# Screening of Selected Contaminants in Sediments of Escambia Bay, Pensacola, FL.

Dr. Carl J. Mohrherr
Center for Environmental Diagnostics and Bioremediation
University of West Florida

Dr. Johan Liebens
Department of Environmental Studies
University of West Florida

Dr. K. Ranga Rao
Center for Environmental Diagnostics and Bioremediation
University of West Florida

June 15, 2009

# Foreword

This study is a component of the "Assessment of Environmental Pollution and Community Health in Northwest Florida" supported by a USEPA Cooperative Agreement award X-9745502 to The University of West Florida (Project Director: Dr. K. Ranga Rao). The contents of this report are solely the responsibility of the authors and do not necessarily represent the official views of the USEPA. The study was undertaken because of the increasing concern for environmental pollution and potential impacts on human health in Northwest Florida. It was designed to assess environmental impacts of PCBs and other toxic pollutants in Escambia Bay and River. The KS series of samples was collected by Kristen Anne Smith under supervision of Dr. J. Caffrey. Kristal Walsh managed the spatial databases for the project and drafted the maps. Her assistance has been invaluable. Jeffrey Jackson helped with the fieldwork and Michael Somerville helped with some laboratory procedures.

# Table of Contents

# List of Tables

# List of Figures

# Executive Summary

This study assessed the profiles of PCBs, dioxins/furans, and other common urban and industrial pollutants in sediment of the Escambia Bay and River System in Florida. The primary objective of this Task of PERCH (Partnership for Environmental Research and Community Health) was to examine spatial patterns and concentrations of PCBs and toxic polychlorinated dioxins/furans relative to environmental and human health concerns. PAHs, total petroleum hydrocarbons, organochlorine pesticides, and selected trace metals were also analyzed for.

Escambia Bay is a large shallow estuary of about 36 miles$^2$ in surface area and is located between Escambia and Santa Rosa Counties in northwest Florida. It is a micro-tidal system with an average tidal range of 50 cm. It is dominated by the flows of the Escambia River and its associated channels, the White and Simpson Rivers. The freshwater flow from the rivers follows the western side of Escambia Bay as it flows south towards Pensacola Bay. In Florida the river consists of multiple channels and is approximately 58 miles long but further north in Alabama it is a single channel named the Conecuh River. The total length of the river is about 230 miles for its extent in both Florida and Alabama. An assessment of environmental impacts from initial colonization, logging, dredging, and industrialization was conducted prior to commencement of the project to aid in placement of sampling sites. Historical USEPA environmental studies were reviewed as were also the steps that were undertaken to curtail industrial pollution and aid in the environmental recovery of Escambia Bay during the 1970’s.

Initially most human impacts to this system were from logging and agricultural activities. The construction of railroads and intense logging appear to have had only minor impacts. This changed after World War II when Escambia Bay was subjected to intense point source pollution coinciding with construction and operation of chemical and municipal facilities that released effluents that included large quantities of nitrogen containing wastes. There were immense fish kills, and commercial fisheries such as the white shrimp fishery were adversely impacted.

In 1970 and 1972 (Stein et al., 1970a,b; USEPA, 1972) the forerunner to the US EPA and then the US EPA conducted interstate conferences on the Escambia Bay and River. Intense federal actions took place during the following years that resulted in a diminution of surface releases from industries and sewage treatment plants to the Escambia Bay and River System. Fish kills eventually became rarer and less extensive in nature. However, the original pollutants that contaminated the system have persisted in the sediments. A GIS database (DeBusk et al., 2002) has data from several US EPA and NOAA studies of Escambia Bay sediments and shows the presence of metals and organic substances of concern (SOCs).

The present study is the most complete and systematic study to date of Escambia Bay and River System sediments relative to the number of samples, areas sampled, and the analyses employed. This study was intended to complement related PERCH studies on PCBs, dioxins/furans, and other SOCs in seafood tissues. In Escambia Bay recent PERCH studies showed elevated TEQ levels in shellfish and diverse fin fish species that exceeded the US EPA screening values (SV) and thresholds (ST) for dioxins/furans and dioxin-like PCBs (Karouna-Renier et al., 2007;

Snyder and Rao, 2008). This has raised concerns in the community about the environmental and human health impacts of PCBs and other pollutants in the Escambia Bay and River System.

Chemical analyses of the sediment samples were preformed by the laboratories of Columbia Analytical Systems using approved US EPA and State of Florida methodology. Analyses were performed for PCB congeners, dioxins/furans, organochlorine pesticides, PAHs, petroleum hydrocarbons, and total organic carbon. Sediment particle size analysis were done in-house at the Soils Laboratory at UWF. For the purposes of this study the Escambia Bay and River were divided into five sections:

1. Lower bay (south of the I-10 Bridge),
2. Upper bay (between I-10 bridge and US 90 causeway),
3. Lower wetlands (north of US 90 causeway up to the join of the north electrical high tension transmission line and old gas pipe line),
4. Lower river (between river's mouth and Solutia, Inc. to the north), and
5. Upper river (north of the Solutia, Inc. facility)

With the exception of DDT there were no SOCs in the sediments that exceeded the probable effects level concentration (PEL). However, many samples exceeded the threshold effects level concentration (TEL) for more than one SOC, suggesting the possibility of impact to sediment fauna. The TEL indicates the threshold concentration at which negative impacts to benthic fauna could *possibly* occur, but such impacts do not become *probable* until the PEL is exceeded. The TEL and PEL are not protective relative to the accumulation of persistent organic pollutants (POPs) and other SOCs in seafood.

*Total PCBs:* Total concentrations for the 209 PCB congeners in the sediments ranged from 0.9 ug/kg to 125.9 ug/kg with a mean of 17.9 ug/kg. Sixteen samples exceeded the FDEP TEL of 21.6 ug/kg, no sample exceeded the FDEP PEL of 189 ug/kg. The concentrations of the PCBs generally varied according to the region in the Escambia Bay and River System. Overall, the lower Escambia River and upper regions of Escambia Bay had PCB concentrations about the TEL. There were two samples that stood out from the other samples due to their higher concentrations and also their locations. One was located in Thompson's Bayou, adjacent to where the thermal canal from the Crist Steam Plant bypasses it, and had a PCB concentration of 93.5 ug/kg. The other sample had the highest concentration of all the samples (125.9 ug/kg) and was collected near the Monsanto-Solutia spill site. It appears that there is significant PCB contamination in the sediments in this stretch of the river and that according to FDEP SQAGs it can impair sediment quality. It would be remarkable if this contamination has persisted in an area subjected to dredging and tow boat prop wash since the 1969 release at Monsanto without additional PCB import. In the lower wetlands adjacent to the lower river the mean PCB concentration was 14.1 ug/kg and for the lower Escambia Bay the mean was 11.9 ug/kg. Upriver of the spill site the mean concentration was lower (5.06 ug/kg).

*Total dioxins/furans:* The concentration range for toxic dioxins/furans was 22 ng/kg -11,004 ng/kg with a mean of 1863.8 ng/kg. The dioxin/furan congener profile is similar to what has been observed in the local bayous in other PERCH studies in that octachlorodibenzo-p-dioxin (OCDD) is the dominant congener in the sediment on the basis of mass concentration.

*Summed dioxin/furan and dioxin-like PCB TEQ:* The mean summed TEQ of dioxins/furans and dioxin-like PCBs for the sediments is 2.6 ng/kg. Dioxins/furans contribute about 92% and PCBs about 8% of the total TEQ. In seafood tissues this relationship is reversed. In the striped mullet *Mugil cephalus* the overall TEQ was 75.305 ng/kg and resulted from a dioxin/furan contribution of 0.3 ng TEQ /kg and a dioxin-like PCB contribution of 75.005 ng TEQ /kg (Snyder and Rao, 2008). This shows that the dioxin-like PCB bioaccumulation factors can be very high in fishes in Escambia Bay and River and, consequently PCBs seem to present the highest health risk to human consumers of local seafood. For summed TEQ about 33% of the samples exceeded the NOAA TEL but not the NOAA AET and an additional 23% of the samples exceeded both the TEL and AET. This implies that about 56% of samples exhibited summed dioxin/furan and dioxin-like PCB TEQ toxicities that could impact sediments adversely. Spatially, the dioxin-like PCB distribution does not coincide with the dioxin/furan TEQ distribution. This is likely due to differences in origin and possibly to different interactions with transporting and degradation processes.

*Indicator (dominant) PCB congeners:* Indicator or dominant PCB congeners are those that comprise about 3 to 7 percent of the average PCB sediment profile. There were six elutions that were 3.8% in concentration or greater in the current study, including the toxic dioxin-like PCB 118 which could be used in screening studies for sediment or tissue accumulation.

*Origins of PCBs*: The overall profile for the sediment PCBs shows attributes of degradation via dechlorination that makes forensic determinations of the parent material difficult. The forensic evidence suggests the possibility that other Aroclors beside A1254, which allegedly was spilled at the Monsanto-Solutia site, contributed to the current PCB profile. This would not be unusual because of the multiple potential sources that are present in and about the Escambia Bay and River System. The possibility of other undocumented PCB releases is to be expected for a bay and river system with multiple industries in its watershed.

*Pesticides:* Only 4,4'-DDT was detected in the sediments with only one exception when two DDT byproducts were detected in the bay. DDT was detected in 25% of the sediment samples. All detected 4,4'-DDT concentrations were above the FDEP PEL (4.77 ug/kg) except one sample that only exceeded the TEL (1.19 ug/kg). The DDT was generally associated with the wetlands and river. Its presence is of concern as some of these areas may serve as nurseries for marine life and DDT could impact fish and shrimp populations.

*PAHs:* For the light molecular weight PAH category there were only 4 samples that exceeded the TEL and for the heavy molecular weight PAH and the sum of the light and heavy PAH categories only two samples each exceeded the TEL. No samples for these three groups exceeded the PEL. The current study detected much lower concentrations for the sum of light and heavy molecular PAHs (range of 2.4 to 2859 ug/kg and average of 238.2 ug/kg) than previous studies (Debusk et al., 2002). Seven out of ten samples reported by 1991-93 studies in Debusk et al. (2002) ranged from 1033 to 14,590 ug/kg. The PAH concentrations detected during the current study in Escambia Bay and River were also much lower than what was reported by PERCH studies in Bayous Texar, Chico, and Grande (Mohrherr et al., 2005; 2006; 2008).

*Total petroleum hydrocarbon:* Seven out of 57 samples had low but detectable concentrations of total petroleum hydrocarbons. One of the detections was in the bay, two were in minor channels of the Escambia River, and four detections were in or near to the main channels of Escambia River. The observed concentrations suggest total petroleum in sediments is not of environmental concern in Escambia Bay and River.

*Metals:* A total of 14 common metals were analyzed in sediments and included aluminum, arsenic, cadmium, calcium, chromium, copper, iron, lead, magnesium, mercury, nickel, selenium, tin, and zinc. Ten of these can be considered to be common trace metals: arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, tin, and zinc. Some of these trace metals exceeded their TEL, but not PEL. Overall, there were frequent exceedances of the TEL near an Air Products outfall in the upper region of Escambia Bay. It is not clear if the metals originate from this outfall or were carried to the sediments from other parts of the system. Total arsenic appeared to represent the greatest toxic metal impact to the sediments. It was detected in all 57 sediment samples and 30 samples exceeded the TEL. The basin area (deeper regions of Escambia Bay) appears to be the most contaminated with arsenic. Total cadmium in sediments was detected in 46 sediment samples and 16 samples exceeded the TEL. Total chromium was detected in all 57 sediment samples and 14 samples exceeded the TEL, especially in the lower part of the bay. Total copper was detected in 55 sediment samples but only 4 samples exceeded the TEL. Total lead was detected in all 57 sediment samples and 11 samples exceeded the TEL. Total nickel was detected in all 57 sediment samples and 16 samples exceeded the TEL, especially in the bay's basin. Total zinc was detected in all 57 sediment samples and 6 samples exceeded the TEL. Total selenium was detected in 42 sediment samples and total tin in 35 samples but there are no FDEP SQAGs for these two metals. These observations for trace metals indicate that their concentrations are not extremely elevated but, because they exceed the TEL in some samples, have the potential to negatively impact bottom dwelling organisms.

*Total mercury:* Total mercury was detected in 48 out of 57 sediment samples and had a mean concentration of 0.07 mg/kg. Two samples in the lower bay exceeded the TEL of 0.13 mg/kg but none exceeded the PEL of 0.696 mg/kg. Overall, according to the FDEP SQAGs for mercury the health of sediment dwelling organisms is unlikely to be impacted by the levels of mercury. However, mercury has been found to exceed seafood screening levels in some fishes in the Escambia and Conecuh River (FDEP, 2006; USEPA, 2007) and more study is required to understand why tissue residue mercury is above screening levels for human consumption.

*SQAG and remediation:* There currently are no applicable state or federal guidelines that are protective relative to accumulation of SOCs in upper trophic level consumers that include many seafood species. Currently the evidence suggests that in the absence of more information the only safe cleanup level for PCBs relative to human consumption of seafood will be sediment concentrations that are below current analytical detection limits. The surface area of Escambia Bay is about one billion square feet, strongly suggesting that remediation of such acreage will be extremely expensive. It is possible that additional modeling studies will allow protective sediment cleanup goals to be determined that would lower future remediation costs.

# 1. Introduction

Escambia Bay and River are of recreational, economic, environmental, and aesthetic importance to the people of northwest Florida. The citizens and governments of Escambia and Santa Rosa Counties as well as the State of Florida and the federal government have been concerned over the environmental state of the Escambia Bay and River System over the years. The concern stems from massive fish kills caused by the severe deterioration of the environmental conditions due to point source releases from industrial and municipal sources that led to eutrophication. The water column currently does not appear to contain significant amounts of most of the pollutants that were present in previous years (Olinger et al., 1975). However, it appears that some of these pollutants or substances of concern (SOC) still persist in the sediments and are present in seafood tissue. The present study of sediments of the Escambia Bay and River system complements a related PERCH Project that is concerned with Persistent Organic Pollutant (POPs) in seafood tissue. Currently, there are advisories for the Escambia River in Florida for PCBs in mullet (Snyder and Rao, 2008; FDOH, 2007) and mercury in largemouth bass (FDOH, 2007). PERCH studies have also shown the presence of PCBs in shellfish and fin fish species in the Escambia Bay and River (Karouna-Renier et al., 2007; Snyder and Ra, 2008). The presence of PCBs in seafood has been coincidently correlated by the public to a 1969 release of PCBs from a former Monsanto Company plant (Duke et al., 1970) located on the lower Escambia River (Figure 1.0-1) because the PCBs may be persisting in the sediments.

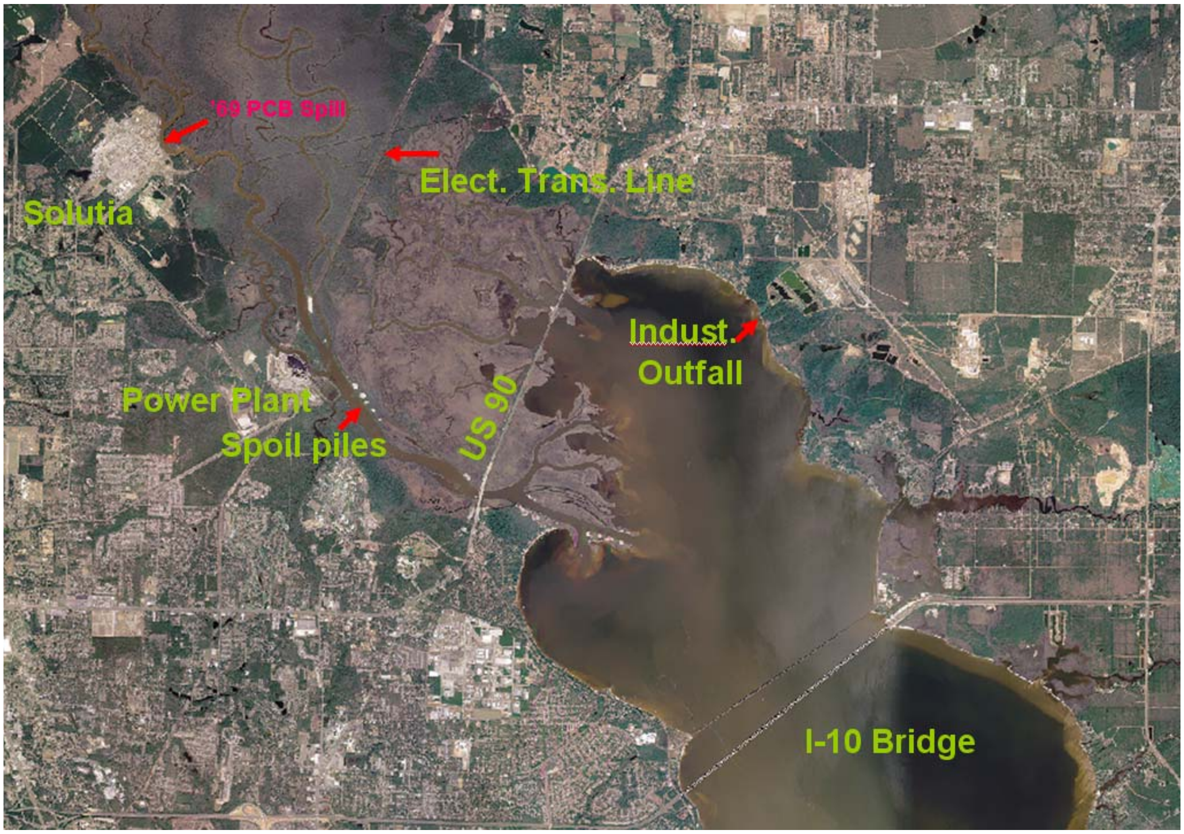


Figure 1.0-1. Aerial photograph of lower Escambia River and upper Escambia Bay (2004).

Figure 1.0-1 is a composite based on 2004 aerial photos showing the locations of some of the major industries and structures that have impacted the upper bay and lower river. It is quite evident that the bay and river have been subjected to impacts from anthropogenic activities. On the lower river is Solutia, Inc., a major chemical industrial facility that used to be a Monsanto Chemicals plant, a regional power plant (Crist Steam Plant), spoil piles from dredging activities, electrical transmission lines, and the US Highway 90 bridge over the Escambia River that continues as a causeway that crosses wetlands and demarcates in part the upper extension of Escambia Bay. On Figure 1.0-1 the site of the 1969 PCB release is indicated by a red arrow. The Solutia, Inc. facility was owned by Monsanto Company in 1969 at the time of the PCB release. Two bridges, for I-10, and the CSX Railroad, cross the bay. There are also two industrial facilities in the Pace-Floridatown area that in the past have discharged to the eastern shore of the bay.

The Pensacola News Journal announced on June 10, 2008 that Monsanto Company, Pharmacia Corporation, and Solutia, Inc. were listed as the defendants in a civic action presented to the Circuit Court of Escambia County, FL that alleges past and continuing release of PCBs in the Escambia River (Rabb, 2008). Currently there is extensive local public interest in PERCH studies of the Escambia Bay and River due to PERCH project findings of the presence of PCBs in seafood that were reported by local media.

The primary objective of this PERCH Task was to evaluate spatial patterns in PCB and dioxin/furan concentrations in sediments in Escambia Bay and River. Other contaminants analyzed in the sediments were: PAHs, organochlorine pesticides, and trace metals.

## 1.1. Description of Escambia Bay

### 1.1.1. Geological attributes

Escambia Bay is a shallow estuary located between Pensacola Bay and the Escambia River with depths varying from very shallow in the delta and wetlands to 17.7 ft (5.4 meters) at the junction of Escambia and Pensacola Bays (Figure 1.1.1-1). It is classified as a micro-tidal, partially stratified, drowned river valley estuary (Schroeder et al., 1999; Murrell et al., 2004). The surface area of Escambia Bay is about 36 square miles with a mean depth of 8 ft. This makes Escambia Bay the largest bay of the Pensacola Bay System which has a total surface area of 54.1 square miles (Table 1.1.1-1; Thorpe et al., 1997). The Escambia River is about 230 miles long and is called the Conecuh River in Alabama. The Escambia River has an annual mean discharge of ~200 $m^3 s^{-1}$ and contributes 80% of the surface water that enters the Pensacola Bay System. East Bay, another component of the Pensacola Bay System, receives the flows of the Blackwater, East, and Yellow Rivers that contribute ~20% of the surface flow (Murrell et al., 2004; Thorpe et al., 1997). Escambia Bay and River also have extensive wetlands at the western end of the bay where the Escambia River and its channels empty into the bay. The wetland area to the east and adjacent to US Highway 90 is separated from the downstream influence of the Escambia River and is likely saline. It consists mainly of emergent herbaceous vegetation. Wetlands near the river and well upstream of tidal influence are characterized by wet forests that have been subjected to logging activities, including dredging of channels for access and probably construction of temporary impoundments. Many minor channels exist in the Florida part of the watershed some of which, such as the White and Simpson Rivers, branch off of the Escambia River itself to enter the bay without rejoining the main trunk (Figure 1.0-1).

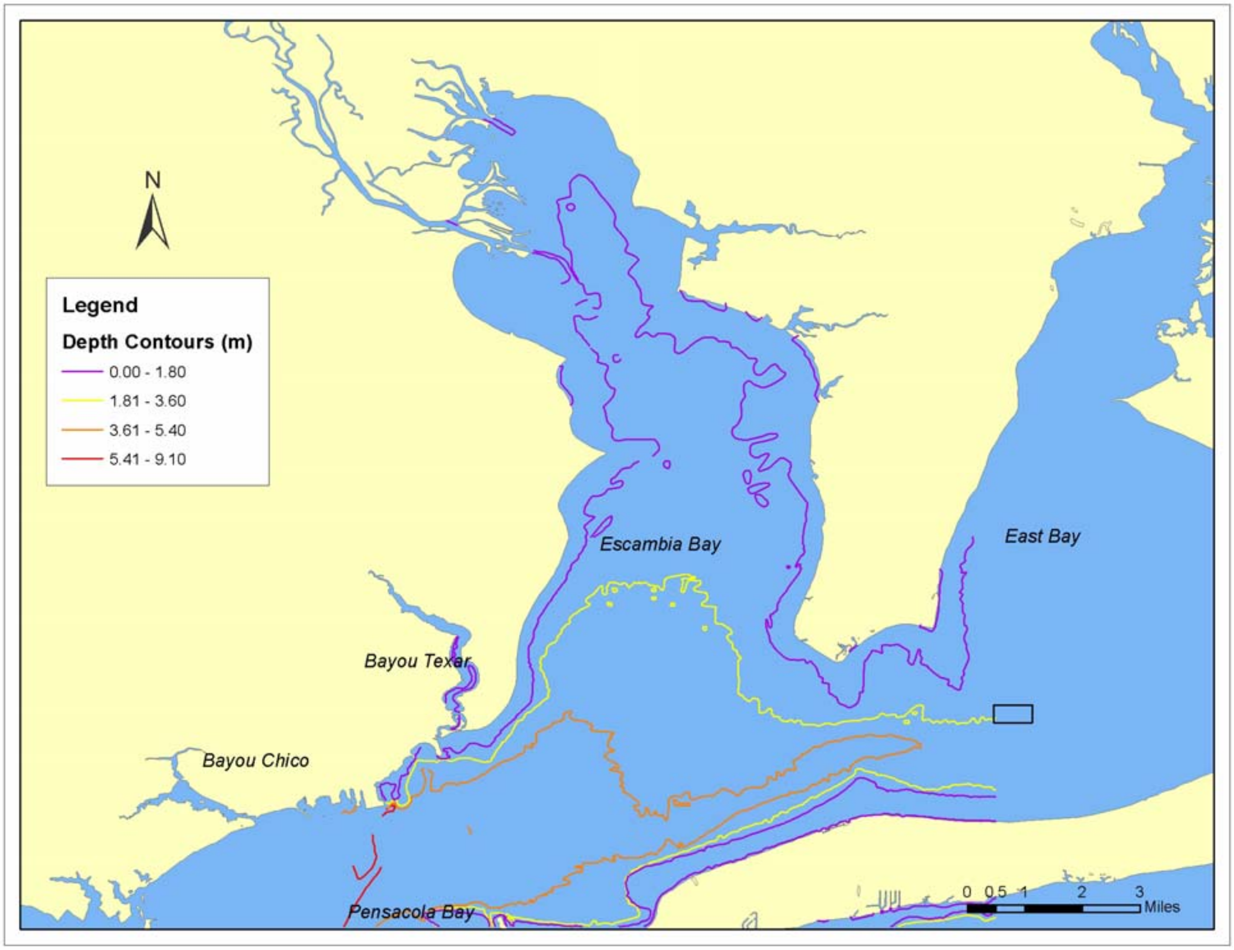


Figure 1.1.1-1. Bathymetry [m] of Escambia Bay.

Table 1.1.1-1. Surface areas of Pensacola estuaries (Thorpe et al., 1997).

| Water Body | Surface Area (mi$^2$) | Mean Depth (ft.) |
|---|---|---|
| Pensacola Bay | 54.1 | 19.5 |
| Bayou Grande | 1.5 | 9.0 |
| Bayou Chico | 0.4 | 6.0 |
| Bayou Texar | 0.6 | 6.1 |
| East Bay | 43.9 | 7.9 |
| East Bay Bayou | 1.7 | 3.9 |
| Escambia Bay | 36.0 | 8.0 |
| Mulatto Bayou | 0.3 | 4.9 |
| Blackwater Bay | 9.8 | 6.3 |
| Catfish Basin | 0.3 | 3.9 |
| Santa Rosa Sound | 42.4 | 8.9 |

### 1.1.2. Environmental status of Escambia Bay and River

In February 2006, the Florida Department of Environmental Protection (FDEP, 2006) classified the Escambia River as 3F or suitable for recreation, propagation, and maintenance of a healthy, well-balanced population of fish and wildlife in fresh water. Its impairments included mercury that was stated to be present in fish tissue in concentrations that exceed the Florida Department of Health guidelines. In Alabama the river also has a fish consumption advisory for mercury (ADPH, 2008). Fecal coliform bacteria are also found to be above guidelines with concentrations of >400 colonies /100 ml. The Escambia Bay is classified as 3M (suitable for recreation, propagation, and maintenance of a healthy, well-balanced population of fish and wildlife in marine waters) with impairments from nutrients for total nitrogen, and total phosphorus, and bacteria exceeded SEAS (Shellfish Evaluation & Assessment Section requirements) thresholds (FDEP, 2006).

### 1.1.3. Recreation and fisheries

The Escambia Bay and River System is considered to be a valuable natural resource, the waters of which are used for commercial harvesting of shellfish (crabs, oysters, and shrimp), recreational fishing, bathing and boating activities. There is at least one public beach on Escambia Bay and there are other sites that also have sandy shores suitable for beach activities. There are several publicly maintained boat launches on the Escambia Bay and River as well as three commercially operated launching sites that are dedicated to recreational fishing activities and are located adjacent to where US Highway 90 crosses the Escambia River delta and wetlands. Sport fishing on the river includes bluegill, red ear sunfish, black crappie, largemouth bass and many other species. Tetrapod species are also hunted and include: frogs, turtles, alligators, deer, feral hogs, small game, and turkeys and water fowl. During field trips numerous trot lines were observed in the minor channels of the Escambia River. On Escambia Bay commercial fishing activities include crabbing (blue crabs, *Callinectes* sapidus) and oyster culture (American oysters, *Crassostrea virginica*). The scallop industry has collapsed, partially due to the disappearance of seagrass beds (BARC, 2005).

Recreational fishing includes the typical fish that are present in inshore marine waters of the northern Gulf of Mexico. Porpoises do make an appearance and were also observed in the Bay during this study. During sampling in the lower portion of Escambia Bay the Florida Lancelet *Branchiostoma floridae* was observed in shallow sandy areas of the western shore. Oysters are a commercially harvested species of Escambia Bay but oyster harvesting is prohibited north of the I-10 bridge. The lower bay has 20,173 acres that are conditionally approved and 3,153 acres that are conditionally restricted for oyster harvesting. Oyster harvesting season is from October 1st through June 30th. Management of this shellfish area is based on Escambia River discharge and rainfall. Shellfish harvesting area maps and the open/closed status of harvesting areas are available at www.FloridaAquaculture.com (BARC, 2005).

### 1.1.4. Submerged aquatic vegetation

Submerged aquatic vegetation (SAV) decline was significant in Escambia Bay from the 1940s through the early 1970s (Olinger et al., 1975). By 1974, SAV beds in Escambia Bay were almost nonexistent (Windsor, 1985; Rogers and Bisterfield, 1995). Between 1974 and the early 1990s there is a data gap but a 1992 USGS survey showed a significant improvement in the distribution of SAV in Escambia Bay (Figure 1.1.4-1). The increase in SAV coverage has been attributed to reduced nutrient loadings, achieved through improved wastewater treatment methods. Mapping and monitoring of SAV in the Pensacola Bay System in 1998 showed continuing improvement in upper Escambia Bay. Seagrass beds in areas characterized by lower salinities are recovering faster than those associated with higher salinity (Lores and Specht, 2001; USEPA, 2004). The distribution of SAV has been most recently studied by Lewis et al. (2008). Lewis et al., (2008) suggested that the changes in coverage are likely due to naturally occurring and anthropogenic factors but it was not possible to differentiate the relative contributions of these factors. It was concluded that the ability of seagrasses to exist long-term in the Pensacola Bay System is uncertain due to the adverse effects of rapid urbanization in the watershed.

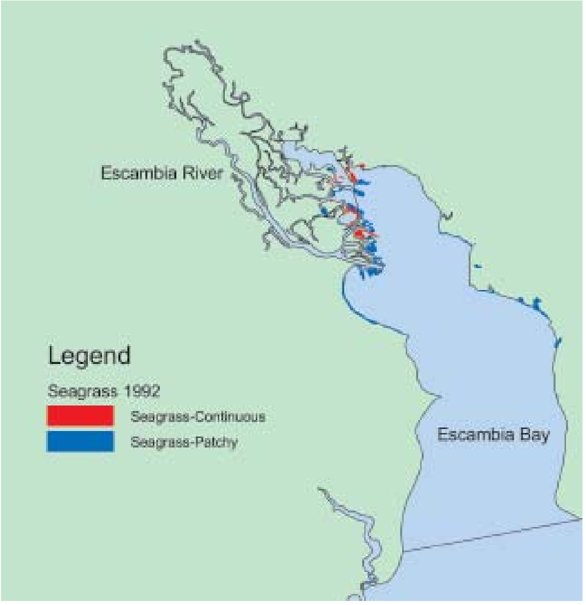


Figure 1.1.4-1. A 1992 survey of the extent of submerged aquatic vegetation in Escambia Bay (USEPA, 2004).

## 1.2. History of the environmental decline

Historically the overall quality of Escambia Bay and the rest of the Pensacola Bay System was environmentally in dire straits in the late 1960’s and early 1970’s. Escambia Bay and Pensacola Bay had the sole category 2 designation (estuary with marginal and/or deteriorating water quality with respect to dissolved oxygen depletion) in the northeastern part of the Gulf of Mexico in the late 1960’s (Windsor, 1985).

The Pensacola Bay System was studied extensively in the 1970s by the USEPA. At that time, significant releases of industrial chemicals and improperly treated sewage wastes occurred on a regular basis. The losses of seagrass beds and changes in the biological community structures of the bay were reported. The Pensacola Bay System had been known throughout the nation as a prime white, pink and brown shrimping area as well as a sport fishing paradise prior to industrial and other releases. Thick mats of rotting vegetation were blamed on the chemical industries as were the hundreds of fish kills reported annually in the system. Shrimp landings declined from 902,000 pounds in 1968, to 236,000 in 1969, 52,000 in 1970, and 17,000 in 1971. Severe dissolved oxygen depletion resulted from a combination of high waste discharges and poor circulation, and led to many fish kills in the late 1960s and early 1970s. In 1970 there were 41 fish kills in Escambia Bay and 32 in Pensacola Bay. The numbers of dead fish were reported in square miles in 1971: one square mile of dead fish in Mulatto Bayou (an embayment of Escambia Bay) and 10 square miles of dead game fish and menhaden along the eastern shore of Escambia Bay.

### 1.2.1. System decline

The system decline, which apparently began in the 1950s, was largely attributed to industrial and domestic point source discharges. Public concern over the deterioration of the system resulted in a number of initiatives in the late 1960s and early 1970s, including research, conferences, and regulatory enforcement actions. One major research activity was the Escambia Bay Recovery Program implemented in the early 1970s by the USEPA. The USEPA concluded that industrial and domestic point source discharges significantly contributed to the poor condition of the system. The USEPA also put forth regulatory action on point source discharges, both adjacent to the bay and upstream along the Escambia and Conecuh Rivers in Florida and Alabama. As a result of these actions, as well as state and federal enforcement that followed, large point source discharges to the system were diminished or ceased, thereby meeting the more stringent permitting criteria (Thorpe et al., 1997).

The report by Olinger et al. (1975) was the research product of the Escambia Bay Recovery Program put into effect by the USEPA. This work characterized conditions of the Escambia Bay as of 1975 and remained the most comprehensive analysis completed to date for the bay, until the current study. The report concluded that because of poor circulation and flushing characteristics, the assimilative capacity of the Pensacola Bay system was extremely limited, and Escambia Bay in particular was barely able to assimilate natural inputs of nutrients and oxidizing materials. Most of the particulate material entering the Escambia Bay was from point and nonpoint waste sources and tributary rivers and was found to be retained in the system. Release of point and nonpoint pollution has been reduced since 1975, but the basic physical processes that control circulation and flushing in the system are unchanged. Nonpoint source pollutant loading is still occurring and such pollutant loading includes suspended sediments contributed by nonpoint sources throughout the basin, chronically-elevated nutrient levels, resuspension by wind events of previously deposited nutrients, and high turbidity. Recent data from Escambia Bay indicate that water quality problems continue to persist (FDEP, 2006). There is increasing developmental pressure on the estuary's shorelines that is causing additional habitat loss and nonpoint source pollutant loading. Although limited aspects of these issues have been the focus of past research, the overall dynamics, and functioning of this poorly flushed system are not understood such that the fate of contaminants like PCBs can be accurately predicted.

### 1.2.2. Threatened species

There are rare and imperiled fish and mussel species in the Escambia River watershed. The fish species include gulf sturgeon *(Acipenser oxyrhynchus desotoi)*, bluenose shiner *(Pteronotropis welaka)*, saltmarsh topminnow *(Fundulus jenhunsi)*, crystal darter *(Crystallaria asprella)*, and harlequin darter *(Etheostoma histrio)*. Six mussel species are also listed by the U.S. Fish and Wildlife Service as threatened (FDEP, 2004). Declining populations of several fish and mussel species have merited concern from the federal government with the Gulf coast sturgeon *Acipenser oxyrinchus desoto*i being one of the most outstanding species relative to protection of critical habitat (Federal Register, 1998; 2008). The U.S. Fish and Wildlife Service and National Marine Fisheries Service designated the Gulf sturgeon to be a threatened subspecies, pursuant to the Endangered Species Act of 1973. The listing became official on September 30, 1991. A total of 14 units along the Gulf of Mexico have been designated as critical habitat for the Gulf sturgeon by the U.S. Fish and Wildlife Service, including the Escambia Bay and River system (Figure 1.2.2-1) (Federal Register, 1998, 2008; http://www.fws.gov/alabama/gs/unitmaps.htm and http://www.fws.gov/alabama/gs/riverine_maps.pdf ).

## 1.3. History of exploitation and pollution of the Escambia Bay and River

The exploitation of the Escambia Bay and River and resulting environmental impacts began with the earliest phases of European presence in the area, if not earlier.

### 1.3.1. Earliest historical occurrences

Timber, hydropower, wildlife, live stock raising, and agriculture would have been the obvious natural resources that were initially exploited, with the lumber industry being most important. Fishing and hunting would also have been important food resources. Hydropower was used to operate machinery and mills, and was the major source of power used to run the earliest saw mills and to handle agriculturally related tasks (Figure 1.3.1-1). Many water powered mills were in use prior to the civil war but, in the case of saw mills, were replaced with steam powered lumber mills when this technology became available.

In 1821 Pensacola officially passed from Spanish to American control and exploitation and development progressed. The extensive forests consisting predominantly of pine were commercially valuable. A businessman, E. F. Skinner, in 1874 purchased a large amount of timber land and operated a lumber mill at Gull Point on the western shore of Escambia Bay. Skinner also built the first logging railroad in Florida that was constructed with steel rails. A hurricane destroyed the Skinner mill and James G. Pace from Hazelhurst, Georgia, purchased what was left of Skinner's assets including approximately 100,000 acres of timber. The lumber mill at Gull Point was purchased by Pace and was moved north of Escambia Bay. The Pace sawmill provided employment for over 200 men from 1907-1927. The sawmill operated its own narrow-gauge railroad for logging that ran through Santa Rosa County from Floridatown to Jay but did not connect to any other railroads (Nugent, 2000).

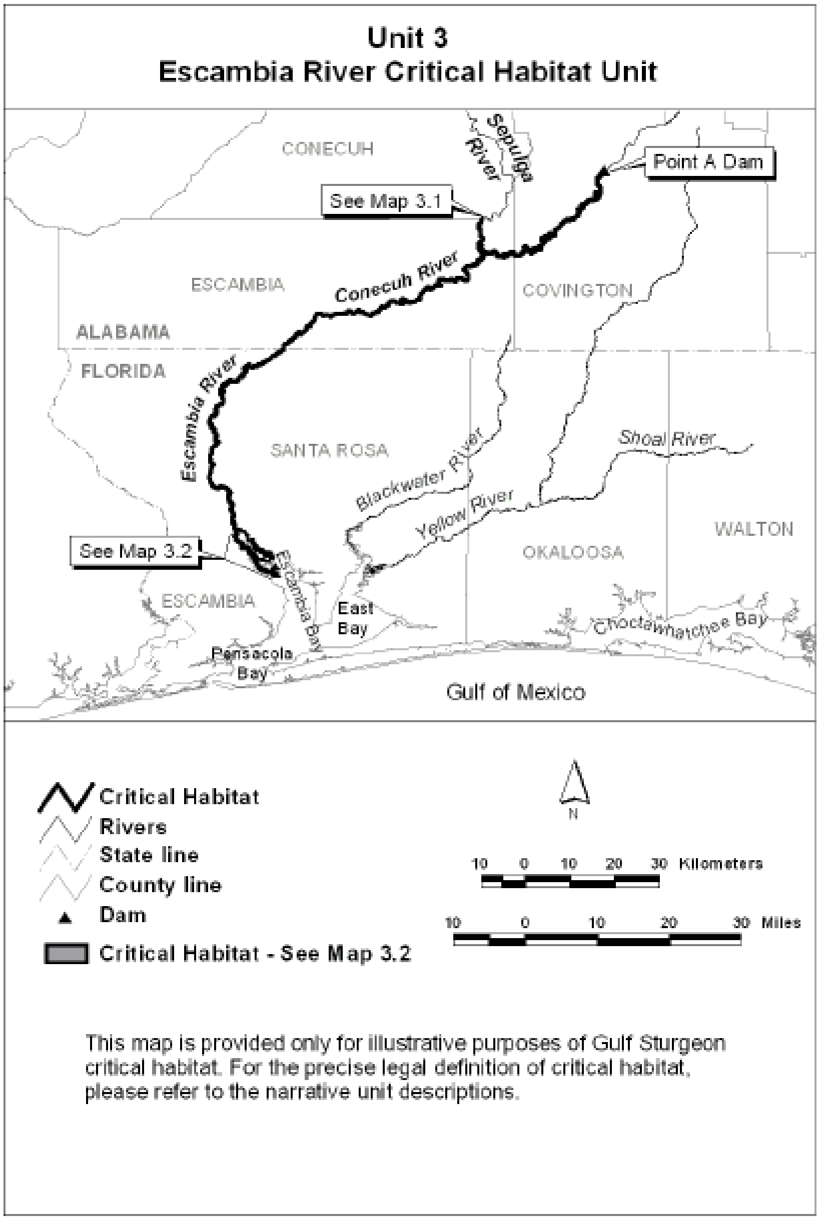


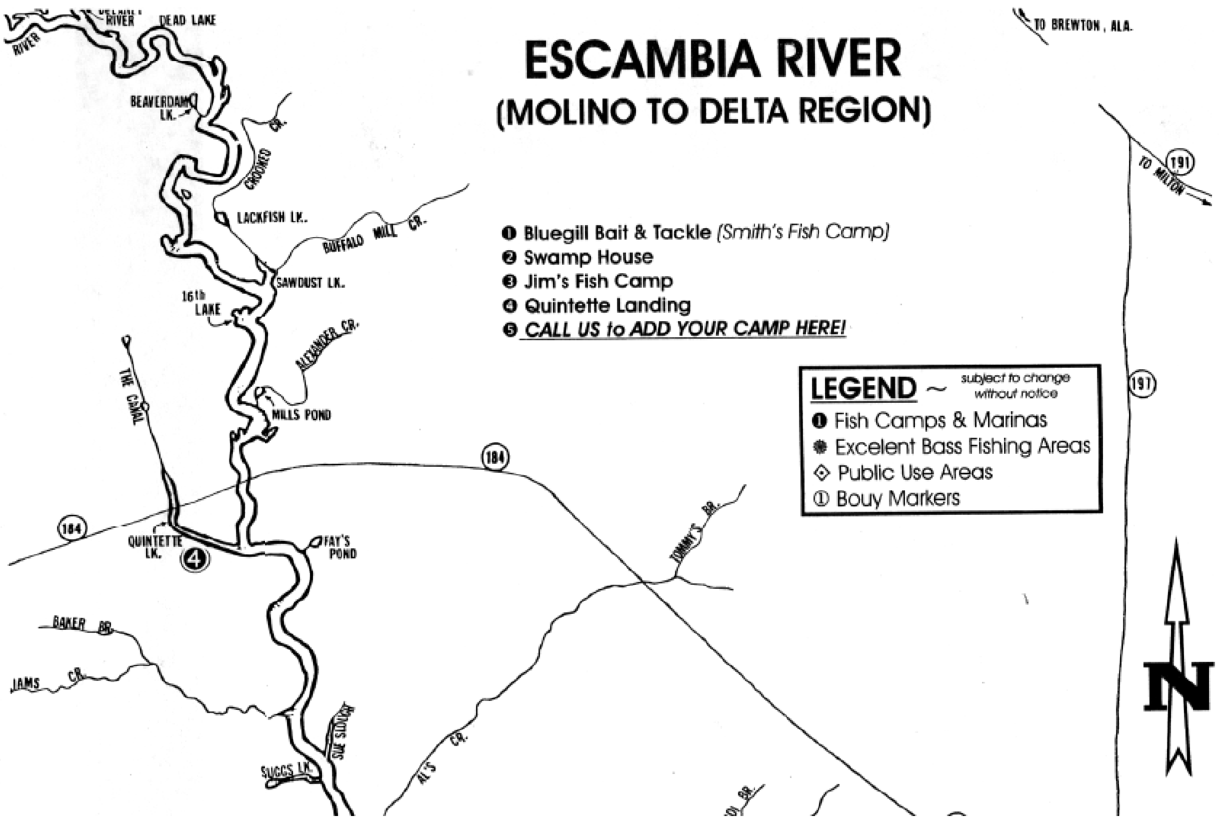
Figure 1.2.2-1. Escambia Bay and River System: Critical habitat map for Gulf coast sturgeon.

Figure 1.3.1-1. Barnett Mill Creek in Pace, FL, site of an early American saw mill circa 1820 (note the cribbing in the water). This mill served the Floridatown community, one of the oldest communities in this area (UWF, 2008).

### 1.3.2. Logging and dredging

Logging activities also began to go inland following the waterways to allow access to the wetlands which besides pine had a significant quantity of bottomland hardwoods and cypress. Several rail lines were constructed by lumber companies to facilitate lumber transport in Northwest Florida and nearby Alabama. Prior to the coming of the railroads timber rafts were floated down the river for transport. The river was initially the only practical means of transport for felled logs and timbers to the saw mills and to ships for maritime transport. Initially the river and its tributaries were blocked by snags, log jams, marl reefs, and sand bars. There was also a bar at the river's mouth that impeded the entrance of tugs, seriously interfering with navigation where the log rafts were made ready to be towed to saw mills or ships. To overcome these obstacles the first congressional appropriation was made in 1833 and again in 1880, then again in 1909 to improve the waterway (Senate Report, 1910). The Florida portion of the river has numerous channels that branch off from the main channels and either rejoin or eventually empty separately into Escambia Bay. The flows into these channels may have been augmented by the previously mentioned snags and log jams that diverted flows from the main trunk into these other channels. Besides the federal government dredging of the main channel there appears to have been substantial dredging activities of the various interconnecting channels of the Escambia River by loggers. Examples of dredging of these other channels are presented in Figures 1.3.2-1a&b that show a map of the lower Escambia River where manmade changes of the river system are obvious. Two very obvious dredged channels are depicted in Figure 1.3.2-1a. North of Florida State Highway 184 is a straight channel called The Canal that was obviously dredged to extend a previously existing channel. In Figure 1.3.2-1b is shown a straight canal labeled as the "Old Gas Pipe Canal" that was intended for transmission presumably of natural gas. Coming from the Crist Steam Plant are also two major power lines that extend across the wetlands with canals that transmit electrical power to Santa Rosa County. There are many other examples of dredged or augmented channels.

The scars upon the land from past logging activities can persist for many years after logging. Figure 1.3.2-2 shows an aerial view of a region of the Escambia River wetlands near Cantonment, FL. Surface scarring of the soils that appears to have been caused by logging is clearly noticeable. This area is labeled as 32 in the figure and shows a series of drag marks radiating from Suggs Lake. Suggs Lake was likely dredged to admit a barge with a steam powered winch that dragged logs towards the lake. The lake may also have had a temporary earthen dam constructed on it. Above Suggs Lake one can also observe Sue Slough that due to its straightness appears to have been dredged. Railroads were also constructed to carry logs and lumber to and from the lumber mills, especially on the upper watershed of the Escambia River (Figure 1.3.5-1) (Buckman, 2003).



1.3.2-1a. Upper portion of the Florida portion of the Escambia River. North of highway 184 is a waterway to the west titled “The Canal”.

