SEDIMENT CONTAMINATION, BY HABITAT, IN THE TAMPA BAY ESTUARINE SYSTEM (1993–1999): PAHs, PESTICIDES AND PCBs

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Abstract. More than 760 Tampa Bay (Florida, U.S.A.) sediment samples have been analyzed for organic contaminants (PAHs, organochlorine pesticides, and PCBs) since 1993. Data were analyzed to assess status by habitat (defined by overlapping salinity zones and sediment type). The habitats most degraded by PAHs and pesticides were generally located in lower salinity, fine-grained sediment habitats, which are typically confined to the Hillsborough River. PCB contamination was more common in mesohaline waters of the Palm and Hillsborough rivers. Higher salinity portions of the bay, where medium to coarse sand-sized sediments predominate, showed little evidence of contamination by PAHs, PCBs and pesticides other than lindane.

Keywords: PAHs, PCBs, pesticides, sediment quality, Tampa Bay

1. Introduction

Tampa Bay is one of the largest estuaries in Florida, encompassing more than 1000 km^2 (Clark and MacAuley, 1989) and with a watershed of approximately 596 000 km^2 (Zarbock, 1991). The Port of Tampa is the largest industrial port in Florida, and Port Manatee, on southeastern Tampa Bay, ranks fourth (Tampa Bay Regional Planning Council, 1986; Tiffany and Wilkinson, 1989). Tampa Bay and its tributaries provide spawning and nursery areas for fishes of commercial and sport value, as well as habitat for forage species (Springer and Woodburn, 1960; Peebles *et al*., 1991).

Tampa Bay's sediments have been the object of several short-term, spatially intensive investigations (Doyle *et al*., 1985, 1989; Brooks and Doyle, 1991, 1992; Long *et al*., 1991, 1994, 1995; Daskalaskis and O'Connor, 1994; Seal *et al*., 1994; Carr *et al*., 1996). As part of the management plan for Tampa Bay (Tampa Bay National Estuary Program, 1996), an annual bay-wide monitoring program for sediment contaminants and benthic macroinvertebrates commenced in 1993.

Organic sediment contaminants, including polycyclic aromatic hydrocarbon (PAHs), organochlorine pesticides (OCLs), and polychlorinated biphenyls (PCBs) are a 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). They may also extert sublethal effects on aquatic organisms (e.g., altered reproductive

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success; Stahlschmidt-Allner *et al*., 1997) that could alter the composition and structure of biotic communities (Carman *et al*., 1995; Murdoch *et al*., 1997).

The Tampa Bay Estuary Program (McConnell *et al*., 1996) has reviewed potential risks associated with contaminated sediments in Tampa Bay. Increased ecological risk was associated with the OCLs DDT, heptachlor, heptachlor epoxide, and lindane, high molecular weight PAHs (HPAHs), the individual PAHs fluoranthene and benzo(a)pyrene, and PCBs (McConnell *et al*., 1996). There was also potential for human health risk via consumption of fish from areas of Tampa Bay contaminated by chlordane and heptachlor. Additional 'contaminants of concern' for Tampa Bay include chlordane, dieldrin, endosulfan, and mirex (Frithsen *et al*., 1995).

Sediment contaminants in Tampa Bay are, in fact, associated with adverse effects on the resident biota. McCain *et al*. (1996) reported that at least four species of fish (*Arius felis*, *Sciaenops ocellatus*, *Fundulus grandis*, and *F. majalis*) collected in one segment of Tampa Bay had elevated tissue concentrations of chlordane, DDT, PAHs, and PCBs sufficient to contribute to morphological and histochemical changes. More recently, Fisher *et al*. (2000) showed not only that oysters (*Crassostrea virginica*) accumulated PAHs, PCBs, and OCLs, but that in many cases, the elevated concentrations were associated with increased physiological or behavioral defense mechanisms.

This article summarizes the distribution of organic contaminants within Tampa Bay, by habitat (defined by salinity zone and sediment type), for 1993 and 1995–1999.

2. Methods

2.1. Study design

A probabilistic design, using seven strata, was adopted for Tampa Bay's sediment monitoring program (Coastal Environmental, Inc., 1994). The strata were the seven recognized bay segments (cf. Lewis and Whitman, 1985): Old Tampa Bay, Hillsborough Bay, Middle Tampa Bay, Lower Tampa Bay, Boca Ceiga Bay, Terra Ceia Bay, and the Manatee River (Figure 1). Within each stratum, sample sites were selected at random and with known probability. Sites are re-randomized annually (except in the Manatee River and Terra Ceia Bay). This design yields approximate unbiased estimates of the measured variables (Coastal Environmental, Inc., 1994).

All samples were collected during late August through mid-October. Starting in 1995, four tributaries to Tampa Bay (Hillsborough River, Palm River, Alafia River, and Little Manatee River), which had a low selection probability with the original design, were added as separate subsegments. More than 760 samples have been analyzed for organic contaminants since 1993. Figure 1 shows the sample locations for 1993 and 1995–1999 (organic contaminants were not analyzed during 1994).

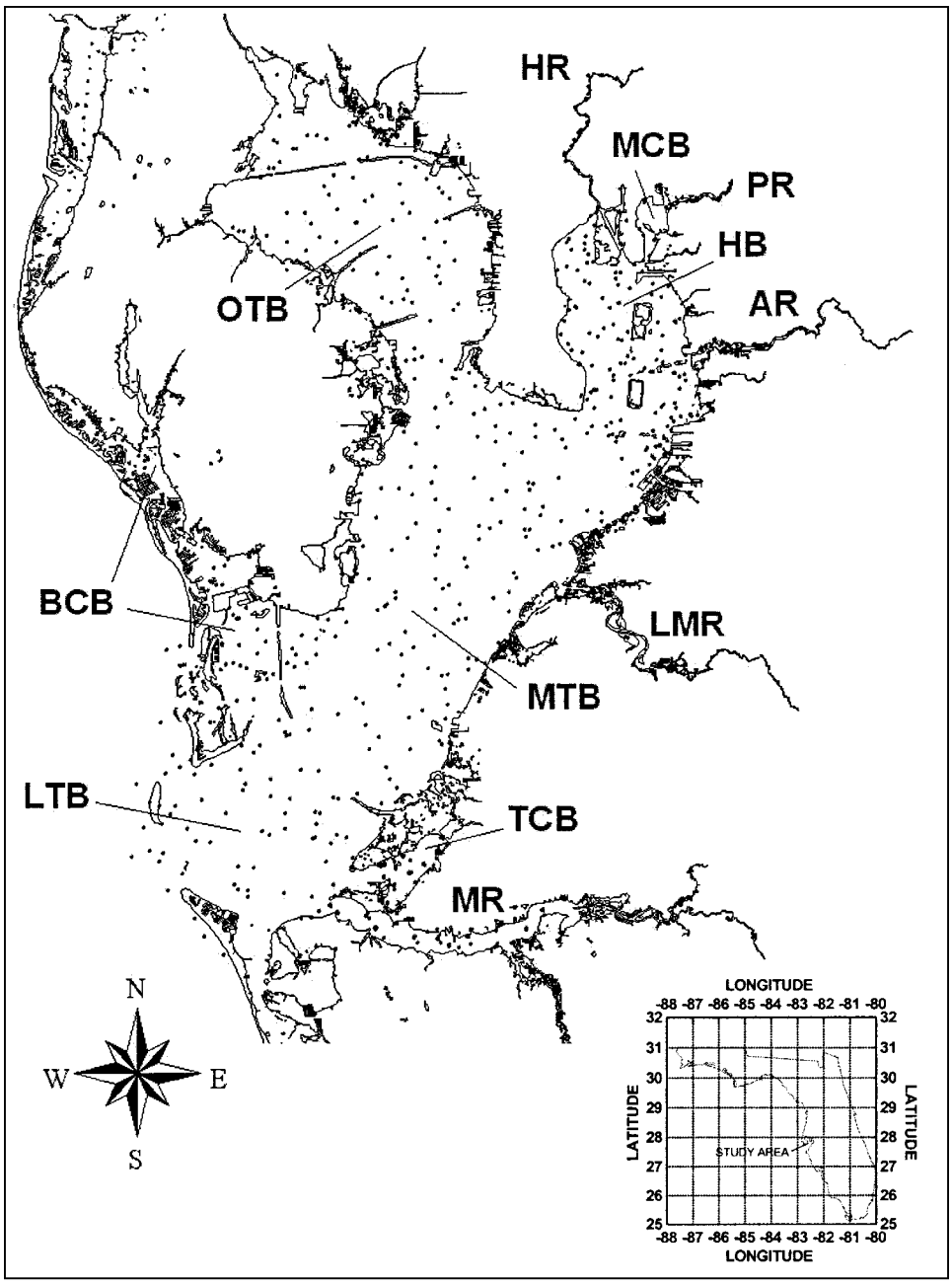

Figure 1. Location of sediment sampling stations in Tampa Bay, FL, 1993 and 1995–1999. Primary bay segments (strata) are Old Tampa Bay (OTB), Hillsborough Bay (HB), Middle Tampa Bay (MTB), Lower Tampa Bay (LTB), Boca Ciega Bay (BCB), Terra Ceia Bay (TCB), and Manatee River (MR). The Hillsborough River (HR), Palm River (PR), McKay Bay (MCB), Alafia River (AR), and Little Manatee River (LMR) are also shown.

2.2. FIELD METHODS

Sediments were collected with a 0.04 m^2 stainless steel Young grab sampler. During 1993 all implements were rinsed with ambient bay water; since 1995 they have been scrubbed with Liquinox, rinsed in ambient bay water, and rinsed with pesticide grade isopropanol.

The upper two centimeters of sediment were removed (using either a stainless steel or Teflon trowel) and spooned into a stainless steel beaker. Sediments from several grabs were composited to ensure there was a sufficient amount of sediment for chemical analyses. Sediments were spooned into chemically cleaned 500-mL glass jars (Teflon lined caps). Field duplicates were collected at approximately 10% of the sample sites for quality assurance.

Sediment samples for determination of the percentage of silt + clay (%SC) were collected with a syringe from a separate grab sample collected for characterization of the benthic community.

2.3. LABORATORY METHODS

During 1993, the Skidaway Institute of Oceanography (Savannah, GA), courtesy of U.S. EPA-Gulf Breeze, analyzed the samples using methods described in U.S. EPA (1993). Quality assuarance/quality control (QA/QC) procedures and criteria were after Heitmuller and Valente (1993).

Beginning in 1995, our agency's laboratory analyzed sediment samples using Soxhlet extraction and EPA Method 8080 for OCLs and PCBs and Method 8270 for PAHs. The samples were air-dried for 3 days, spiked with surrogate compounds and then extracted in a soxhlet apparatus for 16 hr with 100% methylene chloride. Extracts were passed through a column of sodium sulfate and concentrated, under nitrogen, to 1.0 mL using a Zymark TurboVap II concentrator. The concentrates were mixed with activated copper to remove sulfur. 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 (30 m $\times$ 0.25 mm $\times$ 0.25 μm film thickness) was used for the analysis.

Samples were analyzed for OCLs 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 (30 m $\times$ 0.53 mm $\times$ 0.5 μm film thickness) was used for primary analysis and a Supelco SPB-50 column (30 m $\times$ 0.32 mm $\times$ 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 OCLs by a commercial laboratory (Southern Analytical Laboratory, Oldsmar, FL) using EPA Method 8080.

TABLE I

Characterization of Tampa Bay sediments: Predicted ranges of % silt + clay for Wentworth size classes (ϕ)

Mean ϕ	% Silt + clay	Sediment type
0	<1.70	Coarse sand
1	≥1.70 < 4.51	Medium sand
2	≥4.51 < 11.35	Fine sand
3	≥11.35 < 25.95	Very fine sand
>4	≥25.95	mud

TABLE II

Number of samples within habitats: By salinity zone and sediment type. Tampa Bay 1993 and 1995–1999

	Limnetic (<4 ppt)	Oligohaline (≥2 < 14 ppt)	Mesohaline (≥11 < 18 ppt)	Polyhaline (≥16 < 27 ppt)	Euhaline (≥24 ppt)
Coarse sand (<1.70% SC)	8[a]	5[a]	7[a]	39	49
Medium sand (≥1.70 < 4.51% SC)	12	16	23	136	192
Fine sand (≥4.51 < 11.35% SC)	12	23	26	114	162
Very fine sand (≥11.35 < 25.95% SC)	8[a]	5[a]	10	49	50
Mud (≥25.95% SC)	8[a]	5[a]	13	48	33

[a] Excluded from data analyses.

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, pers. commun., 19 March 1997).

The method for determining %SC was a modification (Versar, Inc., 1993) of Plumb (1981). Between 20 g wet weight (mud) and 50 g (sand) of sediment was treated with sodium hexametaphosphate to break aggregates, then wet sieved

(0.62 mm) and dried. Both sand (≥0.62 mm) and silt-clay (<0.62 mm) fractions were weighed. %SC = (silt-clay weight/sand weight + silt-clay weight) × 100.

2.4. DATA ANALYSES

Contaminant concentrations <MDL (Appendix A) were treated as 0.5*MDL in the data analyses. Statistical analyses (e.g., regression, correlation) were carried out using SYSTAT 10 (SPSS, Inc., 2000).

Data were post-stratified by habitat. Habitats were defined by salinity zone (Bulger *et al*., 1990) and sediment type. Bulgar *et al*. (1990) identified five overlapping salinity zones based upon the distributions of aquatic fishes and invertebrates: euhaline (≥24 ppt), polyhaline (≥16 < 27 ppt), mesohaline (≥11 < 18 ppt), oligohaline (≥2 < 14 ppt), and limnetic (<4 ppt).

