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### Abstract

During more than 60 years, sedimentation on the Palos Verdes Shelf has been dominated by time-varying inputs of municipal wastewater from the Los Angeles County Sanitation Districts (LACSD) and debris from the Portuguese Bend Landslide (PBL). The present study examines the depositional history of wastewater-derived organic contaminants at a site approximately 6–8 km downcurrent from the outfall system. Sediments at this location are impacted by contributions from both sources, but the relative influence of the sources has changed over time. Two classes of hydrophobic organic contaminants (chlorinated hydrocarbons, long-chain alkylbenzenes) were determined in sediment cores collected in 1981 and 1992. Using molecular stratigraphy, we determined average sedimentation rates (cm/year) and mass accumulation rates ( $\text{g cm}^{-2} \text{ year}^{-1}$ ) for the following periods: 1955–1965, 1965–1971, 1971–1981 and 1981–1992. The results show that sedimentation and mass accumulation rates increased from 1955 to 1971 and decreased from 1971 to 1981. These trends are consistent with historical information on the emission of suspended solids from the outfall system, indicating that the discharge of wastes dominated sedimentation at the site during this period. In the 1980s and early 1990s, however, mass accumulation rates increased in spite of continually decreasing emissions of wastewater solids. Several lines of evidence indicate that this increase was due to mobilization of debris from the PBL during and after unusually strong winter storms in the 1980s. As a result, heavily contaminated sediments deposited during the years of greatest waste emissions (i.e. 1950–1970) have been buried to greater sub-bottom depths, thereby reducing their availability for mobilization to the overlying water column. These results highlight the dynamic nature of sedimentation in contaminated coastal ecosystems and its importance to the long-term fate and effects of toxic substances. Published by Elsevier Science B.V.

*Keywords:* Palos Verdes Shelf; sedimentation rates; stratigraphy; deposition; DDT; PCBs

### 1. Introduction

Since 1937, treated municipal wastewater has been discharged to waters of the Palos Verdes Shelf from submarine outfalls operated by the Los Angeles

County Sanitation Districts (LACSD; see Fig. 1 in Eganhouse et al., 2000). The LACSD effluent is derived from domestic and industrial sources and has historically contained a wide variety of inorganic and organic contaminants. Many of these contaminants, including the insecticide, DDT (+ metabolites), and the polychlorinated biphenyls (PCBs), partition strongly to particulate matter. Consequently, they have tended to accumulate in sediments of the Palos

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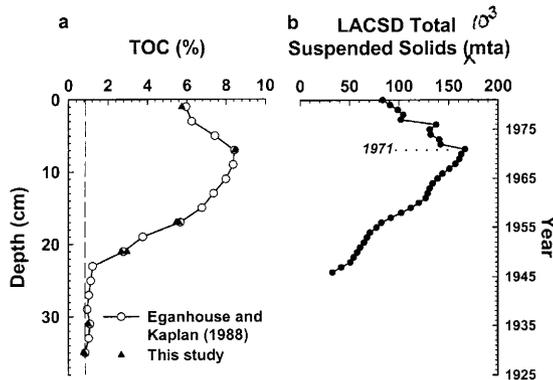


Fig. 1. (a) Vertical concentration profile of TOC in core 3C1 (1981) and (b) total suspended solids mass emission rates (mta = metric tons/year) from the LACSD treatment plant from 1946 to 1981. Dashed line indicates approximate 'background' concentration of TOC.

Verdes Shelf (Young et al., 1976a; MacGregor, 1976; Stull et al., 1986a).

Tissues of biota indigenous to the Palos Verdes Shelf have also been shown to contain elevated concentrations of hydrophobic organic contaminants such as the DDTs and PCBs (cf. references in Young et al., 1991). Several lines of evidence indicate that bottom sediments are the principal source of contamination to the benthos. For example, Young et al. (1988) demonstrated that the bioaccumulation of these compounds by benthic organisms continued long after emissions of the contaminants from the outfalls were curtailed or eliminated (ca. the early to mid-1970s). Moreover, they observed that DDT/PCB mean concentration ratios in muscle tissue of *Microstomus pacificus* (Dover sole) from the Palos Verdes Shelf more closely resembled those of outfall sediments than the LACSD effluent. In studies of mussels deployed in cages near the outfalls, Young et al. (1976b) found the rate and extent of bioaccumulation of DDT and PCBs decreased with increasing elevation above the seafloor. Because of the persistence of these compounds and their potential long-term ecological effects (Ferraro et al., 1991), the fate of the waste-impacted deposit continues to be a subject of concern (Renner, 1998).

Previous studies have shown that the most heavily contaminated sediments are adjacent to and northwest of the outfalls with highest accumulations centered roughly along the 60-m isobath (Stull et al.,

1986a; Lee, 1994a). This pattern reflects the dominantly poleward-moving subsurface currents that flow along the continental shelf in this region (Hickey, 1992). Sediments collected downcurrent from the outfalls on the mid- to outer shelf (i.e. 45–100 m water depth) can be characterized as a three-layer system (Lee, 1994a; Swift et al., 1996). The upper 15–20 cm of the sediment column has relatively low and fairly uniform concentrations of waste-derived contaminants (e.g. DDT, PCBs). Bulk densities are low (1.4–1.5 g/cm<sup>3</sup>), increasing slightly with depth, and organic carbon concentrations are marginally elevated (1.5–3.5%). This is a biologically active zone, and the sediments in this layer are believed to have accumulated during the period of declining effluent solids emissions (> 1971). Emissions of DDT and PCBs also decreased dramatically during this period because of stringent source control measures implemented by the LACSD in the early 1970s (Stull and Tang, 2000; Fig. 7c in Eganhouse et al., 2000). Underlying the surficial layer is a 20–25 cm thick interval of heavily contaminated sediments having lower bulk densities (1.2–1.3 g/cm<sup>3</sup>), more silt and clay (Drake, 1994b), and elevated organic carbon concentrations (3–10%). This is the 'effluent-affected layer' (EAL), so-called because it is believed to have been deposited during the period of increasing wastewater solids and contaminant emissions (ca. 1940–1971; Stull and Tang, 2000). Below the EAL lie uncontaminated or only slightly contaminated native sediments (i.e. pre-effluent: ≤ 1937) of variable thickness. The native sediments have higher bulk densities (1.8–2.1 g/cm<sup>3</sup>) and lower organic carbon concentrations (≤ 1%). Along the 60-m isobath, the boundary between native and (overlying) contaminated sediments is quite distinct (Hampton et al., 2000; Lee, 1994a). While these features primarily reflect the historical record of waste emissions from the outfall system, other sources of sediment, including debris from the Portuguese Bend Landslide (PBL), cliff erosion and natural biogenic detritus, can make significant contributions to the shelf (Kayen et al., 1994).

Several studies have documented the recovery of the benthic community during the 1970s, 1980s and 1990s as effluent emissions were on the decline (Stull and Tang, 2000 and references therein). An important consequence of these changes is the poten-

tial for increased upward transport of contaminants from the heavily contaminated subsurface layer via bioturbation (Los Angeles County Sanitation Districts, 1988; Stull et al., 1996). Two groups have recently developed numerical models for the purpose of predicting the long-term fate of effluent-affected sediments on the Palos Verdes Shelf (Drake et al., 1994 + appendices; Sherwood et al., 1996; Niedoroda et al., 1996). These models incorporate bioturbation, resuspension, lateral advection, molecular diffusion and desorption processes. In both models, bioturbation is the principal mechanism by which heavily contaminated sediments are mixed upward into the less contaminated surficial sediment layer. The single most important parameter affecting the outcome of model simulations is sedimentation rate. This is because the rate of sedimentation determines the effectiveness with which heavily contaminated sediment can be buried below depths at which significant bioturbation is occurring.

Application of conventional radioisotopic methods of dating of sediments on the Palos Verdes Shelf is complicated by non-steady sedimentation that has occurred over the last 50 + years and the possibility of variable fluxes of tracer species (e.g.  $^{210}\text{Pb}$ ; Wheatcroft and Martin, 1994; Swift et al., 1996; Paulsen et al., 1999). In addition, the shelf is inhabited by an increasingly diverse and changing benthos whose activities result in mixing of sediments and alteration of its physical and chemical properties (Stull et al., 1996). These difficulties have led to the use of molecular stratigraphy (Eganhouse and Kaplan, 1988) and correlations between contaminant profiles in sediment cores collected at different times (Kettenring, 1981; Wheatcroft and Martin, 1994) for estimation of average sedimentation rates over specific time intervals. In this paper, we attempt to reconstruct the depositional history of two classes of organic contaminants (chlorinated hydrocarbons, long-chain alkylbenzenes) at a waste-impacted site on the Palos Verdes Shelf. Our approach is to relate information on the known or likely rates of release of these substances from the outfalls to vertical concentration profiles of the contaminants of interest. In an earlier paper, Eganhouse and Kaplan (1988) described the organic geochemistry of a sediment core collected by the LACSD in 1981 (station 3C; Fig. 1 in Eganhouse et al., 2000). In 1992, as part of

a larger study undertaken by the U.S. Geological Survey (USGS), we collected another core near this location (station 522; cf., Fig. 1 in Eganhouse et al., 2000). By comparing data for sediment cores collected in 1981 and 1992 we sought to improve our understanding of sedimentation processes operative during the 1980s and to extend the chronology of sediments collected at station 3C in 1981. In this context, our primary objective was to develop estimates of sedimentation and mass accumulation rates for comparison with those developed by other investigators.

## 2. Materials and methods

### 2.1. Sampling

Details of the procedures used for sampling and analysis of sediments can be found in a companion paper (Eganhouse et al., 2000). A brief description is given here. Sediments have been sampled by the LACSD in odd-numbered years since 1981 using a custom-built thin-walled gravity corer (Bascom et al., 1982). One such core was collected by the LACSD in 1981 at station 3C (cf., Fig. 1 in Eganhouse et al., 2000), and a portion was provided to us for further organic geochemical analyses (Eganhouse and Kaplan, 1988). Station 3C is approximately 6–8 km downcurrent from the outfall system at a water depth of 61 m. This is at roughly the same depth as the outfall diffuser ports (i.e. 48–63 m; Drake, 1994a). Consequently, sediments at station 3C are moderately contaminated by wastewater effluent. This station is also proximal to the PBL, and, as we will show, debris from the landslide has contributed to sedimentation at this general location. In 1992 and 1993 the USGS collected box cores during cruises aboard the R/V *Farnella* and R/V *Sproul*, respectively. Data presented here are for two USGS box cores collected at station 522 (cf., Fig. 1 in Eganhouse et al., 2000): 124B1 (33°43.84'N, 118°24.08'W; water depth = 57 m, 7/1992) and 209B1 (33° 43.81', 118° 24.08'; water depth = 59 m, 3/1993). Cores taken at this station were near, but slightly inshore of, those collected by the LACSD at station 3C in 1981. Upon recovery, each box core

was subcored. One subcore, designated by the suffix, *-DDT*, was used for determination of trace organics (DDT + metabolites, PCBs, long-chain alkylbenzenes) and elemental abundance (total organic carbon — TOC, total nitrogen — TN). Another subcore, designated by the suffix, *-SS*, was taken for stratigraphy/sedimentology studies (cf., Barber et al., 1994; Drake, 1994b). The *-DDT* subcores were immediately frozen onboard ship and maintained frozen until sectioning (2-cm intervals) had been completed. The *-SS* subcores were split lengthwise and maintained in sealed core tubes under refrigeration ( $\approx 4^{\circ}\text{C}$ ) until analyses for elemental abundance could be performed.

