Historical record and fluxes of DDTs at the Palos Verdes Shelf Superfund site, California

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HIGHLIGHTS

- Historical trends of DDTs at the Palos Verdes Shelf Superfund site were examined.
- Very high concentrations of DDTs were found in the sediment core 8C and adjacent cores.
- Peak concentrations of DDTs in sediment cores are linked to the discharge of these chemicals between the 1940s–1980s.
- The estimated total deposition of DDTs is fairly close to that reported for industrial wastewater discharge in this area.

GRAPHICAL ABSTRACT

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ABSTRACT

Marine sediments at many locations in the world are contaminated with a wide range of persistent organic pollutants. The Palos Verdes Shelf (PVS) is located in the ocean off the coast of Los Angeles, California and has been listed as a Superfund site by the US EPA since 1997, because of heavy contamination of DDTs and PCBs. However, little is known about the historical trend in the deposition of DDTs as a result of decades-long discharge of wastewater effluents. In this study, sediment cores were taken from the PVS site and determined for DDT and its metabolites including DDE and DDD (denoted as DDTs). Individual DDTs were found in the majority (95%) of the samples analyzed. The highest Σ DDT concentrations were found in three cores along the 60-meter isobath with geometric means of 31300, 7490, and 5010 ng/g dw and medians of 82400, 17300, and 5200 ng/g dw, respectively. Among DDT congeners, *p,p'*-DDE, *o,p'*-DDE and *p,p'*-DDD were predominant, contributing to approximately 54%, 27%, and 14% of the Σ DDTs in sediment. The vertical profiles of concentrations of contaminants in the sediment cores were examined. For most of the cores, a steady increase in the concentrations of DDTs during 1940s to 1980s was observed, while the concentrations declined gradually toward the surficial layers. On the basis of the mass flux of DDTs calculated and the area of the PVS Superfund site, we estimated the total deposition amount of DDTs in sediment and the deposition amount of Σ DDTs in this region during 1947–1971 was 132 tons, which was fairly close to what was reported in earlier studies for industrial wastewater discharge in the PVS site (870–1450 tons). Our

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findings suggest that the elevated levels of DDTs in sediment from the PVS site are linked to the discharge of these contaminants between the 1940s–1980s.

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1. Introduction

The Palos Verdes Shelf (PVS) site, located off the coast of Los Angeles, California, has been proposed as a typical Superfund site by the U.S. Environmental Protection Agency (US EPA) since 1997, due to heavy contamination by several persistent organic pollutants (POPs), specifically, dichlorodiphenyltrichloroethane (DDT) and its main degradation products dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD) (denoted as DDTs), as well as polychlorinated biphenyls (PCBs) (Eganhouse and Pontolillo, 2008; Fernandez et al., 2012; Quensen et al., 2001; Venkatesan et al., 1996; Zeng and Venkatesan, 1999). Contamination of DDT in the PVS ocean floor is largely due to decades (1947–1983) of wastewater discharge via the outfall of the Joint Water Pollution Control Plant (JWPCP) operated by the Los Angeles County Sanitation District (LACSD) and disposal of residual DDT wastewater by Montrose Chemical Company, once the largest DDT manufacturer in North America (Stull et al., 1996; Venkatesan et al., 1996). It is estimated that over 44 km² of sediment in the PVS Superfund site is heavily contaminated with DDT and its metabolites DDE and DDD. High total concentrations of DDT, DDE, and DDD (up to 200 µg/g) in sediment samples collected from PVS have been reported (USEPA, 2009b, 2013).

