

(i.e., steady-state concentration) in the fish. Halter and Johnson showed that fathead minnows (*Pimephales promelas*) exposed to PCBs for 32 days at approximately 20 °C had not yet achieved a steady-state concentration (9).

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Phthalate Ester Concentration Variations in Dated Sediment Cores from the Chesapeake Bay[†]

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■ Concentrations of several phthalate esters were measured in dated sediment cores to determine their environmental accumulation over the past century. The analytical constraints of the limited sample size of the core sections and of laboratory contamination were overcome by taking advantage of the mass spectrometer as a highly selective and sensitive detector. All phthalates detected showed definite increases in concentration toward the sediment surface. These rates of accumulation were correlated to the respective synthetic production rates in the U.S. for the corresponding years. The accumulation rate of bis(2-ethylhexyl) phthalate in one of the sediment cores showed a very close parallel to its production rate ($R = 0.96$).

Introduction

Phthalate esters are some of the most ubiquitous and commonly reported organic compounds in the near coastal marine environment (1). The majority of phthalate esters found in the environment are considered to be due to anthropogenic inputs from various sources which include sewage treatment plants (2), paper and textile mills (3), and refuse incineration (4), as well as plasticizer chemical plants (5). There also have been claims of the natural occurrence of phthalate esters (6), although most of these studies lack sufficient proof of the absence of environmental pollution or laboratory contamination.

While the input levels to the environment of these compounds from possible natural sources most likely have

not increased during the past century, anthropogenic phthalate esters would be expected to increase in response to their increased use. Since the most highly produced phthalate ester, bis(2-ethylhexyl) phthalate (DEHP), has been shown to be detrimental to the reproduction of marine organisms at parts per billion (ppb) levels in water (7) and has recently been found to be carcinogenic in mice (8), it is important to know how rapidly the environmental level of DEHP and other phthalate esters is increasing.

Historical records of other anthropogenic substances such as lead (9), trace metals (10), chlorinated hydrocarbons (11, 12), and polynuclear aromatic hydrocarbons (PAH) (12-15) have been found in strata of sediment deposited in the past century. The historical changes in phthalate ester levels should also be recorded in sediment provided the phthalates persist after they are adsorbed and deposited with the sediment. Phthalate esters have been shown to resist biodegradation under anaerobic conditions (16). These conditions are found within the first few centimeters of sediment in many areas of the Chesapeake Bay (17).

Phthalate esters were introduced to the high polymer materials market in the 1920s, and DEHP was first synthesized in 1933 (18). The production rates of total phthalates, DEHP, dibutyl phthalate (DBP), and diethyl phthalate (DEP) (19) are shown in Figure 1. While the rate of DEHP production has shown a rapid increase since 1949 when its production figures were first reported, DBP and DEP have shown lesser increases since 1945. The plasticizer industry predicts future yearly increases of 6% in plasticizer production in the 1980s (20). Two dated sediment cores were analyzed in the present study in order to determine the historical rates of phthalate ester influx to the Chesapeake Bay. A highly sensitive and selective gas chromatographic-mass spectrometric (GC-MS) analytical scheme which uses a minimal number of steps and