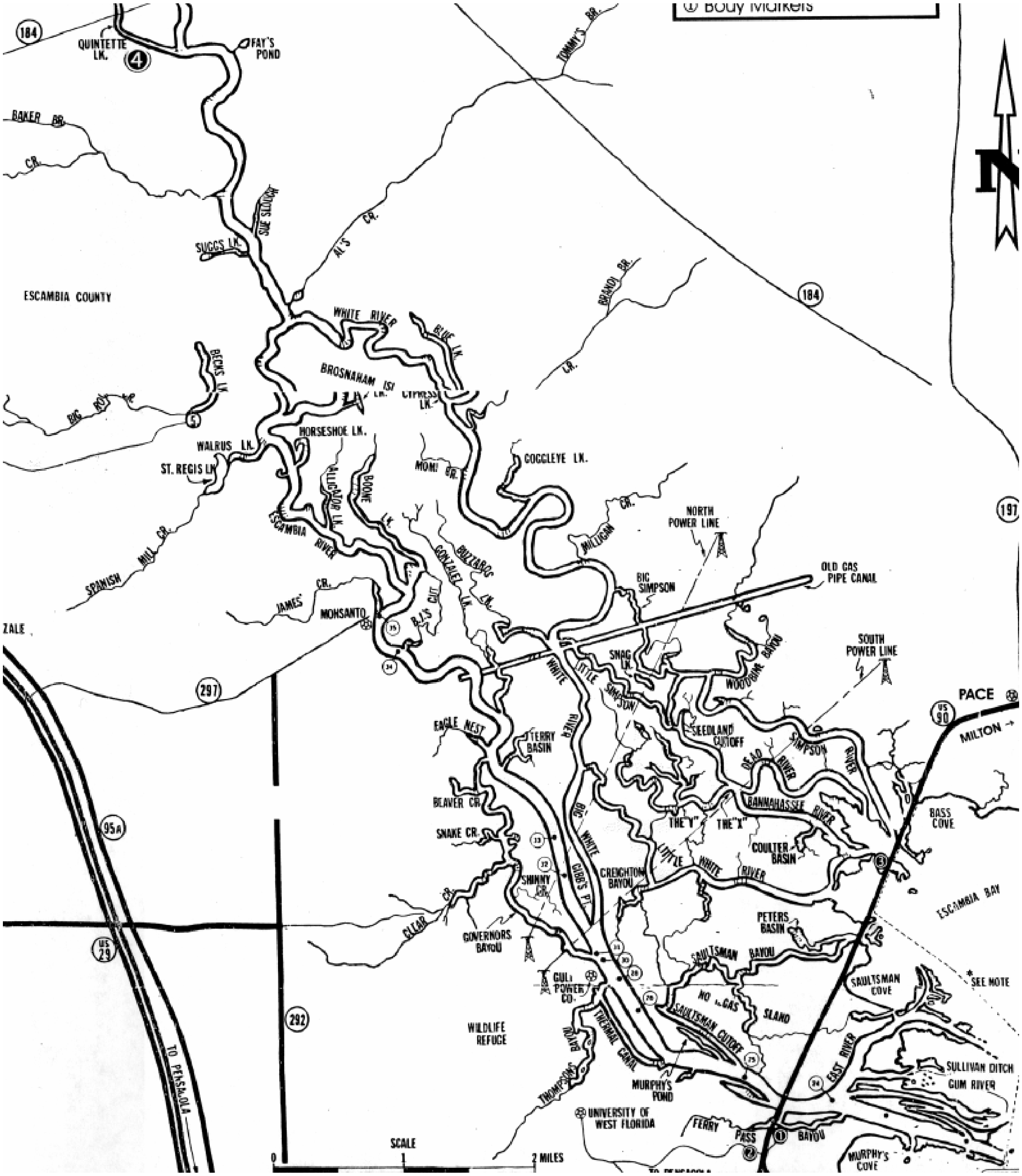


Figure 1.3.2-1b. Escambia River south of State Highway 184.

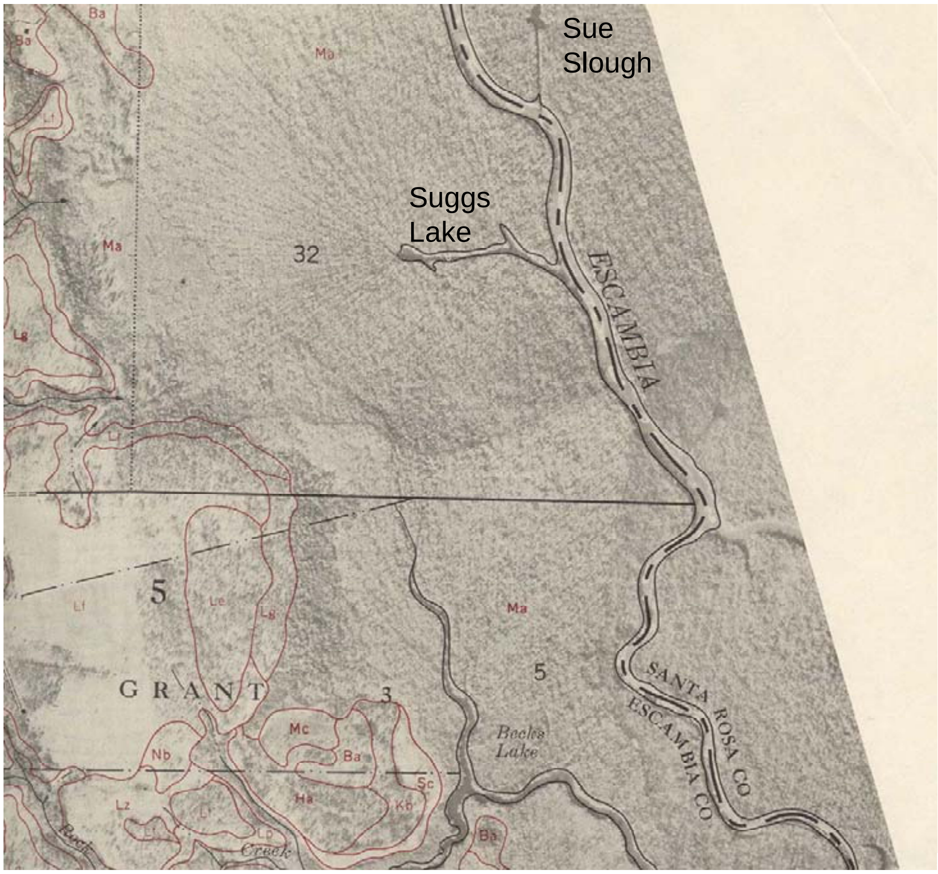


Figure 1.3.2-2. Timber scratch near Beck’s lake, Escambia River, FL. (Walker, 1960).

Figure 1.3.5-1. Logging in southern Alabama about 1911 (The Alger-Sullivan Historical Society, 2006).

### 1.3.5. Dredging and barge transport

With the construction of the Crist Steam Generating Plant in the 1940's and the Monsanto facility in the 1950's a need for barge transport of coal and chemicals arose. This necessitated the dredging of the lower Escambia River to facilitate the transport. Parts of the bay and lower river periodically undergo maintenance dredging to keep the channel navigable for barges and tugs. Barges carrying coal going to the Crist Plant and barges with liquids contained in tanks going to and fro to Solutia were routinely observed during PERCH field trips to the River. Dredge spoils from past dredging activities have been deposited in piles all along the river banks between Solutia, Inc., the site of the PCB spill, and the mouth of the river (see Figure 1.0-1, note white piles near the mouth of the Escambia River). The possible presence of SOCs in these spoil deposits, and possible environmental impacts, have not been investigated. Spoil materials have also been deposited in other areas resulting in the formation of Macky Island that is a small spoil island at the mouth of the Escambia River. The Army Corps of Engineers is currently using Macky Island as a disposal site for spoils dredged from the lower Escambia Bay and River. The spoil material is said to consist of sand. This 10 year dredging project will dispose the spoils such that it will create a 42-acre marsh habitat on the 26-acre island's south side. This is an $800,000 project that requires a FDEP maintenance permit for dredging the river. The U.S. Army Corps of Engineers will do the dredging and the maintenance permit was issued for ten years (Nov. 23, 2005 to Nov 23, 2015) (FDEP, 2005)).

Figure 1.3.5.-1. Macky Island as it will appear after construction of mitigation wetlands.

The permit states that the channel depth will be maintained to a depth of 12 feet mean lower low water plus 2 feet of allowable overdredge and 2 feet for advance maintenance for a 12.5 mile segment from Escambia Bay to Mile 7 of the Escambia River. The 5 ft authorized channel from the Escambia River Mile 7 to the Florida/Alabama border (~51 miles) will not be maintained under this permit. The initial dredging event will remove approximately 187,000 cubic yards of material which will be used for the construction of berms at the mitigation site or deposited within a self-contained upland disposal site at Macky Island. Disposal of spoils on and about Macky Island will result in 10.0 acres loss of wetlands that will be offset by a mitigation that will create a lagoon on the south side of Macky Island that will enclose 42 acres of Escambia Bay. Dredge disposal spoils will be used for construction of the mitigations areas. The final stage is presented in Figure 1.3.5-1 showing Macky Island Phase III (FDEP, 2005).

### **1.3.6. Bridge construction**.

The construction of bridges across the rivers and bays of the Pensacola Bay System was essential to the growth of the Pensacola metropolitan region, but bridges have also been claimed to have impeded tidal and other currents (Olinger et al., 1975). The original railroad bridge constructed in 1882 (Buckman, 2003) was criticized during the first interstate conference on the pollution in the Escambia Bay and River for having closely spaced support pilings of treated wood that impeded currents (Stein et al., 1970; Olinger et al., 1975). In recent years the original railroad bridge was replaced with a bridge of modern design that utilizes more widely spaced concrete pilings. Construction of the original I-10 Escambia Bay bridge was begun by 1960, as shown in Figure 1.3.6-1 (Stein et al., 1970). During the first interstate conference on the state of Escambia Bay (Stein et al., 1970) it was concluded that the entire upper section of Escambia Bay upstream of the railroad bridge was in a state of accelerated eutrophication as shown by unstable dissolved oxygen variation resulting from algal activity, high carbon, nitrogen, and phosphorus concentration, and oxygen demanding sludge deposits. The lower part of the bay was stated to contain some sludges, but was not as badly afflicted due to better water exchange with Pensacola Bay (Stein et al., 1970; Olinger et al., 1975).

The I-10 bridge was rebuilt and completed in 2008 after destruction of the original by Hurricane Ivan in 2004. The replacement and reconstruction of bridges results in disturbances of the sediments. Typically the construction of most bridges requires that pilings be driven into the sediments. Very often water jets are used to aid in driving the pilings into soft sediments and this process displaces sediments. Below, in Figure 1.3.6-2, is shown what appears to be water jetting and pile driving activities for new pilings intended for replacement of the lower Escambia River Bridge on US Highway 90 between the river's mouth and Crist Steam Plant in 2004.

Figure 1.3.6-1. View of I-10 Pensacola Bay Bridge under construction: Pensacola, FL, 1960 **(**The Florida Memory Project, 2008).

Figure 1.3.6-2. Construction activities at new US Highway 90 bridge over Escambia River. At the left, red arrow indicates pipe attached to piling that channels water to the water jet. To the right a pile driver being used to drive pilings is suspended from a crane. (Photos C.J. Mohrherr, Jan. 2004).

### 1.3.3. US Highway 90 causeway and wetlands

Prior to the construction of the railroad bridge across the Escambia Bay ferryboats were the only method for freight and passengers to cross the Escambia Bay and lower Escambia River. Apparently the railroad bridge was not dual use requiring pedestrian and animal drawn wagons to cross by private boat or ferry boat services. A series of causeways and bridges were constructed over the Escambia River, its delta and upper regions of Escambia Bay in 1929 to allow the crossing by the newly constructed US Highway 90 (Drive the Old Spanish Trail, 2004). The environmental impact of this project upon the Escambia River delta and wetlands and Escambia Bay likely involved alterations of tidal flow and changes in salinity. Figure 1.3.3-1 shows a 2004 aerial photograph of US Highway 90 crossing the Escambia River delta and wetlands and Escambia Bay. Parts of the causeway consist of bridges that cross the Escambia River and its minor branches like the Little White and Simpson Rivers. Many parts of the causeway consist of raised earth. The basic design of the structure goes back to 1929 when the only considerations were issues of navigation and flooding. Apparent regrowth of trees is present in some parts of the Escambia River delta adjacent to the river, likely because of the large input of freshwater. The wetlands more distant from the Escambia River are characterized by emergent herbaceous vegetation. Some areas adjacent to the raised road bed, however, do contain shrubs. The delta and wetlands areas are of great interest for the presence of PCBs in sediments because wetlands typically are important nurseries and feeding areas for many types of fishes and shellfish that are consumed by humans.

## 1.4. Potential sources of pollution

### 1.4.1. Sediment pollution in Escambia Bay

Sediments, and fine sediments in particular, can be considered to be a form of pollution. Sedimentation is the most common form of pollution that is seldom commented upon by the public as long as navigation is not impeded. Activities associated with logging, including dredging and straightening of waterways, drainage of wetlands, and felling and dragging of logs, would have resulted in erosion of the soils and an increase in the sediment load of streams and rivers. This increased sediment load would have resulted in undocumented increased sediment disposition in Escambia Bay. Much of the initial industrialization of northwest Florida was integral with the lumber industry in the form of sawmills and later facilities for turpentine extraction (Figure 1.4.1-1). The lumber industry is still very active in northwest Florida and adjacent regions of Alabama, but now relies more upon heavy terrestrial logging equipment and logging trucks than upon water borne equipment to harvest and transport logs. The environmental impact of these activities has not been documented but it seems quite likely that the unpaved access roads and deforestation have resulted in soil erosion. During the 20th century farming in northwest Florida became more prevalent making the environment more likely to be impacted from increased erosion and runoff from applied fertilizers. After felling of the forests, especially in more recent years there has been increased construction of home sites, towns, farming, and roads that has also probably resulted in increased erosion and then sedimentation.

### 1.4.2. Industrial pollution and other point sources

The Lower Escambia Bay and River have a long documented history of pollution from industrial sources in Escambia County, FL, and also upriver in Alabama. There were at one time multiple major dischargers of industrial wastes on the Escambia Bay and River with the most impacting releases coming from chemical industries. The Escambia Bay and River eventually reached such a state of deterioration that a series of three interstate conferences on the pollution in the Escambia Bay and River were held (Stein et al., 1970a,b; USEPA 1972). There were several local industries that were known to have significantly contributed to the pollution mediated impacts upon the Pensacola Bay System with most of the impacts in about the Escambia Bay and River watershed (Figure 1.4.2-1). These releases to the local waterways are now regulated by Federal, State, and County regulations and these point releases have either been eliminated or the impacts drastically diminished.

Figure 1.3.3-1. US 90 crossing over the Escambia Bay and River.

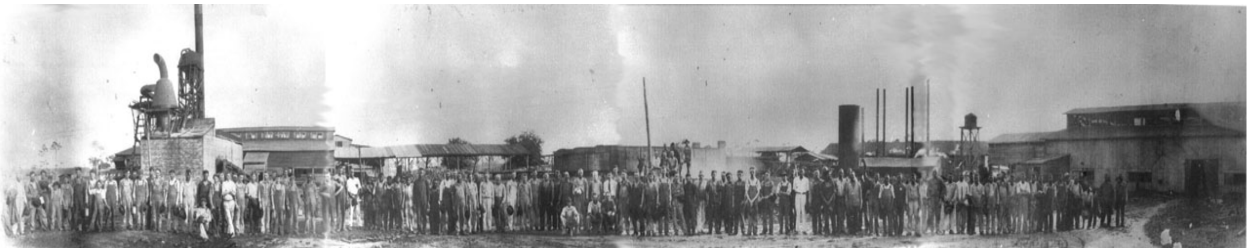


Figure 1.4.1-1. Photo of Pace lumber mill facility (Copyright © 2001-2002 Friends of Pace Area Library, Pace, Florida). Mill operated in Pace, FL from 1907-1927 and provided employment for over 200 men.

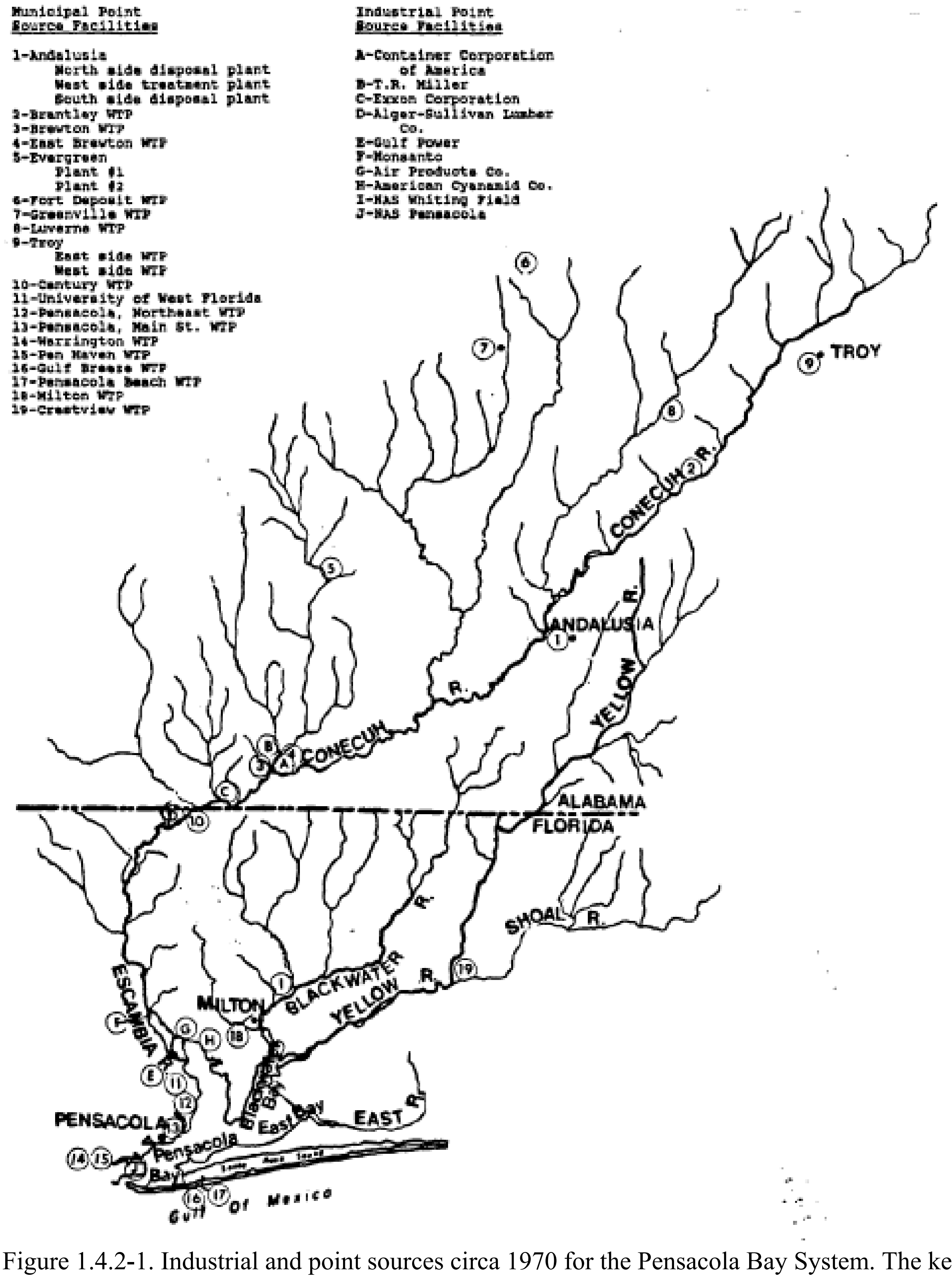


Figure 1.4.2-1. Industrial and point sources circa 1970 for the Pensacola Bay System. The key to the industrial sources for the Escambia watershed is: A-Container Corporation of America, B-T. R. Miller, C-Exxon Corporation, D-Alger-Sullivan Lumber Co., E-Gulf Power, F- Monsanto, G-Air Products and Chemicals, Inc., H- American Cyanamid Co.(Olinger et al, 1975).

In the past the impact of nutrient releases and other wastes was very detrimental to the environmental quality of the Bay. Olinger et al. (1975) reported that the diversity of the fish communities was inversely related to nutrient content in the water column. That is, species diversity was depressed in areas with high nutrient concentrations, whereas diversity was improved in waters with low nutrient levels. The major acute impairments to the Bay in the past have been due to excess nutrients that resulted in eutrophication and bacteria derived from sewage, but excess nutrients and coliform bacteria are by definition highly biodegradable and once the source(s) of the nutrients and sewage are regulated to what the system can handle the problem goes away. However, metals and the POPs like PCBs, dioxins/furans, and DDT are potentially more impacting upon environmental and human health due to their persistence and they can remain bound to sediment particles long after their releases to environment are stopped. Removal of the sources that release POPs may not result in a significant immediate drop in POP sediment concentrations. POPs absorbed to particulates of the sediments persist for many years and are available to the biota resulting in eventual bioaccumulation in the upper levels of the food chain. PCBs, dioxins/furans, and pesticides are among the most common POPs that are routinely looked for in sediments. Metals which do not degrade can also remain bound to the sediments.

In the summer of 1969 there was a reported release of a PCB-containing material from the Monsanto Chemical Company Plant into the waters of the Escambia River (Duke et al., 1970). The fate of these pollutants is uncertain and there is strong evidence that they are still present in the sediments. There are other possible industrial sources for PCBs. As late as 1988 at least one local industry had a permit that allowed discharge of PCBs to Escambia Bay. However, the possession of a permit for PCB disposal or release does not constitute evidence that PCB was actually released to the Bay by the permittee.

Recently, International Paper a large regional landowner with holdings within the watershed announced that segments or potentially all of its 6.8 million acres of U.S. forestlands may be put up for sale (International Paper, 2005). This will open up undeveloped forest lands to urbanization that results typically in increased erosion and pollutant transport to local water ways. Other sources of nutrients and sediments are from nonpoint sources, mainly from agricultural operations, that also affect the water quality in Escambia Bay. Much of the nutrient and sediment loading to the Bay is through the Escambia River. For instance, loading from nonpoint sources in Escambia Bay for biological oxygen demand, total nitrogen and total phosphorus represent 27.8, 16.3, and 37.7 percent of total loading respectively (NWFWMD, 1993). Nonpoint sources in Alabama contribute a significant load of nutrients and sediment of this total. Significant related environmental impacts have been documented in Escambia Bay, including high turbidity, chronic problems with elevated nutrient levels, and resuspension by wind events of previously deposited nutrients and sediments (NWFWMD, 1991).

Information taken from studies in the 1990's by DeBusk et al. (2002) showed that nutrients, heavy metals, PAHs, and pesticides were all elevated in Escambia Bay in general and in the northern part in particular. The Debusk et al. (2002) database shows that for total PAH seven out of ten samples reported in 1991-93 range from 1033 to 14,590 ug/kg. Arsenic, nickel, cadmium and chromium consistently presented the most serious impact for the bay, based on sediment quality assessment guidelines.

### 1.4.3. Monsanto Chemical Company site

The Monsanto Chemical Company through its subsidiary Chemstrand Company setup a nylon plant on the Escambia River in 1953 (Figures 1.4.3-1 & 1.4.3-2). Almost immediately complaints about pollution were voiced when this facility began operating. Chemstrand, the initial owner, claimed it was unaware of any toxic materials or harmful pollutants contained in its plant's discharge. Investigation showed, however, that this facility was one of the principal sources of the serious pollution of Escambia Bay. It was for this reason that regulators ordered the facility to stop discharging wastewater into the Escambia River (Special Grand Jury, 1999). In 1961, the Chemstrand name was changed to the Monsanto Textile Company and in more recent years this plant operated under the name of Solutia, Inc., which was originally part of Monsanto. From 1953 to 1962 nylon production increased by 300 percent and by an additional 400 percent during 1963 to 1972. The principal products of the plant included nylon intermediates and finished nylon. A corresponding increase in concentrated wastes generated at the plant were collected in a separate system and disposed by deep well injection. Other releases reported by the company consisted of cooling water and materials from spills that were as of 1975 discharged through two outfalls into the Escambia River. The north outfall received effluents from the yarn manufacturing area and the research and development building. The main outfall received effluents from the remainder of the plant. Sanitary wastes were treated by a primary treatment plant and then discharged into a lagoon, which supplied makeup water for cooling towers. The chemical oxygen demand load discharged by the Pensacola Plant from 1954 to 1972 was very high. An extremely high average annual load of 61,200 kg/day (135,000 lbs/day) was discharged into the Escambia River in 1955. The waste load decreased until 1959, and then increased until 1963, when a peak average annual load of 33,100 kg/day (73,000 lbs/day) was discharged (Olinger et al., 1975). The high five day biochemical oxygen demand (BODs) load discharged by the facility also decreased by 92.6 percent between September 1969 and January 1975 based on USEPA monitoring studies. Mean monthly BODs waste loadings (self-monitoring data) indicated discharges varied considerably, but a general downward trend did occur. Total nitrogen and phosphorus discharges decreased by 93.8 and 96.5 percent, respectively, between September 1969 and January 1975, based on USEPA monitoring data. Mean monthly self-monitoring data indicated the quantity of total nitrogen discharged was relatively constant during 1971 through 1974. During the same period, the mean monthly total phosphorus effluent load was extremely variable and no trends were obvious (Olinger et al., 1975).

The installation of waste injection wells was used to reduce the releases to the Escambia River (Olinger et al., 1975). In 1998 the plant drew 8 million MGD of groundwater from wells and 21.5 MGD from the Escambia River, for use in manufacturing and cooling processes (Special Grand Jury Report, 1999). The Solutia, Inc. facility recycles most of the water it uses, and deep well injects the rest (approximately 2.8 MGD) into the lower Floridan aquifer. The injected wastewater has remained confined to the immediate plant area. Monitoring wells show that after 30 years the plume was still within two miles of point of injection, and it is not expected to migrate into the sand and gravel aquifer used for drinking water wells or surface waters (Special Grand Jury Report, 1999).

Figure 1.4.3-1. Chemstrand Corporation, Pensacola, FL, 1960 (The Florida Memory Project, 2008).

Figure 1.4.3-2. Aerial view of the Chemstrand Corporation Chemical Plant, Pensacola, FL. 1960 (The Florida Memory Project, 2008).

### 1.4.4. Air Products and Chemicals, Inc.

The Air Products and Chemicals, Inc. facility, formerly called the Escambia Chemical Company, is located in Pace, FL adjacent to Escambia Bay (Figure 1.4.4-1 & 1.4.4-2). Within the local drainage area near the site are industrial ponds with an outfall indicated by a white arrow on the figure. The plant was built in 1955 to make fertilizer and was the source of several environmental problems, including air, groundwater, and surface water contamination. It also was one of the principal sources of the serious pollution of Escambia Bay that occurred in the 1960s. In 1969, the plant was sold to Air Products and Chemicals, Inc. The plant produced ammonium nitrate, ammonia, nitric acid, amines, urea, dinitrotoluene (DNT), and polyvinyl chloride. In 1970, methanol and mixed fertilizer plants at this facility were closed. The wastewater treatment system at the plant consisted of a 3.2 ha (8.0 acre) anaerobic lagoon, followed by four aerobic lagoons with a total area of 29.4 ha (72.5 acres) that finally discharged into Escambia Bay. The plant had a serious problem with contaminated groundwater, which accounted for 50 percent of the total nitrogen in the plant effluent. The plant reduced this problem by improved housekeeping and by intercepting contaminated groundwater before it entered the Pensacola Bay System (Olinger et al., 1975). Based on USEPA studies, BOD, total nitrogen, and total phosphorus were reduced by 78, 78, and 95 percent, respectively between September 1969 and January 1975 (Olinger et al., 1975). Table 1.4.4-1 shows the overall nutrient output of Air Products, Inc. from 1974 to 1986. Over most years there was a general decline with a notable exception in 1985 for total nitrogen.

Figure 1.4.4-1. Air Products and Chemicals, Inc. site on the northeast shore of Escambia Bay.

Figure 1.4.4-2. Escambia Chemical Company plant, Pensacola, FL, 1956. From: The Florida Memory Project (2008).

In the 1990’s all process water, which was drawn from wells, evaporated in manufacturing, except 1.0 MGD, which, together with an additional 0.3 MGD, was discharged into Escambia Bay after treatment. This process wastewater contained nitrogen, phosphorus, suspended solids, biological oxygen demanding substances, chemical oxygen demanding substances, and ammonia (Special Grand Jury Report, 1999). Currently Air Product’s facility’s biggest environmental problem on site appears to be contaminated groundwater. Air Products and Chemicals, Inc. began producing DNT in 1966 at their plant and ceased production in 1975 when this activity was moved to their Pasadena, TX facility. Releases containing DNT have contaminated the groundwater and issued on Sept 29, 1989 was a corrective action order pursuant to RCRA 3008(h) to complete a RCRA Facility Investigation relative to dinitrotoluene contamination by the 2, 6-DNT isomer. A final decision was issued by USEPA on Aug 23, 1994 relative to treatment of soil and ground water wastes (USEPA, 1994). Currently, Taminco Methylamines, Inc. is reported to be operating at this site. Taminco was reported to have reached an agreement with Air Products and Chemicals, Inc. in 2006 to acquire Air product's higher amines and methylamines.

Table 1.4.4-1. Annual loading (lbs/yr) to Escambia Bay by Air Products and Chemicals Inc. (FL DER, unpublished data, (Reidenauer and Shambaugh. 1986)).

| Year | Total N | T/P04 | TSS | T/COD |
|---|---|---|---|---|
| 1974 | 367,765 | 10.096 | 97,313 | 376,814 |
| 1975 | 331,604 | 11,710 | 73,964 | 381,162 |
| 1976 | 314,987 | 8,340 | 72,579 | 314,511 |
| 1977 | 170,371 | 9,260 | 60,784 | 308,505 |
| 1978 | 210,315 | 9,576 | 68,097 | 403,736 |
| 1979 | 181,824 | 9,438 | 62,045 | 376,324 |
| 1980 | 124,365 | 6,314 | 67,106 | 332,022 |
| 1981 | 70,385 | 3,930 | 46,230 | 287,948 |
| 1982 | 88,825 | 5,344 | 55,017 | 337,258 |
| 1983 | 91,435 | 6,411 | 53,361 | 311,074 |
| 1984 | 89,234 | 5,637 | 63,939 | 282,569 |
| 1985 | 117,697 | 5,435 | 48,426 | 299,634 |
| 1986 | 49,328 | 3,743 | 33,410 | 168,921 |

Westlake PVC formerly also operated on the Air Products site. It used vinyl chloride to make PVC and discharged the waste through Air Products and Chemicals, Inc. The waste was blended with groundwater and discharged into Escambia Bay, together with Air Product wastewater. This plant is currently closed (Special Grand Jury Report, 1999).

### 1.4.5. American Cyanamid

The Sterling Fibers facility, formerly known as American Cyanamid, is situated next to the Air Products and Chemicals, Inc. facility. Sterling made synthetic fiber and previously discharged its wastewater into Escambia Bay. It was one of the principal sources for pollution of Escambia Bay in the 1960's, when it discharged large amounts of acrylonitrile wastes containing cyanide, into Escambia Bay. The plant had produced acrylic polymer from acrylonitrile and methyl-methacrylate monomers to make fibers commencing in 1958. The monomers were reacted, washed, stored, and, when needed, dissolved in sodium thiocyanate solvent. Solvent recovery was built into the manufacturing process, and more than 99 percent of the solvent was recovered and reused (Olinger et al., 1975). Treatment facilities at the plant consisted of two 1.6 ha (4.0 acre) baffled lagoons. The discharge to the lagoons was composed of process and primary treated sanitary wastewaters. The effluent was discharged into Escambia Bay through a 1524 meter (5000 ft) submerged outfall with three diffusers spaced at intervals of 183 m (600 ft). Under the terms of the American Cyanamid Company NPDES permit (No. FLOOO2593), the facility was to commence discharging into a deep well disposal system by May 31, 1975. This deep well system was intended to be an interim method of waste disposal. The company was required to perform treatability and pilot plant studies for surface treatment of the total plant waste by 1978 (Olinger et al., 1975). Four studies of the American Cyanamid Plant were performed by USEPA and its predecessor agencies on these discharges (Olinger et al., 1975).

Table 1.4.5-1 shows that discharges to Escambia Bay declined from 1976 to 1986 (Reidenauer and Shambaugh, 1986). Later, Sterling Fibers stopped discharging directly into the bay and began using a 160 acre spray field to dispose 500,000 gallons of process wastewater a day (Special Grand Jury Report, 1999).

Table 1.4.5-1. Annual loading (lbs/yr) 1976 thru 1986 to Escambia Bay by American Cyanamid (Reidenauer and Shambaugh, 1986).

| year | BOD | TSS | TN |
|---|---|---|---|
| 1976 | 169,360 | 144,540 | 317,915 |
| 1977 | 35,770 | 109,500 | 211,335 |
| 1978 | 73.000 | 97,090 | 187,610 |
| 1979 | 51,465 | 101,105 | 176,660 |
| 1980 | 27,740 | 78,110 | 166,805 |
| 1981 | 20,440 | 60,955 | 119,720 |
| 1982 | 21,535 | 41,610 | 95,630 |
| 1983 | 26,280 | 38,325 | 111,690 |
| 19$4 | 30,368 | 43,800 | 144,905 |
| 1985 | 22,964 | 55,449 | 132,738 |
| 1986 | 11,145 | 32,345 | 35,373 |

A recent query of the USEPA Envirofacts Warehouse showed only a minimal amount of activity at the Sterling Fibers site (Table 1.4.5-2). This suggests that this facility is operating for brief intermittent periods of time.

### 1.4.6. Gulf Power Corporation

Gulf Power is a subsidiary of Southern Company and is one of the largest regional electric companies in the United States. It operates the Crist Steam Plant in Pensacola. The Gulf Power Corporation steam plant is located 5.3 km (3.5 mi) upstream of the mouth of the Escambia River on Governor's Bayou (Figures 1.4.6. 1 a&b). It is named for James F. Crist, president of Gulf Power from 1948 to 1955. Initially called the Pensacola Steam Plant, it was first brought on-line on January 1, 1945. In the preceding years during World War II, limited construction supplies had precluded the construction of the much-needed plant, forcing Gulf Power to barge in a surplus floating Navy generating unit, which operated on pilings for one year and helped meet the rapidly increasing demand. The plant's first generating unit had a capacity of 22,500 kilowatts. More units were added over the years, with the 500,000-kilowatt Unit 7 coming on-line in August 1973 (Pensapedia, 2008). The Crist Steam Plant uses large quantities of river water (an average of 24.1 MGD), which it returns to the river after use, to cool its boilers via a thermal canal that runs under Thompson Bayou. It also uses small quantities of well water (an average of 2.2 MGD in 1999) as process water for the boilers, most of which is evaporated, with the rest (an average of 0.225 MGD) discharged, after treatment, into the Escambia River (Special Grand Jury Report, 1999).

Table 1.4.5-2 Releases from Sterling Fibers site in 2006.

| Air | | Underground Injection | | Land Surface | |
|---|---|---|---|---|---|
| Chemical Name | Release [lbs/yr] | Chemical Name | Release [lbs/yr] | Chemical Name | Release [lbs/yr] |
| ammonia | 5 | acrylonitrile | 1170 | ammonia | 4161 |
| chlorine | 5 | ammonia | 1853 | nitrate compounds | 6388 |
| chlorine | 5 | nitrate compounds | 2172 | | |
| ethylene glycol | 5 | | | | |
| ethylene glycol | 5 | | | | |
| methanol | 5 | | | | |
| methanol | 5 | | | | |

Figure 1.4.5-1. American Cyanamid Company chemical plant, Pace, FL, 1959 (The Florida Memory Project, 2008).

Imagery ©2008 DigitalGlobe, The Florida Department of Environmental Protection, GeoEye, Map data ©2008 Tele Atlas - Terms of Use

Figure 1.4.6-1a. Aerial view of Crist Steam Plant on Governor's Bayou and Escambia River.

Figure 1.4.6-1b. Surface view of Crist Steam Plant on Governor's Bayou and Escambia River

Air emissions are the main environmental impact of power plants. A news release from Overland Park, KS. (May 7, 2007) by the consulting firm of Black & Veatch announced that they had been selected by Gulf Power Company to provide detailed engineering, as well as procurement and construction support for the addition of a wet flue gas desulphurization system (scrubber). The scrubber system at the Crist Steam Plant was to enhance air quality in the region by significantly removing sulfur dioxides, fine particulates and oxidized mercury emissions (Black & Veatch Holding Company, 2008).

The EPA mandated Toxic Release Inventory (TRI) data for the Crist plant in 2006 show that the major chemical releases include ammonia, hydrochloric acid, hydrogen fluoride, and sulfuric acid (Table1.4.6-1). Release for common toxic metals like arsenic, chromium, copper, lead, mercury, and nickel ranged mostly from about 200-400 lbs/ year. Zinc and some other metals were higher. Total yearly dioxin/furan emission was 0.485 lbs.

Table 1.4.6-1. Crist Steam Plant 2006 Toxics Release Inventory data .

| Chemical name | Total air emissions [lbs] |
|---|---|
| Ammonia | 22,800 |
| Hydrochloric acid (1995 and after "acid aerosols" only) | 2,400,000 |
| Hydrogen fluoride | 420,000 |
| Sulfuric acid (1994 and after "acid aerosols" only) | 280,000 |
| Arsenic compounds | 320 |
| Barium compounds | 2400 |
| Chromium compounds (except chromite ore mined in Transvaal) | 340 |
| Copper compounds | 230 |
| Lead compounds | 282.9 |
| Manganese compounds | 680 |
| Mercury compounds | 327.3 |
| Nickel compounds | 380 |
| Vanadium compounds | 440 |
| Zinc compounds | 1300 |
| Dioxin and dioxin-like compounds | 0.485 |

### 1.4.7. Former City of Pensacola northeast wastewater treatment plant

This wastewater treatment plant began operation in 1962 and served a population of approximately 11,000. The design flow of the plant was 3800 $m^3$/day (1.0 mgd). The waste underwent screening preparation, grit removal, primary settling, biological treatment using trickling filters, chemical treatment, secondary settling effluent chlorination, and disposal through a 550 m (1,804 ft) outfall line discharging into Escambia Bay just south of Devils (Gull) Point in 1.4 m (4.5 ft) of water . The effluent from the Northeast Wastewater Treatment Plant was sampled by the US Department of Interior in September 1969, and 207 kg/day (457 lbs/day) of BODs, 765 kg/day (1,688 lbs/day) of total nitrogen, and 97 kg/day (213 lbs/day) of total phosphorus were measured. The flow was estimated at 3800 $m^3$/day (1.0 mgd), but the City of Pensacola claimed that the flow was about 1900 $m^3$/day (0.5 mgd) during the study. Another survey was conducted by USEPA in March 1972 and indicated the discharge contained 159 kg/day (351 lbs/day) of BODs, 60 kg/day (132 lbs/day) of total suspended solids, 87 kg/day (191 lbs/day) of total nitrogen, and 25 kg/day (56-lbs/day) of total phosphorus. The effluent flow of the plant was 1.900 $m^3$/day (0.5 mgd) during this study. The Northeast Wastewater Treatment Plant was given a NPDES permit that permitted enlargement to treat 1.85 mgd. This NPDES permit also stated that operation of the plant would be discontinued when the Main Street sewage Treatment Plant could serve this area on or before June 30, 1977. The Northeast Sewage Treatment Plant has since been removed. There were also other sewage treatment plants that polluted the Escambia River (Figure 1.4.2-1) (Stein, 1970a,b).

### 1.4.8. Container Corporation of America

The Container Corporation of America, Brewton, Alabama, was an integrated craft paper mill that began operation in December 1957 with an average daily production of 272 MT/day (300 tons/day). Production increased to 1043 MT/day (1150 tons/day) of paperboard in 1975, of which approximately 50 percent was bleached. Wastewaters from this facility were from the unbleached pulp process, bleach plant, and wood yard. Unbleached pulp process wastewaters were treated in a clarifier, liquid oxygen applicator, aeration basin, and oxidation pond; and then the wastes flowed through a creek, swamp, and six natural lakes before discharging into the Conecuh River, about 80 km (50 mi) upstream of Escambia Bay. Bleach, plant, and woodyard effluents went directly to the creek, swamp, and lake system. Sanitary wastewaters were discharged into the clarifier to provide nutrients for treatment of unbleached pulp process wastewaters. Effluent loadings from the Container Corporation of America Mill decreased between 1969 and 1975. In 1975 the BOD loading was 30 percent less than in 1969 (Olinger et al., 1975). A 1999 Grand Jury Report stated that “For example, the plant is not even required to monitor and report the amount of nitrogen, phosphorus or other nutrients in the effluent” (Special Grand Jury Report, 1999). A recent query of the EnviroMapper for Envirofacts for this region found 2006 TRI facility release data (Table 1.4.8.-1) to surface waters for the pant. The plant currently is owned by Georgia-Pacific.

Table 1.4.8-1. Georgia-Pacific, Brewton, plant 2006 TRI data for chemicals released to surface water.

| Chemical name | Release Amounts [lbs/yr] |
|---|---|
| Acetaldehyde | 1100 |
| Ammonia | 11000 |
| Catechol | 100 |
| Formaldehyde | 3000 |
| Formic acid | 1500 |
| Lead compounds | 670 |
| Manganese compounds | 88000 |
| Methanol | 40000 |
| Naphthalene | 10 |
| Phenol | 15 |
| Polycyclic aromatic compounds | 22 |
| Zinc compounds | 4000 |

### 1.4.9. New Emerald Coast Utilities Authority sewage treatment plant

The Emerald Coast Utilities Authority (ECUA) is building a new municipal sewage treatment plant. The site, referred to as the Central Water Reclamation Facility (CWRF), will replace the 72-year-old Main Street Wastewater Treatment Plant. The new site is a 327-acre parcel on property purchased from Solutia, Inc., located on the Escambia River (Figure 1.4.9.1a&b). The site was found to best meet the criteria set forth by ECUA for the new facility. The site's location is well-buffered from its nearest residential neighbors and is expected to avoid complaints of bad odors, unlike the current Main Street Facility. In addition to the 327 acres that will serve as the location of the new plant, nearly 2,000 more acres have been purchased by ECUA to contribute to the buffering of the new plant. The inland site is well above the category five flood elevation making the plant safe from flooding due to river floods or hurricanes. The site offers industrial reuse of effluent water to the Crist Steam Plant and to other regional industrial users. The International Paper Cantonment, FL. paper mill is planning to use up to 5 million gallons per day of highly treated wastewater from the planned ECUA treatment. It is claimed that reuse of the domestic wastewater will reduce groundwater consumption and decrease pollutant loadings to regional ground and surface waters. In addition, the agreement delivers "smart growth" benefits by expanding regional wastewater treatment capacity in advance of anticipated development in the area. Further, the effluent from this project will be used to restore wetlands for improved water quality (FDEP, 2001).

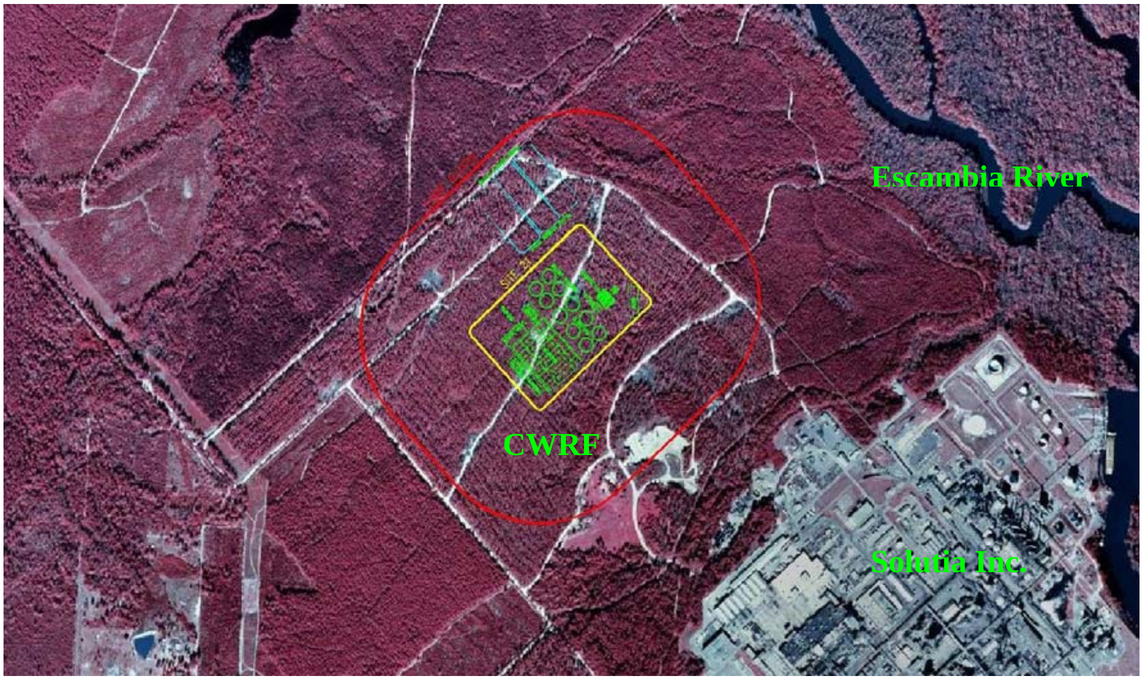


Figure 1.4.9-1a: Location of new ECUA sewage treatment plant (CWRF).

Figure 1.4.9-1b. Site progress at location of new ECUA treatment plant as of October 2008 (ECUA, 2008)

### 1.4.10. Current environmental status

Currently, with the federal pollution regulations enforced by RCRA, NPDES, CERCLA and federally compliant state programs, all of the previously mentioned facilities have reduced their point discharges to surface waters of the Escambia Bay and River. However, a recent USEPA report stated that for the upper Escambia Bay it was verified as impaired for chlorophyll a (USEPA, 2007). Excess chlorophyll a is associated with an excess of nutrients, which may be linked to eroded sediments. The western shore of Escambia Bay is more heavily urbanized than the eastern shore, but both have sources of nutrients and sediments. There are also inputs of sediments and nutrients into Escambia Bay from human activities upriver that include agricultural activities, industries, unpaved surface roads, and urban centers (USEPA, 2005).

## 1.5. Currents and tides

Movement of water in Escambia Bay is complicated because freshwater enters the bay via the main channels of the Escambia River and the Little White and Simpson Rivers in the north and salt water enters from the south. Salinity data from an August 1973 study indicated that more freshwater flows down the western side of Escambia Bay than the eastern side. This may be due to the Coriolis force which is caused by the earth's rotation. In the past waste discharges into the bay instead of being carried towards Pensacola Bay were sometimes transported to the upper Escambia Bay and remained in the system for a longer period than the flushing time for the bay would suggest. Wind is an influential factor in causing these current reversals (Olinger et al., 1975). Based on field flow estimations, about 25 percent of the total flow of the Escambia River basin enters the northwestern section of upper Escambia Bay through the Little White and Simpson Rivers. This freshwater inflow travels seaward along the Escambia River delta and not throughout the entire northeast section of the upper bay. Discharges from American Cyanamid Co. and Air Products and Chemicals, Inc. facilities tended to accumulate in the vicinity of the Air Products outfall (Olinger et al., 1975). The effluent from Air Products and Chemicals, Inc. stayed close to the shore north and south of the Air Products outfall. Circulation caused most of the discharge from the American Cyanamid plant to be transported north toward Floridatown instead of seaward during a September 1974 survey. Effluent from the Air Products and Chemicals Inc. plant remained concentrated in the nearshore zone, north and south of the discharge point during the August 1974 survey. Both effluents entered Bayou Mulat (Olinger et al., 1975). Escambia Bay is a microtidal estuary (0 – 50 cm tides), but strong winds readily magnify tidal levels.

## 1.6. Pollutants in seafood

Findings reported in a PERCH quarterly progress report (May 20, 2005) submitted for the current Cooperative Agreement to EPA show that mullet and large mouth bass collected from the lower Escambia River contain high concentrations of total PCBs and dioxins/furans, and dioxin-like PCBs (Figure 1.6-1). The TEQs found in largemouth bass (3.09 ng/kg) and mullet (2.14 ng/kg) were an order of magnitude higher than the USEPA recreational screening threshold (ST) for dioxins/furans and dioxin-like PCB which is 0.26 TEQ ng/kg. The PCB concentrations found in largemouth bass (52,697 ng/kg) and mullet (84,104 ng/kg) were stated to be extraordinarily high compared to the EPA's recreational fisher ST for total PCBs (2,000 ng/kg). The PCB concentrations found in largemouth bass from lower the Escambia River were about 65 times higher than those found in samples from upper Escambia River. Additional seafood sample data from upper Escambia Bay were obtained during construction of the new I-10 bridge across Escambia Bay. Explosives were used underwater to demolish part of the old bridge structure on either side of the shipping channel resulting in mortality of fishes in the vicinity. Five species of fish were obtained from the blast site, including nine individuals of sheepshead (*Archosargus probatocephalus*), one composite sample of white trout (*Cynoscion arenarius*), two individuals of spotted seatrout (*Cynoscion nebulosus*), three composites of croaker (*Micropogonias undulatus*), and four individuals of mullet (*Mugil cephalus*) (Table 1.6.-1 ). Eight of the samples exceeded the EPA TEQ ST of 0.26 ng/kg for dioxin/furans only, and none were above 0.5 ng/kg. The TEQ for the dioxin-like PCBs however ranged from low values for the white and spotted sea trout (0.778-4.22 ng/kg) to the highest value recorded for a mullet at 75.0 pg/kg, or nearly 300 times the EPA ST for total TEQ (Table 1.6.-1, Snyder and Rao, 2008). This data indicates that the impacts of PCBs that were banned many years ago have accumulated in seafood tissues in amounts sufficient to pose significant health risks to human health.

