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Abstract

Municipal wastes discharged through deepwater submarine outfalls since 1937 have contaminated sediments of the Palos Verdes Shelf. A site approximately 6–8 km downcurrent from the outfall system was chosen for a study of the diagenetic fate of organic contaminants in the waste-impacted sediments. Concentrations of three classes of hydrophobic organic contaminants (DDT + metabolites, polychlorinated biphenyls (PCBs), and the long-chain alkylbenzenes) were determined in sediment cores collected at the study site in 1981 and 1992. Differences between the composition of effluent from the major source of DDT (Montrose Chemical) and that found in sediments suggests that parent DDT was transformed by hydrolytic dehydrochlorination during the earliest stages of diagenesis. As a result, p,p'-DDE is the dominant DDT metabolite found in shelf sediments, comprising 60–70% of ΣDDT. The p,p-DDE/p,p'-DDMU concentration ratio decreases with increasing sub-bottom depth in sediment cores, indicating that reductive dechlorination of p,p'-DDE is occurring. Approximately 9–23% of the DDE inventory in the sediments may have been converted to DDMU since DDT discharges began ca. 1953. At most, this is less than half of the decline in p,p'-DDE inventory that has been observed at the study site for the period 1981–1995. Most of the observed decrease is attributable to remobilization by processes such as sediment mixing coupled to resuspension, contaminant desorption, and current advection. Existing field data suggest that the in situ rate of DDE transformation is 10^2–10^3 times slower than rates determined in recent laboratory microcosm experiments (Quensen, J.F., Mueller, S.A., Jain, M.K., Tiedje, J.M., 1998. Reductive dechlorination of DDE to DDMU in marine sediment microcosms. Science, 280, 722–724.). This explains why the DDT composition (i.e. o,p'-, p,p'-isomers of DDE, DDD, DDT) of sediments from this site have not changed significantly since at least 1972. Congener-specific PCB compositions in shelf sediments are highly uniform and show no evidence of diagenetic transformation. Apparently, the agents/factors responsible for reductive dechlorination of DDE are not also effecting alteration of the PCBs. Two types of long-chain alkylbenzenes were found in the contaminated sediments. Comparison of chain length and isomer distributions of the linear alkylbenzenes in wastewater effluent and surficial sediment samples indicate that these compounds undergo biodegradation during sedimentation. Further degradation of the linear alkylbenzenes occurs after burial despite relatively invariant isomer compositions. The branched alkylbenzenes are much more persistent than the linear alkylbenzenes, presumably due to extensive branching of the alkyl side chain. Based on these results, p,p'-DDE, PCBs, and selected branched alkylbenzenes are sufficiently persistent for use in molecular stratigraphy. The linear alkylbenzenes may also provide information on

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depositional processes. However, their application as quantitative molecular tracers should be approached with caution. Published by Elsevier Science B.V.

Keywords: DDT; PCBs; diagenesis; aromatic hydrocarbons; sediment cores; Palos Verdes Shelf

1. Introduction

The Palos Verdes Shelf off Los Angeles, CA, has been the subject of intensive biological, geochemical, and geophysical investigations for nearly 30 years. Studies initiated in the late 1960s/early 1970s led to recognition that municipal wastewater effluent discharged from submarine outfalls operated by the Los Angeles County Sanitation Districts (LACSD; Fig. 1) was impacting the local ecosystem (cf., Refs. in SCCWRP, 1973; Mearns et al., 1991). This and other evidence of coastal degradation led sanitation authorities to form the Southern California Coastal Water Research Project (SCCWRP), an organization whose mission is to assess the effects of human activity on the ecosystem off southern California. Somewhat later (1981), the LACSD initiated biennial benthic sediment chemistry surveys of the Palos Verdes Shelf. The studies of SCCWRP, the LACSD, and many other researchers have resulted in a massive amount of data on the distribution of inorganic and organic contaminants in sediments and biota at this site. Many of these results were summarized in the proceedings of a sediment dynamics workshop held in 1987 (LACSD, 1988). More recently, the US Geological Survey (USGS) undertook a large multidisciplinary research program, the principal objectives of which were: (1) to map the spatial distribution of specific organic pollutants (Lee, 1994a) and (2) to predict the fate of the contaminated sediment deposit (Drake et al., 1994). The present work was initiated as part of the latter objective. The fate of the deposit is of considerable interest because of the potential for long-term effects on the indigenous biota and questions concerning the persistence of the contaminants (Renner, 1998).

The organic contaminants of greatest concern on the Palos Verdes Shelf are DDT and the polychlorinated biphenyls (PCBs). These substances were released by the LACSD in association with municipal wastewater for a period spanning roughly 45 years. [The discharge histories of DDT and the PCBs are discussed in detail by Eganhouse and Pontolillo (2000).] Based on analyses of sediment cores collected by the USGS in 1992 and the LACSD in 1989, Lee (1994a) and Stull et al. (1996) have described the mass distribution of p,p'-DDE (I, Appendix A) and PCBs at this site. The contaminants are concentrated in fine-grained sediments deposited on the shelf and slope to water depths of at least 500 m. They have also been found in several offshore basins (MacGregor, 1976; Reed et al., 1977; Venkatesan, 1998; Venkatesan et al., 1980; Zeng and Venkatesan, 1999), suggesting the importance of farfield transport. On the Palos Verdes Shelf, an effluent-affected layer of variable thickness (5–> 60 cm thick) overlays native sediments. The contaminated deposit is estimated to comprise a volume of approximately 9–10 million m^3 (Lee, 1994a; Murray, 1994), and various investigators have placed the mass of total DDT in shelf and upper slope sediments at 100–250 tons (Lee, 1994a; MacGregor, 1976; McDermott et al., 1974). The most heavily impacted area is adjacent to and northwest of the outfall system. Contaminant isopleths are roughly centered on the 60-m isobath, the approximate depth at which the outfall diffusers terminate (Fig. 1). The distribution pattern reflects the direction of prevailing subsurface currents, which tend to carry effluent particles upcoast along bathymetric contours (Drake et al., 1994; Stull et al., 1996). Vertical concentration profiles of p,p'-DDE in sediments along the 61-m isobath typically show a subsurface maximum corresponding to the time of peak DDT emissions from the outfall system. This is believed to have occurred in the late 1960s/early 1970s.

The subject of this paper is the diagenetic fate of selected organic contaminants (DDT + degradation products, PCBs, and the long-chain alkylbenzenes) deposited in sediments of the Palos Verdes Shelf from ca. 1950–1992. A companion paper discusses the depositional history of these compounds over the same time period (Eganhouse and Pontolillo, 2000). Although many previous studies have generated information on the spatial distribution of the chlorinated hydrocarbons in sediments of the Palos Verdes

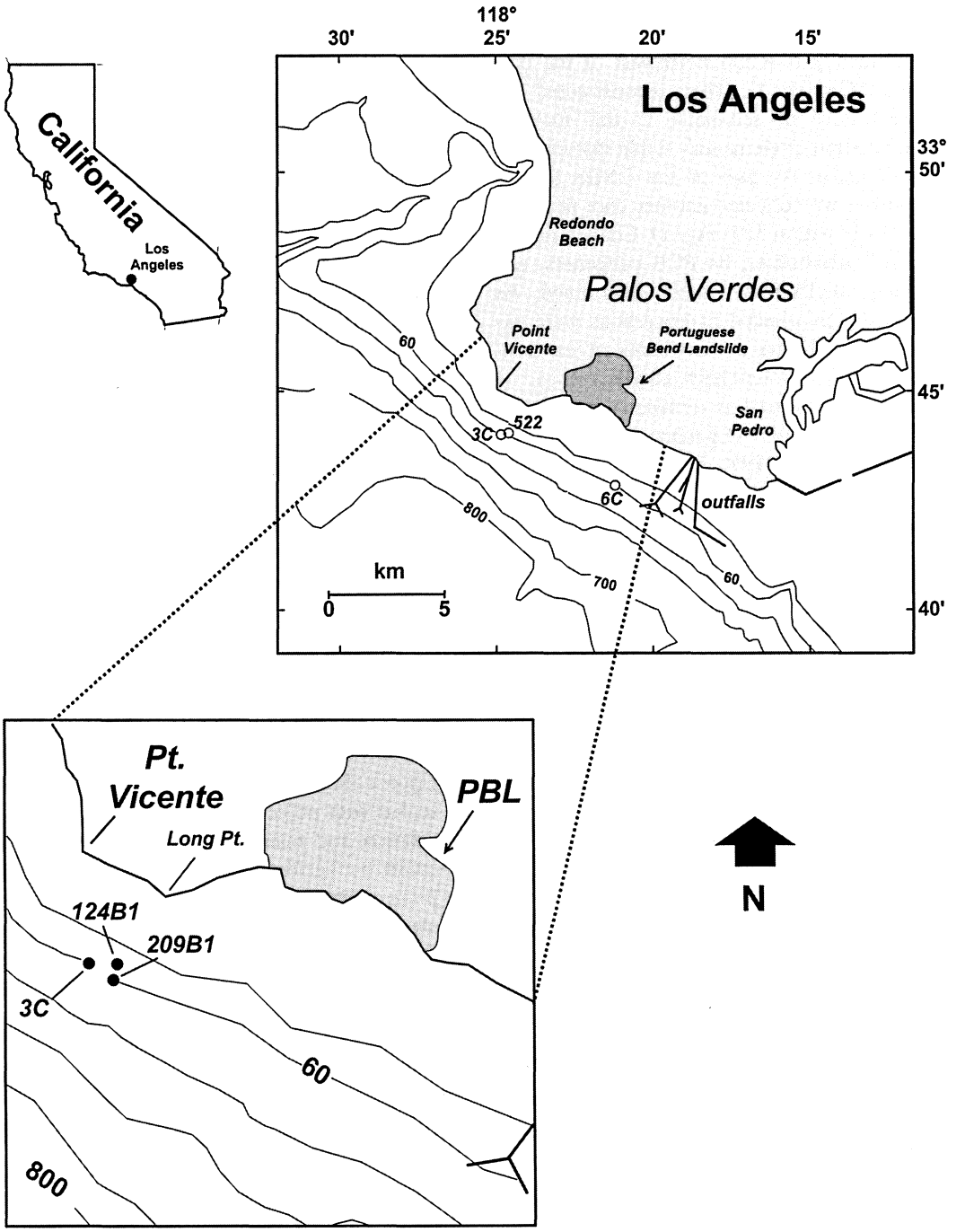


Fig. 1. Location map of the Palos Verdes Shelf showing LACSD and USGS stations where coring was conducted, the Portuguese Bend Landslide and the LACSD outfalls. Water depths given in meters. Core 209B1 from station 522 is identified for purposes of discussion found in Eganhouse and Pontolillo (2000).

Shelf, only one (MacGregor, 1976) explored possible diagenetic processes, and this was limited to DDT. Earlier, Eganhouse and Kaplan (1988) described the organic geochemistry of a sediment core collected in 1981 approximately 6–8 km northwest of the outfalls (station 3C, Fig. 1). They reconstructed the depositional history of sediments at this location using a combination of elemental, stable isotopic and molecular evidence. As part of the USGS studies described above, we collected another core near this location in 1992 (station 522; Fig. 1). Concentrations of seven DDT metabolites, 84 PCB congeners, and 38 long-chain alkylbenzenes were determined. As noted above, the chlorinated hydrocarbons were examined because they are contaminants of environmental concern. The long-chain alkylbenzenes, on the other hand, are viewed as molecular markers of municipal waste at this site (Eganhouse et al., 1983a; Zeng and Venkatesan, 1999). Here, we report new data for these trace organics in the core collected in 1992. Our interpretations rely on comparison of core profiles and an examination of the large body of historical data that has accumulated since 1970. The objective of this work is to understand the post-depositional fate of the DDTs, PCBs, and long-chain alkylbenzenes and to assess the suitability of these compounds as markers of waste contamination at this site. The findings are used in the companion paper to develop estimates of average sediment accumulation rates for comparison with rates developed by other investigators (cf., Refs. in Drake, 1994; Niedoroda et al., 1996).

2. Materials and methods

2.1. Sampling

Sediment cores were obtained during several cruises on the Palos Verdes Shelf. The LACSD collects gravity cores (Bascom et al., 1982) on a systematic sampling grid during odd numbered years (cf., Lee, 1994a,b for locations and procedures). The cores that are most relevant to the present study come from station 3C (33°43.84′N, 118°24.13′W; Fig. 1). This station is approximately 6–8 km downcurrent from the wastewater outfall system at a water depth of 61 m. Sediments at this location are moderately impacted by the effluent discharge (Stull et al., 1996) and are proximal to the Portuguese Bend Landslide (PBL), an important source of sediment to the shelf (Kayen et al., 1994). One of the cores collected at this station in 1981 (3C1) was provided to us by the LACSD for geochemical analyses (Eganhouse and Kaplan, 1988).

