



In-Situ Measurements of Chlorinated Hydrocarbons in the Water Column off the Palos Verdes Peninsula, California

Eddy Y. Zeng, Charlie C. Yu, and Kim Tran

ABSTRACT

Spatial distributions of dichloro-diphenyl-trichloroethane (DDT) and its primary metabolites (*p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDD, *o,p'*-DDD, *p,p'*-DDE, and *o,p'*-DDE; designated as DDTs hereinafter) and polychlorinated biphenyls (PCBs) in the water column off the Palos Verdes Peninsula, California, were measured in the winter and summer seasons of 1997 using an *in-situ* sampling method. The concentrations of DDTs ranged from 0.6 to 15.8 ng/L, while those of PCBs ranged from 0.06 to 1.14 ng/L at eight sampling stations. The spatial distribution patterns of DDTs and PCBs in the water column, as well as the DDT/PCB concentration ratio, were similar to those found in the sediment. The vertical profiles of DDTs and PCBs during both sampling seasons exponentially decreased with increasing distance from the sea floor. In addition, the partitioning characteristics of DDTs and selected PCB congeners indicated a tendency of mobilization from sediment to water. All of these findings strongly suggest that contaminated sediments are a main source of DDT and PCB inputs to the water column surrounding the study site.

INTRODUCTION

Sediments on the Palos Verdes Shelf (PVS), California, are known to contain highly elevated levels of DDT, largely due to the historical discharge of DDT-enriched industrial wastes via the outfall system of the Joint Water Pollution Control Plant (JWPCP) operated by the County Sanitation Districts of Los Angeles County (CSDLAC) (Venkatesan *et al.* 1996). Polychlorinated biphenyls (PCBs) are also present in the sediment, at lower concentrations than DDTs. The mass emission of DDTs from the JWPCP outfall has declined to a record low of 1.9 kg/year in 1995, the result of a DDT manufacturer ceasing inputs of DDT-containing wastes to the treatment plant in 1970. The mass emission of PCBs had reached undetectable levels before 1995 (Raco-Rands 1997).

However, sediments heavily contaminated with DDTs and PCBs remain a potential source of contamination to the water column and therefore are a concern to the decision makers managing coastal resources.

While peak concentrations at various locations have gradually moved downward inside the sediment column, the upper sediment layers near the JWPCP outfall still contain DDTs in the neighborhood of parts per million (Stull *et al.* 1996). One possible explanation for the high levels of DDTs remaining in the top layer of sediment is the continuous deposition of new particles with relatively low but detectable DDT contamination. An alternative explanation is that historically deposited DDTs might continue to be remobilized upward inside the sediment column. The latter mechanism, along with a combination of resuspension and dispersion processes, would result in widespread distribution and possible enhanced bioavailability of DDTs, since suspended DDTs presumably are more bioavailable and more easily subject to redistribution than sediment-bound DDTs.

In this study, we attempted to distinguish between these two hypotheses by measuring suspended DDTs and PCBs on the PVS. An *in-situ* sampling method (Tran and Zeng 1997) was employed that processed large volumes of water, in order to achieve sufficient detection sensitivity. The objectives of the investigation were (1) to obtain the spatial and vertical distributions of DDTs and PCBs in the water column; (2) to estimate the masses of these contaminants in the water column of the PVS; and (3) to assess the tendency for these contaminants to partition between the dissolved and particulate phases. The information gained from this research was used to determine whether contaminated sediments are an important source of DDTs and PCBs in the region and whether these historically deposited contaminants are being remobilized.

METHODS

Sample Collection

Field sampling was conducted during the winter season (from January 13 to March 4) and summer season (from June 23 to July 21) in 1997. Eight stations around

the PVS were sampled; six stations were located at the 60-m depth contour and two were located at the 30-m and 150-m depths, respectively (Figure 1).

Water column samples were collected by deploying an INFILTREX 100 water pumping system (Axys Environmental Systems Ltd., Sidney, British Columbia, Canada) at a depth of ~1 m above the ocean floor from all the sampling locations. In addition, samples were also taken at depths of 2, 5, 20, and 35 m above the ocean floor at Station 6C. Two replicates were collected at Station 6C (1-m depth) for both sampling seasons, as well as at Station 0C (1-m depth) in the summer of 1997. Before each long-term deployment, a one-hour pumping operation using two filters was performed to measure total suspended solids (TSS). The average TSS content was 27.4 ± 2.7 mg/L in the winter sampling and 25.6 ± 3.7 mg/L in the summer sampling, but did not show any consistent pattern with location and depth.

Each sample was collected at a specific location for 3 to 5 d, with 6 to 8 GF/F glass fiber filters (142 mm diameter and 0.7 μ m pore size) installed in a filter assembly. A Teflon column packed with precleaned XAD-II resins was connected to the filter assembly to extract dissolved organics from the filtrates. The sample volume processed varied from ~1,100 to ~2,300 liters, determined from the pumping speed preset by a built-in microprocessor and the total pumping time recorded. Upon retrieval of the sampler, glass fiber filters loaded with particles were carefully removed from the filtration assembly and placed in precleaned petri dishes. The Teflon column was also detached from the sampling system. The filters and Teflon column, wrapped in aluminum foil, were transported to the laboratory in an ice chest.

