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Phthalic Acid Esters, Total DDTs, and Polychlorinated Biphenyls in Marine Samples from Galveston Bay, Texas

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Two halogenated hydrocarbon pollutants which have received much attention are polychlorinated biphenyls (PCBs) and the pesticide DDT, including its degradation products. Prior to 1970, PCBs were extensively used as plasticizers, hydraulic fluids, and dielectrics for transformers and large capacitors. Because of their wide distribution, environmental persistence and toxicity, their use in the U.S. has now been drastically curtailed. DDT, a chlorinated hydrocarbon, was used widely in the U.S. until its use was restricted in the early 1970s. Even though it is now rarely used in the U.S., DDT and its degradation products are still found in environmental samples. Both acute and chronic effects of PCBs and DDT on marine organisms have been studied in the laboratory (NIMMO et al. 1975; VERNBERG et al. 1977).

Phthalic acid esters have also received attention as a marine pollutant (GIAM et al. 1978). These compounds, which are nearly ubiquitous, are added to synthetic plastics to impart flexibility and improve the natural properties of these materials. Non-plastic materials such as cork, glasswool, Teflon sheets, and aluminum foil have also been found to contain the most prevalent of the phthalates, di(2-ethylhexyl) phthalate (DEHP).

The Galveston Bay system is one of the most economically important estuaries along the Texas Gulf Coast. Its economic importance stems from its proximity to a major metropolitan area, which depends on the Bay for transportation of goods, waste disposal, cooling water, recreation and aesthetic appeal. Numerous industrial plants located along the Houston Ship Channel are major potential sources of refractory organic contaminants to the Galveston Bay system. Insecticide utilization in agriculture and in mosquito control along with industrial and domestic waste out-falls provide ample opportunity for these chemicals to reach coastal estuarine systems directly or through run-off following leaching of soil.

Galveston Bay was chosen for this study because of 1) its susceptibility to pollution, 2) its commercial and recreational value, 3) our longstanding interest in marine pollution and 4) our

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participation in evaluating the biological effects of various pollutants in marine organisms. The results reported herein are important because they 1) provide necessary information for the latter study, 2) characterize an important fishing and recreational area, 3) provide baseline data for use in future studies and 4) continue and broaden our extensive studies of pollutants along the Gulf Coast.

MATERIALS AND METHODS

The study area (Figure 1) extends from Morgan's Point, where the Houston Ship Channel joins Galveston Bay, to Bolivar Peninsula and Galveston Island. The area includes Trinity, East and West Bays. Collection sites were selected near suspected point and nonpoint sources of pollution; a relatively non-polluted reference site was also sampled. Site 1 represents a point source from Galveston sewage outfall. Sites 2 and 3 represent point sources from the Houston Ship Channel and Texas City Channel. Site 4 along the Houston Ship Channel is a nonpoint source. Sites 6, 7 and 8 on

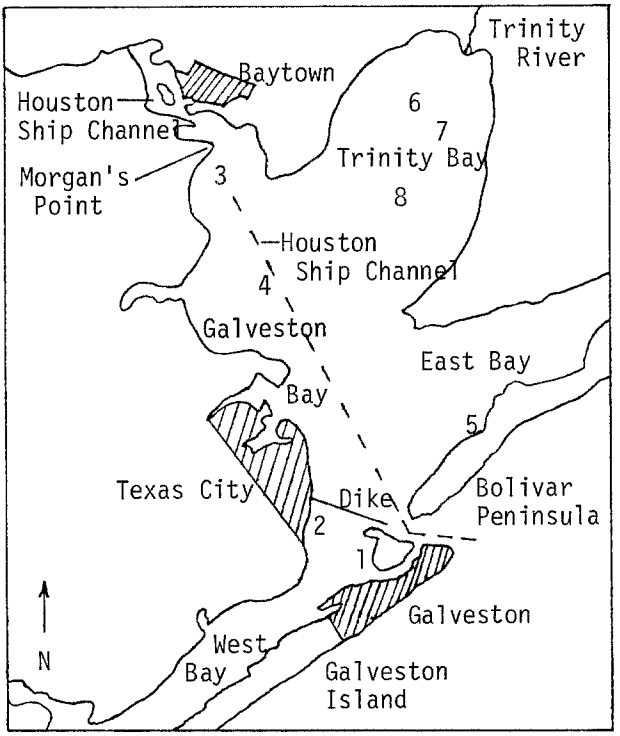

Figure 1. The Galveston Bay System. Samples were collected at the sites indicated (1-8).

