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# Distribution and mass inventory of total dichlorodiphenyldichloroethylene in the water column of the Southern California Bight

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## ABSTRACT

A large-scale survey on the area and depth stratified distribution of dichlorodiphenyltrichloroethane (DDT, mainly *p,p'*- and *o,p'*-dichlorodiphenyldichloroethylene (DDE)) contamination in the water column of the Southern California Bight (SCB) was conducted in 2003-2004 using a solid-phase microextraction-based sampling technique. Dissolved phase DDEs were clearly widespread, with the central SCB containing the highest levels, and the Palos Verdes Shelf sediments have remained the dominant source of DDT compounds to the SCB. The *p,p'*- and *o,p'*-DDE concentrations ranged from <0.073 to 2.6 ng/L and from <0.043 to 0.26 ng/L, respectively, clearly exhibiting elevated with respect to measured values from across the globe. DDEs were hypothesized to have been transported from the historically contaminated zone on the Palos Verdes Shelf to other areas via a repeated process of contaminated sediment resuspension/deposition and short-range advection. Total mass inventories were estimated at 14 and 0.86 kg for *p,p'*- and *o,p'*-DDE, respectively, for the sampled area, resulting in *p,p'*- and *o,p'*-DDE mass inventories for the entire SCB of 230 and 14 kg, respectively. Furthermore, total fluxes of *p,p'*-DDE were estimated to be in the range of 0.8 to 2.3 metric tons per year. These results suggest that the SCB has been and continues to be a significant source of DDT contamination to the global oceans.

## INTRODUCTION

The coastal ocean adjacent to the greater Los Angeles, California, area known as the Southern California Bight (SCB) has been subject to intensive

anthropogenic impacts stemming from steady population growth and increasing urbanization. As a result, more than \$10 million is spent annually on monitoring coastal water quality in the SCB. However, prior and existing monitoring programs have focused on the points of discharge, mainly the outfalls of the four largest wastewater treatment facilities in this densely populated region. Although these monitoring programs have collected copious amounts of high-quality data, they are inadequate in addressing changes on a regional scale (SCCWRP 1998).

To complement these spatially limited monitoring efforts, three regional monitoring programs were conducted in 1994, 1998, and 2003. An integrated approach combining chemistry, toxicology, fish biology, benthic ecology, microbiology and physical oceanography was utilized to assess the regional variability of anthropogenic pollution in the SCB (SCCWRP a - c) in these surveys. Among the large number of parameters measured, the levels of dichlorodiphenyltrichloroethane (DDT) and its metabolites were of particular concern to the coastal management community because previous studies showed these contaminants to be at fairly high concentrations in the water column (Zeng *et al.* 1999) and bedded sediments (Zeng and Vendatesan 1999) of the Palos Verdes Shelf (PVS). This localized area of elevated contamination presumably originated from the discharge of residual DDT wastes via the outfall of the Joint Water Pollution Control Plant operated by the Los Angeles County Sanitation District (Vendatesan *et al.* 1996, Stull *et al.* 1996).

Measurements of water column DDT concentrations can provide valuable information about their environmental fate and potential for ecological

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impacts. Due to the ultra low levels of DDTs in open oceanic environments, large sample volumes would be needed to quantify their concentrations. However, collection and handling of numerous large-volume water samples are labor-intensive, logistically challenging and as a result, extremely costly (Zeng *et al.* 1999).

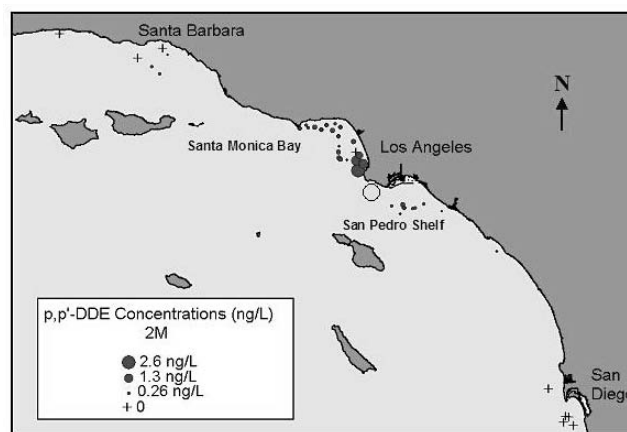
Since the introduction of solid-phase microextraction (SPME) as an alternative to conventional sample preparation tools (Arthur and Pawlizyn 1990), one of its most promising applications has been field sampling of hydrophobic organics (Pawlizyn 1997). While numerous SPME-based methods have been developed for vapor- and aqueous-phase sampling of volatile organics, very few methods have been developed for aqueous phase sampling of nonvolatile compounds. An SPME-based sampler that had been successfully tested and calibrated for DDTs in the oceanic environment (Zeng *et al.* 2004) was recently developed. Because of the cost-effectiveness and operational simplicity of this SPME-based sampling technique, it has the potential to be used in large-scale sampling of water column contaminants.