Although industrial releases of major contaminants, including DDTs, have ceased, sediments in the PVS Superfund site are continuously a source of contaminants to the adjacent water column, and biota living within and above the sediment, like many other Superfund sites (Friedman et al., 2011; Larsson, 1985; Zeng et al., 1999). By using a solid-phase microextraction-based sampling technique, a large-scale survey on DDTs in water column of the PVS and vicinity reported that the *p,p'*- and *o,p'*-DDE concentrations were in the range of <0.073 to 2.6 ng/L and <0.043 to 0.26 ng/L, respectively (Zeng et al., 2005), which was clearly higher than those found for other water column across the globe, e.g. the North Sea, Western Europe (*p,p'*-DDE: ~0.01 ng/L) (Bergqvist et al., 1998), the San Francisco Bay watershed, CA (*p,p'*-DDE: 0.0066–0.23 ng/L; *o,p'*-DDE: ND–0.019 ng/L) (San Francisco Estuary Institute, 1999), and the Pearl River Estuary, China (*p,p'*-DDE: 0.01–0.09 ng/L; *o,p'*-DDE: <0.008–0.02 ng/L) (Luo et al., 2004). Elevated DDTs were detected in surface sediments (0–15 cm) collected from the PVS site with concentrations as high as 25,100, 3350, 11,000, and 1850 ng/g dry weight (dw) for *p,p'*-DDE, *o,p'*-DDE, *p,p'*-DDD, and *o,p'*-DDD, respectively. A national survey on spatial distribution of DDTs in bivalves, collected from the coastal marine environments in the United States during 1986–2009, indicated that bivalves living in areas linked to areas of DDT production or heavy usage, including the southern California and San Francisco area on the west coast, contain elevated concentrations of DDTs in their tissues. For example, the Σ DDTs in bivalves from the PVS site was 731 ng/g dw (Sericano et al., 2014).

Elevated levels of DDTs in the sediment and water column not only pose risk to the marine environment, but also to invertebrates and microorganisms that live within or above the sediment, which in turn harm organisms at upper trophic levels, including bottom-feeding fish, fish-eating birds, marine mammals, and humans. Due to elevated DDT levels accumulated, fish consumption advisories and health warnings have been posted in the Southern California bight (Wolfe and Lowe, 2015). Given the high toxicities of DDTs, e.g., carcinogenicity, endocrine disrupting activity, reproductive and development and effects (Mrema et al., 2013; Rosner and Markowitz, 2013; Su et al., 2014), cleanup strategies and remedial options such as dredging, sand capping and in-situ

sorbent treatment have been explored for Superfund sites to protect human and ecological health (USEPA, 2009a, 2005). Despite such attempts, the PVS site remediation is still a difficult task because the site comprises a large area which extends over 44 km² with sediment layer depth ranging from 150 to 300 ft (USEPA, 2009b).

In view of the potential for continuous release and high toxicity, determination of typical contaminants, including DDTs, in sediment cores and elucidation of sources of environmental pollution arising from anthropogenic activities are imperative to the assessment of risks and for the development of strategies to mitigate exposures. Little is known about the historical trends and chemical fluxes of DDTs at the PVS site, although some studies with respect to the spatial distributions of DDTs have been done in this area (Friedman et al., 2011; Zeng et al., 1999). The objectives of this study were: (i) to determine the concentrations of DDTs, including the *o,p'*- and *p,p'*-isomers of DDT, DDE, and DDD, in sediment core samples collected from the PVS Superfund site; (ii) to determine the composition profiles of contaminants to discuss the environmental behavior and fate of such chemicals in aquatic ecosystem; (iii) to evaluate the spatial distributions and temporal variations in concentrations of contaminants to reveal the current and historical contamination situation in this area of concern; (iv) to calculate the mass flux of contaminants to explore possible links between contamination and anthropogenic activities. Our study fills an important knowledge gap by identifying that industrial wastewater discharge between the 1940s–1980s is the main source for elevated levels of DDTs in the PVS site.

