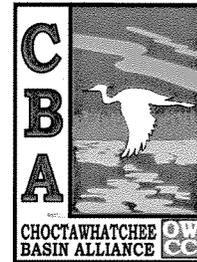


# SEDIMENT ANALYSIS IN CHOCTAWHATCHEE BAY

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## Abstract

A habitat quality survey was conducted in Choctawhatchee Bay at the request of the U.S. Fish and Wildlife Service. Hogtown Bayou in southern Choctawhatchee Bay is a documented frequent location and winter holding area for the Gulf sturgeon, *Acipenser oxyrinchus desotoi*, a federally listed endangered species. Sediment sampling was selected to characterize the chemical integrity of Choctawhatchee Bay. Sampling sites were chosen to represent the extent of the bay and to provide particular focus on certain areas. Focus areas were selected based on historical data from peer review literature and personal knowledge of local citizens.

Sediment samples were collected from 13 sites in Choctawhatchee Bay in a collaborative effort with the U.S. Fish and Wildlife Service and Choctawhatchee Basin Alliance staff. Analyses on sediment samples included metals, pesticides, organochlorines (OC), and polycyclic aromatic (PAH) and aliphatic hydrocarbons (AH). Sediment samples collected from Mullet Creek, Rocky, Tom's, and Hogtown bayous were also subjected to dioxin compound analysis. Overall, sediment contamination in Choctawhatchee Bay was low and found to be comparable to other bays in the Florida panhandle. However, sites in Mullet Creek (pesticides, OC, PAH, AH, metals), Tom's Bayou (OC, AH, metals), Garnier's Bayou (OC, PAH, AH, metals) and Cinco Bayou (OC, PAH) possessed high concentrations of sediment contaminants relative to other sites in Choctawhatchee Bay necessitating further investigation.

## Introduction

Choctawhatchee Bay is located in the western Florida panhandle. The system was originally oligohaline with input primarily from Choctawhatchee River which terminates at the east end of the bay. The Choctawhatchee Bay and River watershed has a drainage area of 5,349 square miles in Florida and Alabama (NFWMD, 1996). Historically, sea water input entered the bay via only periodic breakthroughs to the Gulf of Mexico. A permanent pass to the Gulf of Mexico was opened in 1929 at the west end of the bay (Livingston, 1987). Marine Gulf of Mexico waters flowed through the western pass and combined with the freshwaters from the Choctawhatchee River creating an estuary in transition.

Choctawhatchee Bay has an east to west longitudinal axis that stretches 27 miles long, but is only four miles wide. Average depth of the bay is 22 feet (U.S. Department of Commerce and NOAA, 1997). Choctawhatchee Bay has several small tributaries on the northern shore. Eglin Air Force Base occupies the majority of the immediate drainage basin on the northern shore. While the northern shore has experienced some development, the southern shore of Choctawhatchee Bay has been the site of an exponential increase in urbanized growth over the last few decades (NOAA, 1997).

Previous studies have identified high metal concentrations and low dissolved oxygen in Choctawhatchee Bay and adjoining bayous (Livingston, 1987). Some have speculated that the low dissolved oxygen concentrations result from the unique nature of Choctawhatchee Bay, particularly the dramatic convergence of fresh and marine waters (NOAA, 1997). Choctawhatchee Bay is stratified via a halocline separating freshwater at the surface from

marine waters at the bottom. The lack of mixing and gas exchange between the marine and freshwaters creates a large anoxic zone in the marine (bottom) bay layer is capable of supporting scant life (Livingston, 1987).

A literature review identified areas of concern in Choctawhatchee Bay and distinguished possible problem sources (Livingston, 1987; NOAA, 1997; NFWFMD, 1996). This review revealed that stormwater runoff and increased residential development were responsible for increased nutrient loading to the bay. It was further suggested that these nonpoint source inputs were exacerbating problems in the bayous where water quality was often lower (CBA, 1998). Other reports showed that Choctawhatchee Bay had higher mean organic nitrogen and organic carbon than the four other northwest Florida bays (Escambia, East, Panama City, and Pensacola bays) according to figures from the Environmental Protection Agency (EPA) and the U.S. Army Core of Engineers (Blaylock, 1983). Choctawhatchee Bay also had the third highest mean total phosphorus level (NOAA, 1997). Dr. Livingston, Director of the Center for Aquatic Research and Resource Management and Professor at Florida State University, cited anthropogenic effects and marinas for the cause of harmful stormwater runoff in his 1987 study of the Choctawhatchee Bay system (Livingston, 1997). In 1997 the National Oceanic and Atmospheric Administration (NOAA) performed a study on the bays in the Florida panhandle (NOAA, 1997). Minimal metal enrichment was found bay-wide, but elevated metal concentrations were recorded in Destin Harbor and near Boggy Point. NOAA also found elevated levels of organic contaminants at several locations including: Destin Harbor, Santa Rosa Sound and Boggy Point. Reported concentrations

were of the highest in the nation at the time (U.S. Department of Commerce and NOAA, 1997).

Habitat quality of aquatic systems has been evaluated via surveys of sediment contamination (O'Connor, 1991; US NOAA, 1991; Bolton *et al.*, 1985). The challenge lies in the interpretation of ecological risk posed by sediment contamination (Long *et al.*, 1995). For this reason, many have provided numeric criteria based on reported effects of exposure as a means to estimate relative risk to living organisms (Buchman, 1999; Long *et al.*, 1995; MacDonald, 1993; Persaud, 1992; Di Toro *et al.*, 1991; Long and Morgan, 1990; US EPA, 1989).

To assess the overall ecosystem health of Choctawhatchee Bay, a sediment survey was conducted. The results of this survey were compared to the findings of Long *et al.* (1995) to estimate risk to living resources. Long *et al.* (1995) developed Effects Range Low (ERL) and Effects Range Median (ERM) criteria for evaluating sediment contamination in marine and estuarine environments. Sediment contaminant concentrations exceeding the criterion ERL indicated that adverse negative effects on living resources might increase in incidence from rare to occasional. Sediment contaminant concentrations exceeding the ERM may indicate adverse effects will occur frequently.

## METHODS

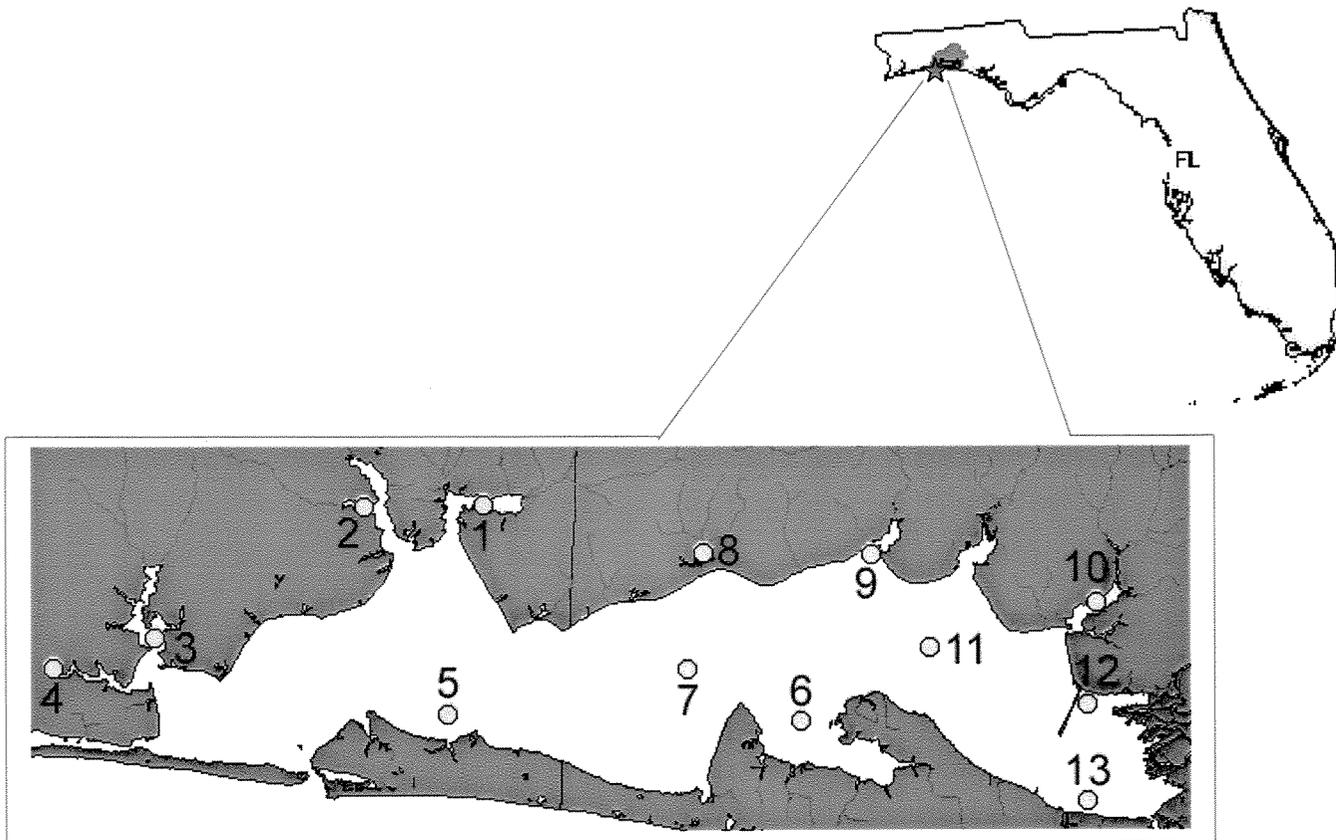
### Sampling Design

The locations of the individual sampling stations were chosen based on historical data from literature review and personal communications with resident scientists. Stations were chosen based on anticipated sediment composition and reported contamination. Station locations were pre-selected, but were altered in cases where field collection of sediments was not feasible.

