Using Bivalves to Assess Levels of Persistent Organic Pollutants in Tampa Bay

by

Jonelle Tamara Basso

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master's of Science
Department of Environmental Science, Policy and Geography
College of Arts and Sciences
University of South Florida St. Petersburg

Major Professor: Henry Alegria, Ph.D.
Foday Jaward, Ph.D.
Steve Geiger, Ph.D.
Christopher Meindl, Ph.D.

Date of Approval:
April 1, 2011

Keywords: Polychlorinated Biphenyls, Polybrominated Diphenyl Ethers, *Perna viridis*, *Crassostrea virginica*

Dedication

For my parents who have ensured that ‘wisdom and knowledge’ are my watch words, my brother Gregory Basso, in loving memory of Matthew Maharaj (1983-2009), and all students who have a passion for learning and are not afraid of academic challenges.

Acknowledgements

I wish to acknowledge my major professor and committee members, Dr. Henry Alegria, Dr. Foday Jaward, Dr. Steve Geiger and Dr. Christopher Meindl, for lending their invaluable expertise, support and guidance throughout the journey of this graduate degree program.

I am deeply indebted to Mr. Michael Drexler, Mr. Anthony Vasilas (FWRI staff), Mr. Lukasz Talalaj, Dr. Liisa Jantunen (Centre for Atmospheric Research Experiments, Canada), Ms. Candice Simmons, Ms. Nicole Easter-Geary, Mr. Frederick Bradley, Mr. Jaeson Clayborn and Dr. Nekesha Williams for analytical chemistry expertise, GIS assistance and knowledge, patience and friendship.

Much gratitude is due to funding through the STREAMS scholarship program (USF), as well as an unending appreciation to Dr. Christopher Meindl for imparting care, knowledge, and patience from the very inception of my graduate career, ensuring my establishment and foundation at USF.

Sincere thanks to Mr. Gregory Basso and Ms. Joanna John for laboratory assistance, Dr. Nicole John-Thomas, UWI, Mona and USF professors for additional academic expertise and support. An immense thank you is extended to my parents, family, and friends for their tremendous love, support and encouragement.

Table of Contents

List of Tables

List of Figures

Using Bivalves to Assess Levels of Persistent Organic Pollutants in Tampa Bay

Jonelle Tamara Basso

ABSTRACT

Persistent Organic Pollutants such as polychlorinated biphenyls (PCBs) and Polybrominated Diphenyl Ethers (PBDEs) have been measured in water and sediment samples as well as marine fauna regionally and globally. PCBs and PBDEs persisting in the environment not only impact organisms inhabiting contaminated ecosystems, but may pose a serious threat to human health. This study seeks to measure the concentrations of these anthropogenic compounds in Tampa Bay waters, with the assumption that a representative fraction of the toxins will accumulate in bivalve tissue. Through GC ECD analysis, it was shown that there is an incidence of PCBs and PBDEs in the Tampa Bay area, with the highest quantity of POP observed in visceral bivalve tissue being 25.93pg/g (25.93 ppb) for BDE-99, and was recorded for the TECO Power Plant Manatee sample site in September 2009, using the green mussel as an indicator. Data obtained for this research will be used for continuous biomonitoring purposes. Comparable studies identify maximum POP concentrations permissible prior to a need for advisory to be 14,600pg/g, which is vastly greater than any value recorded for this study, and helps to conclude that the concentrations of PCBs and PBDEs in Tampa Bay could currently be considered negligible.

Chapter One

Introduction

Background

Persistent organic pollutants constitute a class of contaminants characterized by their persistence, long half-lives in soils, sediments, air and biota, as well as hydrophobicity and lipophilicity (Ramu et al., 2005; Gouin et al. 2000; Jones and de Voogt, 1999; Tilbury et al., 1997). In addition, these chemical compounds exhibit susceptibility to long-range atmospheric transport (Jaward et al. 2004), and demonstrate varying levels of toxicity (Wang et al., 2010; MacKay et al., 2001). Resistance to metabolism in combination with characteristic lipophilicity makes persistent organic pollutants bioaccumulative, and thus susceptible to transport through terrestrial and aquatic food chains. Numerous animal and human studies have linked a wide variety of health problems to exposure to persistent organic pollutants, which include reproductive abnormalities, birth defects, immune system dysfunction, neurological defects and cancer (Andric et al., 2000; Antignac et al., 2008; Barron et al., 1994).

Persistent organic pollutants have received intense international regulatory attention in recent years due to their ubiquity, persistence, high bioaccumulation potential and harmful biological effects (Rodan et al., 1999). The Stockholm Convention on Persistent Organic Pollutants, adopted May 22, 2001 (Karlaganis et al. 2001), remains a global treaty that has banned or severely restricted twelve chemicals: dioxins and furans

(polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans, PCDD/Fs); polychlorinated biphenyls (PCBs), hexachlorobenzene (HCB), dichlorodiphenyltrichloroethanes (DDTs), chlordanes, toxaphene, dieldrin, aldrin, endrin, heptachlor and mirex. Yet despite the implementation of stringent restrictions, substances such as DDT continue to be used illegally for agricultural practices in countries such as Mexico (Alegria et al. 2000). These aforementioned compounds are often referred to as ”legacy” persistent organic pollutants due to their long history of use and release into the environment. Nonetheless, there are numerous additional persistent organic pollutants which are also environmental contaminants and of great concern. Some are both persistent and toxic, and still in widespread production and distribution. Such compounds are currently being used in lesser and more developed industrialized countries throughout the world. These additional persistent organic pollutants are often referred to as “emerging” persistent organic pollutants, and describe “pollutants recently discovered in the environment and known or suspected to cause adverse effects in humans and wildlife.” Examples of “emerging” persistent organic pollutants include several types of brominated flame retardants such as Polybrominated diphenyl ethers (PBDEs), perfluorinated compounds, and polychlorinated naphthalenes (PCNs) (Eljarrat and Barceló, 2003).

Consequently, there has been much interest in the scientific community to understand the fate and transport of persistent organic pollutants in the environment. There is especially a need to investigate emerging persistent organic pollutants. Surprisingly, a review of the literature indicates a paucity of data on these pollutants in Tampa Bay, Florida. While previous reports have illustrated the presence of a number of

these chemicals in biota and sediment in Tampa Bay and elsewhere, these results have been limited and certainly not comprehensive in scope. The U.S. National Oceanic and Atmospheric Administration (NOAA) Mussel Watch Program, for example, uses samples of bivalves for assessment of such pollutants, where Tampa Bay is included as one of their 300 monitoring sites around the country. Of these 300 sites, 7 are monitored for the Tampa Bay area, where date and year are left unrecorded for the report that reflects results for a multi-year period. Considering the sheer size of Tampa Bay, together with the large and ever increasing human population that surrounds it, this lack of data represents an area ripe for pursuit.

One strategy that has been previously employed in determining the fate of persistent organic pollutants is the use of sentinel species (Fisher et al., 2000), which are especially susceptible to these compounds. The oyster *Crassostrea angulata* and the clam *Ruditapes decussates*, for example, were used in a study conducted by Ferreira and Vale (1998), in an effort to analyze and determine the effect of exposure of polychlorinated biphenyls (PCBs) to these bivalves under a controlled laboratory environment. Bivalves are susceptible to bioaccumulation of these pollutants, due to their considerable lipid content, because of their filter feeding characteristics, and since they are sessile in nature. Thus, by deduction, the internal chemical components of bivalves will be indicative of the external local environment of which they are a part. These animals may therefore be useful in helping to indentify pollutants in aquatic environments, especially at point source pollution locations.

Research Project

Within these chapters are detailed results and discussion of the research project with the following objectives: 1) Identification of levels of "legacy" persistent organic pollutants (POPs), particularly polychlorinated biphenyls (PCBs), and "emergent" POPs, specifically polybrominated diphenyl ethers (PBDEs). The green mussel *Perna viridis* and the American oyster *Crassostrea virginica* are the sentinel species used in this study to indicate the extent of PCB and PBDE pollution in Tampa Bay. 2) Determination of any correlation between the incidence of these compounds in the upper, middle and lower Tampa Bay sites, and current land-use patterns. 3) Identification of any difference in bioaccumulation of specific compounds in the two sentinel species engaged. 4) Suggestions for revision of regulatory mandates that are intended to protect humans, terrestrial and aquatic species, but may still be inadequate with respect to human health risk. This is important because of potential exposure to these compounds during commercial harvest and consumption.

Research project location

Tampa Bay, Florida, is the largest open-water estuary in the state, and has a surface area of approximately 1000 km^2 and watershed area of 5700 km^2 (Johansson and Lewis, 1992). This sub-tropical estuary is situated in Central Florida on the Gulf of Mexico coast, is "Y" shaped, and is subdivided into the Lower Tampa Bay, Old Tampa Bay, Hillsborough Bay, and Middle Tampa Bay basins, with an average depth of 4 meters (Chen, 2006).

Figure 1. Map of Tampa Bay, Florida

As seen in Figure 1 (generated in ArcGIS 9.9.2), Pinellas, Hillsborough and Manatee counties surround the Bay area, and contain the highly urbanized cities of Tampa, Clearwater and St. Petersburg.

Tampa Bay exhibits biological diversity and richness, and is fed by significant tributaries and rivers such as the Alafia, Manatee and Hillsborough Rivers. According to Xian et al. (2007), the bay's major drainage basins are named Coastal Old Tampa Bay, Coastal Hillsborough Bay, Hillsborough River, Alafia River, Coastal Middle Tampa Bay, Boca Ciega Bay, Terra Ciega Bay, Coastal Lower Tampa Bay, Manatee River and Little Manatee River. Significant urbanization and development has occurred in all but the Manatee and Little Manatee River basins. The coastal location, amiable climate and recreational facilities are major attractions.

Urbanization has altered the structure and nature of the Bay's ecology causing an increase in total impervious land surface area, as well as having perpetuated water quality modification in terms of organic and inorganic compound inclusion. The average annual non-point source loadings for the Hillsborough, Alafia and Little Manatee Rivers (for Total Suspended Solids) are 2085, 5067, 2521 tons/year respectively (Xian et al., 2007). The Alafia River single-handedly contributes a considerable amount of point and non-point land-based pollution from phosphate mining and other fertilizer manufacturing plants in the watershed (Johansson and Lewis, 1992). Tampa Bay has also accommodated extensive industrialization, where Hillsborough Bay has been an important shipping port. Phosphate mining areas and agricultural lands contribute runoff to the east of the Bay, in addition to processing and power plants located in the same general location. Furthermore, crabs, oysters, mussels and other aquatic creatures are collected for

consumption from the Tampa Bay estuary. Previous research by Karouna-Renier et al. (2007), focused on analysis of dioxins/furans, dioxin-like PCBs and inorganic contaminant levels in blue-crabs *Callinectes sapidus* and oysters *Crassostrea virginica* at Pensacola, Florida. Chemical accumulation of contaminants from organisms positioned lower in the food chain may indicate the potential for biomagnifications within people and therefore require consumption advisories.

Polychlorinated Biphenyls (PCBs)

Polychlorinated Biphenyls (PCBs) form part of a significant class of persistent (Ucan-Marin et al. 2009) organic pollutants (POPs). They are highly stable (Safe et al. 1985), and are useful industrial nonionic toxic chemicals (as are dichlorodiphenyltrichloroethane (DDT), polycyclic aromatic hydrocarbons (PAHs) and other organic pesticides (Novotny, 2003). PCBs may have 1, 4 or 8 chlorines in their structure (vanLoon. 2005), have many (209) congeners, with the compound being a forerunner to the more toxic dioxin product. According to Safe et al. (1985), the most active PCBs congeners, 3,4,4,5'-tetra-, 3,3',4,4'-tetra-, 3,3',4,4',5-penta, and 3,3',4,4',5,5'-hexachlorobiphenyl, are substituted at para and two or more meta positions. These congeners are illustrated in figure 2 below. Relative congener toxicity mirrored biological potencies. The wide use of these organic soluble compounds include instances in transformers, use as dielectric and heat transfer fluids, flame retardants, plasticizers, and wax extenders (Safe et al. 1985). Residues have been identified in lakes, rivers, human adipose tissue, blood and breast milk, fish and aquatic wildlife, and in almost

every constituent of the global ecosystem. PCBs and PBDEs are structurally similar (having comparable physical-chemical properties), and may therefore behave analogously in the environment. (Ter Schure et al., 2004). They bring forth common toxic and biological effects. Thymic atrophy (a wasting away syndrome in PCB exposed animals) is characteristically caused by PCBs. Other effects include immunotoxic responses, reproductive problems, porphyria and related liver damage.

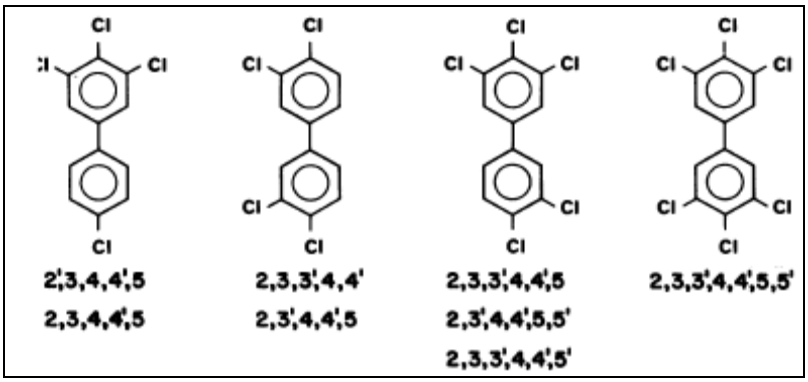


Figure 2. A diagram showing the structure of the most active PCB congeners. Adopted from Safe et al. (1985) PCBs- Structure-Function relationships and Mechanism of Action.

Although most PCB accumulations are limited to urban and industrial areas, compound contamination has been traced to polar regions (Iwata et al. 1993), as well as freshwater and aquatic sediments. Atmospheric transboundary transport enables the distribution of such compounds from their point of use to remote global regions (Alegria et al. 2000). These compounds have very low solubility, and so have large octanol partition coefficients (K_{ow}), ranging between 10^4 and 10^6 L/kg. Persistence is related to the number of chlorinated sites in the two-ring structure. (Novotny, 2003).

PCB partitioning

Environmentalists are concerned with the occurrence of PCBs with respect to their fate and transport in sediments and natural waters. Dioxins and PCBs have limited solubility in water, and because of their large K_{ow}, they tend to partition in soil, especially those with significant organic content (vanLoon. 2005). Experiments conducted by Steen et al. (1978) looked at partitioning of two PCB mixtures (Aroclor 1016 and 1242), where bottom sediment samples were collected with an Eckman dredge (at 4 cm depth), from three ponds in Georgia. Particle size, total organic carbon (TOC) and pH were recorded for each, and the PCB mixtures were provided by the United States Environmental Protection Agency (US EPA). Extraction procedures made use of whole samples, which were centrifuged (10,000 rpm for 20 minutes), decanting the aqueous phase and extracting the isooctane (Steen et al. 1978). Gas chromatography MicroTek® 220 model using nickel (Ni) electron capture was used for analysis. The study showed that PCB partitioning, desorption and adsorption happens quickly with natural sediment. Sediment size and TOC were important for interpretation of partitioning behavior, and it was concluded that other PCB mixers and isomers should partition similarly with sediment. Geographic distribution of soils and Geographic Information Systems (GIS) soil maps can help reveal soil profiles which relate to hydrological profiles (Novotny, 2003), and pollutant movement in the environment, as well as partitioning characteristics. For example, it will take thousands of years for hydrophobic compounds such as DDT and PCB to be removed from one meter of soil column via natural leaching, as opposed to nitrate that will take less than one (1) decade. Removal from soil is primarily by volatilization and biomodification of lower PCBs. This long retention time dictates the

allowable input limits for pollutants in topsoil, and to therefore avoid rapid accumulation of pollutants in the soil (Novotny, 2003). The Hydrologic Simulation Program-Fortran (HSP-F) can be used to model particulate pollutant transport.

Research conducted by V.A. McFarland and J.U. Clarke (1989) have illustrated a trend for larger molecules to be less soluble in octanol (the carbon content which is associated with surface media, such as soil and sediment), and may therefore partition less easily into the site of toxic action within cells.

Half-life/ Half-distance and Distribution

Characteristic travel distance (CTD), or half-distance (analogous to a half-life) for a substance present in a mobile medium related to chemical properties can contribute to coherent assessment of long-range transport potential of environmental pollutants and lead to identifying compounds requiring justified regulation and restriction. (Beyer et al. 2000). PCB concentrations have been determined in air and surface water, with concentrations being greater in the Northern Hemisphere than the Southern (Iwata et al. 1993). Estimations of fluxes by gas exchange across the air-water interface provide insight into the dispersal of organchlorines through oceanic atmosphere depending on their Henry's law constants and the tendency of more transportable ones to deposit into the cold waters as an ultimate sink (Iwata et al. 1993). Once these compounds enter into the gas phase, they are subject to long range transport (Harrad. 2010), hence their ability to reach the poles.

Polybrominated Diphenyl Ethers (PBDEs)

Polybrominated Diphenyl Ethers (PBDEs) are presently considered “emerging” Persistent Organic Pollutants (POPs). They share considerably close physico-chemical similarity to PCBs and dichlorodiphenyltrichloroethane (DDT), and are also bioaccumulative, lipophilic and persistent (Antignac et al. 2008, de Boer et al. 2000, Gouin and Harner, 2003, Ramu et al. 2005). In addition, PBDEs (like PCBs), theoretically possess 209 congeners. The basic chemical structure of a generalized PDBE compound is illustrated in Figure 3 Global PBDE production estimated at 40,000 tons in 1992 (Harner and Shoeib, 2002).

This group of chemical compounds currently has no known geological boundary or limitation, being able to affect even remote reaches of the globe. PBDEs have been chemically engineered for primary use as (reactive and additive) flame retardants, with “the main justification for their utilization” being “their ability to prevent the development of fire by delaying ignition and reducing the combustion rate” (Antignac et al. 2008), and they save lives (Kimbrough et al. 2009). Such chemicals have been added to polymers in materials which include plastics, textiles, (polyurethane) furnishing foam, automobiles, paints, aircraft, and electronic circuitry, all in an effort to avoid fire initiation (Rahman et al. 2001, de Boer et al. 2000). The risk of fire is decreased via this interference “with the combustion of the polymeric materials” (Jaward et al. 2004). According to Covaci et al. (2003), hexabromocyclododecane (HBCD), Tetrabromobisphenol-A (TBBP-A), and Polybrominated biphenyls (PBBs) join PBDEs in being the most used Brominated Flame Retardants (BFRs).

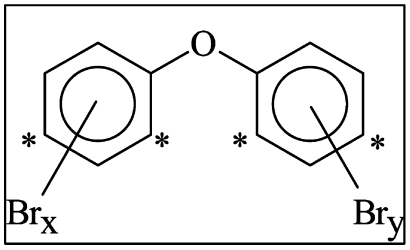


Figure 3. Diagrammatic illustration of the Polybrominated Diphenyl (PBDE) chemical structure, according to Rahman et al, 2001. The asterisks are representative of the most active substitution sites on the rings.

Chemical retention time in the aqueous component of the world's biome will be considerably shorter than in particulate matter, sediment and fatty acid components, where they tend to sorb. This phenomenon leads to the broad distribution of PBDEs in the natural environment and given that they are emerging compounds, it is speculated that they will eventually be observed in greater concentrations than that of PCBs. Their fate, transport and deposition continue to be of environmental (Jurado et al. 2005) and toxicological concern, for both animals and humans. PCB was found in human breast milk collected from mothers in Sweden (Hooper and McDonald., 2000) highlighting a need for a breast milk monitoring program, for the United States population in order to assess current levels. This stems from observing levels from 0.3-98.2 ng/g lipid in human adipose tissue observed in a subset of mothers in Sweden (Hooper and McDonald., 2000). Their results point to the increasing levels of PBDEs, which may present likelihood of developmental toxicity. Reports show that "tetra-BDE congener, BDE-47, and a penta-BDE congener, PBDE-99, the major congeners in human tissue" given to lab mice in 0.7g and 10.5g doses "on postnatal day 10 resulted in permanent aberrations in motor behavior that worsened with age" (Hooper and McDonald. 2000; pg. 391). They conclude that the health of infants and the unborn can be significantly protected from

exposure to these POPs via limiting the exposure and accumulation of POPs in the mother, by possible use of alternatives to persistent organic pollutants that prove to be environmentally friendly.

In 2005, Ramu et al. reported the incidence of PBEs and organochlorines in Hong Kong, using trapped individuals from the *Sousa chinensis* (Indo-pacific humpback dolphin) and *Neophocaena phocaenoides* (finless porpoise) species from 1995-2001. Via analysis of liver, blubber and kidney matter, it was determined that PBDEs were the forth most prevalent class of organohalogen (preceded by DDT, PCBs and chlordanes [CHLs], in that order). Total PBDE concentrations "in the blubber of finless porpoises" were 230-980 ng/g lipid weight and 280 to 6000 ng/g lipid in humpback dolphins (Ramu et al. 2005). The difference in contamination levels between species was attributed to a disparity in habitat. Humpback dolphin live primarily in the western estuarine environment and the finless porpoise live primarily in the oceanic-influenced eastern waters. Three PCB congeners, BDE-47, BDE-99 and BDE-100 constituted approximately 90% of the total PBDEs analyzed (BDE-3, BDE-15, BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, and BDE-209) (Ramu et al. 2005).

Wang et al. (2010) studied organochlorine pesticide incidence across 16 research sites on the Tibetan Plateau for 1 year (July 2007 to June 2008), using passive air sampling procedures. PBDE and PCB were assessed and showed that 22-72% of total PBDEs were BDE 47, and 14-47% were BDE 99. BDE-47 had a "greater reported atmospheric travel distance than BDE-99". The results helped conclude that PBDEs exhibit long range transport (LRAT), as well as local distribution.

