Dispersion of sediment DDTs in the coastal ocean off southern California [☆]

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Abstract

The masses of DDT compounds (DDTs) in surface sediments of the Palos Verdes Shelf (PVS) and Santa Monica Bay (SMB) have declined over the last two decades, following the ban on DDT production in 1970. This mass reduction could result from a number of biological and physical processes, including biodegradation and/or dispersal away from the sites. We integrated existing data with our new data of DDTs from different compartments in the coastal zones off southern California to assess the importance of the dispersal mechanism. The synthesis of the data indicated that: (1) historically deposited DDTs have been remobilized upward in the sediment column; (2) DDTs have been resuspended into the water column; and (3) sewage-derived DDTs have been redeposited into distant areas. Resuspension of DDTs from contaminated sediments was evident from the close correlation between the DDT concentrations in the water column and surface sediment at three locations with different DDT levels. The current distribution patterns for linear alkylbenzenes and DDTs in surface sediments at SMB were also suggestive of dispersal of DDTs. The distribution of DDTs in the surface sediments exhibiting a gradient from the outfalls to offshore and the general spatial distribution pattern in the basins precluded the possibility of either aerial fallout or surface runoff as being an important source of DDTs. These results are consistent with the hypothesis that resuspended DDTs in the discharge zones are being dispersed to distant areas. The percent of DDEs in total DDTs was uniformly high ($\sim 90\%$) in the PVS and SMB sediments, but varied widely in sediments of the Santa Monica and San Pedro Basins. The percent DDEs were particularly low (as low as 10%) in certain subsurface sections of the sediments near two dumpsites containing DDT wastes (from prior to 1970) comprising of low proportions of DDE. However, the top-layers of the basin sediments contained DDT residues with high %DDEs similar to that of sediments on the PVS, suggesting a common source from the historic DDTs in the wastewater discharges. The

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available data is insufficient to confirm the possibility of anaerobic degradation of DDEs in the sediment cores investigated which could also result in the mass reduction of DDTs in the post-1970 sediments. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Usage of DDT compounds (o,p' and p,p' isomers of DDT and their metabolites, o,p'- and p,p'-DDD and DDE; designated as DDTs) has been banned in the United States since 1970, but the fate of historically discharged DDTs remains a source of concern in the Southern California Bight (SCB). The extensive discharge of DDTs via the outfall of the Joint Water Pollution Control Plant (JWPCP; Fig. 1) operated by the County Sanitation Districts of Los Angeles County (CSDLAC) has created a discharge zone on the Palos Verdes Shelf (PVS) where sediments contain elevated levels of DDTs. These sediments may have become significant secondary sources of contaminants.

The mass of DDTs on the PVS has decreased over the last two decades (Young et al., 1976; Lee, 1994). There are at least two possible explanations for this mass reduction. The first one is loss of these compounds by biodegradation. Metabolic products such as DDMU have been detected in sediments around the PVS (Lee, 1994).
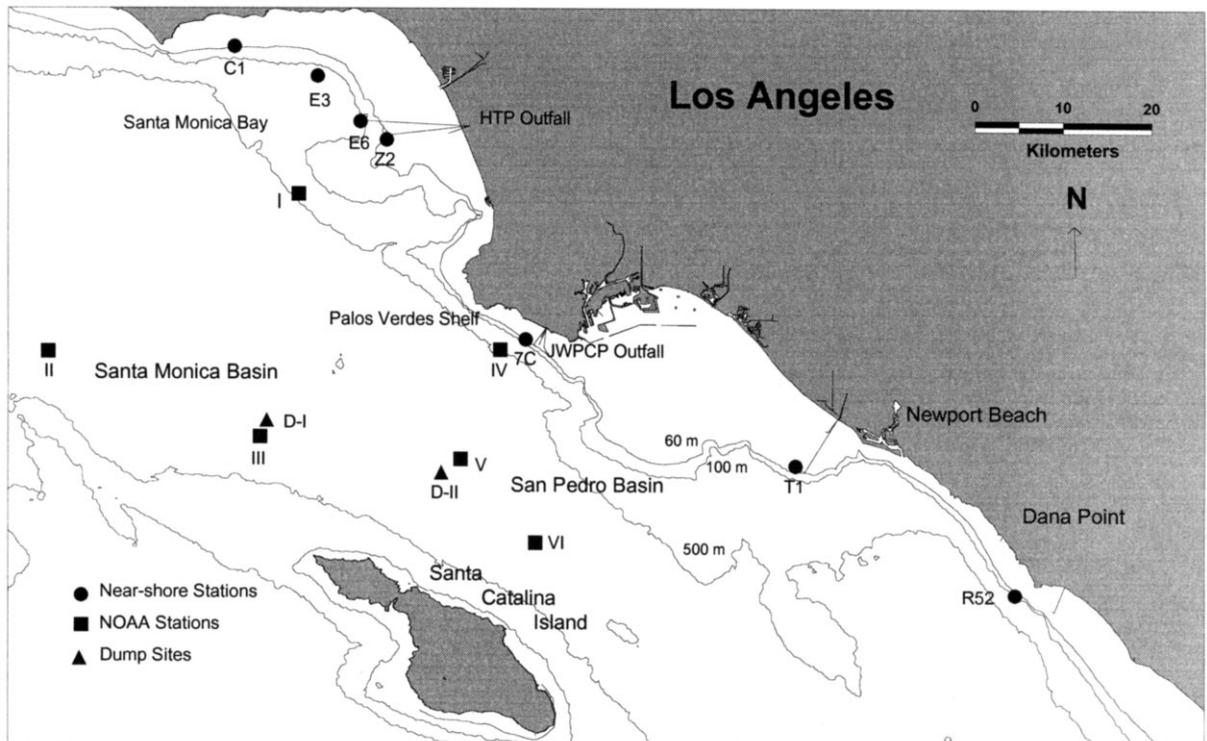

Fig. 1. Map of sampling locations in the Southern California Bight.

