

# Distribution and Mass Inventory of Total Dichlorodiphenyldichloroethylene in the Water Column of the Southern California Bight

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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 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 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 (1).

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 (2–4) 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 (5) and bedded sediments (6) 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 (7, 8).

Measurements of water column DDT concentrations can provide valuable information about their environmental fate and potential for ecological impacts. Due to the ultralow levels of DDTs in open oceanic environments, large sample volumes may 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 (5).

Since the introduction of solid-phase microextraction (SPME) as an alternative to conventional sample preparation tools (9), one of its most promising applications has been field sampling of hydrophobic organics (10). 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. We recently developed an SPME-based sampler that was successfully tested and calibrated for DDTs in the oceanic environment (11). Because of the cost-effectiveness and operational simplicity of the 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 (11) and a statistically randomized area and depth stratified sampling design were employed to fulfill these objectives.

## Materials and Methods

**Study Design.** Sixty-three sites on the continental shelf (30–120 m in depth) between Point Conception, California, and the United States–Mexico international border (Figure S1 and Table S1 in the Supporting Information) were sampled between August 2003 and March 2004. Sites were selected in a total of four latitudinal cross-sections using a stratified random design (12). 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

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**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 <sup>a</sup> (m)	no. of samples		<i>p,p'</i> -DDE				<i>o,p'</i> -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 were treated as zero. <sup>c</sup> Numbers in parentheses represent sample size with detectable target analytes.

the Southern Bight (Dana Point to the international border). This probabilistic design, rather than investigator preselection, 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, a random subsample of hexagon cells was chosen from this population, and one sample was obtained at a randomly selected site within each hexagonal grid cell (12). At each site, SPME samplers (see below) were affixed at up to four depths (measured in meters above the sea floor): 2, 10, 20, and 35 m. 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 detailed elsewhere (11). 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  $\times$  1.5 cm<sup>2</sup> copper casing with 8-mm holes. The SPME samplers were deployed in August–October 2003, October–November 2003, January–February 2004, and March–April 2004 (Table S1 of the Supporting Information). Cleaned sampling devices were attached to a series of 6.4-mm twisted polypropylene ropes with stainless steel hose clamps. The mooring unit was anchored on the seafloor by two anchor chain links and, was suspended in the water column with a subsurface float.

Upon completion of deployment, 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  $-20^{\circ}\text{C}$  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 with two Varian 2000 gas chromatography (GC)/ion trap mass spectrometry (MS) systems (Varian Inc., Walnut Creek, CA) with thermal desorption injection (13). The desorption temperature was programmed from 100 to 280  $^{\circ}\text{C}$  at  $\sim 100^{\circ}\text{C}/\text{min}$  with a 40 min 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/min). Chromatographic separations were made with 60 m  $\times$  0.25 mm i.d. (0.25- $\mu$ m film thickness) DB-5MS columns (J&W Scientific, Folsom, CA) temperature-programmed from 80  $^{\circ}\text{C}$  (hold for 1 min) to 176  $^{\circ}\text{C}$  at a rate of 8  $^{\circ}\text{C}/\text{min}$ , followed by a ramp to 230  $^{\circ}\text{C}$  at a rate of 1.5  $^{\circ}\text{C}/\text{min}$  and a final increase to 290  $^{\circ}\text{C}$  (5

$^{\circ}\text{C}/\text{min}$ ), where it was held for 21 min. 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  $\mu\text{A}$ .

**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 (11). 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 (Tables S2 and S3 in the Supporting Information).

**Data Analysis.** As shown previously (11), the concentration ( $C_w^0$ ) of an analyte in open oceans is simply related to the total amount ( $N_f$ ) of the analyte sorbed on 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.  $K_f V_f$  values calibrated prior to field sampling with the two GC/MS systems (designated as GC/MS-1 and GC/MS-2, respectively) described previously (13) were 3.41 ( $\pm 0.54$ )  $\times 10^5$  and 2.59 ( $\pm 0.97$ )  $\times 10^5 \mu\text{L}$  for *p,p'*-DDE and 5.82 ( $\pm 1.81$ )  $\times 10^5$  and 2.79 ( $\pm 1.13$ )  $\times 10^5 \mu\text{L}$  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 is in the range of  $\pm 10^{\circ}\text{F}$ , which translates into a relative temperature change of less than 5%. Therefore, temperature effects on the measured concentrations were negligible.

The cumulative distribution function (CDF)

$$\text{CDF}_j (\%) = \frac{100\% \times \sum_{i=1}^j \text{AWF}_i}{\sum_{i=1}^n \text{AWF}_i} \quad (1)$$

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  $\text{CDF}_j$  value was paired with the concentration value from the  $j$ th area to generate concentration distribution plots.