PBDE Partitioning

Although PBDE health, toxicological and LRAT issues are of great concern, there is a great paucity of studies, particularly for the Tampa Bay region. The United States National Oceanic and Atmospheric Administration (NOAA) is responsible for the Mussel Watch initiative that assessed PBDEs in bivalves and sediment at locations across Alaska, Puerto Rico, Hawaii and the Continental United States. The Mussel Watch program was established in 1986 "in response to a legislative mandate under Section 202 of Title II of the Marine Protection, Research and Sanctuaries Act (MPRSA) (33 USC 1442)" (Kimbrough et al. 2009; pg. 2). According to Kimbrough et al. (2009), it was determined that human exposure to PBDEs occur as a result of contaminated food consumption (including human breast milk), as well as contaminated dust from the workplace or home. Environmental sources of PBDEs may be from point sources such as industrial outflows of waste materials or discharge during manufacture procedures containing PBDEs, and sewage outflows. Diffuse sources of contamination may be due to the global 'grasshopper effect' of long range transport and deposition of substances, thus resulting in the current PBDE (and other organochlorine pesticide) levels observed in the Inuit people of the Arctic (Bonefeld-Jorgansen and Ayotte. 2002; Jantunen et al. 2000). According to Kimbrough et al. 2009, further circulation methods must be considered, in addition to unintentional spills of contaminated materials, leaching of old, used consumer products and burning of municipal waste. Furthermore, PBDEs are shown to be present in abiotic and biotic media, which include sediment, fish, bivalves, bird eggs, marine and terrestrial mammals and human plasma (Kimbrough et al. 2009; Harner and Shoeib; 2002). This class of chemical contaminants is stated to have "low vapor pressures, very

low water solubility, and high octanol-water partition coefficients (Log K_{OW}) values" (Kimbrough 2009), and thus possess similar environmental behavior to that of other POPs. Furthermore, work by Gouin and Harner (2003) illustrate the use of the principle of steady-state equilibrium, and mass balance modeling, in an effort to explain partitioning and overall persistence of PBDEs into the environment to three components; water, air and octanol.

Half-life/ Half-distance and Distribution

With the capability of bioaccumulation (process whereby chemical storage occurs in the bodies of exposed organisms, and concentration can increase with time) evident, the limitation of data available on such studies makes it unclear as to media-specific degradation and half-life schematics (Gouin and Harner; 2003). According to Hooper and McDonald (2000), 2,2', 4,4'-tetra-(PBDE-47), 2,2', 4,4', 5-penta-(PBDE-99), 2,2', 4,4', 5,5'-hexa-(PBDE-153) are given examples of the 209 congeners of the PBDE group, primarily used for their assistance in impeding fires, albeit releasing bromine (Br). The Penta commercial mixture was shown to have a 25-47 day half life in rodents, with uncalculated equivalents for humans (in years). In terms of toxicity, these examples provide no data on carcinogenic properties, but showed deleterious effects toward neurodevelopment, Ah receptor activity and thyroid activity.

Crassostrea virginica

Crassostrea virginica, also commonly referred to as the American oyster, or Eastern oyster, belongs to the class Bivalvia, order Pteroidea and family Ostreidae. Individuals of the species are found in estuaries and drowned river mouths, along the Eastern North American coastline (ranging from the Gulf of St. Lawrence in Canada to Key Biscayne in Florida), reaches in the West Indies, and possibly to Atlantic South America, though South American taxonomy is not certain. Geographical locations such as the Gulf of Mexico show large prevalence of the species. Oysters "are the keystone species of a diverse community in the estuarine ecosystem", and also shows importance with respect to commercial fishery support along the Eastern North American coastline, supporting more than 10,000 employees in the oyster industry (Sellers et al. 1984).

These sessile organisms possess thicker and heavier left valves, which the American oysters use cement unto substrate. The shell shape and thickness is variable (figure4).

Figure 4. Oysters of variable shape and size are seen cemented on mangrove at Ruskin, Florida. Shell thickness is variable with environmental conditions.

Individuals between 3-5 years in age exhibit a range of length from 10-15 cm. Male and female individuals of the species release gametes into the surrounding water,

with temperature being an important factor in spawning and production of gametes. Tidal cycles and amount of sunlight are additional factors, with actual spawning being initiated by at least one male releasing sperm and pheromone into the surrounding water. Females are capable of producing “23.2 to 85.8 million eggs per spawning, with the number of eggs proportional to the size of the individual” (Sellers et al. 1984). Annual spawning duration lasts from April to October at locations such as the Gulf of Mexico, with longer spawning seasons being characteristic of warmer climate. Following fertilization of gametes, meroplantonic oyster larvae linger in the surrounding water for 2 to 3 weeks after which, the then juvenile oysters attach to substrate. Liquid cement droplet exudes from the juveniles, the foot and velum are lost, and the young oysters are characteristically known as spat, which set in established oyster beds.

Although male and female are distinct in this species (dioecious), gender change is likely. Young oyster individuals are mostly male, with increased conversion to the female gender more apt with age. Like spawning, temperature affects growth (increased death rates with higher temperatures), with greatest growth occurring in the months of August and September, closely following spawning. Other factors affecting growth include surrounding water turbidity, food (planktonic density), salinity (preference for more than 12.5 parts per thousand) and intertidal exposure.

Like the green mussel, Crassostrea virginica is harvested for consumption and is “also one of the predominant species used in mariculture” (Sellers et al. 1984), with market quality being variable, according to annual seasonal changes, and influenced by mortality by various predators (starfish *Asterias forbesi* in saltwater, gastropod oyster drills *Urosalpix cinerea* and *Eupleura caudata* in saltwater, flatworm *Styochus ellipticus*

in brackish water, crabs *Cancer irroratus*, *Callinectes sapidus*, and *Carcinus maenus*), and diseases (*Vibrio* and *Pseudomonas* bacteria, *Dermocystidium* fungus, *Minchinia nelsoni* protozoan causing multinucleate spheroid unknown [MSX], *Minchinia costalis* protozoan).

Oysters are filter feeders, with primary food being naked flagellates of a 3-4 micrometer size range. Being sessile filter feeders, any other compound in that size range also gets filtered, and so this species has been used to determination of surrounding water quality assessment. As a result, the NOAA mussel watch program has adopted the use of this species for assessment of PBDEs around the United States according to legal mandate under Section 202 of Title II, Marine Protection, Research and Sanctuaries Act (Kimbrough et al. 2009). Further research includes, but is not limited to a study conducted by Karouna-Renier et al. (2007), completing screening of organic and inorganic contaminants in *Callinectes sapidus* (blue crabs) and *Crassostrea virginica* at Pensacola, Florida. Analysis was completed for 12 dioxin-like PCBs, mercury, 17 dioxin/furans and other metals, and contamination levels were determined. Screening levels, calculated using U.S. EPA consumption advisories, were compared to results and it was established that blue crabs posed a greater risk to human health than oysters in this scenario. Nonetheless, this sessile species has been shown to be useful in the determination of water quality analysis of the local environment of the American oyster.

Perna viridis

This species of bivalve, also commonly known as the green mussel, is native to the Indo-Pacific. *Perna viridis* is also a Caribbean basin and subtropical southeastern North American invader (Baker et al. 2007) (Figure5). Through anthropogenic practices such as global transshipment traffic and travel, they are easily transported to commercial harbors, such as Tampa Bay. Authors have theorized but not shown that molluscan gametes travel as mobile planktonic larval phases, within the ballast water found in these vessels. Transportation also may include intentional introduction through fisheries shipping and accidental relocation via attachment, seen by ship hull fouling.

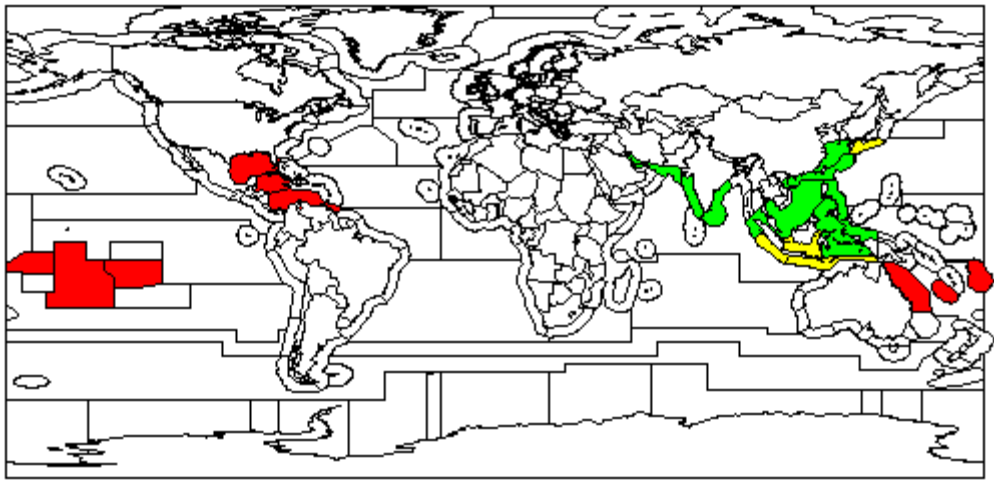


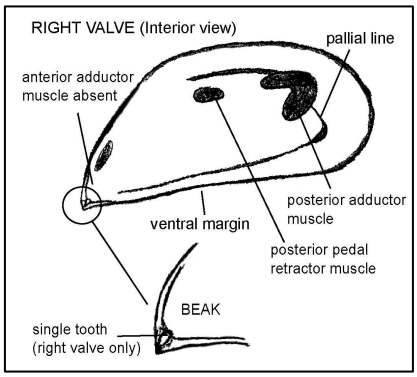
Figure 5. Diagrammatic depiction adopted from the National Introduced Pest Information System (NIMPIS) (2002), of native habitat of Perna viridis (green coloration), as well as crytopgenic regions (yellow), and where the species has been introduced (red).

This species of *Perna* was first observed in Trinidad in 1990 (Buddo et al., 2003; USGS; 2001), and had been subsequently sited in the waters of Jamaica's Kingston Harbor in 1998, and Tampa Bay in 1999 (Baker et al. 2007). It is invasive and as a result,

possesses the capability of displacing naturally occurring fauna in a given locality. University of the West Indies personnel thus sought to monitor ten sites around Kingston Harbor from February 2000 through January 2001, making note of "mussel density, physicochemical parameters, suspended solids, microalgae and gut contents" (Buddo et al. 2003). According to Rajagopal et al. 2006, salinity, availability of substrate (critical for sessile organisms), and human removal are all factors affecting species densities, despite the fact that they thrive well amid environmental fluctuations. *Perna viridis* belongs to the Phylum Mollusca, Class Bivalvia and Mytilidae family. It is an edible bivalve with a diploid number of 30 chromosomes, and is closest related to *Perna perna* (which constitutes 28 diploid pairs). During the pediveliger larval stage (one of its many larval stages), byssal threads are produced from the pedal organ that allows the organism to hold fast to substrata (Figure 6).

This filter feeder utilizes gills for gaseous exchange purposes, as well as for acquisition of nutrients from surrounding waters. As a result, the species booms in regions rich in organic matter, such as bays and estuaries, which include Tampa Bay and Charlotte Harbor (USGS. 2001). Shell length averages 20mm between 2-3 months of age, with a standard life of 3 years, and possessing the capability of reaching up to 6 inches in length. Figure 4 illustrates the measurement of a *Perna viridis* individual used in the study, normally averaging less than 30mm in length. The organism favors environments with a temperature range of 27-32 ^{o}C, and a salinity of at least 16 parts per thousand. Spawning is broadcast, with eggs and sperm being released into surrounding waters, with a peak-spawning time once per annum. Young individuals in the species are brilliant green in color, whereas adults are brown and green.

a.



b.

Figure 6. A graphic representation of Perna viridis species under observation for this study, where in this scenario, the individual measures just shy of 40mm centimeters in length.

In actuality, these filter feeders have the potential to accumulate any organic and inorganic (particulate) matter found in its environment, in addition to the bioaccumulation of material that it may filter (Rajagopal et al. 2006). According to comprehensive research completed by Lee et al. (1999), the Tap Mun, Sai Kung, and Ma Wan shellfish rearing sites in the waters off Hong Kong confirm variable levels of sewage contamination. By sampling and analysis of *Perna viridis* in this region, it was confirmed through antigen capture polymerase chain reaction, that there was incidence of Hepatitis A (HAV) in species individuals at Tam Mun and Sai Kung only, which can subsequently be ingested and made manifest in humans. Conclusions from water samples indicated that the three sites display different fecal coliform quantities according to viral and bacteriological results. At the Tap Mun sample site, mussel fecal coliforms were 7500 per 100g, with a corresponding coliphages value of 4152 per 100g, 470 (per 100mL) water sample faecal coliforms, and water sample coliphages <5 (per 100mL). The Ma Wan site showed much larger values of 12,000 (f. coliforms per 100g),

8125(coliphages per 100g), 140 (f. coliforms per 100mL), 230 (coliphages per 100mL), compared to Sai Kung which had smaller figures of 460 (f. coliforms per 100g), 1000(coliphages per 100g), 61(f. coliforms per 100mL), 155(coliphages per 100mL). This disparity in recorded bacteria levels can be attributed to location variation, albeit, the study proves that it is imperative to "better delineate the public health risk and allow appropriate risk minimization measures to be drawn up" and that "indigenous shellfish could be used as a monitoring tool for indicating the presence of HAV in their surrounding waters" (Lee et al. 1999). Likewise, *Perna* species is able to exhibit bioaccumulation of persistent organic pollutants.

PROJECT HYPOTHESES

The hypotheses of this study are as follows:

1. There is an incidence of Persistent Organic Pollutants (POPs) in Tampa Bay.
2. There is a clear pattern between incidence of POPs and land use in Tampa Bay.
3. There is a clear pattern observed between species type and size in relation to bioaccumulation of POPs in Tampa Bay.

Project significance

Successful completion of this research project will add to the body of literature using sentinel species for identification and quantification of persistent organic pollutants. It may also prove useful in determining the fate and transport of these compounds in the Tampa Bay region, serving as a toxicological study of the movement of pollutants through aquatic and terrestrial food chains. The results of this research project illustrate in detail that the objectives pursued therein were attained, and will add to the body of knowledge of those investigating the identification and quantification of polychlorinated biphenyls and polybrominated diphenyl ethers, in Tampa Bay in particular, but also in the regional and international environment.

Due to the ease of collection of individuals of each species, the study can be repeated locally, nationally and also on an international scale. The enclosed results will furthermore supplement and aid existing regulatory documentation and activity, with pertinence to human health, specific food consumption and consumption advisories.

Additional Geographic Information Systems (GIS) application for environmental monitoring may enhance determination of fate and transport of persistent organic pollutants, and suggestions for appropriate risk assessment. These will be in accordance with ever changing land use characteristics, industrial practices and population dynamics.

Chapter Two

Methodology: Incidence and quantification of Persistent Organic Pollutants in Tampa Bay

Field Collections

Collection of *Crassostrea virginica* and *Perna viridis* was conducted during the months of August, September and October of 2009, and individuals were taken from the Lower, Middle and Upper Estuarine regions. These points included, and are not limited to, Bird Cay sea wall, Boca Ciega Bay, Vinoy sea wall, TECO Power Plant Manatee, Bay Shore sea wall. Site locations were congruent with previously established Florida Fish and Wildlife Research Institute (FRWI) Molluscan laboratory sample and restoration positions. Additional sampling was also conducted in September 2010, October 2010 and January 2011, at the E.G. Simmons Park, Ruskin, the Upper Tampa Bay Park, Hillsborough County, Tampa, and Safety Harbor. Global Positioning System (GPS) coordinates were recorded for each sample sites, as provided in table 1. Individuals were collected at the Vinoy sea wall, TECO Power Plant Manatee and lower estuary locations for more than one consecutive month, in order to demonstrate the repeatability of the

study. Ten individuals of each species were collected at each site; however, where 10 individuals were not found, as many individuals as possible were collected and kept in a freezer in labeled and dated Zip-Lock bags until shucking and individual biological characteristics were recorded.

Global Positioning System (GPS) coordinates were recorded at each site (Figure 7) where specific locations were sampled for consecutive months in an effort to demonstrate the research repeatability. Combination and subsequent analysis of different data layers using Geographic Information Systems (GIS), made it possible to identify areas which are more susceptible to overland flow or physical transportation (Erickson, 1997), one pathway of pollutant transport to the aquatic environment. Industrial areas and other classifications were also determined.

Ambient water temperature (^{0}C), salinity (ppt), dissolved oxygen (%) and dissolved oxygen (mg/L) were measured and recorded using a hand-held YSI Multiparameter Meter at every location, excluding those at Tampa and Ruskin, Florida. Data for the mentioned parameters are offered in table 1. Ten (10) individuals of each species were collected at each site; however, where ten individuals were not found, as many individuals as possible were collected and kept in a freezer in labeled and dated Zip-Lock bag until shucking and individual biological characteristics were recorded.

Table 1. Site location with respective Global Positioning System coordinates, dissolved oxygen (% and mg/L), Temperature and Salinity Data.

Site	Global Positioning System Coordinates		Dissolvd oxygen (%)	Dissolved oxygen (mg/L)	Temperature (^{o}C)	Salinity (ppt)
	Latitude	Longitude				
Vinoy Sea Wall	27N 46’ 6.52”	82W 37’ 5.56”	6.08	3.96	29.9	27.6
Teco Power Plant	27N 48’ 3.74”	82W 24’ 6.90”	76.5	4.50	31.5	25.8
Upper Estuary	27N 53’ 8.82”	82W 26’ 0.56”	13.5	0.90	29.2	25.3
Upper Estuary	27N 53’ 7.22”	82W 29’ 2.55”	39.8	2.74	28.5	22.4
UE Sea Wall Shell	27N 53’ 5.53”	82W 32’ 4.64”	-	-	31.8	26.5
Lower Estuary	27N 44’ 2.78”	82W 41’ 6.35”	24.5	1.68	28.8	33.6
Lower Estuary	27N 44’ 2.36”	82W 41’ 6.08”	22.7	1.50	29.0	33.5
Lower Estuary	27N 43’ 3.92”	82N 44’ 2.62”	58.4	3.81	29.3	35.0
Bird Cay Sea Wall	27N 41’ 1.55”	82W 43’ 1.33”	77.4	4.93	29.3	34.8
Bird Cay Sea Wall	27N41’ 1.25”	82W 43’ 0.42”	99.6	6.30	29.4	34.9
Ruskin E.G. Simmons	N27° 44.1208'	W082° 27.847'	-	-	-	-
Upper Tampa Bay Park	N28° 0.8804'	W082° 38.0303'	-	-	-	-
Safety Harbor	27°59'26.88 "N	82°41'16.8" W	-	-	14.29	24.23

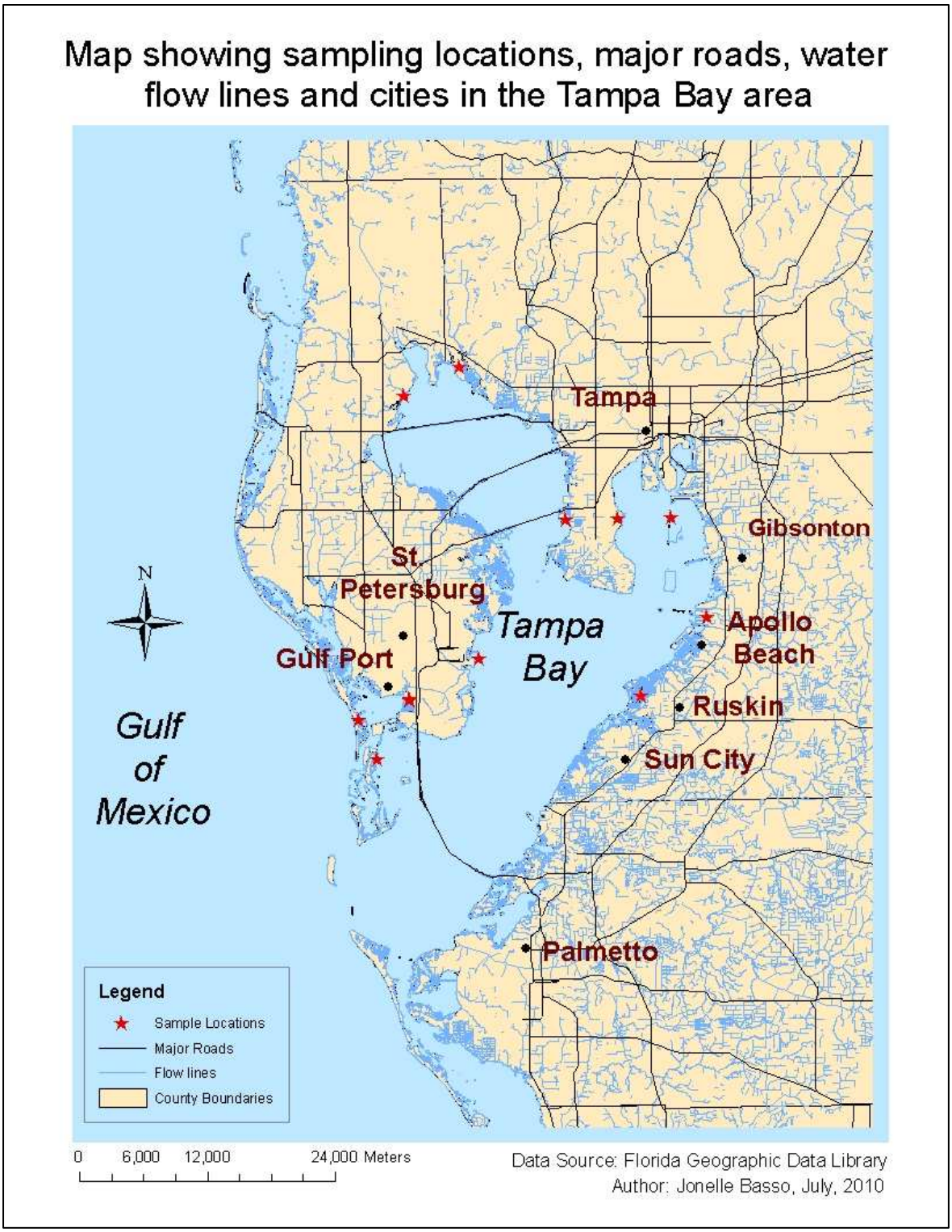


Figure 7. Sample locations map

Sample cleaning and physical examination

Zip-Lock bags containing individual shellfish from each site were removed from freezer conditions and individuals were left to thaw. Each individual was scrubbed placed in pre-cleaned vials after large enough fouling material fixed to the shells was removed. Vials with 25 and 32 milliliter (ml) volumes were baked overnight at 450 ^{0}C in order to kill any organics in or on the glass. Following baking, vials were subsequently washed with pesticide-grade hexane, then pesticide-grade acetone under the laboratory fume hood. The opening of each vial was covered with foil. Lengths (mm), total weight (g), vial weight (g), vial and meat weight (g), meat weight (g) were recorded for every individual (Figure 8. Table 2). Edible (visceral) tissue from each individual was kept frozen in separate vials until required.