In addition, the USGS conducted cruises in 1992 and 1993. On one cruise (R/V *Farnella*, 7/1–13/92) cores were taken with a 0.06 m^2 Naval Electronics Lab (NEL) box corer (Lee and Kayen, 1994). Navigation was primarily by differential geostationary positioning system (GPS); microwave transponder (Delnorte) and non-differential GPS served as backups and were used for comparative purposes (Hamer, 1994). Information concerning station locations and details of the procedures used for collection of sediments with the box corers are provided elsewhere (Lee, 1994a; Lee and Kayen, 1994; Wheatcroft and Martin, 1994). A brief description of the core handling is given here.

Following inspection and careful removal of overlying water, sediments in the box were subsampled using an electrically-driven subcorer with a fixed position piston. As many as three 8.3-cm o.d. cylindrical subcores were obtained from each NEL box core. One subcore, designated by the suffix *-DDT*, was collected in a pre-cleaned polycarbonate liner and was used for determination of trace organics. Upon collection, *-DDT* subcores were immediately sealed with polycarbonate caps, frozen in an upright position and maintained at −20°C until sectioning could be performed. The cores were sectioned at 2-cm intervals while frozen, each section being trimmed of the outer 1 cm to avoid cross-contamination resulting from the coring/extrusion processes. The USGS core of most interest in the present work (124B1) was collected at station 522. Fig. 1 shows the location of station 522 and the approximate position at which core 124B1 (33°43.84′N, 118°24.08′W; water depth = 57 m, 7/92) was obtained. Hereafter, subcore 124B1-*DDT* will simply be referred to as core 124B1.

2.2. Extraction and chromatographic separation of trace organics

Details of the analytical methods used for the 3C1 (1981) sediment core are given in Eganhouse et al.

(1983a). Following is a summary of procedures employed in the analysis of the 1992 sediment core from station 522 (i.e. 124B1). Frozen sediments were thawed and homogenized and an aliquot was weighed into a pre-extracted cellulose thimble. The sediment was spiked with recovery surrogates intended to track the behavior of chlorinated hydrocarbons (PCB congeners 30, 121, 198; IUPAC) and long-chain alkylbenzenes (five 1-phenylalkanes; see below). The sediments were Soxhlet extracted in methanol followed by dichloromethane. After back extraction of the methanol, the dichloromethane extracts were combined and concentrated by rotary evaporation. Water and elemental sulfur were removed by adding excess anhydrous sodium sulfate and activated copper, respectively.

The chlorinated hydrocarbons and long-chain alkylbenzenes were isolated by column chromatography using a 1:2 (v/v) alumina/silica gel column (both 3% deactivated with H_2O). Sediment extracts were separated into three fractions corresponding to: (1) aliphatic hydrocarbons (**F1** — 15 ml hexane), (2) PCBs, DDTs, long-chain alkylbenzenes, PAHs (**F2** — 5 ml of hexane + 30 ml of 30% DCM in hexane), and (3) polar compounds (**F3** — 40 ml methanol). The **F2** fraction was concentrated by rotary evaporation, and a few grains of activated copper were added to ensure removal of traces of elemental sulfur. The **F2** fraction was then transferred quantitatively to a calibrated, 1 dram vial and split volumetrically as follows: 5% DDTs, 25% long-chain alkylbenzenes, 25% PCBs, and 45% archive.

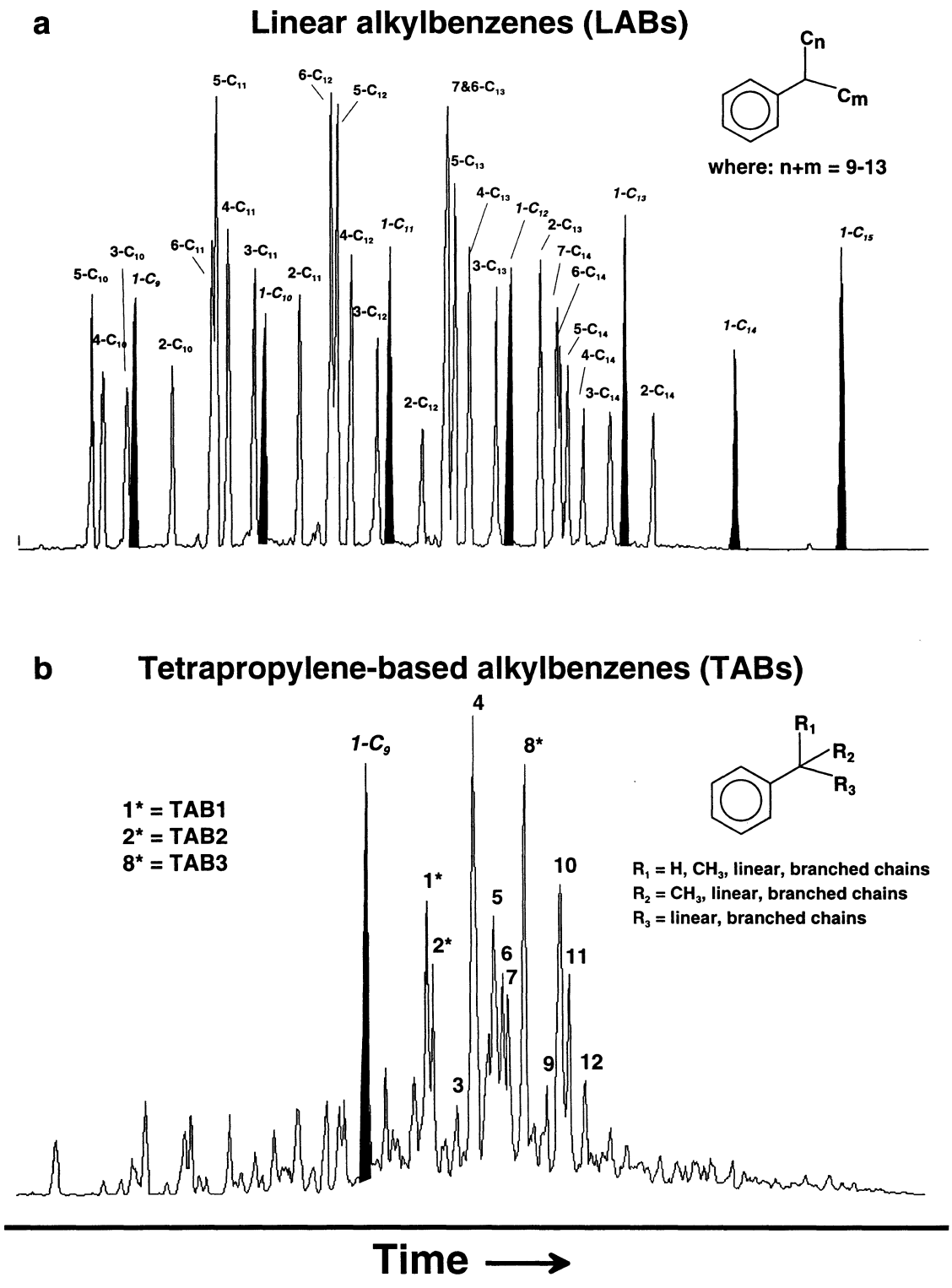
2.3. Instrumental analysis

2.3.1. Chlorinated hydrocarbons

Concentrations of seven DDT compounds (p,p'-DDMU [1-chloro-2,2′-bis(p-chlorophenyl)ethylene, **II**], o,p'-DDE, p,p'-DDE [**I**], o,p'-DDD, p,p'-DDD [**III**], o,p'-DDT, and p,p'-DDT [**IV**]) and 87 PCB congeners were determined using a Hewlett-Packard 5890 Series II high resolution gas chromatograph (HRGC) equipped with a ^{63}Ni electron capture detector (ECD). Splitless injections were made with a Hewlett-Packard 7673A autosampler. The analytical column was a 30 m × 0.25 mm (id) DB-5 fused silica capillary, 0.25 μm film thickness (J&W Scientific).

Prior to analysis, the DDT and PCB splits were taken up in a solution containing three quantitation standards: tetrachloro-*meta*-xylene, and PCB congeners 11 and 207. All compounds (analytes + quantitation standards) were obtained either as certified solutions from National Institute of Standards and Technology (NIST) or from a reputable supplier as neat material with guaranteed purity ≥ 99%. Quantitation of DDTs and PCBs was performed using the internal standard method with seven-level calibration, duplicated at each level. Calibration was verified on a continuing basis, and blanks and matrix spikes were processed and analyzed along with the samples. Method detection limits (MDLs; EPA, 1992) were estimated by analysis of eight replicate samples of precombusted sand (1 g sand + 1 g H_2O) amended with 120–320 pg each of the target analytes (7 DDTs + 84 PCBs + 3 surrogates). MDLs for all DDT compounds, except p,p'-DDD, ranged from 0.1 to 0.7 ng/g; the MDL for p,p'-DDD was 6.1 ng/g dry sediment. With the exception of p,p'-DDT and o,p'-DDT, concentrations of the DDT analytes in sediment samples were found to be 10^3 or more times the estimated MDLs. MDLs for all 87 PCBs ranged from 0.04 to 16.9 ng/g (mean ± 1sd = 1.0 ± 2.5 ng/g). Concentrations of individual PCB congeners in the sediments varied from 260 to < 0.02 ng/g. Concentrations of DDTs and PCBs in blanks were, with few exceptions, below the MDL. Percent recoveries of the surrogates determined in sediment samples were as follows: congener **#30** — 73.8 ± 12.5; **#121** — 76.5 ± 11.8, **#198** — 99.9 ± 20.2 (mean ± 1sd; $n = 35$). Concentrations reported here have not been corrected for recovery. This was to avoid bias caused by application of recovery data for a limited number of surrogates to analytes of widely varying physical properties. Precision is estimated at < 20% based on analysis of five replicate samples of sediment collected from the Palos Verdes Shelf (Hendricks and Eganhouse, 1992).

The identities of the DDTs and PCBs were confirmed by electron capture negative chemical ionization mass spectrometry (EC-NCIMS) using a Hewlett-Packard MS Engine (5989A). Chromatographic conditions and the analytical column were identical to those used in the HRGC/ECD analyses. Full scan mass spectra (0–650 daltons) were acquired at a rate of 1 scan/s and a source pressure of


a
Linear alkylbenzenes (LABs)
Cn
Cm
where: n+m = 9-13
5-C11
6-C12
5-C12
7&6-C13
5-C13
4-C13
1-C12
2-C13
1-C13
1-C15
4-C11
1-C11
4-C12
3-C13
7-C14
6-C14
3-C11
2-C11
1-C10
3-C12
5-C14
4-C14
3-C14
2-C14
1-C14
3-C10
6-C11
5-C10
1-C9
4-C10
2-C10
2-C12
b
Tetrapropylene-based alkylbenzenes (TABs)
1* = TAB1
2* = TAB2
8* = TAB3
1-C9
4
8*
R1
R2
R3
10
1*
5
2*
6
7
11
3
9
12
R1 = H, CH3, linear, branched chains
R2 = CH3, linear, branched chains
R3 = linear, branched chains
Time

2×10^4 Torr using methane as modifying gas. Several PCBs (viz. congeners 99, 83, 151, 170, 189) were affected by interferences with chlordanes and other unidentified substances. These have not been included in the data presented here. Summed concentrations of all identified interference-free PCB congeners are hereafter represented as ΣPCB. Based on the data of Schulz et al. (1989), ΣPCB in the core 124B1 sediments is estimated to be 83.3% of total PCBs.

2.3.2. Long-chain alkylbenzenes

Two classes of long-chain alkylbenzenes were determined in core 124B1. The linear alkylbenzenes (LABs; Fig. 2a) consist of 26 secondary phenylalkanes having alkyl side chains ranging from 10 to 14 carbons in length (hereafter designated j-C_k, where j = position of substitution on the alkyl chain and k = number of carbons in the chain) and five primary phenylalkanes (i.e. recovery surrogates: 1-C_{10}, 1-C_{11}, 1-C_{12}, 1-C_{13}, 1-C_{14}). The tetrapropylene-based alkylbenzenes (TABs; Fig. 2b) are a complex mixture of alkylated benzenes with highly branched side chains (Eganhouse et al., 1983a,b).

The long-chain alkylbenzene split was taken up in a solution containing two quantitation standards, 1-C_9 and 1-C_{15}. An aliquot was analyzed by on-column injection onto a 30 m × 0.25 mm (id) fused silica capillary column (DB-5, J&W Scientific, 0.25 μm film thickness) using a Varian 3400 HRGC interfaced to a Finnigan 800A Ion Trap Detector. Quantitation of the LABs was performed by the internal standard method using seven-level calibration, duplicated at each level with verification on a continuing basis. Quantitation ions used for the LABs were either base peaks, or in cases of potential TAB interference (e.g. 6-C_{11}, 4-C_{11}, 3-C_{11}, 2-C_{11}), characteristic ions that are absent or present at low abundance in the mass spectra of interfering TAB peaks (Eganhouse, 1986). In the case of the TABs, 12 major peaks were determined using a single point secondary calibration standard. Quantitation ions were selected so as to avoid/limit interference as described above. The concentration of ΣTABs represents the sum of the twelve numbered TAB peaks shown in Fig. 2b.