Sample Processing

The procedures for eluting dissolved organic materials from the XAD-II resins and for processing glass fiber filters have been described extensively elsewhere (Tran and Zeng 1997), and only a brief description is given here. Each Teflon column was spiked with surrogate standards (tetrachloro-m-xylene, PCB 65, and PCB 189).

Dissolved organic materials were eluted consecutively with 200 mL of methanol and methylene chloride at a flow rate of 5 mL/min. The methanol fraction was back extracted three times with methylene chloride (50 mL each extraction). Particle-loaded filters were spiked with surrogate standards and extracted three times (16, 6, and 16 h) with methylene chloride (100 mL each extraction) using a roller table. The combined extract for each sample was solvent exchanged to hexane, subjected to sulfur removal (activated copper added to the extract) and clean-up/fractionation using a 1:2 alumina:silica gel glass column, and finally concentrated to 1 mL. Internal standards were added to final extracts before instrumental analyses.

Instrumental Analyses

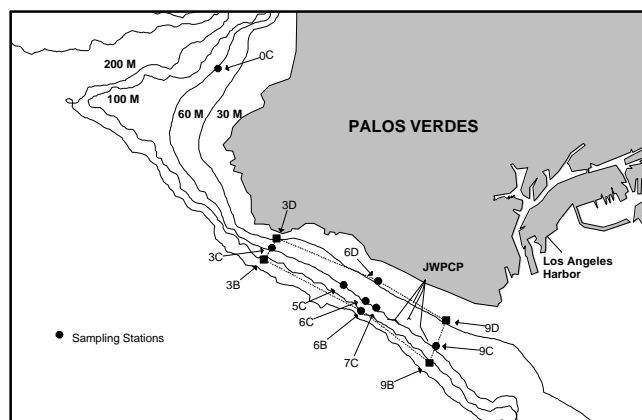
Measurements of DDTs and PCBs were conducted using a Hewlett-Packard (HP) Series II Gas Chromatograph (GC) equipped with a ^{63}Ni electron capture detector (ECD) and a 60 m \times 0.25 mm i.d. (0.25 μ m film thickness) DB-5 column (J&W Scientific Inc., Folsom, CA). The column temperature was initially set at 90 $^{\circ}\text{C}$, programmed to 180 $^{\circ}\text{C}$ at a rate of 6 $^{\circ}\text{C}/\text{min}$, and further ramped to 290 $^{\circ}\text{C}$ at 1 $^{\circ}\text{C}/\text{min}$. Ultra-high-purity helium

was the carrier gas at 2 mL/min at 90 $^{\circ}\text{C}$. Ultra-high-purity nitrogen was the make-up gas at 30 mL/min. Both the injector and detector temperatures were maintained at 280 $^{\circ}\text{C}$. Peak identification was confirmed using an HP Series II GC/5970 mass spectrometer (MS) operated under the same chromatographic conditions as those for the GC/ECD analyses.

Target analytes for the present study were six DDT components (o,p'-DDT, p,p'-DDT, o,p'-DDD, p,p'-DDD, o,p'-DDE, and p,p'-DDE, the sum of which is defined as

total DDTs) and 27 PCB congeners (8, 18, 28, 29, 44, 50, 52, 66, 77, 87, 101, 104, 105, 118, 126, 128, 138, 153, 154, 170, 180, 187, 188, 195, 200, 206, and 209, the sum of which is defined as total PCBs). None of the measured concentrations were corrected for the recoveries of surrogate standards.

FIGURE 1. Map of the Palos Verdes Shelf showing the sampling sites and the Los Angeles Harbor. The dotted area connecting 3D, 3C, 3B, 6B, 9B, 9C, 9D, and 6D indicates where the DDT and PCB masses were estimated.



QA/QC Procedures and Performance

Prepurified XAD-II resins purchased from Rohm and Haas Company (Philadelphia, PA) were further cleaned with methanol and screened using a 0.5 mm-mesh Teflon screen. After packing (about 45 g of resins were used for each column), the resin columns were washed with methanol and methylene chloride, respectively, and soaked in methanol until use. Glass fiber filters were baked at 420 °C for at least 4 h and covered in precleaned petri dishes until they were used. All glassware was washed with water and soap, rinsed with deionized water, and kilned at 420 °C for more than 6 h.

Repeated sampling of water column particles and dissolved organics was conducted once in the winter period (Station 6C at the 1-m depth) and twice in the summer period (Stations 0C and 6C at the 1-m depth). For each deployment, a Teflon column was carried on board and left open during the entire operation. This column was brought back to the laboratory and treated as a field blank. For each batch of up to 10 field samples, a procedural blank and a spiked blank (spiked with target compounds) containing pure solvent and sodium sulfate were processed.

