STATUS OF TAMPA BAY SEDIMENTS: POLYCYCLIC AROMATIC HYDROCARBONS, ORGANOCHLORINE PESTICIDES, AND POLYCHLORINATED BIPHENYLS (1993 & 1995-1999)

Stephen A. Grabe & Joseph Barron



1900 9th Avenue Tampa, FL 33605

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Environmental Protection Commission of Hillsborough County

Richard Garrity, Ph.D. Executive Director

Christopher A. Dunn Director, Water Management Division

Tom Cardinale Assistant Director, Water Management Division

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EXECUTIVE SUMMARY

Monitoring of Tampa Bay sediments for organic contaminants has been on-going since 1993 (excluding 1994). This program targets three classes of contaminants: polycyclic aromatic hydrocarbons, which include combustion products of petrochemicals used by automobiles and other vehicles; organochlorine pesticides, which include chemicals such as DDT and chlordane; and polychlorinated biphenyls, which have been used in electrical transformers. Most organochlorine pesticides and polychlorinated biphenyls are no longer produced because of their adverse effects on the environment.

Polycyclic aromatic hydrocarbon contamination is almost totally confined to low salinity waters: the Lower Hillsborough River, Palm River, and portions of upper Hillsborough Bay. Some sites in the Hillsborough River have concentrations which are likely to be toxic to aquatic life. The highest concentrations were found in the Hillsborough River near I-275 and near the mouth of the Hillsborough. Polycyclic aromatic hydrocarbons were rarely detected in higher salinity waters and in the coarser, sandier sediments found in most of Tampa Bay. The major source of polycyclic aromatic hydrocarbons to the bay is likely urban stormwater runoff, although incinerators and coal-burning power plants also appear to be sources.

The occurrence of pesticides, especially chlordane and DDT, were also generally confined to urban areas (e.g., Lower Hillsborough River, a Culbreath Bayou canal in Old Tampa Bay). Again, low salinity habitats were most affected by pesticides. The majority of Tampa Bay appears unimpacted by pesticides. Sources to the bay appear to primarily be urban stormwater

Polychlorinated biphenyls have been found in very high concentrations in the Palm River, in moderate to high concentrations in the Lower Hillsborough River, and low to moderate concentrations in portions of upper Hillsborough Bay. Polychlorinated biphenyls were only rarely detected elsewhere in the bay.

In general then, the urban tributaries and residential canals are the areas primarily impacted by organic contaminants; the industrial portions of Hillsborough Bay appear less impacted.

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I. INTRODUCTION

Organic contaminants, including polycyclic aromatic hydrocarbon (PAHs), organochlorine pesticides, and polychlorinated biphenyls (PCBs) are an environmental concern because they may be carcinogenic and mutagenic to aquatic life (Eisler 1987; Gassman et al. 1994; McCain et al. 1996; Finley et al. 1997); sublethal effects (e.g., altered reproductive success, fecundity, etc.) of organic contaminants may also affect the composition and structure of benthic communities (Somerfield et al. 1994; Carman et al. 1995; Ward & Hutchings 1996; Murdoch et al. 1997), which could ultimately be expressed as a detrimental effect at higher trophic levels (e.g., fishes, birds). The pesticide DDT and its degradation products have been associated with egg thinning in birds; organochlorine pesticides and PCBs have been linked to reproductive disorders in aquatic animals (Mora 1996; Stahlschmidt-Allner et al. 1997). PCB contamination has adversely impacted commercial and recreational fisheries in the Great Lakes and the Hudson River/New York Harbor area and, more recently, pesticide contamination triggered a health advisory for fish consumption in Collier County, FL (Ross 1995).

PAHs are ring-shaped organic compounds typically associated with the production and combustion of fossil fuels (Eisler 1987). Specific routes to waterways and sediments include atmospheric deposition after incineration, runoff from roadways, and point-source discharges (Hoffman *et al.* 1984; Eisler 1987; Golomb *et al.* 1997; Ianuzzi *et al.* 1997). Runoff and wastewater treatment plant discharges have been specifically cited as the primary sources of PAHs to Tampa Bay (Doyle *et al.* 1985; Frithsen *et al.* 1995).

Synthetic pesticides have been widely used in the U.S. since World War II, starting with the synthesis and application of DDT (Nimmo 1979). Organochlorine pesticides, which tend to be long-lived in the environment, have generally been discontinued in recent years (e.g., toxaphene after 1986 and chlordane after 1988; Bidleman et al. 1998a). Although DDT was discontinued in the 1970s, dicofol, a miticide manufactured from DDT (Kamrin 1997) was

produced until 1986 when registration was temporarily withdrawn. Subsequently it was reregistered when the manufacturing process was modified to significantly reduce the amount of DDT.

Because organochlorine pesticides are generally long-lived (e.g., dieldrin may have a half-life in excess of two decades; Nagami 1997), their residues can constitute an environmental hazard. The presence of organochlorine pesticides in contemporary sediment samples may also reflect local or regional atmospheric transport of volatilized pesticides which were applied to agricultural lands decades ago (Spencer et al. 1996; Nagami 1997; Bidleman et al. 1998a; 1998b) as well as runoff from freshly tilled local farmland (Frithsen et al. 1995). Within the Tampa Bay system, Frithsen et al. (1995) identified agricultural runoff as a primary entry point for chiordane, DDT, dieldrin, and endosulfan.

PCBs are synthetic chlorinated hydrocarbons developed primarily for use as an insulating fluid in electrical equipment; other uses included dust control (during road construction), and in pesticides (Kennish et al. 1992). PCB production was halted after 1977 (Kennish et al. 1992). PCBs enter waterways and become associated with sediments via both point source and non-point source discharges (Kennish et al. 1992) as well as atmospheric deposition after incineration (Finley et al. 1997). The primary source of PCBs to Tampa Bay remains indeterminate since estimates could only be developed for atmospheric inputs (Frithsen et al. 1995). Swain (1983) reports that PCBs have half-lives of 8 to 15 years.

The Tampa Bay Estuary Program (McConnell et al. 1996) reviewed both ecological and human health risks associated with contaminated sediments in Tampa Bay. Increased risk was associated with the organochlorine pesticides DDT, heptachlor, heptachlor epoxide, and lindane, high molecular weight PAHs, the individual PAHs fluoranthene and benzo(a)pyrene, and PCBs. Additional "contaminants of concern" listed for Tampa Bay (Frithsen et al. 1995) include chlordane, dieldrin, endosulfan, and mirex. McConnell et al. (1996) also concluded that there was some potential for human health risk via consumption of fish from those portions of Hillsborough Bay contaminated by chlordane and heptachlor.

At least two studies have shown that sediment contaminants in Tampa Bay specifically can lead to adverse effects on the resident biota. McCain et al. (1996) reported that at least four species of fish (Arius felis [sea catfish], Sciaenops ocellatus [red drum], Fundulus grandis [Gulf killifish] and F. majalis [longnose killifish]) collected from Hillsborough Bay had elevated tissue concentrations of Chlordane, DDT, PAHs, and PCBs sufficient to contribute to morphological and histochemical changes. Fisher et al. (2000) showed not only that the oyster, Crassostrea virginica, accumulated organic contaminants such as PAHs, PCB, and pesticides, but that in many cases, the elevated concentrations of contaminants were associated with increased physiological or behavioral defense mechanisms.

Tampa Bay's sediments have been the object of short-term, spatially intensive investigations by the University of South Florida (Doyle *et al.* 1985; Doyle *et al.* 1989; Brooks & Doyle 1991 & 1992), the National Oceanographic & Atmospheric Administration (Long *et al.* 1991; Long *et al.* 1994; Daskalaskis & O'Connor 1994; Long *et al.* 1995; Carr *et al.* 1996), and the Florida Department of Environmental Protection (Seal *et al.* 1994). Beginning in 1993, an annual baywide benthic/sediment monitoring program was established under the auspices of the Tampa Bay National Estuary Program.

The objective of this report is to summarize all data collected through 1999, with particular emphasis on the 1995-1999. The extents of sediment contamination will be assessed within and across bay segments, within four tributaries, by year, and by habitat type for selected PAHs, organochlorine pesticides, and PCBs.

II. MATERIALS & METHODS

II.1 Study Design

Coastal Environmental, Inc. (1994) designed the benthic/sediment contaminant monitoring program for Tampa Bay after the USEPA's Environmental Monitoring and Assessment Program (USEPA 1990). Tampa Bay is stratified into seven bay segments (cf. Lewis & Whitman 1985): Old Tampa Bay, Hillsborough Bay, Middle Tampa Bay, Lower Tampa Bay, Boca Ceiga Bay, Terra Ceia Bay, and the Manatee River. Sample locations were selected at random and with known probability within each segment; locations are re-randomized annually for all segments except the Manatee River and Terra Ceia Bay. This design yields approximate unbiased estimates of the measured variables (Coastal Environmental, Inc. 1994). All sediment samples were collected during the late August through mid-October "Index Period"; sample locations for 1993 and 1995-1999 (organic contaminants were not analyzed during 1994) are shown in Figure 1 and Appendix Figures A-1 through A-6.

This design was supplemented in 1995 and 1996 by limited sampling of the Lower Hillsborough River, Palm River, Alafia River, and Little Manatee River (1996 only). Beginning in 1997 this aspect of the monitoring program was more rigorously structured with the intent to collect 20-25 samples per tributary during 1997-2000. Sampling of these tributaries was further intensified in 1999. This last modification will produce a database whereby the putative impacts of elements of Tampa Bay Water's "Master Water Plan" (Tampa Bay Water 1998) may be evaluated. Tributary sampling locations during 1995-1999 are shown in Figure 1 and Appendix Figures A-7 through A-10.

In addition to assessing the status of the bay segments and tributaries, data were post-stratified by habitat type. Habitat type was defined by salinity (Venice System; *cf.* Bulger *et al.* 1990) and sediment characteristics (*i.e.*, percent of silt+clay). Five salinity strata were defined: euhaline (≥30 ppt), polyhaline (≥18<30 ppt), mesohaline (≥5<18), oligohaline (≥0.5<5.0), and

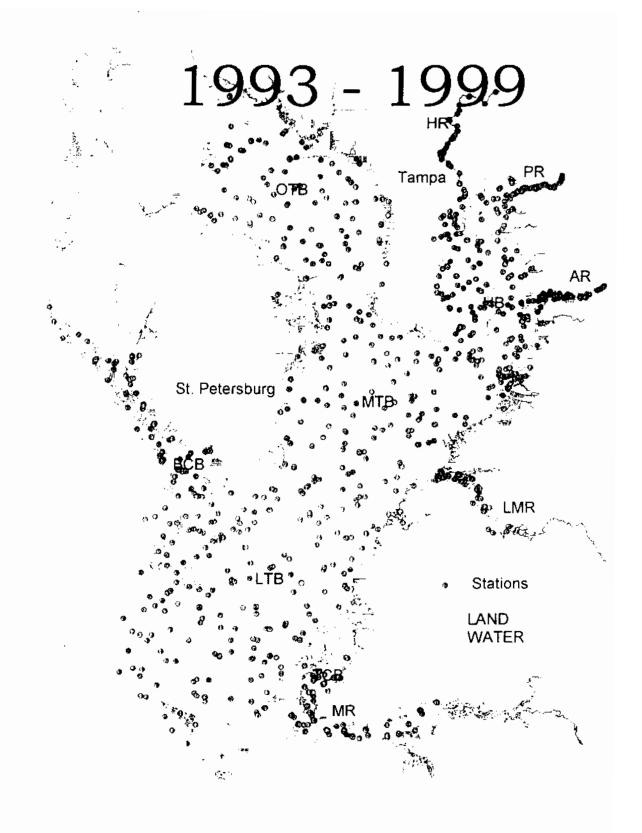


Figure 1. Location of sampling stations in Tampa Bay, 1993 & 1995-1999.

tidal freshwater (<0.5 ppt). Five sediment strata were defined by the percent silt+clay content: <5%, \geq 5%<25%, \geq 25%<75%, and \geq 75% <90%, and \geq 90% (Table 1). Seventeen of the 25 possible "habitats" were identified during 1993-1999, and 13 were retained for data analyses (Table 1).

Table 1. Number of samples (N), by salinity strata, sediment strata, and habitat type, Tampa Bay 1993-1999.

| SALINITY STRATA | N | HABITAT TYPE | N |
|--------------------------------|-----|---------------------------------|-----|
| Polyhaline (>=18<30 ppt) | 720 | Polyhaline <5% SC | 330 |
| Mesohaline (>=5<18 ppt) | 195 | Polyhaline >=5%<25% SC | 188 |
| Euhaline (>=30 ppt) | 159 | Euhaline <5% SC | 80 |
| Tidal Freshwater (<0.5 ppt) | 47 | Mesohaline <5% SC | 75 |
| Oligohaline (>=0.5<5 ppt) | 36 | Mesohaline >=5%<25% SC | 70 |
| No Data | 14 | Polyhaline >=25%<75% SC | 69 |
| | | Euhaline >=5%<25% SC | 66 |
| % SILT+CLAY STRATA (%SC) | N | Mesohaline >=25%<75% SC | 20 |
| <=5% SC | 518 | Tidal Freshwater >=5%<25% SC | 18 |
| >=5%<25% SC | 360 | Tidal Freshwater <5% SC | 15 |
| >=25%<75% SC | 105 | Oligohaline <5% SC | 13 |
| >=75%<90% SC | 11 | Oligohaline >=5%<25% SC | 12 |
| >=90% SC | 1 | Polyhaline >=75% SC | 11 |
| No Data | 172 | Oligohaline* >=25%<75% SC | 7 |
| | | Euhaline* >=25%<75% SC | 5 |
| | | Tidal Freshwater* 25-75% SC | 4 |
| | | High Mesohaline* >=90% SC | 1 |

^{*}excluded from data analyses

II.2 Field Methods

Sediment samples were collected with a 0.04 m² stainless steel Young grab sampler. The sampler was cleaned at each station with ambient bay water during 1993; thereafter the sampler was scrubbed with Liquinox, then rinsed in ambient bay water followed by a rinse with pesticide grade isopropanol (Courtney et al. 1995). The upper two centimeters of sediment were removed with either a stainless steel or Teflon trowel and spooned into a stainless steel beaker. In 1993 both implements were cleaned with ambient bay water only; thereafter they were cleaned with Liquinox and isopropanol (Courtney et al. 1995).

Sediments from several grabs were composited to ensure there was a sufficient amount of sediment for chemical analyses. The sample was then homogenized by thoroughly mixing the contents of the beaker with the trowel. The sample was then spooned into 500-ml glass jars (Teflon lined caps), which had been chemically cleaned (acid wash) in the laboratory. Field duplicates were collected at approximately 10% of the sample sites for quality assurance.

Samples for silt + clay analysis were collected with a syringe from a separate grab sample collected for characterization of the benthic community.

II.3 Laboratory Methods

During 1993 the Skidaway Institute of Oceanography (Savannah, GA), courtesy of USEPA-Gulf Breeze, analyzed the samples using methods described in USEPA (1993). QA/QC were after Heitmuller & Valente (1993).

Since 1995, EPCHC's laboratory analyzed sediment samples using EPA Method 8080 for organochlorine pesticides and PCBs and Method 8270 for PAHs. Through the 1999 samples, extraction was performed using soxhlet extraction. The samples were air dried for 3 days, spiked with surrogate compounds and then extracted in a soxhlet apparatus for 16 hours with 100% methylene chloride. The extracts were then passed through a column of sodium sulfate and concentrated under nitrogen to 1.0 ml using a Zymark TurboVap II concentrator. The concentrates were then mixed with activated copper to remove sulfur. The samples were placed

in silica gel columns and eluted with 100% hexane and then a 40/60 mix of hexane/methylene chloride. The eluted samples were concentrated to 1.0 ml using the Zymark TurboVap II prior to analysis.

A Hewlett Packard 5890 GC fitted with a HP5972 MSD was used for PAH analysis. HP Enviroquant software was used to collect the data. An HP-5MS column (30m x 0.25mm x 0.25 µm film thickness) was used for the analysis.

Samples were analyzed for organochlorine pesticides and PCBs on a Hewlett Packard 5890 GC fitted with an electron capture device. PE Nelson 2600 and Agilent Technologies Chemstation software was used to collect the data. A Supelco SPB-5 column (30m x 0.53mm x 0.5µm film thickness) was used for primary analysis and a Supelco SPB-50 column (30m x 0.32mm x 0.5µm film thickness) was used for confirmation.

During 1996, samples collected from Boca Ciega Bay, Terra Ceia Bay, and Manatee River were analyzed for organochlorine pesticides only by a commercial laboratory (Southern Analytical Laboratory, Oldsmar, FL) using EPA Method 8080.

QA/QC was ensured by the use of matrix spikes and spiked duplicates. Accuracy was determined by analyzing the reference materials; the requirement was that the results be within 80% to 120% of the certified values (T. Heitmuller, *personal communication* 19 March 1997). Precision was determined by comparing the "relative percent difference" between matrix spike duplicates and matrix duplicates; the criterion was that the average relative percent difference be <30% (T. Heitmuller, *personal communication* 19 March 1997). Method detection limits [MDLs] are shown, by year and laboratory, in Appendix B.

The silt+clay content of sediments (as % silt+clay) was determined by wet sieving and drying 20g (mud) to 50g (sand) wet weight of sediment; methods are described in greater detail in Courtney et al. (1995) and Grabe et al. (1996).

II.4 Data Analyses

Contaminant concentrations <MDL (method detection limit) (Appendix B) were treated as 0.5*MDL in the data analyses. "Clean", "Marginal" and "Degraded" sediments were so designated by comparing concentrations of the measured contaminants with the Threshold Effects Level (TEL) and Predicted Effects Level (PEL) concentrations developed by MacDonald Environmental Services, Ltd. (1994) for Florida estuarine sediments (Table 1). The TEL is defined as the contaminant concentration below which adverse biological effects are rarely or never observed. The PEL is defined as the contaminant concentration above which adverse biological effects are likely.

Recent work by NOAA has shown that there is generally a high probability of biological effects when contaminant concentrations exceed the "Effects Range Median" (ERM) (Long et al. 1995b), a contaminant concentration that is similar to the PEL (Table 2). The likelihood of biological effects is quite low when contaminant concentrations are less than the "Effects Range Low" (ERL) (Long et al. 1995b), a contaminant concentration that is similar to the TEL. For example, organic contaminants at concentrations <ERL had biological effects in bioassays between 5% (ppDDE) and 27.3% (Fluorene) of the time. Conversely, at contaminant concentrations >ERM, biological effects were observed between 50% (ppDDE) and 100% of the time (e.g., acenapthylene and low molecular weight PAHs) (Long et al. 1995).

Another approach to identifying contaminated sediments is to compute the ratios of individual contaminant concentrations to their PEL (or ERM) and then average these over all contaminants or over a class of contaminants (PEL quotient). The specific composition of a PEL must be accurately described since all sediment quality monitoring programs do not necessarily include a common suite of variables. PEL quotients were calculated for organochlorine pesticides (chlordane + total DDT + dieldrin + lindane) and low and high molecular weight PAHs.

Table 2. Summary of TEL^a, ERL^b, PEL^a, and ERM^b concentrations (ppb) of organic contaminants.

| CONTAMINANT | TEL | ERL | PEL | ERM |
|----------------------------------|--------|--------|---------|---------|
| A. Organochlorine Pesticides | | | | |
| Chlordane | 2.26 | 0.50 | 4.79 | 6.00 |
| Dieldrin | 0.72 | 0.02 | 4.30 | 8.00 |
| Total DDT | 3.89 | 1.58 | 51.70 | 46.10 |
| Lindane | 0.32 | | 0.99 | |
| | | | | |
| B-1. Low Molecular Weight PAHs | | | | |
| Acenapthene | 6.71 | 16.0 | 88.9 | 500.0 |
| Acenapthylene | 5.87 | 44.0 | 128.0 | 640.0 |
| Anthracene | 46.9 | 85.3 | 245.0 | 1100.0 |
| Fluorene | 21.2 | 19.0 | 144.0 | 540.0 |
| Napthalene | 34.6 | 160.0 | 391.0 | 2100.0 |
| Phenanthrene | 86.7 | 240.0 | 544.0 | 1500.0 |
| Total Low Molecular Weight PAHs | 312.0 | 552.0 | 1442.0 | 3160.0 |
| B-2. High Molecular Weight PAHs | | | | |
| Benz(a)anthracene | 74.8 | 261.0 | 693.0 | 1600.0 |
| Benzo(a)pyrene | 88.8 | 430.0 | 763.0 | 1600.0 |
| Chrysene | 108.0 | 384.0 | 846.0 | 2800.0 |
| Dibenz(a,h)anthracene | 6.22 | 63.4 | 135.0 | 260.0 |
| Fluoranthene | 113.0 | 600.0 | 1494.0 | 5100.0 |
| Pyrene | 153.0 | 665.0 | 1398.0 | 2600.0 |
| Total High Molecular Weight PAHs | 655.0 | 1700.0 | 6676.0 | 9600.0 |
| | | | | |
| B-3. Total PAHs | 1684.0 | 4022.0 | 16770.0 | 44792.0 |
| C. Polychlorinated Biphenyls | | | | |
| Total PCBs | 21.6 | 22.7 | 189.0 | 180.0 |

^a TEL (Threshold Effects Level) and (PEL) Predicted Effects Level after MacDonald Environmental Services, Ltd. (1994)

b ERL (Effects Range-Low) and ERM (Effects Range-Median) after Long & Morgan (1990)

Sediments were designated as "clean" or "healthy" if a contaminant concentration was less than the TEL or if a PEL quotient was ≤0.1. Sediments were of "marginal" status if a contaminant concentration exceeded the TEL and was less than the PEL or if a PEL quotient was >0.1≤1.0. Sediments were designated as "subnominal" or "degraded" if a contaminant concentration exceeded the PEL or if a PEL quotient was >1.0.

Several PAH ratios have been advanced as interpretive tools for identifying possible source(s) of PAH contamination (Table 3). These include the ratios of phenanthrene:anthracene, fluoranthene:pyrene, benz(a)anthracene:chrysene, benzo(b)fluoranthene: benzo(k)fluoranthene, and indeno(1,2,3,c,d)pyrene:benzo(g,h,i)perylene (Benlahcen et al. 1997; Dickhut et al. 2000; McCready et al. 2000). Each ratio is expected to be lower in urban areas where runoff from combustion sources may be the predominant source of PAHs and higher where atmospheric deposition, including coal-fired power plants, predominates.