2. Materials and methods

2.1. Chemicals and materials

Six DDT compounds, including 1,1,1-trichloro-2-(2-chlorophenyl)-2-(4-chlorophenyl)ethane (*o,p'*-DDT), 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (*p,p'*-DDT) and their metabolites 1,1-dichloro-2,4-bis-(chlorophenyl)ethylene (*o,p'*-DDE), 1,1-dichloro-2,2-bis(chlorophenyl)ethylene (*p,p'*-DDE), 1,1-dichloro-2,4-bis(chlorophenyl)ethane (*o,p'*-DDD), and 1,1-dichloro-2,2-bis(chlorophenyl)ethane (*p,p'*-DDD), were purchased from AccuStandard (New Haven, CT). Deuterated compounds *d*₄-*p,p'*-DDE, *d*₈-*p,p'*-DDD, *d*₈-*o,p'*-DDT, and *d*₈-*p,p'*-DDT were purchased from C/D/N Isotopes (Pointe-Claire, Quebec, Canada). Anhydrous sodium sulfate (10–60 mesh; Fisher Scientific, Pittsburgh, PA) and florasil (10–60 mesh; Acros Organics, Morris Plains, NJ) were activated before use in an oven at 400 °C and 130 °C, respectively. Empty SPE cartridges (20 mL) were purchased from Supelco (Bellefonte, PA). All organic solvents, including dichloromethane (DCM), acetone and hexane, were of HPLC grade and purchased from Fisher Scientific. The stock solutions (1 mg/mL) of all target analytes and internal standards were prepared in acetone and stored at –20 °C. The working solutions were prepared from the stock solutions through serial dilution with hexane before use.

2.2. Sample collection and preparation

Marine sediment cores were collected in 2007 from six locations inside the PVS Superfund area off the coast of Los Angeles, CA (Fig. 1), stored in dry ice and transferred to freezers held at –20 °C in the JWPCP Marine Biology Laboratory for storage (LACSD, 2014). The length of these cores were 75, 71, 75, 77, 53, and 77 cm for cores 3C, 6C, 7.5CD,

Fig. 1. Map showing the study area and sampling stations. The Los Angeles County Sanitation District (LACSD) Ocean Monitoring and Research Group collected core samples at six stations in 2007. Station 7.5CD is located at the 50-meter isobath; stations 3C, 6C, 7.5C and 8C are located along the 60-meter isobath; and the station 8CB is located at the 70-meter isobath.

7.5C, 8CB, and 8C, respectively. The cores were sectioned at 2-cm intervals, put in glass jars, and kept frozen until processed for analysis. The sediment cores were dated by ^{210}Pb . Radiometric measurements (^{210}Pb and ^{226}Ra) were collected using low-background gamma counting with well-type intrinsic germanium detectors (Appleby et al., 1986; Schelske et al., 1994). The age of each sediment section was calculated using the constant initial concentration (CIC) model (Nitttrouer et al., 1979). The mean sedimentation rate (MSR) was calculated as the decay constant for ^{210}Pb (-0.031) divided by the slope of the regression of the natural-log of unsupported ^{210}Pb activity (i.e. $^{210}\text{Pb}_{\text{Total}} - ^{226}\text{Ra}$) versus the mid depth cumulative mass (g/cm^2) for each sediment section. The 95% confidence intervals for the mean sedimentation rate in a similar manner were calculated using the 95% confidence intervals for the slope of the regression of the natural-log of unsupported ^{210}Pb activity versus the mid depth cumulative mass.

After mixing, sediment (~ 0.5 g) was accurately weighed (wet weight) and homogenized with anhydrous sodium sulfate (~ 6 g; sediment:sodium sulfate = 1:12, m:m) by a pestle and mortar. One hundred nanograms of stable isotope analogues were spiked as internal standards, and the homogenized sample was extracted with 40 mL of dichloromethane (DCM) and acetone (1:1, v/v) by shaking in an orbital shaker at 250 oscillations/min for 30 min. After centrifugation (3000 rpm, 30 min), the supernatant was transferred to another tube. The residue was extracted one more time with 40 mL of DCM and acetone (1:1, v/v) by shaking. The extracts were combined, concentrated to near dryness under a gentle stream of nitrogen, and reconstituted with

3 mL of hexane and acetone (9:1, v/v). A home-made florisil cartridge (2 g florisil), previously conditioned with 10 mL of hexane, was used for the purification of samples. After loading the sample, the SPE cartridge was washed with 10 mL of hexane and eluted with 15 mL of hexane and acetone (9:1, v/v). The elute was concentrated to near-dryness, reconstituted with 1 mL of hexane and acetone (9:1, v/v), and transferred into a gas chromatographic vial for GC-MS/MS analysis.

