REPORT OF INVESTIGATION

CHEMISTRY AND PARTICLE SIZE ANALYSIS OF UPPER PERDIDO BAY AND ELEVENMILE CREEK BOTTOM SEDIMENTS

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PURPOSE

This investigation was initiated for the purpose of determining the sediment quality of upper Perdido Bay, north of the Highway 90 bridge (Fig. 1), and to evaluate possible sources of contaminants in the bay. Allegations had been made by riparian property owners that the bay has suffered, and continues to suffer, an aesthetic decline caused by large quantities of a fine grained, black material that persists near the sediment-water interface which they believe is of an anthropogenic origin. Their further concern was that this material (which during occasional high water events has been deposited on their property) might contain harmful chemical compounds.

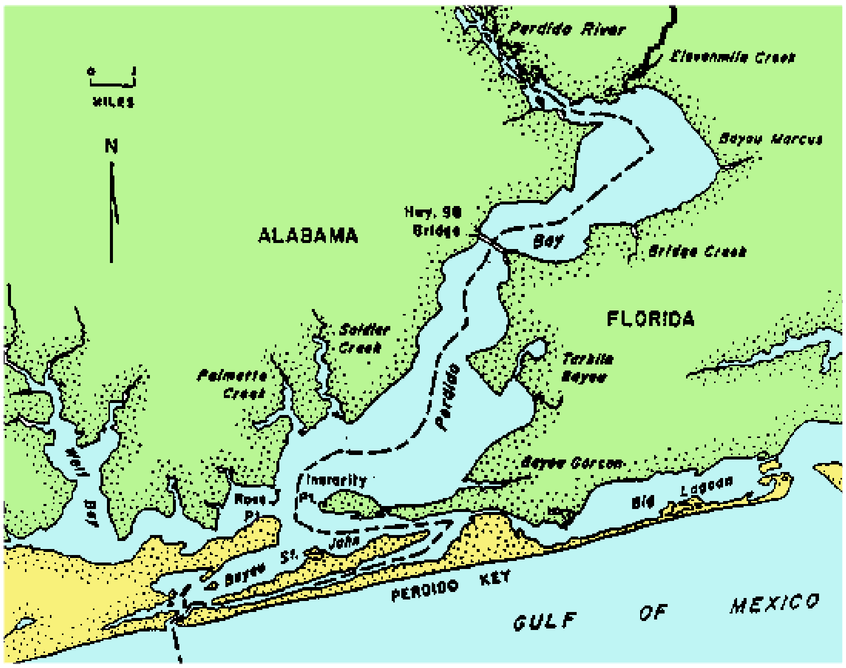

Fig. 1.– Location map showing Perdido Bay and offshore barrier island system (yellow).

General Description and Past Work

The Perdido Bay estuary lies north of the Gulf of Mexico barrier island system and separates the States of Alabama and Florida. The bay covers a surface area of 130 km^2 and has an average depth of 3 meters. It is fed by the Perdido River, which is designated as an Outstanding Florida Water.

A number of previous investigations have been carried out for the purpose of describing the bay's ecology (USEPA, 1999; Brim-USFWS, 1993; Macaulay et al., 1995), sediments (Parker, 1968; Isphording, 1982), its chemistry (Hemming, Brim and Jarvis, 2002; Isphording, 1982; Livingston and Isphording, 1989), as well as the bay's water quality (Schropp et al., 1991), etc. The system is bounded by two barrier islands (Perdido Key and

Santa Rosa Island) and is characterized by both saltwater sounds and marshes. Freshwater influx from the Perdido River (62 m^3/s) causes the upper bay to be distinctly brackish with the result that the bay's average salinity is on the order of 15 parts per thousand (ppt).

Historically, Perdido Bay was predominantly a freshwater system prior to dredging carried out for construction of Perdido Pass and the Intracoastal Waterway. Both the bay and the contributory rivers (Perdido River, Elevenmile Creek, etc.) were essentially pristine waters, however, until introduction of pulp mill wastes into the bay that began in the late 1930s or early 1940s. Areas surrounding the bay have also undergone progressive development for a variety of municipal and private uses causing additional introduction of point and non-point source contaminants to enter the bay. The mill, however, is considered to have had the greatest effect, especially on the upper bay. Wastewater discharges from the mill caused a number of environmental issues to be raised, including low dissolved oxygen, high ammonia, degradation of water color, high specific conductance, elevated iron and zinc levels, and general biological degradation of biological species. Changes in the mill's technology, beginning in the mid-1980's, addressed some of these concerns and did result in improvement of some properties of the wastewater.