### Sample Collection

Thirteen sediment samples were taken from Choctawhatchee Bay over a 2-day period in August 2002 (Figure 1, Table 1) according to the standard operating procedures (PCFO-EC SOP 004) for field collection of sediment samples (Appendix A). The vessel was navigated to the pre-determined stations; if the station was inaccessible or if the sediments at the location were comprised of only sand with no silt or clay components, an alternate location was chosen. In each case the original or the first alternate location was sufficient for sampling. Vessel navigation and positioning were aided by a Garmin Global Positioning System (GPS) 48 Personal Navigator unit and a supplemental navigation map.

Composite samples consisted of three 200 milliliter sub-samples. Samples were collected with a standard ponar 316 stainless steel grab and deposited in a stainless steel tray. The grab sampler and sampling utensils were acid washed with 10% dilute nitric acid, acetone, deionized water and ambient site water before and after each sample was collected. Three shallow grabs were most often sufficient for collecting samples. A stainless steel spoon was used to collect two scoops from the central portion of each grab. Sub-samples were combined in plastics bags, labeled, and placed on ice in a cooler.



**Figure 1** Choctawhatchee Bay sediment stations sampled in August 2002.

**Table 1** Sample information for sediment samples taken by CBA and U.S. Fish and Wildlife Service in the Choctawhatchee Bay in August 2002, Station ID, Location, Latitude and Longitude (decimal degrees).

Station ID	Location	Latitude	Longitude
CBA 1	Rocky Bayou	30.50317	-86.43550
CBA 2	Tom's Bayou	30.50117	-86.49150
CBA 3	Garnier's Bayou	30.44617	-86.58917
CBA 4	Cinco Bayou	30.43233	-86.63667
CBA 5	Mid Bay off Piney Point	30.41667	-86.45000
CBA 6	Hogtown Bayou	30.41667	-86.28333
CBA 7	Mid Bay off Fourmile Point	30.43717	-86.33750
CBA 8	Mullet Creek	30.43233	-86.63667
CBA 9	Mouth of Basin Bayou	30.48550	-86.25167
CBA 10	La Grange Bayou	30.46717	-86.14567
CBA11	Mid Bay off Alligator Point	30.44750	-86.22367
CBA12	East end of Bay North shore	30.42550	-86.14917
CBA13	East end of Bay South shore	30.38533	-86.14900

Each sample was split into different containers relevant to their analytical needs with stainless steel tools that were washed with 10% nitric acid, acetone and deionized water between each sample. Each sample was separated into a clear jar with a Teflon lined lid and two new plastic bags. Samples 1, 2, 6 and 8 were also dolled into brown glass jars with Teflon lined lids to be sent for dioxin compound analysis.

All sediment samples were packed tightly into coolers with ice and bubble wrap. The coolers were shipped by overnight courier with chain of custody that indicated the condition of the samples and the time they were received at the laboratories.

### **Chemical Analysis**

All 13 samples were analyzed for metals, organochlorines, pesticides, aliphatic and polycyclic aromatic hydrocarbons (Table 2) by the Geochemical and Environmental Research Group located on the Texas A&M University campus in College Station, Texas. Wellington Laboratories of Ontario, Canada analyzed selected samples for dioxin and furan compounds. Details of the analytical procedures performed at each lab are described in Appendix H.

**Table 2** Chemical analytes measured in sediment samples taken in Choctawhatchee Bay in August 2002.

<b>Metals</b>	<b>Polycyclic Aromatic Hydrocarbons</b>	<b>Aliphatic Hydrocarbons</b>	<b>Organochlorines and Pesticides</b>
*Silver	*Naphthalene	n Dodecane	Hexachlorobenzene
Aluminium	*Fluorene	n Tridecane	a, b, g and d-BHC
*Arsenic	*Phenanthrene	n Tetradecane	Oxychlorane
Boron	*Anthracene	Cyclohexane	Heptchlor
Barium	*Fluoranthrene	Pentadecane	a, g-Chlordane
Beryllium	*Pyrene	n Hexadecane	t-Nonachlor
*Cadmium	*Benz(a)anthracene	n Heptadecane	Toxaphene
*Chromium	*Chrysene	Pristane	*Total PCBs
*Copper	Benzo(b)fluoranthrene	n Octadecane	*DDT analytes
Iron	Benzo(k)fluoranthrene	Phytane	Dieldrin
*Mercury	Benzo(e)pyrene	n Nonadecane	cis-Nonachlor
Manganese	*Benzo(a)pyrene	n Ecosane	Mirex
Molybdenum	Dibenzo(a,h)anthracene	Total AHs	Dicofol
*Nickel	Benzo(g,h,I)perylene		Dicamba
*Lead	*Total PAHs		Dichloprop
Selenium			Silvex
Strontium			2,4-D
Thallium			2,4,5-T
Vanadium			2,4-DB
*Zinc			Pentachlorophenol

\*Sediment Quality Guidelines available from Long *et al.* 1995

## **Risk Analysis**

The sediment quality guidelines used in this report to interpret much of the sediment data were founded on an effects-based system produced by Long *et al.* (1995). It should be noted that these are interpretive guidelines only. The guidelines are based on two concentration values for each analyte, the ERL and ERM, which delineates three relative safety ranges. The first range includes contaminant concentration values which fall below the ERL. Sediments in this range will cause minimal effects with direct contact and adverse biological effects would rarely be observed. The next range has a lower concentration limit at the ERL and an upper limit at the ERM. Sediment concentrations within this possible effects range would occasionally cause adverse effects in animals with direct contact to the sediments. The third range includes sediment concentration values that are equal to and above the ERM. Biological adverse effects would frequently occur to animals if they were to come in contact with sediments within this probable effects range (Long *et al.* 1995).

Sediment stations were evaluated and scored for relative risk from sediment contamination. This was done for those analytes for which sediment quality guidelines exist from Long *et al.* (1995) including: polycyclic aromatic hydrocarbons (PAHs), organochlorines (OCs), and metals. The system consisted of assigning one point for each chemical concentration that exceeded the ERL value but fell below the ERM value (possible effects range), and two points for each concentration that was above the ERM value (probable effects range). The score for all analytes detected within a sample were then summed to provide a cumulative risk for each sample by chemical class and total analytes.

A similar procedure was followed for the analytes in the aliphatic hydrocarbon (AH) and phenoxy herbicide (PH) chemical classes. However, since sediment quality criteria were not available for these compounds, cumulative risk for each respective class was calculated relative to bay-wide mean concentrations. It was assumed that most elevated sediment contamination would be concentrated near the sources of contamination because the large bay would rapidly dilute most analytes. Using this assumption, it was further given that substantial variation from the mean concentration would indicate differences from background levels. Since the degree of variation about the mean would increase with the variability of the data, standard deviations of the mean were used to determine areas of relatively high concentrations of these contaminants. Sediment concentrations in excess of one deviation above the mean concentration of a given analyte among all 13 sites were given a score of 1. Concentrations greater than 2 standard deviations from the mean were given a score of 2. Scores for each site were summed for PH and AHs, but were not included in the multiple analyte cumulative total like the analytes with sediment quality criteria.

Dioxin toxicity equivalents (TEQs) were calculated for 17 dioxin and furan metabolic analytes found in four sediment samples collected in Choctawhatchee Bay. Assignment of risk levels were based on U.S. Environmental Protection Agency (US EPA) estimated risk to aquatic life associated with dioxin exposure (US EPA, 1993). Using these criteria, a relative risk level was established via Hemming *et al.* (2003) as follows: 0-10 ppt = no risk, 10.01-20 ppt = lowest possible risk level, 20.01-30 ppt = possible risk, 30.01-50 ppt = probable risk, and 50.01-80 = risk to some portion of resource populations if they directly come into contact with the sediments in the sampling areas.

