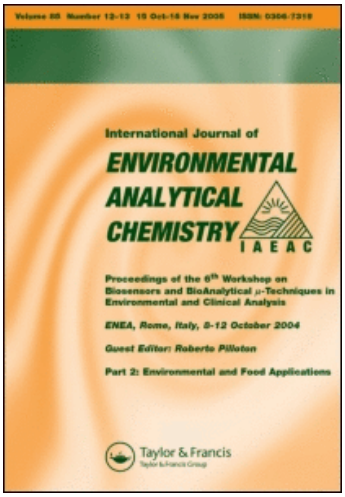

International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Variations of Phthalate Ester Concentrations in Sediments from the Chester River, Maryland

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To cite this Article Peterson, James C. and Freeman, David H.(1984) 'Variations of Phthalate Ester Concentrations in Sediments from the Chester River, Maryland', International Journal of Environmental Analytical Chemistry, 18: 4, 237 — 252

To link to this Article: DOI: 10.1080/03067318408077006

URL: http://dx.doi.org/10.1080/03067318408077006

Inter. J. Environ. Anal. Chem., 1984, Vol. 18, pp. 237–252
0306-7319/84/1804-0237 $18.50/0

Printed in Great Britain

Variations of Phthalate Ester Concentrations in Sediments from the Chester River, Maryland

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(*Received March 21, 1984*)

Phthalate esters discharged from a plasticizer-manufacturing plant were distinguished from those of other sources in the Chester River, Maryland by comparing the distinctive patterns of alkyl phthalate species of the plant to those of sediment samples from sites along the mid-river axis. The magnitude of the changes in individual phthalate species were placed in perspective by charting their concentrations with distance along the river. Short sediment cores were also analyzed to determine the profile of pthalate ester pollution in the Chester River during the previous decade in which the river experienced a significant oyster mortality. A significant level of phthalate ester pollution was found in the Chester River sediment but its source was not found to be the plasticizer plant.

INTRODUCTION

Significant oyster production losses which showed a yearly progression down the Chester River in Maryland were reported during the years following Hurricane Agnes in 1972[1]. Numerous explanations for these losses have been proposed including a suspicion of increasing levels of toxic organic chemicals in the river. Considering all the possible sources of such industrial pollution in

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the Chester River, a producer of phthalate ester plasticizers was considered to be the most likely source compared to two food-processing plants and three sewage-treatment plants. This company reported a spill of 400 kg of organic chemical waste from a holding tank during the storm.

While phthalate esters exhibit relatively low acute toxicity to fish and aquatic invertebrates[2,3], there is evidence that reproductive impairment occurs in invertebrates continuously exposed to as little as 3 μg/l of DEHP[3]. Also, consistent with their lipophilic nature, DEHP and DBP accumulate in fish and aquatic invertebrates with factors ranging from 350 to 3900[2].

The geographical location of the phthalate ester plant (P) and the yearly progression of 100% oyster mortality (1973–1975) is shown in Figure 1. Surprisingly, no agency was charged with the appropriate responsibility so none of the affected oysters was saved. Analyses of oysters or water collected years after the start of the oyster kill would only reflect current levels of phthalate esters. The sediment, however, can act as an historical record of past and current levels of