MDLs for individual LABs ranged from 0.5 to 10.7 ng/g (mean ± 1sd = 5.3 ± 2.8 ng/g), whereas concentrations in sediment samples varied from 290 to < 0.13 ng/g. Blanks and matrix spikes were also analyzed; no LABs or TABs were detected in any processed blanks. Recoveries of the surrogates were as follows: 1-C_{10}: 74.9 ± 12.7%; 1-C_{11}: 74.5 ± 11.0%; 1-C_{12}: 84.7 ± 11.2%; 1-C_{13}: 85.2 ± 11.3%; 1-C_{14}: 85.6 ± 8.1% (mean ± 1sd; n = 35). LAB concentrations were corrected for recovery (cf., Hendricks and Eganhouse, 1992), and concentrations of the 12 TABs were recovery-corrected using 1-C_{11}. This correction is warranted because of similarities between the physical properties of surrogates and corresponding analytes (Sherblom et al., 1992). Precision is estimated at < 12% based on analysis of five replicate grab samples from the Palos Verdes Shelf (Hendricks and Eganhouse, 1992).

3. Results and discussion

3.1. DDT + metabolites

3.1.1. Distribution of DDT in sediments

Concentrations of ΣDDT in the 124B1 subcore range from about 1.3 to 22 μg/g (dry weight). The metabolite, *p,p′*-DDE, represents 60–70% of the ΣDDT in these sediments, and *p,p′*-DDMU comprises 14–25%. The synthetic by-product, *o,p′*-DDT, was not detected in any of the sediment samples, and concentrations of *p,p′*-DDT were low and occasionally below the estimated MDL. Reported concentrations of *p,p′*-DDT must, therefore, be considered maximum estimates. We have identified two other metabolites of DDT using EC-NCIMS (i.e. DDNU [unsym-bis(*p*-chlorophenyl)ethylene; **V**] and DBP [dichlorobenzophenone; **VI**]). However, we were unable to detect other oxygenated metabolites of DDT, such as DDA (**VII**) and DDOH (**VIII**), whose exis-

Fig. 2. High resolution gas chromatograms and structures of (a) linear alkylbenzenes (LABs), and (b) tetrapropylene-based alkylbenzenes (TABs). See text for naming convention of LABs. Numbers above TAB peaks indicate TABs quantitated in this study. Shaded peaks are internal quantitation standards or recovery surrogates.

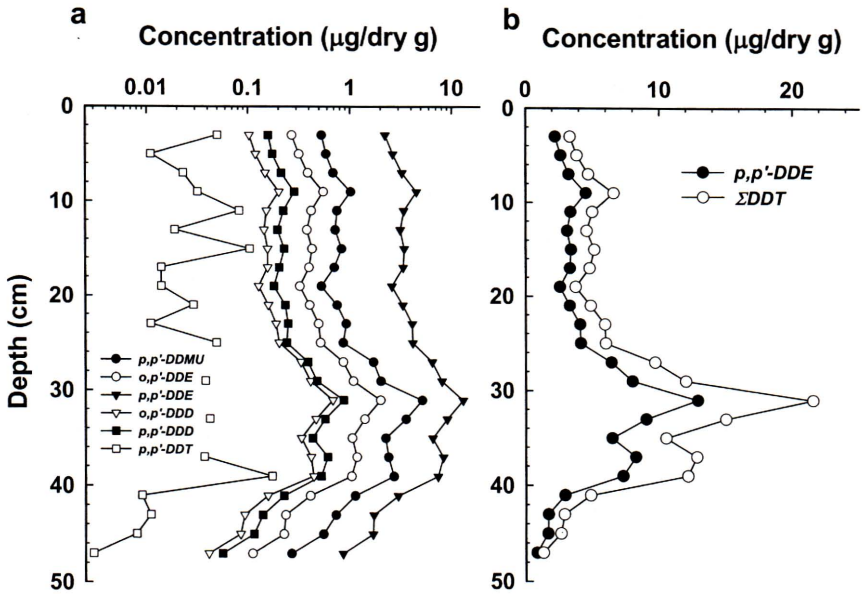


Fig. 3. Vertical concentration profiles of DDTs in core 124B1. (a) DDT + metabolites (note logarithmic scale for abscissa), (b) p,p'-DDE and ΣDDT.

tence had previously been reported in sediments of the Palos Verdes Shelf (cf. Refs. in Gossett, 1988). The results of our oxygenated metabolite studies will be reported elsewhere.

Vertical concentration profiles for the DDT compounds are plotted in Fig. 3a. A logarithmic scale is used for the abscissa to facilitate comparison of the profiles. Concentrations of the DDT compounds,

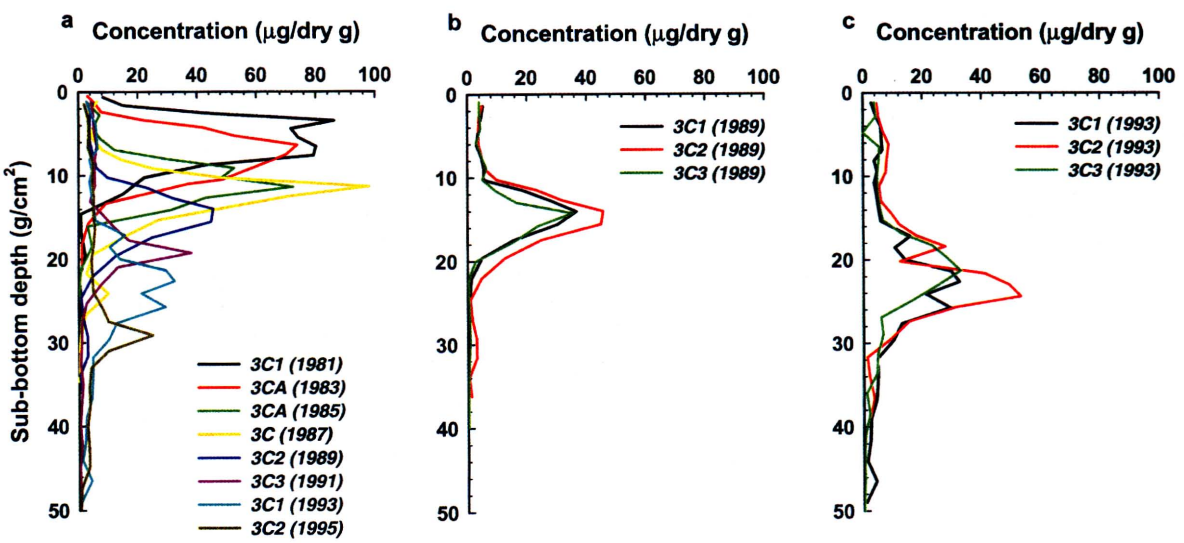


Fig. 4. Vertical concentration profiles of p,p'-DDE in cores collected by the LACSD from station 3C. (a) cores collected from 1981–1995 in odd years, (b) replicate cores collected in 1989, (c) replicate cores collected in 1993. All data are from Lee (1994b).

DDE, DDMU and DDD, are strongly correlated ($r > 0.96$) with each other suggesting that any one of them could be used to characterize the vertical distribution of DDT contamination. Because p,p'-DDE is the dominant and most readily determined DDT compound, we use it in subsequent discussions of DDT patterns. Fig. 3b shows the vertical distribution of p,p'-DDE and ΣDDT in this core. The p,p'-DDE profile is characterized by low and relatively invariant concentrations ($\approx$ 3–4.5 μg/g) within the upper 26 cm of the sediment column, increasing concentrations at greater sub-bottom depths to a subsurface maximum at the 30–32 cm interval ($\approx$ 13 μg/g), a broad interval of heavily contaminated sediments (26–40 cm), and relatively low concentrations below 40 cm (< 3 μg/g). As discussed by Eganhouse and Pontolillo (2000), these features reflect the history of waste emissions.

Fig. 4a shows representative vertical concentration profiles of p,p'-DDE developed by the LACSD for station 3C during odd numbered years from 1981 to 1995. The depth axis is given in units of cumulative g/cm^2 to compensate for the effects of compaction, thereby facilitating comparison of data for different cores. [Mass accumulation for each depth interval was calculated by multiplying the depth interval of the section (2 cm) of interest by the 'dry density' (i.e. g dry sed/cm^3 wet sed) of that section. Mass accumulations to a specified depth represent the summed accumulation from the top of the core to the depth of interest.] Generally speaking, the distributions are characterized by well-defined subsurface maxima. Occasionally (1981, 1985, 1993) a bimodal distribution, such as that observed for core 124B1 (cf., Fig. 3b), is found. The depth to the subsurface maximum increases and the peak concentration decreases with time (cf., Stull et al., 1996). This indicates that the most heavily contaminated sediments are being buried and perhaps redistributed and/or lost.

3.1.2. Temporal changes in DDT inventories (1981–1995)

Fig. 4b and c shows profiles for replicate cores taken by the LACSD at station 3C in 1989 and 1993, respectively. The 1989 profiles exhibit a remarkable degree of uniformity, differing principally in peak concentration. By contrast, replicate cores collected in 1993 show considerable variation in the shape and depth distribution of the p,p'-DDE profile. Differences among the replicate cores are attributable to natural spatial variability, navigational uncertainty, and possible variations due to the coring procedures. To expand on this point, we have also computed inventories of p,p'-DDE reported by the LACSD for cores collected from station 3C along with corresponding data for subcore 124B1 (Table 1). There is a reasonably consistent amount of variation in the p,p'-DDE inventories for replicate cores collected in 1989, 1991, and 1993 (1989: ±28%; 1991: ±18%; 1993: ±23%). Because DDT has no natural source, inventories for cores of different length should be comparable, assuming amounts of p,p'-DDE below the core bases are negligible. This assumption is

Table 1
Inventories of p,p'-DDE, total PCBs, ΣLABs, and ΣTABs at station 3C and 522 (subcore 124B1)

Year collected	Core	Inventory[a] (μg/cm^2)			
		p,p'-DDE	Total PCBs[b]	ΣLABs[c]	ΣTABs[d]
1981	3C1	566	51	106 (16.7)	91 (10.8)
	3C3	523	35	–	–
1983	3CA	534	–	–	–
1985	3CA	402	34	–	–
1987	3C	507	25	–	–
1989	3C1	248	–	–	–
	3C2	358	–	–	–
	3C3	209	–	–	–
1991	3C1	228	–	–	–
	3C2	317	–	–	–
	3C3	245	–	–	–
1993	3C1	407	–	–	–
	3C2	501	–	–	–
	3C3	314	–	–	–
1995	3C1	291	–	–	–
	3C2	252	–	–	–
1992	124B1	209	39	55 (7.5)	30 (6.6)

[a] p,p'-DDE and long-chain alkylbenzene inventories for 3C1 (1981) are based on analyses of Eganhouse et al. (1983a). All other p,p'-DDE inventories and total PCB for cores from station 3C are based on analyses of LACSD.

[b] Total PCBs for 3C cores determined by LACSD using a modified Aroclor method. Total PCBs (ΣPCBs) for 124B1 determined by congener-specific methodology described in the text.

[c] Numbers in parentheses are for 6-C_{12} inventories.

[d] Numbers in parentheses are for TAB3 inventories.

quite reasonable based on comparison of box core and deep gravity core profiles of p,p'-DDE on the Palos Verdes Shelf (Lee, 1994a). Thus, the variation in inventories for replicate cores is not attributable to corer penetration. Rather, it is due to the aforementioned sources of variability.

In general, there appears to have been a decline in the inventory of p,p'-DDE over time since 1981 (Table 1). This trend has been noted previously (Lee, 1994a; Niedoroda et al., 1996). The magnitude of the change (about 50%) exceeds the variability of inventories for replicate cores (about 25%) and is, therefore, considered real (Drake, 1994). Relative to the existing mass of total DDT in the Palos Verdes sediments, which is on the order of 100–200 tons (cf., McDermott et al., 1974; MacGregor, 1976; Lee, 1994a), emissions of total DDT from the LACSD during the period 1981–1995 were negligible (1.2 tons; Stull et al., 1986). Thus, the apparent trend of declining p,p'-DDE inventories could represent loss via resuspension coupled with advective transport and/or desorption. Vertical mixing of the sediments would act to move sediments from deeper, more contaminated layers to the surface where they would be available for resuspension. These are the principal mechanisms upon which recent predictive modeling efforts have concentrated (Drake et al., 1994; Sherwood et al., 1996; Niedoroda et al., 1996). Alternatively, the decline could indicate transformation of p,p'-DDE, a compound which has generally been considered a persistent, if not recalcitrant, organic molecule (Metcalf et al., 1971; Leland et al., 1973; Stull et al., 1996).