## Results

Data are provided in tables and spatially relevant figures. Figures are qualified by estimated sediment exposure risk. Exposure risks were estimated using the sediment quality guidelines of Long *et al.* (1995), deviations from bay-wide mean concentrations, and U.S. Environmental Protection Agency guidelines. Distribution of sediment composition profiles are provided in Table 3 and the composition distribution is shown in Figure 2. Analytes equal to or exceeding sediment quality guidelines (Long *et al.* 1995) are displayed: metals (Table 4), OCs (Table 5) and PAHs (Table 6). Relatively high concentrations for AHs (Table 7) and PHs (Table 8) are provided as well. Figures and estimated risk assessments are provided for three categories of analytes: PAHs (Figure 3), OCs (Figure 4) and metals (Figure 5). A cumulative risk level (Figure 6) was determined by adding scores from all analyte categories at each site. An estimated risk level and need for further evaluation are shown for PHs (Figure 8) and AHs (Figure 9). Results for the dioxin toxicity equivalents (TEQs) calculations are displayed in Table 9 and are spatially illustrated in Figure 7. Complete listings for the raw data collected are provided in the Appendices.

**Table 3** Percent composition of sediment samples taken in Choctawhatchee Bay in August 2002, Gerg ID, Client ID, % Sand, % Silt and % Clay.

Gerg ID	Client ID	% Sand	% Silt	% Clay
C42411	CBA1	32.8	37.7	29.5
C42412	CBA2	46.0	39.7	14.3
C42413	CBA3	23.8	49.8	26.4
C42414	CBA4	97.3	2.2	0.5
C42415	CBA5	90.7	5.2	4.1
C42416	CBA6	95.6	1.8	2.6
C42417	CBA7	42.7	29.9	27.5
C42418	CBA8	76.6	23.4	0.0
C42419	CBA9	99.6	0.2	0.2
C42420	CBA10	27.1	38.4	34.5
C42421	CBA11	39.7	28.1	32.2
C42422	CBA12	73.4	16.8	9.8
C42423	CBA13	87.2	6.8	6.0

**Table 4** Sediment samples taken in Choctawhatchee Bay in August 2002 with metal analytes equal to or exceeding sediment quality guidelines (Long *et al.* 1995): Site, Analyte, Sediment Concentration (ug/g, ppm, dry weight), Effects Range Low (ERL), Effects Range Median (ERM).

Site	Analyte	Sediment Concentration	ERL	ERM
CBA1	Arsenic	17.15	8.2	70
CBA2	Arsenic	11.59	8.2	70
"	Copper	183.83	34	270
"	Lead	57.25	46.7	218
"	Mercury	0.34	0.15	0.71
"	Silver	1.52	1	3.7
CBA3	Arsenic	21.75	8.2	70
"	Lead	58.14	46.7	218
"	Mercury	0.19	0.15	0.71
"	Nickel	22.37	20.9	51.6
CBA7	Arsenic	30.00	8.2	70
"	Nickel	27.96	20.9	51.6
CBA8	Mercury	0.18	0.15	0.71
CBA10	Arsenic	14.66	8.2	70
CBA11	Arsenic	28.82	8.2	70
"	Nickel	25.86	20.9	51.6

**Table 5** Sediment samples taken in Choctawhatchee Bay in August 2002 with organochlorines and pesticide analytes equal to or exceeding sediment quality guidelines (Long *et al.* 1995): Site, Analyte, Sediment Concentration (ng/g, ppb, dry weight), Effects Range Low (ERL), Effects Range Median (ERM).

<b>Site</b>	<b>Analyte</b>	<b>Sediment Concentration</b>	<b>ERL</b>	<b>ERM</b>
CBA1	Total DDT	6.13	1.58	46.1
CBA2	Total DDT	43.20	1.58	46.1
"	Total PCBs	221.63	22.7	180
CBA3	Total DDT	25.25	1.58	46.1
"	Total PCBs	34.43	22.7	180
CBA4	Total PCBs	23.60	22.7	180
CBA7	Total DDT	2.69	1.58	46.1
CBA8	Total DDT	36.17	1.58	46.1
"	Total PCBs	103.75	22.7	180
CBA10	Total DDT	3.24	1.58	46.1
CBA11	Total DDT	2.77	1.58	46.1

**Table 6** Sediment samples taken in Choctawhatchee Bay in August 2002 with polycyclic aromatic hydrocarbon analytes equal to or exceeding sediment quality guidelines (Long *et al.* 1995): Site, Analyte, Sediment Concentration (ng/g, ppb, dry weight), Effects Range Low (ERL), Effects Range Median (ERM).

Site	Analyte	Sediment Concentration	ERL	ERM
CBA2	Acenaphthylene	94.7	44	640
"	Anthracene	191.3	85.3	1100
"	Benzo(a)anthracene	345.2	261	1600
"	Benzo(a)pyrene	436.1	430	1600
"	Dibenzo(a,h)anthracene	66.4	63.4	260
"	Total PAHs	12935.3	4022	44792
CBA3	Acenaphthylene	56.3	44	640
"	Anthracene	115.4	85.3	1100
"	Total PAHs	8382.7	4022	44792
CBA4	Anthracene	103.8	85.3	1100
"	Benzo(a)anthracene	437.5	261	1600
"	Benzo(a)pyrene	599.6	430	1600
"	Chrysene	474.5	384	2800
"	Dibenzo(a,h)anthracene	86.7	63.4	260
"	Fluoranthene	1491.6	600	5100
"	Pyrene	1331.3	665	2600
"	Total PAHs	21618.0	4022	44792
CBA8	Total PAHs	719.6	4022	44792

**Table 7** Sediment samples taken in Choctawhatchee Bay in August 2002 with relatively high concentrations of aliphatic hydrocarbon: Site, Analyte, Sediment Concentration (ug/g, ppb, dry weight), mean+1 standard deviation (SD), mean+2 standard deviations (SD).

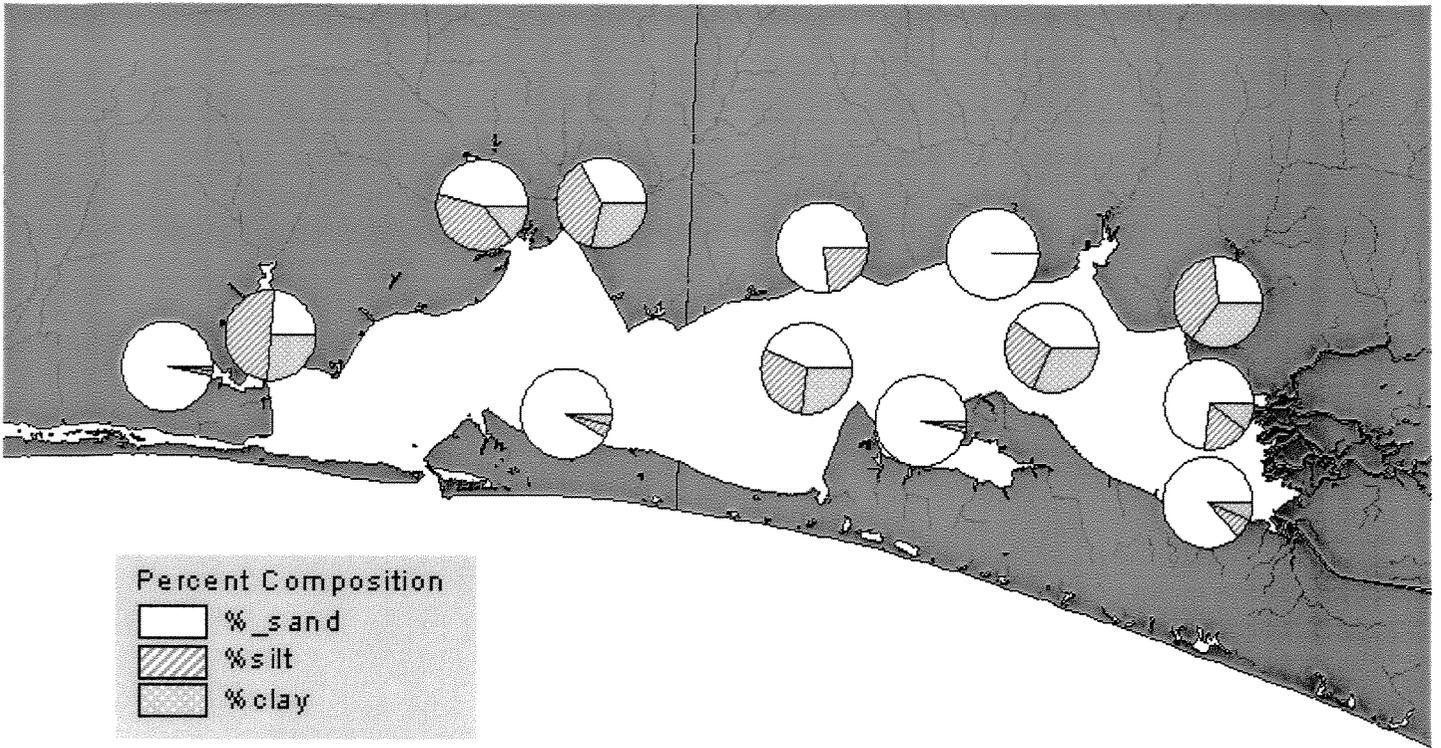
<b>Site</b>	<b>Analyte</b>	<b>Sediment Concentration</b>	<b>mean+1SD</b>	<b>mean+2SD</b>
CBA1	n-C10	20	17	28
"	n-C11	82	64	104
"	n-C15	238	101	161
CBA2	n-C10	19	17	28
"	n-C12	7	3	6
"	n-C13	12	9	14
"	n-C14	16	11	16
"	n-C17	1382	1240	1927
"	Pristane	51	49	82
CBA3	n-C10	33	17	28
"	n-C11	130	64	104
"	n-C13	13	9	14
CBA8	n-C16	81	37	58
"	n-C17	2411	1240	1927
"	Pristane	116	49	82
"	n-C18	302	114	196
"	Phytane	218	83	142
"	n-C19	2700	979	1719
"	n-C20	666	250	432
"	n-C21	1921	783	1294
"	n-C22	1591	599	1028
"	n-C23	4165	1584	2704
"	n-C24	3060	1184	2004
"	n-C25	11334	4610	7698
"	n-C26	5174	1987	3371
"	n-C27	42436	15441	27055
"	n-C28	11021	4056	7058
"	n-C29	111996	40896	71498
"	n-C30	21874	7949	13938
"	n-C31	43749	16402	28232
"	n-C32	3197	1239	2094
"	n-C33	8504	3370	5630
"	n-C34	47711	17171	30299
"	Total Alkanes	324262	119800	207926
CBA10	n-C13	10	9	14
CBA11	n-C12	6	3	6
"	n-C14	12	11	16