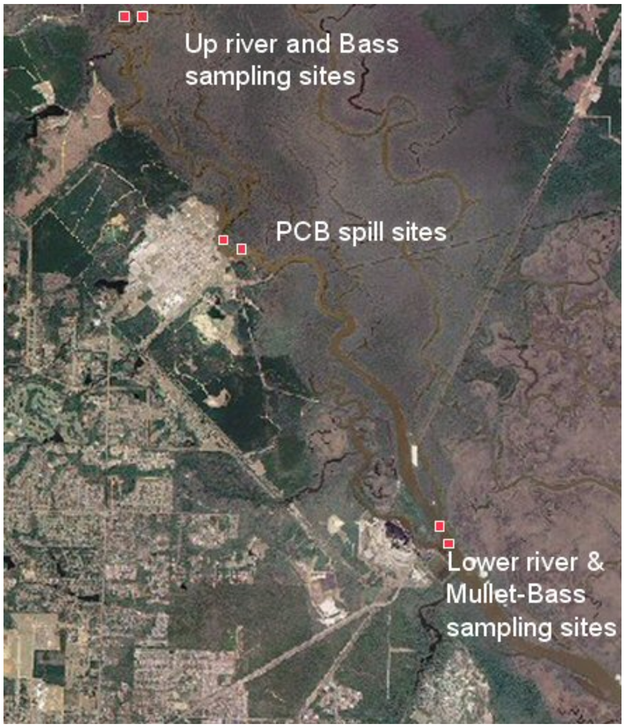


Figure 1.6-1. Lower Escambia River adjacent to Solutia, Inc., and Crist Power Plant. The red squares are locations considered for sediment samples.

## 1.7. Sediment studies in the 1990’s

Data of sediment SOCs obtained from Escambia Bay in the 1990’s by several studies conducted by USEPA, State of Florida, and NOAA are tabulated in the Debusk et al. (2002) database. The database contains data for metals, PAHs, pesticides, PCBs, and nutrients. Members of the DDT family pesticides (Table 1.7-1) and Mirex (Table 1.7-2) were the most commonly detected chlorinated pesticides, but there were also trace amounts of A-Chlordane, Endosulfans, Dieldrin, Endrins, and Heptachlor epoxide. Mirex was not detected in the present study in contrast to DDT that was detected. In past studies p,p’DDT (also known as 4, 4’DDT) was not detected although its isomer o,p’DDT and its degradation products (DDE and DDD) were frequently detected in the bay’s sediments (figure 1.7-1a&b). Table 1.7-3 lists the current FDEP SQAGs for DDT and its byproducts.

Table 1.6-1. PCBs and dioxins in Escambia Bay fishes. From: Snyder and Rao (2008).

| Species | Composite | Lipid [%] | $\mathrm{TEQ}_{\mathrm{DF}}$ [ng/kg] | $\mathrm{TEQ}_{\mathrm{P}}$ [ng/kg] | $\mathrm{TEQ}_{\mathrm{DFP}}$[1] [ng/kg] | Total PCBs[2] [ng/g] |
|---|---|---|---|---|---|---|
| Archosargus probatocephalus | 070917M | 1 | 0.27 | 2.324 | 2.594 | 41.1 |
| Archosargus probatocephalus | 070917I | 0.8 | 0.19 | 3.031 | 3.221 | 54.1 |
| Archosargus probatocephalus | 070917S | 1.8 | 0.4 | 4.183 | 4.583 | 173.0 |
| Archosargus probatocephalus | 070917J | 0.7 | 0.17 | 5.176 | 5.346 | 87.7 |
| Archosargus probatocephalus | 070917K | 0.7 | 0.17 | 4.986 | 5.156 | 83.7 |
| Archosargus probatocephalus | 070917O | 0.6 | 0.16 | 3.202 | 3.562 | 73.4 |
| Archosargus probatocephalus | 070917L | 2.6 | 0.46 | 12.489 | 12.949 | 192.0 |
| Archosargus probatocephalus | 070917N | 1.6 | 0.36 | 6.019 | 6.379 | 165.0 |
| Cynoscion arenarius | 070917F | 0.3 | 0.19 | 1.751 | 1.941 | 336.0 |
| Cynoscion arenarius | 070917U | 0.6 | 0.16 | 4.218 | 4.378 | 192.0 |
| Cynoscion arenarius | 070917T | 0.3 | 0.12 | 1.063 | 1.183 | 70.9 |
| Cynoscion arenarius | 070917E | 0.6 | 0.19 | 3.715 | 3.905 | 105.0 |
| Cynoscion arenarius | 070917H | 0.2 | 0.16 | 0.793 | 0.953 | 27.0 |
| Cynoscion arenarius | 070917G | 0.3 | 0.2 | 0.778 | 0.978 | 26.3 |
| Micropogonias undulatus | 070917R | 2.4 | 0.24 | 3.768 | 4.008 | 303.0 |
| Micropogonias undulatus | 070917Q | 1.5 | 0.23 | 2.947 | 3.177 | 174.0 |
| Micropogonias undulatus | 070917P | 3.6 | 0.34 | 5.806 | 6.146 | 274.0 |
| Mugil cephalus | 070917D | 4.4 | 0.42 | 22.053 | 22.473 | 678.0 |
| Mugil cephalus | 070917C | 2.2 | 0.27 | 43.226 | 43.696 | 1010.0 |
| Mugil cephalus | 070917A | 3.9 | 0.26 | 13.202 | 13.662 | 284.0 |
| Mugil cephalus | 070917B | 3.5 | 0.3 | 75.005 | 75.305 | 1580.0 |

1. US EPA screening level for combined dioxin/furan and PCB TEQ ($\mathrm{TEQ}_{\mathrm{DFP}}$)= 0.26 ng/kg. State of Florida screening level for $\mathrm{TEQ}_{\mathrm{DFP}}$ has not been established.
2. US EPA screening level for total PCB = 20 ng/g. State of Florida screening level for total PCB = 50 ng/g.

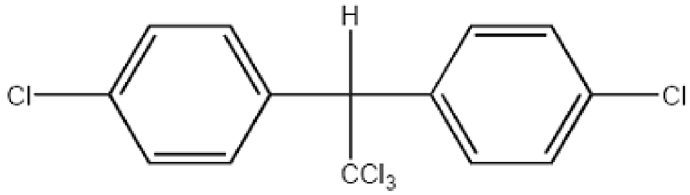


Figure 1.7-1a. Structure of *p,p'*-DDT

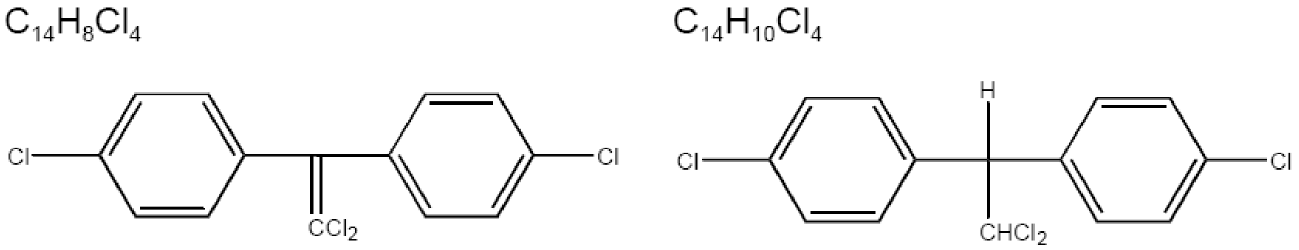


Figure 1.7-1b. Structures of *p,p*'-DDE (left) and *p,p*'-DDD(right)

Table 1.7-1. Results from previous studies for DDTs, DDDs, and DDEs (DeBusk et al., 2002).

| Site Label | 44DDD | 24DDD | 44DDE | 24DDE | 44DDT | 24DDT | SUM_DDT | Tot DDT |
|---|---|---|---|---|---|---|---|---|
| EPA1 | 0.1 | 0.0 | 0.1 | | | | 0.3 | |
| EPA3 | 0.4 | 0.1 | 0.7 | | | 0.3 | 1.5 | 0.3 |
| EPA4 | 0.7 | 0.3 | 1.5 | | | 1.1 | 3.4 | 1.1 |
| EPA5 | 0.4 | 0.1 | 0.8 | | | 0.5 | 1.8 | 0.5 |
| EPA6 | 0.3 | 0.2 | 0.6 | | | 0.3 | 1.3 | 0.3 |
| EPA7 | 0.4 | 0.3 | 1.2 | | | 0.8 | 2.7 | 0.8 |
| EPA8 | 0.3 | 0.2 | 0.6 | | | 0.5 | 1.6 | 0.5 |
| EPA9 | 0.3 | 0.2 | 0.6 | | | 0.5 | 1.5 | 0.5 |
| EPA10 | 0.2 | 0.1 | 0.5 | | | 0.3 | 1.0 | 0.3 |
| EPA11 | 0.3 | 0.2 | 0.9 | | | 0.4 | 1.7 | 0.4 |
| EPA12 | 0.4 | 0.2 | 0.9 | | | 0.4 | 1.9 | 0.4 |
| ESC01 | | | 1.4 | | | | 1.4 | |
| ESC01 | | | 1.4 | | | | 1.4 | |
| ESC02 | | | 2.0 | | | | 2.0 | |
| ESC03 | | 2.4 | 1.7 | | | | 4.1 | |
| ESC04 | | 1.0 | 1.1 | | | | 2.1 | |
| ESC05 | | 0.7 | 1.1 | | | | 1.8 | |
| ESC05 | | 1.8 | **2.2**[1] | | | | 4.0 | |
| ESC06 | | 1.8 | 1.7 | | | | 3.6 | |
| ESC07 | | 0.5 | 1.0 | | | | 1.5 | |
| ESC08 | | 0.7 | 1.4 | | | | 2.0 | |

Table 1.7-1. Results from previous studies for DDTs, DDDs, and DDEs (DeBusk et al., 2002) (cont'd.).

| Site label | 44DDD | 24DDD | 44DDE | 24DDE | 44DDT | 24DDT | SUM_DDT | Tot DDT |
|---|---|---|---|---|---|---|---|---|
| ESC09 | | | | | | | | |
| ESC10 | | | | | | | | |
| ESC11 | | 1.4 | 1.1 | | | | 2.5 | |
| ESC12 | | 1.4 | 0.8 | | | | 2.2 | |
| ESC13 | | 5.6 | 1.3 | | | | 6.9 | |
| ESC14 | | 10.7 | **5.3** | | | | 16.0 | |
| ESC16 | | 10.6 | **4.9** | | | | 15.5 | |
| ESC17 | | | | | | | | |
| ESC18 | *8.4*[2] | | **6.8** | | | | 15.3 | |
| ESC20 | **7.3** | | **4.4** | | | | 11.7 | |
| ESC21 | | | | 2.5 | | | 2.5 | |
| ESC22 | | | | | | | | |
| ESC23 | | | **4.9** | | | | 4.9 | |
| ESC24 | | | **5.2** | | | | 5.2 | |
| ESC25 | | | | | | | | |
| ESC25 | | | | | | | | |
| ESC26 | *14.8* | | **5.9** | | | | 20.7 | |
| ESC27 | | | **4.1** | | | | 4.1 | |
| ESC28 | | | **6.2** | | | | 6.2 | |
| ESC30 | | | **7.4** | | | | 7.4 | |
| ESC30 | | | **1.6** | | | | 1.6 | |
| ESC31 | | 5.6 | | | | | 5.6 | |
| ESC32 | | | **4.5** | | | | 4.5 | |
| ESC33 | | 14.7 | **5.7** | | | | 20.4 | |
| ESC34 | | 3.7 | | | | | 3.7 | |
| ESC35 | | | | | | | | |
| ESC36 | | 8.0 | **4.8** | | | | 12.8 | |
| ESC37 | | | | | | | | |
| ESC38 | | | **5.5** | | | | 5.5 | |
| ESC40 | | | **4.9** | | | | 4.9 | |
| ESC42 | | | **4.4** | 2.7 | | | 7.1 | |
| ESC43 | | | **5.2** | | | | 5.2 | |
| ESC44 | | | | | | | | |
| ESC45 | | | **4.8** | 2.6 | | | 7.4 | |
| ESC47 | | | | | | | | |
| PCOLA01 | | | | | | | | |
| PCOLA42 | | 0.7 | 0.2 | | | | 0.8 | |
| PCOLA47 | | 1.2 | 0.4 | | | | 1.6 | |
| PCOLA47 | | 1.9 | 0.7 | | | | 2.6 | |
| NOAA24 | 0.5 | 1.0 | 1.0 | 0.5 | | 0.1 | 3.1 | 0.6 |

1. Bolded concentrations exceed the FDEP TEL.
2. Italicized-underlined concentrations exceed the FDEP PEL.

Table 1.7-2. Results from previous studies for non-DDT detected pesticides.

| Site label | A-chlordane | Dieldrin | Endosulfan | Endosulfan I | Endosulfan II | Endrin | Endrin aldehyde | Heptachlor | Mirex |
|---|---|---|---|---|---|---|---|---|---|
| EPA1 | 0.0 | | | 0.4 | 1.2 | | | | |
| EPA3 | 0.1 | | | 0.8 | 2.5 | | | | |
| EPA4 | 0.1 | | | 1.0 | 1.5 | | | | |
| EPA5 | 0.1 | | | 0.9 | 0.9 | | | | |
| EPA6 | 0.2 | | | 0.9 | 0.8 | | | | |
| EPA7 | 0.2 | | | 0.7 | 0.4 | | | | |
| EPA8 | 0.2 | | | 0.9 | 0.4 | | | | |
| EPA9 | 0.2 | | | 1.1 | 0.3 | | | | |
| EPA10 | 0.1 | | | 1.1 | 0.4 | | | | |
| EPA11 | 0.2 | | | 1.1 | 1.2 | | | | |
| EPA12 | 0.2 | | | 0.9 | 0.3 | | | | |
| ESC01 | | | | | | | | | 29.6 |
| ESC01 | | | | | | | | | 30.5 |
| ESC02 | | | | | | | | | 31.7 |
| ESC03 | | | | | | | | | 29.6 |
| ESC04 | | | | | | | | | 24.1 |
| ESC05 | | | | | | | | | 25.2 |
| ESC05 | | | | | | | | | 30.3 |
| ESC06 | | | | | | | | | 27.3 |
| ESC07 | | | | | | | | | 24.3 |
| ESC07 | | | | | | | | | 25.9 |
| ESC08 | | | | | | | | | 29.7 |
| ESC09 | | | | | | | | | 14.9 |
| ESC10 | | | | | | | | | 14.7 |
| ESC11 | | | | | | | | | 26.0 |
| ESC12 | | 1.4 | | | | | | | 18.1 |
| ESC13 | | 1.9 | | | | | | | 21.0 |
| ESC14 | | | | | | | 0.9 | | 63.3 |
| ESC16 | | | | | | | 1.4 | | 66.2 |
| ESC17 | | | | | | | | | 64.7 |
| ESC18 | | | | | | | | | 69.8 |
| ESC20 | | | | | | | | | 61.3 |
| ESC21 | | | | | | | | | 63.5 |
| ESC22 | | | | | | | | | 62.5 |
| ESC23 | | | | | | | | | 56.1 |
| ESC24 | | | | | | | | | 65.7 |
| ESC25 | | | | | | | | | 54.6 |
| ESC26 | | | | | | | | | 63.0 |
| ESC27 | | | | | | | | | 56.2 |
| ESC28 | | | | | | | | | 62.2 |
| ESC30 | | | | | | | | | 91.3 |
| ESC30 | | | | | | | | | 20.3 |
| ESC31 | | | | | | | | | 55.5 |
| ESC32 | | | | | | | | | 71.5 |
| ESC33 | | | | | | | | | 64.6 |
| ESC34 | | | | | | | | | 58.0 |

Table 1.7-2. Results from previous studies for non-DDT detected pesticides (cont'd).

| Site label | A-chlordane | Dieldrin | Endosulfan | Endosulfan I | Endosulfan II | Endrin | Endrin aldehyde | Heptachlor | Mirex |
|---|---|---|---|---|---|---|---|---|---|
| ESC35 | | | | | | | | | 61.9 |
| ESC36 | | | | | | | 0.9 | | 57.5 |
| ESC37 | | | | | | | | | 57.6 |
| ESC38 | | | | | | | | | 67.2 |
| ESC40 | | | | | | | | | 63.8 |
| ESC42 | | | | | | | | | 70.9 |
| ESC43 | | | | | | | | 3.2 | 69.9 |
| ESC44 | | | | | | | | | 63.6 |
| ESC45 | | | | | | | | | 70.3 |
| ESC47 | | | | | | | | | 67.9 |
| PCOLA01 | | | 5.3 | | | | | | 10.8 |
| PCOLA42 | | | | | | | | | 11.1 |
| PCOLA47 | | | | | | | | | 19.8 |
| PCOLA47 | | | | | | | | | 19.6 |
| NOAA24 | 1.7 | 0.1 | | | | 1.0 | | | 0.5 |

Table 1.7-3. State of Florida SQAGs [ug/kg].

| Pesticide | TEL | PEL |
|---|---|---|
| p,p’-DDD (44DDD ) | 1.22 | 7.81 |
| p,p’-DDE (44DDE) | 2.07 | 374 |
| p,p’-DDT (44DDT) | 1.19 | 4.77 |
| Total DDT (Sum p,p’DDT and o,p’DDT) | 3.89 | 51.7 |

### 1.7.1. PCBs in Escambia Bay sediments

At least five studies of Escambia Bay sediments have analyzed for PCBs. The studies were carried out in the 1990’s and most of the data are not generally available to the public. The DeBusk et al. (2002) database contains the data from four of these studies:

1. USEPA Environmental Monitoring and Assessment Program Study, 1991-1994
2. USEPA Pensacola Bay Intensive Study, 1992
3. USEPA Pensacola Bay Study, 1996
4. National Oceanic and Atmospheric Administration study, 1993-1994

The fifth study, EA Engineering, Science, and Technology (1999) is the most recent one and is not included in the DeBusk et al. (2002) database. The data these studies generated varied greatly, due in part to the heterogeneous distribution of PCBs, but probably also due to different analyses, analytical laboratories, and possibly differing collection methodologies (Figure 1.7.1-1) (Bunch, 2006). All but one of the studies was of surface sediment; the EA (1999) study was intended to give information about an upcoming dredging project and consisted of 4 mixed sediment cores. Additional sampling by the present study is justified by the varying results of these earlier studies and also the passage of time. The sampling of the past studies was limited in scope and insufficient to give a systematic overall view of PCB concentrations. Additionally, the data can not be summed and used to depict PCB sediment profiles because of differences in the congeners that were analyzed for. The disparity between the results suggests that a new and systematic study of Escambia Bay and River is called for. The current PERCH study is a single study utilizing the standard EPA Analytical Method 1668A for a complete assessment that covers the bay and the Florida portion of the river to allow analyses of any spatial pattern that could give insight into the origin and distributions of the PCBs. The current study includes the full complement of 209 PCB congeners, which has never been analyzed before in the bay. Additionally, the sediments have never been analyzed for dioxins/furans, as the current study does.

This PERCH study also extends to areas of the Escambia Bay System that have never been sampled for SOCs (DeBusk et al., 2002). The unstudied areas are the wetlands, canals, delta of the Escambia River, and the Escambia River itself. It is quite probable that many species of seafood frequent these areas at some point of their life cycle and knowledge of the PCB and dioxin/furan profiles are important to providing data for future studies of POP bioaccumulation in seafood species.

Approximately 18 years have passed since the last PCB studies were conducted in the Bay and the current distributions of the PCB contaminated sediments of Escambia Bay are not known. In the intervening years since the first detections in Escambia River water in 1969, flooding and tropical storms have repeatedly impacted the area. Most recently between 2004 and 2008 the bay system was impacted by storm surges and winds from Hurricanes Ivan, Katrina, Dennis, and Ike. These strong wind events might have resulted in resuspension, dislocation, and/or burial of contaminated sediments since the last studies in the 1990's. Other events that may have impacted sediment distribution have been bridge construction and demolition in Escambia Bay. The original CSX railroad bridge pilings were water jetted up in the 1980's and a new railroad bridge was constructed. Due to Hurricane Ivan the original I-10 bridge was seriously damaged and a new bridge was recently constructed to replace it. There is periodic dredging to maintain the barge shipping channel to the Gulf Power Crist Steam Plant and Solutia facilities located just north of the mouth of the Escambia River that also could affect sediment PCB concentrations.

## 1.8. Data Gaps

To address the above mentioned data gaps the current PERCH study has been extended to areas that have not been previously studied. It will determine if there are significant concentrations of POPs in wetlands that may be important in the life cycles of shellfish and fishes and provide habitat for adult fish, wildfowl, and game animals. In these areas fishing and hunting also occurs. All of these activities represent potential pathways through which POPs can enter food webs and impact human populations. We have collected for assessment the available environmental data for Escambia Bay, its wetlands, and its local tributaries (this includes areas that were never studied for PCBs) and are making them publicly available in this report. Transport of contaminated sediments from bridge construction/repair, releases by industries, dredging, and barge traffic are possible scenarios for impacts. Environmental and possible human impacts from PCBs and dioxin/furans and other SOCs such as heavy metals, PAHs, and pesticides are evaluated in accord with the most appropriate Federal and State of Florida Assessment Guidelines and other existing applicable standards. The purpose of the study is to fill in existing data gaps for a timely assessment of the environmental state of Escambia Bay sediments and to provide information of relevance to location of oyster beds and other aquaculture, health related assessments of commercial and recreational fishing, dredging of shipping channels, and bridge construction.

Figure 1.7.1-1. Total PCBs [ug/kg] in Escambia Bay sediments (Bunch, 2006).

# 2. Methods

Accessible information concerning the environmental conditions of Escambia Bay and River was compiled through an exhaustive literature search. For this effort we drew in part upon another component of the PERCH Project, the PERCH Bibliography (http://fusionmx.lib.uwf.edu/perch/index.cfm) which is a fully searchable database of bibliographical materials pertaining to the environment of Northwest Florida. The purpose of the literature search was to assess what was known about the environmental quality and impacting releases of the Escambia Bay System. This information allowed evaluation of how the present project could further the existing knowledge. A GIS database of spatially referenced data collected during the literature search was constructed by manually entering and digitally importing the data and by converting them to common spatial parameters. In the field, the GIS was used in combination with a WAAS enabled hand held GPS receiver (Garmin GPS V) to navigate to the sampling locations.

There were two sampling series: the KS series that was collected in 2005 by Kristen Anne Smith under supervision of Dr. J. Caffrey and the EG series that was collected from December 2007 to May 2008 by the authors. The KS series of samples was collected at 12 sites and has been reported on in the scientific literature (Smith and Caffrey, 2009). At each of the KS sites three shallow 8 cm diameter cores were composited. At least 200 ml of sediment were taken and transferred into a glass container, and frozen immediately. For the EG series a total of 57 sediment grab samples were collected with a ponar grab from a boat. For each grab sample five local grab samples were joined and mixed thoroughly prior to further processing. The composited samples were placed into dedicated sampling containers and sent to the analytical laboratory the day of sampling. KS samples were analyzed for PCBs only. EG samples were analyzed for PAHs, metals, pesticides, PCBs, total petroleum hydrocarbons, TOC (total organic carbon) and dioxins/furans.

Analytical methods followed standard procedures. Total petroleum was analyzed by the FDEP FL-PRO method. The FL-PRO analysis is designed to measure concentrations of total petroleum hydrocarbons (TPH) in water and soil/sediment in the alkane analytical range of C8-C40. The method is based on a solvent extraction and gas chromatography procedure (using a Flame Ionization Detector). Silica cleanup is a mandatory part of the procedure, designed to remove potential interferences from animal and vegetable oil and grease and biogenic terpenes. Other organic compounds, including chlorinated hydrocarbons, phenols and phthalate esters are detected and the total concentration values of TPH for the FL-PRO may include these compounds in the results. USEPA SW-846 methods were used for PCBs by 1668A and for dioxins/furans by 1613B. Specific PAHs [naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, acenaphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno (1,2,3-cd)pyrene, dibenz(a,h)anthracene, and benzo(g,h,i)perylene] were analyzed by USEPA SW-846 method 8270 C, with Simultaneous Ion Monitoring (SIM). This method was used to achieve detection (MDL) and reporting limits (RL) that were lower than the Florida marine sediment quality assessment guidelines (SQAGs) (MacDonald, 1994a, b). SIM is the most sensitive gas chromatography/ mass spectrometry method that is generally available for PAH detection. The target analytes are extracted by EPA method 3550 using dichloroethane (methylene chloride), separated by gas chromatography, then identified and quantitated by mass spectrometry. SIM is a method in which the detector lingers at a few selected masses for much longer than when using the typical "full scan mode", thus increasing the sensitivity of the detector to those masses and lowering both the method detection limit (MDL) and reporting limit (RL) for the analytes. Organochlorinated pesticides were analyzed by EPA Method 8081A which is a gas chromatography method that is similar to EPA Method 8082 that is used to detect PCBs. It employs fused-silica, open tubular capillary columns with electron capture detection. The 8081 analyses were run for the following pesticides: alpha-BHC, gamma-BHC (Lindane), beta-BHC, delta-BHC, heptachlor, aldrin, heptachlor epoxide, gamma-chlordane, alpha-chlordane, 4,4'-DDE, endosulfan I, dieldrin, endrin, 4,4'-DDD, endosulfan II, 4,4'-DDT, endrin aldehyde, methoxychlor, endosulfan sulfate, endrin ketone, toxaphene, tetrachloro-m-xylene, decachlorobiphenyl. The EPA Method 3550 was used for the extraction.

Mercury (Hg) was determined by Method 7471A for sediments by cold vapor atomic absorption. For all other trace metal determinations the samples were prepared according to SW-846 Method 6010, Acid Digestion of Sediments, Sludges, and Soils. Per the method, aluminum (Al), calcium (Ca), iron (Fe), magnesium (Mg), nickel (Ni), selenium (Se), tin (Sn), cadmium (Cd), copper (Cu), zinc (Zn), arsenic (As), chromium (Cr), and lead (Pb) were prepared for graphite furnace atomic absorption spectrometry (GFAAS). The other metals were prepared for flame atomic absorption spectrometry (FLAAS). The digestates were analyzed according to Standard Method 3111 for FLAAS or USEPA Method 200.9 for GFAAS. Samples for particle size analysis were manually mixed and homogenized in the lab while being air dried. After air drying, samples were crushed with mortar and pestle to break up aggregates. Analyses were then performed by dry, Ro-tap, sieving for the sand fractions (2 mm - 0.063 mm) and by the pipette method for clays (procedure 3A1 of Burt (2004)). We preferred to use the pipette method over the often employed hydrometer method because the pipette method is generally considered to be more accurate.

The chemical analysis were performed by Columbia Analytical Systems of Jacksonville, FL; their high resolution mass spectrometry laboratory in Houston, TX, performed the analyses for PCB and dioxin/furan congeners. Particle size analyses were performed at the Soils Lab, Department of Environmental Studies, University of West Florida.

To calculate a TEQ for the dioxins/furans and dioxin-like PCBs the TEF of each congener present in a mixture was multiplied by the respective mass concentration and the products were summed to represent the 2,3,7,8-TCDD TEQ of the mixture, as determined by the following equation (USEPA, 2003b):

$$\text{TEQ} \cong \Sigma i{-}n\left(\text{Congener } i \times \text{TEF } i\right)+\left(\text{Congener } j \times \text{TEF } j\right)+ \ldots.+\left(\text{Congener } n \times \text{TEF } n\right)$$

The TEF values used were those for humans/mammals established in 2005 by the WHO (Van den Berg et al., 2006) (Table 2.0-1).

Table 2.0-1. TEF values for dioxins/furans and dioxin-like PCBs [ng/kg toxic equivalents of 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)] (Van den Berg et al., 2006).

| Compound | WHO 1998 TEF | WHO 2005 TEF |
|---|---|---|
| | Chlorinated dibenzo-p-dioxins | |
| 2,3,7,8-TCDD | 1 | 1 |
| 1,2,3,7,8-PeCDD | 1 | 1 |
| 1,2,3,4,7,8-HxCDD | 0.1 | 0.1 |
| 1,2,3,6,7,8-HxCDD | 0.1 | 0.1 |
| 1,2,3,7,8,9-HxCDD | 0.1 | 0.1 |
| 1,2,3,4,6,7,8-HpCDD | 0.01 | 0.01 |
| OCDD | 0.0001 | 0.0003 |
| | Chlorinated dibenzofurans | |
| 2,3,7,8-TCDF | 0.1 | 0.1 |
| 1,2,3,7,8-PeCDF | 0.05 | 0.03 |
| 2,3,4,7,8-PeCDF | 0.5 | 0.3 |
| 1,2,3,4,7,8-HxCDF | 0.1 | 0.1 |
| 1,2,3,6,7,8-HxCDF | 0.1 | 0.1 |
| 1,2,3,7,8,9-HxCDF | 0.1 | 0.1 |
| 2,3,4,6,7,8-HxCDF | 0.1 | 0.1 |
| 1,2,3,4,6,7,8-HpCDF | 0.01 | 0.01 |
| 1,2,3,4,7,8,9-HpCDF | 0.01 | 0.01 |
| OCDF | 0.0001 | 0.0003 |
| | Non-ortho–substituted PCBs | |
| 3,3',4,4'-tetraCB (PCB 77) | 0.0001 | 0.0001 |
| 3,4,4',5-tetraCB (PCB 81) | 0.0001 | 0.0003 |
| 3,3',4,4',5-pentaCB (PCB 126) | 0.1 | 0.1 |
| 3,3',4,4',5,5'-hexaCB (PCB 169) | 0.01 | 0.03 |
| | Mono-ortho–substituted PCBs | |
| 2,3,3',4,4'-pentaCB (PCB 105) | 0.0001 | 0.00003 |
| 2,3,4,4',5-pentaCB (PCB 114) | 0.0005 | 0.00003 |
| 2,3',4,4',5-pentaCB (PCB 118) | 0.0001 | 0.00003 |
| 2',3,4,4',5-pentaCB (PCB 123) | 0.0001 | 0.00003 |
| 2,3,3',4,4',5-hexaCB (PCB 156) | 0.0005 | 0.00003 |
| 2,3,3',4,4',5'-hexaCB (PCB 157) | 0.0005 | 0.00003 |
| 2,3',4,4',5,5'-hexaCB (PCB 167) | 0.00001 | 0.00003 |
| 2,3,3',4,4',5,5'-heptaCB (PCB 189) | 0.0001 | 0.00003 |

# 3. Results and Discussion

## 3.1. Study regions

For the purposes of this study the Escambia Bay and River were divided into five regions (Figure 1.0-1):

1. Lower bay (south of the I-10 Bridge),
2. Upper bay (between I-10 bridge and US 90 causeway),
3. Lower wetlands (north of US 90 causeway up to the join of the north electrical high tension transmission line and old gas pipe line),
4. Lower river (between river's mouth and Solutia, Inc. facility to the north), and
5. Upper river (north of the Solutia, Inc. facility)

## 3.2. Total PCBs

Detected PCB concentrations in the EG and KS series of samples ranged from 0.9 to 125.9 ug/kg with a mean of 17.9 ug/kg. Sixteen of the 68 samples exceeded the FDEP TEL of 21.6 ug/kg (Table 3.2-1). No samples exceeded the FDEP PEL of 189 ug/kg.

Table 3.2-1. Total surface sediment PCB concentrations [ug/kg] for Escambia Bay and River.

| Sample ID | PCB concentration | Sample ID | PCB concentration |
|---|---|---|---|
| EG1 | 22[1] | EG36 | 5.4 |
| EG2 | 3.8 | EG37 | 6 |
| EG3 | 13.9 | EG38 | 19.4 |
| EG4 | 2.4 | EG39 | 2.5 |
| EG5 | 5 | EG40 | 48.2 |
| EG6 | 18.2 | EG41 | 1.9 |
| EG7 | 15 | EG42 | 2.2 |
| EG8 | 34.9 | EG43 | 43.9 |
| EG9 | 3.6 | EG44 | 6.6 |
| EG10 | 71.2 | EG45 | 93.5 |
| EG11 | 15.4 | EG-46 | 5 |
| EG12 | 3 | EG-47 | 2.8 |
| EG13 | 1.8 | EG48 | 24.4 |
| EG14 | 21.1 | EG49 | 12.7 |
| EG15 | 10.1 | EG50 | 54.9 |
| EG16 | 4.8 | EG51 | 55.2 |
| EG17 | 3.2 | EG52 | 30.6 |
| EG18 | 7.9 | EG53 | 14.2 |
| EG19 | 1 | EG54 | 11.4 |
| EG20 | 1.6 | EG55 | 14.9 |
| EG21 | 6 | EG56 | 6.7 |

Table 3.2-1. Total surface sediment PCB concentrations [ug/kg] for Escambia Bay and River (cont'd.).

| Sample ID | PCB concentration | Sample ID | PCB concentration |
|---|---|---|---|
| EG22 | 18 | EG57 | 3.3 |
| EG23 | 1 | KS1 | 2.1 |
| EG24 | 12.1 | KS2 | 7.9 |
| EG25 | 15 | KS3 | 2.3 |
| EG26 | 1.4 | KS4 | 11.6 |
| EG 27 | 1.7 | KS5 | 0.9 |
| EG 28 | 16 | KS6 | 45.1 |
| EG 29 | 1.8 | KS7 | 118.1 |
| EG 30 | 15.4 | KS8 | 1.1 |
| EG 31 | 25.5 | KS9 | 26.1 |
| EG 32 | 23.9 | KS10 | 6.2 |
| EG33 | 9.6 | KS11 | 1.5 |
| EG34 | 11 | KS12 | 125.9 |
| EG35 | 3.9 | Mean | 17.9 |

1. Underlined font indicates concentrations greater than the FDEP TEL of 21.6 ug/kg

### 3.2.1 Upper Escambia Bay

The mean concentration for the 17 samples in the upper bay (EG1, EG3, EG4, EG6, EG7, EG-8, EG9, EG10, EG18, EG31, EG33, EG35, EG51, EG52, EG53, KS7, and KS2) was 26.7 ug/kg, which exceeds the FDEP TEL (Figure 3.2-1a). This suggests that within this region the ability of the sediments to support benthic fauna may be impaired. The highest PCB concentration of the upper bay of 118.1 ug/kg (sample KS7) is not far from the discharge of the Escambia River (Figure 3.2-1a&b ), but it is also not far from the next highest concentration of 71.2 ug/kg (EG10) that is near an outfall by the Air Products and Chemicals, Inc. facility. Previous studies have shown that water transported pollutants get trapped by currents in the upper bay (Olinger et al., 1975). Obviously, the Escambia River is a likely PCB source for the upper bay, but the presence of another high concentration adjacent to the Air Products and Chemicals, Inc. outfall suggests that multiple PCB origins may exist. Assigning a PCB release point is difficult because the distribution of sediments by local transporting mechanisms is not well understood for the bay due to confounding influences from currents from the various river channels, tidal transport, and wind driven waves that can become quite intense during tropical storms (Olinger et al., 1975). It appears likely that PCBs have accumulated in this area due to its proximity to fluvial transport of sediments and suspended particles, but surface water transport from adjacent drainages, such as Pace Mill Creek, Mulat Bayou, the Air Products and Chemicals, Inc. outfall, a buried outfall from American Cyanamid, and other regional sources, may also have contributed to PCB sediment concentrations. It is not readily apparent if there is only a single source or if there are multiple source origins for the PCBs of upper Escambia Bay on the basis of spatial patterns.

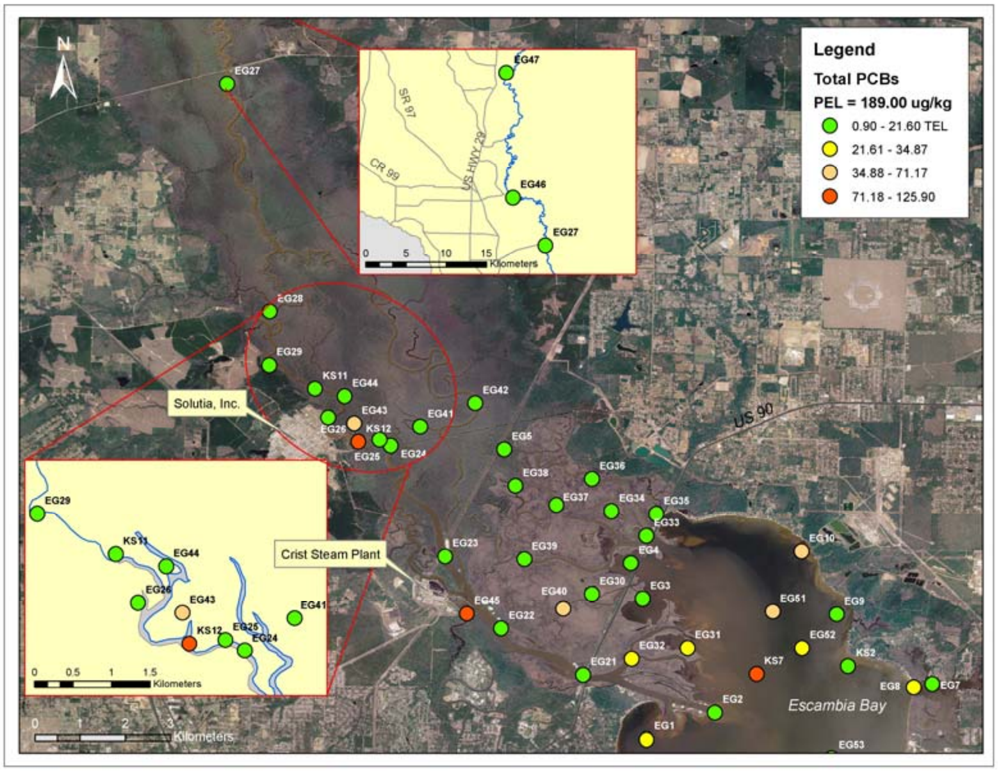


Figure 3.2-1a. Total sediment PCBs for upper Escambia Bay and River and lower wetlands.

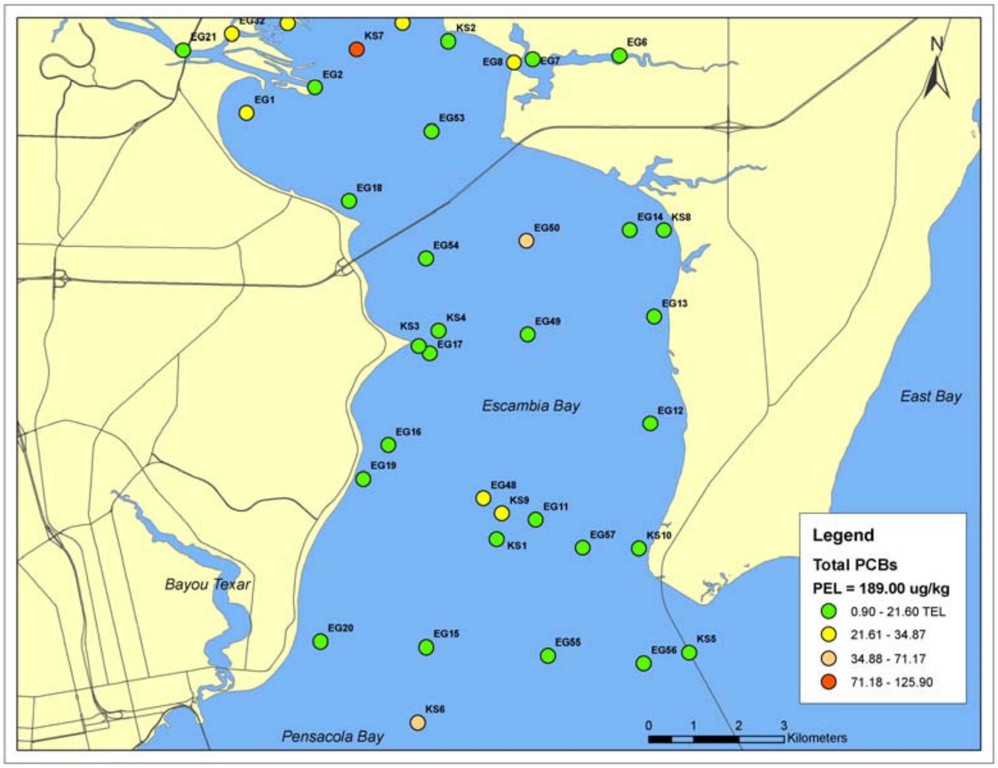


Figure 3.2-1b. Total sediment PCBs for Escambia Bay.

### 3.2.2. Lower Escambia Bay

For the lower bay (Figure 3.2-1b) a total of 24 samples was collected with an averaged concentration of 11.9 ug/kg. This average is less than the FDEP TEL and less than half of the mean concentration of 26.7 ug/kg observed for the upper bay. Only 4 out of the 24 samples were above the TEL and concentrations ranged from 0.9-54.9 ug/kg. Samples taken from the shoreline that consisted primarily of sand had very low concentrations of total PCBs. It is generally accepted that PCBs and many other pollutants tend to be associated with fine sediment particles (Knezovich et al., 1987) that accumulate in the deeper, less dynamic parts of a waterbody. For Escambia Bay, particularly in its lower portion, the winds generate significant wave action that may be sufficient to wash the coarser sands onto the shore line and result in the finer particles settling into the deeper regions of the bay. The overall lower concentrations of the lower bay as compared to the concentrations of the upper bay may be due to their greater distances away from the major sources of PCBs.

### 3.2.3. Lower river

The Escambia River is the major source of fresh water for Escambia Bay and also for the Pensacola Bay System (Olinger et al., 1975; Thorpe et al., 1997) and it is the main source of sediments for Escambia Bay. The initial reports of a major PCB release in the Escambia River in 1969 (Duke et al., 1970) has focused attention on the Escambia River as a source of PCBs to Escambia Bay, but the literature shows very little in the way of sediment sampling in the river. To remedy this shortcoming, the present study divided the Escambia River into lower Escambia River as the segment between the river's mouth and the Solutia, Inc. facility, and upper Escambia River going from Solutia, Inc. north to the Alabama state border. These segments also included areas of inlets within 200 feet of the river. Eleven samples (EG2, KS12, EG24, EG25, EG43, EG26, EG21,~~ ~~EG22~~,~~ EG23, EG32, EG45) were taken in the lower Escambia River and ranged in total PCB concentration from 1.0 to 125.9 ug/kg. The lower river mean concentration was 31.1 ug/kg with a total of four out of the 11 concentrations being greater than the TEL.

Thompson's Bayou was sampled about 100 ft from the river at the point where the Gulf Power Crist Steam Plant sends its thermal canal underneath the bayou. The concentration of this obviously disturbed sediment was 93.5 ug/kg (Sample EG45). Sample EG23 located upriver from the Crist Plant was 1.02 ug/kg (Figure 3.2-1a). Several samples were taken adjacent to the Solutia, Inc. facility and are listed in Table 3.2-1. Concentrations for two of these samples were above the TEL. Sample KS12 at 125.9 ug/kg had the highest concentration of all the samples analyzed in this study. The next highest concentration was 43.9 ug/kg (sample EG43) taken in B.J.'S Cut, a small dredged bypass, about 150 ft from the river. It appears that there are significantly PCB contaminated sediments in this stretch of the river that according to SQAGs can impair sediment quality. The PCB concentrations have a spotty distribution that is likely determined by sediment characteristics, which are influenced by natural fluvial erosion and deposition, prop wash from tugboats, and dredging. However, Pearson's product moment correlation coefficients do not show a strong correlation between PCB concentrations and sediment characteristics (Table 3.2.7-1). The strongest correlation is with organic matter content (r=0.42) while sand, as noted above, has a negative even though moderate correlation (r= -0.33).

Table 3.2.7-1. Pearson's product moment correlations for PCB concentrations and sediment characteristics.

| Sediment characteristic | Correlation coefficient |
|---|---|
| Organic matter | 0.42 |
| Sand | -0.33 |
| Silt | 0.26 |
| Clay | 0.29 |

### 3.2.4. Upper river

Sediments in the upper river (samples EG27, EG46, EG47, EG28, EG29, EG44, & KS1) did contain PCBs, but at reduced concentrations compared to the lower river. The mean was 5.06 ug/kg and the range was 1.54 to 16.0 ug/kg. Sample EG44, taken just upriver from the Monsanto facility release site, had a concentration of 6.6 ug/kg. Sample KS1 taken slightly up river from EG44 was 1.54 ug/kg. Sample EG29 was taken further up the river and also had a low concentration (1.8 ug/kg), but in EG28 further north the concentration was 16.0 ug/kg. This sample would appear to be upriver from activities emanating from the Monsanto Chemical Company site and yet has a significant PCB concentration. The PCBs found at this site could originate in the local watershed or come from further up river. Sample EG27, taken just south of the Quintette Road - Escambia County Highway 184 bridge, had a low PCB concentration of 1.7 ug/kg. Much further up river the concentrations of samples EG46&47 were 5.0 and 2.8 ug/kg. While these concentrations are not high, they are as high as some of lower range samples that were taken in Escambia Bay.

### 3.2.5. Upper wetlands

The samples taken north of the northern Gulf Power electrical transmission line & old gas pipe line in the White River and Milligan Creek (EG41&42) had low PCB concentrations (1.9 ug/kg and 2.2 ug/kg respectively). These locations would seem to be distant from the hydraulic influence of river water coming from the 1969 spill site and yet do still show PCBs, albeit at low concentrations.

### 3.2.6 Lower wetlands

The wetlands adjacent to the lower river that lie south of the join of the Northern Transmission Line & Old Gas Pipeline and north of US Highway 90 consist mainly of emergent herbaceous vegetation. The samples EG39, EG5, EG36, EG37, EG34, EG30, EG38, and EG40 in these lower wetlands had a mean of 14.1 ug/kg. This is less than the mean of 26.7 ug/kg for the upper bay. The highest concentration in the lower wetlands was 48.2 ug/kg (Sample EG40 in Saultsman Bayou), which exceeds the FDEP TEL but all other concentrations in the lower wetlands were below the FDEP TEL.

### 3.2.7 Overall view of PCB concentrations

Escambia River sediments throughout the Florida portion of the river were found to have PCBs. Areas of the river near the Monsanto spill site and also downstream had one sample each that was several times higher than the FDEP TEL, but below the PEL. The fact that sedimentary PCBs are still found to be present in segments of a river that is periodically dredged and traversed by barge traffic attests to the persistence of these pollutants but also suggests that PCBs may still be entering these areas of the lower river. The presence of mostly trace detections of PCBs north of the Solutia, Inc. (old Monsanto) site suggests that at least some PCBs may be entering the system from upriver sources that could possibly include watersheds in Alabama. Beside surface water origins there is also atmospheric disposition of PCBs that may contribute to upstream sediment PCB concentrations (Eisler, 1986).

Overall, the Escambia Bay and River System is generally less polluted with PCBs than Bayous Texar, Chico, and Grande, which were assessed by previous PERCH studies. However, one of the major concerns from the viewpoint of public health is that of uptake of sediment PCBs into biota, especially fish that are consumed by the local human population. It is possible that PCB sediment concentrations lower than the TEL may accumulate to exceed USEPA and State of Florida SVs and STs in the tissues of consumed seafood. The FDEP TEL and PEL were not designed to address this issue. Other site specific studies must be performed to assess this.

## 3.3. PCB TEQ

### 3.3.1. Dioxin-Like PCBs

The most common dioxin-like PCB congener on the basis of mass is PCB 118 (Table 3.3.1-1 and Figure 3.3.1-1). It is about 61% of the PCB mass in the EG series and 64% in the KS series. It only accounts for between 3% and 13% of the total TEQ due to its relatively low TEF value. PCB 126 is the most toxic congener and constitutes less than 1% of the total dioxin-like PCBs but accounts for 76 to 93% of the TEQ. In the KS series PCB 126 was 0.54% of the total PCB mass versus the 0.11% in the EG series, which explains in part why some of the KS series samples had elevated TEQs. An example of this is sample KS12 that has a total PCB concentration of 125.9 ug/kg concentration with a TEQ of 6.51 ng/kg.