PRESENT INVESTIGATION

This study was undertaken to identify and describe the physical and chemical properties of the bottom sediments in the upper bay and the grayish-black, suspended material present near the base of the water column, immediately above the sediment-water interface.

On December 27, 2003, bottom sediment samples were collected by a diver (Mr. Rick Schaeffer, Escambia County Health Department) from fifteen sites (see Fig. 2) within the bay using a polycarbonate tube that could be sealed from both ends, following collection. The unusual black material was observed at sites 9, 11, 13, and 14 and consisted of a sand-silt-clay-colloid mixture whose thickness varied from 4" to 6". Samples of the material were acquired at sites 9 and 14 for analysis. Similar material was also associated with sample locations M-1 and M-1-A in Elevenmile Creek.

In addition to those acquired in the bay, two additional bottom sediment samples were collected by Mr. David Ellis from the small lagoon located immediately west of the mouth of Elevenmile Creek (L-1 and L-2). Eight samples were also collected from bottom sediments in Elevenmile Creek and one sample, for "background" purposes, from Eightmile Creek where it crosses Alternate Highway 90. Locations of these samples are given in Table 1.

LABORATORY ANALYSIS

Size frequency distribution analyses were carried out on each of the samples collected in the bay and on all river samples using ASTM Method D 422-63 (combined sieve and hydrometer analysis). The dark gray sand-silt-clay colloid material was collected at sites 9

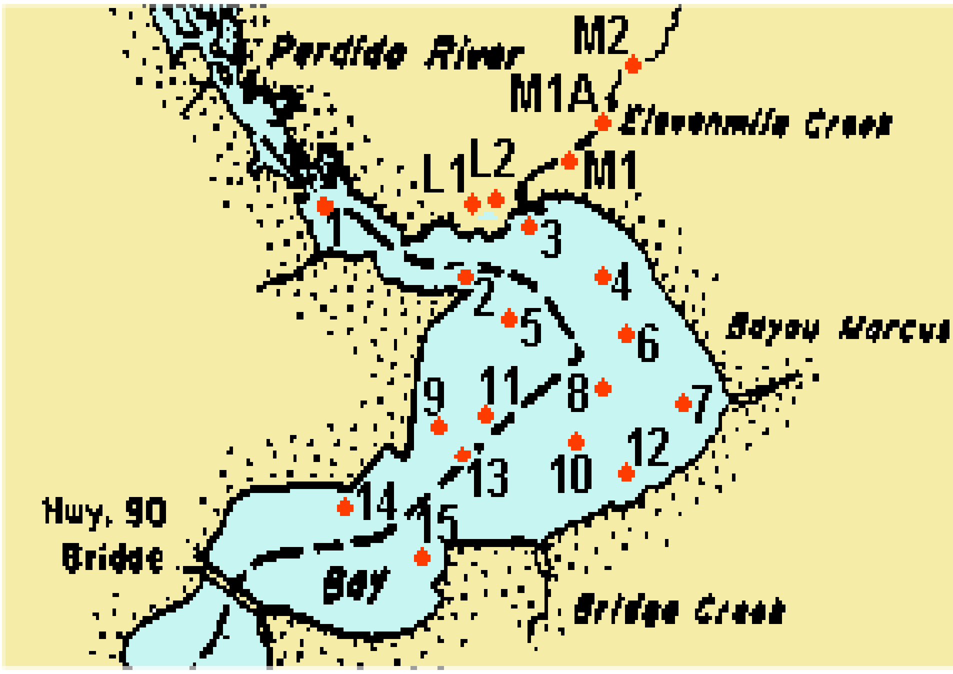

Fig. 2.– Sample location sites in upper Perdido Bay and lower reach of Elevenmile Creek.