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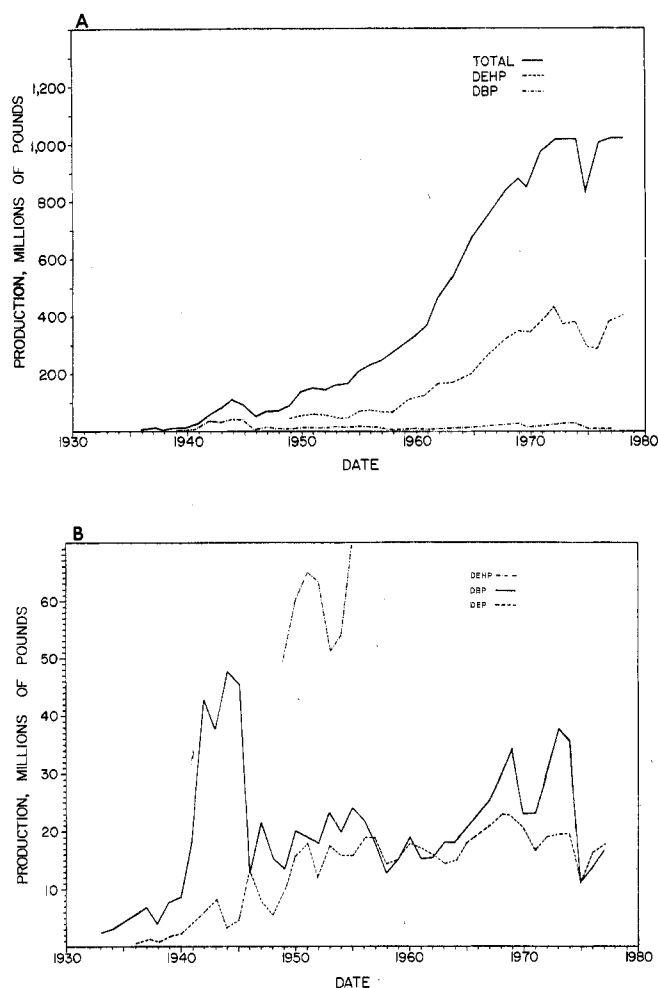


Figure 1. Phthalate ester annual production rates (19), millions of pounds per year.

reagents was employed (5). In this way small samples sizes, limited by the size of the core slices, can easily be analyzed with low background levels. This procedure avoids laboratory contamination problems that are commonly encountered with phthalate ester determinations (21).

Experimental Section

Subsurface sediment cores were collected with a gravity corer aboard the R/V *Retriever* in June 1979, at the sites illustrated in Figure 2 (no. 55 and 62). These sediment cores were chosen for their lack of apparent bioturbation as determined from radiographs of the core structure. Duplicate cores were dated by using sedimentation rates determined by the ^{210}Pb constant initial concentration (CIC) method (22).

The two cores for organic analysis were cut into 10-cm cylindrical sections. The external 1-cm portion of each 6.7-cm diameter slice that had closest contact with the cellulose acetate butyrate core liner was removed. This outer portion was used for total organic carbon analysis. The inner portions were placed in clean aluminum weighing boats and dried in a vacuum oven at 45 °C for 48 h with a stream of purified air. The stream of air for drying core 55 was purified by a trap consisting of sodium sulfate and XAD-2 resin. An additional trap of charcoal was added before the drying of core 62. Spiked sediment samples subjected to the drying process were found to give recoveries of $90 \pm 7\%$, $95 \pm 6\%$, and $95 \pm 2\%$ for DEP, DBP, and DEHP, respectively. The dried sediment (1–2% residual moisture content) was pulverized and homogenized with a mortar and pestel.

