APPENDIX D
PSD REPORT (FLUEN POINT ENVIRONMENTAL)

Palos Verdes Shelf 2013 Water Column Passive Samplers Deployment: Data Summary

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Executive Summary

In September 2013, two passive sampling methods were employed to determine dissolved concentrations of dichlorodiphenyltrichloroethane breakdown products (DDTs), and polychlorinated biphenyls (PCBs) in the water column above the Palos Verdes Shelf Superfund site. This work was in follow-up to a similar passive sampling program completed in 2010 and used polyethylene strips (PE) and solid-phase microextraction fibers (SPME). The current work replicated results indicating increasing dissolved DDT and PCB concentrations with proximity to sediment bed, and increasing dissolved concentrations in a north-west direction along the shelf until Station 4C when the concentrations begin to decrease again. Dissolved concentrations of DDTs measured in this work were within a factor of three of those measured using identical methods three years previously in 2010. Application of temperature correction factors to PE-determined concentrations reduced the calculated dissolved concentrations by an average factor of two. Employment of performance reference compounds to correct for disequilibrium between SPME and water column increased calculated DDT concentrations by an average factor of three. Similar biases in DDT concentrations determined using the two passive sampling devices remained, however, with PE methods generating higher dissolved DDT concentrations than SPME methods by an average factor of two.

Introduction

The Palos Verdes Shelf (PVS) Superfund site off the coast of California near Los Angeles County is a 320-acre site contaminated with dichlorodiphenyltrichloroethane (DDT) and its breakdown products, and polychlorinated biphenyls (PCBs). Biennial sampling of bulk sediment suggests that contaminant concentrations in shelf sediments are decreasing. Monitoring of water column concentrations is needed to determine if a similar trend exists in the waters above the contaminated zone. Passive water sampling methods have shown promise as inexpensive tools for determining time-averaged, low-concentrations of persistent organic pollutants in marine environments. In addition, passive samplers can be deployed concurrently at multiple stations and depths in the water column.

In September 2010, two techniques using passive sampling devices (PSDs) were employed to measure the freely-dissolved concentrations (C_W) of DDTs and PCBs at eleven stations throughout the PVS and at a background station (T11) (Figure 1). Solid-phase microextraction fibers (SPME) and polyethylene strips (PE) were used. Following month-long deployments, full equilibration between SPME and the water column was assumed, while the transfer of performance reference compounds (PRCs) from PE was used to calculate the fractional equilibration between PE and water column. Using these methods, elevated DDT and PCB freely dissolved concentrations were detected throughout the water column and all around the PVS site. In addition, values of C_W determined using PE for individual compounds were three times greater than those determined using SPME. Two possible explanations for this difference are that the equilibrium assumption for SPME samplers is incorrect, or that the partitioning coefficients used to calculate C_W from polymer concentrations are inaccurate (Fernandez et al., 2012).

Given the need to establish baseline water column concentrations and to understand temporal changes of dissolved DDT and PCB concentrations above the contaminated zone while improving passive sampling methodologies, the following objectives were pursued in the 2013 PSD sampling event:

(1) compare water column concentrations of DDTs and PCBs generated using PE passive sampling methods in this work to those measured using the same methods in 2010,
(2) compare water column concentrations of DDTs determined using SPME and PE, while using PRCs to determine fractional equilibration of both types of samplers, and
(3) determine if deeper water stations, not sampled in 2010, differed from stations along the 60 meter isotherm.

Materials and Methods

Sampler materials and preparation were as described in Fernandez et al. (2012) with the addition of steps for loading SPME fibers with PRCs. Pre-cleaned SPME fibers were loaded in a solution of acetone/methanol/DI water (4:4:2, v/v) containing PCBs 50, 98, 155, and 184 (AccuStandard, New Haven, CT, USA), and ^{13}C-labeled PCB 52, PCB 128, and p,p'-DDE (Cambridge Isotope, Andover, MA, USA). The nominal concentration of the PRCs in solution was 0.5 mg/L. Fibers were immersed in a 20-mL glass tube stirred at 250 rpm by a Teflon-covered stir bar (8 mm × 1.5 mm) for 4 h in a dark room maintained at ≈ 22 °C. Pre-loaded fibers were rinsed with DI water, air dried for 2 min, rinsed with methanol and air dried for another 2 min, retracted into the needle and stored in 40-mL scintillation vial in freezer (-20°C) until use.