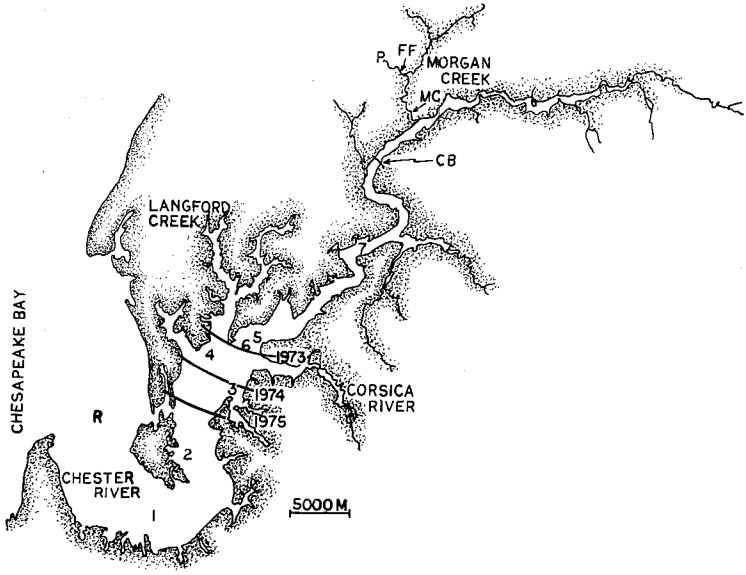

FIGURE 1 Map of the Chester river illustrating sample site locations. Solid bars indicate the yearly progression of 100% oyster mortality.

hydrophobic substances in the estuarine environment[4,5]. Therefore, the sediment was chosen as the matrix to analyze in order to compare the relative contribution of phthalate esters from the plasticizer plant to the overall phthalate ester pollution in the Chester River.

Three approaches were taken to examine the situation.

1) Phthalate ester distribution patterns: Recently, Sheldon and Hites[6] studied the movement of industrial effluents in river water by monitoring unique compounds from a specific source. Because phthalate esters are ubiquitous pollutants, this approach was not applicable. Instead, we have studied the possible uniqueness of the pattern of phthalate species of a single industrial source in order to distinguish its discharge from other unknown phthalate ester sources.

2) Variation of individual phthalate ester concentrations along the mid-river axis: The sediment concentrations can be compared provided that the adsorptive capacity of the sediments from the chosen sites along the river are similar. This depends on the similarity in the particle size distribution and total organic carbon content of the sediment[4,5]. The sediment sample sites were chosen to favor collection of sediments containing finer particles which have the greatest adsorptive characteristics.

3) Variation of phthalate ester concentrations with depth below the sediment surface: Assuming an estimated 0.8 cm/year sedimentation rate in the Chester River[7], the occurrence of the waste tank spill or other similar episodic events in the previous decade should be recorded as elevated concentrations in segments of the top 8–10 cm of sediment. Short sediment "cores" were analyzed to investigate the occurrence of such an event.

To reduce the chance of laboratory contamination commonly encountered in the analysis of phthalate esters[8,9], the number of sample manipulation steps was minimized. This protocol, described in detail elsewhere[10], consisted of ultrasonic extraction of dried sediment followed by direct analysis of the concentrated crude extract by glass capillary GC–MS.

EXPERIMENTAL

Sediment samples were obtained with a Vanveen grab sampler at the sites marked in Figure 1 aboard the Chesapeake Biological

Laboratory research vessel, the *Aquarius*, in June 1978. At the sites numbered 1 to 7, a short brass coring tube was inserted through a sliding panel at the top of the Vanveen sampler to obtain a short core of the top 10 cm of sediment. Duplicate cores were taken at each site. One core was promptly sliced every 1 cm on site. The second core was homogenized with a spatula. The sediment was stored at 3°C before drying.

The sediment was dried in thin layers (0.5–1 cm) on aluminum foil in a vacuum oven at 45°C under a stream of purified air. Studies of the air-drying step revealed little or no loss (>90% recovery) of phthalates. The dried sediment was pulverized and homogenized with a mortar and pestel.

The dry sediment (5 g) was extracted ultrasonically (Branson 220 ultrasonic cleaning bath, 150 W) with methylene chloride at a 2:1 solvent to sediment ratio for 2 min at 25°C. Deuterated anthracene internal standard was added before the addition of the solvent. After the vial was centrifuged at 2500 g for 15 min, the supernatant was removed and the extraction was repeated two more times with fresh solvent. The three extracts were combined and concentrated with a stream of nitrogen to 200 μl.

