# FLOCCULE CHARACTERIZATION OF THE

#### SATILLA ESTUARY

A THESIS

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The Faculty of the Division of Graduate

Studies and Research

By

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# FLOCCULE CHARACTERIZATION OF THE

SATILLA ESTUARY

Approved:

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Date a	pproved	i by Cha	irman:	12-7	2-74

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#### SUMMARY

Stations on the Satilla Estuary were occupied at different seasons and at different salinities. A relationship between water chemistry and river hydrodynamics and the chemical and physical properties of the floccules found at the fresh water-salt water interface was established. The formation of the floccules was thought to be caused by coprecipitation of metals and dissolved organic carbon (DOC), since a close metal-organic association had been observed in the Satilla River water (Beck et al., 1974).

At the initial appearance of salt water (3 - 50 ppm Na) organicrich floccules occur which are not observed upstream in the Satilla River water. The organic carbon content of the floccules decreases with increasing salinity (> 50 ppm Na). DOC decreases proportional to the mixing with sea water. Therefore the organic floccules do not appear to originate immediately by precipitation of the DOC, and thus the composition of the floccules is not quite understood. The suspended particulate organic carbon (POC) appears to be incorporated with the resuspended bank material in the mixing zone and eventually becomes included in the marshes.

Dissolved metals show a rapid decrease seaward and are assumed to be incorporated into the floccules. However, the increase of metals in suspended particulate matter observed in the mixing zone is not attributed to this incorporation only. An increase in the concentration of the suspended material in the mixing zone due to resuspension of bank material is related to the increase of metals in the particulate matter and masks the precipitational feature of the dissolved metals.

# CHAPTER I

#### INTRODUCTION

The Satilla River drains the Coastal Plain of Georgia and is characterized by low pH values, high dissolved organic carbon (DOC), and a dissolved inorganic load which is low in the major sea water elements but contains appreciable amounts of Fe, Al and  $SiO_2$  (Beck <u>et al.</u>, 1974). The suspended load of the Satilla is low relative to other east coast rivers (Neiheisel and Weaver, 1967). Rains flush the Coastal Plain swamps and increase the organic matter and metal content of the river waters. The Satilla waters have been observed to change in pH and organic carbon content with the seasons (Beck, 1972).

The dark color of the Satilla river waters decreases at the interface of fresh water and salt water. During this transition, large concentrations of floccules which are not present upstream are now observed, appearing dependent on the current velocity. Bank resuspension appears to be one source of the floccules. Turbulent agitation of the water and floccules seems to be responsible for transporting high floccule concentrations in response to current velocities.

Association of metals and organic matter in the river waters has been observed by Beck <u>et al.</u>, 1974. The dissolved metals of the river have been shown to decrease rapidly in concentration with little salt water influence (Beck, 1973) and it is possible that associated dissolved organic material behaves similarly. This rapid decrease appears to be due to removal of metals from solution rather than to dilution with sea water.

Floccules occurring at the salt water - fresh water interface are suspected to result from coprecipitation of metals and organic matter from solution. It was proposed to investigate the chemical composition of the floccules and their morphology at both macroscopic and microscopic levels, and to include the associated water chemistry. These investigations at various salinities and time were to establish a mechanism for floccule formation. This mechanism would also be pertinent to the transport and deposition of trace metals through the estuary. River particulate matter, including metal-organic material, has been reported to incorporate trace metals (Windom et al., 1971a).

Other complications also to be considered in this mechanism of floccule formation are the influence of suspended seaward-derived material and resuspended bottom and bank sediments of the estuary.

#### Hydrodynamics

The Satilla Estuary appears to be similar in hydrodynamics to the Chesapeake Bay Estuary, as described by Schubel (1971). The low river discharge (relative to the tidal influence) of the Satilla River changes substantially with the seasonal rains. These changes are adequate to shift the position of the mixing zone of the river and sea waters. High river discharge, occurring during the high spring and summer rains, pushes the mixing zone seaward resulting in less

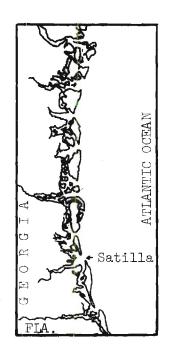
influence of tidal fluctuations. The Satilla Estuary can be characterized as changing from a partially mixed to a homogeneous type estuary, according to Schubel's (1971) classification. This is substantiated by the existence of a slight salt wedge, which changes with river discharge to minimal salinity variations with depth. Another similarity of the Satilla and Chesapeake Bay Estuaries is observed in the mixing zone. The mixing zone, assumed as the location of the beginning influence of the salt wedge on fresh water, contains a high suspended load. This load is assumed to be derived from several sources. Landward transport of fine seaward-derived sediment (Mead, 1969) in the Satilla Estuary, adds to the high suspended load (Neiheisel and Weaver, 1967; Windom et al, 1971a). Resuspended bottom and bank material due to tidal and river discharge fluctuations also increases the suspended load at the mixing zone.

#### CHAPTER II

#### PROCEDURE

Each of seven fixed stations in the Satilla Estuary were occupied hourly through a complete tidal cycle. (See map, Figure 1). Stations 1 and 2, occupied August 24-30, 1973, through a 24 hour period, are designated summer stations. Stations 3 and 4, occupied October 18-20, 1973, through a 24 hour period, are designated fall stations. Stations 5 and 6, occupied December 14-18, 1973 during a rainy period for a period of 6 hours each, are designated winter stations. Station 7, occupied March 17, 1974, 1974, through a 12 hour period, is designated spring station (see Table 1). Water samples were collected from a fifteen station traverse of the estuary on March 16, 1974 within a period of 3 hours (Figure 1).

Water samples were collected hourly at a constant depth at each station (Table 1). The water was filtered through 0.45 µm HA Millipore filters (47 and 142 mm in diameter) and stored in polypropylene bottles. The particulate matter on the filter paper was stored in a covered petri dish. The filtered water samples were later analyzed for total Fe, Al, organic carbon, Na, pH and absorbance at 425 nm (A425). The particulate fraction was analysed for the amount of suspended matter and for Fe, Al, Zn, organic carbon concentrations. Clay minerals were determined by X-ray diffraction. Scanning electron microscopy was employed for morphological studies. In addition, macrophotography of



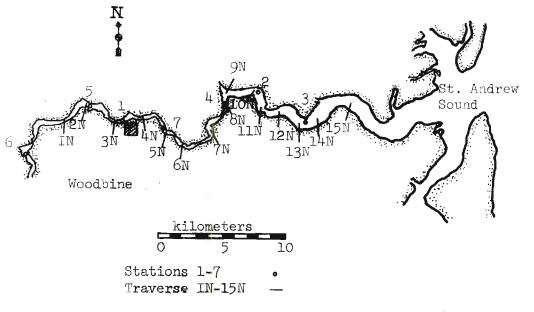


Figure 1. Index Map and Sample Locations of the Satilla Estuary

Stations	Date	River Discharge* (cfs)	Depth of Sample (ft.)	Range of Salinities (%)
l	8/24/73	2640	8	0 - 0.5
2	8/26/73	1960	12	0.5 - 6.5
3	10/18/73	265	10	9.0 - 21.4
) <sub>4</sub>	10/19/73	252	8	3.1 - 11.6
5	12/14/73	287	6	0.0 - 0.7
6	12/17/73	329	12	0.0 - 0.7
7	3/17/74	1100	0	0.0 - 0.6
Traverse	3/16/74	1100	0	0.0 - 15.1

# Table 1. Stations, River Discharges, Depth of Sampling, and Salinity Ranges

\* Data from U.S.G.S. gaging station at Atkinson, Ga.

the suspended floccules was performed in situ. Other measurements made at various depths include salinity and current velocities (Tables 2-8).

### Field Procedures

Figure 2 shows the apparatus used for sample collection. A reel of coaxial wire was mounted on an A-frame and extended over the side of the boat. A Price current meter and 30 pound lead weight were suspended on the wire, and measurements were taken hourly at several depths. Above the current meter, 3/4" plastic tubing was taped to the wire and connected to a small all-plastic battery-operated pump. Water was collected from various depths in this fashion. A salinity probe was fastened to the wire above the tubing, and a Beckman salinometer was used to read salinity, conductivity and temperature aboard boat.

A ten liter Plexiglas cylinder was filled with a water sample and connected to a 142 mm diameter, 0.45  $\mu$ m Millipore filter (Brown <u>et al.</u>, 1970). The cylinder was pressurized by means of a hand pump. The water and filter were changed during the even hours (every two hours) and the amount filtered recorded for determination of suspended load concentration. A reduction in pore size in the 0.45  $\mu$ m filters over the two hour filtering period due to clogging was taken into consideration. Precautions were taken to reduce contact of the water sample with metal. Water was washed through the filters before collection to reduce contamination by the filter. pH of the filtrate was measured <u>in situ</u> by use of a glass electrode and an Orion 407 pH meter. Buffers spaced at intervals of 1.0 pH units were used for

Table 2. Chemical and Physical Data

STATION 1

.