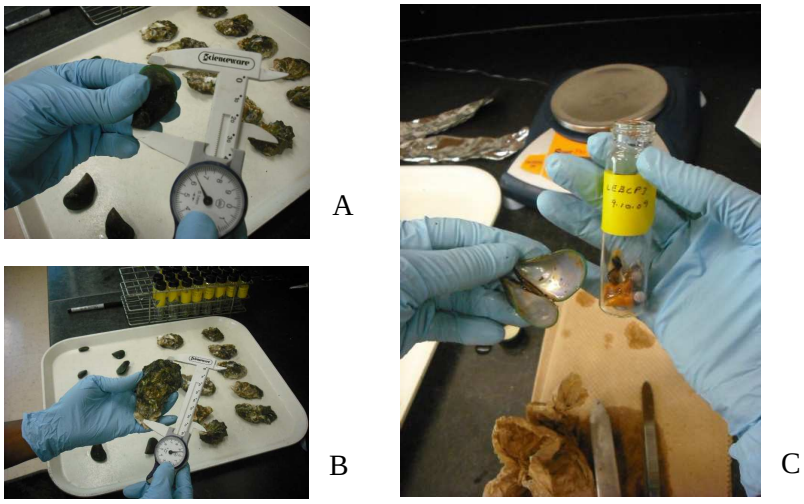


Figure 8. Illustration of measuring lengths of *P. viridis* (a) and *C. virginica* (b), and already shucked visceral matter from the third *P. viridis* individual (c) from the Lower Estuary, Boca Ciega area, Tampa Bay, Florida.

Table 2. Average total weight, vial weight, vial and meat weight, meat weight and length for all individuals of *C. virginica* and *P. viridis* used in the study.

Species	Total weight (g)	Vial weight (g)	Vial and meat weight (g)	Meat weight (g)	Length (mm)
C. virginica	23.45	19.69	23.10	3.41	52.56
P. viridis	12.07	20.40	23.93	3.53	45.30

The frozen visceral tissue was taken out of the freezer and left to thaw. The visceral matter was subsequently removed from the amber vials and weighed in a watch glass on a Mettler Toledo AB104-S model sensitive scale. A maximum of 30 (± 0.5) grams of wet weight visceral tissue was used, homogenized, and an adequate measure of Hydromatrix was added to absorb any water from the sample.

Nine polychlorinated biphenyls (PCBs) of the existing 209 possible congeners, were acquired as NIST standards and were in close association with the International Council for the Exploration of the Sea (ICES) set which is most used in studies of marine environments. Furthermore, eight BDE standards were also employed herein, which is within considerable agreement with research carried out by Ramu et al (2005).

Samples underwent Soxhlet extraction, Silica/Alumina chromatography for sample clean up, followed by Gel Permeation Chromatography (GPC) procedure to remove lipid content. Samples were analyzed at the environmental chemistry laboratory at the University of South Florida St. Petersburg (USFSP). Measurement and analysis of each target analyte was performed using a Gas Chromatography Electron Capture

Detector (GC ECD). Subsequent quantification was achievable via comparison of response factors of samples to analyte calibration curves made at seven differing concentrations varying between 1 ppb and 100 ppb.

Extraction

Soxhlet condensers and all other glassware required for Soxhlet extraction were initially left in a weak hydrochloric acid bath for at least 24 hours. Glassware was then washed with reverse osmosis (RO) water, followed by a wash with pesticide grade Acetone and air dried for at least 10 minutes. Axis Premium soil amendment/ Hydro Matrix (Eagle Picher Filtration and Minerals Inc.) was left to bake for at least 10 hours at 650 ^{0}C, and subsequently kept at 120 ^{0}C. Soxhlet bodies were set up in the fume hood in preparation for extraction, and additional materials, such as disposable Pasteur pipettes, round bottom flasks, and steel wool were baked at 450^{0}C for at least 10 hours.

The Soxhlet extraction equipment was assembled and placed accordingly in the fume hood (see figure 3). A 1:1 solvent ratio was created using 100 mL of Pesticide residue analysis grade Hexanes (Acros), and 100mL of (ECD tested for pesticide analysis) Dichloromethane (Acros). The heating mantle was set at power 3, extraction was left to proceed for at least 12 hours, and the sample was subsequently left to cool. The Soxhlet was dismantled, with the samples stoppered immediately.

On completion of extraction, the 200 mL of 1:1 Hexane: DCM was required to be evaporated to a much smaller volume, and thus, the Rotary evaporator equipment was set up (figure 9).

A.

B.

Figure 9. The set up of two Soxhlet extractors on heating mantles with power on, in the laboratory, is shown for *C. virginica* samples collected at Ruskin and the Upper Tampa Bay Park, Florida (a). The rotary evaporator set up, with connection to a cold water source to feed into the coils, in addition to connect to the motor for production of the vacuum (b).

The water bath temperature was set to approximately 40-45^{0}C. The glass attachment joining the flask to the rotary evaporator (as seen in figure 9), was cleaned as thoroughly as possible with pesticide grade A40-4 acetone (Fisher Scientific), in an effort to avoid contamination from previous sample rotary evaporator experiments. The flask was attached to the equipment, secured with a clip, and lowered into the water bath. Rotation was set at 5, with cold water being allowed to flow through the coils, making the functioning of the machine more efficient. The vacuum was turned on, the seal set, and tightened slowly, in an effort to avoid the entire sample from being sucked up into the vacuum itself. The sample was evaporated to approximately 2 (± 0.5) mL. The rotation was stopped, and the flask was lifted from the water bath. The seal was removed and the pump was taken off. The sample was transferred to a 25 mL test tube with at least four (4) small washes of hexane. Additional solvent was evaporated via the use of a nitrogen

evaporator, whereby dichloromethane, was switched out with Pesticide grade (packaged under nitrogen) isooctane (Fisher brand); achieving a final volume of 1 mL.

Silica-alumina clean up procedure

Silica-alumina columns were set up in accordance with analytical chemical laboratory procedures adopted from Foday Jaward, PhD, University of South Florida, Tampa. aluminium oxide (Al_2O_3), neutral, 60-325 mesh Brockman Activity 1 (Fisher Scientific), and Silica Gel, sorbent, extra pure 70-230 mesh (Fisher Scientific), were used as the stationary phase of these columns. Glass wool was plugged fairly firmly to the bottom of the glass column with the aid of a glass rod, which had been previously rinsed with 1:1 hexane: DCM.

Two (2) (± 0.05) grams of activated alumina (previously baked for at least 10 hours), was placed in a small beaker. Four (± 0.5) grams of activated silica was placed in a second small beaker. The alumina was slurry packed in the column with 1:1 hexane: DCM, with silica subsequently added. As the silica settled accordingly, approximately 1cm of sodium sulfate anhydrous, certified ACS granular (Fisher scientific) (also previously baked for at least 10 hours), was added t o the column, being very careful to avoid allowing the column from becoming dry prior to the application of the sample undergoing clean up procedure. Next, two column volumes of 1:1 hexane: DCM was washed through the column. As the silica-alumina column ‘just’ became dry, a weighed, clean and labeled 32mL test tube was placed beneath the column and the sample was applied. Using four small washings of hexane, the test tube which contained the sample,

prior to clean up was thus adequately washed of sample traces and aided to retain as much of the sample for clean up procedure. Approximately 25mL of 1:1 Hexane: DCM was collected, and consequently concentrated to roughly 0.5mL via use of a nitrogen evaporator.

This procedure is in good association with methods used as part of sediment core analysis of PAHs, PCBs, DDTs and heavy metals concluded for the Mississippi River Delta, Galveston Bay and Tampa Bay, and conducted by P.H. Sanatschi et al. in 2001. In addition, this same procedure was used to "fractionate the extract" (Brasher, A.M.D., and R.H.Wolff. 2004), in the study of researching relationships between land use and PCBs, organochlorine pesticides, and other chemicals in Hawaii in which bed-sediment samples and fish of varying species (collected in accordance with protocols standard for the NAWQA) were studied.

As the sample approached a 0.5mL volume, solvents were switched out using small washings of iso-octane. This was repeated 3 or 4 times following. Studies conducted by M. Bazzanti et al. (1997), used comparable procedure in their efforts to determine the distribution of PCB congeners, including PCB 153 and 180, in the aquatic environment at the River Arrone, located within close proximity to Rome, Italy.

Gel-Permeation Chromatography (GPC) clean-up procedure

GPC methodology was adopted from Jaward et al. (2004). Small GPC columns were cleaned via (weak) acid bath, and then flushed with hexane, DCM, and acetone. The columns were set up, and 6 (± 0.5) grams of Bio-Beads, S-X3, 200-400 (Bio-Rad Labs Inc.), which were previously soaked in 1:1 hexane: DCM for at least 10 hours and allowed not to become dry, were added to the column (as seen in figure 10).

The small columns were then cleaned by allowing at least 30mL of 1:1 Hexane: DCM to pass through them. As the solvent level became close to that of the Bio-Beads, the tap situated to the bottom of the column was turned to the closed position. A waste vial was placed under the column, the sample was carefully applied, and the tap then turned open. Washings of the sample were applied to the top of the column as the liquid neared the level of the bio-beads within. The column was then filled to the top with 1:1 Hexane: DCM, exhibiting caution in avoiding dispersion of bio-beads in the process. One 15mL and one 1mL fraction (16mL) of the solvent was collected in a vial, was labeled as waste, and discarded accordingly.

A.

B.

Figure 10. Illustration of the general gel-permeation chromatography set up with two columns, each holding eight (8) grams of bio-beads, with the tap closed to the bottom (A). The six port nitrogen evaporator is also shown, set up in the laboratory and iso-octane (contained in the wash bottle- bottom center of picture), was used to switch out solvents (B).

The then clean, labeled, collecting vials were placed beneath the column in order to collect fractions 3, 4, 5 of the eluent; each 1mL, 15mL, and 15mL respectively. An additional 15mL fraction (fraction 6), was collected as a precautionary method for capturing any compounds that eluated at a later stage from the column. 46mL (approximately 50mL) of solvent was collected, which was subsequently evaporated under a stream of nitrogen, to an approximate volume of 1mL. Again, solvents were switched using 3 or 4 washes of isooctane, and evaporating to a final volume of approximately 0.5mL.

Florisil Clean up procedure

The Florisil® cleanup method used for this study was derived from published literature from Alegria and Shaw (1999) with respect to pesticide quantification and analysis.

The method was first tested on a procedural method blank, together with another sample to test for clean-up effectiveness of the procedure, using one eighth of all materials used in the literature, then repeated with the prescribed methodology.

Sixty to 100 mesh Florisil® (Fisher Scientific) was prebaked at 500^{o}C for at least 10 hours, or overnight. One gram of Florisil® was weighed and dry packed into a micropipette. It was deactivated with approximately 25µL of W5-4 High Performance Liquid Chromatography (HPLC) grade, submicron filtered water (Fisher Scientific), and overlain with roughly 0.0625g of anhydrous sodium sulfate. The column was pre-eluted with roughly 12.5mL of 1:1 hexane: DCM. The sample was added and approximately 10mL of solvent was collected, and brought to just about 0.5mL by use of a nitrogen evaporator, with solvent exchange accomplished using isooctane (3 or 4 small washings).

One glass column was filled with 8g of prebaked Florisil® which was deactivated with 200µL of HPLC grade, submicron filtered water (Alegria and Shaw., 1999). This stationary phase of the column was overlain with roughly 0.5g of anhydrous sodium sulfate, and pre-eluted with 100mL of 1:1 hexane: DCM. The samples were subsequently added to the column and 25mL of solvent was collected, which was concentrated to approximately 0.5mL, via use of a nitrogen evaporator in the laboratory. Solvent was also exchanged using isooctane, with 3 or 4 small washings.

Analysis

All samples were analyzed using a Gas Chromatography Electron Capture Detector (GC ECD), using a narrow 2-30m x 0.25mm gas chromatography column. Each batch of samples was analyzed together with a method procedural blank. The analysis time was 82 minutes, with an injection volume of 1.0uL. A temperature of 100^0C was held for 2 minutes, ramped up to 140^0C, held at 220^0C for 10 minutes, 240^0C for 5 minutes, then at 300^0C for 15 minutes. A calibration curve was created and results were recorded in pictogram per microliter (pg/uL).

Additional analysis was carried out on all samples through an external laboratory, using Gas Chromatography Mass Spectrometry (GC MS) equipment, done in an effort to improve accuracy of detection. An internal standard was added in order to help with the identification of PCB and PBDE congeners, and methodology specific to the laboratory was used. Results were recorded in pg/uL.

Quality Control

For quality control, four spiked samples containing 100 ppm concentration of dieldrin and dichlorodiphenyltrichloroethane (DDT) were treated in the same manner as the other collected samples, in an effort to test for accuracy of the extraction, clean up and analytical procedures. In addition one procedural blank (containing no sample or

contaminant), was used per every four samples and treated with comparable technique. These spiked and blank samples served as controls since a preparatory concentration in each was known.

Geographic Information Systems Overlay mapping

ArcGIS version 9.2 was used to generate basic Geographic Information Systems (GIS) mapping, in an effort to identify differences in elevation and land use patterns to remotely determine those areas that are more likely to accumulate greater amounts of PCB and PBDE compounds, whether via water or air partitioning and deposition.

Land use data was derived from the South West Florida Water Management District (SWFWMD) GIS data source for the various blocks covering Tampa Bay, and a map illustrating land use for the area was generated. A level 1 reclassification of land use was created, giving rise to the 8 spatial classes (urban land, agricultural land, range land, forest land, water, wetland, barren land, and transport/ utility), with appropriate color scheme (Jeer and Bain. 1997).

Table 3. Summary of the data layers used for GIS mapping, along with the sources, file, and data type.

Data Layers	Sources	File	Data Type
County boundaries	Florida Geographic Data Library (FGDL)	cntbnd.shp	Polygon
Land use	South West Florida Water Management District (SWFWMD)	Lu08-saras_ne Lu08-saras_nw Lu08-stpet_se Lu08-stpet_sw Lu08-stpet_ne Lu08-stpet_nw Lu08-tarpo_se Lu08-tarpo_sw	Polygon
City points	Florida Geographic Data Library (FGDL)	Citylocations.shp	Point
Hydrography (Flow lines)	United States Geological Survey (USGS): National Hydrography Dataset (NHD)	Block 03100202 Block 03100203 Block 03100204 Block 03100205 Block 03100206 Block 03100207	Polygon

Chapter Three

Results

Biological findings

Crassostrea virginica individuals were collected at 12 sites (Figure 11 and Table 4). *Perna viridis* were collected at 6 of those 12 sites, since they were not observed at the other sample sites. *Crassostrea virginica* individuals were larger in size, and therefore corresponded with a greater mass of visceral (meat) matter, than *Perna viridis* individuals. It was observed that visceral matter increased with increasing shell length in both C. virginica (figure x) and P. viridis (figure x). Average *C. virginica* total weight, meat weight and length were 24.16g, 3.38g and 52.50 mm. *P. viridis* had corresponding averages of 12.07g, 3.53g and 45.30 mm respectively.

Table 4. Average total weight, meat weight and length for all individuals of C. virginica and P. viridis used in the study

Species	Total weight (g)	Meat weight (g)	Length (mm)
C. virginica	24.16	3.38	52.50
P. viridis	12.07	3.53	45.30

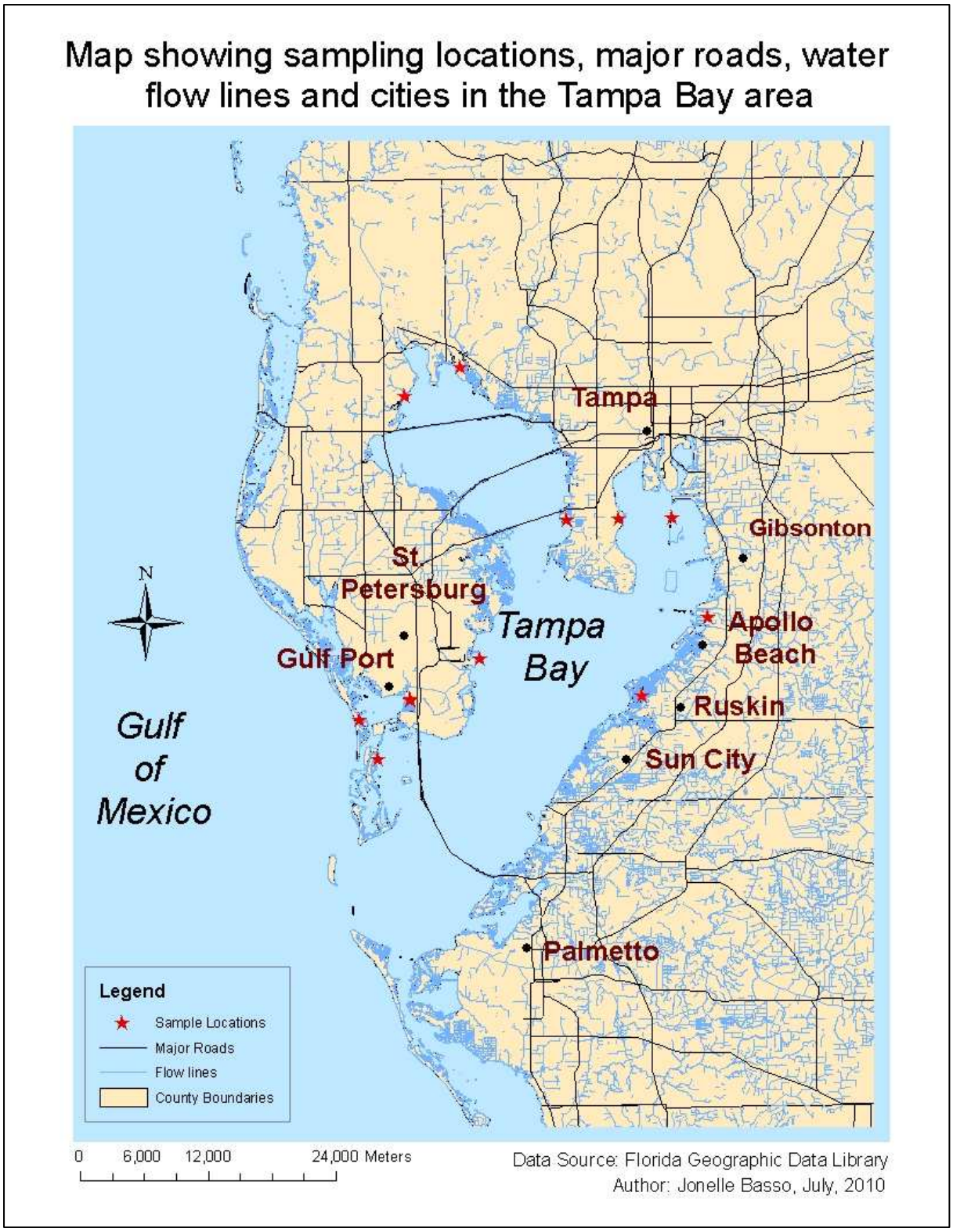


Figure 11. Sample locations map.

For each species, relationships between average lengths (mm) per sample site, average total weight (g) per sample site, as well as average visceral weight per sample site are represented in the form of bar charts (see figures 13 through 19 below). Mean oyster weights ranged from 11.69 grams and 43.95 grams, which is seen in Figure 13. Mean mussel visceral weights ranged from 2.15 grams to 5.58 grams (figure 18). Mean oyster shell heights ranged from 39.57 mm to 65.51 mm (figure 15). Mean oyster total weights ranged from 0.55-29.26 grams (figure 13). Mean green mussel visceral weights ranged from 0.16-8.91 grams (figure 18). Mean green mussel shell lengths ranged from 14.60-69.60 mm (figure 19).