Although only %SC data were collected for this program, Long *et al*. (1994) analyzed their Tampa Bay sediment samples for both %SC and mean grain size (ϕ). These data were used to develop a relationship between %SC and mean ϕ. Table Curve 2D ver. 5.0 (AISN Software, 2000): %SC = 1/(0.0097 + 1.575*e^{ϕ}) adjusted $r^2 = 0.947$).

Ranges of %SC corresponding to five Wentworth size classes (cf. Percival and Lindsay, 1997) were then estimated (Table I). The eighteen habitats (of 25 possible) which had at least ten samples were included in the data analyses (Table II).

The association between low (LPAH) and high (HPAH) molecular weight PAHs, four OCLs, total PCBs and %SC were also examined using Table Curve 2D Ver. 5.0 (AISN Software, 2000). The selected curves and equations were derived from 'simple' equations (exponential, power, linear) and not from more complex (higher order polynomials) equations.

'Clean' and 'degraded' sediments were designated by comparing measured contaminant levels with the Threshold Effects Level (TEL) and Predicted Effects Level (PEL) developed for Florida estuarine sediments (MacDonald Environmental Sciences, Ltd., 1994; MacDonald *et al*., 1996) (Appendix B). The TEL is the contaminant concentration below which adverse biological effects are rare or never observed. The PEL is the contaminant concentration above which adverse biological effects are likely.

PEL quotients (measured concentration/PEL) were calculated for individual contaminants as well as for classes of contaminants (e.g., total PAHs, total PCBs). Sediments were designated as 'clean' if a contaminant concentration was less than the TEL or if a PEL quotient was ≤0.1. Sediments were designated as 'degraded' if a contaminant concentration exceeded the PEL or if a PEL quotient was >1.0.

Source identification of PAHs from field samples has generally relied upon interpretation of one or more ratios of selected PAHs (Benlachen *et al*., 1997; Dickhut *et al*., 2000; Soclo *et al*., 2000; Van Metre *et al*., 2000; Walker and Dickhut, 2001). PAHs are considered to be derived from pyrogenic (incomplete combustion) rather than petrogenic (e.g., oil spills) sources when LPAH:HPAH ratios

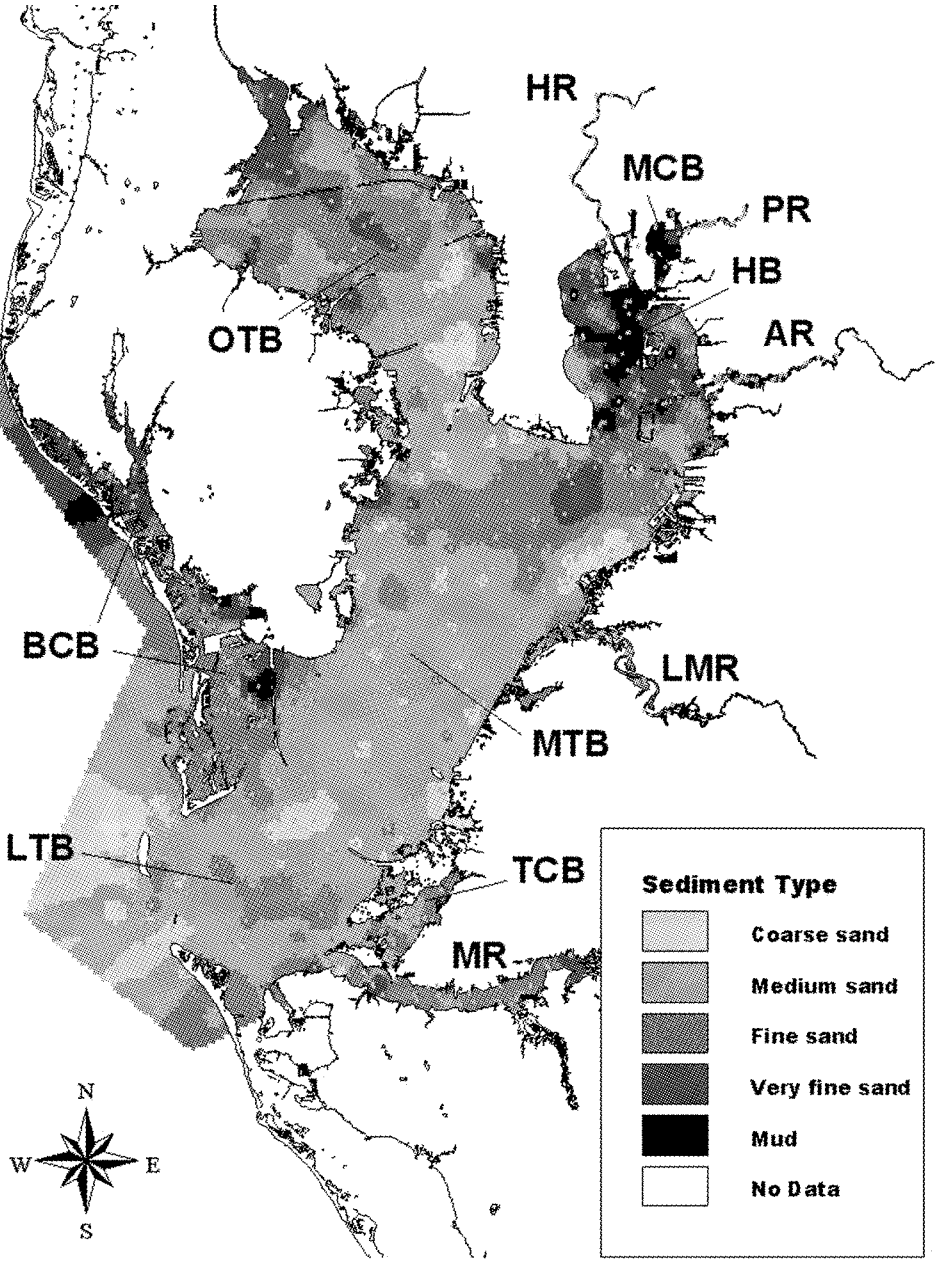

Figure 2. Distribution of sediment types in Tampa Bay, FL, 1993 and 1995–1999.

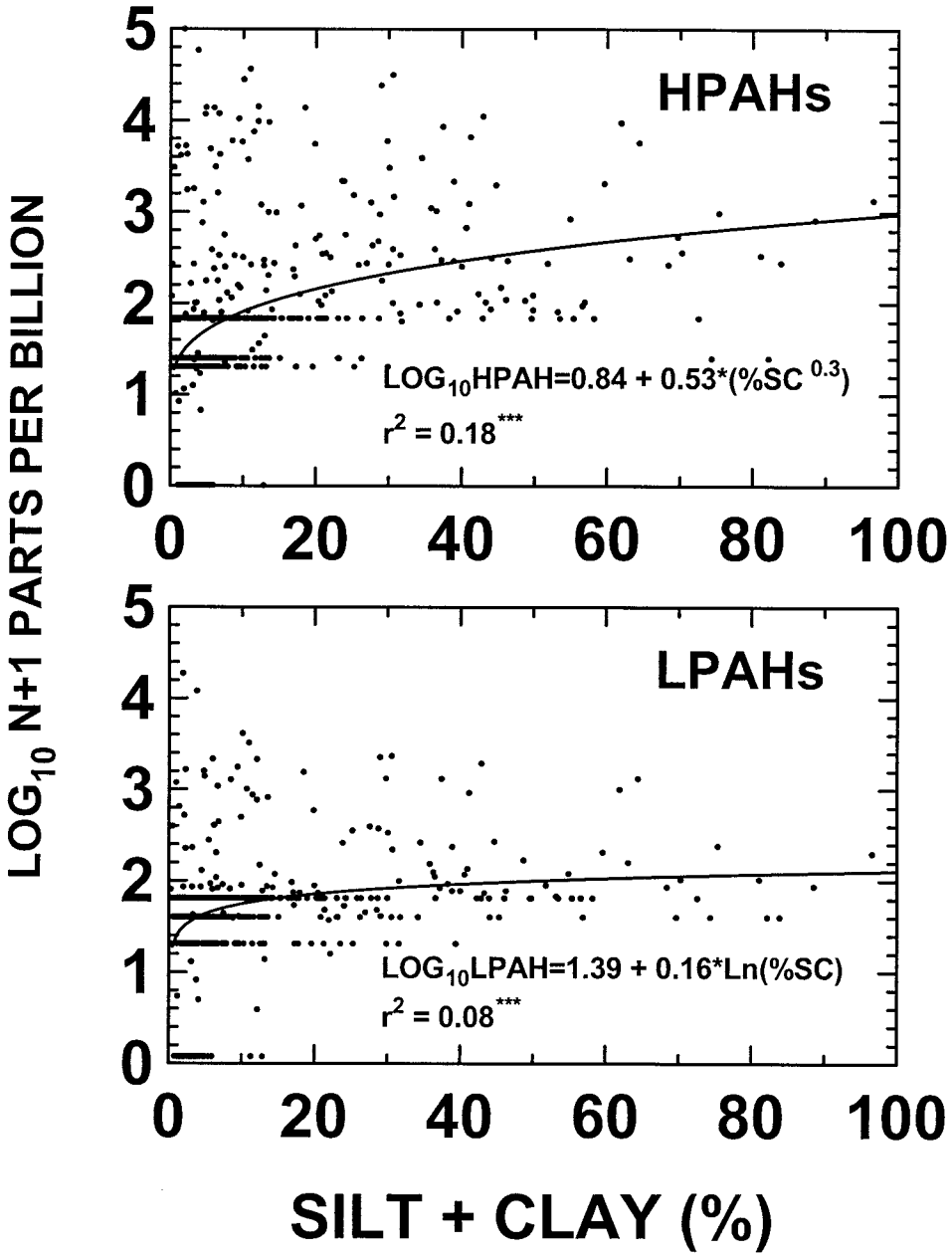

Figure 3. Association between % silt + clay and both high (HPAHs) and low (LPAHs) molecular polycyclic aromatic hydrocarbons in Tampa Bay, FL, 1993 and 1995–1999.

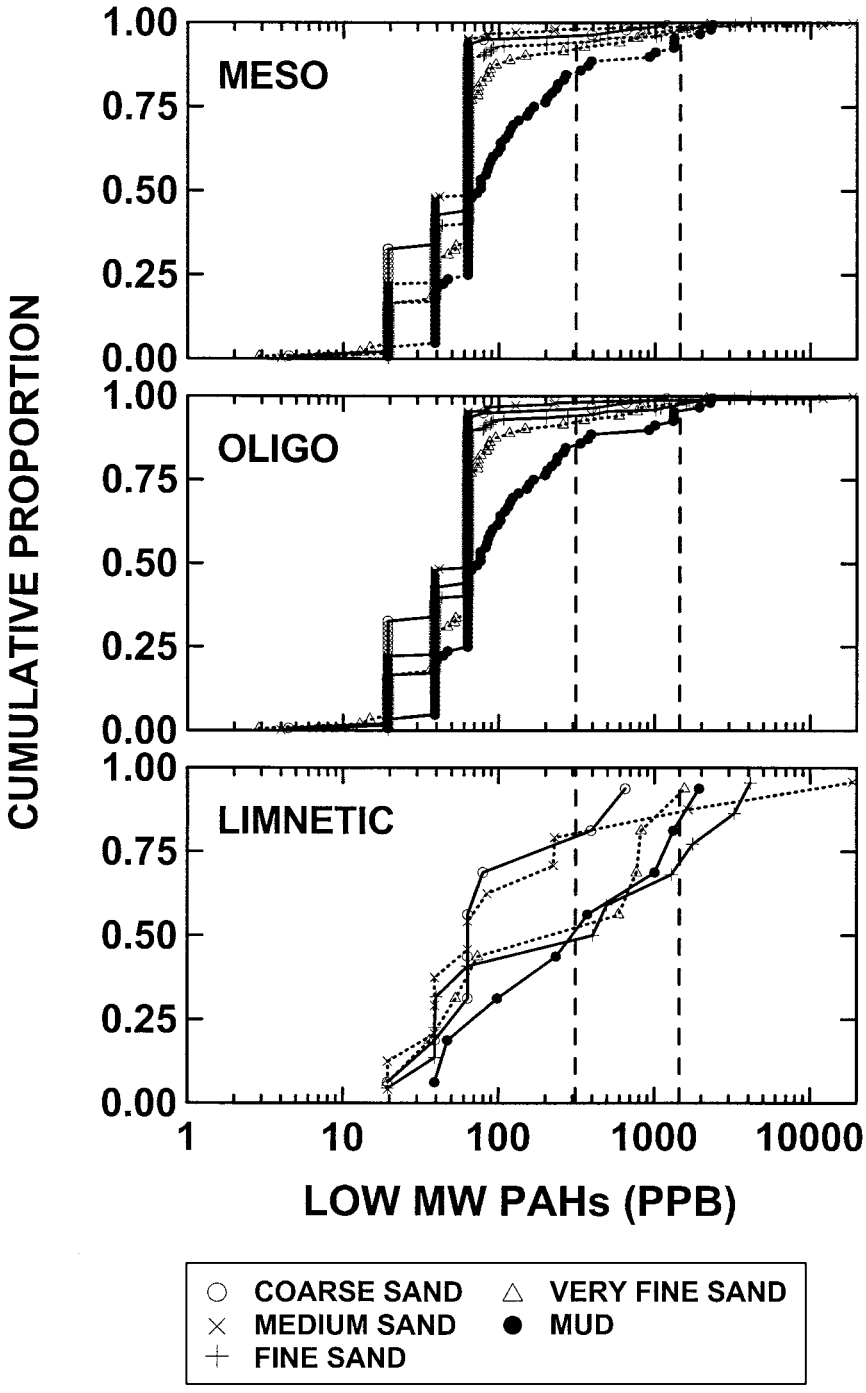

Figure 4. Cumulative distribution function plots of low molecular weight PAHs in Tampa Bay, FL (1993 and 1995–1999): By salinity zone and sediment type. Vertical lines demarcate the TEL (312 ppb) and PEL (1442 ppb).

