

Response to Comment on “In Situ Measurements of Chlorinated Hydrocarbons in the Water Column off the Palos Verdes Peninsula, California”

SIR: Thank you for the opportunity to respond to Paulsen et al.’s comments (1) on our previous publication (2) documenting the distribution of DDT and PCB concentrations in the water column of the Palos Verdes Shelf (PVS), California. While Paulsen et al. have made valuable remarks on the long-debated issue of DDT contamination on the PVS (3), they fail to invalidate the two key conclusions of our paper: (i) the water column concentrations of total DDT and PCB at all the sampling locations (and depths) exceeded the discharge limits established by the California Ocean Plan (4) and (ii) the primary source of DDT contamination in the water column appeared to be the PVS sediments.

Paulsen et al. disagree with our second conclusion but apparently not with the first one. Our second conclusion was based on four observations/arguments. First, the spatial distribution of DDTs (and PCBs) in the water column at the 1-m depth from the ocean floor exhibited a pattern similar to that of sediment *p,p'*-DDE (5), i.e., the highest concentration occurred around stations 6C and 7C near the Joint Water Pollution Control Plant (JWPCP) outfall system (Figure 1 in ref 2). Second, the water column concentrations of DDTs (and PCBs) decreased exponentially with increasing distance from the ocean floor. Third, the characteristics of partitioning of DDTs and PCBs between the surface sediment and overlying water, assessed from the measured DDT and PCB concentrations and two sets of empirical parameters (6, 7) relating K_{oc} and K_{ow} , favored a thermodynamic process that transported DDTs (and PCBs) from the sediment to the overlying water. Lastly, external sources, such as the JWPCP outfall, aerial deposition, and land-derived runoff, appeared inadequate to account for the distribution and magnitude of DDT contamination in the PVS water column. Paulsen et al. appear to disagree only with the third and last arguments. Our responses to their comments are presented below.

Thermodynamic Driving Force. Paulsen et al. argue that the higher porewater concentrations of *p,p'*-DDE near the sediment–water interface than inside the sediments (8) provided a driving force for the diffusion of DDTs from the sediment–water interface into the sediments. They also argue that the $\log K_{ow}$ value for *p,p'*-DDE should be higher than 5.83 as cited in our publication (2) and that a higher $\log K_{ow}$ value would negate our conclusion that loss of DDTs from the sediment to the overlying water was thermodynamically possible via diffusion. However, Paulsen et al.’s first argument does not contradict our conclusion mentioned above based on the assessment of partitioning of DDT and PCB compounds between the sediments and the overlying water. In fact, the large difference between the concentrations of *p,p'*-DDE in the overlying water [~ 5 ng/L (2)] and in the surface sediment porewater [~ 80 – 100 ng/L (8)] is in favor of the diffusion of *p,p'*-DDE from the sediment–water interface to the overlying water. This is further corroborated by the fact that the concentrations of DDTs (and PCBs) in the water column decreased exponentially with increasing distance from the sediment–water interface at station 6C (2).

The interpretation by Paulsen et al. of partition coefficients and available field data (2, 8), which is the basis of their