Sample No.	Location	UTM Coordinates	
M-1	Approximately ½ mile north of mouth of Elevenmile Creek	464380	3370423
M-1-A	Approximately 3/4ths mile north of mouth of Elevenmile Creek	464806	3370849
M-2	Approximately 1 mile north of mouth of Elevenmile Creek	not determined (~1 mile from mouth)	
A	Eightmile Creek at Alternate HW-90	468811	3373535
B	Elevenmile Creek at HW-90	467774	3374060
C	Bridge at Elevenmile Creek at Alternate HW-90, just south of I-10	467114	3378111
D	Elevenmile Creek at HW-297A	468367	3279514
E	Elevenmile Creek at HW-186 (Kingsfield Road)	469148	3382417
F	West side of HW-297A, 2 miles south of HW-184 (Muscogee Road)	not determined	

Table 1.– Location map for samples collected in Elevenmile Creek and Eightmile Creek.

and 14 in the bay, and at river site M-1-A, and was analyzed by Laser Diffraction by Kenneth Pye Associates, Ltd., Berkshire, England. Sample M-2 was also analyzed by Laser Diffraction. The results of all sediment analyses are appended to this report.

Most of the samples collected from the bay and river were sent to STL Laboratories, Mobile, Alabama for determination of AOX (Adsorbable Organic Halides) and a full suite of metals, which included Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Se, Sb, Sn, Tl, Ti, V, and Zn. Three samples of the dark gray sand-silt-clay colloid material collected at sites 9, 14, and M-1-A were analyzed for AOX, semivolatiles, and the above metals. Sample 3, collected in the bay at the mouth of Elevenmile Creek, was similarly analyzed. Five samples were not chemically analyzed either because the high sand content of these samples made it unlikely that any significant adsorbable metals/organics would be present (Sites B, C, and D) or because of the close proximity of another sample that was chemically analyzed (L-1). Percent carbon and nitrogen analyses were carried out by the Dauphin Island Sea Lab on twenty-three of the samples (see Table 4). A LECO Carbon-sulphur analyzer was used to determine the carbon content of the sand-silt-clay-colloidal samples M-1-A, 9, and 14. All analyses are included in the Appendix of this report.

Results of Analyses

Bottom Sediment Particle Size.– Sediment particle size distributions were compared for samples from the upper bay from investigations carried out by Parker (1968), Isphording (1982), Livingston and Isphording (1988), and the present study, whose samples were collected in December 2003. The results are summarized in Table 2, below, for samples from each investigation whose proximity to each other would permit meaningful comparisons. Descriptions of the samples were made using Shepard's (1954) sediment classification system.

Parker 1968		**Isphording, 1982**		**Livingston and Isphording (1988)**		**This Study (Dec., 2003)**	
Sample No.	Description	Sample No.	Description	Sample	Description	Sample	Description
76	Silty-clay	39	Sand	48	Clayey-silt		
80	Clayey-silt	40	Silty-clay	50A	Sand-Silt-Clay	15	Sandy-silt
82	Silty-sand	41	Clayey-silt	14	Silty-sand	13	Clayey-silt
						(or) 11	Sandy-silt
87	Sand-Silt-Clay	42	Sand	54	Clayey-sand	12	Sand
				(or) 15	Silty-clay		
92	Silty-sand	43	Clayey-sand	12	Silty-sand	6	Silty-sand
94	Sandy-silt	44	Clayey-silt	10	Silty-clay	3	Silty-clay
85	Sand			57	Sand	5 (or 1)	Sand
84	Silty-sand					2	Silty-sand
93	Sandy-silt			56	Sandy-silt	4	Silty-sand
90	Silty-sand					7	Clayey-silt
86	Sand-Silt-Clay			53	Sand-Silt-Clay	8	Silty-sand
78	Sand-Silt-Clay			50C	Silty-Clay	14	Clayey-silt
85	Sand					9	Silty-sand

Table 2.– Particle size descriptions for sediments from upper Perdido Bay for this investigation and historical studies.