As a component of the SCB 2003 Regional Survey, the goals of this study were to determine the spatial distributions of DDT compounds in the water column of the SCB, examine the transport and fate of these contaminants, and estimate the mass inventories and ocean-going flux of individual DDT compounds. The previously developed SPME-based sampling technique (Zeng *et al.* 2004) and a statistically randomized area and depth stratified sampling design were employed to fulfill these objectives.

## METHODS

### Study design

Sixty-three sites on the continental shelf (30 - 120 m depth) between Point Conception, California, and the United States-Mexico international border (Figure 1) were sampled between August 2003 and March 2004. Sites were selected in a total of four latitudinal cross-sections using a stratified random design (Stevens 1997). The four strata differentiated by latitude were designated the Northern Bight (Point Conception to Point Dume), Santa Monica Bay (Point Dume to Palos Verdes), San Pedro Shelf (Palos Verdes to Dana Point), and the Southern Bight (Dana Point to the international border). This probabilistic design, rather than investigator pre-selection,



**Figure 1. Distribution of p,p'-DDE at 2 m above the seafloor in the Southern California Bight. Solid circles represent data from the present study, while the single open circle (station 6C on the Palos Verdes Shelf) represents an average concentration of 3.8 ng/L (n = 3) obtained from a previous study conducted in May - June 2003.**

ensured that sites were representative and could be extrapolated to the response of the entire stratum. For all strata, a systematic component was added to the selection process to minimize clustering of sample sites. The systematic element was accomplished by placing a hexagonal grid over a map of the sampling area, selecting a random sub-sample of hexagonal cells from this population, and obtaining one sample at a randomly selected site within each hexagonal grid cell (Stevens 1997). At each site, SPME samplers (see below) were affixed at up to four depths: 2, 10, 20, and 35 m above the sea floor. A fifth sample per site was collected 2 m below the air-water interface (surface).

### Sample collection

The procedures for constructing and deploying SPME-based samplers were outlined by Zeng *et al.* (2004). Briefly, a typical SPME-based sampler consisted of a glass fiber coated with poly(dimethylsiloxane; PDMS, 100- $\mu$ m nominal thickness; part no. 57341-U, Supelco, Bellefonte, PA) supported within a 15 x 1.5 cm<sup>2</sup> copper casing with 8-mm holes. SPME-based samplers were deployed in August - October 2003, October - November 2003, January - February 2004, and March - April 2004. Cleaned sampling devices were attached to a series of 6.4-mm twisted polypropylene rope with stainless steel hose clamps. The mooring unit was anchored on the seafloor by two anchor chain links and suspended in the water column with a subsurface float.

Upon deployment completion, SPME samplers were carefully removed from the moorings. The fiber assemblies were detached from the copper casing, and the PDMS-coated fiber tips were rinsed briefly with deionized water before being retracted into the protective sleeves. The samplers were placed in aluminum-foil-lined Petri dishes and cooled with dry ice during transport to the laboratory where they were stored at -20°C until analysis. Overall, a total of 152 SPME samplers (including four replicates) were recovered and successfully processed, representing a successful sampling rate of 69.4%.

### Sample analysis

Field-deployed SPME fibers were processed using two Varian 2000 gas chromatography (GC)/ion trap mass spectrometry (MS) systems (Varian Inc., Walnut Creek, CA) with thermal desorption injection (Zeng *et al.* 2005). The desorption temperature was programmed from 100°C to 280°C at ~100°C/minute with a 40 minute hold at the maximum temperature. Chromatographic conditions used for the GC/MS systems were identical except for a slight difference in carrier gas flow rates (1.0 and 1.3 ml/minute). Chromatographic separations were made with 60 m x 0.25 mm-id (0.25-µm film thickness) DB-5MS columns (J&W Scientific, Folsom, CA) temperature-programmed from 80°C (hold for 1 minute) to 176°C at a rate of 8°C/minute, followed by a ramp to 230°C at a rate of 1.5°C/minute, and a final increase to 290°C (5°C/minute) where it was held for 21 minute. Mass spectra were acquired from 100 to 504 m/z with a scan rate of 0.7 scans per second and an emission current of 15 µA.

### Quality assurance/quality control

Quality assurance/quality control (QA/QC) procedures adopted in this study were similar to those used in the method development phase (Zeng *et al.* 2004). In addition, a number of SPME samplers attached to several duplicate moorings were deployed to examine the precision of the field measurements. Of these field replicates, two moorings with five samplers at three depths were recovered. Analysis of the recovered replicates resulted in an average standard relative difference of 23% for *p,p'*-dichlorodiphenyldichloroethylene (DDE). Concentrations of *o,p'*-DDE in these samples were below the reporting limits.