Table 3.3.1-1. Proportion of dioxin-like PCBs in total mass concentration and combined TEQ.

| Congener | 2005 TEF | % mass EG series | % mass KS series | % TEQ EG series | % TEQ KS series |
|---|---|---|---|---|---|
| PCB-77 | 0.0001 | 5.50 | 4.86 | 3.85 | 0.83 |
| PCB-81 | 0.0003 | 0.03 | 0.13 | 0.07 | 0.07 |
| PCB-105 | 0.00003 | 19.20 | 19.80 | 4.03 | 1.02 |
| PCB-114 | 0.00003 | 0.63 | 0.39 | 0.13 | 0.02 |
| PCB-118 | 0.00003 | 61.44 | 63.47 | 12.89 | 3.28 |
| PCB-123 | 0.00003 | 0.73 | 0.00 | 0.15 | 0.00 |
| PCB-126 | 0.1 | 0.11 | 0.54 | 76.28 | 93.61 |
| PCB-156&157 | 0.00003 | 9.03 | 7.33 | 1.89 | 0.38 |
| PCB-167 | 0.00003 | 2.98 | 2.97 | 0.63 | 0.15 |
| PCB-169 | 0.03 | 0.00 | 0.02 | 0.00 | 0.82 |
| PCB-189 | 0.00003 | 0.35 | 0.29 | 0.07 | 0.01 |

Overall there is similarity in the profiles for mass concentration and TEQ for the EG and KS series of samples (Figures 3.3.1-1 and Figure 3.3.1-2). On the basis of mass concentration and TEQ the highly toxic PCB 126 is higher for the KS series than for the EG series. Figure 3.3.1-2 also includes the mass of dioxin-like PCBs from the hepatopancreas of the blue crab, *Callinectes sapidus*. This group of crabs was collected off the Gaberrone shore of Escambia Bay on the west side of the bay and south of the I-10 bridge. The profiles in the crab tissue and sediments show similarities with PCB-118 being the most prevalent congener. Concentrations of PCB congeners 77 and 105 are substantially higher in the sediments but concentrations for congeners 156-157 and 167 are lower.

## 3.4. PCB Congeners

### 3.4.1. PCB congener profiles

All samples from this study were analyzed by the same laboratory. EPA method 1668A was employed for both series of sediment samples (EG and KS series) but different numbers of elutions were obtained for the two groups. The KS series samples were collected and analyzed during 2005-06 and resulted in 135 separate elutions. The ES series was analyzed in 2007-08 and resulted in 166-168 separate elutions for the 209 congeners due to advances in the analytical instruments used by the lab (Table 3.4.1-1a and Table 3.4.1-1b, see appendix).

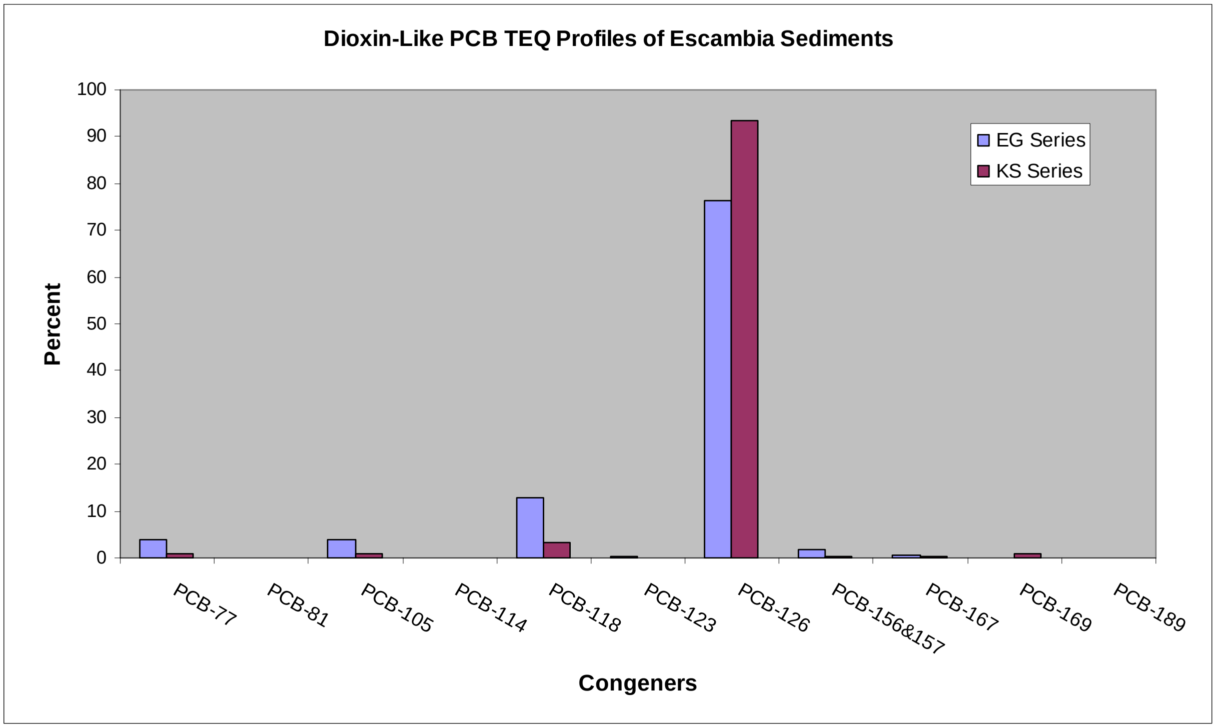


Figure 3.3.1-1. Dioxin-like PCB TEQ profiles in sediments in Escambia Bay and River.

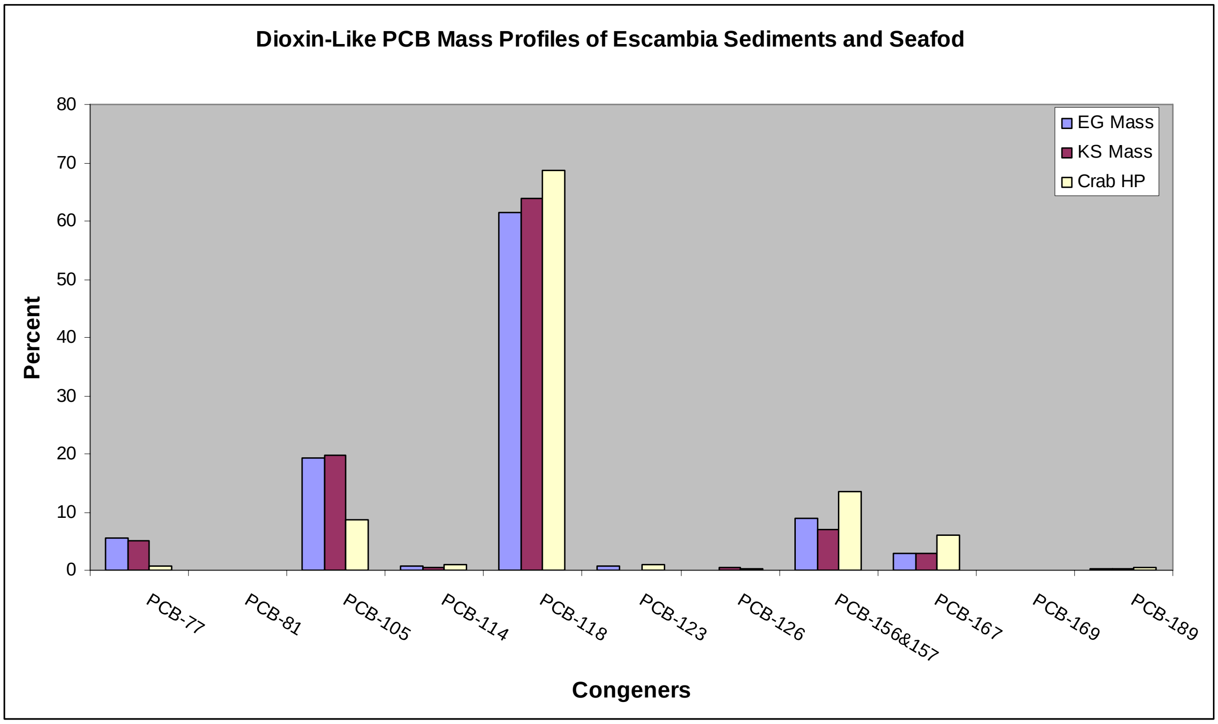


Figure 3.3.1-2. Dioxin-like PCB mass concentration profiles in Escambia Bay and River.

### 3.4.2. Indicator PCB congeners and field screening

Dominant PCBs can be used for field screening if remediation of contaminated sediments in Escambia River or Bay is ever pursued. The dominant PCB congeners that comprise about 3 to 7 percent of the average PCB sediment profile are called indicator PCB congeners and are of value for screening determinations in scenarios for which the PCB profile has been established by recent studies. An example would be for site cleanup where analyses that only detect the indicator PCBs are employed since they are often less expensive and time consuming when screening an area for PCBs. There is no absolute necessity that screening analyses have to detect all 209 congeners if there is already current information on what PCBs profiles are like in the Escambia Bay and River System. The presence of the indicators strongly suggests that remainder of the suite of PCBs congeners is also present. The advantage of using analyses for only a few indicator PCB congeners is that the analysis is simpler resulting in lower costs and often will shorten the analytical time from weeks to hours to obtain screening results.

Table 3.4.2-1. Potential indicator PCBs and elutions in Escambia Bay and River sediments.

| Order | EG Series | % | KS Series | % |
|---|---|---|---|---|
| 1 | 129+138+163 | 6.8 | 110+115 | 6.0 |
| 2 | 153+168 | 5.6 | 129+138 +160+163 | 5.3 |
| 3 | 118 | 5.6 | 153 +168+141 | 4.6 |
| 4 | 110 | 5.0 | 118 | 4.3 |
| 5 | 90+101+113 | 5.0 | 147+134+149 | 4.3 |
| 6 | 147+149 | 3.8 | 83 +99+112 | 3.9 |
| 7 | 49+69 | 3.1 | 90 +101+113 | 3.9 |

### 3.4.3. Origins of PCBs in Escambia Bay and River.

Aroclors are mixtures of PCB congeners that are made up to a fixed chlorine percentage. That percentage usually varies slightly with each batch. For example, for Aroclor 1254 the 54 specifies that it is to contain 54% chloride saturation and Aroclor 1268 would have 68% chlorination. A general comparison between weathered PCBs or assigning a probable single source to an Aroclor is difficult because exposure to normal environmental processes results in dechlorination, thus causing alterations of the original congener profile of the parent Aroclor(s). It is made even more difficult by the fact that there can be multiple releases of different Aroclors that along with the weathering can make deciphering the origins even more difficult. But keeping such limitations in mind we did attempt to compare the homologue profiles of Aroclor 1254 mixtures to the analytical results for our samples. Aroclor 1254 was stated to be the Aroclor that was released from Monsanto Chemical Company in 1969 (Duke et al., 1970) and it is reasonable to compare some of the different known formulations of Aroclor 1254 with the averages of chlorine homologues from samples collected from Escambia Bay and River.

Each Aroclor batch can differ from other batches of the same Aroclor as is in shown in Table 3.4.3-1. The mean total chlorination percent of the four Aroclor 1254 batches shows that it ranges from about 52 % to 55 %. Our homologue sediment data has about 49% chlorination and it could be postulated that the lower degree of chlorination is due to weathering, i.e. dechlorination. It is difficult to ascertain what the original profile of the PCBs was since dechlorination can unequally attack some congeners and chlorination homologue classes depending upon the specific ambient conditions. Anaerobic dechlorination of Aroclor 1254 would be expected to result in a greater quantity of the mono, di, tri, and tetra congeners and a reduction of the hexa , hepta, and octa congeners and in contrast aerobic dechlorination would reduce the di, tri, and tetra congeners. Table 3.4.3-1 shows that the sediment samples were slightly higher for the nona, octa and heptaCB's and also higher for the less chlorinated congeners i.e. monoCB, diCB, and triCB. The lower chlorinated congeners can also be derived from other Aroclors such as A1221, A1232, A1016, A1242 and A1248 which do not have hepta, octa, and nona homologues. The chlorination homologue profile does suggest dechlorination has occurred. The presence of the heavier hepta, octa, and nona congeners would be consistent with the presence of a more chlorinated Aroclor such as A1260, A1262, or 1268 being present in the mixture. The Screening Quick Reference Table for Aroclor PCB Composition (Buchman, 2008) shows some other forensic ratios that can also be applied. The indicator or prominent congeners of A1254 are listed as PCBs 118, 110, 101, 95, 138, and 153 and all of these were in elutions that comprised at least 3% of the total EG series profiles (see above). PCB 137 is listed as an unique congener of A1254 and PCB 137 was found to compose 0.21 % of the total profile and so is consistent with the presence A1254. The ratio of PCB 118/PCB 203 is 33 which is closer to that of A1248 (73) than A1254 (230-370). The ratio of PCB 31/PCB118 was 0.14 which is closer to that of A1260 and A1262 (0.1) than A1254 (0.01-0.04). The mass of PCB 153 is supposed to range from 4.7 to 6.1% of the total mass which in the EG series of samples was 5.6%, and thus is within the range of A1254. Buchman (2008) states that there should be only a trace (0.05-0.5%) of PCB 202. In the EG sediment samples this congener was 0.09%.

In summary, there is a documented release that contained A1254. What is lacking here is precise knowledge of the congeners that were present when the Aroclor containing material was released in 1969. There does not appear to be any available data showing the congener profile for the original material that was released from the Monsanto Chemical Company facility in 1969. The overall profile for the sediment PCBs shows attributes of degradation via dechlorination that makes forensic determinations of the parent material difficult. The forensic evidence suggests that A1254 may have been a source for the PCBs in the sediment samples but leaves open the possibility that other Aroclors beside A1254 were also released. Multiple releases would not be unusual due to the large number of potential sources that are present in and about the Escambia Bay and River System.

Table 3.4.3-1. Chlorine homologue content for EG series and four different batches of Aroclor 1254.

| Chlorine homologues | EG series | A 1254[1] | A 1254[2] | A1254[3] | A1254[4] | Squirt [5] |
|---|---|---|---|---|---|---|
| Monochlorobiphenyls | 0.9 | 0.002 | 0 | 0 | 0 | 0 |
| Dichlorobiphenyls | 5.8 | 0.1 | 0.2 | 0 | 0 | 0 |
| Trichlorobiphenyls | 8.4 | 0.4 | 1.3 | 0 | 0 | 2.1 |
| Tetrachlorobiphenyls | 18.6 | 4.9 | 10.3 | 17.11 | 17.47 | 14.3 |
| Pentachlorobiphenyls | 33.1 | 71.4 | 59.1 | 28.06 | 23.18 | 53.2 |
| Hexachlorobiphenyls | 25.2 | 22.0 | 26.8 | 49.10 | 55.99 | 26.6 |
| Heptachlorobiphenyls | 6.7 | 1.4 | 2.7 | 5.73 | 3.56 | 3.8 |
| Octachlorobiphenyls | 1.1 | 0 | 0.04 | 0 | 0 | 2.1 |
| Nonachlorobiphenyls | 0.2 | 0.04 | 0.04 | 0 | 0 | trace 202 |
| Total calculated chlorination | 48.60 | 51.97 | 52.04 | 54.3 | 54.50 | ? |

1 and 2. From Frame et al. (1996)
3 and 4. From Kodavanti et al. (2001)
5. Squirt Table for A1254 (Buchman, 2008)

### 3.5. Dioxins/Furans

The dioxins or CDDs (Chlorinated dibenzo-p-dioxins) are a class of related chlorinated hydrocarbons that are structurally similar, but differ in regards to the number and position of chlorine groups. The basic structure is a dibenzo-p-dioxin molecule comprised of two benzene rings joined via two oxygen bridges at adjacent carbons on each of the benzene rings (Figure 3.5-1). There are eight homologues of CDDs, monochlorinated through octachlorinated. Each homologous class contains one or more isomers or congeners. The family of CDDs contains 75 congeners; 2 monochlorodibenzo-p-dioxins (MCDD), 10 dichlorodibenzo-p-dioxins (DCDD), 14 trichlorodibenzo-p-dioxins (TrCDD), 22 tetrachlorodibenzo-p-dioxins (TCDD), 14 pentachlorodibenzo-p-dioxins (PeCDD), 10 hexachlorodibenzo-p-dioxins (HxCDD), 2 heptachlorodibenzo-p-dioxins (HpCDD), and a single octachlorodibenzo-p-dioxin (OCDD). The seven 2,3,7,8-chlorine substituted congeners are the most toxic CDD congeners, with 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) being the most toxic and most extensively studied. This compound is often called "TCDD" or merely "dioxin" in the popular literature. The furans or CDFs (chlorinated dibenzofurans) are similar to the CDDs except for that there is only one oxygen atom (position ‘10’) that occurs for furans and none at position ‘5’ (Figure 3.5-2). The CDF’s then compose a similar family of chemicals known as chlorinated dibenzofurans. These chemicals also contain one to eight chlorine atoms attached to the carbon atoms of the parent chemical, dibenzofuran. The CDF family contains 135 individual compounds (known as congeners) with varying health and environmental effects. Of these 135 compounds, those that contain chlorine atoms at the 2,3,7,8-positions of the parent dibenzofuran molecule are especially harmful as is also the case with the CDDs. Most CDDs and CDFs are produced in very small amounts as unwanted impurities of certain products and high temperature processes or combustions utilizing chlorinated compounds. These chemicals are not very soluble in water and there is no known beneficial use for them.

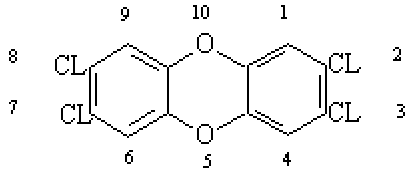


Figure 3.5-1. Structure of TCDD. TCDD is the most toxic dioxin. Dioxins that have chlorine atoms in the 2,3,7 and 8 positions are toxic.

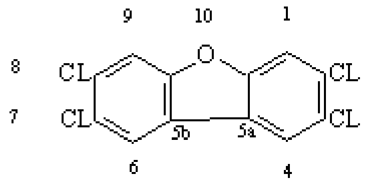


Figure 3.5-2. Structure of TCDF. TCDF is the most toxic furan. Furans that have chlorine atoms in the 2,3,7 and 8 positions are toxic.

Currently available experimental evidence indicates that the aryl hydrocarbon receptor (AHR) mediates dioxin's known physiological roles, as well as most, if not all, of the toxic effects of dioxin through alterations in gene expression. Relative toxicity of dioxin-like molecules are expressed as TEF derived from the relative affinity that a pollutant molecule has with the AHR receptor (Bunger et al., 2003; Stevens and Bradfield, 2008). Dioxins/furans and dioxin-like PCBs are thought to exert physiological effects upon mammals (mice) via the AHR. The AHR is a ligand activated gene transcription factor that in mammals is well known as a mediator of the toxicity of environmental pollutants, including its prototype ligand, dioxin. Upon binding agonists (i.e., dioxins/furans), the AHR translocates from the cytoplasm to the nucleus, where it forms a heterodimer with the aryl hydrocarbon nuclear translocator protein (Bunger et al., 2003; Stevens and Bradfield, 2008). This heterodimeric complex interacts with dioxin-responsive elements within the genome and upregulates the transcription of a battery of xenobiotic metabolizing enzymes (XMEs). These regulated XMEs include the cytochrome P450s Cyp1a1, Cyp1b1, and Cyp1a2 and the phase II enzymes Gst-a1 and Ugt1–06 (Bunger et al., 2003). The cytochrome P450 enzyme system consists of a group of enzymes involved in drug metabolism and is found in high levels in the liver. These enzymes change many drugs, including anticancer drugs, into less toxic forms that are easier for the body to excrete. The phase II or post-oxidative biotransformation system comprises an array of enzymes that catalyze the incorporation of a new hydrophilic endogenous chemical into hydrophobic molecules, thereby decreasing its polarity and eventual toxicity (Bunger et al, 2003). Dioxins can also cause changes in mammalian T Cells resulting in immunological changes. The toxic effects of dioxins/furans include thymic atrophy, chloracne, tumor promotion, wasting, and can even lead to death in laboratory animals (Stevens et al., 2008). The most important consideration is for risk assessments to human health where the dioxins/furans and dioxin-like compounds are considered to be carcinogenic to humans by International Agency for Research on Cancer (IARC, 1997) and the USEPA (2008).

It has strongly been suggested that dioxin-like compounds impact living organisms via endocrine disruption. TCDD is on the U.S General Accounting Office (GAO) list of 20 reproductive and developmental toxicants, and the effects of chronic exposure to TCDD on reproduction in rodents have been well documented (Gregoraszczuk, 2008). Endocrine disruptors include industrial chemicals like pesticides, polychlorinated biphenyls (PCBs), dioxins/furans, and other synthetic chemicals. Organochlorine industrial chemicals have been extensively used in the production of plastics, flame retardants, pesticides, drugs, and a host of other commercial products. Growing evidence suggests that the reproductive system is one of the most sensitive targets for the adverse effects of these compounds. Ligand binding results in interaction with the dioxin response element on the DNA, resulting in transcription of a group of enzymes active in steroid and xenobiotic metabolism. Therefore dioxin-like molecules may interfere with vertebrate reproduction by altering the production of steroid hormones (Gregoraszczuk, 2008; OECD, 2006). There appears currently to be no evidence for a receptor in invertebrate animals groups that binds to dioxin-like compounds.

### 3.5.1. Total dioxin/furan concentration in sediments

In the EG series of sediment samples the total concentration of the 17 congeners that are considered to have significant toxicity ranges between 22 ng/kg and 11,004 ng/kg, with a mean of 1863.8 ng/kg (Table 3.5.1-1). The proportion that the toxic congeners comprise of the total dioxin/furan concentration ranges from 77 to 99% and has a mean of 87%. This shows that the nontoxic component of the dioxin/furan total is minor. If in the future some dioxin-like toxicity is found for these congeners it would likely only represent a modest increase in total overall toxicity (ATSDR, 1994; 1998).

Table 3.5.1-1. Mass concentration [ng/kg dry weight] of toxic dioxin/furan congeners and their percentage of total dioxins/furans.

| Sample | 17 toxic congeners | % of total | Sample | 17 toxic congeners | % of total |
|---|---|---|---|---|---|
| EG1 | 2136 | 85 | EG31 | 1868 | 87 |
| EG2 | 205 | 86 | EG32 | 2921 | 90 |
| EG3 | 1292 | 86 | EG33 | 1384 | 85 |
| EG4 | 234 | 88 | EG34 | 1921 | 86 |
| EG5 | 1523 | 89 | EG35 | 940 | 87 |
| EG6 | 265 | 82 | EG36 | 679 | 89 |
| EG7 | 1688 | 87 | EG37 | 2355 | 92 |
| EG8 | 1490 | 81 | EG38 | 4882 | 90 |
| EG9 | 1590 | 84 | EG39 | 1146 | 92 |
| EG10 | 91 | 88 | EG40 | 6645 | 90 |
| EG11 | 311 | 80 | EG41 | 697 | 93 |
| EG12 | 550 | 83 | EG42 | 865 | 93 |
| EG13 | 27 | 83 | EG43 | 6289 | 93 |
| EG14 | 5592 | 83 | EG44 | 556 | 91 |
| EG15 | 1351 | 80 | EG45 | 1345 | 90 |
| EG16 | 412 | 82 | EG46 | 3991 | 94 |
| EG17 | 253 | 83 | EG47 | 3371 | 94 |
| EG18 | 723 | 85 | EG48 | 2660 | 79 |
| EG19 | 69 | 87 | EG49 | 1105 | 83 |
| EG20 | 178 | 82 | EG50 | 3587 | 83 |
| EG21 | 357 | 88 | EG51 | 1144 | 86 |
| EG22 | 644 | 90 | EG52 | 504 | 85 |
| EG23 | 29 | 99 | EG53 | 2801 | 85 |
| EG24 | 1949 | 93 | EG54 | 1955 | 83 |
| EG25 | 1334 | 93 | EG55 | 3508 | 77 |
| EG26 | 334 | 89 | EG56 | 1222 | 79 |
| EG27 | 1042 | 94 | EG57 | 409 | 80 |
| EG28 | 8791 | 91 | Mean | 1864 | 87 |
| EG29 | 22 | 94 | Range | 22-11,004 | 77-99 |
| EG30 | 11004 | 86 | | | |

The congener profile of the 17 toxic PCDDs/PCDFs is superficially similar to what has been observed in the local bayous (Mohrherr et al., 2005; 2007; 2008) in that octachlorodibenzo-p-dioxin (OCDD) is the dominant congener on the basis of mass concentration (Table 3.5.1-2 and Figure 3.5.1-1). A comparison with data from these bayous, that are also components of the Pensacola Bay System, does show some differences in trends.

For example, the OCCD concentration is higher in Escambia Bay and River than in Bayou Chico (94% vs. 85%) but most other congeners are lower in Escambia Bay and River ( 1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin (HpCDD) is 5% vs. 12%, Octachlorodibenzofuran (OCDF) is 0.9% vs. 1.3%). These differences suggest differences in the origin of these compounds but may also be the result of differential degradation.

Table 3.5.1-2. Comparison of dioxin/furan profiles.

| Congener | % River and Bay | % Bayou Chico |
|---|---|---|
| TCDD | 0.001 | 0.001 |
| 1,2,3,7,8-PeCDD | 0.009 | 0.020 |
| 1,2,3,4,7,8-HxCDD | 0.028 | 0.058 |
| 1,2,3,6,7,8-HxCDD | 0.101 | 0.307 |
| 1,2,3,7,8,9-HxCDD | 0.245 | 0.227 |
| 1,2,3,4,6,7,8-HpCDD | 4.583 | 11.892 |
| OCDD | 93.810 | 85.166 |
| 2,3,7,8-TCDF | 0.015 | 0.074 |
| 1,2,3,7,8-PeCDF | 0.003 | 0.059 |
| 2,3,4,7,8-PeCDF | 0.005 | 0.015 |
| 1,2,3,4,7,8-HxCDF | 0.014 | 0.068 |
| 1,2,3,6,7,8-HxCDF | 0.017 | 0.034 |
| 1,2,3,7,8,9-HxCDF | 0.001 | 0.002 |
| 2,3,4,6,7,8-HxCDF | 0.022 | 0.036 |
| 1,2,3,4,6,7,8-HpCDF | 0.263 | 0.648 |
| 1,2,3,4,7,8,9-HpCDF | 0.016 | 0.045 |
| OCDF | 0.868 | 1.349 |

Figure 3.5.1-2 and Table 3.5.1-3 show the relative proportion for homologue chlorination for tetra through octa-homologues for the dioxin/furan congeners. When all congeners are accounted for the relative proportion for OCCD declines to about 82% from 94% (Tables 3.5.1-2 and 3.5.1-3.) as other non-toxic dioxins/furans are accounted for.

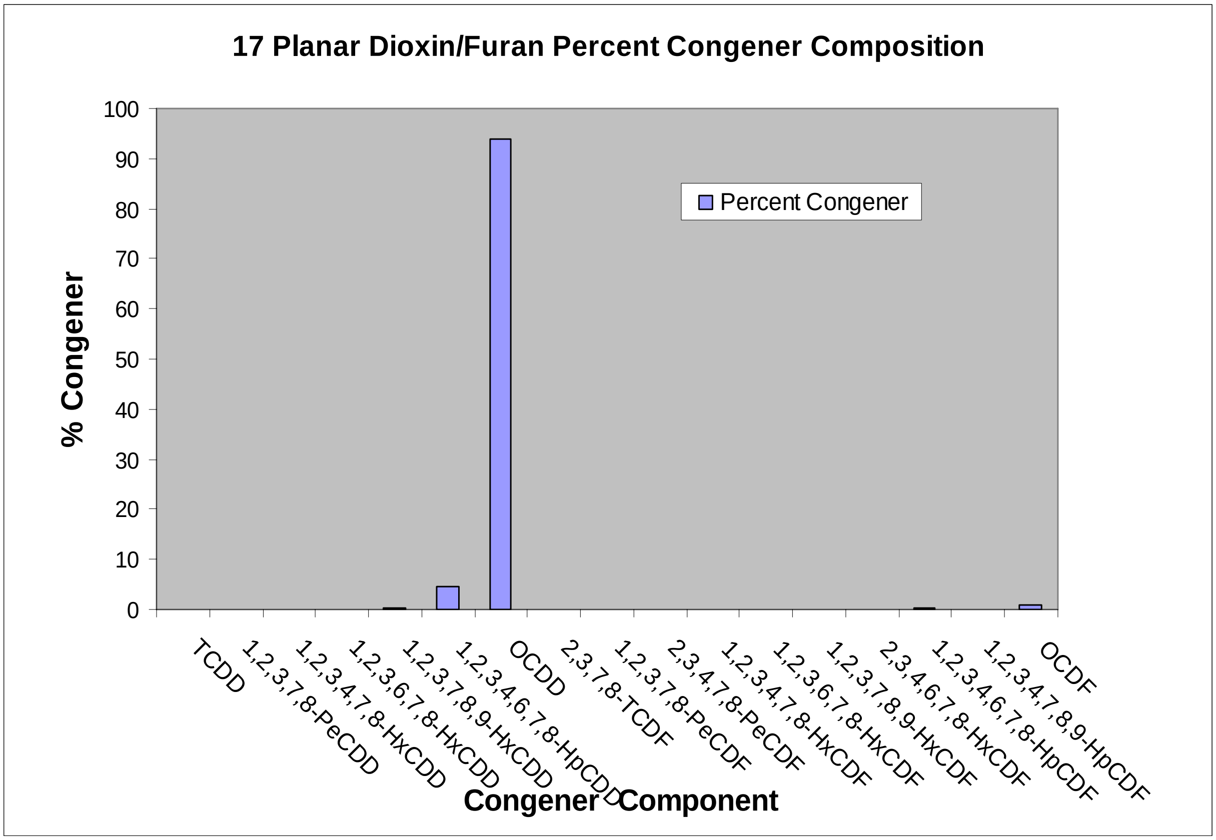


Figure 3.5.1-1. Average dioxin/furan profiles for the 17 toxic dioxin/furan congeners in sediments in Escambia Bay and River.

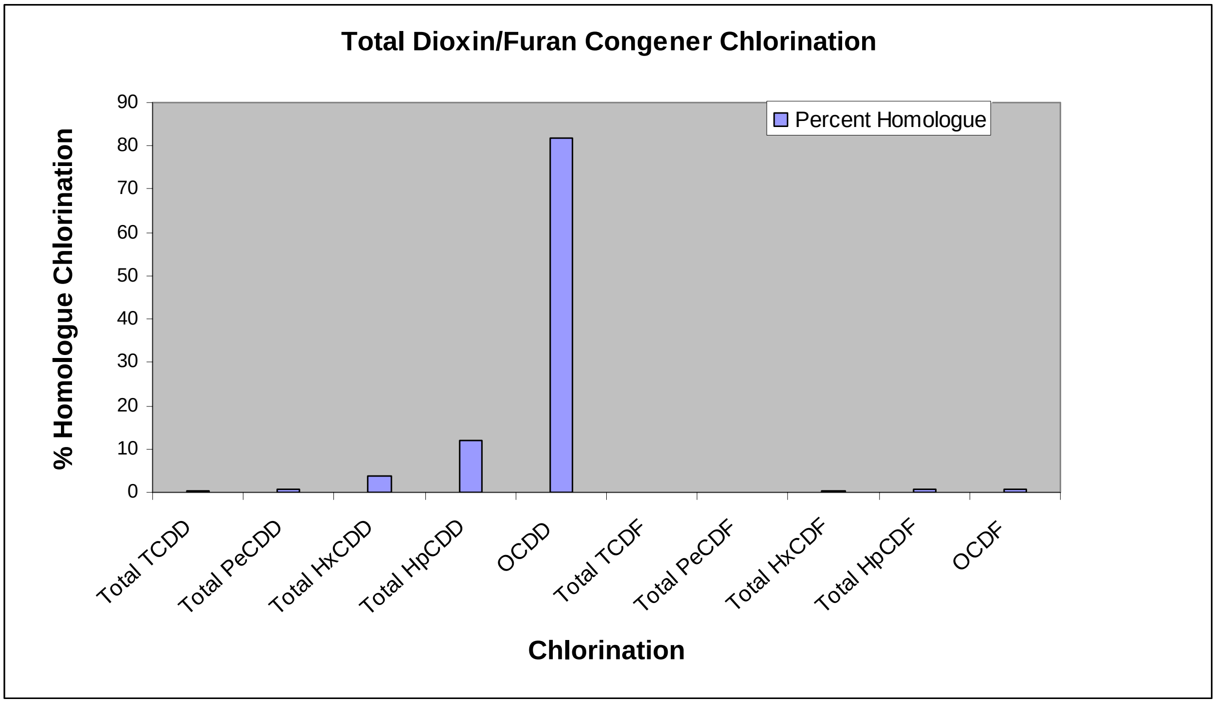


Figure 3.5.1-2. Proportion of homologue chlorination for tetra through octa-homologues.

Table 3.5.1-3. Relative proportion [%] of tetra through octa-homologues.

| Chlorination homologues | Proportion [%] |
|---|---|
| Total TCDD | 0.28 |
| Total PeCDD | 0.55 |
| Total HxCDD | 3.43 |
| Total HpCDD | 11.88 |
| OCDD | 81.88 |
| Total TCDF | 0.06 |
| Total PeCDF | 0.08 |
| Total HxCDF | 0.27 |
| Total HpCDF | 0.62 |
| OCDF | 0.76 |

### 3.5.2. Dioxin/Furan TEQ

Even though OCCD makes up nearly 94% of the total toxic dioxin/furan mass concentration it is responsible for only about 22% of the 2005 TEF based TEQ and 8.2% of the 1998 TEF based TEQ (Table 3.5.2-1). The higher 2005 TEF for OCDD of 0.0003 has caused the more plentiful OCDD to comprise a larger percentage of the total TEQ. Congener 1,2,3,7,8,9-HxCDD makes about 5% of the total congener mass and yet makes up about 35% to 40% of the total TEQ toxicity. The more toxic congeners such as PeCDD, and TCDF composed about 0.025% of the mass but yet make up approximately 9% to 10% of the total TEQ toxicity.

Table 3.5.2-1. Dioxin/furan congener mass concentration and sediment toxicity.

| Congener | concentration ng/kg | 2005 TEF | % '05 TEF | 1998 TEF | % '98 TEF |
|---|---|---|---|---|---|
| TCDD | 0.001 | 1 | 0.6 | 1 | 0.7 |
| 1,2,3,7,8-PeCDD | 0.009 | 1 | 6.8 | 1 | 7.8 |
| 1,2,3,4,7,8-HxCDD | 0.028 | 0.1 | 2.2 | 0.1 | 2.5 |
| 1,2,3,6,7,8-HxCDD | 0.101 | 0.1 | 7.7 | 0.1 | 8.8 |
| 1,2,3,7,8,9-HxCDD | 0.245 | 0.1 | 18.8 | 0.1 | 21.4 |
| 1,2,3,4,6,7,8-HpCDD | 4.583 | 0.01 | 35.1 | 0.01 | 40.0 |
| OCDD | 93.810 | 0.0003 | 21.6 | 0.0001 | 8.2 |
| 2,3,7,8-TCDF | 0.015 | 0.1 | 1.2 | 0.1 | 1.3 |
| 1,2,3,7,8-PeCDF | 0.003 | 0.03 | 0.1 | 0.05 | 0.1 |
| 2,3,4,7,8-PeCDF | 0.005 | 0.3 | 1.1 | 0.5 | 2.1 |
| 1,2,3,4,7,8-HxCDF | 0.014 | 0.1 | 1.0 | 0.1 | 1.2 |
| 1,2,3,6,7,8-HxCDF | 0.017 | 0.1 | 1.3 | 0.1 | 1.5 |
| 1,2,3,7,8,9-HxCDF | 0.001 | 0.1 | 0.1 | 0.1 | 0.1 |
| 2,3,4,6,7,8-HxCDF | 0.022 | 0.1 | 0.2 | 0.1 | 1.9 |
| 1,2,3,4,6,7,8-HpCDF | 0.263 | 0.01 | 2.0 | 0.01 | 2.3 |
| 1,2,3,4,7,8,9-HpCDF | 0.016 | 0.01 | 0.1 | 0.01 | 0.1 |
| OCDF | 0.868 | 0.0003 | 0.2 | 0.0001 | 0.1 |

Total dioxin/furan TEQs ranged from 0 ng/kg to 15.9 ng/kg using 2005 TEF and from 0 ng/kg to 14.4 ng/kg using 1998 TEF with respective means of 2.4 and 2.1 ng TEQ/kg (Table 3.5.2-2). NOAA most recently published SQAGs for sediment TEQs with a TEL of 0.85 ng/kg, AET of 3.4 ng/kg, and PEL of 21.5 ng/kg (Buchman, 2008). No sediment samples exceeded the PEL. About 37% of the samples had 2005 TEQs above the TEL and an additional 25% showed values above the AET. Of the 14 concentrations exceeding the AET six were in deeper portions of Escambia Bay (samples EG14, 48, 50, 53, 54 and 55), three were in the lower wetlands (EG30, 38 and 40). The remaining samples exceeding the AET were in the river ranging from the east Escambia River channel to near the Alabama border. Samples EG32 (East Channel) and EG43 were either adjacent to or south of the Monsanto spill site and the remaining three samples (EG28, 46 and 47) were located in the upper river segment.

Table 3.5.2-2. Total dioxin/furan TEQ [ng/kg].

| Sample | 2005 TEF based | 1998 TEF based | Sample | 2005 TEF based | 1998 TEF based |
|---|---|---|---|---|---|
| EG1 | 2.8[1] | 2.4 | EG30 | **15.9** | **14.4** |
| EG2 | 0.2 | 0.2 | EG31 | 2.3 | 2 |
| EG3 | 1.8 | 1.6 | EG32 | **3.4** | 3.1 |
| EG4 | 0.3 | 0.2 | EG33 | 2.2 | 2 |
| EG5 | 1.7 | 1.5 | EG34 | 2.7 | 2.3 |
| EG6 | 0.4 | 0.4 | EG35 | 1.4 | 1.2 |
| EG7 | 2.2 | 1.9 | EG36 | 0.8 | 0.6 |
| EG8 | 2.1 | 1.8 | EG37 | 2.7 | 2.3 |
| EG9 | 2.7 | 2.5 | EG38 | **5.2** | **4.3** |
| EG10 | 0.1 | 0.1 | EG39 | 1.3 | 1.1 |
| EG11 | 0.4 | 0.3 | EG40 | **7.7** | **6.7** |
| EG12 | 0.7 | 0.6 | EG41 | 0.8 | 0.6 |
| EG13 | 0 | 0 | EG42 | 0.9 | 0.8 |
| EG14 | **7.9**[2] | **7.1** | EG43 | **5.5** | **4.3** |
| EG15 | 1.8 | 1.6 | EG44 | 0.7 | 0.6 |
| EG16 | 0.5 | 0.5 | EG45 | 1.6 | 1.4 |
| EG17 | 0.3 | 0.3 | EG46 | **4.4** | **3.7** |
| EG18 | 0.9 | 0.8 | EG47 | **3.4** | 3 |
| EG19 | 0.1 | 0 | EG48 | **4.3** | **4** |
| EG20 | 0.2 | 0.2 | EG49 | 1.5 | 1.4 |
| EG21 | 0.4 | 0.3 | EG50 | **5.3** | **4.9** |
| EG22 | 0.7 | 0.6 | EG51 | 1.7 | 1.6 |
| EG23 | 0 | 0 | EG52 | 0.6 | 0.6 |
| EG24 | 2.1 | 1.8 | EG53 | **4** | **3.4** |
| EG25 | 1.4 | 1.1 | EG54 | **3.8** | **3.4** |
| EG26 | 0.4 | 0.3 | EG55 | **5.6** | **5.1** |
| EG27 | 1 | 0.8 | EG56 | 1.7 | 1.4 |
| EG28 | **13.4** | **12.1** | EG57 | 0.5 | 0.5 |
| EG29 | 0 | 0 | | | |

1. Underlined quantities indicate that only the TEL (0.85 ng/kg) has been exceeded
2. Bolded quantities indicate that the AET (3.4 ng/kg) has been exceeded.

### 3.6. Combined dioxin/furan and dioxin-like PCB TEQ

The average summed 2005 TEF based TEQ is 2.6 ng/kg of which dioxins/furans contribute about 92% (Table 3.6-1). Sample series KS did not include an analysis for dioxins/furans and the total TEQ only included the TEQ of dioxin-like PCBs. For combined TEQ about 33% of the samples exceeded the TEL, and an additional 23% of the samples exceeded both the AET and TEL.

Table 3.6-1. Combined dioxin/furan and dioxin-like PCB TEQ.

| Sample | Diox TEQ'05 | PCB TEQ'05 | Sum TEQ'05 | Sample | Diox TEQ'05 | PCB TEQ'05 | Sum TEQ'05 |
|---|---|---|---|---|---|---|---|
| EG1 | 2.788[1] | 0.26 | 3.048 | EG36 | 0.768 | 0.007 | 0.775 |
| EG2 | 0.216 | 0.009 | 0.225 | EG37 | 2.677 | 0.016 | 2.693 |
| EG3 | 1.821 | 0.319 | 2.14 | EG38 | **5.15** | 0.555 | **5.706** |
| EG4 | 0.265 | 0.007 | 0.273 | EG39 | 1.326 | 0.007 | 1.333 |
| EG5 | 1.697 | 0.012 | 1.709 | EG40 | **7.727** | 1.212 | **8.938** |
| EG6 | 0.407 | 0.063 | 0.469 | EG41 | 0.774 | 0.003 | 0.777 |
| EG7 | 2.238 | 0.064 | 2.302 | EG42 | 0.945 | 0.003 | 0.948 |
| EG8 | 2.074 | 0.111 | 2.185 | EG43 | **5.512** | 0.147 | **5.659** |
| EG9 | 2.695 | 0.008 | 2.702 | EG44 | 0.667 | 0.016 | 0.683 |
| EG10 | 0.081 | 2.318 | 2.399 | EG45 | 1.579 | 1.25 | 2.829 |
| EG11 | 0.354 | 0.037 | 0.391 | EG46 | **4.423** | 0.009 | **4.433** |
| EG12 | 0.662 | 0.004 | 0.666 | EG47 | 3.36 | 0.046 | **3.406** |
| EG13 | 0.023 | 0.003 | 0.026 | EG48 | **4.291** | 0.056 | **4.347** |
| EG14 | **7.856**[2] | 0.797 | **8.654** | EG49 | 1.547 | 0.365 | 1.911 |
| EG15 | 1.833 | 0.019 | 1.852 | EG50 | **5.34** | 0.164 | **5.504** |
| EG16 | 0.532 | 0.078 | 0.61 | EG51 | 1.708 | 0.219 | 1.927 |
| EG17 | 0.313 | 0.007 | 0.32 | EG52 | 0.648 | 0.091 | 0.739 |
| EG18 | 0.884 | 0.178 | 1.061 | EG53 | **3.986** | 0.412 | **4.398** |
| EG19 | 0.056 | 0.002 | 0.057 | EG54 | **3.778** | 0.204 | **3.982** |
| EG20 | 0.236 | 0.003 | 0.239 | EG55 | 5.64 | 0.404 | **6.044** |
| EG21 | 0.363 | 0.006 | 0.368 | EG56 | 1.655 | 0.014 | 1.669 |
| EG22 | 0.688 | 0.063 | 0.75 | EG57 | 0.549 | 0.063 | 0.612 |
| EG23 | 0.019 | 0.001 | 0.02 | KS1 | NA | 0.003 | 0.003 |
| EG24 | 2.099 | 0.041 | 2.139 | KS2 | NA | 0.029 | 0.029 |
| EG25 | 1.36 | 0.028 | 1.389 | KS3 | NA | 0.005 | 0.005 |
| EG26 | 0.366 | 0.002 | 0.368 | KS4 | NA | 0.73 | 0.73 |
| EG27 | 1.024 | 0.002 | 1.026 | KS5 | NA | 0.001 | 0.001 |
| EG28 | **13.41** | 0.022 | **13.43** | KS6 | NA | 0.067 | 0.067 |
| EG29 | **0.018** | 0.001 | **0.02** | KS7 | NA | 5.503 | 5.503 |
| EG30 | **15.94** | 0.045 | **15.98** | KS8 | NA | 0.001 | 0.001 |
| EG31 | **2.305** | 0.366 | **2.671** | KS9 | NA | 0.833 | 0.833 |

Table 3.6-1. Combined dioxin/furan and dioxin-like PCB TEQ (cont'd).

| Sample | Diox TEQ'05 | PCB TEQ'05 | Sum TEQ'05 | Sample | Diox TEQ'05 | PCB TEQ'05 | Sum TEQ'05 |
|---|---|---|---|---|---|---|---|
| EG32 | 3.393 | 0.505 | **4.098** | KS10 | NA | 0.026 | 0.026 |
| EG33 | 2.154 | 0.29 | 2.444 | KS11 | NA | 0.001 | 0.001 |
| EG34 | 2.651 | 0.503 | 3.155 | KS12 | NA | **6.51** | **6.51** |
| EG35 | 1.363 | 0.174 | 1.538 | | | | |

1. Underlined quantities are above the NOAA TEL 0.85 ng/kg but not the AET.
2. Bolded quantities are above the AET of 3.4 ng/kg. No samples exceeded the PEL of 21.5 ng/kg.

While the average summed TEQ is 2.6 ng/kg there were only 11 sediment samples that had dioxin-like PCB TEQs above 0.50 for 2005 TEFs (Table 3.6-2). This shows that the majority of the combined TEQ comes from dioxin/furan congeners and not dioxin-like PCBs. Two of the samples, KS7 and KS12 had dioxin-like TEQs that were above the AET of 3.4 ng/kg (Buchman, 2008) and these samples also had the highest total PCB concentration.

Table 3.6-2. Samples with PCB 2005 TEQ above 0.50.

| Sample | 2005 TEQ[1] |
|---|---|
| KS12 | 6.51 |
| KS7 | 5.50 |
| EG10 | 2.32 |
| EG45 | 1.25 |
| EG40 | 1.21 |
| KS9 | 0.83 |
| EG 14 | 0.80 |
| KS4 | 0.73 |
| EG38 | 0.56 |
| EG 32 | 0.51 |
| EG 28 | 0.50 |

1. Ascending sorting

Figure 3.6-1 shows the overall greater contribution of dioxin/furans to total TEQ for the EG sample series from the river and upper Escambia Bay. For the KS series the total TEQ is derived only from PCBs because this series did not include dioxin/furan analyses.