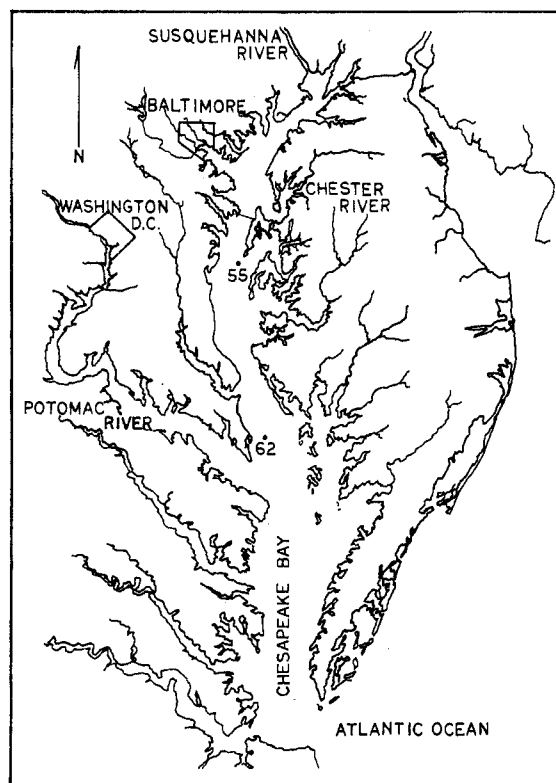


Figure 2. Map of the Chesapeake Bay illustrating sampling sites 55 and 62 (site 55: $38^{\circ}48'30''$ N, $76^{\circ}23'30''$ W; site 62: $38^{\circ}10'30''$ N, $76^{\circ}14'$ W).

The dry sediment 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 at the start of the extraction. After the vial was centrifuged at 2500 g for 15 min, the liquid supernatant was removed, the extraction was repeated twice more with fresh solvent, and the three extracts were combined. Extraction recoveries from spiked sediment were $96 \pm 4\%$, $90 \pm 4\%$, and $95 \pm 10\%$ for DEP, DBP, and DEHP, respectively.

Concentrated extracts (200 μL) were analyzed, with no further cleanup, 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 (DMP), monitored at m/e 163), was monitored for quantitation. The identities of individual phthalates were confirmed in each case by the coincident peak ratios of two additional characteristic ions. Fragment ions of selected PAH's were also monitored and quantitated (m/e 228 for 1,3-benzanthracene, chrysene, and triphenylene).

Methylene chloride was distilled twice before use for extraction. All glassware was washed, rinsed, and baked overnight in an annealing oven at 400 °C. Matrix blanks consisting of Fuller's earth (Attaclay, Englehard Chemicals, Attapulgus, GA), treated at 1000 °C and therefore practically organic-free, were used for laboratory background determinations. This material was baked overnight at 400 °C before use. Portions of this material equal to the sample size were carried through the entire analytical procedure, including the drying step. The possibility of phthalate ester migration from the plastic core liner into the wet sediment was ruled out by the results of an examination of the inner and outer portions of deeper sediment slices. These showed no increase in concentration closest to the liner. A more detailed description of the phthalate ester extraction and analysis procedure is in

Table I. Phthalate Ester Concentrations in Sediment Core Sections

Core 55 (ppb \pm Standard Deviation) (n) ^a									
core depth, cm	dates	%C	DEP (\pm 8)	DPP	DAP	DIBP	DBP	DHP	DEHP (\pm 24)
0-10	1974-1979	3.06	42 (3)	13 (2)	<1	5.6 (2)	89 \pm 7 (3)	5.6 (1)	180 (3)
10-20	1968-1974	2.98	49 (2)	13 (1)		8.6 (2)	82 \pm 8 (3)	<3	145 (2)
20-30	1963-1968	3.02	35 (2)	12 (1)	8.7 (1)	<1	66 \pm 15 (3)		124 (2)
30-40	1957-1963	2.80	18 (2)	7.0 (1)	9.2 (1)	4.3 (1)	93 \pm 30 (3)		84 (2)
40-50	1952-1957	2.56	19 (2)	4.0 (1)	4.2 (1)		66 \pm 9 (3)		34 (2)
50-60	1946-1952	3.45	18 (2)	6.2 (2)	8.3 (1)	4.3 (1)	53 \pm 5 (3)		28 (2)
60-70	1940-1946	2.78	34 (2)	5.5 (1)	8.8 (2)		66 \pm 13 (3)	3.5 (1)	21 (2)
70-80	1935-1940	2.82	19 (2)	3.3 (1)	7.0 (1)	3.6 (2)	50 \pm 4 (3)	4.0 (1)	22 (2)
80-90	1929-1935	2.87	22 (2)	<1	6.8 (2)	3.0 (1)	49 (2)	2.9 (1)	20 (2)
90-100	1923-1929	2.27	19 (2)		9.2 (2)	13.4 (2)	34 \pm (3)	4.6 (1)	29 (2)
blank			16	<0.3	<0.5	<0.3	4	<0.5	<0.5
Core 62 (ppb \pm Standard Deviation) (n) ^b									
core depth, cm	dates	%C	DEP	DPP		DBP		DEHP	
0-10	1972-1979	2.81	22 (2)	5.9 (2)		27 (2)		12 (1)	
10-20	1964-1972	2.33	16 (2)	3.3 (2)		38 (2)		7.3 (1)	
20-30	1956-1964	2.26	15 (2)	2.8 (2)		32 (2)		9.9 (1)	
30-40	1948-1956	2.28	14 (2)	1.0 (1)		40 (2)		10.7 (1)	
40-50	1940-1948	2.35	14 (2)	2.9 (1)		32 (2)		5.2 (1)	
50-60	1932-1940	2.27	13 (2)	2.6 (2)		37 (2)		7.4 (1)	
60-70	1924-1932	2.25	9.0 (2)	1.6 (2)		19 (2)		<2.6	
70-80	1916-1924	2.19	5.8 (1)	1.4 (1)		33 (2)			
80-90	1908-1916	2.15	5.2 (1)	<1		32 (2)			
90-100	1900-1908	2.18	6.4 (1)			21 (2)			
100-110	1892-1900	1.95	3.3 (1)			20 (2)			
110-120	1884-1842	1.92	3.1 (1)			16 (2)			
blank			1	<0.3		1		<0.5	