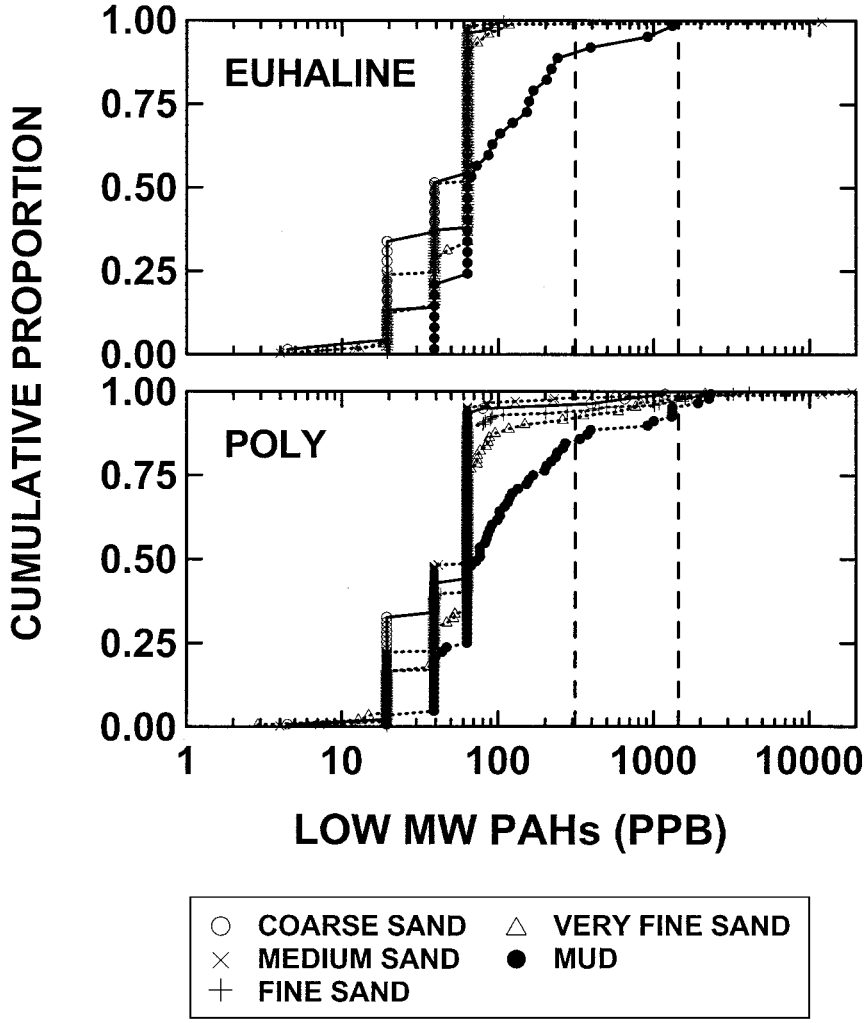

Figure 4. (continued)

are low (Soclo *et al.*, 2000; Stout *et al.*, 2001), phenathrene:anthracene ratios are <10, and fluoranthene:pyrene ratios are >0.6 (Benlachen *et al.*, 1997; Stout *et al.*, 2001). Automotive emissions may be characterized by indenopyrene: benzo(g,h,i)-perylene ratios close to 0.33 (Dickhut *et al.*, 2000; Walker and Dickhut, 2001), benzo(a)anthracene:chrysene ratios near 0.53 (0.25–0.75; Dickhut *et al.*, 2000; Walker and Dickhut, 2001) and benzo(b)fluoranthene:benzo(k)fluoranthene ratios >1 (Dickhut *et al.*, 2000). Emissions from coal-fired electric generating stations, which do operate on Tampa Bay, may be identified by indenopyrene: benzo(g,h,i)-perylene ratios near 1.09 (0.75–1.3; Dickhut *et al.*, 2000; Walker and Dickhut, 2001) and benzo(b)fluoranthene:benzo(k)fluoranthene ratios >3.5 (Dickhut *et al.*, 2000).

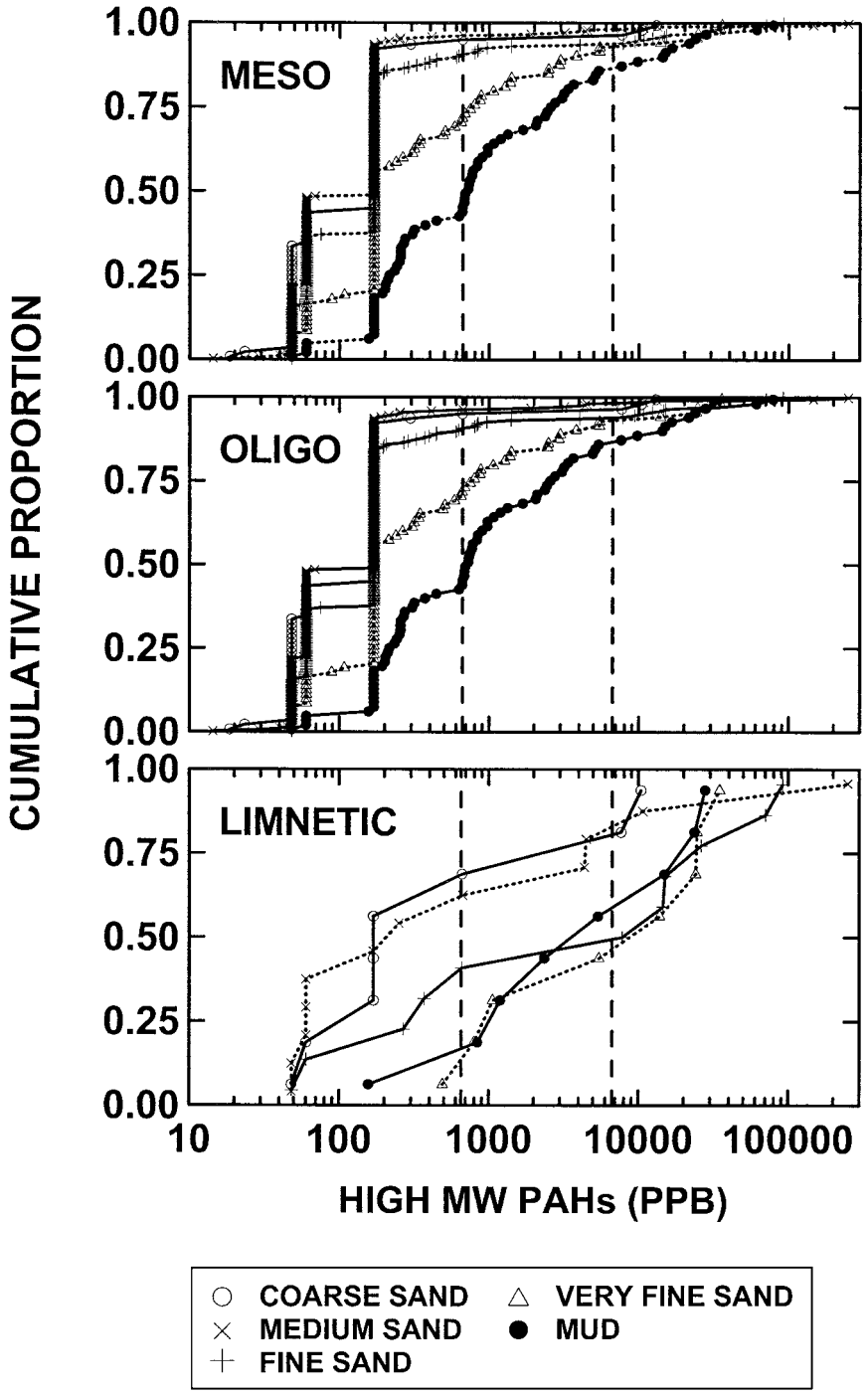

Figure 5. Cumulative distribution function plots of high molecular weight PAHs in Tampa Bay, FL (1993 and 1995–1999): By salinity zone and sediment type. Vertical lines demarcate the TEL (655 ppb) and PEL (6676 ppb).

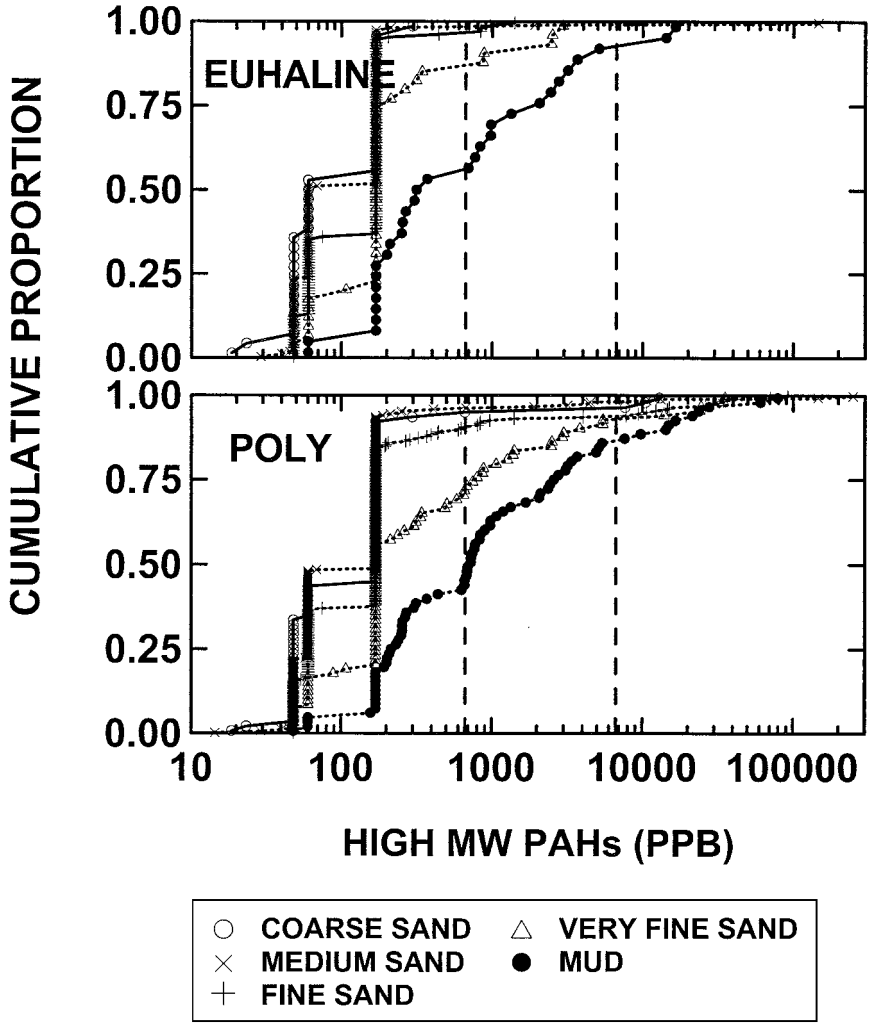

Figure 5. (continued)

These ratios were calculated from samples in which the concentration of at least one isomer in the pair was >MDL.

3. Results

3.1. HABITATS

Euhaline salinities and medium to fine sand-size sediments predominated in Tampa Bay during the late summer through fall sampling periods (Table II and Figure 2). Euhaline salinities and medium to fine sand-size sediments are generally located in

lower Old Tampa Bay and Middle Tampa Bay gulfward to upper Lower Tampa Bay. Coarse sand-size sediments were generally located in Lower and Middle Tampa Bays (Figure 2). Lower salinity sites were relatively rare and tended to be restricted to three of the tributaries; mud habitats (>25.95% SC) were most common in polyhaline waters located in Hillsborough Bay.

3.2. Polycyclic aromatic hydrocarbons

PAHs were detected (>MDL) in 24.1% of the samples (Table III). Concentrations of both LPAHs ($r^2_{1,703} = 0.08$) and HPAHs ($r^2_{1,703} = 0.18$) were significantly associated ($p < 0.001$) with the %SC (Figure 3). LPAHs occurred at concentrations up to 18,800 ppb (Hillsborough River). Between 16 and 27% of samples collected from fine and medium sand sized sediments in limnetic waters exceeded the PEL (Figure 4). HPAHs were detected in concentrations of up to 99 800 ppb (Hillsborough River). More than half of the samples collected from fine sand sized sediments in limnetic waters exceeded the PEL and >14% of the samples collected from mud-sized sediments in oligohaline, mesohaline, and polyhaline waters exceeded the PEL (Figure 5). The 17 highest PEL quotient sites, including 13 with a PEL quotient >1, were located in the Hillsborough River.

Isomer ratios (Table IV) suggest that PAHs were derived from pyrolytic sources, notably automotive emissions. LPAH:HPAH ratios were generally <0.1; phenanthrene:anthracene ratios <10 occurred in 77% of the samples and 83% had fluoranthene: pyrene ratios >0.6 < 1.5; benzo(a)anthracene:chrysene ratios were generally <1; and ratios of benzo(b)fluoranthene:benzo(k)fluoranthene were generally >1 < 3 (Table IV). Indenopyrene: benzo(g,h,i)perylene ratios, however, were generally >0.8.