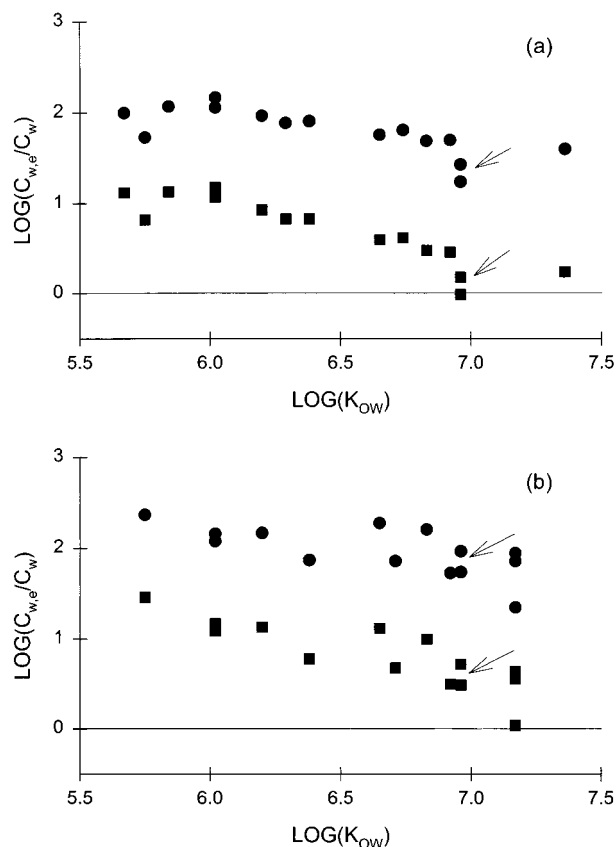


FIGURE 1. Correlation of $\log(C_{w,e}/C_w)$ with $\log K_{ow}$ for DDT components and selected PCB congeners partitioning between the sediment and the water column dissolved phase at station 6C (1 m from the sea floor) modified from Figure 4 in ref 2. Arrows point to the revised values of $\log(C_{w,e}/C_w)$ for *o,p'*-DDE and *p,p'*-DDE using a new value of $\log K_{ow}$ (6.96) for DDE. Samples were collected in (a) winter 1997 and (b) summer 1997. Circles and squares are derived using *a* and *b* values obtained by Schwarzenbach and Westall (6) and Karickhoff et al. (7), respectively.

second argument, is incorrect. First, the measured porewater concentrations (C_w) of DDTs obtained by Eganhouse (8) are not necessarily at equilibrium with the sediment DDT concentrations. The true K_p can be expressed as $C_p/C_{w,e}$ with C_p being the solid-phase concentration and $C_{w,e}$ being the dissolved phase concentration equilibrating with the solid phase. The measured porewater concentration, C_w , obtained by Eganhouse (8) could not be used to calculate K_p unless an equilibrium partitioning between the sediment and the sediment porewater was assured. In fact, the difference between $C_{w,e}$ and C_w dictates the magnitude of thermodynamic driving force. Second, K_{ow} is another equilibrium parameter characterizing the partitioning of a specific compound between octanol and water. K_{ow} may not be calculated directly from the measured porewater concentration C_w for the same reason discussed above. The equation of $\log K_{oc} = a \log K_{ow} + b$ is simply a tool to estimate K_{oc} from K_{ow} , since K_{oc} is more difficult to obtain practically as compared to K_{ow} . The values of *a* and *b* proposed by Schwarzenbach and Westall (6) and Karickhoff et al. (7) represented the high and low ends of K_{oc} values measured experimentally. Third, the K_{ow} value for *p,p'*-DDE quoted by Paulsen et al. appears to be at the high end of a range of K_{ow} values obtained by different researchers using various experimental techniques (9). A large variation in the reported