2.3. Instrumental analysis

Identification and quantification of DDTs were performed with a Varian 3800 gas chromatograph (GC) coupled with a Varian 1200 triple-quadrupole mass spectrometer (MS/MS) (Varian Instruments, Sunnyvale, CA) (Jia et al., 2014). An aliquot of sample extract (1 μL) was injected into the inlet at 240°C and the separation was achieved on a DB-5MS Ultra Inert capillary column ($60\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$, Agilent, Wilmington, DE). Helium (purity 99.999%) was used as the carrier gas at a flow rate of 1 mL/min and argon (99.999%) was used as the collision gas. The oven temperature was programmed to start at 80°C and hold for 1 min, increase by $10^\circ\text{C}/\text{min}$ up to 210°C , and further to 300°C at $5^\circ\text{C}/\text{min}$ and hold for 5 min. The MS/MS was operated in electron ionization (EI) mode at 70 eV with multiple reaction monitoring (MRM), and the MRM transitions of ions monitored are listed in Table 1. The transfer line and ionization source temperatures were 300° and 250°C , respectively. Calibration standards

Table 1
Conditions of GC–MS/MS method for target analytes.

Chemical	Precursor ion (m/z)	Product ion (m/z)	Collision energy (eV)
<i>o,p'</i> -DDE	247	176	30
<i>p,p'</i> -DDE	247	176	25
<i>d₄-p,p'</i> -DDE	255	184	30
<i>o,p'</i> -DDD	236	165	25
<i>p,p'</i> -DDD	236	165	20
<i>d₈-p,p'</i> -DDD	243	173	22
<i>o,p'</i> -DDT	236	165	25
<i>d₈-o,p'</i> -DDT	243	173	22
<i>p,p'</i> -DDT	236	165	25
<i>d₈-p,p'</i> -DDT	243	173	22

were prepared in *n*-hexane and analyzed under the same conditions on the same day of analysis.

2.4. Quality assurance and quality control (QA/QC)

The mean recoveries of target analytes spiked into procedural blanks (400 ng) ranged from 79.9% (*p,p'*-DDD) to 135% (*p,p'*-DDE) and those spiked into sample matrices (400 ng) ranged from 110% (*p,p'*-DDE) to 144% (*o,p'*-DDD) (Table 2). The internal standards (isotope labeled analogues) were spiked in all samples (100 ng) before analysis and their mean recoveries were in the range of $105 \pm 38.2\%$ (*d₈-p,p'*-DDE) to $115 \pm 39.7\%$ (*d₈-p,p'*-DDD). Quantification was by the isotope-dilution method, i.e., the reported concentrations were adjusted by the recoveries of the internal standards, *d₄-p,p'*-DDE for *o,p'*- and *p,p'*-DDEs, *d₈-p,p'*-DDD for *o,p'*- and *p,p'*-DDDs, *d₈-o,p'*-DDT for *o,p'*-DDT, and *d₈-p,p'*-DDT for *p,p'*-DDT. Several samples were randomly selected ($n = 4$ for each batch) and analyzed in duplicate and the coefficient variation between the concentrations were <15% for the target compounds. The limits of quantitation (LOQs) were 0.1 ng/g for *o,p'*-DDE, *p,p'*-DDE, and *o,p'*-DDD, 0.2 ng/g for *p,p'*-DDD, 0.4 ng/g for *o,p'*-DDT, and 1.0 ng/g for *p,p'*-DDT, respectively (Table 2); which were calculated from the value of the valid lowest acceptable calibration standard and a nominal sample weight of 0.5 g. A midpoint calibration check standard was injected as a check for instrumental drift in sensitivity after every 20 samples, and a pure solvent (hexane) was injected as check for carry-over of analytes from sample to sample. Instrumental calibration was verified by the injection of 12 point calibration standards at concentrations ranging from 0.1 to 1000 ng/mL, and the regression coefficient (r) of the calibration curve was >0.99.

2.5. Data analysis

Difference between groups was determined by one-way analysis of variance (ANOVA) using Origin 8.6 (OriginLab Corporation; Northampton, MA). The value of $p < 0.05$ was considered significant. Concentrations below the LOQ were substituted with a value equal to LOQ divided by the square root of 2. Moisture content of each sediment sample was determined before weighed for extraction. All data were expressed on a dry weight basis, unless otherwise stated.