3.3. Organochlorine pesticides

Twenty-one OCLs have been identified from Tampa Bay sediments (Table V). The most frequently detected were DDD, DDE, and total chlordane. The least frequently detected were α-hexachlorocyclohexane (α HCH) and endosulfan I.

Chlordane concentrations were positively associated with %SC, although this explained only 3% of the variance (Figure 6). More than 40% of samples collected from limnetic fine sand-size sediments exceeded the PEL and >15% of samples collected from mud-sized sediments in oligohaline, mesohaline, and polyhaline waters exceeded the PEL. In euhaline habitats <4.3% of samples exceeded the PEL (Figure 7).

DDT and its metabolites were detected in up to 19% of the samples (Table V). Total DDT concentrations were positively correlated with %SC (Figure 6). More than 15% of samples collected in oligohaline, mesohaline, and polyhaline waters with mud-sized sediments exceeded the TEL and >25% of samples in limnetic waters with fine and medium sand-size sediments exceeded the TEL (Figure 8).

TABLE III

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

PAH	N	% Occurrences >MDL[c]	Mean (ppb)	Median (ppb)	Maximum (ppb)
LPAHs					
Acenapthene[a]	729	4.1	11.8	11.0	533.0
Acenapthylene[a]	729	2.9	10.0	11.0	414.0
Anthracene[a]	728	7.3	19.7	10.0	2210.0
Biphenyls	57	1.8	0.009	0.003	0.4
Fluorene[a]	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[a]	57	3.5	0.1	0.005	5.5
2,6-Dimethylnaphthalene	57	3.5	0.1	0.003	4.5
2,3,5-Trimethylnaphthalene	57	1.8	0.01	0.002	0.4
Phenanthrene[a]	729	14.4	86.6	12.0	15324.0
1-Methylphenanthrene	57	10.5	1.3	0.002	29.8
Total LPAHs	730	15.7	150.9	63.5	18802.0
HPAHs					
Benzo(a)anthracene[b]	729	16.6	93.2	10.5	11221.0
Benzo(a)pyrene[b]	730	16.4	118.7	12.0	13636.0
Benzo(e)pyrene	57	7.0	1.2	0.003	33.0
Chrysene[b]	729	17.3	129.2	11.0	16946.0
Dibenz(a,h)anthracene[b]	729	11.2	45.9	11.0	3919.0
Fluoranthene[b]	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[b]	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
Total HPAHs	730	22.2	806.6	68.0	99818.0
Total PAHs	730	24.1	1311.2	167.5	157269.0

[a] Included in computation of total low molecular weight PAHs.
[b] Included in computation for total high molecular weight PAHs.
[c] MDL = Method Detection Limit.

TABLE IV

Mean (range) PAH isomer ratios: By habitat (n ≥ 5 for at least one variable with concentration >MDL). Tampa Bay, 1993 and 1995–1999

Habitat	LPAH: HPAH	PHEN: ANTH	FLUO: PYRE	BENZA: CHRYS	BBF: BBK	INDENO: BGHIP
Euhaline – Medium sand	–[a]	–	0.8 (0.4–1.3)	–	–	–
Euhaline – Fine sand	–	8.5 (3.1–13.5)	0.9 0.5–1.3)	0.7 (0.4–1.0)	2.9 (1.1–6.8)	2.3 (0.8–7.0)
Euhaline – Very fine sand	0.04 (0.02–0.06)	–	0.8 (0.1–1.0)	0.7 (0.5–0.9)	2.4 (0.8–6.5)	1.4 (<0.1–6.3)
Euhaline – Mud	0.15 (0.03–0.63)	6.6 (2.7–15.3)	0.9 (0.1–1.3)	0.8 (0.5–1.1)	3.0 (0.9–11.5)	1.4 (0.8–7.0)
Polyhaline – Medium sand	0.3 (<0.1–1.4)	–	0.8 (0.4–1.3)	–	–	–
Polyhaline – Fine sand	0.13 (<0.01–0.72)	8.6 (3.1–16.8)	0.9 (0.5–1.3)	0.7 (0.5–1.0)	2.9 (0.9–7.5)	1.4 (<0.1–7.0)
Polyhaline – Very fine sand	0.04 (0.02–0.06)	12.1 (<0.1–36.1)	0.9 (0.5–1.3)	0.8 (0.2–2.2)	1.9 (0.6–6.5)	1.5 (<0.1–7.0)
Polyhaline – Mud	0.10 (0.03–0.63)	7.3 (2.5–20.0)	0.8 (0.1–1.4)	0.8 (0.5–1.1)	2.9 (1.2–11.5)	1.2 (0.5–7.0)
Mesohaline – Fine sand	0.16 (0.02–0.72)	7.7 (2.8–16.8)	1.0 (0.6–1.2)	0.7 (0.5–0.8)	1.8 (1.1–3.7)	0.9 (0.8–1.1)
Mesohaline – Very fine sand	–	–	0.9 (0.6–1.3)	0.8 (0.6–1.0)	1.6 (1.4–1.9)	0.9 (0.8–1.0)
Mesohaline – Mud	0.05 (0.03–0.06)	7.4 (2.5–17.4)	0.8 (0.3–1.0)	0.7 (0.6–0.9)	2.7 (1.4–5.6)	1.3 (0.5–5.1)
Oligohaline – Fine sand	–	–	1.0 (0.9–1.2)	–	2.3 (0.8–4.8)	–
Oligohaline – Mud	–	–	–	–	–	–
Limnetic – Medium sand	–	12.6 (3.3–38.2)	1.2 (1.1–1.3)	0.7 (0.7–0.8)	1.7 (0.9–2.3)	2.1 (0.8–7.7)
Limnetic – Fine sand	0.05 (0.03–0.70)	5.0 (3.1–8.1)	0.9 (0.8–1.1)	0.7 (0.6–0.8)	1.8 (0.8–4.3)	1.0 (0.9–1.1)
Limnetic – Very fine sand	0.04 (<0.01–0.05)	11.1 (5.3–23.2)	0.9 (0.7–1.1)	0.7 (0.3–0.8)	2.0 (1.3–4.6)	0.9 (0.9–1.0)
Limnetic – Mud	–	7.1 (3.9–19.4)	0.8 (0.1–1.4)	0.9 (0.7–1.4)	3.0 (1.2–11.5)	2.0 (0.8–8.3)
All	0.09 (<0.01–1.40)	7.7 (<0.1–38.2)	0.9 (<0.1–1.4)	0.7 (0.2–2.2)	2.3 (0.6–11.5)	1.3 (<0.10–8.3)

[a] – = n < 5.

PHEN:ANTH = Phenanthrene:Anthracene, FLUO:PYRE = Fluoranthene:Pyrene, BENZA:CHRYS = Benzo(a)anthracene:Chrysene, BBF:BBK = Benzo(b)fluoranthene: Benzo(k)fluoranthene, INDENO:BGHIP = Indeno (1,3,3-c,d)pyrene: Benzo(g,h,i)perylene.

TABLE V

Inventory of organochlorine pesticides detected from Tampa Bay and its tributaries, 1993 and 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)
αHCH	461	0.65	0.09	0.05	0.8
Aldrin	769	1.30	0.23	0.30	5.8
βHCH	461	3.04	0.16	0.08	1.4
Chlordane	769	17.42	1.76	0.50	166.0
δHCH	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 epoxide	165	4.85	0.04	0.02	0.94
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

Dieldrin and lindane were each detected in approximately 3% of the samples (Table V). Inferences about their distributions are affected by the paucity of data points >MDL. More than 8% of samples collected from fine sand-size sediments in limnetic waters exceeded the PEL for dieldrin and almost 12% of samples collected in mud-sized sediments exceeded the TEL (Figure 9). In the case of lindane, the PEL was exceeded in >2% of samples collected from euhaline coarse sand-size habitats (Figure 10).

Other OCLs 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 V). Highest concentrations of endosulfan sulfate ocurred in the Hillsborough River in limnetic

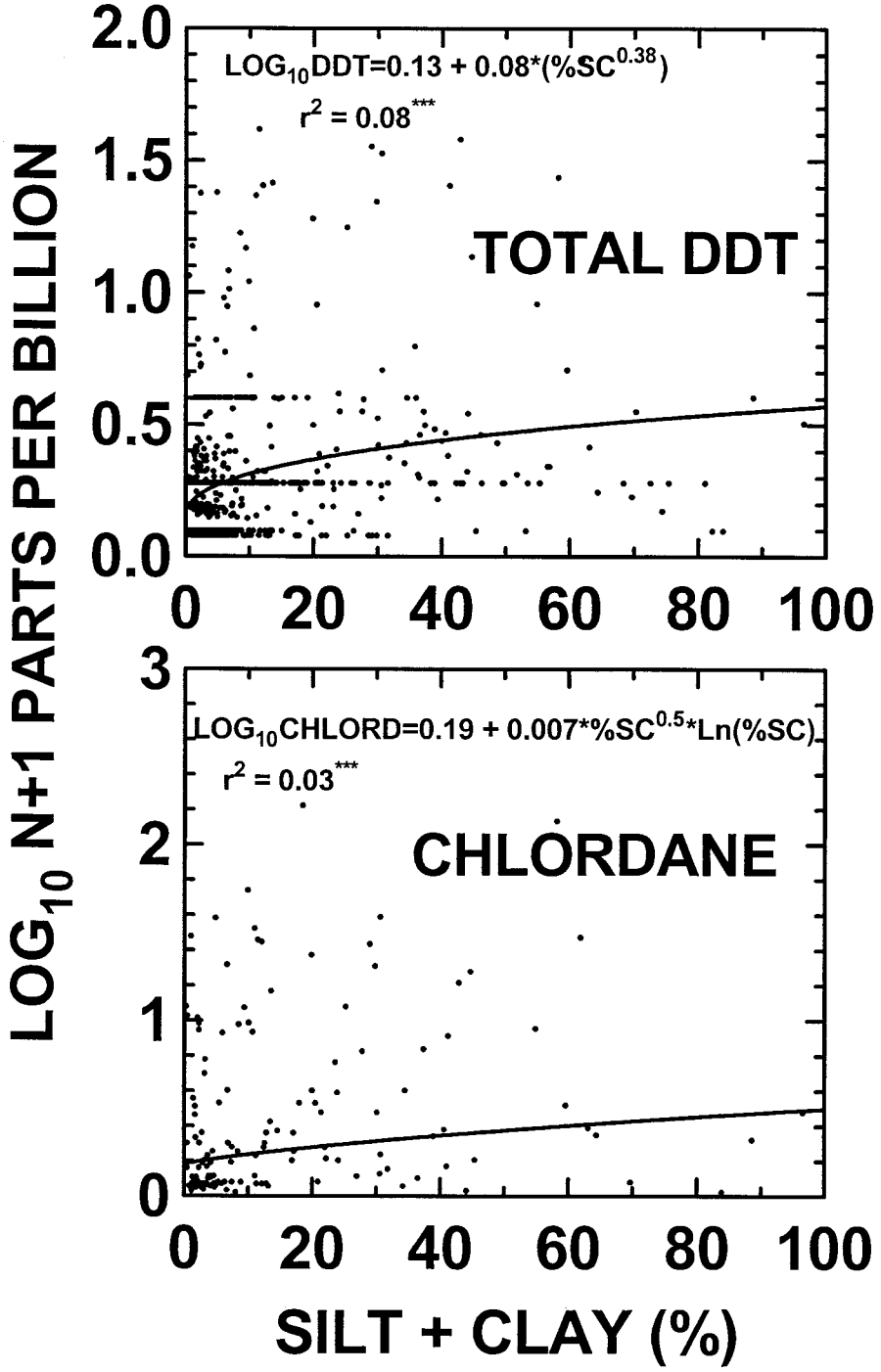

Figure 6. Association between % silt+clay and the organochlorine pesticides DDT, chlordane, lindane, and dieldrin in Tampa Bay, FL, 1993 and 1995–1999.