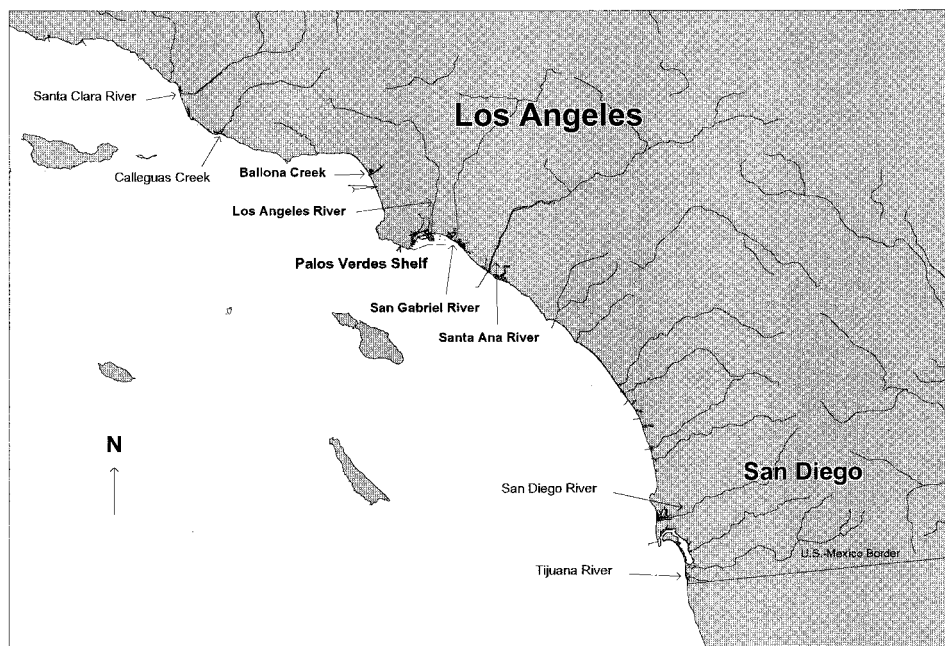


FIGURE 2. Map of the Southern California Bight showing eight major rivers and creeks sampled during 1986–1987 and 1987–1988 in a previous study (10).

TABLE 1. Mass Emissions (kg) of DDTs and PCBs from Major Rivers and Creeks to the Southern California Bight in 1986–1987 and 1987–1988^a

sampling time	1986–1987			1987–1988		
	DDTs	PCBs	PCB/DDT	DDTs	PCBs	PCB/DDT
Ballona Creek						
high flow	2.1	2.0	0.95	7.7	7.0	0.91
low flow	0.3	0.7	2.3	0.2	0.7	3.5
Los Angeles River						
high flow	9.7	18.8	1.9	19.8	38.4	1.9
low flow	1.0	1.9	1.9	0.9	1.9	2.1
San Gabriel River	7.0	18.5	2.6	6.9	18.4	2.7
Santa Ana River	1.0	1.4	1.4	1.5	2.0	1.3
Sum of Four Rivers	19.8	40.7	2.1	35.9	65.8	1.8
total ^b	29.4	54.3	1.8	62.1	102.0	1.6

^a Edited from ref 10. DDTs include *o,p'*-DDT, *p,p'*-DDT, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDE, and *p,p'*-DDE. PCBs include Aroclor 1242 and Aroclor 1254.

^b Also include Santa Clara River, Calleguas Creek, San Diego River and Tijuana River in addition to the four rivers listed (Figure 2).

K_{ow} values for DDT and DDE compounds was also noted (9). Even if the higher K_{ow} value ($\log K_{ow} = 6.96$ instead of 5.83) for DDE is used, only the lower points representing *o,p'*-DDE and *p,p'*-DDE in Figure 4 in ref 2 are brought down close to zero; the higher points remain greater than zero. Figure 1 depicts the modified correlation between $\log(C_{w,e}/C_w)$ and $\log K_{ow}$ using the higher K_{ow} value for DDE. The thermodynamic driving force still favored the diffusion of DDT and PCB compounds from the surface sediment to the overlying water. Finally, higher than expected C_p/C_w (not K_p) values as quoted by Paulsen et al. actually favors the diffusion of *p,p'*-DDE from the sediment to the sediment porewater, since $\log(C_{w,e}/C_w) = \log(C_p/C_w) - \log K_p$.

Alternate Sources of DDTs. Paulsen et al. do not dispute our assessment of the JWPCP outfall system and aerial deposition being insignificant sources contributing DDTs to the PVS water column. However, they suggest that land-derived runoff inputs, instead of the PVS sediments, are responsible for the presence of significant amounts of DDT compounds in both the water column and the surface sediments. The possible land-derived inputs of DDTs might not be thoroughly examined in our previous publication (2), and we appreciate this opportunity to revisit the issue.

Besides the Los Angeles Harbor, other significant runoff sources most adjacent to the PVS include Los Angeles River, San Gabriel River, Santa Ana River, and Ballona Creek (Figure 2). In a study cited by Paulsen et al., the Southern California Coastal Water Research Project (SCCWRP) measured DDTs, PCBs, and other contaminants in eight largest rivers and creeks in southern California and estimated the mass emissions of these contaminants in 1986–1987 and 1987–1988 (10). The four rivers and creeks mentioned above were included in SCCWRP's study. Re-analysis of the results from this study (10) clearly rules out the possibility of land-derived inputs as a significant source of DDTs to the PVS based on three arguments.