Field deployments of passive samplers Samplers were deployed on September 5th and 6th, 2013. PE samplers loaded with PRCs (^{13}C-4,4'-DDT, -4,4'-DDE, -4,4'-DDD, -PCB28, -PCB52, -PCB118, and -PCB128) were deployed at 16 stations on the PVS and at one background station T11 (see Figure 1). SPME samplers, also loaded with PRCs (^{13}C-4,4'-DDE, PCB 50, ^{13}C-PCB 52, PCB 98, ^{13}C-PCB 128, PCB 155, and PCB 184), were co-deployed with PE samplers on the same mooring lines at five stations on the PVS (4C, 7C, 8C, 9C, and W3) and at the background station. As in the 2010 sampling program, samplers were deployed at three depths at each station: 5 m below the surface (near-surface); mid-column; and 5 m above the sediment-water interface (near-bottom). PE and SPME samplers were deployed in triplicate at each station/depth. Water temperature and conductivity were measured using conductivity-temperature-depth meter (CTD) casts at the time of retrieval.

Samplers were recovered in the same order they were deployed 32 days later, on October 8th and 9th, 2013. The problem of PE sampler loss during deployment, encountered during the 2010 sampling campaign was solved by the use of stainless steel wire for threading of sampler polymer to the deployment gear. Some losses of samplers still occurred. Surface samplers were most often missing with one surface sampler missing from station 7C, and all three surface samplers missing from stations 8C and 9C. One near-bottom sampler from station W3 was missing. Also, an entire mooring line from station W5 was not recovered. While all SPME samplers were recovered, two failed before they could be analyzed, one of three from near-bottom at station 4C, and one of three from near-bottom at station 7C. All retrieved samplers were transported to the Southern California Coastal Water Research Programs (SCCWRP) laboratory facilities on ice for storage and analysis.

Partition coefficients Two sets of PE-water partition coefficients (K_{PEW}) for DDTs and PCBs were used in this study. One set was determined from laboratory measurements (in seawater) and published values (see Fernandez et al. (2012) and references therein). These partition coefficients were originally used to calculate C_W from the mass of PCBs and DDTs taken up by samplers in the study completed in 2010. In addition, incorporating recent advancements in passive sampling methods, these partition coefficients were adjusted for the effects of water temperature and salinity following Lohmann (2012) (Table 1). Calculated values using both sets of partition coefficients are reported here. SPME-water partitioning coefficients ($K_f V_f$) used to calculate freely-dissolved water concentrations from the mass of DDTs and PCBs in SPME were the same as those used in the 2010 study (Table 1).

Calculation of dissolved DDT and PCB concentrations SPME-water and PE-water partition coefficients were used to calculate C_W, where PRCs were used to determine the fractional

equilibration, f_{eq}, of both samplers with the water-column. For SPME, the following calculation was applied:

$$C_{W(SPME)} = \frac{N_f/(K_f V_f)}{f_{eq}} \quad (1)$$

while for PE, this equation was used:

$$C_{W\ (PE)} = \frac{C_{PE}/K_{PEW}}{f_{eq}} \quad (2)$$

For both samplers, Equation 3 is used to determine f_{eq}:

$$f_{eq} = \frac{C^0_{PRC} - C_{PRC,t}}{C^0_{PRC}} \quad (3)$$

For these three equations, N_f is the mass of target chemical in the SPME fiber, K_f is the SPME-water partition-coefficient (L_W/L_{PDMS}), V_f is the volume of sorptive coating (L_{PDMS}), C_{PE} is the concentration of target chemical in the polyethylene sampler (ng/kg_{PE}), K_{PEW} is the PE-water partition coefficient (L_W/kg_{PE}), C^0_{PRC} is the initial concentration of loaded PRCs in the unexposed samplers, and $C_{PRC,t}$ is the concentration of PRC in the sampler after deployment.