Table 3. PAH isomer ratios for emission sources (adapted from Benlahcen et al. 1997; Dickhut et al. 2000; McCready et al. 2000)

| SOURCE | BENZ(A): CHRYS | BENZO(B)FL: BENZO(K)FL | INDENO: BENZOPER | PYRENE: FLUORAN | PHEN: ANTHRAC |
|---------------------------|-------------------|---------------------------|---------------------|--------------------|------------------|
| VEHICULAR EMISSIONS | 0.53 | 1.26 | 0.33 | 1.0 | <10 |
| COAL | 1.11 | 3.70 | 1.09 | | |
| MUNICIPAL INCINERATORS | | | 1.0 | | |

Benz(a):Chrys=Benz(a)anthracene:Chrysene; Benz(b):Benz(k)=Benzo(bfluoranthene:Benzo(k)fluoranthene; Ind:Benz(ghi)=Indeno(1,2,3,c,d)pyrene:Benzo(g,h,i)perylene; Phen:Anth=Phneanathrene:Anthracene; Pyr:Fluor=Pyrene:Fluoranthene

The ratio of heptachlor:heptachlor epoxide is useful in identifying possible sources of the pesticide chlordane (Jantunen *et al.* 2000). Heptachlor is a component of technical chlordane and heptachlor epoxide is a metabolite of heptachlor. The breakdown of heptachlor primarily takes place in soils (Jantunen *et al.* 2000). Where the ratios of heptachlor to heptachlor epoxide are >1, urban residential emissions rather than agricultural applications are the most likely source of the chlordane (Jantunen *et al.* 2000).

The ratio of DDT:DDE may be useful in determining whether the DDT present has been recently applied or a residue of historical use. Tavares et al. (1999) suggested that, in Brazil, where the ratio was >0.91, DDT use was likely within the past five years.

One-way analysis of variance [ANOVA] (Sokal & Rohlf 1981) was used to test whether mean concentrations ($\log_{10} n+1$ ppb) of a contaminant were equal among Bay Segment-Year combinations and by habitat type (combinations of salinity strata and % SC content of the sediments). Where the main effect was statistically significant (p<0.05), equality of means was tested a posteriori by the Bonferroni method (Neter et al. 1985).

Regression and correlation analysis (Neter *et al.* 1985) was applied to determine the association among selected variables, including percent silt+clay and low molecular weight PAHs, high molecular weight PAHs, individual organochlorine pesticides, and PCBs.

Statistical analyses were carried out using SYSTAT 10 (SPSS 2000).

III. RESULTS

III.1 Habitats

Polyhaline salinities (Figures 2-7) and sediments of <5% silt+clay (Figure 8) have predominated within the study area during the targeted "Index Period" (cf. Table 1). This habitat is generally found from lower Old Tampa Bay and Middle Tampa Bay gulfward to upper Lower Tampa Bay. Oligohaline salinities and sediments of >75% silt+clay were relatively rare and tended to be confined to the Lower Hillsborough River.

III. 2 Polycyclic Aromatic Hydrocarbons

Twenty-four PAHs have been identified from Tampa Bay sediments since the inception of the monitoring program in 1993 (Table 4). Overall, PAHs were detected (>MDL) in 24.6% of the samples. Concentrations of both low molecular weight PAHs $(r_{1,703}=0.25)$ and high molecular weight PAHs $(r_{1,703}=0.38)$ were significantly associated (p<0.001) with the percent silt+clay (Figure 9). Each of the 12 PAHs comprising the low molecular PAH and high molecular weight PAH subgroup were significantly (p<0.05) correlated with each other with three exceptions: the associations of Acenapthylene with Anthracene, Chrysene, and Phenanthrene.

Low molecular weight PAHs were found in 16 % of samples and at concentrations up to 18,800 ppb (Lower Hillsborough River). ANOVA showed that there were significant differences in mean low molecular weight PAH concentrations by habitat $(F_{13,673}=11.4; p<0.001)$. Mean concentrations were highest in tidal freshwaters with sediments of 5% to 25% silt+clay and in oligohaline waters with sediments of 25% to 75% silt+clay (Figure 10); these sites were primarily found in the Lower Hillsborough River. Lowest concentrations were found in polyhaline and euhaline waters with sediments of <5% silt+clay. On a percentage basis, the most degraded habitats included oligohaline waters (20% to 33% of samples >PEL), tidal freshwaters of <5% silt+clay (60% of samples >TEL) (Table 5). PEL quotients in euhaline waters were all <0.1.

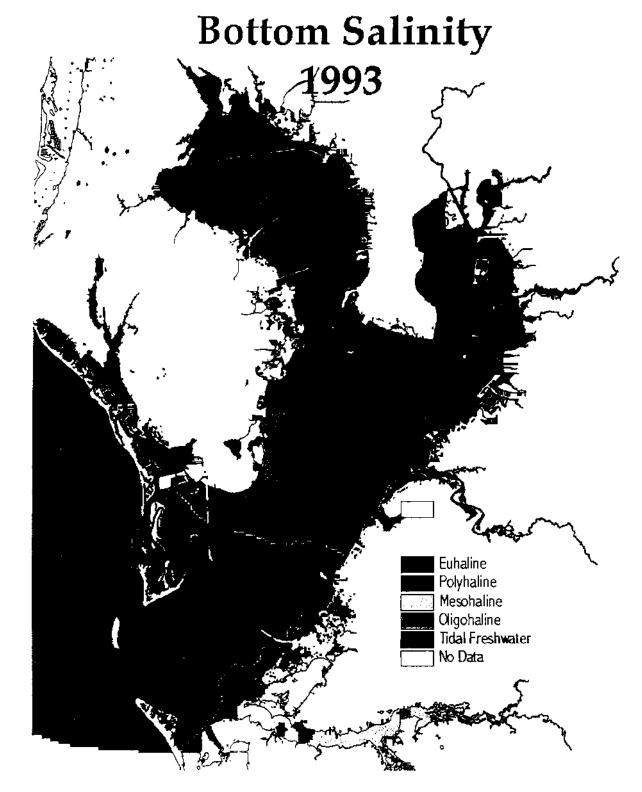


Figure 2. Distribution of salinity zones in near-bottom waters of Tampa Bay, 1993 Index Period.

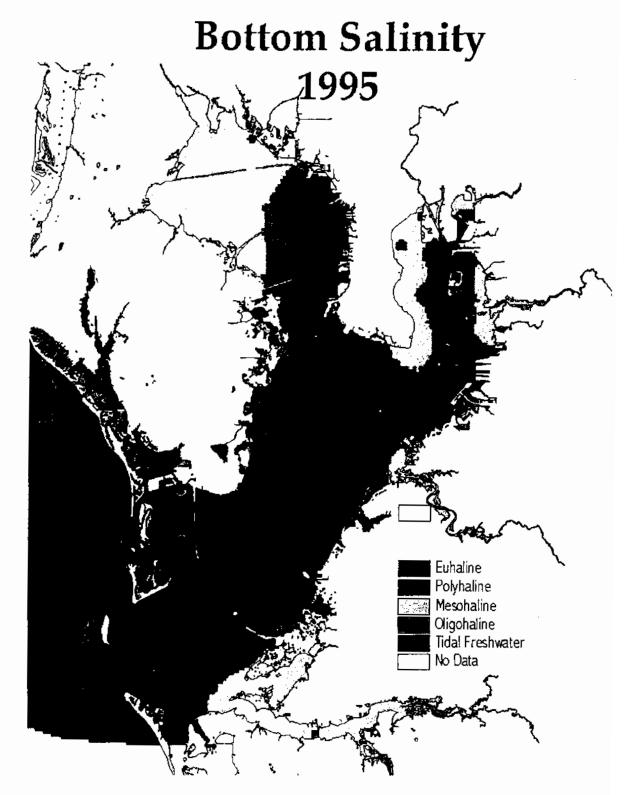


Figure 3. Distribution of salinity zones in near-bottom waters of Tampa Bay, 1995 Index Period.

Bottom Salinity

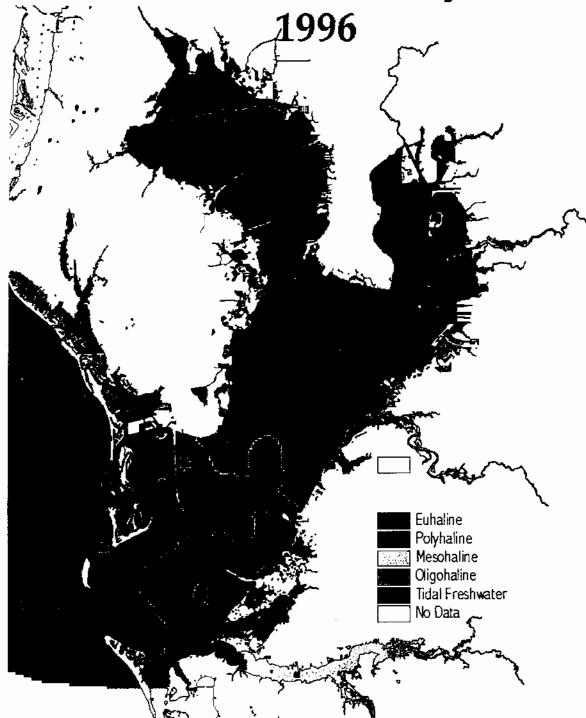


Figure 4. Distribution of salinity zones in near-bottom waters of Tampa Bay, 1996 Index Period.

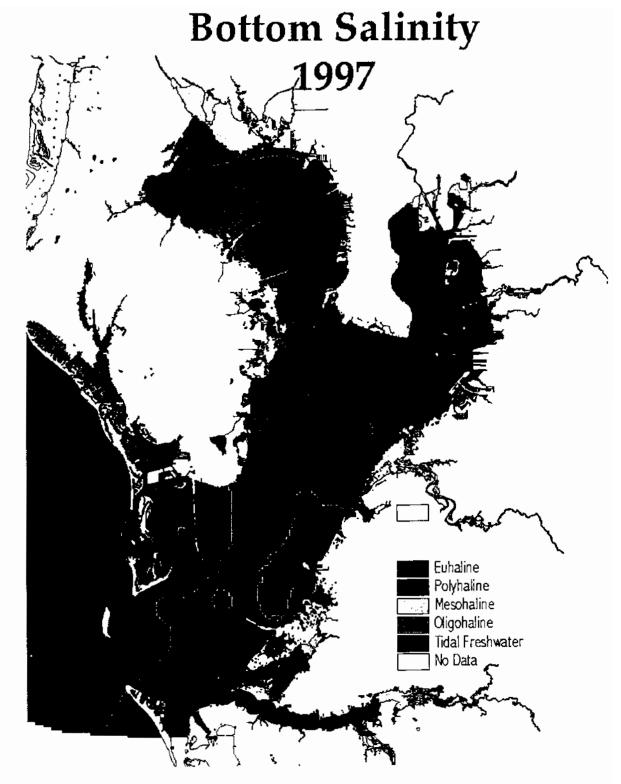


Figure 5. Distribution of salinity zones in near-bottom waters of Tampa Bay, 1997 Index Period.

Bottom Salinity

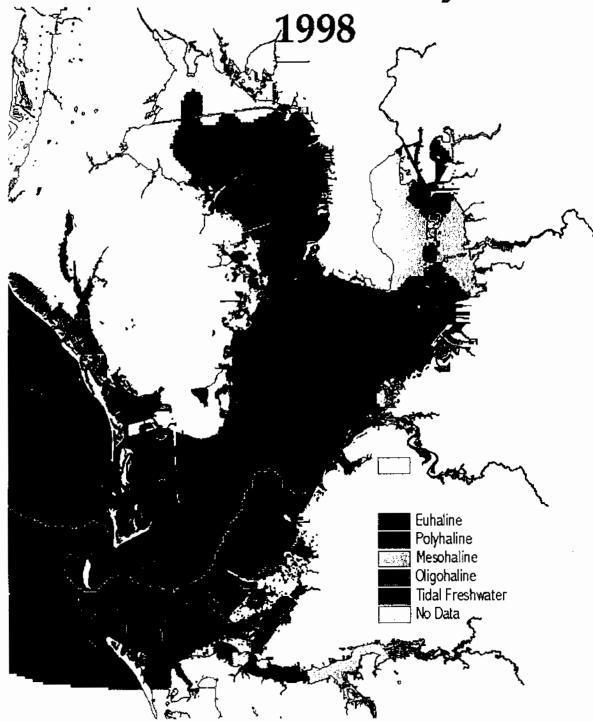


Figure 6. Distribution of salinity zones in near-bottom waters of Tampa Bay, 1998 Index Period.

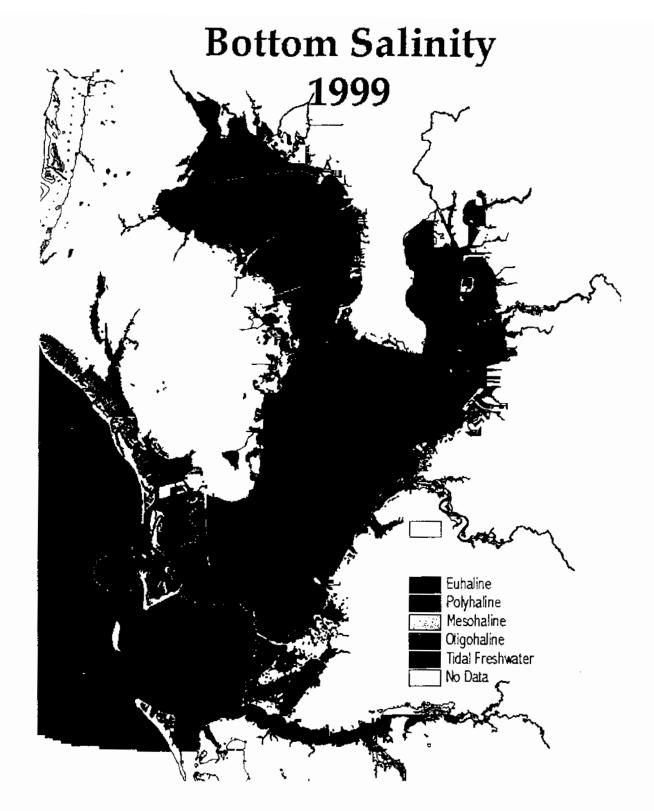


Figure 7. Distribution of salinity zones in near-bottom waters of Tampa Bay, 1999 Index Period.

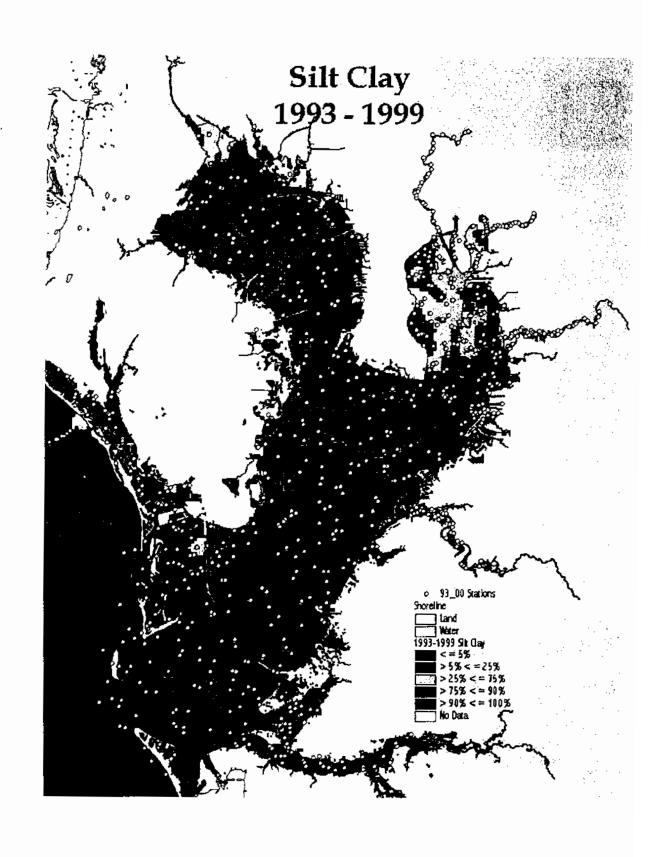


Figure 8. Percent silt+clay content of Tampa Bay sediments, 1993-1999.

Table 4. Inventory of PAHs detected from Tampa Bay and its tributaries, 1993 & 1995-1999: Number of samples (N), percent of samples with concentrations >MDL, mean, median, and maximum concentration (ppb).

| РАН | N | % Occurrences >MDL*** | Mean (ppb) | Median ` (ppb) | Maximum (ppb) |
|------------------------------|-----|-----------------------|---------------|-------------------|------------------|
| Low Molecular Weight PAHs | | | | | |
| Acenapthene* | 729 | 4.1 | 11.8 | 11.0 | 533.0 |
| Acenapthylene* | 729 | 2.9 | 10.0 | 11.0 | 414.0 |
| Anthracene* | 728 | 7.3 | 19.7 | 10.0 | 2210.0 |
| Biphenyls | 57 | 1.8 | 0.009 | 0.003 | 0.4 |
| Fluorene* | 729 | 4.4 | 12.0 | 11.5 | 629.0 |
| Naphthalene | 729 | 7.4 | 11.2 | 8.0 | 367.0 |
| 1-Methylnaphthalene | 57 | 1.8 | 0.01 | 0.003 | 0.8 |
| 2-Methylnaphthalene* | 57 | 3.5 | 0.1 | 0.005 | 5.5 |
| 2,6-Dimethylnaphthalene | 57 | 3.5 | 0.1 | 0.003 | 4.5 |
| 2,3,5- | 57 | 1.8 | 0.01 | 0.002 | 0.4 |
| Trimethylnaphthalene | | | | | |
| Phenanthrene* | 729 | 14.4 | 86.6 | 12.0 | 15324.0 |
| 1-Methylphenanthrene | 57 | 10.5 | 1.3 | 0.002 | 29.8 |
| | | | | | |
| High Molecular Weight PAHs | | | | | |
| Benzo(a)anthracene** | 729 | 16.6 | 93.2 | 10.5 | 11221.0 |
| Benzo(a)pyrene** | 730 | 16.4 | 118.7 | 12.0 | 13636.0 |
| Benzo(e)pyrene | 57 | 7.0 | 1.2 | 0.003 | 33.0 |
| Chrysene** | 729 | 17.3 | 129.2 | 11.0 | 16946.0 |
| Dibenz(a,h)anthracene** | 729 | 11.2 | 45.9 | 11.0 | 3919.0 |
| Fluoranthene** | 729 | 18.8 | 214.0 | 13.0 | 30436.0 |
| Benzo(b)fluoranthene | 730 | 19.3 | 167.1 | 15.0 | 19768.0 |
| Benzo(k)fluoranthene | 730 | 17.1 | 86.4 | 9.5 | 8684.0 |
| Perylene | 57 | 8.8 | 1.3 | 0.002 | 29.8 |
| Benzo(g,h,i)perylene | 675 | 18.2 | 109.0 | 12.0 | 10197.0 |
| Pyrene** | 729 | 21.9 | 206.6 | 10.0 | 23660.0 |
| Indeno (1,3,3-c,d)pyrene | 729 | 17.3 | 98.3 | 8.5 | 10758.0 |

^{*} included in computation of total low molecular weight PAHs

^{**}Included in computation for total high molecular weight PAHs

^{***}MDL= Method Detection Limit

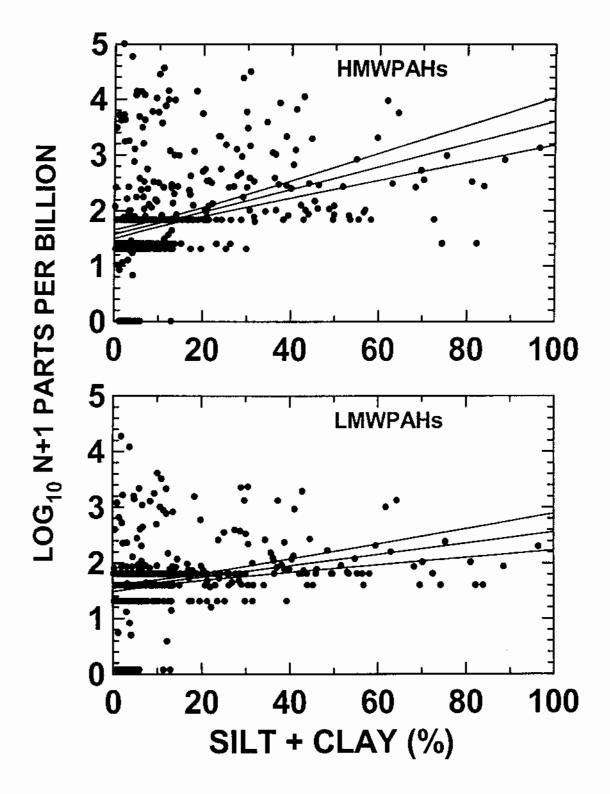


Figure 9. Association between low molecular weight polycyclic aromatic hydrocarbons (LMWPAH) and high molecular weight polycyclic aromatic hydrocarbons (HMWPAH) and percent silt+clay. Tampa Bay, 1993 & 1995-1999. Regression line and 95% confidence limits are shown.

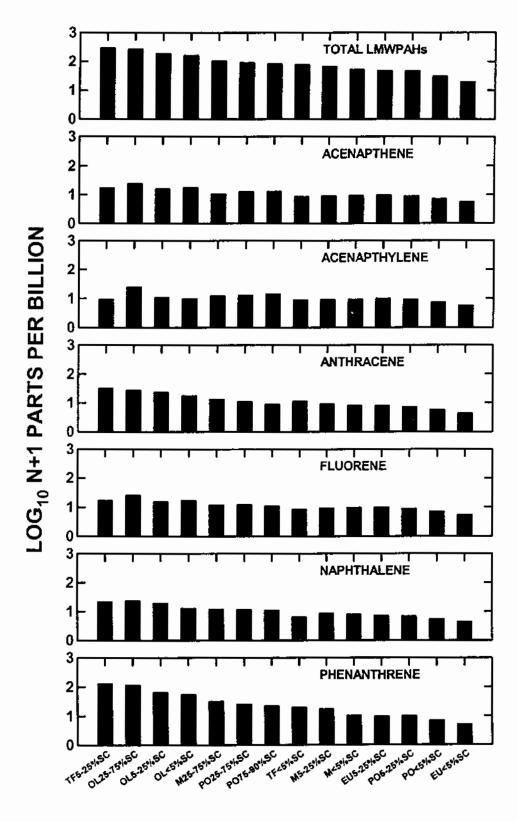


Figure 10. Mean concentrations (ppb) of low molecular weight PAHs by habitat type. Tampa Bay, 1993 & 1995-1999.