The concentrated extracts were analyzed with no further clean-up steps by glass capillary (20 m, SE-52 WCOT) GC–MS (Hewlett Packard, model 5992) in the selected ion monitoring mode. Ion mass 149, characteristic of phthalate esters (except for dimethyl phthalate, base peak: m/e 163) was monitored for quantitation. The identities of individual phthalates were confirmed in each case by the coincident peak area ratios of two additional characteristic ions. Ion mass 188 was monitored for the detection of the internal standard, d-10 anthracene. Standard solutions of d-10 anthracene and phthalate esters were injected to determine the individual phthalate ester:d-10 anthracene response factors.

A single unfiltered water sample was extracted with methylene chloride at a 7:1 water to solvent ratio. The 100 ml extract was concentrated to 1 ml with a Buchi rotary evaporator. This extract was analyzed in the same manner as the sediment extracts.

Methylene chloride was distilled twice before use for extraction. All glassware was washed, rinsed and baked overnight in an annealing oven at 400°C. All exposed parts were covered by baked aluminum foil for storage. Matrix blanks consisting of Attaclay

(Englehard Chemicals, Attapulgus, GA) were used for laboratory background determinations. Pure standards of dimethyl (DMP), diethyl (DEP), diallyl (DAP), diisobutyl (DIBP), dibutyl (DBP), dihexyl (DHP), di(2-ethylhexyl) (DEHP) and di-n-octyl (DnOP) phthalate were obtained from Analabs (New Haven, CN) and Chem Service (West Chester, PA). Heptylnonyl (7,9P), octyldecyl (8,10P), diisodecyl (DIDP) and di-n-decyl (DnDP) phthalate were obtained from Tenneco Chemicals, Inc. (Saddlebrook, NJ).

The total organic carbon was determined with a Perkin Elmer carbon-hydrogen-nitrogen (CHN) analyzer after HCL treatment to remove the carbonate carbon. The sediment grain size analysis was performed using a rapid sediment analyzer (sand fraction) and a Coulter counter particle analyzer (silt-clay fraction) after inorganic and organic carbon was removed by HCL and H_2O_2 treatment, respectively.

RESULTS AND DISCUSSION

The geochemical data describing the sediment samples are in Table I. The particle size distribution data were plotted in a Shepard classification diagram (Figure 2)[11]. The majority of collected samples have a mean grain size smaller than 10 μm and cluster around the silty-clay classification region. This agrees with the sampling pattern since these samples were taken from the deeper channel portions of the river where fine sediments preferentially collect[7]. The only exceptions were the Chestertown Bridge (CB) and the Frye farm (FF) samples which have substantial amounts of sand and have mean grain sizes larger than 75 μm. These two sediments also have a lower organic carbon content. Therefore, they would likely have lower adsorption capacities for a given phthalate ester than the other samples. The concentrations reported for these sites should be considered low for comparison purposes.

Eleven phthalate ester species quantitated from Chester River, Morgan Creek, discharge pond sediment and discharge pond water are presented in Table II. The phthalate ester pattern at each site was then plotted as shown in Figure 3. The data are plotted as per cent abundance relative to the homologue of highest concentration.

In the discharge pond just beyond the phthalate ester plant outfall, the same distinctive pattern was found in the sediment as in

TABLE I

Location, particle size distribution, moisture and organic carbon content of Chester River sediment samples.

Site	Lat/Long	% H_2O	% C	Mean grain size	% sand	% silt	% clay	Classification
Pond	39°12′15″ / 76°04′45″	52	2.6	8.47	0.15	50.48	49.37	clayey silt
Frye Farm (FF) (Morgan Creek at Rt. 213)			1.6	3.67	68.05	12.74	19.21	clayey sand
Morgan Creek (MC) at Rt. 291			3.8	9.10	6.34	33.27	60.39	silty clay
Chestertown Bridge (CB)			1.3	1.48	84.93	6.11	8.96	sand
Site 7	39°09′13″ / 76°04′13″	52	2.8	9.49	3.49	30.58	65.93	silty clay
Site 6 Spaniard Point	39°05′44″ / 76°08′49″	57	2.8	9.37	1.82	29.77	68.41	silty clay
Site 5 Spaniard Point	39°05′52″ / 76°08′49″	51	2.3	10.46	0.00	19.14	80.86	clay