Results and Discussion

PRCs in PE and SPME As mentioned above, one difference between this study and the previous passive sampler deployment at this site was that PRCs were loaded into both the PE and SPME samplers. This was performed in order to determine the proximity to equilibration with the water column of both types of samplers. As observed in the 2010 campaign, PRCs indicated that PE samplers and the water column were more closely equilibrated for ^{13}C-*p,p*'-DDD (avgerage f_{eq} for all samplers = 92%) than for ^{13}C-*p,p*'-DDE (average f_{eq} for all samplers = 60%). Also, each PE sampler showed a decreasing degree of equilibration with increasing degree of chlorination in PRCs, with the average f_{eq}= 95% for ^{13}C-PCB 28 and average f_{eq}=26% for ^{13}C-PCB 128. These patterns were expected, as the distribution between PE and water for less hydrophobic compounds reaches equilibrium levels more quickly than for more hydrophobic compounds (Booij et al., 2002). In the 2013 deployment, a similar equilibration pattern was observed for PCB PRCs in SPME fibers with average f_{eq}=59% for PCB 50 and average f_{eq}=22% for PCB 184.

While no pattern in degree of equilibration with depth of deployment is observed in the SPME samplers, PE samplers appear to be more equilibrated with the water column in the near-surface samplers as compared to the near-bottom samplers. For example, f_{eq} of DDE in PE sampler averaged 97% (± 2% (one standard deviation (SD), n=14)) in the near-surface deployment, 55% (±12%) in the mid-column deployments, and 43% (±13%) in the near-bottom deployments. Similar patterns are seen for all other PRCs. This equilibration pattern is expected considering the decreasing temperature with depth and currents at different depths affecting contaminant transport into and out of the polymer. Larger K_{PEW} and slower molecular diffusivity within the polymer due to lower temperature would cause the mass transfer rates between sampler and water to decrease, leading to slower equilibration. No patterns in sampler equilibration with distance from shore, or distance along the shelf were observed.

Comparison of C_W determined using PE and SPME methods To compare the level of agreement between C_W determined using the two types of samplers in the current study to the level of agreement observed in the 2010 study, the same K_{PEW} values were applied to calculate $C_{W,PE}$. These K_{PEW} values do not include corrections for temperature effects. Similar bias was observed in the current study as had been observed in 2010. Dissolved concentrations of *p,p'*-DDE, *o,p*'-DDE, and *p,p*'-DDMU calculated from PE data were generally higher than those calculated from SPME data (Figure 2), and the bias increased with depth (and disequilibration) of the sampler. If PRCs had not been used to correct for disequilibrium between SPME and the water column, the observed bias would have been even greater. Correcting for temperature effects on K_{PEW} reduces the bias observed between sampling methods (Figure 3). For example, PE-determined C_W remain generally higher than SPME-determined C_W, but the bias is reduced to an average factor of 1.4 for *p,p*'-DDE and 6.0 for *o,p*'-DDE.

As previously noted, several parameters must be incorporated to calculate C_Ws when using passive samplers. Currently, the way these parameters are applied is not standardized across all types of samplers. For example, different types of samplers (i) use different partition coefficients (K_f, K_{PEW}); (ii) adjust estimated C_W concentrations for non-equilibrium while others assume equilibrium; and (iii) include the effects of salinity and temperature on partition coefficients. As a result of the differences, variations in the calculated dissolved concentrations can occur. In this study, these differences are readily observable in the dissolved concentrations of individual DDT compounds (Tables 2 through 7). The development of standards and standard operating procedures for PSDs remains a work in progress; consequently, it is critical to understand that the values presented represent values specific to a type of sampler using unique parameters. Given these considerations, it is not possible to state which values are the "correct" ones – rather these values should be used to bracket likely environmental concentrations and examine general concentration trends.