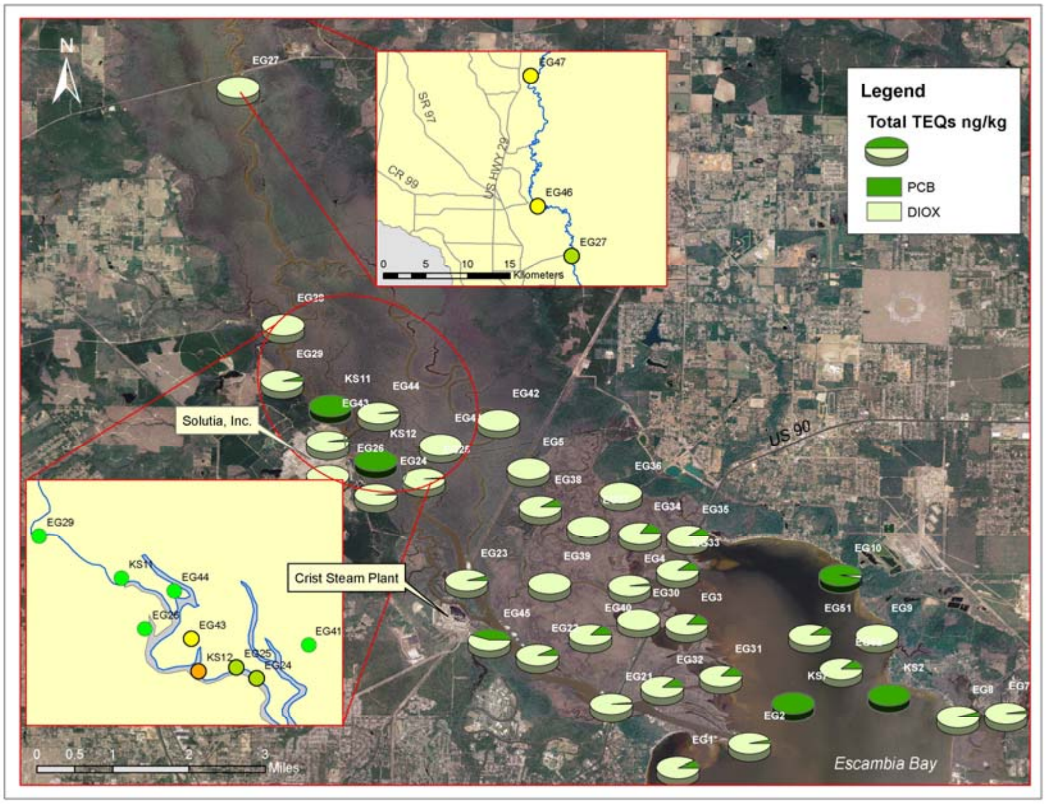


Figure 3.6-1. Relative PCB and dioxin/furan TEQ composition for river and upper bay sediments.

### 3.6.1 Spatial distribution of combined TEQ

On Figures 3.6-1a&b is shown the spatial distribution of the combined TEQ in portions of the river and upper bay. Samples EG46 and EG47, which are on the upper river, have TEQs above the AET. Sample EG28 with the second highest TEQ is also on the river north of the Monsanto-Solutia spill site and the highest TEQ (EG30) is in lower wetlands in Peter's Basin. For Escambia Bay there is a group of concentrations above the AET that are just south of the I-10 bridge (EG14, 50, & 54). The other EG samples above the AET in the bay are EG48, 53, and 55 with the only common factor being that these samples were taken away from the shoreline and near the I-10 and CSX rail bridges. More investigation is needed to establish a causal relationship, if one exists, with these structures and the dioxin/furan concentrations observed in samples EG48, 53, and 55.

The upper bay had 12 samples with a mean TEQ of 2.2 ng/kg, which is above the NOAA TEL. Of these samples seven exceeded the TEL and two other samples (EG53 and KS7) also exceed the AET with TEQs of 4.3 ng/kg and 5.5 ng/kg respectively (Figure 3.6-1a). The range for 24 samples in the lower bay was 0.001-8.7 ng/kg with a mean of 1.6 ng/kg for combined TEQ (Figure 3.6-1b). Only three samples exceeded the TEL and five also exceeded the AET. In the lower river the combined TEQ ranged from 0.02 ng/kg to 6.51 ng/kg with a mean of 2.2 ng/kg. Three of the samples exceeded the TEL and three additional samples exceeded the AET.

In the lower wetlands the samples had the highest overall TEQ with a mean TEQ of 5.04 ng/kg and a range of 0.78 to 15.98 ng/kg, three samples only exceeded the TEL and three samples also exceeded the AET (Figure 3.6-1a). For the upper river there were seven samples with a mean of 3.28 ng/kg and a detected range of 0.003 to 13.43 ng/kg. Two samples exceeded the TEL and three exceeded the AET (Figure 3.6-1a). There were two samples for the upper wetlands, samples EG41 and EG42, that had TEQs of 0.777 ng/kg and 0.948 ng/kg respectively, thus exceeding the TEL.

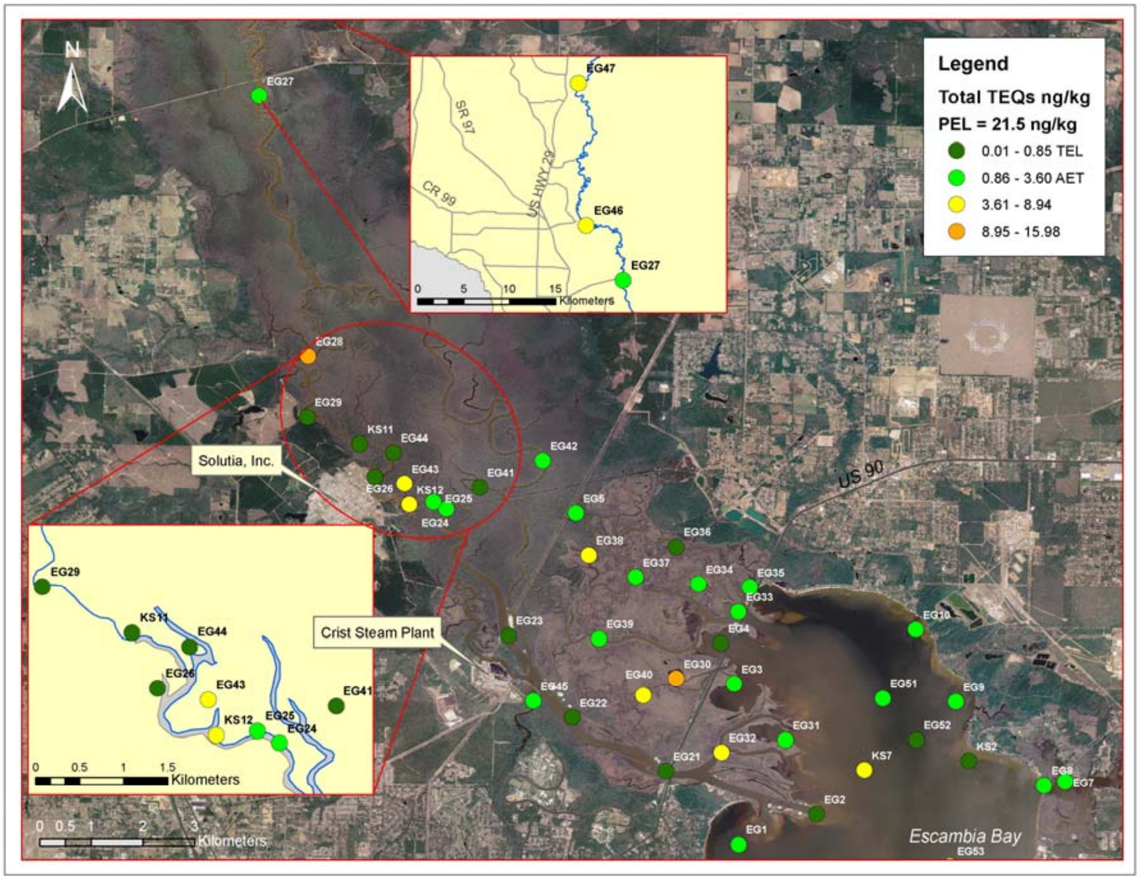


Figure 3.6-1a. Total combined TEQ in Escambia River and the upper Escambia Bay.

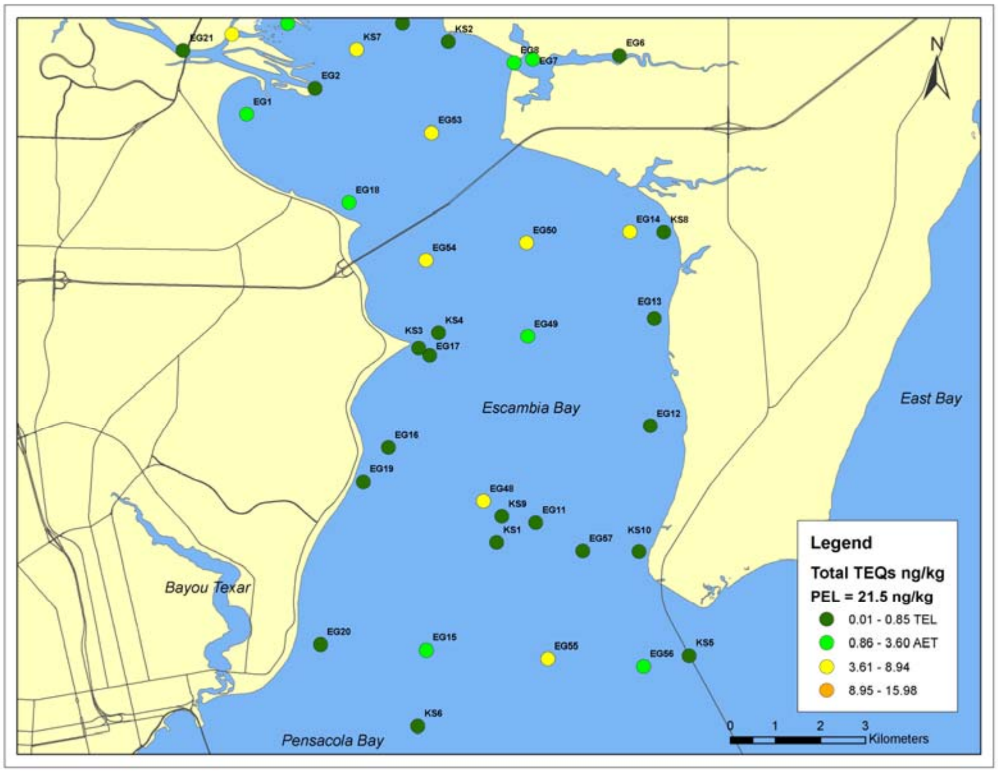


Figure 3.6-1b. Total combined TEQ in Escambia Bay.

## 3.7. Pesticides

The standard suite of organochlorine pesticides was analyzed by EPA Method 8081 that included the following pesticides: alpha-BHC, gamma-BHC (Lindane), beta-BHC, delta-BHC, Heptachlor, Aldrin, Heptachlor Epoxide, gamma-Chlordane, alpha-Chlordane, 4,4'-DDE, Endosulfan I, Dieldrin, Endrin, 4,4'-DDD, Endosulfan II, 4,4'-DDT, Endrin Aldehyde, Methoxychlor, Endosulfan Sulfate, Endrin Ketone, and Toxaphene. Only 4,4'-DDT and, in one sample (EG20), two of its degradation products were detected. DDT was detected in 25% (14 out of 57) of the samples (Table 3.7-1; Figure 3.7-1a&b). All detected 4,4'-DDT concentrations were above the FDEP PEL (4.77 ug/kg) except for EG39 where it only exceeds the TEL (1.19 ug/kg ). The FDEP TEL for p,p'-DDE is 2.07 ug/kg and the TEL for p,p'-DDD is 1.22 ug/kg. With the exception of sample EG20 all detections were found to be associated with the wetlands and river areas of the study. Sample EG3 was found on the bay side of US Highway 90, at the mouth of an inlet that can be considered to be part of the wetlands area.

An explanation for the presence of the DDT in the river sediments and wetlands and only one detection in the bay is not immediately apparent. The data shows none of the common byproducts and degradation products. The DDT concentrations were high enough for detection of DDT byproducts as is shown by the fact that all DDT concentrations are above FDEP SQAGs. Also for the single bay sample EG20, byproducts were detected. DDT detected in previous studies within Escambia Bay also did show the presence of the common DDT technical byproducts such as DDD and DDE (DeBusk et al. (2002). The environmental presence of DDT would be expected to diminish since by federal mandate in January 1, 1973, all uses of DDT in the United States were canceled with an exception for emergencies for public health uses and a few other uses permitted on a case-by-case basis (ATSDR, 2002). This suggests that the detected DDT in the system has been in the environment for 35 or more years. A possible hypothesis is that the DDT in the river and wetlands has been attached to particles in such a way that there has been no detectable degradation since the original application or release of DDT and that this particulate bound DDT must have persisted as such since the 1973 ban or earlier. Many POPs will bind to carbon and other particles. A comparison of DDT to TOC (total organic carbon) yielded a Pearson r correlation coefficient of 0.16 denoting no significant correlation. However, our analyses did not distinguish between black carbon and the other constituents of TOC. Black carbon is a product of weathering of graphitic carbon in rocks and of incomplete combustion of fossil fuels and vegetation. Grass fires, brush fires, and controlled burns are common to the wetland areas and may also provide black carbon. Extremely efficient sorption to black carbon pulls highly toxic PAHs, PCBs, dioxins/furans, polybrominated diphenylethers and pesticides into sediments and soils. This increased sorption is general, but strongest for planar (most toxic) compounds at environmentally relevant, low aqueous concentrations. Black carbon generally comprises about 9% of total organic carbon in aquatic sediments, and then may reduce uptake in organisms by up to two orders of magnitude (Koelmans et al., 2006).

Table 3.7-1. DDT and related byproducts [ug/kg] in sediments in Escambia Bay and River.

| Samples | 4,4'-DDT | Samples | 4,4'-DDT |
|---|---|---|---|
| EG1 | ND | EG30 | ND |
| EG2 | ND | EG31 | ND |
| EG3 | **48** | EG32 | ND |
| EG4 | ND | EG33 | ND |
| EG5 | ND | EG34 | ND |
| EG6 | ND | EG35 | ND |
| EG7 | ND | EG36 | **5.9 i** |
| EG8 | ND | EG37 | **13 i** |
| EG9 | ND | EG38 | **9.1 i** |
| EG10 | ND | EG39 | **1.5** |
| EG 11 | ND | EG40 | **13 i** |
| EG 12 | ND | EG41 | **14** |
| EG 13 | ND | EG42 | **7.4 i** |
| EG 14 | ND | EG43 | **51** |
| EG15 | ND | EG44 | **20** |
| EG16 | ND | EG45 | **17** |
| EG17 | ND | EG46 | **20** |
| EG18 | ND | EG47 | **18** |
| EG19 | ND | EG48 | ND |
| EG20[1] | **130 i** | EG49 | ND |
| EG21 | ND | EG50 | ND |
| EG22 | ND | EG51 | ND |
| EG23 | ND | EG52 | ND |
| EG24 | ND | EG53 | ND |
| EG25 | ND | EG54 | ND |

Table 3.7-1. DDT and related byproducts [ug/kg] in sediments in Escambia Bay and River (cont'd).

| Samples | 4,4'-DDT | Samples | 4,4'-DDT |
|---|---|---|---|
| EG26 | ND | EG55 | ND |
| EG27 | ND | EG56 | ND |
| EG28 | ND | EG57 | ND |
| EG29 | ND | | |

1: 4,4'-DDE concentration is 0.47 ug/kg and 4,4'-DDD is 1.7 ug/kg.

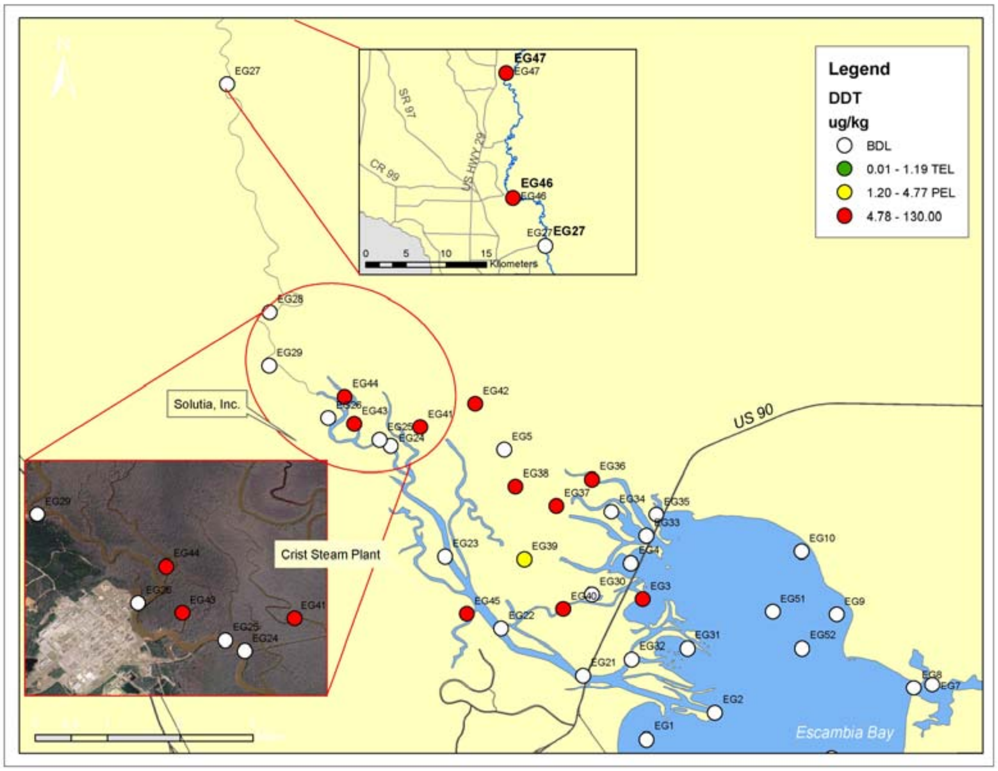


Figure 3.7-1a. DDT in sediments in Escambia River and upper Escambia Bay.

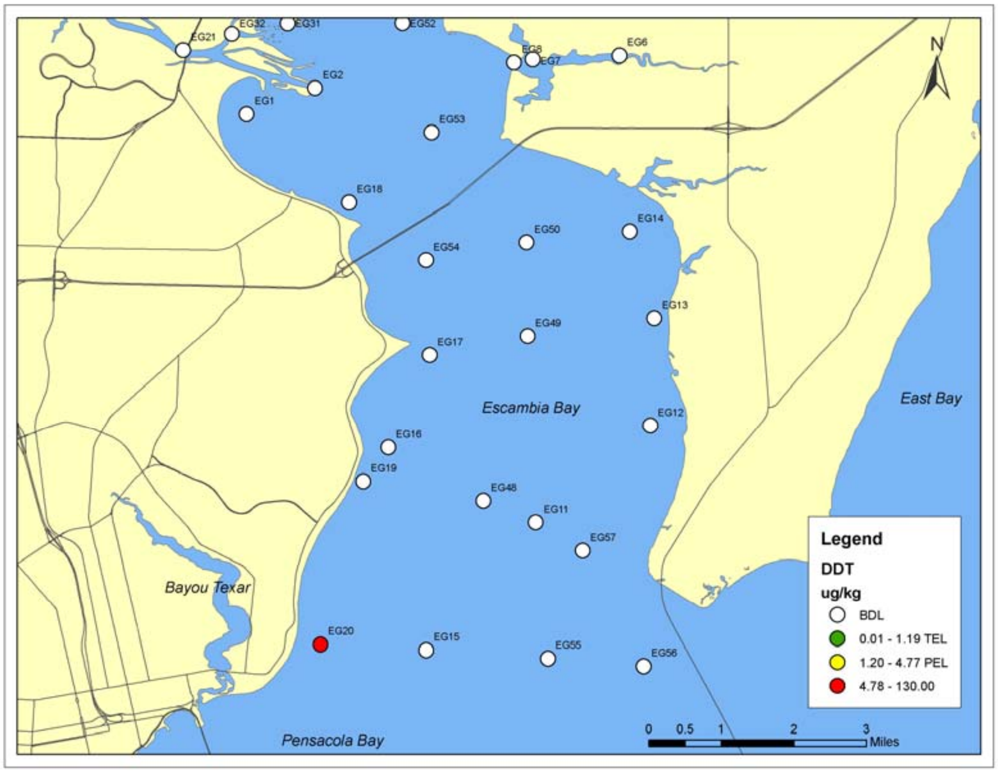


Figure 3.7-1b. 34b. DDT in sediments in Escambia Bay.

The presence of DDT in the lower wetlands is of concern. From its location adjacent to Escambia Bay and from the vegetation it appears that this area is brackish and could serve as nurseries and feeding areas for fish, crustaceans, and animals. DDT does accumulate in fish and shrimp as has been demonstrated by many studies. A recent study (Wandiga et al., 2004) found that the fish *Gobious keinesis* and the white shrimp *Panaeus setiferus* had bioaccumulation factors of 270 and 351 respectively for uptake of DDT. The white shrimp used in the study was the species that occurred in Escambia Bay but suffered serious decline in the late 1960's (Olinger et al., 1975). Long term exposure to this pesticide could certainly prove to be detrimental to the shrimp fishery in Escambia Bay. The impact of these DDT contaminated sediments merits further study relative to impacts upon Escambia Bay and River fauna.

## 3.8. PAHs

The PAH concentrations were much lower in Escambia Bay and River compared to what was reported by PERCH studies in Bayous Texar, Chico, and Grande (Mohrherr et al., 2005, 2006, & 2008). Out of 57 samples only 4 exceeded the TEL for the LMW PAH and only two exceeded the TEL for the HMW PAH and L&H PAH (sum of the light and heavy PAH) (Table 3.8-1). No samples exceeded the PEL. Data from the Debusk et al. (2002) database shows that for total PAHs seven out of ten samples range from 1,033 ug/kg to 14,590 ug/kg. In the current study much lower concentrations were observed (2.4 ug/kg to 2,859 ug/kg) (Table 3.8-1). The low L&H PAH concentrations of the individual congeners were frequently non-detects. Dibenzo(a,h)anthracene had the greatest number of exceedances of the TEL (10 exceedances out of 57 samples) and naphthalenes were the second most common analyte to exceed SQAG (6 exceedances of the TEL and 7 of the TEL). Overall all the light PAHs exceeded SQAGs more frequently (26 cases) than did the heavy PAH species (17 cases). In general, exceedances of SQAG were limited and the bay and river do not appear to be adversely impacted by PAHs according to FDEP SQAG criteria except in a few instances. Results for individual PAH congeners are listed in Tables 3.8-2a&b.

Figures 3.8-1a&b show the spatial distributions of the sum of the light and heavy PAHs (L&H PAH). The four highest PAH concentrations were samples EG33, 34, & 35 near US Highway 90 that was undergoing repair and a boat launch and fishing store, and sample EG8 near the CSX Railroad trestle at Bayou Mulat, which is at least partially constructed out of treated wood. The proximity of the samples with high PAH concentrations to these features points to a possible source for the PAHs. Of note is that adjacent to Solutia, Inc. there is a slight elevation in PAH concentration for four samples (EG25, 26, 43, & 44) (Figure 3.8-1b) and also for some samples in lower Escambia Bay, especially where it meets Pensacola Bay, although all of these were below SQAGs.

All sediment samples were subjected to two separate analyses for PAHs: a full scan by EPA Method 8270C SV and a scan with very low minimal detection limits by 8270 using SIM (Simultaneous Ion Monitoring) for 18 PAHs and PCP (pentachlorophenol). The SV indicates that the data was derived from EPA method 8270 run without SIM. Normally only the 8270 SIM data are reported since its minimum detections limits are usually lower giving better quantifications of the analytes. In Escambia Bay for most cases the higher minimal detection limits of the 8270 SV resulted in non-detect results. However the results of both 8270 analyses are considered when reporting results. The concentrations for PAHs for EG33SV and EG34SV were elevated compared to their respective 8270 SIM results. We confirmed with the contracted analytical laboratory that the QA/QC was valid and have reported this data.

Table 3.8-1. PAHs [ug/kg] in sediments in Escambia Bay and River.

| analyte[1] | detections out of 59 samples | mean of detections | range LL | range UL | mean of all 59 samples | TEL | PEL | samples exceeding TEL | samples exceeding PEL |
|---|---|---|---|---|---|---|---|---|---|
| Naph | 18 | 43.1 | 1.3 | 270 | 13.2 | 34.6 | 391 | 6 | 0 |
| 2-Men | 21 | 42.9 | 2.6 | 360 | 15.3 | 20.2 | 201 | 7 | 2 |
| 1-Men | 16 | 28.2 | 1.5 | 190 | 7.6 | none | none | NA | NA |
| Aceny | 1 | 37 | 37 | 37 | 0.6 | 5.9 | 128 | 1 | 0 |
| Acthene | 4 | 108 | 16 | 210 | 7.3 | 6.7 | 88.9 | 4 | 2 |
| Fluor | 8 | 36.2 | 5 | 88 | 4.9 | 21.2 | 144 | 4 | 0 |
| Phen | 18 | 79.3 | 4.4 | 540 | 24.2 | 86.7 | 544 | 2 | 0 |
| Anth | 28 | 15.4 | 1.7 | 120 | 7.3 | 46.9 | 245 | 2 | 0 |
| LMW | 36 | 119.2 | 3 | 928 | 72.7 | 544 | 1442 | 4 | 0 |
| Flrant | 40 | 53.7 | 0.86 | 89 | 36.4 | 113 | 1494 | 2 | 0 |
| Pyrene | 52 | 58.3 | 0.82 | 710 | 51.4 | 153 | 1398 | 2 | 0 |
| Chrys | 38 | 36.2 | 1.2 | 64 | 25.7 | 108 | 846 | 2 | 0 |
| BzaA | 38 | 32 | 1 | 51 | 22.8 | 74.8 | 693 | 2 | 0 |
| BzbF | 18 | 57 | 6.7 | 260 | 18.4 | none | none | NA | NA |
| BzkF | 20 | 44 | 0.97 | 210 | 15.7 | none | none | NA | NA |
| BzaP | 24 | 42 | 1.5 | 210 | 17.8 | 88.8 | 763 | 2 | 0 |
| InPy | 22 | 22 | 1.3 | 78 | 8.6 | none | none | NA | NA |
| DzaA | 16 | 11.59 | 2.1 | 45 | 3.5 | 6.2 | 135 | 10 | 0 |
| BzPe | 26 | 25.7 | 0.87 | 120 | 11.7 | none | none | NA | NA |
| HMW | 53 | 183.4 | 1.68 | 2140 | 164.9 | 655 | 6676 | 2 | 0 |
| S L&H | 55 | 255.5 | 2.4 | 2859 | 238.2 | 1684 | 16770 | 2 | 0 |
| Total | 55 | 320.5 | 2.4 | 3491.1 | 298.8 | none | none | NA | NA |

[1] PAH abbreviations: Naph: Naphthalene; 2-Men: 2-methylnaphthalene; 1-Men: 1-methylnaphthalene; Acen: Acenaphthylene; Athen: Acenaphthene; Fluor: Fluorene; Phen: Phenanthrene; Anth" Anthracene; LMW: Light molecular weight PAH total; Flrant: Fluoranthene; S L&H: sum of LMW and HMW PAHs.

Table 3.8-2a. LMW PAHs [ug/kg] in sediments in Escambia Bay and River.

| Sample ID | Naph | 2-Men | 1-Men | Acen | Athen | Fluor | Phen | Anth | LMW |
|---|---|---|---|---|---|---|---|---|---|
| EG1 | <4.2 | <13 | <9 | <22 | <22 | <13 | <27 | <5 | 0 |
| EG2 | <0.68 | <2 | <1.5 | <3.3 | <3.4 | <2 | <4.4 | <0.81 | 0 |
| EG3 | <4.2 | <13 | <8.9 | <21 | <22 | <13 | <27 | <5 | 0 |
| EG4 | 14i | 15i | 7.5i | <13 | <14 | 8.3i | 20i | <3 | 57.3 |
| EG5 | <7.6 | <23 | <17 | <39 | <40 | <23 | <49 | <9 | 0 |
| EG-6 | <2.8 | <8 | <5.9 | <14 | <15 | <8 | <18 | <3.5 | 0 |
| EG7 | <3.1 | <9 | <6.6 | <16 | <17 | <9 | <20 | 8.8i | 8.8 |
| EG8 | 44 | 15i | 8.1i | <15 | 26i | 38 | 440 | 120 | 683 |
| EG9 | <3.5 | <9.7 | <7.1 | <17 | <18 | <9.7 | <22 | <4 | 0 |
| EG10 | <4.8 | <15 | <11 | <25 | <26 | <15 | <32 | <5.8 | 0 |
| EG11 | 83 | 29i | 13i | <31 | <32 | <18 | <39 | <7.3 | 112 |
| EG12 | <3.5 | 12i | <7.1 | <17 | <18 | <9.6 | <22 | <4 | 12 |
| EG13 | 6.2 | 3i | <1.4 | <3.2 | <3.6 | <1.9 | <4.1 | <0.75 | 9.2 |
| EG14 | 76 | 19i | <11 | <24 | <25 | <14 | <31 | <5.6 | 95 |
| EG15 | <6 | 23 i | <13 | <31 | <32 | <18 | <39 | <7.2 | 23 |
| EG16 | <2.4 | 13 i | 6.2 i | <13 | <13 | <7 | 28 i | 13 i | 54 |
| EG17 | <2.8 | 18 i | 8.3 i | <15 | <15 | <8.2 | 32 i | 17 i | 67 |
| EG18 | <0.64 | 3.1 i | 1.5 i | <3.5 | <3.6 | <1.9 | 4.4 i | 1.9 i | 9.4 |
| EG19 | <0.64 | <1.9 | <1.4 | <3.5 | <3.6 | <1.9 | <4.2 | <0.77 | 0 |
| EG20 | <2 | 9.3 i | 4.2 i | <9.8 | <11 | <5.7 | 17 i | 5.7 i | 32 |
| EG21 | <1.2 | 3.6 i | <2.5 | <5.8 | <6.1 | <3.6 | 7.9 i | 4.5 i | 15.8 |
| EG22 | <0.63 | 2.6 i | <1.4 | <3.2 | <3.5 | <1.9 | 5.2 i | 2.5 i | 10.3 |
| EG23 | <0.63 | <1.9 | <1.4 | <3.2 | <3.6 | <1.9 | <4.1 | <0.76 | 0 |
| EG24 | <3.9 | <12 | <8.3 | <20 | <21 | <12 | <25 | 9.3 i | 9.3 |
| EG25 | <3.5 | <9.7 | <7.1 | <17 | <18 | <9.7 | 29 i | 10 i | 39 |
| EG26 | <2.9 | <8.3 | <6.1 | <15 | <15 | <8.3 | 21 i | 9.5 i | 30.5 |
| EG27 | <0.65 | <1.9 | <1.4 | <3.5 | <3.3 | <1.9 | <4.2 | <0.77 | 0 |
| EG28 | <8.1 | <24 | <18 | <42 | <43 | <24 | <53 | <9.7 | 0 |
| EG29 | <0.64 | <1.9 | <1.4 | <3.5 | <3.6 | <1.9 | <4.2 | <0.77 | 0 |
| EG30 | <4.8 | <15 | <11 | <25 | <26 | <15 | <31 | <5.8 | 0 |
| EG31 | <2.2 | <6.5 | <4.8 | <12 | <12 | <6.5 | <15 | <2.7 | 0 |
| EG32 | <2.1 | <6.2 | <4.6 | <11 | <12 | <6.2 | <14 | <2.6 | 0 |
| EG33SV | 160i | 230i | 120i | <93 | 180i | 87i | <64 | <54 | 657 |
| EG33 | <2.5 | <7.4 | <5.4 | <13 | <14 | <7.4 | <17 | <3 | 0 |

Table 3.8-2a. LMW PAHs [ug/kg] in sediments in Escambia Bay and River (cont'd).

| Sample ID | Naph | 2-Men | 1-Men | Acen | Athen | Fluor | Phen | Anth | LMW |
|---|---|---|---|---|---|---|---|---|---|
| EG34SV | 270i | 360i | 190i | <150 | 210i | 88i | <110 | <85 | 928 |
| EG34 | <4 | <12 | <8.5 | <21 | <21 | <12 | <26 | <4.7 | 0 |
| EG35 | 21 | 10 | 7.1 | 37 | 16 | 19 | 540 | 76 | 719 |
| EG36 | 7.4 i | <14 | 15 i | <24 | <24 | <14 | <30 | 12 i | 19.4 |
| EG37 | 8.4 | <15 | <11 | <25 | <26 | <15 | <31 | 13 | 21.4 |
| EG38 | 8.6 | <21 | <16 | <36 | <37 | <21 | <46 | 17 | 25.6 |
| EG39 | 1.3 i | <2 | 2.1 i | <3.6 | <3.3 | <2 | <4.3 | 1.7 i | 3 |
| EG40 | 5.1 i | 9.4 i | 5.4 i | <7.9 | <8.2 | 5 i | 14 i | 4.6 i | 38.1 |
| EG41 | 13 i | 24 i | 14 i | <19 | <20 | 14 | 28 | 8.6 i | 87.6 |
| EG42 | 6.7 i | 11 i | <7.2 | <17 | <18 | <9.8 | <22 | 7.6 i | 25.3 |
| EG43 | 34 i | 70 | 34 i | <38 | <39 | 30 i | 70 i | 20 i | 224 |
| EG44 | 11 i | 21 | 14 i | <14 | <15 | <7.9 | 28 i | 7 i | 67 |
| EG45 | 6.6 | <12 | <8.7 | <21 | <22 | <12 | <27 | 5.3 i | 11.9 |
| EG46 | <4.4 | <13 | <9.4 | <23 | <23 | <13 | <29 | <5.2 | 0 |
| EG47 | <4.8 | <14 | <11 | <25 | <25 | <14 | <31 | <5.7 | 0 |
| EG48 | <6 | <18 | <13 | <31 | <32 | <18 | <39 | 9.3i | 9.3 |
| EG49 | <5.3 | <16 | <12 | <27 | <28 | <16 | <35 | <6.4 | 0 |
| EG50 | <4.3 | <13 | <9.2 | <22 | <23 | <13 | <28 | <5.1 | 0 |
| EG51 | <5 | <15 | <11 | <26 | <27 | <15 | <33 | <6 | 0 |
| EG52 | <3.4 | <11 | <7.6 | <18 | <19 | <11 | <23 | <4.2 | 0 |
| EG53 | <5.1 | <15 | <11 | <26 | <27 | <15 | <33 | 6.2i | 6.2 |
| EG54 | <4.9 | <15 | <11 | <25 | <26 | <15 | <32 | 8.5i | 8.5 |
| EG 55 | <6.1 | <18 | <14 | <32 | <33 | <18 | 58i | 12i | 70 |
| EG 56 | <5.7 | <17 | <13 | <29 | <31 | <17 | 44i | 10i | 54 |
| EG 57 | <4.4 | <13 | <9.5 | <23 | <24 | <13 | 40i | 8.9i | 48.9 |

[1] PAH abbreviations: Naph: Naphthalene; 2-Men: 2-methylnaphthalene; 1-Men: 1-methylnaphthalene; Acen: Acenaphthylene; Athen: Acenaphthene; Fluor: Fluorene; Phen: Phenanthrene; Anth" Anthracene; LMW: Light molecular weight PAH total; Flrant: Fluoranthene; S L&H: sum of LMW and HMW PAHs.

[2] Bold faced font indicates that the concentration is equal to or exceeds the FDEP TEL.

[3] Italicized underlined font indicates that the concentration is equal to or exceeds the FDEP PEL.

[4] < indicates a nondetect showing that the result is below the MDL indicated by the number following.

[5] I indicates that the reported value is between the laboratory method detection limit and the laboratory practical quantitation limit.

Table 3.8-2b. HMW PAHs [ug/kg] in sediments in Escambia Bay and River.

| Sample ID | Flran | Pyrene | Chrys | BzaA | BzbF | BzkF | BzaP | InPy | DzaA | BzPe | HMW | L&H | Total PAH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| EG1 | 19i | 24i | 12i | 13i | 8.6i | 10i | 9.5i | <7.1 | <4.2 | 6.5i | 77.5 | 77.5 | 102.6 |
| EG2 | 2.2i | 2.4i | 1.2i | 1i | <1.1 | 0.97i | <1.5 | <1.2 | <0.68 | <0.86 | 6.8 | 6.8 | 7.77 |
| EG3 | 13i | 16i | 7.3i | 5.4i | 6.7i | 5.6i | <8.9 | <7.1 | <4.2 | <5.3 | 41.7 | 41.7 | 54 |
| EG4 | 12i | 9.9i | 4.4i | 3.1i | <4 | 3.5i | <5.4 | <4.3 | <2.5 | <3.2 | 29.4 | 86.7 | 97.5 |
| EG5 | 21 | 29 | 11 | 8.8 | <12 | <9.6 | <17 | <13 | <7.6 | <9.6 | 69.8 | 69.8 | 69.8 |
| EG6 | <3.2 | 6.7i | <2.6 | <2.7 | <4.3 | <3.3 | <5.9 | <4.7 | <2.8 | <3.3 | 6.7 | 6.7 | 6.7 |
| EG7 | 71 | 74 | 70 | 49 | 72 | 55 | 49 | 28 | 8.6i | 32 | 321.6 | 330.4 | 517.4 |
| EG8 | 700 | 500 | 290 | 270 | 240 | 210 | 210 | 120 | 45 | 120 | 2015 | 2698 | 3396.1 |
| EG9 | <3.9 | 4.7i | <3.1 | <3.5 | <5.2 | <4.2 | <7.1 | <5.7 | <3.5 | <4.2 | 4.7 | 4.7 | 4.7 |
| EG10 | <5.6 | 17i | 7.8i | 6.3i | 8.5i | 8.2i | <11 | <8.2 | <4.8 | <6.2 | 31.1 | 31.1 | 47.8 |
| EG11 | 44 | 41i | 24i | 23i | <9.5 | <7.7 | 23i | 16i | <6.1 | 20i | 155 | 267 | 316 |
| EG12 | 13i | 11i | 6.4i | <3.2 | <5.2 | <4.2 | <7.1 | <5.6 | <3.5 | 6i | 30.4 | 42.4 | 48.4 |
| EG13 | 0.86i | 0.82i | <0.59 | <0.62 | <0.99 | <0.8 | <1.4 | <1.1 | <0.63 | <0.8 | 1.68 | 10.88 | 10.88 |
| EG14 | 12i | 12i | <4.5 | <4.6 | <7.4 | <6 | <11 | <8 | <4.7 | <6 | 24 | 119 | 119 |
| EG15 | 53 | 51 | 40 i | 33 i | <9.4 | <7.7 | 33 i | 24 i | 7.8 I | 28 i | 217.8 | 240.8 | 292.8 |
| EG16 | 30 | 27 | 16 | 15 i | <3.8 | <3.1 | 12 i | 8.2 i | 2.5 i | 9.6 i | 102.5 | **156.**5 | 180.5 |
| EG17 | 30 | 26 | 15 i | 14 i | <4.4 | <3.4 | 13 i | 9.2 i | <2.8 | 11 i | 98 | 165 | 193.3 |
| EG18 | <0.74 | 2.3 i | <0.6 | <0.62 | <1 | <0.81 | <1.4 | <1.1 | <0.64 | 0.87 i | 2.3 | 11.7 | 14.07 |
| EG19 | <0.74 | <0.65 | <0.6 | <0.63 | <1 | <0.82 | <1.4 | <1.1 | <0.64 | <0.82 | 0 | 0 | 0 |
| EG20 | <2.3 | 15 | 9.8 i | 9.7 i | <3 | <2.5 | 10 i | 6.8 i | 2.1 i | 8.7 i | 46.6 | 78.6 | 98.3 |
| EG21 | 11 | 21 | 7.4 i | 7 i | <1.8 | <1.5 | 4.9 i | <2 | <1.2 | 2.3 i | 51.3 | 67.1 | 69.4 |
| EG22 | 5 | 4.6 | 2.5 i | 1.5 i | <0.98 | <0.8 | 1.5 i | 1.3 i | <0.63 | 1.5 i | 15.1 | 25.4 | 28.2 |
| EG23 | <0.73 | 2.5 i | <0.6 | <0.62 | <0.99 | <0.8 | <1.4 | <1.1 | <0.63 | <0.8 | 2.5 | 2.5 | 2.5 |
| EG24 | 41 | 80 | 32 | 28 | <6.1 | <4.9 | 22 i | 7.5 i | <3.9 | 11 i | 203 | 212.3 | 230.8 |
| EG25 | 56 | 92 | 37 | 31 | <5.2 | <4.2 | 24 | 10 i | 4.1 i | 15 i | 244.1 | 283.1 | 308.1 |
| EG26 | 68 | 110 | 30 | 27 | <4.4 | <3.4 | 16 i | 5.1 i | <2.9 | 7 i | 251 | 281.5 | 293.4 |
| EG27 | <0.75 | <0.66 | <0.61 | <0.63 | <1.1 | <0.82 | <1.4 | <1.1 | <0.65 | <0.82 | 0 | 0 | 0 |
| EG28 | <9.4 | <8.3 | <7.6 | <7.9 | <13 | <11 | <18 | <14 | <8.1 | <11 | 0 | 0 | 0 |
| EG29 | <0.74 | <0.65 | <0.6 | <0.63 | <1 | <0.82 | <1.4 | <1.1 | <0.64 | <0.82 | 0 | 0 | 0 |
| EG30 | <5.6 | 14 i | <4.6 | <4.7 | <7.6 | <6.1 | <11 | <8.2 | <4.8 | <6.1 | 14 | 14 | 14 |
| EG31 | <2.6 | 2.4 i | <2.1 | <2.2 | <3.3 | <2.8 | <4.8 | <3.8 | <2.2 | <2.8 | 2.4 | 2.4 | 2.4 |
| EG32 | <2.5 | 12 i | 5.5 i | 6 i | <3.5 | <2.7 | <4.6 | <3.4 | <2.1 | <2.7 | 23.3 | 23.3 | 23.3 |

Table 3.8-2b. HMW PAHs [ug/kg] in sediments in Escambia Bay and River (cont'd.).

| Sample ID | Flran | Pyrene | Chrys | BzaA | BzbF | BzkF | BzaP | InPy | DzaA | BzPe | HMW | L&H | Total PAH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| EG33SV | <59 | <69 | <110 | <54 | <98 | <79 | <93 | <88 | <110 | <79 | 0 | 690 | 777 |
| EG33 | <2.9 | 6.8i | <2.4 | <2.5 | <4 | <3.2 | <5.4 | <4.3 | <2.5 | <3.2 | 6.8 | 6.8 | 6.8 |
| EG34SV | <93 | <110 | <170 | <85 | <160 | <130 | <150 | <140 | <170 | <130 | 0 | 928 | 1118 |
| EG34 | <4.6 | 15i | 12i | 9.5i | <6.2 | <5.1 | <8.5 | <6.7 | <4 | <5.1 | 36.5 | 36.5 | 36.5 |
| EG35 | 76 | 710 | 300 | 270 | 260 | 210 | 190 | 78 | 30 | 77 | 2140 | 2859 | **3491.1** |
| EG36 | <5.3 | 23 i | 13 i | 11 i | <7.2 | 12 i | <9.8 | <7.8 | <4.6 | <5.8 | 47 | 66.4 | 93.6 |
| EG37 | 39 | 45 | 24 | 21 | 7.8 | 24 | <11 | <8.2 | <4.8 | <6.1 | 129 | 150.4 | 182.2 |
| EG38 | 52 | 60 | 31 | 29 | 20 | 33 | <16 | <12 | <7 | <8.9 | 172 | 197.6 | 250.6 |
| EG39 | 3.9 i | 5.5 | 2.2 i | 1.7 i | <1.1 | <0.84 | <1.5 | <1.2 | <0.66 | <0.84 | 13.5 | 16.3 | 18.4 |
| EG40 | 9 i | 8.6 i | 4.4 i | 3.8 i | <2.5 | <2 | <3.6 | <2.7 | <1.6 | <2 | 25.8 | 63.9 | 69.3 |
| EG41 | 12 i | 35 | <3.3 | <3.4 | <5.8 | <4.7 | <7.9 | <6.3 | <3.7 | <4.7 | 47 | 134.6 | 148.6 |
| EG42 | 30 | 28 | 17 i | 8.3 i | <5.3 | <4.3 | <7.2 | <5.7 | <3.6 | <4.3 | 83.5 | 108.6 | 108.6 |
| EG43 | 28 i | 150 | <6.9 | <7.2 | <12 | <9.3 | <16 | <13 | <7.3 | <9.3 | 178 | 402 | 436 |
| EG44 | 65 | 81 | 39 | 33 | 26 | 25 | <5.8 | <4.6 | <2.7 | <3.3 | 218 | 285 | 350 |
| EG45 | 37 | 52 | 21 i | 18 i | <6.4 | <5.2 | <8.7 | <6.9 | <4.1 | <5.2 | 128 | 139.9 | 139.9 |
| EG46 | 33 | 42 | 22 i | 14 i | 16 i | <5.6 | <9.4 | <7.4 | <4.4 | <5.6 | 111 | 111 | 127 |
| EG47 | <5.5 | <4.9 | <4.5 | 6.8 i | <7.4 | <6.1 | <11 | <8.1 | <4.8 | <6.1 | 6.8 | 6.8 | 6.8 |
| EG48 | 75 | 69 | 50 | 46 | 68 | 49 | 58 | 42 | 15i | 48 | 313 | 322.3 | 529.3 |
| EG49 | 31i | 31i | 21i | 20i | 29i | 21i | 21i | 16i | 5.9i | 18i | 129.9 | 129.9 | 213.9 |
| EG50 | 23i | 25i | 19i | 19i | 25i | 22i | 22i | 15i | 5.5i | 18i | 113.3 | 113.3 | 193.3 |
| EG51 | 29i | 35 | 21i | 17i | <7.8 | <6.4 | 19i | 14i | <5 | 15i | 121 | 121 | 150 |
| EG52 | 25 | 26 | 25 | 18i | 24i | 21i | 19i | 12i | 3.7i | 13i | 116.7 | 116.7 | 186.7 |
| EG53 | 42 | 46 | 30i | 29i | 45 | 32i | 35 | 22i | 7.8i | 25i | 189.8 | 196 | 320 |
| EG54 | 54 | 66 | 43 | 33i | 60 | 49 | 47 | 29i | 9.5i | 33 | 252.5 | 261 | 432 |
| EG55 | 120 | 110 | 64 | 59 | <9.6 | <7.8 | 68 | 51 | 16i | 61 | 437 | 507 | 619 |
| EG56 | 89 | 86 | 51 | 51 | 57 | 46 | 53 | 36i | 11i | 41 | 341 | 395 | 575 |
| EG57 | 72 | 67 | 44 | 41 | 53 | 43 | 48 | 32 | 11i | 39 | 283 | 331.9 | 498.9 |

[1] PAH abbreviations: Naph: Naphthalene; 2-Men: 2-methylnaphthalene; 1-Men: 1-methylnaphthalene; Acen: Acenaphthylene; Athen: Acenaphthene; Fluor: Fluorene; Phen: Phenanthrene; Anth: Anthracene; LMW: Light molecular weight PAHs; Fant: Fluoranthene.

[2] Bold faced font indicates that the concentration is equal to or exceeds the FDEP TEL.

[3] Italicized underlined font indicates that the concentration is equal to or exceeds the FDEP PEL.

[4] < indicates a nondetect showing that the result is below the MDL indicated by the number following.

[5] I indicates that the reported value is between the laboratory method detection limit and the laboratory practical quantitation limit.