## 2.2. Elemental abundance

Sediments from the core collected by the LACSD at station 3C in 1981 (core 3C1) were analyzed for TOC and TN by wet acidification, sealed tube combustion and cryogenic separation/vacuum line manometry (Eganhouse and Kaplan, 1988). Sediments collected by the USGS in 1992–1993 (i.e. subcores 124B1-*SS*, 124B1-*DDT* and 209B1-*DDT*) were treated for carbonate removal by the acid vapor acidification method of Hedges and Stern (1984) and analyzed in duplicate on a Carlo Erba EA1108 ele-

mental analyzer. The instrument was calibrated daily at five levels using acetanilide, and all samples were blank corrected. A daily calibration curve obtained by linear regression with forcing through the origin provided correlation coefficients  $> 0.999$ . Method detection limits (MDLs; Environmental Protection Agency, 1992) were 0.007% (TOC) and 0.003% (TN). Measured concentration ranges of the sediment samples were 0.7–3.5% (TOC) and 0.05–0.28% (TN). Accuracy and precision was assessed by analyzing replicate samples of a standard reference material, PACS-1, obtained from the National Research Council of Canada. PACS-1 is a marine sediment with a certified total carbon content of  $3.69 \pm 0.11\%$ , and a non-certified TOC content of 3.56%. Replicate analysis ( $n = 5$ ) of PACS-1 yielded the following results: total carbon —  $3.68 \pm 0.13\%$ , TOC —  $3.53 \pm 0.05\%$ , and TN —  $0.265 \pm 0.003\%$ .

## 2.3. Trace organics

Details of the methods used for determination of DDTs and long-chain alkylbenzenes in the 3C1 (1981) core can be found in Eganhouse et al. (1983). Similar information for the 124B1-*DDT* core along with details of the methods used for congener-specific determination of PCBs is given in Eganhouse et al.

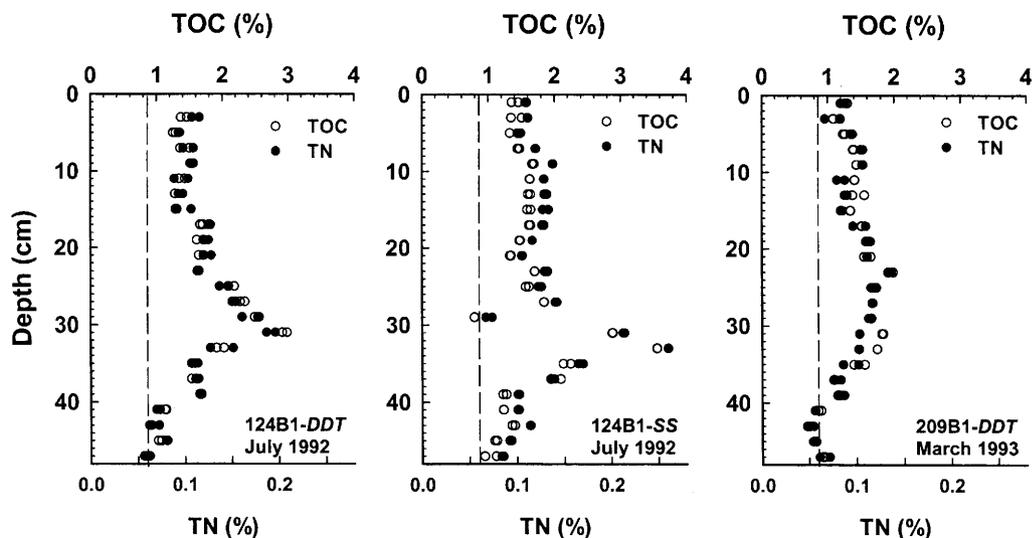


Fig. 2. Vertical concentration profiles of TOC and TN in cores collected from station 522 in 1992–1993. Dashed line indicates approximate 'background' concentration of TOC.

(2000). Seven DDT compounds (*o,p'*- and *p,p'*-isomers of DDE, DDT, DDD + *p,p'*-DDMU) and 87 PCB congeners were determined by high resolution gas chromatography/electron capture detection (HRGC/ECD) with confirmation by electron capture-negative chemical ionization HRGC/mass spectrometry. Hereafter,  $\Sigma$ DDT refers to the summed concentrations of the seven DDT compounds, and  $\Sigma$ PCB is the summed concentrations of all PCBs free of non-PCB interference (73 congeners in all).

Two varieties of long-chain alkylbenzenes, the linear alkylbenzenes (LABs) and the tetrapropylene-based alkylbenzenes (TABs) were determined by HRGC/mass spectrometry (cf., Fig. 2 in Eganhouse et al., 2000). The LABs consist of 26 secondary phenylalkanes having alkyl chains 10–14 carbons in length. Individual LABs are designated  $j$ -C<sub>*k*</sub> where  $j$  = position of substitution on the alkyl chain and  $k$  = number of carbons in the chain. For example, 6-phenyldecane is given as 6-C<sub>12</sub>. Hereafter,  $\Sigma$ LAB refers to the summed concentrations of 26 LAB compounds. The TABs are a complex mixture of phenylalkanes produced by Friedel–Crafts alkylation of benzene using tetrapropylene (Ötvös et al., 1973). Twelve major peaks, representing approximately 30% by weight of the TAB mixture, were quantified according to methods described in Eganhouse et al. (1983, 2000). The summed concentrations of these 12 TAB peaks are given as  $\Sigma$ TAB. One of the 12 peaks, TAB3, is a highly persistent contaminant (Eganhouse et al., 2000) that serves here as a molecular marker of waste-derived TABs.

### 3. Results and discussion

#### 3.1. Elemental abundance

##### 3.1.1. Sedimentary record of waste emissions

Fig. 1a shows the concentration of TOC in core 3C1 (1981) based on the wet acidification/sealed tube combustion technique (Eganhouse and Kaplan, 1988). Also shown are results from this study using the vapor acidification/elemental analyzer procedure. The data sets are in good agreement. TOC concentrations in the sediment core range from 0.9% to 8.4%. The vertical concentration profile is smooth and is characterized by a subsurface maximum at a

depth of 6–8 cm. [Note: Because the core was collected in 1981, the three-layer system described earlier was not yet fully established]. Concentrations at or below approximately 0.85% organic carbon (dashed line) are found at intervals deeper than about 26 cm. These are typical of background concentrations found in sediments from the narrow continental shelf off southern California (Eganhouse and Venkatesan, 1993). Previous work has shown that less than 25% of the organic carbon and nitrogen in sediments below 26 cm in the 3C1 (1981) core is derived from wastewater effluent (Eganhouse and Kaplan, 1988). Thus, these are largely native sediments deposited prior to the onset of waste emissions in 1937.

The sediment core profile can be compared with data on the release of suspended solids from the LACSD's outfall system from 1946 to 1981 (Fig. 1b). The LACSD services a large portion of metropolitan Los Angeles and has undergone substantial change in its 60+ year history. Presently, the outfall system consists of two simultaneously operating multiport diffusers, a 229-cm diameter wye-shaped outfall completed in 1956 and a 305-cm diameter dogleg completed in 1965 (cf., Fig. 1 in Eganhouse et al., 2000). A detailed description of the history of the outfall system and the evolution of waste treatment practices can be found elsewhere (Schafer, 1989; Stull et al., 1996). In general, mass emissions of suspended solids increased with population almost monotonically between 1946 and 1971. After 1971 solids emissions declined as a result of improved treatment (Stull and Haydock, 1986). The similarity between the vertical TOC concentration profile in the 3C1 (1981) core and the trend in solids emissions from the LACSD from 1946 to 1981 suggests that sediments at this location faithfully record the history of waste discharge. This conclusion is supported by the stable isotopic composition ( $\delta^{15}\text{N}$ ,  $\delta^{13}\text{C}$ ) of the sedimentary organic matter and the vertical distribution of waste-derived contaminants at this site (Eganhouse and Kaplan, 1988).

##### 3.1.2. Spatial variability in sedimentary organic matter content

Fig. 2 shows vertical concentration profiles of TOC and TN for subcores 124B1-DDT and 124B1-SS collected in July 1992 and for subcore 209B1-DDT

collected in March 1993. Subcores 124B1-*DDT* and 124B1-*SS* were taken from a single box, and the 8.9 cm (od) core liners were positioned within a few centimeters of each other. Therefore, the profiles for the 124B1 subcores provide an indication of the small-scale spatial variability in organic matter content of Palos Verdes Shelf sediments at this location. In general, TOC and TN concentrations for the 124B1 subcores fall within 0.8–3.6% and 0.06–0.26%, respectively, and the profiles have similar shapes consistent with the three layer system described earlier. However, the 124B1-*DDT* core profiles exhibit subsurface maxima at 30–32 cm, whereas the maxima in the 124B1-*SS* subcore are at a depth of 32–34 cm. In addition, the 124B1-*SS* subcore has a deflection to minimum concentrations at a depth of 28–30 cm. This feature is not seen in our data for the 124B1-*DDT* subcore, but it has been reported by Costa and Bailey (1994) for split samples of the 124B1-*DDT* subcore. It may be a small-scale anomaly that reflects non-local mixing by deep burrowing benthic organisms (Wheatcroft and Martin, 1994; Swift et al., 1996). Although minor, these differences are not artifacts of sampling or analytical procedures. They reflect spatial variability that exists over vertical and horizontal distances on a scale of a few centimeters (Murray, 1994). Similar variations have been noted for bulk density profiles of replicate cores from the Palos Verdes Shelf (Kayen, 1994).