Table 2
Limit of detection (LOD), limit of quantification (LOQ), and recoveries (% mean $\pm$ SD) from spiked blanks and matrices for target analytes in sediment.

Chemical	LOD (ng/mL)	LOQ (ng/g)	Blank spike (%)	Matrix spike (%)
<i>o,p'</i> -DDE	0.05	0.1	105 ± 4.20	129 ± 51.3
<i>p,p'</i> -DDE	0.05	0.1	135 ± 4.81	110 ± 39.2
<i>o,p'</i> -DDD	0.05	0.1	94.7 ± 3.76	144 ± 36.6
<i>p,p'</i> -DDD	0.1	0.2	79.9 ± 0.154	115 ± 39.5
<i>o,p'</i> -DDT	0.2	0.4	126 ± 7.43	123 ± 23.0
<i>p,p'</i> -DDT	0.5	1.0	124 ± 8.48	133 ± 12.7

3. Results and discussion

3.1. Concentrations and profiles of DDTs

Geometric mean (GM) and median concentrations of DDTs (*o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDT, and *p,p'*-DDT) in sediment core samples collected from six locations in the PVS Superfund site, are shown in Table 3. The highest concentration of *p,p'*-DDE was found in sediment from core 8C (GM: 9560 ng/g, median: 28,400 ng/g, detection rate: 94.7%); followed, in decreasing order, by *p,p'*-DDD (5650 ng/g, 14,200 ng/g, 94.7%), *o,p'*-DDE (5110 ng/g, 21,500 ng/g, 92.3%), and *p,p'*-DDT (1950 ng/g, 3840 ng/g, 94.9%). The total concentration (sum of DDTs: Σ DDTs) of the six target compounds was compared among the six cores studied. Sediment samples from core 8C contained the highest Σ DDT concentration (GM: 31,300, median: 82,400 ng/g), which was approximately 4–6 times higher than that found for cores 7.5C (7490, 17,300 ng/g) and 6C (5010, 5200 ng/g), and 1–2 orders of magnitude higher than those found for cores 7.5CD (2170, 5500 ng/g), 8CB (1450, 2930 ng/g) and 3C (364, 752 ng/g) (Table 3). The Σ DDT concentrations in core 8C (maximum: 910,000 ng/g) were 2 orders of magnitude

Table 3
Concentrations (ng/g dw) and profiles of target analytes in sediment cores from the PVS Superfund site.

	<i>o,p'</i> -DDE	<i>p,p'</i> -DDE	<i>o,p'</i> -DDD	<i>p,p'</i> -DDD	<i>o,p'</i> -DDT	<i>p,p'</i> -DDT	Σ DDTs
Core 3C ($n = 38$)							
GM	98.4	170	2.74	23.2	0.396	11.5	364
GSD	15.1	10.2	18.7	9.18	2.68	4.49	7.89
Median	231	374	9.87	55.0	0.283	8.48	752
95P	3220	3170	144	509	6.69	310	7330
Max	4810	7450	270	801	11.0	1380	13,600
DR (%)	92.1	97.4	63.2	92.1	10.5	100	100
Core 6C ($n = 36$)							
GM	1700	2710	42.7	262	1.72	52.3	5010
GSD	4.14	4.35	9.84	4.32	6.49	6.67	4.32
Median	1690	2940	58.8	289	1.55	25.5	5200
95P	13,700	22,600	655	2070	43.7	3500	37,900
Max	38,000	50,800	833	3000	103	15,500	102,000
DR (%)	100	100	94.4	100	55.6	100	100
Core 7.5CD ($n = 38$)							
GM	405	870	21.4	190	2.07	86.6	2170
GSD	51.6	17.7	22.5	19.2	9.33	21.5	15.1
Median	1760	2170	53.0	474	1.12	70.5	5500
95P	10,300	15,000	524	3510	71.9	6250	35,500
Max	15,000	20,200	909	6540	746	13,500	39,800
DR (%)	84.2	94.7	78.9	92.1	52.6	78.9	94.7
Core 7.5C ($n = 39$)							
GM	1840	2910	104	1040	13.6	260	7490
GSD	10.7	9.64	24.0	8.80	16.6	9.62	9.59
Median	3310	5080	260	1640	52.2	262	17,300
95P	21,700	36,400	2450	13,500	326	9700	75,100
Max	26,300	43,600	3060	69,300	1400	59,100	108,000
DR (%)	100	100	89.7	100	69.2	100	100
Core 8CB ($n = 27$)							
GM	178	749	11.5	165	2.44	40.4	1450
GSD	69.3	10.8	33.9	13.0	12.4	15.3	13.1
Median	828	1200	59.2	424	0.283	53.9	2930
95P	14,100	13,900	586	3210	84.0	1600	33,100
Max	14,500	14,600	624	4500	111	17,800	45,500
DR (%)	81.5	100	70.4	96.3	44.4	77.8	100
Core 8C ($n = 39$)							
GM	5110	9560	663	5650	44.4	1950	31,300
GSD	50.1	19.3	24.8	15.6	31.1	19.5	17.0
Median	21,500	28,400	2170	14,200	182	3840	82,400
95P	129,000	115,000	10,700	71,400	1950	61,000	311,000
Max	152,000	136,000	11,900	160,000	3180	577,000	910,000
DR (%)	92.3	97.4	92.3	97.4	71.8	94.9	97.4