STAIL	.011 1						S 0	LUB	LΕ	(Dec	kman)	(Spec	+ 7 )	PAR	ТІСՍ	LATE		
Time	Depth	Curr. Vel. cfs	Sus. Conc. mg/l	рН	Sal. %	Na ppm	Al ppm	Fe ppb	T.C. ppm	n.C. ppm	O.C. ppm	(Spec A425 x 10		%c	Al ppm	Fe ppm	Zn ppm	% Mont.
01 02	8 8	2.60	21.2	4.48	.05	2.9	520	1005	20.6	0	20.6	1.96	21.11	17.4	41,678	20,838	208	0 43
03 04	8 8	.51 1.78	15.2	4.51	.02	3	540	1300	21.6	0	21.6	2.03	21.89	17.7	57,381	36,888	148	33 41
05 06	8 8	1.80 1.29	16.9	4.56	.04 .05	3.2	440	980	21	0	51	1.99	21.44	17.2	61,333	46,958	173	47
07 08	8 8	·79 .66	18.5	4.43	.05 .06	3.2	590	1290	23	0	23	2.11	22.73		62,849	35,614	126	36 44
09 10	8 8	1.71 2.50	18.5	4.41	.07 .04	3.	500	1270	20.1	0	20.1	2.03		16.96	59,979	39,460	158	11 0
11 12	8 8	2.50 2.70	16.9	4.51	.06	3	470	1340	21.6	0	21.6		22.83		88,300	38,631	392	0 46
13 14	8 8	2.52 1.27	17.6	4.55	.06	3	530	1350	24.6	0	24.6		23.01		55,566	33,333	170	0
15 16	8 8	.74	19.5	4.43	.06	3		1335	23	0	23		21.99		57,480	34,490	159	42
17 18	8 8 8	1.87 1.76	17.4 18	4.95 4.49	.08	3 3.4	500 490	1250 1125	21	0	21	1.97 2.70	21.24 29.42		63,546 66,350	40,619 48,020	157 196	37 39
19 20 21	8 8	1.57 .23 1.62	10	4.49	.05 .05 .05	3.5	490 460	935	19.9 19.6	0	19.9 19.6	2.70	29.42		63,483	40,020 38,219	196 156	35 41
22 23 00	8 8 8	2.31 2.44 2.75	17.4	4.52	.04 .04 .04	3		1305	19.6	0	19.6	2.01		18.47	63,316	36,934	158	45 36 0

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# Table 3. Chemical and Physical Data

STATI	ON 2						SO	LUE	LE	Dee		( [ ] ] ]	+ 7 \	ΡΑF	тіси	LATE		
Time	Depth	Curr. Vel. cfs	Sus. Conc. mg/l	рH	Sal. %	Na ppm	Al ppm	Fe ppb	T.C. ppm	(Bec n.C. ppm	kman) 0.C. ppm	(Spec A425 x 10	to	%c	Al ppm	Fe ppm	Zn ppm	% Mont.
00	10	2.62	145	5.92	.42	200	270	755	34	4.3	30	2.19	23.7	6.79	87,975	41,516	114	40
Ol	10	2.50		5.46	.05													29
02 03	10 10	2.19 1.29	168	5.42 5.61	.05	50	340	920	33.3	1.1	32	1.96	21.1	7.48	87,619	41,673	102	34 20
03	10	1.06	63.7	5.51	.05	45	360	1000	21.6	0	21.6	1.94	20,88	7 80	90,318	39,948	130	20
05	10	1.84	00.1	5.57	.06	4)	000	7000	Δ <b>Τ</b> ΙΟ	U	21.0	1.94	20.00	1.09	90,510	39,940	UCT	43
06	10	1.67	196	5.62		180	270	775	29.7	1	38.7	2.09	22.56	7.0	91,725	41,494	109	41
07	10	1.29			1.11													26
08	10	.76	55.6	5.89	1.90		210	640	20.6	1	19.6	1.70	18.28	7.2	89,182	39,697	122	44
09	10				.07													
10	10																	
11 12	10 10	2.22	103	5.65	.08	39	370	900	26.3	0	26.3	1.95	20.97	8 96	85,931	41,012	129	42
13	10	2.09	102	رە.ر	.05	29	210	900	20.3	U	20.3	1.95	20.91	0.20	0,951	41,012	129	42
14	10	1.59	97.6	5.38	.07	18	420	1120	21	0	21	1.97	21.2	8.75	86,573	40,063	118	<u>~ 1</u>
15	10	1.49	21.12	5.55	.05					-					,,,,,			34
16	10	2.11	190	5.53	.08	63	400	845	19.6	2.5	17.1	1.99	21.43	7.4	87,686	40,804	104	40
17	10	2.22		5.82	.3													50
18	10	1.89	136.	5.93	1.27		50	670	30.6	0	30.6	1.81	19.39	6.99	89,518	40,047	110	
19	10	1.48	(	6.51	3.18		300	210		0	3= (	7 (7		( 10	00 (0-	20 010	105	24
20	10 10	.81 21	67.7	6.44	5.60	1900	T00	340	24.6	8	15.6	T.0T	17.26	6.43	83,695	38,043	125	30
21 22	10	·34 2.48	58.2	6.50 6.19	1 28	1500	125	415	27.3	3.4	13.6	1 5)	16.42	6 67	86,789	34,489	124	0 34
23	10	2.92	JU.2	6.10	2.36		16)	717	-1.2	5.4	T).O	1.74	10.72	0.01	00,102	5~,-09	⊥ <b>∠</b> -+	45
					50													

STATION 2

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Table -	4.	Chemical	and	Physical	Data
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STATION 3

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DIAL.							S C	LUB	LE	(Bec	kman)	(Spec	+1)	PAR	TICU	LATE		
Time	Depth	Curr. Vel. cfs	Sus. Conc. mg/l	рH	Sal. %	Na ppm	Al ppm	Fe ppb	T.C. ppm	n.C. ppm	0.C. ppm	A425		%c	Al ppm	Fe ppm	Zn ppm	% Mont.
00 01		1.73 1.62	119 116	7.12 7.11		4550 3450	14 14	174 220	22	13.5	8.5	.86	8.9	6.13	85,808		122	56
02 03		1.38 .829	102 48	7.15	17.6	5750 6100	10	207 203	23.5	17	6.5	.67	6.75	5.96	84,496	38,849	102	уо 45
04 05		.44 .94	34.6 65.6	7.37 6.84	18.3	6050 5950	10	183 183	27.9	22.5	5.4	.66	6.67	6.15	74,538	34,357	110	50
06 07		.94 1.24	43.1	7.37	18.2	6000 4250		203 183	24.2	17.5	6.7	.63	6.33	5.91	82,225	37,288	106	
08 09		.87 1.55	213.5 50.4	4.12	12.0 9.1	4100 2900	14	233 250	23	12.2	10.8	.88	9.11	6.03	88,659	39,029	106	45
10 11		.49 1.01	68.3 122		11.97			267 220	20.5	11	9.5	1.02	10.7	6.07	83,186	36,620	109	46
12 13		1.85 1.63		6.65	13.75 15.9	4850		163 250	22.4	14	8.4	.82	8.44	5.92	88,544	36,944	1,01	33
14 15		1.40			17.6			183	23	18	5.5	.65	6.56	5.76	87,917	38,006	105	
16 17		.94 1.51	29.5	6.95 7.15	21	6950 6560		193 250	25 01-0	20	5	.49 .62	4.78	5.84	89,831	31,492	145	60
18 19		1.62 2.10	85.4 156	6.95 6.93	19.0 16.7 14			174	24.2	18.5		.02 .87	6.62	5.37	88,051	39,391	107	
20 21 22		.81 .58 .35	127.8 52 85.1	6.99 6.80 6.96	14 12.1 9.6			174 203	22.9 21	14.3		.07	9.0 10.1	5.94 6.70	88,387 81,397	41,280 39,342	136 104	50
23		.35	۲.(0	7.20		3420 3800		203	61 -	17.2	9.1	•91	TO·T	0.10	01,391	JY, 342	104	47

Table	5.	Chemical	and	Physical	Data
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STATION 4

							S C	LUI	3 L E	(Pee	kman)	(Spec	+ 7 )	ΡA	RTICU	LATE		
Time	Depth	Curr. Vel. cfs	Sus. Conc. mg/l	рH	Sal. %	Na ppm	Al ppm	Fe ppb	T.C. ppm	n.C. ppm	0.C. ppm	A425		%c	Al ppm	Fe ppm	Zn ppm	% Mont.
00	15 15	2.06	221. 140	6.45 6.55		1450 1095		408 462	20 23	6 5.5	14 17.5		15.1	6 57	84,614	48.076	106	33
02	15	.81	47.2	6.58		1075		563	25.5	5	20.5	1.42		0.71	04,014	40,010	TOO	48
03	15	2.55	112.7	6.30	-	1650		330	22.5	7.1	15.4	1.24	13.6	6.09	85,624	38,584	100	
04	15	2.03	318.5	6.38	-	1800		350	30	7.3	22.7	1	20 (	( 53	00.007			50
05 06	15 15	1.82 1.30	190 269	6.57 2.58		2400 2750		303 313	23 28	9 8 8	14 19.2	1.14	12.6	0.51	89,991	38,313	111	38
07	15	1.19	45.9	6.42		3250		240	21		10.2	1.02	10.7	6.53	78,493	35,465	137	00
08	15	.51	28	6.39		3300												57
09 10	15	1.23	56	6.38	9.54	3050	0	250						6.23	82,897	36,213	122	
11	15	1.91	122	6.43		1200		496	19.5	5.5	14	1.37	14.6	6.85	82,105	39,604	111	
12 13	15 15	1.34 1.21	122 34.2	6.53 6.53		1005 900		553	23	F 2	7 7 7	a ko	14.8	7 00	P3 003	38,510	170	48
13	15	1.56	34.2	6.42		1250		627 462	23	2.3	17.7	1.40	14.0	7.92	81,021	30,510	170	46
15	15	2.48	133	6.46		1700		330	23.5	7.8	15.7	1.22	12.4	6.50	85,366	41,928	113	
16	15	2.39	154	6.53		2150		333										42
17	15	2.06	168 64	6.62		2750		240	20	10	10	1.07	11.0	6.34	100,186	38,686	95	44
18 19	15 15	1.52 .05	64 36.3	6.55		3200 3750		240 183	25.2	12 3	12.9	.94	9.8	3.26	82,249	34,610	110	44
20	15	1.43	44	6.61		3350		100	32		11.5	• ) 4	2.0	J.20	02,249	J <b>4,</b> 010	TTO	47
21	15	1.91	152	6.51		2700		233	20.5	10.5		1.08	11.3	6.24	83,682	38,202	96	
22	15	1.85	215	6.43		2250		07.0	28	-	19.5	3 00	2.0		00 500	12.050	176	38
23	15	1.62	195	6.28	5.24	1700	31	313	22.2	7.1	15.1	1.20	12	6.57	83,509	41,252	116	