For both subcores the maximum concentrations ( $\text{TOC}_{\text{max}}$ ) are lower and the depths at which they occur are considerably greater than those observed

for the 3C1 (1981) core (cf. Figs. 1 and 2; Table 1). In addition, it would appear that the box corer used in 1992/1993 did not penetrate as deeply into the pre-effluent sediments as the gravity corer did in 1981. Bulk density profiles presented by Kayen (1994) support this conclusion. Linear regression analysis of the TOC vs. TN data for both of the 124B1 subcores yields high correlation coefficients ( $r^2 \geq 0.98$ ) with slopes corresponding to average C/N ratios of 14.4–15.7. These are similar to ratios reported by Eganhouse and Kaplan (1988) for core 3C1 (1981; C/N = 10.6–17.8). There is no systematic variation in the C/N ratio with depth to indicate diagenetic alteration of the organic matter or changes in composition of the source materials over time. Thus, it is reasonable to conclude that the sedimentary organic matter represented by these profiles is largely refractory, and its abundance can be used as an indicator of the presence of LACSD effluent particles (Eganhouse and Kaplan, 1988).

Examination of the profiles for subcore 209B1 reveals that concentrations of TOC and TN are generally lower (0.7–2.0% and 0.05–0.14%, respectively) than observed for the 124B1 subcores, and the profiles are relatively featureless. Core 209B1 was collected with the same box corer near (within  $\approx 50$  m) but in deeper water than the 124B1 core (Fig. 1 in Eganhouse et al., 2000). However, sampling occurred on a separate cruise that took place approximately 9 months later. The differences between the 124B1 and 209B1 profiles must primarily reflect variability over spatial scales defined by navi-

Table 1  
Distribution and inventories of TOC in sediment cores from the Palos Verdes Shelf (1981–1993)

Station/ core	Date collected	Analyzed by	Length (cm) <sup>a</sup>	Depth to $\text{TOC}_{\text{max}}$ (cm)	$\text{TOC}_{\text{max}}$ (%)	Inventory ( $\text{mg}/\text{cm}^2$ ) <sup>b</sup>	
						TOC	$\text{TOC}_{\text{EAL}}^c$
3C1	4/81	LACSD	36 (26)	11	5.6	709 (67)	608 (79)
3C1	4/81	Eganhouse and Kaplan (1988)	36 (26)	7	8.4	924 (75)	796 (85)
3C3	4/81	LACSD	36 (26)	9	5.4	625 (66)	535 (78)
3C1	5/87	LACSD	40 (32)	17	6.8	883 (70)	802 (77)
124B1- <i>DDT</i>	7/92	this work	48 (44)	31	3.0	743 (41)	697 (49)
209B1- <i>DDT</i>	3/93	this work	49.5 (42)	23	1.9	698 (37)	636 (42)
3C1	7/93	LACSD	58 (48)	31	2.6	703 (39)	605 (47)

<sup>a</sup>Numbers in parentheses are the depths to the base of the EAL.

<sup>b</sup>Numbers in parentheses represent the percent of the TOC inventory that is derived from wastewater effluent. See text for explanation.

<sup>c</sup> $\text{TOC}_{\text{EAL}}$  is the TOC inventory from the core top to the base of effluent-affected layer.

gational systems that were used to position the ships during sampling. Differential GPS was employed during collection of both 124B1 and 209B1 cores and is accurate to  $\pm 10$  m (Hamer, 1994). Hence, the sampling locations shown in Fig. 1 of Eganhouse et al. (2000) are reasonable representations of the positions and uncertainties in position for these cores. Given that 209B1 was collected in deeper water and slightly nearer the outfalls, it is surprising that the profiles for this core show little correspondence to the 124B1 core profiles. Based on comparison of replicate box cores, Drake (1994a) has concluded that there is more spatial variation in grain size distribution at station 522 than at station 556 (near station 6C, Fig. 1 of Eganhouse et al., 2000). Thus, the differences in TOC/TN profiles found for cores 209B1 and 124B1 are likely due to spatial variability on the scale of tens of meters in the vicinity of stations 3C/522.

### 3.1.3. Fate of effluent-derived TOC

Table 1 provides data on the depth-integrated inventories of TOC and TN in the subcores described above. Also shown are data produced by the LACSD for cores collected from station 3C in the years 1981, 1987 and 1993 along with thicknesses of the EAL as determined from TOC and bulk density profiles. Comparison of results obtained by this laboratory and the LACSD for TOC in core 3C1 (1981) shows that the concentrations determined by the two laboratories were highly correlated ( $r^2 = 0.96$ ). However, data obtained by the LACSD were systematically lower by about 20%. This difference is reflected in the TOC inventories determined in the 3C1 (1981) core based on analytical results from the two laboratories (709 vs. 924 mg/cm<sup>2</sup>). The TOC inventories calculated from LACSD data for the period 1981–1993 are variable and exhibit no discernible temporal trend. Because organic carbon is not derived solely from effluent particles, comparing inventories for cores of different length could lead to bias. Therefore, we have computed inventories of TOC within the effluent-affected layer (TOC<sub>EAL</sub>). The inventories are uniformly lower, but the same between-core relationships are observed. We also estimated the proportion of TOC that is derived from effluent particles using the two-source mixing equations presented in Eganhouse and Kaplan (1988).

These calculations show that approximately 39–70% of the mass of organic carbon in the LACSD cores came from wastewater particles. While TOC inventories have not changed measurably from 1981–1993, the proportion (and, hence, the inventory) of effluent-derived organic carbon has decreased by approximately 40%. During this same period there is no systematic increase in the C/N ratio. This indicates that diagenesis is not responsible for the decrease in effluent-derived TOC inventories in the 3C cores.

The most likely explanation for the observed decline in effluent-derived TOC inventories is that sedimentary organic matter has been redistributed by physical and/or biological mixing processes and subsequently lost by resuspension and advective transport away from the site. According to this scenario, deposition of fresh, relatively uncontaminated sediment would partially compensate for losses in the TOC inventory. This interpretation is consistent with the declining maximum TOC concentrations (TOC<sub>max</sub>) and the apparent burial of the TOC concentration peak (depth to TOC<sub>max</sub>) in the cores over time (Table 1). It is also consistent with an observed decline in the inventory of *p,p'*-DDE at station 3C during the 1980s which is believed to be on the order of 50% (Eganhouse et al., 2000; Drake, 1994a; Niedoroda et al., 1996).

The only USGS cores analyzed in our laboratory from station 522 for which inventories could be computed are 124B1-*DDT* and 209B1-*DDT*. These cores have total and effluent-derived TOC inventories that are comparable to the most recent data developed by the LACSD (i.e. 3C1-1993). Thus, with respect to particulate organic carbon, station 522 appears to fall within the same sedimentary regime as station 3C.

## 3.2. Molecular stratigraphy

### 3.2.1. Background and assumptions

We now consider the depositional history of the organic contaminants at this site and evaluate whether molecular stratigraphy can be used to estimate average sedimentation and mass accumulation rates for periods spanning the history of wastewater discharge (ca. 1940–1992). Molecular stratigraphy relies upon the ability to relate the rate of input of a chemical into a sedimentary system with its vertical distribu-

tion in a sediment column (Valette-Silver, 1993). If the temporal variation of the input is known, dates can be assigned to sediment horizons that correspond to inflections in the input function. Successful application of this approach depends on the validity of three primary assumptions: (1) the marker should be unique to a given source, (2) the marker should be conservative or degrade, react, or be removed in a known or predictable manner, and (3) the stratigraphy of the sediments should be largely preserved.

Concerning the first assumption, existing data indicate that the DDTs, PCBs and long-chain alkylbenzenes found in sediments of the Palos Verdes Shelf are overwhelmingly, if not exclusively, derived from the LACSD. This assertion is based on three observations. First, all of these compounds have been found at elevated concentrations in the LACSD final effluent, and the industrial and/or domestic sources of these anthropogenic compounds to the effluent have been identified (Carry and Redner, 1970; Southern California Coastal Water Research Project, 1973; Eganhouse et al., 1983; Hendricks and Eganhouse, 1992). Second, there is no evidence for significant contributions of these anthropogenic contaminants to the Palos Verdes Shelf from alternate sources (Eganhouse and Venkatesan, 1993). Finally, vertical concentration profiles of these and other contaminants in Palos Verdes Shelf sediments correlate well with existing information on historical release rates from the outfalls and production/consumption rates in the United States (Eganhouse et al., 1983; Stull et al., 1988).

The second assumption concerns the extent to which these waste-derived contaminants can be considered conservative tracers. All are hydrophobic with log octanol–water partition coefficients in the range,  $\approx 4.0$ – $10$  (Sherblom et al., 1992; see references in Hansch and Leo, 1982 and Mackay et al., 1992). Consequently, they sorb strongly to organic-rich particles and accumulate in bottom sediments. In a companion paper (Eganhouse et al., 2000), we examined the diagenetic fate of the DDTs, PCBs and long-chain alkylbenzenes on the Palos Verdes Shelf. Our data show that a small but unknown fraction of  $p,p'$ -DDE in the 124B1-DDT core has likely been transformed to  $p,p'$ -DDMU over the 50 years since DDT was first released to the Palos Verdes Shelf. The rate of transformation is sufficiently slow that

the composition of 'total DDT' (i.e.  $p,p'$ - and  $o,p'$ -DDT, DDE, DDD) has not changed measurably since sediment cores were first collected and analyzed in the early 1970s. Transformation of  $p,p'$ -DDE to  $p,p'$ -DDMU during the period 1971–1992 is estimated at  $\leq 10\%$ . Moreover, based on LACSD core data for 1989, 1991 and 1993 no measurable change in the total mass of  $p,p'$ -DDE on the Palos Verdes Shelf appears to have occurred over time scales of a few years (total mass  $p,p'$ -DDE = 112, 118 and 119 metric tons, respectively; H. Lee, 1999, personal communication). Thus, we believe that  $p,p'$ -DDE is effectively preserved in this system and can be used reliably as a molecular tracer of DDT input. Eganhouse et al. (2000) also present evidence that the composition of the PCBs in sediments from station 522 is extremely uniform throughout all core sections, giving no indication of post-depositional alteration. Concentrations of PCBs and DDTs are highly correlated, and downcore distributions are similar to existing information on mass emission rates from the LACSD. The above relationships lend additional support to the assertion that these chlorinated hydrocarbons are well preserved. Similarly, TAB3, a major peak in the complex mixture of TABs, was found to be a highly persistent tracer of the TABs. By contrast, our data suggest that the most abundant LAB, 6-C<sub>12</sub>, believed to be among the most persistent LABs, has likely undergone significant degradation following burial. Consequently, this molecular marker is considered to be less reliable for purposes of molecular stratigraphy than  $p,p'$ -DDE, TAB3 and the PCBs. We have included 6-C<sub>12</sub> in the analytical discussions to follow because, despite some limitations, this compound yields very similar results to those obtained with the other markers. We do not rely exclusively on this compound for our interpretations but include it here for the sake of completeness.