### Data analysis

As shown previously (Zeng *et al.* 2004), the concentration ( $C_w^0$ ) of an analyte in open oceans is simply related to the total amount ( $N_f$ ) of the analyte sorbed in the SPME sampler by  $N_f = K_f V_f C_w^0$ , where  $K_f$  is the partition coefficient of the analyte between the SPME fiber and the aqueous phases and  $V_f$  is the volume of the SPME fiber coating (PDMS) phase. The  $K_f V_f$  values calibrated prior to field sampling with the two GC/MS systems (designated as GC/MS-1 and GC/MS-2, respectively) described previously (Zeng *et al.* 2005) were  $3.41 (\pm 0.54) \times 10^5$  and  $2.59 (\pm 0.97) \times 10^5$  µL for *p,p'*-DDE, and  $5.82 (\pm 1.81) \times 10^5$  and  $2.79 (\pm 1.13) \times 10^5$  mL for *o,p'*-DDE. On the basis of these values and the instrumental detection limit of 0.025 ng (both systems), the reporting limits were 0.073 and 0.097 ng/L for *p,p'*-DDE, and 0.043 and 0.090 ng/L for *o,p'*-DDE. The nearshore annual temperature variation was in the range of ±10°F, which translated into a relative temperature change of less than 5%. Therefore, temperature effects on the measured concentrations were negligible.

The cumulative distribution function (CDF),

$$CDF_j (\%) = \frac{100\% \times \sum_{i=1}^j AWF_i}{\sum_{i=1}^n AWF_i} \quad (1)$$

where AWF is the area weighting factor for the site-specific hexagonal (actual) area and  $n$  denotes the total number of areas included in the calculation, was used to compare the concentration distribution at different depths. Each  $CDF_j$  value was paired with the concentration value from the  $j$ th area to generate concentration distribution plots.

## RESULTS

### Water column concentrations of *p,p'*-DDE and *o,p'*-DDE

The sample collection information and distribution data are summarized in Table 1. Excluding replicates, the number of samples acquired and processed were 43, 44, 14, 21, and 26 for the depths of 2, 10, 20, and 35 m from the seafloor and 2-m below the sea surface, respectively, out of 63, 63, 21, 28, and 38 SPME samplers deployed. The *p,p'*-DDE

**Table 1. Deployment success and concentration distribution (minimum, maximum, and area-weighted mean; ng/L) versus depth of p,p'-DDE and o,p'-DDE in the water column of the Southern California Bight as measured by solid-phase microextraction samplers.**

depth (m) <sup>a</sup>	# of samples		p,p'-DDE				o,p'-DDE			
	deployed	collected	min.	max.	mean <sup>b</sup>	standard error <sup>c</sup>	min.	max.	mean <sup>b</sup>	standard error <sup>c</sup>
2	63	43	<0.073	2.6	0.19	0.046 (33)	<0.043	0.22	0.015	0.0046 (11)
10	63	44	<0.073	2.1	0.22	0.043 (35)	<0.043	0.26	0.015	0.0048 (13)
20	21	14	<0.073	0.26	0.065	0.018 (7)	<0.043	<0.043	<0.043	
35	28	21	<0.073	1.1	0.049	0.024 (13)	<0.043	0.18	0.015	0.0067 (4)
surface	38	26	<0.073	0.22	0.053	0.022 (8)	<0.043	<0.043	<0.043	

<sup>a</sup> Water depth defined as the distance from the water-sediment interface; "surface" defined as 2-m below the air-water interface.  
<sup>b</sup> Calculation of mean values included results that were below detection limits but identifiable with GC-MS (Tables S2 and S3 in the Supporting Information), and nondetectables treated as zero.  
<sup>c</sup> Numbers in parentheses represent sample size with detectable target analytes.

was detected in 33, 35, 7, 13, and 8 samples corresponding to these depths, representing detectable rates of 77%, 80%, 50%, 62%, and 31%. Concentrations of p,p'-DDE ranged from nondetectable (<0.073 ng/L) to 2.58 ng/L, with area weighted mean values ( $\pm$ standard errors) of 0.19 ( $\pm$ 0.05), 0.22 ( $\pm$ 0.04), 0.065 ( $\pm$ 0.018), 0.049 ( $\pm$ 0.024), and 0.053 ( $\pm$ 0.022) ng/L, respectively, at the five depths. By comparison, o,p'-DDE was detected in 11, 13, 0, 4, and 0 samples at these same depths, representing detectable rates of 26%, 30%, 0%, 19%, and 0%, respectively. In addition, concentrations of o,p'-DDE ranged from nondetectable (<0.043 ng/L) to 0.26 ng/L with area weighted mean values ( $\pm$ standard errors) of 0.015 ( $\pm$ 0.005), 0.015 ( $\pm$ 0.005), 0.0051 ( $\pm$ 0.0027), and 0.015 ( $\pm$ 0.007) ng/L, respectively, at individual depths. The mean concentrations of p,p'-DDE were similar for samples collected at the depths of 2 and 10 m, and were also similar for samples collected at the other three depths. For o,p'-DDE, the mean concentrations were essentially identical at the depths of 2, 10, and 35 m, the value at the 35-m depth is based on only four samples with detectable o,p'-DDE and thus has a substantially higher relative uncertainty. Furthermore, no o,p'-DDE was detected in samples collected from the depths of 20 and 2 m below the sea surface.

