Sediment and water pollution in Bayou Chico, Pensacola, FL.

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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 toxic pollutants in Bayou Chico with an emphasis on possible superfund site impacts upon the Bayou. Kristal Flanders managed the spatial databases for the project and drafted the maps. Her assistance has been invaluable. Gustav Cancro, Brian Bradley and Nicholas Balderston helped with the fieldwork and some laboratory procedures.

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ABBREVIATIONS and ACRONYMS

- 2378 TCDD Tetrachlorodibenzo-p-dioxin
- ACW American Creosote Works Superfund Site
- AET Apparent Effects Threshold
- APHA -American Public Health Association
- AST Above ground storages tanks
- ATSDR Agency for Toxic Substances and Disease Registry
- BP Years before present
- CERCLA Comprehensive Environmental Response, Compensation, and Liability Act
- Cfs Cubic feet per second
- CWA Clean Water Act
- DNAPL Dense Non-Aqueous Phase Liquid
- DNT Dintrotoluene
- DWS Drinking water standard (used on maps)
- ECHD Florida Department of Health Escambia County Health Department
- ECUA Emerald Coast Utilities Authority
- DGPS Differential GPS
- FDEP Florida Department of Environmental Protection
- FDEP MCL Florida Department of Environmental Protection, Maximum Contaminant Level
- FDOT Florida Department of Transportation
- FLAAS Flame atomic absorption spectrometry
- ECHD Florida Department of Health Escambia County Health Department
- GCTL Groundwater Cleanup Target Level
- GFAAS Graphite furnace atomic absorption spectrometry
- GIS Geographical Information Systems
- HAL Health advisory level
- HMW High molecular weight
- HRL Health reference level
- HPLC High Performance Liquid Chromatography
- HDPE High density polyethylene

IARC - The International Agency for Research on Cancer (IARC), part of the World Health Organization.

LDPE - Low density polyethylene

LMW - Low molecular weight

LNAPL - Light non-aqueous phase liquid

MPRSA - Marine Protection, Research and Sanctuaries Act

MCL - Maximum contaminant level

MEK - Methyl ethyl ketone

MPZ - Main producing zone of the aquifer

NPL - National Priorities List

OMV - Omni-Vest Landfill

OU1 - Operational Unit 1

OU2 - Operational Unit 2

PAH - Polycyclic Aromatic Hydrocarbons or Polynuclear Aromatic Hydrocarbon

PCA - Principal component analysis

PCE - Tetrachloroethene

PEL - The probable effects level are concentrations above which adverse effects on biota are probable.

PERCH - Partnership for Environmental Research and Community Health

PCB - Polychlorinated biphenyls are a group of synthetic polychlorinated aromatic hydrocarbons.

pCi or picoCurie - One trillionth of a Curie; A unit of radioactivity which is equal to 3.7 x 1010 Bq (Becquerel)

PCP - Pentachlorophenol

PLI - Pollution load index

POPs - Persistent Organic Pollutants

ppb - Parts per billion (ppb or 1µg/L)

ppt - For salinity parts per thousand

P&A - Pensacola and Atlantic Railroad

PRP - Principal responsible party

r - Correlation coefficient, reflects the degree of linear relationship between two variables.

RCRA - Resource Conservation and Recovery Act

RI/FS - Remedial investigation/feasibility study

RO - Reverse osmosis

ROD - Record of Decision

- RPM Revolutions per minute
- SIM Selected ion monitor mode
- SCL Soil cleanup level
- SO₄ Sulfate ions
- SDWA Safe Drinking Water Act
- SOC Substance of concern
- SV Screening value
- SVOC Semivolatile organic compounds
- TCE Trichloroethene
- TEL Threshold effect level
- TEQ Dioxin toxic equivalents
- TMDL Total maximum daily loads
- USACE United States Army Corps of Engineers
- USEPA United States Environmental Protection Agency
- USEPA TAL Target analytes list for metals
- USEPA TCL VOCs Target compound list volatile organic compounds

EXECUTIVE SUMMARY

The PERCH (Partnership for Environmental Research and Community Health) Project on Bayou Chico was designed to address community concerns relating to environmental health issues for Bayou Chico. The Bayou has a long history of industrial pollution and is generally considered to be the most polluted of the three urban bayous in the Pensacola area. Point sources and non-point sources have led to high levels of pollutants - including trace metals, PAHs, PCP, dioxins/furans and PCBs. The Bayou is also adjacent to the American Creosote Works site, a Priorities List site that may be affecting the Bayou. Additionally, the Bayou is subject to urban runoff and stormwater discharges into it. Pollutants affecting the water quality of the Bayou, and the effect of water quality on bayou flora and fauna, have been the subject of many investigations. The State of Florida classifies Bayou Chico as suitable for recreational uses and as suitable for the propagation of fish and wildlife.

Human activities have likely adversely affected Bayou Chico from the time European settlers entered the area. Initial impacts would have been caused by land clearing for agricultural and logging activities, and military encampments. Industrial development of the area started in the 1820s and 100 years later the Bayou was allegedly so polluted that logs could be stored in the Bayou without fear of shipworm damage. By the 1950s governmental entities within the State of Florida were aware that environmental problems existed in the Pensacola Bay System and its bayous. Fish kills were common in the 1950s and 1960s and remedial dredging was considered. More recently, efforts have been undertaken to reduce pollution and its adverse effects, including elimination of some industrial and domestic waste water releases that previously entered the Bayou.

Review of the scientific literature shows that the quality of the water and sediments in Bayou Chico has been and still is affected by an assortment of pollutants. In the 1970s organic pollutants were found to be many times the typical values for coastal sediments. PCBs and dioxins were first studied in the 1990s and detected at high levels. A recent PERCH study found elevated levels of PCBs and dioxins/furans in seafood from the Bayou. Trace metals were studied by a series of investigations and invariably were found to be elevated in the main part of the Bayou and between two topographic constrictions in the northern half of the Bayou. Organisms are affected by the pollution of the Bayou and show diminished density and diversity. Two nearby industrial sites have well documented environmental problems but their impacts on the Bayou are not well known.

The present study initially used existing environmental data to examine the location and concentration of contaminants affecting water and sediment quality of the Bayou. The data were incorporated into a geographic information system (GIS) and were utilized in prioritizing research efforts based on perceived gaps in the existing information.

Several gaps were found to be present in the existing information about the environmental state of Bayou Chico, even though the Bayou has been studied extensively. One outstanding question is if relationships exist between the elevated PCB and dioxin/furan levels encountered by another PERCH project in seafood from the Bayou and pollution of the Bayou's

water and sediments. The presence of petroleum storage tanks and human activities that use petroleum products suggest that petroleum contamination may be present in the Bayou, but this has not been fully addressed by any other study. The present study focused on two polluted industrial sites that are located close to the Bayou. The pollution at these sites has been studied, but the potential influence of the pollutants on the Bayou has not been thoroughly evaluated. Plans exist to dredge the navigation channel of Bayou Chico and to dispose the dredge spoil in a sand pit a short distance north of the Bayou. Because of the geology of the area the sand pits may hydrologically communicate with groundwater and additional consideration of the potential implications of the pollution of the sediments that will be dredged is warranted.

The fieldwork of this project took place June to October 2005. The bathymetry of the Bayou was surveyed with an echosounder and differential GPS. Seven vibracores with depths up to 2.91 m were collected at the mouth of the Bayou and just outside the Bayou off Sanders Beach in Pensacola Bay. Three other cores, up to 1.65 m were collected south of the Omni-Vest site. On land, just north of Sanders Beach six manual soil borings were carried out. In the Bayou 22 composite sediment samples were obtained with a ponar grab sampler. At seven sites surface water samples were collected with a Van Dorn sampler.

Total petroleum was found in all samples, a result that is not unusual for an urban water body. Total petroleum was lowest near the mouth of the Bayou, in spite of the location of petroleum storage tanks in that area, but increased markedly in the north and main sections of the Bayou. Low levels near the mouth are consistent with an exchange in that area of bayou water and sediment with less polluted materials from Pensacola Bay. Sediment quality guidelines for Florida marine sediment do not appear to exist for total petroleum but comparison with other studies shows that levels of petroleum in Bayou Chico are comparable to those in marine sediments near industrial and port facilities elsewhere. Qualitative analysis of the composition of total petroleum suggests that the predominant petroleum hydrocarbons are in the heavy oil range in the arms of the Bayou, and of diesel range in the main body.

Some sediments at 2 m depth at Sanders Beach have high levels of PAHs that are of creosote origin. Given that creosote was used at ACW and that groundwater movement at ACW is towards Sanders Beach this seems to indicate that pollutants from the ACW site are impacting these sediments. However, the PAHs may also come from other sources since it appears that part of the beach is underlain by anthropogenic materials. Surface sediments at Sanders Beach, and shallow and deep sediments in the nearby mouth of Bayou Chico, have relatively low PAH concentrations and show no evidence for a creosote origin. In the Bayou PAHs are present in high concentrations in surface sediments and appear to have a non wood treating origin, indicating they did not originate at the ACW site.

Dioxins/furans are also contaminants of concern at ACW but they are not present at high concentration in the Sanders Beach area or the mouth of the Bayou. Dioxin/furan TEQs are high in the rest of the Bayou and often exceed their AET. Among other places, they were found to be high near the spoil island in the Bayou where another PERCH study collected blue crabs that were high in dioxin/furan TEQ. PCP was also found in areas of the Bayou distant from the ACW. The dioxin/furan TEQs and PCP concentrations were not high near the seemingly obvious source at ACW. However, congener profiles are consistent with an origin from wood treating

wastes and statistical analysis show a relationship between congener profiles at the mouth of the Bayou and in groundwater at the ACW site. This strongly suggests that the ACW site is affecting the lower part of Bayou Chico. The high PCP level and dioxin/furan TEQ elsewhere in the Bayou imply that either wastes from ACW are transported over longer distances than previously known or that dioxins/furans and PCP were released into the Bayou in some other and unknown way.

The present study is the first known to us that examines the full suite of 209 PCB congeners in Bayou Chico sediments. For PCB mass concentration five sites out of seventeen exceed the PEL and an additional eight exceed the TEL. This shows that PCBs are a ubiquitous component of Bayou sediments and together with the dioxins/furans they are likely to present a hazard to human health due to their potential for bioaccumulation in seafood. Their presence has been confirmed in Bayou Chico seafood by a related PERCH study.

Concentrations and profiles of dioxin-like PCB and dioxin/furan congeners were compared for sediments from the present study and tissues of the blue crab <u>Callinectes sapidus</u> Rathbun and the oyster <u>Crassostrea virginica</u> Gmelin from another PERCH study (Karouna-Renier et al., 2006). PCB 118 is the most common dioxin-like PCB in sediments and tissues. Bioaccumulation is higher for dioxin-like PCBs than for dioxins/furans in all tissues. The crab hepatopancreas consistently have higher concentrations for dioxin-like PCBs and dioxins/furans than do oyster tissues; crab muscle tissue has the lowest concentrations. Profiles of dioxin-like PCBs in tissues reflect more closely the profiles in sediments than do dioxin/furan profiles. Principal component analysis and cluster analysis demonstrate, however, that the profiles for the tissues are more similar to each other than to the profiles for the sediments from the collection stations. This indicates that the organisms bioaccumulate the various congeners selectively, although there is some influence of the profiles in the sediments on the organisms. The most predominant dioxin/furan congeners in both sediments and tissues were OCDD and 1,2,3,4,6,7,8-HpCDD.

Other semivolatile organic compounds were either not detected or present at very low concentrations. Volatile organic compounds were also either below detection limit or present at very low concentrations. Some volatile organic compounds are substances of concern at the Omni-Vest and the ACW sites but the present study did not find evidence that these substances are affecting Bayou Chico or the Sanders Beach area.

We tested for 9 trace metals in surface sediments from 26 sites. Thalium was not detected, Sb was detected in one sample, Cd in 11, Hg in 23, and As, Cr, Cu, Pb, and Zn were detected in all 26 samples. The respective TELs are exceeded by As, Cr, and Cd; the PEL is exceeded by Cu, Pb, Hg, and Zn. The latter four metals also exceeded their PEL in Bayou Texar, as shown in another PERCH study, but did not reach the levels they reach in Bayou Chico. Even compared to other urbanized or industrialized catchments the Bayou Chico levels are high. Since most of the metals exceed their TEL or PEL they can be assumed to have negative impacts on biota in the Bayou. The lowest trace metal concentrations are present at the mouth of the Bayou, as is the case for most pollutants, due to the interaction with the less polluted sediment and water from Pensacola Bay. The highest concentrations are generally reached near the spoil island and between the two constrictions in the northern part of the Bayou. Observations for trace metals in

samples south of the Omni-Vest site corroborate findings for VOCs and fail to show an influence of the Omni-Vest site on the Bayou.

The US Army Corps of Engineers has submitted a permit application for the dredging of the navigation channel in Bayou Chico and the disposal of the spoils in a sand pit northwest of the Bayou. Results from a study by EA (2000), used to support the application, seem to be based on a deficient sampling scheme and somewhat superficial data analysis. Two of the six sampling locations of EA (2000) are located in the northern section of the navigation channel. This section of the channel is in the most polluted region of the Bayou, as shown by the present and several previous studies. It seems that a thorough evaluation of the environmental quality of the sediments to be dredged can only be made with more samples from that section. Spoils from the section of the navigational channel located in Pensacola Bay are being considered for nourishment of Sanders Beach. It appears that only surface samples have been studied in this region. It is suggested that sediment cores also be studied because previous dredge spoils have been dumped in areas of Pensacola Bay that are adjacent to Bayou Chico.

Another potential issue is the behavior of the contaminants in the spoils after disposal. The pH, Eh and salinity of the sediments will change after disposal, which is likely to affect (i.e. increase) the mobility of the pollutants. Elutriation with bayou water, as carried out for the permit application may not be the most appropriate test to represent the environmental conditions and pollutant behavior after disposal. Relying on the upward gradient of the aquifer at the disposal site to help minimize contamination of the aquifer by pollutants that would leach from the spoils may not be appropriate because this gradient could potentially diminish or even reverse.

Many of the pollutants examined in the present study exceed regulatory guidelines, including PAHs, dioxins/furans, PCBs and trace metals. Even though these pollutants may be unlikely to directly affect humans, because of limited direct contact of people with the sediments of Bayou Chico, they do have the potential to indirectly affect humans. A case in point are the elevated levels of dioxin/furan TEQ and some trace metals found in seafood by another PERCH project. Negative effects on the living environment are also manifested in the reduced populations of some biota. The present study did not find evidence of an effect of the ACW site on the surface environment at Sanders Beach. This is particularly noteworthy because part of the beach area is in front of the Pensacola Yacht Club ditch that at one time has been a major release point to the Bay of creosote wastes from ACW. However, some deeper sediments at Sanders Beach are heavily polluted. The Omni-Vest landfill site to the north of Bayou Chico does currently not seem to affect the Bayou via Jackson's Brach Creek. Considering the most likely sources for the encountered pollution, solutions for the poor environmental condition of Bayou Chico include reduction of inputs from industry and stormwater.

1.0 INTRODUCTION

Bayou Chico is a small urban bayou that through much of its modern history has been characterized by industrial, commercial, and non-point activities that have polluted its sediments and water. The contamination of sediments in Bayou Chico, and many other water bodies of the United States, has emerged in recent years as an ecological and human health issue of concern. The EPA and others estimate that approximately 10 percent of the sediment underlying our nation's surface water is sufficiently contaminated with toxic pollutants to pose potential risks to fish and to the humans and wildlife that eat fish and shellfish. This represents about 1.2 billion cubic yards of contaminated sediment out of the approximately 12 billion cubic yards of total surface sediments (upper five centimeters) where many bottom-dwelling organisms live, and where exchange processes between the sediment and overlying surface water occur. Additionally, approximately 300 million cubic yards of sediments are dredged from harbors and water ways annually to maintain commerce, and about 3 to 12 million cubic yards of those are sufficiently contaminated to require special handling and disposal (USEPA, 1998).

Contaminated sediments can affect fish and wildlife by contributing to the bioaccumulation and biomagnifications of contaminants in the food chain. The contaminated sediments pose a threat to human health when the pollutants in the sediments bioaccumulate in edible aquatic organisms. There are numerous examples of cases where fish consumption advisories or bans have been issued for Persistent Organic Pollutants (POPs) such as polychlorinated biphenyls (PCBs), mercury, and dioxins because of the transfer of the pollutants into the food chain (USEPA, 1998). A related PERCH study is presently investigating the bioaccumulation of POPs in seafood tissues (PERCH Task A: Bioaccumulation of chemical contaminants in seafood in the Pensacola Bay region).

2. GEOGRAPHIC DESCRIPTION

2.1. Physiography

Bayou Chico is located in Escambia County, Florida and has a surface area of 216 acres (Map 1). It is the smallest of three urban bayous in Pensacola and the most heavily industrialized waterway in the area. The lower regions of the Bayou include its mouth that opens to Pensacola Bay and a west branch that connects to Jones Creek that carries the drainage coming from the Jones Swamp watershed. The upper Bayou begins at an abrupt constriction (site of former rail bridge, Map 1) south of the W. Navy Blvd. bridge. The Bayou immediately widens just north of this constriction. After a short distance, at the W. Navy Blvd. Bridge, the Bayou abruptly constricts again. To the north of this second constriction it widens again somewhat to next bifurcate into two branches forming the top of a T. The northwest branch of the T connects to Jackson's Branch Creek and the northeast branch receives a stream simply called the Northeast Branch Tributary. Jackson's Branch Creek flows through an area of three flooded, abandoned sand mines (Clark Sand Pits) that contains the Omni-Vest Landfill (OMV), an abandoned hazardous waste site (Map 1). The eastern shore of the lower Bayou and nearby Sanders Beach are underlain by the Sand and Gravel aquifer that has been contaminated by releases from the American Creosote Works Superfund Site (ACW) just to the north. Presently, land use around the lower Bayou is predominantly commercial and light industry related mostly to boating (Figure 1). These activities include the Pensacola Marine Complex, a shipyard, marinas, and petroleum barge off-loading with large above ground storage tanks. The upper regions of the Bayou are mainly residential.



Figure 1: Patti Shipyard on the north bank of the main body of Bayou Chico.

The Bayou initially was formed as a minor tributary by the downcutting of the Escambia River during the glacial stages of the Pleistocene Epoch (Stone and Morgan, 1991). At the peak of the last major glacial stage (about 18,000 BP), sea-level was approximately 350-450 ft below today's level (Curray, 1960) and the Northwest Florida shoreline was 15-20 miles more seaward. The Escambia River eroded a very deep channel to the lower Gulf baselevel. This resulted in the precursor of Bayou Chico also cutting an entrenched relatively steep-sided valley. Jones Creek, Jackson's Branch Creeks, and the Northeast Tributary were all smaller streams feeding into the entrenched precursor of the Bayou. At the beginning of the Holocene interglacial, a rapid rise in sea-level occurred ending about 6,000 BP. Flooding formed the modern estuary system called the Pensacola Bay System, including Bayou Chico (Curray, 1960; BARC, 2005).

The watershed of the Bayou is approximately 6,630 acres. Land surface elevations range from sea level to a maximum of about 90 ft above sea level. Elevations are highest in the northern portion of the watershed (near New Warrington road and Mobile Highway, Map 1). Here, elevations range from about 70 to 90 feet above sea level with the surface topography being relatively flat. This area corresponds to the highest of several relict marine terraces found in the watershed. Moving south off this terrace, the land surface drops sharply along an east-west lying escarpment. Across the escarpment, which runs generally along and parallel to Jackson's Street, elevations drop about 50 ft. This drop occurs over a distance of about 2,000 ft. The northeast tributary lies on the east side of Bayou Chico and flows from east to west along the toe of the escarpment. Jackson's Branch lies on the west side of the Bayou and flows from west to east along the toe of the escarpment. Roughly three quarters of the watershed lies below this principal escarpment. Much of that area is characterized by a ridge-and-swale topography. Land surface elevations are generally less than 25 feet above sea level and the land is relatively flat. Several low, relict terraces and shorelines are present. These features generally parallel the coast and trend in a southwest-northeast direction. The principal surface drainage feature in the watershed (Jones Creek) lies in a broad, shallow swale between two ridges. This swale extends eastward into Bayou Chico, becoming one of its principal arms. In the headwaters of Jones Creek is a large wetland known as Jones Creek Swamp. The flat terrain, low permeability soils and poor drainage result in a relatively high water table in the extreme western portion of the watershed. The area east of Bayou Chico and within the city limits of Pensacola is relatively flat. Elevation here ranges from sea level to about 20 ft above sea level (Stone and Morgan, 1991).

The Bayou and its watershed lie in the coastal plain province, a major physiographic division of the United States. Geologically the region consists principally of unconsolidated sands, silts, and clays deposited before the shoreline of the continental mainland reached its present position. The region has a humid, warm-temperate climate. Summers are long and warm, and winters are short and mild. The average summer temperature at Pensacola is slightly more than 80° F, the average winter temperature is 55° F. The annual rainfall is fairly high at nearly 62 inches on average. Rainfall is well distributed throughout the year, with a peak in July and August, and often falls as heavy afternoon thunderstorms.

2.2 Clean Water Act classification

The water quality of Bayou Chico is classified on the FDEP's 1998 303(d) List as 3M or suitable for recreation, propagation, and maintenance of a healthy, well-balanced population of fish and wildlife in marine water. This system of classification is not based on the chemical composition or toxicity of the sediments and is based completely on the water column. However, the Bayou was also listed as impaired or polluted relative to coliform bacteria and mercury in

fish tissues. A more recent 2002 assessment on an EPA website listed pathogens and organic enrichment/low DO as reasons for impairment. The impairment was listed as occurring in the upper arms, including the one receiving water from Jackson's Creek and closest to the proposed disposal site for dredge spoils. The Bayou was still classed as 3M in 2006 (FDEP, 2006b).

2.3 Tidal flow

Bayou Chico is a mesohaline tidal estuary. Its tidal regime is microtidal and diurnal, with a periodicity of approximately 25 hours. The mean tidal range is 1.15ft. Mean high tide is + 0.94ft NAVD88, mean low tide is -0.22 ft NAVD88. The movement of marine waters via tidal actions into and out of an estuary is essential to maintenance of its environmental health. We used a 2004 aerial orthophoto collected by USGS and processed for the Northwest Florida Management District to measure the width of the Bayou at its mouth. At the narrowest points, just southeast of Pensacola Yacht Club, the width was no more than 66 m or 217 ft. The horizontal positional accuracy of the orthophoto is estimated to be 0.08 m. Tidal flow into and out of the upper arms of the Bayou appears to be further restricted by the approaches of a bridge for W. Navy Blvd. and the remnants of a former railroad bridge (Map 1). Flow velocity measured at 60 % of the depth between these two constrictions at mid-tide between high and low tide was 0.2 ft/sec southward; between low and high tide it was 0.2 ft/sec northward. Flow at the surface was visually observed to be wind driven.

2.4 Sedimentation and bathymetry

In Bayou Texar, about 7 km northeast of Bayou Chico, sedimentation studies have shown that large volumes of sediment are accumulating (Liebens et al., 2006). According to Stone and Morgan (1991) the same is happening to Bayou Chico. Sand is allegedly reworked from Pensacola Bay to the lower reaches of Bayou Chico while the fine sediments are carried and deposited further up stream but very few scientific data are available on which to base such statements. Stone and Morgan (1991) also state that during the past 100-150 years natural and primarily inorganic sediments from throughout the Bayou Chico drainage basin have been progressively filling in the Bayou with sediments that contain trace metals and organics from residential, commercial, and industrial activities. The fact that dredging is necessary periodically to maintain the barge channel does suggest that sediment accumulation has been taking place and sedimentation would be consistent with general knowledge about urban bayous. However, there have been no long term studies to quantify or characterize sediment accumulation in Bayou Chico. A report by Glassen et al. (1977) includes a figure showing that most of the Bayou's bottom is covered with "sludge" (Map 2). In some areas the accumulations of sludge are more than 10 ft. thick. Glassen et al. (1977) commented that generally the contact between the sludge and underlying sand is distinct, suggesting that the depositional environment in the Bayou underwent a sudden rather than gradual change. The sudden change in sedimentation might coincide with onset of heavy pollution from industry such as Newport Industries releasing large quantities of wastes in about 1916 or the erosion resulting from the felling of the original forests. On the basis of data collected from 48 sampling stations it was calculated that the total volume of sludge contained within the Bayou was on the order of 2 million m³. The deeper sludge layers were thought to occur in areas that had been dredged or had been filled in. The smallest sludge accumulation occurred at the Bayou's mouth, the northeast central Bayou, at the extremities of the upper Bayou's arms, and in a narrow fringe around the shoreline (Glassen et al., 1977).

Sludge settled into the deepest basin areas of the Bayou and had not been deposited where wave, tide, or inflow action was concentrated as a result of shallow depths or narrow constrictions.

An early map (Map 3) from Pensacola Harbor and Bar, Florida Survey shows the 1822 bathymetry of the Bayou. The bottom contours and sediments on that map are very different from what is found today. It appears that there was no navigable channel from the Bay to the Bayou. It has been suggested that dredging events after the 1926 hurricane resulted in changes in the lower part of the Bayou (Killam, 1981a-e). According to local attorney Tom Ratchford, who represented a Pensacola citizen group seeking to cleanup Bayou Chico in 1981, the natural mouth of Bayou Chico was literally closed by the 1926 hurricane. It was claimed that the new manmade channel which connects the Bayou to the Bay probably had an impact on the degree of natural tidal action in the Bayou. There is no evidence to confirm or deny this assertion for changes in tidal flushing due to changes in the entrance channel. By 1977 the dredged channel present during World War II had filled in with unconsolidated sediment (Glassen et al., 1977). Unfortunately, we only have dredging plans made prior to World War II (Map 4) and no actual bathymetric data of the Bayou. More recently Bayou Chico was described as shallow in most places with the dredged channel having mid-depths of 8 ft and maximum depths of up to 18 ft (Wood and Bartel, 1994). The present study shows that some limited portions of the channel exceed 18 ft in depth.

3. SEDIMENT AND WATER POLLUTION: LITERATURE REVIEW

It is common to blame point pollution as the primary cause for environmental deterioration but in many cases estuaries are more impacted by non-point pollution from stormwater runoff from construction sites, roads, malls, residences, parks, golf courses, etc. However, in the case of Bayou Chico industrial point pollution does appear to have had significant environmental impact. The Bayou has a long history of industrial pollution (Matheson, 2004). Presently it has shipbuilding activities, unloading of petroleum tanker barges to large AST (above ground storages tanks), and contains numerous marinas in its lower reaches. It is predominantly residential in its upper reaches.

3.1 History of urbanization and industrial impacts on Bayou Chico

One of the most important aspects of Bayou Chico's environmental history has been the role of concerned citizens with the environmental situation of Bayou Chico. In recent years there has been a Bayou Chico Association which has attempted to prevent industrial pollution of the Bayou. Their thoughts on the Bayou are probably best summed up in a letter sent by LaVerne Matheson, a past president of the Bayou Chico Association, to The Pensacola News Journal (Matheson, 2004):

"Until 1916 Bayou Chico was a pristine bayou used by Gen. Bernardo Galvez in the late 1700s, Gen. Andrew Jackson in the early 1800s, and then Braxton Bragg in the Civil War. This was evidently the place to camp with the troops: clean water, white sand bottoms and springs.

....It surely was a beautiful and clean body of water. Then in 1916 Newport Industries built a plant on the Bayou to process pine stumps into turpentine and other Naval supplies. Supposedly the pine stumpage was all that remained from the total sale of longleaf pine in Northwest Florida. Newport Industries needed the water to transport the stumps to the plant, but also as a place to dispose of the waste. Bayou Chico was the recipient. In 1927 Armstrong Industries moved to Pensacola and built a plant on Bayou Chico. They used a byproduct from Newport Industries, and then Armstrong disposed of their cellulose fiber waste into Bayou Chico. In 1954 Don T. Turner, sanitarian, and William M. Beck Jr., biologist, of the Florida Health Department completed their studies of contaminants in Bayou Chico. The report states as follows: "The bulk of the solid material now deposited on the bottom in Bayou Chico is cellulose fibers characteristic of those originating from wood. These fibers break down very slowly; therefore, the great depth of sludge found on the bottoms (2 feet to 10 feet) is understandable.

In the late 1950s the homeowners filed a lawsuit against the large corporations, requesting they cease dumping their waste into Bayou Chico. The Bayou Chico Association won the lawsuit and the corporations were told to cease dumping their waste into the Bayou immediately. The Bayou Chico Association is still active and still trying to restore Bayou Chico to its one-time pristine condition. We don't have our eyes watering from turpentine fumes around the Bayou anymore.

In the 1950-60s there was very little evidence of fish in the water or birds around the Bayou. Today Bayou Chico has an abundance of bird life and fish and the dolphins come into the Bayou to feed. You can also find oysters and shrimp in the Bayou.

Will Bayou Chico be pristine by the year 2030? I doubt it! ...".

Mr. Matheson expresses a commonly held belief that point industrial pollution is to blame for the majority of Bayou Chico problems. It is difficult to document the original environmental conditions of Bayou Chico, but from historical study we can see a progression of events that prestaged the deteriorated ecological state that was observed on Bayou Chico in the 1950's. An increase in population and human activities is generally associated with environmental impacts. Reviewing the development as reflected by human activities on Bayou Chico can give insights relating to origins and types of environmental impacts that have occurred.

One of the earlier documented uses of Bayou Chico was for military encampments. The upper reaches of Bayou Chico were used for the maintenance of troops, and Spanish troops during the Battle of Pensacola found it a good place for a military camp. In the early 19th century there was a site on the Bayou known as Cantonment Clinch that was reportedly used by General Jackson during the campaigns in the War of 1812 when he defeated Spanish forces in Pensacola. A permanent military post was set up at the head of Bayou Chico in about 1821 because of a yellow fever epidemic that caused the Pensacola population to flee the city for the county side. The site went out of military use in 1829 and was used again by confederate forces during the Civil War (Killam, 1981a-e).

A British map from 1780 shows the beginning of exploitation of what has become the Pensacola area (Gauld and Des Barres, 1780; Map 5). An excerpted portion of this map shows significant differences in the mouths of Bayous Chico and Texar from what is observed today. There is very little development evident from this map. However, parcels of land had been surveyed for presumably future development of natural resources. In the various parcels shown on this map one can see a parcel drawn over a wetland area in lower Carpenter's Creek. Timber at that time was a readily exploitable resource. The Pensacola Bay System with its bayous and rivers provided transport routes from the land to sea. A sawmill was constructed there on Carpenter's Creek in 1767 (Pensacola Historical Society, 2004) just north of Bayou Texar. This demonstrates that the British Colonists of the time were using the timber resources of Northwest Florida around Carpenters Creek. Even though the British forces lost out to the Spanish in the fighting that began in 1781, tree felling and removal if not actually occurring on Bayou Chico during British rule would have eventually spread to this watershed. Tree removal is often accompanied by erosion and an increase in sedimentation of adjacent waterways. We have no records of environmental deterioration in Bayou Chico during the 18th and 19th centuries. However an increase in development that was gradual at first is evident from study of the few available documents. A general rule of the environmental thumb is that increased development causes increased impacts on adjacent waterways through increased runoff. A map of Pensacola Harbor and Bar, Florida Survey, 1822 shows no development in lower Bayou Chico (Map 3). In a period of about five years it can be seen that there was some development on the lower Bayou as is demonstrated by a map of property plats drawn in 1827 for the Bayou Chico area (Map 6). A fort and hospital were present at the northern end of the Bayou and a bridge and other structures at its mouth (Butler, 1827). By the latter part of the 19th century there was substantially more development in Pensacola. During the post-Civil War reconstruction period Pensacola became a boom town thanks to the yellow pine industry and shipping. The Pensacola water front in general showed a significant increase in activities by the 1880's and by this time rails links were completed with a bridge over Escambia Bay. In 1882 the Pensacola and Atlantic Railroad (P&A) bridge was completed across Escambia Bay. The P&A line to Chattahoochee was completed in August of that year finally giving Pensacola a rail route to the east (Buckman, 2003). Between 1865 and the early 1900's, northwest Florida and Pensacola became leading producers of yellow pine. During the 1880s there were 16 wharves over a 5 km stretch from Bayou Texar to Bayou Chico (Port of Pensacola, 2004). An 1895 map of the Bayou shows that

the Bayou was for the most part still undeveloped with the exception of an area near its mouth (Map 7). This area had a bridge on "Military Road" which later became known as Barrancas Avenue. The map shows the Bayou as it was before present day development and dredging changed the shoreline of many areas of the Bayou (Brown's Marine, 2006). The map also shows a second bridge with rails possibly for passenger trolleys and/or trains. Brent's Lumber Mill was at the Bayou's mouth and jutted out into the Bay connected by a bridge of some sort to the mainland (Map 7). Sanborn Insurance maps of the period also depict these structures for the mill (Stave, 1992). The projection of Brent's mill into Pensacola Bay alleviated the need for ships to navigate into the Bayou for log and lumber transport. It is not known what the depth of the Bayou entrance was at this time. The mill was in a good location to receive lumber from the interior by rail or road and after sawing to transport the lumber by boat. The presence of lumber mills was a dominant influence on this part of the Bayou for many years. The Weis-Fricker Mahogany Lumber Mill and Storage Yard operated on the Bayou for many years under the names of Patterson Lumber Co., Weis-Patterson, and Weis-Fricker. Ships would dock at the Port of Pensacola and discharge mahogany logs into the Bay (Stave, 1992). A small boat would "raft" the logs up and tow the "rafts" to the Bayou to await sawing at the mill (Brown's Marine, 2006). In the early twentieth century Pensacola was the major world port for the export of yellow pine. James R. McGovern stated in a description of the history of Pensacola that nature had endowed the hinterlands of Pensacola with majestic growths of long leaf pine which could be converted into excellent lumber for export (McGovern, 1976). There were approximately 16 mills operating in the vicinity of Pensacola in 1900. The presence of Brent's Mill is definitive proof that the lumber industry was established on the Bayou by this time. The presence of lumber mills was a dominant influence on this part of the Bayou for many years.

The industry and population near Bayou Chico does not appear to have initially increased when the rest of Pensacola was booming due to the production of yellow pine lumber (McGovern, 1976). Pensacola at this time began to develop naval stores industries to extract tars and turpentines. One such historic site (Pensacola Tar and Turpentine Company) on Escambia Bay can still be observed as cinders, rusting ferrous remnants, and two large concrete vats at about two hundred yards west of where Creighton Road dead ends on Escambia Bay. This is a hazardous waste site that apparently has had wells installed for ground water treatment. After the yellow pine timber resources were depleted Pensacola's economy was threatened but new source of raw materials for the naval stores industry was found. In 1916, Newport Industries set up an industrial process that was able to utilize the stumps remaining from the felled yellow pine forests to extract naval stores and Bayou Chico was used as a disposal site for the waste product. The stumps left by the felling of very large trees were a most significant resource that could be obtained with most of the cost presumably being the extraction of the stumps out of ground and transport to Newport (McGovern, 1976; Appleyard, 2004). Newport Industries subjected stumps to new techniques for the extraction of rosins and turpentine. It initially used 150 tons of stumps per day and employed over 200 workers. A large percentage of the pine stumps would have remained after extraction as a form of contaminated lignin-cellulose wastes. Some of it might have been used for fuel, but undoubtedly a significant amount of it would have been disposed of in the Bayou. In 1921 Weis-Fricker came to Bayou Chico and found that the chemical pollution present in the Bayou killed the teredo shipworm worm allowing Weis-Fricker to store mahogany logs shipped from South America in the Bayou without fear of shipworm damage to the submerged logs awaiting sawing (Killam, 1981a; Appleyard, 2004).

American Creosote Works was established in 1902 several city blocks to the west of the Bayou. It remained active until 1981 when the company filed for bankruptcy. Before 1950, creosote was the primary preservative chemical, and after 1950 pentachlorophenol (PCP) became the preferred chemical. Prior to 1970, operators discharged liquid process wastes into two unlined, 80,000-gallon percolation ponds, and these wastewaters also flowed to follow a drainage course into Bayou Chico and Pensacola Bay. This drainage in part was by a ditch, also characterized as an intermittent stream, that flowed through property that currently belongs to the Pensacola Yacht Club. This waste stream was observed to leave creosote appearing deposits on the adjacent Sanders Beach (Rostad and Pereira, 1987). Later, workers drew wastewaters off the ponds periodically and discharged them into designated "spillage areas" on site. Additional discharges occurred when heavy rainfall flooded the ponds, which then overflowed their dikes.

The beginning of World War I in Europe in 1914 had a stimulatory effect upon the economy of Pensacola in general and the Bayou Chico area specifically. A shipyard was reopened as the Naval Air Station in 1914 on nearby Bayou Grande and in 1917 the Pensacola Shipyard was opened on Bayou Chico (McGovern, 1976). For Pensacola Shipyard a site on Bayou Chico was selected and the Gulf, Florida, and Alabama Railroad built a spur to the site. The Escambia County Commissioners built a lift bridge over Bayou Chico. The rail line that crossed Bayou Chico allowed passenger trolleys to cross the Bayou to transport laborers from Pensacola to what is now NAS (Naval Air Station, Pensacola) and other parts of the Pensacola area. Increases in population during the war resulted in housing construction, some of which occurred in the Bayou's watershed (McGovern, 1976).

The Pensacola Street Car Company provided mass transit service with mule drawn cars for Pensacola. In 1888, the company operated a 3½-mile system with ten cars and a stable of 32 mules. At this time, the Pensacola Terminal Company purchased the system and added a ninemile steam powered service. This new service connected downtown Pensacola with Fort Barrancas located on the present Naval Air Station. Pensacola Terminal Company ran into financial difficulty and in 1897 was sold to the Pensacola Electric Terminal Railway, which in November of 1897 converted the mule drawn service to an electric trolley system. The old street railway was rebuilt to accommodate electric trolleys and commenced operations in March 1898. The line to Fort Barrancas continued steam-powered operations. Pensacola Electric Company's transit operations peaked in 1918, at which time the system consisted of 21.4 miles of track and 45 passenger cars. By 1931, the 30-year railway franchise was expiring and Gulf Power Company, the successor to the Pensacola Electric Company, supported by the Chamber of Commerce, decided that public transit needs would be better served by buses rather than railways (Escambia County Area Transit, 2006).

On January 2, 1926 one of Pensacola's most serious if not the worst industrial accident occurred resulting in the deaths of 15 men due to an explosion of a retort at Newport Chemical (Pensacola Journal, 1926). The damage was estimated to amount to \$200,000 in 1926 dollars. The explosion occurred in the retort building in a retort 20 feet in diameter and six feet deep. So hot were the flames that the reinforced glass in the windows of the structure melted and hung like icicles from the steel window sashes. Steel girders as large as a man's waist were twisted and bent by the intense heat. Automobiles belonging to employees of the company that were parked 150 yards from the retort building were completely demolished. The tires were blown off and in some instances the glass in the windshields melted. The building which housed the retort unit of the plant was demolished, only the steel frame and supports of the retort remained standing (Pensacola Journal, 1926).

In 1929 Armstrong Chemical was constructed on the Bayou to use wood byproducts left over from Newport's processes. In 1938 the Strook Wittenburg Company, later known as Ashland Oil and Refining, came initially to use the rosins derived from Newport's activities for the synthesis of rosins used for adhesives and in later years produced synthetic resins from petrochemicals. The industrial activity of the Bayou continued through World War II. In February 1942 Pensacola Shipyard and Engineering employed 7,000 workers, but it failed in a year. It was reconstituted as Smith's Shipyards and employed 900 workers, built 4 tankers, four barges, and several army tugs (McGovern, 1976). Weis-Fricker Mahogany Company supplied 300 contractors with plywood and related materials to make aircraft and other items (McGovern, 1976). By the 1950's Bayou Chico and other local water ways were in an obviously degraded state. Citizen groups were alarmed and this concern ultimately led to court action against Newport, Armstrong, and the City of Pensacola in an effort to stop the industrial release of untreated waste. Litigation was settled in 1957 when a court order was issued mandating primary treatment of industrial waste. In the late 1950's water quality improved but fish kills continued and waste was still entering the Bayou (Killam, 1981a,b,c)

Efforts were made at this time to implement remedial dredging of the Bayou as recommended by state health officials. In 1958 former Congressman Bob Sikes asked the US Army Corps of Engineers (USACE) to dredge Bayou Chico in connection with other improvements at the Port of Pensacola. The USACE said no, and Sikes then tried unsuccessfully to interest the US Navy on the basis of benefits related to defense (Killam, 1981a,b,c). Bayou Chico remained environmentally impaired and fish kills continued throughout the 1960's. The Weiss Fricker Lumber Company during the 1960's was reported to have complained about the anti-pollution requirements mandated by the court to cleanup Bayou Chico since this threatened the continuance of the antifouling properties of bayou waters. Weiss Fricker Lumber Company's procedure included storing logs in the Bayou since wood boring organisms were killed by the toxic bayou waters (Killam, 1981a,b,c).

Prior to 1971 there were at least eight industrial and domestic waste sources discharging directly into Bayou Chico (Glassen et al., 1977), and in addition American Creosote Works discharged contaminated stormwater into the Bay just outside of the Bayou's mouth (Pratt et al., 1993). By 1971, three of the industrial companies, Ashland Chemical, Newport Division of Tenneco Chemicals, and Armstrong Cork Co., that had released direct discharges into the Bayou diverted their discharge to the Main Street sewage plant. Armstrong Cork Co. and Newport Division of Tenneco Chemical jointly built a four inch forced main to tie into the municipal sewage system in 1971 (Pratt et al., 1993). Pratt et al. (1993) also state that a fourth unnamed industrial polluter ceased discharge at this time. However, industrial discharge of pollutants may have continued through overflowing stormwater ponds and percolation of waste waters into the aquifer (Thorpe et al., 1997). Additionally, Newport still continued to release wastes into the Bayou from impoundments (Thrope et al., 1997). Newport, through the years, has changed its processes and has undergone changes in ownership. Presently it is owned by Reichhold Chemicals. Originally, Newport's processing included heated retorts as part of its extraction procedures for removal of product from pine stumps. Later, when known as Newport Division of Tenneco Chemicals, it utilized various solvents including a blend of naptha-toluene extraction solvents. Major chemicals in use included phenols, toluene and ethylbenzene. Discharges of these solvents must have inhibited biological activity to a great extent (Glassen et al., 1977). According to local people, one could moor a boat in Bayou Chico and in a week or two the boat's bottom would be free of barnacles and piling timbers seemed to last 'forever' as boring

organisms were not a problem (Glassen et al., 1977). The Newport facility had twelve unlined impoundments for both process water and stormwater. Approximately 150,000 gallons per day of industrial wastewater was routed to the unlined impoundments. Stormwater runoff from the plant site was also routed to the impoundments after being processed (in later years) through an oil/water separator. During heavy rains, stormwater runoff which could not be accommodated by the basins was discharged from the oil/water separator directly to Bayou Chico. A consent order was executed on June 15, 1984, by the Florida Department of Environmental Protection (FDEP) to effect clean-up of contaminated ground water and cease indirect discharge of industrial wastewater and stormwater (from process areas) to Bayou Chico (Thorpe et al., 1997; NWFWMD, 1990).

Four of the point sources identified by Glassen et al. (1971) were domestic wastewater treatment facilities: Moreno Courts, Pen Haven, Correy Field, and Warrington waste treatment plants. The Corry field plant was diverted to the Warrington Plant in 1971. Pratt et al. (1993) reviewed FDER files for the permitting history and previous waste disposal practices of historical point sources of pollution. The authors estimated that the annual mean daily discharges from the remaining three sewage plants in the mid to late 1970's were: Moreno: 0.17 million gallons per day (Mgal/d); Pen Haven: 0.40 Mgal/d, and Warrington Plant about 1 Mgal/d. Pratt et al. (1993) calculated that the three plants combined had an estimated total for Biological Oxygen Demand (BOD) Constituents of 45,400 lbs/ year, Total Suspended Solids (TSS) at 41,600 lbs/ year, Total nitrogen at 47,900 lbs/ year, and Total phosphorus at 4,760 lbs/ year. The Moreno Courts output was diverted to percolation/evaporation ponds in April 1980. The Warrington plant, to which the Pen Haven had been diverted in 1983, was finally diverted from Bayou Chico to the ECUA Main Street waste water treatment plant in November of 1990 (Pratt et al., 1993; Thorpe et al., 1997).

A general estimate of the discharges to the Bayou by industry can be made based on De Sylva (1955), Musgrove (1965), Glassen et al. (1977), and USACE (1977). Newport Industries and Armstrong Cork Co. were discharging material with a very high BOD. They were discharging cellulose and several kinds of oil sludge similar to asphalt. Newport Industries had thirteen wells drilled between 1915 and 1954 (Musgrove, 1965). Pumpage started at 2,000,000 gal/d in 1916 and through the years grew to 8,000,000 gal/d by 1939. A significant portion of this pumpage must have been returned to the Bayou either directly from an outfall or via the groundwater from percolation/evaporation ponds. It can be calculated that for these two industries the BOD and total solids that entered the Bayou must have been about 3,000,000 lbs/ year each. Presently, most point pollution from waste water of domestic and industrial origin has been removed from the Bayou. Non-point pollution is still an issue with probable inputs from marinas, shipbuilding, metal recycling, and stormwater.