Site 4 Grays Inn Point	39°05′15″ 76°11′03″	53	2.4	8.18	6.21	44.07	49.72	silty clay
Site 3 Gordon Point	39°04′12″ 76°09′55″	49	2.4	7.69	20.62	31.25	48.12	sand-silt-clay
Site 2 Piney Point	39°02′18″ 76°09′55″	58	3.4	9.15	0.91	35.61	63.48	silty clay
Site 1 Buoy Rock	38°59′31″ 76°12′50″	57	2.9	9.06	3.44	34.84	61.72	silty clay
Site "R" Chester River, Mouth	39°02′54″ 76°16′06″	65	2.9	8.71	3.79	38.97	57.24	silty clay

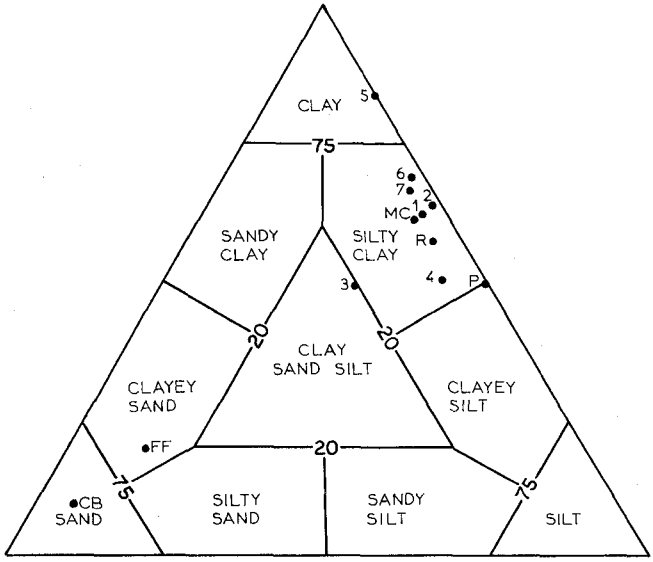

FIGURE 2 Shepard diagram showing the classification of sediment samples based on percentages of clay, silt and sand. Numerical values refer to the percentages defining the boundaries.

the water. They both consisted of higher molecular weight phthalates, with DEHP and DIDP being the major components. Analyses of sections of a sediment core of the pond revealed a sharp increase in phthalate concentration towards the sediment surface with no significant change in the phthalate ester distribution pattern. While the pond water contains waste water released only in recent months (the pond's mean residence time was calculated to be 30 days), the sediment concentrations represent the average input over several years. The close similarities of relative phthalate concentrations in the water and the sediment suggests that this array of phthalate esters can be considered constant and characteristic of the plant. This characteristic pattern might then be used as a tracer to determine the plant's contribution to the total phthalate ester pollution in the Chester River.

The pattern found in the pond is quite evident in the Frye farm sample, (FF) 2 km downstream. However, at the Morgan Creek site (MC) this pattern is lost. The DIDP peak was not detected at this site while DEP and DBP have joined DEHP as the dominant