Comparison of C_W determined in current study with those observed in 2010 To directly compare values between the two studies, SPME-determined ΣDDT C_W without PRC adjustments and PE-determined concentrations without temperature corrections were compared to the values calculated in 2010. ΣDDT includes concentrations of *p,p*'- and *o,p*'- congeners of DDE, and DDD and non-detects were not included in the sum. Parent DDTs were below detection limits in the 2010 study and were not analyzed in the 2013 work. SPME-determined concentrations in the current study were within a factor of two of those determined in 2010 when samplers were not corrected for disequilibrium using PRC (Figure 4). PRC corrections to SPME increased the calculated concentrations by an average factor of three. Similarly, PE-determined ΣDDT C_W in this study were within a factor of three of those found in 2010 (Figure 5). Correcting for the effects of temperature in this work reduced the calculated concentrations, but they remained within an average factor of three of those measured in 2010. As we consider them to be the most accurate, data analysis for the remainder of this report will focus on the PRC and temperature effects corrected values.

General concentration trends PE-determined values will be used to illustrate spatial trends at the site as SPME samplers were only deployed at a limited number of stations. Also, the larger mass of PE samplers allows for the detection of PCBs and DDTs occurring at very low concentrations such as DDNU and many PCB congeners.

Total detectable dissolved DDT (ΣDDT C_W) determined using PE ranged from 41 pg/L at the surface at Station W4, to 10,500 pg/L near the bottom at Station 4C (Figure 6). Total detectable PCBs (ΣPCB C_W) ranged from 1 pg/L at the surface and mid-column of the T11 background station, to 309 pg/L near the bottom of Station 4C (Figure 7). Stations T11 and 4C also had the lowest and highest dissolved concentrations, respectively, in the 2010 study.

As previously observed, concentrations of DDTs and PCBs appear to increase with depth in the water column and distance from the Sanitation Districts' outfall at White Point in a north-west direction along the shelf through station 4C. Concentrations then decrease to the north-west of station 4C with similar concentrations observed in the water column at Station 3C and 1C (Figures 6, 7, 8, and 9). In the cross-shelf direction (i.e., along transects perpendicular to the shoreline), dissolved concentrations of DDTs and PCBs appear to be highest near the 60 m isobath, except at the stations nearest the outfall (8DC, 8C, W4) where the highest concentrations are observed at Station 8DC (Table 8, Figures 10 and 11).

In addition to the stations investigated in the 2010 study, five additional stations (W1-W5) were sampled in this work. These stations were added to provide additional data for the boundary

conditions of a box model for PVS. Results of this modeling work will be reported separately. However, modeling indicates that the highest dissolved concentrations would be expected near Station 4C if currents carry water in a generally along the shelf until the area where Long Point begins to affect flow trajectories. Stations W2, W3, and W4 are located along the 200m isobath to the south and west of the stations studied in 2010. While the general trend of increasing concentration with water depth was also observed at these stations, the mid-column deployments were sampling water 100 m below the surface. Along PVS where the most contaminated sediments are found, these deeper stations (W3 and W4) show lower near-bottom DDT and PCB concentrations than the shallower stations along transects perpendicular to the shoreline (Figures 10 and 11). In the area down-current of the shelf (W1 and W2), near-bottom DDT and PCB concentrations are similar at the 60m and 200m stations (Tables 8 and 9).