Recently, Quensen et al. (1998) reported the formation of DDMU from the anaerobic microbial degradation of DDEs in the PVS sediments from their microcosm studies. The presence of such metabolic products is suggestive of biodegradation because they were not expected to be present in the original sediments and, therefore, were likely formed in situ. The second possible explanation is that material has mobilized upward in the sediment, resuspended into the water column, and transported from the site to other areas of the SCB; the net result is dispersion of buried DDTs from the discharge zone to other distant areas. Depending on whether the biodegradation or dispersal mechanism is dominant, the bioavailability of historically discharged DDTs may alternatively be decreasing or increasing. Differentiating between these hypotheses is an important challenge to decision makers responsible for coastal water quality management.

The importance of dispersal as a mechanism for depleting the DDT inventory around known sources could reasonably be assessed by examining whether (1) buried DDTs have been mixed upward in the sediment column after the discharge of DDT residues via sewer systems was banned in early 1970s and the DDT mass emissions have drastically reduced since then; (2) DDTs in sediments have been released into the water column, resulting in a net flux of DDTs from the sediment bed; and (3) whether resuspended DDTs have been effectively transported into areas farther away from known historical input sources.

DDTs found, especially at surface sediments in distant areas such as the San Pedro and Santa Monica Basins, could have originated from the historical discharge zones from the JWPCP outfall at the PVS, as well as (in a much less amount than those from the JWPCP outfall) from the outfall of the Hyperion Treatment Plant (HTP; City of Los Angeles) in Santa Monica Bay (SMB) (Fig. 1). In addition, Montrose Chemical Company dumped acid wastes containing DDTs at two locations in the Santa Monica and San Pedro Basins, respectively, until the late 1960s (Chartrand et al., 1985) and DDTs in the vicinity could reflect this source as well (Venkatesan et al., 1996).

Since linear alkylbenzenes (LABs) are residues in detergents manufacturing processes and are almost exclusively disposed into the marine environment via sewage outfalls, presence of LABs has been used effectively as an indication for sewage-derived materials in southern California (Eganhouse et al., 1988; Zeng et al., 1997). Therefore, concurrent analyses of the distributions of DDTs and LABs would help identify the occurrence of sewage-derived DDTs. In addition, previous work on several sediment cores clearly demonstrate the presence of sewage-derived carbon in the Santa Monica and San Pedro Basins (Venkatesan and Kaplan, 1990; Venkatesan, 1995).

The dispersal mechanism of DDTs was first discussed in a series of recent publications (Niedoroda et al., 1996; Stull et al., 1996; Swift et al., 1996). Particularly, it was proposed that the ongoing release of DDT-contaminated particles from the discharge region was caused by bioturbation and physical transport of surface sediments due to storms and current flows (Niedoroda et al., 1996).

This article presents new data from analyses of a sediment core near the PVS, and integrates previously collected data to further assess whether dispersal is an important mechanism leading to depletion of DDT from the discharge zones in the SCB. The sediment data are used to elucidate the temporal change and spatial distribution of DDTs. A recent sampling at the PVS near the JWPCP outfall and two other locations with relatively less DDT impacts provided an opportunity to examine the DDT concentrations in the water column and sediment at the same locations (Tran and Zeng, 1997). Another study that collected water column samples at eight locations on the PVS, with varying distances from the JWPCP outfall (Fig. 2), also reported data suggesting the contaminated sediments on the PVS to be an important source of DDTs (Zeng et al., 1999). Additionally, the DDE profiles in sediment cores help verify the presence of sewage-derived DDTs in the Santa Monica and San Pedro Basin sediments (Venkatesan, 1994).
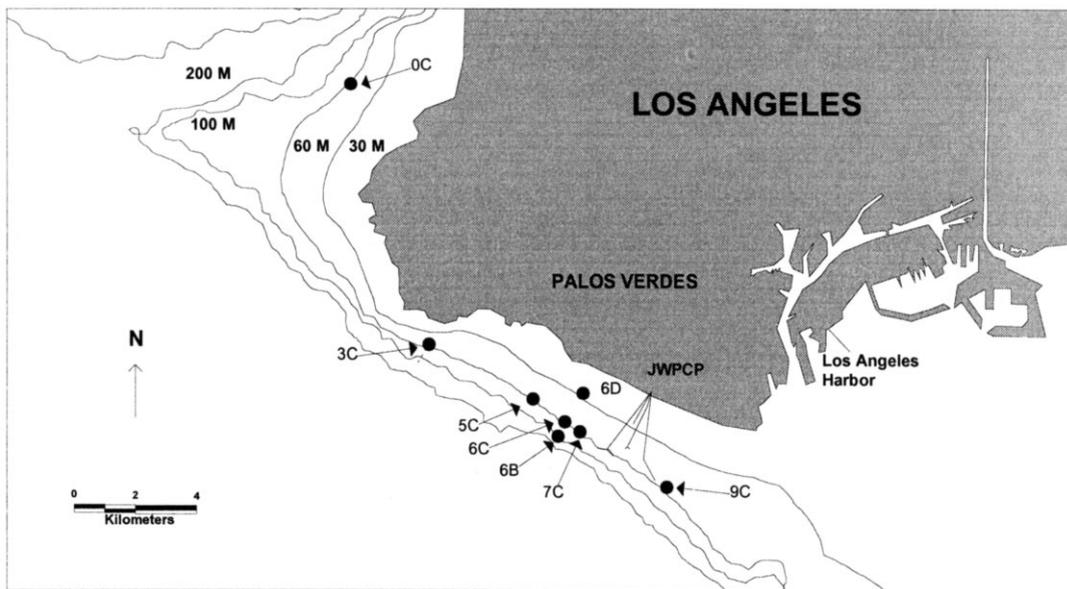
Fig. 2. Map showing the water column sampling locations on the Palos Verdes Shelf.