Table 5. Percentage of samples with low molecular weight PAH <TEL, >=TEL<PEL and >=PEL: by habitat type (salinity zone and % SC content). Tampa Bay, 1993 & 1995-1999.

| | EU | EU | PO / | PO | PO محر عد | PO 275 | M Fox | M 5.2502 | M 26.7502 | OL. | 70° | 0L | TF | TF |
|--|------|------|------|-------|-----------|--------|----------|----------|--------------|------|------|------|------|------|
| ACENAPTHENE | ? | 9/10 | | | | | | | | 200 | | | | |
| <tel <<="" th=""><th>41.3</th><th>15.2</th><th>31.8</th><th>22.8</th><th>4.7</th><th>0</th><th>30.0</th><th>33.3</th><th>41.2</th><th>20.0</th><th>33.3</th><th>16.7</th><th>30.0</th><th>30.0</th></tel> | 41.3 | 15.2 | 31.8 | 22.8 | 4.7 | 0 | 30.0 | 33.3 | 41.2 | 20.0 | 33.3 | 16.7 | 30.0 | 30.0 |
| >TEL <pel< th=""><th>58.7</th><th>84.8</th><th>8.79</th><th>76.5</th><th>93.0</th><th>100</th><th>70</th><th>63.9</th><th>52.9</th><th>0.09</th><th>45.5</th><th>66.7</th><th>70.0</th><th>0.09</th></pel<> | 58.7 | 84.8 | 8.79 | 76.5 | 93.0 | 100 | 70 | 63.9 | 52.9 | 0.09 | 45.5 | 66.7 | 70.0 | 0.09 |
| >=PEL | 0 | 0 | 4.0 | 0.7 | 2.3 | 0 | 0 | 2.8 | 5.9 | 20.0 | 22.2 | 16.7 | 0 | 10.0 |
| Figure 1 state of 1 state of 1 | | | | | | | | | | | | | | |
| ACENAPIHYDENE | 413 | 15.2 | 31.8 | 23.5 | 4.7 | 0 | 30.0 | 33.3 | 35.3 | 20.0 | 33.3 | 16.7 | 30.0 | 40.0 |
| >=TEL <pel< th=""><th>58.7</th><th>84.8</th><th>68.2</th><th>76.5</th><th>95.3</th><th>001</th><th>70.0</th><th>66.7</th><th>58.8</th><th>80.0</th><th>66.7</th><th>66.7</th><th>70.0</th><th>0.09</th></pel<> | 58.7 | 84.8 | 68.2 | 76.5 | 95.3 | 001 | 70.0 | 66.7 | 58.8 | 80.0 | 66.7 | 66.7 | 70.0 | 0.09 |
| >=PEL | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 5.9 | 0 | 0 | 16.7 | 0 | 0 |
| | | | | | | | | | | | | | | |
| ANTHRACENE | , | 00. | 000 | 1 | 3 50 | 901 | | 1 | 7 60 | 18 | ,,,, | 3 | 0 | |
| <tel< th=""><th>20 °</th><th>80</th><th>98.8</th><th>7.8.7</th><th>93.0</th><th>00</th><th>92.3</th><th>71.6</th><th>82.4</th><th>80.0</th><th>55.6</th><th>50.0</th><th>90.0</th><th>50.0</th></tel<> | 20 ° | 80 | 98.8 | 7.8.7 | 93.0 | 00 | 92.3 | 71.6 | 82.4 | 80.0 | 55.6 | 50.0 | 90.0 | 50.0 |
| >=TEL <pel< th=""><th>0</th><th>0</th><th>0.8</th><th>0.7</th><th>0.7</th><th></th><th>/:/</th><th>5.5</th><th>11.7</th><th>10.0</th><th>7.77</th><th>20.0</th><th>10.0</th><th>40.0</th></pel<> | 0 | 0 | 0.8 | 0.7 | 0.7 | | /:/ | 5.5 | 11.7 | 10.0 | 7.77 | 20.0 | 10.0 | 40.0 |
| >=PEL | 0 | 0 | 04 | 0.7 | C | 0 | 0 | 2.8 | 5.9 | 10.0 | 22.2 | 0 | 0 | 10.0 |
| FLUORENE | | | | | | | · · · | | | | | | | |
| <tel< th=""><th>100</th><th>001</th><th>99.2</th><th>98.7</th><th>93.0</th><th>001</th><th>0.26</th><th>94.4</th><th>82.4</th><th>80.0</th><th>2.99</th><th>50.0</th><th>100</th><th>0.09</th></tel<> | 100 | 001 | 99.2 | 98.7 | 93.0 | 001 | 0.26 | 94.4 | 82.4 | 80.0 | 2.99 | 50.0 | 100 | 0.09 |
| >=TEL <pel< th=""><th>0</th><th>0</th><th>0.4</th><th>1.4</th><th>7.0</th><th>0</th><th>5.0</th><th>5.6</th><th>17.6</th><th>10.0</th><th>33.3</th><th>50.0</th><th>0</th><th>30.0</th></pel<> | 0 | 0 | 0.4 | 1.4 | 7.0 | 0 | 5.0 | 5.6 | 17.6 | 10.0 | 33.3 | 50.0 | 0 | 30.0 |
| >=PEL | 0 | 0 | 0.4 | 0 | 0 | 0 | 0 | 0 | 0 | 10.0 | 0 | 0 | 0 | 10.0 |
| | | | | | | | | | | | | | | |
| NAPTHALENE | | | į | , | i | , | | | | | | | | |
| <tel< th=""><th>8</th><th>8</th><th>99.2</th><th>9.96</th><th>76.7</th><th>0.09</th><th>95.0</th><th>91.7</th><th>76.5</th><th>80.0</th><th>66.7</th><th>66.7</th><th>8</th><th>40.0</th></tel<> | 8 | 8 | 99.2 | 9.96 | 76.7 | 0.09 | 95.0 | 91.7 | 76.5 | 80.0 | 66.7 | 66.7 | 8 | 40.0 |
| >=TEL <pel< th=""><th>0</th><th>0</th><th>9.0</th><th>2.7</th><th>22.7</th><th>40.0</th><th>5.0</th><th>8.3</th><th>23.5</th><th>10.0</th><th>22.2</th><th>16.7</th><th>٥</th><th>60.0</th></pel<> | 0 | 0 | 9.0 | 2.7 | 22.7 | 40.0 | 5.0 | 8.3 | 23.5 | 10.0 | 22.2 | 16.7 | ٥ | 60.0 |
| >=PEL | 0 | 0 | 0 | 0.7 | 0 | ٥ | 0 | 0 | 0 | 10.0 | -:- | 16.7 | ٥ | 0 |
| PHENANTHRENE | | | | | | | | | | | | | | |
| <tel< th=""><th>82</th><th>82</th><th>8.86</th><th>98.7</th><th>86.0</th><th>001</th><th>94.9</th><th>86.1</th><th>76.5</th><th>0.09</th><th>55.6</th><th>50.0</th><th>80.0</th><th>40.0</th></tel<> | 82 | 82 | 8.86 | 98.7 | 86.0 | 001 | 94.9 | 86.1 | 76.5 | 0.09 | 55.6 | 50.0 | 80.0 | 40.0 |
| >=TEL <pel< th=""><th>0</th><th>0</th><th>4.0</th><th>0.7</th><th>11.7</th><th>0</th><th>0</th><th>8.3</th><th>11.8</th><th>20.0</th><th>11.1</th><th>16.7</th><th>20.0</th><th>20.0</th></pel<> | 0 | 0 | 4.0 | 0.7 | 11.7 | 0 | 0 | 8.3 | 11.8 | 20.0 | 11.1 | 16.7 | 20.0 | 20.0 |
| >=PEL | 0 | 0 | 8.0 | 0.7 | 2.3 | 0 | 5.2 | 5.6 | 11.8 | 20.0 | 33.3 | 33.3 | 0 | 40.0 |
| | | | | | | | | | | | | | | |
| Total Low Molecular Weight PAHs | | | | | | | | | | | | | | - |
| <tel< th=""><th>100</th><th>100</th><th>98.8</th><th>98.7</th><th>93.0</th><th>001</th><th>95.0</th><th>61.7</th><th>76.5</th><th>80.0</th><th>55.6</th><th>50.0</th><th>80.0</th><th>40.0</th></tel<> | 100 | 100 | 98.8 | 98.7 | 93.0 | 001 | 95.0 | 61.7 | 76.5 | 80.0 | 55.6 | 50.0 | 80.0 | 40.0 |
| >=TEL <pel< th=""><th>0</th><th>0</th><th>0.4</th><th>0.7</th><th>7.0</th><th>0</th><th>2.5</th><th>5.5</th><th>17.6</th><th>0</th><th>11.1</th><th>16.7</th><th>20.0</th><th>50.0</th></pel<> | 0 | 0 | 0.4 | 0.7 | 7.0 | 0 | 2.5 | 5.5 | 17.6 | 0 | 11.1 | 16.7 | 20.0 | 50.0 |
| >=PEL | 0 | 0 | 0.8 | 0.7 | 0 | 0 | 2.5 | 2.8 | 5.9 | 20.0 | 33.3 | 33.3 | 0 | 10.0 |
| | | | | | | | | | | | | | | |

EU=euhaline (>30 ppt); PO=polyhaline (18-30 ppt); M=mesohaline (5-18 ppt); OL=oligohaline (0.5-5 ppt); TF= tidal freshwater (<5 ppt)

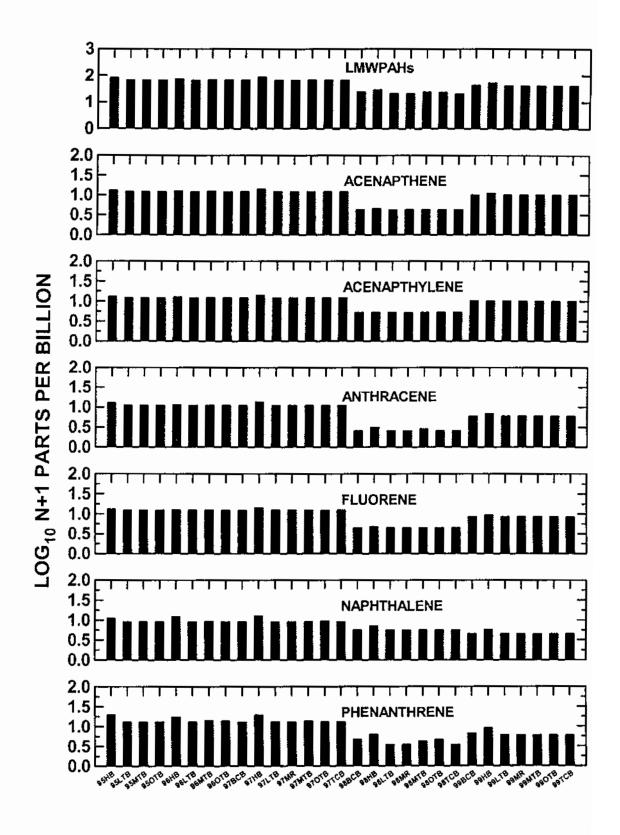


Figure 11. Mean concentrations (ppb) of low molecular weight PAHs by bay segmentyear. Tampa Bay, 1993 & 1995-1999.

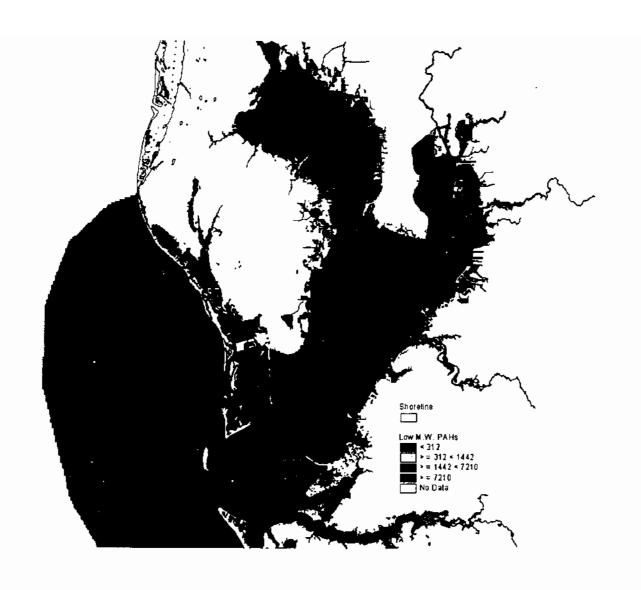


Figure 12. Spatial distribution of low molecular weight PAHs(ppb) in Tampa Bay, 1993 & 1995-1999.

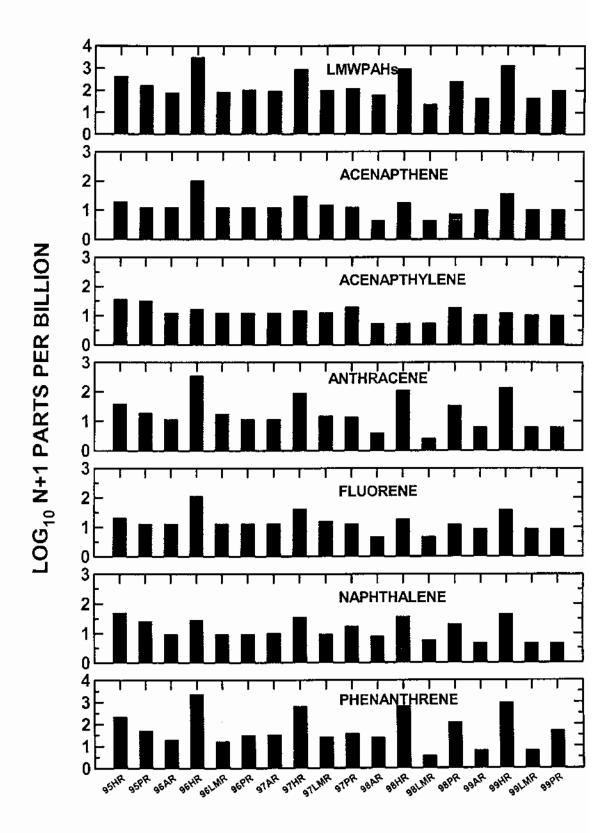


Figure 13. Mean concentrations (ppb) of low molecular weight PAHs by tributary-year. Tampa Bay, 1995-1999.

ANOVA showed that the mean concentrations of low molecular weight PAHs differed among Bay Segment-Year combinations (F _{28,531}=28.6;p<0.001). Within each year, mean concentrations were generally higher in the Hillsborough Bay (Figure 11) segment and approximately 4.5% of Hillsborough Bay samples exceeded the TEL for low molecular weight PAHs (Table 5; Figure 12).

Within the tributaries, concentrations during each year were highest in the Lower Hillsborough River and were lowest during 1998 in the Little Manatee and Alafia rivers (Figure 13). Within the tributaries, almost 40% of Lower Hillsborough River samples exceeded the TEL and >90% of the samples exceeded the TEL (Table 6; Figure 14).

High molecular weight PAHs were detected in 23% of the samples and at concentrations of up to 99,800 ppb (Lower Hillsborough River). Fluoranthene and Pyrene were the two PAHs found in highest concentrations (Table 4). ANOVA showed that there were significant differences in mean high molecular weight PAH concentrations by habitat ($F_{13,673}$ =23.2; p<0.001). Mean concentrations were highest in tidal freshwaters with sediments of 5% to 25% silt+clay and in oligohaline waters with sediments of 5% to 75% silt+clay (Figure 15); these sites were primarily found in the Lower Hillsborough River. Lowest concentrations were found in polyhaline and euhaline waters with sediments of <5 % silt+clay.

On a percentage basis, the most degraded habitats included oligohaline and tidal freshwaters with sediments of 5% to 25% silt+clay and oligohaline waters of 25% to 75% silt+clay (30% to 33% of samples >PEL) (Table 7). Euhaline waters were the least degraded.

ANOVA showed that mean high molecular weight PAH concentrations differed among Bay Segment-Year combinations ($F_{22,537}$ =2.0; p<0.01). Mean concentrations were, again, highest in the Hillsborough Bay segment (Figure 16). Approximately 7% of Hillsborough Bay samples exceeded the TEL for high molecular weight PAHs (Table 8; Figure 17).

Table 6. Percentage of samples with LMWPAH concentrations <TEL, >=TEl<PEL, and >=PEL: by bay segment and tributary, Tampa Bay 1993 & 1995-1999.

PRIMARY BAY SEGMENTS

TRIBUTARIES

| | | PF | HIMAK | I DA | 1 SEG | TATENTA 1 | ıs | | IKI | UIAI | CTF2 |
|---|------|------|-------|------|-------|-----------|-----|--------------|--------------|------|--------------|
| | OTB | HB | MTB | LTB | BCB | TCB | MR | HR | PR | AR | LMR |
| ACENAPTHENE | F | | | | | | | |] | | |
| <tel< td=""><td>30.5</td><td>22.9</td><td>30.8</td><td>29.5</td><td>33.3</td><td>30.8</td><td>100</td><td>12.9</td><td>18.2</td><td>16.1</td><td>26.1</td></tel<> | 30.5 | 22.9 | 30.8 | 29.5 | 33.3 | 30.8 | 100 | 12.9 | 18.2 | 16.1 | 26.1 |
| >=TEL <pel< td=""><td>69.5</td><td>75.5</td><td>69.2</td><td>70.5</td><td>66.7</td><td>69.2</td><td>0</td><td>61.5</td><td>81.8</td><td>83.9</td><td>73.9</td></pel<> | 69.5 | 75.5 | 69.2 | 70.5 | 66.7 | 69.2 | 0 | 61.5 | 81.8 | 83.9 | 73.9 |
| >=PEL | 0 | 1.6 | 0 | 0 | 0 | 0 | 0 | 25.6 | 0 | 0 | 0 |
| ACENAPTHYLENE | | | | | | | | <u> </u> | | | |
| <tel< td=""><td>30.5</td><td>23.7</td><td>30.8</td><td>29.5</td><td>33.3</td><td>30.8</td><td>100</td><td>22.6</td><td>9.1</td><td>16.1</td><td>26.1</td></tel<> | 30.5 | 23.7 | 30.8 | 29.5 | 33.3 | 30.8 | 100 | 22.6 | 9.1 | 16.1 | 26.1 |
| >=TEL <pel< td=""><td>69.5</td><td>74.7</td><td>69.2</td><td>70.5</td><td>66.7</td><td>69.2</td><td>0</td><td>77.4</td><td>90.9</td><td>83.9</td><td>73.9</td></pel<> | 69.5 | 74.7 | 69.2 | 70.5 | 66.7 | 69.2 | 0 | 77.4 | 90.9 | 83.9 | 73.9 |
| >=PEL | 0 | 1.6 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| ANTHRACENE | | | | | - | | | | <u> </u> | | |
| <tel< td=""><td>100</td><td>96.2</td><td>100</td><td>100</td><td>100</td><td>100</td><td>100</td><td>19.4</td><td>90.9</td><td>100</td><td>91.3</td></tel<> | 100 | 96.2 | 100 | 100 | 100 | 100 | 100 | 19.4 | 90.9 | 100 | 91.3 |
| >=TEL <pel< td=""><td>0</td><td>3.8</td><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td><td>55.0</td><td>9.1</td><td>0</td><td>8.7</td></pel<> | 0 | 3.8 | 0 | 0 | 0 | 0 | 0 | 55.0 | 9.1 | 0 | 8.7 |
| >=PEL | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 25.6 | 0 | 0 | 0 |
| FLUORENE | | | | | | | | | | | |
| <tel< td=""><td>100</td><td>96.2</td><td>100</td><td>100</td><td>100</td><td>100</td><td>100</td><td>35.5</td><td>90.9</td><td>100</td><td>95.7</td></tel<> | 100 | 96.2 | 100 | 100 | 100 | 100 | 100 | 35.5 | 90.9 | 100 | 95.7 |
| >=TEL <pel< td=""><td>0</td><td>3.8</td><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td><td>51.7</td><td>9.1</td><td>0</td><td>4.3</td></pel<> | 0 | 3.8 | 0 | 0 | 0 | 0 | 0 | 51.7 | 9.1 | 0 | 4.3 |
| >=PEL | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 12.8 | 0 | 0 | 0 |
| NAPTHALENE | | | | | | | | | | | |
| <tel< td=""><td>100</td><td>87.8</td><td>100</td><td>100</td><td>100</td><td>100</td><td>100</td><td>32.3</td><td>68.2</td><td>96.8</td><td>100</td></tel<> | 100 | 87.8 | 100 | 100 | 100 | 100 | 100 | 32.3 | 68.2 | 96.8 | 100 |
| >=TEL <pel< td=""><td>0</td><td>10.6</td><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td><td>58.1</td><td>31.8</td><td>3.2</td><td>0</td></pel<> | 0 | 10.6 | 0 | 0 | 0 | 0 | 0 | 58.1 | 31.8 | 3.2 | 0 |
| >=PEL | 0 | 1.6 | 0 | 0 | 0 | 0 | 0 | 9.6 | 0 | 0 | 0 |
| PHENATHRENE | | | | | | | | <u> </u> | | | |
| <tel< td=""><td>100</td><td>96.2</td><td>100</td><td>100</td><td>100</td><td>100</td><td>100</td><td>3.2</td><td>59.1</td><td>100</td><td>95.7</td></tel<> | 100 | 96.2 | 100 | 100 | 100 | 100 | 100 | 3.2 | 59.1 | 100 | 95.7 |
| >=TEL <pel< td=""><td>0</td><td>1.6</td><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td><td>32.8</td><td>36.4</td><td>0</td><td>4.3</td></pel<> | 0 | 1.6 | 0 | 0 | 0 | 0 | 0 | 32.8 | 36.4 | 0 | 4.3 |
| >=PEL | 0 | 2.4 | 0 | 0 | 0 | 0 | 0 | 64.0 | 4.5 | 0 | 0 |
| LOW MW PAHS | | | | | | | | | | | |
| <tel< td=""><td>100</td><td>95.5</td><td>100</td><td>100</td><td>100</td><td>100</td><td>100</td><td>9.7</td><td>90.9</td><td>100</td><td>95.7</td></tel<> | 100 | 95.5 | 100 | 100 | 100 | 100 | 100 | 9.7 | 90.9 | 100 | 95.7 |
| >=TEL <pel< td=""><td>0</td><td>3.7</td><td>0</td><td>0</td><td>0</td><td>0</td><td>0</td><td>51.6</td><td>9.1</td><td>0</td><td>4.3</td></pel<> | 0 | 3.7 | 0 | 0 | 0 | 0 | 0 | 51.6 | 9.1 | 0 | 4.3 |
| >=PEL | 0 | 8.0 | 0 | 0 | 0 | 0 | 0 | 38.7 | 0 | 0 | 0 |

OTB= Old Tampa Bay; HB= Hillsborough Bay; MTB=Middle Tampa Bay; LTB=Lower Tampa Bay; BCB=Boca Ciega Bay; Ciega Bay; TCB=Terra Ceia Bay; MR=Manatee River; HR= Hillsborough River; PR=Palm River; AR=Alafia River; TLMR= Little Manatee River

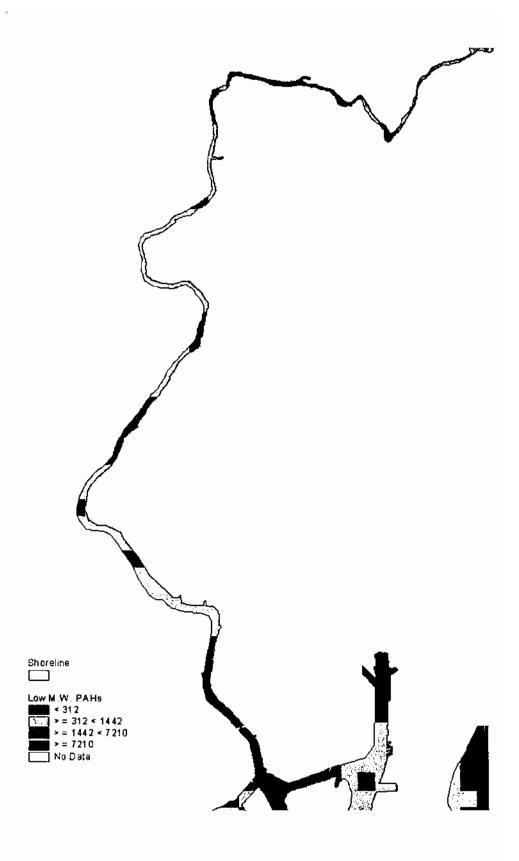


Figure 14. Spatial distribution of low molecular weight PAHs (ppb) in the Lower Hillsborough River, 1995-1999.