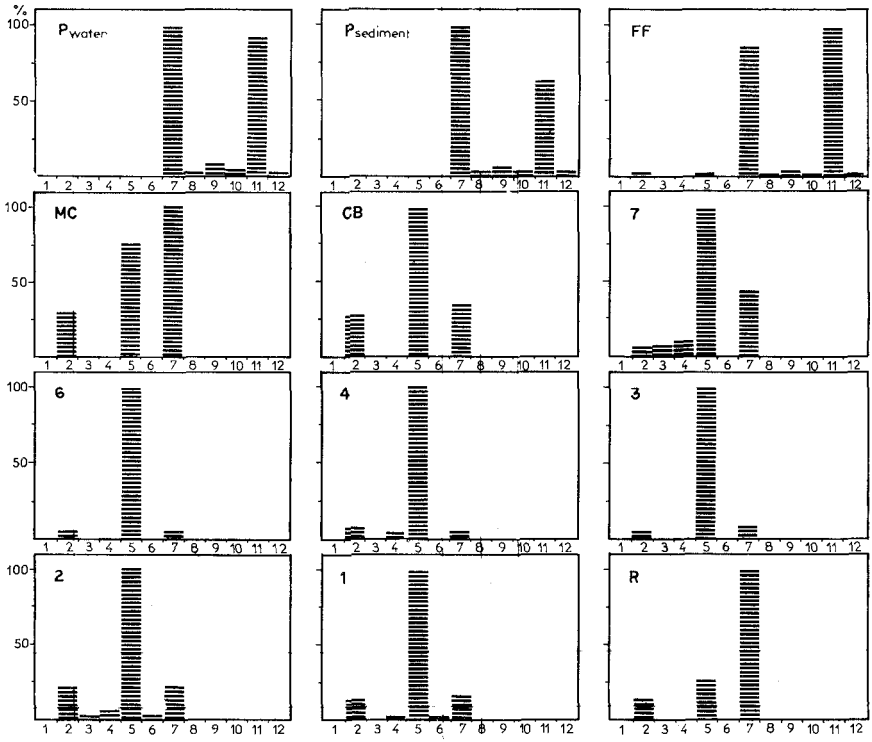

FIGURE 3 Phthalate ester distribution patterns in Chester river sediment. Per cent abundances are based on the highest concentration measured at each site (1=DMP, 2=DEP, 3=DPP, 4=DIBP, 5=DBP, 6=DHP, 7=DEHP, 8=DnOP, 9=7,9 P, 10=8,10 P, 11=DIDP, 12=DnDP).

species. From the Chestertown bridge to the region of highest oyster mortality at sites 4, 5 and 6, the pattern changes more slowly to one in which DBP is the single dominant species. According to a plant spokesman from the plasticizer plant, only relatively insignificant amounts of DBP have ever been produced at the Chestertown plant. This is supported by the minimal concentrations of DBP in the pond sediment. Also it is highly unlikely that the pattern shift from DEHP to DBP is a result of biodegradation or weathering of DEHP. DBP has not been shown to be a metabolite of DEHP. Studies suggest that bio-degradation of phthalate esters proceeds first to the phthalic half-ester (mono-2-ethylhexyl phthalate), then to phthalic acid[12,13].

TABLE II

Phthalate ester concentrations in Chester River sediments

Site	Phthalate ester concentrations (ppb ± standard deviation; (n))				
	DEP	DAP	DIBP	DBP	DHP, ppb
Pond sediment (TP) ($\times 10^3$)				0.2 ± 0.1 (3)	
Pond water					
Frye Farm (FF)	11 ± 2 (3)	< 2	< 1	59 ± 23 (4)	< 3
Morgan Creek (MC)	14 (2)			45 ± 8 (4)	
Chestertown Bridge (CB)	16 ± 1 (3)			49 ± 11 (6)	
Site 7	41 ± 21 (5)	4.3 ± 1.8 (5)	6.8 (2)	50 ± 11 (5)	
Site 6	40 ± 15 (5)	5.2 ± 2.3 (5)		900 ± 440 (5)	6.4 ± 1.3 (5)
Site 5	26 ± 5 (5)	3.5 ± 1.1 (5)	2.9 ± 0.7 (4)	560 ± 230 (5)	2.4 ± 0.5 (5)
Site 4	44 ± 10 (5)	2.5 ± 0.7 (4)	27.6 ± 13 (5)	740 ± 290 (5)	
Site 3	25 ± 2 (3)			430 ± 150 (5)	
Site 2	36 ± 16 (5)	5.5 ± 1.5 (5)	9.2 ± 4.2 (5)	186 ± 93 (5)	3.7 ± 0.9 (5)
Site 1	32 ± 12 (5)		3.5 ± 1.5 (5)	185 ± 79 (5)	3.5 ± 0.7 (5)
Site R	11 ± 2 (6)	1.8 ± 0.6 (4)	2.6 ± 0.9 (4)	28 ± 4 (6)	