^a Deposition rate: 17.8 mm/year (10 cm = 7.9 year); n = number of replicates (individual extraction); ppb = ng/g of dry sediment. ^b Deposition rate: 12.6 mm/year (10 cm = 5.6 year).

preparation and will be published elsewhere.

Results and Discussion

The quantitative results of the analysis of seven phthalate esters in 10-cm sections of sediment cores from sites 55 and 62 are presented in Table I. Also included are the total carbon content and the inclusive dates calculated for each section.

Higher phthalate ester concentrations were found at the site closest to Baltimore Harbor and the Susquehanna River. These are areas of high industrial activity and dense population, and they are both established sources of organic chemical pollution in the Bay (23, 24).

The Kent Island dredge spoil disposal area is approximately 25 km north of site 55, and this is not expected to have a great effect on either coring site. Contour maps of trace metals in the Bay constructed by Helz et al. (25) do not show anomalously elevated concentrations in the region near site 55 which might result from movement of this disposed material. In addition, Zabawa and Schubel (26) noted that during Hurricane Agnes in June 1972 the amount of sediment that accumulated south of the Bay bridge (10 km north of site 55) was only a few millimeters in thickness.

The concentrations of DEHP, DBP, and DEP are plotted relative to depth and age of respective sediment layers in Figure 3. All of the phthalates show a definite increase in concentration toward the sediment surface, with DEHP in core 55 showing the most dramatic increase. These profiles suggest that these phthalate esters are of anthropogenic origin since they chronologically follow the increasing commercial use of these compounds (Figure 1). However, low levels of phthalates are found at sediment depths that predate their initial production. Several possible factors could explain their occurrence: (1) incorrect dating of sediment strata; (2) natural production

of phthalate esters; (3) laboratory contamination; (4) transport of phthalates by burrowing organisms or physical mixing.

The sedimentation rates used to determine the geochronology of the sediment strata were based on well-tested techniques of excess ²¹⁰Pb measurement (22, 27). These ²¹⁰Pb activity profiles are published elsewhere (25). Comparisons to previously published reports (10, 28, 29) show that the sedimentation rate of 17.8 mm/year at site 55 (38°48'30" N, 76°23'30" W) is roughly the mean of the measurements of 10 and 30 mm/year made by Goldberg et al. (10) in the same vicinity (38°56'80" N, 76°25'18" W and 38°57'43" N, 76°22'49" W, respectively). There are no sedimentation rates published for sites within 40 km of site 62 in previous work.