STATI	ONS 5 8	<b>.</b> 66																
						S 0	L U	BLE		(		PARTICULATE (Spect1)						
Time	Depth	Curr. Vel. cfs	Sus. Conc. mg/l	рН	Sal. %	Na ppm	Al ppm	Fe ppb	T.C. ppm	(Bec n.C. ppm	kman) O.C. ppm	(Spec A425 x 10		%с	Al ppm	Fe ppm	Zn ppm	% Mont.
Stati	on 5												•••					
09 10	10 10	1.18	272	6.12 6.0	.04 .04	205 235	90	305	14	.8	13.2	• 74	7.6	5.96	93,173	48,612	127	
11 12	10 10	.46 1.62	107	6.11 6.17	.04 .04	180 234	68	370	16.2 17	.8 0	15.4 17	.76	7.78	5.6	89.213	53,835	162	
13	10	1.73	290	6.30	.04	375	107	260	18.5	1.2	17.3	.80	8.22	5.4	94,360	45,857	128	
Stati	on 6																	
08 09	12 12	1.51 1.51	159	5.79 5.73	.02 .02		88.8 125	430 495	5.5	.83	4.67	.76	7.78	4.95	93,565	47,727	123	
10	12	1.51	133	5.69	.02	40.5	12	520	13.5	1	12.5	.76	7.78	6.97	108,958	51,816	110	
11 12	12 12	1.37 .30	194	5.71 5.91	.02	37 32	130 128	530 440	12	.8	11.2	.76	7.78	6.83	87,995	44,749	104	
13 14	12 12	1.37 1.62	152	5.91 5.92	.02 .02	31 40	113 140	505 540	13	.07	12.9	•77	7.89	6.63	94,512	41,159	120	
15 16	12 12	1.89 1.89	181	5.93	.02 .02	43 63	120 103	460 420	12.5	.8	11.7	.76	7.78	6.28	108,348	49,734	260	

Table 6. Chemical and Physical Data

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011111	011						SC	) L U I	βLΕ	(Doc	kman)	(Spec	.+ 7 \	ΡΑR	TICU	ГАТ Е		
Time	Depth	Curr. Vel. cfs	Sus. Conc. mg/l	рН	Sal. %	Na ppm	Al ppm	Fe ppb	T.C. ppm	n.C. ppm	O.C. ppm	(3pec A425 x 10		%c	Al ppm	Fe ppm	Zn ppm	% Mont.
11	0			5.37		20.5		875										
12	0			5.32		7.5		high	21.5	0	21.5	1.17	12.3					
13	0			5.41		8.5	107	835	15	0	15	.76	7.78					
14	0			5.32		8.5		950	15.8	0	15.8	.8	8.22					
15	0			5.40		8.0	146	1150	15.5	0	15.5	.77	7.89					
16	0			5.36		6.5	86	650	14.3	0	14.3	.74	7.56					
17	0			5.32		7.5		high	16.1	0	16.1	.82	8.44					
18	0			5.32		7.5	104	830	15.6	0	15.6	.78	8.00					
19	0			5.39		8.0		high	15.8	0	15.8	•79	8.1					
20	0			5.46		10.0	125	975	15	0	15	.76	7.78					
21	0			5.53		13.5	132	1030	15	0	15	.76	7.78					
22	0			5.58		10.5	113	900	15.6	0	15.6	.78	8.0					

Table 7. Chemical and Physical Data

STATION 7

							S O	LUB	ЪLЕ	(Ber	kman)	(Spec	+1)	ΡΑΕ	RTICU	LATE		
tation	Depth ft	Curr. Vel. cfs	Sus. Conc. mg/l	рH	Sal. %	Na ppm	Al ppm	Fe ppb	T.C. ppm	n.C. ppm		A425 x 10	to	%c	Al ppm	Fe ppm	Zn ppm	% Mont.
lN	0			5.25		5		930	15.5	0	15.5	.77	7.89				-	
2N	0			5.26		5.5		800	14.3	0	14.3	.74	7.56					
3N	0			5.27		5.5		650	15.6	0	15.6	.78	8.0					
4N	0			5.30		6 6		800	14.25	0	14.3	.70	7.1					
5N 6N	0			5.13 5.34		ь 6.5		1080 840	16.1 15	0 0	16.1 15	.82 .76	8.4 7.78					
7N	0			5.66		12		1040	15.5	0	15.5	.77	7.89					
8N	õ			6.25		300		670	15.5	õ	15.5	.77	7.89					
9N	0			6.52		600		520	13.5	0	13.5	.71	7.22					
lon	0			7.03		1950		420	12.2	0	12.2	.61	6.11					
12N	0			7.29		3450		320	7	0	7	• 39	3.67					
13N	0			7.41		3950		250	6.76	0	6.75	• 36	3.33					
14N	0			7.53		4000		270	11.25	0	11.25	•55	5.44					
15N	0			7.61		4480		260	6.5	0	6.5	.34	3.11					
BANK	CORES																	
a														5.2	78,420	35,863	86	
Ъ														5.4	85,450	34,654	95	
с														5.3	84,363	34,370	101	
d														5.2	84,615	32,923	120	
е	r													6.5		37,716	91	
g														6.4	75,691	30,874	77	

Table 8. Chemical and Physical Data

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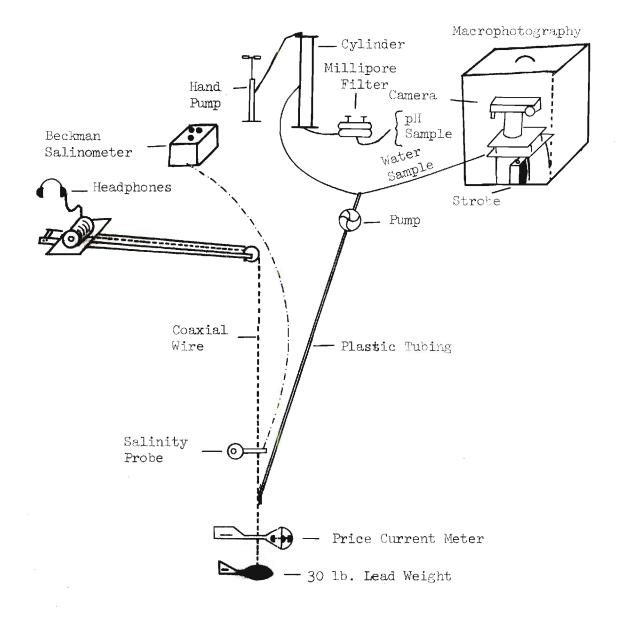


Figure 2. Instrumentation Apparatus

calibration. Filtered water was collected in two bottles. All bottles in this study were polypropylene and washed with nitric acid. A water sample was collected in a 250 ml bottle containing 0.5 ml of 6N redistilled HCl for analyses of total Fe, Al, and Na; a 30 ml bottle of filtrate was collected and refrigerated for analyses of organic carbon. The suspended particulate matter was collected on a preweighed filter paper and stored in a washed petri dish for determination of amount of suspended matter and concentrations of Al, Fe, Zn and organic carbon.

Water samples from odd station hours and the traverse were filtered with a Millipore syringe through a 42 mm diameter, 0.45  $\mu$ m HA Millipore filter. Similar storage precautions were taken. A filtrate sample, collected in a 125 ml bottle containing 0.5 ml of 3N redistilled HCl was used for metal analyses. An additional 30 ml of the filtrate sample was collected and kept refrigerated for analyses of dissolved organic carbon. The particulate matter on the 42 mm diameter filter paper was stored in washed petri dishes and used for clay mineral analyses by X-ray diffraction.

Macrophotography of the suspended particles was done <u>in situ</u> with a 35 mm Nikkormat camera having a 55 mm micro lens placed at l:l focal range and focused by adjustment of the mounted camera on a movable rail. Photographs of the particles were used to estimate size, shape and concentration variations in the estuary.

#### Laboratory Analyses

Water samples were analyzed within two weeks of collection.

Al was analysed by atomic absorption spectrophotometry (AAS) using Al-oxine complex extracted into methyl isobutyl ketone (MIBK) (Fishman, 1972). Seventy-five ml of previously acidified sample were buffered at pH 8 - 8.1 by addition of 7.5 ml of a THAM-HCl buffer. The metals were extracted by addition of 7.5 ml MIBK-0.533 percent oxine. Total Fe and Na were measured directly using AAS. Dissolved organic carbon (DOC), analyzed by a Dow-Beckman Model 915 Carbonaceous Analyser (dual channel), was determined as the difference between total dissolved carbon and inorganic carbon (Van Hall and Stenger, 1967; EPA, Water Quality Office, 1971).

Calibration standards for total carbon were prepared from desalted, freeze-dried river water organic matter, using the compositional formula reported by Martin, 1973. Calibration standards for inorganic carbon were prepared from sodium carbonate (EPA, Water Quality Office, 1971).

Dissolved organic carbon was also measured indirectly by determining the absorption at 425 nm (A425) of the filtered water samples. Beck and Reuter (1974) report a linear relationship between A425 and concentration of DOC (slight metal effect).

The organic carbon values obtained from the Dow-Beckman Model 915 Carbonaceous Analyser were found to be linearly related to the A425 values as has been shown by Beck and Reuter (1974). The results of the two methods are compared in Tables 2-8 at each station. It is believed that length of storage before analyses effected the values obtained from the Dow-Beckman Model 915 Carbonaceous Analyzer. DOC

concentrations as determined by the absorption measurements, show less scatter when plotted against metals and therefore are used hereafter as DOC values instead of the Dow-Beckman Model 915 Carbonaceous Analyser values.