2. Methods

2.1. Sample collection

Three sets of sediment samples were investigated. The sampling stations as well as two dumpsites, D-I and D-II, are depicted in Fig. 1. The first set comprising of the sediment core 7C ($\sim$ 80 cm), was collected using a modified gravity core (SCCWRP, 1982) on 10 October 1995, frozen immediately, and sliced into 1-cm sections later using a stainless steel hand saw. The sample analysis procedures are described below. The second set, including sediment cores E6, E3, Z2 and C1, were collected using the modified gravity corer in June 1994 and cut every 2 cm onboard using a stainless steel blade. The analyses of these samples were described previously (SCCWRP, 1995). The third set consists of sediments collected from the Santa Monica and San Pedro Basins using a Slow Entry Soutar Box corer. These stations were sampled for a National Oceanic and Atmospheric Administration (NOAA)'s National Status and Trends program in 1991 and analyzed following the protocol validated by the interlaboratory calibration exercise coordinated by the National In-

stitute of Standards and Technology (Gaitherburg, MD, USA). The cores were age-dated by Pb-210 and are labeled here from I to VI (Venkatesan, 1994).

The first water column sampling was conducted using an Infiltrex 100 sampler (Axys Environmental Systems Ltd., Sidney, BC, Canada) in April 1996 and samples were collected at a depth of 1 m above the sea floor (Tran and Zeng, 1997). In addition, surficial sediments (top 2 cm) were also collected using a 0.1-m^2 Van Veen grab sampler (Stubbs et al., 1987). Three stations were sampled: 7C near the JWPCP outfall, T1 near the Orange County Sanitation District (OCSD) outfall, and R52 off Dana Point (Fig. 1). The second water column sampling was conducted during the winter (from January to March) and summer (from June to July) seasons in 1997 (Zeng et al., 1999), employing the same sampler as used in the first water column sampling. Samples were collected at a depth of 1 m above the sea floor from eight locations and at additional depths of 2, 5, 20 and 35 m above the sea floor from Station 6C (Fig. 2). Sampling and analytical procedures for the water column samples are described elsewhere (Tran and Zeng, 1997; Zeng et al., 1999)

and the sediment samples were processed using the procedures described below.

2.2. Analyses of 7C sediments

Typically ~ 30 g wet wt. from selected sections of the 7C sediment core were spiked with surrogate standards and extracted three times with methylene chloride using a roller table. The extract was subject to sulfur removal with activated copper granules and chromatographic column clean-up/fractionation using a 1:2 alumina/silica gel glass column. The fraction containing LAB and DDT compounds was concentrated to 1 ml using a Zymark TurboVap 500 concentrator (Zymark Corporation, Hopkinton, MA, USA). Appropriate amounts of internal standards were added to the final extract before instrumental analysis. The surrogate standards used were 1-phenyl nonane for LAB measurements and tetrachloro-*m*-xylene, PCB 65, and PCB 189 for DDT measurements.

Samples were analyzed using an Hewlett-Packard (HP) 5890 II gas chromatograph with a 5970 mass selective detector (GC-MSD) for LABs and an HP 5890 II equipped with a ^{63}Ni electron capture detector (GC-ECD) for DDTs. Chromatographic separation was achieved by a 60-m $\times 0.25$-mm i.d. (0.25-μm film thickness) DB-5 column (J & W Scientific, Folsom, CA, USA). The internal standards were 1-phenyl pentadecane for LABs and 2,4,6-trichlorobiphenyl (PCB congener 30) and 3,3′,4,4′,5,5′-hexachlorobiphenyl (congener 169) for DDTs. Quantitation of DDTs was based on a 5-point calibration curve for individual DDT components. Quantitation of LABs was performed in two steps. The composition of the LAB mixture was determined using 1-phenyl LABs (from C_{10} to C_{14}) and then the characterized LAB mixture was used as a calibration standard to quantify LAB components in samples (Zeng and Yu, 1996).

The GC-MSD and GC-ECD instrumental parameters were similar to those given previously (Zeng and Yu, 1996; Zeng et al., 1999). The detection limits for individual LAB and DDT components were 200 ng/g and 10 ng/g, respectively, for 1 g of dry sample. Recoveries of the

Table 1
Concentrations (ng/g dry sediment) of total DDTs and LABs at the near-shore surface sediments

Station	Depth (m)	DDTs	LABs
7C (0−1 cm)[a]	60	12 500	311
E6 (0−2 cm)[b]	100	93	9330
Z2 (0−2 cm)[b]	60	14	245
E3 (0−2 cm)[b]	60	29	40
C1 (0−2 cm)[b]	60	41	18

[a] Results from the present study.
[b] Results from a previous study (SCCWRP, 1995).

surrogate standards spiked into samples prior to extraction were as follows: 1-phenyl nonane — $83 \pm 33\%$, tetrachloro-*m*-xylene — $105 \pm 5\%$, PCB 65 — $106 \pm 6\%$, and PCB 189 — $103 \pm 8\%$. The LAB and DDT concentrations were all normalized to dry sediment weights (part per million or part per billion); they were not corrected for the surrogate standard recoveries.

The ratio of the concentrations of internal (6-phenyl dodecane and 5-phenyl dodecane) to external (4-phenyl dodecane, 3-phenyl dodecane, and 2-phenyl dodecane) isomers of phenyl dodecanes (designated as I/E) was calculated. This ratio is directly proportional to the degree of biodegradation of LAB compounds (Takada and Ishiwatari, 1990).