Quantitation was done using a five-point calibration method. For each instrumental analysis batch, a continuing calibration standard solution was analyzed to examine the validity of the five-point calibration curves for all the target analytes. In addition, two check standard solutions (SRM 2261 and SRM 1493; National Institute of Standards and Technology, Gaithersburg, MD) containing six DDT components (o,p'- and p,p'-DDT, DDD, and DDE) and 20 PCB congeners, respectively, were also analyzed at the end of each batch to verify the consistency of instrument performance.

Field samples were analyzed in six batches. The relative percent difference between continuing calibration and the five-point calibration was within $\pm 20\%$ for 190 out of 192 total measures. The average recoveries of surrogate standards were greater than 60% except for tetrachloro-m-xylene, which was recovered 50% on average (with standard deviations less than 15%). None of the field and procedural blank samples contained detectable amounts of target analytes. Recoveries of check standards were between 85% to 100%. Detection limits were typically 0.01 ng/L for individual components with a sample size of 1,000 L. Actual detection limits were adjusted based on actual sample sizes.

RESULTS AND DISCUSSION

Distribution of Organic Compounds in the Water Column

This study directly measured the water column concentrations of organochlorines in a wide range of locations on the PVS. Total DDTs were detectable in all the samples (Table 1), ranging from 0.5 to 9.7 ng/L in the dissolved phase and from 0.1 to 10.0 ng/L in the particulate phase. The volume-normalized concentrations of DDTs in the particulate and dissolved phases were almost identical. Since the TSS concentrations were approximately 26 mg/L at these sampling locations, the particle-normalized concentrations of DDTs in the particulate phase ranged from 3.0 to 360 ng/g dry weight. Spatially, the highest concentration was found in proximity to Station 6C, while the lowest concentration was found at Station 6D, a near-shore location. Along the 60-m isobath, Station 0C contained the lowest DDT concentration. In all of the samples, p,p'-DDE constituted more than 70% of the total concentrations, and more than 85% of detectable DDT compounds were o,p'-DDE and p,p'-DDE (Table 1).

The concentrations of PCBs ranged from 0.06 to 1.14 ng/L (Table 2), approximately an order of magnitude lower than concentrations of DDTs. Only one sample (particulate sample from Station 6C-35M) contained non-detectable PCBs (<0.007 ng/L). Similar to the results associated with DDTs, the particulate and dissolved PCB concentrations were almost identical. The highest PCB concentration occurred at Station 6C and the lowest concentration was found at Station 6D; Station 0C contained the lowest PCB concentration among the stations located at the 60-m isobath.

These results indicate that DDTs and PCBs are widely distributed in the water column off Palos Verdes. They remain detectable by the *in-situ* sampling method in areas as far as Station 0C and at distances as high as 35 m above the sea floor at Station 6C (Tables 1 and 2).

A previous sampling by Green *et al.* (1986) that used a similar sampling approach was conducted at a location 1 km inshore of the two active outfalls (Figure 1) at a distance of 20 m from the sea floor (with a water depth of 30 m). The concentration of total DDTs measured in the previous sampling was 3.8 ng/L (Green *et al.* 1986), comparable to but at the low range of the measured values of the present study (Table 1). Green *et al.* (1986) did not detect any PCBs with a detection limit of 0.5 ng/L (100 L of water processed). The majority of the measured PCB concentrations obtained from the present study were below 0.5 ng/L, with some measurements as low as 0.06 ng/L (Table 2). These lower levels of PCBs

TABLE 1. Concentrations of DDTs in water column and average percent of p,p'-DDE and total DDE.^a

Station	Winter Sampling			Summer Sampling		
	Dissolved (ng/L)	Particulate (ng/L)	Total (ng/L)	Dissolved (ng/L)	Particulate (ng/L)	Total (ng/L)
0C-1M-1	1.6	0.7	2.3	2.4	2	4.4
0C-1M-2				2.6	1.6	4.2
0C-1M (AVE)				2.5 (0.1)	1.8 (0.3)	4.3 (0.4)
3C-1M	2.9	1.6	4.5	4.4	3.1	7.6
5C-1M	4.5	4.7	9.2	4.2	6.2	10.4
6C-1M-1	7.2	7	14.2	3.8	3.2	7
6C-1M-2	9.7	5.2	14.9	4.9	5.5	10.4
6C-1M (AVE)	8.4 (1.7)	6.1 (1.3)	14.5 (3.0)	4.4 (0.8)	4.3 (1.6)	8.7 (2.4)
6C-2M	5.9	10	15.8	4.8	5.5	10.3
6C-5M	4.5	3.1	7.6	4.5	4.1	8.6
6C-20M	2.3	0.5	2.8	1.4	0.6	2
6C-35M	0.6	0.2	0.8	0.5	0.1	0.6
7C-1M	5.8	4.1	9.9	3.2	2.3	5.5
9C-1M	3.4	2	5.3	2.9	2.1	5
6B-1M	3	2.4	5.4	3.1	2.6	5.6
6D-1M	4.2	3	7.2	1.5	1.5	3
% of p,p'-DDE ^b	72 (4)	77 (3)	71 (4)	78 (5)		
% of total DDEs ^c	87 (4)	86 (3)	86 (3)	89 (4)		

a Numbers in parentheses are standard deviations.
b Defined as concentration of p,p'-DDE relative to the total DDT concentration.
c Defined as concentrations of p,p'-DDE and o,p'-DDE relative to the total DDT concentration.