Particulate matter on the 42 mm diameter filter was mounted on glass slides for clay mineral analyses by X-ray diffraction. A Norelco diffraction unit was used with Ni filtered Cu K<sub> $\alpha$ </sub> radiation. The slides were treated with ethylene glycol and rotated from 2° = 20 to 40°. The peak heights of the 7 Å kaolinite peak and the 17 Å montmorillonite peak were measured to determine the relative proportion of each. This method of analysis is not a representative percentage of each clay in the sample. However, it can be used as a method to determine abundance of one mineral relative to another. It should be noted that the montmorillonite peak is broad, containing montmorillonite mixed layered with vermiculite and/or chlorite (Windom <u>et al</u>., 1971b; Neiheisel and Weaver, 1967). In this paper only the peak heights of the montmorillonite were considered.

Untreated water samples from the Satilla River were also collected for studing the morphology of the floccules using the scanning electron microscope. Floccules were prepared for analyses by evaporation of river water on filter paper, and by freeze-drying of the river water particulate matter. The second preparation techique apparently caused less disturbance of the floccule's original structure.

#### CHAPTER III

#### RESULTS

Tables 2-7 contain the analytical data for stations 1 - 7 and Table 8 contains the analytical data for the traverse. Data pertaining to the physical relations from these tables (current velocities, suspended load, salinities) are presented in Figures 7 and 8. Also from these tables, the analytical data pertaining to the water chemistry are presented in Figures 9 - 14, and the data on the chemistry of the particulate matter are presented in Figures 15 - 20. Figure 21 shows the clay mineralogy data.

It is important when comparing data between stations to keep in mind that not all stations were sampled at the same season of the year. It is assumed that data from the same season (data from station 1 and 2, etc.) show valid relationships. Attempts to interpolate data of different seasons is speculative. Some seasonal data do show similarities. Of the chemical parameters measured, summer and fall data are similar and winter and spring data also are similar. However, the summer and fall data are completely different from the winter and spring data.

During low discharge of the Satilla River, salt water advances further upstream than during high discharge of the river. The location of the mixing zone in the estuary therefore changes in accordance to the discharge of the Satilla River. Because of the shifting position

of the mixing zone, the salinities, reported as Na concentrations, at each station are used to measure the seaward progression of the stations rather than using the location of the station in the estuary. Thus station 1 is the upstream station, followed by stations 7, 6, 2, 4 and 3 in order of increasing salinity.

#### Nature of the Floccules

The morphology of the floccules in aqueous suspension was observed under the microscope, both during agitation and after settling. They appeared reddish-brown and oval shaped, and their size was very much dependent on the water motion. The floccules exhibited a honeycomb, hexagonal arrangment of fibers forming chains, whose length determined the size of the floccule. The general hydrophilic character is illustrated by relatively little compaction of the floccules upon settling. Resuspension occurred readily with water motion.

Figures 3 - 6 are scanning electron microscope (SEM) images of floccules. An X-ray diffraction technique for elemental composition was used with the SEM to differentiate clays, organic material, and silica. Figure 3 shows floccules of clays and diatom tests oriented at right angles. These types of floccules do not appear to have undergone compaction, and are similar to those found for flocculated clays (Sides and Barden, 1970). Figure 4 shows parallel oriented clays and diatom tests.

Suspended particulate matter of the Satilla River was collected by evaporation of water in a petri dish. The solid compacted particulate matter was then observed using the SEM for floccule structures

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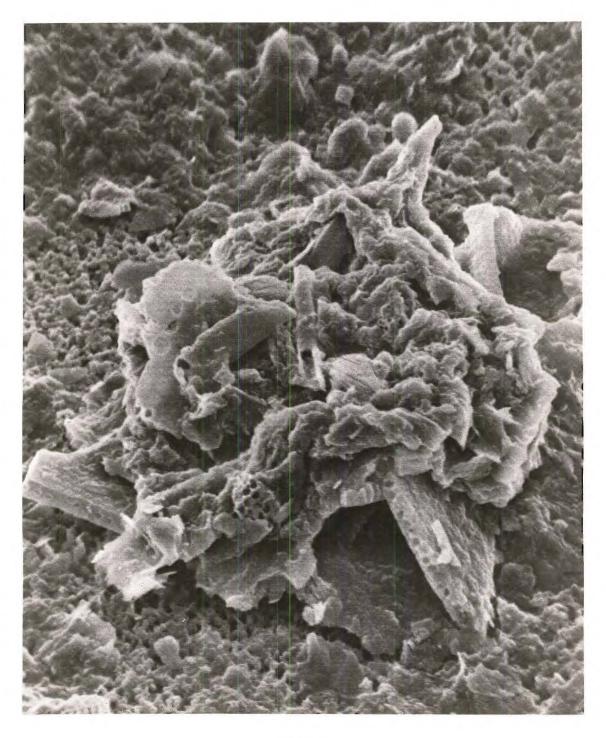
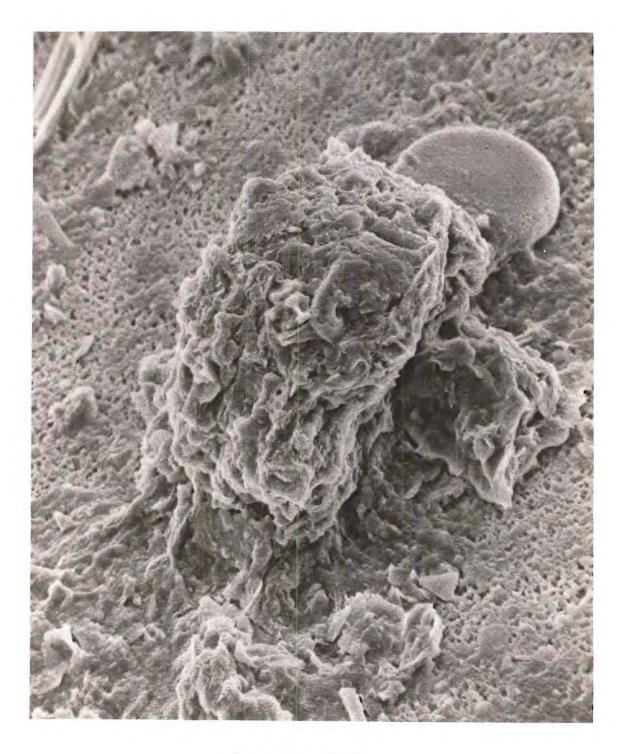




Figure 3. SEM Photograph Illustrating Right Angle Flocculation (Magnification 4488x)



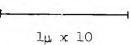
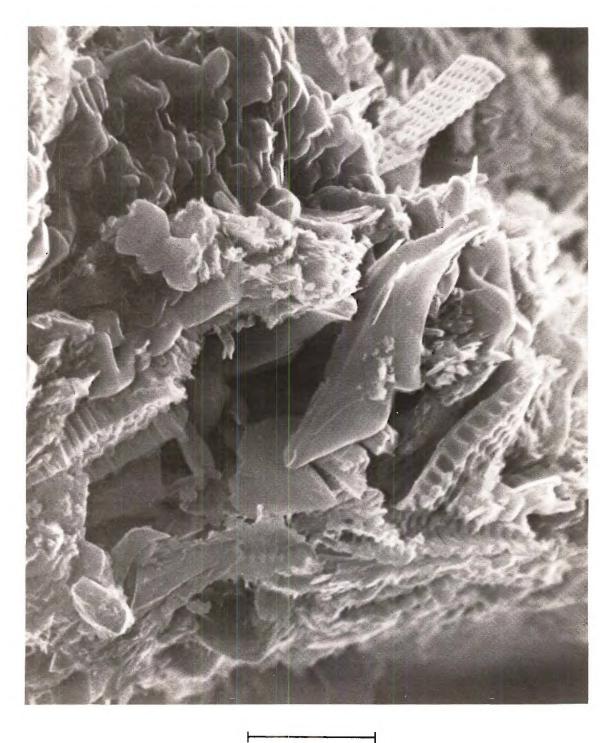


Figure 4. SEM Photograph Illustrating Parallel Oriented Flocculation (Magnification 2244x)

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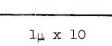


Figure 5. SEM Photograph Illustrating Compacted Floccules (Magnification - 3344x)

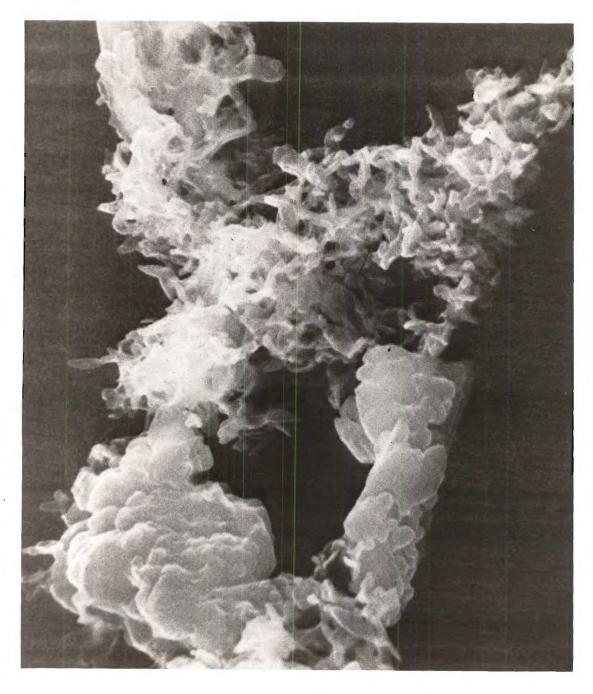




Figure 6. SEM Photograph Illustrating Organic Material and Clay Aggregate Forming a Floccule (Magnification 9537x) (Figure 5). No previous floccule structures are observed. The compacted particulate matter was then resuspended in water with a magnetic stirrer and again observed with the SEM. Floccules appeared very similar to Figure 4, with parallel oriented clays and diatom tests. This type floccule, which has undergone compaction and resuspension, is believed typical of resuspended bank and bottom sediments. Figure 6 shows the original structure of freeze-dried river floccules. The association of organic matter and clay aggregates is shown. The hexagonal fiberous material shown in this photograph is assumed to be organic matter since no elements were detected by the analyzer on the SEM (carbon is not detectable by the analyzer).