3.1.3. DDT composition of wastewater effluent

To better understand the composition of the source material and processes that may have affected DDT metabolite composition of wastewater effluent following release from the outfalls, we evaluated LACSD monitoring data collected from 1971 to present. We also examined historical information on the Montrose Chemical effluent, sewer water collected downstream from the Montrose plant (Carry and Redner, 1970; Redner and Payne, 1971), and sediments from the Palos Verdes Shelf (McDermott et al., 1974; unpublished LACSD data). These data do not include concentrations of the metabolite, p,p'-DDMU. Thus, for purposes of the following discussion, 'total DDT' represents the summation of p,p'- and o,p'-isomers of DDD, DDE, and DDT.

Montrose Chemical produced DDT from 1947 to 1982. In 1953, they were issued a permit by the City of Los Angeles to discharge their wastes into the sewer system serviced by the LACSD. The primary DDT-bearing wastes were caustic process liquors that were treated for pH and solids removal prior to release. As the result of a sewer survey conducted by the LACSD in 1969, Carry and Redner (1970) determined that high concentrations of DDT were present in the trunk sewers. A subsequent survey revealed that the principal source of the DDT was Montrose Chemical, the world's largest manufacturer of DDT at that time (MacGregor, 1974). In April of 1970, Montrose began hauling its caustic wastes to a landfill, and by June 1971 it had ceased all inputs to the LACSD treatment system. From December 1970 to July 1971, the LACSD cleaned the sewer lines of sediment, mobilizing significant quantities of historical DDT deposits that eventually passed through the waste treatment plant. Fig. 5a summarizes information on the DDT composition of samples collected from (1) the Montrose plant effluent in 1970–1971, (2) the downstream sewer (July–December 1970), (3) the LACSD effluent (1971–1990), and (4) Palos Verdes Shelf sediments (1972, 1981, 1992).

To our knowledge direct information on the DDT content and composition of the Montrose plant effluent prior to 1970 does not exist. However, average data for 18 samples collected in 1970–1971 indicate that 'total DDT' compositions were dominated by p,p'- and o,p'-DDT (DDT/DDE/DDD $\approx$ 75:20:5). Clearly, the DDT wastes being discharged from the plant had already undergone some degradation as evidenced by the presence of DDE and DDD (MacGregor, 1974). Because the major degradation product was DDE, and because the wastes were caustic before pH adjustment, it is reasonable to assume that a portion of the DDT had been dehydrochlorinated abiotically (Wolfe et al., 1977 and Refs. therein). Samples collected in the sewer downstream from the Montrose plant following termination of the caustic waste inputs (i.e. after April, 1970) had significantly higher abundances of DDEs and especially, DDDs (DDT/DDE/DDD = 14:38:48). Based on differences in the composition of the Montrose effluent and the downstream sewer samples, Carry and Red-

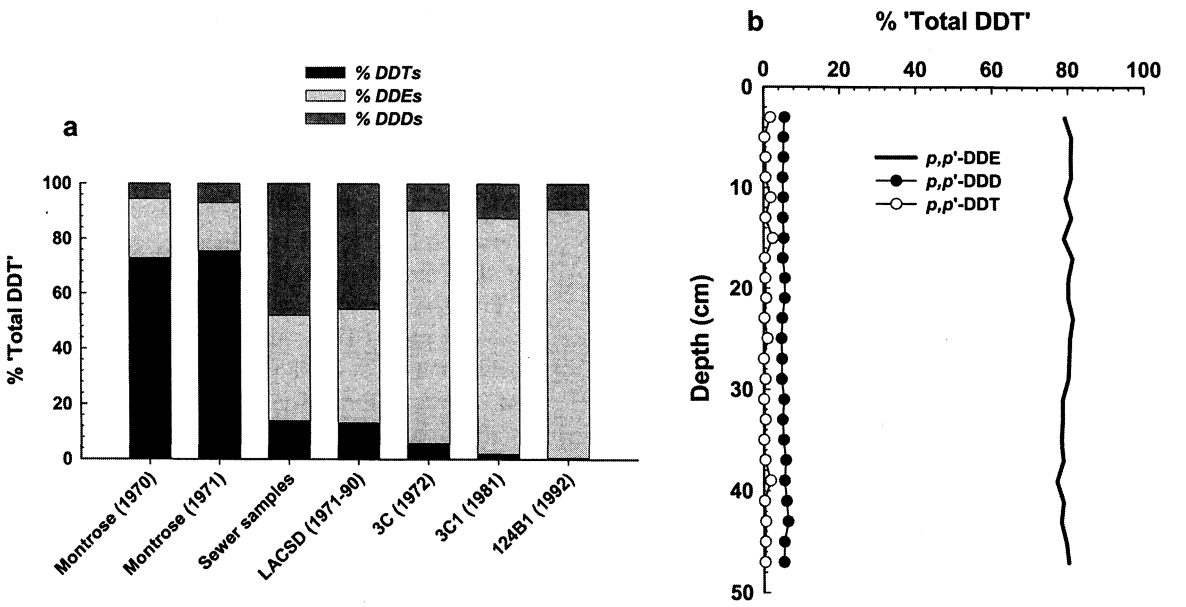


Fig. 5. Composition of 'total DDT' in (a) Montrose effluent 1970–1971 and sewer lines (Redner and Payne, 1971), LACSD effluent 1971–1990 (LACSD annual monitoring reports), sediment cores (3C 1972 — McDermott et al., 1974; 3C1 1981 — LACSD; 124B1 1992 — this study), (b) p,p'-DDE, p,p'-DDD, and p,p'-DDT as a percent of 'total DDT' in 124B1 core.

ner (1970) concluded that DDT residues in the sewer samples had come principally from historical deposits in the sewer lines, not fresh effluent from the Montrose plant. The increased relative abundance of DDDs in the deposits undoubtedly resulted from reductive dechlorination of DDT, a process that can occur abiotically (cf., Refs. in Sayles et al., 1997 and Boul, 1995) or through microbial activity (Esaac and Matsumura, 1980). These same deposits, which were mobilized during the sewer cleaning operations of December 1970–July 1971, continued to enter the LACSD plant for many years after discharge of the Montrose effluent had ceased. Thus, the average compositions of the downstream sewer samples taken after April 1970 and the LACSD effluent (1971–1990) are virtually identical (Fig. 5a).

3.1.4. Early diagenesis

Average compositional data for three cores collected at or near station 3C are shown in Fig. 5a. In all cases, 'total DDT' is dominated by DDE (84–90%) with minor amounts of DDD ($\lesssim$ 10%) and smaller amounts of DDT ($<$ 1–6%). Fig. 5b illustrates the uniformity of the DDT composition in core 124B1. It is reasonable to assume that the composition of the effluent discharged from Montrose between 1953 and 1971 was similar to that shown for the Montrose effluent samples collected in 1970–1971. The composition of the influent to the LACSD plant between 1953 and April 1970, thus, probably resembled a mixture of the Montrose effluent and the deposits in the sewer lines as reflected in the downstream sewer samples collected after April 1970. Carry and Redner (1970) found a reduction of $>$ 90% in DDT loading following removal of the caustic waste discharge in April 1970. It follows then that the composition of the influent to the LACSD treatment plant from 1953 to April 1970 should have been dominated by that of the Montrose effluent, not the sewer sediments. The LACSD used primary treatment through 1971, and residence times of wastes passing through the sedimentation tanks were, at most, a few hours. Sludge was digested anaerobically for about 15 days and centrifuged, after which the centrate (i.e. supernatant) was recombined with the primary effluent (J. Stull, personal communication, 1999). Given these short residence times, it is likely that little, if any, degradation occurred during passage of the DDT-bearing wastes through the LACSD plant. The effluent composition must, there-

fore, have been similar to the influent composition. This conclusion is supported by the similarity between the LACSD effluent composition (1971–1990) and the sewer samples taken downstream from Montrose after April 1970. Because the vast majority of the DDT was discharged to the ocean before April 1970, it is most relevant to compare the DDT composition of the Montrose effluent (ca. 1970–1971) with that of the sediments.

The data in Fig. 5a show that most of the parent DDT likely to have been present in the pre-1970 LACSD effluent was transformed following release from the outfalls. Assuming no significant degradation of DDE or DDD, the compositional data indicate that almost all of the parent DDT was converted to DDE (rather than DDD). Moreover, this transformation must have been complete by the time the 1972 core was collected because no significant change in composition was seen between 1972 and 1992. It is most likely that the DDT → DDE transformation occurred under oxidizing conditions during the earliest stages of diagenesis. If so, degradation of DDE and DDD would have been limited because both of these compounds are quite stable in the presence of oxygen (Metcalf et al., 1971; You et al, 1996). It is highly unlikely that the DDT → DDE transformation occurred under reducing conditions because reductive dechlorination of DDT to DDD would have been favored (Aislabie et al., 1997; Lal and Saxena, 1982). Dehydrochlorination could have been mediated biologically or by abiotic processes during transport of DDT-bearing waste particles through the water column and before their burial in the sediment column at depths below which conditions were reducing. Previous research has shown that DDE is the major metabolite found in higher marine animals (e.g. MacGregor, 1974) and usually the dominant product of DDT degradation in algae (Bowes, 1972; Rice and Sikka, 1973). It seems unlikely that higher organisms could have metabolized a major fraction of the DDT undergoing sedimentation on the shelf. Conversion of DDT to DDE by phytoplankton would be limited by the inherent inefficiency of this process (Johnsen, 1976; Lal and Saxena, 1982). Moreover, because wastes discharged from the deepwater LACSD outfalls ordinarily do not rise above the thermocline (Hendricks and Eganhouse, 1992), the availability of DDT to phytoplankton in the photic zone would be limited. For the same reason, photolytic decomposition would likely be insignificant. This leaves hydrolysis as the most likely mechanism for dehydrochlorination of DDT.

Wolfe et al. (1977) found that DDE was the major product of DDT hydrolysis within the pH range of 5–9. They showed that the half-life of DDT was inversely related to pH at values greater than about 7 and that the dehydrochlorination rate constant for DDT was approximately seven times that of DDD at 27°C and pH 9. Thus, all things being equal, dehydrochlorination of DDT proceeds much more rapidly than dehydrochlorination of DDD. The authors presented an equation relating the half-life of DDT in aqueous solution at pH 8 (near that of seawater) to the hydrolytic rate constant and the fraction of DDT in solution. Using the rate constant (2.5×10^{-8} s^{-1}) of Wolfe et al. (1977) and data presented by Zeng et al. (1999) on the fraction of 'dissolved' DDT near station 3C (≈ 0.63), we calculate that DDT would likely have had a half-life of approximately 1.3–1.4 years in waters of the Palos Verdes Shelf. At higher pH, the half-life would be considerably shorter. It is possible that the presence of surface active materials, especially synthetic surfactants, in the effluent may have served to enhance the solubility of DDT (Sayles et al., 1997; Kile and Chiou, 1989). This, too, would tend to increase the rate of hydrolysis.

Notwithstanding differences between the experimental conditions used by Wolfe et al. (1977) and those that probably existed on the Palos Verdes Shelf at the time of major DDT emissions, the calculated half-lives for DDT appear plausible. Estimated sedimentation rates for station 3C during the period 1955–1971 range from 0.8 to 1.3 cm/year (Eganhouse and Pontolillo, 2000; Drake, 1994). Whereas initial deposition of aggregated effluent particles would likely occur within days (Hendricks and Eganhouse, 1992), incorporation into the sediments and burial would take place on a time scale of a few years. It is probable that the upper few centimeters of the sediment were sufficiently oxidizing to bring about the DDT → DDE transformation. Once buried below depths at which conditions were reducing, however, residual parent DDT would undergo dehydrochlorination at greatly reduced rates or not at all. Unless further reductive transformations were to occur (see discussion below), the DDT composition

would effectively become fixed. This scenario is largely consistent with the relationships shown in Fig. 5a and the remarkable uniformity of DDT composition indicated in Fig. 5b.

3.1.5. Reductive dechlorination of DDE

We now examine processes operating in the sediment column following burial of DDT-bearing effluent particles below depths where conditions were reducing. Our focus is primarily on *p,p'*-DDE because it is the dominant DDT compound in these sediments (Fig. 5), and its fate and effects are the focus of much current interest (Renner, 1998). A large body of data exists on the reductive dechlorination of DDT to DDD. This transformation can occur abiotically through redox reactions involving zero-valent metals (e.g. Fe) or metal-coenzyme complexes, reduced metal porphyrins and other metalloproteins derived from living systems (cf., Refs. in Boul, 1995). Dechlorination of DDT can also be mediated by a variety of microorganisms under anaerobic conditions (Esaac and Matsumura, 1980). By comparison, very little information exists on the reductive dechlorination of DDE. Sayles et al. (1997) reported reduction of DDE by zero-valent iron in the laboratory, and there are a handful of studies indicating transformation by microorganisms from non-marine environments (Aislabie et al., 1997; Agarwal et al. 1994; Bumpus et al., 1993; Ledford and Chen, 1969). However, DDE has usually been regarded as a metabolic product (Rochkind et al., 1986) that is highly persistent in the marine environment (MacGregor, 1974; Stull et al., 1996).