are attributed to the higher volumes of water sampled in the present study than were taken by Green *et al.* (1986). Since the sampling locations were different in these two studies, it is difficult to assess the observed concentration difference. Green *et al.* did confirm that the DDT concentrations in the water column off Palos Verdes were in the range of several parts per trillion.

Another previous sampling (Tran and Zeng 1997) in October/November 1995 and April/May 1996 at Station 7C yielded total DDT concentrations of 5.4(±0.1) and 11.7(±3.6) ng/L, respectively; concentrations of total PCBs were below detection limits and 4.3(±2.1) ng/L, respectively. These results were comparable to the results obtained from the present study (Tables 1 and 2). In addition, concentrations of 0.2 ng/L for total DDTs and <0.01 ng/L for total PCBs were determined at a reference location, Station R52 (at 1 m above the sea floor), off Dana Point (Tran and Zeng 1997). These measurements can be considered as background DDT and PCB concentrations in the water column of the Southern California Bight near the sea floor.

The California Ocean Plan (SWRCB 1997) establishes criteria for managing ocean discharge including

limits for DDTs and PCBs to protect human health. The 30-d average concentrations permitted in receiving waters off California are 0.17 ng/L for DDTs and 0.019 ng/L for the sum of Aroclors, respectively. The water column concentrations obtained from the present study exceed these limits at all of the sampling locations (the difference in PCB congener-specific measurement and Aroclor-based quantitation methods is not significant enough to reverse this conclusion).

Estimation of DDT and PCB Masses in the Water Column and Fluxes Across the Palos Verdes Shelf

The data presented above allowed us to estimate the masses of DDTs and PCBs in the water column. The mass, M , of a specific component equals the product of the concentration, C , times the volume, V , i.e., $M = C \times V = C \Delta x \Delta y \Delta z$, where x and y are two horizontal distances and z is designated as the vertical depth. Since only a limited number of stations were sampled and vertical distribution of target analytes was measured at one station (Station 6C), the masses were estimated only for the area bounded by the dotted lines connecting Stations 3D, 3C, 3B, 6B, 9B, 9C, 9D, and 6D (Figure 1), which

TABLE 2. Concentrations of total PCBs in water column.^a

Station	Winter Sampling			Summer Sampling		
	Dissolved (ng/L)	Particulate (ng/L)	Total (ng/L)	Dissolved (ng/L)	Particulate (ng/L)	Total (ng/L)
0C-1M-1	0.1	0.04	0.14	0.24	0.19	0.43
0C-1M-2				0.23	0.16	0.39
0C-1M (AVE)				0.23 (0.01)	0.18 (0.02)	0.41 (0.03)
3C-1M	0.18	0.1	0.28	0.43	0.51	0.94
5C-1M	0.26	0.25	0.51	0.46	0.68	1.14
6C-1M-1	0.36	0.29	0.65	0.4	0.26	0.66
6C-1M-2	0.79	0.31	1.1	0.63	0.37	1
6C-1M (AVE)	0.58 (0.30)	0.30 (0.02)	0.88 (0.32)	0.52 (0.16)	0.32 (0.08)	0.84 (0.24)
6C-2M	0.37	0.52	0.89	0.54	0.56	1.11
6C-5M	0.27	0.14	0.41	0.62	0.32	0.94
6C-20M	0.2	0.01	0.21	0.19	0.08	0.28
6C-35M	0.06	<0.007	0.06	0.16	0.05	0.21
7C-1M	0.46	0.19	0.65	0.37	0.19	0.56
9C-1M	0.19	0.12	0.31	0.14	0.16	0.3
6B-1M	0.2	0.13	0.33	0.32	0.21	0.52
6D-1M	0.29	0.19	0.48	0.53	0.14	0.67

a Numbers in parentheses are standard deviations.

covers an area of ~20 km².