A comparison of water column concentrations of DDEs from around the globe suggests that the concentrations of DDEs documented herein were generally at the high end of reported values (Table 1). In Lake Malawi of Southeast Africa, for example, the dissolved p,p'-DDE concentration was below 0.027 ng/L (Karlsson 2000). Maldonado and Bayona (2002) reported p,p'-DDE concentrations of between 0.0015 ng/L (open water) to 0.0060 ng/L

(estuary) for the northwestern Black Sea. In the North Sea, Bergqvist *et al.* (1998) obtained an average concentration of ~0.01 ng/L for p,p'-DDE following a flood episode in Western Europe. In rivers and streams draining traditionally agricultural regions of Northern California, p,p'- and o,p'-DDE ranged from 0.0066 to 0.23 ng/L and from nondetectable to 0.019 ng/L, respectively (SFEI 1999). At two locations in the Pearl River Delta (China), a region that has been subject to rapid economic expansion since the early 1980s, p,p'- and o,p'-DDE ranged from 0.01 to 0.45 ng/L, and from <0.008 to 0.18 ng/L, respectively (Luo *et al.* 2004). Estuarine waters of the Pearl River (downstream from the delta) and open water of the northern South China Sea contained p,p'-DDE concentrations of 0.140-0.886 and 0.039-0.054 ng/L, respectively (Luo 2004). In contrast, very high levels of p,p'-DDE in the Pearl River Estuary (20.1 - 175 ng/L) and South China Sea (5.85 - 29.1 ng/L) were reported by another group of researchers (Zhang *et al.* 2002). The same group of researchers also obtained very high concentrations of p,p'-DDE at three other locations in China's Daya Bay, Guangdong Province (0.2 - 6.9 ng/L; Zhou *et al.* 2001), River Wuchuan, Fujian Province (25.1 - 81.4 ng/L; Zhang *et al.* 2002a), and Tonghui River near Beijing (3.71 - 208 ng/L; Zhang *et al.* 2004). However, these extremely high levels are deemed questionable, because the sediment-water concentration ratios for p,p'-DDE obtained from these studies were inconceivably low based on its  $K_{ow}$ .

In 1989 - 1990, Iwata *et al.* (1993) determined that the maximum concentration of p,p'-DDE in surface seawater at locations far removed from direct land-based sources was 0.0079 ng/L. The mean value for p,p'-DDE in this large-scale study of per-



sistent organochlorines was 0.0008 ng/L (Iwata *et al.* 1993). Thus, the levels of *p,p'*-DDE in the nearshore region of the SCB were 1 - 2 orders of magnitude greater than those in other coastal regions and approximately 3 orders of magnitude higher than the global oceanic background values reported by Iwata *et al.* (1993).