the Trinity Bay represent point sources from oil platforms. Site 5 in East Bay was believed to be relatively non-polluted and was selected as the reference site. Surface water samples were collected at all sites in solvent-cleaned, one-gallon glass containers. Sediment samples were collected with a stainless steel Ekman grab sampler and placed into solvent-cleaned, quart Mason jars. Samples were collected from July 1, 1978, to May, 1979.

Solvents used in this study were pesticide quality. Distilled water was purified by continuous extraction with petroleum ether in a 20-liter extractor. The petroleum ether was changed at 24-h intervals until a 50-fold concentration demonstrated no impurities by gas chromatography.

Glassware and other equipment were washed with Micro cleaning solution (International Products Corp.), rinsed with distilled water and heated at 320°C overnight. Just prior to use, glassware was rinsed with pesticide-grade petroleum ether.

Other details of sampling and analytical procedures for marine samples have been reported (GIAM 1976; GIAM et al. 1975a; HARVEY & GIAM 1976; MURRAY et al. 1980). The sources of and techniques for removing background contamination during the analysis of phthalates and PCBs have also been discussed in detail (GIAM & CHAN 1976; GIAM & WONG 1972; GIAM et al. 1975b).

RESULTS AND DISCUSSION

Concentrations of total DDTs (including various isomers of DDT and DDE), PCBs and DEHP detected in water samples from eight collection sites in the Galveston Bay system are given in Table 1. Total DDTs ranged from <0.01 to 3.5 ng/ℓ with an average concentration of 0.38 ng/ℓ. Total DDTs along the Mississippi Delta have been reported to range from 0.01 to 2.9 ng/ℓ, with an average of 1.7 ng/ℓ, while concentrations along the Gulf Coast ranged from 0.01 to 0.6 ng/ℓ with an average of 0.35 ng/ℓ (GIAM et al. 1978). In general, the values reported in this study fall within the range reported for the Mississippi Delta and Gulf Coast.

PCB concentrations ranged from <0.01 to 70 ng/ℓ with an average of 3.1 ng/ℓ. These values are somewhat higher than those reported for the Mississippi Delta and Gulf Coast. Water samples from the Mississippi Delta contained from 1.7 to 3.3 ng/ℓ with an average of 2.5 ng/ℓ, while concentrations along the Gulf Coast ranged from 0.1 to 3.1 ng/ℓ with an average of 1.6 ng/ℓ (GIAM et al. 1978).

DEHP concentrations in water ranged from <2 to 12,000 ng/ℓ with an overall average of 600 ng/ℓ (Table 1). Disregarding Site 2, the values reported in this study (range, <2 to 1600 ng/ℓ; average, 250 ng/ℓ) are slightly higher than those along the Mississippi Delta and Gulf Coast. Concentrations reported for

TABLE 1. Concentrations of Total DDTs, PCBs and DEHP in Water from Galveston Bay, Texas