Finally, we consider the assumption that the stratigraphy of surficial sediments collected at stations 3C and 522 has been preserved. Data for the 3C1 (1981) and 124B1-DDT cores clearly show that there has been vertical mixing of the sediments in the period 1981–1992 (Fig. 3). This is evidenced by the presence of TABs (as illustrated by TAB3) in all sections of the 124B1-DDT core despite the fact that TABs were not detected in the LACSD effluent in

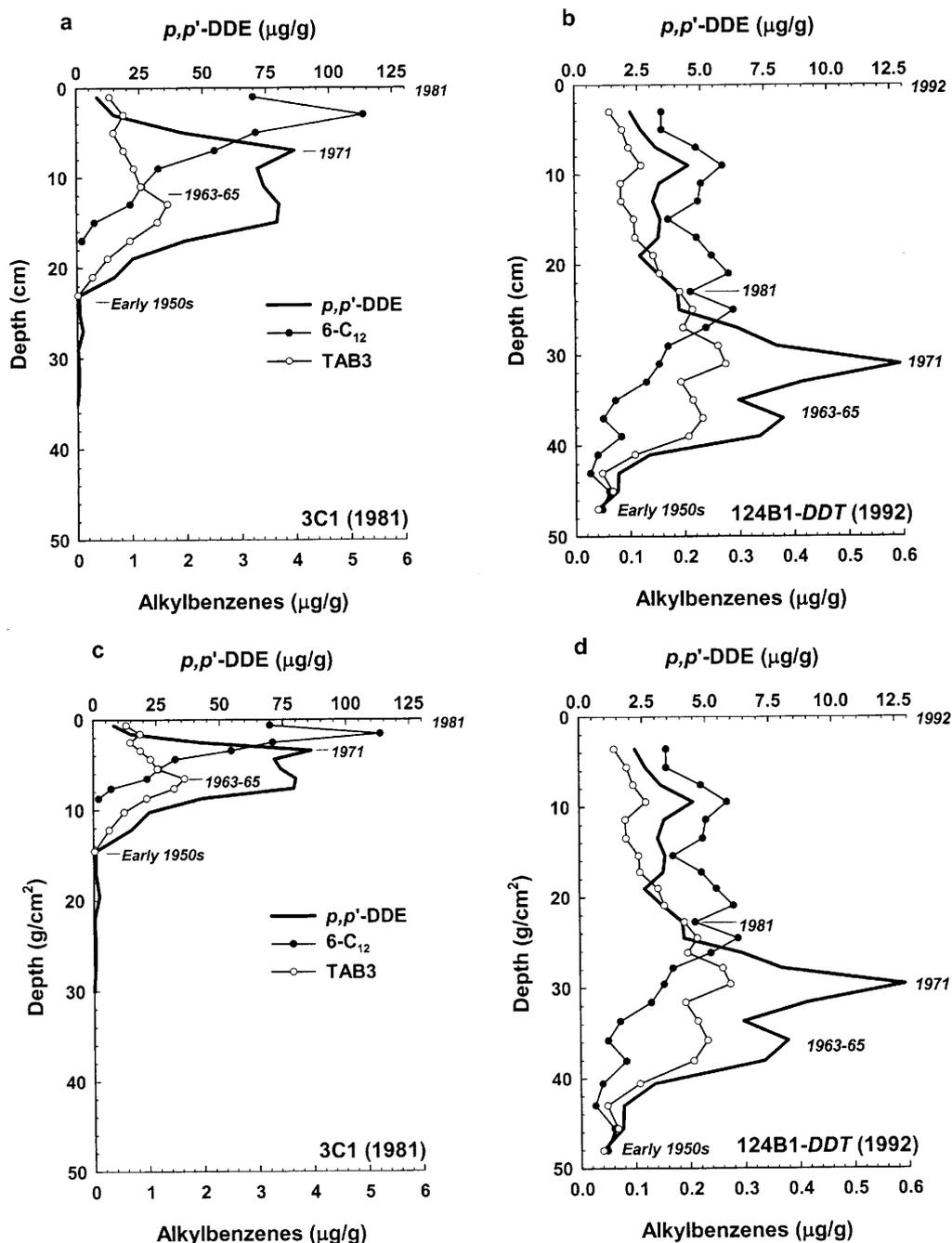


Fig. 3. Vertical concentration profiles of molecular markers  $p,p'$ -DDE,  $6\text{-C}_{12}$  and TAB3 in sediment cores from the Palos Verdes Shelf: (a,c) core 3C1 (1981), (b,d) core 124B1-DDT. See text and Table 2 for basis of tentative date assignments.

1979 and 1990 (Eganhouse et al., 1983; Hendricks and Eganhouse, 1992). The same argument can be made for the DDTs (and PCBs) because these com-

pounds have not been released in significant quantities by the LACSD since 1980 (Fig. 4). Finally, excess  $^{210}\text{Pb}$  profiles in cores collected at station 522

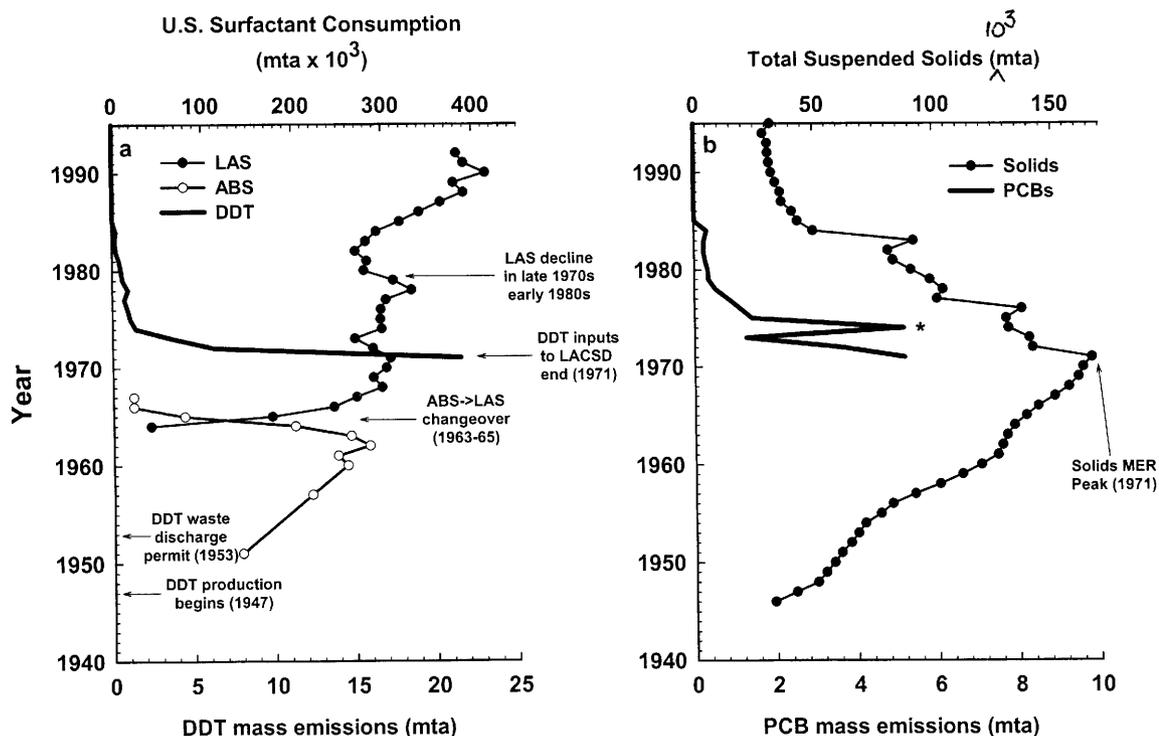


Fig. 4. Source trends for chemicals associated with markers used for molecular stratigraphy: (a) plot of U.S. surfactant (LAS — linear alkylbenzenesulfonates, ABS — tetrapropylene-based alkylbenzenesulfonates) consumption rates and LACSD total DDT mass emission rates (mta = metric tons/year), (b) LACSD total suspended solids mass emission rates (1946–1992) and  $\Sigma$ PCBs (1970–1992). \* 2/3 of this amount discharged between October and December of 1974 (Stull et al., 1988).

in 1992–1993 and 3C in 1991 show irregular or near-constant activities in the upper 20 cm of the sediment column rather than a log-linear decline (Wheatcroft and Martin, 1994; Swift et al., 1996; Paulsen et al., 1999). This indicates that rapid sedimentation and/or mixing must have occurred during the time period represented by that depth interval.

Based on modeling studies of Drake et al. (1994), no more than the upper 2 cm of the Palos Verdes Shelf sediments are likely to be reworked by physical resuspension resulting from storm-generated waves. This process is evidenced by the formation and destruction of wave ripples on the sea floor at water depths of 40–63 m (Drake, 1994a; Edwards and Chezar, 1994). Niedoroda et al. (1996) have also shown that erosion and redeposition of surficial sediments near station 6C on the shelf (cf., Fig. 1 in Eganhouse et al., 2000) during three unusually extreme storms of the 1980s was in the range of 1–4

cm. This is likely to be true for other locations at the same water depth (such as stations 3C and 522) and indicates that mixing of sediments on the Palos Verdes Shelf by physical processes is limited to the upper few centimeters of the sediment column. Thus, while storm waves may have been responsible for upward mixing of heavily contaminated layers of sediment in the past (for example ca. 1983), these processes are no longer capable of mobilizing the bulk of the contaminants because the latter are buried at greater sub-bottom depths.