To add independent evidence of age to the dating of the sediment strata, profiles of representative PAH concentrations were determined to act as event markers during the past century. These concentrations in cores 55 and 62 are presented in Table II. The concentrations of benz[a]anthracene, chrysene, and triphenylene (C₁₈H₁₂) were plotted as histograms as a function of depth, normalized to each other according to corresponding dates in Figure 4. The two core profiles, which are representative of the other PAH species measured, correlate well with each other. They are also remarkably similar to results of similar experiments in the literature. Grimmer and Bohnke (13), Pahl and Carpenter (14), and Hites et al. (15) published profiles of PAH's in sediments from northern Germany, northwest Washington, and Rhode Island, respectively. Their profiles and those from this study exhibit two major maxima after a precipitous rise beginning between 1900 and 1910. One maximum occurs between 1915 and 1925 and the other between 1940 and 1950. These investigators agree in that the major source of these PAH's is the combustion of fossil fuels, especially

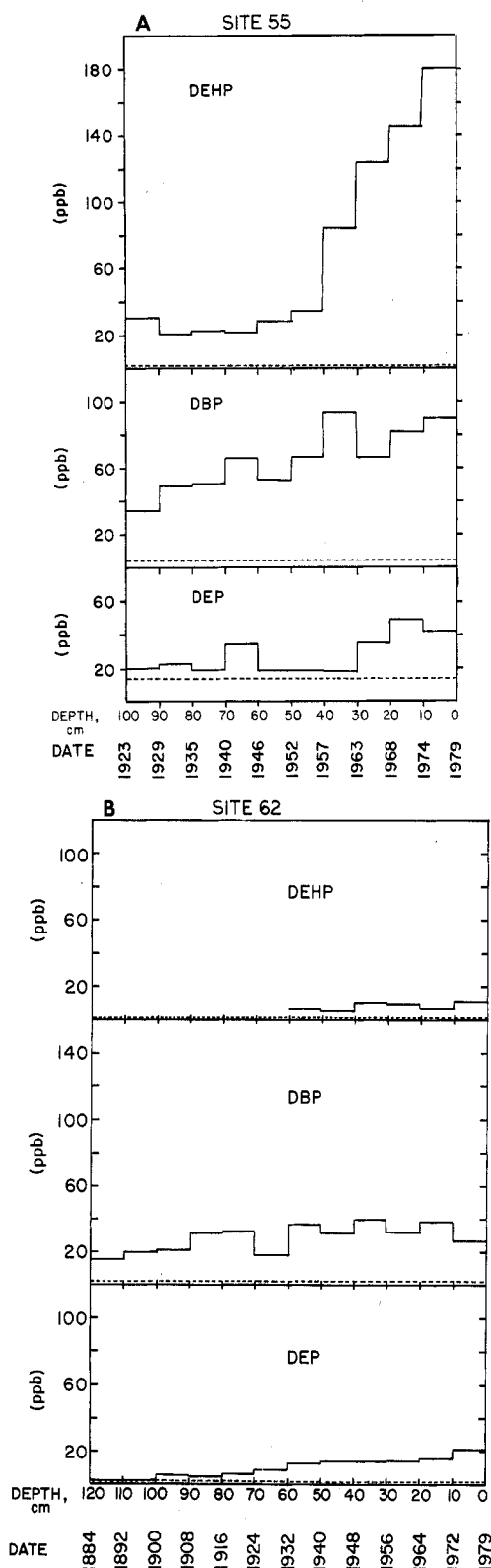


Figure 3. Variation of phthalate ester concentrations as a function of sediment depth and time. Dates were estimated by ^{210}Pb dating methods (22). The dotted lines represent background levels measured during the analysis of each core.

coals (13, 15). The production of bituminous coal and lignite in the U.S. parallels this pattern with a rapid increase from 1900 to 1925, followed by a minimum around 1931 and another maximum between 1940 and 1959 (30). These figures and results strongly support the deposition rates established for these cores. The dates are therefore considered to be accurate to within 5 years. The PAH