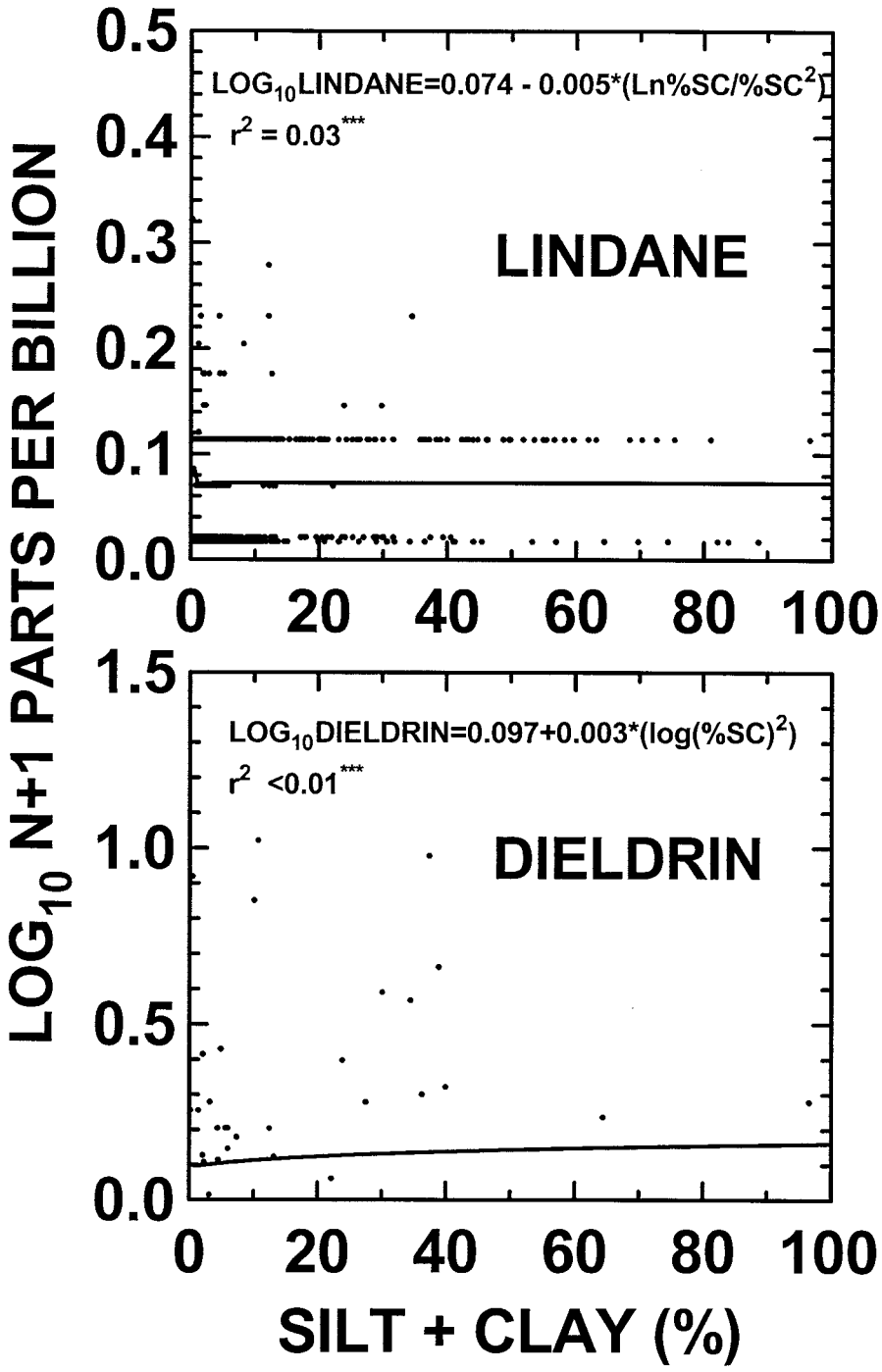

Figure 6. (continued)

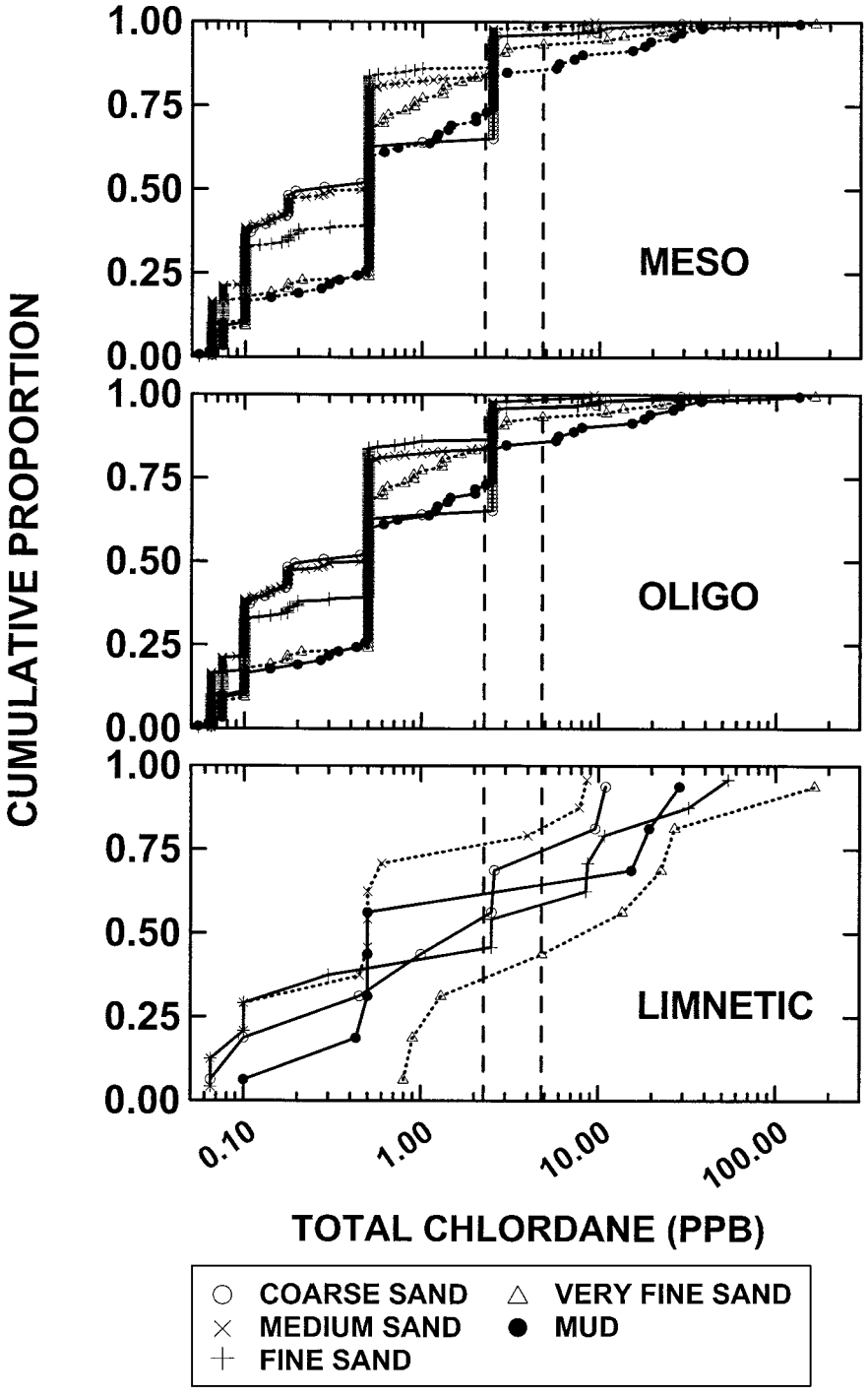

Figure 7. Cumulative distribution function plots of chlordane in Tampa Bay, FL (1993 and 1995–1999): By salinity zone and sediment type. Vertical lines demarcate the TEL (2.26 ppb) and PEL (4.79 ppb).

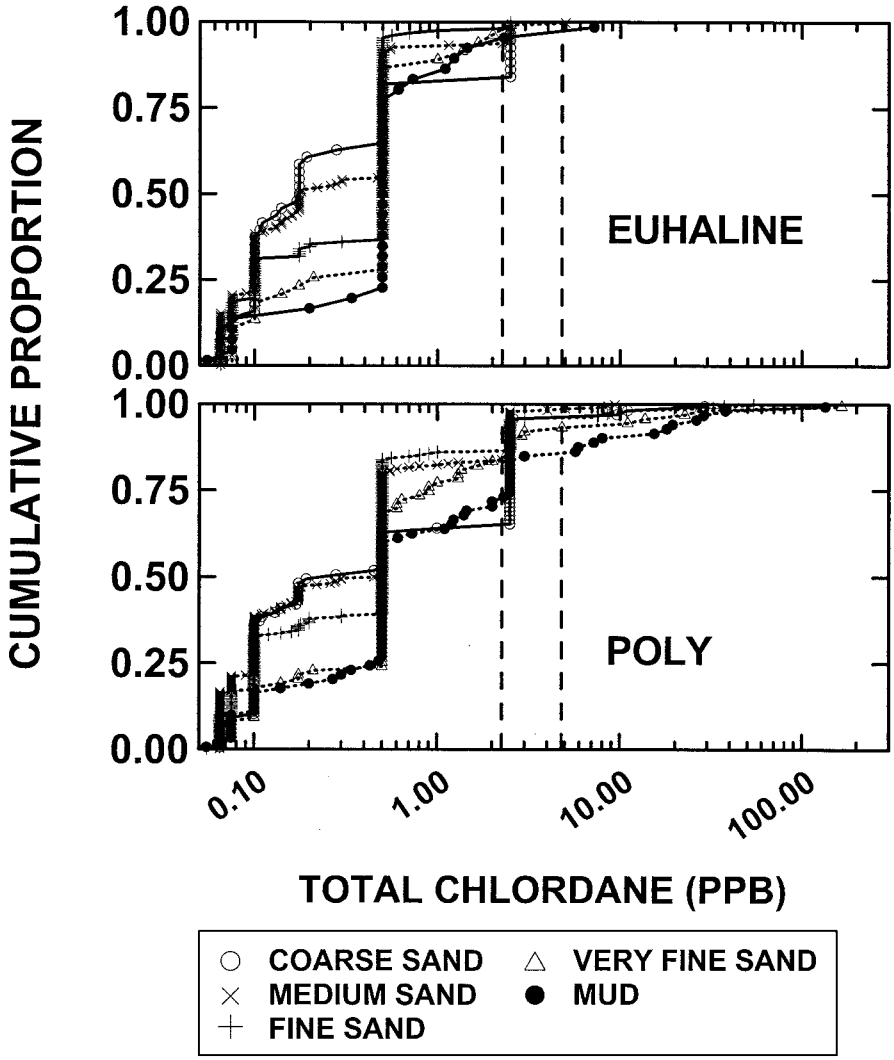

Figure 7. (continued)

waters with very fine sand size sediments and polyhaline muds. Endosulfan I and II maxima occurred in polyhaline very fine sand-size sediments located in Hillsborough Bay and McKay Bay respectively. Heptachlor and heptachlor epoxide occurred in approximately 4 to 5% of the samples (Table V). Highest concentrations of heptachlor occurred in mesohaline fine sand-size sediments and polyhaline muds in Hillsborough and Middle Tampa Bay. Highest concentrations of heptachlor epoxide were found in polyhaline muds and fine sand-size sediments in polyhaline waters in Hillsborough Bay. Mirex was detected in 2.6% of samples

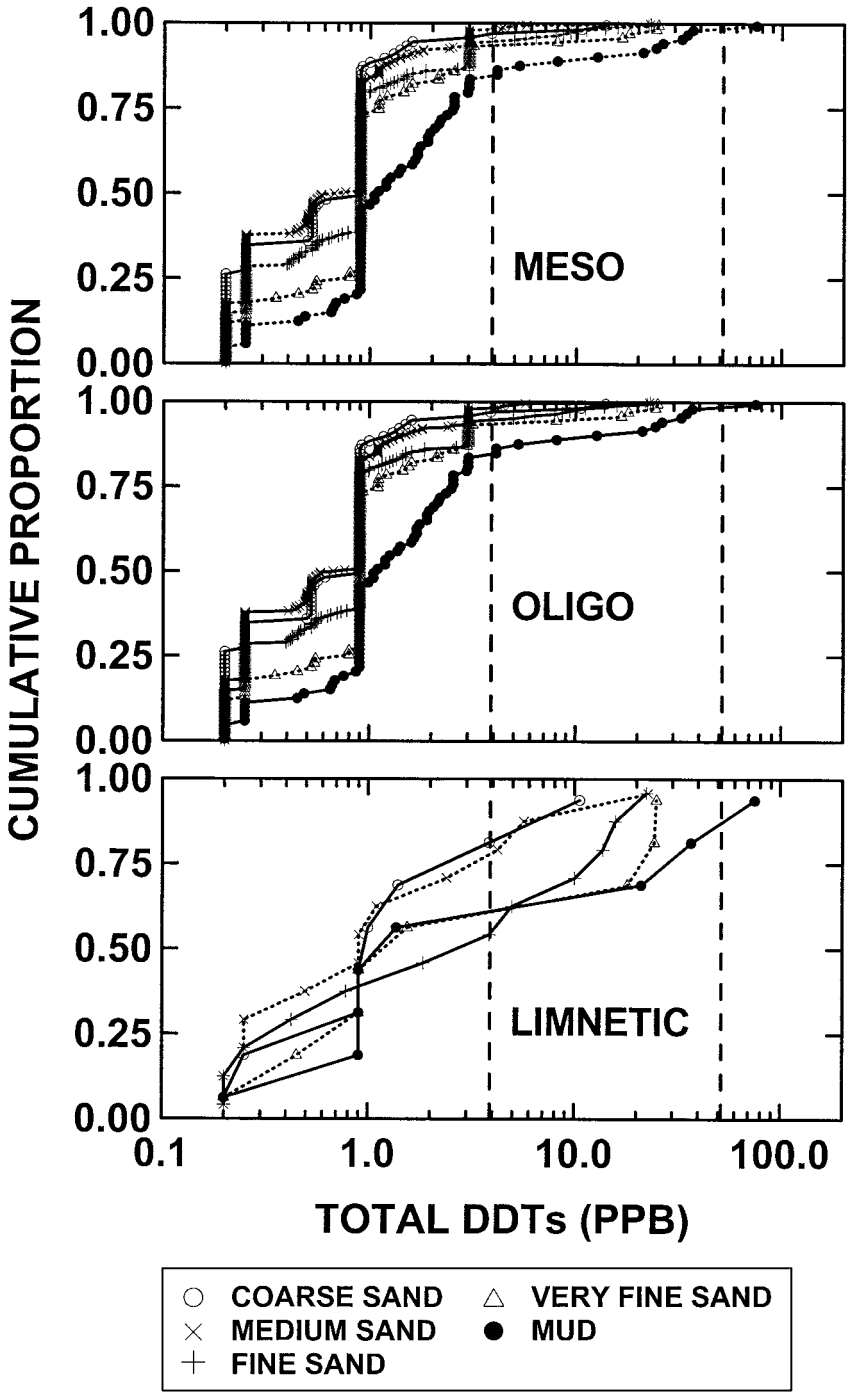

Figure 8. Cumulative distribution function plots of total DDTs in Tampa Bay, FL (1993 and 1995–1999): By salinity zone and sediment type. Vertical lines demarcate the TEL (3.89 ppb) and PEL (51.7 ppb).