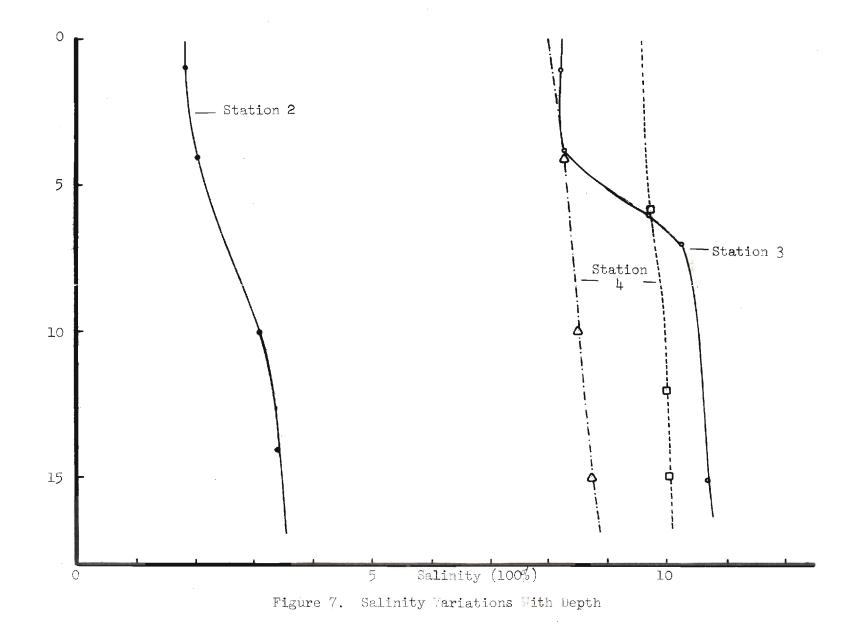
# Physical Relationships

River discharge has a direct influence on the mixing and circulation patterns of different types of estuaries (Schubel, 1971). Salinity measurements over a depth profile are used to distinguish these patterns. Data on salinity variations with depth given in Table 9 and plotted in Figure 7 appear to be intermediate between patterns of a partially mixed and a homogeneous type estuary (Schubel, 1971). The river discharge is insufficient to develop a pronounced salt gradient with depth. Tidal fluctuations dominate the mixing of fresh water and salt water. This diminishes the salt wedge effect and tends to develop a homogeneous mixing of the waters.

Other characteristics of the circulation pattern of the Satilla estuary are analogous to the Chesapeake Bay Estuary (Schubel, 1971). A zone of high concentrations of suspended matter is reported at low

	ation 2 @ . 1900	St Hr	ation 3 @ . 1000		ation <sup>1</sup> 4 @ . 1700	Station 4 @ Hr. 1800			
Depth	Salinity	Depth	Salinity	Depth	Salinity	Depth	Salinity		
14'	3.4	17.5'	10.8	13'	8.7	15'	10.06		
10'	3.18	15'	10.71	7'	8.5	12'	10.00		
<u>1</u> , •	2.06	71	10.38	21	8.2	0'	9.78		
1'	1.84	<u>)</u> + 1	8.31						
		01	8.29						

# Table 9. Variations of Salinity With Depth



salinities in the estuary. Table 10 shows the ranges of concentrations of suspended matter at different stations in the Satilla Estuary. An increase of concentration of suspended matter appears between station 1 and 2, as the salt water-fresh water interface is encountered. The high concentration of suspended matter decreases gradually with increasing salinities (see stations 3 and 4). It is assumed that a zone of high suspended load occurs at the maximum limit of the salt wedge. The seaward decrease in this load is believed to be due to sea water dilution (Schubel, 1971).

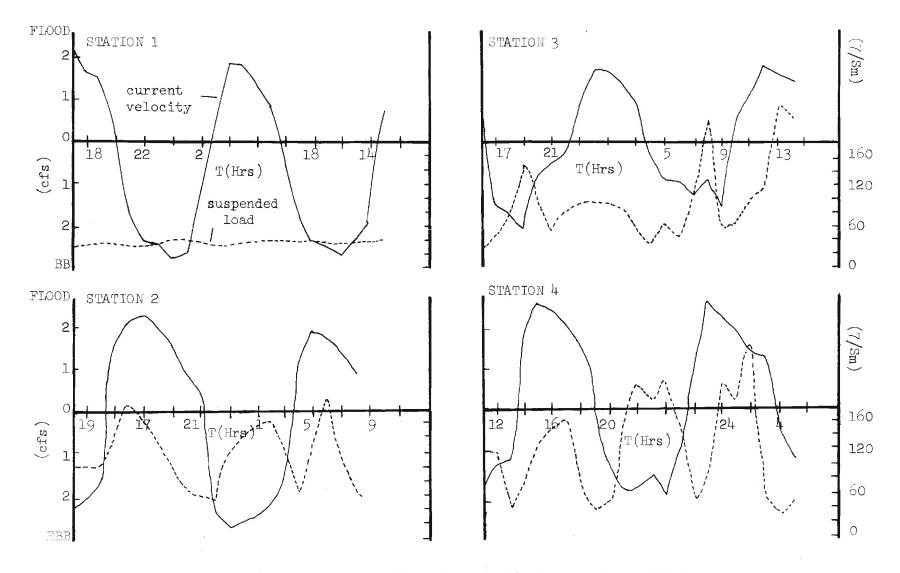
Current velocity and concentrations of suspended matter are related to time through a tidal cycle as shown in Figure 8. The suspended load appears to correspond to current velocity for stations 2-6. Schubel (1971) found a similar relation for the Chesapeake Bay Estuary. This relationship is possibly elated to resuspension of sediments at the upstream salt wedge limit. The relatively fresh waters at station 1 do not show this relationship of suspended load following current velocity. Possibly the particulate matter in this region of the river is not derived from resuspended bank sediments. The characteristics of the suspended load change between station 1 and the other stations (as will be shown in the chemistry of the particulate matter).

#### Water Chemistry

In the upstream reaches of the Satilla Estuary, the salinity measurements were not sufficiently accurate for measuring the mixing of fresh water and salt water. Na concentrations were used as a

Station	Range of Suspended Concentrations mg/1.
	16 - 21
6	130 - 190
5	106 - 290
2	63 - 165
)+	34 - 268
3	43 - 229
	·

Table 10.	Downstream	Station	Progression	and Ranges
	of Concent:	ration of	' Suspended	Matter



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Figure 8. Current elocity and uspended Load During a Tidal Cycle

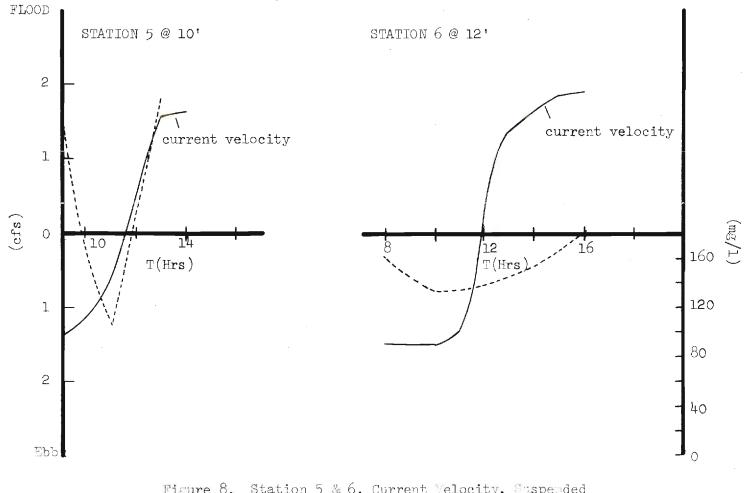


Figure 8. Station 5 & 6, Current Velocity, Suspended Load During a Tidal Cycle Figure 8. Continued

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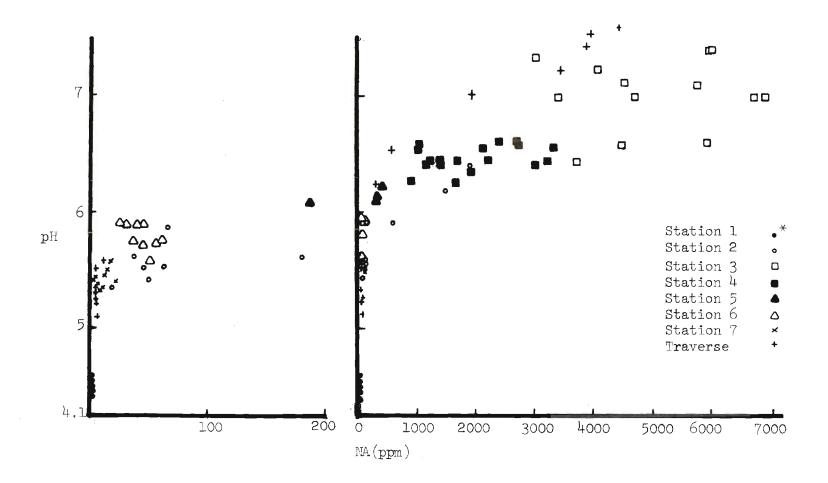
measure of salt water influence since values were obtainable to less than a ppm. Satilla River waters have Na concentrations between 5 to 7 ppm (Beck, 1972) and small increases in Na due to sea water addition can be determined.

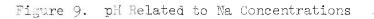
The pH of the Satilla Estuary increases with salt water influence (see Figure 9). pH values during the summer show an abrupt increase at initial Na influence (until 50 ppm). The pH values during the other seasons are higher than during the summer. During the winter, the river water has the highest pH values, however, the rapid increase is also observed at initial Na influence (until 50 ppm). This relationship is also shown by values in the traverse. Beck (1972) has reported similar results for a series of traverses through the Satilla Estuary. After 50 ppm Na and with higher salt water influence, pH values show a linear increase.