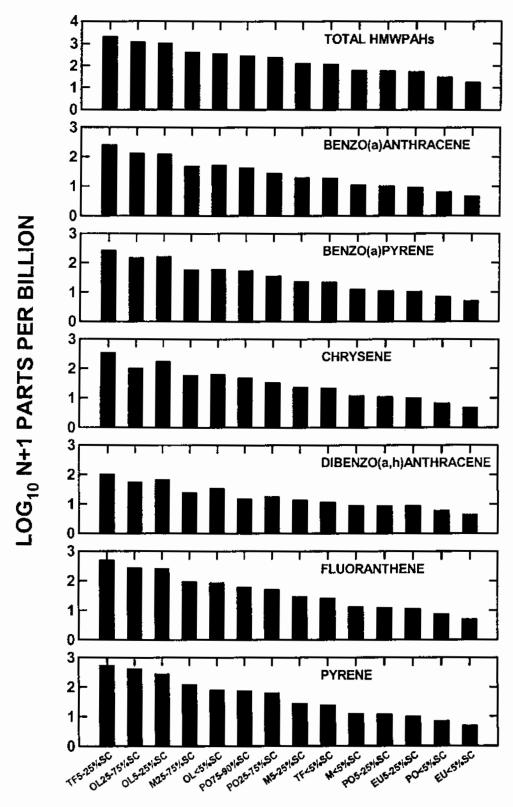


Figure 15. Mean concentration (ppb) of high molecular weight polycyclic aromatic hydrocarbons by habitat type. Tampa Bay, 1993 & 1995-1999

Table 7. Percentage of samples with HMWPAH <TEL, >=TEL<PEL and >=PEL: by habitat type (salinity zone & %SC). Tampa Bay, 1993 & 1995-1999.

| i E | OL, TF TF 25-75% <5% \$-25%. | | 50.0 80.0 40.0 | 16.7 20.0 30.0 | 33.3 0 30.0 | | 66.7 80.0 40.0 | 0 20.0 10.0 | 33.3 0 50.0 | | 50.0 80.0 40.0 | 20.0 | 33.3 0 40.0 | | 16.7 40.0 20.0 | 50.0 50.0 20.0 | 33.3 10.0 60.0 | | 50.0 80.0 40.0 | 16.7 20.0 20.0 | 33.3 0 40.0 | | 33.3 80.0 40.0 | - | 33.3 0 50.0 | | 50.0 80.0 40.0 | 16.7 20.0 30.0 | 2 |
|--------|---------------------------------|-------------------|---|---|-------------|----------------|---|---|-------------|----------|---|---|-------------|---|--|--|----------------|--------------|--|--|-------------|--------|--|--|-------------|--------------------|--|------------------------------------|---|
| | 5-25% | | 44.4 | 22.2 | 33.3 | | 44.4 | 22.2 | 33.3 | | 44.4 | 22.2 | 44.4 | | 33.3 | 22.2 | 44.4 | | 44.4 | 22.2 | 44.4 | | 4.44 | 22.2 | 33.3 | | 44.4 | 22.2 | |
| | OL <\$% | | 0.09 | 30.0 | 0.01 | | 0.09 | 30.0 | 10.0 | | 8 | 30.0 | 10.0 | | 30.0 | 40.0 | 30.0 | | 0.09 | 30.0 | 10.0 | | 60.0 | 30.0 | 10.0 | | 0.09 | 30.0 | |
| | 25-75% | | 9.07 | 17.6 | 8.11 | | 70.6 | 17.6 | 11.8 | | 70.6 | 17.6 | 8.1.8 | | 29.4 | 47.0 | 23.6 | | 70.6 | 17.6 | 11.8 | | 70.6 | 17.6 | 11.8 | | 70.6 | 17.6 | |
| Z | 5-25% | | 86.1 | 8.3 | 5.6 | | 83.3 | 8.3 | 8.3 | | 86.1 | 5.5 | 8.4 | | 34.3 | 54.1 | 9711 | | 83.3 | 11.1 | 5.6 | | 83.3 | = | 5.6 | | 1.98 | 8.3 | |
| 2 | %\$> | | 92.3 | 5.1 | 2.6 | | 92.5 | 5.0 | 2.5 | | 92.3 | 5.1 | 2.6 | | 40.0 | 55.0 | 8.0 | | 92.3 | 2.6 | 5.2 | | 92.3 | 2.5 | 5.2 | | 92.5 | 5.0 | |
| MH | 75-90% | | 0.09 | 40.0 | 0 | | 0.03 | 40.0 | 0 | | 0.09 | 40.0 | 0 | j | 20.0 | 80.0 | 0 | | 0.09 | 40.0 | 0 | | 0.09 | 40.0 | 0 | | 0.09 | 40.0 | |
| N.I. | 25-75% | | 74.4 | 21.0 | 4.6 | | 76.7 | 21.0 | 2.3 | | 76.7 | 18.7 | 4.6 | | 18.6 | 74.5 | 6.9 | | 72.1 | 25.6 | 2.3 | | 72.1 | 23.3 | 4.6 | | 74.4 | 25.9 | |
| EN | 5-25% | | 0.96 | 3.3 | 0.7 | | 95.3 | 3.3 | 4.1 | | 0.96 | 3.3 | 0.7 | | 38.9 | 60.4 | 0.7 | | 94.0 | 5.3 | 0.7 | | 0.96 | 3.3 | 0.7 | | 0.96 | 3.3 | |
| | % \$> | | 98.4 | 0.8 | 8.0 | | 4.86 | 8.0 | 0.8 | | 98.4 | 4.0 | 1.2 | | 52.3 | 46.5 | 1.2 | | 98.4 | 0.8 | 0.8 | | 8.86 | 0.4 | 8.0 | | 98.4 | 8.0 | |
| . Od | 5-25% | | 8.7.8 | 2.2 | 0 | | 97.8 | 2.2 | 0 | | 87.6 | 2.2 | 0 | | 30.4 | 9.69 | 0 | | 8.76 | 2.2 | 0 | | 8.76 | 2.2 | 0 | | 8.76 | 2.2 | |
| Ğ | %\$> | | 8 | 0 | 0 | | 8 | 0 | 0 | | 100 | 0 | 0 | | 001 | 0 | 0 | | 100 | 0 | 0 | | 82 | 0 | 0 | | 8 | 0 | |
| | | BENZ(a)ANTHRACENE | <tel< th=""><th>>=TEL<pel< th=""><th>>=PEL</th><th>BENZO(a)PYRENE</th><th><tel< th=""><th>>=TEL<pel< th=""><th>>=PEL</th><th>CHRYSENE</th><th><tel< th=""><th>>=TEL<pel< th=""><th>>=PEL</th><th>DIBENZ(a<h)anthracene< th=""><th><tel< th=""><th>>=TEL<pe1,< th=""><th>>=PEL</th><th>FLUORANTHENE</th><th><tel< th=""><th>>=TEL<pel< th=""><th>>≖PEL</th><th>PYRENE</th><th><tel< th=""><th>>=TEL<pel< th=""><th></th><th>TOTAL BICH MW PAHS</th><th><tel< th=""><th>>=TEL<pel< th=""><th></th></pel<></th></tel<></th></pel<></th></tel<></th></pel<></th></tel<></th></pe1,<></th></tel<></th></h)anthracene<></th></pel<></th></tel<></th></pel<></th></tel<></th></pel<></th></tel<> | >=TEL <pel< th=""><th>>=PEL</th><th>BENZO(a)PYRENE</th><th><tel< th=""><th>>=TEL<pel< th=""><th>>=PEL</th><th>CHRYSENE</th><th><tel< th=""><th>>=TEL<pel< th=""><th>>=PEL</th><th>DIBENZ(a<h)anthracene< th=""><th><tel< th=""><th>>=TEL<pe1,< th=""><th>>=PEL</th><th>FLUORANTHENE</th><th><tel< th=""><th>>=TEL<pel< th=""><th>>≖PEL</th><th>PYRENE</th><th><tel< th=""><th>>=TEL<pel< th=""><th></th><th>TOTAL BICH MW PAHS</th><th><tel< th=""><th>>=TEL<pel< th=""><th></th></pel<></th></tel<></th></pel<></th></tel<></th></pel<></th></tel<></th></pe1,<></th></tel<></th></h)anthracene<></th></pel<></th></tel<></th></pel<></th></tel<></th></pel<> | >=PEL | BENZO(a)PYRENE | <tel< th=""><th>>=TEL<pel< th=""><th>>=PEL</th><th>CHRYSENE</th><th><tel< th=""><th>>=TEL<pel< th=""><th>>=PEL</th><th>DIBENZ(a<h)anthracene< th=""><th><tel< th=""><th>>=TEL<pe1,< th=""><th>>=PEL</th><th>FLUORANTHENE</th><th><tel< th=""><th>>=TEL<pel< th=""><th>>≖PEL</th><th>PYRENE</th><th><tel< th=""><th>>=TEL<pel< th=""><th></th><th>TOTAL BICH MW PAHS</th><th><tel< th=""><th>>=TEL<pel< th=""><th></th></pel<></th></tel<></th></pel<></th></tel<></th></pel<></th></tel<></th></pe1,<></th></tel<></th></h)anthracene<></th></pel<></th></tel<></th></pel<></th></tel<> | >=TEL <pel< th=""><th>>=PEL</th><th>CHRYSENE</th><th><tel< th=""><th>>=TEL<pel< th=""><th>>=PEL</th><th>DIBENZ(a<h)anthracene< th=""><th><tel< th=""><th>>=TEL<pe1,< th=""><th>>=PEL</th><th>FLUORANTHENE</th><th><tel< th=""><th>>=TEL<pel< th=""><th>>≖PEL</th><th>PYRENE</th><th><tel< th=""><th>>=TEL<pel< th=""><th></th><th>TOTAL BICH MW PAHS</th><th><tel< th=""><th>>=TEL<pel< th=""><th></th></pel<></th></tel<></th></pel<></th></tel<></th></pel<></th></tel<></th></pe1,<></th></tel<></th></h)anthracene<></th></pel<></th></tel<></th></pel<> | >=PEL | CHRYSENE | <tel< th=""><th>>=TEL<pel< th=""><th>>=PEL</th><th>DIBENZ(a<h)anthracene< th=""><th><tel< th=""><th>>=TEL<pe1,< th=""><th>>=PEL</th><th>FLUORANTHENE</th><th><tel< th=""><th>>=TEL<pel< th=""><th>>≖PEL</th><th>PYRENE</th><th><tel< th=""><th>>=TEL<pel< th=""><th></th><th>TOTAL BICH MW PAHS</th><th><tel< th=""><th>>=TEL<pel< th=""><th></th></pel<></th></tel<></th></pel<></th></tel<></th></pel<></th></tel<></th></pe1,<></th></tel<></th></h)anthracene<></th></pel<></th></tel<> | >=TEL <pel< th=""><th>>=PEL</th><th>DIBENZ(a<h)anthracene< th=""><th><tel< th=""><th>>=TEL<pe1,< th=""><th>>=PEL</th><th>FLUORANTHENE</th><th><tel< th=""><th>>=TEL<pel< th=""><th>>≖PEL</th><th>PYRENE</th><th><tel< th=""><th>>=TEL<pel< th=""><th></th><th>TOTAL BICH MW PAHS</th><th><tel< th=""><th>>=TEL<pel< th=""><th></th></pel<></th></tel<></th></pel<></th></tel<></th></pel<></th></tel<></th></pe1,<></th></tel<></th></h)anthracene<></th></pel<> | >=PEL | DIBENZ(a <h)anthracene< th=""><th><tel< th=""><th>>=TEL<pe1,< th=""><th>>=PEL</th><th>FLUORANTHENE</th><th><tel< th=""><th>>=TEL<pel< th=""><th>>≖PEL</th><th>PYRENE</th><th><tel< th=""><th>>=TEL<pel< th=""><th></th><th>TOTAL BICH MW PAHS</th><th><tel< th=""><th>>=TEL<pel< th=""><th></th></pel<></th></tel<></th></pel<></th></tel<></th></pel<></th></tel<></th></pe1,<></th></tel<></th></h)anthracene<> | <tel< th=""><th>>=TEL<pe1,< th=""><th>>=PEL</th><th>FLUORANTHENE</th><th><tel< th=""><th>>=TEL<pel< th=""><th>>≖PEL</th><th>PYRENE</th><th><tel< th=""><th>>=TEL<pel< th=""><th></th><th>TOTAL BICH MW PAHS</th><th><tel< th=""><th>>=TEL<pel< th=""><th></th></pel<></th></tel<></th></pel<></th></tel<></th></pel<></th></tel<></th></pe1,<></th></tel<> | >=TEL <pe1,< th=""><th>>=PEL</th><th>FLUORANTHENE</th><th><tel< th=""><th>>=TEL<pel< th=""><th>>≖PEL</th><th>PYRENE</th><th><tel< th=""><th>>=TEL<pel< th=""><th></th><th>TOTAL BICH MW PAHS</th><th><tel< th=""><th>>=TEL<pel< th=""><th></th></pel<></th></tel<></th></pel<></th></tel<></th></pel<></th></tel<></th></pe1,<> | >=PEL | FLUORANTHENE | <tel< th=""><th>>=TEL<pel< th=""><th>>≖PEL</th><th>PYRENE</th><th><tel< th=""><th>>=TEL<pel< th=""><th></th><th>TOTAL BICH MW PAHS</th><th><tel< th=""><th>>=TEL<pel< th=""><th></th></pel<></th></tel<></th></pel<></th></tel<></th></pel<></th></tel<> | >=TEL <pel< th=""><th>>≖PEL</th><th>PYRENE</th><th><tel< th=""><th>>=TEL<pel< th=""><th></th><th>TOTAL BICH MW PAHS</th><th><tel< th=""><th>>=TEL<pel< th=""><th></th></pel<></th></tel<></th></pel<></th></tel<></th></pel<> | >≖PEL | PYRENE | <tel< th=""><th>>=TEL<pel< th=""><th></th><th>TOTAL BICH MW PAHS</th><th><tel< th=""><th>>=TEL<pel< th=""><th></th></pel<></th></tel<></th></pel<></th></tel<> | >=TEL <pel< th=""><th></th><th>TOTAL BICH MW PAHS</th><th><tel< th=""><th>>=TEL<pel< th=""><th></th></pel<></th></tel<></th></pel<> | | TOTAL BICH MW PAHS | <tel< th=""><th>>=TEL<pel< th=""><th></th></pel<></th></tel<> | >=TEL <pel< th=""><th></th></pel<> | |

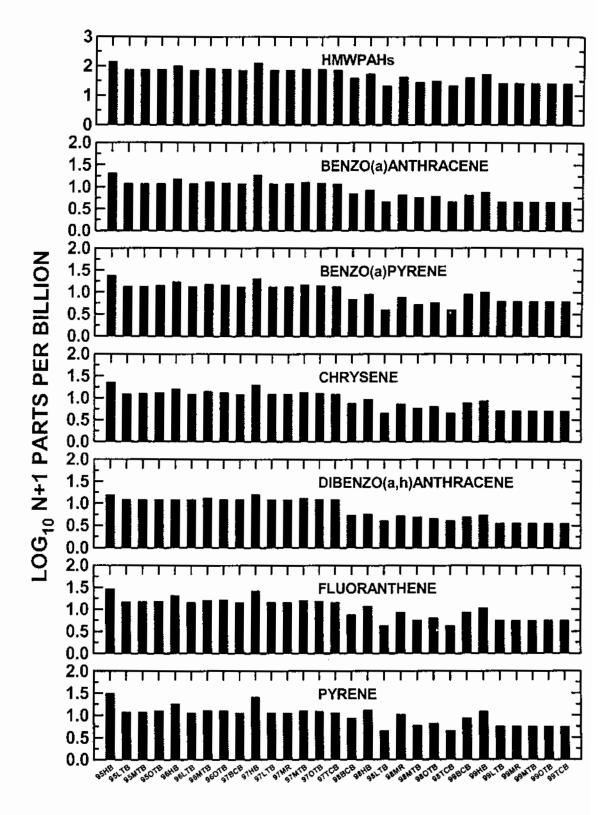


Figure 16. Mean concentrations (ppb) of high molecular weight PAHs by bay segmentyear. Tampa Bay, 1993 & 1995-1999.

Table 8. Percentage of samples with HMWPAH Concentrations <TEL, >=TEl<PEL, and >=PEL: by bay segment and tributary, Tampa Bay 1993 & 1995-1999.

| | | PRIN | IARY | BAY | SEGN | MENT | S | TI | RIBU' | FARI | ES |
|---|----------|------|-------------|------|------|------|------|------|------------|------|------|
| | ОТВ | HB | MTB | LTB | BCB | TCB | MR | HR | PR | AR | LMR |
| BENZ(a)ANTHRACENE | <u> </u> | | ì | | 1 | | | | [<u>-</u> | | |
| <tel< td=""><td>100</td><td>93.1</td><td>97.7</td><td>100</td><td>96.8</td><td>100</td><td>97.4</td><td>3.2</td><td>40.9</td><td>96.8</td><td>91.3</td></tel<> | 100 | 93.1 | 97.7 | 100 | 96.8 | 100 | 97.4 | 3.2 | 40.9 | 96.8 | 91.3 |
| >=TEL <pel< td=""><td>0</td><td>4.5</td><td>2.3</td><td>0</td><td>3.2</td><td>0</td><td>2.6</td><td>45.6</td><td>54.6</td><td>3.2</td><td>8.7</td></pel<> | 0 | 4.5 | 2.3 | 0 | 3.2 | 0 | 2.6 | 45.6 | 54.6 | 3.2 | 8.7 |
| >=PEL | 0 | 2.4 | 0 | 0 | 0 | 0 | 0 | 51.2 | 4.5 | 0 | 0 |
| BENZO(2)PYRENE | | | | | | | | | - | | |
| <tel< td=""><td>100</td><td>91.7</td><td>97.7</td><td>100</td><td>96.8</td><td>100</td><td>97.4</td><td>3.2</td><td>40.9</td><td>100</td><td>95.7</td></tel<> | 100 | 91.7 | 97.7 | 100 | 96.8 | 100 | 97.4 | 3.2 | 40.9 | 100 | 95.7 |
| >=TEL <pel< td=""><td>0</td><td>6.7</td><td>1.5</td><td>0</td><td>3.2</td><td>0</td><td>2.6</td><td>32.0</td><td>54.6</td><td>0</td><td>4.3</td></pel<> | 0 | 6.7 | 1.5 | 0 | 3.2 | 0 | 2.6 | 32.0 | 54.6 | 0 | 4.3 |
| >=PEL | 0 | 1.6 | 0.8 | 0 | 0 | 0 | 0 | 64.8 | 4.5 | 0 | 0 |
| | <u> </u> | | | | | | | | | | Ť |
| CHRYSENE | | | | | | | | | <u> </u> | | ļ |
| <tel< td=""><td>100</td><td>93.1</td><td>97.7</td><td>100</td><td>96.8</td><td>100</td><td>97.4</td><td>3.2</td><td>40.9</td><td>100</td><td>91.3</td></tel<> | 100 | 93.1 | 97.7 | 100 | 96.8 | 100 | 97.4 | 3.2 | 40.9 | 100 | 91.3 |
| >=TEL <pel< td=""><td>0</td><td>4.5</td><td>1.5</td><td>0</td><td>3.2</td><td>0</td><td>2.6</td><td>35.2</td><td>54.6</td><td>0</td><td>8.7</td></pel<> | 0 | 4.5 | 1.5 | 0 | 3.2 | 0 | 2.6 | 35.2 | 54.6 | 0 | 8.7 |
| >=PEL | 0 | 2.4 | 0.8 | 0 | 0 | 0 | 0 | 61.6 | 4.5 | 0 | 0 |
| DIBENZ(a,b)ANTHRACENE | | | | | | | | | †··· | | |
| <tel< td=""><td>100</td><td>36.4</td><td>46.2</td><td>45.1</td><td>57.1</td><td>100</td><td>100</td><td>0</td><td>4.5</td><td>30.0</td><td>56.5</td></tel<> | 100 | 36.4 | 46.2 | 45.1 | 57.1 | 100 | 100 | 0 | 4.5 | 30.0 | 56.5 |
| >=TEL <pel< td=""><td>0</td><td>60.4</td><td>53.0</td><td>54.9</td><td>42.9</td><td>0</td><td>0</td><td>12.9</td><td>77.5</td><td>70.0</td><td>43.5</td></pel<> | 0 | 60.4 | 53.0 | 54.9 | 42.9 | 0 | 0 | 12.9 | 77.5 | 70.0 | 43.5 |
| >=PEL | 0 | 3.2 | 0.8 | 0 | 0 | 0 | 0 | 87.1 | 18.0 | 0 | 0 |
| FLUORANTHENE | | | : | | | | | + | | | |
| <tel< td=""><td>100</td><td>91.7</td><td>97.7</td><td>100</td><td>96.8</td><td>100</td><td>97.4</td><td>3.2</td><td>36.4</td><td>93.5</td><td>91.3</td></tel<> | 100 | 91.7 | 97.7 | 100 | 96.8 | 100 | 97.4 | 3.2 | 36.4 | 93.5 | 91.3 |
| >=TEL <pel< td=""><td>0</td><td>6.7</td><td>2.3</td><td>0</td><td>3.2</td><td>0</td><td>2.6</td><td>35.2</td><td>59.1</td><td>6.5</td><td>8.7</td></pel<> | 0 | 6.7 | 2.3 | 0 | 3.2 | 0 | 2.6 | 35.2 | 59.1 | 6.5 | 8.7 |
| >=PEL | 0 | 1.6 | 0 | 0 | 0 | 0 | 0 | 61.6 | 4.5 | 0 | 0 |
| DVDCNIC | | | | | | | | | | | |
| PYRENE | | | | | | | | 1 | | | |
| <tel< td=""><td>100</td><td>92.4</td><td>98.5</td><td>100</td><td>96.8</td><td>100</td><td>97.4</td><td>3.2</td><td>36.4</td><td>93.5</td><td>91.3</td></tel<> | 100 | 92.4 | 98.5 | 100 | 96.8 | 100 | 97.4 | 3.2 | 36.4 | 93.5 | 91.3 |
| >=TEL <pel< td=""><td>0</td><td>4.4</td><td>1.5</td><td>0</td><td>3.2</td><td>0</td><td>2.6</td><td>32.0</td><td>59.1</td><td>6.5</td><td>8.7</td></pel<> | 0 | 4.4 | 1.5 | 0 | 3.2 | 0 | 2.6 | 32.0 | 59.1 | 6.5 | 8.7 |
| >=PEL | 0 | 3.2 | 0 | 0 | 0 | 0 | 0 | 64.8 | 4.5 | 0 | 0 |
| High Molecular Weight PAHS | | | | | | | | | | | : |
| <tel< td=""><td>100</td><td>93.2</td><td>97.7</td><td>100</td><td>96.8</td><td>100</td><td>97.4</td><td>3.2</td><td>40.9</td><td>96.8</td><td>91.3</td></tel<> | 100 | 93.2 | 97.7 | 100 | 96.8 | 100 | 97.4 | 3.2 | 40.9 | 96.8 | 91.3 |
| >=TEL <pel< td=""><td>0</td><td>5.2</td><td>2.3</td><td>0</td><td>3.2</td><td>0</td><td>2.6</td><td>44.8</td><td>54.6</td><td>3.2</td><td>8.7</td></pel<> | 0 | 5.2 | 2.3 | 0 | 3.2 | 0 | 2.6 | 44.8 | 54.6 | 3.2 | 8.7 |
| >=PEL | 0 | 1.6 | 0 | 0 | 0 | 0 | 0 | 52.0 | 4.5 | 0 | 0 |

Within the tributaries, the Hillsborough River was also, again, the most degraded (Figure 18): >50% of Lower Hillsborough River samples exceeded the PEL and >96% of the samples exceeded the TEL (Table 8; Figure 19). Almost 60% of the Palm River samples exceeded the TEL. Old Tampa Bay, Lower Tampa Bay, and Terra Ceia Bay segments have shown no evidence of contamination by high molecular weight PAHs.