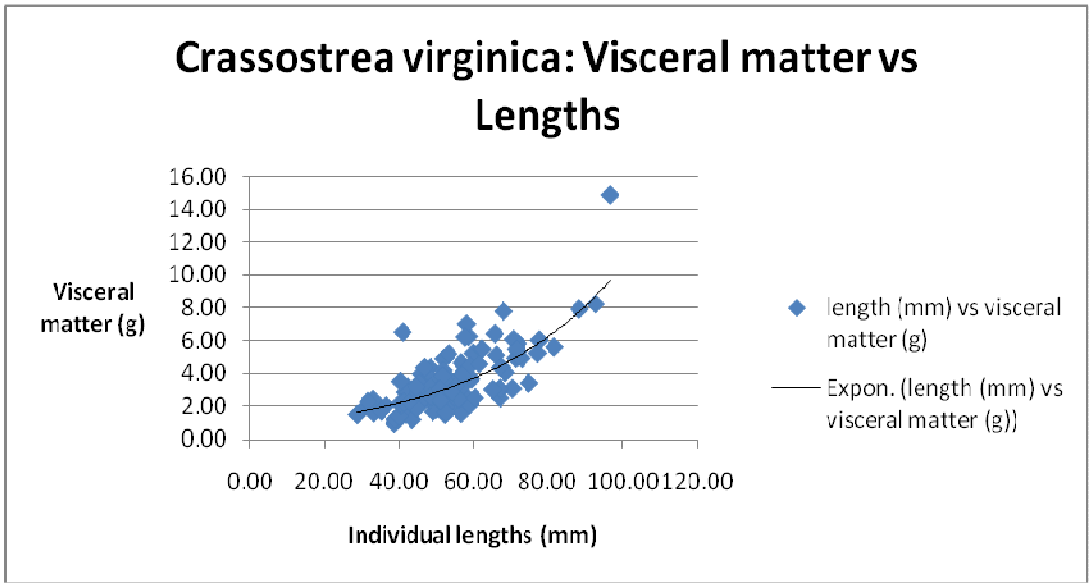


Figure 12. *C. virginica* visceral matter versus lengths

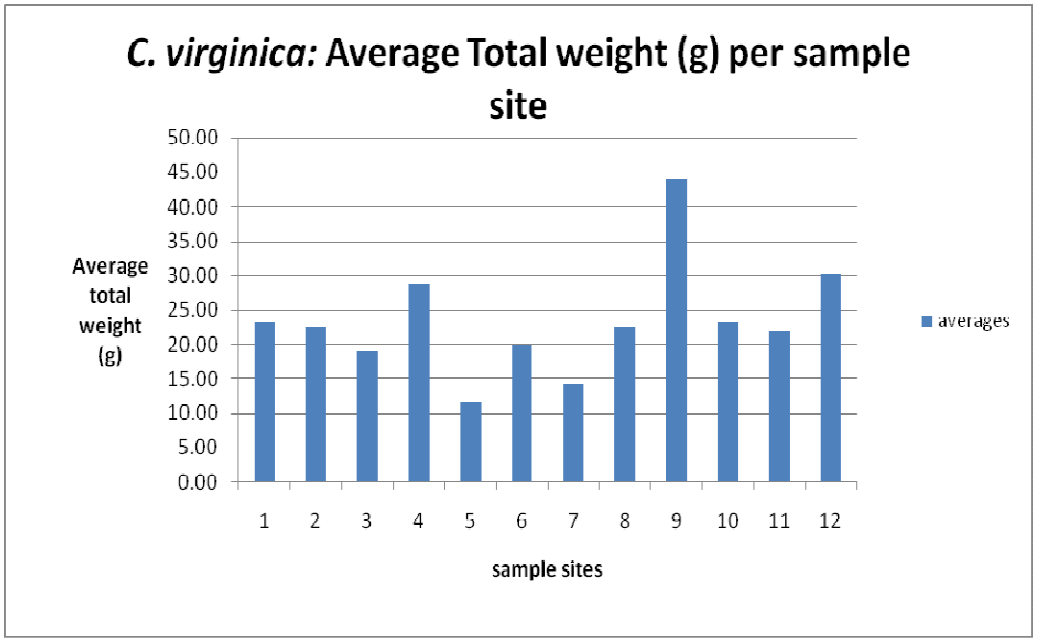


Figure 13. *C. virginica* average total weight (g) per sample site

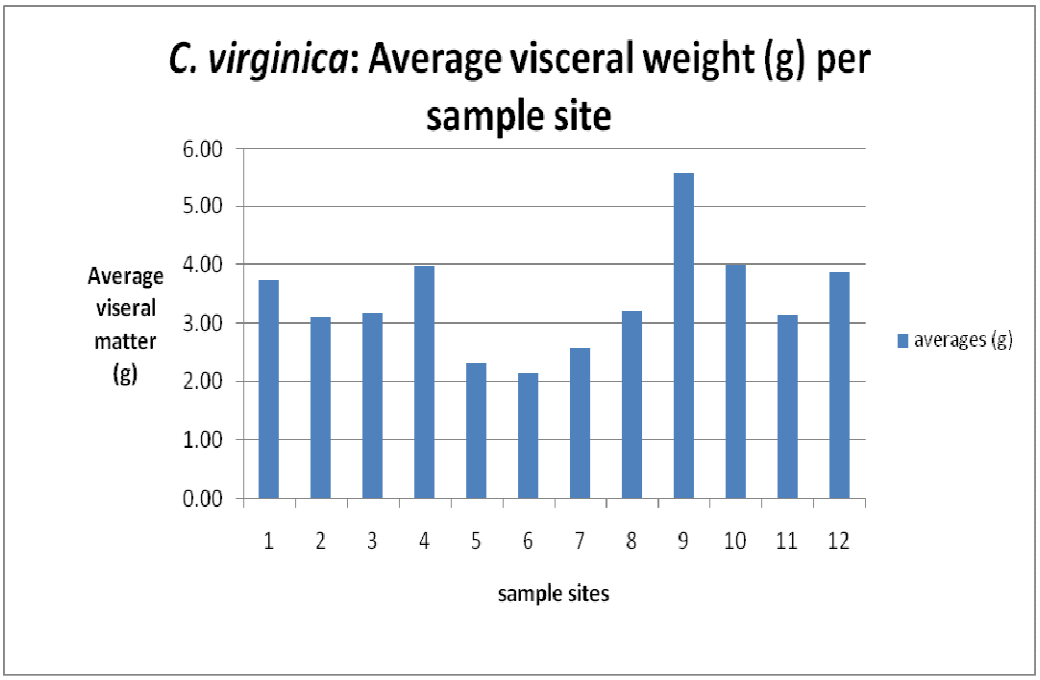


Figure 14. *C. virginica* average visceral weight (g) per sample site

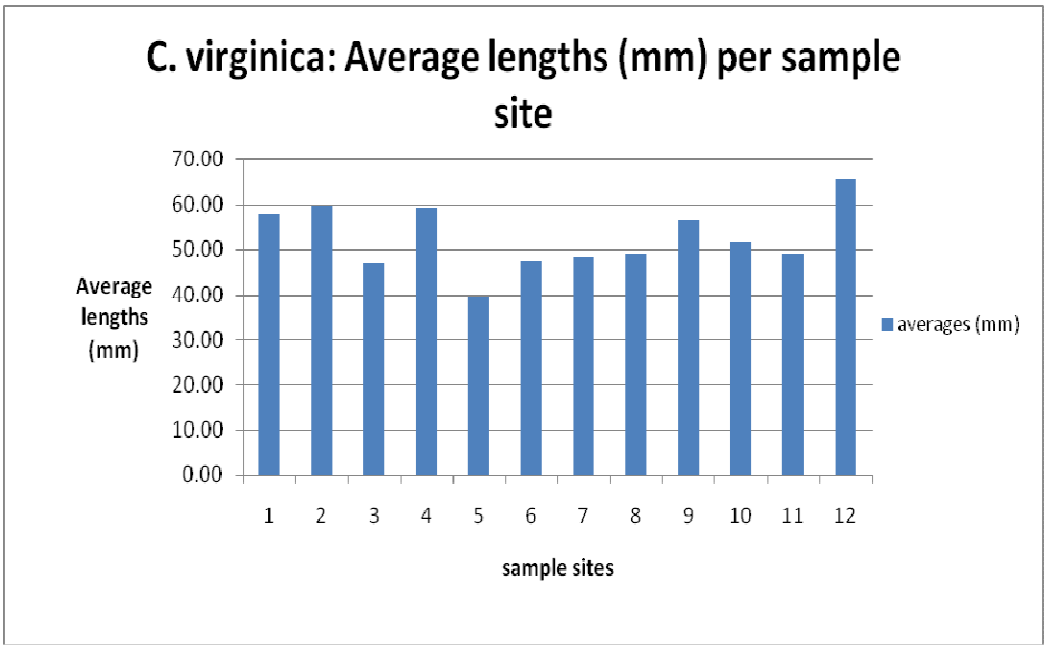


Figure 15. *C. virginica* average lengths (mm) per sample site

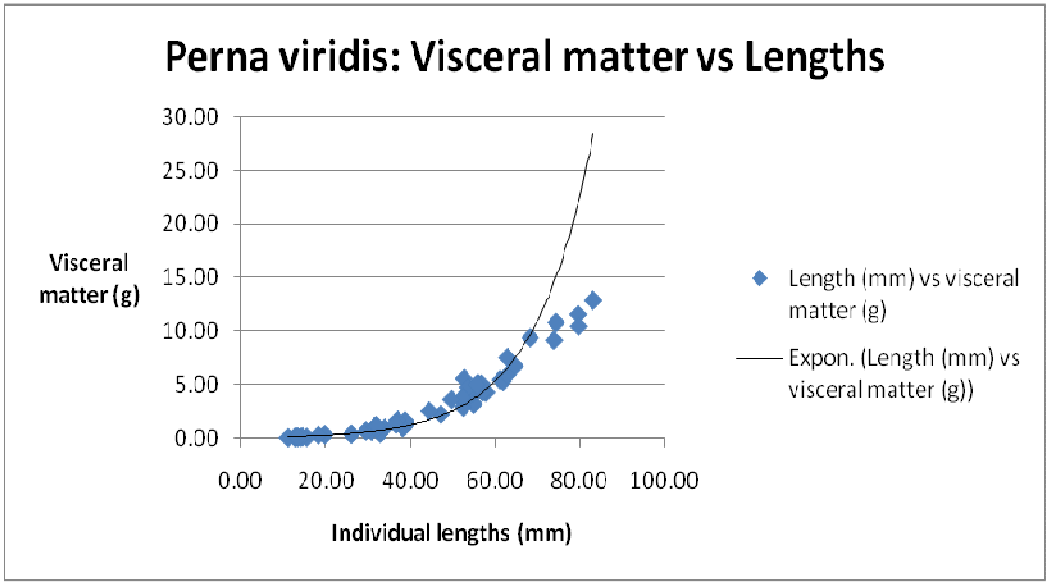


Figure 16. *P. viridis* visceral matter versus lengths

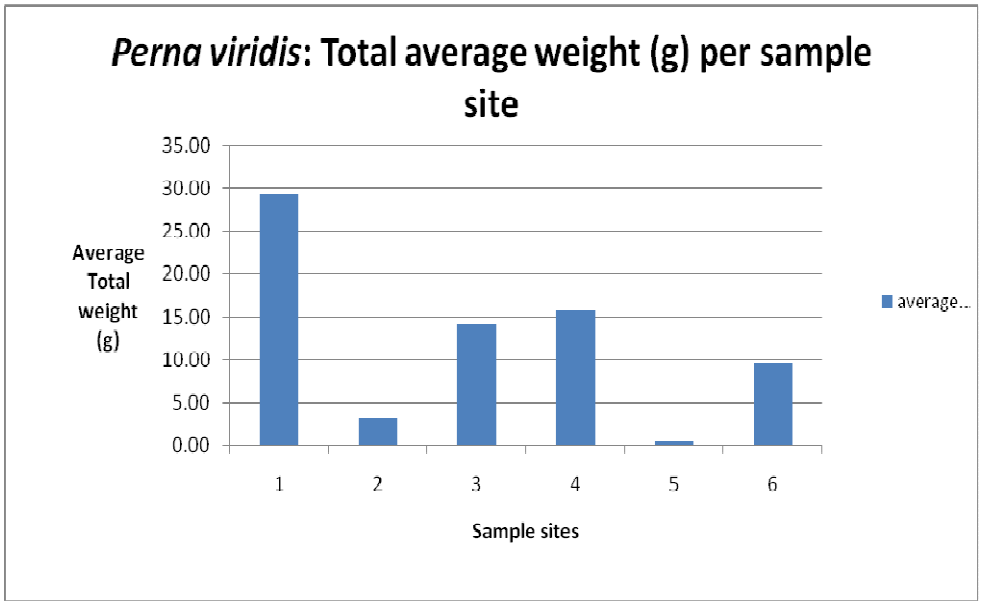


Figure 17. *P. viridis* total average weight (g) per sample site

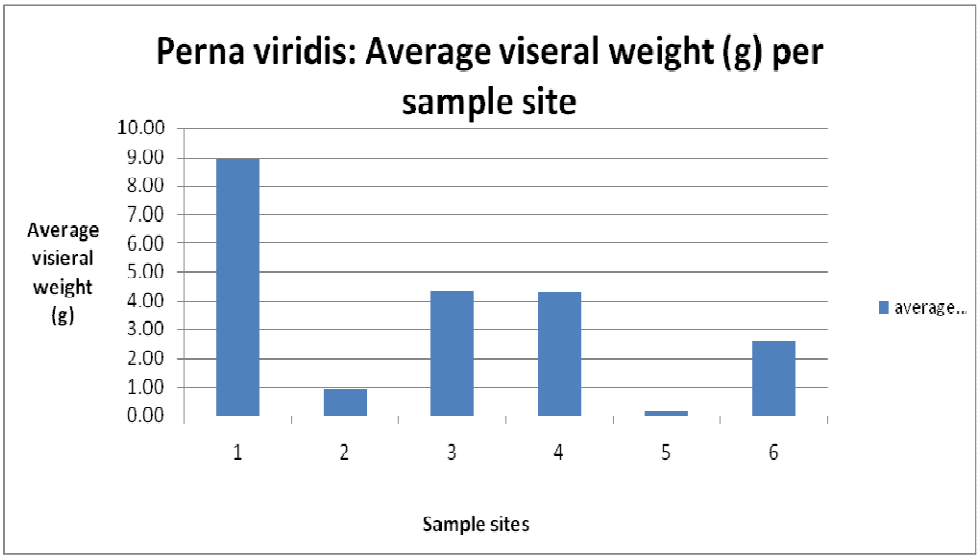


Figure 18. *P. viridis* average visceral weight (g) per sample site

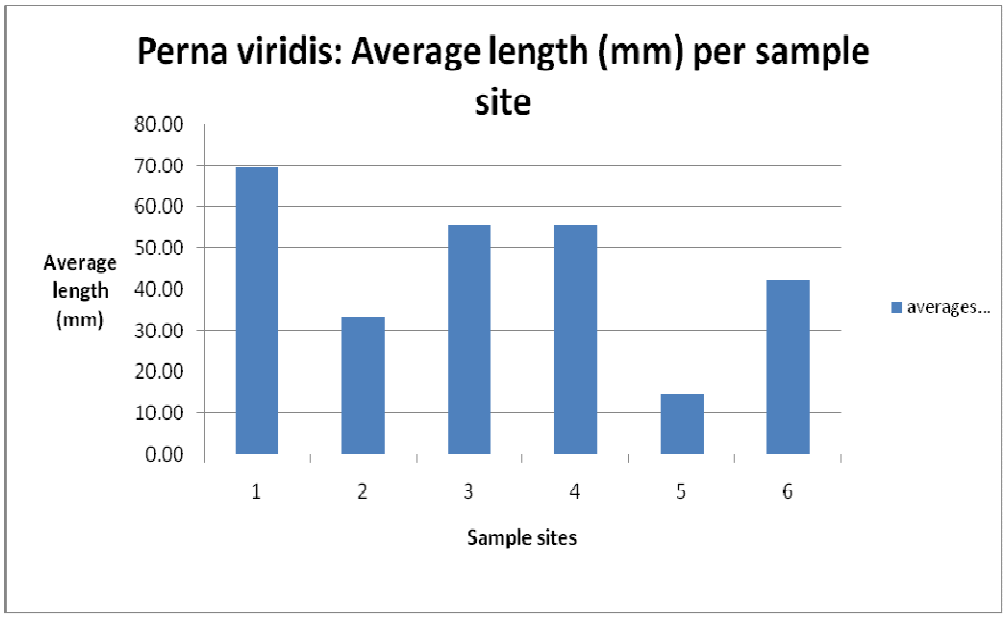


Figure 19. *P. viridis* average length (mm) per sample site

Oysters were collected at more locations than green mussels (table). At many sample sites *Perna viridis*, were not found.

Table 5. Sample sites, codes, species collected, weight of species edible tissue (in grams) and total Hydromatrix weight (in grams) used in Soxhlet extraction

Site	Code	Species Collected		Weight (g)	Total Hydromatrix weight (g)
		P. viridis	*C. virginica*		
Boca Ciega Bay	BCB P 8.12.09	x		17.9595	55.2829
Boca Ciega Bay	BCB C 8.12.09		x	20.8575	21.3601
Vinoy SeaWall	VSW C 8.10.09		x	10.0606	30.6803
Vinoy SeaWall	VSW P 8.10.09	x		23.6260	40.1301
Vinoy SeaWall	VSW C 9.01.09		x	13.2513	20.9780
Vinoy SeaWall	VSW P 9.10.09	x		26.8507	30.0375
Bay Shore SeaWall	BSSW C 9.01.09		x	6.4689	20.1745
Lower Estuary Bird Cay	LEBC P 9.10.09	x		9.7960	20.5395
Upper Estuary	UE C 9.08.09		x	9.6208	20.0929
Lower Estuary	LEC 9.10.09		x	15.1967	20.4559
Lower Estuary	LE C 9.10.09		x	22.6765	30.2723
Lower Estuary	LE C 10.20.09		x	12.3370	20.1367
Gandy Bridge	GB C 9.08.09		x	7.5231	20.0348
Upper Estuary	UE P 9.08.09	x		0.8635	6.0547
Teco Power Plant	TPP P 9.01.09	x		6.0092	16.0175
Teco Power Plant	TPP C 9.01.09		x	11.2199	20.0379
Teco Power Plant	TPP P 8.10.09	x		31.5013	40.3215
Teco Power Plant	TPP C 8.10.09		x	16.7417	30.0890
Ruskin E.G. Simmons	RUC 9.25.10		x	31.5963	35.6472
Upper Tampa Bay Park	UTBC 10.01.10		x	30.7914	32.7591
Safety Harbor	SHC 01.28.11		x	27.3158	31.8463

At the Gandy Bridge sampling site, the American oyster (*C. virginica*), was the only species found. Baker et al. (2007), and Steve Geiger, Ph.D. (FL FWC- FWRI, personal communication) mentioned that harvesting of the green mussel (*P. viridis*), was widespread in that area, but may no longer be a prevalent population of that region.

Gas Chromatography Electron Capture Detector (GC ECD) primary environmental chemical analysis results

As a result of quality control procedure, 18.119ppb of 4,4' DDT and 22.686ppb of Dieldrin was detected, where these were distinct peaks (figure 20). The largest and first peak on the chromatogram represents the isooctane (solvent) burning off during the 30 minute run time in the ECD. Other compounds are represented by the peaks seen roughly at 18 minutes and 23 minutes into detection.

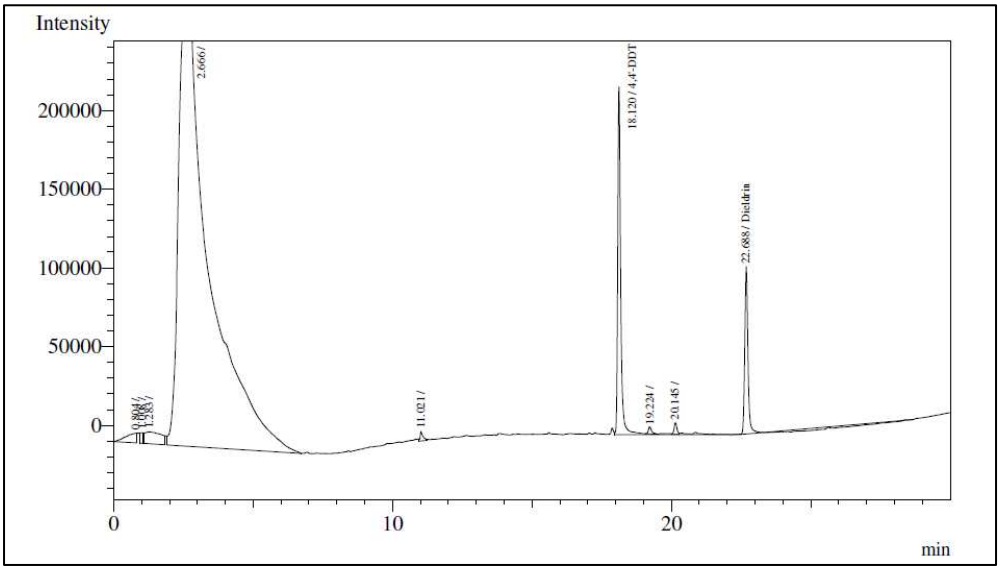


Figure 20. Trial test sample (FT2) spiked iso-octane with 4,4' DDT, Dieldrin, with peaks and parts per billion (ppb) concentrations identified.

The concentrations of PCBs and PBDEs in *C. virginica* samples from September 01, 2009 and October 10, 2009, and that for P. viridis samples for the same dates were similar (Figure 21). According to figure, the general peaks of the chromatograms are similar, and beg the question of whether is there any significant difference in bioaccumulation in these species with respect to PCBs and PBDEs.

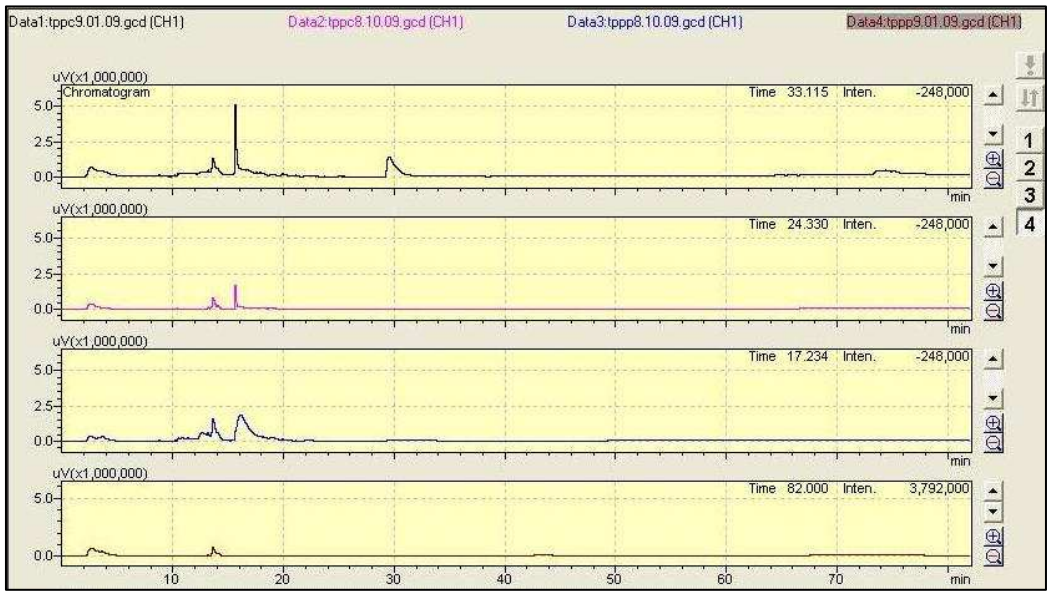


Figure 21. A comparison of C. virginica and P. viridis samples, collected in September and October of 2009 at the Teco Power Plant Manatee, located at the middle estuary area of Tampa Bay

General preliminary observations

Peaks observed in sample chromatograms indicate only trace quantities of both PCBs and PBDEs. The maximum value was 292.8ppb of BDE 153, analyzed at Boca Ciega Bay for August 12, 2009 (see table 6).