The vertical concentrations of chlorinated hydrocarbons at Station 6C generally decreased with increasing distance from the sea floor (Figures 2 and 3), with the maxima occurring near the bottom (1 or 2 m above the sea floor). The concentrations varied exponentially with the water column depth which we described using a first-order function:

$$C = A e^{-kz} \quad (1)$$

where

C is concentration (ng/L or $\mu\text{g}/\text{m}^3$) of a compound or a group of compounds, z is distance (m) from the sea floor, k is rate constant (m^{-1}), and A is an integral constant. A regression analysis on the DDT and PCB data at Station 6C (Tables 1 and 2) using Eq. (1) yielded a series of distribution functions or profiles (Table 3). One common feature in these functions is that the rate constant is greater in the particulate phase than in the dissolved phase. These exponential regression fits are also shown in Figures 2 and 3. Three assumptions were made in the mass estimation:

- (I) The rate constant, k , was the same at all of the sampling locations for a specific component group and a specific sampling time and obtained from the vertical profiles at Station 6C (Table 3).
- (II) A values at stations other than 6C were estimated

using the measured concentration values at the 1-m depth (Tables 1 and 2), i.e., $A = C(1\text{ m})/e^{-k}$. For locations along the 30-m and 150-m isobaths (but not sampled), we assumed that the concentration gradient between Stations 6C and 6D or 6C and 6B can be applied to other station pairs. For example, the concentration at the 1-m depth at Station 3D can be estimated by $C_{3D}(1\text{ m}) = C_{3C}(1\text{ m}) \times [C_{6D}(1\text{ m})/C_{6C}(1\text{ m})]$.

- (III) In calculating the total mass, integration along the z axis was done by using vertical profiles similar to those for Station 6C (Table 3). Integration along the x or y axes would be approximated by a simple arithmetic average approach.

After performing a series of calculations based upon the measured data (Tables 1 and 2), vertical profiles at Station 6C (Table 3), and the three assumptions discussed above, masses of DDTs and PCBs in the water column of the PVS were obtained (Table 4). It is interesting to note that more DDTs and PCBs are present in the dissolved phase than in the particulate phase (defined as particle size greater than 0.7 μm), although these compounds are highly hydrophobic.

Annual fluxes of DDTs and PCBs across the PVS (and therefore discharged to areas outside the PVS) were calculated from water column masses multiplied by average water turnover rates. Longshore and cross-shore

FIGURE 2. Water column vertical profiles of total DDTs at Station 6C and curves represent exponential regression fits from eqs (3) to (6).

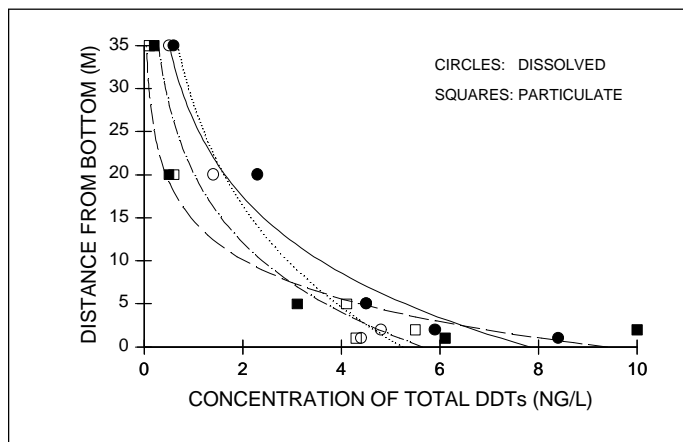
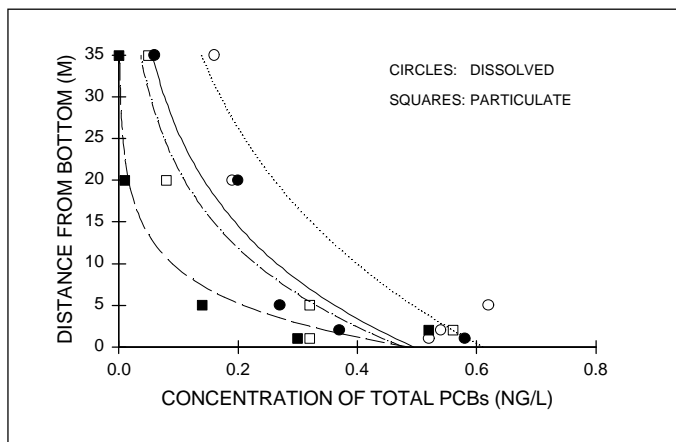


FIGURE 3. Water column vertical profiles of total PCBs at Station 6C and curves represent exponential regression fits from eqs (7) to (10).



fluxes were considered separately. The average longshore and cross-shore lengths of the designated area (Figure 1) are 10.6 and 1.7 km, respectively. The water turnover rates could be estimated from current speeds, but the difficulty was that current speeds tend to vary with locations and seasons on the PVS. After reviewing existing data from studies of this area (SCCWRP 1993, Lee 1994), we assumed that the average net longshore and cross-shore bottom current speeds were 5 and 1 cm/s, respectively. Therefore, the longshore water turnover rate was 149 times/year. Given the DDT and PCB masses in the designated area (Table 4), the longshore fluxes of DDTs and PCBs across the PVS were 186 and 22 kg, respectively, in 1997 (the winter and summer measurements were averaged). Similarly, the cross-shore fluxes of DDTs and PCBs were 232 and 27 kg, respectively. Hence, the total fluxes of DDTs and PCBs across the PVS were 418 and 49 kg, respectively (Table 4).