3.2 Pollution

3.2.1 Early studies

By 1950's there was a perception of environmental problems in the Pensacola Bay System by State of Florida authorities. Scientists were sent to investigate the lower Escambia River and Bay and Bayou Chico (De Sylva, 1955). De Sylva (1955) presented a grim picture of a water body that was heavily impacted by industrial waste disposal on the basis of a one day site visit. This visit was by request of the State Board of Conservation and was precipitated at least in part by an extensive fish kill. It was concluded that the most serious pollution was coming from two industrial plants and considerably lesser amounts from three domestic waste treatment plants. De Sylva (1955) concluded that the combined discharge from the industrial plants had an unusually high BOD, equivalent to that which would be found in raw sewage from a city of more than 100,000 people. The industrial plants discharged solids in the form of cellulose and several kinds of oil sludge similar to asphalt. The water was covered with a film of scum and a layer of sludge from 2 to 10 ft thick was present on the bottom. The entire area had an odor of hydrocarbons distinctive of tars and rosins. The shoreline of the Bayou was covered with layers of accumulated hydrocarbon sludge. As a consequence of these conditions, the Bayou was almost completely devoid of life, particularly in the lower part.

A Florida State Board of Health memorandum, dated February 14, 1969, described the results of a bottom survey in the upper portion of Bayou Chico and mentions that strong tar-like odors were noted. In April and May of 1969 the Florida State Board of Health conducted water quality surveys of the Bayou in response to the problems caused by the multitude of point and non-point sources discharging to Bayou Chico at that time (Pratt et al., 1993). The U.S. Army Corps of Engineers evaluated sediments in 1971 and 1974, and water quality in January and September of 1972. A draft report (USACE, 1977; quoted by Glassen et al., 1977) described sediments and water quality within the Bayou but is not available for further interpretation.

3.2.2 Polycyclic aromatic hydrocarbons (PAHs)

The PAHs are compounds composed of two or more aromatic (benzene) rings. PAHs may be divided into two groups, depending upon their mass: low-molecular-weight PAHs, containing three or fewer aromatic rings, and high-molecular-weight PAHs, containing more than three aromatic rings. PAHs can have multiple origins with oil spills and combustion products being important sources in typical urban environments. They are released into the environment by incomplete combustion and pyrolysis of organic materials such as coal, wood, fuel, garbage, tobacco, and meat. A major source of ambient PAHs is believed to be motor vehicle combustion emissions, particularly in urban areas. Motor vehicle emissions can contribute 46-90% of the mass for individual PAHs in ambient airborne particles in urban areas (Dunbar et al., 2001; Harrison et al., 1996; Nielsen, 1996). PAH constituents known to cause cancer are also present in creosote, a wood preserving agent used in wood treating facilities such as ACW (ATSDR, 1990; 1992a, b). By weight, creosote is composed of about 85% PAH, 12% phenolic compounds, and 3% heterocyclic nitrogen, oxygen, and sulfur compounds. PAHs are not particularly soluble in water, but adsorb well to particulate matter, and are therefore usually concentrated in soil or attached to dust particles or marine sediments. Because of the low solubility PAH levels in water are typically low. PAHs are known to cause environmental deterioration upon accumulating in sediments, as reflected in FDEP sediment quality assessment guidelines (Table 1). Removal of PAHs from the environment occurs most rapidly for 2-ring forms than for the heavier PAH forms via volatilization and biodegradation. Under anaerobic conditions the lighter forms will degrade under nitrate and sulfide reducing conditions and the heavier forms (4-6 rings) tend to adsorb to sediments becoming less available than the lighter 2 and 3-ring forms. The 3-ringed forms due to their availability exert more acute toxic effects (Brenner et al., 2002). In Bayou Chico, potential PAH sources past and present include the wood treating industry, municipal sewage discharges, industries related to boating and ship building, petroleum transport and storage, stormwater, naval stores, and wall board manufacturing. One of the objectives of the present study was to determine if the former ACW site could have impacted Bayou Chico through releases of wood-treating wastes that contained PAHs of creosote or diesel origin.

PAH Compound	TEL ² [μg/kg]	PEL ³ [µg/kg]	Carcinogenic IARC ⁴
	LMW (Light Molecular Weight) PAHs		ght) PAHs
Acenaphthene	6.71	88.9	No listing
Acenaphthylene	5.87	128	No listing
Anthracene	46.9	245	Not classifiable
Fluorene	21.2	144	Not classifiable
2-methylnaphthalene	20.2	201	No listing
Naphthalene	34.6	391	Possibly
Phenanthrene	86.7	544	Not classifiable
Sum LMW-PAHs⁵	312	1,442	No listing
	HMW (Heavy Molecular Weight) PAHs		
Benz(a)anthracene	74.8	693	Probably
Benzo(a)pyrene	88.8	763	Probably
Chrysene	108	846	Not classifiable
Dibenzo(a,h)anthracene	6.22	135	Probably
Fluoranthene	113	1,494	Not classifiable
Pyrene	153	1,398	Not classifiable
Sum HMW-PAHs ⁶	655	6676	No listing
Sum LMW&HMW ⁷	1684	16,770	No listing
	PAHs not assigned SQAG by FDEP		
Benzo(b)fluoranthene	na	na	No listing
Benzo(g,h,i)perylene	na	na	No listing
Benzo(k)fluoranthene	na	na	No listing
Indeno(1,2,3-cd)pyrene	na	na	No listing
1-Methylnaphthalene	na	na	No listing

Table 1: PAH SQAGs¹ [µg/kg] and IARC listing.

¹: SQAGs: Sediment quality assessment guidelines adopted by the FDEP.

²: TEL: Threshold effects level (MacDonald ,1994a,b). Within this range, concentrations of sediment-associated contaminants are not considered to represent significant hazards to aquatic organisms.

³: PEL: Probable effects levels (MacDonald ,1994a,b), lower limit of the range of contaminant concentrations that are usually or always associated with adverse biological effects

⁴ IARC: The International Agency for Research on Cancer is part of the World Health Organization. Agents with *sufficient evidence* of carcinogenicity in experimental animals and *inadequate evidence* of carcinogenicity in humans will ordinarily be placed in the category *possibly* carcinogenic to humans. When there is strong evidence that carcinogenesis in experimental animals is mediated by mechanisms that do operate in humans, the agent may be upgraded to *probably* carcinogenic to humans. The classification scheme allows for down-grading to *not classifiable*

as to its carcinogenicity to humans if there is strong, consistent evidence that the mechanism of carcinogenicity in experimental animals does not operate in humans or is not predictive of carcinogenic risk to humans. ⁵: Sum LMW-PAHs refers to FDEP TEL and PEL values determined for the sum of 7 light molecular weight PAHs ⁶: Sum HMW-PAHs refers to FDEP TEL and PEL values determined for the sum of 6 heavy molecular weight PAHs

⁷: Sum LMW&HMW refers to the sum of the concentrations of each of the 13 low and high molecular weight PAHs having FDEP SQGL. While the mode of action of LMW and HMW PAHs is thought to differ, these substances are sometimes grouped in assessments of sediment quality. This results in a derivation of a TEL of 1,684 ug/kg and a PEL of 16,770 ug/kg. (MacDonald, 1994a,b). The actual Total PAH of this 8270C SIM Analyses includes an additional 5 PAHs.

PAHs can be transported to aquatic sediments via groundwater discharge from an aquifer into sediments, via stormwater deposition, air deposition from grass and forest fires and vehicle exhaust, and petroleum product spills. PAHs tend to partition from water into sediments at ratios based on their molecular weight. Larger PAHs tend to partition preferentially into sediments with relatively small concentrations of PAHs showing up in water due to their lower solubilities. After a spill on the ground the heavier of the PAHs upon entering an aquifer sink to the bottom of the aquifer to form a layer of Dense Non-Aqueous Phase Liquid (DNAPL). The lighter PAHs float on water as the Light Non-Aqueous Phase Liquid (LNAPL) layer. LNAPL PAHs such as naphthalene also tend to be more soluble and enter the water column and then evaporate to the atmosphere or are transformed to alkyl forms (Van Mouwerik et al., 1998). There is a considerable amount of DNAPL under ACW and Sanders Beach (Bechtel Environmental, 1996). It is possible that some of this DNAPL has or could migrate via the aquifer toward the beach or Bayou and contaminate the waters and sediments of Bayou Chico.

3.2.3 Pentachlorophenol (PCP)

Pentachlorophenol (PCP) is a manufactured chemical that does not occur naturally. Technical grade PCP that is used in industry, and was routinely used at ACW, is more toxic than pure PCP due to by-products. By-product contaminants of PCP production include various dioxins and furans. PCP was widely used as a pesticide and wood preservative but since 1984 the purchase and use of PCP has been restricted to certified applicators. It is no longer available to the general public, but is still used industrially as a wood preservative for utility poles, railroad ties, and wharf pilings. PCP can be found in the air, water, and soil. It enters the environment through evaporation from treated wood surfaces, industrial spills, and disposal at uncontrolled hazardous waste sites. PCP is broken down by sunlight, other chemicals, and microorganisms within a few days to months (Rao, 1978; ATSDR, 2001). Studies of workers show that exposure to high levels of PCP can cause the cells in the body to produce excess heat. When this occurs, a person may experience a very high fever, profuse sweating, and difficulty breathing. The body temperature can increase to dangerous levels, causing injury to various organs and tissues, and even death. Liver effects and damage to the immune system have also been observed in humans exposed to high levels of PCP for a long time (ATSDR, 2001). The USEPA has determined that PCP is a probable human carcinogen and the International Agency for Cancer Research (IARC) considers it a possible human carcinogen. In drinking water the USEPA and FDEP MCL has been set at 1 ppb or 1µg/L (ATSDR, 2004). For coastal sediments the AET is 17 ug/kg (NOAA, 1999). A TEL or PEL for coastal sediments has not yet been determined by FDEP. PCP was detected in monitoring wells near the ACW site (BEM, 2005) but PCP data for the bayou sediments do not seem to exist except for very limited data from EA (2000) that showed no detections.

3.2.4 Other hydrocarbons

A study of Bayou Chico in 1977 found that 13 out of 16 sediment cores had more oil and grease near the surface than at depth (Glassen et al., 1977). The highest oil and grease concentrations were found on the south side of the main part of the Bayou and in the northern arms. Concentrations of solvent extractable organics in these areas were about 100 times higher than those in typical coastal sediments. The high concentrations were attributed to petroleum releases, industrial activities, and stormwater runoff (Glassen et al., 1977).

Stone and Morgan (1991) reported that two of their twelve cores had a strong turpentine odor in the upper parts of the sediment core and chemical analysis detected retene (1-methyl-7-isopropylphenanthrene) at concentrations of 250 and 300 ppm. Retene is an indicator for coniferous wood combustion and various industries on the Bayou could have released it as wood and bark remnants from sawmills, wood-treatment plants, and naval stores operations are commonly combusted to provide heat for boilers and other industrial processes that require heat (Holmes, 1989).

3.2.5 Dioxins/furans

Dioxins/furans and dioxin-like compounds are ubiquitous environmental contaminants that are very stable against chemical and microbiological degradation and therefore persistent in the environment. The major sources of dioxins/furans are combustion processes, such as waste incineration and metal smelting and refining. Dioxin/furan contamination is also associated with the production and the use of pentachlorophenol (PCP) at wood treating sites. Other sources of localized dioxins/furans hotspots include spills from PCB filled electrical equipment such as transformers and capacitors, each of which may contain several kilograms of PCBs and hundreds of milligrams of dioxins/furans. Paper mills in the past produced dioxins/furans (mainly the 2,3,7,8-TCDD congener) during a chlorine bleaching process (ATSDR, 1998). Agent orange, a herbicide once employed by the Department of Defense, and tested at Eglin Air Force Base 30 miles to the east of Bayou Chico, contained dioxins/furans. The active ingredient (herbicide 2,4,5-T) was contaminated with minute amounts of dioxins/furans as a by-product of the manufacturing process (Frumkin, 2003). Dioxins/furans are fat-soluble and thus tend to bioaccumulate in the lipids of animal tissues and in the food chain. Food presumably contaminated by environmental dioxins/furans is the major source for human exposure to dioxins/furans, especially fatty foods: dairy products (butter, cheese, and fatty milk), meat, eggs, and fish. Some subgroups within the society (e.g., nursing babies and people consuming large quantities of dairy products and fish) may be highly exposed to these compounds and are thus at greater risk (ATSDR, 1998).

Dioxin/furan compounds include polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). The chlorinated dibenzodioxins include 75 individual compounds and the dibenzofurans include 135 compounds. They are tricyclic aromatic compounds with similar physical and chemical properties. There are also dioxin-like polybrominated dibenzo-p-dioxins (PBDDs or BDDs), polybrominated dibenzofurans (PBDFs or BDFs), and polychlorinated biphenyls (PCBs). Dioxin-like refers to the fact that some polyhalogenated compounds assume similar structural conformations and similar physicalchemical properties that invoke a common battery of toxic responses. The brominated compounds with dioxin-like activity were not included in the PERCH Bayou Study. The dioxinlike PCBs are included in this study. The most widely studied congener of this general class of compounds is 2,3,7,8tetrachlorodibenzo-p-dioxin (TCDD). This compound, often called simply "dioxin," is the most toxic and is used as the reference for calculations of toxicity. The structure of TCDD and several related compounds are shown in Figure 2. These individual compounds are referred to technically as congeners. Out of 75 congeners of dioxins, 7 appear to have dioxin-like toxicity. Out of the 135 possible congeners of furans, 10 appear to have dioxin-like toxicity. This makes a total of 17 individual dioxins/furans congeners exhibiting dioxin-like toxicity. Certain of the PCBs are structurally and conformationally similar to dioxins/furans (Figure 2). There are 209 PCB congeners with 12 of the 209 congeners appearing to have dioxin-like toxicity.



Figure 2: Chemical Structure of 2,3,7,8-dioxin (TCDD) and representative dioxin-like compounds.

Dioxins bring about a wide spectrum of biochemical and toxic effects in experimental animals. These effects depend on species, strain, gender, age and tissue. For the most part, the mechanisms of the impacts are still obscure. Dioxins/furans and dioxin-like PCBs persist and bioaccumulate in fatty tissues of animals and humans because of their hydrophobic nature and resistance towards metabolic breakdown in the body. It appears that because they are fat-soluble and not very soluble in water, they can not be readily excreted in urine and animals are not able to metabolize them. The excretion is so slow that their so called half-life is many years, which means that it takes years for the human body to get rid of 50 % of the compound once it has been become incorporated into the tissues. Because dioxins are mixtures, every compound has a different half-life, but as a rule of thumb an average half-life is ten years. This long half-life

makes them highly cumulative compounds, i.e., they accumulate in the body over the decades even at a low exposure (ATSDR, 1998).

In humans, a wide variety of health effects have been linked to high exposures to dioxins, including mood alterations, reduced cognitive performance, diabetes, changes in white blood cells, dental defects, endometriosis, decreased male/female ratio of births and decreased testosterone and elevated thyroxin levels in neonates. Presently in humans the effects have been proven to include chloracne (skin disease with severe acne-like pimples). The effect that has caused the greatest public concern is cancer. In 2003 USEPA characterized TCDD as "carcinogenic to humans" (USEPA, 2003b). There is still some uncertainty of the relationship between dioxin and cancer, especially at lower concentrations (National Academy, 2006). Another concern in the society are possible developmental effects. (ATSDR. 1998) Dioxins are one of the contaminants listed by the ATSDR as being present at the ACW site (ATSDR, 1992b).

Dioxin and dioxin-like toxicity is expressed as Toxic Equivalents (TEQ). To determine the TEQ all the toxic dioxins/furans and dioxin-like PCBs have been assigned a Toxic Equivalency Factor (TEF). TEFs compare the potential toxicity of each dioxin-like compound comprising the mixture to the well-studied and understood toxicity of TCDD, the most toxic member of the group. TEFs were established though review of toxicological databases along with considerations of chemical structure, persistence, and resistance to metabolism. That information has been used to ascribe specific "order of magnitude" TEFs for each dioxin-like congener relative to TCDD, which is assigned a TEF of 1.0. The most recent system of TEQ assessment (Van den Berg et al., 1998) has TEF values for 17 dioxins/furans and 12 PCBs.

Screening studies by PERCH are being done to assess accumulation of contaminants in fish and shellfish from the Pensacola Bay System. These studies indicate that oysters and/or crabs collected from Bayou Chico contain substantially elevated levels of various contaminants, including dioxins and dioxin-like polychlorinated biphenyls (PCBs) (Karouna-Reneir et al., 2006). The combined toxicity equivalent quotients (TEQ) for dioxins/furans and dioxin-like PCBs for a composite sample of oysters from Bayou Chico was about 23 times higher than the EPA-recommended screening value for recreational fisheries. The dioxins/furans accounted for 55-60% of the TEQ load in crab and oyster samples and dioxin-like PCBs for the rest (Karouna-Reneir et al., 2006).

3.2.6 Polychlorinated biphenyls (PCBs)

PCBs are a family of chemical compounds formed by the addition of chlorine to biphenyl (Figure 3). This is a two-ring structure comprising two 6-carbon benzene rings linked by a single carbon-carbon bond. There are 10 possible substitution positions for chlorine in the two aromatic rings resulting in 209 possible combinations. Molecules with a single chlorine substituent are called "monochlorobiphenyl" (or just "chlorobiphenyl"). Molecules with two chlorines are called "dichlorobiphenyl", and those with three through ten chlorines, in order, are called: "tri...", "tetra...", "penta...", "hexa...", "hepta...", "octa...", "nona...", and "decachlorobiphenyl". Each of the possible chlorine substitutions results in a specific PCB called a congener. The name of a congener specifies the total number of chlorine substituents and the position of each chlorine. For example: 4, 4'-dichlorobiphenyl is a congener comprising the biphenyl structure with two chlorines. The dioxin-like PCBs have four or more lateral chlorines with one or no substitution in the ortho position (Figure 2, Figure 3). The ortho positions are the carbons adjacent to the biphenyl linkage

between the two phenyl groups (positions 2 or 2' and 6 or 6'). These compounds are sometimes referred to as coplanar, meaning that they can assume a flat configuration with rings in the same plane (Van den Berg et al., 1998). Each of the individual PCB congeners has its own unique chemical, physical, and toxicological properties. Each congener has a unique number based upon the International Union of Pure and Applied Chemistry (IUPAC) naming system (ATSDR, 2000). There is also a BZ nomenclature (Ballschmiter and Zell, 1980) that is presently identical for congener number, but expresses the chemical name in a different form for some of the congeners.



Figure 3: General PCB structure

Commercial mixtures of PCBs formerly produced in the United States were known mostly by the trade name Aroclor. Aroclors were sold based upon their overall level of chlorination and were mixtures of multiple PCB congeners. Each Aroclor mixture contained a different blend of individual PCB congeners (Table 2). Aroclor 1254 indicated a PCB mixture with an overall chlorine content of 54%. It is now known that certain congeners in commercial PCB mixtures weather more rapidly than others upon release to the environment, resulting in PCB mixtures in the environment that can be significantly different than the original product. Because traditional laboratory analyses are intended to detect the Aroclor mixtures of PCBs, individual congeners are not routinely reported. These analysis rely upon chromatographic pattern matching between the environmental sample and pure Aroclor mixtures and it is not uncommon for laboratories to list high concentrations of PCBs as 'non-detected' for severely weathered environmental samples. This is not because PCBs are absent, but rather, because the detected pattern no longer resembles the Aroclor mixtures used as the standard of comparison (Schwartz et al., 1987). The traditional Aroclor approach has been supplanted in recent years by analyses for specific PCB congeners with detection limits less than 1 ppt (part per trillion). Our study for Bayou Chico employed method 1668A for the analyses of the 209 PCB congeners (Fikslin and Santoro, 2003).
Congener No.	Chlorine substitution	Aroclor	Aroclor	Aroclor	Aroclor	Aroclor
(PCB No.)	(IUPAC No.)	1016	1242	1248	1254	1260
4	2,2'	4.36	3.99		•	
8	2,4'	10.30	8.97			
18	2,5,2'	10.87	9.36	9.95		
28	2,4,4'	14.48	13.30			
31	2,5,4'	4.72	4.53	9.31		
42	2,3,2',4'			7.05		
52	2,5,2',5'	4.35	4.08	8.36		
53	2,5,2',6'			6.30		
70	2,5,3',4'			6.38	4.75	
91	2,3,6,2',4'				5.00	
99	2,5,2',3',4'				6.10	
101	2,4,5,2',5'				6.98	5.04
110	2,3,6,3',4'				8.51	
118	2,4,5,3',4'				8.09	
138	2,3,4,2',4',5'					5.01
149	2,3,6,2',4',5'					9.52
153	2,4,5,2',4',5'					8.22
180	2,3,4,5,2',4',5'					7.20
185	2,3,4,5,6,2',5'					5.65

Table 2: Major PCB congener constituents of five Aroclors.

^a Values less than approximately 4% are not included.

PCBs are called persistent organic pollutants (POPs) due to toxicity, persistence, and biomagnification as they move up through the food chain. PCBs are among the most stable organic compounds known and accumulate in animal and human tissues. Even though PCBs are no longer commercially produced in the United States, high levels of these chemicals remain in poultry and fish in various parts of the country. PCBs are highly soluble in lipids and are known to biomagnify (concentrate) in human tissues. PCB congeners with higher percentages of chlorine tend to bioaccumulate to higher concentrations in tissue. Because of the persistence of PCBs in environmental media, analyzing for the presence and concentration of PCBs is important in conducting risk assessments (ATSDR, 2000). Most PCB manufacture and new use was prohibited in the United States in 1978 under TSCA (the Toxic Substances Control Act). TSCA was enacted in 1976 by Congress to give EPA the ability to track the vast number of industrial chemicals currently produced or imported into the United States.

Bayou Chico with its history of industrial pollution would be expected to contain PCBs in its sediments. Previous studies in Bayou Chico included only PCB analyses for selected congeners with a maximum of 26 individual detections. Past data for PCBs in Bayou Chico sediments can be found in the Pensacola Bay System GIS Database (DeBusk et al., 2002), Lewis et al. (2001b), and EA (2000). Several of these studies reported PCB concentrations above the TEL and PEL. These results are not unexpected for an urban bayou in an industrial setting. Unfortunately there was a lack of a uniform standard for PCB congener analyses and there were four different congener lists employed and none of these lists includes all of the dioxin-like PCBs. The present study of Bayou Chico used the 209 congener assay to assure that sufficient data was obtained on dioxin-like PCB TEQ data for comparison with results of the PERCH seafood study.

Sediment samples from Bayou Chico and Pensacola Bay were also analyzed for PCB congeners by Waller et al. (1998). The analyses showed that the sediments of Bayou Chico and, to a lesser extent, those of nearby Pensacola Bay were more contaminated than those collected elsewhere in the southeastern US. The concentrations of organic contaminants found in the sediments were directly related to organic carbon content and particle size of the sediments and to their proximity to the sources of point and non-point loading from the watershed (Waller et al.,

1998). Lewis et al. (2001b) reported mean total PCB values of 103.1 ug/kg that exceed the TEL (21.6 ug total PCBs/kg dry wt for estuarine and marine sediments in Florida) and Waller et al. (1998) reported values of a similar range with some individual values exceeding the PEL (189 µg total PCBs/kg dry wt). These PCB total values are not complete since the analyses did not include all 209 PCB congeners.

3.2.7 Trace metals

A report by the U.S. Army Corps of Engineers in 1977 is one of the first to report trace metal data for the water and sediment from Bayou Chico (Pratt et al., 1993). The report is a compendium of information and data collected from a number of sources. It consists mainly of appendices containing data that, at this point in time, are probably unobtainable. One of the appendices presents data for particle size distribution, Pb, Zn, and Hg for 25 sediment samples (Pratt et al., 1993). The samples were apparently collected from six separate stations, the locations of which are not clearly identified.

Glassen et al. (1977) analyzed sediment samples to determine trace metal concentrations in surface and sub-surface materials of Bayou Chico. Iron, Zn, and Pb concentrations were found to be higher than would be expected for a "natural" bayou (Glassen et al., 1977). The authors noted that of the metals examined, Fe, Zn, and Pb were most likely of non-natural origin. Relatively high concentrations of Ni (75 mg/kg max) and Pb (1484 mg/kg max) observed in the surface sediments of the northern branches of the Bayou were attributed to the impacts of urban stormwater runoff because these elements are often associated with traffic. These concentrations are well above the current day PEL levels for these metals (Table 3). The authors observed that, in general, Bayou Chico sediments were not excessively contaminated with metals.

Table 3: Current TEL and PEL [mg/kg] for trace metals (MacDonald, 1994a,b).								
	As	Cd	Cr	Cu	Hg	Pb	Ni	Zn
TEL	7.24	0.676	52.3	18.7	0.13	30.2	15.9	124
PEL	41.6	4.21	160	108	0.696	112	42.8	271

T 11 20 1 1 0 11 1004 1)

Stone and Morgan (1991) studied trace metal concentrations of subsurface sediments in Bayou Chico. The cores collected by this study were longer (deeper) than cores collected by other studies. As expected, metal concentration in their samples generally showed a strong correlation (>0.7) with silt and clay, due to the electrochemical properties of these sediment size fractions. Copper, Pb, and Zn showed correlation coefficients with clay that were below 0.7. Cadmium and Co had very low correlation coefficients. Between the metals, correlation coefficients of more than 0.9 were found for Cr and Fe, Cr and Al, Cu and Zn, and Fe and Al. Strong relationships were also found for other combinations of metals but Co and Cd correlated poorly with the other metals. The highest metal concentrations were usually found in the top 2 ft. In two cores high metal levels were found at depth (8 ft to 15 ft), which was interpreted by the authors as evidence for the percolation of metal-rich water through the sandy sediments. Metal enrichment, defined in the study as the ratio of the concentration of a given metal to the concentration of that metal in the deepest layer, was evident near the top of all cores with the exception of two cores that presumably were taken in disturbed sediments. The depth of metal enrichment varied throughout the Bayou but was deepest in cores in the northern and central parts of the Bayou. Maximum enrichment depth in those areas was about 7 ft. This was to be expected according to the authors because sources for metals were located in those areas and

because natural flushing of the Bayou was thought to be low there. In the lower portion of the Bayou, between the old Pace Blvd. bridge (State Road 292) and the new Barrancas Ave. bridge constructed in 1999, the depth of metal enrichment was between 0.4 ft and 1.2 ft. The authors explained this relatively small enrichment depth by a greater flushing capacity of the Bayou and the input of relatively uncontaminated sediment from Pensacola Bay. High enrichment of surface layers was encountered in the NW branch of the upper Bayou, between the two constrictions, and in one core near the southern shore between the two bridges. The authors compared their results with those from Glassen et al. (1977) and noted that both studies found the highest concentrations in the surface and near-surface layers between the topographic constrictions at W. Navy Blvd. and the railroad to the south of it, and in the NW branch of the northern Bayou. Between the two constrictions the PEL was exceeded in the surface sediments by Pb, Ni, and Zn; in the NW branch the PEL was exceeded by Cu, Pb, and Zn. The PELs for Cu, Zn, Pb, and Ni were exceeded in six, five, four, and two samples out of 12 respectively. Cadmium and Cr exceeded their respective TELs in two samples. Metal concentrations decreased between 1977 and 1991 in most of the Bayou (Stone and Morgan, 1991). In the NW branch, however, Fe, Cr, Pb, Mn, and Ni increased in that time period and Cu and Ni increased in several other parts of the Bayou (Stone and Morgan, 1991).

Four other sediment cores were obtained in the early 1990s and analyzed for Al, Cu, Hg, Cr, Ni, Co, and Mn (Wood and Bartel, 1994). Specific depth information is not available for samples from these cores. The site with the most metals above the TEL and PEL was located between the old Pace Blvd. and new bridge near the mouth of the Bayou. The TEL was exceeded by Cr and Cd, and the PEL was exceeded by Cu, Hg, Pb, and Zn. Based on normalization of the data with Al concentrations, and comparison with other data in the state, the high values of these metals were ascribed by the authors to anthropogenic enrichment. Sites in the western finger of the Bayou and the NE branch of the northern Bayou had relatively low concentrations of trace metals. Based on reinterpretation of the results from Stone and Morgan (1991), Wood and Bartel (1994) concluded that the two studies show general agreement and that they indicate that sediments near the mouth of the Bayou were the most polluted. Wood and Bartel (1994) did not sample the NW branch of the northern Bayou where other studies found high concentrations of trace metals (Stone and Morgan, 1991; Glassen et al., 1977). Even though concentrations in the western finger of the Bayou were relatively low (Stone and Morgan, 1991; Wood and Bartel, 1994), some evidence suggests that anthropogenic enrichment may have taken place there as well (Wood and Bartel, 1994).

Long et al. (1997) found elevated levels of Cu, Pb and Hg in surface sediments of the Bayou. In a broader regional context, the Pensacola Bay System was found to show a higher frequency of exceedances of metal background concentrations than Choctawhatchee, St. Andrew and Apalachicola Bays. This was attributed to the high level of metal contamination in Bayou Chico (Long et al., 1997).

Surface samples were analyzed for 13 trace metals by Waller et al. (1998). Raw data were not provided in the report but concentrations for the metals were compared with criteria for biological effects from Long and Morgan (1990). In some samples Cd, Cu, and Pb exceeded the concentration above which biological effects are predicted to occur 10% of the time, and Hg, Ni, Ag, and Zn exceeded the concentration above which biological effects are predicted to occur 50% of the time. The highest concentrations of As, Cd, Cr, Pb, Ni, and Ag were found in the northern part of the Bayou north of the W. Navy Blvd. bridge. These high concentrations were interpreted as being the result of anthropogenic input via freshwater (Waller et al., 1998). High

levels of As, Cr, Pb, and Ag in sediments of Jackson's Branch Creek and the Northeastern tributary were seen by the authors as evidence of continued loading of metals to the northern Bayou via these waterways. The high values for the northern Bayou are in part in contradiction with those of Stone and Morgan (1991) and Wood and Bartel (1994) who found low metal concentrations in sediments in the NE branch of the northern Bayou. Relatively high concentrations of As, Cu, and Hg were found in the western finger of the Bayou, and in sediments in Jones Creek which feeds into the finger. This result also is in contradiction with both the Stone and Morgan (1991) and Wood and Bartel (1994) studies who found relatively little trace metal pollution in the western finger. It is possible, of course, that the apparent contradictions are due to local variations in metal content of the sediments or they may represent variations over time. Sediments in Pensacola Bay had low metal concentrations, with the exception of Cu which was elevated (3.6 mg/kg - 187.4 mg/kg). The concentrations in the Bay were considerably higher than concentrations found in coastal water bodies elsewhere in the Southeastern United States by an environmental reconnaissance study (Waller et al., 1998).

Another study that was carried out in the first half of the 1990s (Lewis et al., 2001b) found Cu and Zn to be the generally most elevated metals with means of 118.7 mg/kg and 565.7 mg/kg respectively. These means exceed the PEL for these metals. Lead, which was not detected in water (see below) was detected in all sediment samples and had a mean concentration of 88.1 mg/kg. The maximum concentration encountered for Pb (283 mg/kg) exceeded the PEL for this metal. Concentrations for all metals were considerably less in Pensacola Bay near the mouth of Bayou Chico than in the Bayou itself. Metal concentrations for different sampling dates over the two year study period varied by a factor of 2.0 to 2.6 (Lewis et al., 2001b). The spatial trend was a decrease in sediment contamination towards the mouth of the Bayou, but spatially explicit data were not provided (Lewis et al., 2001b).

The occurrence of moderate As contamination and moderate to high Pb and Cu contamination of the sediments in Bayou Chico increased between the 1980s and 1990s (DeBusk et al., 2002). Relatively few data were available for Ni concentrations during the 1980s but data suggest that the concentrations increased to moderate levels in the 1990s. Moderate contamination of Cd remained unchanged between the two time periods. High levels of Cr and Hg contamination were found in Bayou Chico in the 1980s but data indicate that the contamination decreased from the 1980s to the 1990s. DeBusk et al. (2002) also report that the Florida Coastal Sediment Contaminants Atlas (Seal et al., 1994) indicates areas of Cd, Cr, Cu, Pb, and Zn enrichment in sediments of Bayou Chico.

The FDER collected stormwater quality data between November 1978 and November 1979 from three stormwater outfalls on Bayou Chico (Pratt et al., 1993). Two outfalls were located on the east side of the Bayou and one on the west side. Stormwater quality data was obtained from ten storm events and during each event seven samples were collected for a total of 210 samples. Additionally, one set of base flow samples was collected at each outfall at the beginning of the project. No flow data was collected during the course of stormwater sample collection. The maximum concentration for Cr, Cu, Pb, Hg, Ni, and Zn were 17, 50, 890, 2, 13 and 2160 µg/l respectively. With the exception of Cr, these maximum concentrations exceed the class III minimum standards.

Freshwater input into Bayou Chico was studied in the three creeks that drain into the Bayou (Pratt et al., 1993). Water samples were collected during baseflow and storm conditions. Chromium, Ni, Cd, and As were found to be below detection level most of the time. Copper and Hg exceeded their respective class III minimum standards in four out of 36 samples (Table 4).

These four samples were all from the Jackson's Branch Creek, which was sampled about ¹/₄ mile east of State Road 295. Zinc and Fe were generally detected during baseflow, and Zn, Fe, Al, and Pb were detected during stormwater runoff. During stromwater runoff the Pb concentration exceeded the class III minimum standards in all three creeks at least some of the time. In Jones Creek 15 out of 24 samples exceeded the standard. In Jackson's Branch Creek all samples exceeded the standard and one sample had a Pb concentration of 240 µg/l, or about 75 times the class III minimum standard. Zinc exceeded the class III minimum standards in 10 out of 24 samples from Jackson's Branch Creek. In the NE tributary Zn exceeded the standard in two out of 24 samples and in Jackson's Branch Creek it did not exceed the standard. Generally, the highest mean values of all pollutants were found in Jackson's Branch Creek and the lowest mean values in Jones Creek. These findings are consistent with results for sediments in these areas (Stone and Morgan, 1991; Wood and Bartel, 1994). Lead and Zn in stormwater were found to have correlation coefficients of about 0.9 with turbidity and TSS, which is not surprising given the affinity of metals for fine-grained particles. Assuming that the data from the relatively short study are representative of the overall water quantity and quality in the three creeks, total loading from the freshwater input into Bayou Chico was estimated at 647 lb/yr and 1857 lb/yr for lead and zinc respectively. For Pb almost the complete annual load is contributed by stromwater runoff while for Zn about 75% - 80% of the loading occurs during storms.

Metal	Marine water	Fresh water
Cu	2.9	11.8
Hg	0.025	0.012
Pb	5.6	3.18
Zn	86	106

Table 4: FAC 17-302 water quality standards for class III water bodies¹.

¹: Modified from Pratt et al. (1993), units are $\mu g/l$.

In 1994 Bayou water was tested for metals by two studies (Waller et al., 1998; Lewis et al., 2001b). Both studies found that only Cu was present in appreciable amounts. Copper concentrations exceeded the Gold Book criteria (USEPA, 1986) for marine and for fresh water at sites in all zones of the Bayou (Waller et al., 1998). The highest Cu level recorded in the study was 41 μ g/l, but concentrations close to this maximum were found at several sites throughout the Bayou and in one station in Pensacola Bay near the mouth of the Bayou (Waller et al., 1998). The mean concentration for Cu (6.6 μ g/l with BDL equated to 0; 18.7 μ g/l with BDL excluded) exceeded state (FDER, 1993) and national (USEPA, 1999a) guidelines for marine water quality in another study (Lewis et al., 2001). When mean concentrations were determined excluding below detection limit results, Cd (13.7 μ g/l) and Ni (29.5 μ g/l) also exceeded the state and national guidelines (Lewis et al., 2001b).

3.2.8 Biota

The Bayou Assessment Framework Project by Waller et al. (2000) utilized 17 sampling stations, 14 of which were in Bayou Chico and 3 in nearby Pensacola Bay (Figure 4). Three additional stations, S1, S2, and S3, were located in three tributary streams. In May of 1994 an intensive field survey was conducted and benthic macroinvertebrates, zooplankton, and phytoplankton communities were sampled at each of the sampling stations. The collected data consisted of chemical, physical, and biological information. Species abundance information was

obtained on replicate samples and these count data were used to determine Brillouin diversity and Richness (number of taxa) and other criteria. Statistical analyses were performed to detect statistical differences between stations and zones and to explore relationships between sediment characteristic (% sand, silt, and clay), presence of sediment contaminants and the structure of the biological communities.



Figure 4: Location of Waller et al. (2000) sampling stations.

The highest values for Brillouin Diversity were found at stations nbc3b, nbc28, and nbc6 and the lowest values were observed at nbc14, nbc17b, nbc26. Two of the highest values occurred in Pensacola Bay and all of the lowest values were found in Zone 3 of Bayou Chico. Bayou Chico sampling stations showing higher diversity index values were nbc33, nbc11, and nbc12b. However, their index values were considerably lower than those occurring in Pensacola Bay.

The highest number of benthic macroinvertebrate taxa present (richness based on genera) were found at stations nbc3b, nbc28, and nbc 6 and the lowest numbers were found at nbc14, nbc17b, and nbc26. Zone 1 was markedly richer in fauna and Zone 3 was depauperate of benthic macroinvertebrates and had extremely low richness values. Zone 1 had the highest mean Brillouin Diversity and Zones 3 and 4 had the lowest. Zone 1 also had the highest mean number of organisms per gram sample. The fewest organisms per gram of sample were found in Zones 3 and 4. The annelid Capitellida was the dominant macroinvertebrate phyla present in the Bayou. Amphipods, gastropods, and tubificid groups were absent from Zones 4 and 5.

Waller et al. (2000) attempted to correlate sediment type (particle size) and sediment contaminants to benthic macroinvertebrate populations. They concluded that Bayou Chico was

very heterogeneous with regards to the chemical and physical properties of sediments. This heterogeneity also exists within zones. Both the highest and lowest macroinvertebrate diversity and richness were associated with sand dominated sediments. This seems to be at odds with the current wisdom that sediments dominated by sand, contain less organic and inorganic contaminants than sediments dominated by silt and clay fractions and should have greater diversity. It is possible that the briefness of the sampling period may have played a role in the observed results.

Zooplankton samples were collected only in Bayou Chico and not in the Bay. Brillouin diversity was calculated and the highest genera abundance was observed at stations nbc18, nbc26, and nbc 19 that were located in Zone 3. The lowest values were found at stations nbc33 (Zone 3) and nbc3b (Zone 4). Richness or quantity of genera present had a different pattern. It was highest at stations nbc19, nbc33, and nbc26 in Zone 3. The lowest richness was found at stations nbc10, nbc11, and nbc12b all located in Zone 5.

Phytoplankton in the Bayou and Bay showed the highest Brillouin diversity at nbc11, nbc12b, and nbc10 in Zone 5. The lowest values were at stations nbc19 (Zone 3), nbc23 (Zone 3), nbc9 (Zone 1), and nbc6 (Zone 1). The richness was similar at most stations with nbc17b being the highest. Pensacola Bay sampling stations nbc3b and nbc9 were the lowest (Zone 1). The phytoplankton assemblage had a higher diversity and richness in the Bayou than in the Bay. Zone 5 was most diverse. Zones 1 and 2 had the lowest overall richness and diversity.

Lores et al. (2002) examined spatial and temporal patterns in zooplankton community composition and abundance in coastal areas of the Gulf of Mexico. Spatial and temporal differences in zooplankton community composition and abundance from 10 stations from the Pensacola Bay System were determined. The three main bayous of the system were found to be impacted by urban and industrial development and differences were noted between the bayous and the Bay. Bayou Chico came out ahead of Bayou Texar and was behind Bayou Grande. The mean biovolume of zooplankton was highest in Pensacola Bay (0.38 ml/m³) followed by Bayou Grande (0.21 ml/m³), Bayou Chico (0.14 ml/m³), and Bayou Texar (0.06 ml/m³). Mean zooplankton abundances (organisms per m³) in Pensacola Bay (3,100 per m³) and Bayou Grande (3,000 per m³) were more than double the abundances in Bayou Texar (1,400 per m³) and Bayou Chico (1,100 per m³).

Butts and Lewis (2002) studied the species number and diversity in sediments from the lower Bayou and used the percentage of pollution sensitive taxa to indicate community integrity, stability, and health. Undesirable shifts in community structure were characterized by increased dominance of burrowing infaunal forms (polychaetes), decreased dominance of epifaunal forms and predators, and an increase in the polychaete/bivalve ratio. Epifaunal forms are generally considered more sensitive to environmental stress in contrast to infaunal forms such as certain oligochaete and polychaete worms. Depending on the sampling location infaunal organisms comprised 73-100% of the taxa. Approximately 57-100% of the taxa were indicative of organic enrichment and the dominant species at most stations were Streblospio benedicti and Mediomastus ambiseta. Spatial differences in community composition were obvious, but no consistent trend seaward and no relationship to sediment particle size was obvious. At three stations diversity and density were too low to calculate diversity index values. Species number at these stations averaged 3.0 (\pm 1) and mean individual number was 36.3 (\pm 6.0). Organic indicator organisms comprised between 92% and 100% of the total taxa. No predator species were identified at these three stations, and the polychaete/bivalve ratios ranged between 97% and 100%. In contrast, a total of 16-21 species and 98-158 individuals were collected from two other

stations, one of which was at the mouth of the Bayou and the other in the northern part. The percentage of organic indicator organisms was lower in these sediments (57% and 58%) and, unlike elsewhere, epifaunal species were identified (5% and 6%).

Bayou Chico sediments were determined at some sites to be toxic to rooted vascular plants. Lewis et al. (2001a) determined toxicities of whole sediments for benthic invertebrates in three urbanized Florida bayous/estuaries, including Bayou Chico. The results of the bioassays, conducted for 7 to 28 days, were compared for interspecific differences and to effects-based, sediment quality assessment guidelines. A consistent inhibitory or stimulatory response of the examined plant species was observed for some sediments from Bayou Chico. Specific locations for the sampling stations were not given but assuming that the sampling stations were the same as in Butts and Lewis (2002) the toxic sediments were from the northern part and western finger of the Bayou.

Toxicity testing was also performed by Waller et al. (1998). The authors stated that contamination was widespread in the Bayou and Bay. It was not known if the sediment contamination was biologically available to benthic and water column organisms. A limited number of toxicity tests were performed. The first test used <u>Ampelisca abdita</u>, a small shrimp-like amphipod that constructs tubes of fine sand grains. Testing for sediment mortality to <u>Ampelisca abdita</u> resulted in acceptable rates except for one site. Toxicity to fathead minnow (<u>Pimephales promelas</u>) and the cladoceran (<u>Ceriodaphnia dubia</u>) were tested in Jones Creek, Jackson's Branch and the northeast branch. For the fish there was no sediment toxicity observed, but for the clodoceran toxicity was observed from Jackson's Branch Creek sediments.

The toxicity of sediments in Pensacola, Choctawhatchee, St. Andrew and Apalachicola Bays was determined as part of bioeffects assessments performed by NOAA's National Status and Trends Program (Long et al., 1997). Bayou Chico was consistently the worst relative to toxicity assays. For amphipod toxicity there was only one site out of 12 that was toxic. Data from a Microtox^r test indicated that all of the samples from Bayou Chico were toxic. Results of Mutatox^r tests for all stations tested in Bayou Chico provided a genotoxic response. Sea urchin fertilization tests showed that most of the 1994 samples from Bayou Chico were highly toxic in all porewater concentrations, whereas none collected in 1993 was toxic in any porewater concentrations. The relationships between toxicity and solid-phase (bulk) sediment chemistry were explored in a multistep approach. Microtox^r test results were highly correlated with the concentrations of chlorinated compounds, including DDTs, PCBs, and total pesticides. To a lesser degree, Microtox^r test results were significantly correlated with the concentrations of some trace metals and PAHs. Sea urchin fertilization was highly correlated with the concentrations of PAHs, numerous trace metals, and DDT. Urchin embryo development was primarily correlated with the concentrations of unionized ammonia, and to a lesser degree, PAHs, three trace metals, and the pesticide dieldrin. Additional statistical analysis strongly suggested that mixtures of toxicants, co-varying with each other, contributed significantly to the observed toxicity. The relationships between measures of toxicity and chemical concentrations differed considerably among the four bays. Based upon these analyses, it appeared that the concentrations of zinc, high molecular weight PAHs, two DDD/DDT isomers, total DDT, and dieldrin were most closely associated with toxicity in the Pensacola Bay System, including Bayou Chico. Cadmium, Cu, Pb, and low molecular weight PAHs were moderately associated with toxicity in Pensacola Bay and Bayou Chico. Spearman-rank correlations failed to show significant correlations between toxicity and chemical concentrations in samples from Bayou Chico and Apalachicola Bay. However, there were numerous obvious associations between elevated chemical levels and

toxicity. Most notable among these were the concentrations of DDT isomers, total DDT, silver, the sum of PAHs, and dieldrin. Urchin fertilization was correlated with a number of trace metals, DDT, and ammonia. Concentrations of some metals and DDT exceeded effects based numerical guideline values. Microtox^r test results were highly correlated with complex mixtures of substances, including many trace metals and organic compounds. Toxicity occurred in all four bays but the most severe toxic responses and the highest incidences of toxicity occurred in Bayou Chico.