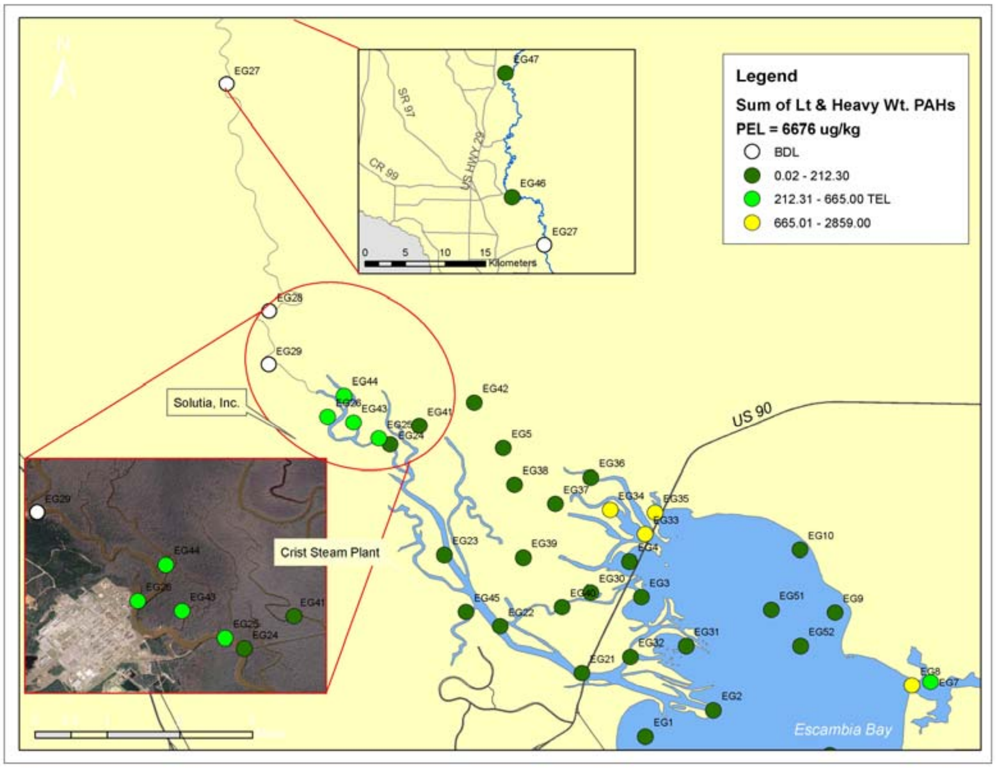


Figure 3.8-1a. Sum of light and heavy weight PAHs in sediments in Escambia River and upper bay.

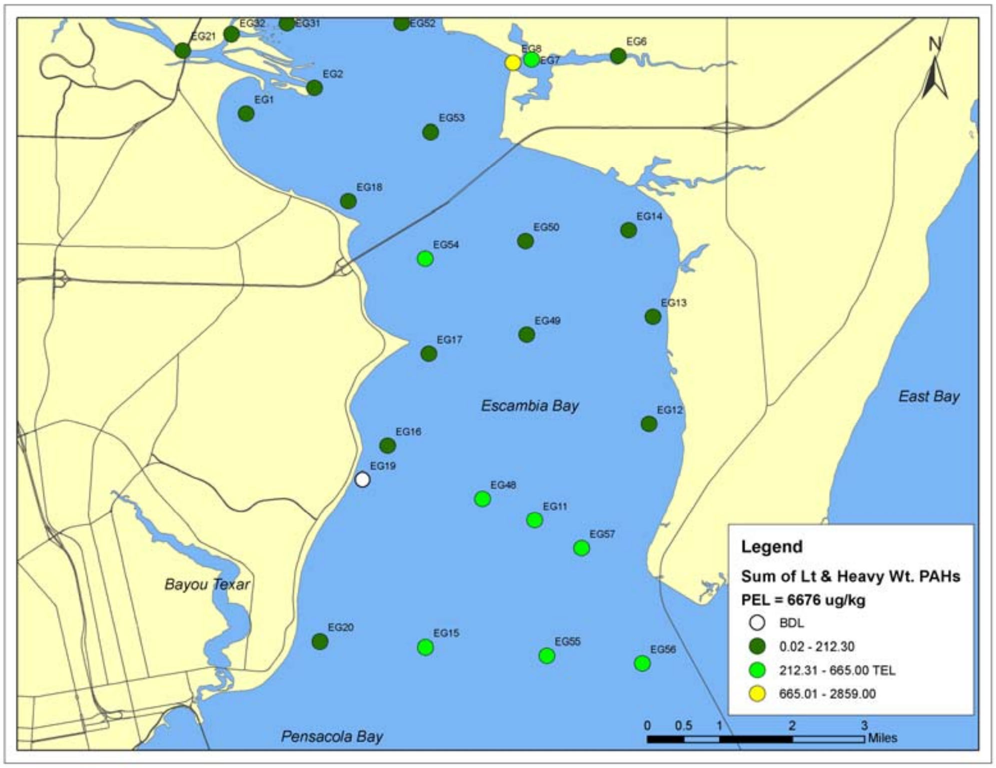


Figure 3.8-1b. Sum of LMW and HMW PAHs in sediments in Escambia Bay.

### 3.8.1. PAH origins

PAHs can have multiple origins with oil spills and combustion products being among the most important sources in typical urban environments. Ratios based on concentrations of specific PAHs present within a sediment sample have been employed to obtain evidence that suggests the probable origins of PAH mixtures (Rostad and Pereira, 1987; Yunker et al., 2002). The ratios can be correlated with one of four sources: petroleum release; combustion of petroleum products; combustion of grass, wood, and/or coal; and creosote origin. For Escambia Bay and River the detected PAH concentrations were insufficient to calculate ratios. Over all the frequent nondetects for the PAH congeners needed for the calculation, fluoranthene, phenanthrene, pyrene, anthracene, pyrene, indeno(1,2,3-c,d), & benzo(g,h,i) perylene, resulted in the majority of samples having incalculable ratios making analysis of origins unfeasible via this methodology.

## 3.9. Total petroleum hydrocarbon

In Table 3.9-1 and Figure 3.9-1a&b detections for total petroleum hydrocarbons occurred in only seven out of 57 samples with only one of the detections being in Escambia Bay (Sample EG55). Two of the remaining detections were minor channels of the Escambia River System (EG41&42) and all of the other detections were in or near to the main channels of Escambia River (Figure 3.9-1a&b). Petroleum hydrocarbons were found in minimal quantities in and about the Escambia River and it does not appear to be accumulating in Escambia Bay as is suggested by the presence of only a single detection in the Bay (Figure 3.9-1b and sample EG55).

Table 3.9-1. Total petroleum hydrocarbons [mg/kg] in sediments in Escambia Bay and River.

| Sample | TPH | Sample ID | TPH | Sample ID | TPH |
|---|---|---|---|---|---|
| EG1 | <52 | EG20 | <8 | EG39 | <8.2 |
| EG2 | <8.5 | EG21 | <43 | EG40 | <84 |
| EG3 | <52 | EG22 | <7.9 | EG41 | **120 i** |
| EG4 | <11 | EG23 | <7.9 | EG42 | **99 i** |
| EG5 | <95 | EG24 | <48 | EG43 | **150 i** |
| EG-6 | <35 | EG25 | <42 | EG44 | <34 |
| EG-7 | <39 | EG26 | <36 | EG45 | **200** |
| EG-8 | <37 | EG 27 | <8.1 | EG-46 | **120 i** |
| EG-9 | <41 | EG 28 | <110 | EG-47 | **98 i** |
| EG-10 | <60 | EG 29 | <8 | EG48 | <75 |
| EG 11 | <76 | EG 30 | <60 | EG49 | <67 |
| EG 12 | <41 | EG 31 | <28 | EG50 | <54 |
| EG 13 | <7.9 | EG 32 | <27 | EG-51 | <63 |
| EG 14 | <59 | EG33 | <32 | EG-52 | <44 |
| EG15 | <75 | EG34 | <50 | EG-53 | <62 |
| EG16 | <30 | EG35 | <8 | EG-54 | <60 |
| EG17 | <35 | EG36 | <57 | EG 55 | **160i** |
| EG18 | <8 | EG37 | <61 | EG 56 | <72 |
| EG19 | <8 | EG38 | <87 | EG 57 | <55 |

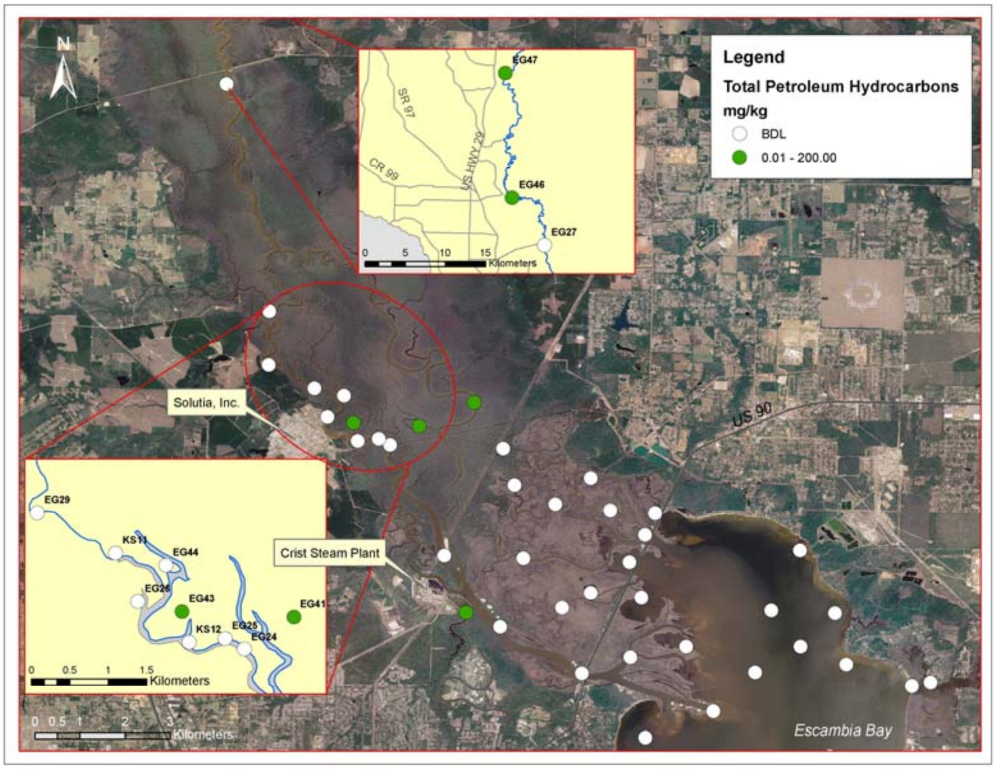


Figure 3.9-1a. Total petroleum hydrocarbons in sediments in Escambia River and upper bay.

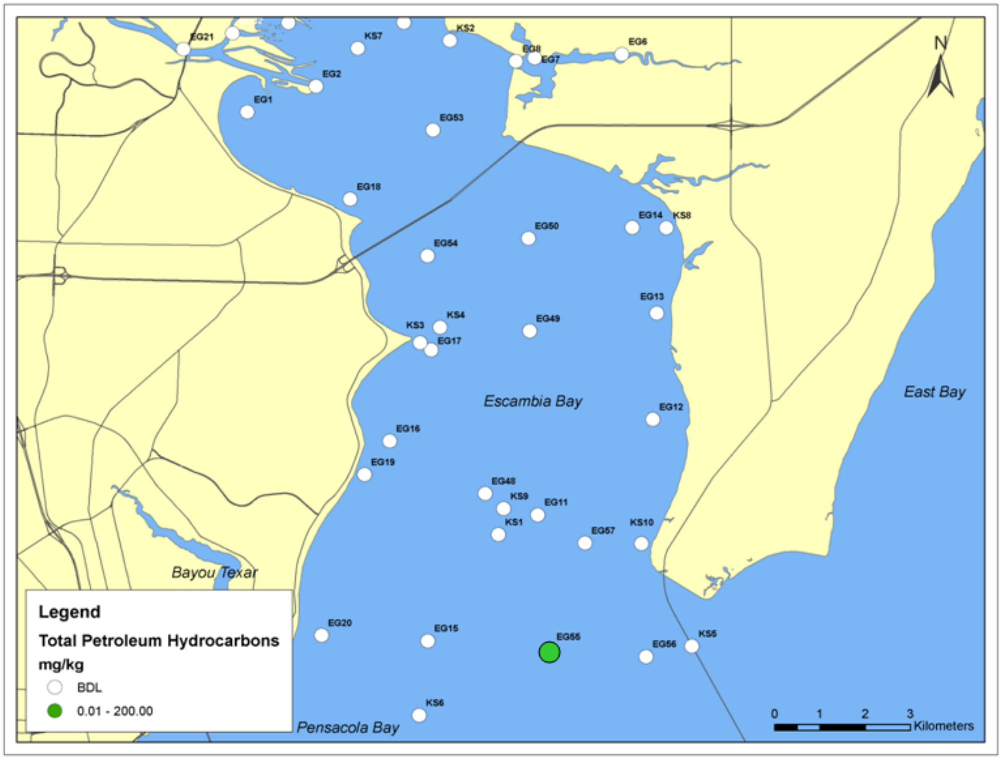


Figure 3.9-1b. Total petroleum hydrocarbons in sediments in Escambia Bay.

### 3.10. Total organic carbon

Hyland et al. (2005) found that organic matter in sediments is an important source of food for benthic fauna. In a study covering 7 coastal regions of the world: the northern Black Sea (Crimean and Caucasian coasts); eastern Mediterranean Sea (Greece); North Sea (Ekofisk oil field); Firth of Clyde and Liverpool Bay, UK; Seto Inland Sea, Japan; Boston Harbor and Massachusetts Bay, USA, and estuaries of the southeastern USA it was found that an overabundance of organic carbon caused reductions in species richness, species abundance, and biomass due to oxygen depletion and buildup of toxic by-products (ammonia and sulphide) associated with the breakdown of these materials. Increasing organic content of sediment was observed to be often accompanied by other chemical stressors co-varying with sediment particle size (Hyland et al., 2005). Results suggested that risks of reduced species richness from organic loading and other associated stressors in sediments should be relatively low at TOC concentrations less than about 10 mg/g, high at concentrations greater than about 35 mg/g, and intermediate at concentrations in between. It was proposed to use total organic carbon (TOC) as critical points for a general screening-level indicator of sediment impact. This would be used to evaluate the likelihood of reduced sediment quality and associated bioeffects over broad coastal areas receiving organic wastes and other pollutants from human activities (Hyland et al., 2005). On this basis it appears that the sediment of the Escambia Bay and River is not stressed by total organic carbons. The TOC range was 0 mg/g to 5.7 mg/g, that is well below the 10 mg/g limit that is associated with low stress.

Table 3.10-1. Total organic carbon [mg/g] in sediments in Escambia Bay and River.

| Sample | TOC | Sample | TOC | Sample | TOC | Sample | TOC |
|---|---|---|---|---|---|---|---|
| EG1 | 2.6 | EG16 | 0.24 | EG 30 | 1.5 | EG44 | 0.98 |
| EG2 | 0.56 | EG17 | 0.24 | EG 31 | 2.2 | EG45 | 1.4 |
| EG3 | 0.77 | EG18 | 0.27 | EG 32 | 0.77 | EG-46 | 5.7 |
| EG4 | 1.5 | EG19 | 0.18 | EG33 | 0.61 | EG-47 | 1.5 |
| EG5 | 4.0 | EG20 | 0.28 | EG34 | 1.5 | EG48 | 3.9 |
| EG-6 | 2.2 | EG21 | 0.44 | EG35 | 0.28 | EG49 | 2.7 |
| EG-7 | 2.4 | EG22 | 0.19 | EG36 | 0.87 | EG50 | 2.3 |
| EG-8 | 1.2 | EG23 | 0.0 | EG37 | 1.0 | EG-51 | 2.0 |
| EG-9 | 0.9 | EG24 | 0.76 | EG38 | 2.4 | EG-52 | 1.7 |
| EG-10 | 1.7 | EG25 | 0.79 | EG39 | 0.72 | EG-53 | 2.9 |
| EG 11 | 2.44 | EG26 | 0.81 | EG40 | 1.5 | EG-54 | 2.6 |
| EG 12 | 2.1 | EG 27 | 0.32 | EG41 | 1.2 | EG 55 | 4.3 |
| EG 13 | 0.37 | EG 28 | 2.1 | EG42 | 4.5 | EG 56 | 3.9 |
| EG 14 | 1.5 | EG 29 | 0.0 | EG43 | 2.3 | EG 57 | 2.6 |
| EG15 | 0.86 | | | | | | |

## 3.11. Trace metals

A total of 14 common metals were analyzed in sediments collected from the Escambia Bay and River for the EG series. The studied metals were: aluminum (Al), arsenic (As), cadmium (Cd), calcium (Ca), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), magnesium (Mg), mercury (Hg), nickel (Ni), selenium (Se), tin (Sn), and zinc (Zn). Ten of these can be considered to be common trace metals: arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, tin, and zinc. None of the metals exceeded its FDEP PEL, suggesting that high level sediment pollution is not present in the Escambia Bay and River sediments (Table 3.11-1). However, all metals exceeded their respective TELs, indicating that some negative effects on bottom dwelling organisms are possible. Arsenic had most TEL exceedances (30 out of 59 samples), mercury the fewest (2 exceedances). Selenium and tin, for which a TEL is not available, had the lowest number of detections (Table 3.11-1).

Table 3.11-1. Summary statistics for metals [mg/kg] in sediments in Escambia Bay and River.

| analytes | detections | mean | lower range | upper range | TEL | PEL | samples exceeding TEL | samples exceeding PEL |
|---|---|---|---|---|---|---|---|---|
| Arsenic | 57 | 10.6 | 0.27 | 35 | 7.24 | 41.6 | 30 | 0 |
| Cadmium | 46 | 0.6 | 0.085 | 2.5 | 0.676 | 4.21 | 16 | 0 |
| Chromium | 57 | 35.1 | 0.66 | 91 | 52.3 | 160 | 14 | 0 |
| Copper | 55 | 9.5 | 0.3 | 20 | 18.7 | 108 | 4 | 0 |
| Lead | 57 | 17.4 | 0.33 | 50 | 30.2 | 112 | 11 | 0 |
| Mercury | 48 | 0.07 | 0.007 | 0.47 | 0.13 | 0.696 | 2 | 0 |
| Nickel | 57 | 10.3 | 0.28 | 26 | 15.9 | 42.8 | 16 | 0 |
| Selenium | 42 | 1.3 | 0.12 | 3.5 | NA | NA | NA | NA |
| Tin | 35 | 2 | 0.79 | 5.4 | NA | NA | NA | NA |
| Zinc | 57 | 60.9 | 1.2 | 144 | 124 | 271 | 6 | 0 |

Concentrations of arsenic, chromium, lead, nickel and zinc are highly correlated with clay content ($r > 0.8$), a relationship that has been observed in many other studies (Table 3.11-2). Tin has a modest correlation with clay, and selenium does not seem to be affected by clay content or any of the other measured sediment characteristics (Table 3.11-2). Sand content is generally negatively correlated with the metal concentrations, reflecting the lack of chemical binding capacity of the sand, which in the area consists predominantly of quartz. Organic matter has an intermediate to high correlation with the metal concentrations, except for selenium and tin. These often strong correlations illustrate the influence sediment characteristics have on metal concentrations and distribution in the study area.

Table 3.11-2. Pearson product-moment correlation coefficient for sediment metals.

| Metal | Clay | Silt | Clay + Silt | Sand | Organic matter |
|---|---|---|---|---|---|
| As | 0.83 | 0.41 | 0.78 | -0.78 | 0.54 |
| Cd | 0.49 | 0.53 | 0.62 | -0.62 | 0.61 |
| Cr | 0.84 | 0.57 | 0.87 | -0.87 | 0.66 |
| Cu | 0.78 | 0.63 | 0.87 | -0.87 | 0.8 |
| Pb | 0.86 | 0.52 | 0.86 | -0.86 | 0.66 |
| Hg | 0.56 | 0.38 | 0.58 | -0.58 | 0.52 |
| Ni | 0.86 | 0.65 | 0.93 | -0.93 | 0.77 |
| Se | -0.06 | 0.02 | 0.02 | 0.02 | 0.08 |
| Sn | 0.37 | 0.03 | 0.27 | -0.27 | 0.23 |
| Zn | 0.83 | 0.67 | 0.92 | -0.92 | 0.74 |

### 3.11.1. Total arsenic

Total arsenic is an element that is widely distributed in the Earth’s crust (ATSDR, 2005a). Inorganic arsenic occurs naturally in soil and in many kinds of rock, and is common in soils and sediments of Escambia and Santa Rosa Counties (Liebens et al., 2009). Total arsenic was detected in all sediment samples (Table 3.11-3, see appendix). The detected sediment arsenic can originate from natural geological formations, from improper disposal of wastes, and also from its use in agricultural pesticides. The past use of inorganic arsenic pesticides, primarily on cotton fields with in the river’s drainage, may have significantly contributed to the presence of arsenic.

The mean of total arsenic sediment concentrations was 10.6 mg/kg, ranging from 0.27 to 35 mg/kg. A total of 30 samples exceeded the TEL of 7.24 mg/kg and none exceeded the PEL of 41.6 mg/kg. Overall arsenic is the biggest contributor to metal sediment toxicity on the basis of FDEP SQAG exceedances. The basin area (deeper regions of Escambia Bay) appears to be the most arsenic contaminated region of the Escambia Bay and River System. The Pearson product-moment correlation coefficient shows a strong positive correlation of 0.83 between clay content and arsenic concentration (Table 3.11.1-2). This suggests that arsenic is associated with the smallest diameter sediment particles of less than 2 µm, which can be expected to accumulate mostly in the less dynamic deeper parts of Escambia Bay.

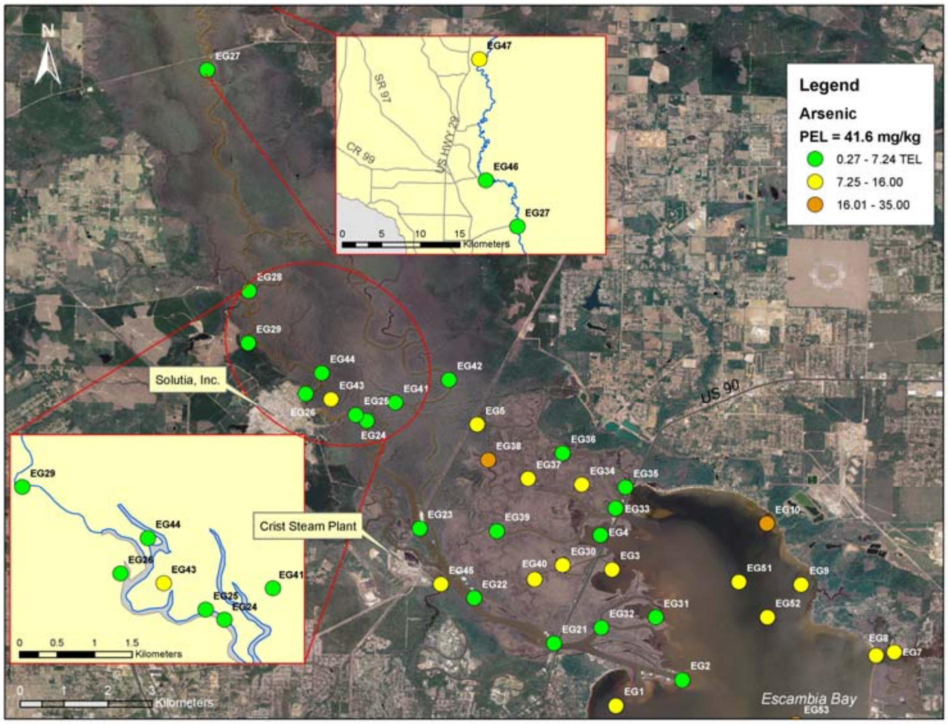


Figure 3.11.1-1a. Arsenic in Escambia River and upper bay sediments.

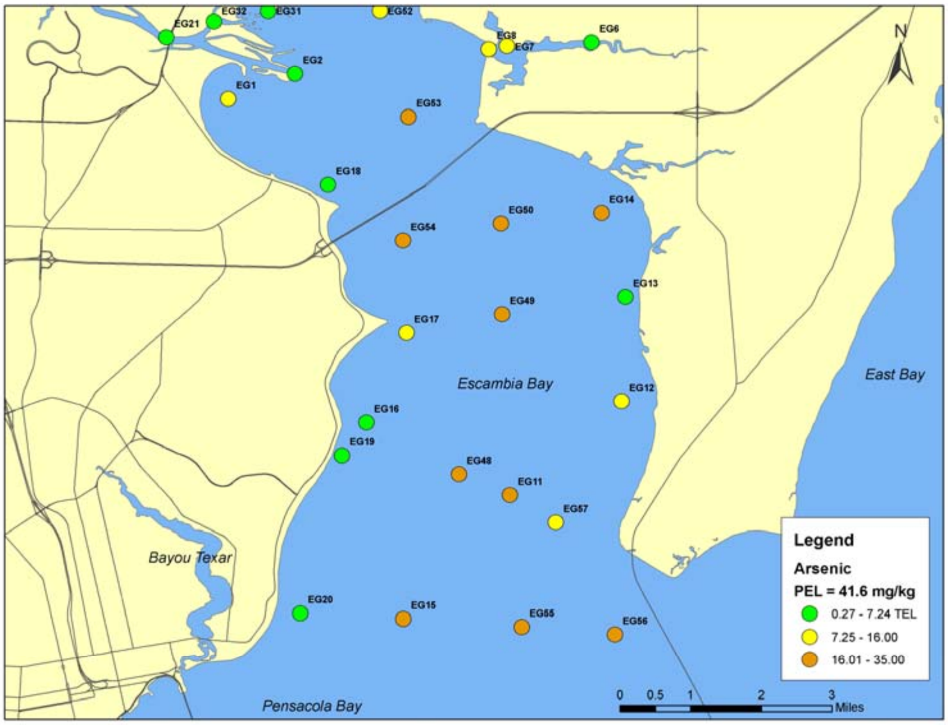
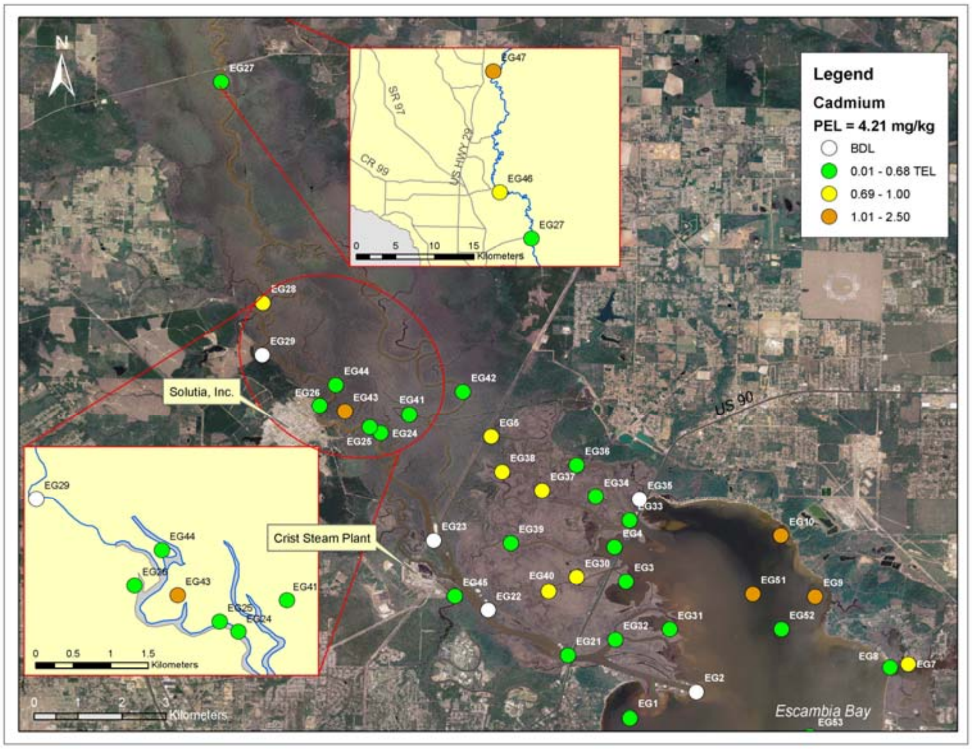


Figure 3.11.1-1b. Arsenic in Escambia Bay sediments.

### 3.11.2. Total cadmium

The presence of cadmium in sediments is always of concern since it is a metal that is not known to be essential for plant or animal life but has a high toxicity. Cadmium was detected in 46 sediment samples at a mean concentration of 0.6 mg/kg and range of 0.085 mg/kg to 2.5 mg/kg (Table 3.11-3, see appendix). A total of 16 samples exceeded the TEL of 0.676 mg/kg and none exceeded the PEL of 4.21 mg/kg. The distribution of the higher concentrations does not constitute a definite pattern except for a clump of the higher concentrations near the Air Products and Chemicals site (samples EG9, 10, & 51) (Figure 3.11.2-1a). Detection at EG10 occurred also for several other trace metals. This trio of samples could be related to releases from this site since cadmium is associated with industrial uses and processes. For example, it is used extensively in electroplating, which accounts for about 60% of its use (Nordic Council of Ministers, 2003). There were two higher concentrations detected on the river, sample EG43 (B.J.'s Cut near the Solutia, Inc. site) and EG47 upriver. This pattern was also observed with some of the other trace metals. Two higher concentrations were also detected in the lower bay (Figure 3.11.2-1b). Pearson's correlation showed a weaker correlation with clay than was seen with many of the other metals (r = 0.49) (Table 3.11.1-2). Moderate correlations were observed with organic matter (r = 0.61) and clay + silt (0.62). The moderate correlation of cadmium to organic matter does agree with the findings of Kaschl et al. (2002) showing cadmium to form binding complexes with the organic ligands present in compost. The highest complexing capacities for cadmium were found for the most humified ligands in that study. It may be possible that competition between organic matter and clay particles results in a lower correlation for clay.



3.11.2-1a. Cadmium in Escambia River and upper bay sediments.

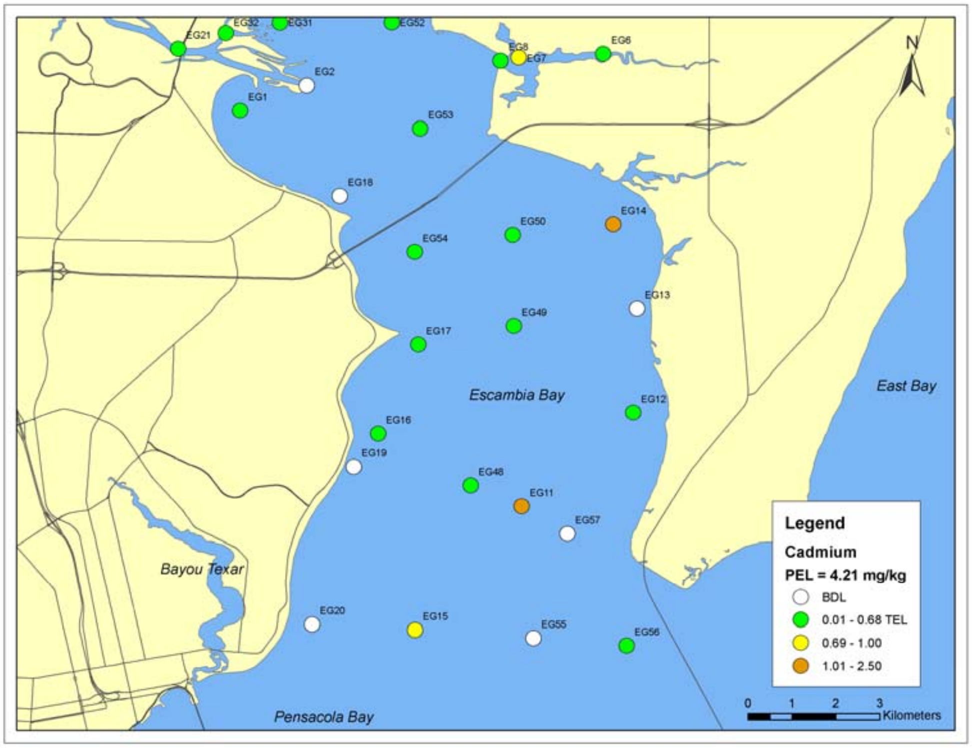


Figure 3.11.2-1b. Cadmium in Escambia Bay sediments.

### 3.11.3. Total chromium

Total chromium was detected in all 57 sediment samples, which is not unusual since chromium is a commonly occurring element found in rocks, animals, plants, soil, and in volcanic dust and gases. The elevated amounts of the chromium that are found in the hydrosphere, pedosphere, atmosphere and biosphere can primarily be attributed to industrial emissions. The natural emissions into the atmosphere are quoted as being roughly 58,000 tons per year, whereas anthropological emissions are almost up to 100,000 tons per year (BMZ , 2008; ATSDR, 2000c). The mean sediment concentration of chromium was 35.1 mg/kg and the range was from 0.66 mg/kg to 91 mg/kg. A total of 14 samples exceeded the TEL of 52.3 mg/kg and none exceeded the PEL of 160 mg/kg (Table 3.11-3, see appendix). The lower part of the bay had the greatest number of detections above the TEL (Figure 3.11.3-1b). There were two additional samples in the upper bay near the Air Products and Chemicals site (EG10 & EG 51), one in B.J.'s Cut Off near Solutia, Inc. on the river (sample EG43) and another in the wetlands at EG38 that had elevated concentrations. Pearson product-moment correlation showed a high correlation (r = 0.84) for clay content and total chromium. However, there is a moderate correlation of 0.66 between chromium and organic matter content. This suggests that much of the chromium in sediment is associated with the smallest particles of less than 2 μm, but there is still a moderate association with other components of the sediments.

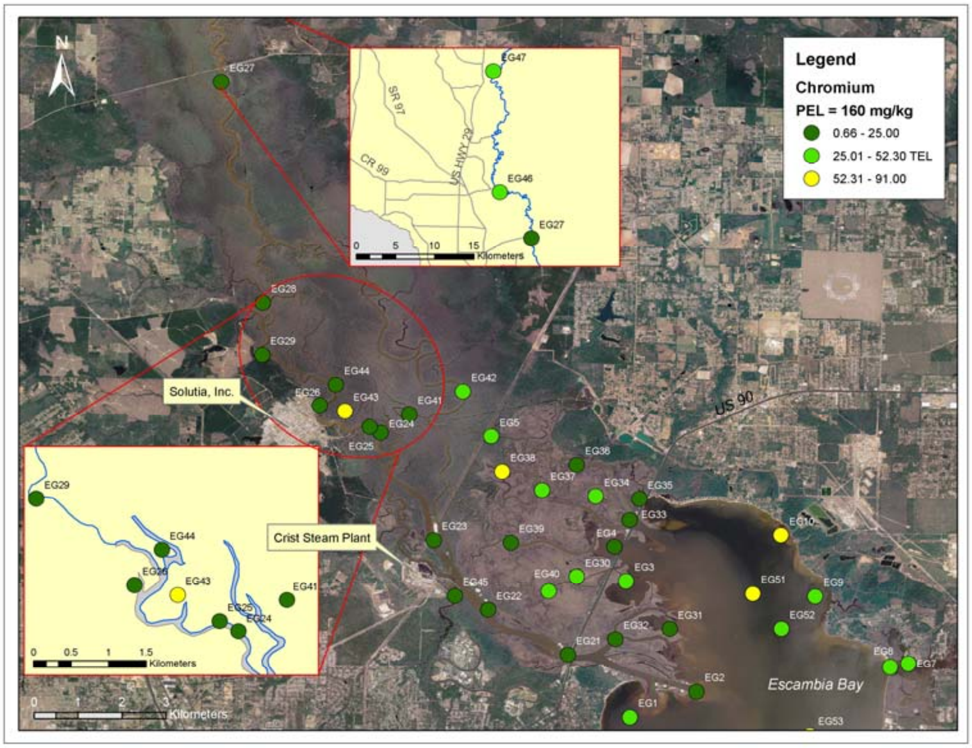


Figure 3.11.3-1. Chromium in Escambia River and upper bay sediments.

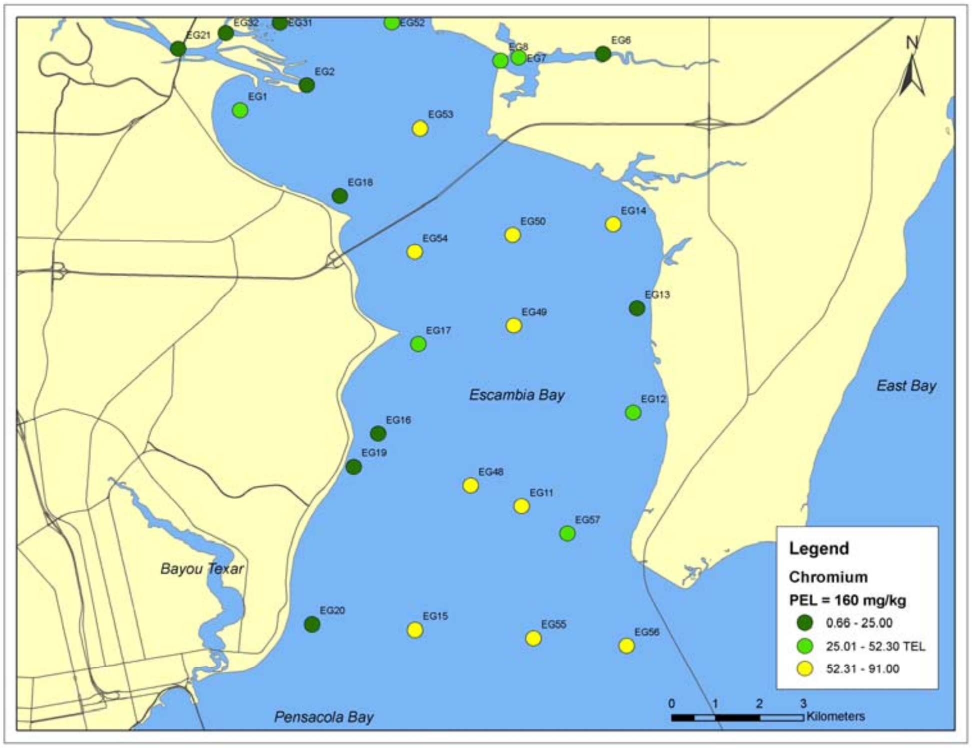


Figure 3.11.3-1b. Chromium in Escambia Bay sediments.

### 3.11.4. Total copper

Total Copper is a widespread element in the environment as indicated by an estimated 640,000 tons of copper being released annually into the environment by industries in 2000 (ATSDR, 2004). Copper was detected in 55 samples out of 57 (Table 3.11-3, see appendix). The mean sediment concentration of copper was 9.5 mg/kg and the range was from 0.3 mg/kg to 20 mg/kg. A total of 4 samples exceeded the TEL of 18.7 mg/kg and none exceeded the PEL of 108 mg/kg. In the wetlands, samples EG40 and EG38 exceeded the TEL and in the Bay EG11 and again EG10 exceeded the TEL (Figures 3.11.4-1a&b). Only one of these sites (EG10) appears to be near a likely point source which is near an Air Products and Chemicals outfall. For the sediments there does not appear to be a major overall impact on the basis of SQAG from copper in Escambia Bay and River sediments. Pearson product-moment correlation showed a high correlation of 0.78 between clay content and total copper, but the correlation for silt was moderate (0.63); for clay + silt it was high (0.87) ; for organic matter it was high (0.8); and for sand it was high but negative (-0.87). It appears that copper has a high attraction for the clay particulates and organic matter.

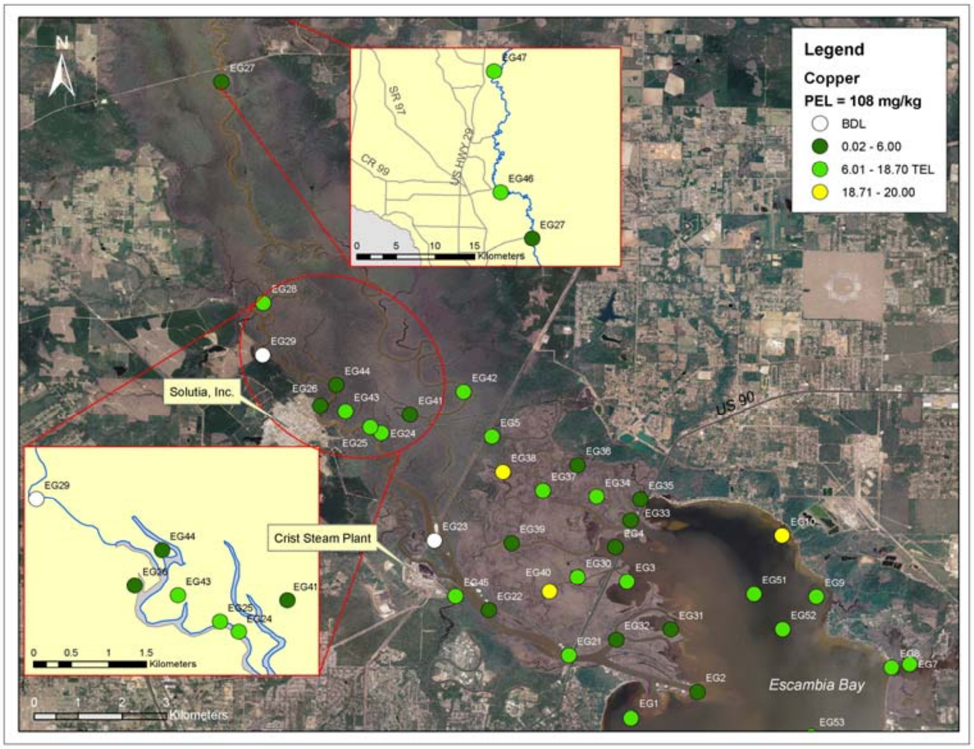


Figure 3.11.4-1a. Copper in Escambia River and upper bay sediments.

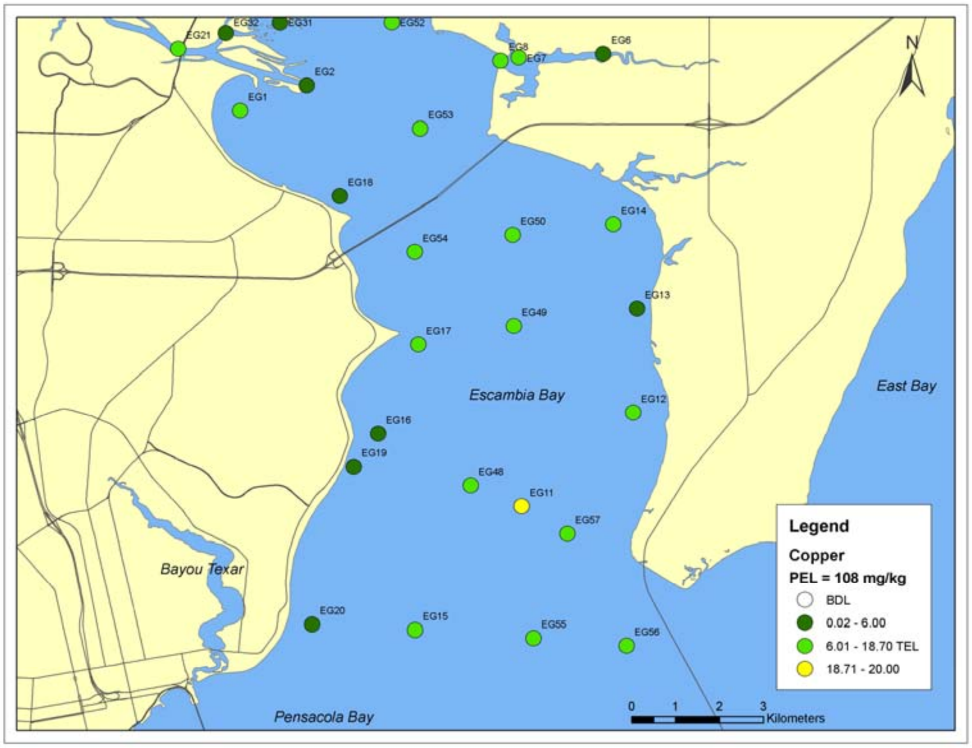


Figure 3.11.4-1b. Copper in Escambia Bay sediments.

### 3.11.5. Total lead

Lead has been widely distributed by anthropogenic activities that include construction, production and use of small arms ammunition, brass and pewter, paints and protective coatings, glass and crystal, ceramic glazes, and water lines and pipes and more recently cable covering, caulking, solder, fuel additives and lead acid storage batteries (Ostrom et al., 2004). The widespread use of lead is likely responsible for its detection in all 57 sediment samples (Table 3.11-3, see appendix). The mean sediment concentration of lead was 17.4 mg/kg and the range was from 0.33 mg/kg to 50 mg/kg. A total of 11 samples exceeded the TEL of 30.2 mg/kg and none exceeded the PEL of 112 mg/kg. The locations of the samples exceeding the TEL include eight detections in the lower bay, two in the upper bay including sample EG10 near the Air Products and Chemicals outfall, and one in the wetlands (Figures 3.11.5-1a&b). Pearson product-moment correlation coefficients show a high correlation (r = 0.86) between lead and clay content and a moderate correlation (r = 0.66) between lead and organic matter, suggesting that lead is most highly associated with the clay components of the sediments.

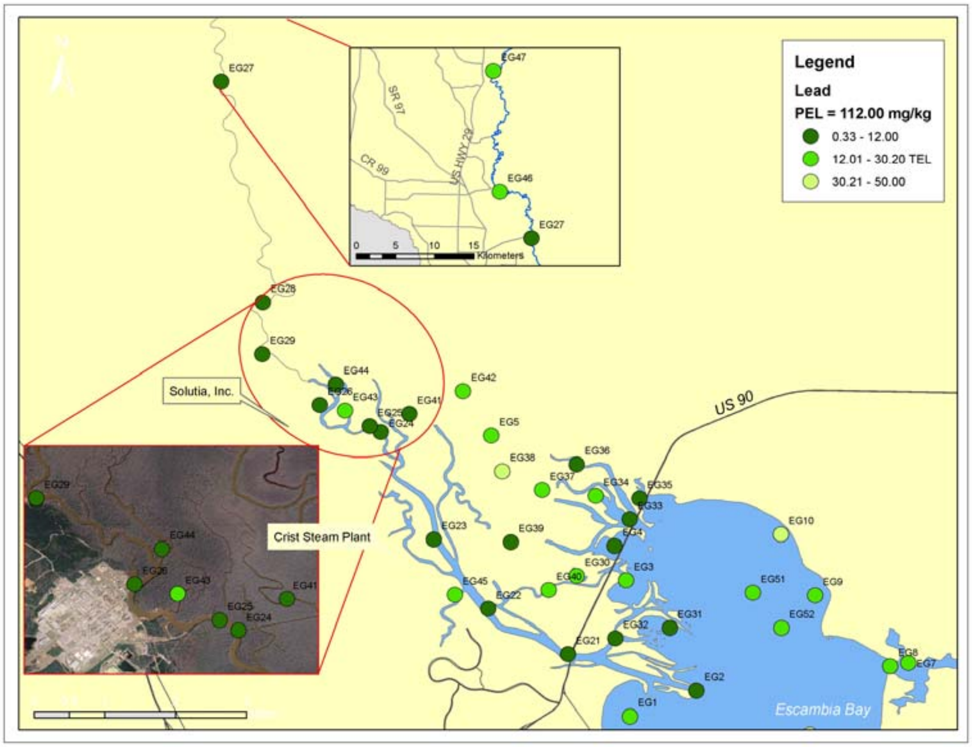


Figure 3.11.5-1a. Lead in Escambia River and upper bay sediments.

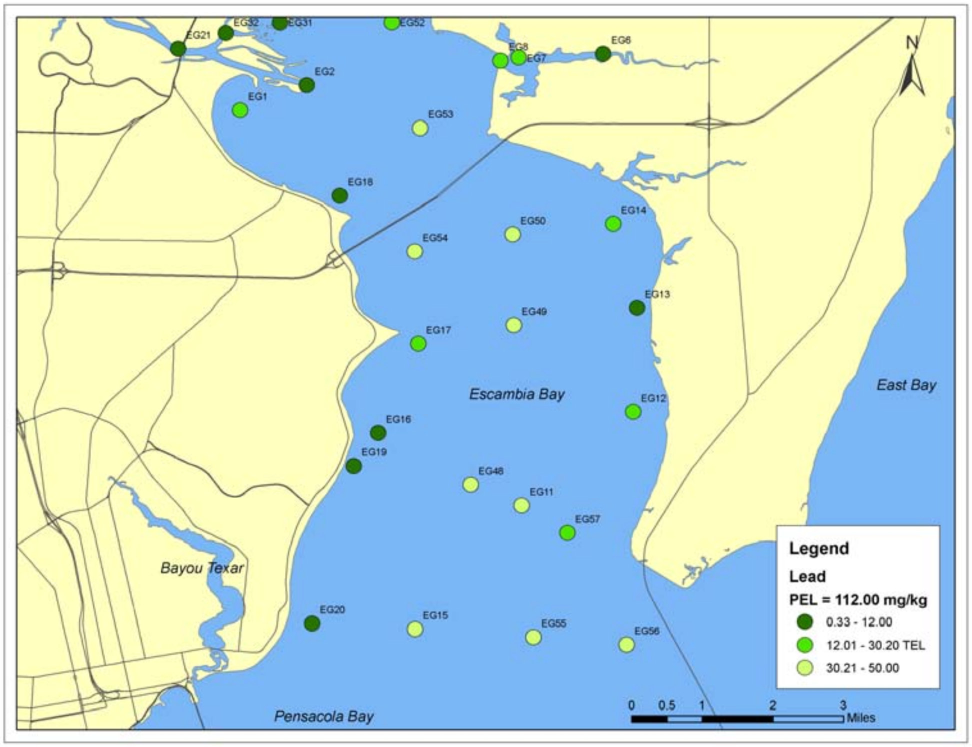


Figure 3.11.5-1b. Lead in Escambia Bay sediments.