Recent microcosm studies have demonstrated the potential for microbial degradation of *p,p'*-DDE to *p,p'*-DDMU in Palos Verdes sediments via reductive dechlorination (Quensen et al., 1998). While we have no data on the in situ redox conditions of sediments from the 124B1 core, it is likely that the sediments were reducing within a few centimeters of the sediment–water interface at the time the core was collected (Berelson et al., 2000). If one assumes that the *p,p'*-DDE/*p,p'*-DDMU ratio of contaminated effluent particles deposited on the Palos Verdes Shelf remained constant during the main period of DDT release (ca. 1947–1970), transformation of *p,p'*-DDE to *p,p'*-DDMU might be evidenced by a decrease in this ratio with depth in the sediment column. A similar argument can be made for transformation of *p,p'*-DDD to *p,p'*-DDMU via dehydrochlorination. However, the latter reaction would likely require aerobic conditions that are not considered favorable for DDD degradation (You et al., 1996). The *p,p'*-DDE/*p,p'*-DDMU and *p,p'*-DDD/*p,p'*-DDMU ratios in core 124B1 are plotted in Fig. 6a.

In the 124B1 core, both ratios tend to decrease, albeit irregularly, with increasing depth. The observed pattern is consistent with a loss of precursor (*p,p'*-DDE,-DDD) and/or generation of product (*p,p'*-DDMU) in these sediments. However, when plotted as a per cent of ΣDDT, the abundance of *p,p'*-DDD in the 124B1 core (Fig. 6b) is seen to be uniform. This indicates that the gradual decline in *p,p'*-DDD/*p,p'*-DDMU ratio with depth is due to the increasing relative abundance of *p,p'*-DDMU, not transformation of *p,p'*-DDD to *p,p'*-DDMU. Fig. 6b also shows the abundance of *p,p'*-DDE, *p,p'*-DDMU and the sum, [*p,p'*-DDE + *p,p'*-DDMU], as percentages of ΣDDT. The *p,p'*-DDE and *p,p'*-DDMU profiles show little, if any, change in the upper 28 g/cm^2 but decrease and increase, respectively, below that depth. The profiles are mirror images of each other. Thus, the summed abundance (i.e. [*p,p'*-DDE + *p,p'*-DDMU]) is essentially

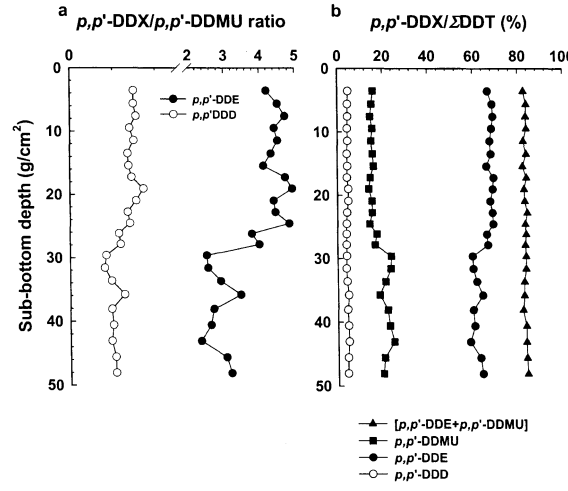


Fig. 6. (a) DDT metabolite/*p,p'*-DDMU ratio profiles in core 124B1, (b) DDT compound abundances as percent of ΣDDT in core 124B1.

constant throughout the core. The relatively constant percentages of p,p'-DDE and p,p'-DDMU found in the upper 28 g/cm^2 is consistent with evidence indicating rapid sedimentation and/or mixing during the period 1981–1992 (cf., Eganhouse and Pontolillo, 2000). The inverse relation between the p,p'-DDE and p,p'-DDMU profiles supports the hypothesis that p,p'-DDE was transformed into p,p'-DDMU, whereas the near constancy of the summed abundance indicates the attainment of mass balance.

In order to achieve a mass balance, the system would either have to be at steady state or be closed with respect to DDE and DDMU. Under steady state conditions, the rate of formation of DDMU would equal the rate of formation of DDE. Assuming the sediments were anoxic within a few centimeters of the sediment–water interface, it is reasonable to conclude that conversion of DDT to DDE would be unlikely to occur at a significant rate at depths in the sediment column where reducing conditions prevailed. Instead, transformation of DDT to DDD would be preferred. Examination of p,p'-DDT/p,p'-DDE ratios for this core reveals no discernible trend with depth, and there is no apparent correlation between concentrations of p,p'-DDE and p,p'-DDT ($r^2 = 0.01$; Fig. 3a). Moreover, the 'total DDT' composition of the sediments has not changed appreciably since at least 1972 (Fig. 5a). Finally, the abundance of p,p'-DDT in the 124B1 core is uniformly low ($0.7 \pm 0.7\%$ ΣDDT). Thus, it could support production of only a minor fraction of the p,p'-DDE pool. Together, these results suggest that diagenetic transformation of DDT to DDE following burial in reducing layers is insignificant. We conclude that steady state conditions do not exist and therefore, cannot explain the mass balance.

A closed system with respect to DDE and DDMU would require that p,p'-DDE not be produced in significant quantities from p,p'-DDT and that p,p'-DDMU be a dead-end product. By analogy to the DDE → DDMU transformation (Quensen et al., 1998), it may be inferred that DDNU could be produced by reductive dechlorination of DDMU. However, we know of no studies demonstrating this reaction pathway in marine sediments. It is also conceivable, though not demonstrated, that under appropriate conditions, DDNU could be produced by dehydrochlorination of DDMS (**IX**). However, this again would likely require oxidizing conditions. We were unable to detect the presence of DDMS in sediments from the 124B1 core. However, we have tentatively identified trace amounts of DDNU using EC-NCIMS. The mass balance for DDE/DDMU and the lack of any evidence for DDT → DDE conversion suggest that these trace amounts of DDNU may have been produced prior to incorporation into the sediments. However, we presently have no data to directly test this hypothesis.

Quensen et al. (1998) conducted microcosm experiments with sediments collected from LACSD stations 3C, 5C, and 8C (Fig. 1). Separate microcosms were amended with ^{14}C-labeled p,p'-DDE and p,p'-DDD. They demonstrated transformation of DDE to DDMU under both sulfate-reducing and methanogenic conditions. However, the rate and extent of conversion were significantly greater under methanogenic conditions. Recoveries of the ^{14}C activity in all experiments for both autoclaved and live microcosms were 86–93%. Of the recovered materials, more than 99.3 % was attributable to DDE, DDD, or DDMU. This is consistent with our hypothesis that the DDMU is effectively a dead-end product in the Palos Verdes sediments, and that transformation of DDE to DDMU, if occurring, is doing so as a closed system. Moreover, Quensen et al. (1998) found much lower transformation rates of DDD; only trace quantities of DDMU were formed in the DDD spiking experiment. This finding is consistent with our conclusion that DDE, not DDD, is the primary precursor of any DDMU generated in these sediments.

Although the metabolite ratio profile of the 124B1 cores is consistent with the DDE → DDMU transformation hypothesis, it is of interest to know whether this feature is common to sediments of the Palos Verdes Shelf. Costa and Bailey (1994) report data similar to those depicted in Fig. 6a for nine of 10 sediment cores collected at water depths of 54–207 m. The remaining core showed no discernible trend with depth. These profiles do not exhibit characteristic patterns that would indicate a shelf-wide time-varying source function. Thus, we interpret the decreasing trends in the p,p'-DDE/p,p'-DDMU ratio observed in the cores to reflect diagenetic transformation processes that were operative after these materials were incorporated into the sea floor.

3.1.6. DDE dechlorination vs. remobilization

From the limited data available, it is not possible to determine exactly how much of the apparent decline in p,p'-DDE inventories at 3C (1981–1995) might be explained by post-depositional transformation of p,p'-DDE to p,p'-DDMU. Any such assessment depends on assumptions about the origin of DDMU in these sediments. Alternative hypotheses for the origin of DDMU include: (1) some of the DDMU originated directly from the LACSD effluent, (2) some of the DDMU was produced by dehydrochlorination of DDD after waste discharge during the early stages of diagenesis, or (3) all of the DDMU was derived from DDE following burial. Because no measurements were made of DDMU in the LACSD effluent, we cannot directly evaluate hypothesis 1. However, given the composition of the Montrose effluent (Fig. 5a), it seems unlikely that significant quantities of DDMU existed in the LACSD effluent ca. 1953–1971. This is because the predominance of the metabolite, DDE, indicates oxidizing conditions, and reductive dechlorination of DDE would not be expected to occur. Moreover, the low rate of hydrolysis of DDD relative to DDT at circum-neutral to alkaline pH as demonstrated by Wolfe et al. (1977), would result in little, if any, DDMU production via dehydrochlorination of DDD. By the same line of reasoning, hypothesis 2 appears untenable. Hypothesis 3 is viable, but no data exist on concentrations of p,p'-DDMU in sediments prior to 1992 other than anecdotal observations by MacGregor (1976). Unable to chromatographically separate o,p'-DDE and p,p'-DDMU, MacGregor (1976) reported that the inventory of components constituting the o,p'-DDE/p,p'-DDMU peak in sediments collected near the outfall between 1971 and 1972 had increased relative to the inventories of p,p'-DDE, DDD, and DDT. He suggested, among other things, that this might reflect metabolism.

Limits for the transformation of DDE to DDMU can be estimated as follows. First, we consider the change in relative abundance of p,p'-DDE as found in the 124B1 core. This implies that some unknown fraction of the existing inventory of p,p'-DDMU was originally deposited in the sediments and was not formed in situ by reductive dechlorination of DDE (hypotheses 1 and 2). For this computation, it is assumed that the system is closed and that the initial fraction of the ΣDDT represented by p,p'-DDE was 69.3%, the maximum abundance observed in core 124B1. Applying the difference between the observed % ΣDDT represented by p,p'-DDE at each depth and 69.3% to the mass of ΣDDT per unit area at each depth in the core, we compute the mass of p,p'-DDE in each depth interval that could have been transformed to DDMU. Summing these masses over depth, we obtain an estimate of the total inventory of DDE that may have been transformed (20 $\mu g/cm^2$). This represents about 10 % of the existing inventory of p,p'-DDE or 9 % of the hypothetical combined post-depositional p,p'-DDMU + p,p'-DDE inventories ($20 + 209 = 229$ $\mu g/cm^2$; cf., Table 1).

The second approach assumes that all of the p,p'-DDMU in core 124B1 was derived from p,p'-DDE following burial (hypothesis 3). Accordingly, the inventory of p,p'-DDMU (62 $\mu g/cm^2$) in core 124B1 represents approximately 23% of the combined inventories of p,p'-DDMU and p,p'-DDE. The upper limit of the range (i.e. hypothesis 3) of these estimates accounts for less than half the apparent decline in p,p'-DDE inventories at station 3C from 1981 to 1995 ($\approx 50\%$). It is important to note, however, that the upper limit we have calculated reflects transformations that could have occurred over a period of roughly 40 years ($\sim$ 1953–1992). One can argue that physical and biological transport processes effecting loss of DDT would largely be nonspecific with respect to the various metabolites because of similarities in their physical properties. Under these conditions, resuspension, desorption and advection would tend to cause a decrease in the inventory of p,p'-DDE without measurably affecting its relative abundance. This is consistent with our observations (Fig. 5a). The strong similarity between the DDT compositions of the 1981 and 1992 cores suggests that transformation of DDE to DDMU must have been slow (Zeng and Venkatesan, 1999) and that reductive dechlorination was of minor importance relative to physical/biological mobilization over the period 1981–1995.

3.1.7. Transformation rates

The transformation rates observed in the laboratory experiments conducted by Quensen et al. (1998) were 0.17 and 0.85 nmol/g sediment/day for sul-

Table 2
Inventory ratios of ΣLAB/ΣTAB, 6-C_{12}/TAB3, 6-C_{12}/p,p'-DDE, and TAB3/p,p'-DDE in cores 3C1 (1981) and 124B1 (1992)

Ratio	3C1 (1981)	124B1 (1992)
ΣLAB/ΣTAB	1.16	1.90
6-C_{12}/TAB3	1.54	1.14
6-C_{12}/p,p'-DDE	0.012	0.036
TAB3/p,p'-DDE	0.019	0.031

fate-reducing and methanogenic conditions, respectively. Using these rates and assuming zeroth order kinetics, it would take only 2.1 and 0.43 years to transform 50% of the DDE to DDMU in the 3C1 (1981) core under sulfate-reducing and methanogenic conditions, respectively. Higher order kinetics would result in more rapid transformation. Clearly, such rates cannot apply to this field site. We can estimate apparent in situ transformation rates corresponding to hypotheses 1 and 3 using sedimentation rates determined for core 124B1 from molecular stratigraphy (see Table 2 in Eganhouse and Pontolillo, 2000). Depth-integrated rates corresponding to hypotheses 1 and 3 are 0.0001 and 0.001 nmol/g sediment/day, respectively. These rates are two to three orders of magnitude lower than those obtained in the microcosm experiments of Quensen et al. (1998).