However, with corrections to raw data (summarized in the table 7 and 8), according to weight, Limit of Detection (LOD) and method blank corrections (Table 7), the highest value identified (27.45pg/g) was recorded at the Teco Power Plant Manatee (*Perna viridis* sample) for the BDE-99 congener (Table 8).

Table 6. Representative sample of the raw data (with concentrations in pg/UL) collected for 7 of the samples. Additional data includes the weights of the visceral weights ground up for analysis

weight	20.86	6.47	7.52	9.80	15.20	10.06	6.01
	bcbc 8.12.09	bsswc 9.01.09	gbc 9.08.09	lebcp 9.10.09	lec 9.10.09	vswc 8.10.09	tppp 9.01.09
BDE-28			31.8		9.303	64.796	
BDE-47	32.7	10.2	14.5	24.0	10.676	25.112	10.964
BDE-100	129.3	15.7	31.0	28.4	29.341	18.449	19.424
BDE-99	82.8	25.3	73.2	11.0	56.128	41.387	167.506
BDE-154	210.9	10.5	37.6		12.336	8.915	22.371
BDE-153	292.8	16.0	68.0	23.9	16.879	7.28	17.703
BDE-183		8.9					
PCB-28							
PCB-52						60.781	
PCB-90/101		16.2	20.1	10.3	30.53	28.725	8.266
PCB-152	67.6						9.509
PCB-118	60.2	33.1	8.0	8.5	8.76	26.805	7.603
PCB-138	13.2	10.1	8.4	8.4	9.246	10.714	9.082
PCB-157		7.9	8.2				
PCB-180	14.4	10.2		11.5	10.228	11.477	10.393

Table 7. Summary of PBDE and PCB congers analyzed at USF St. Petersburg, but corrected according to Limits of Detection (LOD) and method blank corrections for Boca Ciega Bay, Gandy Bridge, Lower Estuary, TECO Power Plant Manatee, and Vinoy sea wall locations.

	Final Conc pg/g						
	bcbc 8.12.09	bsswc 9.01.09	gbc 9.08.09	lebcp 9.10.09	lec 9.10.09	vswc 8.10.09	tppp 9.01.09
BDE-28			3.06			5.57	
BDE-47	1.07		0.56	1.40		1.47	
BDE-100	5.60		2.45	1.62	1.11		
BDE-99	3.41	2.10	8.17		2.92	2.95	**25.93**
BDE-154	**10.11**	1.62	5.00		0.81	0.89	3.72
BDE-153	**13.64**	1.20	7.94	1.60	0.57		1.58
BDE-183		1.38					
PCB-28							
PCB-52						6.04	
PCB-90/101		1.66	1.95	0.49	1.65	2.31	0.47
PCB-152	3.03						0.87
PCB-118	2.58	4.13	0.22	0.22	0.16	2.03	0.21
PCB-138	0.63	1.56	1.12	0.86	0.61	1.06	1.51
PCB-157							
PCB-180	0.21			0.14		0.14	

Table 8. Summary of PBDE and PCB congers analyzed at USF St. Petersburg, but corrected according to Limits of Detection (LOD) and method blank corrections for Vinoy sea wall, Ruskin, Upper estuary, TECO Power plant Manatee, and Upper Tampa Bay Locations.

	Final Conc pg/g					
PBDE	**vswp 8.10.09**	**ruc 9.25.10**	**uec 9.08.09**	**uep 9.08.09**	**tppc 9.01.09**	**utbc 10.01.10**
BDE-28						
BDE-47		0.23	0.52	3.17		
BDE-100		1.33				
BDE-99	0.48	0.13	1.41		3.86	
BDE-154		0.33			1.52	
BDE-153			0.38		0.53	
BDE-183				9.53		0.27
PCB-28						
PCB-52						
PCB-90/101	0.77	0.06	1.35		0.45	
PCB-152			1.30		1.10	
PCB-118	0.70		0.54	4.10	1.60	
PCB-138	0.52	0.30	1.15	11.22	0.77	0.28
PCB-157						
PCB-180						

It was theorized that since most sites were within areas that are categorized as urban or agricultural, that the general recorded quantities for POPs for all site would be similar, however this was not the case. A test for association for POPs was conducted for the lower, middle, and upper estuary regions, where it was found that a bias existed for PCBs at the upper estuary region (Tables 9 and 10). The calculated chi squared value (for association) was 19.25921, which is greater than table values of confidence, leading to the conclusion that there is an association of POPs with different estuary regions, with a bias for PCBs in the upper estuary. The distribution of observed total PCBs are not normally distributed, as seen when compared to expected values (Figures 22 and 23).

Table 9. Observed (o) and expected (e) were used to calculate the chi squared value, by using the equation $\sum$ (o-e)2/e. Total Chi squared was calculated to be 19.25921. The chi squared table value at df 2 is 5.991 for p= 0.05, and 9.210 for p= 0.01. The Ho is rejected if the chi square calc is greater than the table value, which is true here.

o-e	$(o-e)^2$	e	$(o-e)^2/e$	
6.03	36.34228	40.96	0.887229	
6.30	39.64639	74.02	0.535592	
-12.32	151.9055	33.91	4.479006	
-6.03	36.34228	18.10	2.008032	
-6.30	39.64639	32.71	1.212186	
12.32	151.9055	14.99	10.13716	
				chi
			19.25921	squared

Table 10. The observation of individual chi squared values for different regions, with direct relation to the two groups of POPs shows a bias for PCBs in the upper estuary.

	chi sq	
	PBDE	PCB
lower	0.8872291	2.0080319
middle	0.5355923	1.2121856
upper	4.4790063	**10.137164**

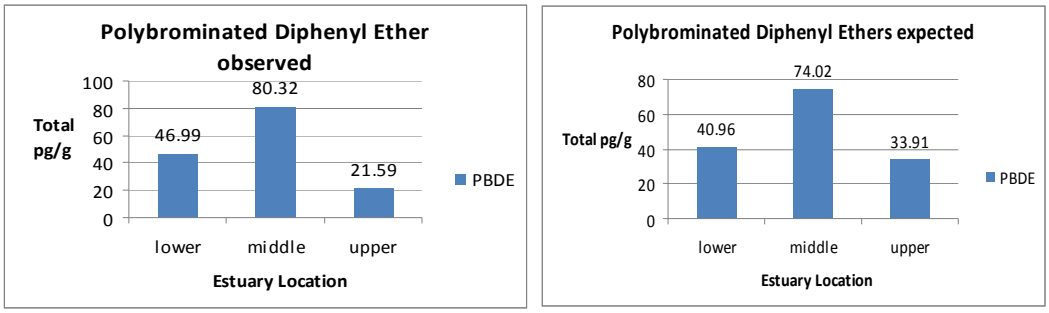


Figure 22. Observed and expected total PBDE in pg/g for lower, middle and upper estuary regions.

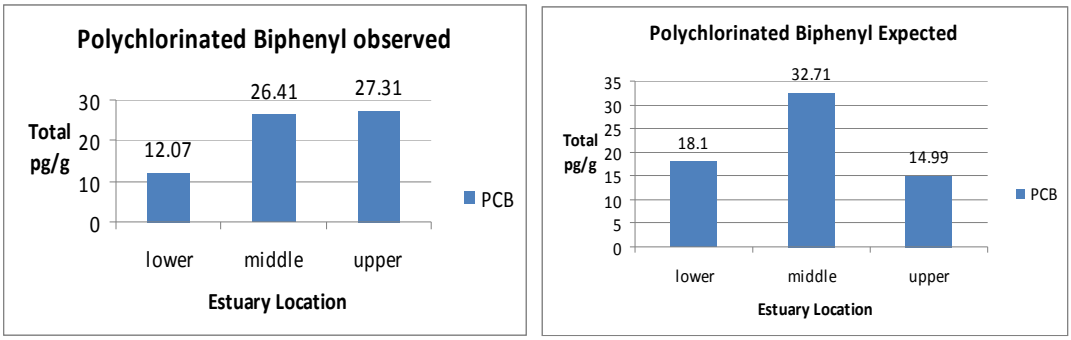


Figure 23. Observed and expected total PCB in pg/g for lower, middle and upper estuary regions.

PBDE quantities ranged from 0.27 to 25.93pg/g, and PCB values ranged from 0.14 to 11.22pg/g.

Secondary observations and analysis

All samples that were analyzed at the environmental chemistry laboratories at USF St. Petersburg will be further analyzed and verified by means of external laboratory expertise, in order to confirm the results determined at USF, and complete a more thorough analysis with many more congeners.

GIS mapping

The level 1 reclassified designation of land use for Tampa Bay is seen in Figure 24. The Digital Elevation Model (DEM) map was produced (figure 25), as well as a three tiered reclass of the DEM (figure 26). An overlay of the DEM reclass and land use reclass led to the generation of a risk assessment map, outlying high risk and low risk areas (figure 27). Lower lying areas, agricultural and urban areas were of most importance. Areas of lower elevation are prone to greater probability of runoff to surrounding aquatic environments and depositional trends of these compounds. Agricultural and urban lands are much more prone to greater use of pesticides and persistent organic pollutant use in comparison to other land use designations.

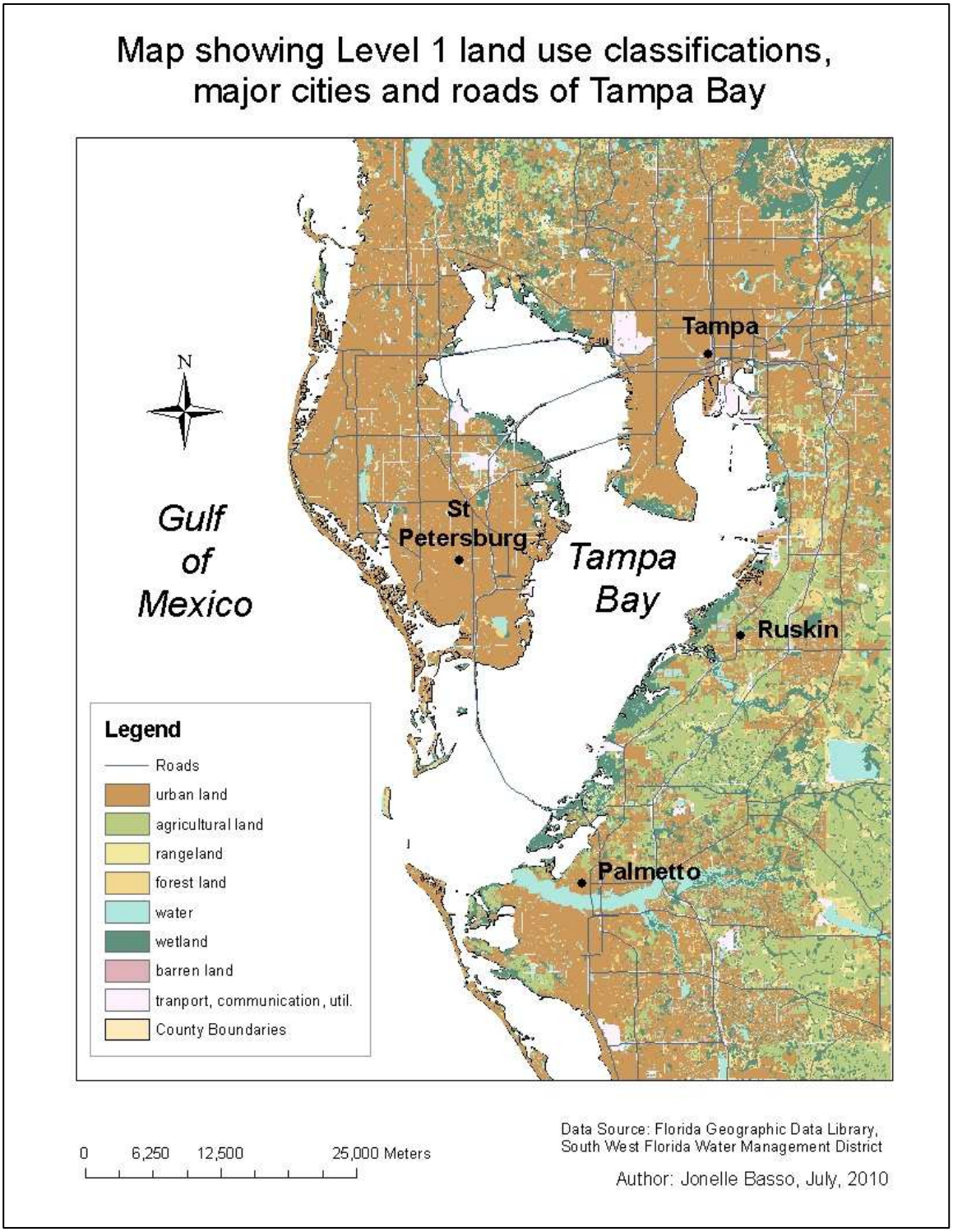


Figure 24. Level 1 reclassification of land use, Tampa Bay

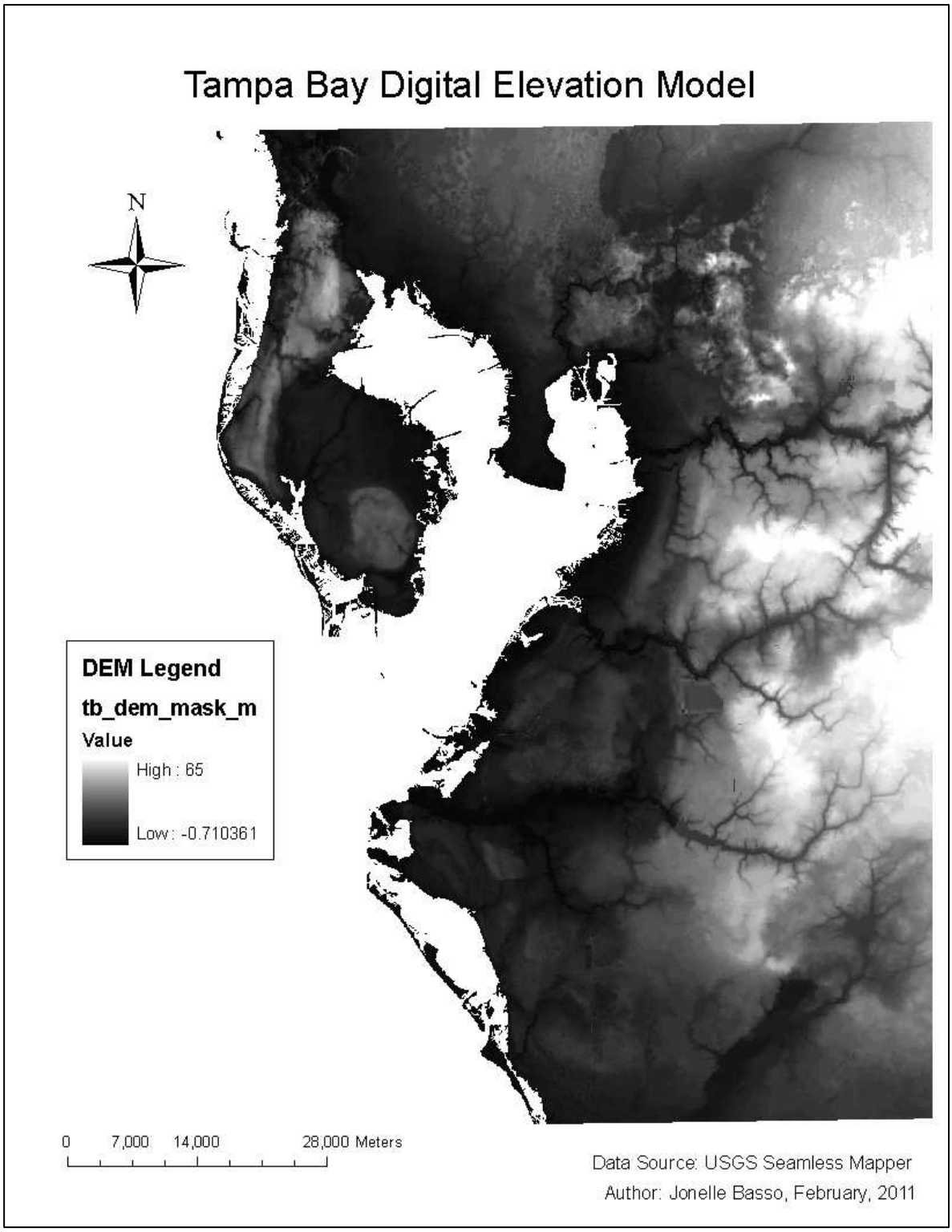


Figure 25. Digital Elevation Model (DEM), Tampa Bay. Higher elevation appears lighter, and lower elevations are of darker color.

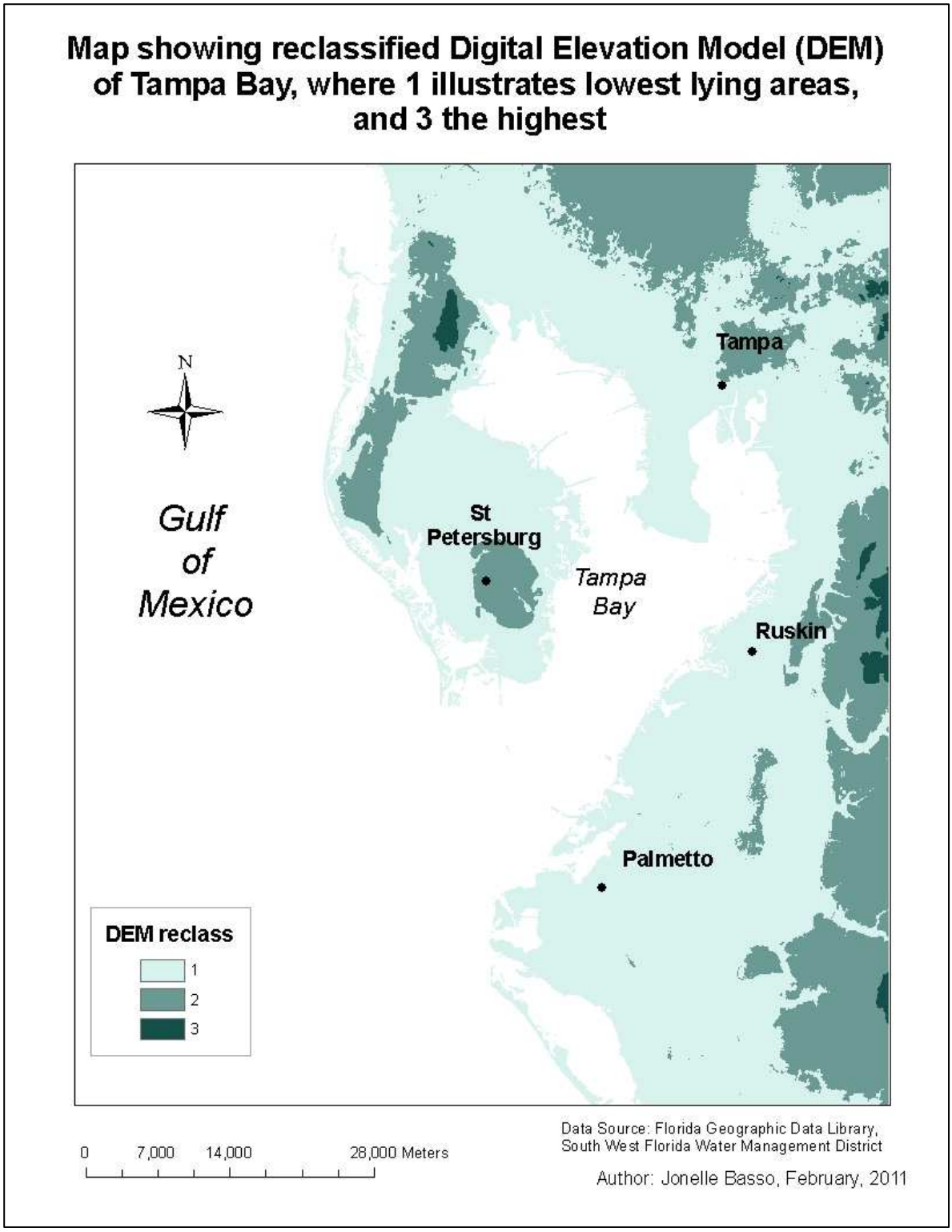


Figure 26. DEM reclassified into 3 levels of high (darkest shade of blue), medium (lighter shade of blue), and low (lightest blue) elevation, Tampa Bay.