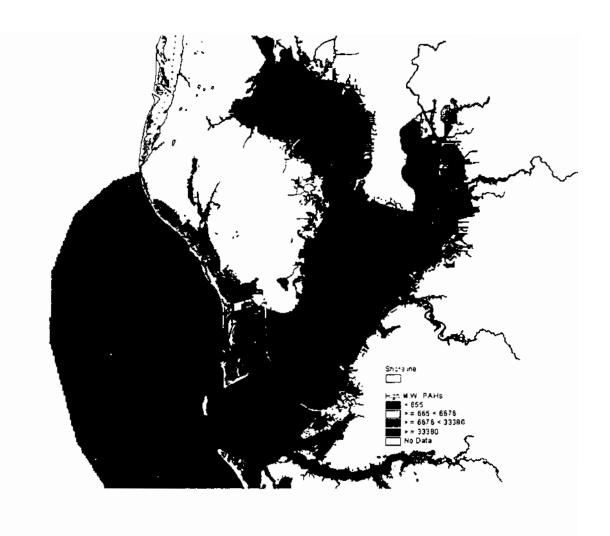


Figure 17. Spatial distribution of high molecular weight PAHs (ppb) in Tampa Bay, 1993 & 1995-1999.

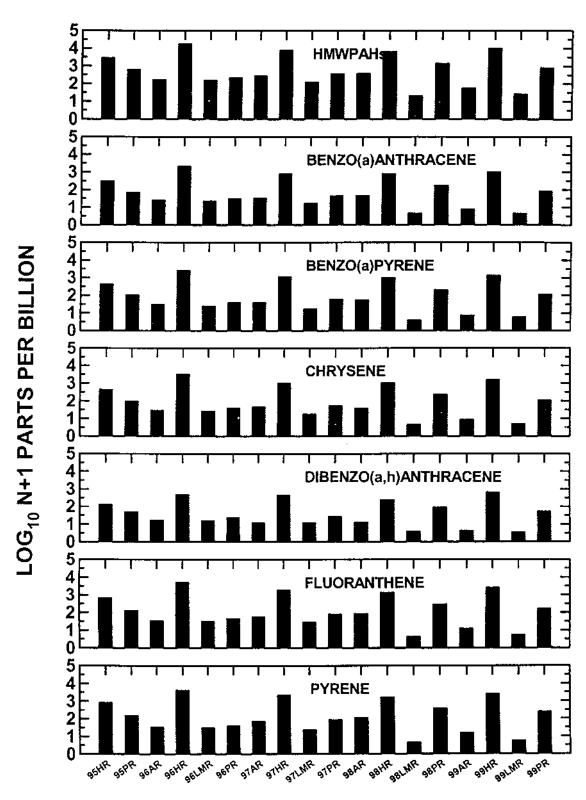


Figure 18. Mean concentrations (ppb) of high molecular weight PAHs by tributary-year. Tampa Bay, 1995-1999.

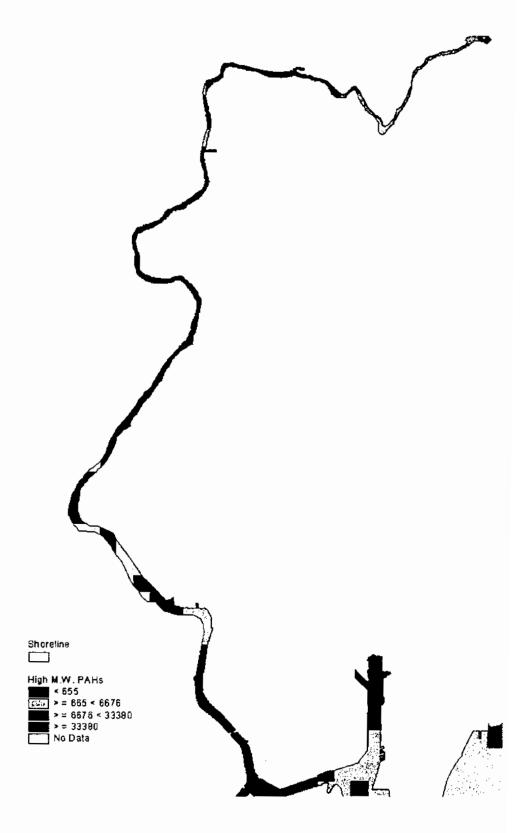


Figure 19. Spatial distribution of high molecular weight PAHs (ppb) in the Lower Hillsborough River, 1995-1999.

Ratios of benzo(a)anthracene:chrysene were generally <1:1 (Table 9). Benzo(b)fluoranthene: benzo(k)fluoranthene and phenanthrene:anthracene ratios were generally >1:1. Ratios of indeno(1,2,3,c,d)pyrene:benzo(g,h,i)perylene and pyrene:fluoranthene were generally close to1:1.

Table 9. Summary of PAH isomer ratios: Number of samples >MDL (N), Mean by bay segment and tributary, minimum, maximum, mean and median for all data.

| | Benz(a):Chry | Benz(b):Benz(k) | Ind:Benz(ghi) | Phen:Anth | Pyr:Fluor |
|-----------|--------------|-----------------|---------------|-----------|-----------|
| N >MDL | 125 | 144 | 130 | 107 | 152 |
| SEGMENT | | | | | _ |
| OTB | 0.61 | 1.3 | 0.96 | 2.6 | 1.0 |
| HB | 0.81 | 1.6 | 0.89 | 3.8 | 1.2 |
| MTB | 0.71 | 1.5 | 0.94 | 5.5 | 1.0 |
| LTB | ND | ND | ND | ND | ND |
| ВСВ | 0.58 | 1.3 | 0.92 | 16.4 | 1.0 |
| TCB | ND | ND | ND | ND | ND |
| MR | ND | ND | ND | ND | ND |
| TRIBUTARY | | | | | |
| HR | 0.71 | 1.8 | 0.96 | 6.9 | 0.9 |
| PR | 0.68 | 1.7 | 0.90 | 6.2 | 1.3 |
| AR | 0.75 | 1.4 | 0.89 | 3.8 | 1.1 |
| LMR | ND | ND | ND | ND | ND |
| MIN | 0.16 | 0.57 | 0.04 | 0.02 | 0.69 |
| MAX | 7.6 | 11.5 | 8.3 | 6736.0 | 10.7 |
| MEAN | 0.81 | 2.3 | 1.2 | 105.9 | 1.5 |
| MEDIAN | 0.73 | 1.6 | 0.92 | 5.5 | 1.1 |

Benz(a):Chrys=Benz(a)anthracene:Chrysene; Benz(b):Benz(k)=Benzo(bfluoranthene:Benzo(k)fluoranthene; Ind:Benz(ghi)=Indeno(1,2,3,c,d)pyrene:Benzo(g,h,i)perylene; Phen:Anth=Phncanathrene:Anthracene; Pyr:Fluor=Pyrene:Fluoranthene

ND= not detected

III.3 Organochlorine Pesticides

Twenty-one organochlorine pesticides have been identified from Tampa Bay sediments since the inception of the monitoring program in 1993 (Table 10). The most frequently detected (> MDL) pesticides were DDD, DDE, and total chlordane. The least frequently detected pesticides were a-hexachlorocyclohexane(AHCH) and endosulfan I. Four pesticides have had TELs and PELs established (MacDonald Environmental 1994): chlordane, total DDT, dieldrin, and lindane.

Chlordane concentrations were positively associated with percent silt+clay, although <3% of the variance was explained by percent silt+clay (Figure 20). Mean chlordane concentrations were significantly different between habitat types (F 13,710=13.3; p<.001). The mean concentration exceeded the PEL in tidal freshwaters where the percent silt+clay of the sediments ranged between 5% and 25% and in oligohaline waters with sediments of 5% to 75% silt+clay (Figure 21). Based upon the percentage of samples collected exceeding the PEL, lower salinity waters were more degraded (Table 11). The least contaminated habitats were euhaline waters with sediments containing < 25% silt+clay.

Mean concentrations also differed significantly for Bay Segment-Year combinations (F 29,543=40.4; p<0.001). Highest concentrations were detected in Old Tampa Bay, Hillsborough Bay, Lower Tampa Bay, and Middle Tampa Bay during 1995 (Figure 22)—although these were unduly influenced by a "high" (5 ppb) MDL. Almost 4% of Hillsborough Bay samples exceeded the PEL (Figure 23); in all other segments <2% exceeded the TEL (Table 12). One site in Old Tampa Bay (Culbreath Bayou) had a chlordane concentration >160 ppb.

Within the four smaller tributaries, chlordane concentrations were highest in the Lower Hillsborough River during every year except 1996 (Figure 24). Contamination was most widespread in the Lower Hillsborough River (Figure 25) and undetected in the Little Manatee River (Table 12).

Table 10. Inventory of organochlorine pesticides detected from Tampa Bay and its tributaries, 1993 & 1995-1999: Number of samples (N), percent of samples with concentrations > MDL, mean, median, and maximum concentration (ppb).

| | N | % Occurrences >MDL | Mean (ppb) | Median (ppb) | Maximum (ppb) |
|--------------------|-----|--------------------|---------------|-----------------|------------------|
| АНСН | 461 | 0.65 | 0.09 | 0.05 | 0.8 |
| ALDRIN | 769 | 1.30 | 0.23 | 0.30 | 5.8 |
| внсн | 461 | 3.04 | 0.16 | 0.08 | 1.4 |
| CHLORDANE | 769 | 17.42 | 1.76 | 0.50 | 166.0 |
| DHCH | 461 | 1.74 | 0.23 | 0.15 | 3.0 |
| DDD | 769 | 18.99 | 0.49 | 0.10 | 56.3 |
| DDE | 769 | 18.60 | 0.81 | 0.55 | 34.9 |
| DDT | 769 | 6.24 | 0.31 | 0.25 | 12.03 |
| DIELDRIN | 769 | 2.99 | 0.33 | 0.45 | 9.5 |
| ENDOSULFAN I | 730 | 0.96 | 0.53 | 0.25 | 4.9 |
| ENDOSULFAN II | 624 | 6.57 | 0.12 | 0.05 | 2.88 |
| ENDOSULFAN SULFATE | 674 | 4.15 | 0.18 | 0.25 | 2.90 |
| ENDRIN | 769 | 9.23 | 0.18 | 0.15 | 2.64 |
| ENDRIN ALDEHYDE | 675 | 4.74 | 0.10 | 0.05 | 3.0 |
| ENDRIN KETONE | 675 | 2.22 | 0.15 | 0.15 | 5.1 |
| HEPTACHLOR | 766 | 3.78 | 0.78 | 0.50 | 1.9 |
| HEPTACHLOR | 165 | 4.85 | 0.04 | 0.02 | 0.94 |
| EPOXIDE | | | | | |
| LINDANE | 731 | 2.60 | 0.19 | 0.30 | 1.1 |
| METHOXYCHLOR | 675 | 4.44 | 0.10 | 0.10 | 2.5 |
| MIREX | 461 | 2.60 | 0.17 | 0.20 | 3.02 |
| TOXAPHENE | 164 | 3.66 | 0.21 | 0.20 | 1.3 |

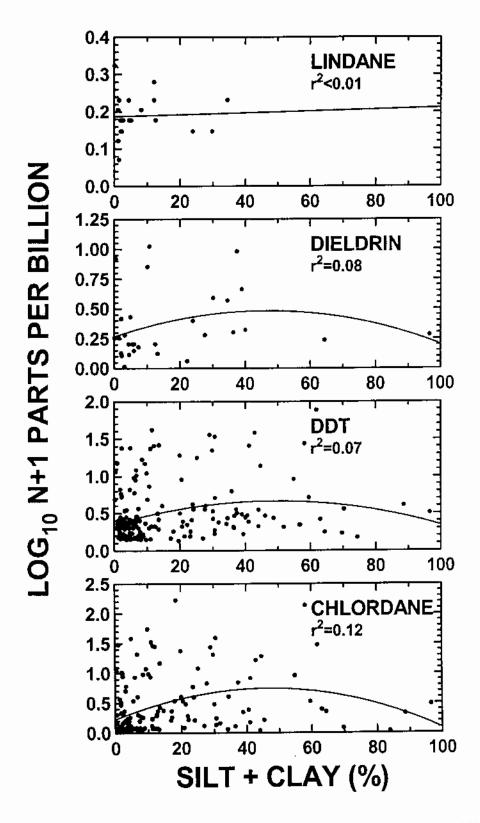


Figure 20. Association between chlordane, total DDT, dieldrin, and lindane (ppb) and percent silt+clay. Tampa Bay, 1993 & 1995-1999.

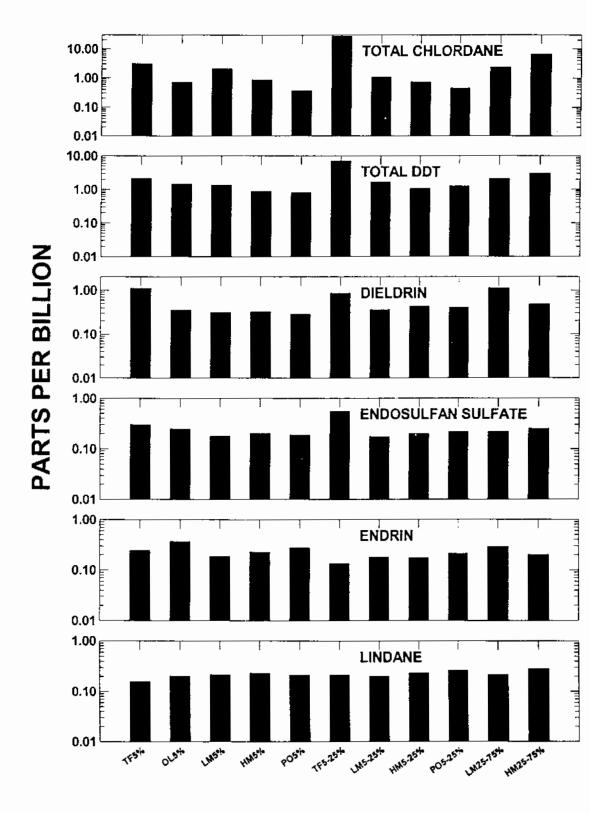


Figure 21. Mean concentrations (ppb) of selected pesticides by habitat type. Tampa Bay, 1993 & 1995-1999.

Table 11. Percentage of samples with pesticide concentrations <FEL, >=TEL<PEL and >=PEL: by habitat type (salinity zone & %SC). Tampa Bay, 1993 & 1995-1999.

| | EU | Ugi | PO | PO | P0 | PO | M | M | LM | OL | OL | 01 | TF | TF |
|---|------|------|------|------|------|------|------|------------|------|------|------|------|------|------|
| | <2% | 5- | %\$> | 5- | 25- | 75- | <5% | 5- 250% | 25- | %\$> | 5- | 25- | %5> | 5- |
| CHLORDANE | | 2/2 | | | | | | | | | | | | |
| <tel< th=""><th>98.5</th><th>100</th><th>80.2</th><th>90.3</th><th>74.4</th><th>100</th><th>54.8</th><th>76.2</th><th>59.2</th><th>70.0</th><th>40.0</th><th>2.99</th><th>0.09</th><th>40.0</th></tel<> | 98.5 | 100 | 80.2 | 90.3 | 74.4 | 100 | 54.8 | 76.2 | 59.2 | 70.0 | 40.0 | 2.99 | 0.09 | 40.0 |
| >=TEL <pel< th=""><th>1.5</th><th>0</th><th>18.6</th><th>9.1</th><th>16.3</th><th>0</th><th>42.9</th><th>19.0</th><th>23.5</th><th>10.0</th><th>10.0</th><th>0</th><th>20.0</th><th>10</th></pel<> | 1.5 | 0 | 18.6 | 9.1 | 16.3 | 0 | 42.9 | 19.0 | 23.5 | 10.0 | 10.0 | 0 | 20.0 | 10 |
| >=PEL | 0 | 0 | 1.2 | 9.0 | 9.3 | 0 | 2.4 | 4.8 | 17.3 | 20.0 | 50.0 | 33.3 | 20.0 | 50.0 |
| TOTAL DDT | - | | | | | | | | | | | | | |
| <tel< th=""><th>100</th><th>100</th><th>98.8</th><th>98.1</th><th>83.7</th><th>100</th><th>95.2</th><th>92.9</th><th>88.2</th><th>70.0</th><th>70.0</th><th>2.99</th><th>100</th><th>50.0</th></tel<> | 100 | 100 | 98.8 | 98.1 | 83.7 | 100 | 95.2 | 92.9 | 88.2 | 70.0 | 70.0 | 2.99 | 100 | 50.0 |
| >=TEL <pel< th=""><th>0</th><th>0</th><th>1.2</th><th>1.9</th><th>16.3</th><th>0</th><th>4.8</th><th>7.1</th><th>11.8</th><th>30.0</th><th>30.0</th><th>33.3</th><th>0</th><th>50.0</th></pel<> | 0 | 0 | 1.2 | 1.9 | 16.3 | 0 | 4.8 | 7.1 | 11.8 | 30.0 | 30.0 | 33.3 | 0 | 50.0 |
| >=PEL | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | | | | | | | | | | | | | | |
| DIELDRIN | | | | | | | | | | | | | | |
| <tel< th=""><th>100</th><th>100</th><th>8.86</th><th>99.4</th><th>90.7</th><th>100</th><th>100</th><th>97.6</th><th>82.4</th><th>90.0</th><th>100</th><th>100</th><th>80.0</th><th>0.06</th></tel<> | 100 | 100 | 8.86 | 99.4 | 90.7 | 100 | 100 | 97.6 | 82.4 | 90.0 | 100 | 100 | 80.0 | 0.06 |
| >=TEL <pel< th=""><th>0</th><th>0</th><th>1.2</th><th>9.0</th><th>9.3</th><th>0</th><th>0</th><th>2.4</th><th>11.8</th><th>10.0</th><th>0</th><th>0</th><th>10.0</th><th>10.0</th></pel<> | 0 | 0 | 1.2 | 9.0 | 9.3 | 0 | 0 | 2.4 | 11.8 | 10.0 | 0 | 0 | 10.0 | 10.0 |
| >=PEL | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 5.9 | 0 | 0 | 0 | 0 | 0 |
| | | | | | | | | | | | | | | |
| LINDANE | | | | | | | | | | | | | | |
| <tel< th=""><th>95.2</th><th>100</th><th>97.5</th><th>98.0</th><th>100</th><th>100</th><th>97.5</th><th>97.2</th><th>94.1</th><th>100</th><th>001</th><th>100</th><th>100</th><th>96</th></tel<> | 95.2 | 100 | 97.5 | 98.0 | 100 | 100 | 97.5 | 97.2 | 94.1 | 100 | 001 | 100 | 100 | 96 |
| >=TEL <pel< th=""><th>4.8</th><th>0</th><th>2.1</th><th>2.0</th><th>0</th><th>0</th><th>2.5</th><th>2.8</th><th>5.9</th><th>0</th><th>0</th><th>0</th><th>0</th><th>10</th></pel<> | 4.8 | 0 | 2.1 | 2.0 | 0 | 0 | 2.5 | 2.8 | 5.9 | 0 | 0 | 0 | 0 | 10 |
| >=PEL | 0 | 0 | 0.4 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | | | | | | | | | | | | | | |
| PESTICIDE PEL | | | | | | | | | | | | | | |
| OUOTIENT | | | | - | | | | | | | | | | |
| <0.1 | 65.2 | 42.9 | 53.8 | 46.1 | 32.6 | 0.09 | 42.9 | 47.6 | 29.4 | 30.0 | 40.0 | 33.3 | 40.0 | 30.0 |
| >=0.1<1.0 | 34.8 | 57.1 | 45.8 | 53.9 | 62.8 | 40.0 | 54.7 | 50.0 | 64.7 | 70.0 | 30.0 | 33.3 | 0.09 | 50.0 |
| >=1.0 | 0 | 0 | 0.4 | 0 | 4.6 | 0 | 2.4 | 2.4 | 5.9 | 0 | 30.0 | 33.3 | 0 | 20.0 |
| | | İ | | | | | | | | | | | | |

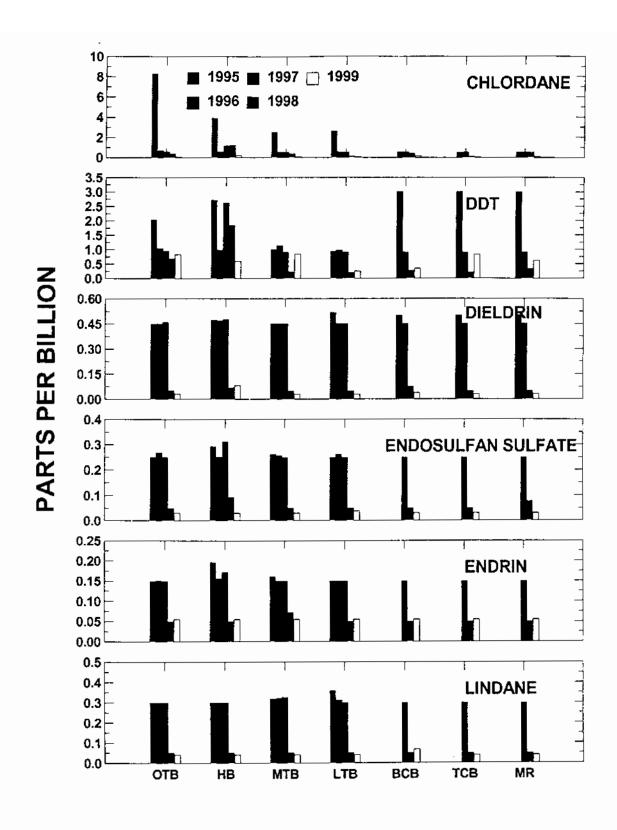


Figure 22. Mean concentrations (ppb) of selected pesticides by bay segment-year. Tampa Bay, 1993 & 1995-1999.