Table 2
%DDEs (*o,p′*-DDE and *p,p′*-DDE) in total DDT in the sediments near the JWPCP and HTP outfalls

Station		%DDEs
7C (*n* = 18; 0−71 cm)[a]	AVE	91.6
	STDEV	4.4
E6 (*n* = 20; 0−94 cm)[b]	AVE	93.9
	STDEV	2.0
Z2 (*n* = 7; 0−22 cm)[b]	AVE	94.9
	STDEV	0.5
E3 (*n* = 7; 0−30 cm)[b]	AVE	93.5
	STDEV	0.8
C1 (*n* = 5; 0−18 cm)[b]	AVE	93.4
	STDEV	0.5

[a] Results from the present study.
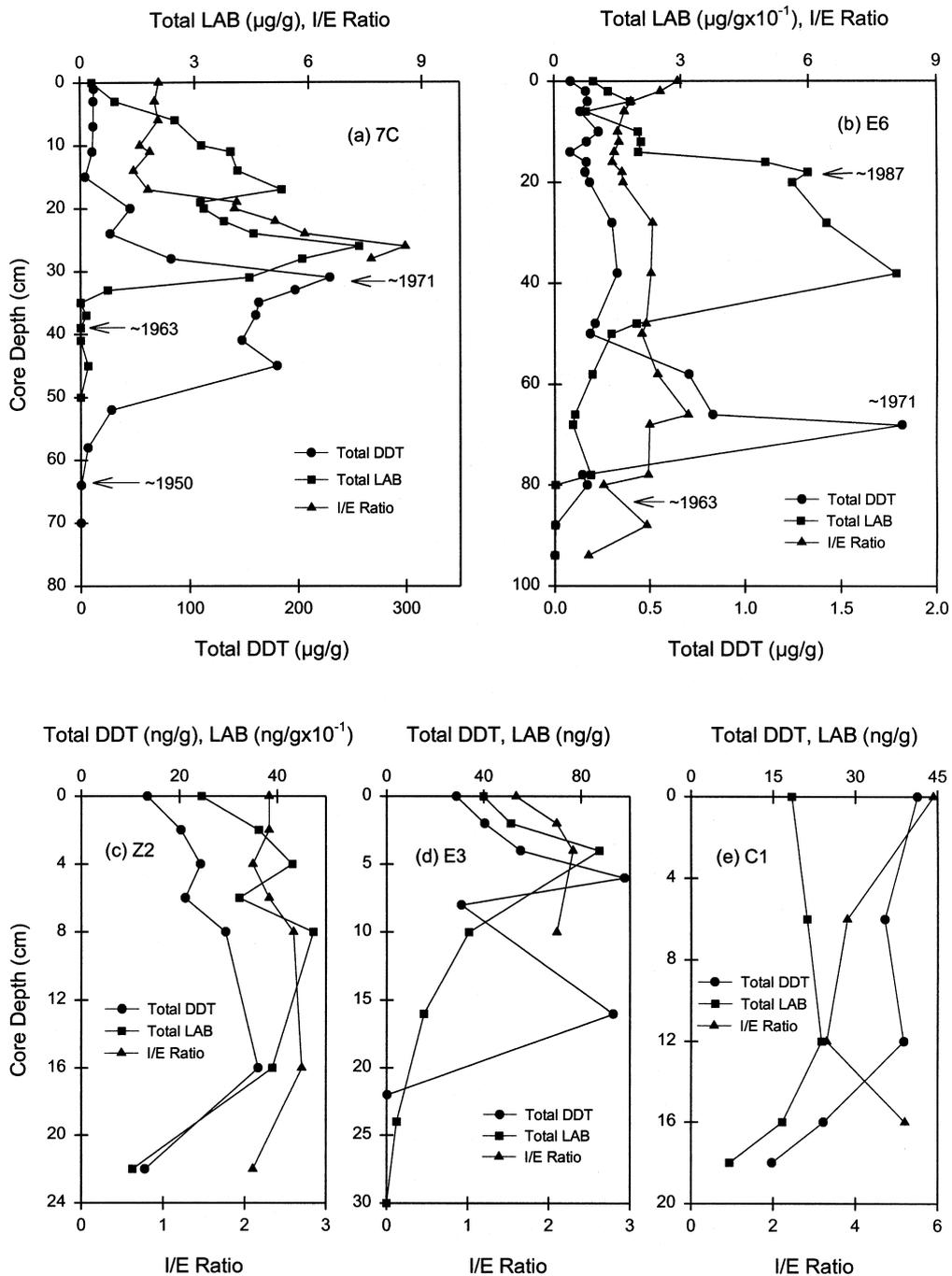[b] Results from a previous study (SCCWRP, 1995).

Fig. 3. Profiles of total DDT and LAB concentrations and I/E ratios in the sediment cores collected from (a) 7C at the Palos Verdes Shelf near the JWPCP outfall; (b) E6 in Santa Monica Bay (SMB) near the HTP 7-mile outfall; (c) Z2 in SMB near the HTP 5-mile outfall; (d) E3 in SMB; and (e) C1 (reference) in SMB (see Fig. 1).

3. Results and discussion

3.1. Spatial and temporal distributions of DDTs in near-shore sediments

The new data comprising profiles of DDT and LAB concentrations and I/E ratios in the station 7C sediment are shown in Fig. 3a. In addition, DDT and LAB concentrations at the 7C surface sediment, as well as the %DDEs values from the 7C sediment core are presented in Tables 1 and 2. These data will be evaluated in association with other previously collected data.

DDT and LAB concentrations at the top sediment sections (2 cm at Stations E6, Z2, E3, and C1 and 1 cm at Station 7C) vary over a wide range (Table 1). The DDT concentration was highest at 7C, while the LAB concentration peaked at E6; the maximum DDT or LAB concentration was at least an order of magnitude higher than the concentration levels in the rest of the samples. Stations 7C and Z2 are near the JWPCP and HTP 5-mile outfalls, respectively; surface sediments from these stations contained similar LAB levels. Within SMB, the surface sediment layers at E6 contained relatively higher DDT content than the other sites (Fig. 3b−e).