**Table 8** Sediment samples taken in Choctawhatchee Bay in August 2002 with relatively high concentrations of chlorophenoxy herbicides: Site, Analyte, Sediment Concentration (ug/g, ppb, dry weight), mean+1 standard deviation (SD), mean+2 standard deviations (SD).

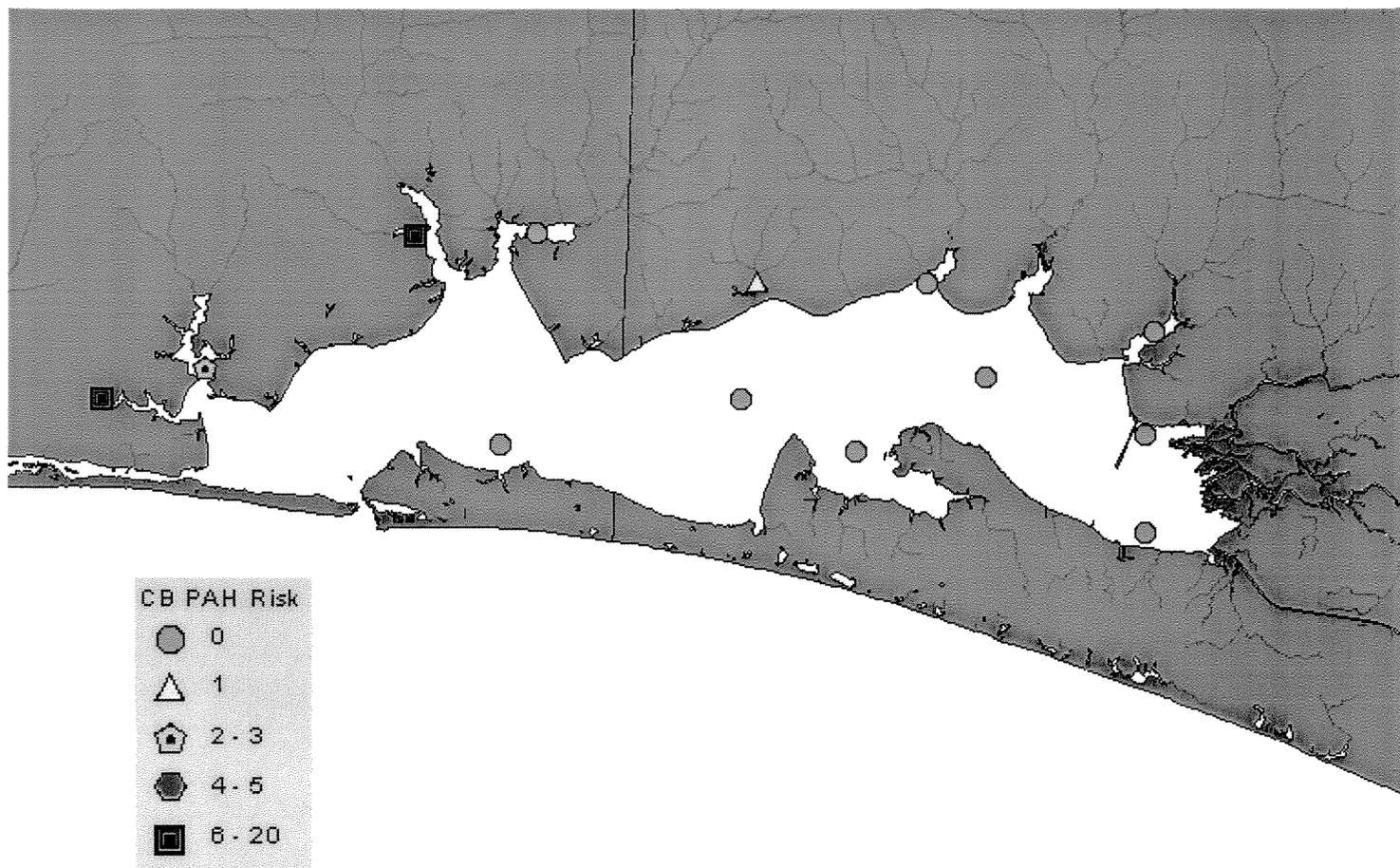
Site	Analyte	Sediment		
		Concentration	mean+1SD	mean+2SD
CBA1	Dicamba	320	210	355
"	2,4-D	370	304	516
"	Dichlorprop	620	461	781
"	2,4-DB	260	211	339
CBA2	2,4,5-T	1322	567	971
CBA8	Total Phenoxy Herbicides	4551	1986	3300
"	Dicamba	451	210	355
"	2,4-D	714	304	516
"	Dichlorprop	1049	461	781
"	2,4-DB	445	211	339
"	2,4,5-T	744	567	971
"	Silvex	1147	440	751

**Table 9** Dioxin total toxicity equivalents (TEQs) relative to 2,3,7,8-tetrachlorodibenzodioxin in sediment samples taken in Choctawhatchee Bay in August 2002: Site, TEQs (ppt).