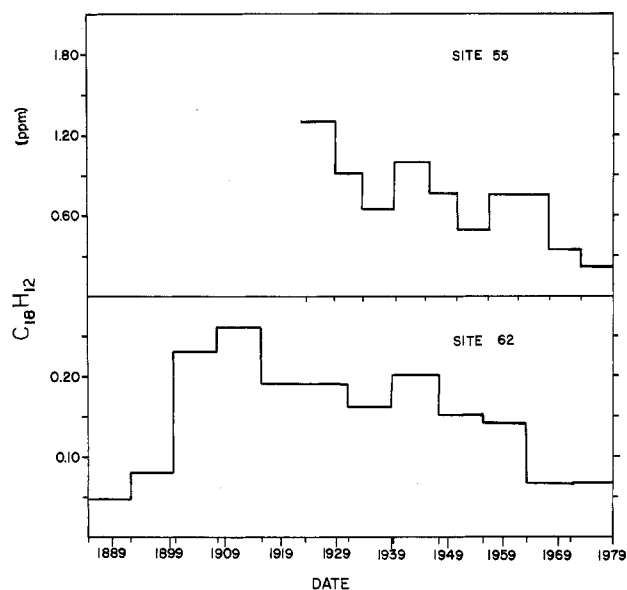


Figure 4. Variation of the summed concentrations of benz[a]-anthracene, chrysene, and triphenylene ($\text{C}_{18}\text{H}_{12}$) as a function of sediment depth and time at sites 55 and 62.

patterns do not correlate with those of phthalate esters. Separate sources for these two compound classes is evident.

While the constant concentration value of DEHP (29 ppb) in deeper sections of core 55 may suggest natural occurrence of this product, the disappearance of DEHP in core 62 (below the limit of detection, <2.5 ppb) in turn discourages such a conclusion. On the other hand, DBP does not show such a disappearance, and the possibility of its natural occurrence cannot be simply discarded. This is supported by Miyoshi and Harada's (31) demonstration of DBP production from acetylene precursors by a soil bacterium.

The results of carefully measured blanks and the analysis of inner- and outer-core portions do not support laboratory contamination as the source of measured DEHP or DBP in deep strata. However, the background levels of DEP found in core 55 (19 ppb) can be attributed to laboratory contamination (16 ppb). These DEP blank levels were dramatically decreased in core 62 (1 ppb) after the addition of charcoal to the sediment-drying chamber trap.

Finally, the explanation most consistent with the data is that phthalates, in trace amounts, were transported to lower portions of the core via restricted burrowing of benthic organisms and/or diffusive migration without disrupting the basic structure of the upper sediment strata. Venkatesan et al. (12) came to similar conclusions in explaining the occurrence of polychlorinated hydrocarbons in deep core sediments from the Southern California Bight (San Pedro Basin). The defined profiles of the phthalates and PAH's are indications that extensive mixing has not occurred relative to the 10-cm sampling interval. Goldberg et al. (10) estimated the mixed zone in sediment near site 55 to be approximately 5 cm, which is half the thickness of the core sections analyzed.

Regardless of whether the background concentrations are due to sediment layer mixing or natural production, the phthalate ester gradient measured in the sediment cores parallels the reported phthalate ester production rate for the corresponding years. This is best illustrated by the DEHP profile in core 55, which is superimposed on the production rate of the same compound in Figure 5. To quantitate the goodness of this fit, correlation analyses were performed for DEHP, DBP, and DEP in each core.