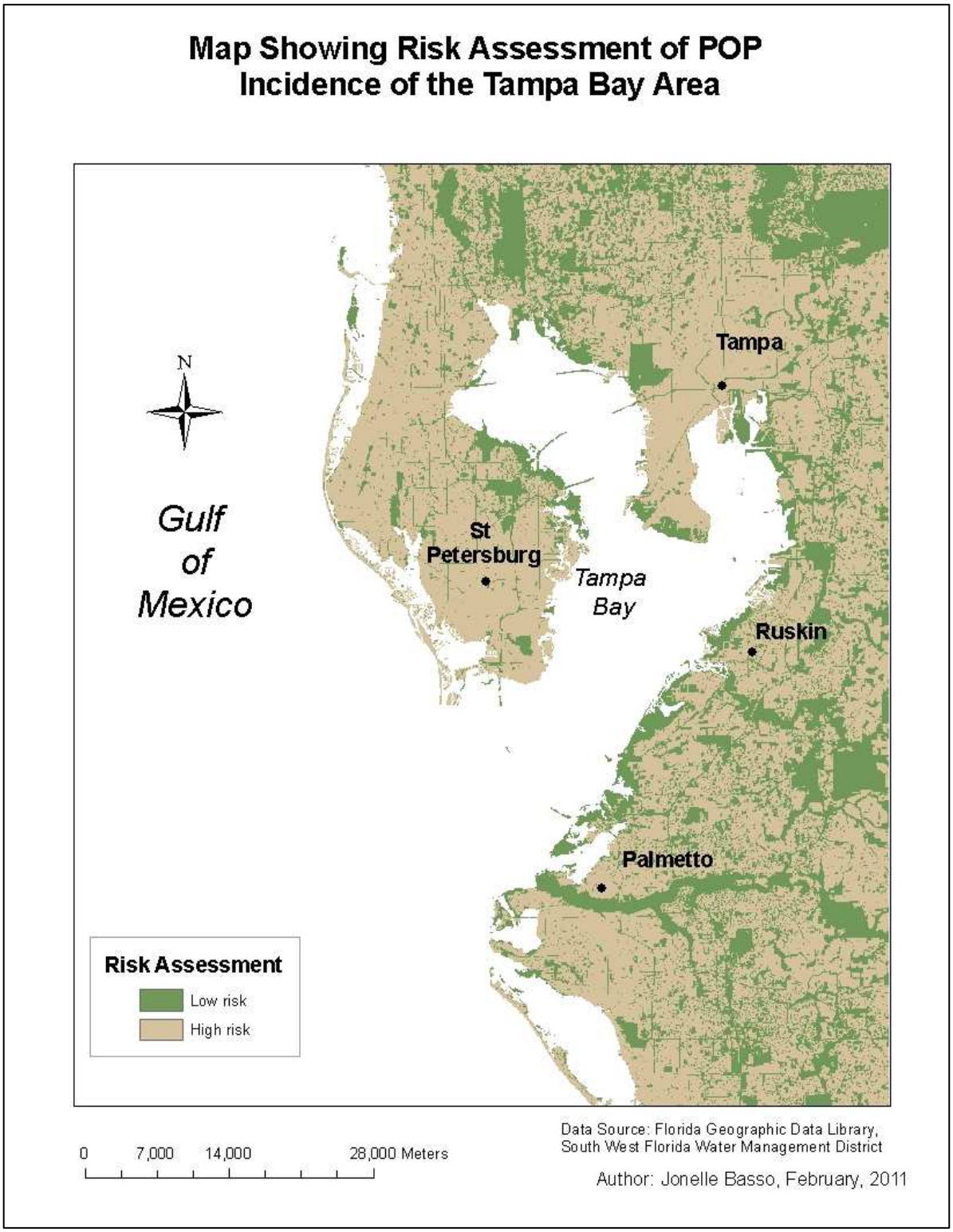


Figure 27. Overlay of land use and reclassified DEM layers, identifying areas that may be more prone to incidence of PCBs/PBDEs in Tampa Bay (high risk), and those less prone (low risk).

Chapter Four

Discussion

The study has proved that, through GC ECD analysis, there is an incidence of PCBs and PBDEs in the Tampa Bay area, with the highest quantity of POP observed in visceral bivalve tissue being 25.93pg/g (25.93 ppb) for BDE-99. This value was recorded for the TECO Power Plant Manatee sampling site in September 2009, using the green mussel as an indicator. This level of contaminant is expected for an industrial or urban area. By using the America oyster in August 2009, the Boca Ciega Bay sample site had 10.11pg/g and 13.64pg/g of BDE-154 and BDE-153 respectively. This may be due to possible ship wrecks in the bay, or due to the slow local water column circulation, because the area is now more of a bayou. According to the GIS land use map, it is considered an urban low lying region, and an area of high risk for POP incidence. One other site in the upper estuary, using the green mussel in September 2009 recorded the highest PCB value in the study. 11.22pg/g of PCB-138 was recorded at the site.

It was theorized that since Tampa Bay is dominated by urban or agricultural development, the recorded quantities for PCBs and PBDEs at all sample sites would be similar, however this was not the case. A clear pattern of POP incidence in relation to land use was not observed, and may be due to a variety of local environmental factors. A test for association for PCBs and PBDEs was conducted for the lower, middle, and upper estuary regions, where it was found that a bias existed for PCBs at the upper estuary

region. The calculated total chi squared value (for association) was 19.25921, which is greater than table values of confidence, leading to the conclusion that there is an association of PCBs and PBDEs with different estuary regions, with a bias for PCBs in the upper estuary. The distribution of observed total PCBs are not normally distributed across the bay, as seen when compared to expected values.

There was also no clear pattern observed between species, in relation to bioaccumulation and individual size. Each species is capable of having different chemical concentrations, even when environmental conditions are identical (O'Conner, 2002). When internal chemical concentrations of species are taken into account, together with factors such as metabolic activity, environmental degradation of congeners before filtration through sessile filter feeders, and degradation within bivalves, the rate of bioaccumulation becomes greatly complex in relation to a clear understanding of the actual bioaccumulation process. Literature addresses the degradation of POPs in the environment, via photodegradation, biodegradation, and biotransformation of these compounds through plant-microbe interactions (de Boer et al., 2000; Kohler et al., 1988; Mackova et al., 2007). Photodegradation and biodegradation processes in essence suggests that perhaps the amount of PCBs and PBDEs observed during analysis may be less than what is really present in the environment. The literature also suggests that through biotransformation, it is perhaps made possible that specific PCB and PBDE congeners are no longer made available through consumption, due to the metabolic activities of the American oyster and the green mussel. A more complete statistical analysis related to this PCB and PBDE incidence study will be provided in future research in order to better identify a significant difference between bioaccumulation of

PCBs and PBDE between both species, and also identify a significant difference within each specific species of bivalve.

PBDE quantities ranged from 0.27 to 25.93pg/g, and PCB values ranged from 0.14 to 11.22pg/g. According to Binelli and Provini (2004), the maximum POP concentrations permissible prior to a need for advisory is 14,600pg/g, which is much greater than any recorded value for this study. Therefore, although POPs are present in Tampa Bay, even the sample site with the highest concentration of 25.93pg/g is still well below that recommended for safe seafood consumption.

Studies have shown that PCB mixtures such as the commercial product Arochlor 1248, that mix tri-, penta- and tetrachloro congeners, result in carcinogenic and toxicant actions in range of mammalian tissue, and has been tested and proven for deleterious effects in rodents under laboratory conditions (Andric et al., 2000). The two benzene ring structure of PCBs is physico-chemically similar to that observed in PBDEs, and it is therefore suggested that due to this structural similarity that both families of compounds will react similarly in the environment, and within food chains. Lower brominated PBDEs have already been shown to exhibit hepatotoxicity (chemically-driven liver damage), affect thyroid hormone levels by stimulating thyroid dysfunction disorders, and neurobehavioral problems in rodents (Antignac et al., 2008). It is because of these effects that research is being conducted to identify environmental effects of PBDEs, potential human and animal health risks, including risk of cancer since its structurally similar counterpart, the PCB group, has been shown to bring about carcinogenic activity.

In the United States, the NOAA's mussel watch program continues to assess up to 300 sites around the country and Puerto Rico, all in an effort to assess PBDE chemical

contamination in US coastal waters. According to Kimbrough et al. (2009), dry weight summary estimates for the 7 sites monitored in Tampa Bay suggest medium (1-270ppb lipid weight) contamination levels of PBDEs. Values are representations for 2004-2007, where oysters were the sole monitoring species utilized for the study. Data is limited, whereby sample dates for the 3-year period are not provided, and due to the magnitude of the report, specific analytes are also omitted for these locations, thus failing to provide an indication of those pollutants that are cause for concern. Yet the report provides a comparison to a 1996 NOAA report, where Cockroach Bay, Papys Bayou and Naverez Park PBDE levels are shown to increase from a low (below detection limits) to a medium concentration from 1996 to 2007, although the other sites remained only moderately contaminated. In comparing PBDE values from the 1996 NOAA report to the 2009 NOAA report, it is shown that all sample sites have a medium classification, with concentrations ranging between 8-220ppb lipid weight. The project findings are in accordance with NOAA report findings, where medium concentrations of PBDEs were observed for all sites, with PBDE concentrations ranging from 0.48-25.93pg/g. In estuarine waters in Pensacola, Florida, Karouna-Renier et al. (2007) analyzed oysters for PCBs (among other contaminants), and found that previous reports for the urbanized watershed of Galveston Bay, Texas and Tampa Bay, Florida identified toxic equivalency factors (TEFs) to be 2.7-55.5pg/g and 0.3-14.5pg/g for the dioxin, furan, and PCB groups of chemicals. The TEF was calculated in an effort to create a method for evaluation of health risks closely related to these chemical compounds, and is used in reassessment procedure. The study itself reported TEFs ranging from 0.29- 5.90pg/g for this group of compounds, and these levels were determined to possibly pose a threat to human health

based on 46 g/day consumption rate. Continued monitoring of their sample sites was deemed necessary. In order to determine the TEF of a particular congener, it is assigned an “order of magnitude” for relative toxicity compared to the most potential halogenated aromatic hydrocarbon; as a result a direct comparison of this project’s range of 0.06-11.22pg/g should not be carried out, but suggests that results are environmentally realistic, and further monitoring should be completed for future research.

Chapter Five

Conclusions and Recommendations

PCBs have been included as one of the world's dirty dozen chemicals according to the Stockholm Convention on Persistent Organic Pollutants (United National Environmental Programme (Lallas, 2001). The Basel Convention, governing the international transboundary movements of hazardous materials, interacts with international conventions such as the Stockholm Convention. The Basel Convention offers technical guidelines on POP waste, particularly with respect to PCB waste management (Krueger, 2001). Training tools have been implemented to help developing nations in their transition to using (Basel Convention) guidelines in accordance with their economies. One such tool is the implementation of regional workshops such as Environmentally Sound Management of PCBs and POP waste. Objectives include spreading increased awareness of POP wastes and best available techniques and practices for handling them. In addition, expert meetings have been organized by the World Health Organization to determine toxic equivalency factors for PCBs and other dioxins and furans in humans and wildlife (Van den Berg et al. 1998). Due to the toxic and persistent characteristics of organochloride pesticides such as DDT have been banned in the United States (Novotny, 2003), and global PCB production has been curtailed. However, much produced material is still in use and many developing countries desperately seek the

significant benefits DDT and PCBs provide people despite the environmental problems they cause (vanLoon, 2005).

From the study, the following were identified:

1. This study shows that there is an incidence of persistent organic pollutants in the Tampa Bay area, with specific reference to polychlorinated biphenyls and polybrominated diphenyl ethers.

2. An obvious pattern between the incidence of persistent organic pollutants and land use in Tampa Bay was not seen.

3. A clear pattern between species type and size in relation to bioaccumulation of persistent organic pollutants in Tampa Bay was not observed.

The quantity of contaminants, as well as the type of congeners identified is a reflection of the health of the bay, but may be influenced by factors such as population density, overland flow of contaminants into the watershed, the amount of materials being used in the bay that contain these contaminants, rainfall events, tidal cycles, circulation of currents in the bay, and other factors that extended beyond the scope of the study, and indeed leave much unanswered. Through personal interview with Dr. Steve Geiger, it was mentioned that the average size of the American oyster, and even the green mussel have diminished in size, and average life expectancy has also decreased. As a result, a

true bioaccumulative representation of compounds in the water column may remain unknown.

This study supports the use of sentinel species in the identification of persistent organic pollutants at various locations, and therefore helps assess water quality of the environment in which specific species are found. A range of bivalve species continues to be used in United States national reports (Kimbrough et al. 2009). Through this project, it was shown that there is an incidence of persistent organic pollutants in Tampa Bay. The highest POP value observed in visceral bivalve tissue was 25.93pg/g for BDE-99. In comparable studies in the Great Lakes, researchers argued that the maximum POP concentrations permissible prior to need for a public health advisory is 0.0146×10^6pg/g (Binelli and Provini, 2004), which is a vastly greater value than any recorded for this study.

One might assume that the concentrations of PCBs and PBDEs in Tampa Bay could be considered negligible. However, due to the possibility of accumulation of persistent organic pollutants both in the human body, and magnification along food chains, it is strongly and duly recommended to continue to adhere to local, regional, and international mandates. The Stockholm convention (enforced in 2004) is one such international mandate, which is a demonstration from the international community to the commitment and agreement on a legal framework geared toward the protection of human health and the environment, via reduction and elimination of the 12 persistent organic pollutants (Karlaganis et al., 2001). National legislative mandates include the Marine Protection Research and Sanctuaries Act (MPRSA [1988]), in response to which NOAA established the Mussel Watch program in 1986. The Act calls for continuous monitoring

conducted in order for marine environmental health assessments to be completed, and include monitoring of biota, the water column and sediment to assess levels of contaminants. This need is addressed under Section 202 of Title II (33 USC 1442). The activities and approach of the NOAA National Status and Trends Program, which includes the Mussel Watch Program, is included in the NOAA Authorization Act (1992), and are coded under the National Coastal Monitoring Act provisions (Title V, MPRSA) (Kimbrough et al. 2009). Added importance is due to the difficulty in containment of POPs. Factors such as long range transport and long half-lives of these compounds cause negative health effects on people while others continue to reap the benefit of continued POP use. (Bonefeld-Jorgensen and Ayotte, 2002).

Natural environmental degradation of some PBDEs and PCBs may decrease the risk of carcinogenic results. However, with environmental degradation, the lower brominated and chlorinated PBDEs and PCBs may result, tend to bioaccumulate more efficiently, and are considered to be more dangerous contaminants.Therefore risk assessments are recommended, taking into consideration factors such as exposure duration, body weight, food-chain multiplier and ingestion rate. Particular emphasis is made with respect to the cooking of seafood, where the method of preparation influences the amount of pollutants that is ingested (Barron et al., 1994; Novotny, 2003; vanLoon, 2005).

Adherence to mandates incorporates, but is not limited to, such legislation as the Stockholm Convention, which has included new POPs in addition to the original dirty dozen. Of the new POPs included in the Stockholm convention, BDE 47, 99 153, 154, 175 and 183 are included in the ambit of the convention. Out of these 6 Brominated

Diphenyl Ether congeners, BDE 47, 99, 153, 154 and 183 were tried and tested in analysis, and were present. The study is not only a primary attempt at identifying quantity of POPs in Tampa Bay, but the study supports international concern for these compounds in terms of persistence in the environment.

Project limitations

Samples were collected from August 2009 through to January 2011, with some samples undergoing extraction within a shorter time period than others. These photosensitive PCBs and PBDEs may have undergone weathering, and so the recorded concentrations may indeed be less than what is in fact present in the watershed aquatic system. With degradation of PCBs and PBDEs, there stood the risk of being incapable of seeing peaks of contaminants on the chromatograms following analysis using the GC ECD. Since the average oyster and mussel size was small, and the average size of individuals of this species is on the decline, there also stood the chance that PCBs or PBDEs did not have an extended time period to amass in the organisms, and therefore, the project results may better represent short time accumulation, if any at all, as opposed to accumulation of persistent organic pollutants over a longer time frame. In addition, sample collection through every season of the year, seasonal rainfall and abnormal rainfall events, tidal cycles, and current circulation factors were beyond the scope of the study.

Future trends and research

Seeing as these species of oyster and mussel have been identified in countries such as Trinidad and Tobago, and Jamaica, a similar study can be conducted in other locations, in order to complete a comparable assessment for these and other territories in terms of PCB and PBDE concentrations. Furthermore, there is added value to the faction of the population who consume seafood, and appropriate advisories can be established where required.

Also, because there is the assumption of analogous deleterious effects of PBDEs to that of PCBs (due to physico-chemical similarity), additional analytical chemistry results and investigation may help strengthen, or refute this alleged connection. Additional statistical tests can also be completed in the future, so as to directly identify significant differences in bioaccumulation between and among species, as well as significant differences in land use in relation to pollutant incidence. In order to further emphasize the role of GIS technology, environmental modeling can also be added to future research so to remove the static nature of the study. GIS will also enable additional factors, such as rainfall, census data, and current circulation, to be taken into account, as well as allow for predictions on future trends to be made with respect to aquatic contamination, and partitioning of these pollutants into the aquatic environment.

REFERENCES

Alegria, H.A, and T.J. Shaw. Rain Deposition of Pesticides in Coastal Waters of the South Atlantic Bight. Environmental Science and Technology. 1999, 33, 850-856.

Alegria, H.A., Bidleman, T.F., and T.J. Shaw. Organochlorine Pesticides in Ambient Air of Belize, Central America. Environmental Science and Technology. 2000, 34, 1953-1958.

Andric, S.A., Kostic, T.S., Stojilkovic, S.S., and R.Z. Kovacevic. Inhibition of Rat Testicular Adrogenesis by a Polychlorinated Biphenyl Mixture Aroclor 1248. Biology of Reproduction. 2000, 62, 1882-1888.

Antignac, J., Cariou, R., Maume, D., Marchand, P., Monteau, F., Zalko, D., Berrebi, A., Cravedi, J.; Andre, F., and B. Le Bizec. Exposure assessment of fetus and newborn to brominated flame retardants in France: preliminary data. Mol. Nutr. Food Res. 2008, 52, 258-265.

Baker, P., Fajans, J.S, Arnold, W.S., Ingrao, D.A., Marelli, D.C., and S.M. Baker. Range and Dispersal of a Tropical Marine Invader, The Asian Green mussel, Perna viridis, in Subtropical Waters of the Southeastern United States. Journal of Shellfish Research. 2007, 26 (2), 345-355.

Barron, M.G., Yurk, J.J., and D.B. Crothers. Assessment of Potential Cancer Risk from Consumption of PCBs Bioaccumulaed in Fish and Shellfish. Environmental Health Perspectives. 1994, 102 (6-7), 562- 567.

Bazzanti, M., Chiavarini, S., Cremisini, C., and P. Soldati. Distribution of PCB Congeners In Aquatic Ecosystems: A Case Study. Environment International. 1997, 23 (6), 799-813.

Bennett, D.H., Scheringer, M., McKone, T.E., and K. Hungerbuhler. Predicting Long-Range Transport: A Systematic Evaluation of Two Multimedia Transport Models. Environmental Science and Technology. 2001, 35, 1181-1189.

Beyer, A., Mackay, D., Matthies, M., Wania, F., and E. Webster. Assessing Long-Range Transport Potential of Persistent Organic Pollutants. Environmental Science Technology. 2000, 34, 699-703.

Binelli, A. and A. Provini. Risk for human health of some POPs due to fish from Lake Iseo. Ecotoxicology and Environmental Safety. 2004, 58, 139-145.

Birch, G.F., and S.E. Taylor. Distribution and Possible Sources of Organochlorine Residues in Sediments of a Large Urban Estuary. Australian Journal of Earth Sciences. 2000, 47, 749-756.

Bjorklund, E., von Holst, C., and E. Anklam. Fast extraction, clean-up and detection methods for the rapid analysis and screening of seven indicator PCBs in food matrices. Trends in Analytical Chemistry. 2002, 21, 39-52.

Bonefeld-Jorgensen, E.C. and P. Ayotte. Toxicological Properties of Persistent Organic Pollutants and Related Health Effects of Concern for the Arctic Populations. AMAP Assessment. 2002: Human Health in the Arctic. 57-74.

Brasher, A.M.D., and R.H. Wolff. Relations Between Land Use and Organochlorine Pesticides, PCBs, and Semi-Volatile Organic Compounds in Streambed Sediment and Fish on the Island of Oahu, Hawaii. Archives of Environmental Contamination Toxicology. 2004, 46, 385-398.

Buddo, D.S.A, Steele, R.D., and E.R. D'Oyen. Distribution of the Invasive Indo-Pacific Green Mussel, Perna viridis, In Kingston Harbour, Jamaica. Bulletin of Marine Science. 2003, 72 (2), 433-441.

Chen, Z. Monitoring Water Quality in Tampa Bay: Coupling in Situ and Remote Sensing. 2006.

Covaci, A., Voorspoels, S., J. de Boer. Determination of brominated flame retardants, with emphasis on polybrominated diphenyl ethers (PBDEs) in environmental and human samples- a review. Environment International. 2003, 29, 735-756.

De Boer, J., de Boer, K., and J.P. Boon. Polybrominated Biphenyl and Diphenylethers. The Handbook of Environmental Chemistry. 2000. Vol 3. Park K.

Eljarrat, E. and D. Barceló. Priority lists for persistent organic pollutants and emerging contaminants based on their relative toxic potency in environmental samples. Trends in Analytical Chemistry. 2003, 22 (10), 655-665.

Erickson, M.D. 1997. Analytical Chemistry of PCBs. Lewis Publishers, Boca Raton and New York.

Ferreira, A.M., and C. Vale. PCB Accumulation and Alterations of Lipids in Two Length Classes of the Oysters *Crassostrea angulata* and of the Clam *Ruditapes decussates*. Marine Environmental Research. 1998, 45 (3), 259-268.

Fisher, W.S., Oliver, L.M., Winstead, J.T., and E.R. Long. A survey of Oysters Crassostrea virginica from Tampa Bay, Florida: Associations of Internal Defense Measurements with Contaminant Burdens. Aquatic Toxicology. 2000, 51, 115-138.

Gouin, T. and T. Harner. Modeling the environmental fate of the polybrominated diphenyl ethers. Environment International. 2003, 29, 717-724.

Gouin, T., MacKay, D., Webster, E., and F. Wania. Screening Chemicals for Persistence in the Environment. Environmental Science and Technology. 2000, 34, 881-884.

Harner, T. and M. Shoeib. Measurement of Octanol-Air Partition Coefficients (KOA) for POlybrominated Diphenyl Ethers (PBDEs): Predicting Partitioning in the Environment. Chemical and Enginerring Data. 2002, 47 (2), 228-232.

Harrad, S. 2010. Persistent Organic Pollulants. Wiley. United Kingdom.

Hooper, K. and T.A. McDonald. The PBDEs: An Emerging Environmental Challenge and Another Reason for Breast-Milk Monitoring Programs. Environmental Health Perspectives. 2000, 108 (5), 387-392.

Iwata, H., Tanabe, S., Sakal, N., and R. Tatsukawa. Distribution of Persistent Organochlorines in the Oceanic Air and Surface Seawater and the Role on Their Global Transport and Fate. Environmental Science and Technology. 1993, 27, 1080-1098.

Jantunen, L.M.M., Bidleman, T.F., Harner, T. and W.J. Parhurst. Toxaphene, Chlordane, and other Organochlorine Pesticides in Alabama Air. Environmental Science and Technology. 2000, 34, 5097-5105.

Jaward, F.M., Farrar, N.J., Harner, T., Sweetman, A.J., and K.C. Jones. Passive Air Sampling of PCBs, PBDEs, and Organochlorine Pesticides Across Europe. Environmental Science and Technology. 2004, 38, 34-41.

Jeer, S. and B. Bain. Traditional color coding for land use. American Planning Association. 1997.

Johansson, J.O.R., and R.R. Lewis. Recent improvements of water quality and biological indicators in Hillsborough Bay, a highly impacted subdivision of Tampa Bay, Florida, USA. Sicence of the Total Environment suppliment 1992, 1199-1215.