An inspection of the sediment descriptions indicates that while some minor changes in sample particle sizes have taken place, locally, in the upper bay over the past 35 years (1968

-2003) no drastic changes in the sediment regimen have occurred. Residential (and municipal) construction have undoubtedly increased runoff in the Perdido River watershed, resulting in an expansion of the size of the delta at the mouth of the Perdido River. As the delta has become larger, its trap efficiency has increased with the result that somewhat higher quantities of coarse-grained sediments are now being deposited within the delta and an increased amount of finer grained sediment is now being carried through the delta and into the bay. For example, Parker's (1968) sample 90, a sandy-silt, has now been replaced by a clayey-silt (sample 7, this study). The same is also seen where Parker's sample 85 (a sand) is now represented by a silty-sand (sample 9, this study). Exceptions to this trend are present and likely result from sediment changes influenced by erosion associated with construction in areas immediately adjacent to the bay. One apparent change that is germane to this study, however, can be seen when sediments deposited at the mouth of Elevenmile Creek are compared. Parker's (1968) sample 94 was described as a sandy-silt (the sample contained 37% sand, 50% silt, and 13% clay). Since that time, the sediments deposited at the mouth of the creek have clearly changed. The 1982 sample from the creek mouth is described as a clayey-silt; that from the 1988 study was a silty-clay, and the sample acquired in December 2003 was also a silty-clay. The latter was composed of 6% sand (a significant decrease from 1968), 46% silt, and 48% clay (a significant increase). Because the exposed sedimentary formations undergoing erosion within the Elevenmile Creek watershed are largely sands and silts, with only minor clays, the increase in the quantity of clay-size material is almost certainly anthropogenic material associated with discharge from the mill.

Laser diffraction analyses were carried out to define the particle size distribution of the dark gray sand-silt-clay-colloidal phase that was found at a number of locations in the upper bay and which is also present in Elevenmile Creek. This material is unusual in that it occurs as a colloidal-like suspension just above the sediment-water interface and consists of particles that range in size from slightly over 1 millimeter in size, down to extremely fine grained, colloidal material that is less than 0.0005 millimeters (0.5 µm) in diameter (see Table 3). This material is atypical of Perdido Bay sediments and its presence in Elevenmile Creek undoubtedly identifies it as an effluent component from the IP Mill. Further, the very fine grained nature of this material would mean that it is easily carried in the water column of Elevenmile Creek and is therefore continuously being discharged into the bay. The fact that the material is found as a suspended phase above the bottom water-sediment interface would indicate that a significant portion of the "sand" and "silt" sized components consist of both low specific gravity organic materials and flocculated clay particles.

Sample No.	Largest Size (µm)	Smallest Size (µm)	Mean (µm)	%Sand	%Silt	%Clay	%Colloid (<0.5 µm)
9	1377	0.00004	79.82	67	29	4	0.72
14	1041	0.00007	68.74	52	40	8	0.43
M-1-A	1041	0.00004	50.77	47	45	8	0.75

Table 3.– Textural properties of sand-silt-clay-colloidal phase.

Chemical Analyses.– Table 4 contains a synopsis of the combined data for the organic and inorganic chemistry of the sediment data. Of particular significance are the results of analyses for samples from the dark gray, sand-silt-clay-colloidal phase. This material possesses a number of distinctive chemical features, in addition to the unusual particle size seen on Table 3.

Samples M-1-A (Elevenmile Creek) and 14 are especially similar and are characterized by high AOX (adsorbable organic halides), aluminum, arsenic, chromium, iron, zinc and carbon levels. AOX is, historically, associated with paper mills. Though new processes in use have markedly reduced chlorine discharges from most mills, AOX compounds still provide a distinctive fingerprint for effluent discharge. These compounds continue to be discharged into Elevenmile Creek and International Paper's request for renewal of their wastewater discharge permit, dated February 18, 2004, lists a "Daily Maximum" value for AOX compounds at 234 pounds/day and a "Maximum 30 day average" value of 217 pounds per day. The permit request further estimates that the company will discharge up to 28.8 million gallons per day of treated effluent of which some 30 % of the flow will enter lower Elevenmile Creek near the mouth of the creek, and the remaining 70 % is expected to flow through a wetlands area with several small, tidal lakes before entering Perdido Bay.