### Spatial distribution pattern

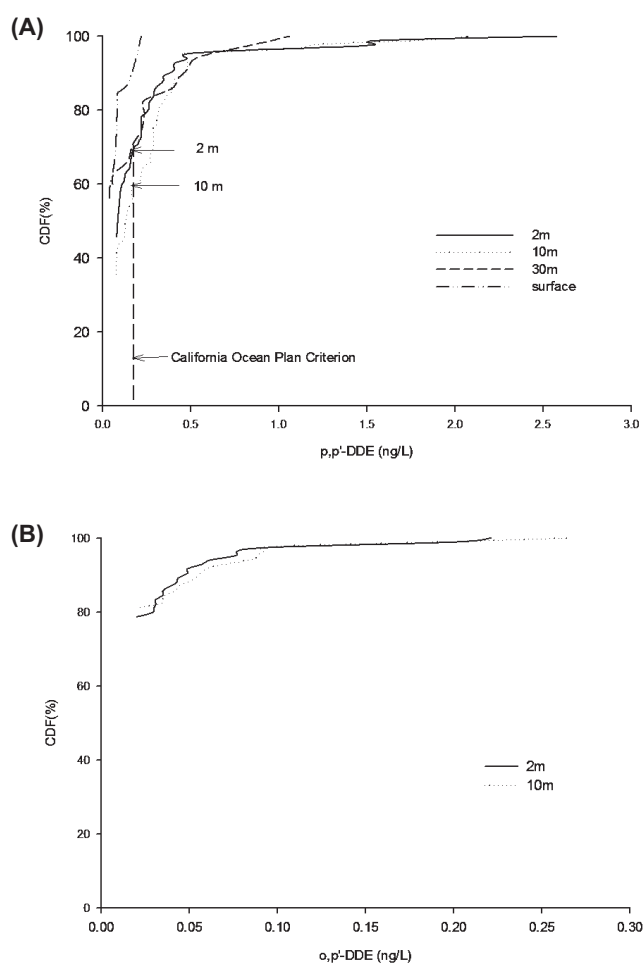
The highest levels of *p,p'*-DDE (also *o,p'*-DDE, data not shown) were detected in Santa Monica (SMB) adjacent to the PVS where sediments are known to contain highly elevated levels of DDT contamination (Figure 1; Stull *et al.* 2004, Lee 1994). Due to the randomized nature of the sampling design, no sampling site was selected for the PVS. However, SPME-based water column sampling conducted in June - July 2003 (Zeng *et al.* 2004) at station 6C near the Joint Water Pollution Control Plant outfall obtained slightly higher *p,p'*-DDE and *o,p'*-DDE concentrations than the highest concentration values acquired in the present study for both the 2- and 10-m depths. Specifically, these concentrations of *p,p'*-DDE were ~4 and 2 ng/L, whereas those of *o,p'*-DDE were ~0.6 and 0.3 ng/L at the 2- and 10-m depth of station 6C, respectively (Zeng *et al.* 2004). In comparison, the highest *p,p'*-DDE concentrations reported herein were 2.6 and 2.1 at the 2- and 10-m depths, respectively, and the highest *o,p'*-DDE concentrations were 0.22 and 0.26 ng/L at the 2- and 10-m depths, respectively (Table 1).

The area distribution of DDEs can be assessed from the plots of CDFs versus concentrations of *p,p'*- and *o,p'*-DDE (Figure 2). From a regulatory standpoint, the California Ocean Plan (SWRCB 1997) requires that the 30-day average concentration permitted in receiving waters off California must not exceed 0.17 ng/L for total DDTs (sum of six DDD, DDE and DDT isomers). Considering only *p,p'*-DDE, approximately 30% and 40% of the areas at the depths of 2- and 10-m (Figure 2), respectively, are in violation of this requirement.

## DISCUSSION

### Comparison of geographical subpopulations

With a reasonably large and equitable sample size among strata, the randomized sampling design utilized in this study would have allowed for a statistically rigorous spatial comparison of DDE concentrations at each water depth. However, the limited number of samples with detectable target analytes



**Figure 2. Cumulative distribution functions (CDFs) of *p,p'*-DDE (A) and *o,p'*-DDE (B) at various water column depths. Also marked in part A is the 30-day average concentration of 0.17 ng/L for DDTs permitted in receiving waters off California.**

made a meaningful comparison for most of the contaminant-geographic subpopulation pairings impossible. Thus, only three subpopulations (SMB, San Pedro Shelf, and Santa Barbara) were compared for *p,p'*-DDE at 2- and 10-m depths. Data for both DDE analytes were compared for SMB and San Pedro Shelf at all of the depths (Table 3). In this assessment, some concentration values that were below the reporting limits but identifiable by GC/MS were included to increase the statistical power. For both the 2- and 10-m depths, *p,p'*-DDE concentrations were as follows: SMB > San Pedro Shelf > Santa Barbara. At the other three depths, there was no significant difference in this parameter between SMB and the San Pedro Shelf. For *o,p'*-DDE, the contamination levels at the 2- and 10-m depths were similar for SMB and the San Pedro Shelf. Meaningful comparisons at the other depths were

**Table 2. Comparison of global water column levels (ng/L) of p,p'- and o,p'-DDEa.**

	p,p'-DDE	o,p'-DDE	Year
Lake Malawi, Southeast Africa	<0.027		1998 (14)
Northwestern Black Sea surface water			
Danube Estuary	0.0059-0.0060		1995 (15)
Odessa depression	0.0037		1995 (15)
offshore Bulgaria-Romania border	0.005		1995 (15)
slope	0.0017		1995 (15)
open sea	0.0015		1995 (15)
North Sea, Western Europe	~0.01		1995 (16)
San Francisco Bay watershed, CA	0.0066-0.23	nd-0.019	1999 (17)
China			
Baiertang, Pearl River Delt <sup>a</sup>	0.01-0.09	<0.008-0.02	2002 (18)
Macao coast, Pearl River Delt <sup>a</sup>	0.06-0.45	0.01-0.18	2002 (18)
Pearl River Estuary <sup>b</sup>	0.140-0.886		2002-2003 (19)
northern South China Sea <sup>b</sup>	0.039-0.054		2002-2003 (19)
Pearl River Estuary <sup>b</sup>	20.1-175		2000 (20)
northern South China Sea <sup>b</sup>	5.85-29.1		2000 (20)
Southern California Bight, CA	<0.073-2.58	<0.043-0.264	2003-2004 <sup>c</sup>

<sup>a</sup> Operationally defined dissolved concentrations, except Southern California Bight data (this study).