Niederoda *et al.* (1996) estimated that approximately 12.6 tons of p,p'-DDE were removed from the central PVS during the two-year period from 1987 to 1989. Other estimates of total sediment DDT masses on the PVS suggested a DDT mass reduction in the order of 10 to 20 metric tons per year from 1972 to 1992 (Lee 1994, Young *et al.* 1976). Our estimate of DDT loss due to current dispersal was substantially lower than these estimates. It should be noted that the DDT flux estimated in this study (Table 4) was highly dependent upon the current speeds used. Therefore, estimates using different techniques should be conducted during the same period of time to achieve a more true comparison. Nevertheless, physical transport of DDTs to other areas is a viable mechanism leading to the reduction of DDT mass in sediments of the PVS.

Partitioning Between Dissolved and Particulate Phases

Partitioning of an organic compound between the particulate and dissolved phases can be expressed in the form of the total organic carbon (TOC) normalized partition coefficient (K_{oc}):

$$K_{oc} = C_{oc}/C_{w,e} = C_p/(f_{oc} \times C_{w,e}) \quad (2)$$

where C_{oc} and C_p denote particulate phase concentrations, but are normalized to TOC content and dry sample weight, respectively; $C_{w,e}$ is the concentration of the same compound in the dissolved phase at equilibrium state; and f_{oc} is the fraction of TOC in the solid sample. The tendency for a specific compound to partition in the dissolved phase can be evaluated by the ratio of $C_{w,e}/C_w$ (C_w is measured concentration in water) or chemical fugacity (Achman *et al.* 1996):

$$\log(C_{w,e}/C_w) = \log(C_p/C_w) - \log K_{oc} - \log f_{oc} \quad (3)$$

K_{oc} values are not available readily, but can be related to the octanol-water partition coefficient, K_{ow} , an attainable parameter. Ideally, K_{oc} would equal K_{ow} under strictly equilibrium conditions. Such an equality is not warranted in reality. A more practical correlation can be expressed as $\log K_{oc} = a \log K_{ow} + b$ with a and b being determined from experiments. Substituting $\log K_{oc}$ in Eq. (3) with this expression yields the following equation:

$$\log(C_{w,e}/C_w) = \log(C_p/C_w) - a \log K_{ow} - b - \log f_{oc} \quad (4)$$

Two sets of a and b have been proposed which may represent the high and low ends of K_{oc} values measured experimentally. Schwarzenbach and Westall (1981)

TABLE 3. Estimated values of A and k in Eq. (1) for the DDT and PCB data at Station 6C.

Sampling Time	Component	A		k	
		Estimated	S.E. ^a	Estimated	S.E. ^a
Winter 1997	Dissolved DDTs	7.8	0.9	0.078	0.028
	Particulate DDTs	9.4	3.0	0.15	0.13
	Dissolved PCBs	0.49	0.08	0.062	0.031
	Particulate PCBs	0.49	0.18	0.17	0.15
Summer 1997	Dissolved DDTs	5.2	0.4	0.059	0.013
	Particulate DDTs	5.7	0.7	0.086	0.032
	Dissolved PCBs	0.61	0.07	0.043	0.015
	Particulate PCBs	0.48	0.1	0.073	0.045

^aS.E.=Standard error.

obtained $a=0.72$ and $b=0.49$, while Karickhoff *et al.* (1979) obtained $a=1.0$ and $b=0.21$. A $C_{w,e}/C_w$ value of greater than 1 indicates that the organic compound has a tendency (thermodynamically achievable) to move from the particulate phase to the dissolved phase.

Relationships between $\log(C_{w,e}/C_w)$ and $\log K_{ow}$ were calculated for p,p'-DDE, o,p'-DDE, p,p'-DDD, o,p'-DDD, and selected PCB congeners in the filtrate (dissolved) samples of 6C-1M and the sediment from Station 6C (unpublished results) (Figures 4a and 4b). The higher and lower values for each pair of $\log(C_{w,e}/C_w)$ represent estimates using the regressions of K_{oc} by Schwarzenbach and Westall (1981) and Karickhoff *et al.* (1979), respectively. All the estimated $\log(C_{w,e}/C_w)$ values were above the equilibrium line for both the winter and summer seasons (Figures 4a and 4b). This suggests that sediment-bound DDTs and PCBs can be transported to the surrounding water body thermodynamically, even without any physical forces. One possible mechanism is diffusion (Achman *et al.* 1996).