The profiles of the LAB and DDT concentrations in the 7C and E6 sediments clearly correlate with the timelines of wastewater discharge histories. In sediment core 7C (Fig. 3a), the initial increase in the LAB concentration at ∼ 35 cm was apparently due to the beginning of discharge of LABs in domestic wastes in the early 1960s when LABs replaced tetrapropylene-based alkylbenzenes as detergent raw materials. This observation is consistent with the declining concentration of DDTs from the depth of 30 cm upward (Fig. 3a), as a result of the ban on the discharge of these compounds via sewer systems in 1970 (Young et al., 1975). The mass emission of DDTs from the JWPCP outfall reached 1.9 kg/year in 1995 (Raco-Rands, 1997), compared to approximately 20 t/year in 1971 (Young et al., 1975). In sediment core E6, detectable LABs started to show up at ∼ 78−80 cm and the DDT concentration peaked at ∼ 68−70 cm (Fig. 3b); the depth difference between these two events is consistent

with what is observed with the 7C sediment core. As the operation of the HTP 7-mile sludge outfall ceased in 1987, sharp declines in the sediment concentrations of both LABs and DDTs occurred accordingly (Fig. 3b).

The vertical profiles of DDTs and LABs at Stations Z2, E3 and C1 do not show consistent trends (Fig. 3c,d) possibly because of the slower sedimentation rates at these locations compared to Stations E6 and 7C. Since the sediment cores were sliced at every 2 cm, each section may have represented a relatively long period of sedimentation; thus variations in DDT concentrations due to the same historical events as described above would be smoothed. However, DDTs remained detectable at the surfaces of these sediments

The timeline established above for the near-shore sediment contamination enables a comparison of DDT concentrations at an identical deposition time but at different sampling times. McDermott et al. (1974) extensively sampled surface sediments in 1973 around the sewage outfalls in southern California, including stations 7C and E6. The DDT concentrations obtained represented approximately the maximum values at that time. Stull et al. (1986, 1996) reported DDT profiles of sediment core 7C collected in 1981 and 1989. Maximum DDT concentrations can be obtained from both of these measurements. Their data are plotted along with the results from the present study in Fig. 4. Maximum DDT concentrations at 7C and E6 have gradually decreased over the last 20 years, a strong indication that the DDT masses at these sites have indeed declined, which is consistent with mass estimates reported previously. Young et al. (1976) estimated a mass of 156 t of total DDTs (sum of all DDTs, DDDs and DDEs) in 1972, although they believed that their number was rather low. Studies conducted in 1989 (Lee, 1994) estimated p,p'-DDE to be 122 t, while the United States Geological Survey (USGS) estimated its mass at 67 t in 1992 (Lee, 1994). In addition, Niedoroda et al. (1996) suggested that 12.6 t of p,p'-DDE were reintroduced into the marine environment from the central PVS region over the 2-year period of 1987−1989, with 1.2 t being redistributed on the northwest side of the shelf and 6.2 t being
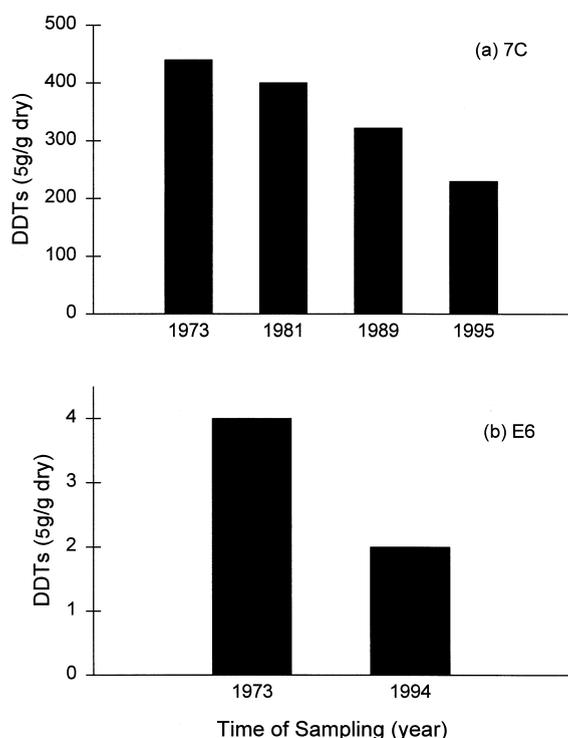
Fig. 4. Comparison of maximum DDT concentrations at sediments (a) 7C and (b) E6 sampled at different times. The DDT concentration at sediment 7C collected in 1989 was estimated from the maximum p,p'-DDE concentration (Stull et al., 1996) assuming that p,p'-DDE constituted 90% of total DDTs.

transported to the deep slope; the remaining 5.2 t could presumably have been transported to regions beyond the monitored sediment.

3.2. Mechanisms leading to DDT mass reduction

A relatively stabilized level of DDTs in the top 15-cm stratum in the profiles of cores 7C and E6 is rather striking (Fig. 3a,b). Stull et al. (1996) also noticed remarkably constant concentrations of p,p'-DDE in the upper sediment layers at two other stations (6C and 3C; Fig. 2) on the PVS. Apparently, DDTs are present in the surface sediments even after the discharge of such material was banned approximately three decades ago. These results, along with the observation mentioned above that the maximum DDT concentrations at PVS and SMB have continuously declined, are consistent with the possibility of buried

DDTs being remobilized upward in the sediment column via bioturbation (Swift et al., 1996).