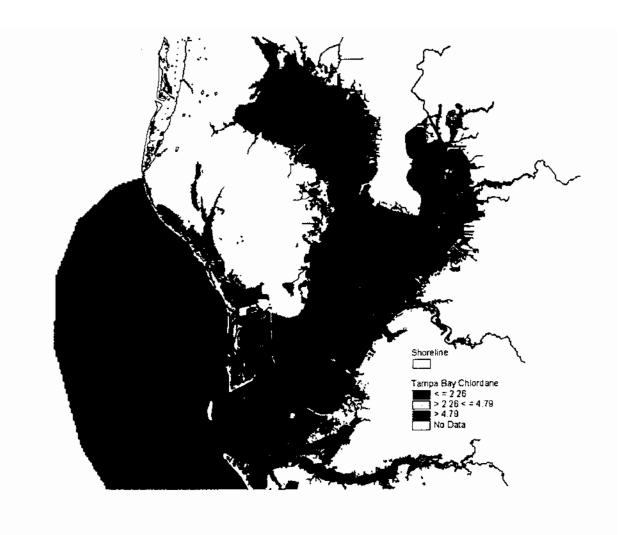


Figure 23. Spatial distribution of Chlordane (ppb) in Tampa Bay, 1993 & 1995-1999.

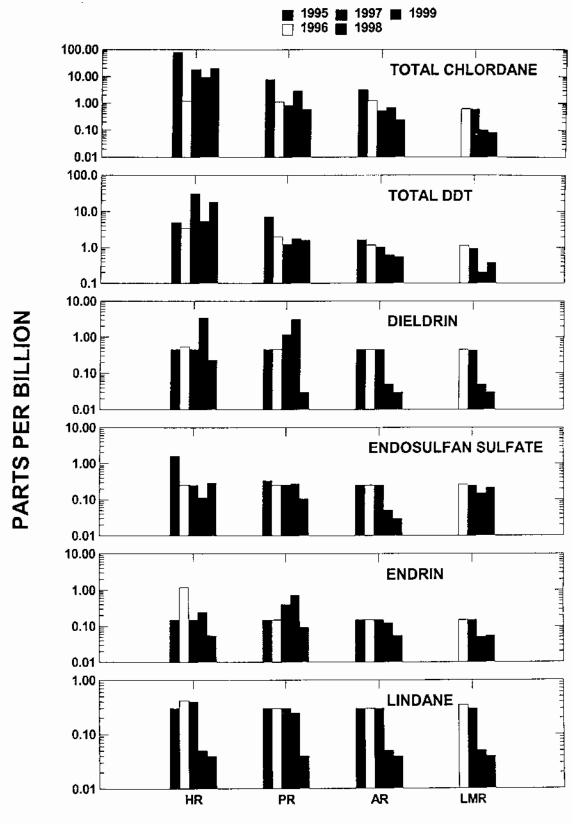


Figure 24. Mean concentrations (ppb) of selected pesticides by tributary-year. Tampa Bay, 1995-1999.

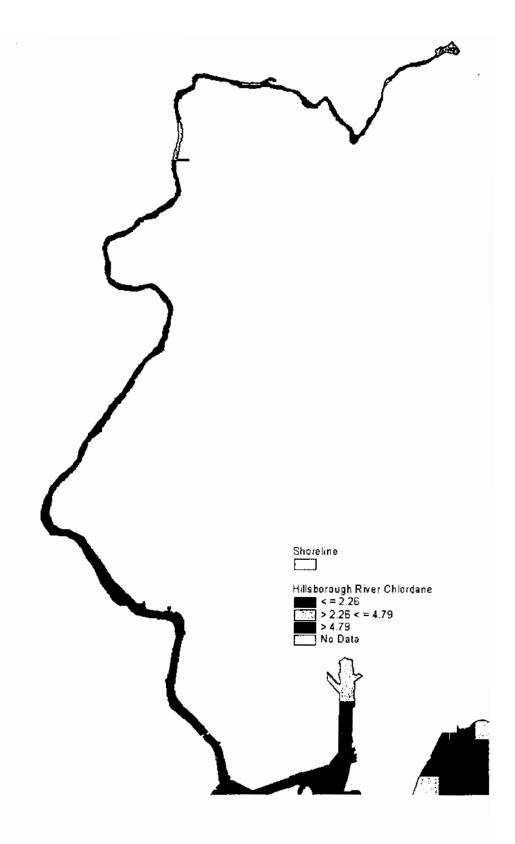


Figure 25. Spatial distribution of Chlordane (ppb) in the Lower Hillsborough River, 1995-1999.

Table 12. Percentage of samples with pesticide concentrations <TEL, >=TEL<PEL and >=PEL: by bay segment and tributary. Tampa Bay, 1993 & 1995-1999.

| | | PRI | MARY | BAY S | SEGMI | ENTS | | | TI | RIBUT | ARIE | S |
|---|----------|------|------|-------|-------|------|------|---|----------------|-------|------|------|
| | OTB | HB | MTB | LTB | BCB | TCB | MR | | HR | PR | AR | LMR |
| CHLORDANE | [| | | | | : | | | | | | |
| <tel< td=""><td>98.1</td><td>96.2</td><td>99.2</td><td>99.2</td><td>98.8</td><td>100</td><td>98.1</td><td></td><td>12.9</td><td>72.7</td><td>93.5</td><td>100</td></tel<> | 98.1 | 96.2 | 99.2 | 99.2 | 98.8 | 100 | 98.1 | | 12.9 | 72.7 | 93.5 | 100 |
| >=TEL <pel< td=""><td>1.0</td><td>0</td><td>0.8</td><td>0</td><td>1.2</td><td>0</td><td>0</td><td></td><td>12.9</td><td>18.2</td><td>3.2</td><td>0</td></pel<> | 1.0 | 0 | 0.8 | 0 | 1.2 | 0 | 0 | | 12.9 | 18.2 | 3.2 | 0 |
| >=PEL | 1.0 | 3.8 | 0 | 0.8 | 0 | 0 | 1.9 | | 74.2 | 9.1 | 3.2 | 0 |
| TOTAL DDT | | | | | | | | | | | | |
| <tel< td=""><td>98.1</td><td>95.2</td><td>99.2</td><td>100</td><td>100</td><td>100</td><td>100</td><td></td><td>25.8</td><td>86.4</td><td>100</td><td>100</td></tel<> | 98.1 | 95.2 | 99.2 | 100 | 100 | 100 | 100 | | 25.8 | 86.4 | 100 | 100 |
| >=TEL <pel< td=""><td>1.9</td><td>4.8</td><td>0.8</td><td>0</td><td>0</td><td>0</td><td>0</td><td></td><td>71.0</td><td>13.6</td><td>0</td><td>0</td></pel<> | 1.9 | 4.8 | 0.8 | 0 | 0 | 0 | 0 | | 71.0 | 13.6 | 0 | 0 |
| >=PEL | 0 | 0 | 0 | 0 | 0 | 0 | 0 | | 3.2 | 0 | 0 | 0 |
| DIELDRIN | | | | | | | | | | | | |
| <tel< td=""><td>100</td><td>97.0</td><td>100</td><td>98.4</td><td>100</td><td>100</td><td>100</td><td></td><td>80.6</td><td>72.7</td><td>100</td><td>100</td></tel<> | 100 | 97.0 | 100 | 98.4 | 100 | 100 | 100 | | 80.6 | 72.7 | 100 | 100 |
| >=TEL <pel< td=""><td>0</td><td>3.0</td><td>0</td><td>1.6</td><td>0</td><td>0</td><td>0</td><td></td><td>9.7</td><td>22.8</td><td>0</td><td>0</td></pel<> | 0 | 3.0 | 0 | 1.6 | 0 | 0 | 0 | | 9.7 | 22.8 | 0 | 0 |
| >=PEL | 0 | 0 | 0 | 0 | 0 | 0 | 0 | | 9.7 | 4.5 | 0 | 0 |
| LINDANE | | | | | | | | | - - | | | |
| <tel< td=""><td>100</td><td>100</td><td>94.6</td><td>95.9</td><td>98.4</td><td>100</td><td>100</td><td></td><td>90.3</td><td>90.9</td><td>100</td><td>95.8</td></tel<> | 100 | 100 | 94.6 | 95.9 | 98.4 | 100 | 100 | | 90.3 | 90.9 | 100 | 95.8 |
| >=TEL <pel< td=""><td>0</td><td>0</td><td>5.4</td><td>3.9</td><td>1.6</td><td>0</td><td>0</td><td></td><td>9.7</td><td>9.1</td><td>0</td><td>4.2</td></pel<> | 0 | 0 | 5.4 | 3.9 | 1.6 | 0 | 0 | | 9.7 | 9.1 | 0 | 4.2 |
| >=PEL | 0 | 0 | 0 | 0.8 | 0.8 | 0 | 0 | | 0 | 0 | 0 | 0 |
| PESTICIDE | <u>-</u> | | | | | | | _ | | | | |
| PEL | | | | | | | | | | | | |
| QUOTIENT | | | | | | | | | | | | |
| <0.1 | 47.6 | 38.6 | 46.2 | 45.1 | 68.7 | 70.6 | 73.1 | | 0 | 31.8 | 45.2 | 58.3 |
| >=0.1<1.0 | 51.4 | 59.0 | 53.8 | 54.9 | 31.3 | 29.4 | 26.9 | | 61.3 | 63.7 | 54.8 | 41.7 |
| >=1.0 | 1.0 | 2.4 | 0 | 0 | 0 | 0 | 0 | | 38.7 | 4.5 | 0 | 0 |

DDT and its metabolites were detected in up to 19% of the samples (Table 10). Total DDT concentrations were positively correlated with percent silt+clay (Figure 20). DDT concentrations differed significantly between habitat type ($F_{13,710}=11.4$; p<.001). Mean exceeded the TEL in tidal freshwaters and oligohaline waters with sediments of 5% to 25% silt+clay and in mesohaline waters with sediments of 25% to 75% silt+clay (Figure 21). Within habitat types, lower salinity sites had more frequent exceedences of the TEL by DDT (Table 11). None of samples collected to date exceeded the PEL. Overall, lowest median DDT concentration occurred in euhaline waters with sediments of <5% silt+clay.

Mean concentrations also differed significantly among Bay Segment-Year combinations $(F_{29,543}=17.1; p<0.001)$. Highest mean were detected in the Manatee River during 1996 and

Hillsborough Bay in 1995 (Figure 22)--although high MDLs bias this pattern (cf. Appendix A). Almost 5% of Hillsborough Bay samples did have DDT concentrations >TEL (Table 12; Figure 26).

Within the tributaries, the Lower Hillsborough River had the highest mean concentration during each year (Figure 24) and almost 75% of the samples exceeded the TEL (Table 12; Figure 27). To date there has been no evidence of DDT contamination in either the Alafia or Little Manatee rivers.

At sites where both DDT and DDE concentrations were both >MDL, DDT:DDE ratios ranged from 0.03:1 to 134:1, with a median ratio of 0.74:1. The five highest ratios (>20:1) were found in 1998 Hillsborough River samples where the total DDT concentration ranged from 1.3 to 10.5 ppb; the five lowest ratios (<0.07:1) were found in the Hillsborough River during 1997 where DDT concentrations ranged from 21.1 to 75 ppb (Figure 28). At the sites where total DDT concentration >TEL the median DDT:DDE ratio was 0.08:1.

Dieldrin was only detected in 3% of the samples (Table 10) and inferences about its distribution are affected by the paucity of data points >MDL. The association with percent silt+clay was not significant (Figure 20). Dieldrin concentrations appeared to differ by habitat type with concentrations >TEL found in low mesohaline waters with sediments containing 25% to 75% silt+clay and tidal freshwaters with sediments with sediments of <5% silt+clay (Figure 21). Almost 6% of samples in mesohaline waters with sediments of 25% to 75% silt+clay exceeded the PEL (Table 11).

There did not appear to be differences in mean dieldrin concentration by Bay Segment (Figure 22), although there did appear to be differences between years which could be attributed to variations in the MDL (cf. Appendix A). Three percent of Hillsborough Bay samples

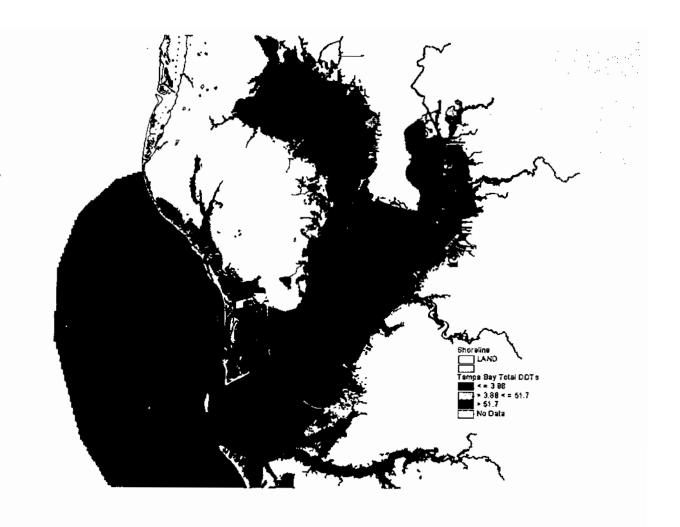


Figure 26. Spatial distribution of total DDT (ppb) in Tampa Bay, 1993 & 1995-1999.

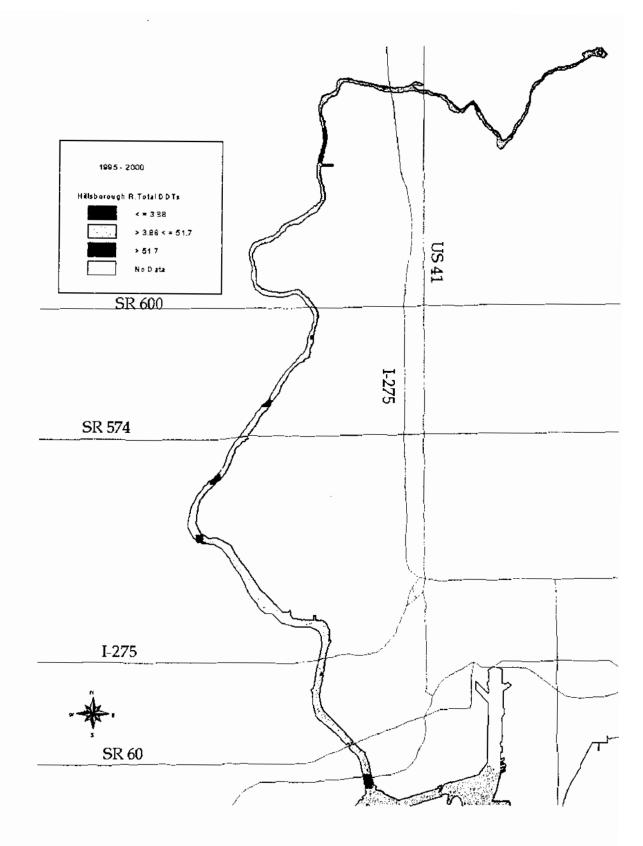


Figure 27. Spatial distribution of total DDT (ppb) in the Lower Hillsborough River, 1995-1999.

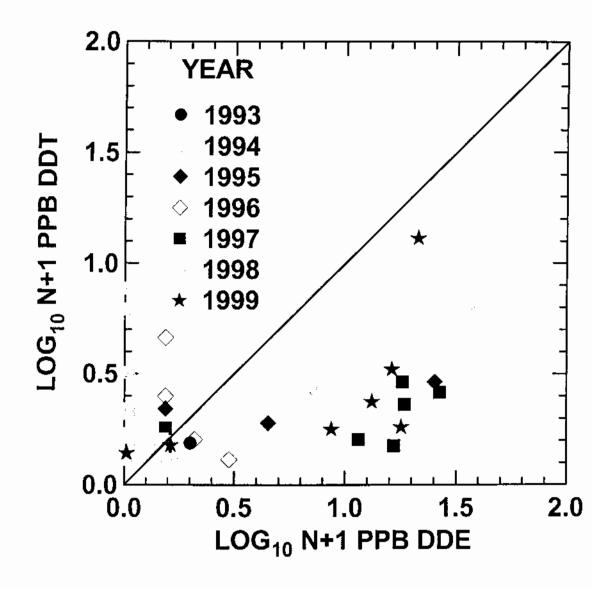


Figure 28. Association between total DDTs and DDE. Tampa Bay, 1993 & 1995-1999

exceeded the TEL for dieldrin (Table 12). Within the tributaries (Table 12), the Palm River showed the most extensive contamination by dieldrin (>27% of samples >TEL). Both the Alafia and Little Manatee rivers were "clean" with respect to dieldrin.

Lindane was only detected in 2.6% of the samples (Table 10). The association with percent silt+clay was not statistically significant (Figure 20). There did appear to be some differences in lindane concentrations by habitat with somewhat lower mean concentrations in low salinity/coarse sediment habitats (Figure 21). Concentrations somewhat lower concentrations in low salinity/coarse sediment habitats (Figure 21). Lindane concentrations exceeded the PEL in a single sample from Lower Tampa Bay and exceeded the TEL in 18 samples (7 from Middle Tampa Bay and 4 from Lower Tampa Bay) (Table 12). Within the tributaries (Figure 21), marginal levels of contamination were observed in <10% of the samples from the Lower Hillsborough, Palm, and Little Manatee rivers. To this date, the Alafia River appears uncontaminated with respect to Lindane (Table 12).

Other pesticides identified as being of concern for Tampa Bay included endosulfan, heptachlor, heptachlor epoxide, and mirex. Endosulfan sulfate, endosulfan I and endosulfan II were detected in 4.2%, 6.6%, and 1.0% of the samples respectively (Table 10). Highest concentrations of endosulfan sulfate and/or its metabolites (Figures 22 & 23) occurred in the Lower Hillsborough River (endosulfan sulfate, endosulfan I & II), Hillsborough Bay (endosulfan I), and McKay Bay (endosulfan II). Heptachlor and heptachlor epoxide occurred in approximately 4% to 5% of the samples (Table 10). Highest concentrations occurred in Hillsborough Bay (heptachlor and heptachlor epoxide) and Middle Tampa Bay (heptachlor) (Figure 22). Mirex was detected in 2.6% of samples (Table 10) with concentrations >1 ppb in samples from McKay Bay (EPCHC unpubl. data) and the Palm River (Figure 22).

Overall pesticide burdens, based upon the PEL Quotient of the above four pesticides, indicate that there are at least moderate levels of contamination in all habitats within Tampa Bay (Table 10; Figure 29). Lower salinity habitats were generally more contaminated than higher salinity habitats (Figures 30-33). PEL Quotients >1 were only observed in the Old Tampa Bay and Hillsborough Bay segments (Figure 29), a consequence of elevated chlordane levels at a few locations (Figure 23). Almost 40% of the Lower Hillsborough River samples had PEL Quotients >1.0 for chlordane and none of the samples had PEL Quotients <0.1 (Table 12). Of

the four pesticides for which PEL quotients exist, the PEL quotients for chlordane and DDT were positively correlated (r=0.46; p<0.001) as were those for lindane and dieldrin (r=0.24; p<0.001).

III. 4 Polychlorinated Biphenyls

Detectable levels of PCBs occurred in 17.6% of the samples collected: 8.8% of the samples collected from the seven primary bay segments and 68.5% of the tributary samples. Concentrations above the PEL occurred in 0.3% of the bay samples (in the Hillsborough Bay segment) and in 7.4% of the tributary samples (primarily the Palm River). PCB concentrations were positively associated with the percent silt+clay ($r_{1.704}$ =0.40; p<0.001) (Figure 29).

Mean PCB concentrations differed significantly by habitat ($F_{13,674}$ =7.5; p<.001). Mean concentrations were highest in mesohaline waters with sediments of 25% to 75% silt+clay and tidal freshwaters with a silt+clay content of 5% to 25%; lowest mean concentration occurred in euhaline waters and in polyhaline waters with sediments of 5% to 25% silt+clay (Figure 30). PCB contamination was most frequent in samples collected in oligohaline waters with sediments of 5% to 25% silt+clay and mesohaline waters of 25% to 75% silt+clay (Table 13).

ANOVA showed that the mean PCB concentrations differed among Bay Segment-Year combinations ($F_{28,531}$ =102.7; p<0.001) (Figure 30). However, 1995-1997 data were biased by relatively high MDLs (cf. Appendix A). For the 1998 and 1999 data, highest concentrations occurred in Hillsborough Bay during 1998. Overall, only Hillsborough Bay had PCB levels exceeding the PEL (Table 14; Figure 31); values >TEL were only found in Hillsborough Bay and Middle Tampa Bay.