### Dissolved Organic Carbon (DOC)

Figure 10 shows a correlation of dissolved organic carbon as measured indirectly by A425 and Na. A linear decrease of DOC occurs seaward during all seasons. During the summer, high DOC values in low Na value waters decrease with a greater slope than during the fall or winter, which initially are lower in DOC values. This is also evidenced by the spring traverse.

The concentrations of DOC in fresh waters, which appear to be strongly dependent on the season, decrease seaward in a fashion typical of dilution by sea water. It has been expected that the trend of the DOC values would indicate precipitation from solution, similar to the





\* The same symbols in this figure for station and traverse points will be used in following figures.

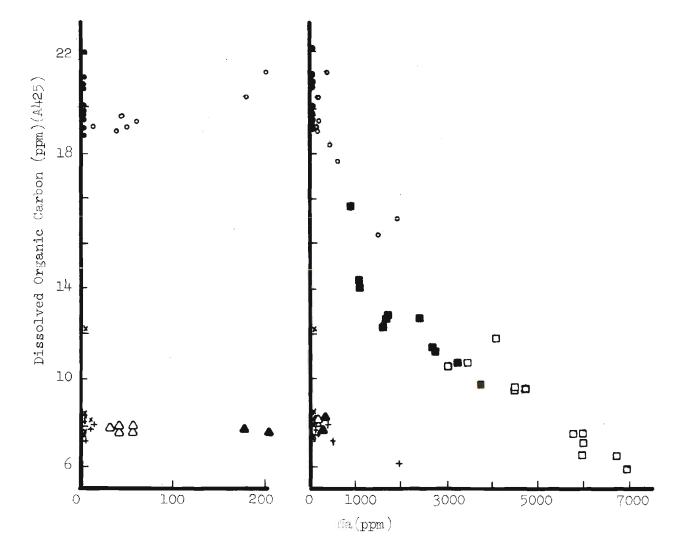


Figure 10. Na Concentrations Related to DOC

dissolved metals as will be shown next. However, this was not found.

Figure 11 shows the relation of DOC values and pH. DOC values during the summer show a decline at a pH of 5.5. This is directly related to the rapid pH increase at initial Na influence (until 50 ppm) noted in Figure 9.

# Dissolved Al and Fe

Figure 12 illustrates the relation of dissolved Fe and Al to Na. This relationship is similar to that reported by Beck, 1972. High concentrations of metals occur in fresh waters during the summer. The metal concentrations decrease rapidly at low Na values which is indicative of precipitation. A lower metal concentration in relatively fresh waters is observed in the fall and winter. At high Na concentrations during the fall, a linear decrease of the metal concentrations is noted, which is more indicative of dilution. The dissolved metals are believed to be incorporated into the floccules by precipitation (as will be shown in the section on the chemistry of the particulate matter). The dissolved metal concentrations are related to pH values in Figure 13.

The seasonal association of dissolved metals and DOC appears to exist in relatively fresh waters. During the summer both high DOC and high metal concentrations are observed in the upstream waters during the fall and winter. Salt water apparently precipitates the dissolved metals and dilutes the DOC concentrations. Figure 14 illustrates the relationship of DOC and dissolved Al and Fe concentrations. The concentrations of metals during the summer decrease rapidly at high DOC values. It is suggested that the metals are being removed

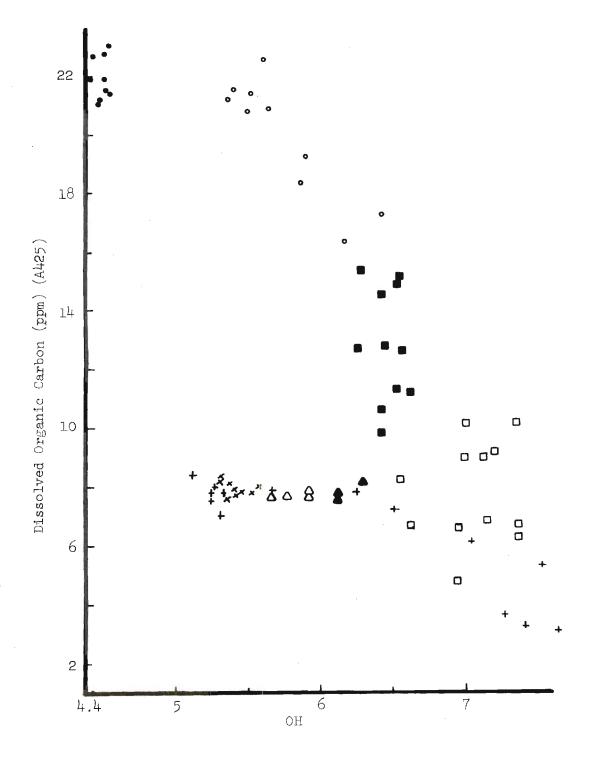


Figure 11. pH Related to DOC

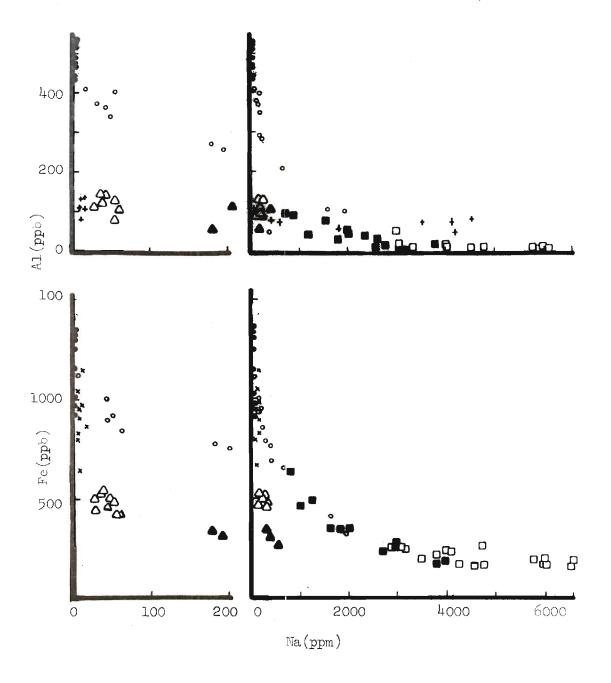


Figure 12. Dissolved Al and Fe Related to Na Concentrations

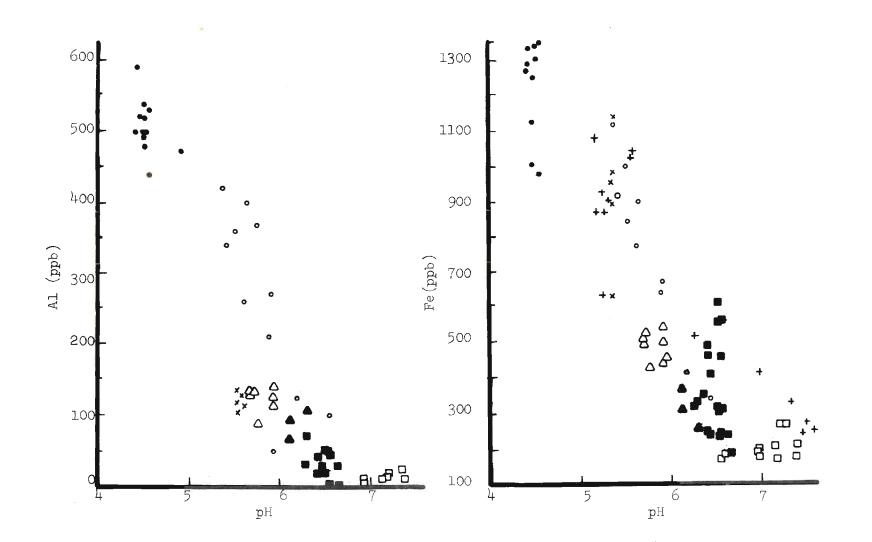
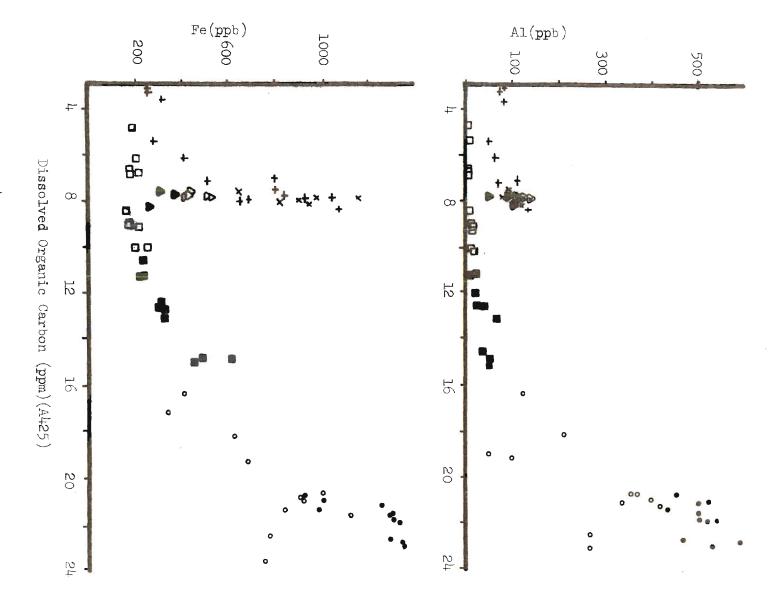


Figure 13. Dissolved Al and Fe Related to pH

Figure 14. Dissolved Fe and Al Related to DOC



from the system while the DOC is only being diluted. With higher salinities, which are observed during the fall, the dissolved metal concentrations and the DOC decrease similarly. This is believed to be due to the decrease by dilution for metals at higher Na concentrations and to the dilution of the DOC seaward. The low, but relatively constant, DOC values during the winter show a marked decrease in the dissolved metal concentrations.