Bioturbation, on the other hand, has been and continues to be an important process for mobilizing contaminants on the Palos Verdes Shelf. Bottom camera surveys have revealed the pervasive nature of biological activity on the shelf in the form of tracks, trails, burrows, mounds and a diverse array of macrofauna not ordinarily recovered by box corers (Edwards and Chezar, 1994). Stull et al. (1986b)

documented the invasion from 1973–1977 of the echiuran worm, *Listriolobus pelodes*, an active bioturbator. Using  $^{234}\text{Th}$  as a short-term tracer of particle motion in the upper sediment column (0–8 cm), Wheatcroft and Martin (1996) estimated biodiffusivities of  $49 \pm 12 \text{ cm}^2/\text{year}$  at station 522. They found that approximately 44% of the benthic macrofauna were present within the upper 2 cm and 94% were in the upper 8 cm of the sediment column. Polychaete annelids were numerically dominant. Similar results have recently been reported by Stull et al. (1996). The authors hasten to point out, however, that numerous other species, including burrow excavating mud shrimp (e.g. *Neotrypaea* sp., *Callianassa* spp., *Axiopsis spinulicauda*), have been found in sieved sediments from various locations on the shelf including the vicinity of station 522/3C. These organisms are capable of burrowing deep into the sediment column (> 20 cm) and can displace particles over longer distances. Although no burrowing shrimp were found in the 124B1-SS core (Barber et al., 1994), they were observed in sediments from several locations near station 522 (Wheatcroft and Martin, 1994). Together, these results suggest that biological activity is a key process contributing to the mixing of surficial sediments on the Palos Verdes Shelf. Given the similarities between the contaminant profiles in the 3C1 (1981) core and deeper portions of the 124B1-DDT core (Fig. 3), it would appear that mixing has not homogenized the effluent-affected sediment layer. Based on our knowledge of established trends in the composition of the benthos (Stull et al., 1996), it is reasonable to conclude that intense bioturbation at stations 3C/522 has probably been restricted to depths of less than about 20 cm and that such deep bioturbation has been prevalent only in recent years. This is consistent with assumptions used by Drake et al. (1994) in predictive modeling of sediments in the vicinity of station 3C and from the previously mentioned distribution of excess  $^{210}\text{Pb}$  activity (Wheatcroft and Martin, 1994; Swift et al., 1996). It is also consistent with findings of Swift et al. (1996) who show that biodiffusion rates below depths of 20 cm are two to three orders of magnitude lower than those at the sediment–water interface. For purposes of the following discussion, therefore, we assume that intense bioturbation of the 124B1-DDT core is limited to the upper 20 cm. Prior to

1992 intense bioturbation of sediments in the vicinity of stations 3C/522 was undoubtedly restricted to much shallower sub-bottom depths. This is indicated by the high concentrations of *p,p'*-DDE in the 1981 3C1 core (Fig. 3a) and the steep decline in concentrations of *p,p'*-DDE with increasing sub-bottom depth. Moreover, systematic benthic biological surveys have shown that shallow burrowing infaunal species predominated during the 1970s and 1980s (Stull et al., 1996; Stull and Tang, 2000). Taken together, these observations support the assumption that the stratigraphy of the heavily contaminated sediment layers in cores 3C1 (1981) and 124B1 (1981) has largely been preserved.

### 3.2.2. Core profiles

Fig. 3 shows vertical concentration profiles of *p,p'*-DDE, 6-C<sub>12</sub> and TAB3 in the 3C1 (1981) and 124B1-DDT cores with depth scales in units of cm and g/cm<sup>2</sup>. [Note: Although not shown here for sake of clarity, the distribution of PCBs effectively mimics that of *p,p'*-DDE; cf. Eganhouse et al., 2000]. These three compounds are used as indicators of the DDTs, LABs and TABs, respectively, as described by Eganhouse et al. (2000). Tentative dates have been assigned to specific depth horizons of the 3C1 core according to the rationale discussed at length by Eganhouse and Kaplan (1988). Briefly, the assignments are based on U.S. consumption rates of alkylbenzenesulfonates (R. Modler, 1994, personal communication), information on the likely initiation and termination of DDT inputs to the LACSD (Carry and Redner, 1970; Redner and Payne, 1971), and emission rates of DDT ( $\geq 1971$ ) and suspended solids (1946–1992) from the LACSD outfalls. These source trends are illustrated in Fig. 4.

We have also made tentative assignments of dates to the 124B1-DDT core profiles based on similarities to the patterns seen in the 3C1 (1981) core. These assignments correspond to (1) the onset of U.S. ABS (and, therefore, TAB) production/consumption, DDT production, and buildup of effluent-derived sediments on the outer shelf — *early 1950s*, (2) the onset of LAS (and, therefore, LAB) production/consumption and termination of U.S. ABS consumption — *mid-1960s*, (3) the rapid decrease in DDT and PCB emissions following source control and the maximum in suspended solids emissions — *1971*,

(4) the short-term decrease in LAS consumption in the late 1970s/early 1980s that coincides with an abrupt decline in LAB concentration at the 0–2 cm interval in the 3C1 (1981) core, and (5) the time of core collection — 1992. From these assignments we have calculated average sedimentation and mass accumulation rates for four time intervals (Table 2).

### 3.2.3. Sedimentation and mass accumulation rates based on molecular stratigraphy

The data given in Table 2 indicate that average sedimentation rates (cm/year) at station 3C for the time interval 1955–1981 varied between 0.7 and 1.3 cm/year. This can be compared with the natural background rate believed to be in the range, 0.1–0.2 cm/year (Hampton et al., 2000; Los Angeles County

Sanitation Districts, 1988; Swift et al., 1996; Wheatcroft and Martin, 1994). Highest rates were found in the 1965–1971 period (1.3 cm/year), a time when wastewater solids emissions reached a peak. Rates during 1955–1965 and 1971–1981 fall within a restricted range (0.7–0.8 cm/year), slightly lower rates being observed during the 1970s when wastewater solids emissions were on the decline. Fig. 5a presents sedimentation rates for station 3C from the present study along with data developed by other investigators using trace metal (Kettenring, 1981) and *p,p'*-DDE (Wheatcroft and Martin, 1994; Niedoroda et al., 1996) stratigraphies. In general, for the period 1955 to 1980 the various estimated sedimentation rates at station 3C are in reasonable agreement. Moreover, the time variation in sedimentation rate is generally consistent with the hypothesis that wastewater emissions exerted a dominant control on sedimentation in this general location from 1955 to 1981 (Drake, 1994a). When mass accumulation rates ( $\text{g cm}^{-2} \text{ year}^{-1}$ ) are computed by applying average dry densities for the depth intervals identified in Table 2 (Fig. 5b), similar relations are observed among the time periods. The rates obtained during 1955–1981 range from 0.3 to 0.7  $\text{g cm}^{-2} \text{ year}^{-1}$ . [These can be compared to the presumed natural background mass accumulation rate (for sediments deposited just prior to construction of the outfall) of 0.2  $\text{g cm}^{-2} \text{ year}^{-1}$  (Niedoroda et al., 1996)]. However, mass accumulation rates during the 1965–1971 period are somewhat elevated relative to the other time intervals. Again, existing data based on trace metal and *p,p'*-DDE stratigraphies developed by others are reasonably comparable with the data developed in this study from molecular stratigraphy.

We now turn to results obtained from core 124B1-DDT (station 522). As shown in Table 2, sedimentation rates (cm/year) for all intervals within the 1955–1981 time period are comparable to those at station 3C. On a mass accumulation rate basis, however, the rates estimated for sediments from station 522 (core 124B1-DDT) are systematically higher than those calculated for station 3C. As will be shown, this is due to the higher dry densities of the sediments at station 522 than station 3C at corresponding depth intervals. The most striking feature of the data in Table 2, however, is the high estimated sedimentation and mass accumulation rates

Table 2

Estimated sedimentation and mass accumulation rates for cores 3C1 (1981) and 124B-DDT (1992) based on molecular stratigraphy

Core	1955– 1965 <sup>a</sup>	1965– 1971 <sup>b</sup>	1971– 1981 <sup>c</sup>	1981– 1992 <sup>d</sup>
<i>3C1</i>				
cm/year	0.8	1.3	0.7	–
$\text{g cm}^{-2} \text{ year}^{-1\text{e}}$	0.6	0.7	0.3	–
<i>124B1-DDT</i>				
cm/year	0.9	1.3	0.8	2.1
$\text{g cm}^{-2} \text{ year}^{-1}$	1.1	1.4	0.9	2.2

<sup>a</sup>1955 was chosen because it preceded installation of the 229-cm 'we' deepwater outfall by 1 year and followed by 2 years the issuing of the DDT discharge permit to Montrose Chemical. This is also 5 years after the ABS surfactants assumed dominance in the U.S. market, whereas 1965 is the mid-point of the ABS–LAS transition.

<sup>b</sup>1971 was chosen to represent the time of maximum emissions of suspended solids from the LACSD and the onset of rapid decline in DDT and PCB emissions.

<sup>c</sup>1981 was chosen based on the correlation between molecular stratigraphies of 3C1 (1981) and 124B1-DDT (1992) cores, a decline in LAS consumption that occurred in the late 1970s/early 1980s, and the assumption that the upper surface of the 3C1 core represented contemporary deposits.

<sup>d</sup>1992 was assigned based on the assumption that the upper surface of the 124B1-DDT core represented contemporary deposits (ca. 1992).

<sup>e</sup>Mass accumulation rates ( $\text{g cm}^{-2} \text{ year}^{-1}$ ) determined as compaction-corrected mass accumulation for the depth intervals depicted in Fig. 3 and the corresponding assigned time intervals. See Fig. 4 for information on input trends.