A recent report by List (1997) suggests that anaerobic biodegradation of DDE to DDMU is active in the PVS sediments, based on the following observations. It is known from several studies that the DDT mass has decreased at the region of highest concentration in the sediment cores. The decrease in the maximum concentration of p,p'-DDE measured is nearly a factor of three from 600 to 212 ppm from 1970 to 1991 and far exceeds any decrease in the concentration of metals (Galloway, 1972; Stull et al., 1986, 1988; Swartz et al., 1991; Huh et al., 1992; Lee, 1994). The peak concentrations of metals, historically deposited in the sediments together with DDTs, apparently have not declined significantly since they were first measured in 1970−1971 (Galloway, 1972). Therefore, List (1997) argues that since metals are complexed with organics and incorporated into the sediment matrix, it is highly unlikely that only DDT-like components are flushed out of the sediments by bioturbating organisms, leaving behind the metals in place intact. Further, the presence of DDMU in sediments can only be a result of anaerobic biodegradation of DDE. Thus, the losses of p,p'-DDE and total DDTs recorded by the CSDLAC and USGS are attributed to the transformation of DDD to DDMS and other metabolites not measured, and DDE to DDMU (measured only in the study by the USGS) and other metabolites.

An alternative hypothesis, therefore, is that DDT could be biodegraded to a series of metabolites such as DDD, DDE, DDMU, etc. For example, DDE could be formed from DDT via dehydrochlorination, an oxidative process whereas, formation of DDD involves reductive dechlorination of DDT (Mohn and Tiedje, 1992). DDMU can be produced from DDE by a similar reductive dechlorination process in anaerobic conditions (Rochkind-Dubrinsky et al., 1987). Hill and McCarty (1967) have demonstrated the reduction of DDT and DDD in anaerobic sewage sludge at 35°C in approximately 2−4 days. Experiments with marine sediments and radiolabeled DDT showed that biodegradation could transform DDT into DDD, DDE, DDOH and DDNS,

although DDMU was not noted and it is not clear if it was even looked for in this study (Patil et al., 1972). These authors also found DDE to be the major biodegradation product in their studies of DDT and ocean water. Recently, the formation of DDMU from DDE, specifically, has been demonstrated in marine microcosm study of Quensen et al. (1998), where the sediment samples form the PVS were incubated statically at 22–25°C. Despite only minimal differences in many of the parameters such as grain size, pH, and trace metals content, Quensen et al. (1998) found significant differences in the rates and extents of DDE dechlorination among the sediments from the three sites investigated.

In the absence of measurements of other metabolites such as DDMU in our study, the role of biodegradation can neither be precluded nor its extent evaluated in the decline of the maximum concentration of DDTs (or DDDs/DDEs) in the region. However, these degradation processes would be much slower in natural anaerobic environments because of the lower ambient temperature. Considering that the sea water temperature is approximately 4°C and that hypooxic conditions of the sediments in the study area may not facilitate the reductive dechlorination as effectively as the anaerobic conditions would (Quensen et al., 1998), it can be reasonably assumed that DDE would be dechlorinated rather minimally and at a much slower rate (Hill and McCarty, 1967). If biodegradation is the only or the dominant mechanism reducing the DDE mass in the sediments, then a uniform decrease in the DDE levels in the surface layers should be expected since DDE would be metabolized to other compounds. This is not the case in the sediment cores we have investigated. The DDE level is nearly constant or varies within a very narrow range in the post-1970 horizons in most of the cores. This would imply remobilization of the underlying sediments from historic deposits.

3.3. Resuspension of sewage-derived DDTs from contaminated sediments

The water column and sediment data from a recent study (Tran and Zeng, 1997) are summa-

Table 3
Distribution of p,p'-DDE (ng/g dry sample) in the water column and sediment samples collected in April 1996 (Tran and Zeng, 1997)

Station	Water column particle ($n = 2$)	Surface sediment ($n = 3$)
7C[a]	174 ± 5	7880 ± 930
T1[b]	0.74 ± 0.15	1.50 ± 0.26
R52[c]	0.90 ± 0.66	5.28 ± 0.67

[a] Near the JWPCP outfall.
[b] Near the OCSD outfall.
[c] Off Dana Point, California.

rized in Table 3. Due to the low levels of DDTs generally found in the water column samples, only p,p'-DDE was chosen for comparison and no %DDEs could be calculated for most water column samples. The substantially higher DDT concentration in 7C water column particles than in T1 and R52 samples corresponds to the sediment DDT distribution (Table 3). Such correlation appears to rule out the possibility of significant DDTs contributions from sources other than the contaminated sediments. The concentration of p,p'-DDE was approximately 200 times higher in the water column particles from Station 7C than in those from Stations T1 and R52, while it was between 1500 and 5000 times higher in the surface sediments of 7C than in the latter stations. This may be attributed to lateral transport of suspended particles containing DDTs from the PVS area. Such a mechanism, although remains to be verified with more investigations, is consistent with the dispersal hypothesis.

Another sampling at the PVS by Zeng et al.

Table 4
Distribution of total DDTs (ng/l) in the water column samples collected in 1997[a] (see Fig. 2 for sampling stations)

Station	Winter sampling	Summer sampling
0C	2.3	4.3
3C	4.5	7.6
5C	9.2	10.4
6C	14.5	8.7
7C	9.9	5.5
9C	5.3	5.0

[a] Edited from Zeng et al. (1999).

(1999) in 1997 indicated that the maximum concentration of total DDTs in the water column was centered around the area near the JWPCP outfall, a known source for DDT inputs prior to the 1970s. The water column concentrations of DDTs generally decreased with increasing distance from the JWPCP outfall (Table 4). In addition, DDT concentrations in water column samples collected from Station 6C exponentially decreased with increasing distance from the sea floor (Zeng et al., 1999). These findings are consistent with the hypothesis that contaminated sediments on the PVS are presently a main source of DDT inputs to the water column.