The discrepancy between laboratory and field results most likely has its origin in a number of factors, not the least of which is the lack of aging of the sediment-DDE slurry in the microcosm experiments. Under field conditions on the Palos Verdes Shelf, the vast majority of the DDT has been deposited for 30 years or more. Data to be published elsewhere will show that sediments off Palos Verdes strongly bind DDE (Eganhouse, 2000). This binding likely limits DDE's biological availability, thereby increasing its resistance to biodegradation (Pignatello and Xin, 1996; Hatzinger and Alexander, 1995). Moreover, studies of Berelson et al. (2000) indicate that the dominant terminal electron acceptors coupled to carbon oxidation on the Palos Verdes Shelf are oxygen and sulfate. Given the greatly reduced transformation rates observed by Quensen et al. (1998) under sulfate-reducing vis-a-vis methanogenic conditions, the low rate of conversion indicated by our field data is quite reasonable.

3.2. Polychlorinated biphenyls

Concentrations of ΣPCBs in the 124B1 core range from 0.2 to 2.4 μg/g. Fig. 7a shows vertical concen-

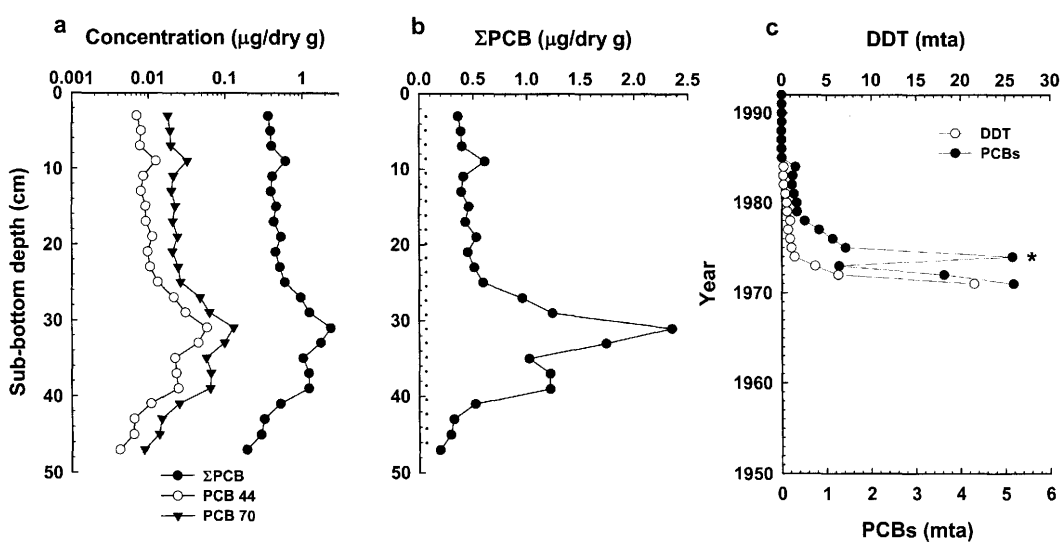


Fig. 7. (a,b) Vertical concentration profiles of PCB congeners and ΣPCB in core 124B1, (c) historical emissions (mta = metric tons/year) of PCBs and DDT from the LACSD 1971–1992 (data from SCCWRP annual reports, 1973–1993; V. Raco, personal communication). Dotted line represents $MDL_{\Sigma PCB}$. * 2/3 of this amount discharged between October and December of 1974 (Stull et al., 1988).

tration profiles of ΣPCB and two representative PCB congeners (44 and 70) in sediments from the 124B1 subcore. Again, concentrations are plotted using a logarithmic scale for purposes of comparison. The profiles are remarkably similar to those obtained for p,p'-DDE (cf. Figs. 3b and 7b) at this location, and linear regression analysis of ΣPCB and ΣDDT concentrations yields a correlation coefficient (r^2) of 0.98. Correlations of this sort have been noted before for sediments from the Palos Verdes Shelf (Lee, 1994a; Murray, 1994; LACSD, 1992; Stull et al., 1988), indicating that these two classes of chlorinated hydrocarbons have had remarkably similar discharge histories and/or depositional fates. Monitoring data for chlorinated hydrocarbons in the LACSD effluent exist since 1971. From these data, it is clear that emissions of these halocarbons declined precipitously in succeeding years and tracked each other closely (Fig. 7c).

Fig. 8 illustrates the average composition (in terms of chlorination level) of the PCBs in sediments from core 124B1. All peaks represented entirely or predominantly by PCBs of a given degree of chlorination have been summed and plotted as a percentage of the ΣPCB concentration. The order of dominance for the PCB homolog groups is

$$Cl_5 \gg Cl_4 > Cl_6 > Cl_7 \cong Cl_3 > Cl_8 > Cl_2 \geq Cl_9 \approx Cl_1, Cl_{10}.$$

The composition of this mixture varies only in minor detail throughout the core as reflected by the small error bars. Either the composition of the PCB source(s) did not change appreciably over the period during which PCBs were deposited at this location or the sediments (and associated PCBs) have been mixed efficiently throughout the period of sedimentation. In view of the shape of the vertical concentration profile (Fig. 7b) and its correspondence to available LACSD discharge data (Fig. 7c), the latter hypothesis is untenable. Also shown in Fig. 8 are distributions for three common Aroclor mixtures based on compositional data developed by Schulz et al. (1989). Nearly identical distributions were reported for these same Aroclors by Frame (1997).

Comparison of the distribution plots suggests that the PCBs in core 124B1 are derived primarily from Aroclor 1254 with possible smaller contributions from Aroclors 1242 and 1260. Multiple linear regres-

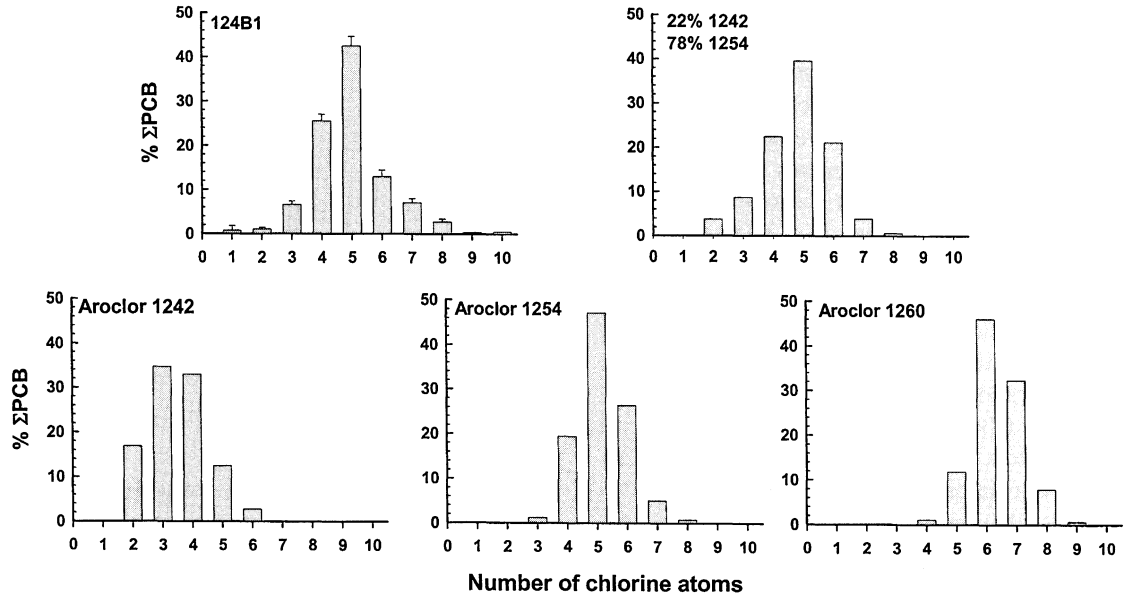


Fig. 8. Distribution of PCBs by chlorination level in core 124B1 (mean ± 1sd), optimal mixture of Aroclors 1242 and 1254 based on multiple linear regression analysis (see text for explanation) and three common Aroclors (Schulz et al., 1989).

sion analysis provides an optimal composition consisting of 22% 1242 + 78% 1254 ($r^2 = 0.96$). However, the average distribution in sediments of core 124B1 is not simply a mixture of the Aroclors shown here.

One possible explanation for the discrepancy is that the PCBs were altered following release from the outfall system. LACSD has reported effluent monitoring data for the period 1971–1984 with average annual total PCB compositions of 56–78% Aroclor 1242, the remainder being comprised of Aroclor 1254. In view of the uniformity of the PCB compositions found throughout the 124B1 core, any post-discharge alteration would seem to have occurred prior to burial in the bedded sediments. However, given the uncertainties in quantitation of PCBs by the "Aroclor method" used by the LACSD and difficulties in comparing such results with data based on congener-specific methods (Eganhouse and Gossett, 1991), no firm conclusions can be reached about the significance of the difference between effluent and sediment PCB compositions.

To investigate the potential for reductive dechlorination of PCBs in these sediments, we examined the composition of PCB congeners that were chromatographically resolved from other PCBs of the same degree of chlorination and were determined to be free of interference by EC-NCIMS (48 of 84 targeted congeners). The distributions of these PCBs, representative plots of which are shown in Fig. 9, are, for all intents and purposes, identical. This provides convincing evidence that reductive dechlorination of PCBs is not occurring in sediments from this location. Whatever agents (biotic or abiotic) are responsible for bringing about conversion of DDE to DDMU in these sediments are not also dechlorinating the PCBs. It is possible that PCB dechlorination is inhibited by the presence of co-contaminants (Sokol et al., 1994) or is limited by the relatively low sediment PCB concentrations (Sokol et al., 1995), reduced bioavailability (Zwiernik et al., 1999) or other, as yet unknown, factors (Bedard and Quensen, 1995). Alternative explanations for the differences between the PCB distribution in the core and the three Aroclors (Fig. 8) include: (1) mixtures analyzed by Schulz et al. (1989) may differ in composition from those discharged in the LACSD effluent, or (2) other Aroclors, not included in the Schulz et al. (1989) analysis, may be present in the sediments. Without congener-specific information on the PCB composition of wastewater effluent, it is not possible to differentiate between these alternatives.

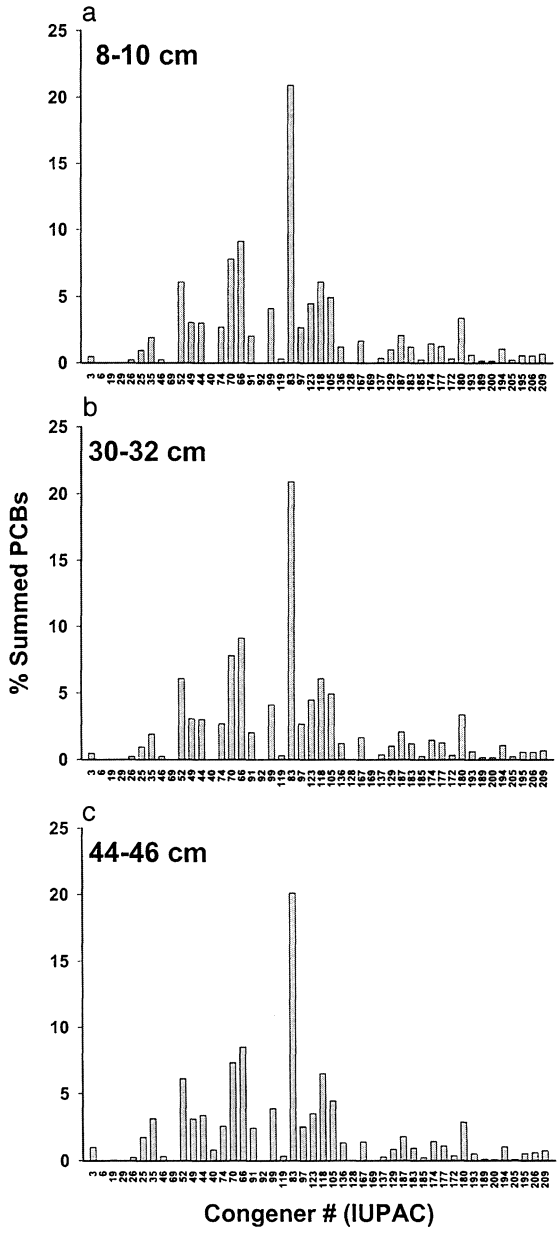


Fig. 9. Composition of interference-free PCB congeners in sediments from core 124B1: (a) 8–10 cm, (b) 30–32 cm, (c) 44–46 cm.