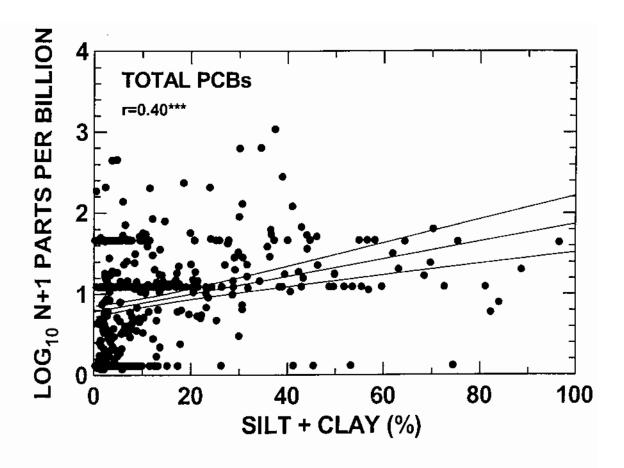


Figure 29. Association between total PCBs and percent silt+clay (regression line and 95% confidence limits): Tampa Bay, 1993 & 1995-1999.

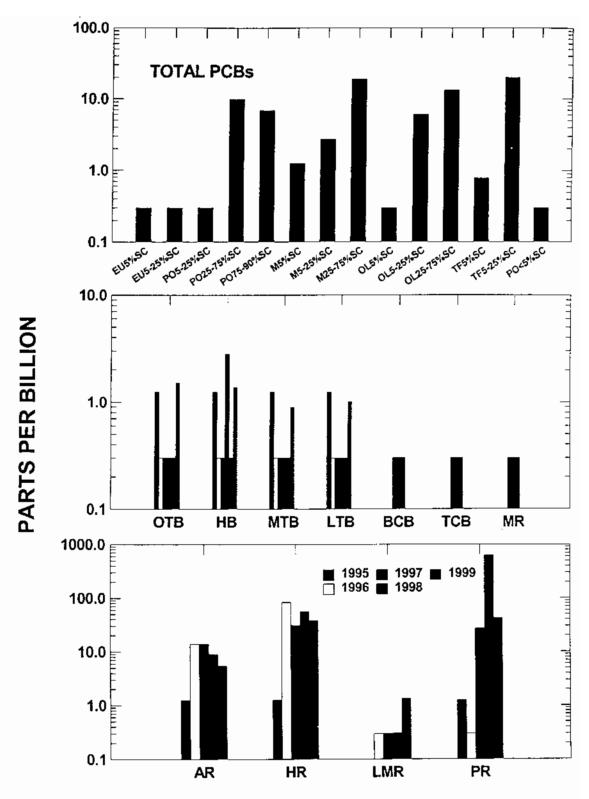


Figure 30. Mean concentrations of total PCBs (ppb) by habitat type, bay segment by year, and tributary by year,. Tampa Bay, 1993 & 1995-1999.

Table 13. Percentage of samples with PCB concentrations <TEL, >=TEL<PEL and >=PEL: by habitat type (salinity zone & %SC). Tampa Bay, 1993 & 1995-1999.

| | BU | ЭÜ | PO | PO | PO | PO | M | M | M | OF | OL | 10 | TF | TF |
|---|-----|-------|-----------|-------|--------|--------|------|-------|--------|------|-------|--------|------|-------|
| | 2% | 5-25% | 2% | 5-25% | 25-75% | 75-90% | 2% | 2-25% | 25-75% | 2% | 5-25% | 25-75% | 5% | 5-25% |
| PCBs | | | | | | | | | | | | | | |
| <tel< td=""><td>100</td><td>100</td><td>99.2</td><td>0.96</td><td>8.69</td><td>80.0</td><td>97.5</td><td>9.08</td><td>58.8</td><td>80.0</td><td>60.0</td><td>2.99</td><td>80.0</td><td>0.09</td></tel<> | 100 | 100 | 99.2 | 0.96 | 8.69 | 80.0 | 97.5 | 9.08 | 58.8 | 80.0 | 60.0 | 2.99 | 80.0 | 0.09 |
| >=TEL <pel< td=""><td>0</td><td>0</td><td>0</td><td>4.0</td><td>30.2</td><td>20.0</td><td>0</td><td>16.7</td><td>23.5</td><td>20.0</td><td>30.0</td><td>33.3</td><td>20.0</td><td>40.0</td></pel<> | 0 | 0 | 0 | 4.0 | 30.2 | 20.0 | 0 | 16.7 | 23.5 | 20.0 | 30.0 | 33.3 | 20.0 | 40.0 |
| >=PEL | 0 | 0 | 8.0 | 0 | 0 | 0 | 2.5 | 2.7 | 17.6 | 0 | 10.0 | 0 | 0 | 0 |
| | | | | | | | | | | | | | | |

Table 14. Percentage of samples with PCB concentrations <TEL, >=TEL<PEL, and >=PEL: by bay segment and tributary, Tampa Bay 1993 & 1995-1999.

| | | PR | PRIMARY BAY SEGMENTS | BAY SE | GMENT | S | | | FRIBUTARIES | ARIES | |
|---|-----|------|----------------------|-------------|-------|-----|-----|------|--------------------|-------|------|
| | OTB | HB | MTB | MTB LTB BCB | BCB | TCB | MR | HR | PR | AR | LMR |
| PCB | | | | | | | | | | | |
| <tel< th=""><th>100</th><th>86.2</th><th>99.2</th><th>100</th><th>100</th><th>100</th><th>100</th><th>22.6</th><th>45.4</th><th>93.5</th><th>95.8</th></tel<> | 100 | 86.2 | 99.2 | 100 | 100 | 100 | 100 | 22.6 | 45.4 | 93.5 | 95.8 |
| >=TEL <pel< th=""><th>0</th><th>12.2</th><th>8.0</th><th>0</th><th>0</th><th>0</th><th>0</th><th>64.5</th><th>31.8</th><th>6.5</th><th>4.2</th></pel<> | 0 | 12.2 | 8.0 | 0 | 0 | 0 | 0 | 64.5 | 31.8 | 6.5 | 4.2 |
| | | | | | | | | | | | |

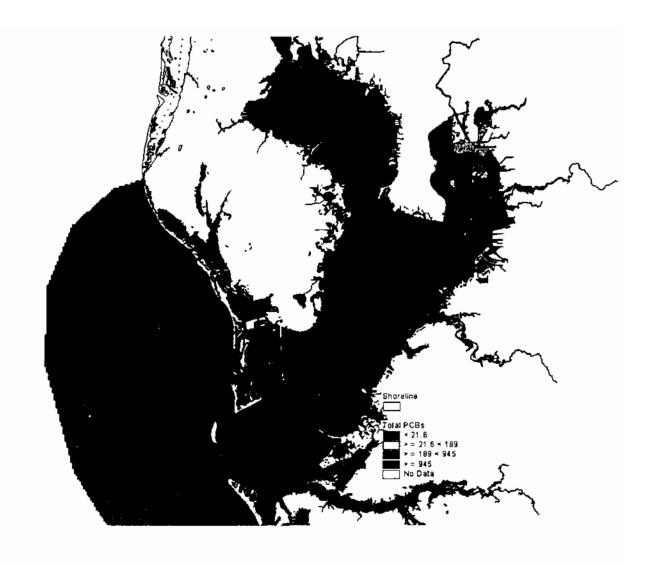


Figure 31. Spatial distribution of total PCBs (ppb) in Tampa Bay, 1993 & 1995-1999.

The samples collected from the Palm River during 1998 had unusually high concentrations of PCBs compared to other years and other tributaries (Figure 30). More than 20% of the Palm River samples (Figure 32) and almost 13% of the Lower Hillsborough River (Figure 33) samples had PCB concentrations >PEL. More than 60% of the Lower Hillsborough River samples and >30% of the Palm River samples had PCB concentrations >=TEL<PEL (Figures 32 & 33; Table 14

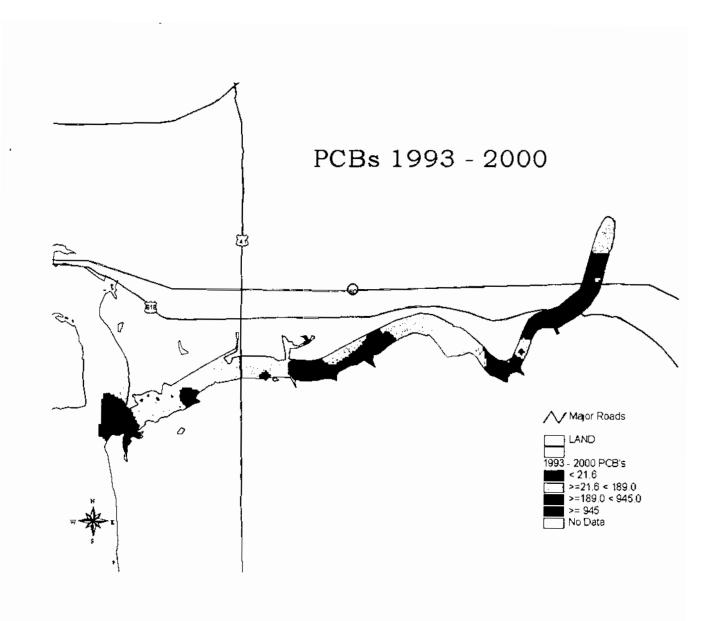


Figure 32. Spatial distribution of total PCBs in the Palm River, 1995-1999.

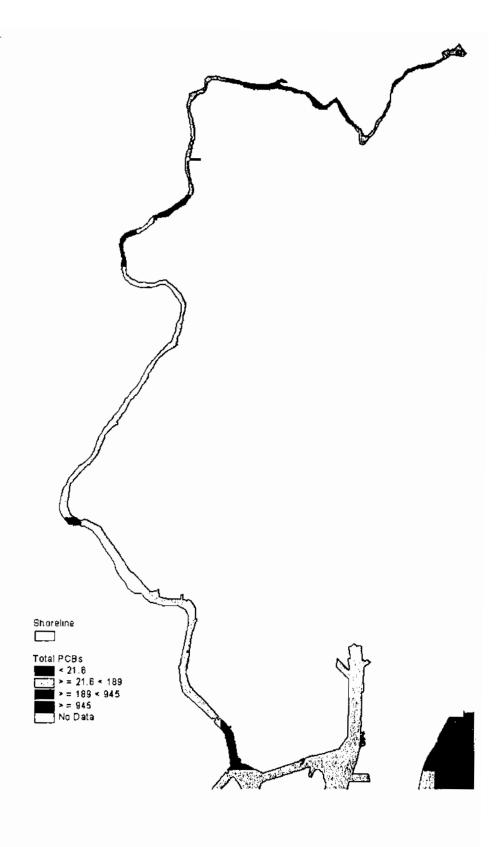


Figure 33. Spatial distribution of total PCBs (ppb) in the Lower Hillsborough River, 1995-1999.

IV. DISCUSSION

McConnell et al. (1996) identified several chemical contaminants which were likely to confer both ecological and human health risk in several subareas of Hillsborough Bay, western Old Tampa Bay, Boca Ceiga Bay, and portions of Middle Tampa Bay. These included the PAHs, benzo(a)pyrene, benzo(b)fluoranthene, and benza(a)anthracene, the organochlorine pesticides chlordane, DDT, endrin, heptachlor, and lindane, and PCBs.

In this monitoring program, PAHs, chlordane, and DDT were each shown to occur at concentrations likely to affect biotic communities in the Lower Hillsborough River and both DDT and chlordane were also detected at high concentrations in eastern Old Tampa Bay. PCBs concentrations at three sites in the Palm River were between three and five time higher than the PEL (MacDonald Environmental Services, Ltd. 1994). Western Old Tampa Bay, Boca Ceiga Bay, and Middle and Lower Tampa Bay sediments showed little or no evidence of contamination by organic chemicals.

Mean concentrations of PAHs were highest in tidal freshwaters with sediments of 5% to 25% silt+clay and in oligohaline waters with sediments of 25% to 75% silt+clay-- sites which were primarily found in the Lower Hillsborough River. Lowest concentrations were found in polyhaline and euhaline waters with sediments of <5% silt+clay. On a percentage basis, the habitats most degraded by low molecular weight PAHs included oligohaline waters (20% to 33% of samples >PEL) and tidal freshwaters of <5% silt+clay (60% of samples >TEL). For high molecular weight PAHs, the most degraded habitats included oligohaline and tidal freshwaters with sediments of 5% to 25% silt+clay and oligohaline waters of 25% to 75% silt+clay (30% to 33% of samples >PEL). Euhaline waters were least degraded by PAHs.

Stormwater runoff of automotive combustion products is likely the primary source of PAHs to Tampa Bay sediments, based upon calculated PAH isomer ratios (Benlahcen *et al.* 1997; Dickhut *et al.* 2000; McCready *et al.* 2000). Benzo(a)anthracene:chrysene,

benzo(b)fluoranthene : benzo(k)fluoranthene, and pyrene : fluoranthene ratios were generally >1:1 and phenanthrene:anthracene ratios were generally >2. However, there were samples in which the ratios were intermediate between vehicle emissions and those characteristic of coal-

fired power plants and/or incinerators. The ratio of indeno(1,2,3,c,d)pyrene:

benzo(g,h,i)perylene were generally close to 1:1, which is more characteristic of atmospheric deposition from coal-fired power plants and municipal incinerators (Dickhut *et al.* 2000).

Where the source of PAHS is runoff, the ratios of

indeno(1,2,3,c,d)pyrene:benzo(g,h,i)perylene are closer to 0.3:1 (Dickhut et al. 2000).

Therefore, at least three possible sources of PAHs to Tampa Bay sediments include stormwater runoff, coal-fired power plants, and municipal incinerators.

The pesticide chlordane was detected in approximately 17% of the samples--- similar to the percentage observed statewide (16%) by Seal *et al.* (1994). Chlordane concentrations were positively associated with percent silt+clay, although only a small fraction (<3%) of the variability was explained by percent silt+clay.

Mean chlordane concentrations were significantly different between habitat types and by Bay Segment x Year. The mean concentration exceeded the PEL in tidal freshwaters where the silt+clay content of the sediments ranged between 5% and 25% and the median concentration in oligohaline waters with sediments of 5% to 25% silt+clay exceeded the TEL; these locations were generally in the Lower Hillsborough River. Based upon the percentage of samples collected exceeding the PEL, lower salinity waters (e.g., Hillsborough River) were more degraded than higher salinity waters with coarser-grained sediments. The highest concentration reported to date (>30 times the PEL of 4.79 ppb), however, is from a site in Culbreath Bayou, a residential canal system in eastern Old Tampa Bay.

This pattern is consistent with the uses of chlordane and its affinity for finer-grained sediments. Chlordane was widely used in commercial pest control, especially as a termiticide, up until 1988. Shigenaka (1990) reported that during 1974-1976 between 35% and 68% of the Chlordane produced was used in commercial pest control, between 10% and 30% was used for "home and garden" applications, and the remainder was used in agriculture. However, Frithsen et al. (1995) estimated that, of the approximately >1000 kg year which enters Tampa Bay annually, 77% is from agricultural runoff and only 21% is from urban runoff. Of the approximately 220 kg per year entering the bay via runoff, 53 kg is from the Hillsborough

River and 97 kg is from Hillsborough Bay as a whole. Given that pesticides in general tend to bind to finer-grained particles (Birch & Taylor 2000), and chlordane does show an affinity for finer-grained sediments in this study, it is not surprising that chlordane in the sediments is detected more often in tributaries, especially those draining urban areas. Chlordane derived from agricultural runoff either is not reaching the bay, or if it does enter the bay it does so in areas where coarser-grained sediments predominate (cf. Brooks & Doyle 1998) and binding by chlordane is minimized.

The ratio of heptachlor to heptachlor epoxide is another potentially useful tool for identifying likely sources of Chlordane to bay sediments. Jantunen et al. (2000) report that where the atmospheric ratios of heptachlor to heptachlor epoxide are "high" (>1), urban residential emissions rather than agricultural applications are the source of the Chlordane. The explanation lies, in part that heptachlor epoxide is a byproduct of the microbial breakdown of heptachlor, a process that occurs primarily in soils (Jantunen et al. 2000). Unfortunately, both heptachlor and heptachlor epoxide were only analyzed during a single year and in only one sample was the ratio based upon concentrations >MDL for both pesticides.

DDT and its metabolites were detected in 6% (DDT) to 19% (DDD) of the samples; this is lower than the statewide frequencies reported by Seal *et al.* (1994): DDTs and DDEs up to 28% and DDD in 46% of the samples. Total DDT concentrations were positively associated with percent silt+clay. Total DDT concentrations differed significantly between habitat type, with the highest mean concentrations (>TEL) in tidal freshwaters with sediments of 5% to 25% silt+clay (*i.e.*, Lower Hillsborough River). Overall, lowest mean DDT concentration occurred in euhaline waters with sediments of <5% silt+clay. Generally, DDT concentrations at lower salinity sites (primarily Lower Hillsborough River) exceeded the TEL more frequently than at higher salinity sites. None of samples collected to date exceeded the PEL.

There were also significant differences in mean DDT concentration for the Bay Segment x Year interaction. During 1996, the highest concentrations were detected in Boca Ciega Bay, Terra Ceia Bay, and the Manatee River—a pattern biased by high MDLs. If 1996 data are excluded, no samples exceed the TEL in these segments. Almost 5% of Hillsborough Bay samples exceeded the TEL for total DDTs. Within the tributaries, the Lower Hillsborough

River had the highest median concentrations during each year and almost three quarters of the samples exceeded the TEL. Both the Alafia and Little Manatee rivers show no evidence of contamination by DDT or its metabolites in the samples collected to date.

DDT:DDE ratios were generally low, especially at the higher DDT concentrations. The ratios were relatively high where DDT concentrations were low. Tavares *et al.* (1999) suggested that, in Brazil, where the ratio was >0.91, DDT use was likely within the past five years. It is unlikely that DDT has been used recently in the Tampa Bay area; therefore the high ratios (occurring at the lowest concentrations) may be spurious. The low ratios, especially those occurring at higher DDT concentrations, are consistent with cessation of DDT use in the 1970s. Whether the use of the miticide dicofol (Kelthane), which is manufactured from DDT (Kamrin 1997) could contribute to the observed distributional patterns is unknown.

Frithsen *et al.* (1995) estimate that agricultural runoff contributes approximately 95% of the 1660 kg year⁻¹ reaching the bay. Urban runoff is estimated to only account for 4% of the loading. The Hillsborough River is listed as the largest contributor to urban runoff (0.9%). Given the distribution of DDT in Tampa Bay, it seems that urban runoff is the source of DDT in the sediments. DDT from agricultural areas does not appear to reach the bay --or if it does, the DDT does not bind to the [coarser] sediments (*cf.* Birch & Taylor 2000).

Contrasting with the patterns for DDT and chlordane in this study, and for pesticides in general (Birch & Taylor 2000), Dieldrin concentrations were not positively associated with percent silt+clay—although the prevalence of samples <MDL confounds this association. Dieldrin concentrations appeared to differ by habitat types with highest concentrations (>TEL) in mesohaline waters with sediments containing 25% to 75% silt+clay (Palm River 1997 and 1998) and tidal freshwaters with sediments of <5% silt+clay (Lower Hillsborough River 1998). Almost 6% of samples in low mesohaline waters with sediments of 25% to 75% silt+clay exceeded the PEL. Three percent of Hillsborough Bay samples exceeded the TEL for dieldrin. Within the tributaries, the Palm River showed the most extensive contamination by dieldrin (>27% of samples >TEL). Frithsen et al. (1995) estimate that agricultural runoff contributes

approximately 99% of the 770 kg year⁻¹ of dieldrin reaching the bay. Urban runoff seems the more likely source of dieldrin to the bay's sediments although the fate of agricultural runoff of dieldrin is uncertain.

Lindane is one of the few organochlorine pesticides still in use. It is used on a variety of crops, and also occurs in shampoos and lotions for the control of lice and mites in humans (Kamrin 1997). Lindane was only rarely (<3%) detected and the association with percent silt+clay was influenced by the MDLs. There did appear to be differences in lindane concentrations by habitat, with lower concentrations in low salinity/coarse sediment habitats. Concentrations exceeded the PEL in a single sample from LTB and exceeded the TEL in 18 samples (7 from MTB and 4 from LTB). Within the tributaries, marginal levels of contamination (>TEL<PEL) were observed in <10% of the samples from the Hillsborough, Palm, and Little Manatee rivers. The Alafia River was "clean" with respect to lindane. Frithsen *et al.* (1995) did not provide any estimates for Lindane sources and loadings to the bay.

Other pesticides identified were too rarely collected or TELs/PELs have not been established which provides context for their observed concentrations. Endosulfan is still in use as an agricultural insecticide (Kamrin 1997). It is of special concern because it has been implicated in more fish kills nationwide (1980-1989) (Pait et al. 1992).

Frithsen *et al.* (1995) estimated that agricultural runoff contributes approximately 95% of the 480 kg year⁻¹ of endosulfan reaching the bay. Urban runoff accounted for the remainder—although estimates of atmospheric deposition were not made.

PCBs were detected in almost 18% of the samples collected; this is markedly lower than the 55% reported statewide by Seal et al (1994). PCBs were most frequently detected in the Palm and Lower Hillsborough rivers and were generally <MDL in other bay segments and tributaries. Although Maruya et al. (1997) did not find any significant association between percent silt+clay and PCBs in Gulf of Mexico sediments, within Tampa Bay there was a statistically significant (p<0.001), positive correlation. However, this association explained only 16% of the variance. Pierard et al. (1996) showed that PCB congeners with four or less chlorine atoms preferentially bound to finer sediments and the more chlorinated congeners

bound preferentially to coarser substrata and vegetative detritus. Since the Tampa Bay samples are analyzed as Aroclors (which are mixtures of congeners) rather than congeners, we do not know how the distribution of PCBs is affected by sediment characteristics.

PCB concentrations differed significantly by habitat, bay segment, and year. Mean concentrations were highest in mesohaline waters with sediments of 25% to 75% silt+clay and tidal freshwaters with a silt+clay content of 5% to 25%. These sites generally occurred in the Palm (especially 1998) and Lower Hillsborough rivers, and to a lesser extent in Hillsborough Bay proper. Although atmospheric deposition was the only source of PCBs evaluated for Tampa Bay by Frithsen *et al.*(1995), stormwater runoff (Kennish *et al.* 1992) or leaching from an abandoned landfill on the north shore of the Palm River (HDR Engineering 1994) are a more likely source given the locations of the highest concentrations. HDR Engineering (1994) alluded to data showing high PCB concentrations in Palm River sediments, but did not present the data or cite the actual source of these data.