First, the mass emissions of DDTs and PCBs from Ballona Creek and Los Angeles River in 1986–1987 and 1987–1988 showed strong seasonal variations corresponding to periods of high and low flows (Table 1). On the other hand, the water column concentrations of DDTs and PCBs measured in January/March 1997 (wet weather season) and June/July 1997 (dry weather season) were essentially the same (2). If land-derived inputs were the dominant source of contamination, there would have been a substantial seasonal difference in the concentrations of DDTs and PCBs in the water column

of the PVS. Second, the ratio of the PCB and DDT mass emissions varied from 0.9 to 3.5 for the runoff sources (Table 1), while the ratio of PCB and DDT concentrations in the water column (as well as in sediments) of the PVS was approximately 0.1 (2). Unless a large portion of PCBs is lost during transportation, DDTs found in both the water column and surface sediment on the PVS are unlikely to significantly derive from land-derived inputs. Lastly, the sufficiently low annual mass emission of DDTs measured in 1987–1988 from Los Angeles River or even from all eight major rivers and creeks (Table 1) simply could not account for the magnitude of DDT contamination in the surface sediments of the PVS, as shown below.

To simplify the process of calculation, we consider the same area defined previously (2), which is about ~20 km². The United States Geological Survey (USGS) analyzed a large number of sediment cores for DDTs (as well as other contaminants) collected from the PVS in 1992 (11). Among the 45 surface sediment samples, total DDT concentrations ranged from 0.014 to 27.1 µg/g (dry weight based) with an average of 5.5 µg/g and a median value of 4.1 µg/g. Using an average concentration of 2 µg/g (or 1 µg/g wet sediment weight), the mass emission of DDTs to the sediments within the designated area is estimated to be 160 kg/yr using the sedimentation rate of 800 mg cm⁻² yr⁻¹ cited by Paulsen et al. As a comparison, the DDT mass emissions from Los Angeles River, the four rivers most adjacent to the PVS, and all the eight rivers and creeks in 1987–1988 were 19.8, 35.9, and 62.1 kg, respectively (Table 1). It is important to note that dilution and dispersion processes would substantially reduce the amount of land-derived DDTs available for transport to the PVS.

Shelf Sedimentation Dynamics. Paulsen et al. also comment on an ancillary part of our study which estimated the flux rate of DDTs across the PVS. Paulsen et al. contend that our estimated DDT flux rate would lead to the conclusion that the PVS is eroding at a prodigious rate. Although this flux estimate was preliminary and based on a model with limited field data (2), we do not believe that Paulsen et al.'s suggestion is valid. It is possible that exchange of DDT-bound particles from the PVS with newly depositing particles containing little or no DDTs may result in a net flux of DDTs from the PVS to areas outside the PVS. In addition, loss of DDTs through the surface sediments can be offset by continuous upward remobilization of buried DDTs inside the sediment column. The latter process helped to maintain a relatively steady concentration profile of DDTs near the surface sediments.

Lastly, Paulsen et al. point out that the peak metals concentrations in sediment cores had remained approximately constant, while the peak DDT concentrations had

steadily declined (11). Paulsen et al. therefore conclude that transfer of DDTs from sediments to the overlying water is impossible without affecting the metals concentrations. However, one scenario may explain why DDTs are being moved upward in the sediment column while the concentration levels of trace metals remain steady. The mass emission data compiled by SCCWRP indicated that trace metals inputs in 1996 from four major municipal wastewater treatment plants in southern California dropped to about 10% of those in 1971, while the DDT inputs were decreased by more than four orders of magnitude over the same period (12). The mass emissions of trace metals and DDTs from the JWPCP outfall system approximately followed the same trend. It is thus quite possible that the steadiness of trace metals concentrations may be due to new inputs of freshly discharged particles enriched with trace metals but containing essentially no DDTs.

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Eddy Y. Zeng* and Kim Tran

Southern California Coastal Water Research Project
7171 Fenwick Lane
Westminster, California 92683

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