As shown in Table 1, determination of PCB concentrations in sediments from this station was con-

ducted by the LACSD in 1981, 1985, and 1987. The data for duplicate cores taken in 1981 suggest a significant amount of variability. Nevertheless, the inventories for cores collected in 1985 and 1987 are progressively lower than those obtained in 1981. The decline in PCB inventory cannot be explained by degradation processes because, as noted above, PCB composition is effectively uniformed throughout the 124B1 core. Rather, the apparent decline of the PCB inventories must be due to the same physical and biologically-mediated transport processes (cf., Eganhouse and Pontolillo, 2000) believed to be primarily responsible for the decreasing inventories of p,p'-DDE at station 3C from 1981 to 1995.

3.3. Long-chain alkylbenzenes

3.3.1. Distribution in sediments

Both varieties of long-chain alkylbenzenes were found in core 124B1. As discussed by Eganhouse et al. (1983a), the presence of these compounds in sediments of the Palos Verdes Shelf is attributable primarily, if not exclusively, to the discharge of alkylbenzenes from the LACSD outfall system. LABs have been found in many wastewater effluent streams (Takada and Eganhouse, 1998) where they normally arise from disposal of commercial detergents containing LAS surfactants. LAS surfactants, in turn, contain LAB residues ($\lesssim 1.0\%$ by weight) due to incomplete sulfonation (Eganhouse et al., 1983b, Takada and Ishiwatari, 1987).

Fig. 10a and b shows the distribution of ΣLABs and ΣTABs in cores 3C1 (1981) and 124B1. The concentrations of both classes of long-chain alkylbenzenes in the 124B1 core are lower than for sediments from 3C1 (1981) by more than an order of magnitude. The reasons for this difference are discussed below. In order to obtain ΣLAB concentrations, the abundances of 26 individual LABs were determined (one exception: 7-C_{13} and 6-C_{13} are not chromatographically resolved). This contrasts with the ΣTAB data which represent the summation of 12 major characteristic TAB peaks identified by Eganhouse et al. (1983a,b) in early work with these compounds (cf. Fig. 2b). Thus, 'ΣTAB' concentrations are not estimates of the 'total TAB' content of the sediments. Rather, they are a subset of it. We have also made estimates of 'total TAB' concentrations using the relative abundance of three significant TAB peaks (TAB1, TAB2, TAB3; cf., Fig. 2b) in our calibration standard solution. The ΣTAB and average estimated 'total TAB' concentrations are well correlated ($r^2 = 0.88$), but the latter are believed to be biased due to coelution of TABs and alteration of certain TABs during diagenesis (see discussion below). ΣTAB concentrations are approximately 30% of the estimated 'total TAB' concentrations.

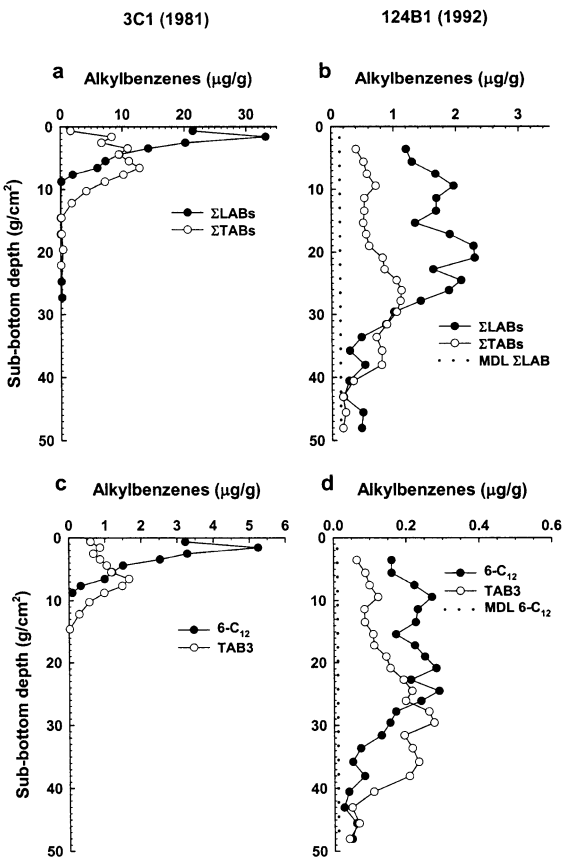


Fig. 10. Vertical concentration profiles of long-chain alkylbenzenes in sediment cores from the Palos Verdes Shelf: (a) ΣLABs, ΣTABs in core 3C1 (1981) (Eganhouse et al., 1983a), (b) ΣLABs, ΣTABs in core 124B1, (c) 6-phenyldodecane (6-C_{12}) and TAB3 in core 3C1 (1981) (Eganhouse et al., 1983a), (d) 6-phenyldodecane (6-C_{12}) and TAB3 in core 124B1. Dotted lines represent MDLs.

The profiles for the 3C1 (1981) and 124B1 cores have several features in common. First, both cores exhibit ΣLAB and ΣTAB profiles characterized by

highest concentrations within defined intervals below the sediment–water interface, and the ΣLAB and ΣTAB profiles overlap. In the 3C1 (1981) core, the profiles are smooth, and subsurface maxima for both alkylbenzene types are prominent features. In the 124B1 core, the profiles are considerably more complex. Concentrations of ΣLABs and ΣTABs in the deepest intervals of the 124B1 core are close to the limit of detection, whereas in the 3C1 (1981) core, LABs were near or below detection limits at sub-bottom depths exceeding about 9 g/cm^2.

Fig. 10c and d are profiles of selected alkylbenzenes in the 3C1 (1981) and 124B1 cores. Hereafter, use is made of individual alkylbenzene concentrations to avoid errors associated with summing concentrations of multiple analytes. We have chosen 6-phenyldodecane (6-C_{12}) to represent the LABs because the C_{12} homologs are the most abundant LABs, and 6-phenyldodecane is believed to be the most persistent isomer within this chain length group. TAB3 was selected because it is a major component identified in all samples. It is a single (or possibly more than one) C_{12}-benzene, and mass spectra for this peak in the unaltered calibration mixture and in the 3C1 (1981) and 124B1 sediments are identical (Eganhouse et al., 1983a). While there is evidence that some TABs may degrade (see discussion below), TAB3 is highly persistent. As shown in Fig. 10, concentration profiles for summed (i.e. ΣLAB and ΣTAB) and selected alkylbenzenes exhibit similar features. The major notable difference is that the relative abundance of 6-C_{12} vs. TAB3 in sediments from the 124B1 core is lower than ΣLAB vs. ΣTAB. This is explained by the fact that ΣTAB concentrations are approximately 30% of the 'total TABs', whereas ΣLAB concentrations include all known LABs in these samples. At the same time, 6-C_{12} and TAB3 represent nearly the same proportions of the ΣLABs and 'total TABs' (approximately 6–10%).

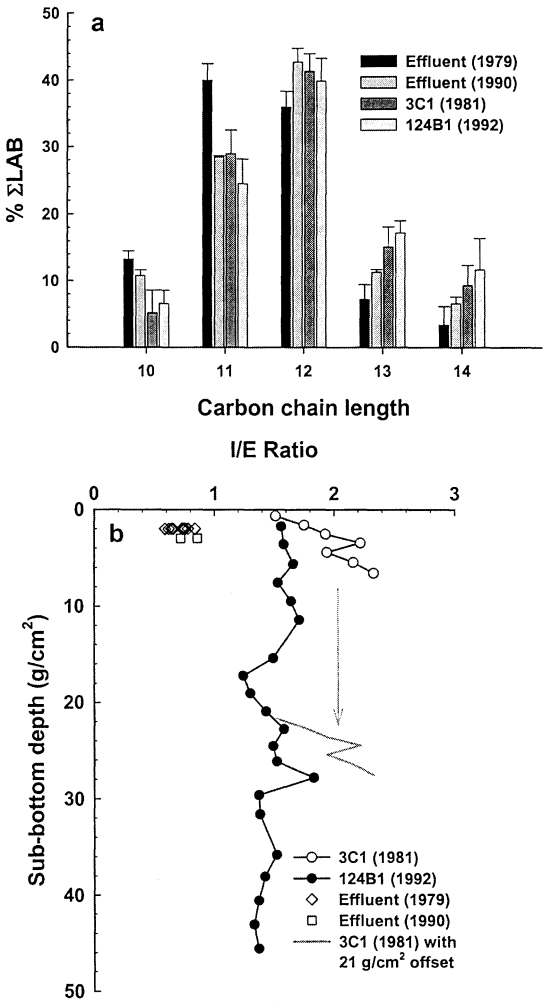


Fig. 11. (a) Chain length and (b) isomer composition of the linear alkylbenzenes. LACSD effluent (1979 — Eganhouse et al., 1983a; 1990 — Hendricks and Eganhouse, 1992), 3C1 (1981) core (Eganhouse et al., 1983a), 124B1 (this study). See text for explanation of I/E ratio and shaded 3C1 (1981) profile with 21 g/cm^2 mass accumulation offset.

3.3.2. Chain length distribution

The chain length distribution of LABs in sediments from the 3C1 (1981) and 124B1 cores and in LACSD effluent samples collected in 1979 and 1990 is shown in Fig. 11a. In general, the order of chain length abundance in the 124B1 sediments is

$$C_{12} > C_{11} > C_{13} > C_{14} > C_{10}.$$

The only exception is the occasional reversal of C_{10} and C_{14} chain length groups. This pattern is very similar to that found for the 3C1 (1981) core. By contrast, LACSD effluent samples collected in 1979 are dominated by the C_{11} homolog group. Effluents from both periods (1979, 1990) have higher relative abundances of the shorter chain length homologs (C_{10}, C_{11}) and lower relative abundances of the longer chain length homologs (C_{13}, C_{14}) than do the

sediments. This difference probably reflects the selective loss of LABs with shorter chain lengths due to their higher aqueous solubilities and/or greater susceptibility to biodegradation (Murray et al., 1987; Sherblom et al., 1992; Raymundo and Preston, 1992).

3.3.3. Isomeric composition

To investigate the potential role of biodegradation, we examined the isomeric composition of the LABs. An index, the 'I/E ratio', has been proposed by Takada and Ishiwatari (1987, 1989) as a means of expressing the relative abundance of isomers within a given chain length. This ratio (for the C_{12} group) is defined as

$$\text{I/E ratio} = [6\text{-}C_{12} + 5\text{-}C_{12}]/[4\text{-}C_{12} + 3\text{-}C_{12} + 2\text{-}C_{12}],$$

where 6-C_{12} and 5-C_{12} compounds are called the 'internal' isomers because the benzene ring is attached to the innermost carbons on the alkyl chain (Fig. 2a). The 4-C_{12}, 3-C_{12}, and 2-C_{12} compounds are, thus, the 'external' isomers. The impetus for computing such a ratio is the fact that under aerobic conditions the external isomers biodegrade more rapidly in aquatic environments than the internal isomers (Eganhouse et al. 1983a; Takada and Ishiwatari, 1989, 1991; Bayona et al., 1986). Thus, the I/E ratio increases as aerobic degradation proceeds. Laboratory experiments have indicated that degradation of the LABs under anaerobic conditions is very slow and does not result in alteration of the isomer composition (Takada and Ishiwatari, 1989; Steber et al., 1995). Studies of the LACSD effluent in 1979 and 1990 yielded I/E ratios for the C_{12}-LABs within the range, 0.59–0.86. This contrasts with ratios obtained for the 3C1 (1981) and 124B1 cores of 1.2–2.3 (Fig. 11b). Because physical processes cannot explain the observed differences in isomeric composition (Sherblom et al., 1992; Takada and Ishiwatari, 1989), we conclude that the LABs from cores 3C1 (1981) and 124B1 must have undergone biodegradation following release from the LACSD outfall system.

3.3.4. Biodegradation

Examination of Fig. 11b reveals that the I/E ratios in core 3C1 (1981) are higher than in the 124B1 core, and there is a trend of increasing ratios with greater sub-bottom depth in the 3C1 core. No such trend is obvious in the 124B1 core profile. If one assumes that the I/E ratio of particles deposited on the sea floor have not changed over the period represented by the upper 9 g/cm^2 of the 3C1 (1981) core, the increasing trend in I/E ratio would indicate that degradation of the LABs continued following burial. Alternatively, the ratios may reflect temporal variations in the composition of the LABs at the time they were incorporated into the sediments. The lack of any systematic increase in I/E ratio with depth in the 124B1 core seems at odds with the 3C1 (1981) profile and suggests that once the LABs were incorporated into the sediment bed, biodegradation stopped or was reduced.