### Chemistry of the Suspended Particulate Matter

The suspended particulate matter in the Satilla Estuary appeared to be mostly composed of floccules (from observation and analytical data). The chemical analyses of the particulate matter are shown in Figures 15 - 20. Formation of floccules have been attributed to clay flocculation (Neiheisel and Weaver, 1967) and from resuspension of bank material (Schubel, 1971). The flocculation of clays (Van Oiphen, 1963) occurs at the interface of fresh water and salt water where a high electrolyte environment is encountered. The high concentration of suspended matter observed at this transition is apparently caused by flocculation of suspended particulate matter (Schubel, 1971). In the Satilla Estuary, however, this is not assumed to be the major process for floccule origin since the suspended clay load of the river is low. The resuspension of bank material at the upstream limit of the salt wedge (~ 50 ppm Na) is assumed to be a major mechanism for floccule origin in this zone since suspended floccules occuring at the mixing zone appear to be chemically similar to the bank material. However, it is observed that the suspended floccules occurring prior

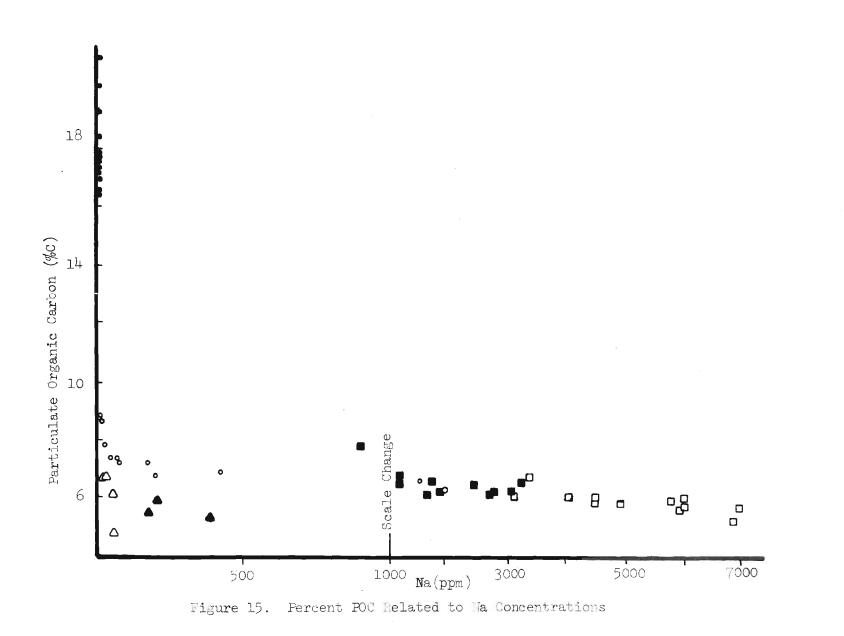
to the mixing zone in the region less than 50 ppm Na, are chemically different from the resuspended floccules. If it is assumed that the river floccules are deposited on the banks, these chemical differences between bank material and the floccules occurring upstream from the mixing zone need to be further investigated.

### Particulate Organic Carbon (POC) of the Floccules

The seaward decrease of organic carbon in the floccules is shown in Figure 15. During the summer, organic-rich floccules occur at initial sea water influence (~ 3 ppm Na). The organic carbon of the floccules decreases rapidly until concentrations of 50 ppm Na are reached. The higher Na values represented by the fall, show a more gradual decrease in organic carbon concentrations seaward. The organic carbon concentrations in the particulate matter are lower in the winter than in the other seasons.

There are two types of floccules which occur in the transition from fresh water to salt water. Prior to the mixing zone, at low Na values (3 ppm) floccules occur which are rich in organic carbon (17 percent C). In the mixing zone at Na concentrations of 50 ppm, the floccules contain lower organic carbon concentrations. The organic carbon concentration of the bank material ( $\sim 5.5$  percent C, Table 8) is comparable to that for the organic carbon of floccules in the mixing zone ( $\sim 9$  percent C). The particulate matter of the mixing zone is therefore assumed to be comprised of resuspended bank material. Figure 16 shows the correlation of pH and POC. This plot is expected because of the relation of pH and Na shown in Figure 9.

The relation of POC and DOC concentrations is illustrated in



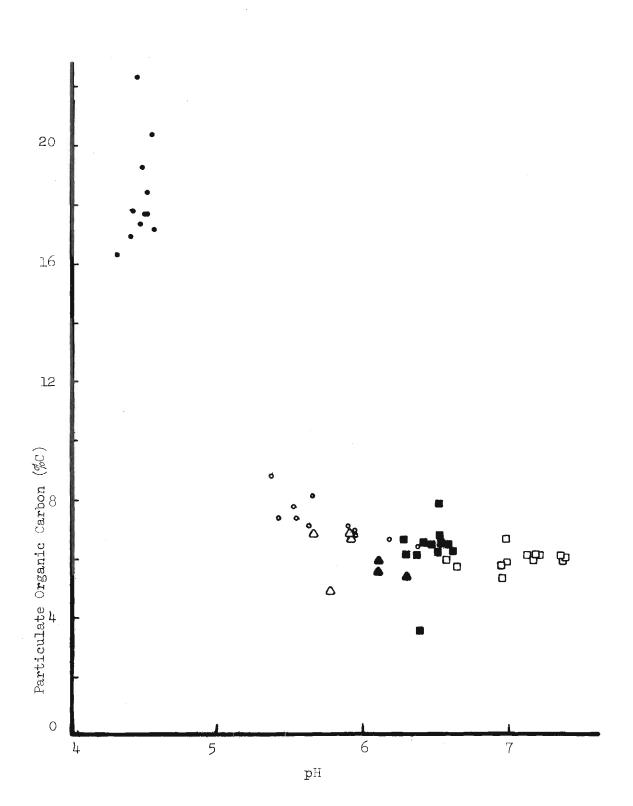


Figure 16. Percent POC Related to pH

Figure 17. The floccules in the relatively fresh waters of station 1 have high POC values at relatively constant high DOC values. With increasing salinity, the POC values of the floccules at station 2 show an abrupt decrease and the DOC values remain relatively constant. At higher salinities represented by the fall and winter stations, lower POC and DOC values are shown to linearly decrease seaward. DOC values which were shown to decrease seaward by dilution, cannot be correlated with the POC values which decrease abruptly as the mixing zone is encountered. The problem of the origin of carbon in the floccules is obviously not yet well understood.

### Particulate Fe, Al and Zn Concentrations

The influence of increasing salinity on particulate Fe and Al concentrations is shown in Figure 18. During the summer, these metal concentrations increase with increasing Na values until 50 ppm. From this point on seaward, the metal concentrations gradually decline. At low Na values, higher metal concentrations occur during the winter than during the summer. The increase in metal concentrations until 50 ppm Na concentrations is possibly due to the precipitation of the dissolved Al and Fe shown in Figure 12. It should also be noted that the high concentrations of suspended matter occur at this point of maximum particulate Al and Fe concentrations (50 ppm Na). This increase, which is due to resuspended bank material (composed mostly of clays) has an effect on the increased metal concentrations. The high concentrations of Al and Fe associated with these clays probably masks the metals contributed by precipitation of DOC. Figure 19 illustrates the relation