Site	Phthalate ester concentrations (ppb ± standard deviation; (n))					
	DEHP	Dn OP	7,9 P	8,10 P	DIDP	Dn DP
Pond sediment (TP) ($\times 10^3$)	1200 ± 100 (5)	12 ± 3 (3)	33 ± 7 (3)	24 ± 4 (3)	690 ± 220 (3)	11 (2)
Pond water	110 (1)	1.0 (1)	3.2 (1)	1.4 (1)	102 (1)	< 1 (1)
Frye Farm (FF)	4800 ± 95 (5)	62 (2)	200 ± 12 (3)	210 ± 30 (3)	540 ± 17 (3)	59 (2)
Morgan Creek (MC)	53 ± 14 (4)	< 5	< 5	< 5	< 5	< 10
Chestertown Bridge (CB)	20 ± 9 (6)					
Site 7	22 ± 8 (5)					
Site 6	44 ± 4 (5)					
Site 5	25 ± 3.9 (5)					
Site 4	23 ± 5 (5)					
Site 3	32 ± 13 (5)					
Site 2	42 ± 3 (5)					
Site 1	45 ± 5 (5)					
Site R	110 ± 9 (6)					

(n) = number of replicates (individual extractions); ppb = ng/g of dry sediment.

In addition, DBP degrades and is metabolized faster than DEHP under aerobic conditions[2,12]. Other losses due to volatilization or hydrolysis should not significantly affect the distribution of phthalates in the water[14].

The pattern again changes from site 4 to site R to one showing an increasing contribution by DEHP. From these patterns it appears that beyond the Frye farm site, the phthalates discharged from the plant do not contribute significantly to the total phthalate ester pollution in the river. Rather, the changing patterns along the axis of the river indicate the likelihood of multiple sources of phthalate esters. The pattern at site R at the mouth of the river is likely the result of pollution from the Chesapeake Bay transported into the river by fine sediment in the sub-surface water. In fact, this pattern is quite similar to that which we have reported in sediment from the center of the Chesapeake Bay[15]. A different pattern is evident in sites 4, 5, and 6 indicating an alternate source for the pollution in the oyster mortality zone. The source appears either to be along the Langford Creek, the Corsica River or between sites 6 and 7.

The sediment concentrations of DEHP and DBP were plotted as a function of distance from the mouth of the Chester River in Figure 4. The DEHP concentration decreases 4 orders of magnitude within a distance of 8 km between the pond and the Morgan Creek site. The Morgan Creek would be expected to dilute the plant effluent by a factor of 100. Yet the sediment reflects a factor of 10,000 difference in water concentrations at the two sites. The difference is likely due to the effectiveness of the pond to function as a tertiary waste-treatment facility.

Beyond the Morgan Creek, the DEHP concentration shows little change, ranging from 20 to 45 ppb, until a rise to 110 ppb is encountered at the mouth of the river. The elevated concentration of DEHP at the mouth of the river can be explained by the model proposed by Munson[16] for the transport of chlorinated hydrocarbons from the Chesapeake Bay up the Chester River. Hydrophobic organics adsorbed to the fine sediment are carried by the bottom waters of the estuarine bimodal flow system in the direction opposite to the flow of the surface waters. This model is further supported by measurements of polynuclear aromatic hydrocarbon pollution concurrent with this work which showed the highest concentrations at the mouth of the Chester River and a decrease with distance upstream[14].