GM = Geometric mean; GSD = geometric standard deviation; 95P = 95th percentile; Max = maximum; DR (%) = detection rate (%).

higher than those found for sediments in other seriously polluted sites, e.g. Ji Canal (mean: 340, maximum: 5400 ng/g) in Tianjin (a city with abundant industries and agricultures in northern China) (Tao et al., 2007), Hong Kong harbor (maximum: 7400 ng/g) (Lin et al., 2009) and Macao Harbor (maximum: 7400 ng/g) (Mai et al., 2002) in the Pearl River Delta, South China.

To assess the environmental risk of DDT pollution, many classification systems were proposed, among which, the Norwegian one is the most comprehensive regarding environmental quality standards (Bakke et al., 2010). Five pollution classes were divided in the Norwegian guidelines, based on ecotoxicological effects: class I (<0.5 ng/g dw; pollution status: background) represents background conditions in pristine areas; the upper limits for classes II (0.5–20 ng/g dw; good) and III (20–490 ng/g dw; moderate) are based on the predicted no effect concentrations for chronic and acute exposures to that compound, respectively; the upper limit of class IV (490–4900 ng/g dw; bad) is specified as concentrations between two and five times the predicted no effect concentrations (depending on the compound); class V (>4900 ng/g dw; very bad) represents concentrations above the class IV. According to this classification, cores 8C (GM: 31,300 ng/g dw), 7.5C (7490 ng/g dw) and 6C (5010 ng/g dw) were in class V (very bad pollution), cores 7.5CD (2170 ng/g dw) and 8CB (1450 ng/g dw) were in class IV (bad pollution), and core 3C (364 ng/g dw) was in class III (moderate pollution) (Table 3). This indicates that the sediment core samples collected from the PVS site were heavily polluted by DDTs.

Technical DDTs are usually composed of 75% *p,p'*-DDT, 15% *o,p'*-DDT, 5% *p,p'*-DDE, and <5% others (Yang et al., 2007). DDT can be biodegraded to DDE under aerobic conditions and to DDD under anaerobic conditions in the environment (Metcalf, 1973). The percentage composition of individual DDTs to Σ DDT concentrations is shown in Fig. 2. The predominant congener was *p,p'*-DDE, representing $54 \pm 8.2\%$ (mean $\pm$ SD; for the six cores) of the total DDT concentrations in sediment, followed, in decreasing order, by *o,p'*-DDE ($27 \pm 7.3\%$), *p,p'*-DDD ($14 \pm 6.9\%$), and *p,p'*-DDT ($4.4 \pm 2.5\%$). A similar pattern was observed for sediments from each core studied, indicating the existence of similar sources of DDTs in sediment cores collected from the PVS site. Given the fact that DDT (sum of *p,p'*-DDT and *o,p'*-DDT) accounted for <5% of Σ DDTs, which was far less than the percentage (~90%) in the technical DDT formulation (Fig. 2), there seemed no fresh technical DDT input in this region (Metcalf, 1973).