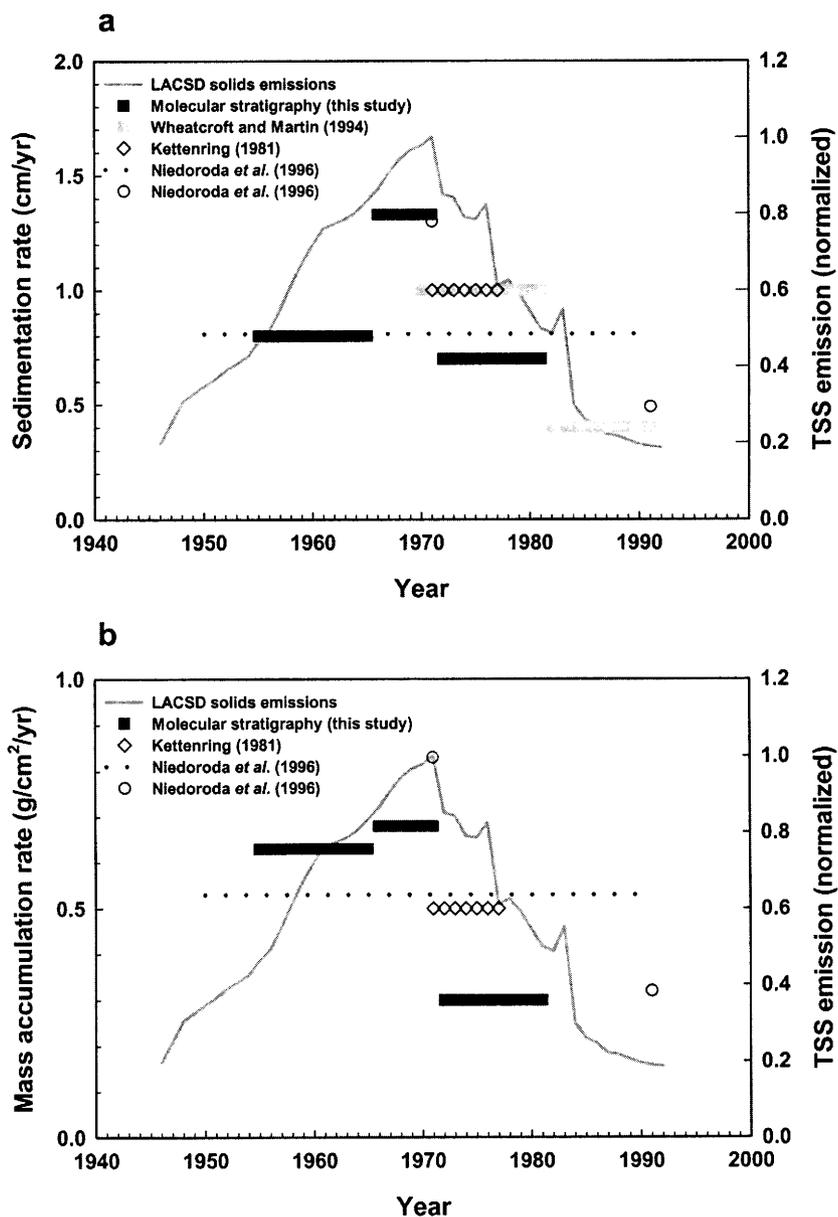


Fig. 5. Sedimentation rates and mass accumulation rates determined by various investigators for station 3C (1950–1991) plotted along with LACSD suspended solids mass emission rates (normalized to 1971 value): (a) sedimentation rate (cm/year), and (b) mass accumulation rate ( $\text{g cm}^{-2} \text{ year}^{-1}$ ). Widths of symbols and bars do not reflect uncertainties in estimates.

at station 522 during the period 1981–1992 (i.e. 2.1 cm/year,  $2.2 \text{ g cm}^{-2} \text{ year}^{-1}$ ). If these estimates are accurate, it signifies that sedimentation during the 1981–1992 period was significantly higher at station 522 than that seen in earlier decades. Moreover,

these rates are 4–5 times greater than those estimated at station 3C for 1991 by Niedoroda et al. (1996) and 1981–1991 by Wheatcroft and Martin (1994). This apparent discrepancy remains to be explained.

Because of the likelihood of bioturbation in the upper sediment column and uncertainties in the date assignments that may have been caused by vertical mixing, we investigated other approaches for establishing sedimentation and mass accumulation rates at station 522 during the 1981–1992 period. Three approaches were considered. The first was a statistically based alignment of the marker profiles for the 3C1 (1981) and 124B1-*DDT* cores. For this analysis we assumed that optimal alignment of the profiles would yield a depth or mass accumulation offset corresponding to the time interval between core collection. The second approach relied upon a comparison of the inventory distribution of the markers in the 3C1 (1981) and 124B1-*DDT* cores. Finally, we examined the change in inventory distribution of *p,p'*-DDE in cores collected from station 3C from 1981–1995 and compared that directly to data for core 124B1-*DDT*.

#### 3.2.4. Corroboration of rates based on core profile alignment

The first approach is a statistically based procedure for optimizing alignment of the 1981 and 1992 core profiles. It allows one to determine the corresponding depth (cm) and mass accumulation ( $\text{g}/\text{cm}^2$ ) offsets which can then be transformed to sedimentation rates and mass accumulation rates through application of the time between core collection (11.2 years). Concentrations of *p,p'*-DDE, 6- $\text{C}_{12}$ ,  $\Sigma\text{PCBs}$  and TAB3 were computed at nominal mass accumulation intervals ( $1 \text{ g}/\text{cm}^2$ ) in the 3C1 and 124B1-*DDT* cores by linear interpolation. The concentration profiles were then subjected to regression analyses as a function of depth (cm) and mass accumulation ( $\text{g}/\text{cm}^2$ ) offset. The results of this exercise for all offsets with three or more cases are shown in Fig. 6. The analysis using depth (cm) offsets yielded similar unimodal curves for all four compounds. Optimal alignment was achieved for a narrow range of offsets (20–22 cm) suggesting concordance among the various markers. These offsets correspond to sedimentation rates of 1.8–2.0 cm/year, very close to the rate estimated from molecular stratigraphy (2.1 cm/year; Table 2). The curve for 6- $\text{C}_{12}$  exhibited the broadest range of offsets with high correlation coefficients. This reflects the fact that LABs are found at relatively high concentrations throughout the upper 26

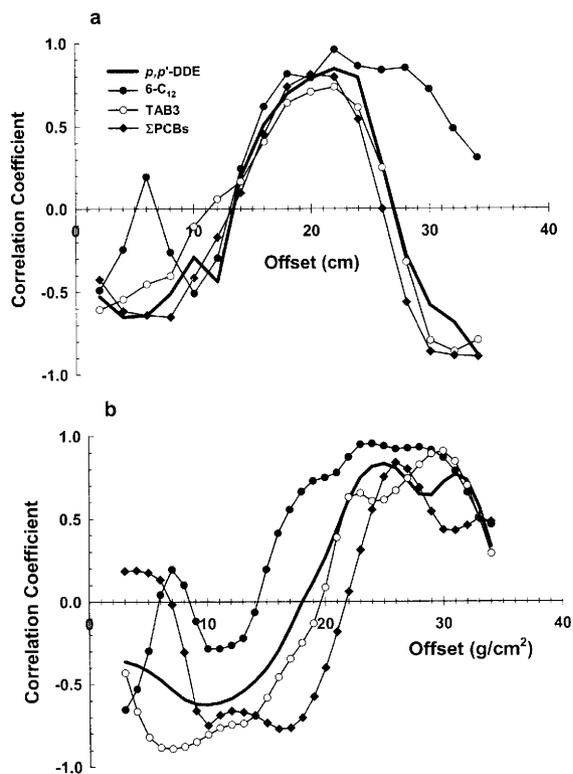


Fig. 6. Core profile alignment curves based on (a) depth (cm), and (b) mass accumulation ( $\text{g}/\text{cm}^2$ ) offsets.

cm of the core due to their continued release from the outfall system.

In the case of the analysis using mass accumulation ( $\text{g}/\text{cm}^2$ ) offsets, the curves are characterized by a broad range of offsets having high correlation coefficients ( $r > 0.6$ ), often with two maxima. The broad range of offsets and the presence of two maxima reflect the dispersion of the contaminant profiles as a result of vertical mixing of the sediments. In general, the range of offsets within which maxima occur is  $\approx 21\text{--}31 \text{ g}/\text{cm}^2$ . Again, the curve for 6- $\text{C}_{12}$  exhibits the broadest range of high correlation coefficients. Applying a time difference of 11.2 years (the period between core collection) to this range yields sediment accumulation rates for the 1981–1992 period of  $1.9\text{--}2.8 \text{ g cm}^{-2} \text{ year}^{-1}$ . The lower limit of the range corresponds to alignment of the upper edges of the subsurface maxima, whereas the upper limit of the range reflects alignment of the lower edges of the subsurface maxima. This mass

accumulation rate range encompasses the estimate of  $2.2 \text{ g cm}^{-2} \text{ year}^{-1}$  based on molecular stratigraphy (Table 2). The lower limit of the range still exceeds the estimated mass accumulation rates for station 522 prior to 1981.

### 3.2.5. Corroboration of rates based on comparison of inventory distributions

The second approach for estimating average sedimentation and mass accumulation rates at station 522 ca. 1981–1992 involves computation of what we have termed the ‘normalized cumulative inventory’ (NCI) profile. For each of the compounds of interest, cumulative inventories were calculated starting at the bases of the 3C1 (1981) and 124B1-DDT cores. The cumulative inventories were normalized to the total inventory, yielding a profile whose abscissa ranges from zero to 1. Example NCI profiles for *p,p'*-DDE are shown in Fig. 7. Normalization is performed to overcome the potential bias that may result from

spatial variation of contaminant inventories. It also minimizes the possible effect of differences in analytical technique. Spatial variations in contaminant concentration and distribution tend to confound comparisons of cores based on absolute concentrations or inventories.

Several assumptions were made for this analysis: (1) the compounds are persistent, (2) the masses of these compounds in sediments below the core bases are negligible, and (3) no losses of surficial sediment occurred at the time of core collection. We have previously provided evidence in support of the first assumption for all compounds with the possible exception of 6-C<sub>12</sub> (Eganhouse et al., 2000). The second assumption appears quite reasonable in view of the fact that bulk density and effluent-derived contaminant distributions indicate that both corers penetrated the native sediment horizon (cf., Kayen, 1994; Figs. 1–3). Also, as described in Lee et al. (2000), there is a high correlation ( $r = 0.96$ ) between the

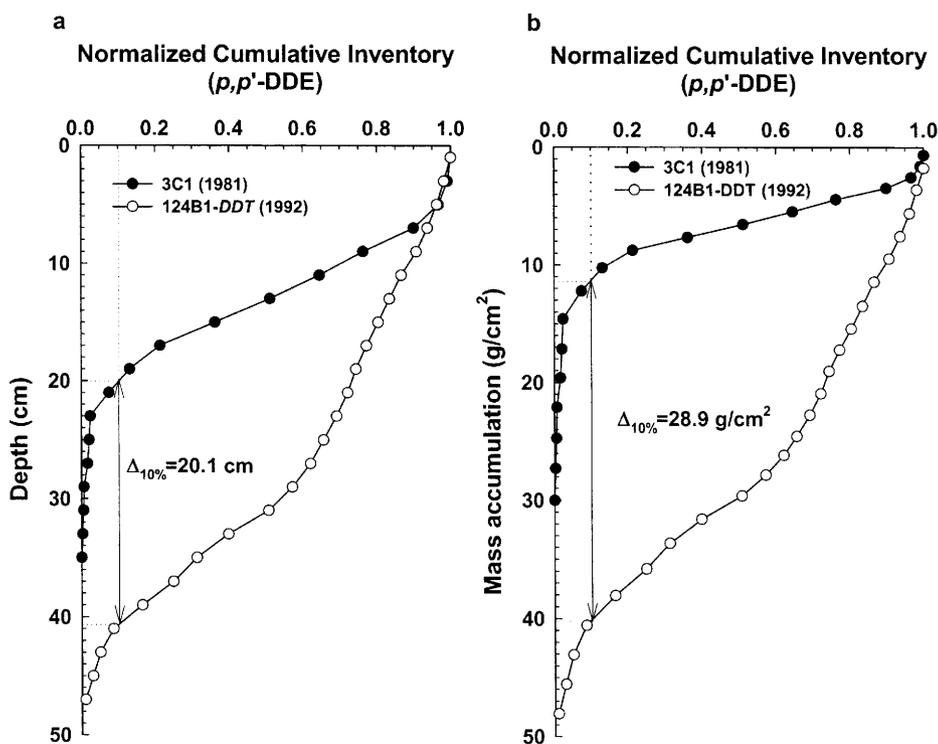


Fig. 7. Normalized cumulative inventory profiles for *p,p'*-DDE in 3C1 (1981) and 124B1-DDT cores plotted according to: (a) depth (cm), and (b) mass accumulation ( $\text{g/cm}^2$ ).  $\Delta_{10\%}$  = the difference in depth (cm) or cumulative mass ( $\text{g/cm}^2$ ) between cores 3C1 (1981) and 124B1-DDT at 10% inventory cutoff.

thickness of the EAL as indicated by bulk density profiles and the concentration of *p,p'*-DDE. We discuss the third assumption in more detail below.