Jones, K.C., and P. de Voogt. Persistent Organic Pollutants (POPs): State of the Science. Environmental Pollution. 1999, 100, 209-221.

Jurado, E., Jaward, F., Lohmann, R., Jones, K.C., Simo, F., and J. Dachs. Wet Deposition of Persistent Organic Pollutants to the Global Oceans. Environmental Science and Technology. 2005, 39, 2426-2435.

Karlaganis, G., Marioni, R., Sieber, I., and A. Weber. The Elaboration of the ‘Stockholm Convention’ on Persistent Organic Pollutants (POPs): A Negotiation Process Fraught with Obstacles and Opportunities. Environmental Science and Pollution. 2001, 8 (3), 216-221.

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

Kimbrough, K. L., W. E. Johnson, G. G. Lauenstein, J. D. Christensen and D. A. Apeti. 2009. An Assessment of Polybrominated Diphenyl Ethers (PBDEs) in Sediments and Bivalves of the U.S. Coastal Zone. Silver Spring, MD. NOAA Technical Memorandum NOS NCCOS 94. 87 pp.

Kohler, H.P.E., Kohler-Staub, D. and D.D. Focht. Cometabolism of Polychlorinated Bipheyls: Enhanced Transformation of Arochlor 1254 by Growing Bacterial Cells. Applied and Environmental Microbiology. 1988, 54 (8), 1940-1945.

Krueger, J. 'The Basel Convention and the International Trade in Hazardous Wastes', in Olav Schram Stokke and Øystein B. Thommessen (eds.), Yearbook of International Co-operation on Environment and Development. 2001/2002 (London: Earthscan Publications), 43–51.

Lallas, P.L. The Stockholm Convention on Persistent Organic Pollutants. The American Journal of International Law. 2001, 95 (3), 692-708.

Lee, T., Yam, W.C., Tam, T.-Y., Ho, B.S.W., Ng, M.H., and M.J. Broom. Occurrence of Hepatitis A Virus in Green-Lipped Mussels (*Perna viridis*). Water Research. 1999, 33(3), 885-889.

MacKay, D., McCarty, L.S., and M MacLeod. On the Validity of Classifying Chemicals for Persistence, Bioaccumulation, Toxicity, and Potential for Long-Range Transport. Environmental Toxicology and Chemistry, 2001, 20 (7) 1491-1498.

Mackova, M., Vrchotova, B., Francova, K., Sylvestre, M., Tomaniova, M., Lovecka, P., Demnerova, K., and T. Macek. Biotransformation of PCBs by plants and bacteria-consequences of plant-microbe iterations. European Journal of Soil Biology. 2007, 43, 233-241.

McFarland, V.A., and J.U. Clarke. Environmental Occurrence, Abundance, and Potential Toxicity of Polychlorinates Biphenyl Congeners: Considerations for a Congener-Specific Analysis. Environmental Health Perspectives. 1989, 81, 225-239.

McKinney, J.D. and C.L. Walker. Polychlorinated Biphenyls as Hormonally Active Structural Analogues. Environmental Health Perspectives. 1994, 102 (3), 290-297.

NIMPIS 2002. Perna viridis species summary. National Introduced marine Pest Information System (Eds: Hewitt C.L., Martin R.B., Sliwa C., McEnnulty F.R., Murphy N.E., Jones T., and Cooper S.

Novotny, V. Water Quality: Diffuse Pollution and Watershed Management. 2003. Wiley. New Jersey.

T.P. O'Connor. National distribution of chemical concentrations in mussels and oysters in the USA. Marine Environmental Research. 2002, 53, 117-143.

Rahman, F., Langford, K.H., Scrimshaw, M.D., and J.N. Lester. Polybrominated diphenyl ether (PBDE) flame retardants. Science of the Total Environment. 2001, 275, 1-17.

Rajagopal, S., Venugopalan, V.P., van der Velde, G., and H.A. Jenner. Greening of the Coasts: A review of the *Perna viridis* success story. Aquatic Ecology. 2006, 40, 273-297.

Ramu, K., Kajiwara, N., Tanabe, S., Lam, P.K.S., and T.A. Jefferson. Polybrominated diphenyl ethers (PBDEs) and organochlorines in small cetaceans from Hong Kong waters: Levels, profiles and distribution. Marine Pollution Bulletin. 2005, 51, 669-976.

Rodan, B.D., Pennington, D.W., Eckley, N., and R.S. Beothling. Screening for Persistent Organic Pollutants: Techniques To Provide a Scientific Basis for POPs Criteria in International Negotiations. Environmental Science and Technology. 1999, 33, 3482-3488.

Safe, S., Bandiera, S., Sawyer, T., Robertson, L., Safe, L., Parkinson, A., Thomas, P.E., Ryan, D.E., Reik, L.M., Levin, W., Denomme, M.A. and T. Fujita. PCBs: Structure-Function Relationships and Mechanism of Action. Environmental Health Perspectives. 1985, 60, 47-56.

Santschi, P.H., Presley, B.J., Wade, T.L., Garcia-Romero, B., and M. Baskaran. Historical contamination of PAHs, PCBs, DDTs, and heavy metals in Mississippi River Delta, Galveston Bay and Tampa Bay sediment cores. Marine Environmental Research. 2001, 52, 51-79.

Sellers, M.A., and J.G. Stanley. 1984. Species Profiles: Life Histories and Environmental Requirements of Coastal Fishes and Invertebrates (North Atlantic)-American Oyster. U.S. Fish Wildlife Service, Washington, DC, USA. FWS/OBS-82/11.23. U.S. Army Corps of Engineers, TR EL-82-4. 1984, 15 pp.

Steen, W.C., Paris, D.F., and G.L. Baughman. Partitioning of selected polychlorinated biphenyls to natural sediments. Water Research. 1978, 12, 655-657.

Ter Schure, A.F.H., Larsson, P., Agrell, C., and J.P. Boon. Atmospheric Transport of Polybrominated Biphenyls to the Baltic Sea. Environmental Science and Technology. 2004, 38 (5), 1282-1287.

Tilbury, K.L., Stein, J.E., Medor, J.P., Krone, C.A., and S. Chan. Chemical Contaminants in Harbor Porpoise (Phocoena phocoena) from the North Atlantic Coast: Tissue Concentrations and Intra- and Inter-Organ Distribution. Chemosphere. 1997, 34 (9/10), 2159-2181.

Ucan-Marin, F., Arukwe, A., Mortensen, A., Gabrielsen, G.W., Fox, G.A., and R.J. Letcher. Recombinant Transthyretin Purification and Competitive Binding with Organohalogen Compounds in Two Gull Species (Larus argentatus and Larus hyperboreus). Toxicological Sciences. 2009, 107 (2), 440-450.

USGS. Department of the Interior. Florida Caribbean Science Center. 2001. No. 2001-002. http://www.fcsc.usgs.gov.

Van den Berg, M., et al. Toxic Equivalency Factors (TEFs) for PCBs, PCDDs, PCDFs for Humans and Wildlife. Environmental Health Perspectives. 1998, 106 (12), 775-782.

VanLoon, G.W., and S. J. Duffy. Environmental Chemistry: a global perspective. 2005. Oxford University Press. Oxford and New York.

Wang, X., Gong, P., Yao, T., and K.C. Jones. Passive Air Sampling of Organochlorine Pesticides, Polychlorinated Biphenyls, and Polybrominated Diphenyl Ethers Across the Tibetan Plateau. Environmental Science and Technology. 2010, 44, 2988-2993.

Xian, G., Crane, M., and J. Su. An analysis of urban development and its environmental impact on the Tampa Bay watershed. Environmental Management. 2007, 85, 965-976.

APPENDICES

Appendix I. Biological data recorded for Perna viridis and Crassostrea virginica individuals acquired at all sample sites

Date: 9.10.09						
Site: Lower Estuary (and seawall)						
Species	Sample Code	Total weight (g)	Vial weight (g)	Vial and meat weight (g)	Meat weight (g)	Length (mm)
C. virginica	LEC1 (9.10.09)	38.93	16.97	20.29	3.32	53.10
C. virginica	LEC2 (9.10.09)	54.65	16.85	24.64	7.79	67.90
C. virginica	LEC3 (9.10.09)	12.02	16.96	19.14	2.18	48.70
C. virginica	LEC4 (9.10.09)	16.71	16.99	20.11	3.12	49.30
C. virginica	LEC5 (9.10.09)	15.36	16.92	18.59	1.67	49.00
C. virginica	LEC6 (9.10.09)	15.73	16.97	19.02	2.05	40.40
C. virginica	LEC7 (9.10.09)	23.77	16.92	21.56	4.64	56.60
C. virginica	LEC8 (9.10.09)	18.09	16.97	19.36	2.39	48.10
C. virginica	LEC9 (9.10.09)	17.34	22.29	25.11	2.82	42.00
C. virginica	LEC10 (9.10.09)	12.45	22.03	24.31	2.28	31.60

Date: 8.10.09						
Site: Teco Power Plant						
Species	Sample Code	Total weight (g)	Vial weight (g)	Vial and meat weight (g)	Meat weight (g)	Length (mm)
C. virginica	TPPC1 (8.10.09)	57.51	22.18	30.10	7.92	88.20
C. virginica	TPPC2 (8.10.09)	37.70	22.08	28.10	6.02	77.50
C. virginica	TPPC3 (8.10.09)	12.14	21.77	23.61	1.84	50.00
C. virginica	TPPC4 (8.10.09)	31.40	22.22	26.60	4.38	67.50
C. virginica	TPPC5 (8.10.09)	17.80	22.12	25.87	3.75	55.90
C. virginica	TPPC6 (8.10.09)	15.66	22.08	24.85	2.77	47.10
C. virginica	TPPC7 (8.10.09)	15.50	21.92	25.08	3.16	42.30
C. virginica	TPPC8 (8.10.09)	11.75	22.00	24.20	2.20	43.10
C. virginica	TPPC9 (8.10.09)	18.57	21.80	24.30	2.50	67.00
C. virginica	TPPC10 (8.10.09)	12.50	22.13	24.98	2.85	41.50

Date: 8.10.09						
Site: Teco Power Plant						
Species	Sample Code	Total weight (g)	Vial weight (g)	Vial and meat weight (g)	Meat weight (g)	Length (mm)
P. viridis	TPPP1 (8.10.09)	34.81	21.81	32.61	10.80	74.40
P. viridis	TPPP2 (8.10.09)	28.54	21.74	31.13	9.39	68.30
P. viridis	TPPP3 (8.10.09)	37.06	22.20	33.76	11.56	79.60
P. viridis	TPPP4 (8.10.09)	14.97	22.09	27.66	5.57	52.70
P. viridis	TPPP5 (8.10.09)	41.68	22.04	34.91	12.87	83.10
P. viridis	TPPP6 (8.10.09)	18.06	21.89	26.87	4.98	56.70
P. viridis	TPPP7 (8.10.09)	41.13	21.94	32.40	10.46	79.70
P. viridis	TPPP8 (8.10.09)	30.01	22.13	31.28	9.15	73.90
P. viridis	TPPP9 (8.10.09)	21.06	22.22	29.76	7.54	62.90
P. viridis	TPPP10 (8.10.09)	25.26	21.98	28.73	6.75	64.70

Date: 9.01.09						
Site: Teco Power Plant						
Species	Sample Code	Total weight (g)	Vial weight (g)	Vial and meat weight (g)	Meat weight (g)	Length (mm)
C. virginica	TPPC1 (9.01.09)	34.63	21.88	27.69	5.81	71.80
C. virginica	TPPC2 (9.01.09)	8.50	22.04	22.99	0.95	38.60
C. virginica	TPPC3 (9.01.09)	66.52	21.86	30.09	8.23	92.60
C. virginica	TPPC4 (9.01.09)	17.05	22.19	24.35	2.16	54.90
C. virginica	TPPC5 (9.01.09)	7.62	22.17	23.36	1.19	39.60
C. virginica	TPPC6 (9.01.09)	11.63	22.05	24.33	2.28	54.90
C. virginica	TPPC7 (9.01.09)	10.52	21.65	23.63	1.98	55.90
C. virginica	TPPC8 (9.01.09)	32.50	21.92	26.84	4.92	72.80
C. virginica	TPPC9 (9.01.09)	15.24	21.98	23.55	1.57	56.60
C. virginica	TPPC10 (9.01.09)	20.06	21.99	24.09	2.10	58.80

Date: 9.01.09						
Site: Teco Power Plant						
Species	Sample Code	Total weight (g)	Vial weight (g)	Vial and meat weight (g)	Meat weight (g)	Length (mm)
P. viridis	TPPP1 (9.01.09)	3.42	22.25	23.22	0.97	33.90
P. viridis	TPPP2 (9.01.09)	5.26	21.99	23.36	1.37	39.00
P. viridis	TPPP3 (9.01.09)	2.93	21.92	22.59	0.67	30.80
P. viridis	TPPP4 (9.01.09)	1.53	21.79	22.20	0.41	26.10
P. viridis	TPPP5 (9.01.09)	2.60	21.99	22.70	0.71	29.50
P. viridis	TPPP6 (9.01.09)	3.17	22.04	22.88	0.84	32.60
P. viridis	TPPP7 (9.01.09)	2.10	22.27	23.89	1.62	38.80
P. viridis	TPPP8 (9.01.09)	5.30	21.79	22.78	0.99	38.30
P. viridis	TPPP9 (9.01.09)	3.11	21.95	22.43	0.48	32.90
P. viridis	TPPP10 (9.01.09)	3.31	22.28	23.16	0.88	32.10

Date: 8.10.09						
Site: Vinoy Sea Wall						
Species	Sample Code	Total weight (g)	Vial weight (g)	Vial and meat weight (g)	Meat weight (g)	Length (mm)
C. virginica	VSWC1 (8.10.09)	12.88	21.54	23.56	2.02	32.50
C. virginica	VSWC2 (8.10.09)	16.18	21.97	25.63	3.66	48.50
C. virginica	VSWC3 (8.10.09)	31.31	22.27	25.25	2.98	67.20
C. virginica	VSWC4 (8.10.09)	31.63	22.24	25.10	2.86	50.60
C. virginica	VSWC5 (8.10.09)	21.28	21.69	28.20	6.51	40.90
C. virginica	VSWC6 (8.10.09)	8.70	22.24	24.11	1.87	34.90
C. virginica	VSWC7 (8.10.09)	20.06	21.88	24.63	2.75	57.20
C. virginica	VSWC8 (8.10.09)	17.99	21.94	25.49	3.55	47.60
C. virginica	VSWC9 (8.10.09)	11.24	22.09	24.44	2.35	43.00
C. virginica	VSWC10 (8.10.09)		21.97			

Date: 8.10.09						
Site: Vinoy Sea Wall						
Species	Sample Code	Total weight (g)	Vial weight (g)	Vial and meat weight (g)	Meat weight (g)	Length (mm)
P. viridis	VSWP1 (8.10.09)	12.25	22.02	25.22	3.20	55.00
P. viridis	VSWP2 (8.10.09)	13.67	22.06	26.68	4.62	56.30
P. viridis	VSWP3 (8.10.09)	15.01	22.06	26.36	4.30	57.90
P. viridis	VSWP4 (8.10.09)	11.97	22.05	25.64	3.59	52.20
P. viridis	VSWP5 (8.10.09)	14.64	21.77	26.87	5.10	55.90
P. viridis	VSWP6 (8.10.09)	13.17	21.74	25.98	4.24	54.80
P. viridis	VSWP7 (8.10.09)	13.41	21.79	25.56	3.77	52.80
P. viridis	VSWP8 (8.10.09)	14.08	21.96	26.43	4.47	55.70
P. viridis	VSWP9 (8.10.09)	17.10	22.19	27.65	5.46	61.20
P. viridis	VSWP10 (8.10.09)	15.56	22.02	26.49	4.47	56.80

Date: 9.01.09						
Site: Vinoy Sea Wall						
Species	Sample Code	Total weight (g)	Vial weight (g)	Vial and meat weight (g)	Meat weight (g)	Length (mm)
C. virginica	VSWC1 (9.01.09)	47.60	22.02	28.08	6.06	70.60
C. virginica	VSWC2 (9.01.09)	38.58	22.11	25.51	3.40	74.70
C. virginica	VSWC3 (9.01.09)	17.18	21.98	24.33	2.35	42.50
C. virginica	VSWC4 (9.01.09)	17.66	21.61	24.67	3.06	48.20
C. virginica	VSWC5 (9.01.09)	25.34	21.81	25.86	4.05	68.40
C. virginica	VSWC6 (9.01.09)	34.56	22.17	27.39	5.22	59.70
C. virginica	VSWC7 (9.01.09)	36.99	21.63	26.56	4.93	71.20
C. virginica	VSWC8 (9.01.09)	19.94	21.89	25.18	3.29	51.50
C. virginica	VSWC9 (9.01.09)	23.71	21.85	25.50	3.65	53.10
C. virginica	VSWC10 (9.01.09)	26.42	21.91	25.66	3.75	52.60

Date: 9.01.09						
Site: Vinoy Sea Wall						
Species	Sample Code	Total weight (g)	Vial weight (g)	Vial and meat weight (g)	Meat weight (g)	Length (mm)
P. viridis	VSWP1 (9.01.09)	17.61	22.02	26.97	4.95	55.90
P. viridis	VSWP2 (9.01.09)	19.58	22.11	27.43	5.32	61.90
P. viridis	VSWP3 (9.01.09)	16.36	21.98	26.23	4.25	53.40
P. viridis	VSWP4 (9.01.09)	9.09	21.96	24.20	2.24	47.20
P. viridis	VSWP5 (9.01.09)	12.46	21.81	25.53	3.72	53.40
P. viridis	VSWP6 (9.01.09)	13.99	22.13	26.54	4.41	57.50
P. viridis	VSWP7 (9.01.09)	19.84	22.27	28.16	5.89	62.90
P. viridis	VSWP8 (9.01.09)	15.15	21.89	26.20	4.31	57.00
P. viridis	VSWP9 (9.01.09)	13.79	22.16	25.07	2.91	52.50
P. viridis	VSWP10 (9.01.09)	18.39	22.08	27.18	5.10	56.80

Date: 9.08.09						
Site: Gandy Bridge						
Species	Sample Code	Total weight (g)	Vial weight (g)	Vial and meat weight (g)	Meat weight (g)	Length (mm)
C. virginica	GBC1 (9.08.09)	18.21	21.76	26.12	4.36	48.30
C. virginica	GBC2 (9.08.09)	16.26	22.12	24.16	2.04	36.40
C. virginica	GBC3 (9.08.09)	12.43	21.91	24.26	2.35	44.80
C. virginica	GBC4 (9.08.09)	9.14	21.94	24.27	2.33	44.50
C. virginica	GBC5 (9.08.09)	15.02	21.90	24.82	2.92	48.10
C. virginica	GBC6 (9.08.09)	8.28	22.00	23.72	1.72	29.80
C. virginica	GBC7 (9.08.09)	10.95	21.77	23.66	1.89	42.70
C. virginica	GBC8 (9.08.09)	11.30	21.68	24.08	2.40	32.90
C. virginica	GBC9 (9.08.09)	9.12	21.86	23.46	1.60	33.10
C. virginica	GBC10 (9.08.09)	6.15	22.05	23.75	1.70	35.10

Date: 9.01.09						
Site: Bay Shore Sea Wall						
Species	Sample Code	Total weight (g)	Vial weight (g)	Vial and meat weight (g)	Meat weight (g)	Length (mm)
C. virginica	BSSWC1 (9.01.09)	22.17	22.02	25.18	3.16	56.70
C. virginica	BSSWC2 (9.01.09)	14.34	21.91	23.42	1.51	52.20
C. virginica	BSSWC3 (9.01.09)	17.88	22.12	24.10	1.98	52.50
C. virginica	BSSWC4 (9.01.09)	20.33	22.17	24.14	1.97	44.80
C. virginica	BSSWC5 (9.01.09)	16.75	22.40	24.74	2.34	49.20
C. virginica	BSSWC6 (9.01.09)	19.06	22.05	23.58	1.53	41.60
C. virginica	BSSWC7 (9.01.09)	54.25	21.78	26.88	5.10	66.00
C. virginica	BSSWC8 (9.01.09)	12.21	21.85	23.34	1.49	28.60
C. virginica	BSSWC9 (9.01.09)	10.81	21.68	22.86	1.18	43.40
C. virginica	BSSWC10 (9.01.09)	11.62	22.04	23.24	1.20	38.80

Date: 9.08.09						
Site: Upper Estuary						
Species	Sample Code	Total weight (g)	Vial weight (g)	Vial and meat weight (g)	Meat weight (g)	Length (mm)
C. virginica	UEC1 (9.08.09)	13.40	16.89	19.70	2.81	47.50
C. virginica	UEC2 (9.08.09)	12.59	16.93	19.06	2.13	44.80
C. virginica	UEC3 (9.08.09)	14.33	16.91	19.26	2.35	49.80
C. virginica	UEC4 (9.08.09)	14.96	16.92	19.60	2.68	51.40
C. virginica	UEC5 (9.08.09)	23.99	16.94	20.59	3.65	59.30
C. virginica	UEC6 (9.08.09)	11.40	16.86	19.41	2.55	44.00
C. virginica	UEC7 (9.08.09)	8.60	16.95	18.35	1.40	39.90
C. virginica	UEC8 (9.08.09)	11.28	16.99	19.39	2.40	46.00
C. virginica	UEC9 (9.08.09)	18.66	16.94	19.82	2.88	53.80
C. virginica	UEC10 (9.08.09)	13.33	16.96	19.92	2.96	45.30

Date: 9.08.09						
Site: Upper Estuary						
Species	Sample Code	Total weight (g)	Vial weight (g)	Vial and meat weight (g)	Meat weight (g)	Length (mm)
P. viridis	UEP1 (9.08.09)	1.22	16.89	17.25	0.36	19.80
P. viridis	UEP2 (9.08.09)	0.92	16.87	17.19	0.32	18.30
P. viridis	UEP3 (9.08.09)	0.38	17.01	17.12	0.11	12.80
P. viridis	UEP4 (9.08.09)	0.47	16.93	17.08	0.15	13.30
P. viridis	UEP5 (9.08.09)	0.36	16.88	16.99	0.11	15.60
P. viridis	UEP6 (9.08.09)	0.46	16.87	16.99	0.12	14.10
P. viridis	UEP7 (9.08.09)	0.27	16.98	17.05	0.07	11.10
P. viridis	UEP8 (9.08.09)	0.43	16.93	17.04	0.11	13.00
P. viridis	UEP9 (9.08.09)	0.53	16.93	17.09	0.16	14.50
P. viridis	UEP10 (9.08.09)	0.46	16.95	17.06	0.11	13.50