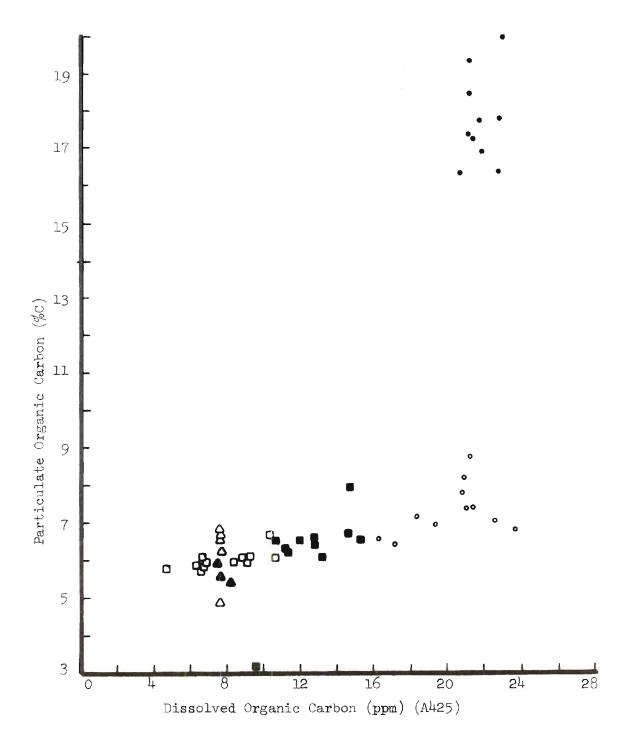


Figure 17. Percent POC Related to DOC

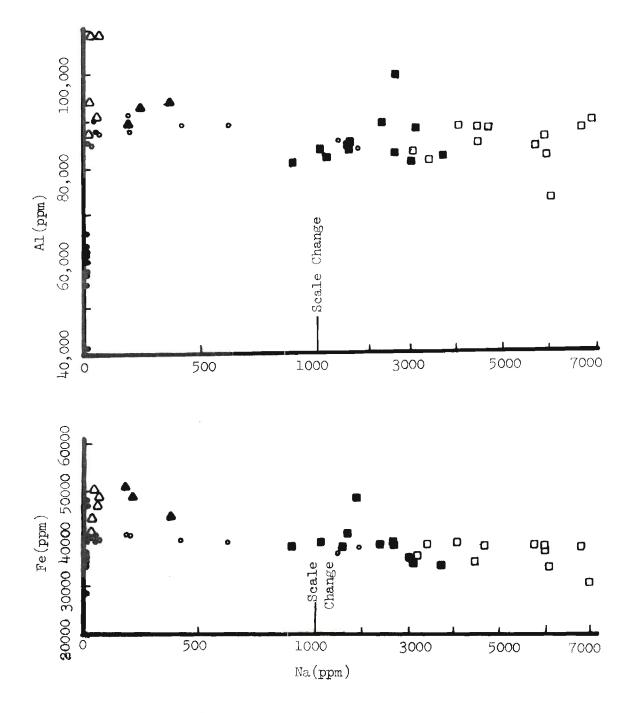


Figure 18. Particulate Al and Fe Concentrations Related to Na Concentrations

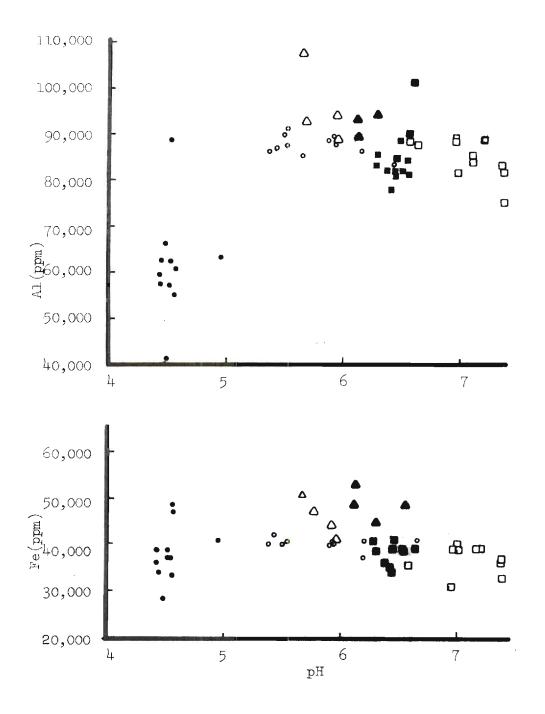


Figure 19. Particulate Al and Fe Concentrations Related to Na Concentrations

of particulate Al and Fe concentrations to pH.

The concentration of particulate Zn is plotted with Na in Figure 20. The data appear to be scattered. However, during the summer, Zn concentrations decrease at initial Na influences (until 50 ppm). At higher Na values, Zn concentrations decrease linearly seaward. With the increasing influence of salt water, Zn concentrations and concentrations of organic carbon in the floccules (see Figure 15) decrease similarly. This suggests a possible association of Zn and POC.

# Clay Mineralogy

Data on the relative amount of montmorillonite to kaolinite in the particulate, given in Tables 2 - 8, are presented in Figure 21. The relative proportion of montmorillonite increases with increasing Na concentrations. The clay mineralogy of Southeastern streams, as described by Neiheisel and Weaver (1967) and Windom et al. (1971b) is comprised of kaolinite, illite, and a montmorillonite mixed-layered with vermiculite and/or chlorite. The Satilla River drainage area lies in the Coastal Plain Province, which is characteristic of relatively high montmorillonite content. The clay mineral composition of suspended matter at station 1 (low Na values) is about 40 percent montmorillonite and 60 percent kaolinite. It has been reported that the seaward increase in montmorillonite is due to landward transport of sediments into the mouth of the Satilla Estuary (Windom et al., 1971a, Neiheisel and Weaver, 1967). These seaward sediments, being high in illite and montmorillonite, enter the estuary after being carried southward by longshore drifts from northern east coast river deposits. This is shown by a greater

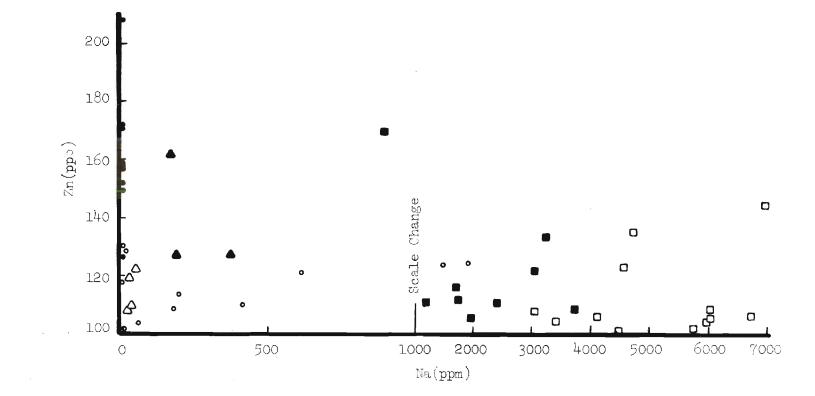


Figure 20. Particulate 7n Concentrations Related to Na Concentrations

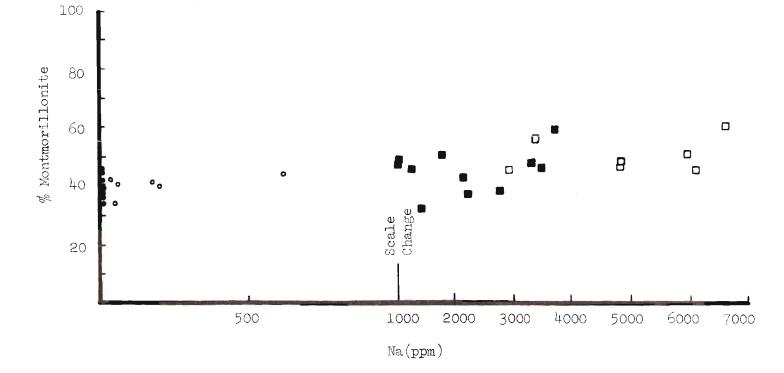


Figure 21. Percent Montmorillonite Related to Na Concentrations

percentage of montmorillonite found near the mouth of the estuary.

Clay stability in suspension also has a bearing on the increasing relative proportion of montmorillonite seaward. Edzwald <u>et al</u>. (1974) reported that montmorillonite has a greater stability in salt water than kaolinite. Thus, Satilla-derived montmorillonite has a longer residence time in the estuary, which is shown by higher percentages with increased salinities.

X-ray diffraction data also showed that at higher salinities, suspended clay samples contained less mixed-layered clays and a purer montmorillonite. The illite content appeared minimal on the diffraction pattern, but a slight increase was noted in the seaward direction, indicating material had been carried from the sea into the estuary.

# Macrophotography

Changes in concentrations of suspended matter, sizes, and shapes of the floccules were observed by photos taken <u>in situ</u>. These changes were noted for different stations and for the tidal fluctuations in each station. A correlation of concentrations of suspended matter and current velocity was observed at stations 2, 3, 4, and 7, but not at station 1. (This is supported by data illustrated in Figure 8.) Surface water showed lower concentrations of suspended matter than bottom waters, as is also reported by Schubel (1971) for the Chesapeake Bay Estuary. This is assumed to be due to resuspension of bottom sediment.

Floccules at station 1 are small (< 0.5 mm) and oval shaped. Floccules located in the mixing zone (located at station 2) changed to a more irregular shape, larger in size ( $\sim 1$  mm) and occurred in higher

concentration. Smaller floccules are observed at higher salinities (station 3).

At several intervals, the same sample was photographed every 10 minutes for an hour. The sample was left undisturbed except for the rocking of the boat during this period. This time lapse macrophotography showed the growth of floccules. Large stringers tended to form rapidly at first, slowing down with increasing time. This mechanism of formation was dependent on the water sample (low salinity waters showed more growth) and the water motion. Slight movements of the water disrupted the growth pattern. It is assumed that the growth of these floccules occurs in a similar fashion at slack tide when the floccules settle from solution. However, because slack tide occurs rapidly, the floccules are limited to their size of growth. The growth of the organic stringers along the banks and bottom tends to incorporate clay aggregates, forming floccules similar to those in Figure 6. Resuspension of these floccules occurs during higher current velocities. The size of these floccules in the water medium would also be controlled by the current velocities within the estuary system.

#### CHAPTER IV

## CONCLUSIONS AND DISCUSSIONS

The Satilla River waters are characteristically clear containing low concentrations of suspended matter. At the estuary two types of floccules are observed. At initial contact of sea water with fresh water (3 - 50 ppm Na), organic-rich floccules are observed. The floccules change to lower concentrations of organic carbon with increasing sea water influence (> 50 ppm Na).

Because of the association of dissolved metals and DOC in the river waters, one might expect that the coprecipitation of these metals and DOC would account for the origin of the organic-rich floccules, which occur prior to the mixing zone. The metals decrease in a precipitational manner and the precipitate is probably incorporated into the floccules and accounts for some of the metals present. The dissolved organic carbon concentrations decrease by dilution with sea water. The organic-rich floccules occurring at station 1 do not appear to originate directly from precipitation of DOC and thus the origin of the organic material in these floccules is not yet well understood.

The floccule chemistry, changing in response to salt water, can possibly be related to the high concentrations of suspended matter which occurs at the mixing zone (approximately 50 ppm Na). The rapid loss in organic carbon in the floccules (Figure 15) which occurs at low Na concentrations, could be attributed to the dilution of carbon with high concentrations of suspended matter. Water with organic-rich floccules (18 percent C) which is found at low Na values (station 1) has low concentrations of suspended matter (~ 18 mg/1, Table 10). There is a 6 fold increase in the suspended matter concentrations between station 1 and 2, or as the mixing zone is encountered (from ~ 18 to ~ 108 mg/1). This dilutes the organic-rich floccules (18 percent C) to 3 percent C. The increase in suspended matter concentrations at the mixing zone is assumed to be attributed to resuspended bank sediment. (Bank sediment is approximately 5.5 percent C, Table 8). Therefore, in the mixing zone it is assumed the addition of 3 percent C from the diluted organic-rich floccules and 5.5 percent C from the resuspended bank sediment yields the 8.5 percent C which is found in this transition zone. Seaward the percent carbon in the floccules decreases, suggesting the deposition of organic matter.

The resuspended bank material is deposited within the estuary, contributing to the build up of the marshes. The association of the organic material with the resuspended bank material describes a mechanism by which the organic material is retained within the marshes of the estuary. A similar mechanism was described by Swanson <u>et al</u>. (1972). In this way metals associated with particulate river water organic material are also assumed retained within the marshes of the estuary. It is not well understood why the organic composition of the marshes is lower than the organic-rich river floccules, since the primary source of marsh sediment is river derived material.

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