<sup>b</sup> Surface water.

<sup>c</sup> Present study.

precluded by a lack of *o,p'*-DDE detections. One salient feature of these data is the apparent decreasing trend in mean DDE concentrations (both isomers) between 10 m from the seafloor and 2 m below the sea surface (Table 3). Moreover, mean DDE concentrations were significantly lower at the surface than at the other depths. This vertical contamination gradient in DDE concentrations, observed in previous studies, has been attributed to the relatively large reservoir of contaminants in SCB bedded sediments (Zeng *et al.* 1999, Zeng *et al.* 2004).

### Transport and fate of DDEs in the Southern California Bight

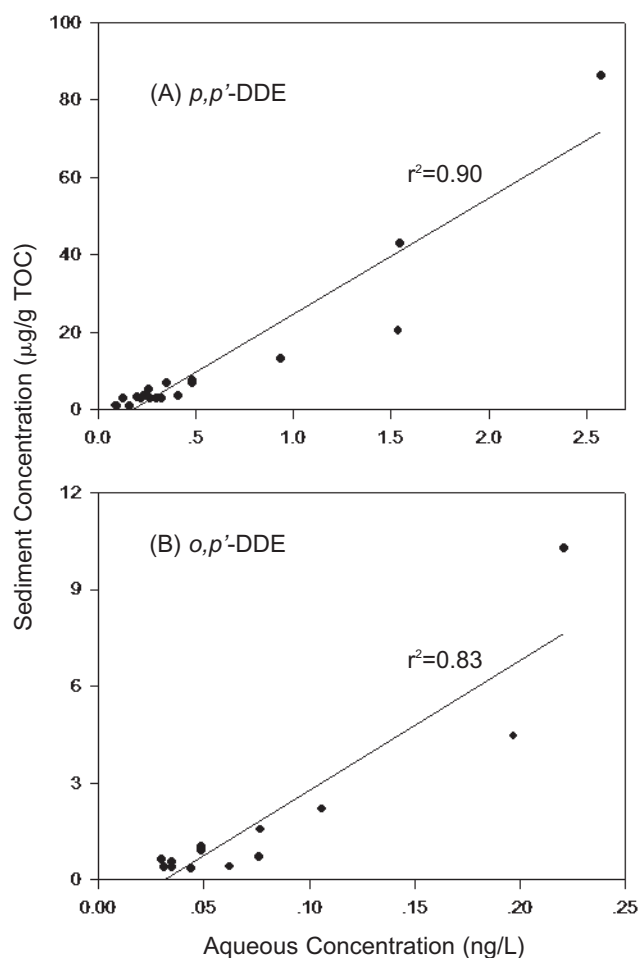
Previous studies suggest that contaminated sediments on the PVS and two dumpsites in the Santa Monica Basin are dominant sources of DDTs in the SCB (Zeng *et al.* 1999, Zeng *et al.* 1999a, Venkatesan *et al.* 1996, Sherwood *et al.* 2002). Because of their location in deep water (800 m), however, the dumpsites are not expected to exert much impact on nearshore areas. The clustering of the highest water column DDE concentrations on/near the PVS (Figure 1) strongly indicates that the PVS sediments remain as the primary source of DDTs within the SCB. Moreover, there are indications that the elevated concentrations associated with the southeastern part of SMB are linked to present-day contaminated sediments on the slope of Redondo Canyon bordering SMB and the PVS (Bay *et al.*

2003). Long-range transport from the PVS to SMB was proposed as a viable mechanism causing the distribution pattern (Bay *et al.* 2003). The results from the present study are consistent with this proposed mechanism, thereby reinforcing the hypothesis that PVS sediments remain as the dominant source of DDT contamination to the nearshore environment.

In areas of the SCB that are relatively distant from the PVS, the presence of DDEs is thought to be a consequence of a repeated cycle of sediment resuspension/deposition and a short-range advection that gradually disperses DDEs from the initial deposition zone. This hypothesis was corroborated by correlation between organic carbon normalized sediment concentrations of *p,p'*- and *o,p'*-DDE and dissolved concentrations at the 2-m water depth (Figure 3). In the absence of significant contaminant transport from outside the PVS area, these correlations suggest a direct link between sediment and the overlying water column, i.e., the water column DDEs were derived from the same (sedimentary) source. Therefore, the transport of DDEs via the water column is sufficiently slow and limited in range so as to maintain sufficient interaction between the sediments and the water.