### 3.11.6. Total mercury

Total mercury was detected in 48 out of 57 sediment samples (Table 3.11-3, see appendix). The mean sediment concentration of mercury was 0.07 mg/kg and the range was from 0.007 mg/kg to 0.47 mg/kg. Two samples (located in the lower bay, Figure 3.11.6-1a&b) exceeded the TEL of 0.13 mg/kg and none exceeded the PEL of 0.696 mg/kg. Overall, according to the FDEP SQAG for mercury the health of sediment dwelling organisms is unlikely to be impacted by the levels of mercury detected since there were only two detections above the TEL. However, mercury has been found to exceed seafood screening levels in some fishes in the Escambia and Conecuh River (FDEP, 2006; USEPA 2007), most likely due to biomagnification through the food chain.

The origin of sediment mercury in Escambia Bay and River is likely due to multiple sources. World wide mercury releases commonly occur from many sources and its volatile nature plays an important role in its environmental fate (ATSDR 1999). The natural global bio-geochemical cycling of mercury is characterized by degassing of the element from soils and surface waters, followed by atmospheric transport, deposition of mercury back to land and surface waters, and sorption of the compound to soil or sediment particulates. Mercury deposited on land and open water is in part revolatilized back into the atmosphere. This emission, deposition, and revolatilization create difficulties in tracing the movement of mercury to its sources. Particulate-bound mercury can be converted to insoluble mercury sulfide and precipitated or bioconverted into more volatile or soluble forms that re-enter the atmosphere or are bioaccumulated in aquatic and terrestrial food chains (ATSDR, 1999). Many manufactured products and fluorescent light bulbs are known to contain mercury that can be released to the environment after improper disposal. Mercury is also transported and distributed by atmospheric process. There is locally the coal powered Crist Steam Generating Plant which released 327.3 lbs of mercury to the atmosphere in 2006 (Table 1.4.6-1). But there are also other coal fired power plants in the southeastern United States that could contribute via atmospheric transport to the mercury concentrations in local sediments.

There are advisories for fish consumption relative to mercury in the Escambia-Conecuh watershed. Within the drainage of the Escambia Bay and River System there is an impounded spring fed lake that in 2003-2004 was found to have mercury contaminated fish. Sampling of 19 largemouth bass from Woodbine Springs/Rock Creek detected an average mercury concentration of 2.33 mg/kg in contrast to the Escambia River where (in 2004) 19 largemouth bass had an average mercury concentration of 0.57 mg/kg (USEPA, 2007). The Woodbine Springs Lake mercury concentration in tissue residue is above all State of Florida screening levels. State guidelines (FDEP, 2006) for consumption of mercury containing seafood state: “fish containing less than 0.5 parts per million are considered safe for unlimited human consumption. Consumption should be limited (one 8 oz serving/wk for non-pregnant adults) for fish with concentrations from 0.5 to 1.5 parts per million of mercury in edible flesh, and fish that have more than 1.5 parts per million in the edible flesh are considered unsafe for any consumption.” The fish in the Escambia River are just over the screening threshold that suggest only one serving per week should be consumed. The fish from Woodbine Springs Lake should not be consumed. The source of the high mercury in Woodbine Springs Lake is not clear. What is of interest is that mercury tissue concentrations in Escambia River fishes are above the screening threshold even though the sediment values are below the SQAG. This demonstrates that the SQAG for mercury is not protective within the Escambia River for human consumption of seafood.

Pearson product-moment correlation showed a moderate (0.56) correlation between mercury and clay and organic matter content and a moderate but negative correlation between mercury and sand (r = -0.58). The lack of high correlation with any specific sediment component may be explained by the chemical properties of mercury, and the sediment. Mercury in the sediments can exist in three forms: elemental mercury, inorganic mercury, and methylmercury that will likely have different affinities for components of the sediments. Inorganic mercury is said to be the most common form and is primarily bound to particulates and organic substances and may not be available for direct uptake by aquatic organisms. The process of methylation of inorganic mercury to methylmercury which is highly bioavailable is thus an important key to the fate of mercury in the environment. Mercury will not likely exist for any great periods of time as elemental mercury since it has a relatively high vapor pressure, a low solubility, does not combine with inorganic or organic ligands, and is not readily available for methylation. Inorganic mercury as the mercurous ion (Hg[I]) combines with inorganic compounds only and cannot be methylated. The mercuric ion (Hg[II]) combines with both inorganic and organic ligands, and can be methylated by biological processes (NOAA, 2005). Measurements of total mercury concentrations in the sediment do not provide information on the form of mercury present, methylation potential, or availability to organisms. The ability of organo-mercury to combine with organic components of the sediments is likely in part responsible for the moderate correlations observed in the current study.

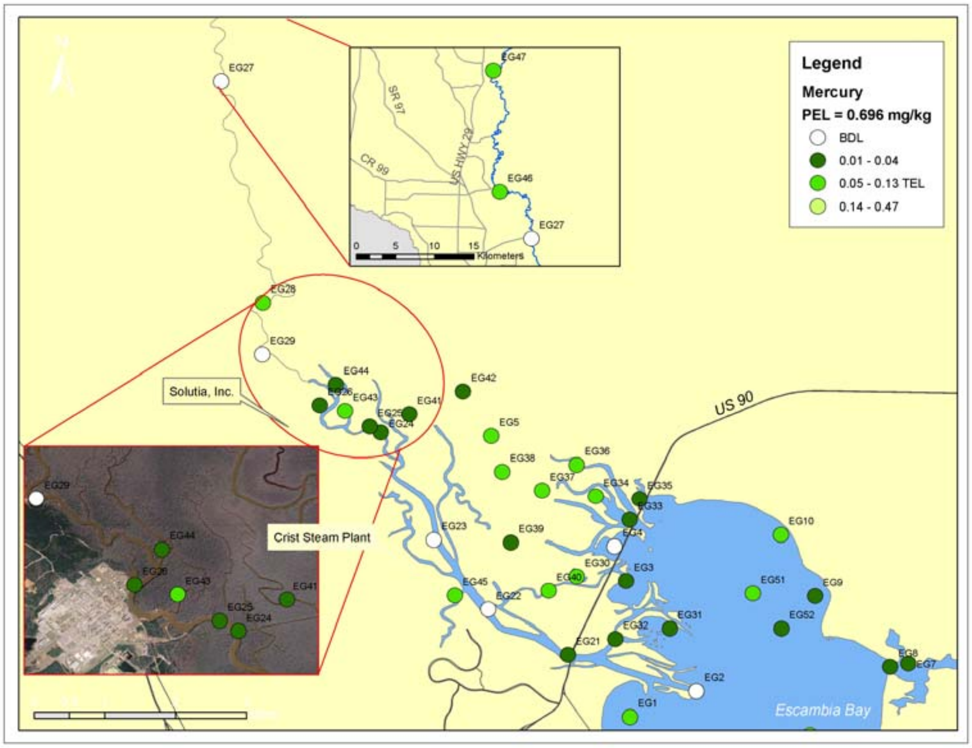


Figure 3.11.6-1a. Mercury in Escambia River and upper bay sediments.

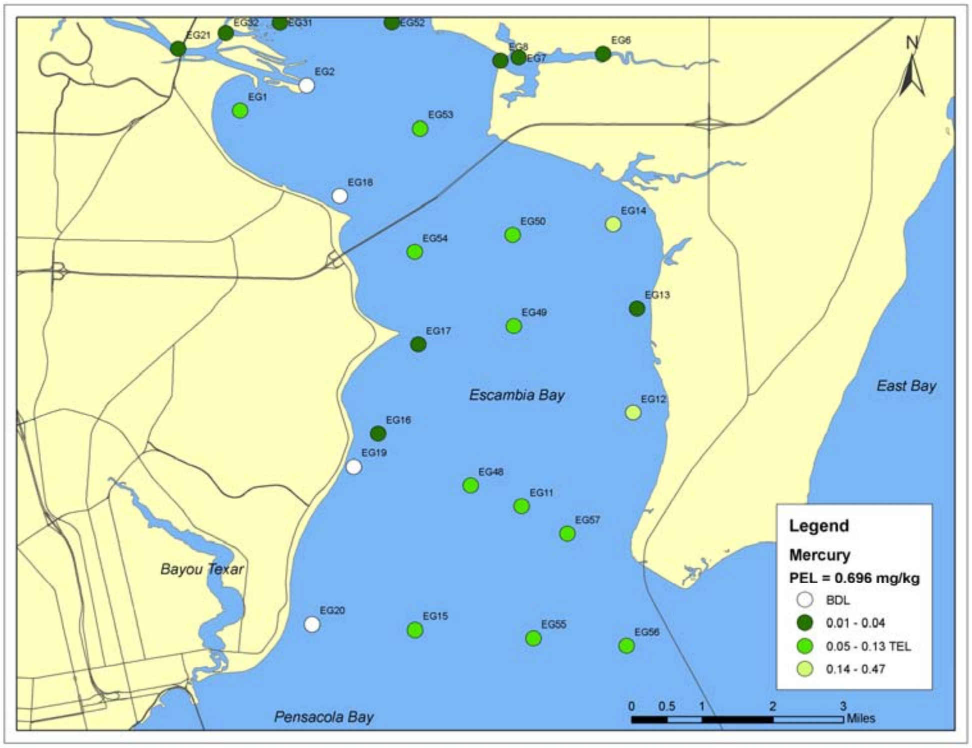


Figure 3.11.6-1b. Mercury in Escambia Bay sediments.

### 3.11.7. Total nickel

Total nickel was detected in all 57 sediment samples (Table 3.11-1). The mean nickel concentration was 10.3 mg/kg and the range was from 0.28 mg/kg to 26 mg/kg (Table 3.11-3, see appendix). A total of 16 samples exceeded the TEL of 15.9 mg/kg and none exceeded the PEL of 42.8 mg/kg. Pearson product-moment correlation showed a high positive correlation (r = 0.86) between nickel content and clay and organic matter content. This suggests that nickel is significantly associated with multiple components of the sediments. For the Escambia River samples EG47 near the Alabama state line and EG43 near the Monsanto site in B.J.'s Cut exceed the TEL (Figure 3.11.7-1a). There were also two exceedances of the TEL in the wetlands south of the northern power transmission line. In the upper bay, samples EG51 and EG10 near the Air Products and Chemicals outfall were also above the TEL (Figure 3.11.7-1a). The proximity of some of the higher nickel concentrations to industrial sites with well established records for releases of SOCs is suggestive of an industrial release for the origin of the nickel. The origins of the nickel for the other sites above the TEL are not obvious. As shown in Figure 3.11.17-1b, nickel is frequently above the TEL in the bay's basin, showing that nickel in some parts of the Escambia Bay could cause a minimum environmental impact.

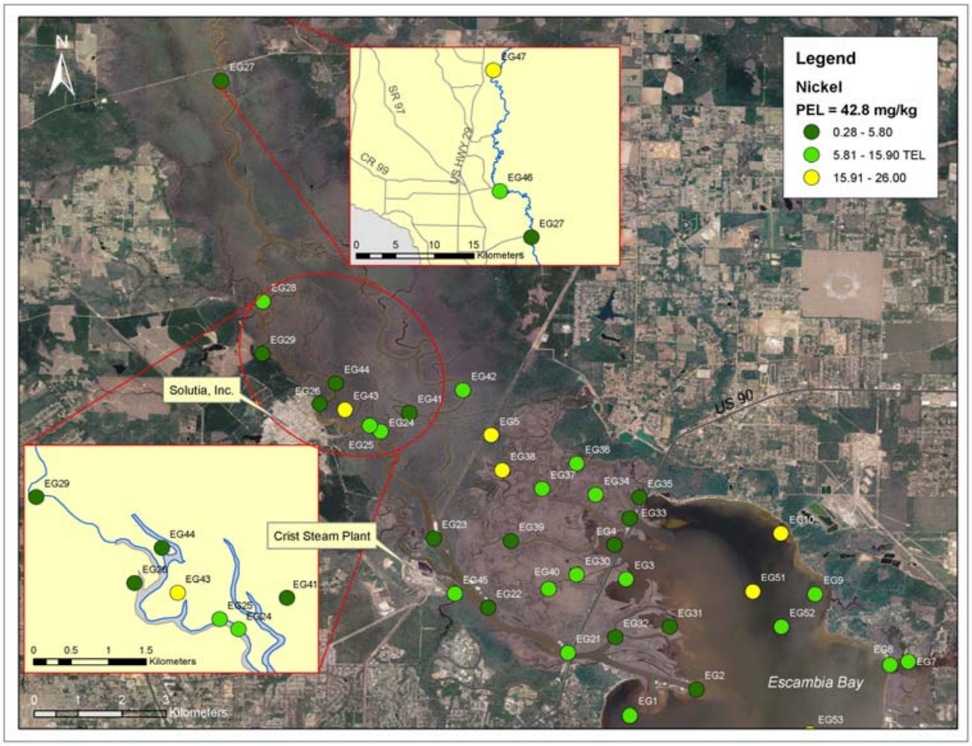


Figure 3.11.7-1a. Total nickel in Escambia River and upper bay sediments.

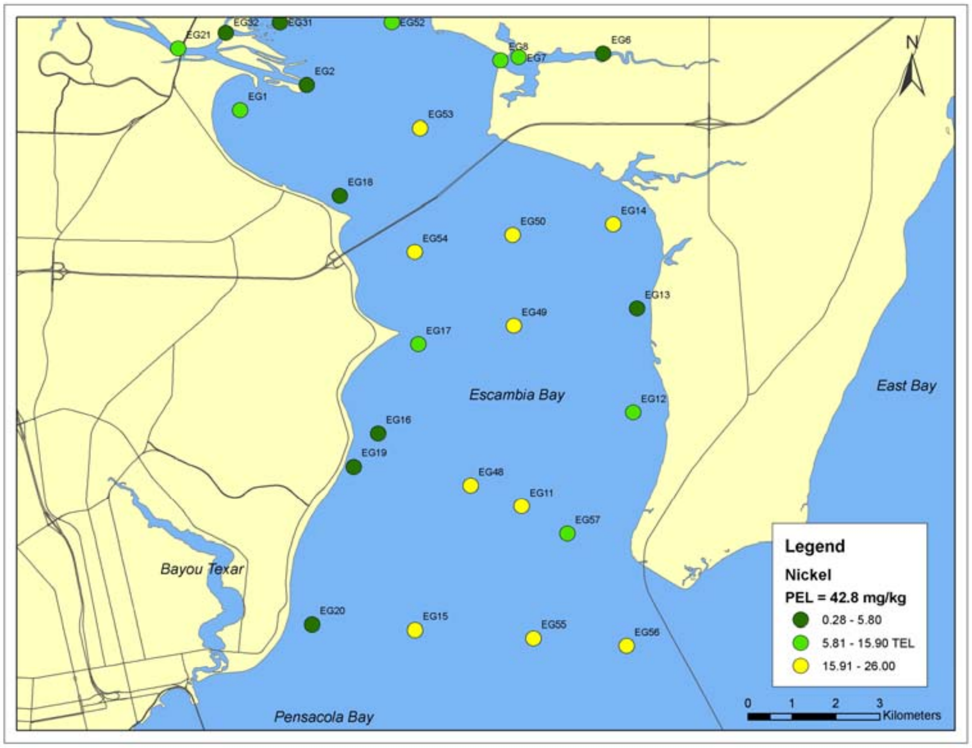


Figure 3.11.7.-1b. Nickel in Escambia Bay sediments.

### 3.11.8. Total selenium

Total selenium was detected in 42 sediment samples. The mean of the 42 detections was 1.3 mg/kg and the range was 0.12 mg/kg to 3.5 mg/kg (Table 3.11-3, see appendix). Overall, selenium concentrations were low with all detections being estimated as indicated by the data qualifier I in the tables. Some of the analytical data had minimal detections in the method blanks and when such blank contamination was no more than 20% of the detected value the qualifier Bl was added to indicate blank contamination. Selenium in the lower river and wetlands was higher than in the bay (Figures 3.11.8-1 a&b). It is interesting to observe that an atmospheric deposition study carried out by PERCH found higher selenium deposition rates just northeast of the wetlands than further south or north (Caffrey et al., 2009). However, it is tedious at best to establish a link between the atmospheric deposition rate and the sediment concentrations due to the limited number of sampling stations for the atmospheric deposition and the influence of the biogeochemical environment on selenium concentrations in the sediments. There is no FDEP SQAG for selenium but the concentrations found in the present study can be considered low (Hamilton and Buhl, 2003) and with one exception (EG 23 just north of Crist Steam Plant) are not of concern for fish and wildlife according to criteria from Lemly and Smith (1987). Pearson product-moment correlation coefficients between selenium concentration and sediment characteristics were all very low (Table 3.11-2). This suggests that selenium content and distribution is not influenced by the sediment characteristics.

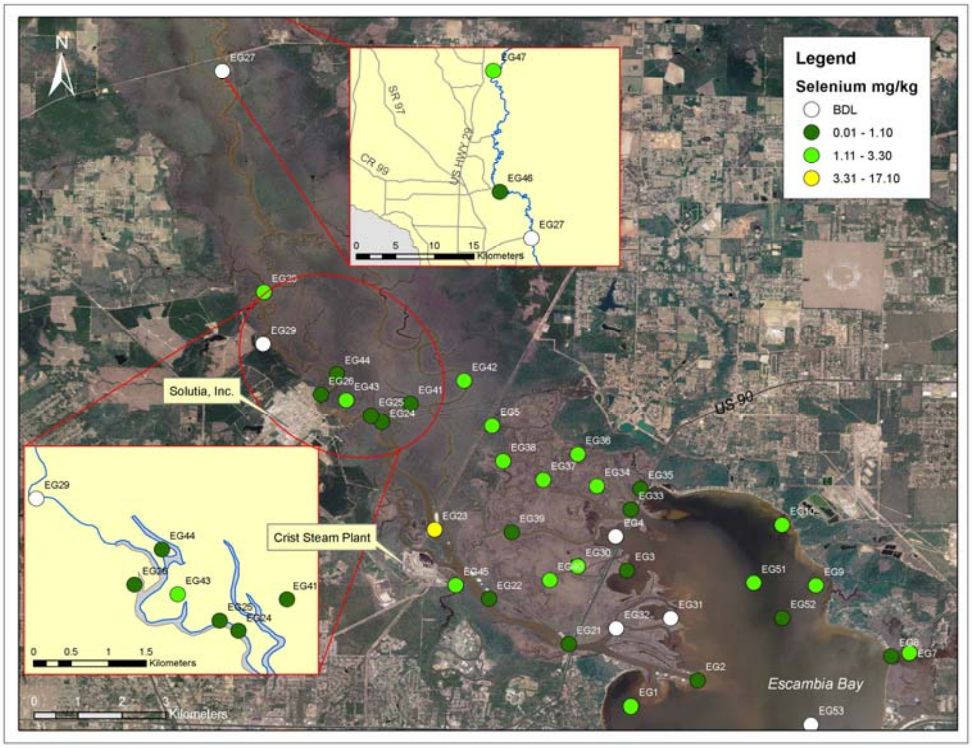


Figure 3.11.8-1a. Selenium in Escambia River and upper bay sediments.

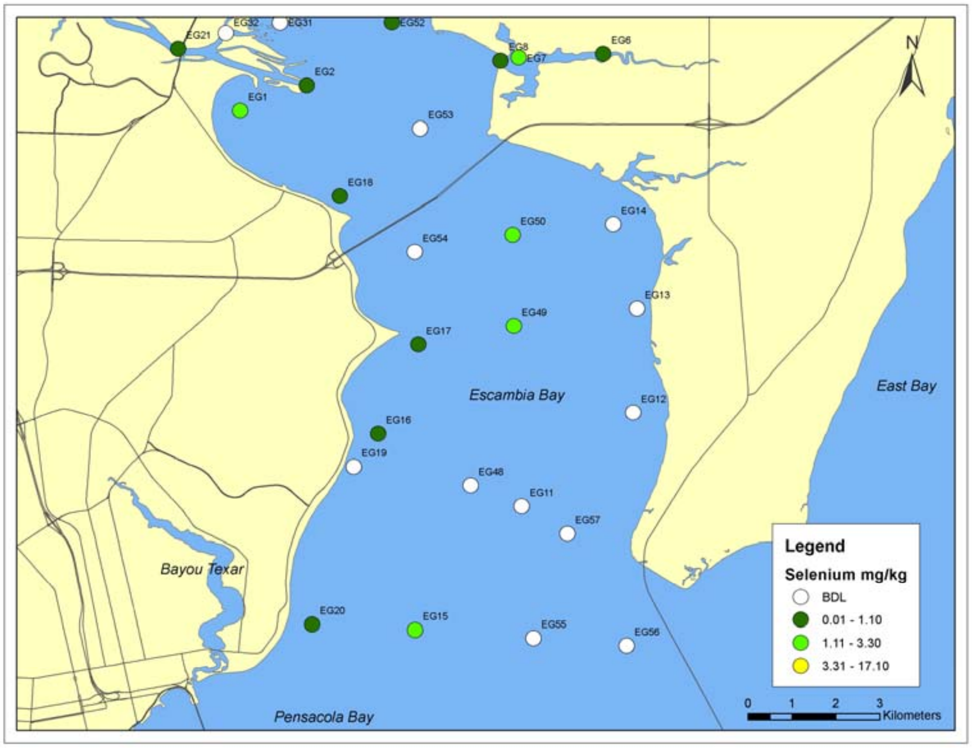


Figure 3.11.8-1b. Selenium in Escambia Bay sediments.

### 3.11.9. Total tin

Total tin was detected in 35 sediment samples, the mean of these 35 detections was 2.0 mg/kg and range was 0.79 mg/kg to 5.4 mg/kg (Table 3.11-1). Overall, sediment concentrations were low and all detections were estimated (Table 3.11-3, see appendix). Some of the analytical samples had minimal detections in the method blanks and when such blank contamination was no more than 20% of the detected value the qualifier Bl was added to the table to indicate blank contamination. The wetlands had the lowest concentrations of total tin with most samples being nondetects (Figure 3.11.9-1a&b). There is no FDEP SQAG for total tin or for the highly toxic organic form tributyltin that has been used as an antifoulant on marine craft. Pearson product-moment correlation coefficients between tin content and sediment characteristics are low (Table 3.11-2). This suggests that tin content and distribution is not substantially influenced by sediment characteristics.

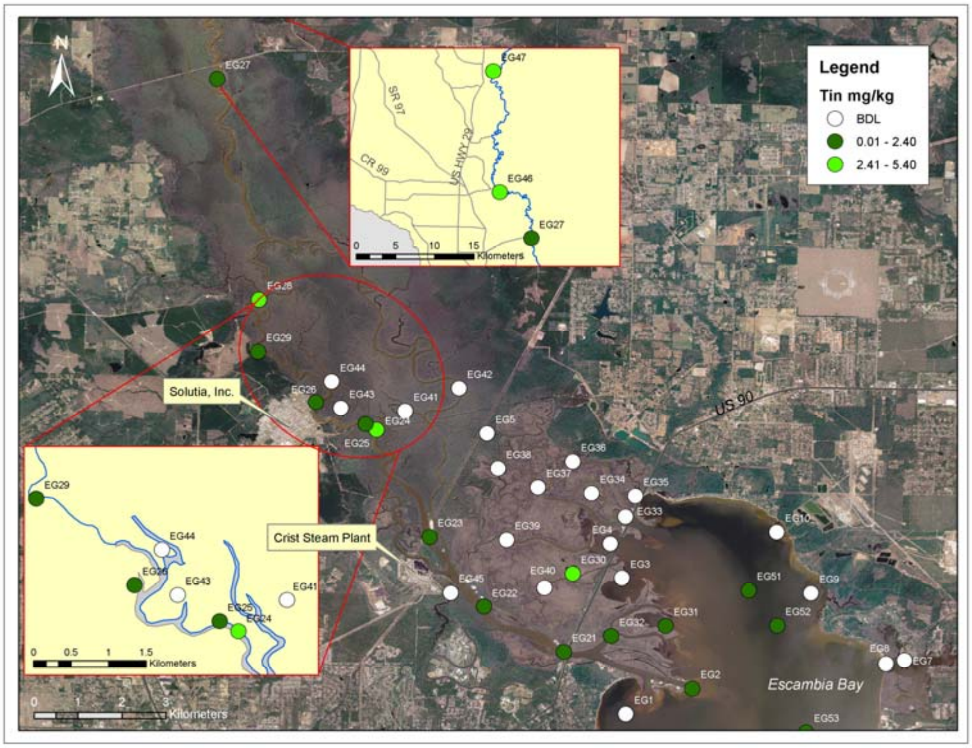


Figure 3.11.9-1a. Total tin in Escambia River and upper bay sediments.

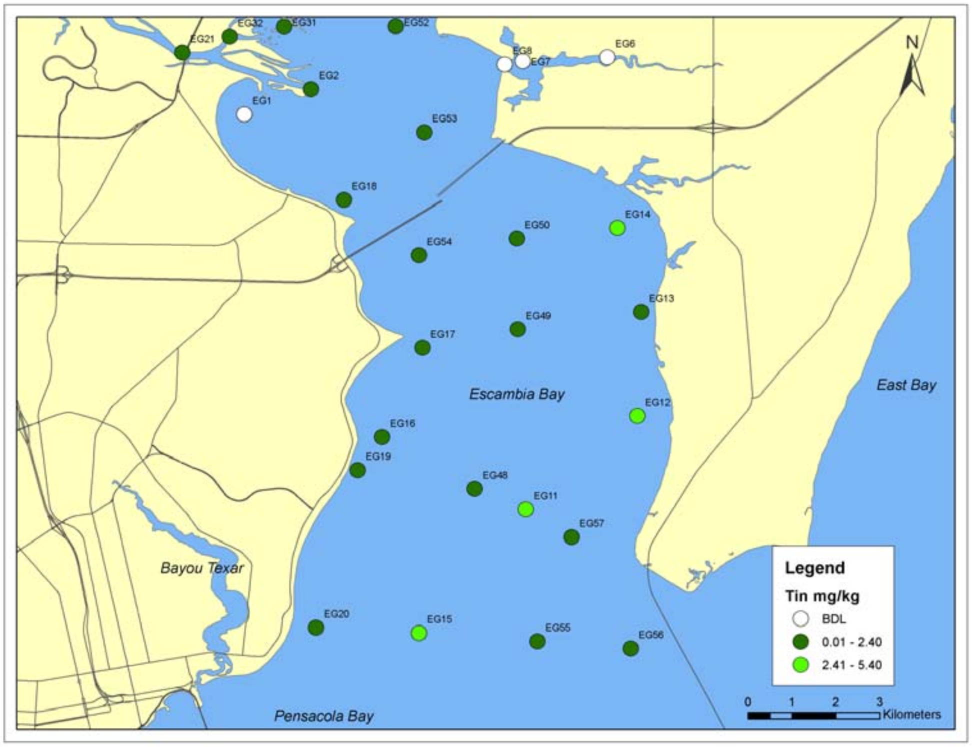


Figure 3.11.9.1b. Total tin in Escambia Bay sediments.

### 3.11.10. Total zinc

Total zinc was detected in all 57 sediment samples, the mean concentration was 60.9 mg/kg and the range was 1.2 to 144 mg/kg (Table 3.11-1). A total of 6 samples exceeded the TEL of 124 mg/kg and none exceeded the PEL of 271 mg/kg. Four exceedances of the TEL were in the lower bay, one was near the Air Products and Chemicals site in the upper bay (EG10), and one in the wetlands (Figures 3.11.10-1a&b). Pearson product-moment correlation between zinc concentration and sediment characteristics was moderate to high (table 3.11-2), suggesting that sediment properties have a strong influence on the zinc content and distribution in sediments of Escambia Bay and River.

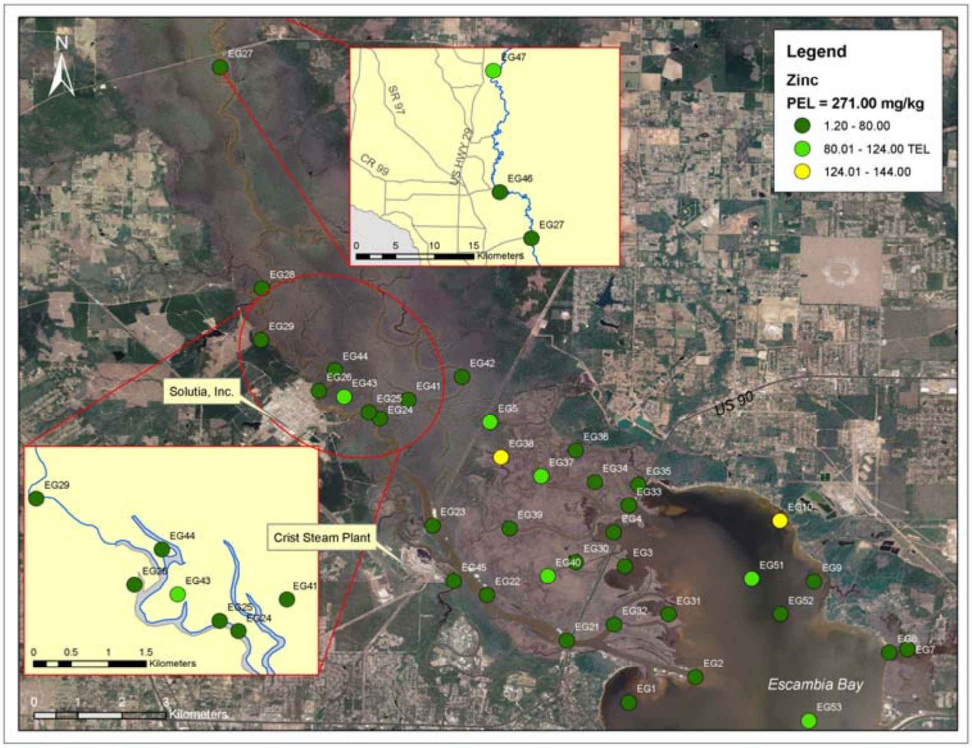


Figure 3.11.10.-1a. Zinc in Escambia River and upper bay sediments.

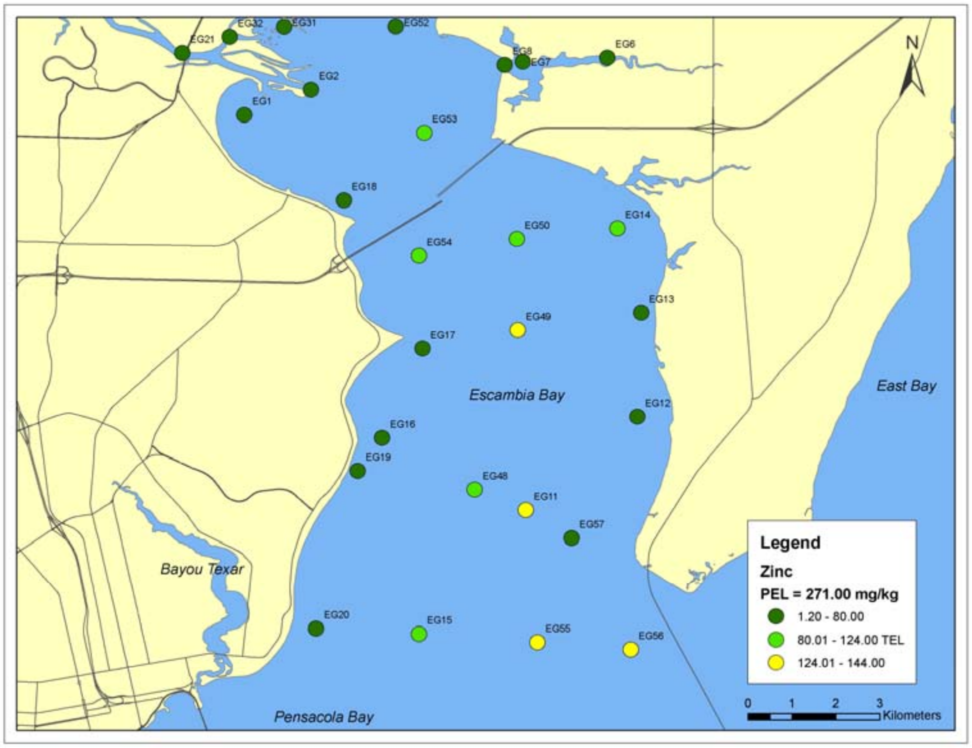


Figure 3.11.10-1b. Zinc in Escambia Bay sediments.

### 3.11.11. Potential sources for trace metals

Certain sites were observed to more frequently have higher trace metal concentrations than other sites. Sample EG10 near the Air Products outfall was consistently above SQAGs for lead, copper, chromium, cadmium, nickel, zinc, and arsenic. Sample EG43 near the Monsanto spill site in B.J.'s Cut and EG38 in the wetlands exceeded the TEL for several metals as did EG47 in northern Escambia County, FL. The proximity of sampling sites EG10 and EG43 to industrial activities is a probable explanation for the origins of the higher concentrations of metals at these sites, but EG 38 is not near any potential source. Site EG47 may be receiving metals from Century, FL. or from sources in Alabama. Sources that could impact the spatial distribution and concentrations of metals also include atmospheric deposition, runoff from roads and urban areas, and burning of coal and diesel fuel at the Crist Plant. However, metal concentrations do not show any clear spatial trend that would point specifically to any one of these sources. PERCH conducted no sampling on Southern Company (owner of the Crist Pant), Monsanto-Solutia or any other private property to ascertain possible surface transport to the Escambia River and Bay System.

In general, atmospheric deposition and surface soils are important sources of pollutants and sediments for estuaries. Atmospheric deposition has been found to be a significant source of nutrients, metals, and semivolatile organics to watersheds (Valigura et al., 2001). For mercury, atmospheric deposition represents 50-90% of the load to US waters (http://nadp.sws.uiuc.edu/). The Crist Power Plant (Table 1.46-1), as do other regional power plants, releases mercury and recent PERCH data for atmospheric deposition of mercury showed that a substantial amount (16 $\mu g/m^2/yr$) enters terrestrial and aquatic habitats from the atmosphere (Caffrey et al., 2009). Only part of this deposition actually reaches the sediments in the Pensacola Bay and River but constructing a mass balance is very complex due to the distinct forms of mercury that have differing volatility characteristics, transport mechanisms by surface water, and biogeochemical characteristics. A recent PERCH study of soil pollution in public places and along highway right-of-ways was conducted for trace metals and locally for dioxins/furans and PAHs (Liebens et al., 2009). Trace metals were found in their highest concentrations by the edge of the road pavement. These soils at the side of the roads are most apt to be transported to waterways due to their proximity to drainages such as swales and ditches, giving more importance to their elevated metal concentrations. What is interesting is that the average concentrations for lead and nickel in the surface soils are above marine sediment SQAGs (Table 3.11.11-1). Arsenic in the soils exceeded the TEL for sediments at the most sites (30 out of 126 samples) (Table 3.11.11-1). The sediment TELs do obviously not apply to surface soils but because many metals tend to be associated with the smallest particles these concentrations at or above the TEL are of concern as the surface soil material can undergo concentrating mechanisms during transportation when coarser sediments are deposited near the shore and finer more contaminated sediments settle out together in the deeper parts of a water body. Arsenic may the be the metal that is of most concern in this regard but it may originate from natural geological formations (ATSDR, 2005a; Liebens et al., 2009). Undoubtedly, trace metal concentrations in sediments are directly related to concentrations soils, but the concentrations actually detected in the sediments result from interplay of many factors.

Table 3.11.11-1. Trace metal concentrations in local soils and FDEP Sediment Quality Assessment Guidelines [mg/kg] (MacDonald, 1994a;b).

| Metals | mean conc. in soils[1] | TEL | mean conc./TEL [%] | # samples over TEL (n=126) |
|---|---|---|---|---|
| Arsenic | 1.87 | 7.24 | 26 | 30 |
| Cadmium | 0.27 | 0.676 | 40 | 16 |
| Nickel | 22.03 | 15.9 | 139 | 16 |
| Chromium | 6.99 | 52.3 | 13 | 14 |
| Lead | 31.22 | 30.2 | 103 | 11 |
| Zinc | 36.64 | 124 | 30 | 6 |
| Copper | 6.32 | 18.7 | 34 | 4 |
| Mercury | 0.0283 | 0.13 | 22 | 2 |

1. Urban soils data from PERCH Study by Liebens et al. (2009).

# 4. Summary and Conclusions

The current study has obtained information for pollutants in sediments in Escambia Bay and River. It is the first study to assess the environmental status of the bay and river with a systematic approach and a full suite of pollutants. It is an essential first step to understanding the impact of PCBs and other pollutants upon the sediments and local seafood.

## 4.1. Pollutant impacts upon sediments: Organics

The detected concentrations of three types of POPs were found to present potential sediment impacts on the basis of SQAGs. These three POPs are the pesticide DDT, dioxins/furans, and PCBs. Most PAH concentrations in the sediments were below SQAGs and are not likely to significantly impact the Escambia Bay and River System. The concentrations of PAHs appear to have declined in Escambia Bay since the concentrations detected by the current study were less than what was reported in previous studies (DeBusk et al., 2002). PAH concentrations for the most part were below the TEL and only infrequently exceeded the PEL.

About 25% of the DDT detections did exceed a SQAG with the detections occurring mainly in the sediments of the river and wetlands. The DDT concentrations in the lower wetlands are of concern and may cause serious impact on fisheries, particularly if these areas serve as nurseries. DDT was frequently detected above the FDEP PEL. It is not known if the detected DDT originated from historic applications and releases that have persisted for many years. It is also possible that the detected DDT originates in part from atmospheric cycling or more recent releases. The presence of DDT in the river suggests that it is being transported to the bay. The presence of DDT with its associated byproducts in detected bay samples from the current and past studies and the nondetection of DDT associated byproducts in the river and wetlands are not readily explainable. The fact that there was only one detection in Escambia Bay in the current study compared to multiple detections in previous studies suggests that DDT concentrations are declining in the surface sediments of the bay. The accumulation and possible impact of DDT upon local seafood tissues is not known but the potential to impact benthic organisms in some areas of the river and wetland areas exists. The presence of DDT in sediments, its possible biomagnification at upper trophic levels, and its probable impact upon commercial and sports fisheries suggests that DDT in the Escambia Bay and River System merits further study.

In the current study, as in past studies, total PCB concentrations did not surpass the FDEP PEL in Escambia Bay. The maximum PCB concentrations in the bay were higher in the past than in the current study. The highest previously reported concentrations were 152 ug/kg and 168 ug/kg (Debusk et al., 2002), the two highest concentrations of the current study were 71.2 ug/kg and 118.1 ug/kg. This suggests a decline in PCB concentrations that while measurable, may not be sufficient to cause a significant change in human health impacts from seafood or other impacts to benthic fauna. It is also possible that the differences between previous studies and the current one are due to spatial differences in PCB concentration. In the current study the mean total PCB mass concentration was highest in the lower river from the site of the Monsanto spill to the river's mouth and in the upper bay between the US Highway 90 causeway and the I-10 Bridge. The mean PCB detections of the lower wetlands, lower bay, and upper river and its wetlands were below the TEL. This suggests that the most serious PCB impacts will occur in the lower river and upper bay.

The PCB profiles suggest that other Aroclor mixtures besides Aroclor 1254, which was spilled at the Monsanto-Solutia site (Duke et al., 1970), may have contributed to the sediment PCBs. However, the degraded nature of the PCBs makes a definitive conclusion difficult. The presence of PCBs in the river suggests that additional PCBs may be entering the bay. It is possible that some PCBs are coming from upriver since all upriver sediment samples had detectable concentrations. Committing large expenditures on remediation should not be initiated until this probable transport is better understood and quantified. The presence of PCBs in the lower wetlands and upper bay especially near the Air Products and Chemicals outfall requires more study. The current model of water transport in Escambia Bay suggests that currents along the eastern side of the bay flow north and that the flow from the river transports sediments south along the western shore of the bay (Olinger et al., 1975). If these models are correct then some of the upper bay PCBs may not have originated solely from river transport into the bay and may have been affected by the northerly currents. Another factor that may influence the concentration and spatial distribution of the PCBs, and other pollutants, in the upper bay are storms, especially tropical storms. Very strong winds and storm surges from tropical systems can drive substantial masses of water towards the upper bay and into the lower wetlands and possibly transport contaminated sediments to these areas. How far upstream into the Escambia River such mechanisms could transport sediments and pollutants is currently not know nor is it clear how subsequent increased fluvial action would counteract the initial sediment transport caused by the storms.

The TEQ component contributed by dioxin-like PCBs was minor when compared to the dioxins/furans. The dioxins/furans contributed the bulk of the sediment TEQ, but a reversal of this ratio was observed in crab (Karouna et al., 2005) and fish tissues(Snyder and Rao, 2008). This appears to be due to a greater bioconcentration rate of PCBs than dioxins/furans. For example, in one mullet sample the total TEQ was 75.305 ng/kg, of which 75.005 ng/kg of TEQ was derived from dioxin-like PCBs (Snyder and Rao, 2008) showing the dominance of dioxin-like PCBs in tissue TEQ.

This is the first reported study of dioxins/furans in sediments in Escambia Bay and River and it is not possible to make any conclusions about long-term changes. There are important differences between the origins of dioxins/furans and PCBs since the overwhelming majority of PCBs are derived from Aroclor releases in contrast to the dioxins/furans that have multiple sources. PCBs only very rarely arise from non-Aroclor sources (Weber et al., 2001; Hu et al., 2008). Dioxins/furans routinely originate from processes that involve organic materials with aromatic components in the presence of chlorine atoms. Dioxins/furans arise from many industrial, also residential activities, bleaching operations, chlorine treated sewage releases, and combustions such as incineration, brush and forest fires. All of these have occurred in the Escambia River watershed. In the past there may have been releases from an upstream paper mill in Alabama (Stein et al., 1970a) and regional coal fired facilities such as Gulf Power's Crist Plant. Historically there were several brick manufacturing enterprises and other industries that employed combustion processes that could have released dioxins/furans on Escambia Bay. Overall it appears likely that dioxins/furans have been and will be produced and will persist for long periods of time in the sediments of the Escambia Bay and River System. The concentrations of dioxins/furans in sediments suggests impacts from dioxins/furans will likely pose long-term risks to bay and river organisms. Sediment core sampling and in-depth analyses of dioxins/furans will be required to predict overall patterns and fates of these POPs.

### 4.2. Pollutant impacts upon sediments: Metals

Trace metal concentrations exceeded the FDEP TEL but not the PEL, as was also observed by other PERCH studies in the sediments of the urban bayous of Texar, Chico, and Grande. The metals that exceeded the TEL included arsenic (30 exceedances), cadmium (16 exceedances), nickel (16 exceedances), chromium (14 exceedances), lead (11 exceedances), zinc (6 exceedances), copper (4 exceedances) and mercury (2 exceedances). A minor trace metal hot spot was observed in upper Escambia Bay near the Air Products and Chemicals outfall. It is not certain if the metals came from the outfall or were transported to that area from other areas of the bay because water transport patterns may hold water borne pollutants in the upper east portion of Escambia Bay (Olinger et al., 1975).

In some cases higher sediment concentrations of metals were correlated with increased concentrations of metals in seafood. This was true of total arsenic, and also cadmium and zinc concentrations that had been found in previous PERCH studies to exceed the US EPA SVs in shellfish tissue from some locations (Karouna-Renier et al., 2007). On the basis of SQAGs it appears that of the metals, arsenic presents the greatest impact to sediments and also presents a significant risk to human consumers of shellfish since some of the crab tissue samples from Escambia Bay did exceed the EPA screening guidelines for arsenic. Mercury was commonly found above the EPA SV in Escambia Bay crab tissues (Karouna-Renier et al., 2007) and above the ST in fishes (FDOH, 2007) even though in only two sediment samples mercury concentrations were detected above FDEP sediment SQAGs. This suggests that sediment concentrations are not reliable indicators for mercury accumulation in seafood tissues. Cadmium was also found to exceed EPA SV in some crab tissue samples in Escambia Bay and zinc was found to exceed the US EPA SV in some oyster tissues (Karouna-Renier et al., 2007).

### 4.3. Sediment SQAGs versus accumulation in seafood.

Concentrations for trace metals, dioxins/furans, and PCBs did exceed SQAGs for impacts on benthic organisms in some of the sediment samples. The lower SQAGs such as the TEL or AET only indicate that the probability of impacts while possible is still statistically less probable than for the PEL or probable effects level. An important observation is that none of the state or federal SQAGs were designed to be protective of the health of humans and upper trophic level wildlife that consume organisms living in the water column, on the sediments, or within the sediments (MacDonald, 1994). Previous PERCH studies show that several metals and dioxins/furans do accumulate in seafood, however it is the accumulation of PCBs that presents the major risk to human consumers of Escambia Bay and River seafood. The upper bay and the lower river showed high PCB concentrations for fish tissues, the lower bay has PCB concentrations in fish and crab above the US EPA SV (Karouna-Renier et al., 2007). Data from a yet unpublished PERCH study (Snyder and Rao, 2008) shows TEQs above the US EPA STs for mullet captured from several regions including the lower Escambia Bay. The current state of knowledge of accumulation of PCBs in seafood tissue and its influence on human health does not allow designating any area of Escambia Bay as safe for consumption of seafood without some awareness of how to best manage risk by humans consuming seafood. These risk management practices include limiting the amount of seafood consumed and removal of the skin prior to cooking and/or consumption.

## 4.4. Remediation

Remediation of contaminated sediments in Escambia Bay is one of the demands of a lawsuit that was recently filed (Rabb, 2008). PERCH takes no position on the merit(s) of this case. However, we will briefly outline some of the technical evaluations that must be considered in making cleanup decisions of sediments. There are currently six known SOCs (arsenic, mercury, cadmium, zinc, dioxins/furans, and PCBs) in the Escambia Bay and River System sediments that recent PERCH studies have shown to pose a health risk to human consumers of seafood. Of these six SOCs PCBs pose the largest risk based on their presence in seafood. Presently, our knowledge of PCBs in Escambia Bay is limited to its presence in the surface sediments and in species of consumed seafood consisting of some fish species, blue crabs, and oysters. We can deduce from this data that fish caught in some parts of the Pensacola Bay System, particularly its bayous, the lower Escambia River, and all of Escambia Bay should only be consumed in accordance with Florida Department of Health (DOH) and US EPA guidelines including certain cautions for rate of consumption and the manner of preparation prior to human consumption. The risk has been estimated for consumption of oysters and crabs from the Pensacola Bay System. Consumption of the entire crab for seventy years for the most contaminated Escambia Bay crab group had a risk of 6.1 cases of cancer per 10,000 people consuming at the Florida-specific consumption rate (46 g day$^{-1}$ ) (Karouna-Renier et al., 2007). This analysis for estimated cancer rate used two contaminant groups that are classified as carcinogens: TEQ (summed dioxins/furans and dioxin like-PCBs) and inorganic arsenic. Relative to human cancer risk the cost of doing nothing will likely be additional cases of cancer that depend upon the amounts of seafood being consumed by the local residents and the accuracy of the risk calculations. The cancer risk could be higher for human consumers of fish since recently a summed TEQ (75.0 pg/kg) was detected in mullet (*Mugil cephalus*) that is much higher than in the most contaminated crab group (Snyder and Rao, 2008).