The same relationships between the filtrate and particle samples were not evaluated, since the average TSS concentrations of 27.4 and 25.6 mg/L, respectively, in two sampling seasons were probably overestimated. While the CSDLAC maintains a comprehensive ocean monitoring program focusing on coastal areas around the

JWPCP outfall on the PVS, TSS is not monitored. Other major wastewater dischargers in southern California have accumulated TSS data in other areas around their outfalls in Santa Monica Bay, off Newport Beach, and off San Diego. The TSS concentrations ranged from <0.1 to 7.9 mg/L (EMD 1993, CSDOC 1998, CSDMWD 1996). However, these measurements were normally conducted using a small sample quantity (~1 L). In our study, we pumped more than 25 L of water into two Whatman GF/F filters with a 0.7 μ m pore size. The prolonged filtration in our measurements may have resulted in filter clogging and therefore increased colloidal materials captured on the clogged filters.

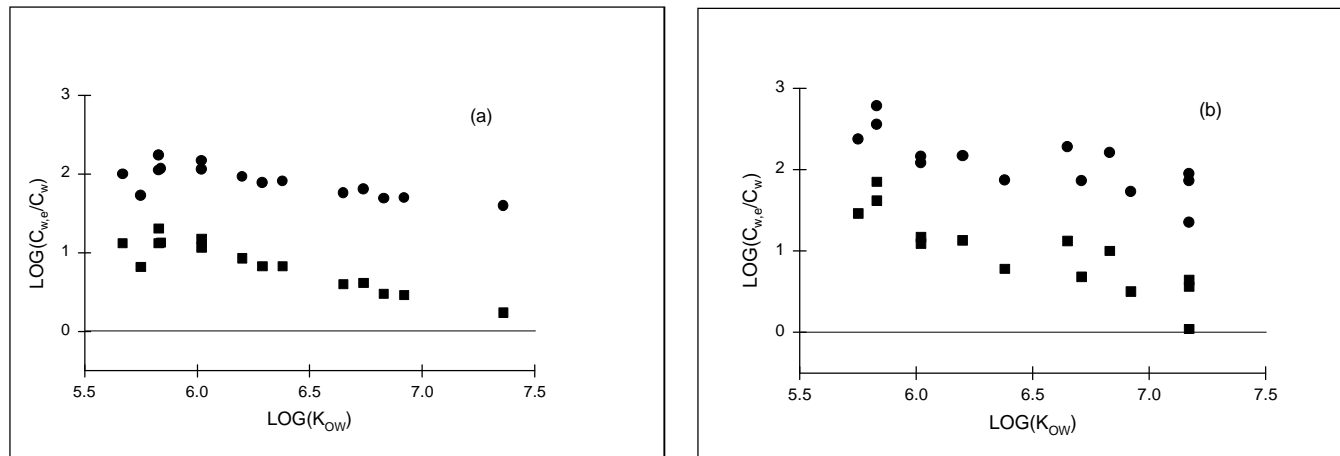
Sources of Contamination to the Water Column

The JWPCP discharged treated sewage via a 1.5-m diameter, 3-outlet outfall (at a 34-m water depth) from 1937 to 1958; via a 1.8-m diameter outfall (at a 34-m water depth) from 1947 to 1966 (used in case of emergency only since the 1960s); via a 2.3-m diameter Y-shaped outfall (at a 64-m water depth) since 1956; and via a 3.0-m diameter L-shaped outfall (at a water depth of 58 m) since 1966 (Stull *et al.* 1986). Stations 7C and 9C are located near the last two outfalls, respectively (Figure 1). The DDT residues were discharged into the JWPCP sewer system by Montrose Chemical Company

TABLE 4. Estimates of total masses of DDTs and PCBs in the water column and the annual fluxes of DDTs and PCBs across the Palos Verdes Shelf.

	Winter 1997			Summer 1997			1997 Net Flux (kg/year)
	Dissolved (g)	Particulate (g)	Total (g)	Dissolved (g)	Particulate (g)	Total (g)	
Total DDTs	830	340	1170	760	570	1330	418
Total PCBs	68	17	85	130	77	210	49

FIGURE 4. Correlation of $\log(C_{w,e}/C_w)$ with $\log K_{ow}$ for DDT components and selected PCB congeners partitioning between sediment and water column dissolved phase at Station 6C (1 m from the sea floor) sampled in (a) winter 1997 and (b) summer 1997. Circles and squares are derived using *a* and *b* values obtained by Schwarzenbach and Westall (12) and Karickhoff *et al.* (13), respectively.



from approximately 1950 to 1970, which eventually was transported to the PVS via the sewage pipes mentioned above (Chartrand *et al.* 1985). As a result, a discharge zone with highly elevated levels of DDT has formed around the Y-shaped outfall, while the area near the L-shaped outfall has significantly lower DDT concentrations. The area near the L-shaped outfall is generally not suitable for deposition due to a combination of geographic setting and bottom currents.