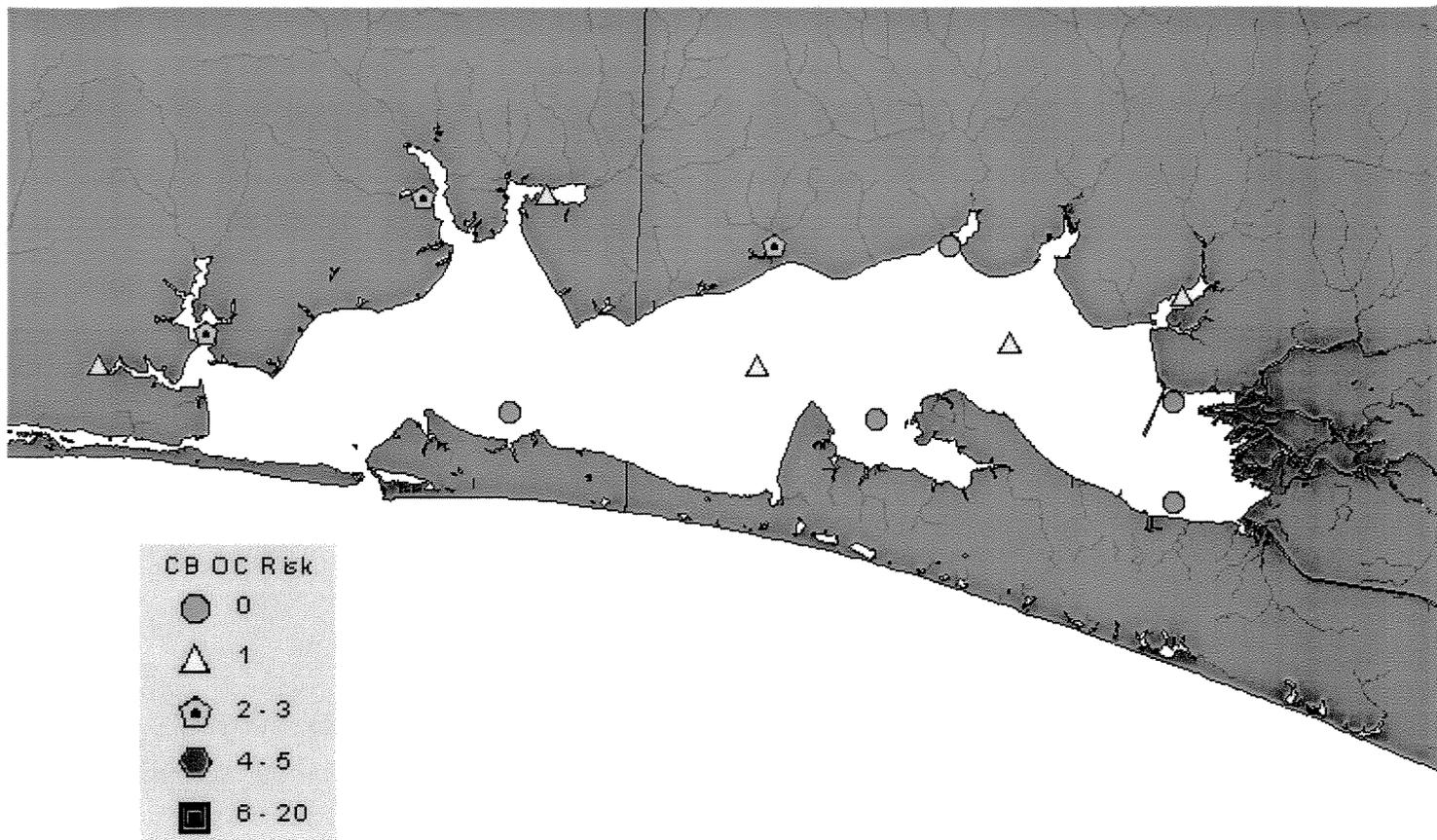
Site	Total TEQs
CBA 1	11.3
CBA 2	25.1
CBA 6	0.787
CBA 8	8.11



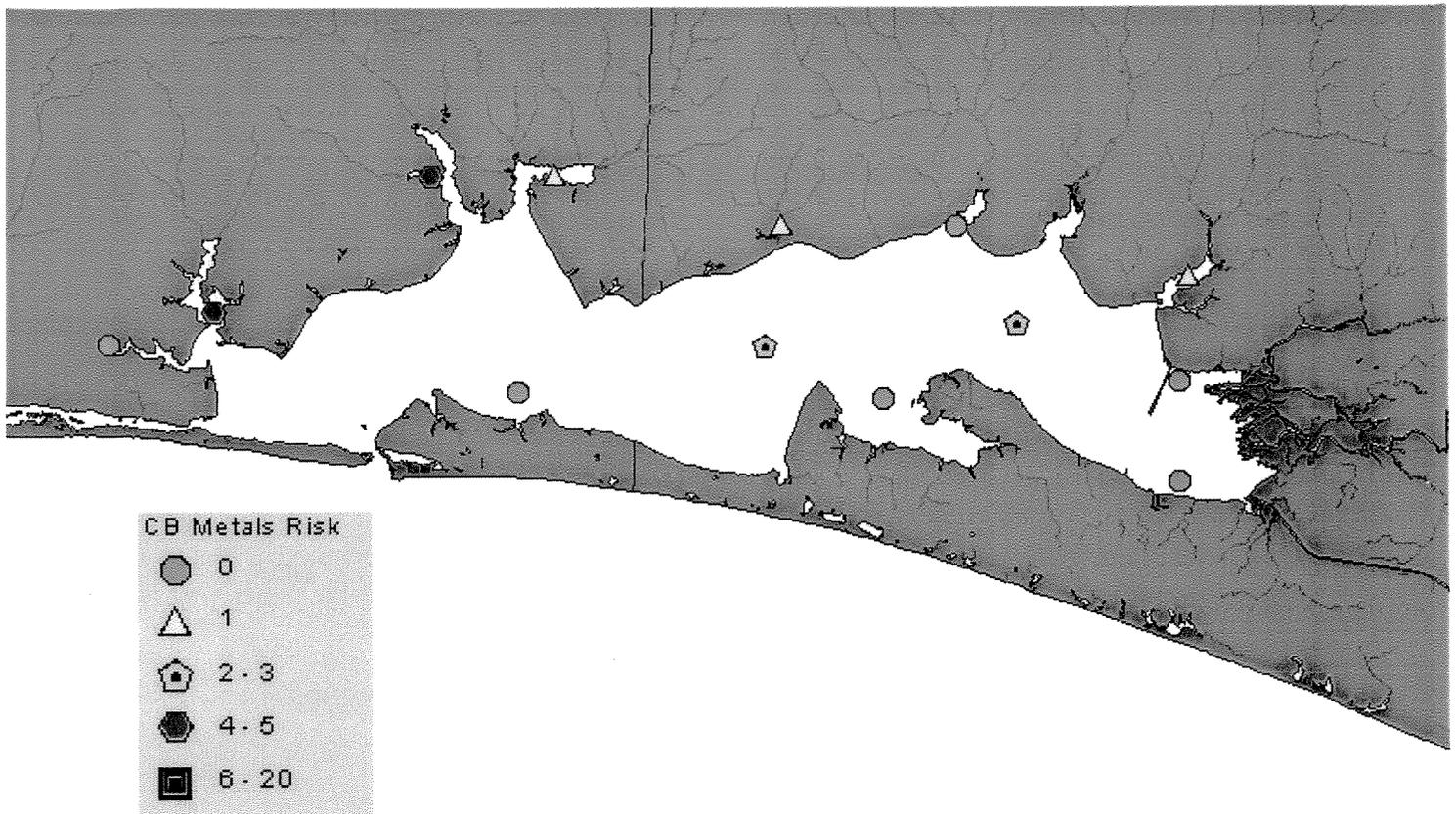
**Figure 2** Sediment composition distribution for sediment samples taken in Choctawhatchee Bay, August 2002.



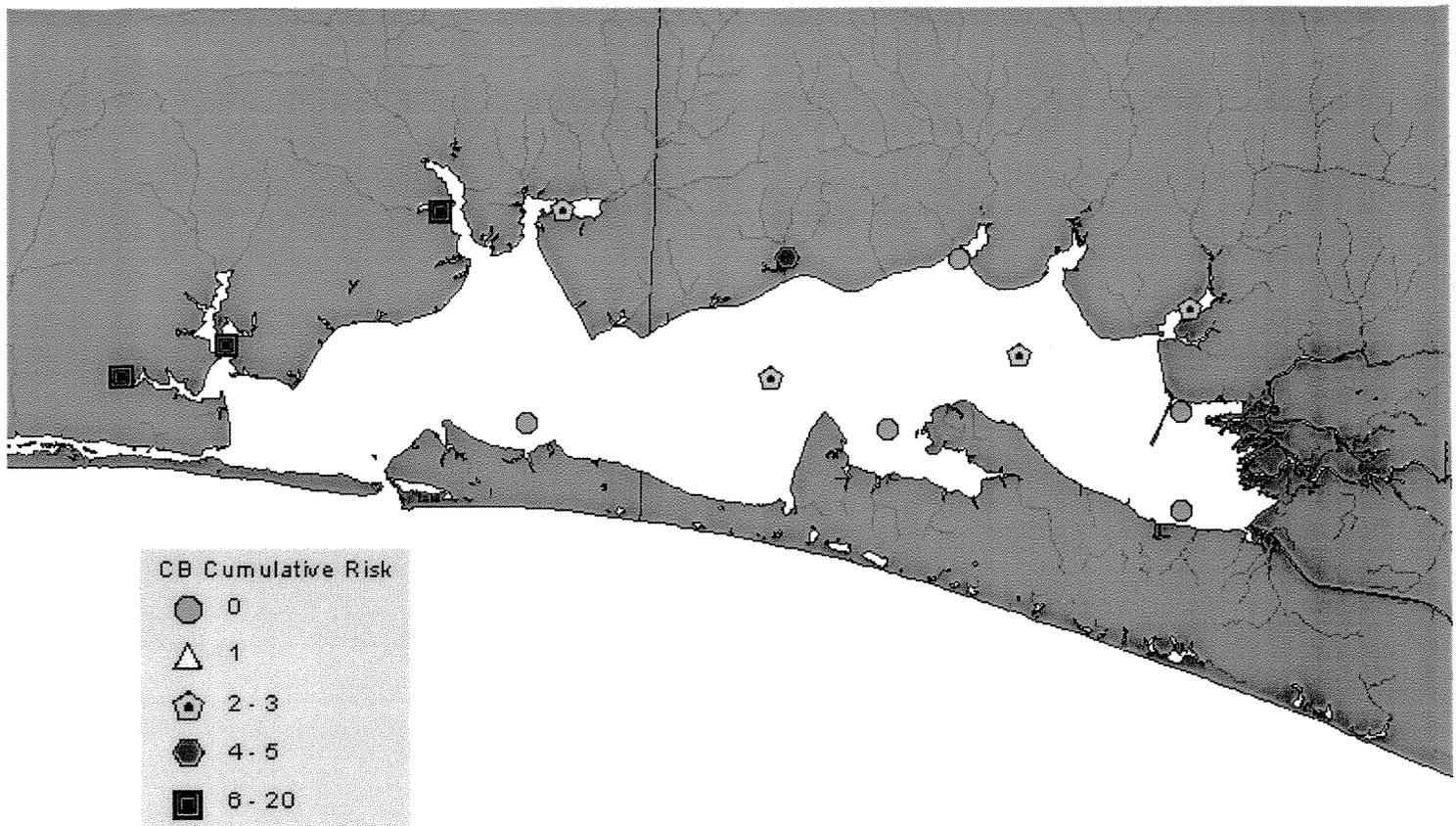
**Figure 3** Estimated risk rank for polycyclic aromatic hydrocarbon (PAH) analytes in sediment samples taken from Choctawhatchee Bay, 2002, exceeding Long *et al.* (1995) sediment quality guidelines.