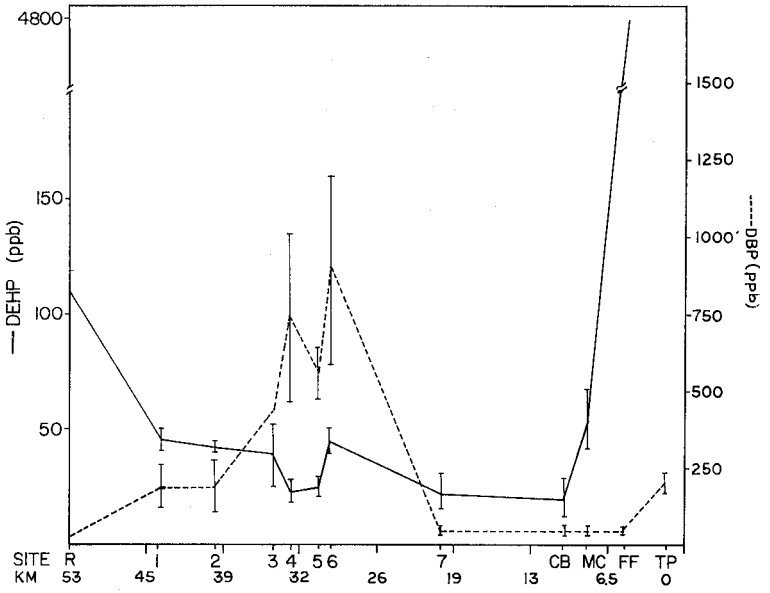

FIGURE 4 Variation of DBP and DEHP concentrations in sediment as a function of distance from the plasticizer factory. Error bars represent one standard deviation.

The variation of DBP concentrations in the river contrasts markedly with the previous model. Figure 4 shows a concentration maximum at sites 4, 5 and 6 and minima at the Chester River mouth and the Morgan Creek. Again, as with the phthalate distribution patterns, this indicates a source of DBP near the confluence of the three tributaries of the river. The concentrations decrease with distance along the upstream and downstream directions from this reference point. These concentrations of phthalate esters found in the Chester River sediment, ranging from 2 to 900 ppb should be compared to 1 to 20 ppm found in Dutch rivers[17], 100 to 200 ppb in Lake Superior[18], 48 to 11,400 ppb in the River Mersey, U.K.[9] and 2 to 176 ppb in the Gulf of Mexico[19].

Short sediment cores (8–10 cm) from the Chester River sites were sliced into 1-cm sections. These were analyzed to determine whether a sudden elevation in sediment concentration had occurred due to a catastrophic spill during the previous decade, assuming relatively little sediment disruption. The results of these analyses are plotted as

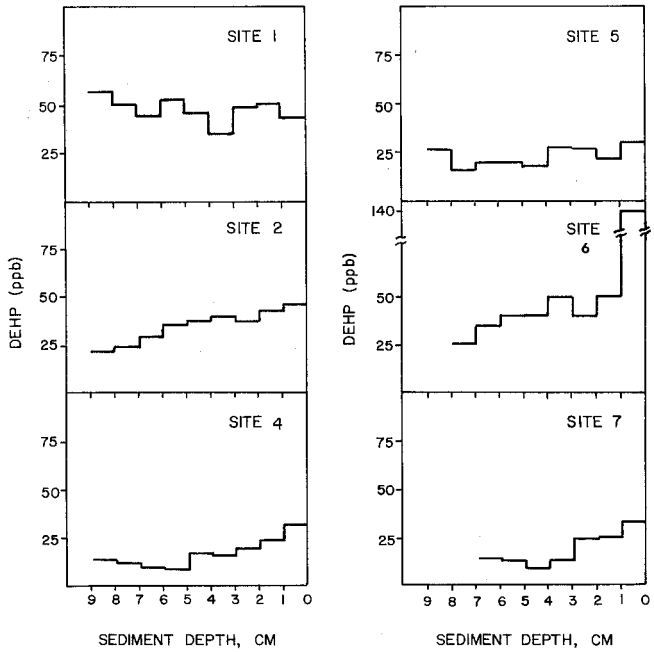

FIGURE 5 DEHP concentration variations with depth of Chester river sediment.