## Results and Discussion

**Water Column Concentrations of *p,p'*-DDE and *o,p'*-DDE.** The sample collection information and distribution data are

summarized in Table 1, and individual concentrations are presented in Tables S2 and S3 of the Supporting Information. Excluding replicates, the numbers 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. *p,p'*-DDE 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 (14). Maldonado and Bayona (15) 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. (16) obtained an average concentration of  $\sim$ 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 (17). 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 (18). 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 (19). 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 (20). The same group of researchers also obtained very high concentrations of *p,p'*-DDE at three other locations in China—Daya Bay, Guangdong Province (0.2–6.9 ng/L) (21), River Wuchuan, Fujian Province (25.1–81.4 ng/L) (22), and Tonghui River near Beijing (3.71–208 ng/L) (23). 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. (24) 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 persistent organochlorines was 0.0008 ng/L (24). 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 about 3 orders of magnitude higher



**FIGURE 1.** Distribution of *p,p'*-DDE 2 m above the seafloor in the Southern California Bight. Red dots represent data from the present study, while the single yellow dot (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 (11).

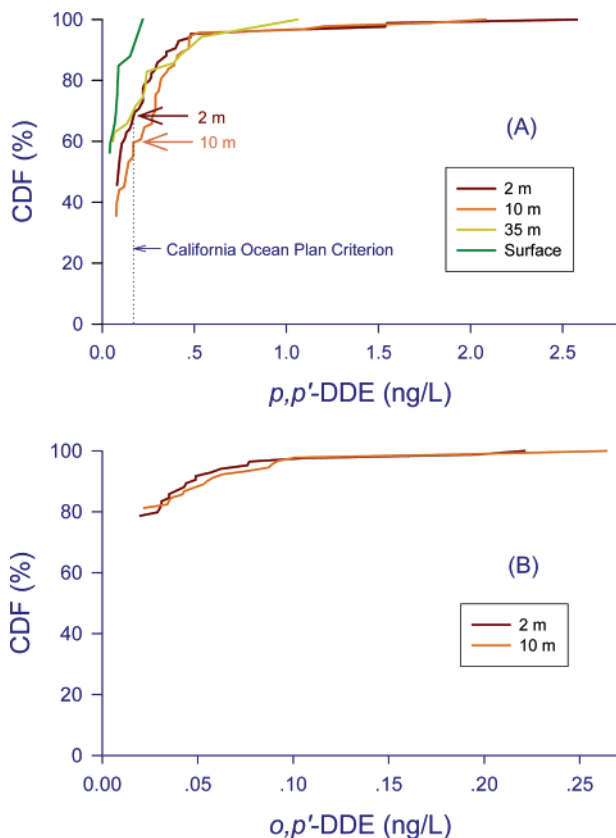
than the global oceanic background values reported by Iwata et al. (24).

**Spatial Distribution Pattern.** The highest levels of *p,p'*-DDE (also *o,p'*-DDE; data not shown) were detected in Santa Monica Bay (SMB) (Figure 1) adjacent to the PVS where sediments are known to contain highly elevated levels of DDT contamination (8, 25). Due to the randomized nature of the sampling design, no sampling site was selected on the PVS. However, SPME-based water column sampling conducted in June–July 2003 (11) 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  $\sim$ 4 and 2 ng/L while those of *o,p'*-DDE were  $\sim$ 0.6 and 0.3 ng/L at the 2- and 10-m depth of station 6C, respectively (11). 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 (26) 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.

**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 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 the 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 (Tables S2 and S3 in the Supporting Information) were included to increase the statistical power. For both the 2- and 10-m depths, *p,p'*-DDE concentrations followed the order: SMB > San Pedro Shelf > Santa Barbara. At the other three depths, there was





**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 (26).

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 or the San Pedro Shelf. Meaningful comparisons at the other depths were 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 (5, 11).

**Transport and Fate of DDEs in the Southern California Bight.** Previous studies suggested that contaminated sediments on the PVS and two dumpsites in the Santa Monica Basin were dominant sources of DDTs in the SCB (5–7, 27). Because of their location in deep water (800 m), however, the dumpsites were 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 (28). Long-range transport from the PVS to SMB was proposed as a viable mechanism causing the distribution pattern (28). The results from the present study are consistent with this proposed mechanism, while in addition 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 the area weighting strategy described in the Materials and 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 nondetectable 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 (again, 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 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  $\text{AWF} \times [10 \times C + (\text{water column depth} - 10) \times C']$ .