### Water column mass inventory of DDE

The total masses of *p,p'*- and *o,p'*-DDE in the water column of the SCB were estimated using the SPME measured concentrations and area-weighting



**Figure 3. Correlation between geographically matched pairs of organic carbon normalized sediment concentration for p,p'-DDE (A) and o,p'-DDE (B) and aqueous concentrations at the 2-m depth above the sediment-water interface throughout the Southern California Bight.**

strategy described in the Methods section. This task was made difficult by the unexpectedly large number of SPME samplers lost during deployment and the additional number of recovered samplers with non-detectable DDEs. To overcome these issues, the concentration distribution with respect to depth was assumed uniform in two depth horizons. Water column concentrations in the first horizon (between 0 and 10 m from the seafloor) was expressed as the mean of the 2- and 10-m depth concentrations, or  $C = [C(2\text{ m}) + C(10\text{ m})]/2$ , where  $C(2\text{ m})$  and  $C(10\text{ m})$  were the measured analyte concentrations at 2 and 10 m, respectively. From 10 m above the seafloor to the surface, the concentration was approximated as  $C' = [(C(z) + C(\text{surface})]/2$  where  $C(\text{surface})$  was the analyte concentration at 2 m below the sea surface and  $C(z)$  was the concentration at depth  $z$ . Assuming

AWF was the actual area of a specific sampling area in this study, the mass inventory within an area with AWF was estimated from  $AWF \times [10 \times C + (\text{water column depth} - 10) \times C']$ .

Through the use of this approach, the mass inventories of p,p'-DDE and o,p'-DDE were estimated at 11 and 0.68 kg, respectively, for a total of 52 sampling sites, representing 78.8% of the total sampling area. By extending the assumption of continuous DDE concentrations to the entire sampling area (~1,820 km<sup>2</sup>), the corresponding mass inventories were 14 and 0.86 kg, respectively. These estimates appear consistent with the previously estimated total dissolved DDT mass of ~0.8 kg in the water column of the PVS (~18 km<sup>2</sup>; Zeng *et al.* 1999), where water column p,p'-DDE was approximately one order of magnitude higher than the mean values for Santa Monica Bay and the San Pedro Shelf in this study (Table 3).

To extend these estimates to the entire SCB, concentrations representing bight-wide averages for p,p'- and o,p'-DDE were assumed to be 0.005 and 0.0003 ng/L, respectively. These were considered reasonable based on interpolation of the measured concentration data (Tables 1 and 2) and the background concentration of p,p'-DDE of 0.0008 ng/L for the North Pacific (Iwata *et al.* 1993). The volume of the SCB was estimated at  $4.5 \times 10^{13}$  m<sup>3</sup> with a digital elevation model, ETOPO-5, using a grid of 5-minute latitude and longitude resolutions (NGDC 1988). Therefore, the mass inventories of p,p'- and o,p'-DDE were estimated at 230 and 14 kg, respectively.

It should be noted that the mass inventory estimates carry some degree of uncertainty stemming from the variability in the analytical procedures, the assumption of continuous distribution of DDEs throughout the entire sampling area, and the use of average concentrations of p,p'-DDE (0.005 ng/L) and o,p'-DDE (0.0003 ng/L) for the entire SCB. To quantify the uncertainty, however, is virtually impossible given the large number of factors involved and the unknown variability associated with each factor. As a result, the mass inventory estimation was intended to provide qualitative constraints for water quality assessment.

### Fluxes of DDEs across the Southern California Bight

In light of the widespread distribution of elevated DDEs in the water column of the SCB, the role of this body of water as a potential contaminant source

**Table 3. Area-weighted mean concentrations and standard errors (ng/L) of p,p'-DDE and o,p'-DDE at various depths of the water column within three major geographical areas of the Southern California Bight.**

		p,p'-DDE								
		Santa Monica Bay			San Pedro Shelf			Santa Barbara		
depth (m) <sup>a</sup>	no. samples	mean <sup>b</sup>	std. error <sup>c</sup>	no. samples	mean <sup>b</sup>	std. error <sup>c</sup>	no. samples	mean <sup>b</sup>	std. error <sup>c</sup>	
2	21	0.54	0.13 (20)	7	0.23	0.03(7)	4	0.12	0.043 (3)	
10	20	0.54	0.12 (18)	7	0.29	0.03 (7)	4	0.17	0.059 (3)	
20	4	0.043	0.065 (1)	5	0.21	0.06 (5)				
35	13	0.35	0.29 (12)	3	0.21	0.19 (3)				
surface	16	0.017	0.029 (4)	8	0.073	0.038 (7)				
		o,p'-DDE <sup>d</sup>								
2		0.051	0.013 (15)		0.022	0.008 (4)				
10		0.058	0.015 (13)		0.031	0.008 (5)				
20		<0.043	<0.043 (0)		0.029	0.013 (4)				
35		0.036	0.047 (7)		0.022	0.013 (2)				
surface		<0.043	<0.043 (0)		0.0045	0.011 (1)				

<sup>a</sup>Water depth was defined as the distance from the water-sediment interface; surface defined as 2-m below the air-water interface.