Because bioturbation is much less likely to have influenced the distribution of contaminants in deeper portions of the sediment column, we examined cutoffs corresponding to 10%, 15% and 20% of the NCIs. As can be seen in comparing Figs. 3 and 7, these cutoffs correspond to the lower portion of the lower shoulders of the marker profiles (i.e. 1981:  $\approx 19$  cm, 10 g/cm<sup>2</sup>; 1992:  $\approx 40$  cm, 39 g/cm<sup>2</sup>). Higher cutoffs would lead to mass accumulation rate estimates increasingly subject to error due to the effects of mixing, whereas estimates from lower cutoffs may be impacted by analytical uncertainty. When the depths or accumulated mass to these cutoffs are determined for both cores, the difference is a reflection of the sedimentation that occurred between the times of core collection. This is illustrated in Fig. 7 where the depth and mass accumulation differences at the 10% NCI cutoff ( $\Delta_{10\%}$ ) for cores 3C1 (1981) and 124B1-*DDT* are depicted. Sedimentation and mass accumulation rates are calculated by dividing the depth and mass accumulation differences at each cutoff by the time elapsed between core collection (i.e. 11.2 years). These data are summarized in Table 3.

The range of sedimentation rates for all compounds (1.7–2.1 cm/year) brackets that deter-

mined by the profile alignment procedure (1.8–2.0 cm/year) and the rate determined by molecular stratigraphy (2.1 cm/year; Table 2). As before, 6-C<sub>12</sub> exhibits a broader range of rates, whereas the other three markers provide sedimentation rates within a relatively narrow range (1.7–1.9 cm/year) that is slightly lower than that determined by molecular stratigraphy. In the case of the mass accumulation rate estimates, the same patterns are observed. A narrow range of estimates (2.4–2.7 g cm<sup>-2</sup> year<sup>-1</sup>) is obtained for *p,p'*-DDE,  $\Sigma$ PCBs and TAB3, whereas 6-C<sub>12</sub> yields rates of 2.2–2.7 g cm<sup>-2</sup> year<sup>-1</sup>. The lower limit of mass accumulation rates determined by the NCI profile method is identical to that determined by molecular stratigraphy (i.e. 2.2 g cm<sup>-2</sup> year<sup>-1</sup>; Table 2). However, it only marginally constrains the rates obtained by the profile alignment approach (1.9–2.8 g cm<sup>-2</sup> year<sup>-1</sup>). Importantly, both profile alignment and NCI profile approaches appear to corroborate the high sedimentation and mass accumulation rates determined by molecular stratigraphy for the 124B1-*DDT* core between ca. 1981 and 1992.

We now consider the effect of losses of surficial sediment during coring operations. If surficial sediments were lost from the gravity cores collected at station 3C, sedimentation and mass accumulation rates determined for the 3C1 (1981) core during the 1971–1981 period would be underestimated. Under these circumstances, rates determined by any of the methods described above for core 124B1-*DDT* for the 1981–1992 period would be overestimated. This might, in turn, be used to explain the unexpectedly high sedimentation and mass accumulation rates we have obtained. One way of circumventing this problem is to examine a series of cores collected at different times with the same coring device. We can reasonably assume that any losses of surficial sediment with the gravity corer used by the LACSD are consistent from core to core (Drake, 1994a). This assertion is based on the modest variation seen among the *p,p'*-DDE inventories in replicate cores taken by the LACSD (18–28%; Eganhouse et al., 2000) and the rigorous core handling procedures that are used (Lee, 1994b). To further investigate the unusually high rates we obtained for the 1981–1992 period at station 522, we examined data generated by the LACSD for cores collected from station 3C during

Table 3  
Estimated sedimentation and mass accumulation rates at station 522 for the period 1981–1992 based on normalized cumulative inventory profile analysis of cores 3C1 (1981) and 124B-*DDT* (1992)

Cutoff	10%	15%	20%
Compound	Sedimentation rate (cm/year)		
<i>p,p'</i> -DDE	1.83	1.86	1.87
$\Sigma$ PCB	1.73	1.73	1.72
TAB3	1.89	1.88	1.84
6-C <sub>12</sub>	2.14	1.95	1.81
	Mass accumulation rate (g cm <sup>-2</sup> year <sup>-1</sup> )		
<i>p,p'</i> -DDE	2.6	2.6	2.6
$\Sigma$ PCB	2.5	2.4	2.4
TAB3	2.7	2.6	2.5
6-C <sub>12</sub>	2.7	2.4	2.2

the period 1981–1995. In this analysis we computed NCIs for *p,p'*-DDE and determined the depths and mass accumulations to the 10%, 15% and 20% cutoffs for each core. These depths and mass accumulations were then plotted as a function of date of

collection (Fig. 8). Because we assume that any surficial sediment losses for these cores were uniform, sedimentation and mass accumulation rates derived from the slopes of the curves are not affected by the coring method.

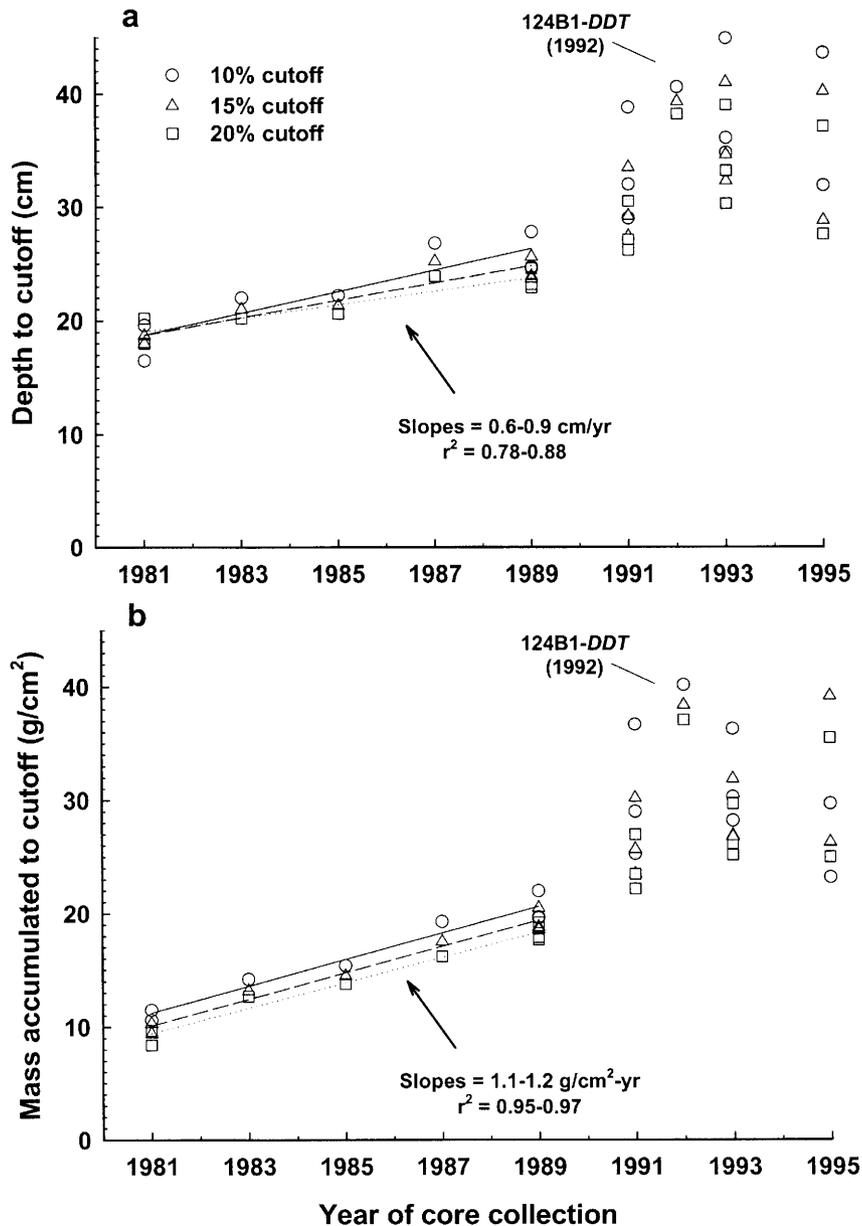


Fig. 8. Temporal trends in sedimentation at stations 3C and 522: (a) depth to 10%, 15% and 20% normalized cumulative inventory cutoffs (*p,p'*-DDE) vs. year of collection, and (b) mass accumulation to 10%, 15% and 20% normalized cumulative inventory cutoffs (*p,p'*-DDE) vs. year of collection.

### 3.3. Temporal trends in sedimentation at stations 3C and 522

#### 3.3.1. Sedimentation and mass accumulation rates

The results plotted in Fig. 8 show that the data fall into two time periods. The interval 1981–1989 appears to be characterized by fairly constant sedimentation and mass accumulation rates. Replicate cores are tightly grouped. Data for 1991, 1993 and 1995, on the other hand, are characterized by much more scatter among replicate cores, and sedimentation appears to have increased markedly ca. 1989–1991. Linear regression analysis of the 1981–1989 data at the 95% confidence interval yields sedimentation rates of  $0.6 \pm 0.3$  cm/year (20% cutoff),  $0.8 \pm 0.3$  cm/year (15% cutoff) and  $0.9 \pm 0.5$  cm/year (10% cutoff). The rates are similar to those determined for station 3C during the 1971–1981 period by molecular stratigraphy (Table 2). However, they are generally higher than, although overlapping with, data reported by Wheatcroft and Martin (1994) ( $0.4 \pm 0.3$  cm/year; Fig. 5a). They performed a similar analysis of 1981–1991 data using a *p,p'*-DDE concentration of  $10 \mu\text{g/g}$  on the lower shoulder as the measurement point. The rates we obtained are also higher than that reported by Niedoroda et al. (1996) for 1991 (0.49 cm/year). The higher rates and steady sedimentation patterns are inconsistent with the concept that sedimentation is controlled by deposition of effluent solids on this portion of the shelf because solids emission continued to decline during this time period (Fig. 5).