Further evidence supporting the resuspension mechanism is available from the comparison of spatial distributions of surface sediment DDTs and LABs in SMB. Presently, DDTs are quite widespread as suggested by the slightly higher sediment DDT concentrations at E3 and C1 than at Z2 (Table 1) which is even closer to the HTP 5-mile and 7-mile outfalls (Fig. 3c–e). In contrast, the concentrations of LABs (representing present-day and continuing discharge) in surface sediments varied over several orders of magnitude among these stations (E6 > Z2 > E3 > C1) (Table 1). Even though the low LAB concentration in station C1 sediments may be partially attributed to greater biodegradation, as reflected by its higher I/E ratios than at the other stations (Fig. 3b–e), the sharp decline in LAB concentration with increasing distance from the HTP outfalls suggests a rapid deposition of sewage-derived organic materials around the discharge area. A similar mechanism would have led to a highly localized distribution pattern for DDTs as well. In contrast, the chronic levels of DDTs with less drastic variation in concentration (yet exhibiting a gradient from the source) presently found in the surface sediments at these locations suggest that the buried DDTs are gradually resuspended from the discharge zone and dissipated to other areas.

Vertical profiles of contaminants reflect discharge history to a certain degree; however, the surface strata in the profiles (Fig. 3a,b) show greater concentration than supported by effluent deposition which suggests amendments from

below. Since remobilization of buried DDTs in the PVS sediments can be initiated by biota (Swift et al., 1996), even in the absence of discharge of DDTs from modern day sewer systems, upward reworking processes would result in fairly substantial DDT concentrations at the top sediment layer.

Aerial fallout and surface runoff may also bring residual DDTs into sediments, but the DDT distribution patterns would be distinct from that resulting from sediment reworking. Aerial fallout would result in a relatively uniform distribution of DDTs in surface sediments and water column throughout the shelf and basins, as opposed to substantially different spatial distributions of DDTs presently observed (Tables 1 and 4). At a given location, aerial fallout also would result in a water column profile of DDT concentrations increasing with increasing distance from the seafloor, opposite to the observed profile (Zeng et al., 1999). Iwata et al. (1993), after their survey on the surface seawater of various oceans (from April 1989 to August 1990), attributed the DDT contamination largely to atmospheric transport. Of the 68 samples collected and analyzed, the highest concentration of DDTs they observed was 0.041 ng/l. By comparison, the water column concentrations of DDTs ranged from 0.6 to 15.8 ng/l on the PVS (Zeng et al., 1999). The much higher DDT concentrations in the water column of the PVS can only be accounted for by inputs from a significant localized source. Surface runoff would have a characteristic imprint of DDT concentrations dictated by the near-shore geographical setting rather than by the relevance to the historically contaminated sediments (Table 1). The above discussion also indicates that the distribution of DDTs in the water column is strongly associated with the level of sediment contamination. Apparently, the data obtained here point to the historically contaminated sediments at the PVS as a major contributor, especially, of the DDT metabolites in the region.

One consequence resulting from resuspension of buried DDTs would be a spatial distribution of DDTs in the water column (near the water–sediment interface) closely related to that in the surface sediments. However, direct measurement

of the fluxes of DDTs between the water−sediment interface in the marine environment remains a difficult task; data are not available in southern California.

3.4. Sewage-derived DDTs in deep-water sediments

Since DDE could be formed from DDT via dehydrochlorination (Mohn and Tiedje, 1992), %DDEs values may be well preserved in sediments under anaerobic conditions. Therefore, %DDEs can be used to differentiate sources of DDT inputs if the original materials contained different DDT compositions. In the near-shore sediments, DDEs were the most abundant components among the six DDT isomers. An average value of %DDEs (percentage of o,p'-DDE and p,p'-DDE in total DDTs) was calculated for the near-shore sediment cores; DDEs are uniformly greater than 90% with small standard deviations (Table 2). On the other hand, o,p'- and p,p'-DDT were the most abundant components in the acid wastes dumped at dumpsites D-I and D-II (Fig. 1) (Chartrand et al., 1985; Venkatesan et al., 1996).

Since the near-shore sediments and water column samples discussed above contain mostly DDEs, the discussion of the basin sediments here will be confined mainly to DDEs (a detailed account of the composition of the DDTs and other chlorinated hydrocarbons will be published elsewhere). These sediments exhibit a wide range of %DDEs in total DDT values (Table 5). Therefore, an average value of %DDEs with standard deviation is given if the variation of %DDEs throughout the consecutive sediment core sections was small; otherwise a depth profile is presented to show the temporal change of %DDEs. At Station III near Dumpsite D-I and Station V near Dumpsite D-II (Fig. 1), %DDEs values are relatively low (mostly below 50%). In contrast, %DDEs values are uniformly high ($> 80\%$) at Station I close to SMB and Station IV near the JWPCP outfall (Fig. 1).

The values of %DDEs in the near-shore sediments (Table 2) are similar to those obtained more than 20 years ago (McDermott et al., 1974), suggesting that the JWPCP and HTP outfalls

Table 5

%DDEs (o,p'-DDE and p,p'-DDE) in total DDT in the sediments around the Santa Monica and San Pedro Basins[a]

Station		%DDEs
I ($n = 13$; 0−14 cm)	AVE	83.5
	STDEV	3.6
II ($n = 4$; 0−2 cm)	AVE	89.7
	STDEV	2.4
	2−2.5 cm	71.8
($n = 2$; 2.5−4 cm)	AVE	27.1
	STDEV	0.7
($n = 3$; 4−7 cm)	AVE	78.3
	STDEV	1.5
III	0−1 cm	21.8
	1−2 cm	55.7
	2−3 cm	32.5
	3−4 cm	28.3
	4−5 cm	10.1
	5−6 cm	11.6
	6−7 cm	56.3
	7−8 cm	30.5
	8−10 cm	52.7
	12−14 cm	54.1
IV ($n = 13$; 0−14 cm)	AVE	87.2
	STDEV	2.9
V ($n = 4$; 0−3 cm)	AVE	85.3
	STDEV	4.7
	3−3.5 cm	30.2
	4−5 cm	22.9
	5−6 cm	10.1
	6−7 cm	47.6
	7−8 cm	56.0
VI ($n = 2$; 0−1 cm)	AVE	83.3
	STDEV	6.4
($n = 7$; 1.5−6 cm)	AVE	71.3
	STDEV	11.6