Date: 8.12.09						
Site: Boca Ciega Bay (Lower Estuary)						
Species	Sample Code	Total weight (g)	Vial weight (g)	Vial and meat weight (g)	Meat weight (g)	Length (mm)
C. virginica	BCBC1 (8.12.09)	20.89	22.03	25.53	3.50	40.22
C. virginica	BCBC2 (8.12.09)	13.99	21.81	24.30	2.49	45.00
C. virginica	BCBC3 (8.12.09)	44.05	16.91	23.16	6.25	58.50
C. virginica	BCBC4 (8.12.09)	49.45	16.97	23.97	7.00	58.00
C. virginica	BCBC5 (8.12.09)	76.94	21.65	28.06	6.41	65.60
C. virginica	BCBC6 (8.12.09)	42.12	16.93	22.37	5.44	61.90
C. virginica	BCBC7 (8.12.09)	21.30	16.91	20.87	3.96	45.90
C. virginica	BCBC8 (8.12.09)	17.12	16.93	20.60	3.67	48.50
C. virginica	BCBC9 (8.12.09)	136.83	22.09	36.96	14.87	96.50
C. virginica	BCBC10 (8.12.09)	16.76	16.88	19.13	2.25	45.50

Date: 8.12.09						
Site: Boca Ciega Bay (Lower Estuary)						
Species	Sample Code	Total weight (g)	Vial weight (g)	Vial and meat weight (g)	Meat weight (g)	Length (mm)
P. viridis	BCBP1 (8.12.09)	6.01	21.96	23.66	1.70	37.00
P. viridis	BCBP2 (8.12.09)	20.62	16.95	21.71	4.76	53.60
P. viridis	BCBP3 (8.12.09)	13.80	17.01	20.80	3.79	52.40
P. viridis	BCBP4 (8.12.09)	14.54	16.93	21.94	5.01	55.70
P. viridis	BCBP5 (8.12.09)	8.28	16.98	19.53	2.55	44.50
P. viridis	BCBP6 (8.12.09)	4.82	16.96	18.03	1.07	31.50
P. viridis	BCBP7 (8.12.09)	4.12	16.88	17.96	1.08	31.60
P. viridis	BCBP8 (8.12.09)	4.23	16.88	18.07	1.19	32.00
P. viridis	BCBP9 (8.12.09)	5.89	16.95	18.31	1.36	36.60
P. viridis	BCBP10 (8.12.09)	14.15	16.87	20.50	3.63	49.70

Date: 10.20.09						
Site: Lower Estuary						
Species	Sample Code	Total weight (g)	Vial weight (g)	Vial and meat weight (g)	Meat weight (g)	Length (mm)
C. virginica	LEC1 (10.20.09)	20.23	16.89	20.23	3.34	46.10
C. virginica	LEC2 (10.20.09)	29.27	16.91	21.80	4.89	51.90
C. virginica	LEC3 (10.20.09)	37.00	16.95	23.16	6.21	57.60
C. virginica	LEC4 (10.20.09)	19.60	16.93	21.11	4.18	51.70
C. virginica	LEC5 (10.20.09)	24.84	16.91	21.36	4.45	58.80
C. virginica	LEC6 (10.20.09)	33.99	16.93	21.29	4.36	67.00
C. virginica	LEC7 (10.20.09)	23.75	16.90	21.25	4.35	46.70
C. virginica	LEC8 (10.20.09)	12.75	16.93	19.60	2.67	49.70
C. virginica	LEC9 (10.20.09)	18.09	16.94	20.34	3.40	45.30
C. virginica	LEC10 (10.20.09)	11.32	16.90	19.10	2.20	40.20

Date: 9.25.10						
Site: Ruskin						
Species	Sample Code	Total weight (g)	Vial weight (g)	Vial and meat weight (g)	Meat weight (g)	Length (mm)
C. virginica	RUC1 (9.25.10)	13.47	16.97	19.22	2.25	41.10
C. virginica	RUC2 (9.25.10)	18.60	16.94	19.52	2.58	44.00
C. virginica	RUC3 (9.25.10)	43.56	16.94	22.42	5.48	62.20
C. virginica	RUC4 (9.25.10)	29.80	16.92	22.10	5.18	53.20
C. virginica	RUC5 (9.25.10)	13.83	16.96	18.85	1.89	44.70
C. virginica	RUC6 (9.25.10)	19.61	16.94	19.52	2.58	54.40
C. virginica	RUC7 (9.25.10)	16.82	16.97	19.23	2.26	42.60
C. virginica	RUC8 (9.25.10)	20.62	16.96	19.98	3.02	54.30
C. virginica	RUC9 (9.25.10)	21.81	16.92	20.10	3.18	48.30
C. virginica	RUC10 (9.25.10)	20.59	16.97	20.15	3.18	44.50

Date: 10.01.10						
Site: Upper Tampa Bay Park						
Species	Sample Code	Total weight (g)	Vial weight (g)	Vial and meat weight (g)	Meat weight (g)	Length (mm)
C. virginica	UTBC1 (10.01.10)	28.17	16.98	21.55	4.57	61.40
C. virginica	UTBC2 (10.01.10)	39.52	17.05	22.28	5.23	77.00
C. virginica	UTBC3 (10.01.10)	37.21	16.99	22.31	5.32	71.90
C. virginica	UTBC4 (10.01.10)	18.31	16.92	19.36	2.44	56.00
C. virginica	UTBC5 (10.01.10)	23.86	16.96	20.03	3.07	70.30
C. virginica	UTBC6 (10.01.10)	22.76	16.96	19.55	2.59	48.20
C. virginica	UTBC7 (10.01.10)	29.23	16.97	20.85	3.88	56.90
C. virginica	UTBC8 (10.01.10)	24.66	16.98	20.06	3.08	66.90
C. virginica	UTBC9 (10.01.10)	46.20	16.92	22.52	5.60	81.50
C. virginica	UTBC10(10.01.10)	33.21	16.97	19.98	3.01	65.00

Date: 01.28.11						
Site: Safety Harbor						
Species	Sample Code	Total weight (g)	Vial weight (g)	Vial and meat weight (g)	Meat weight (g)	Length (mm)
C. virginica	SHC1 (01.28.11)	42.69	16.78	19.63	2.85	51.45
C. virginica	SHC2 (01.28.11)	43.06	17.02	20.86	3.84	51.61
C. virginica	SHC3 (01.28.11)	14.60	16.91	18.53	1.62	52.35
C. virginica	SHC4 (01.28.11)	19.66	16.79	19.29	2.5	60.23
C. virginica	SHC5 (01.28.11)	21.81	16.83	19.86	3.03	50.85
C. virginica	SHC6 (01.28.11)	52.28	16.75	21.79	5.04	71.87
C. virginica	SHC7 (01.28.11)	37.21	16.88	20.11	3.23	55.12
C. virginica	SHC8 (01.28.11)	24.03	16.89	19.23	2.34	51.05
C. virginica	SHC9 (01.28.11)	73.13	16.90	22.37	5.47	71.45
C. virginica	SHC10(01.28.11)	22.79	16.69	19.57	2.88	54.09

Appendix II. Sample sites and species collected, together with sampling months

Site	Species Collected		Sampling Month					
	P. viridis	*C. virginica*	Aug 2009	Sept 2009	Oct 2009	Sept 2010	Oct 2010	Jan 2011
Boca Ciega Bay	x	x	x					
Vinoy SeaWall	x	x	x	x				
Bay Shore SeaWall		x		x				
Lower Estuary Bird Cay	x			x				
Upper Estuary		x		x				
Lower Estuary		x		x	x			
Gandy Bridge		x		x				
Upper Estuary	x			x				
Teco Power Plant	x	x	x	x				
Ruskin E.G. Simmons		x				x		
Upper Tampa Bay Park		x					x	
Safety Harbor		x						x

Appendix III. Raw concentrations in pg/uL of persistent organic pollutants in all samples

weight	20.86	6.47	7.52	9.80	15.20	31.50	10.06	12.34	6.01
	bcbc 8.12.09	bsswc 9.01.09	gbc 9.08.09	lebcp 9.10.09	lec 9.10.09	tppp 8.10.09	vswc 8.10.09	lec 10.20.09	tppp 9.01.09
BDE-28			31.8		9.303		64.796		
BDE-47	32.7	10.2	14.5	24.0	10.676	10.922	25.112	26.514	10.964
BDE-100	129.3	15.7	31.0	28.4	29.341	11.271	18.449		19.424
BDE-99	82.8	25.3	73.2	11.0	56.128	24.149	41.387	12.624	167.506
BDE-154	210.9	10.5	37.6		12.336	10.089	8.915	9.69	22.371
BDE-153	292.8	16.0	68.0	23.9	16.879	13.717	7.28	20.915	17.703
BDE-183		8.9							
PCB-28									
PCB-52							60.781		
PCB-90/101		16.2	20.1	10.3	30.53		28.725	10.306	8.266
PCB-152	67.6								9.509
PCB-118	60.2	33.1	8.0	8.5	8.76	18.984	26.805	9.287	7.603
PCB-138	13.2	10.1	8.4	8.4	9.246	8.204	10.714	10.641	9.082
PCB-157		7.9	8.2			7.866			
PCB-180	14.4	10.2		11.5	10.228	10.427	11.477	10.798	10.393

weight	23.64	31.60	9.62	26.85	16.74	0.86	11.22	30.79
	vswp 8.10.09	ruc 9.25.10	uec 9.08.09	vswp 9.01.09	tppc 8.10.09	uep 9.08.09	tppc 9.01.09	utbc 10.01.10
BDE-28				14.679				
BDE-47		17.508	15.327	15.383		13.04		
BDE-100	9.72	54.621	10.859	14.096	12.122		16.338	
BDE-99	23.087	15.924	25.262	25.83	14.738		54.96	
BDE-154		10.497		8.579			17.092	
BDE-153		6.997	11.929		12.949		14.131	
BDE-183						8.232		8.211
PCB-28							0.495	
PCB-52								
PCB-90/101	23.581	7.414	18.457	12.531	6.195		10.513	4.77
PCB-152			16.844	14.42			16.661	
PCB-118	22.833	7.298	11.577			9.91	24.297	
PCB-138	12.226	9.482	11.041	9.369	8.313	9.692	8.647	8.755
PCB-157		8.116		8.899		8.294	8.479	
PCB-180	10.47	10.792	10.926	11.324	10.205	10.358	10.216	10.187

Appendix IV. Final concentrations in pg/g of persistent organic pollutants in all samples

	Final Conc pg/g								
	bcbc 8.12.09	**bsswc 9.01.09**	**gbc 9.08.09**	**lebcp 9.10.09**	**lec 9.10.09**	**tppp 8.10.09**	**vswc 8.10.09**	**lec 10.20.09**	**tppp 9.01.09**
BDE-28			3.06				5.57		
BDE-47	1.07		0.56	1.40			1.47	1.31	
BDE-100	5.60		2.45	1.62	1.11				
BDE-99	3.41	2.10	8.17		2.92	0.40	2.95		25.93
BDE-154	10.11	1.62	5.00		0.81	0.32	0.89	0.79	3.72
BDE-153	13.64	1.20	7.94	1.60	0.57	0.17		1.03	1.58
BDE-183		1.38							
PCB-28									
PCB-52							6.04		
PCB-90/101		1.66	1.95	0.49	1.65		2.31	0.39	0.47
PCB-152	3.03								0.87
PCB-118	2.58	4.13	0.22	0.22	0.16	0.40	2.03	0.24	0.21
PCB-138	0.63	1.56	1.12	0.86	0.61	0.26	1.06	0.86	1.51
PCB-157									
PCB-180	0.21			0.14			0.14		

			Final Conc pg/g					
	vswp 8.10.09	ruc 9.25.10	uec 9.08.09	vswp 9.01.09	tppc 8.10.09	uep 9.08.09	tppc 9.01.09	utbc 10.01.10
BDE-28				0.22				
BDE-47		0.23	0.52	0.19		3.17		
BDE-100		1.33						
BDE-99	0.48	0.13	1.41	0.53	0.18		3.86	
BDE-154		0.33		0.32			1.52	
BDE-153			0.38		0.28		0.53	
BDE-183						9.53		0.27
PCB-28								
PCB-52								
PCB-90/101	0.77	0.06	1.35	0.26			0.45	
PCB-152			1.30	0.38			1.10	
PCB-118	0.70		0.54			4.10	1.60	
PCB-138	0.52	0.30	1.15	0.35	0.50	11.22	0.77	0.28
PCB-157				0.04				
PCB-180				0.05				

Appendix V. Raw data recorded in pg/uL for Method blanks used for correction of raw data

Raw data pg/ul Method Blanks								
PBDE/ PCB	**mblk1,6.09**	**mblk2,6.09**	**mblk3,6.09**	**mblk5,6.09**	**Mean**	**stdev**	**3xstdev**	**LOD**
BDE-28		8.8			8.8		0.0	2.0
BDE-47				10.3	10.3		0.0	2.0
BDE-100	10.5	17.6	10.1	12.0	12.5	3.5	10.4	**10.4**
BDE-99	10.8	12.5		11.8	11.7	0.9	2.6	**2.6**
BDE-154							0.0	2.0
BDE-153	8.5	8.0			8.2	0.3	1.0	2.0
BDE-183							0.0	2.0
PCB-28							0.0	1.0
PCB-52							0.0	1.0
PCB-90/101	5.2	5.8	5.2	5.6	5.5	0.3	1.0	1.0
PCB-152	4.3				4.3		0.0	1.0
PCB-118	6.2	6.4	6.6	6.2	6.4	0.2	0.5	1.0
PCB-138								1.0
PCB-157				7.9	7.9		0.0	1.0
PCB-180	10.1	10.1			10.1	0.0	0.1	1.0

Appendix VI. External laboratory polychlorinated biphenyl raw data results for sample sites

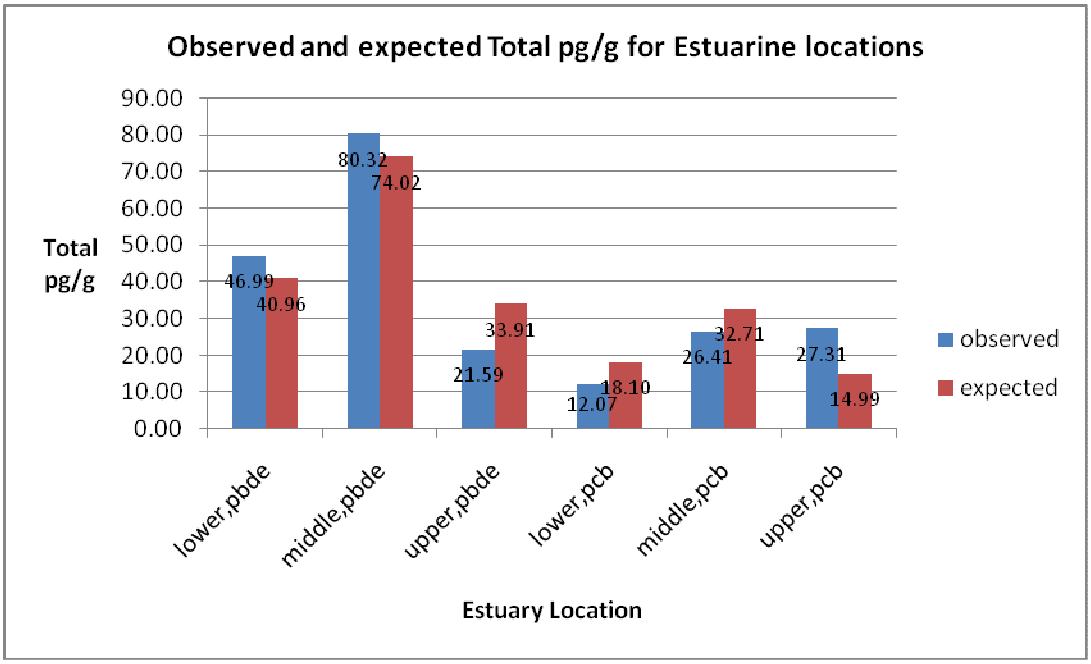
PCB/PBDE	BCB 8.12.09	GBC 9.08.09	LEC 10.20.09	LEL 9.10.09	RUC 9.25.09	SHC 9.28.11	TPPC 8.10.09
PCB 8	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	40.12
PCB 15	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 18	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 17	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 16/32	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 31	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 28	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 33	N.D. d	N.D. d	321.99	N.D. d	N.D. d	N.D. d	N.D. d
PCB 37	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 52	N.D. d	112.08	N.D. d	961.43	822.68	803.81	N.D. d
PCB 49	N.D. d	170.71	N.D. d	1850.9	N.D. d	535.45	N.D. d
PCB 44	N.D. d	598.64	N.D. d	N.D. d	N.D. d	555.46	N.D. d
PCB 42	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 74	N.D. d	N.D. d	N.D. d	1587.12	N.D. d	N.D. d	N.D. d
PCB 70	N.D. d	N.D. d	N.D. d	805.19	N.D. d	N.D. d	N.D. d
PCB 66	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 56/60	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 81	N.D. d	N.D. d	816.39	N.D. d	N.D. d	N.D. d	N.D. d
PCB 77	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 95	N.D. d	N.D. d	N.D. d	1125.37	594.39	397	N.D. d
PCB 101	N.D. d	N.D. d	N.D. d	3063.59	N.D. d	1206.86	N.D. d
PCB 99	N.D. d	N.D. d	N.D. d	2678.95	N.D. d	1116.61	N.D. d
PCB 87	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 110	N.D. d	N.D. d	N.D. d	2557.41	N.D. d	924.25	N.D. d
PCB 123	N.D. d	696.78	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 118	N.D. d	N.D. d	N.D. d	4517.49	N.D. d	1449.05	N.D. d
PCB 114	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 105	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d

PCB/PBDE	BCB 8.12.09	GBC 9.08.09	LEC 10.20.09	LEL 9.10.09	RUC 9.25.09	SHC 9.28.11	TPPC 8.10.09
PCB 126	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 151	N.D. d	137.81	N.D. d	699.73 PG	445	322.3	N.D. d
PCB 149	4356.07	458.27	263.3	3143.46 PG	1873.76	1433.92	509.45
PCB 153	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	4940.07	N.D. d
PCB 137	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 138	N.D. d	N.D. d	298.03	N.D. d	2105.33	1311.05	N.D. d
PCB 128	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 156	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 157	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 187	5513.64	504.6	447.21	2792.81	2318.75	3274.13	589.69
PCB 183	439.38	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 185	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 174	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 177	N.D. d	203.97	N.D. d	1114.68	524.43	N.D. d	N.D. d
PCB 171	N.D. d	N.D. d	N.D. d	1105.36	614.76	N.D. d	N.D. d
PCB 180	N.D. d	165.02	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 170	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 199	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 200	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 203	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 195	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 194	N.D. d	N.D. d	N.D. d	N.D. d	19523.95	N.D. d	N.D. d
PCB 205	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 207	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 208	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 209	N.D. d	N.D. d	N.D. d	460.37	N.D. d	N.D. d	N.D. d

PCB/PBDE	TPPC 9.01.09	TPPP 8.10.09	TPPP 9.01.09	UEP 9.08.09	VSWC 8.10.09	VSWP 8.10.09
PCB 8	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 15	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 18	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 17	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 16/32	N.D. d	N.D. d	N.D. d	N.D. d	204.5	N.D. d
PCB 31	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 28	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 33	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 37	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 52	468.64	N.D. d	N.D. d	394.15	1240.6	217.36
PCB 49	757.09	N.D. d	N.D. d	475.27	3230.46	426.02
PCB 44	579.7	N.D. d	N.D. d	N.D. d	N.D. d	601.74
PCB 42	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 74	2277.86	N.D. d	639.22	N.D. d	N.D. d	N.D. d
PCB 70	230.16	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 66	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 56/60	N.D. d	N.D. d	785.25	N.D. d	N.D. d	N.D. d
PCB 81	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 77	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 95	823.43	N.D. d	N.D. d	335.64	N.D. d	N.D. d
PCB 101	2658.48	N.D. d	N.D. d	1027.94	N.D. d	N.D. d
PCB 99	4163.19	N.D. d	N.D. d	910.01	N.D. d	N.D. d
PCB 87	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 110	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 123	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 118	N.D. d	N.D. d	N.D. d	904.35	N.D. d	1679.94
PCB 114	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 105	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d

PCB/PBDE	TPPC 9.01.09	TPPP 8.10.09	TPPP 9.01.09	UEP 9.08.09	VSWC 8.10.09	VSWP 8.10.09
PCB 126	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 151	1039	N.D. d	N.D. d	N.D. d	N.D. d	567.95
PCB 149	3594.19	1454.02	690.26	950.47	14501.13	1934.59
PCB 153	N.D. d	N.D. d	5964.51	N.D. d	N.D. d	N.D. d
PCB 137	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 138	N.D. d	N.D. d	774.06	N.D. d	N.D. d	N.D. d
PCB 128	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 156	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 157	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 187	5169.48	2094.27	888.57	963.33	13624.24	2264.35
PCB 183	N.D. d	N.D. d	N.D. d	N.D. d	1101.56	752.2
PCB 185	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 174	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 177	1495.33	661.34	N.D. d	430.97	3340.58	847.66
PCB 171	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	358.1
PCB 180	N.D. d	N.D. d	327.31	631.71	N.D. d	1106.02
PCB 170	N.D. d	N.D. d	N.D. d	N.D. d	2323.01	N.D. d
PCB 199	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 200	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 203	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 195	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 194	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 205	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 207	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 208	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d
PCB 209	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d	N.D. d

Appendix VII. Data recorded as comparison of total polychlorinated biphenyl and polybrominated diphenyl ether concentrations in pg/g for all sample sites. Site subdivision recorded according to lower, middle and upper estuarine location



Appendix VIII. Project flowchart