To examine the possibility that the 3C1 (1981) ratio profile might reflect temporal variations in the isomeric composition of sedimenting particles, we carried out a correlation analysis of the I/E ratio profiles in the 3C1 (1981) and 124B1 cores. First, a simulated profile was created for each core by calculating interpolated ratios at 1 g/cm^2 depth increments. The I/E ratios for the two cores were then correlated as a function of depth offset. An offset of 21 g/cm^2 provided the best correlation coefficient ($r^2 = 0.88$). Thus, the upper 6 g/cm^2 of the 3C1 (1981) core corresponds to the 21–27 g/cm^2 interval of the 124B1 core. In this interval of the 124B1 core, the I/E ratio appears also to increase (see shaded profile in Fig. 11b). Data presented in Eganhouse and Pontolillo (2000) show that similar offsets are obtained by correlation analysis of concentration profiles for p,p'-DDE, the PCBs, and the long-chain alkylbenzenes. This suggests that the offset obtained from analysis of the I/E ratio profiles may reflect actual differences in the depositional records preserved in these cores. Thus, the apparent trend found in the 3C1 (1981) core might, in part, reflect temporal variation in the isomeric composition of the LABs rather than the effects of biodegradation. It is interesting to note that Zeng and Venkatesan (1999) recently reported an I/E ratio profile for a core collected adjacent to the outfall system that is very similar to the one observed for core 124B1.

We now consider the reasons for the differences in concentrations of long-chain alkylbenzenes in the 3C1 (1981) and 124B1 cores (Fig. 10). Table 1 lists

inventories of ΣLABs, ΣTABs, 6-C_{12}, and TAB3 for the 3C1 (1981) and 124B1 cores. In all cases, inventories found in the 124B1 core are lower than those found in the 3C1 (1981) core. The percent decreases from 1981 to 1992 are as follows: *p,p′*-DDE — 64%, ΣLAB — 46%, ΣTAB — 67%, 6-C_{12} — 55%, and TAB3 — 39%. To evaluate if these differences reflect temporal changes, we computed inventory ratios for four pairs of constituents, ΣLAB/ΣTAB, 6-C_{12}/TAB3, 6-C_{12}/*p,p′*-DDE, and TAB3/*p,p′*-DDE for the two cores (Table 2). The TABs were not detected in the LACSD effluent in 1979 or 1990 (Eganhouse et al., 1983a; Hendricks and Eganhouse, 1992). Thus, it is presumed that

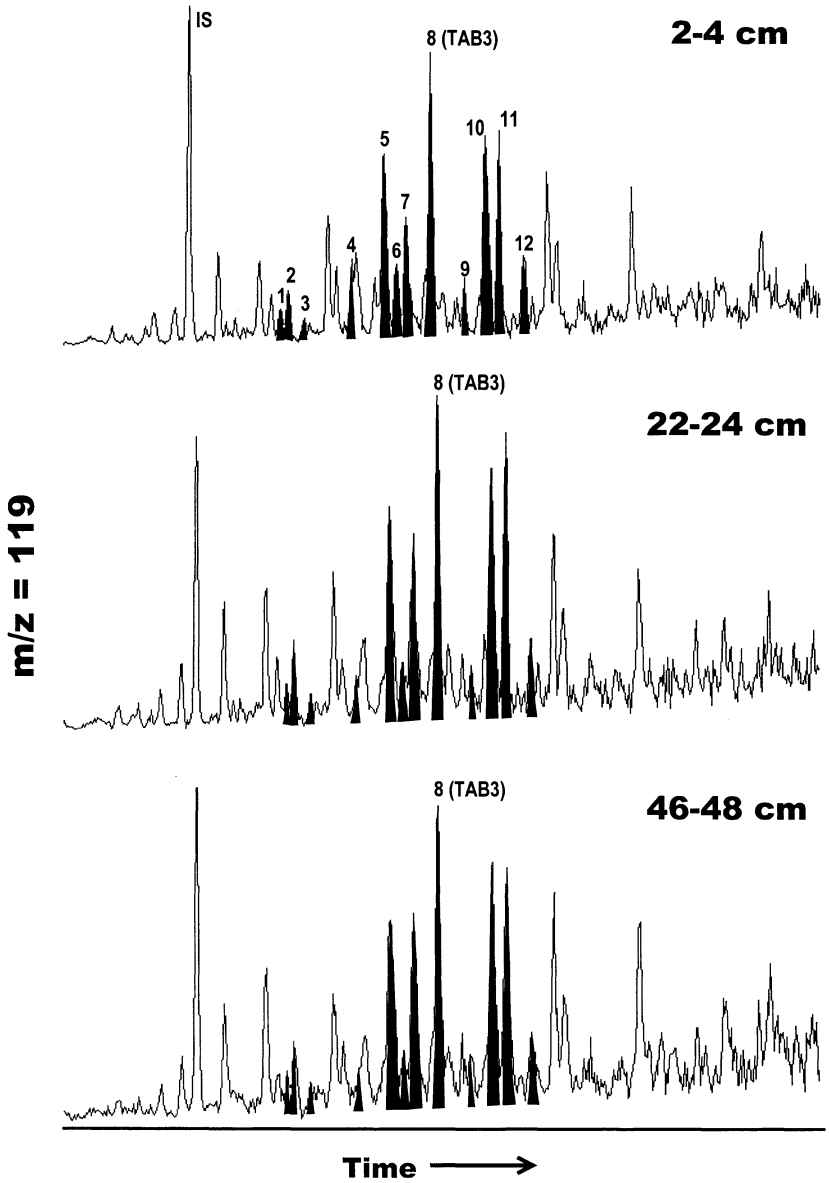


Fig. 12. Extracted ion current profiles ($m/z = 119$) of tetrapropylene-based alkylbenzenes (TABs) in three sections from sediment core 124B1. Peak numbers refer to TABs shown in Fig. 2b. IS = internal standard.

TABs were not introduced to the waste treatment system subsequent to 1979 and perhaps for some unknown period before that time. Similarly, p,p'-DDE was not discharged by the LACSD in significant quantities after 1980 (Fig. 7c). By contrast, LABs were found in the LACSD effluent in both 1979 and 1990. Thus, the ΣLAB/ΣTAB, 6-C_{12}/TAB3, and 6-$C_{12}/p,p'$-DDE ratios are expected to be greater for the 1992 core because LAB emissions continued for at least a decade after TAB and significant p,p'-DDE emissions had ceased. This prediction assumes that all these compounds behave conservatively and that any losses are physical in nature.

The ΣLAB/ΣTAB and 6-$C_{12}/p,p'$-DDE inventory ratios are higher in the 1992 core as expected. However, the 6-C_{12}/TAB3 inventory ratio is lower in the 1992 core, whereas the TAB3/p,p'-DDE inventory ratio is higher. Together, these data indicate that TAB3 is more persistent than 6-C_{12}, p,p'-DDE and other TABs that comprise ΣTAB. The greater persistence of TAB3 relative to 6-C_{12} is most likely due to the presence of a highly branched alkyl side chain that inhibits biodegradation (Boethling, 1993). Fig. 12 shows extracted ion current profiles ($m/z = 119$) of the TABs in three sections of the 124B1 core. Although the profiles exhibit more similarities than differences, subtle changes can be observed with increasing depth. Specifically, peaks 4, 5, 6, and 12 tend to decrease in relative abundance with increasing depth. TAB3, on the other hand, is one of the most persistent TABs. If correct, our interpretation implies that degradation of the LABs, including 6-C_{12}, continues following burial even though there is no observable systematic increase in the I/E ratio (Raymundo and Preston, 1992). This may explain the rather steep decline in LAB concentration with increasing depth in the 3C1 (1981) core (Fig. 10; cf., Eganhouse et al., 1983a) and observations of decreasing LAB inventories at the '106-mile' deepwater disposal site in the New York Bight (Lamoureux et al., 1996). It also explains, in part, the lower maximum concentrations found in the 1992 core as compared with those observed in the 1981 core. Thus, while LABs can provide useful information on depositional processes, application of the LABs as quantitative molecular tracers must be undertaken with caution.

4. Conclusions

Contamination of sediments and biota on the Palos Verdes Shelf is of some concern because of potential long-term ecological effects. In particular, remobilization of the heavily contaminated sediments, now buried several tens of centimeters below the sediment–water interface has been identified as a significant problem (Drake, 1994; Stull et al., 1996, Wheatcroft and Martin, 1996). We have investigated three classes of organic contaminants deposited in shelf sediments for periods of up to 45 years in an effort to understand the diagenetic fate of these compounds. Using historical information on the composition of DDT wastes, we have attempted to reconstruct the pathways of DDT degradation. DDT wastes were discharged to the LACSD sewer system by Montrose Chemical from at least 1953 until 1971. Throughout this period, LACSD effluent composition was most likely dominated by parent DDT. During sedimentation and prior to burial in reducing layers of the sediments, parent DDT appears to have been transformed to DDE via dehydrochlorination. This must have occurred relatively rapidly under oxidizing conditions and probably was not mediated biologically. Evidence from cores taken on the shelf in 1992 suggests that following burial, p,p'-DDE was transformed to p,p'-DDMU by reductive dechlorination. Based on our estimates, approximately 9–23% of the p,p'-DDE was converted to DDMU in the sediments since DDT wastes were first released ($\lesssim$ 1953). Results of LACSD investigations show that inventories of p,p'-DDE at station 3C decreased by about 50% between 1981 and 1995. Because there has been little change in the DDT composition of sediments during this period, transformation of DDE to DDMU cannot be primarily responsible for the observed decrease in inventory. Rather, physical and biologically-mediated remobilization is most likely the major cause. Further evidence for the operation of these processes is discussed in Eganhouse and Pontolillo (2000). Our field data suggest that in situ rates of reductive dechlorination are much slower than those observed by Quensen et al. (1998) in laboratory microcosm experiments, and that over time scales of a decade, p,p'-DDE is a highly persistent marker of waste impact. This accounts for its survival in sediments of the Palos

Verdes Shelf for nearly half a century and its progressive accumulation in myctophid fish from 1949 to 1970 (MacGregor, 1974). Concentrations of ΣPCBs are highly correlated with ΣDDT. This likely reflects the strong similarity in their discharge histories. However, the composition of PCBs in sediment cores are extremely uniform, and there is no indication that reductive dechlorination is occurring. Thus, the PCBs are highly persistent markers of waste contamination in this environment. The correlation between ΣPCB and ΣDDT concentrations in sediments further supports our belief that the DDTs are persistent markers of waste contamination.

The long chain alkylbenzenes are composed of linear (LABs) and branched (TABs) varieties, both of which were and continued to be used as synthetic precursors to the alkylbenzenesulfonate surfactants. Examination of chain length and isomeric compositions of LABs in effluent and sediment samples indicate that these compounds undergo degradation following discharge from the outfalls. Once buried, the isomeric composition of the LABs does not change. However, there is evidence from declining LAB inventories that further degradation of the LABs does occur. Hence, use of the LABs as quantitative molecular tracers must be approached with caution. In general, the TABs are persistent, presumably as the result of branching in the alkyl side chain. However, we have found evidence for alteration of some components of the TABs in sediment cores. Others, such as TAB3, are among the most persistent organic contaminants in sediments of the Palos Verdes Shelf.

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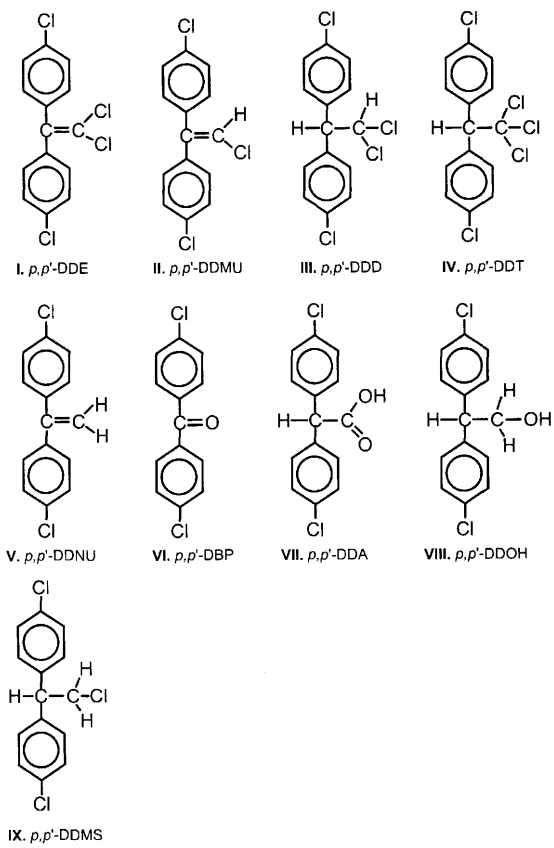
Appendix A



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