In the case of the analysis based on mass accumulation (Fig. 8b), rates at station 3C during the period 1981–1989 were approximately  $1.1\text{--}1.2 \text{ g cm}^{-2} \text{ year}^{-1}$  irrespective of the cutoff used. The extremely narrow range of mass accumulation rates indicates that this analysis is not affected by changes in the *p,p'*-DDE inventories during the period of interest. The rates are more than three times those determined at station 3C by molecular stratigraphy for the 1971–1981 period (Table 2). They also are three times greater than the accumulation rate at 3C proposed by Niedoroda et al. (1996) for 1991 (i.e.  $0.32 \text{ g cm}^{-2} \text{ year}^{-1}$ ). We believe the apparent increase in sedimentation and especially, mass accumulation, rates is due primarily to the influx of coarser, higher density sediment coupled with compaction of the high water

content EAL (Drake, 1994a,b). The result has been a dramatic change in the dry density profiles of the sediments at station 3C during the 1980s (Fig. 9). The reason our estimates greatly exceed the rate proposed by Niedoroda et al. (1996) is that they applied a uniform dry density of  $0.66 \text{ g/cm}^3$  to a sedimentation rate of 0.49 cm/year. This transformation does not account for downcore variations in dry density and the steadily increasing density of the solids that were being deposited at station 3C during the 1980s.

Also plotted on Fig. 8 are data for core 124B1-DDT (1992). The cutoffs for this core are found at greater depths and mass accumulations than might be expected from the 1991 and 1993 cores from station 3C. This suggests that sedimentation and mass accumulation rates at station 522 (core 124B1-DDT) were higher than for station 3C during the early 1990s. They are also well off the trajectory established by the 3C (1981–1989) trend lines. The unusually high rates determined from core 124B1-DDT by molecular stratigraphy for the 1981–1992 period, thus, apparently has its origin in two phenomena: (1) a general increase in sedimentation in the vicinity of stations 3C and 522 that occurred some time after

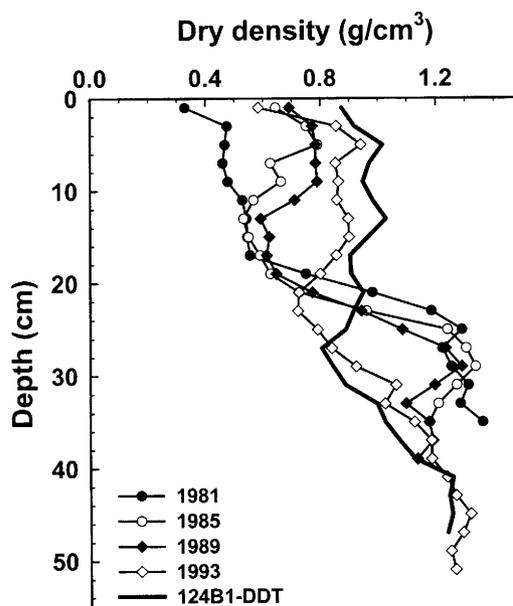


Fig. 9. Dry density profiles for cores collected at stations 3C (1981–1995; Lee, 1994b) and 522 (124B1-DDT; this study).

1989, and (2) the higher sedimentation and mass accumulation rates (at equivalent periods) at station 522 than at station 3C.

### 3.3.2. Evidence for sediment transport pathways

One explanation for the higher sediment accumulation rates observed near stations 3C/522 during the 1980s and early 1990s is the occurrence of several major storms (1982–1983, 1988) coupled with increased erosion of the toe of the PBL in the period 1981–1988 (Drake et al., 1994; Kayen et al., 1994). In particular, the unusually large storm in January 17–18, 1988 may have mobilized landslide and other debris to offshore shelf sediments. Evidence for this comes from a report by Reynolds (1989) which describes the presence of a layer of coarser material (as thick as 5.5 cm at station 6C) that was considered to be a deposit resulting from the January 1988 storm. Data on the quartz composition of surficial sediments (0–2 cm) from station 3C in 1987 plot near to that for the PBL, whereas data for stations located closer the outfall (e.g. 6C, 8C) fall near to that of the effluent (Reynolds, 1987). This indicates a significant input of PBL-derived sediment at and around station 3C. Because core 124B1 was collected in shallower waters than core 3C1 (57 m vs. 61 m), it is conceivable that inputs from the PBL have historically been greater at station 522 than station 3C. This is consistent with the uniformly higher mass accumulation rates we determined in the 124B1-*DDT* core vis-à-vis the 3C1 core (1981) for all time periods (Table 2). One indication of the potential differences in sedimentation at stations 522 (124B1) and 3C is found in the distribution of mass in the “effluent-affected layer” (Drake, 1994a). A tongue of sediment positioned along the inshore perimeter of the USGS sampling grid and apparently emanating from the vicinity of the PBL extends to stations 522 and 3C in a foot-shaped lobe. In this particular area at water depths ranging from 50 to 60 m, a cross-shelf gradient in accumulated mass can be seen. Similar features are found in plots of the percent sand distribution in surficial and EAL sediments (Drake, 1994a), further indicating that coarser sediment originating inshore of these stations, probably from the PBL, is directed offshore near Long Point (cf., Fig. 1 in Eganhouse et al., 2000). Moreover, the distribution of titanite, a

potential mineral marker of the PBL, and the ratio of [amber quartz + chert]/total quartz in shallow sediments are found to coincide with the distribution of accumulated mass (Wong, 1994; Reynolds, 1987). Finally, in X-ray diffraction studies of beach sand from Portuguese Bend and sediments from the 124B1-*DDT* core we have observed dolomite to be a major mineral. Its occurrence in PBL sediment is not unexpected because dolostones are common to the Altamira Shale member of the Monterey Formation, the source of PBL material. Because dolomite is relatively rare in sediments of southern California’s continental shelf, its presence in the 124B1-*DDT* core signals input of PBL material at this location (Kayen et al., 1994). Together, these patterns indicate that the PBL has influenced sediments along the cross-shelf “3” transect.

One remaining question concerns the transport mechanism. Based on analysis of bathymetric, mineralogical and grain size distribution data, Kayen et al. (1994) have proposed that the bulk of PBL debris is transported to the southeast by littoral currents with cross-shelf movement and subsequent entrainment in poleward-flowing subthermocline currents. This is a viable mechanism by which PBL material could find its way to the vicinity of stations 3C/522. However, this does not explain the much greater impact of the PBL on station 3C than station 6C (Drake et al., 1994). Taken together, the available data indicate that some offshore transport from the landslide in a southwesterly direction is likely. If so, poleward-flowing subthermocline currents, directed westward off Long Point by coastal bathymetry, would likely carry PBL sediment to the vicinity of stations 3C/522 (cf., Fig. 1 in Eganhouse et al., 2000; Drake et al., 1994; Noble, 1994). This transport mechanism can be viewed as a local effect. For example, Drake (1994a) has suggested that a cross-shelf gradient in sedimentation results from “...the geometric positions of the two major sediment sources for the shelf, the PBLs and the JWPCP diffusers. Local variability is superimposed on the larger cross shelf and along-shelf trends”. We believe that such a gradient and the delivery of coarser sediment from the PBL is responsible for the higher mass accumulation rates observed for core 124B1-*DDT* than at station 3C over the last 35 years (Table 2). Core 124B1-*DDT* apparently came from a location directly in the trans-

port pathway of the PBL sediment. The fact that core 124B1-*DDT* experienced higher mass accumulation rates at an earlier time than sediments from station 3C is most likely due to a lag in offshore movement of PBL-derived materials.

#### 4. Conclusions

The continental shelf is a dynamic environment. In this regard, the Palos Verdes Shelf is no exception. In recent historic time the dominant sources of sediment to the shelf have been municipal wastewater solids from the LACSD outfall system and debris from the PBL. Inputs of these materials to the shelf have varied over time, and they are introduced to the shelf environment at different locations. This fact combined with prevailing current patterns and resuspension of sediment by storms has given rise to spatial and temporal variations in sedimentation rates on the shelf. By comparing the molecular stratigraphies of two cores, one collected from station 3C in 1981, and another near to, but approximately 50–70 m inshore of 3C, we have determined sedimentation and mass accumulation rates for four periods. These periods span the time during which wastewater effluent has had significant impacts on sedimentation and contamination of this shelf environment. The vertical concentration profiles clearly show that mixing of the sediments has occurred. This is consistent with information from other studies demonstrating that physical resuspension and bioturbation are pervasive on the Palos Verdes Shelf. In spite of the mixing, we were able to estimate approximate sediment accumulation rates using several approaches. These estimates reveal that the area of the shelf near station 3C has been influenced both by effluent solids released from the outfall system and debris from the PBL. During the period 1955–1971, sedimentation and mass accumulation rates at 3C were approximately 0.8–1.3 cm/year and 0.6–0.7 g cm<sup>-2</sup> year<sup>-1</sup>, respectively. Sedimentation then decreased in the 1970s as a result of improvements in waste treatment (0.7 cm/year, 0.3 g cm<sup>-2</sup> year<sup>-1</sup>). During the 1980s, sedimentation rates were steady ( $\approx$  0.6–0.9 cm/year), but mass accumulation rates increased significantly (1.1–1.2 g cm<sup>-2</sup> year<sup>-1</sup>). Because emissions of suspended solids have declined more or

less continuously since 1970, the steady sedimentation rates and increased mass accumulation rates in the 1980s must be due to enhanced input of sediment from the PBL. Mineralogic, grain size and bulk density trends and patterns support this interpretation. The most likely explanation for the increased input of PBL-derived sediment during the 1980s and early 1990s is mobilization of landslide debris by several major storms that occurred in the 1980s. This interpretation is consistent with the generally higher sediment accumulation rates at station 522 (core 124B1-*DDT*) than at station 3C because station 522 is inshore of station 3C and there is a distinct cross-shelf gradient in sedimentation on this portion of the shelf. Because existing models that predict the long-term fate of the effluent-affected deposit are most sensitive to sedimentation rate, the impact of the PBL on shelf sediments near station 3C must be taken into account. All things being equal, the higher sedimentation rates we have determined in the vicinity of stations 3C/522 should lead to increased sequestration of the highly contaminated sediment layers at this location.

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