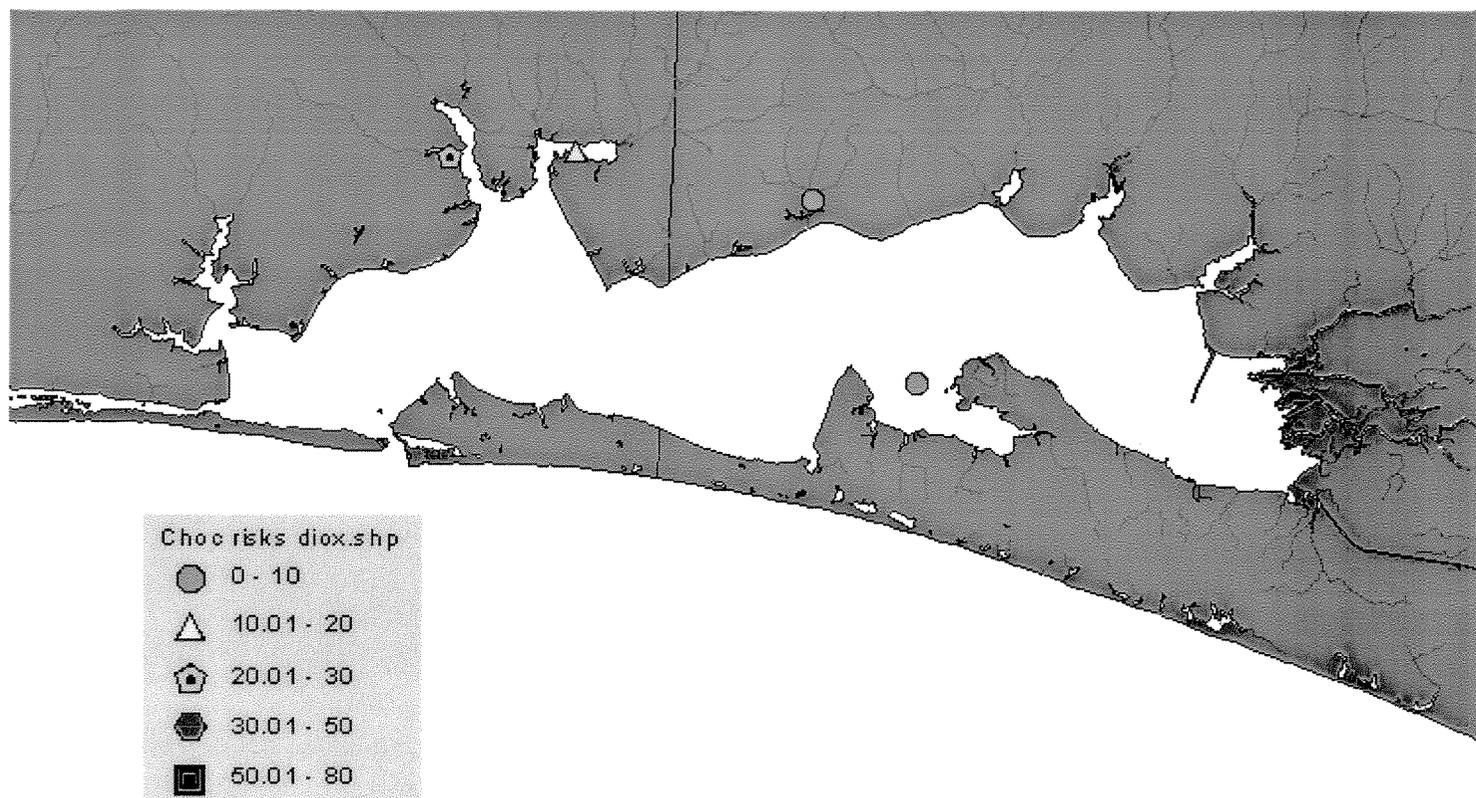
**Figure 4** Estimated risk rank for organochlorine (OC) analytes in sediment samples taken from Choctawhatchee Bay, 2002, exceeding Long *et al.* (1995) sediment quality guidelines.



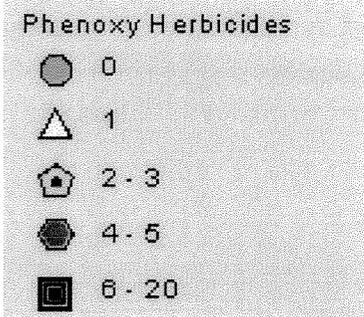
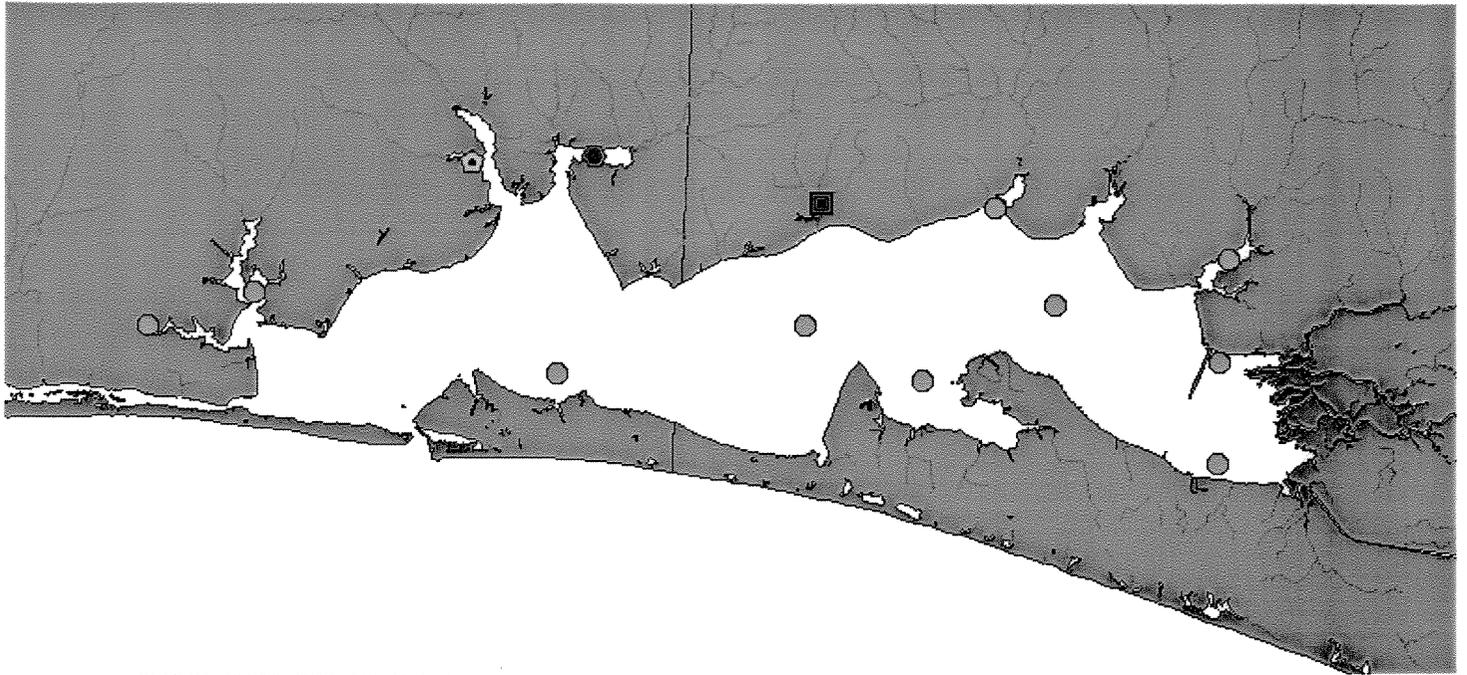
**Figure 5** Estimated risk rank for metal analytes in sediment samples taken from Choctawhatchee Bay, 2002, exceeding Long *et al.* (1995) sediment quality guidelines.