Compound specific results As previously observed, *p,p*'-DDE is responsible for the largest fraction of the ΣDDT at each station/depth (80% on average). Dissolved *p,p*'-DDMU, a DDT form not included in ΣDDT, was observed at nearly the same concentrations as *p,p*'-DDE in the near-surface samplers (average factor of 1.1 ±0.2), while dissolved concentration of *p,p*'-DDMU in the deeper locations averaged 30% of the *p,p*'-DDE concentration at each station/depth (Table 6). Similarly, dissolved *p,p*'-DDNU was observed at water concentrations averaging 44% of *p,p*'-DDE C_W in the near-surface while at an average of 9% of *p,p*'-DDE C_W in the deeper waters (Table 7).

In the 2010 study, PCB congeners 101, 110 and 118 were observed at the highest dissolved concentrations in the near-bottom sample at Station 4C. In the current work, PCBs 101 and 110 were observed to at the highest concentrations at this same station and depth (61 and 46 ng/L, respectively) (Figure 12). In 2010, PCB 118 was determined to have a concentration of 54 pg/L near the bottom at 4C, while in the current study the concentration was determined to be 26 ng/L. In the current study, PCB 87 and PCB 99 were also measured at similarly high concentrations (32 and 31 ng/L, respectively). ΣPCB concentrations measured in this work are also similar to those measured by Burgess et al. at nearby stations during a 2009 study using similar sampling methods (200-400 pg/L at stations located between 5C and 7C and 50-100 pg/L at a station located between 5DC and 7DC) (Burgess et al., 2015).

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Tables

Table 1. Target compounds and sampler-water partition coefficients

Compound	$K_f V_f \times 10^{-4}$ (μL_W)	log K_{PEW} (L_W/kg_{PE})	log $K_{PEW,\ 16ºC}$ (L_W/kg_{PE})	log $K_{PEW,\ 12ºC}$ (L_W/kg_{PE})	log $K_{PEW,\ 11ºC}$ (L_W/kg_{PE})
p,p'-DDE	34.08	5.46	5.61	5.76	5.78
o,p'-DDE	58.24	5.46	5.61	5.76	5.78
p,p'-DDD	9.76	5.26	5.41	5.55	5.58
o,p'-DDD	13.87	5.26	5.41	5.55	5.58
p,p'-DDMU	49.7	5.26	5.41	5.55	5.58
p,p'-DDNU	47.5	4.92	5.07	5.21	5.24
PCB8	2.8	4.85	5.00	5.14	5.17
PCB18	7.93	5.01	5.16	5.30	5.33
PCB28	10.65	5.43	5.58	5.73	5.75
PCB37	12.28	5.58	5.83	5.98	6.00
PCB44	19.05	5.51	5.66	5.81	5.83
PCB49	20.26	5.60	5.75	5.9	5.92
PCB52	20.27	5.59	5.74	5.89	5.91
PCB66	23.11	5.94	6.09	6.24	6.26
PCB70	20.4	5.94	6.09	6.24	6.26
PCB74	20.26	5.94	6.09	6.24	6.26
PCB 77	39.22	6.37	6.52	6.67	6.69
PCB81	25.5	6.21	6.36	6.51	6.53
PCB87	23.75	6.03	6.18	6.33	6.35
PCB99	22.8	6.13	6.28	6.43	6.45
PCB101	25.11	6.12	6.27	6.42	6.44
PCB105	33.58	6.38	6.53	6.68	6.70
PCB110	23.24	6.10	6.25	6.40	6.42
PCB114	29.92	6.38	6.53	6.68	6.70
PCB118	28.66	6.46	6.61	6.76	6.78
PCB119	23.07	6.31	6.46	6.61	6.63
PCB123	28.09	6.46	6.61	6.76	6.78
PCB 126	32.85	6.88	7.03	7.18	7.20
PCB128	20.96	6.46	6.61	6.76	6.78
PCB138	19.2	6.55	6.70	6.85	6.87
PCB149	23.1	6.40	6.55	6.70	6.72
PCB 151	27.25	6.10	6.25	6.40	6.42
PCB153/168	17.59	6.64	6.79	6.94	6.96
PCB 156	17.12	6.98	7.13	7.28	7.30
PCB157	15.7	6.89	7.04	7.19	7.21
PCB158	20.69	6.74	6.89	7.04	7.06
PCB167	14.53	6.98	7.13	7.28	7.30
PCB 169	14.37	7.12	7.27	7.42	7.44