The current PERCH study of Escambia Bay and River sediments has shown the overall extent of the contamination of the sediments. This information has provided the essential first step in what would be necessary to conduct sediment remediation. Additional studies utilizing sediment cores are needed to establish to what depth the contamination extends. Remediation of contaminated soils and sediments is often very expensive, particularly when the surface areas and volumes of the contaminated media are large. The surface area of Escambia Bay is about 36 mile$^2$ or about a billion square feet. This area of approximately one billion square feet only includes Escambia Bay and does not include the wetlands that lie southeast of the northern power line and the old gas pipe line, and parts of the river that had significant concentrations of PCBs and dioxins/furans. Assuming that the legal actions now before the courts or other events were to result in an order to remediate PCBs, the first major technical determination required would be what areas of the Escambia Bay and River System need to be remediated and to what minimal cleanup goals. The State of Florida Soil Cleanup Target Levels as cited in Florida Chapter 62-777 for PCBs cites a leachability cleanup standard based on Marine Surface Water Criteria and also for Freshwater and Surface Water Criteria that is 0.002 mg/kg for PCBs. This criterion is based on leaching tests which were not carried out in this study. Also, there is no suggestion that these standards are protective relative to bioaccumulation of PCBs and it is not clear if these standards are intended to be applied to sediment since they are intended for soil cleanup. The other existing metrics are the FDEP TEL and PEL sediment quality guidelines which do not apply to the TEQ. However, NOAA has assigned a TEL, AET, and PEL for TEQ.

None of these are intended to be protective relative to bioaccumulation of PCBs or other SOCs in seafood relative to cancer risks from human consumption. Other studies, such as construction of a food web, would be needed to determine the biota/sediment accumulation factor (Klečka et al., 2008) and a safe cleanup level. Currently we only have data for sediments and seafood and not in lower trophic levels. If the contamination in the bay were uniform then it would be much easier to calculate a biota/sediment accumulation factor between contaminated fish and the sediments. It would be prudent to obtain more information on the bay prior to taking what will be an extremely expensive course of action. It is our observation that more research is needed to better quantify the relationships between PCBs in seafood and in the sediments.

# 5. References

1. ADPH. 2008. News release Alabama Department of Public Health. Fish Consumption Advisories. www.adph.org

2. Alger-Sullivan Historical Society. 2006. ALGER-SULLIVAN LUMBER, http://www.algersullivan.org/100_years.html

3. ATSDR (Agency for Toxic Substances and Disease Registry). 1994. Toxicological profile for chlorodibenzofurans. ATSDR, Atlanta, GA. 256 p.

4. ATSDR (Agency for Toxic Substances and Disease Registry). 1998. Toxicological profile for chlorinated dibenzo-P-dioxins. ATSDR, Atlanta, GA. 723 p.

5. ATSDR (Agency for Toxic Substances and Disease Registry). 2004. Toxicological profile for DDT, DDE, and DDD. ATSDR, Atlanta, GA. 497 p.

6. ATSDR (Agency for Toxic Substances and Disease Registry). 2004. Toxicological profile for polybrominated biphenyls and polybrominated diphenyl ethers. ATSDR, Atlanta, GA, 639 p.

7. ATSDR (Agency for Toxic Substances and Disease Registry). 2004. Toxicological profile for copper. ATSDR, Atlanta, GA. 314 p.

8. Bandh C., R. Ishaq, D. Broman, C. Näf, Y. Rönquist-Nii, and Y. Zebühr, 1996. Separation for subsequent analysis of PCBs, PCDD/Fs, and PAHs according to aromaticity and planarity using a two-dimensional HPLC system. *Environ. Sci. Technol.* 30: 214–219.

9. BARC (Bay Area Resource Council). 2005. Pensacola Bay watershed management plan. Pensacola, FL. 339 p.

10. Barkovskii, A.L. and P. Adriaens. 1996. Microbial dechlorination of historically present and freshly spiked chlorinated dioxins and diversity of dioxin-dechlorinating populations. *American Society for Microbiology, Environmental Microbiology.* 62(12):4556-4562.

11. Black & Veatch Holding Company. 2007. Press release. http://www.bv.com/wcm/press_release/05072007_1374.aspx

12. BMZ (German Federal Ministry for Economic Cooperation and Development). 2008. Environmental Handbook -Documentation on monitoring and evaluating environmental impacts- Volume III: Compendium of environmental standards http://ces.iisc.ernet.in/energy/HC270799/HDL/ENV/enven/vol327.htm

13. Buchman, M.F. 2008. NOAA screening quick reference tables (SQuiRTs). NOAA OR&R Report 08-1. National Oceanic and Atmospheric Administration, Seattle WA. 34 p.

14. Buckman, R. 2003. Flomaton, Alabama 1861 to 2001: A brief chronological railroad history. The Orderboard, NRHS Tampa Bay Chapter of The Orderboard. Aug 2003 edition.

15. Bunch, C. 2006. Total PCB sediment contaminant report 1991-1999. FDEP Northwest District Watershed Management Section. Northwest District Office, Pensacola, FL.

16. Bunger, M.K., S.M. Moran, E. Glover, T.L. Thomae, G.P. Lahvis, B.C. Lin, and C.A. Bradfield. 2003. Resistance to 2,3,7,8-tetrachlorodibenzo-p-dioxin toxicity and abnormal liver development in mice carrying a mutation in the nuclear localization sequence of the aryl hydrocarbon receptor. *J. Biol. Chem.* 278(20):17767-17774.

17. Caffrey, J.M., W.M. Landing, S. Bagui, and S. Bagui. 2009. Atmospheric deposition of mercury and trace metals to the Pensacola Bay Watershed. University of West Florida, Center for Environmental Research and Bioremediation. 28 p. http://www.uwf.edu/CEDB/perch.cfm

18. DeBusk, W.F., I. Poyer, and L. Herzfeld. 2002. Sediment quality in the Pensacola Bay System. (Technical File Report 02-03). Northwest Florida Water Management District. Havana, FL. 76 p.

19. Díaz-Ferrero, J., M. C. Rodríguez-Larena, L. Comellas, and B. Jiménez. 1997. A review: Bioanalytical methods applied to endocrine disrupting polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans. *Trends in Analytical Chemistry*. 16(10):563-573.

20. Didonato G.T., J.K. Summers, and T.H. Roush. 2003. Assessing the ecological condition of a coastal plain watershed using a probabilistic survey design. *Environmental monitoring and Assessment*. 85(1):1-21.

21. Drive the Old Spanish Trail. 2004. The Old Spanish Trail: History. http://www.drivetheost.com/history.html

22. Duke, T.W., J.I. Lowe, and A.J. Wilson, Jr. 1970. A polychlorinated biphenyl (Aroclor 1254) in the water, sediment, and biota of Escambia Bay, Florida. *Bulletin of Environmental Contamination And Toxicology*. 5(2):171-180.

23. ECUA. 2008. Project Update. http://www.ecua.org/wwtp/default.asp

24. Eganhouse, R.P. Jr. 1975. The measurement of total and organic mercury in marine sediments, organisms and waters. Southern California Coastal Water Research Project, El Segundo, CA. 29 p.

25. Eisler R. 1986. Polychlorinated biphenyl hazards to fish, wildlife, and invertebrates: A synoptic review. Biological Report 85 (1.8). U.S. Fish and Wildlife Service, Laurel, MD. 53p.

26. FDEP. 2001. FDEP news release. http://www.dep.state.fl.us/secretary/news/2001/01-109.htm

27. FDEP. 2004. Water Quality Status Report Pensacola Bay. FDEP Division of Water Resource Management. Tallahassee, FL. 213 p.

28. FDEP. 2005. Consolidated wetland resource permit and intent to grant sovereign submerged lands authorization. Permit/Authorization Number. 0187162-001-D. Tallahassee, FL.

29. FDEP. 2006. Verified List of Impaired Waters for the Group 4 Basins Pensacola (Group 4). Adopted Verified Lists Of Impaired Waters for the Group 4 Basins. http://www.dep.state.fl.us/water/watersheds/assessment/adopted_gp4.htmhttp://www.dep.state.fl.us/water/watersheds/assessment/adopted_gp4.htm

30. FDEP. 2006. Fish Consumption Health Advisories. http://www.dep.state.fl.us/labs/mercury/docs/fhapre.htm

31. FDOH. 2007. Florida Department Of Health issues fish consumption advisory for Escambia River. http://www.escambiahealth.com/recent_hot_topics/2007/fish.htm

32. Federal Register. 1998. Rules and Regulations, Department of Commerce, National Oceanic and Atmospheric, Administration, 50 CFR Part 226, Department of the Interior, Fish and Wildlife Service, 50 CFR Part 17, Endangered and Threatened Wildlife, and Plants; Decision on Designation of, Critical Habitat for the Gulf Sturgeon. Vol. 63, No. 39. Friday, February 27, 1998. http://www.fws.gov/endangered/federalregister/1998/s980227.html

33. Federal Register. 1998. FR Doc. 98–4853 Filed 2–26–98
http://www.fws.gov/alabama/gs/unitmaps.htm
http://www.fws.gov/alabama/gs/riverine_maps.pdf

34. Federal Register. 2008. The purpose of reviews conducted under this section of the Act is to ensure that the classification of species as threatened or endangered on the List of Endangered and Threatened Wildlife and Plants (50 CFR 17.11 and 17.12) is accurate. [Notices] [Page 20702-20704] April 16, 2008 (Volume 73, Number 74). http://www.fws.gov/panamacity/resources/pdf/5-year18speciesFR.pdf

35. Fiedler, H., H. Hoff, J. Tolls, C. Mertens, A. Gruber, and O. Hutzinger. 1994. Environmental fate of organochlorines in the aquatic environment. ECO-INFORMA Press, Bayreuth, Germany. 199 p.

36. Frame G.M., J.W. Cochran, and S.S. Bowadt. 1996. Complete PCB congener distributions for 17 Aroclor mixtures determined by 3 HRGC systems optimized for comprehensive, quantitative, congener-specific analysis. *J. High Resolut. Chromatogr*. 19:657-668

37. Friends of the Pace Library. 2000. http://www.friendsofpacelibrary.org/History/historical_sketch.htm

38. Gobas, F. and J. Wilcockson. 2003. San Francisco Bay PCB food-web model prepared by EVS Environmental Consultants. San Francisco Estuary Institute Contribution 90. San Francisco, CA. 58 p.

39. Gregoraszczu, E.L. 2008. Dioxin exposure and porcine reproductive hormonal activity. http://www.scielo.br/scielo.php?pid=S0102-311X2002000200010&script=sci_arttext&tlng=en.

40. Hamilton, S.J. and K.J. Buhl. 2003. Selenium and other trace metals in water, sediment, aquatic plants, aquatic invertebrates, and fish from streams in southeastern Idaho near phosphate mining operations: September 2000. U.S. Geological Survey, Columbia Environmental Research Center, Yankton, SD. 64 p.

41. Hu. D., A. Martinez, and K.C. Hornbuckle. 2008. Discovery of non-aroclor PCB (3,3′-Dichlorobiphenyl) in Chicago air. *Environ. Sci. Technol*. 42 (21):7873–7877.

42. Hyland J., L. Balthis, I. Karakassis, P. Magni, A. Petrov, J. Shine, O. Vestergaard, and R. Warwick. 2005. Organic carbon content of sediments as an indicator of stress in the marine benthos. *Marine Ecology Progress Series*. 295:91–103.

43. IARC. 1997. Polychlorinated dibenzo-para-dioxins and polychlorinated dibenzofurans. IARC monographs on the evaluation of carcinogenic risks to humans. V. 69. Lyon, France. 666 p. http://monographs.iarc.fr/ENG/Classification/crthgr01.php

44. International Paper. 2005. News Release: International Paper announces plan to transform its business portfolio and performance. Stamford, Conn.

45. Karouna-Renier, N. K., R.A. Snyder, and K.R. Rao. 2005. Assessing fisheries as vectors for toxic materials from the environment to humans- an assessment of potential health risks posed by shellfish collected in estuarine waters near Pensacola, Florida. Center for Environmental Diagnostics and Bioremediation, University of West Florida, Pensacola, FL, 48 p.

46. Karouna-Renier, N.K., R.A. Snyder, J.G. Allison, M.G. Wagner, and K.R. Rao. 2007. Accumulation of organic and inorganic contaminants in shellfish collected in estuarine waters near Pensacola, Florida: Contamination profiles and risks to human consumers. *Environmental Pollution*. 145:474-488.

47. Kasch A., V. Römheld, and Y. Chen. 2002. Cadmium binding by fractions of dissolved organic matter and humic substances from municipal solid waste compost. *J. Environ. Qual.* 31:1885–1892.

48. Klečka G.M. and D.C.G. Muir. 2008. Science-based guidance and framework for the Evaluation and identification of PBTs and POPs: Summary of a SETAC Pellston Workshop, Pensacola, FL. 14 p.

49. Knezovich, J.P., F.L. Harrison and R.G. Wilhelm. 1987. The bioavailability of sediment-sorbed organic chemicals: a review. *Water, Air, and Soil Pollution*. 32:233-245.

50. Kodavanti P.R.S., N. Kannan, N. Yamashita, E.C. Derr-Yellin, T.R. Ward, D.E. Burgin, H.A. Tilson, and L.S. Birnbaum. 2001. Differential effects of two lots of Aroclor 1254: Congener-specific analysis and neurochemical end points. *Environmental Health Perspectives*. 109(11):1153-1161.

51. Koelmans A.A., T.O. Jonker, G. Cornelissen, T.D. Bucheli, P.C.M. Van Noort, and O. Gustafsson. 2006. Review: Black carbon: The reverse of its dark side. *Chemosphere*. 63:365–377.

52. Kriegel, R.V. 1988. Response to the State's Certification of Permit I047-121893 to EPA. Pensacola, FL: FDEP, Northwest District.

53. Lemly, D.A., and , G.J. Smith. 1987. Aquatic cycling of selenium-implications for fish and wildlife. U.S. Fish and Wildlife Service, Fish and Wildlife Leaflet 12, 10 p.

54. Lewis, M.A., R. Devereux, and P. Bourgeois. 2008. Seagrass distribution in the Pensacola Bay System, Northwest Florida. *Gulf Caribb. Res.* 20:21-28.

55. Liebens, J., C.J. Mohrherr, and K.R. Rao. 2009. Pollution of surface soils in Escambia and Santa Rosa Counties, FL. Final Report. Center for Environmental Diagnostics and Bioremediation, University of West Florida, Pensacola, FL, 87 p. http://www.uwf.edu/CEDB/Perch_Pollution_of_surface_soils_in_Escambia_and_Santa_Rosa_Counties.cfm

56. Lores, E. M. and D. T. Specht. 2001. Drought-induced decline of submerged aquatic vegetation in Escambia Bay, Florida. *Gulf of Mex. Sci.* 19(2):161-164.

57. MacDonald, D.D. 1994a. Approach to the assessment of sediment quality in Florida coastal waters. Volume 1 - Development and evaluation of sediment quality assessment guidelines. FDEP Office of Water Policy. Tallahassee, FL. 140 p. http://www.dep.state.fl.us/water/monitoring/docs/seds/vol1/volume1.pdf

58. MacDonald, D.D. 1994b. Approach to the assessment of sediment quality in Florida coastal waters. Volume 2: Application of the sediment quality assessment guidelines. FDEP Office of Water Policy. Tallahassee, FL. 59 p. http://www.dep.state.fl.us/water/monitoring/docs/seds/vol1/volume2.pdf

59. Mohrherr, C.J., J. Liebens, J.E. Lepo, and K.R. Rao. 2005. Profiles of selected pollutants in Bayou Texar, Pensacola, FL. University of West Florida, Center for Environmental Research and Bioremediation, 85 p. http://www.uwf.edu/cedb/perch.cfm

60. Mohrherr, C.J., J. Liebens, and K.R. Rao. 2006. Sediment and water pollution in Bayou Chico, Pensacola, FL. University of West Florida, Center for Environmental Research and Bioremediation, 201 p. http://www.uwf.edu/cedb/perch.cfm

61. Mohrherr, C.J., J. Liebens, and K.R. Rao. 2008. Environmental assessment of sediments and water in Bayou Grande, Pensacola, FL. University of West Florida, Center for Environmental Research and Bioremediation, 175 p. http://www.uwf.edu/cedb/perch.cfm

62. Murrell M.C. and E.M. Lores. 2004. Phytoplankton and zooplankton seasonal dynamics in a subtropical estuary: importance of cyanobacteria. *Journal of Plankton Research.* 26(3):371–382.

63. NOAA. 2005. Mercury in aquatic habitats. http://response.restoration.noaa.gov/topic_subtopic_entry.php?RECORD_KEY%28entry_subtopic_topic%29=entry_id,subtopic_id,topic_id&entry_id(entry_subtopic_topic)=86&subtopic_id(entry_subtopic_topic)=10&topic_id(entry_subtopic_topic)=

64. Northwest Florida Water Management District (NWFWMD). 1991. The Pensacola Bay System surface water improvement and management plan. Northwest Florida Water Management District. Havana, FL.

65. Northwest Florida Water Management District (NWFWMD). 1993. Review of the Pensacola Bay System non-point source 208 Plan methodologies. Northwest Florida Water Management District. Havana, FL.

66. Nugent, E.E. 2000. Pace: A historical sketch. http://www.friendsofpacelibrary.org/History/historyhome.htm

67. OECD. 2006. The use of metabolising systems for in vitro testing of endocrine disruptors. Organization for Economic Co-operation and Development. http://www.oecd.org/dataoecd/42/13/36280446.pdf 125 p.

68. Olinger, L.W., R.G. Rogers, P.L. Force, T.L. Todd, B.L. Mullings, F.T. Bisterfeld, and L.A. Wise II. 1975. Environmental and recovery studies of Escambia Bay and the Pensacola Bay System, Florida. U.S. Environmental Protection Agency. Washington, DC. 471 p,

69. Ostrom, N., M. Wilson, and J. Frampton. 2004. Draft Lead Report. State of California Department of Toxic Substances Control, Hazardous Waste Management Program, Regulatory and Program Development Division. Sacramento, CA. 119 p.

70. Pensapedia. 2008. James F. Crist Generating Plant. http://www.pensapedia.com/wiki/James_F._Crist_Generating_Plant

71. Rabb, S. 2008. Monsanto, (Solutia named in suit) Fifty residents along Escambia Bay are suing the companies they say are responsible for polluting the water and fish near their properties with cancer-causing industrial chemicals. Pensacola News Journal, June 10, 2008.

72. Ravan, J.E. 1985. EPA Journal. http://www.epa.gov/history/topics/epa/15f.htm

73. Reidenauer, J. and C. Shambaugh. 1986. An analysis of estuarine degradations within the Pensacola Bay system and their relationship to land management practices. Florida Dept. of Community Affairs. Tallahassee, FL. 132 p.

74. Schroeder, W. W. and W. J.Wiseman. 1999. Geology and hydrodynamics of Gulf of Mexico estuaries. *In*: Bianchi, T. S., J. R. Pennock, and R. R. Twilley. (eds). Biogeochemistry of Gulf of Mexico estuaries. John Wiley and Sons. New York, NY. 3–28

75. Senate Report. 1910. Senate report on the river and harbor bill by the Committee On Commerce of The United States Senate, April 11, 1910. Government Printing Office. Washington D.C.

76. Smith, K.A. and J.M. Caffrey. The effects of human activities and extreme meteorological events on sediment nitrogen dynamics in an urban estuary, Escambia Bay, Florida, USA. *Hydrobiologia*. 627:67-85.

77. Snyder. R. A. and K.R. Rao. 2008. Bioaccumulation of chemical contaminants in fishes of Escambia Bay. Submitted to UE EPA Region 4 and the Florida Department of Health. http://www.uwf.edu/rsnyder/reports/EscBaybridgefish.pdf.

78. Special Grand Jury. 1999. Report of the Special Grand Jury on air and water quality. Pensacola, FL. The Circuit Court of the First Judicial Circuit in and for Escambia County, FL. 139 p.

79. Steenland, K., J. Deddens, and L. Piacitelli. 2001. Risk Assessment for 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD) based on an epidemiologic study. *Am. J. Epidemiol*. 154:451–8.

80. Stein, M., I.L. Myers, A.N. Beck, N.P. Reed, V.D. Patton, and J.R. Thoman. 1970a. Transcript of proceedings: Conference in the matter of pollution of the interstate waters of the Escambia River Basin (Alabama-Florida) and the intrastate portions of the Escambia Basin within the State of Florida - Volume I. Gulf Breeze, FL. U.S. Government Printing Office. 366 p.

81. Stein, M., I.L. Myers, A.N. Beck, N.P. Reed, V.D. Patton, and J.R. Thoman. 1970b. Transcript of proceedings: Second session of conference in the matter of pollution of the interstate waters of Escambia River Basin (Alabama-Florida) and the intrastate portions of the Escambia Basin and Bay within the State of Florida - Volume II. Gulf Breeze, FL. U.S. Government Printing Office. 303 p.

82. Stevens, E.A., and C.A. Bradfield. 2008. Immunology: T cells hang in the balance. *Nature*. 453:46-47.

83. The Florida Memory Project. 2008. http://www.floridamemory.com/PhotographicCollection/

84. Thorpe, P., R. Bartel, P. Ryan, K. Albertson, T. Pratt, and D. Cairns. 1997. The Pensacola Bay System surface water improvement and management plan: A comprehensive plan for the restoration and preservation of the Pensacola Bay System. *Northwest Florida Water Management District, Program Development Series, 97-2*. 149 p.

85. Ullrich S.M., T.W. Tanton, and S.A. Abdrashitova. 2001. Mercury in the aquatic environment: A review of factors affecting methylation. *Critical Reviews in Environmental Science and Technology*. 31(3):241-293.

86. USEPA. 1972. Transcript of proceedings: Conference in the matter of pollution of the interstate waters of the Escambia River Basin (Alabama-Florida) and the intrastate portions of the Escambia Basin within the State of Florida - Volume III. Gulf Breeze, FL. U.S. Government Printing Office. 673 pp.

87. USEPA. 1994. Statement of basis/Final decision and response to comments summary, Air Products and Chemicals, Inc Pace, FL. USEPA RCRA Compliance Section, Atlanta, GA. 3p.

88. USEPA. 2007. Proposed total maximum daily load (TMDL) for nutrients in Escambia Bay. WBID 548A .USEPA Region 4. Atlanta, GA. 141 p.

89. USEPA. 2008. Persistent bioaccumulative and toxic (PBT) chemical program. http://www.epa.gov/pbt/pubs/dioxins.htm

90. USEPA Gulf Ecology Division. 2005. The ecological condition of the Pensacola Bay System, Northwest Florida (1994 - 2001).USEPA, Gulf Ecology Division. Report EPA/620/R-05/002. 44 p.

91. UWF. 2008. Northwest Florida Mill Survey. UWF Division of Anthropology and Archaeology. http://www.uwf.edu/anthropology/research/industrial/millsurvey/

92. Valigura, R.A. 2001. An introduction to the first assessment of nitrogen loads to US estuaries with an atmospheric perspective. pp. 1-10. *In*: Valigura, R.A., R.B. Alexander, and M.S. Castro (Editors). Nitrogen Loading in Coastal Water Bodies, an Atmospheric Perspective. *Am. Geophys. Un.,* Washington D.C.

93. Van den Berg, M., L.S. Birnbaum, M. Denison, M. De Vito, W. Farland, and M. Feeley. 2006. The 2005 World Health Organization reevaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. *Toxicological Sciences,* 93(2):223–241.

94. Walker, J. H. 1960. Soil survey, Escambia County, Florida. US Department of Agriculture, Soil Conservation Service. Washington, D.C. 87 p

95. Wandiga S.O., I.O. Jumba , W.G. Mutaaga, and J.O. Lalah. 2004. The distribution, metabolism and toxicity of 14c-DDT in model aquarium tanks with fish and sediment simulating a tropical marine environment. *Toxicological and Environmental Chemistry*. 85(4-6):253-268.

96. Weber, R., F. Iino, T. Imagawa, M. Takeuchi, T. Sakurai, and M. Sadakata. 2001. Formation of PCDF, PCDD, PCB, and PCN in de novo synthesis from PAH: Mechanistic aspects and correlation to fluidized bed incinerators. *Chemosphere*. 44(6):1429-1438.

97. White, J.C. , J.E. Ravan, P.J. Traina, J.L. Crockett , Jr. and D. Levin. 1972. Transcript of Proceedings: Third session of conference in the matter of pollution of the interstate waters of Escambia River Basin and the intrastate portions of the Escambia Basin and Bay within the State of Florida. Gulf Breeze, FL. US EPA Region IV. 673 p.

98. Windsor, J.G., Jr. 1985. Nationwide review of oxygen depletion and eutrophication in estuarine and coastal waters: Florida region. Final Report to Brookhaven National Laboratory, Upton, NY and U.S. Department of Commerce, National Oceanic and Atmospheric Administration, Ocean Assessment Division. Department of Oceanography and Ocean Engineering, Florida Institute of Technology, Melbourne, FL. 177 p.

# 6. Appendix: Additional Tables

Table 3.4.1-1a**.** Compositional profiles of the EG series (166-168 elutions).

| Congener | % | Congener | % | Congener | % | Congener | % |
|---|---|---|---|---|---|---|---|
| 129+138+163 | 6.8 | 85+116 | 0.59 | 196 | 0.12 | 55 | 0.013 |
| 153+168 | 5.6 | 56 | 0.58 | 68 | 0.11 | 207 | 0.011 |
| 118 | **5.6**[1] | 177 | 0.56 | 59+62+75 | 0.11 | 80 | 0.011 |
| 110 | 5.0 | 15 | 0.56 | 93+100 | 0.10 | 2 | 0.011 |
| 90+101+113 | 5.0 | 42 | 0.55 | 154 | 0.10 | 150 | 0.010 |
| 147+149 | 3.8 | 136 | 0.53 | 202 | 0.09 | 126 | **0.010** |
| 49+69 | 3.1 | 77 | **0.50** | 103 | 0.09 | 159 | 0.009 |
| 95 | 3.1 | 4 | 0.49 | 117 | 0.09 | 89 | 0.009 |
| 83 | 2.8 | 45+51 | 0.49 | 133 | 0.09 | 181 | 0.008 |
| 44+47+65 | 2.8 | 158 | 0.46 | 176 | 0.09 | 197 | 0.008 |
| 52 | 2.7 | 183 | 0.43 | 195 | 0.08 | 24 | 0.005 |
| 11 | 2.6 | 130 | 0.40 | 206 | 0.08 | 205 | 0.004 |
| 86+87+97+108+119+125 | 2.5 | 64 | 0.35 | 106 | 0.08 | 148 | 0.003 |
| 70+61+74+76 | 2.4 | 164 | 0.33 | 72 | 0.07 | 81 | **0.003** |
| 99 | 2.4 | 171+173 | 0.31 | 123 | **0.07** | 57 | 0.003 |
| 66 | 2.1 | 19 | 0.29 | 63 | 0.06 | 182 | 0.002 |
| 105 | **1.7** | 179 | 0.29 | 139+140 | 0.06 | 104 | 0.002 |
| 8 | 1.7 | 6 | 0.28 | 67 | 0.06 | 152 | 0.001 |
| 180+193 | 1.6 | 198+199 | 0.28 | 120 | 0.06 | 127 | 0.001 |
| 21+33 | 1.6 | 167 | **0.27** | 114 | **0.06** | 111 | 0.001 |
| 41+71+40 | 1.4 | 82 | 0.25 | 208 | 0.06 | 36 | 0.001 |
| 20+28 | 1.4 | 22 | 0.24 | 58 | 0.05 | 9 | 0.001 |
| 135+151 | 1.3 | 134 | 0.23 | 54 | 0.05 | 143 | 0.0005 |
| 132 | 1.2 | 98+102 | 0.22 | 5 | 0.05 | 188 | 0.0002 |
| 128+166 | 1.2 | 194 | 0.22 | 201 | 0.04 | 165 | 0.0002 |
| 32 | 1.19 | 26+29 | 0.22 | 35 | 0.04 | 10 | 0.0000 |
| 170 | 1.09 | 16 | 0.21 | 185 | 0.04 | 14 | 0.0000 |
| 88+91 | 1.04 | 137 | 0.21 | 200 | 0.03 | 23 | 0.0000 |
| 187 | 0.99 | 25 | 0.20 | 131 | 0.03 | 39 | 0.0000 |
| 84 | 0.90 | 27 | 0.19 | 79 | 0.03 | 38 | 0.0000 |
| 92 | 0.83 | 190 | 0.19 | 189 | **0.03** | 78 | 0.0000 |
| 156&157 | **0.82** | 178 | 0.18 | 94 | 0.03 | 121 | 0.0000 |
| 146 | 0.81 | 203 | 0.17 | 12+13 | 0.03 | 155 | 0.0000 |
| 31 | 0.80 | 48 | 0.16 | 34 | 0.03 | 145 | 0.0000 |
| 17 | 0.75 | 60 | 0.16 | 122 | 0.03 | 142 | 0.0000 |

Table 3.4.1-1a**.** Compositional profiles of the EG series (166-168 elutions)(cont'd).

| Congener | % | Congener | % | Congener | % | Congener | % |
|---|---|---|---|---|---|---|---|
| 1 | 0.73 | 209 | 0.16 | 191 | 0.03 | 161 | 0.0000 |
| 141 | 0.64 | 107+124 | 0.15 | 175 | 0.03 | 160 | 0.0000 |
| 174 | 0.63 | 172 | 0.14 | 43+73 | 0.02 | 169 | **<u>0.0000</u>** |
| 37 | 0.61 | 112 | 0.14 | 96 | 0.02 | 184 | 0.0000 |
| 109 | 0.61 | 46 | 0.14 | 162 | 0.02 | 186 | 0.0000 |
| 50+53 | 0.60 | 3 | 0.13 | 7 | 0.02 | 192 | 0.0000 |
| 18+30 | 0.59 | 144 | 0.13 | 115 | 0.019 | 204 | 0.0000 |

1. Bold face and underlined font indicate dioxin-like PCBs.

Table 3.4.1-1b. Compositional profiles of the KS series (135 elutions).

| Congener | % | Congener | % | Congener | % | Congener | % |
|---|---|---|---|---|---|---|---|
| 110+115 | 6 | 45+51 | 0.83 | 197+200 | 0.18 | 7 | 0.035 |
| 129+138 +160 +163 | 5.3 | 128+166 | 0.81 | 26+29 | 0.17 | 34+23) | 0.033 |
| 153 +168 +141 | 4.6 | 85+ 116+117 | 0.75 | 25 | 0.17 | 143 | 0.033 |
| **118** | **4.3** | 170 | 0.72 | 19- | 0.16 | 162 | 0.027 |
| 147+134 +149 | 4.3 | 132 | 0.7 | 201 | 0.16 | 175 | 0.027 |
| 83 +99 +112 | 3.9 | 178 | 0.68 | 208 | 0.15 | 122+**114** | **0.026** |
| 90 +101 +113 | 3.9 | 1 | 0.64 | 11 | 0.14 | 191 | 0.0208 |
| 44+47 +65 | 3.8 | 56+60 | 0.64 | 131+142 | 0.13 | 38 | 0.02 |
| 52+43 +73 | 3.5 | 130+ 137+164 | 0.63 | 190 | 0.12 | **189** | **0.02** |
| **70**+61+ 74+76 | **3.2** | 92 | 0.57 | 2 | 0.12 | 78 | 0.017 |
| 49+69 | 3 | 4 | 0.53 | 209 | 0.11 | 159 | 0.015 |
| 93+100 +98+102 | 2.8 | **156 +157** | **0.49** | 207 | 0.11 | 63 | 0.013 |
| 187+182 | 2.7 | 59+62 +42 +75 | 0.49 | 176 | 0.1 | 89 | 0.011 |
| 5+8 | 2.4 | 15 | 0.47 | 68 | 0.1 | 204 | 0.009 |
| 196 +203 | 2.3 | 136 | 0.46 | 172 | 0.1 | **81** | **0.009** |
| 66+55 | 2.2 | 37 | 0.46 | 103 | 0.1 | 35 | 0.004 |
| 144 | 2.1 | 82 | 0.45 | 80 | 0.09 | 152+150 | 0.004 |
| 180+193 | 2.1 | 177 | 0.45 | 72 | 0.09 | 148 | 0.003 |
| 20+21+28 +33 | 1.9 | 12+13 | 0.42 | 127 | 0.08 | 104 | 0.001 |
| 41+71 +40 | 1.6 | 64 | 0.4 | 133 | 0.07 | **169** | **0.001** |
| 198+199 | 1.51 | 18+30 | 0.38 | 165 | 0.07 | 9 | 0.000 |
| 183+174 +185 | 1.48 | 107+124 | 0.38 | 3 | 0.06 | 48 | 0.000 |
| **105** | **1.34** | 139+140 | 0.37 | 79 | 0.06 | 192 | 0.000 |
| 88+91 | 1.27 | 158 | 0.34 | 39 | 0.05 | 188 | 0.000 |
| 32 | 1.24 | 77 | 0.33 | 36 | 0.05 | 186 | 0.000 |
| 86+87 +97+108 +119+125 | 1.18 | 195 | 0.29 | 94 | 0.05 | 184 | 0.000 |

Table 3.4.1-1b. Compositional profiles of the KS series (135 elutions) (cont'd).

| Congener | % | Congener | % | Congener | % | Congener | % |
|---|---|---|---|---|---|---|---|
| 146+161 | 1.12 | 22 | 0.29 | 58+67 | 0.04 | 155 | 0.000 |
| 31 | 0.94 | 179 | 0.29 | 54 | 0.04 | 145 | 0.000 |
| 135+ 151+154 | 0.91 | 46 | 0.22 | 57 | 0.04 | 14 | 0.000 |
| 194 | 0.9 | 181+ 171+173 | 0.21 | 205 | 0.04 | 121 | 0.000 |
| 50+53 | 0.89 | **167** | **0.2** | 27+16 +24 | 0.04 | 111 | 0.000 |
| 206 | 0.85 | 95 | 0.19 | 120 | 0.04 | 109+106 **+123** | **0.000** |
| 17 | 0.84 | 6 | 0.19 | 126 | 0.037 | 10 | 0.000 |
| 84 | 0.84 | 202 | 0.18 | 96 | 0.035 | | |

Table 3.11-3. Total metal concentrations [mg/kg] in sediments in Escambia Bay and River.

| Sample ID | Al | As | Cd | Ca | Cr | Cu | Fe |
|---|---|---|---|---|---|---|---|
| EG1 | 23100 | 12 | 0.52 i[1] | 1570 | 42 | 13 | 40400 |
| EG2 | 2050 | 1.7 | <0.078[2] | 229 | 4.4 | 1.3 | 4190 |
| EG3 | 17600 | 8 | 0.45i | 1250 | 35 | 10 | 31300 |
| EG4 | 4700 | 2.6 | 0.13i | 514 | 9.9 | 2.6 | 9580 |
| EG5 | 30800 | 9.4 | 0.85i | 2370 | 51 | 13 | 40100 |
| EG-6 | 8,720 | 3.9 | 0.39i | 1,150 | 17 | 5.3 | 14,400 |
| EG-7 | 11,300 | 10 | 0.92i | 4,020 | 36 | 11 | 21,600 |
| EG-8 | 10,900 | 8.4 | 0.63i | 993 | 34 | 9.1 | 19,300 |
| EG-9 | 14,400 | 11 | 1.3 | 1,080 | 47 | 11 | 27,900 |
| EG-10 | 28,500 | 21 | 1.8 | 1,950 | 87 | 20 | 50,400 |
| EG 11 | 41100 | 30 | 1.2i | 5400 | 89 | 19 | 13500 |
| EG 12 | 15500 | 13 | 0.59i | 2260 | 39 | 7.8 | 5980 |
| EG 13 | 758 | 0.51 i | <0.072 | 109i | 2.5 | 0.69 i | 1070 |
| EG 14 | 33100 | 21 | 1.1i | 2420 | 64 | 13 | 13100 |
| EG15 | 41200 | 25 | 0.82 i | 6940 | 72 | 16 | 56800 |
| EG16 | 6800 | 6.4 | 0.19 i | 1550 | 17 | 4.1 | 10500 |
| EG17 | 10500 | 9.8 | 0.31 i | 2310 | 28 | 7 | 17500 |
| EG18 | 1730 | 2.2 | <0.075 | 148 | 5.2 | 1.6 | 3320 |
| EG19 | 421 | 0.38 i | <0.076 | 59 i | 1.8 | 0.3 i | 540 |
| EG20 | 1020 | 1.1 | <0.076 | 417 | 3.1 | 0.72 i | 1500 |
| EG21 | 9730 | 6 | 0.44 i | 896 | 23 | 10 | 18100 |
| EG22 | 1060 | 1.6 | <0.074 | 118 i | 3.6 | 1.9 | 2630 |
| EG23 | 203 | 0.27 i | <0.075 | 22 i | 1.1 i | <0.21 | 631 |
| EG24 | 7790 | 4.3 | 0.65 i | 1170 | 25 | 9 | 15400 |
| EG25 | 9040 | 4.8 | 0.43 i | 988 | 23 | 9.7 | 16600 |
| EG26 | 6380 | 2.5 | 0.27 i | 624 | 17 | 4 | 9150 |
| EG 27 | 1130 | 0.45 i | 0.085 i | 198 | 3.6 | 0.53 i | 2160 |
| EG 28 | 7130 | 4 | 0.89 i | 2630 | 17 | 8.7 | 11900 |
| EG 29 | 210 | 0.41 i | <0.074 | 27iBl | 0.66 i | <0.21 | 880 |
| EG 30 | 16900 | 8.9 | 0.82 i | 1610 | 42 | 15 | 30000 |
| EG 31 | 3500 | 1.8 | 0.14 i | 416 | 8 | 3 | 5890 |
| EG 32 | 4230 | 2.9 | 0.13 i | 334 | 8 | 3.9 | 8080 |
| EG33 | 5370 | 4.5 | 0.24i | 636 | 13 | 3.6 | 12900 |
| EG34 | 15900 | 12 | 0.5i | 1330 | 43 | 12 | 32700 |
| EG35 | 2000 | 1.3 | <0.075 | 259 | 4.5 | 1.3 | 3690 |
| EG36 | 11800 | 6.1 | 0.37 i | 1490 | 23 | 6 | 24000 |
| EG37 | 14500 | 15 | 0.88 i | 2010 | 48 | 13 | 29900 |
| EG38 | 27500 | 21 | 1 i | 2860 | 73 | 20 | 51200 |
| EG39 | 7590 | 5 | 0.23 i | 776 | 18 | 4.9 | 14200 |
| EG40 | 20500 | 16 | 0.8 i | 2780 | 50 | 20 | 41400 |
| EG41 | 6560 | 2.9 | 0.43 i | 1180 | 15 | 4.8 | 10400 |
| EG42 | 11900 | 5.4 | 0.52 i | 1250 | 29 | 6.8 | 19000 |
| EG43 | 24600 | 11 | 1.1 i | 3100 | 56 | 17 | 30900 |
| EG44 | 2480 | 2.6 | 0.32 i | 868 | 7.9 | 3.9 | 6020 |

Table 3.11-3. Total metal concentrations [mg/kg] in sediments in Escambia Bay and River (cont'd).

| Sample ID | Al | As | Cd | Ca | Cr | Cu | Fe |
|---|---|---|---|---|---|---|---|
| EG45 | 13400 | 8.3 | 0.5 i | 2320 | 25 | 15 | 21700 |
| EG-46 | 12900 | 3.7 i | 0.69 i | 1970 | 30 | 7.2 | 23300 |
| EG-47 | 12600 | 7.5 | 1.1 i | 1640 | 35 | 9.5 | 24000 |
| EG48 | 35300 | 24 | 0.39i | 3690 | 64 | 14 | 53600 |
| EG49 | 33100 | 35 | 0.66i | 2420 | 91 | 18 | 54700 |
| EG50 | 23200 | 24 | 0.48i | 2270 | 65 | 12 | 43500 |
| EG-51 | 24400 | 16 | 2.5 | 2210 | 53 | 13 | 52600 |
| EG-52 | 13900 | 13 | 0.4i | 1210 | 45 | 10 | 30700 |
| EG-53 | 26300 | 24 | 0.59i | 2550 | 77 | 17 | 55800 |
| EG-54 | 25200 | 32 | 0.26i | 5630 | 77 | 17 | 56700 |
| EG 55 | 30300 | 29 | <0.27 | 6650 | 80 | 18 | 50700 |
| EG 56 | 27000 | 31 | 0.51i | 6210 | 82 | 17 | 48600 |
| EG 57 | 20900 | 16 | <0.2 | 3230 | 40 | 8 | 38700 |

Table 3.11-3. Total metal concentrations [mg/kg] in sediments in Escambia Bay and River (cont'd).

| Sample ID | Pb | Mg | Hg | Ni | Se | Sn | Zn |
|---|---|---|---|---|---|---|---|
| EG1 | 18 | 4770 | 0.095 | 12 | 1.5 | <1.3 | 75 |
| EG2 | 2 | 574 | <0.006 | 1.4 | 0.15iBl[1] | 0.79iBl | 7.8 |
| EG3 | 15 | 3450 | 0.042i | 11 | 0..8iBl | <1.4 | 57 |
| EG4 | 4.8 | 1010 | <0.007 | 3.1 | <0.05 | <0.82 | 17 |
| EG5 | 22 | 5150 | 0.067i | 17 | 2.9i | <2.6 | 90 |
| EG-6 | 8.2 | 1,880 | 0.012i | 4.6 | 0.55i | <0.93 | 32 |
| EG-7 | 16 | 2,710 | 0.029i | 9.2 | 1.3i | <1 | 59 |
| EG-8 | 20 | 2,760 | 0.015i | 9.2 | 0.93i | <0.97 | 54 |
| EG-9 | 19 | 3,320 | 0.028i | 13 | 1.7i | <1.1 | 73 |
| EG-10 | 34 | 6,150 | 0.057i | 22 | 2.6i | <1.6 | 133 |
| EG 11 | 41 | 12400 | 0.12 | 26 | <0.13 | 5.4i | 144 |
| EG 12 | 18 | 4550 | 0.14 | 11 | <0.07 | 2.8i | 64 |
| EG 13 | 1.2 | 332 | 0.014i | 0.62i | <0.04 | 0.98iBl | 2.3i |
| EG 14 | 26 | 7920 | 0.47 | 18 | <0.1 | 3.2i | 102 |
| EG15 | 37 | 13100 | 0.105 | 21 | 1.4 i | 5 i | 119 |
| EG16 | 8.6 | 2080 | 0.02 i | 4.9 | 0.53 i | 1.9 i | 27 |
| EG17 | 14 | 2860 | 0.029 i | 7.7 | 0.82 i | 2.2 i | 43 |
| EG18 | 2.4 | 453 | <0.006 | 1.3 | 0.12iBl | 1.1 i | 7 |
| EG19 | 1.1 | 152 | <0.006 | 0.28 i | <0.04 | 1 i | 1.2 i |
| EG20 | 2.1 | 508 | <0.006 | 0.77 i | 0.13iBl | 1.2 i | 4.5 i |
| EG21 | 11 | 2540 | 0.031 i | 7.5 | 0.98 i | 2.4 i | 44 |
| EG22 | 1.6 | 217 | <0.005 | 1.2 i | 0.32iBl | 1.2 i | 6.6 |
| EG23 | 0.33 i | 17 i | <0.005 | 0.51 i | 0.17iBl | 1.2 i | 2.5 i |
| EG24 | 12 | 1100 | 0.038 i | 8.6 | 0.76 i | 2.7 i | 54 |
| EG25 | 11 | 1340 | 0.034 i | 8.2 | 0.96 i | 2.3 i | 52 |

Table 3.11-3. Total metal concentrations [mg/kg] in sediments in Escambia Bay and River (cont'd).

| Sample ID | Pb | Mg | Hg | Ni | Se | Sn | Zn |
|---|---|---|---|---|---|---|---|
| EG26 | 7.2 | 1080 | 0.019 i | 5.8 | 0.93 i | 1.7 i | 31 |
| EG 27 | 2.3 | 68 | <0.006 | 1.2 i | <0.04 | 0.95 iBl | 7.2 |
| EG 28 | 12 | 848 | 0.098 i | 8.9 | 2.2 i | 4.2 i | 41 |
| EG 29 | 0.41 i | 7.1 i | <0.006 | 0.89 i | <0.04 | 0.86iBl | 4.5 i |
| EG 30 | 20 | 3360 | 0.069 i | 12 | 2.3 i | 2.9iBl | 72 |
| EG 31 | 3.7 | 549 | 0.011 i | 2.4 | 0.38iBl[3] | 2iBl | 12 |
| EG 32 | 3.4 | 699 | 0.015 i | 2.4 | <0.04 | 0.96iBl | 14 |
| EG33 | 5.9 | 1370 | 0.027i | 3.8 | 0.6i | <0.83 | 25 |
| EG34 | 18 | 3380 | 0.055i | 12 | 1.7i | <1.3 | 79 |
| EG35 | 3 | 426 | 0.007i | 1.2i | 0.14i B | <0.64 | 8 |
| EG36 | 11 | 3350 | 0.088 | 6.5 | 1.7 i | <1.5 | 41 |
| EG37 | 24 | 4110 | 0.069 i | 15 | 2.5 i | <1.6 | 100 |
| EG38 | 35 | 7470 | 0.091 i | 21 | 2.2 i | <2.3 | 130 |
| EG39 | 8.1 | 2030 | 0.009 i | 5 | 0.23 i | <0.66 | 31 |
| EG40 | 24 | 5370 | 0.1 i | 15 | 2.5 i | <2.3 | 94 |
| EG41 | 9.3 | 1230 | 0.033 i | 5.5 | 0.96 i | <1.2 | 31 |
| EG42 | 15 | 1160 | 0.04 i | 11 | 1.4 i | <1.1 | 66 |
| EG43 | 26 | 4420 | 0.093 i | 21 | 3.5 i | <2.4 | 93 |
| EG44 | 5.4 | 500 | 0.025 i | 3.4 | 0.27 i | <0.88 | 21 |
| EG45 | 15 | 1710 | 0.068 | 8.4 | 1.2 i | <1.3 | 59 |
| EG-46 | 17 | 749 | 0.06 i | 12 | 0.5 i | 3 i | 71 |
| EG-47 | 18 | 763 | 0.083 | 16 | 1.5 i | 3.4 i | 109 |
| EG48 | 34 | 10200 | 0.098 | 17 | <1.5 | 0.9i | 90 |
| EG49 | 47 | 8810 | 0.11 | 22 | 1.8i | 0.9i | 127 |
| EG50 | 33 | 6210 | 0.066i | 17 | 1.5i | 0.8i | 99 |
| EG-51 | 28 | 6600 | 0.096 | 16 | 3.2i | 1.6iBl | 103 |
| EG-52 | 22 | 3840 | 0.044i | 12 | 1.1i | 1.1iBl | 80 |
| EG-53 | 40 | 7690 | 0.092 | 20 | <1.3 | 2iBl | 121 |
| EG-54 | 41 | 7410 | 0.09 | 19 | <1.2 | 1.7iBl | 121 |
| EG 55 | 47 | 12200 | 0.1 | 21 | <1.5 | 2iBl | 124 |
| EG 56 | 50 | 10300 | 0.079i | 22 | <1.4 | 1.5iBl | 132 |
| EG 57 | 22 | 7560 | 0.065i | 11 | <1.1 | 1.7iBl | 65 |

1. i is a data qualifier and indicates that the reported value is between the laboratory method detection limit and the laboratory practical quantitation limit.

2. < indicates concentration is less than the MDL (minimum detection limit) and that no analyte was detected.

3. Bl indicates the method blank shows detection of the analyte to at least 20% of its detection in the sample.