Investigations of the spatial distribution of the vertical profiles of p,p'-DDE, the most abundant component of the DDT compounds, revealed that the maximum sediment DDT concentration occurred in proximity to the Y-shaped diffuser at different depths and locations (Stull *et al.* 1996). This variation was apparently related to specific sedimentation conditions. Our present investigation indicates that the water column DDT and PCB concentrations at the 1-m depth from the sea floor exhibited a similar pattern, i.e., the highest concentration was centered around Stations 6C and 7C (Tables 1 and 2). This similarity, along with the nicely fitted exponential profiles of DDT and PCB concentrations at Station 6C shown in Figures 2 and 3, leads us to conclude that sediments near the JWPCP outfall are a main source of DDTs and PCBs present in the water column. The $C_{w,e}/C_w$ values for the water-sediment interface were much greater than one for a group of abundant DDT and PCB compounds (Figure 4), also indicating that these compounds have a strong tendency to move from sediments to the water column.

Before accepting the hypothesis that the waterborne DDTs measured were derived primarily from sediment, we must eliminate several alternative input sources including the JWPCP outfall. Aerial deposition and

land-derived runoff may also contribute to the water column contamination.

Two factors preclude the JWPCP outfall system as a significant source of current DDT inputs. First, the most recent estimate placed the maximum annual average DDT concentration (measured monthly) in the JWPCP final effluent at 4 ng/L (detection limit) in 1995 (Raco-Rands 1997). Using the same argument made by Green *et al.* (1986), a dilution factor of 165 for effluent concentration resulting from the diffusers alone should immediately disperse any residual DDTs to a level of ~ 0.024 ng/L or lower. The concentrations of DDTs measured in the water column ranged from 0.6 to 15.8 ng/L (Table 1). Second, the average DDT/PCB concentration ratios documented from 1971 to 1981 were 2.0 and 16.9, respectively, in the JWPCP final effluents and surficial sediments near the JWPCP outfall (Young *et al.* 1989), while the DDT/PCB concentration ratio currently observed in the water column samples was 12.4 ± 4.5 (calculated from Tables 1 and 2). Since PCBs were not detected in the JWPCP effluent with a maximum detection limit of 900 ng/L (Raco-Rands 1997), it is not clear from the effluent data whether or not the measurable PCBs in the water column (Table 2) were derived from JWPCP effluents.

Aerial deposition is not likely to be a significant source of DDTs or PCBs to the PVS water column, based upon three observations. First, the spatial distribution of these contaminants in the water column was consistent with a sediment contamination pattern (Stull *et al.* 1996), whereas aerial deposition would have yielded a relatively unvarying concentration distribution over a small geographical scale. Second, the exponentially decreasing profiles of DDTs and PCBs with increasing distance

from the sea floor at Station 6C (Figures 2 and 3) are opposite to what would be expected if aerial deposition were a significant source. Last, Iwata *et al.* (1993) collected and analyzed 68 samples from surface water of several oceans mainly affected by atmospheric transport from April 1989 to August 1990; the highest concentration of DDTs was 0.041 ng/L, which is substantially lower than the concentrations of DDTs measured in the present study (from 0.6 to 15.8 ng/L, Table 1).

The most significant land-derived runoff source in the area is the Los Angeles Harbor (Figure 1). An earlier study (Eganhouse *et al.* 1990) indicated that surface sediments at several locations in the harbor contained fairly high concentrations of PCBs. The same study also found that PCB concentrations were generally several times higher than DDT concentrations inside the harbor. The PCB/DDT concentration ratios (~0.1) observed from the present study (Tables 1 and 2) do not indicate any significant impact on the PVS sediments from the Los Angeles Harbor.

Finally, the mechanisms responsible for the observed DDT mass reduction in sediments of the PVS in the 1980s (Lee 1994, Niedoroda *et al.* 1996, Young *et al.* 1976) could affect the significance of sediments as a source of contamination. The presence of suspended DDTs in the water column suggests that DDT mass reduction may be caused by ocean currents carrying suspended DDTs out of the contaminated area. The estimated net flux of DDTs (Table 4) indicates the significance of physical dispersal in reducing the sediment DDT mass. In addition, the wide-spread distribution of DDTs in sediments of the Santa Monica and San Pedro Basins, along with the high percentage of DDEs among the total DDTs in surface sediment (Venkatesan 1994), also suggests that DDTs originally deposited in near-shore regions may have been transported to the basins.

Another mechanism that may reduce the significance of sediments as a source of contamination is biodegradation. A recent publication by Quensen *et al.* (1998) documented evidence for the transformation of DDE into DDMU in a marine microcosm study, where sediments from the PVS were incubated at 22 to 25°C with either sulfate or sodium chloride (both maintaining the same ionic strength). This finding, combined with the *in-situ* detection of DDMU in PVS sediments (Lee 1994), supports the theory that a biodegradation mechanism leads to reduced DDT mass in sediments of the PVS. The biodegradation mechanism would eventually eliminate DDTs within sediments and therefore dismiss sediments as a source of contamination. However, whether *in-situ* biodegradation is effective in transform-

ing DDTs to other less hazardous and less bioavailable metabolites remains a debatable issue (Renner 1998).

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