Closely associated with the AOX levels are the quantities of arsenic, aluminum, iron, chromium, and lead seen in Table 4. Brim (1993) expressed concern over high levels of arsenic in filtered water samples from Elevenmile Creek that (p. 74) were "12.5 times more abundant in Elevenmile Creek than in Perdido River." The levels of arsenic (27 mg/kg) noted by Brim (1993) at his bioassay site (northernmost sample site on Elevenmile Creek) are similar to those observed in this investigation for the sand-silt-clay-colloid sample M-1-A collected near the mouth of the creek (32 mg/kg). Further, while Brim noted that the levels of all metals were below both State and EPA water quality criteria, he observed that metal levels at the northernmost sample collection site in Elevenmile Creek exceeded the widely used aluminum:metal contaminant indicator test for three metals and exceeded sediment quality guideline Threshold Effects Limit concentrations for five metals. A Florida Department of Environmental Protection memo dated 13 May 2004 also expressed concern over several metals that are associated with leachates from the mill (specifically arsenic, lead and chromium). The memo stated that maximum leachate levels of chromium were reported as high as 44.3 µg/l. Both arsenic and lead were noted as present in waste materials at concentrations greater than groundwater standards but it is not yet known whether these metals will leach at concentrations that will cause violations of these standards. All of the metals mentioned above, however, continue to be discharged into the bay and will continue to become adsorbed by the bay's sediments.

The unusually high percentages of carbon seen on Table 5, similarly, are very likely mill-related and originate from organic compounds discharged as effluent. Carbon levels for 69 bay samples given in the Livingston and Isphording study (1988) for Perdido Bay averaged 1.88 percent; similar results (1.89 percent) were obtained by Jackson (1992) for 125 samples collected from Choctawhatchee Bay. George (1988) reported average values from Pensacola Bay as 3.2 percent, Escambia Bay as 2.0 percent, and Blackwater Bay as 1.5 percent.

Table 4.– Adsorbable organic halide (AOX), metals, carbon and nitrogen in Elevenmile Creek and upper Perdido Bay samples. (H) samples are from dark gray sand-silt-clay-colloidal phase. Values shown in red are those considered anomalous or unusually high for Perdido Bay sediments.

Sample	**AOX** (µg/kg)	**Al**	**As**	**Cr**	**Fe**	**Pb**	**Mn**	**Zn**	**Avg. % Carbon**	**Avg. % Nitrogen**
		(Metal Values are in mg/kg)								
A	<2000	1800	<0.6	3.1	1700	7.9	12	12	0.31	0
B									0.064	0
C										
D										
E	<2000	680	<0.6	1.4	700	1.0	5.0	2.9	0.077	0
F	<2000	15000	2.6	14	9300	14	190	22	0.192	0
1L									4.571	0.296
2L	2300	20000	5.6	40	20000	340	86	75	9.034	0.561
M-1	520	580	<0.6	1.0	290	0.70	3.0	6.7	0.046	0
M-1-A **(H)**	7500	31000	32	25	19000	16	20	100	4.221	
M-2										
1										
2	911	3100	1.2	4.7	3900	3.8	11	10	1.504	0.094
3	880	2700	1.3	4.3	3300	2.9	16	8.6		
4	1100	7300	2.6	12.0	9500	7.4	42	32	2.124	0.150
5	1100	1300	<0.6	2.1	1500	1.7	3.5	5.6	0.402	0
6	1700	3300	1.4	5.5	4400	4.3	16	13	0.975	0.065
7	4700	28000	9.2	45	28000	30	97	86	6.197	0.3499
8	2600	16000	4.6	24	18000	13	57	54	3.244	0.2199
9	1700	9400	3.7	14	13000	7.8	37	32	3.814	0.2698
9 **(H)**	950	5300	1.4	8.7	6800	5.5	20	15	5.317	
10	4900	30000	11	41	33000	22	120	83	5.757	0.4038
11	2600	24000	8.4	34	26000	19	93	66	4.152	0.2864
12	570	440	<0.6	<1.0	710	0.5	1.1	3.1	0.115	0
13	9000	28000	10	39	45000	21	120	76	5.686	0.463
14	7000	28000	12.0	40	31000	20	130	71	5.299	0.3944
14 **(H)**	11000	34000	13.0	48	38000	24	20	90	6.855	
15	3900	19000	7.1	28	21000	15	80	58	2.406	0.1765