3.2.9 American Creosote Works site

In the present study the focus upon PAHs at Sanders Beach is due to the nearby presence of the American Creosote Works (ACW) Superfund Site that in the past has released PAHs of creosote and probably of diesel origin along with dioxins and PCP. The 18-acre ACW site is an inactive wood-treating facility in Pensacola located in the Sanders Beach Community just west of downtown Pensacola about 0.3 mile north of where Bayou Chico and Pensacola Bay meet. The ACW site, with EPA_FACIL_ID FLD008161994, is located at the corner of L Street and Barrancas Ave. and is currently in the process of remediation. The surrounding area contains Sanders Beach (a local beach), commercial and residential structures, industry, and the downtown commercial seafood docks and vendors just to the east of the Sanders Beach Community neighborhood. Though the area is served by municipal water supplies, numerous residents and businesses operated private irrigation wells. In February 1981, the U.S. Geological Survey identified phenols in groundwater associated with ACW. Major contaminants in the soil, sediment, and groundwater were volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), pentachlorophenol (PCP), and dioxins/furans from the former woodtreating processes. No public drinking supply wells are within the known zone of contamination.

There is no generally accepted recent model for groundwater transport of contaminants which leaves us with the original model from the 1980's. Groundwater flow from the site was generally proposed as southward toward Pensacola Bay, with mean velocities of about 0.2 m/d (meter per day) (Franks, 1987). In the contaminated part of the aquifer, groundwater velocities range from about 0.05 to 1.0 m/d. Recharge via rainfall is estimated to contribute about 0.2 m/yr (meter per year) to the aquifer. Discharge is to Pensacola Bay (Sanders Beach area) and to a small drainage ditch south of the impoundments. Hydraulic conductivity of the upper two (contaminated) zones ranges between 9 and 20 m/d. Groundwater contamination extends about 600 m south of the contaminant source and vertically to about 30 m below the land surface encompassing only the upper two zones. A north-south cross section illustrates the vertical extent of contamination (Figure 5). Mattraw and Franks (1986) and Franks (1987) reported that the site groundwater was moving predominantly south transporting light non-aqueous phase liquid (LNAPL) fractions at or near the water table, which can rise to within 1 foot of the surface. The water soluble and dense organic phases are transported along a flow path above and below a prominent clay layer. The authors stated that the site's history shows that the Sanders Beach shoreline and the mouth of Bayou Chico have been influenced by past releases of wood treating wastes from ACW to surface waters. A dark sludge band was observed during this period (1980s) on Sanders Beach at low tide, suggesting transport of wood-treating wastes to the Bay. Currently there is no such band visible and surface transport of substances of concern (SOCs) from the ACW via stormwater has been drastically reduced if it occurs at all. At the ACW site ten of fourteen SVOCs detected in monitoring wells (acenaphthene, carbazole, dibenzofuran, 2,4-dimethylphenol, 2-methylphenol, 3&4-methylphenol, 2-methylnaphthalene, naphthalene,

pentachlorophenol and phenol) were above their respective FDEP GCTL regulatory screening values (BEM, 2005).





Remediation of this superfund site is being addressed by the U.S. Environmental Protection Agency (EPA) under two operational units. Operational Unit 1 (OU1) addresses contaminated soil, sludge, and sediment; which represent the source of the contamination at the site. Operational Unit 2 (OU2) addresses the groundwater contamination at the site. The EPA has had the ACW site and the Sanders Beach neighborhood investigated for the above mentioned compounds and there was excavation of contaminated soils from the surrounding neighborhood (USEPA, 2003a).

The Record of Decision (ROD) for OU1 called for excavation of off-site soils that are contaminated above the federal soil cleanup target level. The ROD also called for the construction of a cap to contain the contaminated soil on the ACW site. The cleanup of the groundwater has to date been the removal of dense non-aqueous phase liquids (DNAPL's) that include PAHs and dioxins/furans. As of March 2002, approximately 100,000 gallons of DNAPL's had been removed (USEPA, 2002). The Agency for Toxic Substances and Disease Registry (ATSDR) has investigated the ACW site. In a Public Health Assessment of the site by the ATSDR (1992b) the following chemicals or chemical groups were selected as representative of the distribution and toxicity of the hundreds of individual chemicals associated with this site: Pentachlorophenol; Carcinogenic polycyclic aromatic hydrocarbons (PAHs)-benzo(a)anthracene, chrysenefluoranthene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenzo(a,h)anthracene, indeno(1,2,3-cd)pyrene; dioxins/furans; and benzene.

The EPA is currently investigating the movement of contaminated groundwater from the site. The USACE that is actually directing the field work has most recently been attempting to

establish the extent and movements of the plume emanating from ACW. The most recent report (BEM, 2005) stated that the concentrations of VOCs and SVOCs are above FDEP Groundwater Cleanup Target Level (GCTLs) in both down-gradient and side-gradient offsite monitoring wells. This indicates that additional field investigation is necessary to adequately define the extent of the horizontal and vertical dissolved plume. A more formal trend analysis with calculated plume reduction and graphical analysis will be presented once enough sampling events have occurred to give a statistically sound data set upon which to base calculations and trends.

3.2.10 Omni-Vest site

The Clark Sand Pits area contains a hazardous waste site known as the Omni-Vest Hazardous Landfill (OVLF). Fifty years of sand mining at the site resulted in three large pits with the north pit having a makeshift emergency spillway connecting to Bayou Chico. The three pits are at the foot of a steep wooded escarpment and Jackson's Branch Creek flows to the east between the northern pit and the two southern pits. The hydrology and topography of the area have been heavily influenced by the sand mining operations. The Omni-Vest Landfill (OVLF) site is listed as FDEP Hazardous Waste Case # 50, FLD980845143. The site is approximately six acres and is bounded on the north by the Burlington-Northern railroad tracks, on the south by the former Clark residence. This site is 500 ft north and upgradient from Jackson's Branch Creek and Bayou Chico.

OVLF was a disposal site for various wastes for at least 15 years, and dumping was often not documented. In 1972 OVLF acquired the site and contracted with Reichhold Chemicals to obtain materials identified as "wood chips and wash sand" for use as fill (FDEP, 2006a). Many of the disposed materials contained hazardous chemicals. Soils and sludges in the landfill are contaminated with metals and VOCs (FDEP, 2006a). An estimated 100,000 to 120,000 gallons of terpene are also on-site. The terpene includes benzene, toluene, dichloroethylbenzene, ethylbenzene, and xylenes. A nearby private well at a residence that adjoins the sites' east boundary was sampled and found to be free of contaminants (FDEP, 2006a).

Studies conducted by the FDEP in 1979 and 1980 indicated heavy metal contamination and sludge deposits located at a depth of more than 18 feet. In 1983, the FDEP collected groundwater samples from the site. Data indicated elevated concentrations of chromium, copper, lead, mercury, zinc, ethylbenzene, toluene, xylene, tetrachloroethane, and polynuclear aromatic hydrocarbons (PAHs). Analytical results of sludges indicated toluene concentrations as high as 6,700 mg/kg. Groundwater within the site boundaries was contaminated; however, no contamination was detected in off-site wells (FDEP, 2006a). The site was fenced in April 1985 to limit public access. In May 1986, the FDEP completed additional fencing along the Clark Sand Pond to completely limit all access by unauthorized persons. In September 1996, FDEP sampling of monitoring wells revealed that groundwater contamination remained centered in the northwest area of the site, where total VOC concentrations detected were 6,770 mg/L. Based upon recommendations from the FDEP engineering staff, additional assessment was conducted in September 1998 that confirmed that site contaminants were not migrating offsite.

In September 2004, FDEP assigned the site to ARCADIS Geraghty & Miller (AGM), a State of Florida hazardous waste contractor, to determine the current extent of site contamination. The Draft Site Assessment Report was submitted in May 2005. This report confirmed past investigations that showed contamination has not migrated off property. Two main areas of contamination in soils and groundwater were discovered on the Omni-Vest property, a larger area west of the onsite pond and a smaller area on the eastern portion of the site. Contaminants included terpene products and a lesser amount of VOCs and some metals. Free-phase LNAPL, mainly toluene, was also detected in these areas, primarily near previously installed recovery wells west of the pond. Further work in the western portion of the site, including installation of additional monitor wells, may be necessary to complete the assessment.

The sand pits were recently purchased for Escambia County through a special legislative appropriation and the Pensacola Bay System SWIM program. This is part of an ongoing cooperative effort to increase treatment of stormwater entering Bayou Chico. To avoid overflows, which could lead to the collapse of the bank, the spillway was recently replaced with a more stable structure (NWFWMD, 2004).

3.3 Dredging

Dredging to allow navigation of barge traffic and other commercial shipping is required in Bayou Chico. It is not clear exactly when a shipping channel was first dredged through the lower reaches of the Bayou. A navigable channel would have been required by 1917 for the Pensacola Shipbuilding Company. They had received a contract from the government to build steel ships which would have required a dredged channel to navigate the Bayou. Map 8, dated to 1923 (Overman, 1923), shows that a channel going to Pensacola Bay from Bayou Chico had been dredged and presumably the channel was also dredged in the Bayou. The Bayou appears different on the 1923 map than it did on a 1895 map (Map 7). Dredging may have led to the differences but tropical storms such as the 1906 and 1916 hurricanes and other natural events may have played a role in the changes as well.

A proposed 1935 dredging map (Map 4) by the USACE shows a plan for future dredging of the shipping channel that appears to closely conform to the present shipping channel. There are several businesses and structures that were depicted in this map that are no longer there. On what is now considered to be a spoil island is a structure that was labeled as "B.F. Money Bldg 57-A, U.S. Navy Yard Phila, PA". This structure, as well as a labeled eight story bank site may have been projects that only reached planning stage and were never constructed. At this time there was apparently no active shipbuilding on the Bayou and we do not know if the earlier dredged shipping channels had been maintained. By World War II, ships requiring a dredged channel were being produced and it is likely that the proposed dredging plan had been implemented. The proposed 1935 channel is very similar to the contours of the current shipping channel. A map dated to 1943 and titled as a property survey shows the mouth of Bayou Chico, the lower Bayou channel and part of its extension into Pensacola Bay at that time (Map 9). Apparently some spoils from Bayou Chico had been previously disposed by placing it to either side of the shipping channel going out to the Pensacola Bay. This suggests that some of the pollutants previously present in the Bayou sediments are now in the Bay.

The USACE has commissioned several studies of dredging sediments for Bayou Chico since the 1950s (Glassen et al., 1977; Pratt et al., 1993). Most recently the USACE-Mobile district tasked the EA Engineering, Science, and Technology company to take 6 vibracores from the area to be directly effected by the proposed dredging project on Bayou Chico (EA, 2000). This federal navigation project is described as needed to maintain a 4,400 ft. long, 75 ft. wide channel, and a 250,000 sq. ft. turning basin to a depth of 14 ft below mean low water, plus 2 ft of advance maintenance and 2 ft of allowable overdredge. Vibracore sediment samples were mixed to homogeneity and analyzed for particle analysis, total organic carbon, semivolatile and VOCs,

metals, PAHs, selected PCBs, dioxins/furans, and butyltins (EA, 2000). Analyses of elutriated analytes from the sediments and of site water were also conducted. Presently it is planned to place the spoils for this project in one of the three Clark Sand Pits located near the upper Bayou alongside Jackson's Branch. The disposal of dredging spoils at this site had raised concerns with Peoples Water Service Company of Florida, Inc which does have a drinking water well within 1000 feet of the sand pits (Ma et al., 1999). Apparently the company is more concerned about the chloride in the spoils than the metal or complex organic pollutant molecules that may be present.

Brinson and Keltner's (1981) characterization of stormwater entering Bayou Chico was incorporated into a report which also evaluated the effects of removal of a limited quantity of contaminated sediments on water quality and benthos. Approximately 7,600 cubic meters of unconsolidated sediments were removed from the northeast arm of Bayou Chico by dredging. It should be noted that this area was determined by Glassen et al. (1977) to be not as severely impacted by industrial pollutants as was the main body of the Bayou. Extreme precautionary measures were employed during the study, in conjunction with the removal of the contaminated sediments. In spite of the precautionary measures, the authors determined that: "water samples for the remaining parameters which were monitored during sediment removal activities (i.e., turbidity, TOC, chromium, cobalt, iron, lead, manganese, mercury, zinc, oils and greases, phenolic compounds, pesticides, and PCBs) failed to meet state standards for Class III Waters or to show a reduction of pollutants in the return water" (Glassen et al., 1977). Data were insufficient to determine the long-term effects of sediment removal on benthos; however, total and fecal coliform levels in the water column continued to exceed state water quality standards following removal of contaminated sediments. Stormwater entering the Bayou failed to meet state water quality standards for turbidity, suspended solids, DO, BOD, nutrients, total and fecal coliforms, copper, lead, mercury, zinc, oils and greases, and phenols.

4. OBJECTIVES

The present project was designed to contribute in the following areas:

- Compile all accessible information related to pollution of Bayou Chico, Sanders Beach, and Omni-Vest and identify data gaps;
- Assess the impact of the ACW superfund site to water and sediment quality in Bayou Chico, and indirectly to potentially exposed human populations;
- Characterize selected SOCs of water and sediments in Bayou Chico, Sanders Beach, and Jackson's Branch Creek;
- Assess the relative contribution of potential sources of pollution;
- Establish relationships between pollution and sediment characteristics;
- Assess sediment quality relative to dredging and disposal of dredge spoils.

5. METHODS

Accessible information concerning the environmental conditions of the Bayou was compiled through an exhaustive literature search. For this effort we drew in part upon another component of the PERCH Project, the PERCH Bibliography, a fully searchable database of bibliographical materials pertaining to the environment of Northwest Florida (http://fusionmx.lib.uwf.edu/perch/search.cfm). 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. The purpose of the literature search was to assess what was known about Bayou Chico, Omni-Vest Landfill just north of the Bayou, American Creosote Works just east of the Bayou, and how Bayou Chico was or could be impacted by superfund sites and other potential sources of pollution. This information allowed evaluation of how the present project could further the existing knowledge.

To help identify optimal locations for the sampling sites the bathymetry of the Bayou and Sanders Beach area was surveyed with an echosounder and differential GPS (DGPS). Because we worked only when weather conditions were favorable and when minimal wave action was present on the Bayou we did not use a heave compensator to correct for vertical vessel movement. Accuracy of the echosounder in the given circumstances was 0.06 m as per the manufacturer's specifications (Odom, 2000). The accuracy of the DGPS based on our previous work in the area was 0.5 m (Liebens, 2000). The echosounder was calibrated each day with a bar check, and tide information was recorded at the beginning and end of each day. The tide information was used to post hoc correct the raw echosounder readings for tidal changes. In a GIS the corrected echosounder readings were converted into a bathymetric surface using kriging and a cell size of 15 m for the surface. Optimal sampling locations were identified by project personnel based on the bathymetry of the Bayou, the general location within the Bayou, and specific objectives of the sampling. These locations were marked on an overlay on the bathymetric map in the GIS. 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.

The sampling was conducted during the summer and early fall of 2005. Sediment samples were collected with vibracore equipment and a ponar grab on water, and with a manual soil auger on land. Water grabs were collected with a VanDorn sampler. For vibracores three-inch decontaminated aluminum thin walled irrigation pipe was clamped to a vibracore powered by a portable generator. The vibracore sediment was retained by a plastic core catcher at the bottom and a vacuum plug sealed the top upon retrieval of the coring pipe. In the lab the cores were split lengthwise and the sediments were sampled at mostly regular 1 meter intervals. For the sediment grab samples five local grab samples were joined at each sampling site 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. Sampling equipment was cleaned with soapy water, rinsed with reagent grade solvents, and two rinses of HPLC grade water. The decontaminated equipment was tested with rinsate blanks, and field splits for quality control were also taken.

Analytical methods followed standard procedures. Total petroleum was analyzed by the FDEP FL-PRO method. USEPA SW-846 methods were used for the following: PCBs by 1668A, Dioxin/Furans by 1613B, other semivolatiles by Method 8270C. Specific PAHs (Naphthalene, 2-Methylnaphthalene, 1-Methylnaphthalene, Acenaphthylene, 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 additionally analyzed by US EPA SW-846 method 8270 C, modified for Simultaneous Ion Monitoring (SIM). This method was used to achieve method 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 method that is generally available for PAH detection. The target analytes are extracted into 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. Mercury was determined by Method 7471A for sediments and Method 7470A for aqueous samples by cold vapor atomic absorption. For all other metal determinations the samples were prepared according to SW-846 Method 6010, Acid Digestion of Sediments, Sludges, and Soils. Per the method, antimony, cadmium, copper, thallium, zinc, arsenic, cadmium, chromium, and lead 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 metal, volatile, total organic carbon, and semivolatile analysis were performed by Columbia Analytical Systems of Jacksonville, FL, and 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 Sediments 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):

$$\mathsf{TEQ} \cong \sum_{i=n} \left(\mathsf{Congener}_i \times \mathsf{TEF}_i \right) + \left(\mathsf{Congener}_j \times \mathsf{TEF}_j \right) + \dots + \left(\mathsf{Congener}_n \times \mathsf{TEF}_n \right)$$

The TEF values used were those for humans/mammals from WHO (USEPA, 2003b) (Table 5).

To assess the origin of dioxins/furans, dioxin-like PCBs and PCBs we statistically examined similarities in their profiles with principal component analysis (PCA) and cluster analysis. We applied a varimax rotated PCA and then used hierarchical cluster analysis to identify groups of sampling sites with similar profiles. We also ran hierarchical cluster analysis on statistically standardized raw data by sampling site. The advantage of clustering the standardized raw data instead of principal components is that the standardization eliminates magnitude effects but preserves the original profiles better than PCA, and thus the clustering is run on a dataset that is more closely related to the original data than the set of principal components.

	HUMANS/ MAMMALS	FISH	BIRDS
2,3,7,8-TCDD 1,2,3,7,8-PeCDD 1,2,3,4,7,8-HxCDD 1,2,3,6,7,8-HxCDD 1,2,3,7,8,9-HxCDD 1,2,3,4,6,7,8-HpCDD OCDD	1 0.1 0.1 0.1 0.01 0.001	1 0.5 0.01 0.01 0.001	1 0.05 0.01 0.1 <0.001
2,3,7,8-TCDF 1,2,3,7,8-PeCDF 2,3,4,7,8-PeCDF 1,2,3,4,7,8-HxCDF 1,2,3,6,7,8-HxCDF 1,2,3,7,8,9-HxCDF 2,3,4,6,7,8-HxCDF 1,2,3,4,6,7,8-HpCDF 1,2,3,4,7,8,9-HpCDF 0,200000000000000000000000000000000000	0.1 0.05 0.5 0.1 0.1 0.1 0.1 0.1 0.01 0.0	0.05 0.05 0.1 0.1 0.1 0.1 0.1 0.1 0.01 0.0	1 0.1 1 0.1 0.1 0.1 0.1 0.01 0.01 0.001
3,4,4',5-TCB (81) 3,3',4,4'-TCB (77) 3,3',4,4',5-PeCB (126) 3,3',4,4',5,5'-HxCB (169)	0.0001 0.0001 0.1 0.01	0.0005 0.0001 0.005 0.00005	0.1 0.05 0.1 0.001
2,3,3,4,4',5-PeCB (103) 2,3,4,4',5-PeCB (114) 2,3',4,4',5-PeCB (118) 2',3,4,4',5-PeCB (123) 2,3,3',4,4',5-HxCB (156) 2,3,3',4,4',5'-HxCB (157) 2,3',4,4',5,5'-HxCB (167) 2,3,3',4,4',5,5'-HxCB (169)	0.0001 0.0005 0.0001 0.0005 0.0005 0.0005 0.0001 0.0001	<0.000005 <0.000005 <0.000005 <0.000005 <0.000005 <0.000005 <0.000005	0.0001 0.00001 0.00001 0.0001 0.0001 0.0001 0.00001

Table 5: TEFs for dioxins and dioxin-like PCBs from WHO (USEPA, 2003b). WHO CONSENSUS TEFs FOR MAMMALS, FISH, AND BIRDS

The pollution load index (PLI) is a measure for the overall level of a set of pollutants. Mathematically it is the geometric mean of the concentration factor for a set of pollutants. The concentration factor is the ratio of a pollutant's concentration to its background concentration. In the present study the PLI was determined for trace metals and the lowest value for any particular metal was used as the background concentration. True background concentrations are probably not present in Bayou Chico, given its history of environmental pollution. Nevertheless, the lowest value for a given metal provides a means of standardization for the metal concentrations and is suitable for internal comparison, as is done in the present study.

6. GAPS IN EXISTING DATA

The goals of this study include identifying environmental concerns that have not been fully studied (data gaps) and are related to environmental and human health. The study was designed to not repeat what has previously been studied and is not intended to present a complete environmental assessment of the Bayou. To achieve this we performed a thorough review of the existing environmental literature for Bayou Chico. A GIS database was utilized to evaluate Bayou Chico, Sander Beach, and Omni-Vest data and assess this information for data gaps. We found data gaps for several aspects of Bayou Chico, one of its tributaries, and nearby Sanders Beach.

The greatest weakness of the more recent studies is that many of them were carried out independently of findings of previous studies. However, the diversity of the recent studies has covered most environmental aspects for Bayou Chico and it surrounding areas, but little emphasis has been placed on human health and industrial pollution possibly coming from two industrial waste sites near the Bayou. An environmental assessment of Bayou Chico in the 1990's was published in a report by Waller et al. (1998). The Waller et al. (1998) samples were mostly grabs of sediment and water with analytical data including oxygen, nutrients, biological communities, common pollutants such as metals, selected PCBs, semivolatiles, and pesticides. The major shortcoming of this project was an incomplete characterization of the deeper sediments via vibracoring and little interest in industrial pollution. Metals were studied in vibracores and related to particle size by Stone and Morgan (1991), Wood and Bartel (1994) and EA (2000). Stone and Morgan (1991) also carried out a limited number of analyses for semivolatiles and EA (2000) analyzed elutriates and sediments from 6 vibracores for PCBs, metals, semivolatiles, dioxins/furans, and butyltins.

Previous studies have characterized many aspects of the environment of Bayou Chico and the Sanders Beach area and two nearby industrial waste sites (ACW and OMV) have been studied extensively, mainly by government mandated studies. However, relatively little study has been devoted to assessing the possible impacts of the two sites upon the Bayou or residents living near it. There have been no recent studies directed towards dioxin/furan contamination in soils or sediments on Sanders Beach. The last studies for organics that were directed towards American Creosote Works impacts upon the beach were conducted in the 1980s (Rostad and Pereira, 1987; Elder and Dresler, 1988). At that time the stormwater ditch near the Pensacola Yacht Club was still visibly conveying wastes toward the Bay and creosote was evident about the beach. The more recent studies conducted by USEPA appear not to actually study the sediments under the beach, leaving a data gap. The focus of some recent federally sponsored ACW investigations has been related to adjacent neighborhoods but with little reference to the Bay or Bayou. These investigations suggest that the contaminants of concern (COCs) of this CERCLA site are moving towards the shore and could be deposited into sediments underlying Pensacola Bay and Bayou Chico (Bechtel Environmental, 1996). PERCH was concerned that semivolatiles including carcinogenic PAHs, VOCs, and dioxin/furan contaminants from the site might be entering the sands of Sanders Beach. During the summer months of 2005 this neighborhood beach was observed to be in continuous use from sun bathers, unaccompanied children playing and fishing, daycare children eating lunch, and people just lounging around to relax, consume beverages, and lunch. To assess the potential influence of the SOCs on the users of this public beach we included in our sampling plan vibracore and auger samples on the beach and immediately off the shore from the beach for dioxin/furan, semivolatile, and VOC analysis.

We originally intended to take similar samples from the adjacent Pensacola Yacht Club, but did not succeed in obtaining permission to sample on the property.

PERCH was also concerned that volatiles from the OMV site might be entering the sediments of Jackson's Branch Creek and ultimately Bayou Chico. Therefore, we took vibracore samples for metal and VOC analysis in the sediments of Jackson's Branch Creek just south from OMV.

A PERCH seafood study (Karouna-Renier, 2006) showed that elevated levels of dioxins/furans and PCBs, and other pollutants, are present in crabs and oysters from Bayou Chico. It is difficult to assess the influence of sediment pollution on the seafood because there has been only one very limited study of dioxins/furans in Bayou Chico (EA, 2000). The study consisted of six vibracores taken in the navigational channel. Significant dioxin/furan concentrations were encountered in the sediments suggesting that further study is needed. Lewis et al. (2001b) and Waller et al. (1998) reported on PCBs in the Bayou but the PCB total values from these studies are not complete since the analyses did not include all 209 PCB congeners. Consequently, to assess the effect of sediment pollution on seafood additional samples were collected by the present study from bay and bayou sediments for analyses of dioxins/furans and the 209 PCB congeners.

The presence of a petroleum terminal with storage tanks (Figure 6), constant boating traffic, marinas, boat yards, shipbuilding industry, and urban runoff suggests that current information on petroleum hydrocarbons in surficial sediments is of interest. However, little information on these potential pollutants is available in the Bayou Chico literature. We took samples for analysis with the FL PRO method for C8-C40 hydrocarbons throughout the Bayou.



Figure 6: Barge unloading fuel at petroleum storage tanks.

The data collected during the present study are suitable to support decisions about whether the spoils from proposed dredging in Bayou Chico should be placed in an unlined situation in one of the Clark Sand Pits. Hearn and Baya (2001) conducted a subsurface investigation of the proposed disposal site and took eight cores to a depth of five feet in the southeastern pit. Results show the bottom to be composed of materials ranging from light gray silt, light gray silty sand, dark grey silt, light gray and tan silt, light brown silt, and coarse sand. These data suggest that hydraulic communication between the sand pit and the aquifer and hydraulic transport of pollutants into the aquifer is possible. Because of concerns about dredge spoil disposal and potential adverse impacts to human health and the environmental health of Bayou Chico we reviewed some pertinent literature and formulated recommendations aimed at minimizing potential negative impacts from the dredging and disposal project.

7. RESULTS AND DISCUSSION

7.1 Bathymetry

The bathymetric map shows that in general the Bayou's deepest areas are in the dredged shipping channel with maximum depths exceeding 6 meters occurring primarily south of the Barrancas Ave. bridge (Map 10). To the north the dredged shipping channel ends in a turning basin, but there is also a deeper area just past the turning basin in front of the Patti Shipyard. This deep area may be the result of poorly documented dredging. Some of the deeper spots in the shipping channel may result from natural scour and structure induced scour around the bridge pilings due to tidal currents. The channel extends southward through some sand banks into Pensacola Bay. Out of the shipping channel the remainder of the Bayou is shallow with depths from 1 m to 2 m being predominant. Near the banks the Bayou is very shallow and access by boat to collect depth data was not feasible. North of the Patti Shipyard the Bayou becomes shallower and narrows at the approach remnants of a former railroad bridge. To the north of this bridge the Bayou widens for a short distance and then narrows again for the W. Navy Blvd. bridge. North of this bridge the Bayou bifurcates to two shallow arms that branch apart to form a T with east and west branches. The two arms connect the Bayou with freshwater streams and are less than a meter deep. Near their ends they are overgrown with aquatic vegetation. Coming off the main body of the Bayou to the west is a larger Bayou finger that connects to Jones Creek. This becomes shallower but retains its width as it trends away from the main Bayou. The western shore of the main Bayou north of the Barrancas Ave. bridge has two major widening expansions ranging in depths of 1 m to 2 m. In an earlier sediment typing (Map 2) these areas were shown to contain deep deposits of soft sediment (Glassen et al., 1977). The locations of the sampling sites were selected based on this bathymetric map and a priori knowledge (Maps 11, 12, Table 6). To our knowledge, no other study has methodically considered the detailed bathymetry of the whole Bayou to locate sampling sites.

Table 6: Coordinates of sampling sites.

	<u> </u>	1
SAMPLE_ID	latitude'	longitude
BG-1	30.41396	-87.26118
BG-2	30.41542	-87.25780
BG-3	30.40946	-87.25803
BG-4	30.40758	-87.25736
BG-5	30.40417	-87.25880
BG-6	30.40240	-87.26635
BG-7	30.40466	-87.25313
BG-8	30.40045	-87.24542
BG-9	30.39960	-87.24094
BG-10	30.40361	-87.25361
BG-11	30.39304	-87.23312
BG-12	30.40123	-87.24721
BG-13	30.39514	-87.23186
BG-14	30.40491	-87.25731
BG-15	30.40346	-87.26315
BG-16	30.40991	-87.25836
BGP-1	30.39916	-87.24439
BGP-2	30.40697	-87.25843
BGP-3	30.39999	-87.24285
BGP-4	30.40195	-87.25264
SB-1	30.39993	-87.23758
SB-2	30.39999	-87.23759
SB-3	30.40005	-87.23760
SB-4	30.40013	-87.23762
SB-5	30.40020	-87.23762
SB-6	30.40068	-87.23764
FID-1	30.39958	-87.23661
FID-2	30.39908	-87.23728
FID-2G	30.39919	-87.23733
FID-3	30.39927	-87.23794
FID-4	30.39899	-87.23895
FID-5	30.39934	-87.23954
FID-6	30.39956	-87.24083
FID-7	30.39975	-87.23759
OV-1	30.41396	-87.26445
OV-2	30.41401	-87.26527
OV-3	30.41354	-87.26744
BW-1	30.39304	-87.23312
BW-2	30.40123	-87.24721
BW-4	30.41403	-87.26507
BW-13	30.39949	-87.23750
BW-14	30.40491	-87.25731
BW-15	30.40346	-87.26315
BW-16	30.40991	-87.25836

¹: Latitude is N, longitude is W, units are decimal degrees.

7.2. Semivolatile organic compounds

7.2.1 Total petroleum

Bayou Chico is an industrialized bayou dominated by marine related industries that use diverse petroleum products. There are also fuel storage tanks and a barge transshipment point on the Bayou. Another potential source of bayou petroleum is from stormwater transport in which oil leaking on driveways, streets, and parking lots will ultimately end up in the Bayou. Low levels of petroleum products can be expected to degrade in the presence of bacteria, nutrients, solar radiation, and oxygen (Lepo et al., 2003). However, total petroleum products are expected to persist in Bayou Chico due to continual import via stormwater and from bayou activities related to the maintenance, repair, and use of boats.

There are presently no applicable sediment quality guidelines for this general range of hydrocarbons. A recent discussion of this issue under the auspices of the USACE Seattle District commented upon this issue. Thornburg (2004) found that screening levels for bulk petroleum hydrocarbons in sediment have not been developed due to the widely varying mix of compounds that can be present in total petroleum and a perception that toxicity could be adequately accounted for by considering the toxicity of PAHs that are a constituent of total petroleum. However, there are situations where bulk petroleum hydrocarbons are present in sediment at elevated levels, and individual listed constituents either are absent or are present at levels that would not indicate toxicity. Total petroleum hydrocarbon (TPH) analyses are routinely performed, but it is difficult to relate directly any specific concentration to toxicity. This is due to there having been limited study of the relationship between toxicity threats to sediments by petroleum contamination and the general diversity and variability of TPH constituents. TPH toxicity or other detrimental effects upon the Bayou is not clear and this is reflected in what appears to be an absence of federal or FDEP recognized marine sediment quality assessment guidelines (SOAGs) for total petroleum. More recent theories for assessing the toxicity of petroleum and its constituents to benthic organisms have focused on a narcosis-based approach. Narcosis is a form of toxicity resulting from the presence of foreign molecules in hydrophobic or lipid tissues, which depresses and disrupts various cellular functions (Abernathy et al., 1988; Franks and Lieb, 1978).

The present study utilized the FL PRO method that detects hydrocarbons in the C8 to C40 range. Total petroleum (C8-C40) was generally found at all sites, which is to be expected for an urban bayou/creek system (Table 7). The highest concentration of total petroleum was 930 mg/kg (sample BG-1 located in the upper Bayou's northwest branch) and the lowest was 6.4 mg/kg (sample BG-13, located in Pensacola Bay). An examination of Map 13 shows that total petroleum was low in samples taken in Pensacola Bay, increased slightly inside of the entrance channel of the Bayou and then increased markedly in the main and north sections of the Bayou. The petroleum concentrations observed in Bayou Chico are comparable to those in industrial and harbor settings elsewhere in the world (Metwally et al., 1997; Zheng and Richardson, 1999), but are clearly higher than in environments with little anthropic influence (Hargrave and Phillips, 1975; Keizler et al., 1978; Fowler, 1985).

The FL-PRO is designed to measure concentrations of petroleum hydrocarbons in water and soil/sediment in the alkane range of C8-C40. The MDL is approximately 0.1 mg/L for water and 4 mg/kg for soil/sediment. 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.

Sample ID	mg/kg	Sample ID	mg/kg
BG-1	930	BG-11	13
BG-2	300	BG-12	73
BG-3	340	BGP-1	36
BG-4	50	BGP-2	16
BG-5	170	BGP-3	100
BG-6	65	BGP-4	730
BG-6Dupl.	99	FID-2G	7.2
BG-7	800	BG-13	6.4
BG-8	790	BG-14	390
Bg-9	110	BG-15	170
BG-10	770	BG-16	260

Table 7: Total petroleum hydrocarbons in surface sediments.

The range of C8-C40 can be subdivided into: Gasoline Range Organics (GRO) covers C8-C10, Diesel Range Organics (DRO) covers C10-C28, and Oil Range Organics (ORO) is C28-C40. The FL-PRO analyses performed by Columbia Analytical - Jacksonville, FL, for this study were run over a time period of 15 minutes. A chromatogram of standards shows when each of the standards elutes (Figure 7). All analyses use two surrogates: o-Terpheny ($C_6H_5C_6H_4C_6H_5$) that eluted where C19 alkanes do and is marked by peak 2S and n-Nonatriacontane ($CH_3(CH_2)_{37}CH_3$) that eluted where C39 alkane elutes as marked by peak 3S. Using this information it was possible to determine the probable hydrocarbon range of the observed peaks. It is not possible to separate or distinguish between alkanes and other hydrocarbons with this analysis. We examined the chromatograms obtained during the FL PRO analysis of Bayou Chico sediment samples and observed trends for different ranges relative to the location of the sample.

Examining the chromatograms from the different samples showed that qualitative differences were apparent in the arms of the Bayou as compared to Bayou regions near the navigation channel. The chromatograph of Sample BG-1, located in the NW arm of the upper Bayou (Map 11) shows a broad peak beginning at about C20, just to the right of the narrow 2S peak on the chromatogram (Figure 8A). The top of the broad peak occurs at about C32 in the ORO and the peak remains discernable to C40. This trend is evident, but to a lesser degree, in two other samples from the northern part of the Bayou (BG-2 and BG-16, Figure 8A, Map 11). However, as the sampling sites become closer to the main part of the Bayou, the chromatograms show a cluster of peaks about C20 near the 2S maker in the DRO (Figure 8B, Map 11). This elution pattern becomes more prominent as the sampling sites get closer to the main Bayou. In samples from the main Bayou, but adjacent to Bayou arms, the DRO peak continues to become more prominent relative to elution in the ORO (Figure 8C, Map 11). Within the Bayou near the navigational channel for many samples the DRO peak becomes highly dominant (Figures 9A, B, C; Map 11). This suggests that ORO originates in the arms of the Bayou, possibly the creeks

feeding into these arms, while DRO likely has an origin in the main body of the Bayou. Assigning specific source(s) for these hydrocarbons is not feasible.



Figure 7: FL PRO total petroleum standards and GRO, DRO, and ORO ranges.

It is possible that the predominance of the heavier hydrocarbons in the arms of the Bayou may represent heavier oils transported by stormwater to the Bayou such as engine oils. The peak center about C20 (DRO) could represent diesel fuel spills. However, more precise analytical analyses would be required to unequivocally prove this contention since FL-PRO only distinguishes compounds on the basis of mass and not structure. The petroleum storage tanks near the mouth of the Bayou have always been of concern but sample BGP-1, which was taken near the storage tanks, was actually low in overall TPH. However, the prop wash of tow boats and tidal currents could redistribute any spilled fuel to other parts of the Bayou are qualitatively different from those in the more industrialized areas of the main Bayou in their relative proportions of specific hydrocarbon ranges. These results need to be confirmed by sampling in subsequent years to ascertain that they are not due to some unusual one time event. Future stormwater projects could reduce the ORO range of contamination, and the source of the DRO hydrocarbons need to be determined. If it is due to a point source, then enforcement of existing regulations could conceivably be used to reduce this component.



Figure 8A: Chromatograms representing FL-PRO results for upper Bayou.



Figure 8B: Chromatograms representing FL-PRO results for Bayou arms.



Figure 8C: Chromatograms representing FL-PRO results for main Bayou adjacent to Bayou arms.



Figure 9A: Chromatograms representing FL-PRO results for main body of Bayou.



Figure 9B: Chromatograms representing FL-PRO results for main body of Bayou.



Figure 9C: Chromatograms representing FL-PRO results for main body of Bayou.

7.2.2 Polycyclic aromatic hydrocarbons (PAHs)

Eighteen PAH species were detected via the 8270C SIM analysis: Naphthalene, 2-Methylnaphthalene, 1-Methylnaphthalene, Acenaphthylene, 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, Dibenzo(a,h)anthracene, and Benzo(g,h,i)perylene. A major concern of the project was to achieve analytical results that would give RLs below the FDEP TEL. Table 8 shows the MDL and RL for PAH analytes derived by 8270C SIM for sample FID-5B. The MDLs were for all analyses lower than the TEL, and for most analyses the RLs were also lower than the TEL.

PAH Compound	Reporting Limit	Detection Limit	TEL [ug/kg]	PEL [ug/kg]
	I	LMW (Light Molecular V	Veight) PAHs	
Acenaphthene	4.1	1.3	6.71	88.9
Acenaphthylene	4.1	0.80	5.87	128
Anthracene	4.1	1.47	46.9	245
Fluorene	4.1	0.73	21.2	144
2-methylnaphthalene	4.1	0.76	20.2	201
Naphthalene	4.1	0.61	34.6	391
Phenanthrene	4.1	0.64	86.7	544
Sum LMW-PAHs	na	na	312	1,442
	н	IMW (Heavy Molecular	Weight) PAHs	
Benz(a)anthracene	4.1	0.97	74.8	693
Benzo(a)pyrene	4.1	1.9	88.8	763
Chrysene	4.1	2.3	108	846
Dibenzo(a,h)anthracene	4.1	2.5	6.22	135
Fluoranthene	4.1	0.57	113	1,494
Pyrene	4.1	0.53	153	1,398
Sum HMW-PAHs	na	na	655	6676
Sum LMW&HMW	na	na	1684	16,770
		PAHs not assigned SQ	AG by FDEP	
Benzo(b)fluoranthene	4.1	1.6	NA	NA
Benzo(g,h,i)perylene	4.1	1.5	NA	NA
Benzo(k)fluoranthene	4.1	2.2	NA	NA
Indeno(1,2,3-cd)pyrene	4.1	1.5	NA	NA
1-Methylnaphthalene	4.1	0.75	NA	NA

Table 8: Typical PAH detection and reporting limits and SQAGs^{1,2}.

¹: detection limit and reporting limit are for sample FID-5B.

2: See table 1 for other footnotes

Presently there are only sediment guidelines (TEL and PEL) for 13 of the PAH species. These 13 species likely comprise only a small number of commonly occurring PAHs present in Bayou Chico sediments. The approved USEPA analytical methods used in the present study are set up to detect a set number of PAHs. Our analyses were designed to detect 18 different PAH species. We assume that there are undetected PAH species, but have no direct proof that they are present. Aromatics (including PAHs) are considered to be the most acutely toxic component of petroleum products, and are also associated with chronic and carcinogenic effects. Sixteen of the common PAHs typically analyzed in standard contract laboratory scans have been listed by the Environmental Protection Agency among 126 priority pollutants under the Clean Water Act (Federal Register, 1997). Five of them are also listed among the 25 hazardous substances thought to pose the most significant potential threat to human health at Superfund Sites (Van Mouwerik et al., 1998). There are also IARC (International Agency for Research on Cancer) listings for cancer causing PAHs (Table 3).

7.2.3 PAH origin

PAHs can have multiple origins with oil spills and combustion products being the most important sources in typical urban environments. In the Bayou Chico area the ACW site may be a source through releases of wood-treating wastes that contained PAHs of creosote and diesel origin. Ratios based on concentrations of specific PAHs present within a sediment sample have been employed to obtain evidence that suggests the probable origin of the PAH mixture (Rostad and Pereira, 1987; Yunker et al., 2002). Wood-treating wastes contain PAHs that originate from coal tars used to formulate creosote and may also contain PAHs of petroleum origin since diesel fuel was often employed during wood-treating processes. According to Rostad and Pereira (1987) typical coastal sediment PAHs are not of creosote origin and have less phenanthrene than fluoranthene or pyrene. In the Rostad and Pereira (1987) system normalized ratios for fluoranthene or pyrene to phenanthrene of less than 100 suggest a creosote origin. The authors confirmed this ratio by sampling PAH wastes known to be associated with the ACW site. Yunker et al. (2002) listed four PAH ratio calculations for parent (non-alkylated) PAH compounds. Three of the four ratio calculations were applied to this study (Table 9). The ratios can in principle be correlated with one of four sources: petroleum release; combustion of petroleum products; combustion of grass, wood, and/or coal; and creosote origin. These ratios are general in application and may not adequately predict all specific cases.

ruble 9. 17 m ongin malaator rubbs (1 anker et al., 2002).									
PAH Ratio	Petroleum release	Vehicle, crude oil combustion	Combustion grass, wood, coal	Creosoted wood pilings					
An/(Pn+An) ¹	<0.10	>0.10	>0.10	>0.18					
FI/(FI+Py) ²	<0.40	0.40-0.50	>0.50	>0.62					
IP/(IP+Bghi) ³	<0.20	0.20 to 0.50	>0.50	>0.62					

Table 9: PAH origin indicator ratios (Yunker et al., 2002).

¹: An/(Pn+An)= Ratio of Anthracene/ Anthracene+ Phenanthrene

²: Fl/(Fl+Py) = Ratio of Fluoranthene/ Fluoranthene+ Pyrene

³: IP/(IP+Bghi) = Ratio of Indeno(1,2,3-c,d)Pyrene/ Indeno(1,2,3-c,d)Pyrene+Benzo(g,h,i)Perylene

7.2.3.1 Sanders Beach

Sanders Beach, a public bathing beach, is located a few hundred yards down gradient from the ACW site and may have been impacted by groundwater and surface water transport of wastes from the ACW site. Near the beach is a stormwater ditch that is heavily contaminated with creosote from ACW (USEPA, 2002). Air deposition from the ACW site and in general from other regional sources may also have impacted the beach. We took auger samples from the beach and vibracore samples just offshore (Map 12).

The lower part of the beach and nearby offshore areas presented difficulties in obtaining cores to two meter depth. We encountered absolute resistance to penetration by auger or vibracore at most sampling sites prior to attaining a core of two meters in depth. In some cases we brought material up that appeared to be terracotta fragments that could be debris from old houses, suggesting that part of Sanders Beach may contain fill. There were islands and manmade structures present in the entrance to the Bayou prior to 1906 (Maps 3, 5, 6, 7). Hurricanes in 1906, 1916, and 1926 may have resulted in locational changes in the Bayou's entrance (Killam, 1981a-e) and the precise location of the Brent Lumber Mill (Map 7) is not known relative to the current location of Sanders Beach. The hurricanes and structures all may have led to the accumulation of demolition debris on and near the beach. In Table 10 PAH values obtained from cores taken on a transect (Map 12) on Sanders Beach show great variation in total PAH values. Values for the surface level samples from the cores, designated by suffix A in tables, are generally very low in total PAHs although they reach a maximum of 705 ug/kg for SB-6A. This sample is located very close to a parking lot, which may be the reason for the somewhat higher value for the PAHs. A few of the deeper levels in the cores have very high PAH concentrations. Samples SB-3C and SB-4C have the highest PAH concentrations and were taken at a depth of 2 m (Figure 10). The Rostad and Pereira ratios derived from these samples with the highest PAH concentrations are less than 100, suggesting a creosote origin. Sample SB-4C also exhibited an odor that was characteristic of creosote. One of the Yunker ratios (An/(Pn+An)) for SB-3C suggests an input from non-creosote (or non-coal tar) source since its ratio is 0.14. The remaining ratios for these two samples either exceed the Yunker ratios for creosote origin or are within a 0.03 of achieving the creosote cut off point. The only other sample from 2 m deep was SB-6C and it is a non-detect. Surface sample SB-5A have Rostad and Perreira ratios close to 100, but the very low overall PAH value of 120.8 ug/kg is not as reliable as the higher concentrations used for ratio calculation for SB-3C and SB-4C. All other samples at Sanders Beach have Rostad and Perreira ratios well above 100, indicating a non-creosote origin, and have non-consistent Yunker ratios. Given that the Rostad and Perreira ratios were developed specifically on ACW wastes these results seem to point to an ACW related origin for the PAHs in samples SB-3C and SB-4C. We do not know if there were also combustion products from pine products (bark, woody parts) that might have been used to supply fuel needed for processes requiring heating at ACW. Such combustion can also result in release of PAHs. There is also a possible diesel component in PAHs releases from the ACW. The presence of what appears to be anthropogenic rubble underneath parts of Sanders Beach also could have resulted in deposits of PAHs. Some of the rubble could predate the 1902 startup of ACW or may have been deposited anytime during the 1902 until December 1981 operating period of the plant.