a function of sediment depth in Figures 5 and 6. The DEHP concentrations do not vary greatly in the top 8 cm but cores 2, 4, 6 and 7 do show a slight increase approaching the surface. The DBP concentrations, however, are quite different. The cores contain sections of elevated DBP concentrations 1 to 5 cm below the surface of the sediment, varying in length from 1 to 4 cm. These sharp variations are most likely not the result of physical erosion or bioturbation since these processes tend to diffuse changes rather than accentuate them. These cores suggest that this DBP pollution is a result of one or more short-lived pollution episodes and not due to a continuous build-up.

CONCLUSION

By applying three aproaches to analyze the collected data, phthalate esters from an industrial source were not found to contribute

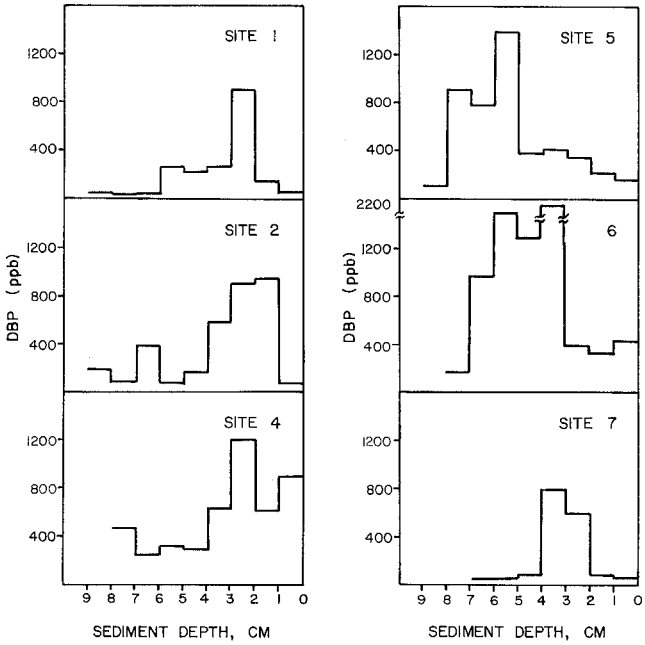

FIGURE 6 DBP concentration variation with depth of Chester river sediment.

significantly to the total phthalate ester pollution in the Chester River. The phthalate ester pattern of the plasticizer plant extends only a few kilometers into the Morgan Creek. In fact, the DEHP concentrations decrease so sharply that the amount of DEHP entering the Chester River from the plant appears to be lower than that entering the river from the Chesapeake Bay.

No evidence of any catastrophic spill from the plant was found in sediment cores from the river. The DEHP concentrations show only a slight positive increase toward the surface of the sediment. Rather, the data indicate an alternate source. The phthalate ester pattern in the oyster mortality zone is distinctly different from that of the plasticizer plant or at the entrance to the river. The DBP concentration maximum of this pattern indicates a source near the confluence of the Langford Creek, the Corsica River, and the main channel of the Chester River. The sharp concentration variations of DBP in the sediment cores suggest that this pollution is a result of isolated episodes rather than a long-term continuous discharge.

These results do not necessarily mean that phthalate esters caused the oyster kill. Rather, they are an indication that an event did occur which roughly coincides chronologically with the loss of the oysters in the Chester River.

Acknowledgement

The authors express appreciation to Darlene Wells for performing the particle size analyses.

This work was supported in part by the Maryland Department of Natural Resources, the National Science Foundation (Grant CHE-77-11313), and GC–MS facility support from the University of Maryland Seagrant Office and Biomedical Research Support Grant, NIHPHS No. RR-07042.

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