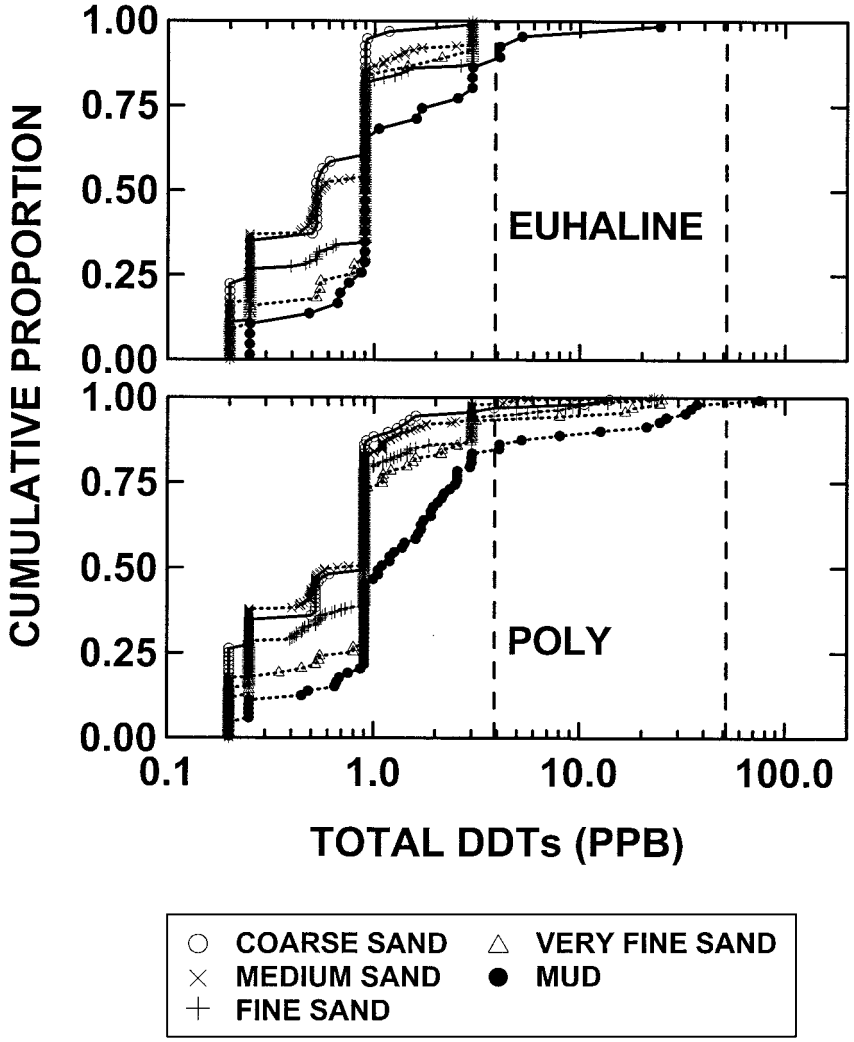

Figure 8. (continued)

(Table V) with concentrations >1 ppb in samples from McKay Bay and the Palm River (polyhaline muds).

3.4. POLYCHLORINATED BIPHENYLS

Detectable levels of PCBs occurred in 17.6% of the samples (8.8% of the bay samples and 68.5% of the tributary samples). PCB concentrations were positively associated with %SC, although this explained only 8% of the variation (Figure 11). Almost 17% of samples collected from medium sand-size sediments in limnetic waters exceeded the PEL (Figure 12). The TEL was exceeded in 47 to 50% of

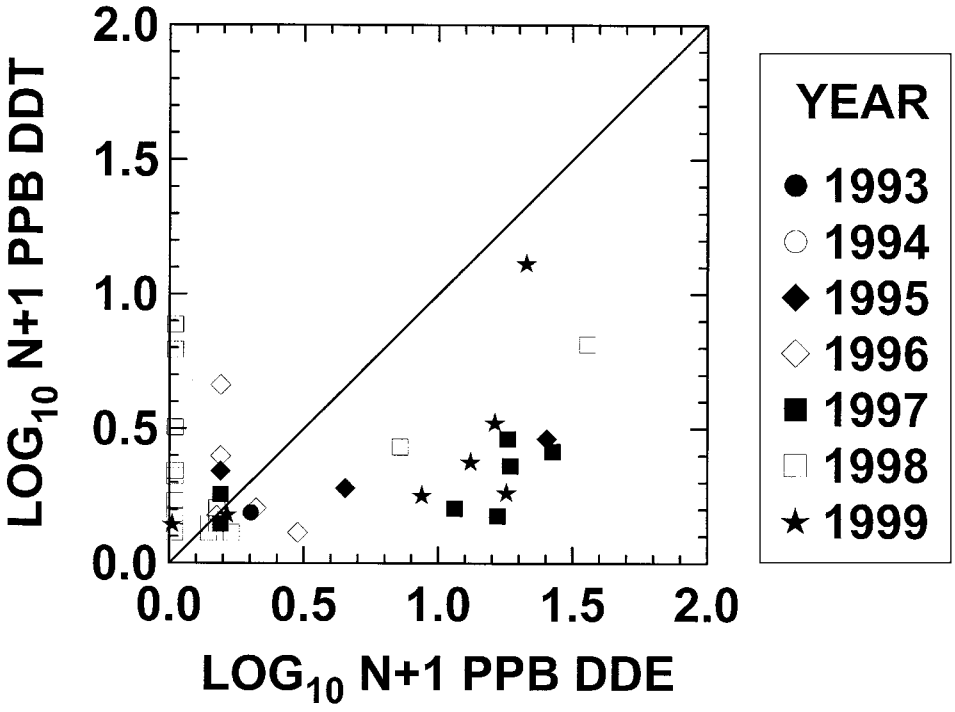

Figure 9. Scatterplot depicting the relationship between DDT and DDE in Tampa Bay, FL (1993 and 1995–1999): By year. Only samples with at least one of the paired concentrations >MDL are plotted.

samples from mud-sized sediments located in all salinity zones except the euhaline zone. Sites with concentrations >TEL < PEL were often indicative of 'high' MDLs in 1995.

4. Discussion

McConnell *et al.* (1996) identified several chemical contaminants that were likely to confer both ecological and human health risk in Tampa Bay. These included the PAHs benzo(a)pyrene, benzo(b)fluoranthene, and benza(a)anthracene, the OCLs chlordane, DDT, endrin, heptachlor, and lindane, and PCBs.

Proportionately, the habitats most degraded by PAHs were limnetic waters with fine sand-size sediments; and muds found in waters with mesohaline and polyhaline salinities. The 17 most contaminated sites were located within the lower Hillsborough River, which receives stormwater runoff from both the City of Tampa and two interstate highways.

Lowest concentrations were found in polyhaline and euhaline waters with medium to coarse sand-size sediments. These were generally located in Lower and Middle Tampa Bays.

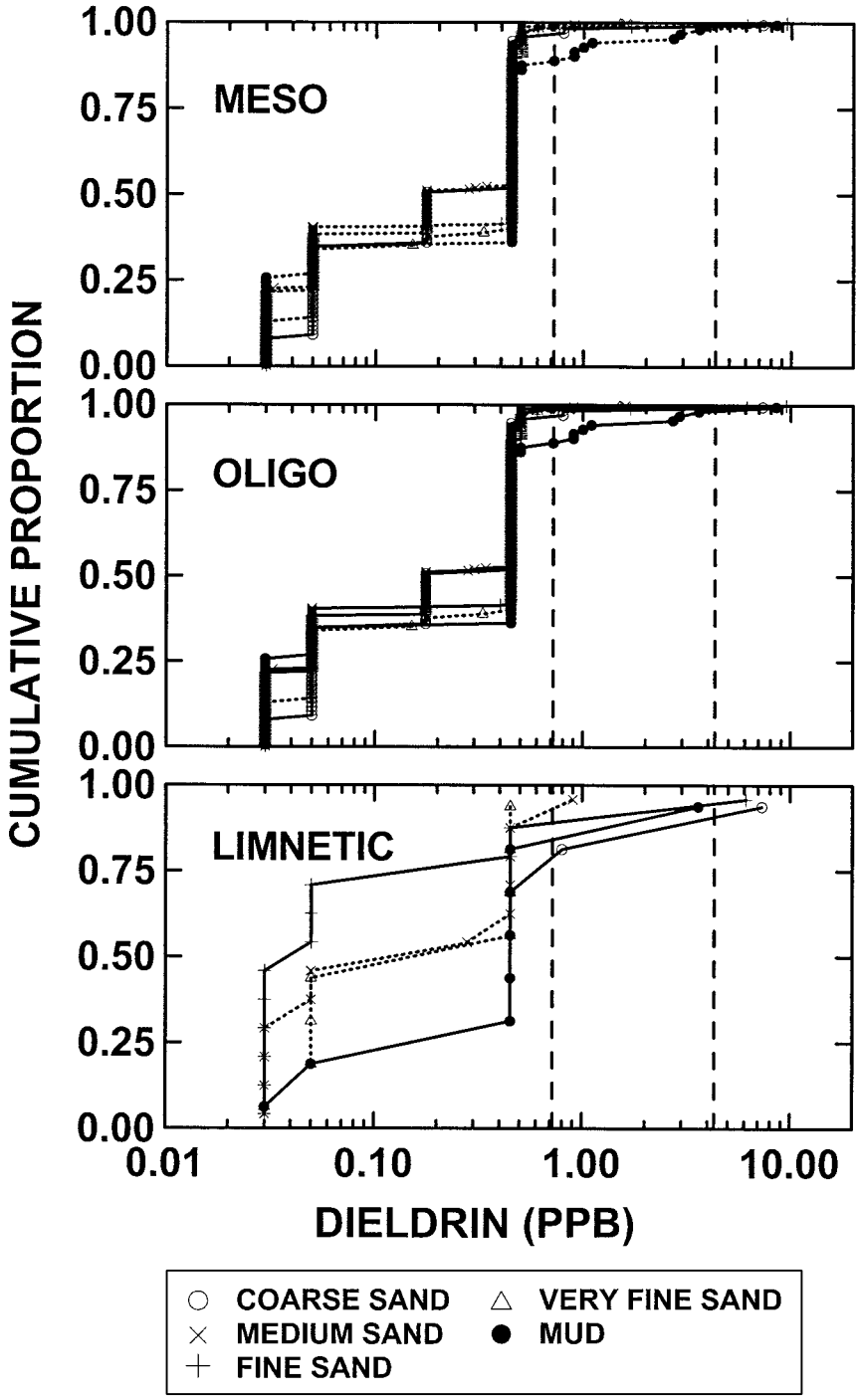

Figure 10. Cumulative distribution function plots dieldrin in Tampa Bay, FL (1993 and 1995–1999): By salinity zone and sediment type. Vertical lines demarcate the TEL (0.72 ppb) and PEL (4.3 ppb).

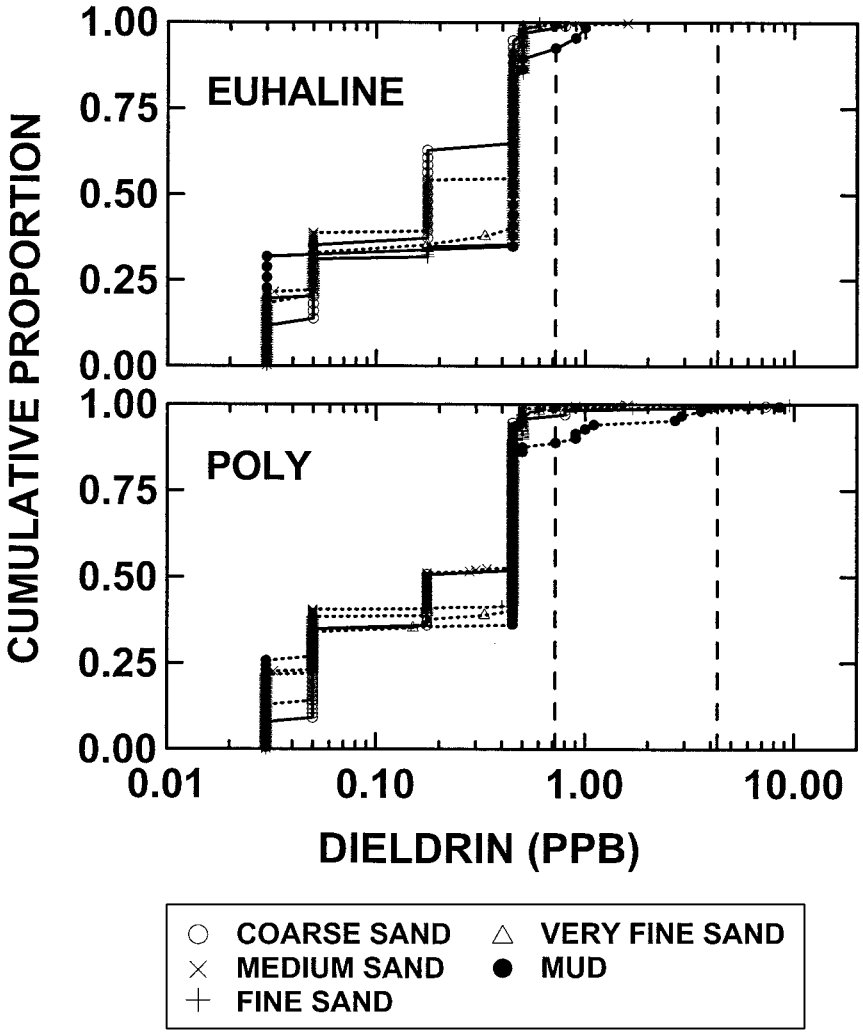

Figure 10. (continued)

Specific routes of PAHs 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 predominant entry route for PAHs to Tampa Bay (Doyle *et al*., 1985; Frithsen *et al*., 1995).