Sample ID	total PAH ¹	fluoranthene/ phenantrene ²	pyrene/ phenantrene ²	An/(Pn+An) ³	Fl/(Fl+Py) ⁴	IP/(IP+Bghi)⁵
SB-1A	29.6	No Ratio	No Ratio	No Ratio	0.53	0.54
SB-1B	187.4	1065	1217	0.35	0.47	0.55
SB-2A	108.4	609	652	0.48	0.48	0.56
SB-2B	270.8	250	210	0.40	0.54	0.50
SB-3A	13.5	No Ratio	No Ratio	No Ratio	0.57	0.54
SB-3B	5,946	180	180	0.97	0.50	0.57
SB-3C	65,840	75	37	0.14	0.67	0.60
SB-4A	40.6	200	162	0.43	0.55	0.54
SB-4B	0	No Ratio	No Ratio	No Ratio	No Ratio	No Ratio
SB-4C	291,940	84	56	0.20	0.60	0.59
SB-5A	120.8	122	94	0.46	0.56	0.53
SB-5B	2268	223	208	0.42	0.52	0.58
SB-6A	704.6	282	223	0.25	0.56	0.55
SB-6B	0	No Ratio	No Ratio	No Ratio	No Ratio	No Ratio
SB-6C	0	No Ratio	No Ratio	No Ratio	No Ratio	No Ratio
ID SB-1A SB-1B SB-2A SB-2B SB-3A SB-3B SB-3C SB-3A SB-4A SB-4A SB-5A SB-5A SB-5B SB-6A SB-6B SB-6C	29.6 187.4 108.4 270.8 13.5 5,946 65,840 40.6 0 291,940 120.8 2268 704.6 0 0	No Ratio 1065 609 250 No Ratio 180 75 200 No Ratio 84 122 223 282 No Ratio No Ratio	No Ratio 1217 652 210 No Ratio 180 37 162 No Ratio 56 94 208 223 No Ratio No Ratio No Ratio	No Ratio 0.35 0.48 0.40 No Ratio 0.97 0.14 0.43 No Ratio 0.20 0.46 0.42 0.25 No Ratio No Ratio	0.53 0.47 0.48 0.54 0.57 0.50 0.67 0.55 No Ratio 0.56 0.52 0.56 No Ratio No Ratio	0.54 0.55 0.56 0.50 0.54 0.57 0.60 0.54 No Ratio 0.59 0.53 0.58 0.55 No Ratio No Ratio

Table 10: Total PAH concentrations [µg/kg] and PAH ratios at Sanders Beach.

¹: Total PAH includes the summed concentrations of the 18 PAHs detected by 8270C in Sanders Beach soils.

²: Rostad/Pereira Ratios are based on calculating Phenanthrene to 100 and calculating the relative percent difference

to Fluoranthene and Pyrene, i.e. (100/ μ g Phenanthrene) x μ g of Phenanthrene, Fluoranthene, or Pyrene.

³: An/(Pn+An)= Ratio of Anthracene/ Anthracene+ Phenanthrene

⁴: Fl/(Fl+Py) = Ratio of Fluoranthene/ Fluoranthene+ Pyrene

⁵: IP/(IP+Bghi) = Ratio of Indeno(1,2,3-c,d)Pyrene/ Indeno(1,2,3-c,d)Pyrene+Benzo(g,h,i)Perylene



Figure 10: Interpreted cross section of total PAH levels at Sanders Beach. Axis scales are in meters, concentrations in μ g/kg. For location of sample sites, see map 12.

7.2.3.2 Offshore Sanders Beach and Bayou mouth

Samples were also collected to assess the possible environmental impacts of ACW wastes upon bayou sediments. The FID series were vibracore sediment samples obtained in shallow waters just off Sanders Beach and the adjacent Pensacola Yacht Club (Maps 11, 12). The surficial sediments of these cores were more strongly subject to wave and current mediated processes than deeper portions of the core. Directly in front of the beach we were not able to obtain cores deeper than a meter likely due to an extension from the beach of the previously mentioned hard layer that was encountered on the beach. For sample cores FID-5 and FID-6,

taken in the Bayou adjacent to the docks of the Pensacola Yacht Club, it was possible to obtain cores to more than 2 m. The vibracore sample series shows Rostad and Perreira ratios reflecting a non-creosote origin (>100) for samples with detectable PAHs (Table 11). The highest total PAH concentrations were from surficial samples and in some cases to level B (1 meter depth). The ratios of An/(Pn+An) show ratios that are characteristic of creosote origin for all samples. The ratios for Fl/(Fl+Py) span the ranges of petroleum origin to all types of combustion but terminate somewhat below the beginning ratio for creosote. The ratios for of IP/(IP+Bghi) span the range between combustion of grass, wood, coal without reaching that of creosote. These results suggest a multiple origin for the PAHs in this area and do not demonstrate a significant contribution from the ACW.

	Total PAH	fluoranthene/ phenantrene ¹	pyrene/ phenantrene ¹	An/(Pn+An) ²	FI/(FI+Py) ³	IP/(IP+Bghi) ⁴
FID-1A	26.7	No Ratio⁵	No Ratio	No Ratio	0.55	0.56
FID-1B	1273.34	118	112	0.20	0.51	0.51
FID-2G	7.7	No Ratio	No Ratio	No Ratio	0.56	No Ratio
FID-2A	28.5	No Ratio	No Ratio	No Ratio	0.54	0.52
FID-2B	17.8	No Ratio	No Ratio	No Ratio	No Ratio	0.58
FID-3A	810.8	134	113	0.21	0.54	0.55
FID-3B	3468	173	173	0.28	0.50	0.56
FID-4A	1443.3	290	246	0.28	0.54	0.56
FID-4B	2734.1	185	413	0.42	0.31	0.58
FID-5A	8017.2	236	627	0.61	0.27	0.58
FID-5B	ND	No Ratio	No Ratio	No Ratio	No Ratio	No Ratio
FID-5C	ND	No Ratio	No Ratio	No Ratio	No Ratio	No Ratio
FID-6A	205.2	357	378	0.27	0.49	0.57
FID-6B	ND	No Ratio	No Ratio	No Ratio	No Ratio	No Ratio
FID-6C	ND	No Ratio	No Ratio	No Ratio	No Ratio	No Ratio
FID-6D	0.88	No Ratio	No Ratio	No Ratio	No Ratio	No Ratio
FID-7A	535.5	206	194	0.49	0.51	0.58

Table 11: Total PAH concentrations $[\mu g/kg]$ and PAH ratios off Sanders Beach.

¹: Ratios are based on calculating Phenanthrene to 100 and calculating the relative percent difference to Fluoranthene and Pyrene, i.e. (100/ μ g Phenanthrene) x μ g of Phenanthrene, Fluoranthene, or Pyrene

²: An/(Pn+An)= Ratio of Anthracene/ Anthracene+ Phenanthrene

³: Fl/(Fl+Py) = Ratio of Fluoranthene/ Fluoranthene+ Pyrene

⁴: IP/(IP+Bghi) = Ratio of Indeno(1,2,3-c,d)Pyrene/ Indeno(1,2,3-c,d)Pyrene+Benzo(g,h,i)Perylene

⁵: No Ratio indicates that at least one of the PAHs required for ratio calculation was not detected in that sample

7.2.3.3 Bayou proper

Surface grab samples taken in other areas away from Sanders Beach and the Pensacola Yacht Club were also analyzed for PAHs (Map 11, Table 12). This was done to verify if there were any observable differences between Bayou and adjacent Bay levels for PAH species. Sample BG-13 taken in the Bay has very low levels of PAHs. The other samples taken in the Bayou at some distance from the ACW site had much higher PAH concentrations. Samples BG-14, BG-15, and BG-16 exhibited ratios that are less suggestive of creosote PAH origins as compared to what was observed in the sample series SB.
	Total PAH	fluoranthene/ phenantrene ¹	pyrene/ phenantrene ¹	An/(Pn+An) ²	Fl/(Fl+Py) ³	IP/(IP+Bghi) ⁴
BG-13	26.7	No Ratio	No Ratio	No Ratio	No Ratio	0.58
BG-14	4,320.7	440	970	0.57	0.31	0.39
BG-15	2,229.6	439	649	0.47	0.40	0.49
BG-16	5,350.4	300	363	0.33	0.45	0.54

Table 12: PAH concentrations [µg/kg] and PAH ratios in Bayou Chico.

¹: Rostad/Pereira Ratios are based on calculating Phenanthrene to 100 and calculating the relative percent difference to Fluoranthene and Pyrene, i.e. (100/ μ g Phenanthrene) x μ g of Phenanthrene, Fluoranthene, or Pyrene

²: An/(Pn+An)= Ratio of Anthracene/ Anthracene+ Phenanthrene

3: Fl/(Fl+Py) = Ratio of Fluoranthene/ Fluoranthene+ Pyrene

⁴: IP/(IP+Bghi) = Ratio of Indeno(1,2,3-c,d)Pyrene/ Indeno(1,2,3-c,d)Pyrene+Benzo(g,h,i)Perylene

7.2.4 Environmental impact of sediment PAHs

7.2.4.1 Sanders Beach

PAH concentrations generally are low for the surface materials near Sanders Beach (Table 13). This may be because PAHs do not reach the surface materials of the area but it is also possible that strong winds or exposure to sunlight prevent accumulation of the PAHs that are detected by our analyses. Three of the samples exceeded Florida guidelines for soil cleanup target levels (SCTL) for Benzo(a)pyrene (0.1 mg/kg SCTL). These samples have also high total PAH levels. Two of them are at 2 m depth (C level) and one at 1 m depth (B level). Benzo[a]pyrene is a carcinogen that is readily absorbed following inhalation, oral, and dermal routes of administration (ATSDR, 1995). Following inhalation exposure, benzo[*a*]pyrene is rapidly distributed to several tissues in rats (Sun et al., 1982; Weyand and Bevan, 1986). The metabolism of benzo[a]pyrene is complex and includes the formation of a proposed ultimate carcinogen, benzo[a]pyrene 7,8 diol-9,10-epoxide (IARC, 1983). The exposure and risk of benzo(a)pyrene to a visitor at Sanders Beach is minimal assuming beach goers do not have contact with materials from these depths. However, for a person that has contact with subterranean soils resulting from digging there is a risk of direct exposure to benzo(a)pyrene at high levels.

		2-Methyl	1-Methyl	Acenaph	Acenaph	
	Naphthalene	naphthalene	naphthalene	thylene	thene	Fluorene
SB-1A	<0.52 ¹	<0.64	<0.63	<0.67	<1.1	<0.61
SB-1B	<0.59	<0.75	<0.73	<0.78	<1.2	<0.71
SB-2A	<0.51	<0.64	<0.63	1.9 IJ	<1.1	<0.61
SB-2B	<0.6	<0.76	<0.75	6.5	<1.2	<0.72
SB-3A	<0.51	<0.64	<0.63	0.67	<1.1	<0.61
SB-3B	11	6.5	3.5 IJ	240	13	33
SB-3C	240	140	320	230	2600 D	4500 D
SB-4A	<0.51	<0.64	<0.63	<0.67	<1.1	<0.61
SB-4B	<0.56	<0.7	<0.69	<0.74	<1.2	<0.67
SB-4C	300 D ²	840 D	2700 D	1500 D	18000 D	25000 D
SB-5A	<0.51	<0.64	<0.63	<0.67	<1.1	<0.61
SB-5B	10	8.4	7.6	48	12	17
SB-6A	<0.69	2.5 IJ ³	2.4 IJ	7.6	4.4 IJ	4.7 IJ
SB-6B	<0.65	<0.81	<0.8	<0.85	<1.3	<0.78
SB-6C	<0.62	<0.78	<0.76	<0.81	<1.3	<0.74

Table 13. F	AH sne	ecies and	nentach	loronhenol	[III]/kg]	at Sander	s Beach
	ALLSPU	Leics and	penaem	lorophenoi	ιμα/και	at Sanuel	s Duaun.

						Benz(a)
	Phenanthrene	Anthracene	Fluoranthene	Pyrene	Chrysene	anthracene
SB-1A	<0.54	<0.68	3.6	3.2 IJ	2.8 IJ	2.6 IJ
SB-1B	4.6	2.5 IJ	49	56	12	13
SB-2A	2.3 IJ	2 IJ	14	15	9.5	9.3
SB-2B	10	6.8	25	21	19	18
SB-3A	<0.54	<0.68	2.8 IJ	2.1 IJ	<2	1.4 IJ
SB-3B	100	3800 D	180	180	130	280
SB-3C	20000 D	3300 D	15000 D	7400 D	2600 D	3100 D
SB-4A	2.6 IJ	2 IJ	5.2	4.2	3.2 IJ	3.1 IJ
SB-4B	<0.59	<0.75	<0.53	<0.49	<2.2	<0.89
SB-4C	64000 D	16000 D	54000 D	36000 D	16000 D	16000 D
SB-5A	7.9	6.8	9.6	7.4	31	13
SB-5B	130	94	290	270	190	180
SB-6A	39	13	110	87	69	54
SB-6B	<0.69	<0.87	<0.61	<0.57	<2.5	<1.1
SB-6C	<0.65	<0.82	<0.58	<0.54	<2.4	<0.98

	Benzo(h)-	Benzo(k)-	Benzo(a)-	Indeno(123	Dihenz(a h)-	Benzo(a h i)-
	fluoronthono	fluoronthono	Denzo(a)-		onthrocono	Denzo(g,n,r)-
	nuorantnene	nuorantnene	pyrene	-ca)pyrene	anthracene	perylene
SB-1A	6.2	1.9 IJ	2.8 IJ	3.5	<2.1	3 IJ
SB-1B	17	6.4	11	8.8	<2.4	7.1
SB-2A	19	6.5	9.7	9.5	2.2 IJ	7.5
SB-2B	47	17	29	32	7.5	32
SB-3A	3.7	<1.9	<1.6	1.9 IJ	<2.1	1.6 IJ
SB-3B	260	89	130	250	50	190
SB-3C	2700 D	600	1800 ⁴	670	200	440
SB-4A	7.1	2.2 IJ	3.4 IJ	4.1	<2.1	3.5 IJ
SB-4B	<1.5	<2	1.7	<1.4	<2.3	<1.4
SB-4C	16000 D	4500 D	11000 D⁴	5100 D	1500 D	3500 D
SB-5A	14	9.1	8.4	7.2	<2.1	6.4
SB-5B	290	140	200 ⁴	190	51	140
SB-6A	100	44	60	51	14	42
SB-6B	<1.7	<2.4	<2	<1.6	<2.6	<1.6
SB-6C	<1.6	<2.3	<1.9	<1.5	<2.5	<1.5

Table 13: PAH species and pentachlorophenol [µg/kg] at Sanders Beach (continued).

 1 : < indicates a nondetect showing that the result is below the minimal detection indicated by the number following the <.

²: D is a data qualifier that indicates that the positive value is the result of an analysis at a secondary dilution factor. ³: I & J are data qualifiers. I indicates that the reported value is between the laboratory method detection limit and the laboratory practical quantitation limit and J is an estimated value (the value was estimated because it was below the calibration curve).

⁴: Bold: Exceeds State of Florida Residential Cleanup Target Levels of 100 ug/kg.

7.2.4.2 Offshore Sanders Beach and Bayou mouth

Tables 12 and 13 show the analytical results for PAH species in cores from near Sanders Beach and the mouth of Bayou Chico. The offshore concentrations were much lower than what was observed at Sanders Beach (Table 10). In this general area sediments are for the most part sand. However, some of the TELs were exceeded for individual PAH species in samples FID-1B, FID-3A, FID-3B, FID-4A, FID-4B, FID-5A, FID-7A (Table 14). For three samples this resulted in guideline exceedence when the individual PAH species were summed for LMW species and HMW species. Two samples, FID-3B and FID-5A, exceeded the TEL for summed LMW and HMW PAHs and FID-4B exceeded only the HMW guideline (Table 15). Sample FID-7A is located in the mouth of the Bayou directly in front of the outlet for the stormwater ditch at the Pensacola Yacht Club. In the 1980's the ditch was observed to carry creosote wastes towards the Bay and beach. The PAH ratios (Table 11) suggest that currently this ditch is not transporting significant amounts of creosote wastes to the Bay.

	•	2-Methyl	1-Methyl		
	Naphthalene	naphthalene	naphthalene	Acenaphthylene	Acenaphthene
FID-1A	< 0.54 ⁴	<0.68	<0.67	<0.71	<1.1
FID-1B	6.7	5.7	7.8	4.9	23 ¹
FID-2G	<0.62	<0.78	<0.76	<0.81	<1.3
FID-2A	<0.61	<0.77	<0.76	<0.80	<1.3
FID-2B	<0.61	<0.76	<0.75	<0.80	<1.3
FID-3A	3.6 IJ ⁵	2.9 IJ	2.6 IJ	13	9.0
FID-3B	21	12	11	29	38
FID-4A	<0.60	<0.76	<0.75	23	2.7 IJ
FID-4B	3.6 IJ	2.7 IJ	1.8 IJ	57	10
FID-5A	8.9	4.6 IJ	2.7 IJ	130	15
FID-5B	<0.60	<0.76	<0.75	<0.79	<1.2
FID-5C	<0.61	<0.77	<0.76	<0.81	<1.3
FID-6A	<1.4	<1.7	<1.7	2.5 IJ	<2.7
FID-6B	<0.61	<0.76	<0.75	<0.80	<1.3
FID-6C	<0.62	<0.78	<0.77	<0.82	<1.3
FID-6D	<0.75	<0.94	<0.93	<0.99	<1.5
FID-7A	<0.61	<0.77	<0.76	10	1.9 IJ
TEL ²	34.6	20.2	NA	5.87	6.71
PEL ³	391	201	NA	128	88.9

Table 14: PAH species and pentachlorophenol lug/kg1 off Sa	anders	Beach
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	Fluorene	Phenanthrene	Anthracene	Fluoranthene	Pyrene
FID-1A	<0.65	<0.57	<0.72	4.3	3.5 IJ
FID-1B	19	170	42	200	190
FID-2G	<0.74	<0.65	<0.83	3.0 IJ	2.4 IJ
FID-2A	<0.73	<0.65	<0.82	3.4 IJ	2.9 IJ
FID-2B	<0.73	<0.64	<0.81	<0.57	<0.53
FID-3A	12	97 TEL	26	130 TEL	110
FID-3B	33	260	100	450	450
FID-4A	5.6	69	27	200	170
FID-4B	15	92	66	170	380
FID-5A	26	110	170	260	690
FID-5B	<0.72	<0.64	<0.81	<0.57	<0.53
FID-5C	<0.74	<0.65	<0.82	<0.58	<0.54
FID-6A	<1.6	9.8	3.6 IJ	35	37
FID-6B	<0.73	<0.64	<0.81	<0.57	<0.53
FID-6C	<0.75	<0.66	<0.83	<0.59	<0.55
FID-6D	<0.90	0.88 IJ	<1.0	<0.70	<0.66
FID-7A	3.7 IJ	18	17	37	35
TEL ²	21.2	86.7	46.9	113	153
PEL ³	144	544	245	1494	1398

		Benz(a)	Benzo(b)	Benzo(k)	Benzo(a)
	Chrysene	anthracene	fluoranthene	fluoranthene	pyrene
FID-1A	2.6 IJ	2.4 IJ	5.8	<2.0	2.7 IJ
FID-1B	97	90	120	52	99
FID-2G	<2.4	<0.98	2.3 IJ	<2.3	<1.9
FID-2A	<2.4	2.8 IJ	6.3	3.0 IJ	3.7 IJ
FID-2B	<2.3	1.9 IJ	5.1	2.6 IJ	3.0 IJ
FID-3A	75	60	88	37	62
FID-3B	390	310	490	180	310
FID-4A	160	110	220	100	150
FID-4B	220	180	500	250	350
FID-5A	1400 D ⁶ PEL	870 PEL	2000 D	560	920 PEL
FID-5B	<2.3	<0.96	<1.6	<2.2	<1.8
FID-5C	<2.4	<0.98	<1.6	<2.2	<1.9
FID-6A	15	16	34	13	20
FID-6B	<2.3	<0.97	<1.6	<2.2	<1.9
FID-6C	<2.4	<1.0	<1.7	<2.3	<1.9
FID-6D	<2.9	<1.2	<2.0	<2.7	<2.3
FID-7A	78	60	100	44	64
TEL ²	108	74.8	NA	NA	88.8
PEL ³	846	693	NA	NA	763

Table 14: PAH species and pentachlorophenol [ug/kg] off Sanders Beach (continued)

	Indeno(1,2,3-	Dibenz(a,h)	Benzo(g,h,i)
	cd)pyrene	anthracene	perylene
FID-1A	3.0 IJ	<2.2	2.4 IJ
FID-1B	67	15	64
FID-2G	<1.5	<2.5	<1.5
FID-2A	3.3 IJ	<2.5	3.1 IJ
FID-2B	3.0 IJ	<2.5	2.2 IJ
FID-3A	40	9.7	33
FID-3B	190	44	150
FID-4A	100	26	80
FID-4B	220	56	160
FID-5A	420	130	300
FID-5B	<1.5	<2.4	<1.5
FID-5C	<1.5	<2.5	<1.5
FID-6A	11	<5.3	8.3 IJ
FID-6B	<1.5	<2.5	<1.5
FID-6C	<1.5	<2.5	<1.5
FID-6D	<1.8	<3.0	<1.8
FID-7A	34	7.9	25
TEL ²	NA	6.22	NA
PEL ³	NA	135	NA

¹: Bold indicates value above TEL ²: TEL, Threshold effects level (MacDonald, 1994a,b). Within this range, concentrations of sediment-associated contaminants are not considered to represent significant hazards to aquatic organisms. ³: PEL. Probable effects levels (MacDonald, 1994a,b). Lower limit of the range of contaminant concentrations that

are usually or always associated with adverse biological effects ⁴: < indicates a nondetect showing that the result if any is below the minimal detection limit that concentration is

indicated by the number following the <

⁵: I & J are Data Qualifiers. I indicates that the reported value is between the laboratory method detection limit and the laboratory practical quantitation limit and J is an estimated value (that the value was estimated since it was below the calibration curve).

⁶: D is a Data Qualifier that indicates that the positive value is the result of an analysis at a secondary dilution factor ⁷: Apparent Effects Threshold (NOAA, 1999)

	LMW-PAHs ¹	HMW-PAHs ²	Sum LMV - HMW ³	Total PAHs ⁴
FID-1A	ND 7	15.5	15.5	26.7
FID-1B	271.3	691	962.3	1273.34
FID-2G	ND	5.4	5.4	7.7
FID-2A	ND	12.8	12.8	28.5
FID-2B	ND	4.9	4.9	17.8
FID-3A	163.5	446.7	610.2	810.8
FID-3B	493	1954	2447	3468
FID-4A	127.3	816	943.3	1443.3
FID-4B	246.3	1356	1602.3	2734.1
FID-5A	464.5	4270	4734.5	8017.2
FID-5B	ND	ND	ND	ND
FID-5C	ND	ND	ND	ND
FID-6A	15.9	123	138.9	205.2
FID-6B	ND	ND	ND	ND
FID-6C	ND	ND	ND	ND
FID-6D	0.88	ND	0.88	0.88
FID-7A	50.6	281.9	332.5	535.5
TEL⁵	312	655	1684	NA
PEL ⁶	1442	6676	16770	NA

Table 15: LMW, HMW, Sum LMV - HMW, and total PAHs for sediments off Sanders Beach.

¹: LMW-PAHs refers to the sum of 7 light molecular weight PAHs.

²: HMW-PAHs refers to the sum of 6 heavy molecular weight PAHs.

³: Sum LMW - HMW refers to the sum of the concentrations of the 13 low and high molecular weight PAHs having FDEP SQGL. While the mode of action of LMW and HMW PAHs is thought to differ, these substances are sometimes grouped in assessments of sediment quality. This results in a derivation of a TEL of 1,684 ug/kg and a PEL of 16,770 ug/kg. (MacDonald, 1994a,b).

⁴: The actual Total PAH of this 8270C SIM Analyses includes 5 PAHs in addition to sum LMW - HMW.

⁵: TEL, Threshold effects level (MacDonald ,1994a,b). Within this range, concentrations of sediment-associated contaminants are not considered to represent significant hazards to aquatic organisms.

⁶: PEL. Probable effects levels (MacDonald ,1994a,b). lower limit of the range of contaminant concentrations that are usually or always associated with adverse biological effects.

⁷: ND means not detected.

7.2.4.3 Bayou proper

In this study most PAH samples were taken near Sanders Beach and the Pensacola Yacht Club (Tables 14, 15; Map 11). However, four PAH samples were taken for background purposes in other areas that were not as likely to be directly impacted by the ACW site (Table 16). Sample BG-13, taken in the shipping channel, has very minimal PAH values. Samples BG-14, BG-15 and BG-16, taken at sites laying between the spoil island and the W. Navy Blvd. bridge, showed higher values with most of the LMW, HMW, and sum of LMW&HMW concentrations being above the TEL. Total PAH concentrations can be influenced by the particle size distribution of the sediment but that was not the case in the present study as the correlation between total PAHs and clay and silt was weak (r < 0.5).

					2	
	Naphthalene	2-Methyl- naphthalene	1-Methyl naphthalene	Acenaph thvlene	Acenaph thene	Fluorene
FID-1A	< 0.544	<0.68	<0.67	<0.71	<1.1	<0.65
FID-2G	<0.62	<0.78	<0.76	<0.81	<1.3	<0.74
FID-2A	<0.61	<0.77	<0.76	<0.80	<1.3	<0.73
FID-3A	3.6 IJ^5	2.9 IJ	2.6 IJ	13	9.0	12
FID-4A	<0.60	<0.76	<0.75	23	2.7 IJ	5.6
FID-5A	8.9	4.6 IJ	2.7 IJ	130 PEL	15	26
FID-6A	<1.4	<1.7	<1.7	2.5 IJ	<2.7	<1.6
FID-7A	<0.61	<0.77	<0.76	10	1.9 IJ	3.7 IJ
BG-13	<0.63	<0.80	<0.78	<0.84	<1.3	<0.76
BG-14	33	9.8 IJ	6.9 IJ	91	34	36
BG-15	<2.0	<2.5	2.9 IJ	36	8.7 IJ	<2.4
BG-16	17	9.4 IJ	7.0 IJ	83	13 IJ	<2.5
TEL	34.6	20.2	NA	5.87	6.71	21.2
PEL	391	201	NA	128	88.9	144

Table 16: PAH species and pentachlorophenol [µg/kg] in surface sediments in Bayou Chico¹.

	Phenan threne	Anthracene	Fluoran thene	Pyrene	Chrysene	Benz(a) anthracene	Benzo(b) fluoranthen e
FID-1A	<0.57 ⁴	<0.72	4.3	3.5 IJ	2.6 IJ	2.4 IJ	5.8
FID-2G	<0.65	<0.83	3.0 IJ	2.4 IJ	<2.4	<0.98	2.3 IJ
FID-2A	<0.65	<0.82	3.4 IJ	2.9 IJ	<2.4	2.8 IJ	6.3
FID-3A	97	26	130	110	75	60	88
FID-4A	69	27	200	170	160	110	220
FID-5A	110	170	260	690	1400 D ⁶ PEL	870 PEL	2000 D
FID-6A	9.8	3.6 IJ	35	37	15	16	34
FID-7A	18	17	37	35	78	60	100
BG-13	<0.67	<0.85	<0.60	<0.56	3.1 IJ	3.0 IJ	2.9 IJ
BG-14	10	130	440	970	240	340	600
BG-15	57	50	250	370	160	140	400
BG-16	190	92	570	690	470	330	1000
TEL	86.7	46.9	113	153	108	74.8	NA
PEL	544	245	1,494	1398	846	693	NA

	Benzo(k)-	Benzo(a)-	Indeno(1,2,3-	Dibenz(a,h)-	Benzo(g,h,i)-
	fluoranthene	pyrene	cd)pyrene	anthracene	perylene
FID-1A	<2.0	2.7 IJ	3.0 IJ	<2.2	2.4 IJ
FID-2G	<2.3	<1.9	<1.5	<2.5	<1.5
FID-2A	3.0 IJ	3.7 IJ	3.3 IJ	<2.5	3.1 IJ
FID-3A	37	62	40	9.7	33
FID-4A	100	150	100	26	80
FID-5A	560	920 PEL	420	130	300
FID-6A	13	20	11	<5.3	8.3 IJ
FID-7A	44	64	34	7.9	25
BG-13	3.8 IJ	<1.9	5.5	4.4	4.0 IJ
BG-14	240	460	230	<7.6	360
BG-15	140	230	170	35	180
BG-16	410	590	420	99	360
TEL	NA	88.8	NA	6.22	NA
PEL	NA	763	NA	135	NA

Table 16: PAH species and pentachlorophenol $[\mu g/kg]$ in surface sediments¹ (continued).

¹: See table 13 for footnotes.

Table 17: LMW, HMW, Sum LMV - HMW, and total	PAH in surface sediments'.
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	LMW-PAHs	HMW-PAHs	Sum LMV - HMV	Total PAHs
FID-1A	ND	15.5	15.5	26.7
FID-2G	ND	5.4	5.4	7.7
FID-2A	ND	12.8	12.8	28.5
FID-3A	163.5	446.7	610.2	810.8
FID-4A	127.3	816	943.3*	1443.3
FID-5A	464.5	4,270	4734.5	8017.2
FID-6A	15.9	12.3	138.9	205.2
FID-7A	50.6	281.9	332.5	535.52
BG-13	ND	10.5	10.5	26.7
BG-14	433.8	2,450	2883.8	4320.7
BG-15	151.7	1185	1336.7	2229.6
BG-16	404.45	2,749	3153.4	5350.4
TEL	312	655	1684	NA
PEL	1442	6676	16770	NA

¹: See Table 15 for footnotes

7.2.5 Health Concerns on Sanders Beach

Residents of the Sanders Beach Community commonly utilize the beach for swimming, sunbathing, picnicking, and related events. This can lead to direct skin contacts of beach goers with contaminated beach soils and sediments. Table 13 shows the PAH concentrations for common PAH species in the soils of Sanders Beach. It is clear that detected PAH concentrations are low for the surface soils of the beach. Exposure to sunlight will degrade PAHs and strong winds may prevent accumulation by transporting it elsewhere. Two of the cores at lower levels had elevated levels of total PAHs (samples SB-3C and SB-4C) and three of the samples

exceeded Florida guidelines for soil cleanup target levels (SCTL) for benzo(a)pyrene (0.1 mg/kg SCTL) (Table 13). Benzo(a)pyrene is a carcinogen that is readily absorbed following inhalation, oral, and dermal routes of administration (ATSDR, 1990). Following inhalation exposure, benzo(*a*)pyrene is rapidly distributed to several tissues in rats (Sun et al., 1982; Weyand and Bevan, 1986). The metabolism of benzo(a)pyrene is complex and includes the formation of a proposed ultimate carcinogen, benzo(a)pyrene 7,8 diol-9,10-epoxide (IARC, 1983). The exposure and risk of benzo(a)pyrene to a visitor at Sanders Beach is minimal if the visitor does not have contact with deeper sediments. However, for a person that has contact with subterranean materials resulting from digging there is a risk of direct contact with the PAhs and benzo(a)pyrene.

7.2.6 Comparison with PAH data in other studies

There is a large body of PAH data from other studies in Bayou Chico. Many of these data are available in the DeBusk et al. (2002) database. Not included in the DeBusk et al. database is a study carried out by EA (2000) for the USACE in which six sediment cores were taken at different locations in the navigation channel and turning basin for dredging information. One sample, BC00-SED-01, showed very high values for PAHs (Table 18) and also relatively high values for dioxins/furans. The averaged total PAH value for the core was 26,458 ug/kg or about 25.7 times greater than the average of EA's other five cores (1,029 ug/kg) that ranged from 0 to 1,706 ug/kg (Table 18). Only our samples SB-3C and SB-4C from Sanders Beach had PAH concentrations that were greater. Our PAH values for bayou sediments were much lower with a maximum value for FID-5A of 8,017.2 ug/kg. We calculated the ratios of PAH species for EA samples and compared the ratios with some of our results for Sanders Beach (Table 19). The ratios for sample BC00-SED-01 are clearly different from those for the other EA samples. The Rostad ratios are much less than those for the other samples and much closer to those for our samples. The Yunker ratios are also much closer to those of SB-3C and SB-4C than to those of the other EA samples. The fluoranthene/phenanthrene ratio for the EA sample is slightly higher than 100 but the pyrene/phenanthrene ratio is clearly in the creosote range (< 100). For the three Yunker ratios EA sample BC00-SED-01 has values that are very close to the cut-off values for creosote (Table 19). The fact that sample BC00-SED-01 was taken from a core in the bottom of the shipping channel elicits more interest because it is possible that its greater depth brought the sample within the influence of the contaminated aquifer coming from the ACW site. The depth of the water was 12 ft and the core tube penetrated an additional 12 ft for BC00-SED-01 which results in a sample depth of 24 ft below mean sea level. The comments in the coring log stated that product was observed on top of core. The core site is less than 600 meters and almost due south from ACW, a position that may coincide with the contaminated groundwater from the ACW which appears to be moving towards the south (Mattraw and Franks, 1986; Franks, 1987). Moreover, the presence of high concentrations of dioxins/furans (42.4 TEQ ng/kg, see below) corroborates that this sample could be affected by wood treating products such as those released at ACW. However, it is also possible that the results for sample BC00-SED-01 represent something local that was dumped in the channel. Samples BC00-SED-02 and BC00-SED-03, which are also located to the SW of the ACW site, do not exhibit the same PAH profiles as BC00-SED-01 (Map 14).

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EA Sample ID	LMW-PAHs ¹	HMW-PAHs ²	Sum LMV - HMV ³	Total PAH ⁴
BC00-SED-01	12,400	14,003	26,403	28,783
BC00-SED-02	603	1,103	1706	2,048
BC00-SED-03	745	938	1683	2,077
BC00-SED-04	ND	ND	ND	ND
BC00-SED-05	288.8	195.6	484.4	591.4
BC00-SED-06	573	699	1272	1,465

Table 18: LMW, HMW, Sum LMV - HMW, and total PAHs [ug/kg] in shipping channel^{1,2}

¹: Based on data from EA (2000) study.

²: See Table 15 for footnotes.

Table 19: Comparison of PAH ratios in EA sediment cores and Sanders Beach soil cores¹.

	Total PAH [μg/kg]	fluoranthene/ phenantrene ^R	pyrene/ phenantrene	An/(Pn+An)	FI/(FI+Py)	IP/(IP+Bghi)
SB-3C ²	65,840	75	37	0.14	0.67	0.60
SB-4C ²	291,940	84	56	0.20	0.60	0.59
BC00-						
SED-01°	28,783	130	89	0.17	0.60	0.58
BC00-						
SED-02°	2,048	631	552	0.41	0.53	0.52
BC00-						
SED-03°	2,077	300	700	0.31	0.30	0.56
BC00-						
SED-04°	ND	No Ratio	No Ratio	No Ratio	No Ratio	No Ratio
BC00-						
SED-05°	591.4	890	1125	0.50	0.44	0.28
BC00-						
SED-06°	1,465	1550	1200	0.70	0.56	0.19

¹: See tables 8 and 9 for footnotes. ²: Results from the present study.

³: Results from EA (2000) study.

The PAH data from the DeBusk et al. (2002) database are represented in Table 20 and Map 15. Values ranged from non-detect to 36,540 ug/kg. The highest concentration reached was 36,540 ug/kg for a sample (NOAA7) taken for a NOAA study in 1997. This and two other samples (NOAA8 and NOAA9) have concentrations for LMW and HMW combined that are above the PEL (Table 20). These three samples were taken at sites south of the current Barrancas Ave. bridge. Table 21 shows origin ratios that we calculated for samples from DeBusk et al. (2002) that had a concentration of at least 1000 µg/kg for total PAHs. Sample EPA27 has one value near the Rostad and Perreira cut-off for creosote origin (100) but the other eight samples do not. Samples NOAA 6, 7 and 8 were in the creosote range for An/(Pn+An) but other samples were not. For Fl/(Fl+Py) ratios none of the samples were near the creosote cut-off and IP/(IP+Bghi) could not be calculated due to incomplete data for these PAHs. Overall these ratios suggest a non-creosote origin for these PAHs. This leaves us with only one sediment sample from the literature, EA sample 1 (Tables 16, 17) that exhibits many characteristics of creosote. As mentioned above, some of our samples from Sanders Beach most likely had a creosote origin.

The current state of groundwater transport of ACW contaminants is not well understood. EPA is currently investigating the movement of contaminated groundwater from the ACW site

(BEM, 2005). This additional field investigation is necessary to adequately define the extent of the horizontal and vertical plume from ACW. The original study of this contaminated aquifer in the site description by Franks (1987) from the U.S. Geological Survey is apparently still the most definitive for the site (see section 3.2.8 above). Sample BC00-SED-01 (EA, 2000) is located to the south of the ACW and could be assumed to be down gradient as far as groundwater movement is concerned leaving open the possibility of impacts from ACW contamination on Bayou Chico.

7.2.7 Pentachlorophenol (PCP)

For Sanders Beach the 8270C analyses showed no detections of PCP at detection limits of 24 to 30 μ g/kg, which is well below the FDEP cleanup level of 7.3 mg/kg (Table 22, Map 12). PCP wastes are often associated with dioxins/furans and only what appeared to be background values for dioxins/furans were encountered in soils and sediments of Sanders Beach. While this study was in progress we requested the analytical laboratory doing the analysis to lower detections limits for PCP for the remainder of the samples to levels below the AET of 17 μ g/kg. The laboratory was able to do so by using 8270C SIM to reach a detection of limit of about 0.49 to 1.7 μ g/kg depending upon the matrix. The results obtained with SIM were below the detection limit for samples taken from off-shore sediments near Sanders Beach (Table 22). However, grab samples taken from surface sediments in the Bayou itself showed detections of PCP above the AET (Table 22). This finding is consistent with the results for dioxins/furans (see next section) that were found in higher concentrations in parts of the Bayou that are distant from ACW and Sanders Beach.

PCP was detected in ACW monitoring wells above its USEPA and FDEP MCL of 1 ppb (BEM, 2005). This seems to suggest that there may be an influence of PCP at ACW on Bayou Chico. However, because of the distance between ACW and the parts of the Bayou with elevated PCP and because of the potential influence of other sources of PCP a clear direct link between the PCP at ACW and in the Bayou can not be established. The PCP may have originated from non-wood treating sources such as pesticides, fungicides, herbicides, algicides, disinfectants, and antifouling paints for which there are potential sources in the marine and chemical industry and the urbanization that have been present on the banks of the Bayou for many years.

The non-detection of PCP in and about Sanders Beach is in agreement with earlier USEPA findings. In 1991, USEPA conducted a dye dispersion and sediment sampling study to determine the presence and concentration of ACW-related compounds within the area of Pensacola Bay influenced by surface water drainage from the Pensacola Yacht Club drainage ditch (USEPA, 1999b). Based on the results of the dye tracer study, the USEPA selected sediment sampling locations near the ditch that were analyzed for organic compounds, pesticides, PCBs, and metals. Results for the ditch and its delta reported no PCP detection. There was detection of PAHs, and dioxin concentrations ranged from 0.069 to 5 ng/kg TEQ.

DataSet	Map Label	LMW PAH	HMW PAH ²	Sum LMW - HMW
EPA_92	EPA27	655.63	1344.7	2,000.33
EPA_96	PCOLA18	154.02	60.89	214.91
EPA_96	PCOLA24	1326.69	10080.85 PEL	11,407.54
EPA_96	PCOLA24	1587.74	13451.94 PEL	15,039.68
NOAA_97	NOAA4	150	1220	1370
NOAA_97	NOAA5	260	3630	3,890.00
NOAA_97	NOAA6	410	2200	2,610.0
NOAA_97	NOAA7	1200	No Data	36,540.0 PEL
NOAA_97	NOAA8	630	No Data	25,980.0 PEL
NOAA_97	NOAA9	1970	No Data	20,680.0 PEL
NOAA_97	NOAA15	70	No Data	70.00*
NOAA_97	NOAA16	250	1	1.00
EPA_CHICO_98	NPB3B	0.1	0.2	0.30
EPA_CHICO_98	NPB3B	0.1	1	1.10
EPA_CHICO_98	NPB3B	0	0.5	0.50
EPA_CHICO_98	NPB6	0	0	0.00
EPA_CHICO_98	NPB9	0.2	No Data	0.20*
EPA_CHICO_98	NBC33	0.3	1.4	1.70
EPA_CHICO_98	NBC30B	2.1	1.9	4.00
EPA_CHICO_98	NBC30B	1.2	0.9	2.10
EPA_CHICO_98	NBC30B	0.7	0.6	1.30
EPA_CHICO_98	NBC28	0.9	0.9	1.80
EPA_CHICO_98	NBC26	0.9	0.8	1.70
EPA_CHICO_98	NBC23	2.3	1.4	3.70
EPA_CHICO_98	NBC19	0.7	0.3	1.00
EPA_CHICO_98	NBC18	1.2	1.3	2.50
EPA_CHICO_98	NBC17B	13.3	16.8	30.10
EPA_CHICO_98	NBC17B	14.5	23.1	37.60
EPA_CHICO_98	NBC17B	9.1	28.8	37.90
EPA_CHICO_98	NBC14	0	0.1	0.10
EPA_CHICO_98	NBC4	0.3	0.5	0.80
EPA_CHICO_98	NBC3B	0.1	0.2	0.30
EPA_CHICO_98	NBC3B	0.1	1	1.10
EPA_CHICO_98	NBC3B	0	0.5	0.50
EPA_CHICO_98	S-1	0	0	0.00
EPA_CHICO_98	S-2	0	0	0.00
EPA_CHICO_98	S-2	0.2	0.1	0.30
EPA_CHICO_98	5-2	0.2	0.1	0.30
EPA_CHICO_98	5-3 ND040D	U	U	0.00
EPA_CHICO_98	NBC12B	3	4.1	7.10
EPA_CHICO_98	NBC12B	3.7	4.2	7.90
	NBC12B	2.9	4.3	1.20
	NBC11	U	1.8	1.80
	NBC10	0.4	1.4	1.80

Table 20: LMW, HMW, Sum LMV – HMW [μ g/kg] from the DeBusk et al. (2002) database¹.

¹: See Table 15 for footnotes. ²: Some PAH analyte results missing form HMW PAH analytes, but all analytical results were combined for Sum LMW - HMW

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	Total	fluoranthene/	pyrene/	An/(Pn+An)	FI/(FI+Pv ⁾	IP/(IP+Bahi)
	PAH	phenantrene	phenantrene		: "(: : ·)	
EPA27	2000	128	203	0.40	0.39	No Ratio
PCOLA24	11408	2070	3158	0.77	0.40	No Ratio
PCOLA24	15040	2253	2802	0.70	0.45	No Ratio
NOAA4	1370	280	713	No Ratio	0.28	No Ratio
NOAA5	3,890	512	1296	No Ratio	0.28	No Ratio
NOAA6	2,610.	231	497	0.12	0.32	No Ratio
NOAA7	36,540.	648	No Ratio	0.14	No Ratio	No Ratio
NOAA8	25,980.	564	No Ratio	0.06	No Ratio	No Ratio
NOAA9	20,680.	283	383	No Ratio	0.42	No Ratio

Table 21: Total PAH concentrations $[\mu g/kg]$ and PAH ratios for selected samples from the DeBusk et al. (2002) database¹.

¹: See tables 8 and 9 for footnotes.

Table 22: Pentachlorophenol concentrations $[\mu g/kg]^1$.

At Sanders	•	Offshore Sanders		Surface sediments	
Beach	concentration	Beach	concentration	in Bayou	concentration
SB-1A	<24	FID-1A	<0.43	BG-13	<0.51
SB-1B	<28	FID-1B	<0.48	BG-14	130
SB-2A	<24	FID-2G	<0.49	BG-15	89
SB-2B	<28	FID-2A	<0.49	BG-16	89
SB-3A	<24	FID-2B	<0.49		
SB-3B	<29	FID-3A	<0.50		
SB-3C	<29	FID-3B	<0.51		
SB-4A	<24	FID-4A	<0.48		
SB-4B	<26	FID-4B	<0.48		
SB-4C	<28	FID-5A	<33		
SB-5A	<24	FID-5B	<28		
SB-5B	<27	FID-5C	<29		
SB-6A	<32	FID-6A	<61		
SB-6B	<30	FID-6B	<28		
SB-6C	<29	FID-6C	<29		
		FID-6D	<35		
		FID-7A	<0.49		

¹: See table 13 for footnotes.

²: Values in bold are above AET of 17 μ g/kg.

7.2.8 Dioxins/furans

7.2.8.1 At Sanders Beach and offshore Sanders Beach and Bayou mouth

Dioxins/furans are USEPA COCs at the ACW site. There is a theoretical possibility that Sanders Beach may have been impacted by releases of these COCs. Dioxin/furan analysis of core samples at the surface and deeper levels for Sanders Beach soils, however, show minimum concentrations that are well below the residential SCTL TEQ of 7 ng/kg (Table 23). It would appear that according to current guidelines dioxin/furan compounds are not a human health or environmental concern at this beach since all results are below the AET of 3.6 ng/kg TEQ for dioxins/furans (NOAA, 1999). Sediments in the waters adjacent to Sanders Beach and at the

mouth of the Bayou were sampled via vibracores. As observed for PAHs and PCP, dioxin/furan concentrations were relatively low at those locations and all concentrations except for one were below the AET (Table 24). The area where the vibracores were located receives drainage from the contaminated stormwater ditch near the Pensacola Yacht Club, but apparently that does not affect dioxin/furan levels in the area to a measurable degree. It is possible that currents may have carried contaminates and contaminated sediments away, but the present study did not examine that possibility.