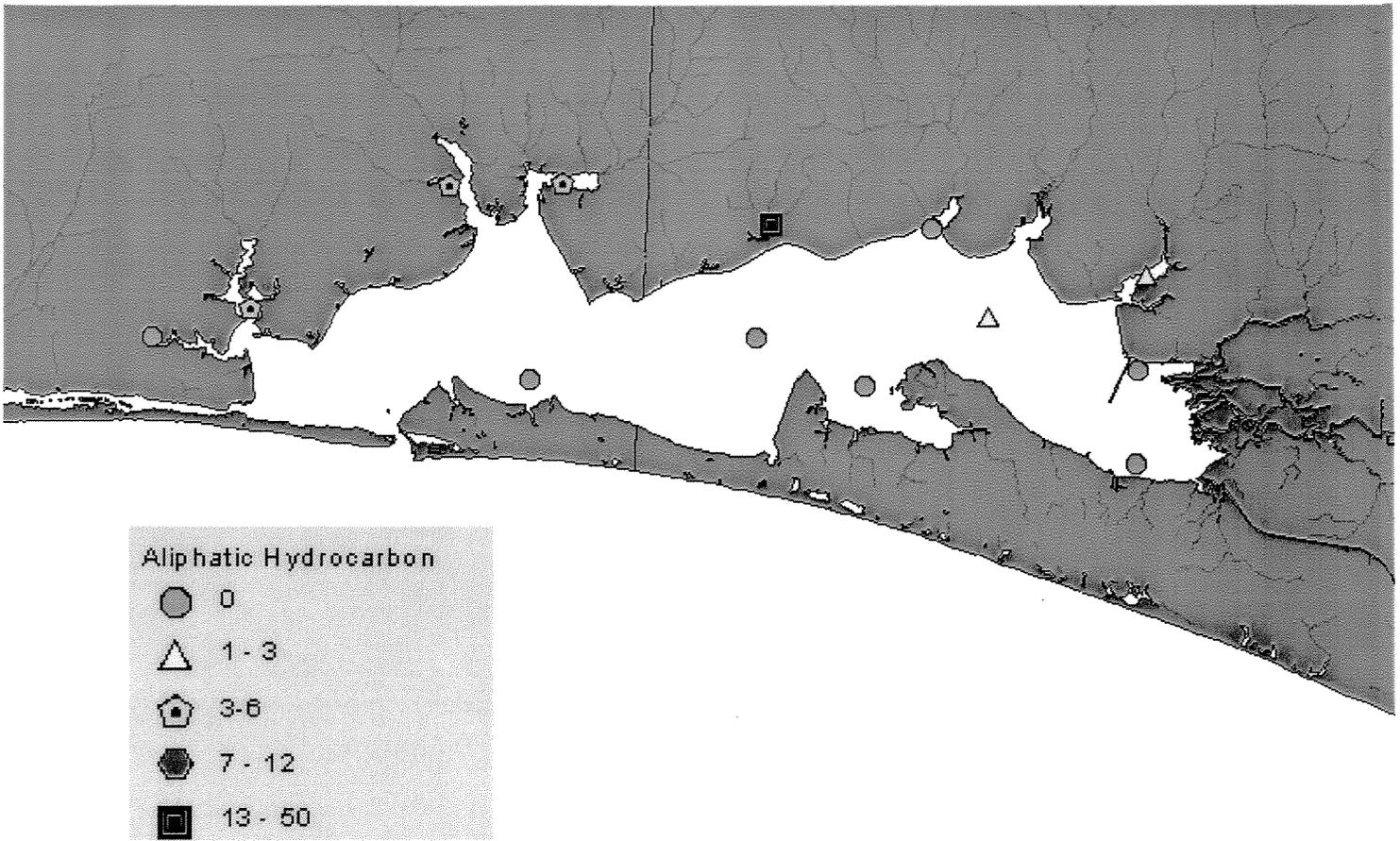
**Figure 6** Estimated risk rank for cumulative analytes (PAH, OC and Metals) in sediment samples taken from Choctawhatchee Bay, 2002, exceeding Long *et al.* (1995) sediment quality guidelines.



**Figure 7** Dioxin toxicity equivalents (TEQs) calculated for dioxin and furan metabolic analytes found in sediment samples collected from four sites in Choctawhatchee Bay, 2002.



**Figure 8** Estimated risk and need for further evaluation ranking scores for phenoxy herbicides in sediment samples collected in Choctawhatchee Bay, 2002.



**Figure 9** Estimated risk and need for further evaluation ranking scores for aliphatic hydrocarbons in sediment samples collected in Choctawhatchee Bay, 2002.

## DISCUSSION

Habitat degradation in Choctawhatchee Bay has been reported (Blaylock, 1983; Livingston, 1997; NOAA, 1997). This study was designed to evaluate Choctawhatchee Bay to assess the current status of the bay, particularly in areas previously reported to be contaminated. Data was not dissimilar from earlier reports.

### Sediment Composition

Sediment composition in Choctawhatchee Bay was comparable to other bay systems of the northeastern Gulf of Mexico (Brim *et al.*, 1998; Brim, 2000; Hemming *et al.* 2002). Sand fractions in Choctawhatchee Bay sediments ranged from a low 27.1% to a high of 99.6% with only 5 of the 13 samples containing less than 70% sand. The silt and clay fractions were correspondingly variable and reciprocal to the sand fractions. Silt ranged from 1.8% to as high 49.8% and clay range from 0.2 to 32.2%. Most samples collected from the deeper central portions of the bay were composed of silt, while sandy samples were collected from the shallow perimeter of Choctawhatchee Bay. Typical samples were a dark olivine color with an occasional sulfurous odor.

### Metals

Arsenic, copper, lead, mercury, nickel, and silver were in excess of sediment quality guidelines at the Effects Range Low (ERL) level, but none exceeded the Effects Range Median (ERM) criteria (Long *et al.*, 1995). Sediment arsenic concentrations most frequently exceeded the sediment criterion with almost half the samples expected to increase the incidence of adverse negative effects on living resources from rare to occasional (ERL, Long

*et al.*, 1995). Mercury and nickel concentrations exceeded their respective ERLs at 3 sites each. Lead surpassed its ERL at 2 sites and both copper and silver at 1 site each. The sediment sample from Tom's Bayou in the northwestern bay possessed all the above metals, except nickel, at concentrations exceeding ERL criteria. Concern prompted an environmental study by the Department of Environmental Protection in the late 90's after the Spence Boat Yard in Tom's Bayou burned to the ground in January of that year (Butts, 1997). Similarly, the adjacent Garnier's Bayou sediments contained all the listed metals, but silver and copper, above the ERL criteria. This localized metals contamination indicates a proximate source. Metal enrichment was found and sources were attributed to runoff from golf courses, marina activity, Chromated Copper Arsenate (CCA) treated dock pilings, antifouling paints, and general stormwater runoff from urban areas after rain event (Butts, 1997). A complete listing of the metal analytes are provided in Appendix G.

### **Polycyclic Aromatic Hydrocarbons (PAHs)**

Like metals contamination, PAH concentrations exceeding ERL often occurred in Tom's Bayou and Garnier's Bayou, but even more frequently in Cinco Bayou, just east of Garnier's Bayou. No other bayou in the Choctawhatchee Bay system was shown to have sediment PAH contamination; however, Mullet Creek did exceed the ERL for total PAHs. The total PAHs criterion was exceeded in each of the three bayous listed above, as was the anthracene ERL criterion. Acenaphthylene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(a)pyrene, and dibenzo(a,h)anthracene were also found to exceed their respective ERLs in 1 to 2 bayous each. High concentrations were found in previous studies and reported sources included runoff, wastewater discharge, and illegal or accidental

dumping (CBA, 1998). As with metal contamination, sediments contaminated with PAHs at concentrations considered to pose ecological risk to fish and wildlife resources were most often found in the bayous of the northwestern bay. A complete listing of the PAH analytes are provided in Appendix F.