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 extension of the assumption of continuous DDE concentrations to the entire sampling area (~1820 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>) (5), where water column *p,p'*-DDE was about an 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 deemed 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 (24). The volume of the SCB was estimated at  $4.5 \times 10^{13}$  m<sup>3</sup> with a digital elevation model, ETOPO-5, with a grid of 5' latitude and longitude resolutions (29). Therefore, the mass inventories of *p,p'*- and *o,p'*-DDE are 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, etc. 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

**TABLE 2. Comparison of Global Water Column Levels (ng/L) of *p,p'*- and *o,p'*-DDE<sup>a</sup>**

	<i>p,p'</i> -DDE	<i>o,p'</i> -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	0.0050		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 Delta	0.01–0.09	<0.008–0.02	2002 (18)
Macao coast, Pearl River Delta	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.

**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**

depth <sup>a</sup> (m)	Santa Monica Bay			San Pedro Shelf			Santa Barbara		
	no. samples	mean <sup>b</sup>	standard error <sup>c</sup>	no. samples	mean <sup>b</sup>	standard error <sup>c</sup>	no. samples	mean <sup>b</sup>	standard error <sup>c</sup>
				<i>p,p'</i> -DDE					
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)			
				<i>o,p'</i> -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.

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

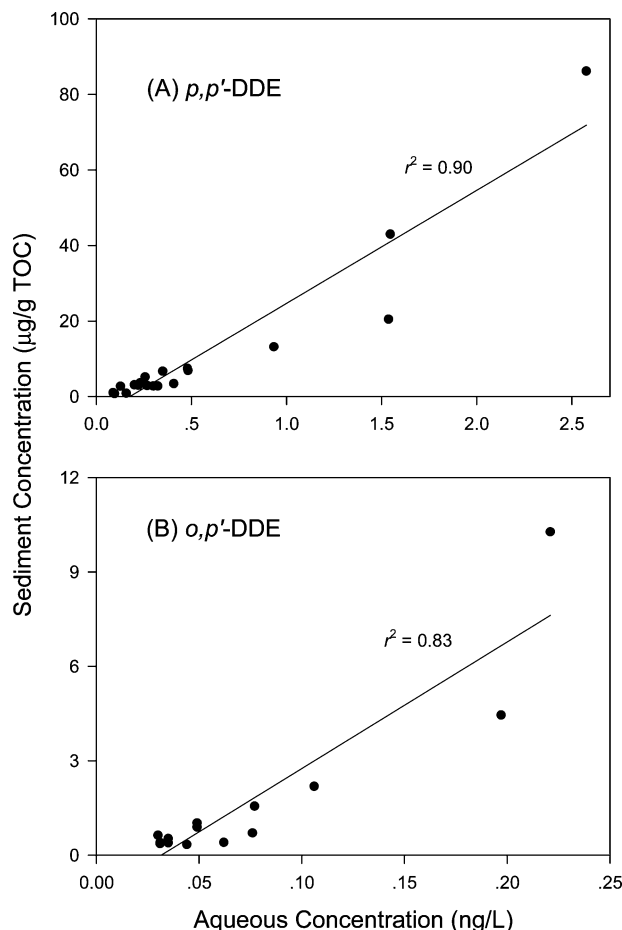
The first method estimated mass fluxes of *p,p'*- and *o,p'*-DDE using published water turnover rates. According to Hickey (30), the entire SCB is flushed within a few weeks during extreme conditions. In other words, the SCB water column can be completely exchanged 5–10 times per year. For the previously 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 because of the complex oceanic conditions in the SCB (30).

The second method employed Fick's law to estimate the flux *F* (31)

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

where *A* is the cross-sectional area of water exchange (approximated as 1 000 000 m × 2000 m = 2 × 10<sup>9</sup> m<sup>2</sup>),  $\kappa_h$  is the horizontal eddy diffusivity (assumed to be 10<sup>3</sup> m<sup>2</sup>/s SCB (32)), and  $\partial C/\partial L$  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 (30). Through the use of eq 2, the annual flux of *p,p'*-DDE out of the SCB is 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 is 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 are quite comparable.

Prior to 1971 when use of DDT compounds was banned, about 1700 metric tons of DDTs were discharged into the



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

PVS through wastewater outfalls (33). 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 ton per year. As mass fluxes likely have decreased with the decline in DDT production/discharge since the 1970s (34), 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 were evenly distributed in the upper 200 m of the water column, or roughly 18% of the background concentration measured by Iwata et al. in the North Pacific (24). If correct, the SCB has indeed been a significant source of DDTs to the global environment.

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### Supporting Information Available

Information about the sampling sites and dates of SPME-based sampler deployment, measured dissolved concentrations of *p,p'*- and *o,p'*-DDE for all samples, and the sampling sites on the continental shelf of the SCB. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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