Sample ID ¹	concentration ng/kg	TEQ (ND = $\hat{0}$) ² ng/kg	TEQ (ND = I/2 DL) ² ng/kg
SB - 1A	59.792	0.113	0.183
SB - 1B	23.611	0.028	0.112
SB - 2A	69.260	0.177	0.232
SB - 2A	48.436	0.056	0.186
SB - 3A	27.222	0.031	0.217
SB - 3B	133.842	0.376	0.525
SB - 3C	507.337	1.094	1.442
SB - 4A	64.206	0.182	0.231
SB - 4B	118.480	0.048	0.511
SB - 4C	84.287	0.302	0.367
SB - 5A	108.170	0.331	0.377
SB - 5B	503.154	1.329	1.376
SB - 6A	845.877	2.294	2.494
SB - 6B	10.881	0.011	0.169
SB - 6C	15.277	0.009	0.181

Table 23: Dioxin/furan concentrations for soil samples at Sanders Beach.

¹: A=surface, B=1 m depth, C=2 m depth.

²: Results below the detection limit (ND) were counted as 0 or $\frac{1}{2}$ the detection limit (DL).

7.2.8.2 Bayou proper

The surface sediment grab samples obtained throughout Bayou Chico were analyzed for dioxins/furans (Table 25) and dioxin-like PCBs (Table 26). Results for individual dioxins/furans for each sample are listed in Table 50 in Appendix 2. Dioxin/furan TEQs from surface sediments in parts of Bayou Chico distant from ACW and Sanders Beach are more elevated than those closer to ACW, and exceed the AET (Map 16, Table 25). The highest TEQs occur in regions of the Bayou that are not closest to the seemingly obvious influence of ACW, and do not seem to be in a known path of any groundwater moving away from ACW. It is possible that currentmediated transport of contaminated sediments from areas closer to the ACW site has occurred in the past, but this contention was not examined by the present study. Combined TEQs (dioxins/furans and dioxin-like PCBs) are lowest in Pensacola Bay and the lower part of the Bayou (Map 17, Table 27). The majority of the TEQs for the other surface grabs within the Bayou are above the AET and also above the state 7 ng/kg SCTL residential clean up level for dioxins/furans. The highest concentration of 118.8 ng/kg TEQ occurs near the spoil island. From this point north and west the remainder of the Bayou has values, with one exception (BG-4), that are considerably above the cited guidelines. The spoil island was one of the sites where blue crabs were collected for the PERCH seafood study that showed high TEQs for tissues (Karouna-Renier et al., 2006) (Figure 11). Dioxin/furan levels are influenced by the relative proportion of

fine sediments at a site, as reflected in the strong correlation between clay and dioxin/furan concentration (r=0.75), and clay and dioxin/furan TEQ (r=0.83).

Sample ID	concentration	$TEQ\left(ND=0\right)^2$	TEQ (ND = $I/2$ DL) ²
	ng/kg	ng/kg	ng/kg
FID - 2G	97.497	0.175	0.275
FID - 1A	134.606	0.291	0.382
FID - 1B	1362.634	3.855 ³	3.922 ³
FID - 2A	144.283	0.296	0.394
FID - 2B	975.097	2.185	2.266
FID - 3A	164.936	0.666	0.721
FID - 3B	847.479	2.115	2.207
FID - 4A	344.692	0.618	0.727
FID - 4B	400.224	0.779	0.869
FID - 5A	627.188	2.210	2.293
FID - 5B	476.252	0.749	0.847
FID - 5C	82.104	0.474	0.570
FID - 6A	148.173	0.263	0.542
FID - 6B	24.336	0.040	0.125
FID - 6C	51.828	1.012	1.107
FID - 6D	78.092	0.154	0.304
FID - 7A	60.913	0.076	0.193

Table 24: Dioxin/furan concentrations for sediment samples off Sanders Beach.

¹: A=surface, B=1 m depth, C=2 m depth, D=3 m depth

²: Results below the detection limit (ND) were counted as 0 or $\frac{1}{2}$ the detection limit (DL).

³: Bold values are above AET of 3.6 ng/kg



Figure 11: Commercial harvesting of crabs between two constrictions in northern part of Bayou.

Sample ID	concentration ng/kg	TEQ (ND = 0) ¹ ng/kg	TEQ (ND = I/2 DL) ¹ ng/kg
BG - 1	6234.7	25.72 ²	26.12
BG - 2	8649.7	29.31	29.56
BG - 3	13390	53.49	53.9
BG - 4	2073.8	5.236	5.279
BG - 5	13440	33.4	33.54
BG - 6	7686.2	22.9	23.08
BG-6Dupl.	16738	46.67	46.82
BG - 7	33102	71.95	72.34
BG - 8	39631	83.62	83.85
BG - 9	1105.9	2.501	2.582
BG - 10	60824	118.8	119.4
BG - 11	265.21	0.15	0.715
BG - 12	4338.7	9.418	9.497
BG - 13	18.937	0.02	0.246
BG - 14	29479	75.43	75.46
BG - 15	17453	45.89	46.07
BG - 16	29834	82.54	82.54

Table 25: Dioxin/furan concentrations for sediment samples in Bayou proper.

¹: Results below the detection limit (ND) were counted as 0 or ½ the detection limit (DL). ²: Bold values are above AET of 3.6 ng/kg.

Sample ID	TEQ (ND = 0) ¹	TEQ (ND = $I/2$ DL) ¹	PCDD/ PCDF TEQ (ND = 0) ¹	PCDD/ PCDF TEQ (ND = I/2 DL) ¹
	ngnig	ng/Ng	ng/kg	ng/kg
BG-1	6.577 ²	6.639	25.720	26.121
BG-2	3.052	3.056	29.307	29.564
BG-3	2.253	2.266	53.491	53.896
BG-4	0.045	0.604	5.236	5.279
BG-5	0.160	0.735	33.398	33.541
BG-6	0.169	0.196	22.905	23.075
BG-6Dupl.	0.152	1.305	46.671	46.819
BG-7	5.816	5.867	71.952	72.343
BG-8	0.292	0.416	83.623	83.851
BG-9	0.041	0.152	2.501	2.582
BG-10	7.940	9.092	118.806	119.374
BG-11	0.005	0.023	0.150	0.715
BG-12	0.050	0.172	9.418	9.497
BG-13	0.965	0.965	0.020	0.246
BG-14	16.787	16.802	75.431	75.462
BG-15	0.303	0.988	45.887	46.074
BG-16	4.777	4.860	4.777	4.860

Table 26: Dioxin-like PCB concentrations for surface sediments in Bayou proper.

¹: Results below the detection limit (ND) were counted as 0 or ¹/₂ the detection limit (DL). ²: Bold values are above dioxin/furan AET of 3.6 ng/kg.

Sample ID	TEQ (ND = 0) 1	TEQ (ND = $I/2$ DL) ¹	Percent dioxin-like PCBs in
Sample ID	ng/kg	ng/kg	combined TEQ
BG-1	32.297 ²	32.761	20.36
BG-2	32.359	32.620	9.43
BG-3	55.744	56.163	4.04
BG-4	5.282	5.883	0.85
BG-5	33.557	34.276	0.48
BG-6	23.074	23.271	0.73
BG-6Dupl.	46.823	48.123	0.32
BG-7	77.768	78.211	7.48
BG-8	83.915	84.268	0.35
BG-9	2.542	2.735	1.61
BG-10	126.746	128.466	6.26
BG-11	0.155	0.738	3.23
BG-12	9.468	9.668	0.53
BG-13	0.985	1.211	97.97
BG-14	92.218	92.264	18.20
BG-15	46.190	47.062	0.66
BG-16	9.553	9.721	50.01

Table 27: Combined dioxin/furan and dioxin-like PCB TEQs for sediment samples in Bayou proper.

¹: Results below the detection limit (ND) were counted as 0 or ¹/₂ the detection limit (DL).

²: Bold values are above AET of 3.6 ng/kg.

7.2.8.3 Dioxin/furan origin

There are many potential sources for environmental dioxins/furans. Congener profiles of the dioxins/furans from Bayou Chico strongly suggest a wood treating origin. Figure 12 shows the average profile of dioxins/furans for surface sediment grab samples BG-1 through BG-16 in Bayou Chico. The six major congeners were: 80% OCCD (Octachlorodibenzo-p-dioxin), 12% HpCDD (1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin), 1% OCDF (Octachlorodibenzo-p-dioxin), 0.6% HpCDF (1,2,3,4,6,7,8-Heptachlorodibenzofuran), 0.3% HxCDD (1,2,3,6,7,8-Heptachlorodibenzofuran), 0.3% HxCDD (1,2,3,6,7,8-Heptachlorodibenzofuran), 0.3% HxCDD (1,2,3,6,7,8-Heptachlorodibenzo-p-dioxin), 1% OCDF (Octachlorodibenzo-p-dioxin), 0.6% HpCDF (1,2,3,4,6,7,8-Heptachlorodibenzofuran), 0.3% HxCDD (1,2,3,6,7,8-Heptachlorodibenzofuran), 0.3% HxCDD (1,2,3,6,7,8-Heptachlorodibenzo-p-dioxin), 0.3% HxCDD (1,2,3,6,7,8-Heptachlorodibenzo-p-dioxin), 0.3% HxCDD (1,2,3,6,7,8-Heptachlorodibenzo-p-dioxin), 0.2% 1,2,3,7,8,9-HxCDD (Hexachlorodibenzo-p-dioxin).

A comparison of congener profiles from laboratory analyses of known sources was made. The closest congener profile match was that of dioxins/furans present in PCP (Schaum, 1997) (Figure 12, Figure 13). Congener profiles for combustion of unleaded gasoline and diesel in internal combustion engines have somewhat similar profiles to PCP with the exception that OCCD of PCP is 70% versus 30-43 % for internal combustion engines. Undoubtedly combustion has contributed dioxins/furans to the Bayou, however the predominant source appears to be wood-treating materials.



Figure 12: Profile of dioxins/furans in samples BG-1 - BG-16.



Figure 13: Profile of dioxins/furans in technical grade PCP used in wood treating (from Schaum, 1997).

A similar profile was calculated for data derived from sediment cores taken by EA (2000) that also detected dioxins/furans during an USACE dredging study. Profiles calculated from these data are very similar to those calculated for the surface grab samples from the present study (Figure 12, Figure 14). Comparison of the dioxins/furans profile from the present study with dioxins/furans profiles from 2004 ground water samples derived from monitoring wells (BEM Systems, 2005) also shows a good agreement (Figure 12, Figure 15). Dioxins/furans from the Escambia Treating Company (ETC) Superfund Site elsewhere in Pensacola (USEPA, 2006) have profiles that are very similar to those from the present study, the EA study, and the BEM Systems study. Studies from the Clarinda Triangle near the ETC site also had OCDD contributing between 70% and 83% of the dioxins/furans concentration (USEPA, 2006). These results were found by USEPA to be consistent with a PCP source for the dioxins/furans. These profiles, particularly the large contribution of OCDD to the total dioxin/furan concentrations, was found to indicate that the ETC site is the likely source for dioxin contamination in Clarinda Triangle surface soils (USEPA, 2006).

The profiles of the dioxins/furans in the surface sediments of the present study indicate a wood treating origin. The profiles are very similar to profiles for ACW groundwater, indicating that the nearby ACW site may be the source for the dioxins/furans. One of the cores (BC00-SED-01) from the EA (2000) study that was taken relatively close to the ACW site and had dioxin/furan profiles indicative of a wood treating origin also had high levels of PAHs that were of creosote origin. This corroborates the contention that at least that part of the Bayou (Map 14) is affected by pollutants from wood treating activities, possibly the ACW site. The present study did not investigate how dioxins/furans may have been transported from the ACW site to bayou sediments but possible explanations include atmospheric transport, groundwater transport, surface water transport, and other releases such as dumping. It is possible that the dioxins/furans entered the Bayou from another wood treating source. For years there was a complex of sawmills and lumber related industry at the site of the former mahogany mill that was located on the west bank of the Bayou (Maps 4). It is not beyond the realm of possibilities that wood treating occurred at this site. In a small facility nearby the Sanders Beach Community wood is currently being treated, but there is no evidence that a waste stream enters bayou waters. We conclude that ACW is the most probable source of dioxins/furans in the Bayou since it released these wastes to ground and surface water and also to the air.



Figure 14: Profile of EA (2000) dioxins/furans data for bayou sediments from six cores.



Figure 15: Profile of BEM Systems (2005) dioxins/furans data for ACW groundwater.

Results for PCA and cluster analysis show that dioxin/furan profiles at sites BG-11 and BG-13 are different from those at the other sites and that at these other sites the profiles are all similar (Figure 16, Figure 17). Figure 16 is based on a hierarchical clustering of the first three components which explained 99% of the variance in the original dataset. Figure 17 is based on hierarchical clustering of the raw dioxin/furan data after standardization. It shows results that are very similar to those of the principal component-based clustering. One difference between the two clustering outcomes is that BG-9 is differentiated from the rest of the samples in the clustering of the standardized data. Sampling sites BG-11 and BG-13 are located in Pensacola Bay and BG-9 is located at the mouth of the Bayou in between the two Bay samples and the other samples (Map 11). This shows that the dioxin/furan profiles in the Bay and Bayou are different, and that profiles at the mouth of the Bayou are somewhat different from both groups. In principle, the different dioxin/furan profiles in the Bay could be due to a different source of dioxins/furans but no such source is evident. Atmospheric deposition of dioxins/furans is possible but it is doubtful that it would create different dioxin/furan profiles in sediments in the Bayou and Bay. A more plausible explanation is that the Bayou acts as the source for the dioxins/furans in the adjacent part of the Bay and thus that dioxins/furans found in the Bay are older and have had more time to develop different profiles through differential degradation of the various congeners. If the Bayou acts as the source for the adjacent part of the Bay dilution by less polluted materials in the Bay, away from the source, also may have led to changes in the profiles because the dilution would lower the concentrations. For the less abundant congeners the concentrations could possibly be reduced to levels below the detection limit of the method, creating profiles with flat segments that are not present in profiles from the Bayou. The latter contention is supported by the raw data for total dioxins/furans (Table 50). The PCA or cluster analysis do not produce evidence for locally distinct sources of dioxins/furans in the Bayou.

We also ran the hierarchical clustering on a dataset containing dioxin/furan data for the sediments and groundwater at the ACW site to statistically verify similarities in profiles described qualitatively earlier in this section. The resulting cluster tree for the standardized data showed that BG-11 and BG-13 are different from all other samples in the dataset. To expand the terminal nodes (horizontal lines on cluster tree graph) and improve the readability of the graph the cluster analysis was run again without these two sites (Figure 18). The result shows that the profiles from the sediments in general are more like each other than like the profiles from the wells. Site BG-9 is an exception and is joined to one of the wells (ACW4) before being added together to another group. This indicates that the dioxin/furan profile at BG-9 is more similar to that of the well than any other site in the dataset. Results from the PCA associate BG-9 less strongly with the wells but still indicate that BG-9 has a profile that is more similar to those of the wells than any other site in the Bayou. Site BG-9 is in the mouth of the Bayou and is closer to the ACW site than the other sites in the Bayou. Site BG-9 is also close to the location of core BC00-SED-01 taken by EA (2000) (Map 11, Map 14). This core had high levels of PAHs and dioxins/furans and profiles of these pollutants indicative of a wood treating origin. All these findings together strongly indicate that the area of the Bayou where BG-9 and BC00-SED-01 are located is influenced by wood treating materials. Considering the nearness of the ACW site and the generally south to southwest movement of the groundwater from ACW it is very likely that the area is influenced by the ACW site. This does not exclude that other parts of the Bayou are also influenced by ACW but the dioxin/furan profiles there are not as similar to those of the groundwater as the profile of BG-9.



Figure 16: Cluster tree for first three principal components based on dioxin/furan data for sediments in Bayou Chico.







Figure 18: Cluster tree for standardized dioxin/furan data for sediments in Bayou Chico and ACW groundwater.

7.2.8.4 Dioxin-like PCBs

Bayou Chico was severely impacted by industrial activities and domestic waste treatment plants. The release of Aroclor PCB mixtures is not an unexpected consequence of such activities and appears to be responsible for dioxin-like PCB contamination of the environment. The presence of dioxin-like congeners in Aroclors is well documented as indicated by Table 30. Aroclors 1254a and 1254g are the most commonly used Aroclor formulations and can contain up to almost 21% of PCB-like IUPAC congener 118.

IUPAC No.	A1016	A1242	A1248a	A1248g	A1254a	A1254g	A1260
77		0.31	0.41	0.52	0.20	0.03	
81		0.01	0.01	0.02	trace		
105	trace	0.47	1.60	1.45	7.37	2.99	0.22
114		0.04	0.12	0.12	0.50	0.18	
118		0.66	2.29	2.35	13.59	7.35	0.48
123		0.03	0.07	0.08	0.32	0.15	
126			trace	trace	0.02	trace	
156		0.01	0.06	0.04	1.13	0.82	0.52
157			0.01	trace	0.30	0.19	0.02
167			0.01	0.01	0.35	0.27	0.19
169							
189					0.01	0.01	0.1

Table 28: Dioxin-like PCB congener distributions for seven Aroclor mixtures (after Frame et al., 1996).

The total TEQ for Bayou Chico sediments includes a contribution from the dioxin-like PCBs (Table 27). The percentages that dioxin-like PCBs comprise of the total TEQ for each sample varies considerably. The average for the 16 surface sediment samples from the present study was 13%. Percentages varied from <1% to $\sim98\%$. The quantities being analyzed are in parts per trillion and at this level the quantities can be extremely minute. Table 29 ranks congeners according to the percent that each congener contributes to the total mass and the percent of total TEQ for the 16 samples. PCB 126 was the most important PCB contributor to TEQ (65%) while PCB 118 on the basis of mass composed more than 53% of all dioxin-like PCBs. This is not surprising since PCB 118 is the only dioxin-like PCB that is a major constituent of an Aroclor. It is present at concentrations of 7.35 to 13.5% in Aroclor 1254. Its presence suggests that Aroclor 1254 may have been an important contributor to the PCBs now present in Bayou sediments. The current major source of Aroclor 1254 and other PCBs is an environmental cycling process of PCBs previously introduced into the environment. Aroclor 1254, and other PCBs, are also currently released to the environment from old landfills containing PCB waste materials and products, incineration of municipal refuse and sewage sludge, and improper disposal of PCB materials such as waste transformer fluid.

Table 29. DIOXIII-IIKE FCDS IOI SUITACE Samples	Table 29:	Dioxin	-like I	PCBs	for	surface	samp	les.
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PCB Congener	IUPAC No.	Aver TEQ	% of total PCB TEQ	Aver. ng/kg	% of aver. total PCBs
3,3',4,4',5-Pentachlorobiphenyl	126	1.852	65.154	18.517	0.520
3,3',4,4',5,5'-Hexachlorobiphenyl	169	0.424	14.930	42.433	1.191
2,3',4,4',5-Pentachlorobiphenyl	118	0.191	6.707	1906.121	53.511
2,3,3',4,4',5-Hexachlorobiphenyl/ 2,3,3',4,4',5'- Hexachlorobiphenyl	156 & 157	0.153	5.391	306.407	8.602
2,3,3',4,4',5,5'-Heptachlorobiphenyl	189	0.104	3.662	57.825	1.623
2,3,3',4,4'-Pentachlorobiphenyl	105	0.083	2.917	829.127	23.276
3,3',4,4'-Tetrachlorobiphenyl	77	0.026	0.930	264.392	7.422
2',3,3',4,5-Pentachlorobiphenyl	114	0.007	0.246	13.973	0.392
2,3',4,4',5,5'-Hexachlorobiphenyl	167	0.001	0.041	117.148	3.289
2,3,3',4,6-Pentachlorobiphenyl	123	0.001	0.021	5.889	0.165
3,4,4',5-Tetrachlorobiphenyl	81	0.00003	0.001	0.260	0.007

The results of PCB analyses available from previous Bayou Chico studies do not allow a complete assessment of dioxin-like PCB impact resulting from Aroclor releases. Previous studies in Bayou Chico included only PCB analyses for selected congener sets with a maximum of 26 individual detections or 28 total detections of congeners if one counts co-elutions out of 209 congeners (Table 30). Unfortunately not only was a smaller analytical set of PCBs employed, but there was a lack of a uniform standard for PCB congener analyses as there were four different PCB sets employed and none of these lists includes all of the dioxin-like PCBs. The present study of Bayou Chico used the 209 congener assay to obtain complete data for derivation of dioxin-like TEQs to support the PERCH seafood study. An examination of Table 30 shows the PCB congener groups that were studied during previous studies conducted between 1994 and 2000. The table shows three PCB sets that were extracted from the DeBusk et al. (2002) database: EPA CHICO 98, NOAA 97, and EPA CHICO 94. The EA (2000) data was from a dredging study of Bayou Chico. The number of analyzed dioxin-like congener sets varied from three to six and the precise dioxin-like congeners differ from one set to the next. The coverage for dioxin-like PCB TEQ in the four data sets varies from 69% for the EPA CHICO 98 set to 96% for the set analyzed for by EA (2000). From the viewpoint of number of analyzed dioxinlike congeners and comparison to the dioxin-like congener TEQ in the present study the EA (2000) PCB set seems to be the most complete of the four data sets.

Results from PCA and cluster analysis for the dioxin-like PCBs show that site BG-13 has a profile that is different from the rest of the sampling sites, as was the case for dioxins/furans (Figure 19). Site BG-14 and BG-15, which are located relatively close to each other more-or-less in the center of the Bayou, have profiles that are more similar to each other than to the other sites. Sites BG-10, BG-4 and BG-6, which are in the same general area as BG-14 and BG-15, are also somewhat different from the rest of the sites. Results for standardized data suggest that the profile at BG-14 is more similar to that at BG-13 than to the one at BG-15 but in any case these three sites are shown to have profiles that are different from the others (Figure 20). The analysis of standardized data does not set BG-10 apart but puts FID-2G and BG-11, two sites in the Bay, into one group. Although Figure 19 and Figure 20 do not give a clear consistent picture they both separate sites in the Bay from sites in the Bayou. As explained for dioxins/furans (section 7.2.8.3), this can in principle be due to a different source but such a source is not known to us. Differential degradation of congeners over time and dilution by materials containing lower concentrations of these pollutants most likely account for the different profiles in the Bay (see section 7.2.8.3). Sites BG-14 and BG-15, and others in that part of the Bayou, may be different from the rest of the sites due to a local source of dioxin-like PCBs. It is not known what exactly that source may be. It is interesting to observe that dioxin-like PCBs, which have characteristics of both dioxins/furans and PCBs, have cluster tree shapes that are in between those of dioxins/furans and PCBs (Figures 16, 17, 19, 20, 21, 22).

7.2.9 Polychlorinated biphenyls (PCBs)

The PCB analyses of the present study included the full list of 209 PCB congeners and their totals were compared to FDEP sediment guidelines. State of Florida sediment quality guidelines presently issue a TEL and PEL for PCBs based upon the total amount present without regard to the number of congeners analyzed for (MacDonald, 1994a,b). Patterns for PCB mass concentrations parallel those of the dioxin TEQ concentrations (Map 18, Map 16). For PCB mass concentration five sites out of seventeen exceed the PEL and an additional eight exceed the TEL

(Map 18, Table 31). PCB concentrations can be affected by particle size of the sediment but that does not seem to be the case in Bayou Chico as correlation coefficients between PCBs and clay and PCBs and silt are weak (r < 0.5). The correlation coefficient between PCBs and petroleum is also weak (r < 0.5).

The average percent for all samples on the basis of total ng of PCBs per kg of sediment is given for each congener in Table 32. Some of the congeners co-elute and this is indicated by $/_{\Pi}$. Co-elute means that during the analysis one or more compounds have identical retention time and the peaks for the compounds run together resulting in just one concentration for 2 or more compounds. This gives a total of 136 separate elutions for the 209 congeners. The first 30 of the elutions have relative abundances of more than 1% and together make up 77% of the total PCB content. The remaining 106 PCB elutions comprise 23% of the total (Table 32).

There is presently no data from local sediments for which the EPA Method 1668 or equivalent methodology has been employed. In the interest of making this data available the PCB results for each congener for the individual samples is listed in Table 51 in Appendix 2.



Figure 19: Cluster tree for first four principal components based on dioxin-like PCB data for sediments in Bayou Chico.



Figure 20: Cluster tree for standardized dioxin-like PCB data for sediments in Bayou Chico.

	EPA CHICO 98	NOAA 97	EPA CHICO 94	EA (2000)
1	PCB 101	PCB 101	PCB 101	BZ# 8
2	PCB 105 ¹	PCB 105	PCB 105	BZ# 18
3	PCB 110/ 77	PCB 118 /108/149	PCB 118 /108/149	BZ# 28
4	PCB 126	PCB 126	PCB 126	BZ# 44
5	PCB 128	PCB_128	PCB_128	BZ# 49
6	PCB_138	PCB_138	PCB_138	BZ# 52
7	PCB_153	PCB_153	PCB_153	BZ# 66
8	PCB_170	PCB_170	PCB_170	BZ# 77
9	PCB_18	PCB_18	PCB_18	BZ# 87
10	PCB_180	PCB_180	PCB_180	BZ# 101
11	PCB_187/182/159	PCB_195	PCB_187/182/159	BZ# 105
12	PCB_195	PCB_206	PCB_195	BZ# 118
13	PCB_200	PCB_187/182/159	PCB_206	BZ# 126
14	PCB_206	PCB_209	PCB_28	BZ# 128
15	PCB_209	PCB_28	PCB_44	BZ# 138
16	PCB_28	PCB29 PCB_52		BZ# 153
17	PCB29	PCB_44	PCB_66	BZ# 156
18	PCB_44	PCB_52	PCB_8	BZ# 169
19	PCB_52	PCB_66	PCB_99	BZ# 170
20	PCB_66	PCB_8		BZ# 180
21	PCB_8	PCB_77		BZ# 183
22	PCB_77			BZ# 184
23	PCB_87			BZ# 187
24	PCB_99			BZ# 195
25				BZ# 206
26				BZ# 209
total	28	25	23	26
congeners	20	20	20	20
dioxin-like	3	4	3	6
Dioxin-like D(B			
TEQ compare	ed 69%	75 7%	74 8%	96%
to present stu	idv		,, .	2070

Table 30: PCB	congeners	with	existing	data	for	Bay	/011	Chico
1 auto 50. 1 CD	congeners	vv I tIII	CAISting	uata	101	Day	ou	Chico.

¹: Congeners in bold are dioxin-like PCBs.

	Table 31: I	PCB mass	concentration	in	surface	sediments	in	Bayou	Chico.
--	-------------	----------	---------------	----	---------	-----------	----	-------	--------

			2
Sample ID	ug/kg ¹	Sample ID	ug/kg ¹
FID-2G	0.57	BG-8	43.83
BG-1	89.85 ²	BG-9	5.50
BG-2	33.28	BG-10	1470.67P
BG-3	37.50	BG-11	0.90
BG-4	8.25	BG-12	7.98
BG-5	21.86	BG-13	42.54
BG-6	26.02	BG-14	403.69P
BG-6Dupl.	22.94	BG-15	191.56P
BG-7	206.61P ³	BG-16	239.29P

 BG-7
 Z00.01P
 BG-10

 1: Tel 21.55 ug/kg and PEL 188.79 ug/kg

 2: Boldface indicates concentration exceeds the TEL

 3: Bold + P indicates concentration exceeds the PEL.

Congener IUPAC No	%	Congener IUPAC No	%	Congener IUPAC No	%	Congener IUPAC No
187/ ₁ 187+182	10.804	59/ _ד 59+62+42+75	0.849	158	0.201	96
180/ _ד 180+193	6.094	146+161	0.841	80	0.201	184
177	4.444	4	0.805	156/ _٦ 156+157	0.193	126
147/ ₁ 147+134+149	4.289	94	0.764	208	0.172	2
153/ _٦ 153+168+141	3.989	83/ ₁ 83+99+112	0.761	77	0.167	63

0.756

0.702

0.692

0.665

0.539

0.527

0.523

0.516

0.514

0.514

0.513

159

95

165

206

1

130/_¬130+137+164

9

46

209

82

207

%

0.015

0.013

0.012

0.011 0.010

0.009

0.008

0.008

0.006

0.005

0.005

0.004

0.004

0.003

0.002

0.001

122/a 122+114

139/_T 139+140

103

136

54

58/ 58+67

133 109/_ד 109+106+**12**

131/_T 131+142

175

57

0.153

0.146

0.128

0

0.107

0.100

0.094

0.089

0.087

0.085

0.082

Table 32: Relative abundance of PCB elutions in Bayou Chico.

32

86/₁86+87+97+108

+119+125

195

56/_T 56+60

201

145

105

64

93/7 93+100+98+

102

45/₁45+5

22

20/7 20+21+28+33

129/ד 129+138+

160+163

198+199 _F/198

178

70/770+61+74+76

135+151+ _ד

154

5/7 5+8

18/_{¬18+30}

196/₁196+203

52/1 52+43+7

90/₁90+101+113

3.640

3.523

3.197

2.829

2.804

2.405

2.291

2.162

2.139

1.994

1.886

167 0.074 194 1.802 176 0.513 89 0.001 170 1.690 202 0.499 205 0.066 0.001 36 179 1.668 25 0.493 12₁12+13 0.060 152/₁152+150 0.001 110/₁110+115 197/_ח 197+200 1.553 0.489 162 0.056 78 0.00024 50+53 F0/_ד 41/1 41+71+40 0.054 1.372 0.391 79 0.00021 7 17 1.363 128/_T 128+166 0.311 183/₁183+174+185 0.047 81 0.00016 181/₁181+171+173 19-0.303 0.042 0.00007 1.277 188 3 44/1 44+47+65 1.258 190 0.297 10 0.039 155 0.00002 66/ 766+55 1.215 192 0.294 107/_ח 107+124 0.039 39 < 0.000001 **118**¹ 0.257 < 0.000001 1.203 148 14 0.038 38 49/₁49+69 1.164 27/1 27+16+24 0.253 189 0.036 < 0.000001 35 < 0.000001 0.245 0.031 31 1.156 84 172 72 0.227 0.027 < 0.000001 85/185+116+117 1.047 88/₇88+91 169 68 15-1.035 6 0.221 191 0 104 < 0.000001 0.953 0.217 < 0.000001 132 127 0.024 11 111 0.018 < 0.000001 26/1 26+29 0.924 34/1 34+23) 0.214 121 120 144 0.909 48 0.211 204 0.017 186 < 0.000001 0.854 0.203 0.015 37 92 143

¹: Boldface indicates PCBs with dioxin-like activity.

Fifty-nine samples analyzed for PCBs by four previous studies are listed in the DeBusk et al. (2002) database (Table 33). None of these previous studies analyzed the complete set of 209 PCB congeners and comparing between these studies is difficult due to differences amongst the analyzed congeners. Most importantly, the previous study with the most congeners (EA, 2000) included only six out of the twelve dioxin-like congeners. The majority of dioxin-like PCB TEQs in that study were from congeners 126 (65% of Bayou Chico TEQ), 169 (15%), 118 (7%), 156&157 (5%), 189 (4%), and 105 (3%). Congener 126 was included in all four previous studies (DeBusk et. al., 2002) but the second most common congener, congener 169, was only covered

in the EA (2000) study. It is conceivable that for the EA (2000) study a different mix of congeners might have yielded different results.

The maximum PCB concentrations for the existing studies were 226.2 and 235.5 ug/kg, compared to 1470.67 and 403.69 ug/kg for the present study. From this, one might conclude that PCB concentration is increasing in the Bayou but the reduced number of congeners analyzed for in the existing studies more than likely explains the lower total values. It is not possible to make a conclusion about changes in total PCB concentration over time in Bayou Chico from comparing past and present studies. Also location is very important since some sites have higher PCB concentrations than other. The same sites should be sampled over time to determine changes in overall PCB concentrations. The data from previous studies and the current study concur in showing that concentrations of total PCB exceed established sediment guidelines in Bayou Chico. The present guidelines do not distinguish between the various PCB analytical methodologies and it could be argued that the TEL and PEL guidelines (21.55 ug/kg and 188.79 ug/kg respectively) should be specific to the PCB analytical method employed.

] = = = = = = = = = = = = = = = = = = =			
Site label	Location	Total_PCB	Site label	Location	Total_PCB
EPA27	Bayou Chico	173.1T ¹	NBC3B	Bayou Chico	66.7T
PCOLA24	Bayou Chico	99.938T	NBC3B	Bayou Chico	70.7T
PCOLA24	Bayou Chico	98.695T	NBC3B	Bayou Chico	94.8T
NOAA4	Bayou Chico	16.76	S-1	Stream	2.2
NOAA5	Bayou Chico	96.34T	S-2	Stream	8.9
NOAA6	Bayou Chico	106.08T	S-2	Stream	3.9
NOAA7	Bayou Chico	16.76	S-2	Stream	10.6
NOAA8	Bayou Chico	16.76	S-3	Stream	No Data
NOAA9	Bayou Chico	16.76	NBC12B	Bayou Chico	235.5P
NOAA15	Bayou Chico	16.76	NBC12B	Bayou Chico	212.8P
NOAA16	Bayou Channel	16.76	NBC12B	Bayou Chico	226.2P
NPB3B	Pensacola Bay	6.9	NBC11	Bayou Chico	101
NPB3B	Pensacola Bay	No Data	NBC10	Bayou Chico	122.2T
NPB3B	Pensacola Bay	No Data	BC1		62.6T
NPB6	Pensacola Bay	No Data	BC2		68.3T
NPB9	Pensacola Bay	9.3	BC4		104.2T
NBC33	Bayou Chico	No Data	BC5		8.2
NBC30B	Bayou Chico	92.7T	BC6		64.5T
NBC30B	Bayou Chico	53.7T	NBC11		101T
NBC30B	Bayou Chico	30.7T	NBC3B		70.7T
NBC28	Bayou Chico	39.8T	NBC3B		94.8T
NBC23	Bayou Chico	223.4P	NBC4		70.4T
NBC19	Bayou Chico	34.1T	NPB9		9.3
	Bayou Chico			Inner Harbour	
NBC18		62.4T	NOAA17	Channel	16.76
NBC17B	Bayou Chico	No Data	NOAA18	Inner Harbour	16.76
NBC17B	Bayou Chico	102.2T	NOAA19	Inner Harbour	16.76
NBC17B	Bayou Chico	78.6T	NOAA20	Inner Harbour	16.76
NBC14	Bayou Chico	17.7	LA94LR05		33.57T
NBC4	Bayou Chico	70.4T	LA94SR10		27.07T

Table 33:	Total PCE	s for Bayou	I Chico	sediments	from	DeBusk	et al.	(2002).	
					-			· · · /·	

¹: Boldface indicates that the TEL (T) or PEL (P) is exceeded. Note: The NOAA total PCB concentrations for samples NOAA4, 7, 8, 9, 15,&16 probably represent transcription errors.

In spite of the above explained difficulties, an attempt was made to evaluate whether or not the results for individual congeners from various studies in Bayou Chico are comparable. The earliest PCB results in the DeBusk et al. database are from 1994 studies that may have actually begun as early as 1991. The sampling of the present study was conducted in 2005 resulting in a maximum time span of 14 years for these studies of PCBs in Bayou Chico. There is some degradation of PCBs in the environment, but any major trend in congener distribution should not change radically for these persistent compounds in such a short time. Profiles based on the relative proportion of each congener to total PCBs for the various datasets in the DeBusk et al. (2002) database combined, for the EA (2000) study, and for the present study were computed and compared (Table 34, Table 35). There appears to be no readily discernable agreement between the profiles. For example, for the DeBusk datasets PCB congener 87 is 30% of the total PCBs. In DeBusk et al. (2002) congener 170 is 5.8%, in the present study it is 1.7%, in the EA (2000) study it is 0.4%. These differences corroborate the earlier made contention that PCB data from the various datasets for Bayou Chico are not comparable.

DeBusk et al. database		Present study	
Congener	Percent of total	Congener	Percent of total
		86/ ₁ 86+87+97+108	
87	30.164	+119+125	0.702
99	9.990	83/ ₁ 83+99+112	0.761
52	6.893	52/ _ד 52+43+7	1.994
44	6.091	44/ ₁ 44+47+65	1.258
170	5.787	170	1.69
101	5.465	90/ ₁ 90+101+113	1.886
28	4.660	20/ ₁ 20+21+28+33	3.64
118/108/149	4.363	118	1.203
105	4.138	105	0.523
77	3.028	77	0.167
180	3.006	180/ _ד 180+193	6.094
66	2.866	66/ ₁ 66+55	1.215
126	1.905	126	0.012
153	1.740	153/ _٦ 153+168+141	3.989
138	1.500	129/ד 129+138+160+163	3.523
29	1.340		0.924
195	1.104		0.692
128	0.989	128/ _ח 128+166	0.311
18	0.931	18/ ₁ 18+30	2.162
110/77	0.905	Not compared	
206	0.818	206	0.116
8	0.780	5+8	2.291
209	0.758	209	0.087
187/182/159	0.756	187/ _ד 187+182	10.804
200	0.022	197/ _ד 197+200	0.489

Table 34: Relative proportion of PCB congeners compared for DeBusk et al. (2002) database and the present study.

EA	(2000)	Present s	study
Congener	Percent of total	Congener	Percent of total
BZ# 101	10.596	90/ ₁ 90+101+113	1.886
BZ# 153	8.337	153/ ₁ 153+168+141	3.989
BZ# 138	7.691	129/ ₁ 129+138+160+163	3.523
BZ# 66	6.548	66/ ₁ 66+55	1.215
BZ# 52	6.185	52/ _T 52+43+7	1.994
BZ# 44	5.580	44/ _q 44+47+65	1.258
BZ# 184	5.419	184	0.013
BZ# 118	5.244	118	1.203
BZ# 169	4.975	169	0.027
BZ# 28	4.962	20/ ₁ 20+21+28+33	3.64
		86/ ₁ 86+87+97+108+119+	
BZ# 87	4.827	125	0.702
BZ# 180	4.168	180/ _ח 180+193	6.094
BZ# 49	3.536	49/ ₁ 49+69	1.164
BZ# 128	3.308	128/ _ח 128+166	0.311
BZ# 126	3.241	126	0.012
BZ# 187	3.025	187/ _ד 187+182	10.804
BZ# 105	2.434	105	0.523
BZ# 156	2.071	156/ _{דן} 156+157	0.193
BZ# 77	1.990	77	0.167
BZ# 18	1.358	18/ ₁ 18+30	2.162
BZ# 195	1.089	195	0.692
BZ# 8	1.035	5+8	2.291
BZ# 209	0.914	209	0.087
BZ# 183	0.524	183/ ₁ 183+174+185	0.047
BZ# 206	0.524	206	0.116
BZ# 170	0.417	170	1.69

Table 35: Relative proportion of PCB congeners compared for EA (2000) and the present study.

Keeping in mind that results for PCBs may vary according to the analytical method used the literature was searched for other studies in the northern Gulf of Mexico. In a study for nearby Choctawhatchee Bay four total PCB sediment concentrations were reported as: 221.6, 34.43, 23.6, and 103.8 ug/kg (Hemming et al., 2005). One of these is above the PEL and the other three are above the TEL. These values are below the higher values of the present study but they show that there are other locales nearby that also have high concentrations of PCBs. There was no report for the individual congeners that were analyzed. Elsewhere, the EPA Gulf Ecology Division at Sabine Island, Florida conducted monitoring of estuaries in the Louisianian Province between 1991 and 1994 (Macauley et al., 1999). This monitoring was done to assess ecological conditions on a regional scale. It was found that over the four years of monitoring, 25.6% of Gulf of Mexico estuarine sediments in the Louisianian Province displayed poor biological conditions, as measured by diverse metrics. This study included analyses of PCBs (Macauley et al., 1999).

In the Macauley et al. (1999) study twenty-two PCB congeners were analyzed from the Louisianian Province sediments. Concentrations of total PCBs (the sum of the congeners) in Gulf of Mexico estuarine sediments ranged from 0–299 ppb. Only <1% of the observations exceeded

the ER-L guideline of 22.7 ug/kg which is only slightly higher than the 21.5 FDEP TEL. Bayou Chico PCB results show that the majority of samples exceeded FDEP sediment quality guidelines (Table 31). Table 36 shows a comparison between the range of congener concentrations of the Macauley et al. (1999) study and that of the present study. Most of the data ranges are not directly comparable due to co-elutions of multiple compounds being compared to those of single elutions. PCB 77 is a single elution in both cases and the Bayou Chico concentration is 60% higher. For PCB 105 the data range for the Macauley et al. (1999) study is about four times higher than the Bayou Chico concentration as is the case for the several other cases of single elutions. However, the total PCB concentration range is 1-299 ug/kg for Macauley et al. (1999) and 0.6-1470.7 ug/kg for the present study of Bayou Chico. EPA Method 1668 used in the present study was not available for use at the time of the Macauley et al. study. The methodology used in that study was likely equivalent to the assays employed by EPA or NOAA during the 1990's in Bayou Chico. Therefore, results in Table 36 are not fully comparable and should only be used for a general qualitative comparison.

Louisianian Province PCBs		Present study	
IUPAC #	Range ug/kg	IUPAC #	Range ug/kg
8	0-1	5+8	ND ¹ -14.6
18	0-11	18+30	0.01-14.9
28	0-14	20+21+28+33	0.01-31.6
29	0-<1	26+29	ND-14.2
44	0-32	44+47+65	ND-9.1
66	0-58	66+55	ND-10.5
77	0-1	77	0.01-1.6
87	0-23	86+87+97+108+119+	ND-79.0
		125	
101	0-35	90+101+113	0.01-23.1
105	0-23	105	<0.01-5.2
110	0-6	110+115	ND-11.7
118	0-36	118	0.01-13.1
126	0-1	126	ND-0.13
128	0-5	128+166	ND-3.3
138	0-18	129+138+160+163	0.02-48.8
153	0-14	153+168+141	ND-79.0
180	0-9	180+193	ND-126.2
187	0-7	187+182	0.03-241.0
195	0-1	195	<0.01-14.5
200	0-<1	197+200	<0.01-12.1
206	0-3	206	ND-1.4
209	0-6	209	<0.01-0.7
Total PCBs	<1-299	Total PCBs	0.6-1470.7

Table 36: Comparison of Louisianian Province PCB concentrations to those of the present study.

¹: ND is non-detect.

Results from PCA and cluster analysis for the PCB congeners show very little systematic differentiation between sampling sites. No large steps between consecutive joins are obvious in the cluster tree graphs and no clear spatial pattern is present in the resulting groups (Figure 21, Figure 22). This suggests that the PCBs were derived from sources with PCBs of similar profile or that sources with different PCB profiles were present in the past but that the PCBs were redistributed more-or-less homogeneously throughout the Bayou. Homogenization through redistribution is likely to occur in Bayou Chico considering that no major current PCB source is known to exist on Bayou Chico and that the Bayou is subject to currents, storm surges, and disturbance of bottom sediments by boating activities in shallow areas. Differential degradation does not seem to affect the PCBs as much as the dioxins/furans, even though PCB profiles at FID-2G and BG-11 in the Bay are still somewhat different from those at most other sites.



Figure 21: Cluster tree for first six principal components based on PCB data for sediments in Bayou Chico.



Figure 22: Cluster tree for standardized PCB data for sediments in Bayou Chico.

7.2.10 Other detected semivolatile organic compounds

In addition to the PAHs four other semivolatiles were detected: carbazole, dibenzofuran, di-n-butyl phthalate, and bis(2-ethylhexyl) phthalate. Carbazole is a nitrogen containing heterocyclic PAH (Figure 12) usually found along with anthracene in coal tar. It is used chiefly in the manufacture of dyes and is also a component of coal tar creosote. Several thousand tons of carbazole are produced each year from coal tar and crude oil. It is used widely in synthesis of dyes, pharmaceuticals, and plastics and is a suspected carcinogen (OSHA, 1999). We found carbazole at seven sites on and near Sanders Beach at concentrations of 32 to 570 ug/kg (Table 19). In the Bayou carbazole was not detected. There are apparently no applicable SQAGs for carbazole but the residential SCTL is 49,000 ug/kg.

Dibenzofuran is a heterocyclic organic compound with the chemical structure shown in Figure 23. It is an aromatic compound that has two benzene rings fused to one furan ring in the middle. All of the numbered carbon atoms have a hydrogen atom bonded to each of them (not shown in the image). It may be found in coke dust, grate ash, fly ash, and flame soot. The general public may be exposed to dibenzofuran through the inhalation of contaminated air or through the consumption of contaminated drinking water or food. Dibenzofuran has also been identified in tobacco smoke (USEPA, 2000). Dibenzofuran was of concern in EPA's Great Waters Program due to its persistence in the environment, potential to bioaccumulate, and toxicity to humans and the environment. Dibenzofuran was found at six sites on and near Sanders Beach at concentrations of 21 to 7,800 ug/kg but not in the Bayou. These concentrations are well below the residential SCTL of 320,000 ug/kg for dibenzofuran.