Automobile emissions are likely the primary source of PAHs to Tampa Bay sediments, based upon calculated PAH isomer ratios. Data collected for an atmospheric deposition study (unpubl. Data, Environmental Protection Commission) also suggest that automobile emissions are a major source of PAHs to Tampa Bay.

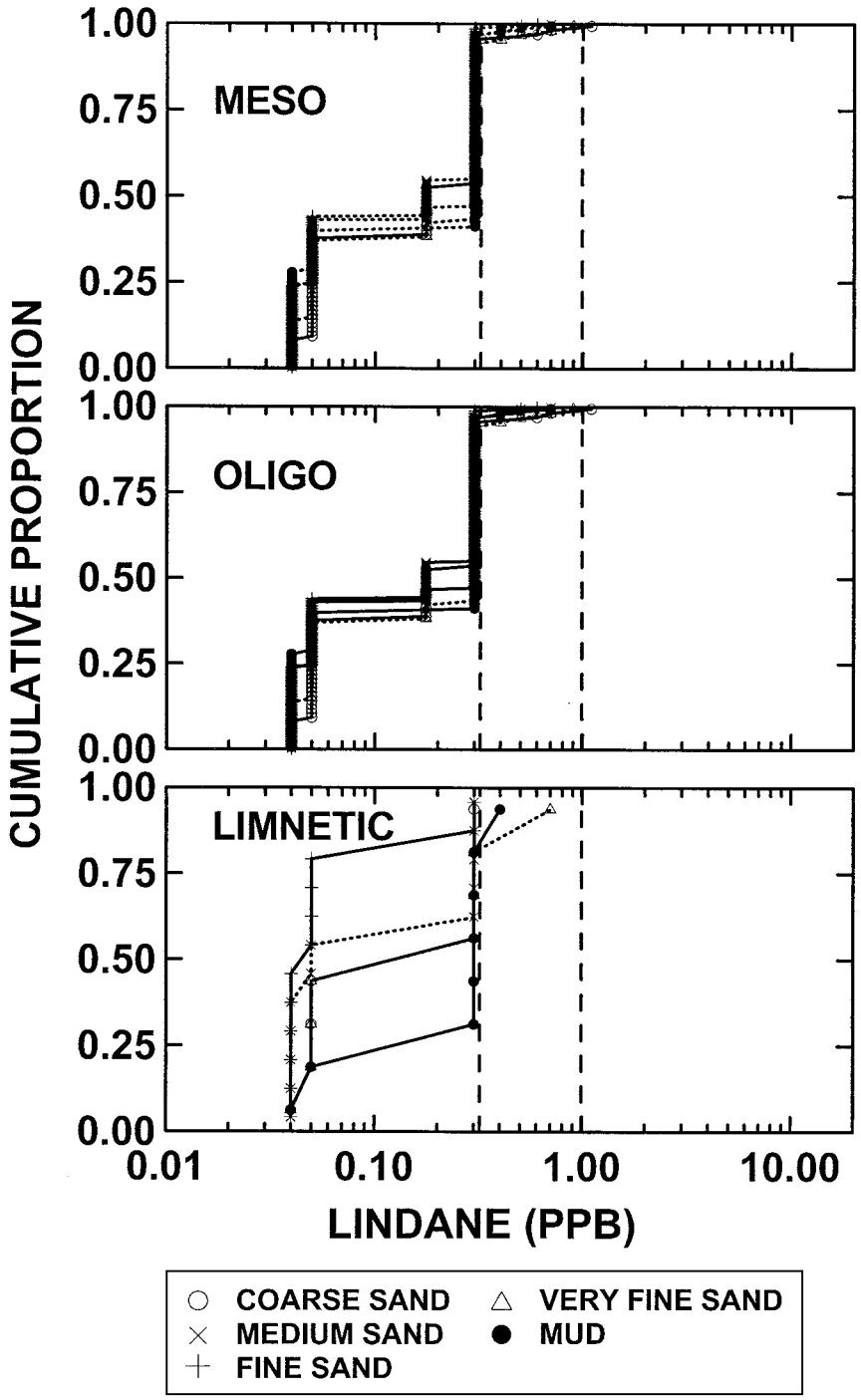

Figure 11. Cumulative distribution function plots lindane in Tampa Bay, FL (1993 and 1995–1999): By salinity zone and sediment type. Vertical lines demarcate the TEL (0.32 ppb) and PEL (0.99 ppb).

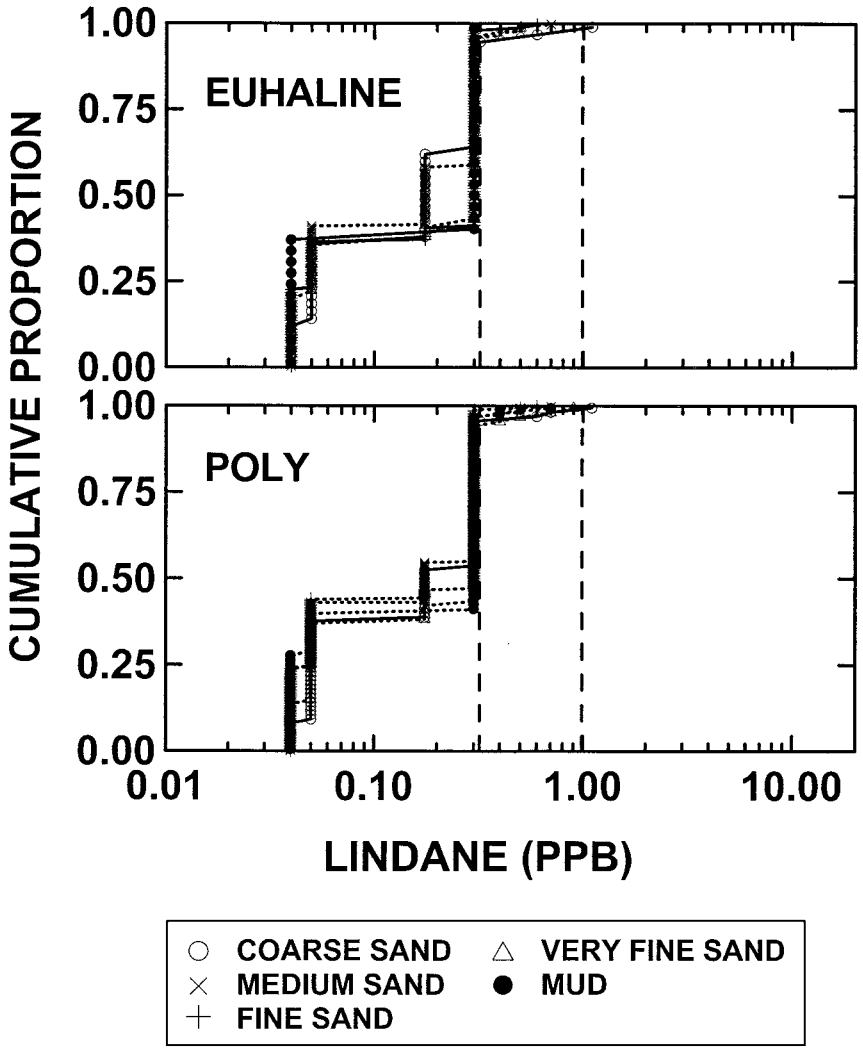

Figure 11. (continued)

The mean ratios of phenathrene:anthracene (2.45), fluoranthene:pyrene (7.07), benz(a)anthracene:chrysene (0.66), and indenopyrene: benzo(g,h,i)perylene (0.45) are within the ranges for vehicular emissions (Bescombes *et al.*, 2001; Walker and Dickhut, 2001).

Mixed sources are, however, likely at a number of sites. Indeno(1,2,3,c,d)-pyrene: benzo(g,h,i)perylene ratios in the sediments are generally >0.55, the upper limit for likely auto emissions (Walker and Dickhut, 2001). The ratios are more similar to those from coal (0.75–1.3; Walker and Dickhut, 2001) and may be indicative of atmospheric deposition from coal-fired power plants (Dickhut *et al.*, 2000). Sediment ratios of benzo(b)fluoranthene:benzo(k)fluoranthene reported here also

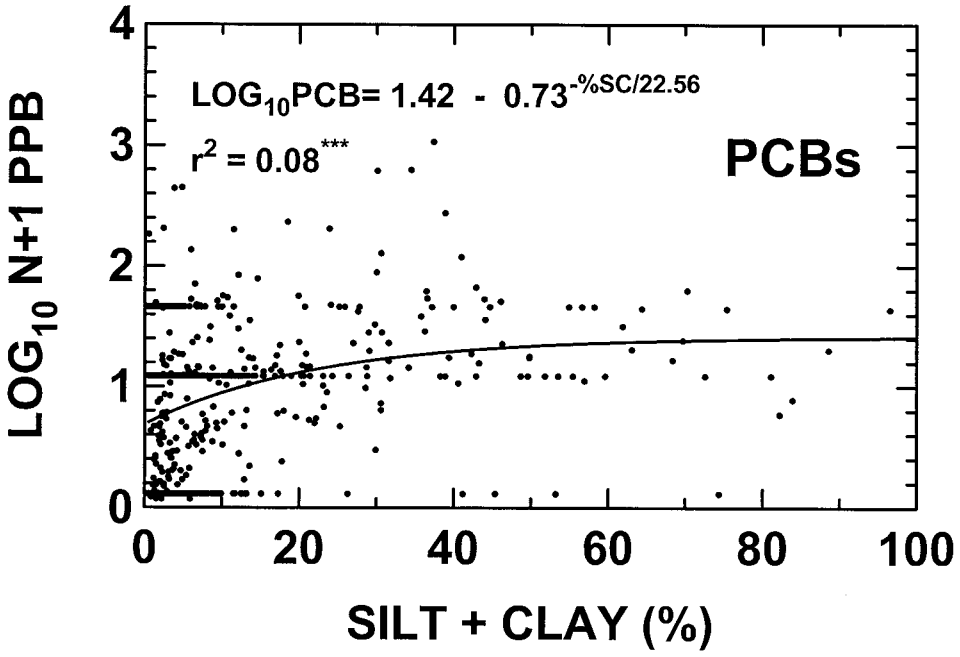

Figure 12. Association between % silt+clay and total PCBs in Tampa Bay, FL, 1993 and 1995–1999.

often exceed the likely ranges automotive emissions (1.26±0.19; Walker and Dickhut, 2001) and are closer to the range reported for coal (3.70±0.17; Walker and Dickhut, 2001). Poor (2002) reports that atmospheric PAH ratios in the Tampa Bay region are sometimes consistent with combustion of oil or coal as the source. The origin of these PAHs may not, however be local since atmospheric concentrations of anthracene, phenanthrene, fluoranthene and pyrene were only weakly associated with sulfur dioxide levels (Poor, 2002).

Source identification of PAHs may be enhanced with the addition of coronene (a marker for exhaust emissions) and retene (a marker for biomass combustion, i.e., municipal incinerators) (Bescombes *et al.*, 2001) to our program beginning in 2001.

Chlordane was detected in approximately 17% of the samples – similar to the percentage observed statewide (16%) (Seal *et al.*, 1994). The distributional pattern for chlordane in Tampa Bay 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, 10 to 30% was used for 'home and garden' applications, and the remainder was used in agriculture. Frithsen *et al.* (1995) estimated that, of the approximately >1000 kg yr^{-1} which enters Tampa Bay annually, 77% is from agricultural runoff and only 21% is from urban runoff. Of the approximately 220 kg