Table II. Variation of PAH Concentrations in Sediment Core Sections (ppb \pm Standard Deviation) (*n*)^a

core depth, cm	dates	phen + anthr	fluor	pyr	b[a]a + chry
Core 55 ^b					
0-10	1974-1979	580 \pm 39 (3)	320 \pm 40 (3)	300 (2)	210 \pm 20 (3)
10-20	1968-1974	600 (2)	430 (2)	420 (2)	330
20-30	1963-1968	1200 (2)	530 (2)	580 (2)	740 (2)
30-40	1957-1963	960 (2)	640 (2)	710 (2)	730 (2)
40-50	1952-1957	540 (2)	430 (2)	400 (2)	490 (2)
50-60	1946-1952	1500 (2)	810 (2)	730 (2)	750 (2)
60-70	1940-1946	1800 (2)	870 (2)	770 (2)	990 (2)
70-80	1935-1940	1200 (2)	920 (2)	740 (2)	480 (2)
80-90	1929-1935	1400 (2)	900 (2)	750 (2)	900 (2)
90-100	1923-1929	1500 (2)	870 (2)	600 (2)	1300 (2)
Core 62 ^c					
0-10	1972-1979	110	73 (2)	50 (2)	66 (2)
10-20	1964-1972	86	100 (2)	78 (2)	65 (2)
20-30	1956-1964	210	68 (2)	45 (2)	140 (2)
30-40	1948-1956	220	160 (2)	74 (2)	150 (2)
40-50	1940-1948	240	130 (1)	68 (1)	200 (1)
50-60	1932-1940	250	160 (1)	99 (1)	160 (1)
60-70	1924-1932	200	160 (1)	130 (1)	190 (1)
70-80	1916-1924	240	170 (1)	140 (1)	190 (1)
80-90	1908-1916	320	280 (1)	220 (1)	260 (1)
90-100	1900-1908	210	220 (1)	150 (1)	230 (1)
100-110	1892-1900	83	80 (1)	66 (1)	77 (1)
110-120	1884-1892	31 (1)	30 (1)	30 (1)	47 (1)

^a *n* = number of replicates (individual extractions); ppb = ng/g of dry sediment. ^b Sedimentation rate, 17.8 mm/year (10 cm = 5.6 year); phen = phenanthrene, anthr = anthracene, fluor = fluoranthene, pyr = pyrene, b[a]a = benz[a]anthracene, chry = chrysene. ^c Sedimentation rate, 12.6 mm/year. (10 cm = 7.9 year).

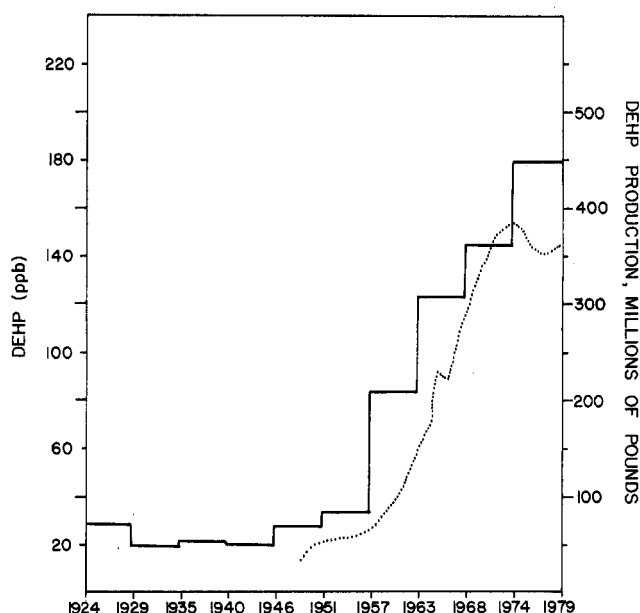
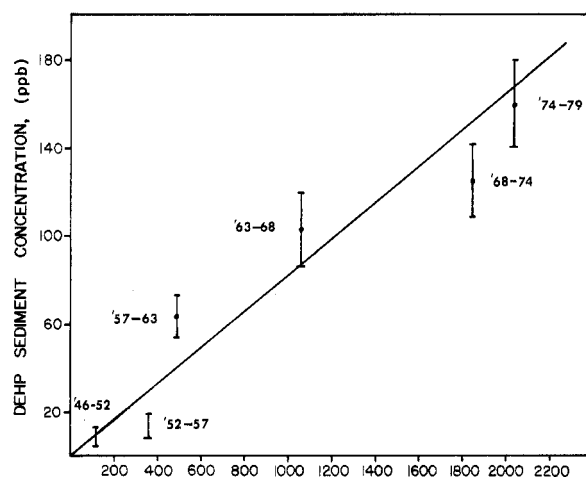


Figure 5. Profile of the annual DEHP production rate (---) superimposed on the DEHP sediment concentration (—) at site 55.