Table 1. (continued) Target compounds and sampler-water partition coefficients

Compound	$K_f V_f \times 10^{-4}$ (μL_W)	log K_{PEW} (L_W/kg_{PE})	log $K_{PEW,\ 16ºC}$ (L_W/kg_{PE})	log $K_{PEW,\ 12ºC}$ (L_W/kg_{PE})	log $K_{PEW,\ 11ºC}$ (L_W/kg_{PE})
PCB170	6.69	6.98	7.13	7.28	7.30
PCB177	9.04	6.79	6.94	7.09	7.11
PCB180	7.35	7.07	7.22	7.37	7.39
PCB183	7.74	6.61	6.76	6.91	6.93
PCB187	8.85	6.91	7.06	7.21	7.23
PCB189	6.34	7.41	7.56	7.71	7.73
PCB194	3.23	7.49	7.64	7.79	7.81
PCB 200	5.06	6.89	7.04	7.19	7.21
PCB201	3.73	7.32	7.47	7.62	7.64
PCB206	1.88	7.77	7.92	8.07	8.09
PCB209	64.1	7.86	8.01	8.16	8.18

Table 2. *p,p*'-DDE concentrations determined using PE with PRC and temperature corrections and SPME with PRC correction (pg/L)

	PE			SPME		
Station	near-surface	mid-column	near-bottom	near-surface	mid-column	near-bottom
BA1C	89	1490	3623			
BA3C	149	1887	3591			
BA4C	126	1606	8793	147	756	1845
BA5C	101	2181	5810			
BA5DC	152	1247	3579			
BA7C	102	1449	5467	147	836	2265
BA7DC	103	837	2505			
BA8C	no data	1208	1238	136	714	1731
BA8DC	56	478	2806			
BA9C	no data	446	1044	109	401	871
BA9DC	78	479	1108			
W1	64	724	1308			
W2	57	293	1009			
W3	59	358	1593	122	522	1843
W4	31	307	1030			
W5	no data	no data	no data			
T11	<6.67	25	39	72	93	<7.48

Table 3. *o,p*'-DDE concentrations determined using PE with PRC and temperature corrections and SPME with PRC correction (pg/L)

	PE			SPME		
Station	near-surface	mid-column	near-bottom	near-surface	mid-column	near-bottom
BA1C	28	259	630			
BA3C	47	337	679			
BA4C	36	302	1674	10	55	148
BA5C	35	399	1119			
BA5DC	43	216	671			
BA7C	34	270	1076	6	61	184
BA7DC	32	167	466			
BA8C	no data	209	247	6	52	140
BA8DC	22	83	525			
BA9C	no data	71	180	5	25	61
BA9DC	28	85	203			
W1	20	129	226			
W2	17	42	159			
W3	17	51	256	5	29	120
W4	10	47	175			
W5	no data	no data	no data			
T11	<6.20	<7.79	<9.46	<3.69	<3.69	<3.69

Table 4. *p,p'*-DDD concentrations determined using PE with PRC and temperature corrections and SPME with PRC correction (pg/L)

	PE			SPME		
Station	near-surface	mid-column	near-bottom	near-surface	mid-column	near-bottom
BA1C	<12.2	16	22			
BA3C	<12.2	20	39			
BA4C	<12.2	21	48	<46.2	<46.2	111
BA5C	<12.2	25	63			
BA5DC	<12.2	22	40			
BA7C	<12.2	17	57	<46.2	58	176
BA7DC	<12.2	<9.16	15			
BA8C	no data	<9.16	26	<46.2	57	143
BA8DC	<12.2	<9.16	34			
BA9C	no data	<9.16	9	<46.2	<46.2	61
BA9DC	<12.2	<9.16	16			
W1	<12.2	<9.16	<8.97			
W2	<12.2	<9.16	16			
W3	<12.2	<9.16	27	<46.2	<46.2	141
W4	<12.2	<9.16	31			
W5	no data	no data	no data			
T11	<12.2	<9.16	<8.97	<46.2	<46.2	<46.2