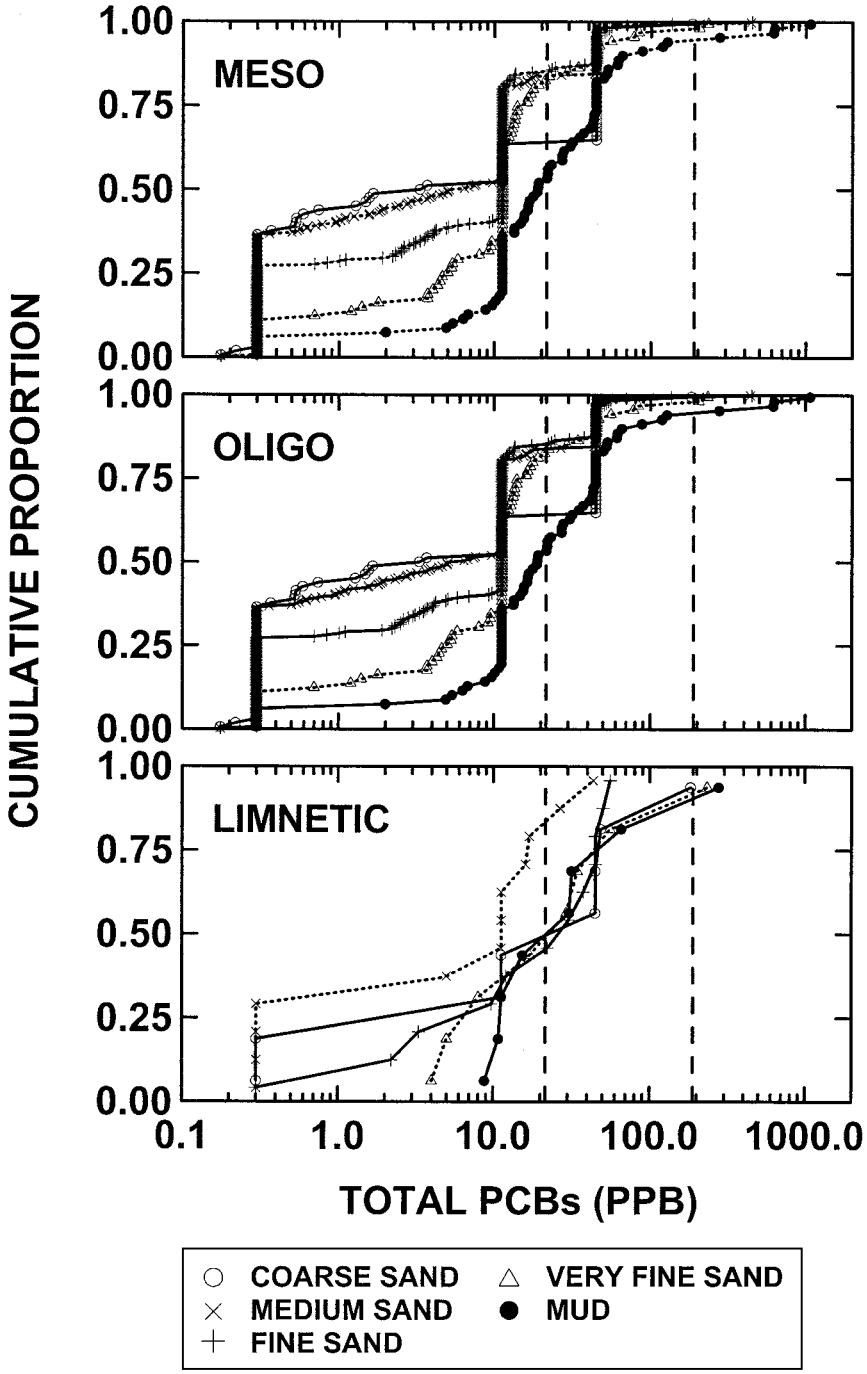

Figure 13. Cumulative distribution function plots of total PCBs in Tampa Bay, FL (1993 and 1995–1999): By salinity zone and sediment type. Vertical lines demarcate the TEL (21.6 ppb) and PEL (189 ppb).

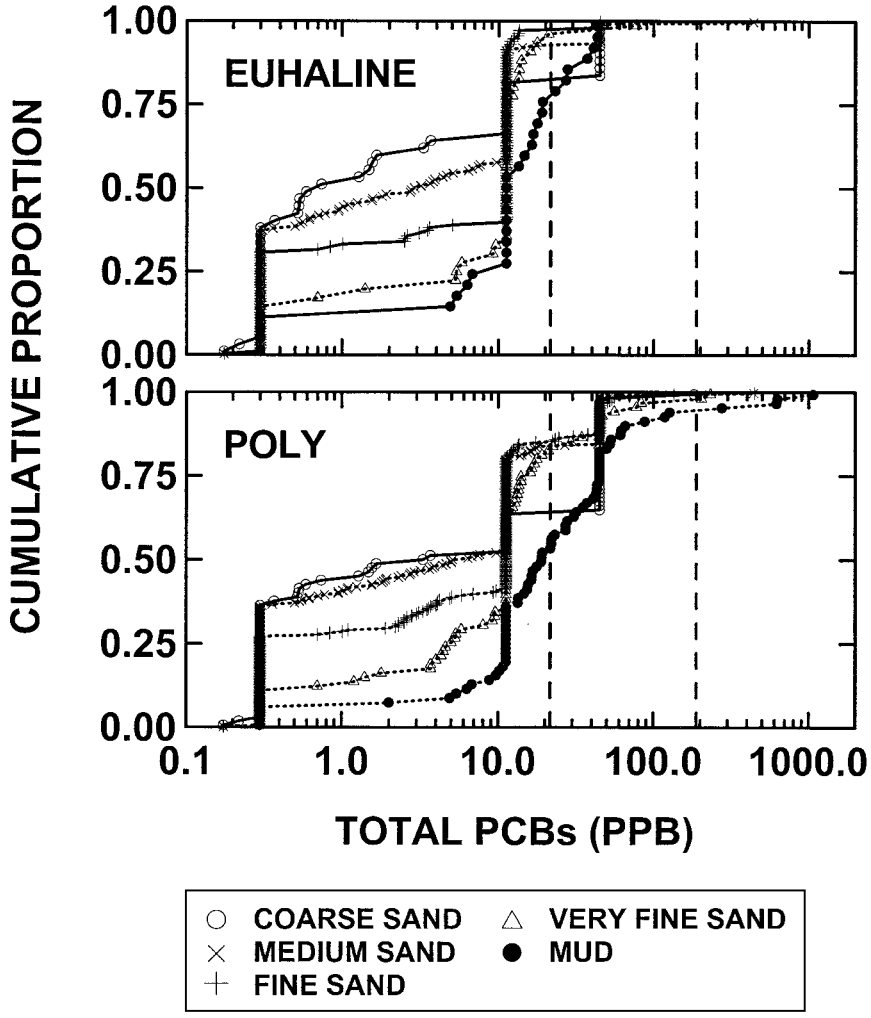

Figure 13. (continued)

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 OCLs in general tend to bind to finer-grained particles (Birch and 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 enters where coarser-grained sediments predominate (cf. Brooks and Doyle, 1998) and binding is minimized.

DDT and its metabolites were detected in 6% (DDT) to 19% (DDD) of the samples. This is lower than statewide frequencies (Seal *et al.*, 1994): DDTs and DDEs up to 28% and DDD in 46% of the samples.

Frithsen *et al*. (1995) estimate that agricultural runoff contributes approximately 95% and urban runoff 4% of the 1660 kg yr^{-1} reaching the bay. The Hillsborough River, where DDT concentration were highest in this study, was listed as the largest contributor to urban runoff (0.9%). DDT from agricultural areas does not appear to reach the bay – or if it does, the DDT does not bind to the sand-size sediments (cf. Birch and Taylor, 2000) prevalent in the lower bay. Whether the use of the miticide dicofol (Kelthane), which is manufactured from DDT (Kamrin, 1997) could contribute to the observed distribution is unknown.

Dieldrin concentrations were not positively associated with %SC – although the prevalence of samples <MDL confounds this analysis. Dieldrin concentrations appeared to differ by habitat, with highest concentrations found in polyhaline muds in both the Palm and Hillsborough rivers.

Frithsen *et al*. (1995) estimate that agricultural runoff contributes approximately 99% of the 770 kg yr^{-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 OCLs still in use, although it was only rarely detected in Tampa Bay sediments. It is applied to a variety of crops, and also occurs in shampoos and lotions for the control of lice and mites in humans (Kamrin, 1997). The distribution of lindane in Tampa Bay was noticeably different from that of the other OCLs. Of 14 sites with concentrations >0.5 ppb, nine were located in euhaline waters and eight were associated with medium to coarse sand-size sediments, and most of these locations were in Middle and Lower Tampa Bay. Frithsen *et al*. (1995) did not provide any estimates for lindane sources and loadings.

Other OCLs were too rarely detected or guidelines have not been established to provide context for the observed concentrations. Endosulfan is still in use as an agricultural insecticide (Kamrin, 1997) and is of special concern because it has been implicated in more fish kills nationwide (1980–1989) than any other OCL (Pait *et al*., 1992). Frithsen *et al*. (1995) estimated that agricultural runoff contributes approximately 95% of the 480 kg yr^{-1} of endosulfan reaching the bay; urban runoff accounted for the remainder. Poor's (2002) more recent data demonstrated that atmospheric deposition could contribute approximately 4 kg yr^{-1} of endosulfan to Tampa Bay.

Because OCLs 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 OCLs 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 b) as well as runoff from freshly tilled local farmland (Frithsen *et al*., 1995).

PCBs enter waterways and become associated with sediments via point 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; Poor, 2002).

PCBs were detected in almost 18% of the samples collected, lower than the 55% reported statewide (Seal *et al*., 1994). Maruya *et al*. (1997) did not find any significant association between %SC and PCBs in Gulf of Mexico sediments, although within Tampa Bay there was a positive and statistically significant association. 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 rather than congeners, we do not know how the distribution of PCBs is affected by sediment characteristics.

PCB concentrations > PEL were found at 10 sites; five were within the mesohaline salinity zone and seven sites had very fine sand and mud sized sediments. These were primarily located in the Palm and Hillsborough rivers. Although atmospheric deposition was the only source of PCBs evaluated for Tampa Bay by Frithsen *et al*. (1995), recent work by Poor (2002) suggests that PCB flux is more likely from sediments to water to the atmosphere than *vice versa*. Stormwater runoff (Kennish *et al*., 1992) or leaching from an abandoned landfill on the north shore of the Palm River (HDR Engineering, 1994) are more likely sources 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.

5. Conclusions

Within Tampa Bay the most contaminated habitats are generally those with salinity <14 ppt and sediments of fine sand and mud sizes – the urban tributaries. The bay proper shows little evidence of contaminated sediments.

Concentrations of PAHs reported for the Hillsborough River have a high likelihood of being toxic to aquatic life. PAHs were rarely detected in higher salinity waters with coarser sediments. Isomer ratios suggest that stormwater runoff is a major contributor of PAHs to bay sediments, although incinerators and coal-burning power plants, possibly removed from the immediate study area, are possible contributors.

The majority of Tampa Bay appears unimpacted by OCLs. The data suggest runoff from urban/residential locales rather than agricultural runoff are primary sources of OCLs to Tampa Bay.

PCBs have been detected found in extremely high concentrations in the Palm River, in moderate to high concentrations in the Hillsborough River, and low to moderate concentrations in portions of upper Hillsborough Bay (mesohaline habitats). PCBs were only rarely detected elsewhere in the bay.

Acknowledgements

Sediment samples were collected by staff of the Environmental Protection Commission of Hillsborough County (EPCHC), the Manatee County Environmental Management Department, and the Pinellas County Department of Environmental Management. The Tampa Bay Estuary Program provided partial financial support for laboratory analyses. B. Goetting produced the maps. T. Cardinale and H. Greening (Tampa Bay Estuary Program) reviewed an earlier draft.

Appendix A

Appendix A

Summary of method detection limits (MDLs) (ppb) of organic contaminants in Tampa Bay sediments, 1993 and 1995–1999

A. OCLs	1993	1995	1996 (EPC)	1996 (SAL[a])	1997	1998	1999
α-Hexachlorcyclohexane [α HCH]	–	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
β-Hexachlorcyclohexane [βHCH]	–	0.2	0.2	–	0.2	0.1	0.16
Chlordane (Total)	0.14	5.0	–	–	–	–	–
α-Chlordane	–	–	0.1	1.0	0.1	0.1	0.04
γ-Chlordane	–	–	0.1	–	0.1	0.1	0.11
δ-Hexachlorcyclohexane [δHCH]	–	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
γ-Hexachlorcyclohexane [Lindane]	0.35	0.2	0.2	1.0	0.2	0.1	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	–	–	–

[a] Southern Analytical Laboratory, Oldsmar, FL.
[b] – = Not analyzed.

Appendix A
(continued)

B. PAHs	1993	1995	1996	1997	1998	1999
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
Benzo(a)pyrene	0.0088	6.0	6.0	6.0	5.8	10.0
Benzo(b)fluoranthene	<0.01	7.5	7.5	7.5	3.6	6.0
Benzo(g)fluoranthene	<0.01	6.0	6.0	–	–	–
Benzo(k)fluoranthene	<0.01	4.8	4.8	4.8	10.7	8.0
Benzo(g,h,i)perylene	–	6.0	6.0	6.0	8.7	6.0
Chrysene	<0.01	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	<0.01	6.5	6.5	–	6.3	9.0
Fluorene	0.005	5.8	5.8	5.8	7.0	15.0
Indenopyrene	<0.01	4.3	4.3	4.3	4.6	2.0
2-Methylnapthalene	0.0099	–	–	–		–
Napthalene	0.0099	4.0	4.0	4.0	9.2	7.0
Perylene	0.0038	–	–	–	–	–
Phenanthrene	0.35	6.0	6.0	6.0	4.8	10.0
Pyrene	<0.01	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

[a] Southern Analytical Laboratory, Oldsmar, FL.
[b] – = Not analyzed.

Appendix B

Appendix B

Summary of TEL[a], and PEL[a] concentrations (ppb) of organic contaminants

Contaminant	TEL	PEL
A. OCLs		
Chlordane	2.26	4.79
Dieldrin	0.72	4.30
Total DDT	3.89	51.70
Lindane	0.32	0.99
B-1. Low molecular weight PAHs		
Acenapthene	6.71	88.9
Acenapthylene	5.87	128.0
Anthracene	46.9	245.0
Fluorene	21.2	144.0
Napthalene	34.6	391.0
Phenanthrene	86.7	544.0
Total LPAHs	312.0	1442.0
B-2. High molecular weight PAHs		
Benz(a)anthracene	74.8	693.0
Benzo(a)pyrene	88.8	763.0
Chrysene	108.0	846.0
Dibenz(a,h)anthracene	6.22	135.0
Fluoranthene	113.0	1494.0
Pyrene	153.0	1398.0
Total HPAHs	655.0	6676.0
B-3. Total PAHs	1684.0	16770.0
C. Polychlorinated biphenyls		
Total PCBs	21.6	189.0

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

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