The lowest concentration for each compound in each core was assumed to be background, and it was subtracted from the other concentrations. In order to take into account the variable time delay assumed for the release of phthalates to the environment after production, the production rates were smoothed over 5-year periods with a 2-year lag. According to the sediment deposition rates, each 10 cm core 55 and core 62 corresponds to 5.6 and 7.9 years, respectively. Therefore, the production levels corresponding to each 10-cm section were calculated by summing fractional quantities covering either every 5.6 or every 7.9 years.

A double-correlation plot relating DEHP concentrations in core 55 and DEHP production is presented in Figure 6. The correlation coefficient of 0.96 indicates a close



DEHP PRODUCTION, MILLIONS OF POUNDS (SUMMED EVERY 5.6 YEARS)

Figure 6. Correlation of DEHP sediment concentration at site 55 with the synthetic production of DEHP during the inclusive dates.

relationship. The DEHP concentrations in core 62 were too low to make a similar correlation. The correlations for DEP and DBP are not quite as strong as DEHP; 0.83 and 0.60 for DEP in cores 55 and 62, respectively, and 0.40 for DBP in both cores. However, the sediment profiles for both compounds do show slightly increasing trends, which, like the production rates, rise slower than DEHP and are detected prior to the appearance of DEHP.

Conclusion

The analytical feasibility of the study of ppb levels of phthalate esters in small-sized samples has been demonstrated. This same technique can be simultaneously applied to other moderately volatile, slightly soluble and persistent compound classes by detection of properly selected characteristic fragment ion species.

Although the data in the study are somewhat limited, several significant implications are evident and further

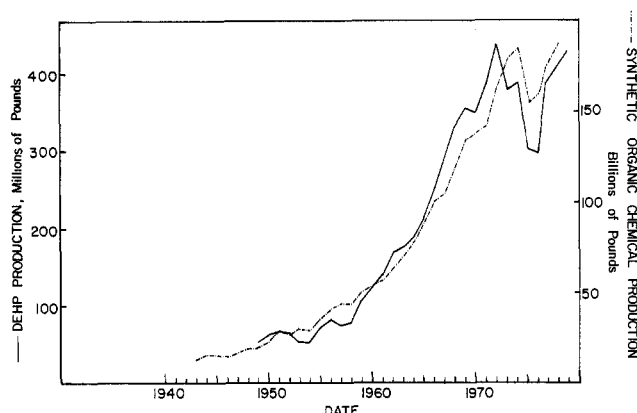


Figure 7. Comparison of the annual production of DEHP (millions of pounds) to the annual production of synthetic organic chemicals (billions of pounds).

verification of the results is warranted. The marine life in the Chesapeake Bay has been exposed to phthalate esters since the 1940s. The DEHP concentration, which appears to be originating in the northern portion of the Bay, is increasing in direct proportion to the synthetic production rate. Future concentration increases are predicted based on the projected increases in industrial production. If the current yearly increases in production (6%/year) do continue, the DEHP pollution in the Bay would double in about 12 years.

The presence of anthropogenic phthalate esters may indicate the presence of other more toxic, synthetic chemicals. The comparison of the annual production of DEHP to that of total synthetic chemicals from 1943 to 1978 (19) is presented in Figure 7. The strong correlation between the two curves indicates that the profile of DEHP pollution not only parallels the production rate of DEHP but the total production rate of synthetic organic chemicals as well. DEHP may therefore be a useful indicator compound in sediment strata of dispersed or aggregate synthetic chemicals which affect the environment, a process that seems to have begun about 3 decades ago.

Acknowledgments

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