<sup>b</sup>Calculation of mean values included results that were below detection limits but identifiable with GC-MS (Tables S2 and S3 in the Supporting Information) and nondetectables treated as zero values.

<sup>c</sup>Numbers in parentheses represent sample size with detectable target analytes.

<sup>d</sup>Four samples each retrieved from 2 and 10 m off Santa Barbara were all nondetectable.

to the adjacent open ocean was further investigated by estimating mass fluxes. In an attempt to constrain such estimates based on parameters with large uncertainties in some cases, two different estimation methods were performed.

The first method estimated mass fluxes of p,p'- and o,p'-DDE using published water turnover rates. According to Hickey (1993), the entire SCB is flushed within a few weeks during extreme conditions. In other words, the SCB water column can be completely exchanged 5 to 10 times per year. For the previously estimated total inventories for p,p'- and o,p'-DDE of 230 and 14 kg, the resultant corresponding annual fluxes were 1.2 - 2.3 metric tons and 69 - 140 kg, respectively. Because these estimates were based on extreme fluctuation conditions, the average annual fluxes of DDEs are expected to be lower. The uncertainty in these estimates mainly stems from the difficulty in obtaining an accurate water flux rate due to the complex oceanic conditions in the SCB (Hickey 1993).

The second method employed Fick's Law to estimate the flux  $F$  (Crank 1975):

$$F = -Ak_h \frac{\partial C}{\partial L} \quad (2)$$

where  $A$  is the cross-sectional area of water exchange (approximated as 1000000 m x 2000 m = 2 x 10<sup>9</sup> m<sup>2</sup>),  $k_h$  is the horizontal eddy diffusivity

(assumed to be 10<sup>3</sup> m<sup>2</sup>/s for SCB (Ledwell *et al.* 1998)), and  $\frac{\partial C}{\partial L}$  is the gradient of solute (p,p'-DDE) across the flux boundary. This gradient was represented as the decrease of 0.0042 ng/L from the SCB (0.005 ng/L average) to the open ocean (0.0008 ng/L) over a 300-km boundary layer, which corresponds to the average width of the California Current (Hickey 1993). Through the use of Equation 2, the annual flux of p,p'-DDE out of the SCB was estimated at 0.84 metric tons. Through the use of the inventory ratio of p,p'-DDE versus o,p'-DDE, the corresponding flux of o,p'-DDE was 50 kg. The uncertainty in these estimates resulted from the large range of possible eddy diffusivities, and to a lesser extent from an inaccurate concentration gradient. Nevertheless, the fluxes of DDEs estimated from the two independent methods were quite comparable.

Prior to 1971 when use of DDT compounds was banned, approximately 1700 metric tons of DDTs were discharged into the PVS through wastewater outfalls (USEPA). Including all DDT inputs, on the order of 2000 metric tons of DDTs have been discharged into the coastal ocean off southern California. Because DDT residues found in the vast majority of the SCB sediments contain a high percentage of p,p'-DDE, the flux of total DDT is currently estimated at ~ 1 metric tons per year. As mass fluxes likely have decreased with the decline in DDT production/discharge since the 1970s (Steinberger *et*



al. 2003), a total of 10 metric tons is a reasonable estimate for DDTs that have entered the global oceans from the SCB. This amount corresponds to a 0.14 pg/L contribution to the global oceanic DDT concentration if these DDTs are evenly distributed in the upper 200 m of the water column, or roughly 18% of the background concentration measured in the North Pacific by Iwata *et al.* (1993). If correct, the SCB has indeed been a significant source of DDTs to the global environment.

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## ACKNOWLEDGEMENTS

The authors are indebted to the Steering Committee of the Southern California Bight 2003 Regional Survey for insightful guidance and opinions; with sincere appreciation to Willie McCarthy and Dennis Wayranch of SEAWORLD (University of California, Los Angeles, CA) and Tom Pesich of Enchanter IV for field assistance, Valerie Raco-Rands for drawing Figure 1, and Nikolay Nezlin for assistance in running the digital elevation model ETOPO-5. Support of E.Y.Z. by the "One Hundred Talents" Program of the Chinese Academy of Sciences is gratefully acknowledged.