Site	ΣDDTs	PCBs	DEHP
1	0.99* (<0.01 - 3.3)**	0.97 (<0.01 - 3.9)	510 (<2.0 - 1600)
2	0.20 (<0.01 - 0.79)	18 (<0.01 - 70)	3000 (90 - 12,000)
3	1.8 (0.04 - 3.5)	1.1 (<0.01 - 4.6)	220 (150 - 300)
4	0.04 (<0.01 - 0.10)	1.1 (<0.01 - 3.4)	470 (58 - 1100)
5	0.01 (<0.01 - 0.04)	0.74 (<0.01 - 2.9)	120 (<2.0 - 290)
6	<0.01 (†)	0.82 (<0.01 - 2.4)	240 (<2.0 - 650)
7	<0.01 (††)	3.2 (††)	120 (††)
8	0.06 (<0.01 - 0.16)	1.4 (<0.01 - 4.1)	54 (<2.0 - 100)
Average, all sites	0.38	3.1	600

*Concentrations are in ng/ℓ; averages are based on four determinations. Samples were collected from July, 1978, to May, 1979.

**Values in parentheses are ranges.

†All were below the limit of detection (0.01 ng/ℓ).

††Only one sample was analyzed.

the Mississippi Delta ranged from 23 to 230 ng/ℓ (average, 70 ng/ℓ), while the Gulf Coast values ranged from 6 to 320 ng/ℓ (average, 130 ng/ℓ; GIAM et al. 1978).

Concentrations of total DDTs, PCBs and DEHP detected in sediment from the eight collection sites are given in Table 2. Concentrations of total DDTs ranged from 0.01 to 1.4 ng/g with an overall average of 0.21 ng/g. Concentrations of total DDTs from the Mississippi Delta ranged from 0.2 to 9.3 ng/g with an average of 4.2 ng/g, while along the Gulf Coast they ranged from 0.2 to 4.0 ng/g

TABLE 2. Concentrations of Total DDTs, PCBs and DEHP in Sediment from Galveston Bay, Texas

Site	ΣDDTs	PCBs	DEHP
1	0.32* (<0.01 - 0.49)**	0.35 (<0.14 - 0.90)	27 (11 - 57)
2	0.23 (<0.01 - 0.53)	2.8 (<0.14 - 5.2)	26 (6 - 38)
3	0.09 (<0.01 - 0.28)	1.5 (<0.14 - 3.3)	30 (1 - 110)
4	<0.01 (†)	0.12 (<0.14 - 0.21)	38 (3 - 100)
5	0.017 (<0.01 - 0.04)	0.10 (<0.14 - 0.14)	9 (3 - 17)
6	0.23 (<0.01 - 0.62)	1.4 (<0.14 - 4.9)	11 (1 - 23)
7	0.49 (<0.01 - 1.4)	1.9 (<0.14 - 7.1)	25 (2 - 58)
8	0.30 (<0.01 - 0.63)	0.33 (<0.14 - 0.84)	13 (<1 - 27)
Average, all sites	0.21	1.1	22

*Concentrations are in ng/g; averages are based on four determinations. Samples were collected from July, 1978, to May, 1979.

**Values in parentheses are ranges.

†All were below the limit of detection.

with an average of 1.3 ng/g (GIAM et al. 1978). Thus, total DDT values reported for sediments from the Mississippi Delta and along the Gulf Coast were substantially higher than those for Galveston Bay.

PCB concentrations ranged from <0.14 to 7.1 ng/g with an overall average of 1.1 ng/g. These values fall within the range reported for the Mississippi Delta and Gulf Coast. PCBs from the Mississippi Delta ranged from 0.2 to 35 ng/g (average, 19 ng/g), while along the Gulf Coast they ranged from 0.2 to 6 ng/g (average, 2.0 ng/g; GIAM et al. 1978).

DEHP concentrations in this study ranged from <1 to 110 ng/g with an overall mean of 22 ng/g. These values are within the range reported for the Mississippi Delta and Gulf Coast. DEHP in the Mississippi Delta ranged from <0.1 to 250 ng/g with an average concentration of 69 ng/g, while for sediments along the Gulf Coast, it ranged from 3.4 to 14 ng/g with an average of 6.6 ng/g (GIAM et al. 1978).

This study revealed that the relative concentrations were DEHP > PCBs > DDTs in both the water and sediments. A similar trend was also observed in the samples from the Mississippi Delta and Gulf Coast.

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