3.2. Vertical profiles of concentrations of DDTs in sediment cores

We examined the vertical profiles in concentrations of DDTs in sediment cores collected from the PVS site. The core 8C has elevated concentrations of all compounds, with levels of Σ DDTs ranging from non-detected (nd) to 910,000 ng/g dw (detection rate: 97%) compared to the core 3C, where levels of Σ DDTs ranged from 3.34 to

13,600 ng/g dw (97%) (Fig. 3). The concentrations of DDTs in samples from core 8C increased steadily from 1940s to 1980s, and the concentrations declined steadily toward the surficial layers. The highest peaks in concentrations in the core 8C were found around sections from the 1980–90s, while the core 3C exhibited a much sharper peak in sections from the 1940–60s. Similar vertical profiles of concentrations of DDTs were found for the cores 8CB and 7.5C. Generally upper layers of all of cores have higher concentrations than bottom layers, peaking around similar depths for DDTs. The peaks in total concentration for the cores show the levels of DDTs are linked to their discharge between the 1940s–80s (USEPA, 2009b, 2013). However there still appears to be discharge of these compounds for several years after they were banned, possibly from sources such as industrial/agricultural runoff. This finding is in accordance with that found for sediment cores in the San Francisco Bay area, in which PCB concentrations steadily increased, peaked around 1970, and gradually declined to the present, due to the phase out during the 1970s in the Bay area and the 1979 federal ban on sales and production (Brinkmann and de Kok, 1980).

3.3. Historical fluxes of DDTs to the Palos Verdes Shelf Superfund site

Mean sedimentation rate (MSR), calculated using excess ^{210}Pb activity which was the subtraction of ^{210}Pb and ^{226}Ra (Appleby et al., 1986; Schelske et al., 1994), was used to evaluate the mass fluxes of DDTs in the sediment cores. The MSR values were respectively calculated as 0.858 g/cm²/yr for the core 8C and 0.593 g/cm²/yr for the core 3C, which are consistent with those of others determined for the same sites reported in earlier studies (Paulsen et al., 1999; Santschi et al., 2001). The MSR value calculated for core 8C (0.858 g/cm²/yr) was used in evaluation of the mass fluxes of these compounds for other four sediment cores collected in the vicinity of core 8C (6C, 7.5C, 7.5CD, and 8CB; Fig. 1). The mass flux of a compound ($\mu\text{g}/\text{cm}^2/\text{yr}$) was calculated by multiplying the concentration of this compound in a sediment section ($\mu\text{g}/\text{g}$) by the MSR ($\text{g}/\text{cm}^2/\text{yr}$). Temporal trends in mass fluxes of Σ DDTs (sum of *o,p'*- and *p,p'*-isomers) in sediment cores are shown in Fig. 4, respectively. The Σ DDT flux in sections from core 8C increased steadily from 1940s to 1980s, and peaked in the section from 1981 (up to 781 $\mu\text{g}/\text{cm}^2/\text{yr}$); afterward, the flux decreased gradually. A similar trend was found for cores 6C, 7.5CD and 8CB. The core 3C was somewhat different with the core 8C, with a peak in the section from 1945 (8.04 $\mu\text{g}/\text{cm}^2/\text{yr}$). These substantial increases in Σ DDT flux from 1940s to 1980s were also consistent with the wastewater discharge and disposal of residual DDT wastewater between 1947 and 1983 (Stull et al., 1996; Venkatesan et al., 1996). In the core 7.5C, the first major increase in the Σ DDT flux occurred between 1960 and 1964, after which the flux remained at approximately 50 $\mu\text{g}/\text{cm}^2/\text{yr}$ through 1977, followed by a slight increase to 50 $\mu\text{g}/\text{cm}^2/\text{yr}$ between 1977 and 1988. The highest Σ DDT flux in section from core 8C (781 $\mu\text{g}/\text{cm}^2/\text{yr}$) were 1–2 orders of magnitude higher than those found for other cores (Fig. 4). The highest peaks in fluxes in these cores were found around sections from the 1970s–1990s, with the exception of the core 3C, for which the highest peaks were in sections from the 1940s–1950s.