Livingston (1992) reported that hypoxia is exacerbated by the release of organic compounds and has caused problems in various parts of the Elevenmile Creek on different occasions. The highly elevated carbon level seen in the lagoon sample 2-L, 9.034 percent, coupled with its high AOX content (2300 µg/kg), is unquestionably a reflection of mill effluent. This lagoon is located near the mouth of Elevenmile Creek and is fed by a small channel that enters the lagoon directly from the creek. Effluent, therefore, is frequently carried into this lagoon, especially during times of high water in the bay. Note also that this sample possesses the highest nitrogen percentage for any of the samples analyzed. High nitrogen levels are characteristic of organisms that thrive on anthropogenic waste products or can be directly of effluent origin. The 2003 Industrial Wastewater request issued by International Paper, again, identifies the mill as the source for a significant amount of this component. The "Daily Maximum" of discharged ammonia was expressed as "14.2mg/l N/1409 pounds/day."

	AOX	(Metal Values are in mg/kg)							**Avg. %**
Sample	(µg/kg)	**Al**	**As**	**Cr**	**Fe**	**Pb**	**Mn**	**Zn**	**Carbon**
M-1-A **(H)**	7500	31000	32	25	19000	16	20	100	4.221
9 **(H)**	950	5300	1.4	8.7	6800	5.5	20	15	5.317
14 **(H)**	11000	34000	13.0	48	38000	24	20	90	6.855

Table 5.– Adsorbable organic halides (AOX), metals, and carbon levels from sand-silt-clay-colloid samples.

Hence, the mill signature is clearly visible in the bay itself. The high nitrogen, carbon, and AOX levels seen in samples 7, 10, 11, 13, and 14, coupled with elevated values for aluminum, arsenic, chromium, iron, and zinc leave little doubt that the principal source of these materials is from mill effluent.

REFERENCES CITED

Brim, M.S., 1993. Toxics Characterization Report for Perdido Bay, Alabama, and Florida. Publication No. PCFO-EC-93-04, U.S. Fish and Wildlife Service, Fish and Wildlife Ecological Services, Panama City, FL 32405, 134 p.

Hemming, J.M., Brim, M.S., and Jarvis, R.B., 2003. A survey of dioxin and furan compounds in sediments of Florida Panhandle Bay systems. Marine Pollution Bulletin, v. 46, No. 4, p. 512-521.

Isphording, W.C., 1982, Sedimentation, Dispersal and Partitioning of Trace Metals in Coastal Alabama Estuarine Sediments. Final Report, R/ER-4, Mississippi-Alabama SEA GRANT Consortium, Ocean Springs, MS, 15 p.

Livingston, R.J. and Isphording, W.C., 1988. Synoptic Analysis of Water and Sediment Quality in the Perdido Drainage System. Final Report, Champion International, Inc., Cantonment, FL, 54 p.

Livingston, R.J., 1992. Ecological Study of the Perdido Drainage System. Summary of Results. Environ. Planning & Analysis, Inc, Tallahassee, FL,. 66 p.

Macauley, J.M., Engle, V.D., Summers, J.K., Clark, J.R., and Flemer, D.A., 1995. Assessment of Water Quality and Primary Productivity in Perdido Bay, a Northern Gulf of Mexico Estuary. EPA /600/J-95/462. Environmental Monitoring Assessment, v. 36, No. 3, p. 191-205.

Parker, N.M., 1968. A Sedimentologic Study of Perdido Bay and Adjacent Offshore Environments. Sedimentological Research Laboratory Contribution No. 23, Florida State University, Tallahassee, FL, 57 p.

Schropp, S.J., Calder, D., Sloane, G.M., Carlton, J.C., Halcomsb, G.L., Windom, H.L., Taylor, B.R., 1991. A report on Physical and Chemical Processes Affecting the Management of Perdido Bay. Results of the Interstate Project, Florida Dept. of Env. Prot. And Ala. Dept. of Environ. Manag.

Shepard , F., 1954. Nomenclature based on sand-silt-clay ratios. Jour. Sedim. Petrol., v.24, p. 151-158.