### **Organochlorines/Pesticides**

Organochlorine (OC) contamination of sediments was only found to exceed sediment quality guidelines for the categories total polychlorinated biphenyls (PCBs) and total dichlorodiphenyltrichloroethane (DDT). Total DDT exceeded the ERL criterion at 7 sites, and was almost more than the ERM criterion in Tom's Bayou. Total PCB sediment concentrations exceeded the ERL in Garnier's Bayou, Cinco Bayou, and Mullet Creek, and were more than the ERM in Tom's Bayou indicating frequent adverse effects may have been expected from organochlorine compound exposure. The distribution of sediments contaminated with OC compounds was quite similar to the distribution of sediments contaminated with metals (described above). This type of contamination was also prevalent in the bayous of the northwestern bay area where metal and PAH contamination were predominant. Most of the areas with elevated organochlorine levels were drainage areas from historical spray fields used in the late 60's and early 70's (U.S. Department of Health and Human Services, 2003). A complete listing of the OC analytes are provided in Appendix E.

### **Dioxin**

Dioxin contamination of sediments in Choctawhatchee Bay was not dissimilar from dioxin concentrations found in the sediments from bay systems across the Florida panhandle

(Hemming *et al.* 2003). The highest dioxin and furan concentrations measured in Choctawhatchee Bay were found in sediments taken from Tom's Bayou. As a result, the highest toxicity equivalency (TEQ) estimate was calculated for this bayou and it was more than twice the estimate for any of the other three samples taken. The Tom's Bayou sample could have imposed possible risk to some natural resource populations if in contact with these sediments; although, the other sites were likely to have posed only negligible risk (USEPA 1993, Hemming *et al.* 2003). However, risk may increase with changes in the distribution of these sediments via storm events or dredge and fill activities. Risk from exposure to dioxin compounds also dramatically increases in more sensitive life stages, different exposure routes (such as filtration feeding), and with concurrent exposure to other contaminants.

Dioxin found in Choctawhatchee Bay sediment may have originated from numerous historical spray fields and burial sites in the bay watershed (U.S. Department of Health and Human Services, 2003). However, natural burning occurrences and industrial processes also generate dioxin compounds (Harte *et al.*, 1991; Hoffman *et al.*, 2003; Schettler *et al.*, 1999; Im *et al.*, 2002). Resulting atmospheric concentrations (<6 pg/m<sup>3</sup> range) in the United States are reportedly low (Smith *et al.*, 1989; Harless *et al.*, 1990; Maisel *et al.*, 1990; Hunt *et al.*, 1990a; CDEP, 1988; Harless *et al.*, 1991; Edgerton *et al.*, 1989; Eitzer *et al.*, 1989; Hunt *et al.*, 1990b), but can be traced to water body loading and sediment sequestering (Lodge and Cook, 1989, Hemming *et al.* 2003). Dioxin compounds are transferred from the sediment compartment to the food chain rather readily in aquatic systems. It is in the food chain that dioxins can be biologically magnified and cause adverse ecological effects (Hoffman *et al.*,

2003; Rhodes *et al.*, 1997; Woodford *et al.*, 1998; Landis and Yu, 1999; Marvin *et al.*, 2000; Kannan *et al.*, 2001; Im *et al.*, 2002). A complete listing of the dioxin analytes are provided in Appendix B.

## **Herbicides**

Substantially more phenoxy herbicide residues were found in the sediment sample taken from Mullet Creek; however, noteworthy concentrations were also found in sediments from Tom's Bayou and Rocky Bayous. The phenoxy herbicides analyzed for in this survey included dicamba, 2,4-D, Dichloroprop, 2,4-DB, 2,4,5-T, and silvex. Dicamba is a synonym for the herbicide trichlopyr, commonly found as the active ingredient in landscaping "weed and feed" and brush control products (MeisterPro 2003). Phenoxy herbicides are systemic pesticides used for controlling woody plants and broadleaf weeds. They are used on lawns, golf courses, rights-of-way, non-irrigation ditch banks and agricultural fields (MeisterPro 2003). All three waterbodies with elevated concentrations of herbicides are lined with private homes, but Mullet Creek also has a drainage connection to a large private development on Lake Sharon.

Although no sediment quality guidelines were available for these chemicals, the literature does suggest that phenoxy herbicide exposure can cause adverse effects (Arias 1994, Arbuckle 1999, Duchnowicz 2002, Kleszczynska 2003). The effects of sediment-associated exposures are less clear (Romero 1998, Dorado and Almendros 2001). In any event, the elevated concentrations found only in certain bay segments indicated probable sub-watershed application of these herbicides and transport to the most proximate waterbody

(Felding *et al.* 1995, Hill *et al.* 2003). Appropriate pesticide management practices, such as adequate buffer zones and application timing and method alterations, could significantly reduce these inputs to the tributaries of Choctawhatchee Bay. A complete listing of the herbicide analytes are provided in Appendix D.

### **Aliphatic Hydrocarbons**

Like phenoxy herbicides, the highest concentrations of aliphatic hydrocarbons (AHs) were found in sediments taken from Mullet Creek, Rocky Bayou, and Tom's Bayous. In addition to these sites, sediments from Garnier's Bayou also possessed noteworthy AH concentrations. While sediments from the above-mentioned bayous were contaminated with higher concentrations of 3 to 5 AH analytes, Mullet Creek sediments were heavily contaminated with over 20 AH analytes. Tom's and Rocky bayous are proximate to the Fort Walton Airport, but the land-use near Mullet Creek is mainly residential and owned by Eglin Air Force Base. Mullet Creek is one of the historical drainage sites from spray fields used in the late 60's and early 70's for testing of spray patterns and equipment. The test site above Mullet Creek was also a drum disposal site during the same time frame (U.S. Department of Health and Human Services, 2003). Mullet Creek is also in the vicinity of the Tri-Village Fire Department which might contribute to high levels of AH in the creek.

AHs are a large component of petroleum, such as fuels and oils, and are found associated with a variety of combustion engines from motor vehicles to aircraft. These products are found at various concentrations throughout the world as a result of the presence of petroleum (Hoffman *et al.* 2003). Because of their wide use, occupational exposure

(Dudley *et al.* 2001, Spencer *et al.* 2002, Ritchie 2003) and environmental fate and transport (Suchanek *et al.* 2000, Lindstrom and Braddock 2002) have been examined. However, sediment quality guidelines are not yet available and risk assessments for this complex mix of analytes are not easily made despite their environmental toxicity and hazard to organisms (Hoffman *et al.* 2003). A complete listing of the AH analytes are provided in Appendix C.

## CONCLUSIONS

The sediment quality of Choctawhatchee Bay was analogous to that reported for sediments of other Bay systems in the Florida panhandle (Brim *et al.*, 1998; Brim, 2000; Hemming *et al.*, 2003; Hemming et a. 2002). The occurrence of sediment contamination was largely site-specific with probable ties to proximate sub-watershed land-uses. More specific study of the distribution of contaminated sediments in these areas may reveal the historic and/or current sources of pollution. Further investigation into the extent of the contamination and the potential ecological risk posed is recommended for Mullet Creek, Rocky Bayou, Tom's Bayou, Garnier's Bayou, Cinco Bayou, and possibly La Grange Bayou.

The cumulative impact of the multiple analytes detected in some sediment samples has not been determined. However, the risk to the ecological systems in these bay areas is likely to far exceed the estimated risk of exposure to individual analytes as proposed by Long *et al.*, 1995. To further compound and intensify the point, heavy contamination of these same areas with contaminants not represented by the effects range categories (phenoxy herbicides and aliphatic hydrocarbons) existed.

## RECOMMENDATIONS

The following recommendations are offered for consideration.

- 1) Conduct a more systematic sediment survey throughout the following water bodies to better assess the extent of contamination, level of contamination (increasing, decreasing, or stable) and possible migration of the contamination to surrounding areas: Mullet Creek, Rocky Bayou, Tom's Bayou, Garnier's Bayou, Cinco Bayou, and La Grange Bayou.
- 2) Conduct a land-use survey evaluating activities, historic and present, that may be related to site-specific contamination.
- 3) Monitor the biological tissues (especially reproductive tissues or eggs) of some resident piscivorous birds, in particular, the brown pelican and osprey for bioaccumulation of these contaminants to determine if remedial actions are needed.
- 4) Monitor the biological tissues (including unfertilized eggs) of coastal resident marine species, particularly spotted seatrout, flounder, redfish, and long-lived, deep-water clam species for bioaccumulation of these contaminants to determine if remedial actions are needed.

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