Di-n-butyl phthalate is an odorless and colorless or faintly yellow oily liquid that does not occur in nature. It is a chemical that is added to hard plastics to make them soft. Di-n-butyl phthalate is used most in polyvinyl chloride plastics and nitrocellulose lacquers. In 1994, more than 17 million pounds (i.e., 7.8 million kilograms) of di-n-butyl phthalate were made. Di-n-butyl phthalate is in many items made of plastics such as carpets, paint, and nail polish. Di-n-butyl phthalate. In water and soil, bacteria break down di-n-butyl phthalate. If di-n-butyl phthalate does not break down in soil, it can get into groundwater. Di-n-butyl phthalate appears to have relatively low toxicity, and large amounts are needed to cause injury. Adverse effects on humans from exposure to di-n-butyl phthalate have not been reported. Di-n-butyl Phthalate was only found in one sample from Bayou Chico (Table 37). Di-n-butyl Phthalate has no SQAG.

Bis(2-ethylhexyl)phthalate, also called DEHP, is a manufactured chemical that is commonly added to plastics to make them flexible. DEHP is found nearly everywhere in the environment because of its use in plastics, but it does not evaporate easily or dissolve in water easily. It dissolves faster in water if gas, oil, or paint removers are present. It attaches strongly to soil particles. DEHP in soil or water can be broken down by microorganisms into harmless compounds. DEHP does not break down easily when it is deep in the soil or at the bottom of lakes or rivers. It is in plants, fish, and other animals, but animals high on the food chain are able to break down DEHP, so tissue levels are usually low. At the levels found in the environment, DEHP is not expected to cause harmful health effects in humans. Most of what we know about the health effects of DEHP comes from studies of rats and mice given high amounts of DEHP. Harmful effects in animals generally occurred only with high amounts of DEHP or with prolonged exposures. Moreover, absorption and breakdown of DEHP in humans is different than in rats or mice, so the effects seen in rats and mice may not occur in humans (ATSDR, 2002). DEHP was found in three Bayou locations but concentrations were below the TEL (182 ug/kg) and SCTL (72,000 ug/kg).

			Di-n-butyl	
	Carbazole	Dibenzofuran	Phthalate	Bis(2-ethylhexyl) Phthalate ¹
SB-3B	79	ND	ND	45
SB-3C	250	710	ND	51
SB-4C	380	7800	ND	58
SB-5B	32	20	ND	ND
FID-3B	39	21	ND	ND
FID-5A	340	58	ND	ND
FID-7A	570	270	ND	ND
BG-16	ND	ND	600	ND

Table 37. Other detected	semivolatile organic	compounds [ug/kg]
	Senni volutile ofguille	compounds [µg/kg]

¹: The Bis(2-ethylhexyl) Phthalate TEL is 182 ug/kg; PEL is 2647 ug/kg.



Figure 23: Structure of other detected semivolatile organic compounds.

7.3 Volatile Organic Compounds (VOCs)

7.3.1 Omni-Vest

Volatile organic compounds (VOCs) were an important component of the waste materials present in the Omni-Vest waste site (FDEP, 2006a). A concern was whether VOCs were being transported in the groundwater to Jackson's Branch Creek, thereby entering Bayou Chico. To verify this, the present study took sediment vibracores (Map 11, Map 19) from Jackson's Branch Creek and collected water samples from the Bayou and creek. Samples were analyzed for the EPA Method 8260B list of volatile organic analytes.

All of the VOC detections were between the laboratory method detection limit and the laboratory practical quantitation limit. The MDL for most compounds was about 1 ppb, showing that the slightest traces of VOCs are detected by this analyses (Table 38). All the detected sample values were flagged with data qualifiers I and J. I indicates that the reported value is between the laboratory method detection limit and the laboratory practical quantitation limit; J indicates a value was estimated because it was below the calibration curve. To determine if there was contamination of the samples either in the laboratory or during sample collecting and transport, method blanks and trip blanks were also analyzed for volatiles. Acetone and dichloromethane (methylene chloride) were detected at trace quantities in most sediment analytical method blanks, many trip blanks, and most sediment samples that were below the reportable limit. These two compounds in question are common laboratory contaminants since they are routinely used in many laboratory procedures. After an examination of the method blanks and trip blanks it was decided that data reported for these two compounds was not reliable and was excluded. A similar decision was made for 1,4-Dichlorobenzene in two samples from near the Pensacola Yacht Club. Much of this sample contamination likely occurred during preparation and extraction of the sample in the laboratory when the sample jars are opened and exposed to the laboratory atmosphere.

The results (Table 38) included trace amounts of several compounds that were reported as being present in the landfill but were not routinely encountered in the blanks. Toluene was detected in vibracore sample OV-1C and 1,4- dichlorobenzene was found at level C (2 m depth) in all three cores. Toluene has been reported as a constituent of the wastes present in the Omni-Vest Site. Its presence in the sediments of Jackson's Branch Creek suggests a possible origin from the waste site. The 1,4- dichlorobenzene was detected at comparable trace quantities at all three sites, including one upstream from where any Omni-Vest leachate could be expected to reach the creek. Consequently, its presence seems to represent background contamination form another source(s). Both toluene and 1,4- dichlorobenzene are present at just barely detectable quantities that do not appear to exceed applicable guidelines.

Three other VOCs were detected near the Omni-Vest site: 2-butanone (MEK or methyl ethyl ketone) in sample OV-3B, trichloroethene (TCE) in sample OV-2C, and tetrachloroethene (PCE) in sample OV-C. MEK is a commonly encountered compound and is manufactured in large amounts for use in paints, glues, and other finishes. It is also a natural product made by some trees and is found in some fruits and vegetables. MEK is usually found in the air, water, and soil of landfills and hazardous waste sites. MEK will not stick to soil and if it is spilled onto soil it will travel through the soil into underground water sources. MEK was detected upstream (OV-3B) but not down gradient from the Omni-Vest site. This suggests that it is not migrating from the Omni-Vest site. The TCE was detected adjacent and slightly down gradient from Omni-Vest. However, this does not clearly implicate Omni-Vest as the origin for this contaminant
because PCE, to which TCE is closely linked, was found upstream. TCE is linked to PCE because TCE is a degradation product of PCE, they have common uses as cleaning solvents, and they are commonly encountered together as ground water contaminants.

Sample ID	2- Butanone (MEK)	Trichloroet hene (TCE)	Tetrachloro ethene (PCE)	Toluene	1,4- Dichloro benzene	o- Xylene	Carbon Disulfide
OV-1B	<1.4	<0.14	<0.075	<0.067	<0.11	<0.046	<1.6
OV-1C	<1.3	<0.13	<0.071	0.58 I,J	0.42 IJ	<0.043	<1.6
OV-2B	<1.4	<0.14	<0.075	<0.068	<0.11	<0.046	<1.9
OV-2C	<1.6	0.68 IJ	<0.085	<0.077	0.61 IJ ¹	<0.052	<1.6
OV-3B	3.4 I, J	<0.14	<0.076	<0.068	<0.11	<0.046	<1.7
OV-3C	<1.6	<0.16	4.5 IJ	<0.077	0.92 IJ	<0.052	<1.8
SB-1B	<1.3	<0.13	<0.072	<0.065	<0.11	<0.044	<1.6
SB-2B	<1.4	<0.14	<0.073	<0.066	<0.11	<0.045	<1.6
SB-3B	<1.4	<0.14	<0.076	<0.068	<0.11	<0.046	<1.7
SB-3C	<1.4	<0.14	<0.077	<0.069	<0.11	0.48 IJ	<1.7
SB-4B	<1.3	<0.13	<0.068	<0.062	<0.097	<0.042	<1.5
SB-4C	1.7 I,J	<0.14	<0.075	<0.067	<0.11	<0.045	<1.6
SB-5B	<1.3	<0.13	<0.072	<0.065	<0.11	<0.044	<1.6
SB-6B	<1.5	<0.14	<0.079	1.6 I,J	<0.12	<0.048	<1.7
SB-6C	<1.5	<0.15	<0.075	0.93 I,J	<0.11	<0.046	<1.6
FID-1B	<1.4	<0.14	<0.074	<0.067	<0.11	<0.045	<1.6
FID-2B	<1.4	<0.14	<0.074	<0.067	<0.11	<0.055	<1.6
FID-3B	<1.7	<0.17	<0.091	0.54 I,J	<0.13	<0.046	6.1 I, J
FID-4B	<1.4	<0.14	<0.076	<0.069	<0.11	<0.046	<1.7
FID-5B	1.4	<0.14	<0.073	<0.066	0.40 I,J	<0.044	<1.6
FID-5C	1.4	<0.14	<0.078	<0.07	0.42 I,J	<0.047	<1.7
FID-6B	<1.4	<0.14	<0.078	<0.07	<0.12	<0.047	1.7
FID-6C	6.0 I,J	<0.15	<0.080	<0.072	<0.12	<0.049	13
FID-6D	5.0 I,J	<0.14	<0.077	<0.07	<0.11	<0.047	4.6 I, J
FID-7B	<1.4	<0.14	<0.077	<0.070	<0.11	<0.047	<1.7

Table 38: Volatile organic compounds in sediments [µg/kg].

¹: Contamination in method blank, value is rejected.

7.3.2 Sanders Beach

Sediments samples from on and around Sanders Beach were also analyzed for VOCs to examine if these products impact the area and potentially pose a threat to human health (Map 12). If VOCs were encountered, the ACW site would be a potential source for them because in a recent report twenty VOCs were encountered during ACW ground water investigations, including acetone, bromodichloromethane, bromomethane, benzene, toluene, carbon disulfide, chloroethane, chloromethane, 1,2-dichloroethane, cis-1,2-dichloroethene, ethylbenzene, 2hexanone, 4-methyl-2-pentanone, methyl ethyl ketone, styrene, tribromomethane, 1,1,2trichloroethane, trichloromethane, vinyl chloride, and total xylenes (BEM Systems, 2005). The results of the present study showed some detections of toluene, o-xylene, carbon disulfide and MEK (Table 38). These VOCs were detected as trace concentrations only and do not appear to present any probable hazard to human health.

7.3.3 Bayou water

Seven water grab samples were taken from the Bayou (Map 11, Map 12), but due to contamination of the trip blanks all of the acetone and dichloromethane detections were considered not valid. Samples BW-2 and BW-13 had trace detections for toluene and m,p,o-xylenes. Site BW-4, which is near Omni-Vest, has no detections of VOCs (Table 39, Map 11). This finding is consistent with results for sediments near the Omni-Vest site that also fail to show an influence of the contamination at the site on Bayou Chico.

	U		
	toluene	m,p-xylene	o-xylene
BW-1	< 0.13	<0.19	< 0.083
BW-2	0.51 I,J	0.22 I,J	0.13 I,J
BW-4	< 0.13	< 0.19	< 0.083
BW-13	0.65 I,J	0.36 I,J	0.16 I,J
BW-14	< 0.13	< 0.19	< 0.083
BW-15	< 0.13	< 0.19	< 0.083
BW-16	< 0.13	< 0.19	< 0.083

Table 39: Volatile organic compounds in water [µg/liter].

7.4 Trace metals

7.4.1 Surface sediments

Trace metals have been studied in the sediments of Bayou Chico by several investigations and have been found to be elevated (see section 3.2.7). In this study we analyzed for As, Cd, Cr, Cu, Hg, Pb, Sb, Tl and Zn. Although Tl and Sb have high concentrations in sediments of stormwater retention ponds in the area (Liebens, 2001) Tl was not detected in the Bayou and Sb was detected in only one sample in the NW branch of the Bayou (Table 40, Map 11). Cadmium was detected in 11 samples out of 26 and Hg in 23 samples. The other metals were detected in all 26 surface sediment samples. The TEL's were exceeded by As, Cr, and Cd. The PELs are exceeded by Cu, Pb, Hg, and Zn. These same four metals were found to exceed their PEL in Bayou Texar by another study of the PERCH project (Mohrherr et al., 2005; Liebens et al., 2006). However, the maximum concentrations for Cu, Pb and Zn are higher in Bayou Chico than Bayou Texar. They also exceed the concentrations observed in some other estuaries in highly urbanized and industrialized catchments (Sarkar et al., 2004; Cave et al., 2005) and in Choctawhatchee Bay, a large estuary about 50 miles east of Bayou Chico (Hemming et al., 2005). These observations indicate that some sediments in Bayou Chico have very high levels of trace metal pollution and that these levels are likely to negatively affect sediment-dwelling biota. The results from the present study are in line with those from another study in Bayou Chico that found Cd, Cu, Pb, and especially Hg and Zn to be elevated (Waller et al., 1998). Although it is difficult to pinpoint specific sources for the metals because of the multiple potential sources for them in the Bayou Chico area, high concentrations for Cu, Pb and Zn are consistent with the shipbuilding and maintenance, and metal recycling and processing activities (Figure 24) that have taken place for many years on the banks of Bayou Chico. Copper, Cr, and As have been used in wood preservatives and must be present in pilings and docks on and near the Bayou. The metals may have leached out of the wood and into the Bayou but, as mentioned before, identifying specific sources is tedious at best. As has been observed in many other settings, the trace metal concentrations correlate highly with clay and total organic carbon (TOC) content because of sorption processes (Table 40). Cadmium has low correlation coefficients because of its well documented low affinity for clay and TOC. The generally high correlation coefficients imply that the spatial distribution of the trace metals in Bayou Chico is determined at least in part by the distribution of sediment characteristics, such as clay content and TOC.



Figure 24: Scrap metal recycling facility on east bank of Bayou Chico.

Table 40: Trace metal concentrations in surface sediments [mg/kg].	
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Sample ID ²	Antimonv ¹	Arsenic ¹	Cadmium ¹	Chromium ¹	Copper ¹	Lead ¹
BG-1	1.2	17.00	1.50	56.0	140.0	290.0
BG-2	<0.56	7.10	< 0.37	23.0	49.0	110.0
BG-3	<1.20	20.00	1.20	48.0	170.0	190.0
BG-4	<0.33	2 70	<0.22	6.3	20.0	12.0
BG-5	<1 10	21.00	1.50	74 0	200.0	150.0
BG-6	<0.78	7 70	0.91	33.0	100.0	71.0
BG-6 duplicate	<0.77	7.40	0.78	30.0	91.0	67.0
BG-7	<0.32	5.60	0.56	14 0	60.0	34.0
BG-8	<0.02	8 10	0.00	18.0	310.0	40.0
BG-0	<0.02	2 10	<0.66	5.6	28.0	40.0 25.0
BG-10	<0.33	16.00	1 20	49.0	170.0	100.0
BG-11	<0.33	0.58	<0.22	20	1 1	16
BG-12	< 0.33	1.20	<0.22	2.3	19.0	5.6
BG-13	< 0.34	<0.20	<0.22	0.7	0.3	0.7
BG-14	<0.96	16.00	<0.64	50.0	120.0	79.0
BG-15	<0.97	13.00	1.00	48.0	150.0	110.0
BG-16	<1.10	22.00	1.60	54.0	180.0	230.0
BGP-2	<0.57	10.00	<0.38	28.0	13.0	12.0
BGP-3	<0.34	1.20	<0.23	3.4	7.9	12.0
BGP-4	<1.30	20.00	1.50	58.0	270.0	120.0
FID-2G	<0.32	0.24	<0.21	0.8	0.7	1.1
FID-5G	<0.33	3.5	<0.22	6.3	13	13
FID-6G	<0.34	0.63	<0.22	1.6	5.7	7.6
OV-1A	<0.32	0.41	<0.22	2.2	0.84	1.6
OV-2A	<0.31	0.5	<0.21	2.2	4.5	6.5
OV-3A	<0.32	0.35	<0.21	1.4	1.5	5
minimum	<0.31	0.20	<0.21	0.68	0.29	0.67
maximum	<1.10	22.00	1.60	74.00	310.00	290.00
mean	-	7.87	0.64	23.76	81.75	65.18
correlation clay	-	0.8	0.1	0.8	0.7	0.5
correl. TOC	-	0.8	0.1	0.8	0.8	0.8
TEL	No TEL	7.24	0.68	52.3	18.7	30.2
PEL	No PEL	41.6	4.21	160	108	112

Sample ID ²	Mercury ¹	Thallium ¹	Zinc ¹
BG-1	0.4100	<0.96	670
BG-2	0.3100	<0.48	50
BG-3	0.4300	<1.00	810
BG-4	0.0270	<0.28	82
BG-5	0.4700	<0.98	1100
BG-6	0.1900	<0.67	440
BG-6 duplicate	0.1900	<0.65	430
BG-7	0.0530	<0.27	240
BG-8	0.1200	<0.27	280
BG-9	0.0570	<0.84	78
BG-10	0.6000	<0.65	920
BG-11	0.0078	<0.28	6
BG-12	0.0220	<0.28	43
BG-13	0.0023	<0.29	2
BG-14	0.5900	<0.82	960
BG-15	0.5700	<0.82	910
BG-16	0.7300	<0.92	890
BGP-2	0.0250	<0.48	66
BGP-3	0.0290	<0.29	45
BGP-4	0.7900	<1.10	1100
FID-2G	<0.0009	<0.27	4
FID-5G	0.0013	<0.28	42
FID-6G	<0.0010	<0.29	35
OV-1A	<0.0010	<0.28	3.3
OV-2A	0.0062	<0.27	9.5
OV-3A	0.0053	<0.27	9.2
minimum	<0.0009	<0.27	1.50
maximum	0.79	<1.10	1100
mean	0.22	-	355
correlation clay	0.7	-	0.8
correl. TOC	0.7	-	0.8
TEL	0.13	No TEL	124
PEL	0.696	No PEL	271

Table 40: Trace metal concentrations in surface sediments [mg/kg] (continued).

¹: <x means below detection limit x. ²: A=surface, B=1 m depth, C=2 m depth.

³: Bold values are above PEL

In general, the lowest metal concentrations are present near the Bayou's mouth and at the two sample sites in Pensacola Bay (Maps 20- 26). This is most likely due to the influence of relatively unpolluted water and sediment from the Bay. The highest concentrations are found in the more interior parts of the Bayou, especially near the spoil island in the center of the Bayou. Several consistent hot spots occur just south and towards the northwest of the island. Concentrations are also consistently high between the two constrictions north of the main body of the Bayou and they are usually high in one of the samples (BG-1) in the NW branch of the upper Bayou's bifurcation. Other studies have reported elevated concentrations in that branch (Glassen et al., 1977; Stone and Morgan, 1991). Waller et al. (1998) also found elevated trace metal concentrations in the NW branch but that study found elevated concentrations at several

locations north of the W. Navy Blvd. bridge. The present study found elevated concentrations in only one out of five samples north of the bridge. Waller et al. (1998) attributed the elevated levels to input from stormwater via the two branches of the bifurcation of the northern Bayou. If this contention is correct our results suggest that stormwater input may be diminishing. This is consistent with findings of another study that indicate that water quality has improved to some extent in the region due to reductions in industrial and municipal point source loading (NWFWMD, 1992). The PLI index map (Map 27) shows that overall the highest metal pollution of the sediments can be found between the two constrictions, south of the spoil island, and to the west of the spoil island. The high index between the two constrictions suggests that pollutants entering from the north are trapped by the southernmost constriction. The sample just south of that southernmost constriction has a low PLI index. This corroborates the argument that the constriction acts as a barrier that greatly limits sediment exchange between the constricted part of the Bayou and its main body.

7.4.2 Bayou water

Antimony, Cd, and Tl were not detected in the water of Bayou Chico. Arsenic, Cr, Cu, Pb, Hg, and Zn were detected in almost all water samples (Table 41). Copper and Hg exceed the state criteria for class II or marine class III surface water in four out of seven samples. Arsenic exceeds the criteria in the samples from the Bayou itself but is below the state criteria in Pensacola Bay, near Sanders Beach and where Jackson's Branch Creek enters the NW branch of the Bayou. (Map 28). Mercury exceeds its criteria in the Bay, between the old Pace Blvd. bridge and new Barrancas Ave. bridge in the lower section of the Bayou and in the central and western portion of the Bayou (Map 29). The lowest Hg levels were found between the two constrictions and in the NW branch. The chromium concentration is also highest in the Bay but is low in the central and western section of the Bayou (Map 30). Arsenic and Pb have spatial distributions that are similar to that of Cu with the highest concentrations in the Bayou and low concentrations in the Bay and at the end of the NW branch of the Bayou (Maps 28, 31, 32). Zinc also has a low concentration in the sample in the Bay but reaches its maximum between the two bridges in the lower section of the Bayou (Map 33). The maximum is well below the state criteria for Zn.

The elevated levels of Cu are consistent with results of Waller et al. (1998) and Lewis et al. (2001b) (range of 1 to 41 μ g/l and mean of 18.7 μ g/l respectively). Waller et al. (1998), however, did not detect other trace metals in appreciable amounts while the present study and Lewis et al. (2001b) did. Lewis et al. (2001b) found relatively high levels of Cd, 13.7. μ g/l on average, but Cd was not detected in the present study. Arsenic exceeds regulatory criteria in the present study but not in the Lewis et al. (2001b) study. The differences between the Lewis et al. (2001b) study and the present can be explained by spatial and temporal changes. The relatively low levels recorded by Waller et al. (1998) are difficult to interpret because raw data are not provided.

The PLI index shows that overall the Bayou water is most polluted with trace metals between the two constrictions and in the western finger of the Bayou (Map 34). This distribution coincides in part with that of sediment pollution by metals, which is also highest between the two constrictions. Sediments in the western finger, however, are generally not highly polluted (Map 27). The PLI for water is lowest in the NW branch of the Bayou as well as in the south in Pensacola Bay and near Sanders Beach. Regulatory criteria from other states and countries obviously do not legally apply to the waters in Bayou Chico but comparison with other criteria helps put our observations in a broader perspective. For instance, the concentrations of Cu and Zn in some samples exceed marine surface water quality guidelines intended to protect aquatic ecosystems in Australia and New Zealand (ANZECC/ARMCANZ, 2000) and would trigger further monitoring and/or assessment in those countries. Copper, As and Hg exceed chronic toxicity values for aquatic life in saltwater according to Rhode Island criteria (Department of Environmental Management, 2000). These observations indicate that especially Cu, but also Hg, are truly elevated in Bayou Chico water. Copper has been used in chromated copper arsenate, a wood preservative that likely is present in wood in and around the Bayou (Weis and Weis, 1996). The copper may have leached from the wood and entered the water column. Other potential sources include the metal recycling and metal processing industries on the banks of the Bayou and input from stormwater. Potential sources of mercury include coal-fired power plants in the area, paints used in the ship-building industry, and improperly disposed of electrical equipment.

	Antimony ¹	Arsenic ¹	Cadmium ¹	Chromium	Copper	Lead
BW-1	<0.00045	0.0027	<0.00013	0.0023	0.0012	0.0003
BW-2	<0.00045	0.0025	<0.00013	0.0015	0.0053	0.0010
BW-4	<0.00045	<0.0002	<0.00013	0.0009	0.0016	0.0005
BW-13	<0.00045	0.0160	<0.00013	0.0007	0.0036	0.0003
BW-14	<0.00045	0.0310	<0.00013	0.0010	0.0061	0.0010
BW-15	<0.00045	0.0370	<0.00013	0.0010	0.0065	0.0013
BW-16	<0.00045	0.0430	<0.00013	0.0016	0.0066	0.0017
mean	-	0.0189	-	0.0013	0.0044	0.0009

Table 41: Trace metal concentrations [mg/l] in water.

	Mercury ¹	Thallium ¹	Zinc
BW-1	0.00005	<0.00004	0.007
BW-2	0.00006	<0.00004	0.030
BW-4	0.00002	<0.00004	0.016
BW-13	<0.00001	<0.00004	0.013
BW-14	0.00004	<0.00004	0.019
BW-15	0.00003	<0.00004	0.019
BW-16	0.00002	<0.00004	0.014
mean	0.00003	-	0.017

¹: \leq x means below detection limit x.

7.4.3 Omni-Vest

Metal concentrations in sediments south of the Omni-Vest site were examined at three depth levels because of concerns about possible leakage of pollutants from this site (FDEP, 2006a). All metals occur at concentrations below their respective TELs (Table 42), with the exception of mercury that equals its TEL in one sample (OV-3C). These observations strongly suggest that trace metals are not leaking from the Omni-Vest site and moving towards Bayou Chico at sediment depths up to 2 m. This contention is consistent with findings for VOCs.

Sample ID ²	Antimony ¹	Arsenic ¹	Cadmium ¹	Chromium1	Copper ¹	Lead ¹
OV-1A	<0.32	0.41	<0.22	2.2	0.84	1.6
OV-1B	<0.32	0.31	<0.21	4	0.49	1.5
OV-1C	<0.27	<0.16	<0.18	0.44	0.2	0.24
OV-2A	<0.31	0.5	<0.21	2.2	4.5	6.5
OV-2B	<0.32	<0.19	<0.21	1.5	0.36	0.7
OV-2C	<0.32	<0.19	<0.21	5.6	1.0	1.1
OV-3A	<0.32	0.35	<0.21	1.4	1.5	5.0
OV-3B	<0.32	1.7	<0.21	7.5	0.82	2.1
OV-3C	<0.39	0.95	<0.26	51	7.8	14
TEL	No TEL	7.24	0.68	52.3	18.7	30.2
PEL	No PEL	41.6	4.21	160	108	112

Table 42: Trace metal concentrations [µg/kg] in sediment cores south of the Omni-Vest site.

Sample ID ²	Mercury ¹	Thallium ¹	Zinc ¹
OV-1A	< 0.00097	<0.28	3.3i
OV-1B	<0.001	<0.27	2.4i
OV-1C	<0.00096	<0.23	<0.8
OV-2A	0.00620i	<0.27	9.5
OV-2B	<0.00088	<0.27	<0.95
OV-2C	0.0082i	<0.27	1.8i
OV-3A	0.0053	<0.27	9.2
OV-3B	<0.001	<0.27	5.7i
OV-3C	0.13 ³	< 0.33	10
TEL	0.13	No TEL	124
PEL	0.696	No PEL	271

¹: <x means below detection limit x.

²: A=surface, B=1 m depth, C=2 m depth.

3: Bold value is above TEL

7.5 Assessment of dioxins/furans, PCBs and trace metals in seafood

A previous PERCH study (Karouna-Reneir et al., 2006) found elevated concentrations of dioxins/furans, dioxin-like PCBs and some trace metals in crabs and oysters from Bayou Chico. As shown in the present study and others (see above) these pollutants are present in the sediments of Bayou Chico. The dioxins and PCBs are not soluble in water but they do adhere to fine particles or become incorporated into small organisms such as algae which can be suspended by currents and enter the water column. Filter feeders such as oysters can readily remove such materials from the water column and their tissues become contaminated by the POPs. Blue crabs are predatory and live upon the bottom and are also able to swim. They will consume small benthic invertebrates and therefore are also exposed to any sediment borne POP that has been incorporated into their prey. Unlike oysters, crabs are not sessile as adults and can readily range over small areas the size of Bayou Chico, likely allowing multiple contacts with contaminated prey. Upon consumption by humans the POPs can readily be incorporated into lipid tissues.

The crabs were collected just outside the mouth of the Bayou (C9), near the Barrancas Ave. bridge (C8), and near the spoil island in the center of the Bayou (C7) (Karouna-Reneir et al., 2006). Oysters were collected from the pilings of the Barrancas Ave. bridge. Trace metal levels were highest for the crabs collected just outside the mouth. This seems to be at odds with results for trace metals in water and sediments as these are generally lowest at the mouth of the

Bayou and in the adjacent Bay. However, because of the mobility of the blue crabs their trace metal levels may not reflect the environment at one particular location and point in time but the general environmental state of the waterbody where they live. Compared to other locations in the Pensacola Bay area, Cu and Zn were most elevated in the crabs from Bayou Chico (Karouna-Reneir et al., 2006). To some extent As and Cd were also elevated. This is consistent with results from the present study and others (Waller et al., 1998; DeBusk et al., 2002) that show that these metals are also elevated in the sediments of Bayou Chico. Results from a previous PERCH study (Liebens et al., 2006) and the present study show that Cu and Zn concentrations in sediments are higher in Bayou Chico than Bayou Texar. The concentrations of these metals in the crabs reflect this difference. Copper and Zn concentrations in sediments are lower in Bayou Grande than in the other two bayous (Lewis et al., 2001b) and this is also reflected in the crab data (Karouna-Renier et al., 2006). Copper and Zn are also elevated in oysters from Bayou Chico. For Cu this is consistent with high Cu concentrations in Bayou Chico water recorded by the present study and others but Zn is not elevated in the water column (Wallace et al., 1998; Lewis et al., 2001b). Zn concentrations in water of Bayous Chico and Texar are comparable (Lewis et al., 2001b) but Zn concentrations in oysters from the two bayous are very different (850 mg/kg for Bayou Chico, 290 mg/kg for Bayou Texar). Compared to these two bayous, Zn concentrations in Bayou Grande are lower for water but higher for oysters. Copper concentrations in the oysters from the three bayous follow the pattern of Cu concentrations in water: comparable in Bayous Grande and Chico, lower in Bayou Texar (Lewis et al., 2001b; Karouna-Renier et al., 2006). These results indicate that in Bayou Chico elevated trace metal concentrations in crabs, and to some extent those in oysters, reflect the environmental conditions of the Bayou.

Tissues of blue crabs and oysters from Bayou Chico contain dioxins/furans and dioxinlike PCBs above US EPA screening value guidelines (SV) (Karouna-Renier et al., 2006). All tissue samples exceeded the SV (0.098 pg/g) for dioxins/furans and dioxin-like PCBs based on a Florida-specific consumption rate of 46 g/day. It would appear that Bayou Chico sediments are the most likely source of these tissue POPs. Blue crabs in particular are of concern since they are commercially harvested for human consumption in Bayou Chico (Figure 11). There appears to be no commercial harvesting of oysters even though there is an oyster reef present near the W. Navy Blvd. bridge.

We compared the profiles for these POPs in sediments adjacent to the seafood sampling stations to profiles in the tissues of the blue crab <u>Callinectes sapidus</u> Rathbun and the oyster <u>Crassostrea virginica</u> Gmelin (Karouna-Renier et al., 2006). Table 43 shows the sediment collecting sites that are associated with the seafood study stations. The dioxin/furan and dioxin-like PCB concentrations of the indicated sediment sampling sites in Table 43 were averaged for comparison with the seafood data (Table 44, Table 45).

Table 45. Seafood study sampling stations and corresponding sediment sampling sites.							
Seafood study designation	Bayou Chico mouth	Bayou Chico bridge	Bayou Chico upper				
Seafood study sample ID	C9	C8	C7				
Term used in present study	bay	Barrancas Ave. bridge	spoil island				
Sediment sample IDs ¹	FID-2G	BG-8	BG-4				
	BG-11	BG-9	BG-5				
	BG-13	BG-12	BG-7				
			BG-10				
			BG-14				

Table 43: Seafood study sampling stations and corresponding sediment sampling sites.

¹: See Map 11 for location.

Table 44. Dioxin-like I CDS in sediments and seafood fissue.										
PCB congener		Sediments ¹		Hepatopancreas ¹				Oysters ¹		
	spoil island	bridge	bay	spoil island	bridge	bay	spoil island	bridge	bay	bridge
<u>77</u>	625.9	45.7	78.3	1310.0	1130.0	578.0	36.3	40.0	10.5	258.0
<u>81</u>	0.9	ND	ND	90.3	65.9	28.6	2.0	2.2	0.5	48.0
105	1929.2	231.1	57.1	9020.0	8350.0	4310.0	197.0	230.0	65.1	1115.0
<u>123</u>	0.0	35.3	ND	615.0	586.0	248.0	9.2	12.9	3.7	102.1
<u>118</u>	4462.0	593.7	116.0	29400.0	26700.0	15600.0	509.0	704.0	220.0	3410.0
114	21.1	10.9	2.5	558.0	562.0	233.0	10.3	16.0	3.6	753.0
<u>126</u>	39.5	ND	2.8	115.0	86.3	58.8	1.9	2.2	0.8	14.4
<u>156+157</u>	768.3	62.3	24.4	2880.0	3163.0	2040.0	36.3	57.0	23.3	214.8
<u>167</u>	299.3	22.6	9.6	1310.0	1360.0	932.0	14.6	23.4	10.0	120.0
<u>169</u>	150.5	ND	0.9	18.3	5.8	23.6	0.3	0.1	0.3	0.5
<u>189</u>	184.1	3.1	6.7	144.0	174.0	121.0	1.3	1.9	0.8	0.4

Table 44: Dioxin-like PCBs in sediments and seafood tissue.

¹: Concentrations are in ng/kg dry wt for sediments and pg/g wet wt for tissues.

Congener		Sediments ¹		He	epatopancrea	s ¹		Muscle ¹		Oysters ¹
	spoil island	bridge	bay	spoil island	bridge	bay	spoil island	bridge	bay	bridge
2,3,7,8-TCDD	0.29	ND	ND	3.50	2.60	1.30	0.10	0.13	0.03	0.62
1,2,3,7,8- PECDD	4.65	2.38	ND	7.60	4.50	3.40	0.17	0.21	0.07	1.40
1,2,3,4,7,8- HXCDD	13.98	6.56	ND	5.10	3.00	2.00	0.09	0.15	0.06	1.19
1,2,3,6,7,8- HXCDD	82.09	42.11	ND	23.10	11.10	7.50	0.43	0.52	0.19	3.35
1,2,3,7,8,9- HXCDD	58.80	27.81	ND	9.50	5.40	3.30	0.22	0.25	0.10	2.30
1,2,3,4,6,7,8- HXCDD	3309.99	1761.44	7.65	61.40	54.70	13.30	1.95	3.64	0.65	9.50
OCDD	23787.99	12762.57	70.60	106.00	121.00	12.70	6.17	16.00	2.04	52.05
2,3,7,8-TDCF	19.76	1.00	ND	22.20	35.50	7.00	0.48	0.64	0.13	4.30
1,2,3,7,8- PECDF	15.65	1.08	ND	5.60	7.00	1.60	0.16	0.21	0.04	0.64
2,3,4,7,8- PECDF	3.32	0.57	0.03	5.00	4.00	2.70	0.10	0.01	0.02	0.78
1,2,3,4,7,8- HXCDF	15.89	4.83	ND	2.70	1.80	1.10	0.08	0.10	0.05	0.04
1,2,3,6,7,8- HXCDF	7.07	3.28	ND	1.70	4.80	0.80	0.05	0.15	0.03	0.60
2,3,4,6,7,8- HXCDF	0.65	ND	ND	0.00	0.10	0.00	0.01	0.04	0.01	0.05
1,2,3,7,8,9- HXCDF	7.15	4.24	ND	1.00	0.50	0.40	0.01	0.04	0.01	0.26
1,2,3,4,6,7,8- HPCDF	145.81	116.38	0.95	6.30	10.00	2.60	0.15	0.39	0.09	0.28
1,2,3,4,7,8,9- HPCDF	10.12	5.97	ND	0.00	0.10	0.00	0.03	0.05	0.01	0.10
OCDF	290.50	285.09	47.97	0.90	1.00	0.10	0.11	0.04	0.08	0.35

Table 45: Dioxins/furans in sediments and seafood tissue.

¹: Concentrations are in ng/kg dry wt for sediments and pg/g wet wt for tissue.

An examination of sediment concentrations for dioxin-like PCBs and dioxins/furans shows that the zone around the spoil island has higher concentrations of these compounds than the mouth of the Bayou. Sediment collecting sites in the adjacent Bay have the lowest concentrations (Table 44, Table 45). In Figure 25 the profiles of dioxin-like PCBs for Bayou Chico sediments are represented for the areas that are adjacent to stations where the blue crabs were collected. The zone around the spoil island has the highest concentrations of dioxin-like PCBs with PCB 118 being the most common one followed in descending order by PCBs 105, 156-157, 77, 167, 189, and 169 (Figure 25). Representing much smaller concentrations are PCBs 114, 126, 123, and 81. Dioxin-like PCB concentrations are many times less at the mouth of the Bayou and even lower in adjacent areas of Pensacola Bay. The highest concentrations of dioxins/furans are also near the spoil island; OCCD and HpCDD are the predominant forms with minor contributions from 1,2,3,6,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDF and OCDF (Figure 26). The other congeners are represented by much lower concentrations that are not visible on the graph (Table 45). All dioxin/furan congener concentrations diminish towards the mouth of the Bayou and overall are even lower in the Bay (Table 45).



Figure 25: Dioxin-like PCB profiles in sediments near seafood sampling stations. Lower Bayou samples are from near Barrancas Ave. bridge.



Figure 26: Dioxin/furan profiles in sediments near seafood sampling stations. Lower Bayou samples are from near Barrancas Ave. bridge

Direct comparison of the concentrations of dioxin-like PCBs in sediment and tissue is not appropriate because concentrations for sediment are in ng/kg dry wt and concentrations for tissue are in ng/kg wet wt. Bearing this in mind it is still possible to examine the profiles. The profiles indicate that dioxin-like PCBs bioaccumulate in crab hepatopancreas (Figure 27). The bioaccumulation is greater than in crab muscle and oysters (Table 44). The concentrations for PCB 118 are particularly elevated in crab hepatopancreas (Figure 27). Table 44 data shows a decline in dioxin-like PCB concentration in crabs collected from regions of lower sediment concentrations suggesting some correspondence between sediment and tissue concentrations.

Dioxin/furan bioaccumulation appears to be different from what was observed for the dioxin-like PCBs in that the degree of bioaccumulation is markedly less for the major congeners even if one notes that sediments are in dry wt versus wet wt for the tissues (Figure 28). The bars for HpCDD and OCCD in figure 28 were cropped and the actual concentrations indicated by numbers since these concentrations are many fold greater than those of the corresponding crab tissues. The major congeners, HpCDD and OCDD, are not concentrated proportionally to the same extent as some of the minor congeners such as PcCDD, TCDD, and TCDF. Table 46 shows the percentage of the total dioxins/furans that each congener represents for crab hepatopancreas and sediments from near the spoil island. The compositions are different as can be seen for OCDD that is 40.52% in hepatopancreas and 85.65% in sediments. A reversal of this trend is seen for some lesser concentrated congeners where they become a larger percentage of the total dioxin/furan composition. For example, 2,3,7,8-TCDD is 1.34% in hepatopancreas versus 0.00% in sediment; 1,2,3,7,8-PECDD is 2.91% versus 0.02%; 1,2,3,4,7,8-HXCDD is 1.95% versus 0.05%; 1,2,3,6,7,8-HXCDD is 8.83% versus 0.30%; and 1,2,3,7,8,9-HXCDD is 3.63% versus 0.21% for hepatopancreas and sediments respectively.



Figure 27: Comparison of dioxin-like PCB profiles in sediments and crab hepatopancreas





Congeners	Hepatopancreas [%]	Sediment [%]
2,3,7,8-TCDD	1.34	0.00
1,2,3,7,8-PeCDD	2.91	0.02
1,2,3,4,7,8-HxCDD	1.95	0.05
1,2,3,6,7,8-HxCDD	8.83	0.30
1,2,3,7,8,9-HxCDD	3.63	0.21
1,2,3,4,6,7,8-HpCDD	23.47	11.92
OCDD	40.52	85.65
2,3,7,8-TDCF	8.49	0.07
1,2,3,7,8-PeCDF	2.14	0.06
2,3,4,7,8-PeCDF	1.91	0.01
1,2,3,4,7,8-HxCDF	1.03	0.06
1,2,3,6,7,8-HxCDF	0.65	0.03
2,3,4,6,7,8-HxCDF	0.00	0.00
1,2,3,7,8,9-HxCDF	0.38	0.03
1,2,3,4,6,7,8-HpCDF	2.41	0.52
1,2,3,4,7,8,9-HpCDF	0.00	0.04
OCDF	0.34	1.05

Table 46: Dioxin/furan profiles in crab hepatopancreas and sediments from near the spoil island.

For dioxin-like PCBs the bioaccumulation in crab muscle is much lower than in the hepatopancreas (Table 45). For example, for PCB 118 in crab muscle the highest concentration is 704 ng/kg wet wt as compared to the lowest hepatopancreas concentration for hepatopancreas of 15,600 ng/kg wet wt. The explanation may lie with the role of muscle versus hepatopancreas in the crab. Muscle tissue consists primarily of protein and receives PCBs via transport from the hemolymph. The muscle also contains a lesser complement of lipids than the hepatopancreas and PCBs tend to accumulate preferentially in lipids (ATSDR, 2000). The hepatopancreas is a digestive organ that contains lipids and is in intimate contact with what the crab may ingest, including POP containing materials. For these reasons the muscle would be expected to contain less PCB than the hepatopancreas. In the crab muscle the pattern for dioxin/furan accumulation is similar to what was observed in the hepatopancreas, but at a reduced scale. In oysters the dioxin-like PCB concentrations are in between the levels observed in crab hepatopancreas and muscle (Table 44), showing a lesser degree of bioaccumulation as compared to crab hepatopancreas. Again, PCB 118 is the most abundant dioxin-like PCB (Figure 29). For oyster dioxins/furans, the concentrations were less than 100 ng/kg wet wt for the most prevalent congener resulting in a truncated scale in the profile presented in Figure 30.



Figure 29: Comparison of dioxin-like PCB profiles in sediments and oysters.





Leatherbarrow et al. (2005) in a review of the fate of sediment contaminants from the San Francisco estuary reported that direct ingestion of sediment is an important mechanism by which benthic organisms assimilate organic contaminants such as PCBs and PAHs. Assimilation of organic contaminants is also highly dependent on specific chemical properties that influence the extent to which they either bioaccumulate or remain associated with recalcitrant fractions of sediment. Leatherbarrow et al. (2005) reported differences in incorporation for organics in that PCBs and pesticides were more readily incorporated by the organisms than were PAHs.

Differences were attributed to differences in sorption affinities for sediment particles between contaminants. Significant variation in PCB accumulation also occurs due to difference in chemical properties of individual congeners. The literature reports that sandworms and shrimp accumulated non-dioxin-like PCB 153 more than other PCB congeners, because they readily metabolized PCBs 52, 101, and 151, all of which have hydrogen atoms at the meta and para sites of the biphenyl molecule. Leatherbarrow et al. (2005) suggest that predictions of bioaccumulation need to take into consideration the varying chemical properties between contaminants as well as between congeners of contaminant classes (e.g., PCBs and PAHs) to accurately reflect the transfer of organic contaminants from sediment to the benthic food web.

The likelihood of sediment being the origin of PCB pollution was reported by Young et al. (1994). Their findings suggested that contaminated sediments on the seafloor were the principal (although not necessarily direct) cause of the relatively high and persistent concentrations of DDT and PCB residues in tissues of seafood fishes and invertebrates from the study area 5-7 years after control of the dominant wastewater input. The study indicated that residues of the higher-molecular-weight chlorinated hydrocarbons, such as DDT and PCB, can be highly persistent once released to coastal marine ecosystems and that their accumulation in surficial bottom sediments is the most likely cause of this persistence observed in the biota. Suarez et al. (2005) studied dioxins/furans and dibenzofurans in the Houston ship channel sediments and in animal tissues (catfish and crabs). In sediments OCDD concentrations were up to three orders of magnitude higher than those for the remaining congeners. For dioxins/furans in sediments and tissues they found that an important observation was the absence of high concentrations of OCDD in tissue relative to the remaining 16 congeners in contrast with what was observed in sediment samples. This correlates well with what was observed in the sediment data of the present study and the tissue results by Karouna-Renier et al. (2006) in that congeners of lesser concentration in sediments appear to contribute proportionately more to the profile in tissues than the more abundant congeners such as OCDD.

To assess the influence of the exposure environment on seafood more quantitatively we statistically examined if the profiles of dioxins/furans and dioxin-like PCBs in crabs and sediments are similar. The statistics are based on the crab hepatopancreas data from Karouna-Reneir et al. (2006) because there are fewer non detects in the data for the hepatopancreas than in the data for the other tissues. We performed hierarchical clustering on principal components and on standardized data to identify groups with similar profiles. The results for the dioxins/furans show that the profiles in the crab hepatopancreas are different from those in sediments. The PCA based clustering algorithm groups the crab profiles (C7, C8, C9) into one homogeneous group that is distinctly different from the group of sediment profiles (Figure 31). Site BG-11 has a profile that is very different from the other sediments, as explained above (section 7.2.8.3), but also from the profiles of crab hepatopancreas. The clustering based on the standardized data separates the profiles in the Bayou sediments, Bay sediments, and crab hepatopancreas into different groups but the dissimilarities are not as pronounced as in the PCA-based clustering (Figure 32). In any case, both approaches indicate that there is no correlation between profiles in the crab hepatopancreas and in sediments from the area where the crabs were trapped. Biological factors seem to be stronger determinants of dioxin/furan profiles in the crab hepatopancreas than profiles in the exposure environment. This is consistent with the qualitative interpretation presented above.



Figure 31: Cluster tree for first three principal components based on dioxin/furan data for sediments and crab hepatopancreas.



Figure 32: Cluster tree for standardized dioxin/furan data for sediments and crab hepatopancreas.