From 1947 to 1971, the world's largest manufacturer of DDT, Montrose Chemical Company discharged processed wastewater into the sewers of Los Angeles County and it is estimated that 870–1450 tons of DDTs were released to the ocean off the Palos Verdes Peninsula (Eganhouse and Pontolillo, 2008; USEPA, 2013). It is estimated that over 44 km² of sediment in the PVS Superfund site is heavily polluted with DDTs. For assessing the sources of DDTs in the PVS site, we examined the deposition of DDTs in sections aging 1947–1971 from the six cores investigated in the present study, by multiplying the sum (299 $\mu\text{g}/\text{cm}^2$) of mass flux of Σ DDTs in each section during 1947–1971 by the area of the PVS site (44 km²). Here the Σ DDT flux in each section was an average value of fluxes in sections from the same depth of six cores (3C, 6C, 7.5CD, 7.5C, 8CB, and 8C). Therefore, the total deposition amount of DDTs in sediments aging 1947–1971 in the PVS site can

Fig. 2. Composition profiles of DDTs in sediment cores from the PVS Superfund site.

Fig. 3. Vertical profiles in concentrations of DDTs in sediment cores from the PVS Superfund site.

roughly calculated as 132 tons, which is fairly close to the estimated discharge of 870–1450 tons by previous studies (Eganhouse and Pontolillo, 2008; USEPA, 2013).

It should be noted that there are several uncertainties in our estimate of deposition of DDTs in sediment from the PVS site. Earlier studies showed that sedimentation on the Palos Verdes Shelf changed with the time-varying inputs of municipal wastewater and the sedimentation rate was affected by bioturbation (Eganhouse and Pontolillo, 2008; Santschi et al., 2001), however we only used mean sedimentation rate (MSR) in calculation of mass flux of contaminants for each core. Further, two cores (3C and 8C) were dated by ^{210}Pb in this study and the MSR value of core 8C was used for other four adjacent cores (6C, 7.5C, 7.5CD, and 8CB) in calculation of fluxes. As the PVS Superfund site covers a large area of sediment (over 44 km²), our discussion on DDT deposition is tempered by the small sample size (six sediment cores collected) from the PVS site; thus, further studies with large sample sizes are needed. On the other hand, the deposited DDTs in sediment can be released to surrounding water column, bioaccumulated by invertebrates and microorganisms that live within or above the sediment,

and transported to other areas via a repeated process of sediment resuspension/deposition and short-range advection (Zeng et al., 2005). These factors are not incorporated in the calculation of total deposition of DDTs in sediment and the calculated deposition amount would be underestimated in this regard. In spite of these, our rough calculation of deposition of DDTs in sediment is near the previous estimate of discharge of DDTs in the PVS site (Eganhouse and Pontolillo, 2008; USEPA, 2013), suggesting that disposal of residual DDT wastewater by Montrose Chemical Company is major source of DDTs in this region.

4. Conclusions

In summary, frequent occurrence (95%) and high concentrations of ΣDDTs (up to 910 $\mu\text{g/g dw}$) were found in sediment cores collected from the PVS Superfund site off the coast of Los Angeles, California, which were far higher than those reported for other highly polluted areas of the world. Among DDT congeners, p,p' -DDE, o,p' -DDE and p,p' -DDD were predominant, accounting for approximately 54%, 27%, and 14% of the total DDT concentrations in sediment. The core 8C has

Fig. 4. Temporal trends in mass flux of Σ DDTs in sediment cores from the PVS Superfund site. The dash lines show the 95% confidence intervals.

elevated concentrations of all compounds, as compared to other sediment cores. Upper layers of all cores generally have higher concentrations than bottom layers, peaking around similar depths for DDTs, which are linked to the discharge of these contaminants between the 1940s and 1980s. Based on the calculated mass flux of DDTs in sediment cores, the total deposition amount of DDTs in sediments aged between 1947 and 1971 in the PVS site is estimated 132 tons, which is fairly close to that (870–1450 tons) reported for industrial wastewater discharge in this area. The study's findings will be crucial to future efforts to understand the human and ecological health significance of DDT contamination in the PVS site and explore potential mitigation operations.

Conflict of interest

We hereby state that we do not have any conflict of interest with regard to submission of this manuscript.

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