[a] Data edited from Venkatesan (1994).

have remained the main chronic sources of the near-shore sediment DDT contamination. By contrast, a large variation in the value of %DDEs is evident in the sediment cores collected from various stations in the Santa Monica and San Pedro Basins (Table 5). The relatively low %DDEs values observed at Stations III and V compared to other stations (Fig. 1) reflect the composition of DDTs in the acid wastes from DDT manufac-

ture dumped at two nearby locations (dumpsites D-I and D-II) in the Santa Monica and San Pedro Basins, respectively, prior to 1968 (Chartrand et al., 1985; Venkatesan et al., 1996). The sediments at these dumpsites contain elevated levels of DDTs and thus, may have become significant secondary sources of contaminants. Apparently, this DDT signature has been well preserved in the deep waters (Venkatesan et al., 1996). Values of %DDEs were substantially lower in tar cake (∼ 1–2%) collected at one of the dumpsites in the San Pedro Basin (Venkatesan et al., 1996) than that measured in contaminated sediments near the outfall areas more than 25 years ago (McDermott et al., 1974). Since DDT can be metabolized to DDE significantly only under aerobic conditions (List, 1997), %DDEs is expected to be characteristic of its source in the basin sediments which are generally hypooxic. Consequently, the low %DDEs (10–30%) in the sediments from the vicinity reflect the composition of the acid wastes from the dumpsites. On the other hand, high values of %DDEs (∼ 83–87%) in sediment cores I and IV are similar to those in the near-shore sediments (Tables 2 and 4).

The temporal change of DDT compositional indices in several basin sediment cores clearly showed the impact of ocean dumping on the sediment DDT contamination (Table 5). Apparently, Station III was most strongly influenced by D-I as illustrated by low %DDE throughout the sediment core. Station V showed considerable influence from D-II. Stations II and VI, which are further away from the dumpsites, showed less impact from D-I and D-II. Stations I and IV being close to the HTP and the JWPCP outfalls, respectively, were strongly impacted by the outfall discharge, as indicated by high %DDEs values throughout the core. At station V, %DDEs fell within a narrow window from 0 to 3 cm (78.5–88.7). This percentage dropped substantially in the 3–6-cm sections to between 10.1 and 30.2. The 3–3.5-cm depth corresponds to year 1970 (Venkatesan, 1994) when DDTs discharge via outfalls was about to cease. Similarly, the 5–6-cm section corresponding to 1942 exhibits the lowest %DDEs content (10.1%). Wastes from

DDT manufacture were generally dumped at designated sites until 1968 (Chartrand et al., 1985) and it is likely that the acid wastes contributed to the low %DDEs of the sediments in the vicinity including station V. Below a depth of 6 cm (pre-1942), total DDTs contents are much less and DDEs are much higher. Similar, but less pronounced, trends are observed also in Station II with relatively low DDEs in the horizons from 2.5 to 4 cm, dating 1948–1959 compared to other sections above and below.

Even if some DDEs have been microbially degraded to DDMU, such loss of DDEs is expected to be minimal as discussed previously. Furthermore, the higher percentages of DDEs generally observed above and below the horizons, corresponding to approximately between 1948 and 1970, in the cores suggest that microbial degradation of DDEs did not play a significant role in the sediments investigated. The distinction between the compositions of DDTs in sewage outfalls and in the dump sites, particularly the %DDEs, appears to be diagnostic of their origin in the study area. These parameters could, therefore, help infer the dominant origin of DDTs as to whether sewage-related DDTs have been dispersed from near-shore areas such as from the JWPCP and HTP outfalls and deposited in the basin sediments or DDT residues from the historic dumpsites have contributed to the sedimentary components.

A detailed study of fecal sterols and trialkylamines (originating from fabric softeners in the household laundry discharges) clearly show the presence of carbon derived from sewage outfalls in the Santa Monica and San Pedro Basins (Venkatesan and Kaplan, 1990; Venkatesan, 1995). Furthermore, the composition of LABs in these sediments (Chalaux et al., 1992) was similar to those of LAB assemblages in the E6, Z2, E3, and C1 sediments collected near-shore. The magnitude of the contaminant impact felt in the sediments is dependent on factors such as the proximity to the source, the grain size, and the refractory nature of the components. Apparently the %DDE values in the sediments reflect the inputs from outfalls and/or the dumpsites.

4. Conclusions

The post-1970s distribution of DDTs in PVS and SMB sediments is mainly associated with two localized sources, i.e. the JWPCP and HTP outfalls. Historically contaminated sediments have become an important source of DDTs, in the modern day sediments. Buried DDTs are being resuspended from the sediments, as suggested by the close correlation between DDT concentrations in sediments and water column particles, and dispersed away from the discharge zones. DDT metabolites such as DDEs, the major DDT component, found at the surface sediment layers in the Santa Monica and San Pedro Basins, were most likely transported by resuspension from the near-shore areas. This is also supported by the fact that LABs have been detected in sediments collected from the Santa Monica Basin. The results imply that gradual remobilization of the historic layers by bioturbation and resuspension has resulted in the decline of the DDT inventory on the PVS. Some sediment horizons exhibit characteristic DDE composition of acid wastes probably remobilized from the historic dumpsites in the basins. It should be noted that the available data is not sufficient to confirm anaerobic degradation of DDE to other compounds in the study region, which could also result in a decrease in the mass of DDTs, especially DDEs, in the sediment horizons.

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