Three Palm River sites had PCB concentrations between 617 to 1073 ppb and two Lower Hillsborough River sites have concentrations >400 ppb. These values are higher than the highest concentrations reported from several northern Gulf of Mexico estuaries (maximum 288 ppb in Bayou Chico; Lewis et al. 2001) and the St. Johns River (Durell et al. 1998), but are comparable to levels found in the N.Y. Harbor area (1973 ppb; Long et al. 1995c). However, these site comparisons could be affected by different methods of summing PCBs. Frignani et al. (2001) noted that when total PCBs are expressed as Aroclors, concentrations are approximately an order of magnitude higher than when the sum is based upon congeners. Data from this study are sums of Aroclors; data from the northern Gulf estuaries, N.Y. Harbor, and St. Johns River are the sums of congeners.

V. CONCLUSIONS

Sediment contaminant monitoring in Tampa Bay for PAHs, organochlorine pesticides, and PCBs commenced in 1993, was excluded from sediment analyses in 1994, and has been ongoing since 1995. Additional sampling began in four tributaries to the bay (Lower Hillsborough River, Palm River, Alafia River, and Little Manatee River) in 1995 and is ongoing.

PAH contamination is almost totally confined to the Lower Hillsborough River, Palm River, and portions of upper Hillsborough Bay. The habitat type most affected were low salinity waters (<5 ppt) with sediments of >5% silt+clay. Concentrations reported for the Lower Hillsborough River are generally high enough to have a high likelihood of being toxic to aquatic life. The highest PAH concentrations were found proximate to major roadways (e.g., I-275). PAHs were rarely detected in higher salinity waters with sediments of lower silt+clay content. Isomer ratios suggest that stormwater runoff is a major contributor of PAHs to bay sediments, although incinerators and coal-burning power plants are also likely contributors.

The occurrence of organochlorine pesticides, especially chlordane and DDT, were also generally confined to urban areas (e.g., Lower Hillsborough River, a Culbreath Bayou canal in Old Tampa Bay). Habitats most affected were low salinity (<5 ppt) waters with sediments of >5% silt+clay. Organochlorine pesticides in these locales are generally at concentrations with a moderate to high probability of being toxic to aquatic life. The majority of Tampa Bay appears unimpacted by organochlorine pesticides. Sources to the bay primarily appear to be urban stormwater runoff since data on these pesticides as well as their metabolites are consistent with a residential rather than an agricultural source.

PCBs have been detected found in extremely high concentrations in the Palm River, in moderate to high concentrations in the Lower Hillsborough River, and low to moderate concentrations in portions of upper Hillsborough Bay. PCBs were only rarely detected elsewhere in the bay. PCBs were associated with finer grained sediments.

In general, the urban tributaries and residential canals are the areas primarily impacted by organic contaminants; the industrial portions of Hillsborough Bay appear less impacted, although the number of samples actually collected in the East Bay, Seddon Channel, and Port Sutton areas are few and no samples have yet been collected in Ybor Channel. We recommend that the Ybor and Seddon Channel areas be considered for targeted sampling in the future and sampling in the tributaries be continued and even increased in the future in the event bay-wide sampling efforts are reduced.

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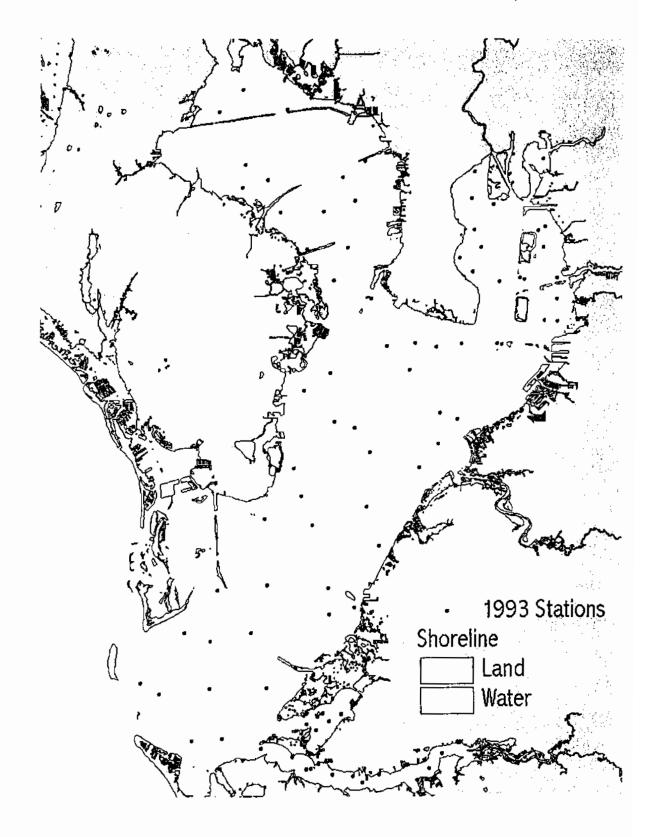
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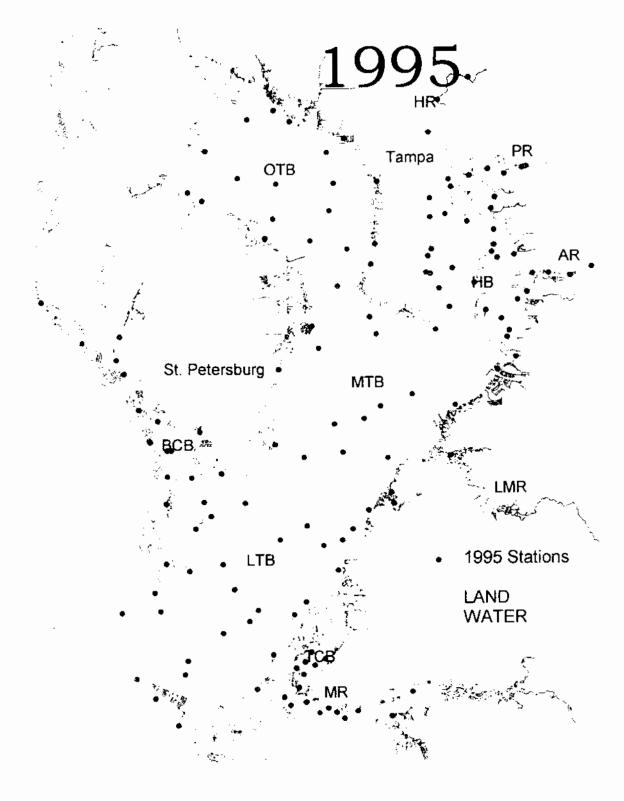
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VII. APPENDICES

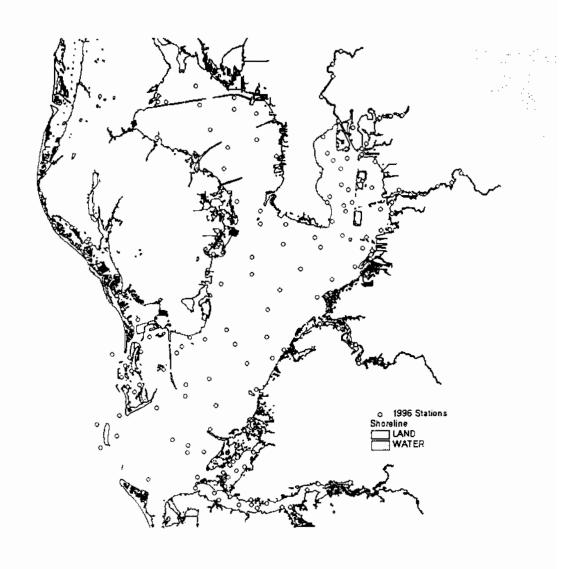
APPENDIX FIGURE A-1 LOCATION OF SAMPLING STATIONS IN TAMPA BAY, 1993



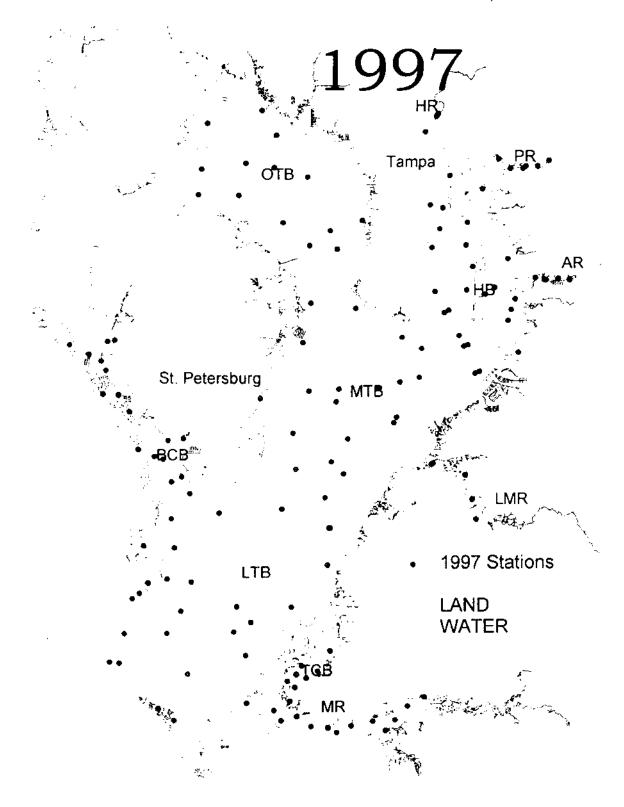
APPENDIX A-2 LOCATION OF SAMPLING STATIONS IN TAMPA BAY, 1995



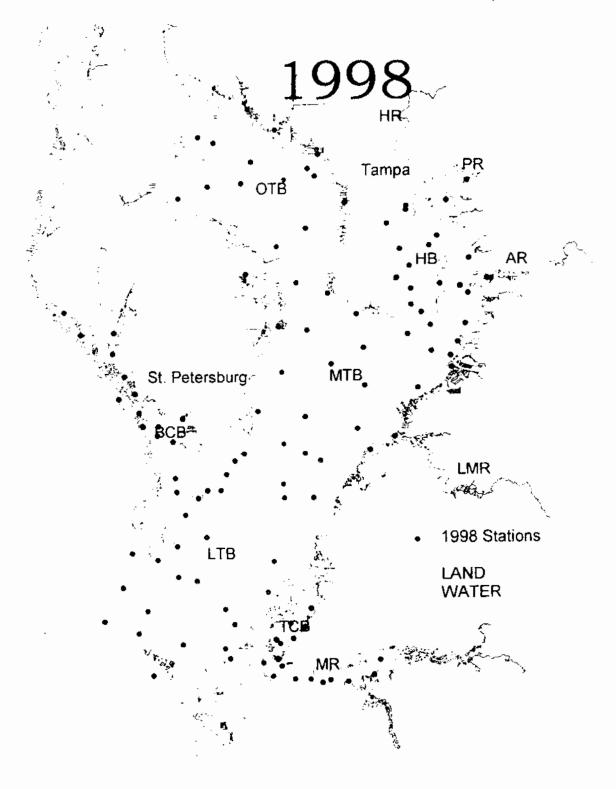
APPENDIX A-3 LOCATION OF SAMPLING STATIONS IN TAMPA BAY, 1996



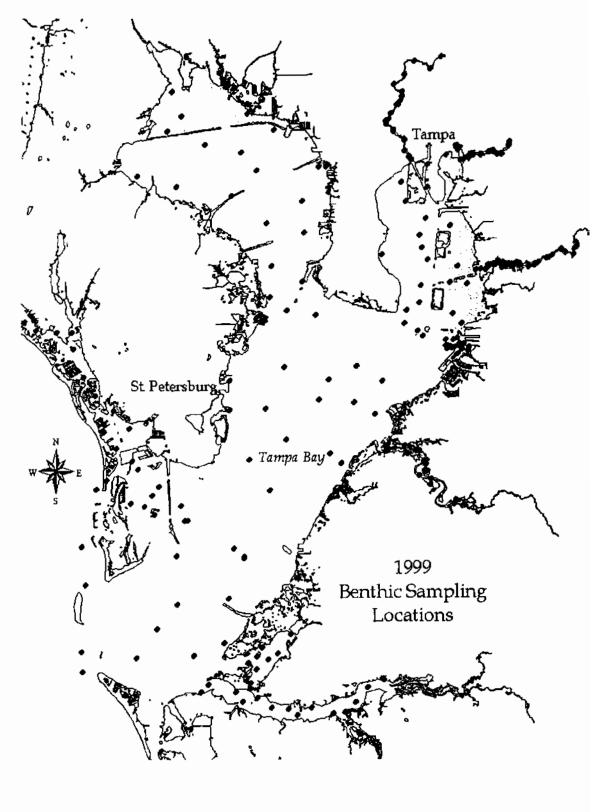
APPENDIX A-4 LOCATION OF SAMPLING STATIONS IN TAMPA BAY, 1997



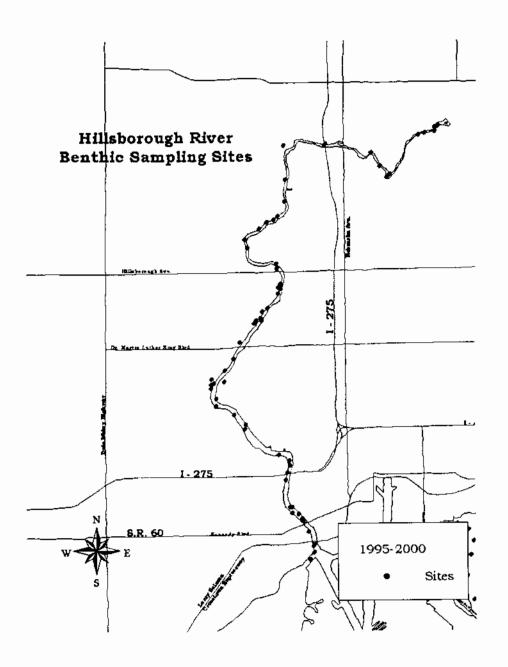
APPENDIX A-5 LOCATION OF SAMPLING STATIONS IN TAMPA BAY, 1998



APPENDIX A-6 LOCATION OF SAMPLING STATIONS IN TAMPA BAY, 1999



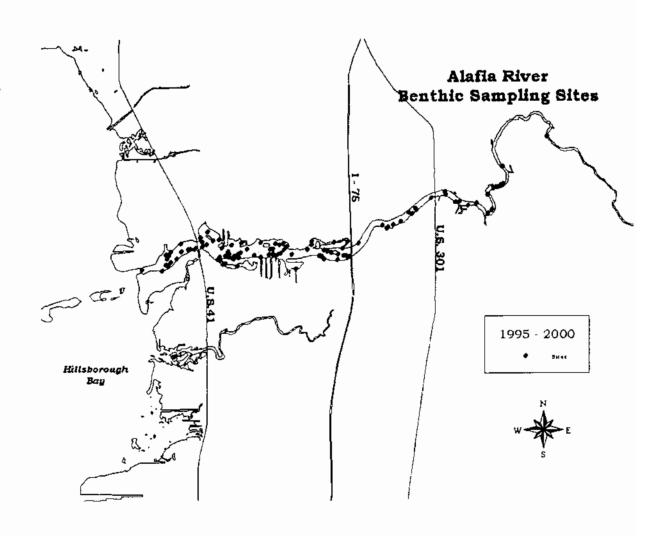
APPENDIX A-7 LOCATION OF SAMPLING STATIONS IN THE LOWER HILLSBOROUGH RIVER, 1995-1999



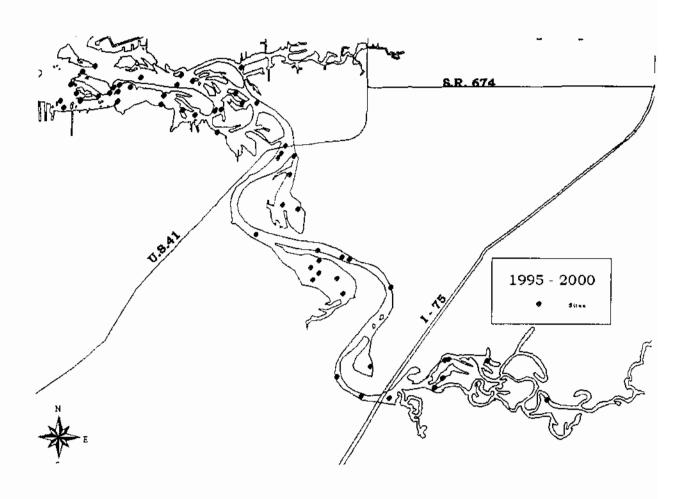
APPENDIX A-8 LOCATION OF SAMPLING STATIONS IN THE PALM RIVER, 1995-1999



APPENDIX A-9 LOCATION OF SAMPLING STATIONS IN THE ALAFIA RIVER, 1995-1999



APPENDIX A-10 LOCATION OF SAMPLING STATIONS IN THE LITTLE MANATEE RIVER 1996-1999



Summary of Method Detection Limits (MDLs) (ppb) of Organic Contaminants in Tampa Bay Sediments, 1993 & 1995-1999.

APPENDIX B

| CONTAMINANT | 1993 | 1995 | 1996 | 1996 (SAL*) | 1997 | 1998 | 1999 |
|----------------------------------|-------|------|-------|----------------|------|------|------|
| | | | (EPC) | (0) | | | |
| A. Organochlorine | | | | | |] | |
| Pesticides | į | ļ | | | | | |
| a-Hexachlorcyclohexane [AHCH] | - | 0.1 | 0.1 | - | 0.1 | 0.1 | 0.4 |
| Aldrin | 0.35 | 0.2 | 0.2 | 1.0 | 0.2 | 0.2 | 0.11 |
| b-Hexachlorcyclohexane [BHCH] | - | 0.2 | 0.2 | - | 0.2 | 0.1 | 0.16 |
| Chlordane (Total) | 0.14 | 5.0 | - | - | - | - | - |
| a-Chlordane | 1- | - | 0.1 | 1.0 | 0.1 | 0.1 | 0.04 |
| g-Chlordane | T- | - | 0.1 | - | 0.1 | 0.1 | 0.11 |
| d-Hexachlorcyclohexane [DHCH] | - | 0.3 | 0.3 | - | 0.3 | 0.2 | 0.03 |
| Dieldrin | 0.066 | 0.2 | 0.2 | 1.0 | 0.2 | 0.1 | 0.06 |
| DDT | 0.32 | 0.1 | 0.1 | 1.0 | 0.1 | 0.1 | 0.38 |
| DDD | 0.35 | 0.1 | 0.1 | 1.0 | 0.1 | 0.2 | 0.07 |
| DDE | 0.175 | 0.3 | 0.3 | 1.0 | 0.3 | 0.1 | 0.05 |
| Endosulfan Sulfate | - | 0.1 | 0.1 | 1.0 | 0.1 | 0.1 | 0.06 |
| Endosulfan I | 0.13 | 0.5 | 0.5 | - | 0.5 | 0.2 | 0.09 |
| Endosulfan II | 0.35 | <0.1 | <0.1 | - | <0.1 | 0.1 | 0.12 |
| Endrin | 0.26 | 0.1 | 0.1 | 1.0 | 0.1 | 0.1 | 0.11 |
| Endri-aldehyde | - | 0.1 | 0.1 | - | 0.1 | 0.1 | 0.15 |
| Endrin Ketone | - | 0.3 | 0.3 | - | 0.3 | 0.3 | 0.13 |
| Heptachlor | 0.09 | 0.8 | 0.8 | 1.0 | 0.8 | 0.2 | 0.13 |
| Heptachlor epoxide | - | 0.7 | 0.7 | 1.0 | 0.2 | 0.1 | 0.08 |
| g-Hexachlorcyclohexane [Lindane] | 0.35 | 0.2 | 0.2 | 1.0 | 0.2 | 1.0 | 0.08 |
| Methoxychlor | - | 0.2 | 0.2 | - | 0.2 | 0.1 | 0.05 |
| Mirex | - | 0.3 | 0.1 | 1.0 | 0.1 | 0.4 | 0.06 |
| Toxaphene | 0.35 | 0.4 | 0.4 | 20.0 | - | - | - |

APPENDIX B (CONTINUED)

Summary of Method Detection Limits (MDLs) (ppb) of Organic Contaminants in Tampa Bay Sediments, 1993 & 1995-1999.

| CONTAMINANT | .1993 | 1995 | 1996 | 1997 | 1998 | 1999 |
|------------------------------|--------|------------|------|------|------|------|
| B. Polycyclic Aromatic | | | | | | |
| Hydrocarbons | ; | ! | | | | |
| Acenapthene | 0.0102 | 5.5 | 5.5 | 5.5 | 6.4 | 18.0 |
| Acenapthylene | 0.0048 | 5.5 | 5.5 | 5.5 | 8.4 | 18.0 |
| Anthracene | 0.0038 | 5.0 | 5.0 | 5.0 | 3.1 | 10.0 |
| Benzo(a)anthracene | 0.0044 | 5.3 | 5.3 | 5.3 | 6.9 | 7.0 |
| Вепго(а)ругепе | 0.0088 | 6.0 | 6.0 | 6.0 | 5.8 | 10.0 |
| Benzo(b)fluoranthene | <.01 | 7.5 | 7.5 | 7.5 | 3.6 | 6.0 |
| Benzo(g)fluoranthene | <.01 | 6.0 | 6.0 | T - | - | - |
| Benzo(k)fluoranthene | <.01 | 4.8 | 4.8 | 4.8 | 10.7 | 8.0 |
| Benzo(g,h,i)perylene | i - | 6.0 | 6.0 | 6.0 | 8.7 | 6.0 |
| Chrysene | <.01 | 5.5 | 5.5 | 5.5 | 6.8 | 8.0 |
| Dibenz(a,h)anthracene | 0.0074 | 5.5 | 5.5 | 5.5 | 5.9 | 5.0 |
| Fluoranthene | <.01 | 6.5 | 6.5 | - | 6.3 | 9.0 |
| Fluorene | 0.005 | 5.8 | 5.8 | 5.8 | 7.0 | 15.0 |
| Indenopyrene | < 01 | 4.3 | 4.3 | 4.3 | 4.6 | 2.0 |
| 2-Methylnapthalene | 0.0099 | ː - | - | - | | - |
| Napthalene | 0.0099 | 4.0 | 4.0 | 4.0 | 9.2 | 7.0 |
| Perylene | 0.0038 | | T | ; - | - | - |
| Phenanthrene | 0.35 | 6.0 | 6.0 | 6.0 | 4.8 | 10.0 |
| Pyrene | <.01 | 5.0 | 5.0 | 5.0 | 6.7 | 9.0 |
| | | | | | | |
| C. Polychlorinated Biphenyls | | : | | | | |
| PCBs (congeners) | 0.35 | 0.35 | - | - | - |] - |
| PCBs (Aroclors) | - | · - | 2.5 | 0.6 | 0.6 | 0.6 |

- Not Analyzed
- * Southern Analytical Laboratory, Oldsmar, FL