Outcomes for dioxin-like PCBs in sediments and crab hepatopancreas are comparable to those for dioxins. The clustering of the standardized data clearly separates the profiles for crab hepatopancreas from those for the sediments. The profiles for crab hepatopancreas are more similar to those of the majority of the sediments than are the profiles of sites BG-13, BG-14 and BG-15 but, nevertheless, there are clear distinctions between the profiles in crab hepatopancreas and sediments (Figure 33). The PCA-based clustering outcomes suggest that the profiles in crab hepatopancreas from near the spoil island and the mouth of the Bayou (C7 and C8 respectively) are similar to the profile at BG-11, a site in the Bay, while the profile from crab hepatopancreas from the Bay (C9) is more similar to profiles in the rest of the sediments (Figure 34). This seems contradictory since C9 is from the Bay and C7 and C8 are from the Bayou. This observation, however, may be consistent with the other findings that show that there is no strong linkage between profiles of dioxins/furans and dioxin-like PCBs in crab hepatopancreas and sediments in the area where the crabs were trapped. Possible explanations are the mobility of crabs and issues related to bioavailability, sequestration, metabolic alteration, and detoxification. Poor agreement between profiles in the exposure environment (water and sediments) and organisms has been found elsewhere for PCBs (Wenning et al., 1995) and dioxins/furans (Suarez et al., 2005).



Figure 33: Cluster tree for standardized dioxin-like PCB data for sediments and crab hepatopancreas.



Figure 34: Cluster tree for first four principal components based on dioxin-like PCB data for sediments and crab hepatopancreas.

7.6 Dredging of navigation channel

7.6.1 Background

The US Army Corps of Engineers (USACE) has submitted a permit application to the FDEP for dredging and disposal of the spoils in the Clark Sand Pits (Map 14). The USACE, Mobile District, received from the FDEP a Notice Of Intent To Issue Wetland Resource Permit on 6/7/05 for the Bayou Chico Maintenance Dredging and Disposal Project (FDEP, 2005). This applies to a project to conduct maintenance dredging of the federal navigation channel in Bayou Chico. The dredging is to result in a shipping channel that is 4,400 ft. long, 75 ft. wide channel with a 250,000 sq. ft. turning basin to a depth of 14 ft below MLW (mean low water), plus 2 ft. of advance maintenance, and 2 ft. of allowable overdredge. The maximum quantity of spoil to be placed in one of the Clark Sand Pits is about 230,000 cubic yards with 60,000 cubic yards of this estimated to be coarse sand. It is not completely clear how the USACE estimated the quantity of spoils and particularly the particle size of the spoils. Six cores were taken by a USACE commissioned study (EA, 2000), but this may be insufficient to reliably estimate the overall particle size for the proposed dredging. Sediments will be hydraulically dredged and pumped to a disposal site at the north Clark Sand Pit. Recently it has been proposed to use some of this spoil for beach renourishment (FDEP, 2005) so the exact volumes to be placed in the sand pit are not vet clear.

The major issue relative to spoil disposal is that the Clark Sand Pits are in direct hydraulic communication with the Sand and Gravel Aquifer (Hearn and Baya, 2001). Peoples Water Service Well #8 is located within 1000 ft of the Clark Sand Pits. It is the proposed

disposal of the dredge material in one of the Clark Sand Pits that is of major concern relative to pollution of the aquifer and the Bayou's water column. Peoples Water Service, due to the proximity of their well #8, did protest that dredge spoils placed in the sand pit could contaminate the well with excess chloride. There is mention in the Notice of Intent To Issue Wetland Resource Permit about provisions of the Clean Water Act, but there is no reference to the Safe Drinking Water Act (SDWA) that was originally passed by Congress in 1974 to protect public health by regulating the nation's public drinking water supply. The SDWA was amended in 1986 and 1996, and requires many actions to protect drinking water and its sources: rivers, lakes, reservoirs, springs, and ground water wells. Consideration of SDWA seems pertinent since this drinking water well is not very distant from the proposed disposal site.

The process of disposal is described as: "... using a hydraulic dredge pipeline that will be floated from the dredge to Jackson's Branch Creek. From that point to the southern end of the north Clark Sand Pit for disposal the pipeline will be laid on the bottom of the creek so as to minimize erosion and damage to vegetation" (FDEP, 2005). The sand pit contains water supplied under a head of pressure from the aquifer. and the groundwater gradient under most conditions is upward with water flowing from the aquifer into the sand pit. A concern of the FDEP with the project was whether sediment contaminants and salinity-related ions (such as sodium and chloride) in the dredge disposal material would migrate from the sand pit into surficial groundwater (FDEP, 2005). The proposed location of the dredged material disposal site was changed from the south sand pit to the north pit to help alleviate concerns of contaminating a potable water well (Peoples Water Well #8), located approximately 1,000 feet from the southwest corner of the southwest pit (FDEP, 2005). The north pit is farther away from the well and is on the opposite side of Jackson's Branch Creek from Peoples Water Well #8. This is expected to reduce the risk of well contamination because the creek will act as a groundwater sink by receiving the flow in the surficial aquifer. The change of the disposal site to a more distant, isolated one suggests that the FDEP and USACE placed some credence in the claim of a potential for ground water contamination.

The Notice Of Intent To Issue Wetland Resource Permit justifies dredging for several reasons. The notice states that the USACE has received reports of navigational restrictions within the channel, associated with progressive shoaling, and that the obstructions have created a boating hazard and have limited shipping commerce. For this reason, the Northwest Florida Water Management District has been working in conjunction with Escambia County, who is serving as the project's local sponsor, to support this project. It was added that vessels passing over the shoals of contaminated sediment have continued to resuspend the pollutants into the water column (FDEP, 2005). The proposed project is designed to improve navigation, but will also be a part of ongoing efforts to restore the water quality in Bayou Chico through the removal of the contaminated sediments. If properly removed from the Bayou, the contaminated sediments will no longer become resuspended.

To apparently minimize the contaminated state of bayou sediments the Notice of Intent stated: "Overall, the analytical data from Bayou Chico show the detection of inconsistent levels of contamination, with samples collected at different places or times containing varying levels of organics and metals" (FDEP, 2005). Although factually correct, the use of the phrase "inconsistent levels" may not be the best way to describe the pollution in the Bayou. SOC tend to accumulate in specific regions of a waterway and not in others resulting in hot spots of contamination and elsewhere in less polluted zones. Consistent levels of pollution throughout a water body and throughout time occur in rare instances. In Bayou Chico there are several hot

spots, one of which appears to exist about the spoil island and appears to cover part of the area to be dredged. A pertinent question, however, is whether there is significant evidence that contamination of the sediments that are to be dredged poses a hazard for disposal in an unlined pond that is in hydraulic contact with the aquifer and the Bayou's water column. Because of the hydraulic contact it is important to have a qualitative and quantitative knowledge of SOCs present and their likely interactions with groundwater prior to disposal. This information is needed to properly predict the possible environmental impacts of the SOC in the sediments that will be dredged.

7.6.2 Review of EA (2000) study

An examination of the EA (2000) sampling pattern (Map 14) shows that most of the samples were obtained southeast (below) of the Barrancas Ave. bridge in what is the cleanest part of the Bayou and only two samples were taken northwest (above) of the Barrancas Ave. bridge. Data from the current study clearly show that the highest amounts of SOC occur northwest of the Barrancas Ave. bridge. Southeast of the Barrancas Ave. bridge parts of the channel attain depths of 18 ft or more and tidal sediment transport with the cleaner Pensacola Bay is more effective as evidenced by what appears to be channel scour. It would appear that this area also will require a lesser amount of dredge spoil removal due to its deeper depths, yet it is here that most of the samples were taken.

Five out of the six EA (2000) samples were above the dioxin/furan AET TEQ of 3.6 ppt (Table 47). Core samples BC00-SED-01 and BC00-SED-06, taken from the area to be dredged, had dioxin levels of 42.4 and 61.8 ng/kg TEQ respectfully, far above the AET. These analytical results are for core samples and it can be assumed that they represent average values for the sediments in the core, all or part of which may become part of the spoils.

Table 47. Dioxin TEQ III EA (2000) sediment cores.						
EA sample ID	TEQ (ND=0) NG/KG	TEQ (ND=1/2) NG/KG				
BC00-SED-01	42.4	42.4				
BC00-SED-02	10.2	10.3				
BC00-SED-03	3.74	3.82				
BC00-SED-04	0.09	0.24				
BC00-SED-05	7.48	7.49				
BC00-SED-06	61.8	61.8				

Table 47: Dioxin TEQ in EA (2000) sediment cores.

Trace metals are perhaps more critical than the organic SOC like the dioxins/furans because pH changes resulting from sediment disturbance are known to mobilize metals from contaminated sediments. This is, among other places, recognized in the Code of Federal Regulations (CFR) 40 CFR §261.24. Several metals exceed the FDEP TEL and PEL guidelines for coastal sediments in cores BC00-SED-01 to BC00-SED-04 taken southeast of the new Barrancas Ave. bridge by EA (2000) (Table 48). There were no exceedances northwest of the new Barrancas Ave. bridge. This is somewhat surprising because the present study and others (DeBusk et al., 2002, Waller et al., 1998; Lewis et al., 2001b) found that general part of the Bayou to be most polluted with metals, and depth of metal pollution is also highest there (Stone and Morgan, 1991). It is possible that variations in metal concentrations on a small spatial scale or over time explain the somewhat unexpected results from EA (2000) but the results would be more robust if more samples had been taken in that part of the navigational channel.

	Arsenic	Cadmium	Chromium	Copper	Lead	Mercury	Nickel	Zinc
BC00-SED-01	2.6	0.29	6.1	28.6T	129P	0.26T	2.6	141T
BC00-SED-02	4.4	0.46	12	59.9T	60.3T	0.3T	5.9	262P
BC00-SED-03	2.7	0.17	5.6	271P ¹	11.3	0.07	1.8	54.9
BC00-SED-04	14.6T ¹	0.12	32.1	7.5	9.2	1.4P	8.8	34.5
BC00-SED-05	2.8	0.12	8.7	13.9	10.5	0.09	2.1	75.7
BC00-SED-06	1.5	0.08	4.4	12.7	7.8	0.1	1.5	79.5

Table 48: Trace metal concentrations [mg/kg] in ES (2000) sediment cores.

¹: Bold values are above TEL (T) or PEL (P).

It is especially clear from the DeBusk et al (2002) data compilation that many samples that were collected either in or nearby the navigational channel exceed FDEP sediment guidelines for metals and organics (Table 45, Map 15). Sample nbc-33 is from the part of the Bayou Chico shipping channel that extends into Pensacola Bay. It has very low to no detections for analytes. Sample NOAA9, as reported in DeBusk et al. (2002), was taken at the mouth of the Bayou adjacent to the navigation channel (Map 15). This sample showed high levels of several metals and PAHs that in the majority of cases exceeded their TEL (Table 49). Sample BC1, a little further into the Bayou, exceeded the TEL for total PCBs. Northwest of the new Barrancas Ave. bridge BC2 exceeds the TEL for PCBs and in the turning basin NOAA4 shows exceedances for As, Cu, Pb, Hg, Zn and PAHs. Nbc17b shows exceedances for three metals and PCBs. BCO-0002 shows exceedances for several metals. These data suggest that the EA (2000) study should be extended to more sampling points.

	Table 49: Data from DeBusk et al.	(2002) for	samples in and	about the navig	gation channel.
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	As ¹	Cd	Cr	Cu	Pb	Hg	Ni	Ag	Zn
NOAA9	13.5T ²	0.64	42.3	63.9T	64.2T	0.258T	13	0.1	314P ¹
S110-01		1.1T	30	230P	100T	0.38T	12		560P
UWF5 1"		2.3T	8.3	120.8P	116P		4.6		87.1T
nbc17b	4.7	0.53	2.7	113.5P	54.3T	0.358T	20.8T	0.59	269P
BCO-0002	5.5	1.5	240P	99T	110T	0.69T		0.17	1300P
NOAA4	7.6T	0.55	34.9	55.6T	43.8T	0.241T	11.2	0.11	354P

	LMW PAH ³	HMW PAH	LMW+HMW	Tot PCB
NOAA9	1990P	5580T	7550T	
BC1				62.6T
BC2				68.3T
nbc17b	12.3	22.9	35.2	90.4T
NOAA4	150	1070T	1220	

¹: Trace metals in mg/kg.

²: Bold values are above TEL (T) or PEL (P).

³: PAHs and PCBs in µg/kg.

7.6.3 Implications of the present study

The present study included surface grab samples and some vibracores that are in or adjacent to the navigation channel (Map 11, Map 12). For dioxins and PCBs the regions of the channel south of Pace Blvd. (the old bridge) were below the TEL except for sample BG-13 in Pensacola Bay that was above the PCB TEL of 21.55 ug/kg (Table 31, Map 18). This was one of the few SOC concentrations that was high in Pensacola Bay sediments. Sample BG-8, taken between Pace Blvd and the Barrancas Ave. bridge was also above the TEL for PCBs. Both of these PCB concentrations are below the SCTL residential clean level of 500 ug/kg for PCBs. Northwest of the Barrancas Ave. bridge PCB concentrations in and about the navigational channel increase dramatically as seen in samples BG-4, 7, 10, and 14 (Table 31, Map 18). Northwest of the Barrancas Ave. bridge there is also evidence of elevated dioxin/furan concentrations that exceed sediment quality guidelines. Grab sample BG-7 taken in the area to be dredged had a combined dioxin/furan-PCB TEQ of 77.77 ng/kg and had a PCB concentration 206.61 ug/kg that is above the FDEP PEL (Table 27, Table 31, Map 11, Map 17, Map 18). Samples BG-10 and BG-14, taken adjacent to the navigation channel, had a combined TEQ of 126.7 ng/kg and 92.3 ng/kg respectively, showing additional evidence of organic contamination in that area.

An examination of metal concentrations shows that the following metals exceed their TEL in or near the navigation channel: As in sample BG-8, Cu in samples BG-7, BG-12 and BG-8, Pb and Zn in BG-7 and BG-8. Zinc and Cu also exceed their PEL near the navigation channel. Sample BG-8 has elevated levels for several metals and is located in the navigation channel between the old Pace Blvd. bridge and the new Barrancas Ave. bridge. These findings from the present study indicate that further study of the pollution of sediments in the navigation channel, and especially in the northern section of channel, is warranted.

7.6.4 Disposal issues

For disposal of wastes as non-hazardous waste in a RCRA permitted landfill there is a list of contaminants that require an analysis via TCLP (RCRA Toxic Characteristic Leaching Procedure). For lead, for example the test determines by leaching with an acidic solution what amount of material will leach out. Five mg/l of lead leaching out of a waste is sufficient to characterize the waste as toxic. The Code of Federal Regulations (CFR) 40 CFR §261.24, outlines the 40 contaminants that require TCLP analysis tests toxicity. The actual quantities are based on extraction of the solid soil or sediment with a specific amount of extraction fluid. The idea being that over time groundwater and surface waters that are below a pH of 7 may release pollutants. The SOC found by PERCH or other studies in the Bayou that are included in the list of 40 by RCRA having Maximum Concentration of Contaminants for Toxicity Characteristic include: Arsenic (As) 5.0 mg/l, Chromium (Cr) 5.0 mg/l, Lead (Pb) 5.0 mg/l, Mercury (Hg) 0.2mg/l, Pentachlorophenol (PCP) 100.0 mg/l, and Selenium (Se) 1.0 mg/l. We are suggesting that these sediments be submitted to testing to determine what can leach out of them in this specific freshwater environment.

The USACE claims that federal law does not require to follow RCRA rules relative to characterization of wastes in this situation. In the permit application of the USACE for the Bayou Chico Dredging and Disposal Project (Received by FDEP on 4/11/00), 2001 Joint application for works in the water of Florida, there is a section about Comments and questions by Peoples Water Service Company of Florida (Enclosure1). According to that section the USACE, was asked:

"Are any of these sediments listed or characteristic hazardous waste that require treatment and/or disposal in a RCRA (or state equivalent) permitted hazardous waste facility? Has a RCRA Toxicity Characteristic Leaching Procedure (TCLP) test been performed on any of the sediment samples? If so, what are the results?" The response was: "No. None of the sediments samples have been listed or (sic) characteristic hazardous waste that require treatment and/or disposal in a RCRA (or state equivalent) permitted hazardous waste that require treatment and/or disposal in a RCRA (or state equivalent) permitted hazardous waste facility. Please be aware of Rule in Federal Register, November 30, 1998 (Vol. 63, No 229)-IX. Dredged Material Exclusion. The rule eliminated the overlap of RCRA Subtitle C with the Clean Water Act (CWA) and Marine Protection, Research and Sanctuaries Act (MPRSA) programs by excluding dredged material under accurate and environmentally sound evaluation of any potential impacts to the aquatic environment. This rule explains why it is not necessary for dredged material to be also regulated by RCRA, when it is regulated by CWA and MPRSA. The materials were tested by the Standard elutriated test for dredged material.....". A remaining concern is that if the cited rule applies, the condition "under accurate and environmentally sound evaluation of any potential impacts to the aquatic environment" is not being met in this situation.

To prevent aquifer contamination the FDEP initially suggested that the applicant consider a liner for the sand pit to prevent downward migration of pollutants (FDEP, 2005). Due to the direction of groundwater flow from the aquifer into the pit (upward gradient), the applicant felt that the liner would not be necessary and potentially would float up and not form an adequate seal and this requirement was dropped (FDEP, 2005). Even if there is positive water pressure with the groundwater flowing upward into the sandpit and then onward towards Jackson's Branch Creek it does not seem to be a good idea to put contaminated sediments into hydraulic contact with an aquifer that is the sole water supply for southern Escambia County. Pressure gradients in an aquifer are subject to changes caused by variations in rainfall and in water well pumping. Gradient changes will be monitored during dredging but in all likelihood not after completion of the dredging, when pollutants can still leach out of the spoils.

A contention with the proposed dredge disposal in the north Clark Sand Pit lies with what appears to be a misapplication of elutriate testing. "The applicant submitted an analysis of potential impacts to groundwater beneath the Clark Sand Pits if sediments dredged from Bayou Chico were to leach into the groundwater, i.e., if there were a downward gradient. The assessment focused first on whether polycyclic aromatic hydrocarbons (PAHs) and metals concentrations in Bayou Chico sediment elutriates exceed Groundwater Criteria under Rule 62-777, F.A.C." (FDEP, 2005). The submitted analysis evaluated elutriate data from sediment core samples that were collected at six locations in Bayou Chico at depths ranging from 2.3 to 9 feet below the top of the sediment column (EA, 2000). The evaluation determined whether groundwater standards would be exceeded assuming there was a net movement of water from the disposal site into the surficial aquifer. The elutriate analysis found only two PAHs at concentrations exceeding Groundwater Criteria. No metals were found at concentrations exceeding primary drinking water standards. "This analysis concluded that the concentrations of PAH's and metals observed in the elutriate samples would be diluted to levels that would not exceed groundwater standards" (FDEP, 2005). The FDEP also stated "most of the metals and organics will be bound to fine particles and remain sequestered in the disposal site; and soluble salts will gradually be flushed back into the Bayou Chico system". The problem with elutriate testing in this instance is comparing bayou estuarine water which has a pH close to 8 (basic) with non-saline ground water that is generally below pH 7, and therefore acidic. Metals and other SOC are often more soluble and mobile under these conditions. It would seem logical to use the

elutriate analyses to determine if dredging activities will pollute the waters of the area being dredged but not to assess the leachate from the spoils since the ambient conditions will be different.

An existing weir structure presently directs the discharge from the north sand pit containment area into Jackson's Branch Creek and back to Bayou Chico. This suggests that whatever leachate leaves from the dredge spoils can reenter the waters of the Bayou and that the many toxic pollutants currently sequestered in bayou sediments could enter the water column of the Bayou. This could lower bayou water quality. In Figure 35 water can be seen to pass over the weir into Jackson's Branch Creek on its way to Bayou Chico and this water could likely carry leachate.



Figure 35: Weir at North Clark Sand Pit circa 2005. Water passes from weir to Jackson's Brach Creek on the left off the photograph.

8. SUMMARY AND CONCLUSIONS

Bayou Chico is a small estuary that has been heavily impacted by pollutants from urban and industrial sources for more than a century. Government documents, studies by consulting firms, and previous scientific research during the last 50 years show that Bayou Chico is polluted with oil and grease, PAHs, dioxins/furans, PCBs, trace metals, and other pollutants. These pollutants have left a heavy impact on sediments and consequently the organisms in the Bayou; pollutants in sediments are toxic to some organisms and have negatively affected community structure. These pollutants can also potentially affect human health as at least some bayou seafood has been shown by PERCH to contain pollutants above accepted guidelines.

The present study found several weaknesses in the current environmental knowledge of the Bayou. It was found that very little information was available on dioxins/furans, a SOC that is elevated in bayou seafood. More information was available for PCBs but the previous studies examined different sets of congeners and no study examined the full suite of 209 congeners, as the present study did. Petroleum storage tanks are located near the mouth of the Bayou but little information on sources of petroleum hydrocarbons in Bayou Chico was available. Two hazardous waste sites are located close to the Bayou and may potentially impact the Bayou or adjacent areas. However, this potential impact has never been fully assessed. Plans to dredge the navigation channel are in an advanced state, but continued evaluation of the available relevant information seems justified. The present study was designed to remedy these shortcomings in the environmental knowledge of Bayou Chico, without unnecessarily duplicating previous efforts.

Outside the shipping channel the Bayou is relatively shallow, 1 to 2 m, and has a flat bottom. Clay content of the bottom sediments is relatively high (up to 38%), away from the mouth of the Bayou. Combined with the low current velocities measured in the Bayou these observations suggest that fine sediments are gradually accumulating in the Bayou. This accumulation undoubtedly favors retention of pollutants as many pollutants are known to have a high affinity for fine sediments. Accumulation of fine sediments in estuaries like Bayou Chico is a natural process but is most likely enhanced by humans in this case. Measures to reduce runoff and erosion throughout the watershed of Bayou Chico, combined with efforts to improve flushing of the Bayou, appear to be the best options to reduce accumulation of fine sediments.

Petroleum was found in all samples but this is not unexpected given the inflow of stormwater from urban areas and the boating and boat repair activities on the Bayou. Petroleum levels were low near the storage tanks at the mouth of the Bayou. In the northern parts of the Bayou the heavier oils predominate while in the main body of the Bayou petroleum from within the diesel range predominates, indicating that petroleum in the Bayou was derived from multiple sources. State FDEP and Federal sediment quality guidelines for petroleum do not seem to exist but petroleum levels in the Bayou are comparable to those in industrial and harbor settings elsewhere.

PAHs at deeper levels in some places under Sanders Beach are very elevated and have profiles that are consistent with an origin at ACW. Sanders Beach is hydrologically downgradient from ACW. These findings indicate that the PAHs may be from ACW, although other origins can not be completely excluded. Surface sediments at Sanders Beach have low levels of PAHs and nearby offshore sediments have PAHs from various sources. This indicates that currently wastes from ACW do not pose a health threat at the beach. The very elevated levels of PAHs at 2 m depth, including benzo(a)pyrene, remain a concern due to the potential for

migration. The fact that some of the offshore surface samples and samples from the main body of the Bayou have PAH concentrations above the TEL is also of concern, regardless of their origin.

Dioxin/furan TEQs are low at and near Sanders Beach. This indicates that dioxins/furans probably do not negatively impact the beach area at this time even though these pollutants were released at ACW to a stormwater ditch adjacent to the beach area. The same is true for VOCs: they were also encountered in groundwater at the ACW site but were detected at and near Sanders Beach in trace amounts only, indicating that they currently do not appear to pose a human health threat.

In the main part of the Bayou dioxin/furan TEQs exceed the federal AET guideline at most sampled locations. These high levels provide an explanation for the elevated dioxin levels found in blue crabs and oysters from the Bayou by a related PERCH project. A generalized profile of the dioxins/furans in the main part of the Bayou is consistent with a wood treating origin but high levels of dioxins/furans were detected in a direction from ACW in which groundwater transport has not been shown to exist. It is possible that transport of contaminated sediments coming from the Yacht Club ditch during previous years could have contaminated the more distant regions of the Bayou. The results of an EA core show the presence of dioxins/furans and creosote material in a region of the navigational channel that is down gradient from the ACW site. Additional cores should be taken in this area and further hydrogeological study of the contaminated aquifer should be undertaken to clarify if groundwater movement may ever have been from ACW towards the areas of the Bayou with the high dioxin/furan levels. Samples collected by the present study close to the ACW site have low levels of dioxin/furan TEQ but at least one of them has a dioxin/furan profile that is similar to profiles in groundwater wells at the ACW site, as indicated by PCA and cluster analysis. This suggests that ACW is a source but wood treating products have been used elsewhere in the area and more local, small scale, releases can not be excluded as the source for the dioxins/furans. PCP, which is a likely source for the dioxins/furans due to the characteristics profiles, may also have been used in the ship building and maintenance industries that have been present in the Bayou since World War One.

Concentrations of PCBs were generally elevated. The TEL was exceeded by eight samples out of seventeen and the PEL by an additional five. As is the case for most pollutants, the lowest levels were encountered at the mouth of the Bayou and the highest in the main body of the Bayou. Profiles of PCB congeners are similar throughout the Bayou indicating that PCBs with similar profiles were released into Bayou Chico or that PCBs from different sources have been redistributed.

Volatile organic compounds are a known pollutant at the Omni-Vest landfill site but no clear evidence was found that the VOCs are leaching into Jackson's Branch Creek. Some VOCs were detected at trace amounts in sediments of the creek. Given the low levels of the VOCs, the precise location of the various samples with respect to the site, and alternative origins for these trace amounts, the presence of the VOCs is judged not to be indicative of leaching from Omni-Vest. This contention is consistent with findings for trace metals that also fail to show an influence of the Omni-Vest site on Jackson's Branch Creek, and thus on the Bayou.

Copper, Pb, Hg and Zn exceeded their respective PEL, and As, Cr and Cd exceeded their TEL, indicating that these trace metals will probably have negative effects on bottom dwelling biota. These trace metal concentrations also exceed concentrations observed by PERCH in Bayou Texar in Pensacola, in other urban and industrial estuaries elsewhere, and in guidelines in other states and countries. This indicates, together with many other observations from the present study, that Bayou Chico is still heavily polluted. The high concentrations for Cu, Pb and Zn are

consistent with the type of industrial activity present on the banks of the Bayou but identifying specific sources is not feasible. High levels of trace metals also explain, at least in part, the elevated levels of some metals found in seafood from the Bayou by another PERCH project.

Plans to dredge the federal navigation channel in Bayou Chico are well advanced. Some of the environmental arguments associated with the support of the plans seem to be based on an imperfect sampling scheme and set of analysis. A very limited number of samples northwest of the Barrancas Ave. bridge was analyzed even though that part of the Bayou is most polluted. One of the samples from the present study located in the northwestern section of the navigational channel had high levels of petroleum, dioxins/furans, PCBs and Cu. This suggests that further sampling of that section of the channel is warranted. It is also recommended that the southeast section of the channel in Pensacola Bay be further investigated if sediments are to be used for beach nourishment because of the possibility of contamination by previous disposal of spoils. (A recent personal communication from an Escambia County, FL employee has informed us that the beach renourishment will probably not occur.) Another concern is the fate of the pollutants in the sediments to be dredged after the spoils are disposed of. The elutriation test carried out with bayou water to evaluate this fate does not represent the long term or even medium term hydrogeochemical conditions of the spoils and may underestimate the mobility of the pollutants in the spoil. It is recommended that other leaching tests be conducted to evaluate the mobility of pollutants in the spoils.

9. REFERENCES

- Abernathy S.G., D. Mackay and L.S. McCarty. 1988. "Volume Fraction" Correlation for Narcosis in Aquatic Organisms: The Key Role of Partitioning. *Environ. Toxicol. Chem.* 7:469-481.
- 2. ATSDR (Agency for Toxic Substances and Disease Registry). 1990. Toxicological Profile for Benzo(a)pyrene. Prepared by ICF-Clement. ATSDR/TP-88-05.
- 3. ATSDR (Agency for Toxic Substances and Disease Registry). 1992a. Toxicological profile for wood creosote, coal tar creosote, coal tar, coal tar pitch, and coal tar pitch volatile. Agency for Toxic Substances and Disease Registry, Division of Toxicology/Toxicology Information Branch. 394 p.
- 4. ATSDR (Agency for Toxic Substances and Disease Registry). 1992b. Public Health Assessment, American Creosote Works Incorporated (Pensacola) Pensacola, Escambia County. Prepared by: Florida Department of Health and Rehabilitative Services under a cooperative agreement with the Agency for Toxic Substances and Disease Registry. <u>http://www.atsdr.cdc.gov/HAC/PHA/pensacola/acw_p1.html</u>
- 5. ATSDR (Agency for Toxic Substances and Disease Registry). 1995. Toxicological profile for polycyclic aromatic hydrocarbons. Division of Toxicology/Toxicology Information Branch. 487 p.
- 6. ATSDR (Agency for Toxic Substances and Disease Registry). 1998. Toxicological profile for chlorinated Dibenzo-p-dioxins. Division of Toxicology/Toxicology Information Branch. 723 p.
- 7. ATSDR (Agency for Toxic Substances and Disease Registry). 2000. Toxicological profile for polychlorinated biphenyls (PCBs). Agency for Toxic Substances and Disease Registry, Division of Toxicology/Toxicology Information Branch. 948 p.
- 8. ATSDR (Agency for Toxic Substances and Disease Registry). 2001. Toxicological profile for pentachlorophenol. Agency for Toxic Substances and Disease Registry, Division of Toxicology/Toxicology Information Branch. 316 p.
- 9. ATSDR (Agency for Toxic Substances and Disease Registry). 2002. Toxicological profile for Di(2-ethyhexyl)phthalate. Division of Toxicology/Toxicology Information Branch. 336 p.
- 10. ANZECC/ARMCANZ. 2000. Australian and New Zealand guidelines for fresh and marine water quality. Australia and New Zealand Environment and Conservation Council, Agricultural and Resource Management Council of Australia and New Zealand, Canberra.
- 11. Appleyard, J. 2004. Armstrong builds wood-related work into 75 years of success. The Pensacola News Journal. July 11, 2004. 13 p.
- 12. Ballschmiter, K. and M. Zell. 1980. Analysis of polychlorinated biphenyls (PCB) by glass capillary gas chromatography. *Fresenius Z. Anal. Chem.* 302:20-31.

- 13. BARC (Bay Area Resource Council). 2005. The Pensacola Bay Watershed Management Plan: An integrated action plan 2005. Pensacola Bay Area Resource Council. 339 p. <u>http://www.wfrpc.dst.fl.us/barc/barc_library.htm</u>.
- Bechtel Environmental, Inc. 1996. Remedial design investigation report for operable unit 2- Phase 1 DNAPL recovery and recycling at the American Creosote Works Superfund Site, Pensacola, Florida. Atlanta, GA: United States Environmental Protection Agency, Region 4. 65 p.
- BEM Systems, Inc. 2005. Final Interim Long-Term Monitoring Report for January 2005, American Creosote Works Superfund Site - Operable Unit II. Pensacola, Florida. Contract DACA01-01-D-0004, Task Order 13. 318 p.
- 16. Bobra, A.M., W.Y. Shiu and D. Mackay. 1985. Quantitative structure-activity relationships for the acute toxicity of chlorobenzenes in daphnia magna Review. *Environ. Toxicol. Chem.* 4:297-306.
- 17. Brinson, S.T. and J.M. Keltner. 1981. Water quality and biological assessment of Bayou Chico, Florida. A two part study: Florida Department of Environmental Regulation. 98 p.
- Brenner, R.C., V.S. Magar, J.A. Ickes, J.E. Abbott, S.A. Stout, E.A. Crecelius and L.S. Bingler. 2002. Characterization and fate of PAH-contaminated sediments at the Wyckoff/Eagle Harbor Superfund Site. *Environ. Sci. Technol.* 36(12):2605-2613.
- 19. Brown's Marina. 2006. 1895 Drawing of Bayou Chico. http://www.brownmarine.com/BAYOU_CHICO.htm.
- 20. Buckman, R. 2003. Flomaton, Alabama 1861 to 2001: A brief chronological railroad history. The Orderboard, NRHS Tampa Bay Chapter of The Orderboard. August 2003 edition, NRHS Tampa Bay Chapter.
- 21. Butler, R. 1827. State of Florida. Pensacola Bay area. <u>http://image8.fcla.edu/cgi/i/image/image-</u> <u>idx?&q1=UF90000133&rgn1=Identifier&type=boolean&view=thumbnail&c=map</u>.
- 22. Burt R. (Editor). 2004. Soil Survey Laboratory Methods Manual. Soil Survey Investigations Report No. 42. USDA – NRCS. Washington, D.C. 700 p.
- 23. Butts, G.L. and M.A. Lewis. 2002. Survey of chemical and biological structure in three Florida bayou-estuaries. *Gulf of Mexico Sci.* 20(1):1-11 p.
- 24. Cave, R.R., J.E. Andrews, T. Jickells and E.G. Coombes. 2005. A review of sediment contamination by heavy metals in the Humber catchment and estuary, and the implications for future estuary water quality. *Estuarine, Coastal, Shelf Sci.* 62:547-557.
- Curray, J.R. 1960. Sediments and history of Holocene transgression, continental shelf, northwest Gulf of Mexico, in F. P. Shepard, F. B. Phleger and T. H. van Andel ,eds., Recent Sediments, Northwest Gulf of Mexico. Tulsa, Oklahoma, The American Association of Petroleum Geologists. 221-266.
- 26. DeBusk, W.F., I. Poyer and L. Herzfeld. 2002. Sediment quality in the Pensacola Bay system. Havana, FL: Northwest Florida Water Management District. NWFWMD Technical File Report 02-03. 76 p. http://www.state.fl.us/nwfwmd/pubs/pnsbaysed/pensacola_bay_sediment.htm.

- 27. De Sylva, D. 1955. Report on Pollution and Fish Mortality in Bayou Chico, Pensacola, Florida. Coral Gables, FL: University of Miami, Marine Lab. 4 p.
- 28. Department of Environmental Management, State of Rhode Island. 2000. Water Quality regulations, Regulation EVM 112-88.97-1.
- 29. Dunbar J., C. Lin, I. Vergucht, J. Wong and J. Durant. 2001. Estimating the contribution of mobile sources of PAH to urban air using real-time PAH monitoring. *Sci. Total Environ.* 279:1–19.
- EA Engineering, Science, and Technology. 2000. Data Report and Evaluation of Dredged Material from Bayou Chico Channel, Pensacola Bay, Pensacola, Florida. Sparks, MD: EA Engineering, Science, and Technology/Savannah Laboratories. 61144.06. August 2000. 137 p.
- 31. Elder, J.F. and P.V. Dresler. 1988. Accumulation and bioconcentration of polycyclic aromatic hydrocarbons in a nearshore environment near a Pensacola (Florida) creosote contamination site. *Enviro. Poll.* 49(2):117-132.
- 32. Escambia County Area Transit. 2006. ECAT History & Profile. <u>http://www.goecat.com/ecathistory.cfm</u>.
- 33. Federal Register. 1997. Proposed Rules. Vol. 62, No. 150 Tuesday, August 5, 1997.
- 34. FDEP. 2005. Notice of intent to issue Bayou Chico maintenance dredging and disposal, File No. 0182865-001-DF. June 7, 2005. <u>http://bcs.dep.state.fl.us/env-</u> <u>prmt/escambia/pending/0182865_Bayou_Chico_Maintenance_Dredging_and_Disposal/0</u> <u>01-DF/Final%20Documents/Bayo%20Chico%20Intent,%20final%20version.pdf</u>
- 35. FDEP. 2006a. OMNI-VEST Landfill Idlewood Drive, west of Keys Court Pensacola, Florida. Bureau of Waste Cleanup HWC# 50 Site description and history. 3 p. http://www.dep.state.fl.us/waste/quick_topics/publications/wc/sites/summary/050.pdf.
- 36. FDEP. 2006b. <u>www.dep.state.fl.us/Water/tmdl/docs/</u> <u>303d lists/group4/adopted/PensacolaVerified 051206.pdf.</u>
- 37. FDEP. No date. Request for additional information. Bayou Chico Maintenance Dredging and Disposal. ERP File Number: 0182865-001-DF, Escambia County.
- FDER (Florida Department of Environmental Regulation). 1993. Criteria for surface water quality classifications. Bureau of Surface Water Management, Tallahassee, FL. 17-302. 530 p.
- 39. Fikslin, T.J. and E.D. Santoro. 2003. PCB congener distribution in estuarine water, sediment and fish samples: Implications for monitoring programs. *Enviro. Monitoring, Assess.* 87:197-212.
- 40. Fowler, S.W. 1985. Coastal baseline studies of pollutants in Bahrain, UAE and Oman. In: ROPME's symposium on regional marine monitoring and research programmes. Al-Ain UAE University. 155-180 p.
- 41. Frame, G.M., J.W. Cochran, and S.S. Boewadt. 1996. Complete PCB congener distributions for 17 Aroclor mixtures determined by 3 HRGC systems optimized for

comprehensive, quantitative, congener-specific analysis. J. High Resol. Chromatogr. 19:657-668.

- 42. Franks, N. and W. Lieb. 1978. Where do general anaesthetics act? *Nature*. 274:339-342.
- 43. Franks, B.J.(Editor). 1987. U.S. Geological Survey program on toxic waste--Groundwater contamination: Proceedings of the Third Technical Meeting, Pensacola, Florida, March 23-27, 1987. Open-file report USGS. 87-109 p.
- 44. Frumkin, H. 2003. Agent Orange and cancer: An overview for clinicians. *CA Cancer J. Clin.* 53:245-255.
- Gauld, G., A.M. and J.F.W. Des Barres. 1780. A chart of the bay and harbour of Pensacola in the Province of West Florida. 1:64,000.
 <u>http://image8.fcla.edu/cgi/i/image/image-</u> idx?&q1=UF90000100&rgn1=Identifier&type=boolean&view=thumbnail&c=map.
- 46. Glassen, R.C., J.E Armstrong, J.A. Calder, R.W.G Carter, P.A La Rock, J.O, Pilotte and J.W. Winchester. 1977. Bayou Chico restoration study. Report prepared for the Florida Department of Environmental Regulation, Tallahassee, Florida. 49 p.
- 47. Hargrave, B.T. and G.A. Phillips. 1975. Estimates of oil in aquatic sediments by fluorescence spectroscopy. *Environ. Poll.* 8:193-197 p.
- 48. Harrison, R., D.J.T. Smith and L. Luhana. 1996. Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, U.K. *Environ. Sci. Technol.* 30:825–832 p.
- 49. Hearn, S. and E. Baya. 2001. Subsurface investigation and report. Pensacola, FL. Thompson Engineering. Project number 01-2116-0058. March 30, 2001. 21 p.
- 50. Hemming, J.M., J.M. Brown, M. Brim and R. Jarvis. 2005. Sediment quality survey of the Choctawhatchee Bay system in the Florida panhandle. *Mar. Pol. Bull.* 50: 889-903.
- 51. Holmes, J. R.. 1989. Ambient concentrations of polycyclic aromatic hydrocarbons (pahs) at selected locations in California. Research notes No. 89-1. April 1989 http://www.arb.ca.gov/research/resnotes/notes/89-1.htm.
- 52. IARC (International Agency for Research on Cancer). 1983. Benzo[a]pyrene. In: IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. Polynuclear Aromatic Compounds. Part 1. Chemical, Environmental and Experimental Data, Vol. 32. World Health Organization, Lyon, France. 33-224 p.
- 53. Keizler, P.D., J. Dale and D.C. Gordon.1978. Hydrocarbons in surficial sediments from the Scotian Shelf. *Geochem. Cosmochem. Acta*. 42:165-172.
- 54. Karouna-Renier, N.K., R.A. Snyder, J.G. Allison, M.G. Wagner and K.R Rao. 2006. Accumulation of organic and inorganic contaminants in shellfish collected in estuarine waters near Pensacola, Florida: Contamination profiles and risks to human consumers. *Enviro. Poll.* (in press).
- 55. Killam, B. 1981a. Bayou Chico: Industry Brings Prosperity, Population and Pollution. Pensacola News Journal. April 14, 1981. p 1A, p 3A.

- 56. Killam, B. 1981a. Bayou Pollution Not Industry Only- Third in series, Pensacola News Journal. April 15, 1981. p 1A.
- 57. Killam, B. 1981b. Bayou Pollution Not Industry Only- fourth in a series, Pensacola News Journal. April 16, 1981. p 1A-2A.
- 58. Killam, B. 1981c. Battle Goes On To Save Bayou From Pollution. Pensacola News Journal. April 17, 1981. p 1A, p 2A.
- 59. Killam, B. 1981d. Bayou Chico: Industry Brings Prosperity, Population and Pollution. Pensacola News Journal. April 14, 1981. p 2A.
- 60. Leatherbarrow, J., J. Ross, N. David and D. Yee. 2005. Final Report: Fate of contaminants in sediment of San Francisco Estuary: A review of literature and data. San Francisco Estuary Institute. March 2005. Regional Monitoring Program for Trace Substances. 61 p.
- 61. Lepo, J.E., C.R. Cripe, J.L. Kavanaugh, S. Zhang and G.P. Norton. 2003. The effect of amount of crude oil on extent of its biodegradation in open water- and sandy beach-laboratory simulations. *Enviro. Tech.* 24(10):1291-302.
- 62. Lewis, M.A., D.E. Weber, R.S. Stanley and J.C. Moor. 2001a. The relevance of rooted vascular plants as indicators of estuarine sediment quality. *Arch. Environ. Contam. Toxicol.* 40:25–34.
- 63. Lewis, M.A., J.C. Moore, L.R. Goodman, J.M. Patrick, R.S. Stanley, T.H. Roush and R.L. Quarles. 2001b. The effects of urbanization on the chemical quality of three tidal bayous in the gulf of Mexico. *Water, Air, Soil Poll.* 127(1-4):65-91.
- 64. Liebens, J. 2000. A simple method to evaluate the impact of tropical cyclones on coastlines: Hurricane Georges and the Gulf Coast. *Shore & Beach*. 68(1):17-24.
- 65. Liebens, J. 2001. Heavy metal contamination of sediments in stormwater management systems: The effect of land use, particle size, and age. *Enviro. Geo.* 41:341-351.
- 66. Liebens, J., C.J. Mohrherr, K.R. Rao and C.A. Houser. Pollution in an urban bayou: magnitude, spatial distribution and origin. *Water, Air, Soil Poll*. in press.
- 67. Long, E.R. and L.G. Morgan. 1990. The potential for biological effects of sedimentsorbed contaminants tested in the National Status and Trends Program. NOAA Technical memorandum NOSOMA 52. U.S. Department of Commerce. National Oceanic and Atmospheric Administration, Rockville, MD.
- 68. Long, E.R., G.M Sloan, R.S. Carr, T. Johnson, J. Biedenbach, K.J. Scott, G.B. Thursby, E. Crecelius, C. Even, H.L. Windom, R.D. Smith and B. Loganathon. 1997. Magnitude and extent of sediment toxicity in four bays of the Florida panhandle: Pensacola, Choctawhatchee, St. Andrew and Apalachicola. Silver Spring, Maryland: National Oceanic and Atmospheric Administration. NOAA Technical Memorandum NOS ORCA 117. 233 p.
- 69. Lores, E.M., M.A. Lewis and Z.A. Malaeb. 2002. Spatial and temporal variability in zooplankton community dynamics in three urbanized bayous of the Pensacola Bay system, Florida, USA. *Gulf and Caribbean Res.* 14:1-11.

- 70. Ma, T., T.R. Pratt, J. Dukes, R.A. Countryman and G. Miller. 1999. Susceptibility of public supply wells to ground water contamination in southern Escambia County, Florida. Northwest Florida Water Management District. 162 p. <u>http://edocs.dlis.state.fl.us/fldocs/nwfwmd/wrsr99-1.pdf</u>.
- 71. 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. Tallahassee, Florida. Florida Department of Environmental Protection, Office of Water Policy. 140 p.
- MacDonald, D.D. 1994b. Approach to the Assessment of Sediment Quality in Florida Coastal Waters: Volume 2: Application of the Sediment Quality Assessment Guidelines. Tallahassee, Florida. Florida Department of Environmental Protection, Office of Water Policy. 59 p.
- Mattraw, H.C., Jr. and B.J. Franks. 1986. Movement and fate of creosote waste in ground water, Pensacola, Florida: U.S. Geological Survey toxic waste ground-water contamination program. Reston, VA. U.S. Geological Survey. Water-supply paper; 2285. 63 p.
- 74. Matheson, L., 2004 Pensacola News Journal Viewpoint: Bayou recovering from contamination. July 31, 2004
- 75. McCarty, L.S. and D. Mackay. 1993. Enhancing Ecotoxicological Modeling and Assessment. *Environ. Sci. Technol.* 27(9):1718-1729.
- 76. McCarty, L.S., D. Mackay, A.D. Smith, G.W. Ozburn, and D.G. Dixon. 1992. Residue-Based Interpretation of Toxicity and Bioconcentration QSARs from Aquatic Bioassays: Neutral Narcotic Organics. *Environ. Toxicol. Chem.* 11:917-930.
- 77. McGovern, J.R. 1976. The emergence of a city in the modern South: Pensacola 1900-1945. DeLeon Springs, Fl: Painter. 250 p.
- 78. Metwally, M.E.S., S. Al-Muzaini, P.G. Jacob and M. Bahloul. 1997. Petroleum hydrocarbons and related heavy metals in the near-shore marine sediments of Kuwait. *Enviro. Intern.* 23(1)115-121.
- 79. Mohrherr, C., 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 Diagnostics and Bioremediation, 151 p
- 80. Musgrove, R.H. 1965. The Pensacola area's water. Tallahassee, FL. Florida Geological Survey. <u>http://fdl.fcla.edu/</u>.
- 81. Nielsen, T. 1996. Traffic contribution of polycyclic aromatic hydrocarbons in the center of a large city. *Atmos. Environ.* 30(20):3481–3490.
- 82. NOAA. 1999. NOAA Screening Quick Reference Tables (SQuiRTs). <u>http://response.restoration.noaa.gov/type_subtopic_entry.php?RECORD_KEY%28entry_subtopic_type%29=entry_id,subtopic_id,type_id&entry_id(entry_subtopic_type)=90&subtopic_id(entry_subtopic_type)=5&type_id(entry_subtopic_type)=2.</u>
- 83. NWFWMD (Northwest Florida Water Management District). 1990. Surface water improvement and management (S.W.I.M.) Program. Point source Assessment of the

Pensacola Bay System, a Working Paper. Northwest Florida Water Management District, April 1990. Water Resource Special Report 90-5.

- 84. NWFWMD (Northwest Florida Water Management District). 1992. A literature-based review of the physical, sedimentary, and water quality aspects of the Pensacola Bay System. Water Resources Special Report 92-5. Northwest Florida Water Management District. Havana, FL.
- 85. NWFWMD (Northwest Florida Water Management District). 2004. Northwest Florida Water Management District 2004 Annual Report.
- 86. Odom Hydrographic systems. 2000. Hydrotrac installation and operation manual. Baton Rouge, LA.
- 87. Overman, C.H. 1923. Survey of Brent Island, Pensacola, Florida for The Bruce Dry Dock Company. Trace from a print signed by Frank Jarrett, civil engineer.
- 88. OHSA. 1999. Appendix C, Basis of OSHA carcinogen listing for individual chemicals <u>www.epa.gov/tri/chemical/appendixc1999pdr.pdf</u>.
- 89. Pensacola Historical Society, 2004. <u>http://www.cherylynstopler.com/history.htm</u>.
- 90. Pensacola Journal. 1926. Pensacola Journal. January 3, 1926. 1 p.
- 91. Pensacola Marine Complex. 2006. <u>http://www.psmc.net/private.htm</u>.
- 92. Port of Pensacola. 2004. History highlights A timeline. http://www.portofpensacola.com/timeline.htm.
- 93. Pratt, T.R., P.F. McGinty, G.Z. Guo, W.C. Hunner and E.F. Songer. 1993. Stormwater assessment of the Bayou Chico watershed, Escambia County, Florida: Surface water improvement and management plan, a comprehensive plan for the restoration and preservation of the Pensacola Bay system, Water Resources Special Report 93-7. Havana, FL: Northwest Florida Water Management District. 218 p.
- 94. Rao, K.R. (Editor). 1978. Pentachlorophenol: Chemistry, Pharmacology and Environmental Toxicology. Plenum Press, New York. 402 p.
- 95. Rostad, C. and W.E. Pereira. 1987. Creosote compounds in snails obtained from Pensacola Bay, FL, near an onshore hazardous-waste site. *Chemosphere*. 16(10-12):2397-2404.
- 96. Sarkar, S.K., S. Franciskovic-Bilinski, A. Bhattacharya, M. Saha and H. Bilionski. 2004. Levels of elements in the surficial estuarine sediments of the Hugli River, northeast India and their environmental implications. *Enviro. Intern.* 30:1089-1098.
- 97. Schwartz, T.R., D.L. Stalling and C.L. Rice. 1987. Are polychlorinated biphenyl residues adequately described by Arochlor mixture equivalents? Isomer-specific principal components analysis of such residues in fish and turtles. *Environ. Sci. Tech.* 21(1):72–76.
- 98. Seal, T.L., F.D. Calder, G.M. Sloane, S.J. Schropp and H.L. Windom. 1994. Florida coastal sediment contaminants atlas: Technical volume. Tallahassee, Fl: Florida Dept. of Environmental Protection
- 99. Stave, B.M. 1992. Fire insurance maps from the Sanborn Map Company archives, late 19th century to 1989, Florida. University Publications of America, Bethesda, MD.
- Stone, G.W. and J.P. Morgan. 1991. Heavy metal concentrations in subsurface sediments Bayou Chico, Pensacola, FL. Institute for Coastal and Estuarine Research, University of West Florida. Rep-05: 12-02-91. 33.
- Suarez, M.P., H.S. Rifai, R.M. Palachek, K.E. Dean and L. Koenig. 2005. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in Houston Ship Channel tissue and sediment. *Enviro. Eng. Sci.* 22(6):891-906.
- 102. Sun, J.D., R.K. Wolff and G.M. Kanapilly. 1982. Deposition, retention, and biological fate of inhaled benzo[a]pyrene adsorbed onto ultrafine particles as a pure aerosol. *Toxicol. Appl. Pharmacol.* 65:231-244.
- 103. Thornburg, T. 2004. Development of SQGs for petroleum hydrocarbons, What analytes and associated SQGs should be used for bulk petroleum hydrocarbons and/or their constituents, such as PAHs? US Army Corps of Engineers, Seattle District. 6 p. <u>http://www.nws.usace.army.mil/publicmenu/DOCUMENTS/DMMO/Combined_Issue_P</u> apers.pdf#search='DRAFT%20RSET%20ISSUE%20PAPER%202%20%E2%80%93%2 0Development%20Of%20SQGs%20For%20Petroleum%20Hydrocarbons'.
- 104. Thorpe, P., R. Bartel, P. Ryan, K. Albertson, T. Pratt and D. Cairns. 1997. The Pensacola Bay System surface water improvement and management plan. Northwest Florida Water Management District. 150 p.
- 105. USACE (US Army Corps of Engineers). 1946. Pensacola Harbor, Florida, Improvement of Bayou Chico, In accordance with Chief of Engineers dated 1943, Property Survey. Mobile Office.
- 106. USACE (US Army Corps of Engineers). 1977. Report on water pollution in Bayou Chico. Draft, Mobile District. Reference quoted according to Glassen et al. 1977.
- 107. USEPA (Environmental Protection Agency). 1986. Quality criteria for water (Gold Book). Document EPA/5-86-001. Washington, DC. 477 p.
- 108. USEPA. 1988a. Estimating toxicity of industrial chemicals to aquatic organisms using structure activity relationships. R.G. Clements, Ed. US Environmental Protection Agency, Washington DC. EPA-560-6-88-001.
- 109. USEPA. 1998b. EPA's Contaminated sediment management strategy. EPA-823-R-98-001. <u>http://www.epa.gov/glnpo/sediment/PCBContaminatedSedimentsStrategy.pdf</u>
- 110. USEPA. 1999a. National Recommended Water Quality Criteria-Correction. EPA-822-7-99-001, Office of Water, Washington DC.
- 111. USEPA. 1999b. EPA Superfund, Record of Decision Amendment: American Creosote Works, Inc. (Pensacola Plant) Amended Record Of Decision Operable Unit 1, American Creosote Works Site, Pensacola, Escambia County, Florida, USEPA Region 4, Atlanta, Georgia. 71p. <u>http://www.epa.gov/superfund/sites/rods/fulltext/a0499500.pdf</u>
- 112. USEPA. 2000. DIBENZOFURAN hazard summary-created in April 1992; Revised in January 2000. Technology Transfer Network Air Toxics Website. <u>http://www.epa.gov/ttn/atw/hlthef/di-furan.html#ref2</u>.
- 113. USEPA. 2002. Fact Sheet American Creosote Works. August 2002. 4 p. http://www.epa.gov/region4/waste/npl/nplfln/acw802fs.pdf.

- 114. USEPA. 2003a. American Creosote Works Site. January 2, 2003. USEPA Region 4.4 p. http://www.epa.gov/region4/waste/npl/nplfln/acw103fs.pdf.
- 115. USEPA. 2003b. Draft dioxin reassessment draft exposure and human health reassessment of 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD) and related compounds: Part III: Integrated summary and risk characterization for 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD) and related compounds. EPA/600/P-00/001Cb. 264 p. www.epa.gov/ncea
- 116. USEPA. 2006. Record of decision: Summary of remedial alternative selection Escambia Wood Treating Company Superfund Site Operable Unit 01 (Soil). USEPA Region 4. Atlanta, Georgia: US Environmental Protection Agency. 519 p.
- 117. Van den Berg, M., L. Birnbaum, A.T.C. Bosveld, B. Brunström, P. Cook, M. Feeley, J.P. Giesy, A. Hanberg, R. Hasegawa, S.W. Kennedy, T. Kubiak, J.C. Larsen, F.X.R. van Leeuwen, A.K. Djien Liem, C. Nolt, R.E. Peterson, L. Poellinger, S. Safe, D. Schrenk, D. Tillitt, M. Tysklind, M. Younes, F. Wærn, and T. Zacharewski. 1998. Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. *Environ. Health Perspect*. 106(120):775-792.
- 118. Van Mouwerik, M., L. Stevens, M.D. Seese and W. Basham. 1998. PAHs. In: Environmental Contaminants Encyclopedia. R. J. Irwin (Editor). National Park Service, Colorado State University. 176 p.
- 119. Waller, T., M. Acevedo, J. Kennedy, K. Dickson, S. Cairns, L. Ammann, W. Walker, D. Burke, F. Mayer and M. Lewis. 1998. Development and evaluation of diagnostic indicators of ecological condition of Gulf of Mexico bayous: Bayou Chico statistical summary and assessment framework. Gulf Breeze, FL: EPA Gulf Breeze Ecology Division. 327 p.
- 120. Waller, T.W., M.F. Acevedao, J.H. Kennedy, K.L. Dickson, S.H. Cairns and L. Ammann. 1998. Development and evaluation of diagnostic indicators of ecological condition of Gulf of Mexico bayous: Bayou Chico statistical summary and assessment framework. EPA Gulf Breeze Ecology Division.
- 121. Weis, J.S. and P. Weis. 1996. Effects of using wood treated with chromated copper arsenate in shallow-water environments: A review. *Estuaries*. 19(2A):306-310.
- 122. Weyand, E.H. and D.R. Bevan. 1986. Benzo(a)pyrene disposition and metabolism in rats following intratracheal instillation. *Cancer Res.* 46:5655-5661.
- 123. Wenning, R. J., D.J. Paustenbach, M.A. Harris and H. Bedbury. 1995. Comparisons of patterns of polychlorinated biphenyl congeners in water, sediment, and indigenous organisms from New Bedford Harbor, Massachusetts. Arch. Enviro. Cont. Toxi. 29(2):271-289.
- 124. Wood, K.A. and R.L. Bartel. 1994. Bayou Chico sediment and water quality data report. Havana, FL: Northwest Florida Water Management District. Technical File Report 94-3. August 1994. 48 p.
- 125. Young, D.R., R.W. Gossett and T.C. Heesen. 1988. Persistence of chlorinated hydrocarbon contamination in a California marine ecosystem. In: Wolfe, D.A. and T.P. O'Conner (Editors). Oceanic Processes in Marine Pollution: Volume 5; Urban wastes in coastal marine environments. pp. 33-41.

- 126. Yunker, M.B, R.W. Macdonald, R. Vingarzan, R.H. Mitchell, D. Goyette and S. Sylvestre. 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Org. Geochem.* 33:489-515.
- 127. Zheng, G.J. and R.J. Richardson. 1999. Petroleum hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) in Hong Kong marine sediments. *Chemosphere*. 38(11)2625-2632.

10. APPENDIX 1: MAPS



Map 1: Location of Bayou Chico.



Map 2: Bayou Chico sediment thickness distribution (Glassen et al., 1977).



Map 3: Pensacola Harbor and Bar, Florida Survey, 1822.



Map 4 Proposed dredging for Bayou Chico, 1935.



Map 5: 1780 British Survey map of Pensacola.



Map 6: 1827 map of Bayou Chico.



Map 7: 1895 map of mouth of Bayou Chico.



Map 8: 1923 map of Bayou Chico.



Map 9: 1943 property survey map.



Map 10: Bathymetric map of Bayou Chico, 2005.



Map 11: Location of sampling sites - overview.



Map 12: Location of sampling sites - Sanders Beach.



Map 13: Total petroleum hydrocarbons.



Map 14: Location of EA (2000) sampling sites. Sample 1 is EA (2000) sample ID BC00-SED-01, Sample 2 is EA (2000) sample ID BC00-SED-02, etc.



Map 15: Location of Bayou Chico sampling sites in DeBusk et al. (2002) database.



Map 16: Dioxin/furan TEQs for surface sediments.



Map 17: Combined dioxin/furan and dioxin-like PCB TEQs for surface sediments.



Map 18: PCB concentrations in surface sediments.



Map 19: Location of OmniVest vibracore sites (OV 1 - 3).



Map 20: Arsenic concentrations in surface sediments.



Map 21: Cadmium concentrations in surface sediments.



Map 22: Chromium concentrations in surface sediments.



Map 23: Copper concentrations in surface sediments.



Map 24: Mercury concentrations in surface sediments.



Map 25: Lead concentrations in surface sediments.



Map 26: Zinc concentrations in surface sediments.



Map 27: Trace metal PLI index for surface sediments.



Map 28: Arsenic concentrations in water.



Map 29: Mercury concentrations in water.



Map 30: Chromium concentrations in water.



Map 31: Copper concentrations in water.



Map 32: Lead concentrations in water.


Map 33: Zinc concentrations in water.



Map 34: Trace metal PLI index for water.



Map 35: Clay content in surface sediments.

11. APPENDIX 1: DIOXIN/FURAN AND PCB DATA

Analyte	BG-1	BG-2	BG-3	BG-4	BG-5	BG-6	BG-7	BG-8
2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)	ND	ND	ND	ND	ND	ND	ND	ND
1,2,3,7,8-Pentachlorodibenzo-p-dioxin (PeCDD)	3.55	3.37	3.08	0.30	2.83	2.51	4.91	6.05
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin (HxCDD)	6.99	9.19	9.64	1.11	8.64	6.88	13.64	16.82
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin (HxCDD)	26.87	36.03	46.52	5.06	40.46	28.86	97.53	109.87
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin (HxCDD)	26.46	17.82	37.10	4.45	33.70	25.39	63.83	71.57
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin (HpCDD)	761.20	1033.70	1568.48	254.64	1737.38	1047.18	4182.93	4668.19
Octachlorodibenzo-p-dioxin (OCDD)	5115.41	7165.28	11206.29	1738.84	11328.47	6386.69	27981.44	33624.10
2,3,7,8-Tetrachlorodibenzofuran (TCDF)	16.13	12.69	78.24	2.82	4.76	4.38	4.22	3.01
1,2,3,7,8-Pentachlorodibenzofuran (PeCDF)	14.00	10.77	63.14	2.19	4.18	3.12	3.39	2.90
2,3,4,7,8-Pentachlorodibenzofuran (PeCDF)	3.82	4.41	10.95	0.40	1.08	1.25	ND	1.47
1,2,3,4,7,8-Hexachlorodibenzofuran (HxCDF)	13.86	16.99	41.46	2.34	7.50	5.67	9.43	12.50
1,2,3,6,7,8-Hexachlorodibenzofuran (HxCDF)	7.41	9.90	15.41	0.95	3.81	3.58	5.16	8.39
1,2,3,7,8,9-Hexachlorodibenzofuran (HxCDF)	ND	ND	3.27	ND	ND	ND	ND	ND
2,3,4,6,7,8-Hexachlorodibenzofuran (HxCDF)	8.08	6.72	6.01	0.69	5.02	4.17	7.99	11.03
1,2,3,4,6,7,8-Heptachlorodibenzofuran (HpCDF)	76.80	107.78	103.13	14.53	84.70	56.16	191.20	309.30
1,2,3,4,7,8,9-Heptachlorodibenzofuran (HpCDF)	7.47	10.57	16.51	1.35	5.63	3.90	10.20	15.66
Octachlorodibenzofuran (OCDF)	146.66	204.48	180.50	44.15	171.46	106.45	526.27	770.47

Table 50: Dioxins/furans in surface sediments in ng/kg¹.

¹: ND denotes non-detect of analyte during analyses.

Analyte	BG-9	BG-10	BG-11	BG-12	BG-13	BG-14	BG-15	BG-16
2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)	ND	ND	ND	ND	ND	1.45	ND	1.44
1,2,3,7,8-Pentachlorodibenzo-p-dioxin (PeCDD)	0.23	7.50	ND	0.87	ND	7.43	4.70	7.04
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin (HxCDD)	0.71	23.42	ND	2.17	ND	22.08	14.20	19.94
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin (HxCDD)	3.43	152.77	ND	13.02	ND	108.57	63.23	89.53
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin (HxCDD)	2.29	109.16	ND	9.57	ND	79.46	52.49	73.64
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin (HpCDD)	128.33	6942.66	10.71	487.81	1.60	3601.23	2165.26	3221.64
Octachlorodibenzo-p-dioxin (OCDD)	933.84	52898.18	111.21	3729.76	16.33	25115.18	14827.78	25662.54
2,3,7,8-Tetrachlorodibenzofuran (TCDF)	ND	6.66	ND	ND	ND	6.86	4.94	54.06
1,2,3,7,8-Pentachlorodibenzofuran (PeCDF)	ND	4.61	ND	0.34	ND	4.89	3.93	39.44
2,3,4,7,8-Pentachlorodibenzofuran (PeCDF)	ND	3.05	ND	0.25	ND	2.21	1.85	8.91
1,2,3,4,7,8-Hexachlorodibenzofuran (HxCDF)	0.63	13.55	ND	1.36	ND	12.66	9.22	33.95
1,2,3,6,7,8-Hexachlorodibenzofuran (HxCDF)	0.41	7.77	ND	1.04	ND	6.09	4.93	16.71
1,2,3,7,8,9-Hexachlorodibenzofuran (HxCDF)	ND	ND	ND	ND	ND	ND	ND	1.61
2,3,4,6,7,8-Hexachlorodibenzofuran (HxCDF)	0.45	11.06	ND	1.23	ND	10.02	7.23	15.48
1,2,3,4,6,7,8-Heptachlorodibenzofuran (HpCDF)	9.87	222.19	1.75	29.97	0.21	198.01	112.93	214.17
1,2,3,4,7,8,9-Heptachlorodibenzofuran (HpCDF)	0.65	13.01	ND	1.61	ND	9.53	6.04	17.64
Octachlorodibenzofuran (OCDF)	25.02	408.60	141.54	59.77	0.80	292.99	174.71	356.33

Table 50: Dioxins/furans in surface sediments in ng/kg (continued).

	1 ²	2	3	4	6	5 ₁ 5+8	7	9	10	11	12+13 _{וד} 12	14
BG-1	28	28.3	41.2	ND	ND	1540	ND	ND	ND	528	ND	ND
BG-2	8.6	6.6	19.9	23.3	ND	ND	ND	ND	ND	179	ND	ND
BG-3	30	10.5	23.1	119	ND	682	ND	ND	ND	285	ND	ND
BG-4	ND	ND	ND	ND	ND	353	ND	ND	ND	299	23.9	ND
BG-5	31.4	10.9	20.9	117	ND	ND	ND	ND	ND	328	ND	ND
BG-6	66.5	ND	49	ND	ND	585	ND	ND	ND	501	ND	ND
BG-7	133	38.3	114	1950	853	9560	ND	407	ND	ND	ND	ND
BG-8	ND	ND	34.5	ND	ND	1280	ND	ND	ND	783	ND	ND
BG-9	ND	ND	ND	ND	ND	155	ND	ND	ND	260	ND	ND
BG-10	309.4	ND	321.4	1789.7	ND	9427.5	814	386.2	ND	ND	ND	ND
BG-11	9.5	13.7	2.6	17.4	ND	ND	ND	ND	ND	52.7	ND	ND
BG-12	9.6	10.8	8.5	36.8	ND	185.2	ND	ND	ND	74.7	17.6	ND
FID-2G	3.3	21.1	2.6	ND	ND	ND	ND	ND	ND	40	ND	ND
BG-13	144.9	18.7	31	876.9	277	2419.3	ND	62.1	33.9	120.4	ND	ND
BG-14	683.3	43.1	162.5	5187.5	1577.1	12769	210.2	603.5	258.5	590.9	526.6	349.6
BG-15	855.1	72.2	200.4	7283.7	1887.6	14634.6	255.7	675.5	427	619	600.2	480.6
BG-16	726.7	51.8	169.8	5565.3	1716.9	10875	264.4	561.3	388.7	549.8	537.3	263

Table 51: PCB congeners in surface sediments in ng/kg¹.

¹: ND denotes non-detect of analyte during analyses. ²: IUPAC congener numbers are in first row.

	15-	17	18/ _¶ 18 +30	19	20/ _T 20+21 +28 +33	22	25	26/ 26+ 29	27/ 27+16 +24	31	32	34/ _ד 34+ 23
BG-1	1170	529	868	111	3310	978	ND	474	127	2400	380	ND
BG-2	305	69.6	117	11.2	119	121	ND	60.6	13.4	316	50.6	ND
BG-3	458	343	570	57.2	1290	355	85.1	195	70.5	899	215	ND
BG-4	144	16	123	14.6	415	138	27	61.3	15.3	312	51.5	ND
BG-5	306	76.3	590	51.4	1070	286	ND	ND	76.2	788	207	ND
BG-6	322	40.4	315	39.3	920	284	ND	137	41.8	405	114	ND
BG-7	3380	5670	8300	853	9120	573	9670	4720	1270	ND	3020	1720
BG-8	347	120	725	81.7	1860	575	204	387	76.7	1540	323	ND
BG-9	48.3	13.5	75.9	8.2	175	52	18.8	34.5	7.8	141	33.9	ND
BG-10	3878.7	5840.4	9835.7	831.9	31641.3	ND	ND	ND	1324.4	2801	3156.4	ND
BG-11	ND	13	10.1	3.7	21.6	4.8	2.4	2.5	1.4	14.8	12.1	3.8
BG-12	85.3	94.3	130	17.1	376.6	95.4	ND	ND	20.8	301.1	57.2	76.1
FID-2G	ND	4.3	5	1.8	13.8	3.8	ND	ND	1	12.1	2.9	ND
BG-13	1234.1	904.9	1522	275.2	3170.4	1062.6	2229.2	232.2	203.2	ND	531	586.7
BG-14	5842.7	7162.3	10509.2	1644.2	17619.2	5585.8	858	2806.8	1301.8	10982.1	3985.7	ND
BG-15	5369.7	8362.9	12780	2434.3	14120.9	4191.4	971	2873	1649	11328.5	4217.6	ND
BG-16	6333	9560.3	14853.5	2221.7	17662.4	ND	ND	14234.2	979.1	ND	5091.3	3722.3

Table 51: PCB congeners in surface sediments in ng/kg (continued).

	36	39	38	35	37	41/ _ח 41+ 71+40	44/ 44+ 47+65	45/ _ד 45+ 51	46	48	49/ד 49+ 69
BG-1	ND	ND	ND	ND	1270	2950	3670	617	144	ND	2320
BG-2	ND	ND	ND	ND	333	204	ND	54.1	16.2	ND	275
BG-3	ND	ND	ND	ND	329	215	ND	208	48.2	ND	891
BG-4	ND	ND	ND	ND	118	189	ND	57	18.6	44.3	220
BG-5	ND	ND	ND	ND	246	467	ND	167	36.1	ND	667
BG-6	ND	ND	ND	ND	248	501	32.3	117	37.3	ND	623
BG-7	ND	ND	ND	ND	3380	7150	ND	2780	474	ND	7930
BG-8	24.1	ND	ND	ND	421	1090	ND	392	129	468	1500
BG-9	ND	ND	ND	ND	35.7	127	ND	46.5	15	50.9	183
BG-10	ND	ND	ND	ND	3253.8	11466.5	9101.9	2837.1	ND	ND	3641.3
BG-11	ND	ND	ND	ND	6.1	11.5	24.5	6.6	1.8	ND	16.9
BG-12	ND	ND	ND	ND	78	248.8	352.3	58.4	17.5	ND	212.7
FID-2G	ND	ND	ND	ND	3.7	10.4	15	3.1	ND	ND	8.6
BG-13	ND	ND	ND	ND	1308.3	828	320.2	329.7	115.3	ND	ND
BG-14	ND	ND	ND	ND	6444.2	5474.6	8589.5	2195.1	433.6	2444.6	4711.5
BG-15	ND	ND	ND	ND	2693.9	3371.5	5647.8	2119.5	236.8	912	3472.5
BG-16	ND	ND	ND	ND	3952.3	4262.7	8135.5	2538.2	787	1896.5	5904.3

Table 51: PCB congeners in surface sediments in ng/kg (continued).

	50/ _ד 50+53	52/ ₁ 52+43+73	54	56/ _ד 56+60	57	58/ _T 58+67	59+62+42 _{(آ} /59 75	63	64	66/ _T 66+55	68
BG-1	419	3690	ND	459	ND	33	3350	ND	1050	1830	ND
BG-2	43.3	518	0.8	200	ND	ND	433	ND	128	420	ND
BG-3	154	1440	2.9	423	ND	28.5	1310	ND	207	769	ND
BG-4	40.1	377	ND	ND	ND	ND	322	ND	96.6	235	ND
BG-5	122	1100	2.7	109	ND	10.2	986	ND	309	514	ND
BG-6	85.2	1060	4.6	ND	ND	ND	968	ND	295	641	ND
BG-7	1840	10900	33.2	3270	ND	ND	11000	ND	1980	4560	ND
BG-8	313	2480	7.4	ND	33.6	ND	1920	ND	920	1430	ND
BG-9	41.4	327	1.6	ND	ND	ND	224	ND	102	166	ND
BG-10	1946.8	9690.7	34.4	4571	ND	ND	ND	196.7	ND	6050.6	ND
BG-11	5.3	27.6	0.6	5.2	ND	ND	ND	ND	7.5	17	ND
BG-12	54.1	335.5	1.7	127.4	ND	ND	39.1	ND	92.3	205.8	ND
FID-2G	3.3	19.7	ND	4.9	ND	ND	ND	ND	5.1	10.1	ND
BG-13	249.3	1158.4	5	ND	ND	ND	ND	ND	569	ND	ND
BG-14	1828.8	8443.2	ND	5312.9	ND	ND	935.7	ND	3704.5	10540.1	ND
BG-15	1899.4	6326.9	ND	2306.7	ND	ND	592.9	ND	2249.9	3522	ND
BG-16	2007.3	7836.4	54.2	2173	ND	70.2	1263.7	76.7	2564.8	3043.3	ND

Table 51: PCB congeners in surface sediments in ng/kg (continued).

	70/ _٦ 70+61+74 +76	72	<u>77</u> ³	78	79	80	<u>81</u>	82	83/ ₁ 83+99+112	84	85/ ₁ 85+116+117
BG-1	3920	ND	183	ND	ND	ND	ND	413	1640	518	ND
BG-2	721	ND	119	ND	ND	58.2	ND	84.2	637	109	ND
BG-3	1600	ND	95.6	7	ND	147	4.7	169	671	257	431
BG-4	489	ND	22.5	ND	ND	ND	ND	16.8	74.6	56.6	143
BG-5	1150	ND	57.7	ND	5.9	ND	ND	113	512	178	458
BG-6	1360	ND	59.9	ND	ND	ND	ND	138	547	169	569
BG-7	10600	ND	640	ND	ND	1060	ND	1150	3560	1280	ND
BG-8	2790	ND	103	ND	ND	ND	ND	301	1000	423	313
BG-9	325	ND	13.6	ND	ND	ND	ND	42.2	149	63.1	44.1
BG-10	20272.4	ND	792.8	ND	ND	1052.3	ND	ND	6440.6	2269	25246.5
BG-11	28.6	ND	1.7	ND	ND	ND	ND	ND	25.8	6.2	ND
BG-12	564.8	ND	20.6	ND	ND	ND	ND	ND	156.2	55.5	ND
FID-2G	22.4	ND	1.2	ND	ND	ND	ND	ND	10.1	3	ND
BG-13	2955.5	ND	231.9	ND	ND	ND	ND	ND	371.8	102.3	ND
BG-14	18459.5	ND	1578.4	ND	ND	1990.6	ND	ND	1969.4	991.4	1173.4
BG-15	6931.5	ND	418.7	ND	ND	729.8	ND	ND	981.6	327.5	567.8
BG-16	6392.2	ND	346.8	ND	ND	685.5	ND	ND	2529.1	ND	936

Table 51: PCB congeners in surface sediments in ng/kg (continued).

³: Bold face font indicates a dioxin-like PCB congener.

	86/ ₁ 86+87 +97+108+ 119+125	88/ 88+91	89	90/ ₁ 90+101+ 113	92	93/ק 93+100+ 98 +102	94	95	96	103	104
BG-1	1350	643	30.4	2940	565	1410	ND	1130	23	ND	ND
BG-2	207	125	ND	957	ND	ND	429	ND	5.2	217	ND
BG-3	347	187	ND	1470	ND	ND	1060	ND	10.9	ND	ND
BG-4	54.4	40.2	ND	269	26.4	201	ND	ND	2.6	ND	ND
BG-5	275	172	ND	1020	48.8	682	ND	ND	8.2	ND	ND
BG-6	253	106	ND	1020	125	590	ND	ND	6	ND	ND
BG-7	2700	1140	ND	6340	1200	ND	4770	ND	83.3	ND	ND
BG-8	617	263	ND	1760	349	1300	ND	ND	19.6	14.4	ND
BG-9	85.9	41.4	ND	280	54.6	201	ND	ND	2.7	3.1	ND
BG-10	10176.6	2365.3	ND	23053.2	1915.4	ND	15524.9	ND	92.4	ND	ND
BG-11	11.6	6.8	ND	24.9	ND	ND	ND	38	ND	ND	ND
BG-12	ND	45	ND	267.3	ND	195.6	ND	ND	0.6	ND	ND
FID-2G	7.6	2.2	ND	14.4	ND	ND	ND	23.4	ND	ND	ND
BG-13	102.2	80.5	ND	720.7	ND	ND	ND	995.5	6.2	ND	ND
BG-14	1737.6	436.9	ND	5354.2	868.1	3738	ND	522.6	49.4	ND	ND
BG-15	599.3	151.4	ND	2955.3	448.3	2379.4	ND	ND	41.6	ND	ND
BG-16	1491.4	563.4	ND	4413.2	ND	3370.3	ND	1469.3	56.9	ND	ND

Table 51: PCB congeners in surface sediments in ng/kg (continued).

	<u>105</u>	107/ ₁ 107+124	109/ _٦ 109+106 +<u>123</u>	110/ _ח 110+115	111	<u>118</u>	120	121	122/ 122+ <u>114</u>	127	<u>126</u>
BG-1	1410	142	ND	6220	ND	3120	ND	ND	49.7	275	58.6
BG-2	308	29.2	ND	1790	ND	725	ND	128	ND	21.5	27.7
BG-3	469	84.4	ND	1800	ND	1100	ND	180	15.3	22.8	20
BG-4	102	3.8	ND	287	ND	202	ND	14.7	ND	ND	ND
BG-5	300	32.1	ND	1200	ND	733	ND	ND	11.1	ND	ND
BG-6	384	36.8	ND	1260	ND	759	ND	38.5	ND	9.5	ND
BG-7	2130	346	ND	11700	ND	4520	ND	ND	90.4	65.1	47.7
BG-8	521	103	106	2580	ND	1350	ND	ND	25.6	ND	ND
BG-9	74.1	16	ND	381	ND	192	ND	ND	2.8	ND	ND
BG-10	5159	ND	ND	ND	ND	13104.7	ND	ND	ND	ND	ND
BG-11	7.9	ND	ND	35.8	ND	23.4	ND	3.3	ND	ND	ND
BG-12	98.3	ND	ND	471.3	ND	239.2	ND	33.4	4.4	ND	ND
FID-2G	5.1	ND	ND	23.8	ND	12	ND	1.7	ND	ND	ND
BG-13	158.2	47	ND	732.3	ND	312.7	ND	127.1	7.5	20.9	8.3
BG-14	1786.1	ND	ND	6655.2	ND	3383.3	ND	ND	ND	218.9	129.6
BG-15	519.8	ND	ND	2807.8	ND	1088.6	ND	ND	ND	ND	ND
BG-16	1197.8	259.6	ND	4873.3	ND	2744.3	ND	ND	44.7	62.9	41.5

Table 51: PCB congeners in surface sediments in ng/kg (continued).

	128/ 128 +166	+29 _آ /129 138+160 +163	130/ _٦ 130+ 137+164	131/ 131+ 142	132	133	135/ _T 135+1 51+154	136	139/ _ח 139+140	143	144
BG-1	804	5040	67.6	ND	1230	ND	170	1.6	24.3	ND	ND
BG-2	372	2750	98.3	11.7	571	12.7	85.9	1.3	18.3	33.8	1860
BG-3	395	2630	95.2	18.5	703	21.8	126	ND	18.5	33.8	ND
BG-4	30.6	229	8.3	ND	ND	ND	224	15.3	ND	ND	216
BG-5	160	1150	37.2	ND	ND	ND	ND	28.5	4	7.8	ND
BG-6	142	1380	ND	ND	ND	ND	34.9	34	ND	5.1	4070
BG-7	957	6300	275	58.8	1750	56.9	246	3.5	52.6	74	1430
BG-8	243	1690	117	ND	ND	ND	1710	ND	11.2	16.2	ND
BG-9	ND	264	18.6	ND	ND	ND	123	35.4	1.6	2.7	ND
BG-10	3340.7	48760.5	199.5	ND	13930.6	ND	56263.6	ND	ND	ND	18243.9
BG-11	6.6	37.5	1	ND	9.3	ND	1.7	ND	ND	ND	ND
BG-12	42.3	254.8	9.3	ND	85.2	ND	7.6	ND	1.8	ND	90.1
FID-2G	3.1	20.5	ND	ND	7	ND	1	ND	ND	ND	11.4
BG-13	ND	1446.1	ND	ND	566.8	28.4	1143.4	ND	12.2	ND	ND
BG-14	1333.1	16703	1504.9	ND	4307	ND	ND	ND	67.8	ND	ND
BG-15	359.5	4286.3	286.9	ND	1557	ND	ND	ND	22.6	ND	ND
BG-16	526.5	6509	103.1	ND	2465.9	ND	7397.3	ND	ND	244.7	ND

Table 51: PCB congeners in surface sediments in ng/kg (continued).

	145	146 146 +161	147/ ₁ 147+134+149	148	152/ 152+150	153/ _ד 153+ 168+141	155	<u>156/╗ 156+</u> <u>157</u>	158	159	162
BG-1	90.7	3540	2020	1040	ND	319	ND	434	232	ND	ND
BG-2	218	ND	1690	1010	1.6	2360	ND	157	158	29.2	21.5
BG-3	259	ND	1910	1030	ND	2240	ND	154	178	14.1	13.1
BG-4	18.8	23.3	2.3	128	15.4	3.8	ND	24.3	10.6	3.7	ND
BG-5	86.4	923	24.5	427	ND	115	ND	88.5	58	ND	ND
BG-6	77.3	110	21.8	463	ND	38	0.5	94.4	65.6	30.5	ND
BG-7	603	ND	3920	2080	ND	4620	ND	535	428	18.3	17.8
BG-8	186	209	64.8	651	ND	66.7	ND	140	130	ND	ND
BG-9	ND	32.9	9.5	ND	ND	10.3	ND	22.8	ND	ND	ND
BG-10	9535.3	5223.9	84924.6	ND	ND	79010.7	ND	2453.5	2770.2	3403.2	1156.5
BG-11	4.2	43.7	50.9	16.4	ND	3.6	ND	3.1	2.1	ND	0.4
BG-12	20.6	213.1	241.8	75.1	ND	ND	ND	24	16.1	ND	ND
FID-2G	2.2	22.5	28.1	9.9	ND	2.5	ND	1.7	1.4	ND	ND
BG-13	251.2	1776.4	ND	ND	ND	299.8	ND	68.5	75.6	35.5	23.4
BG-14	1116.2	3173.7	14151.8	ND	ND	18461.4	ND	674.9	985.4	671.8	265.5
BG-15	917.1	913.3	5714.8	ND	ND	5143.9	ND	199.3	244.8	101.3	61
BG-16	1651.7	7716.5	7578.8	ND	ND	1103.4	ND	350.1	334.1	54.7	36.6

Table 51: PCB congeners in surface sediments in ng/kg (continued).

	165	<u>167</u>	<u>169</u>	170	172	175	176	177	178	179	180/ 180+193
BG-1	263	113	ND	1250	242	ND	167	776	910	415	2790
BG-2	258	85.9	8.6	649	10.6	ND	ND	385	797	408	1580
BG-3	272	57.8	ND	345	ND	ND	ND	335	431	224	887
BG-4	18.8	9.7	ND	ND	11.8	ND	ND	54.6	110	58.9	224
BG-5	98.4	34.1	ND	ND	32.4	ND	ND	114	236	137	498
BG-6	114	49.7	ND	ND	43.9	ND	ND	149	282	150	ND
BG-7	566	158	ND	807	ND	ND	ND	694	960	501	1950
BG-8	177	51.3	ND	ND	47.9	55.2	ND	181	368	199	690
BG-9	28.3	9.5	ND	ND	8.3	10.5	ND	33.9	63.7	32.8	ND
BG-10	ND	1013.2	475	28627.6	ND	ND	12187.8	113915.7	62835.5	39088.7	126229.6
BG-11	6.2	1.2	ND	8.1	ND	ND	ND	ND	11.7	6.8	22.5
BG-12	22.1	7.1	ND	39.8	6	ND	ND	ND	38.5	24.1	105.7
FID-2G	2.7	0.7	ND	5	1.2	ND	ND	ND	8.4	4.7	15.6
BG-13	327.9	27	2.7	834.8	117.4	ND	141.1	536	695.8	405.8	1708.5
BG-14	ND	257.6	277.5	13029.6	ND	ND	1082	6772	8156.5	2890.9	29172.3
BG-15	ND	69.3	ND	1059.9	ND	ND	345.9	1137.7	1691.2	1075.1	3214.4
BG-16	1389.8	129.9	ND	1555.3	312.9	ND	703.1	1527.4	2829.3	1806.4	4139.8

Table 51: PCB congeners in surface sediments in ng/kg (continued).

	181/ ₁ 181+171+173	183/ _{ປີ} 183+174+185	184	186	187/ ₁ 87+182	188	<u>189</u>	190	191	192	195
BG-1	580	ND	ND	ND	3340	ND	28.2	156	ND	166	205
BG-2	156	1210	98.8	ND	2830	ND	17	86.2	ND	87.3	167
BG-3	104	ND	54	ND	1660	0.8	10.8	43.6	ND	41.4	73.1
BG-4	18.7	ND	16.4	ND	412	ND	1.9	15.5	2.7	222	22.2
BG-5	54.3	ND	32.4	ND	1030	ND	7.1	22.7	10.7	ND	35.6
BG-6	69.8	ND	39.9	ND	1270	1.3	8.4	41.7	ND	156	64.6
BG-7	268	ND	ND	ND	3730	ND	24	108	ND	113	178
BG-8	91.1	ND	55.2	ND	1360	ND	8.1	40.4	9.5	682	55.2
BG-9	15.1	ND	10.3	ND	235	ND	ND	7.4	ND	ND	9.4
BG-10	30731.2	ND	ND	ND	241014.3	ND	481.8	5451.5	612.1	5098.3	14498.8
BG-11	ND	28.4	1.5	ND	51.3	ND	ND	ND	0.1	ND	2.2
BG-12	11.7	92	6.1	ND	171.5	ND	1.4	ND	1.1	ND	13.4
FID-2G	2	20.9	1.2	ND	34.1	ND	ND	ND	ND	ND	1.6
BG-13	208.9	ND	7.3	ND	2329.3	ND	20	129.5	24.8	ND	155.9
BG-14	3021.9	ND	ND	ND	32573.1	ND	401.9	1912.2	ND	1691.3	3641.7
BG-15	391.3	ND	ND	ND	6218.1	ND	ND	168	ND	139.9	267.2
BG-16	623	ND	ND	ND	8863.9	ND	30.3	250.3	54.3	ND	297.9

Table 51: PCB congeners in surface sediments in ng/kg (continued).

	194	196/196+ 203	197/ _{דן} 197+ 200	198/ 198+199	201	202	204	205	206	207	208	209
BG-1	533	612	110	887	108	ND	ND	22.7	292	43.2	149	321
BG-2	396	507	67.5	683	89	95.5	30.4	23.3	128	24.4	67.9	130
BG-3	201	217	35.2	372	54.3	66.5	14.8	8.7	123	19.3	47.8	95.6
BG-4	58.2	82.9	10.3	108	15.9	20.3	6.6	2.6	38.4	6.1	11.8	14.8
BG-5	101	180	24.4	219	35.8	41.7	12	4.8	60.9	9.6	30.3	34.2
BG-6	186	268	28.8	317	45.2	58.4	15.2	7.6	109	19.7	41	54.8
BG-7	511	553	138	1020	146	156	ND	21.9	135	32.3	137	209
BG-8	141	273	43.3	315	54.5	61	12	6.6	85.4	16.4	44.2	67.7
BG-9	24.8	47	7	49.9	9.1	10.9	2.1	1.1	21	3.7	7.1	14.4
BG-10	38844	48403.5	12080.6	73951.1	13336.5	12555.8	ND	1238.2	ND	1818.1	3624.7	726.4
BG-11	3.7	15	2.1	9.6	2.6	2.5	ND	ND	4.4	0.8	1.6	2.9
BG-12	69.4	199.9	12	120.1	16	16.9	ND	1.6	209	21.3	63.9	54.1
FID-2G	2.9	12	1.9	7.2	2.2	2.3	ND	ND	2.5	0.6	1.4	1.7
BG-13	293.9	311.5	49.7	385.9	58.1	38	13.4	13.4	66.8	7.8	12.6	85.6
BG-14	8679.6	7449.6	1002.8	10165.1	986.7	685.9	258.9	466.4	1398.8	215	434.5	288.9
BG-15	611.2	678.4	150.1	1045.7	136.9	133	43.8	36.2	307	40.6	82	117.6
BG-16	602.3	1024.2	171.5	1317.6	251.2	247.5	70	27	243.1	46.5	109.3	224

Table 51: PCB congeners in surface sediments in ng/kg (continued).

12. APPENDIX 3: CORE DESCRIPTIONS

OV-1	
0-18 cm	Yellow-brown sand
18-30 cm	Yellowish clayey sand
30-44 cm	Brown to yellow clay
44-49 cm	Yellow-brown clay
49-60 cm	Light tan sand
60-100 cm	Gray sand
100-108 cm	Gray sand with organic inclusions
108-118 cm	Yellow sand
118-120 cm	Gray clay
120-133 cm	Yellow sand
133-135 cm	Dark gray sand
135-150 cm	Tan sand
150-151 cm	Orange sand layer
151-165 cm	Yellowish sand
OV-2	
0-23 cm	Brown sand, some coarse
23-40 cm	Transition from vellowish sand to vellowish clav
40-63 cm	Dark grav sand, some organic material
63-86 cm	Tan sand
86-104 cm	Tan sand with spots of darker materials
104-113 cm	Black mud
113-138 cm	Tan sand: grades from darker to lighter.
138-146 cm	Missing, was taken in field for samples
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OV-3	
0-23 cm	Coarse tan sand, organic inclusions
23-28 cm	Dark gray clay
28-34 cm	Brown clay
34-61 cm	White clay mixed with dark clay
61-100 cm	Tan sand and clay mixed with organic inclusions
100-124 cm	Brown clay mixed with organic inclusions
138-142. cm	Orange and brown clay
FID-1	
0-17 cm	Yellow-white sand
17_30 cm	Sand color changes from white vellow to dark
30-66 cm	Grav sand with organic inclusions
FID-2	
0-20 cm	Gray sand with dark strands
20-47 cm	Sand grades to grayish yellow

FID-3	
0-26 cm	Gray sand with dark band
26-34 cm	Black sand
34-39 cm	Tan sand
39-40 cm	Black organic band
40-46 cm	Dark gray sand with organic material
40-46 cm	Dark tan sand
46-57 cm	Dark gray sand
FID-4	
0-12 cm	Tan sand with dark laver
12-24 cm	Tan sand with dark inclusions
24-50 cm	Tan sand with layers of gray sand
50-63 cm	Coarse vellow sand
FID-5	
0-25 cm	Dark gray sand with shell
25-26 cm	organic material
FID-5 cm	
26-28 cm	Tan sand
28-37 cm	Dark gray clay and sand layers
37-80 cm	Tan sand
80-82 cm	Dark band in sand
82-85 cm	Tan sand
85-95 cm	Sand grades from light tan to dark brown
95-116 cm	Brown sand
116-142 cm	Tan fine sand
FID-6	
0-16 cm	Dark gray to brown sand with organic inclusion
16-30 cm	Sand, grades from dark to yellow brown.
30-32 cm	Dark gray organic band
32-100 cm	Dark tan and gray sand
100-200 cm	Dark tan sand with mottles of organic rich gray sand
200-233 cm	Mottles of tan and gray sand
233-291 cm	Gray sand

Core FID-7 was completely consumed by field samples and was not described.