Table 5. *o,p*'-DDD concentrations determined using PE with PRC and temperature corrections and SPME with PRC correction (pg/L)

	PE			SPME		
Station	near-surface	mid-column	near-bottom	near-surface	mid-column	near-bottom
BA1C	<7.72	7	12			
BA3C	<7.72	9	17			
BA4C	<7.72	8	20	<12.6	16	35
BA5C	<7.72	8	20			
BA5DC	<7.72	7	13			
BA7C	<7.72	<5.78	17	<12.6	17	44
BA7DC	<7.72	<5.78	<5.66			
BA8C	no data	<5.78	8	<12.6	17	38
BA8DC	<7.72	<5.78	9			
BA9C	no data	<5.78	4	<12.6	<12.6	20
BA9DC	<7.72	<5.78	4			
W1	<7.72	<5.78	6			
W2	<7.72	<5.78	8			
W3	<7.72	<5.78	13	<12.6	<12.6	47
W4	<7.72	<5.78	13			
W5	no data	no data	no data			
T11	<7.72	<5.78	<5.66	<12.6	<12.6	<12.6

Table 6. *p,p'*-DDMU concentrations determined using PE with PRC and temperature corrections and SPME with PRC correction (pg/L)

	PE			SPME		
Station	near-surface	mid-column	near-bottom	near-surface	mid-column	near-bottom
BA1C	107	448	993			
BA3C	143	557	1420			
BA4C	115	540	1600	16	89	321
BA5C	111	510	1518			
BA5DC	121	382	1170			
BA7C	89	396	1336	9	87	324
BA7DC	102	234	659			
BA8C	no data	272	527	8	82	244
BA8DC	76	142	737			
BA9C	no data	98	295	8	32	99
BA9DC	107	122	310			
W1	76	285	520			
W2	58	121	288			
W3	59	139	797	8	50	284
W4	36	175	682			
W5	no data	no data	no data			
T11	<12.5	<9.36	<9.17	<7.3	<7.3	<7.3

Table 7. *p,p'*-DDNU concentrations determined using PE with PRC and temperature corrections and SPME with PRC correction (pg/L)

	PE			SPME		
Station	near-surface	mid-column	near-bottom	near-surface	mid-column	near-bottom
BA1C	33	119	279			
BA3C	65	158	376			
BA4C	26	159	382	<6.48	<6.48	21
BA5C	62	151	386			
BA5DC	69	142	336			
BA7C	63	102	243	<6.48	<6.48	14
BA7DC	24	85	173			
BA8C	no data	80	118	<6.48	<6.48	10
BA8DC	28	61	139			
BA9C	no data	27	64	<6.48	<6.48	7
BA9DC	<21.7	38	95			
W1	22	74	133			
W2	34	27	105			
W3	<21.7	31	214	<6.48	<6.48	13
W4	<21.7	42	199			
W5	no data	no data	no data			
T11	<21.7	<16	<16	<6.48	<6.48	<6.48

Table 8. Dissolved ΣDDT concentrations determined using PE with PRC and temperature corrections and SPME with PRC correction (pg/L)

	PE			SPME		
Station	near-surface	mid-column	near-bottom	near-surface	mid-column	near-bottom
BA1C	117	1771	4288			
BA3C	196	2253	4326			
BA4C	162	1937	10535	157	826	2139
BA5C	135	2614	7012			
BA5DC	196	1493	4304			
BA7C	135	1736	6616	154	973	2669
BA7DC	136	1004	2987			
BA8C	no data	1417	1520	142	841	2053
BA8DC	77	561	3374			
BA9C	no data	517	1238	114	426	1013
BA9DC	105	564	1331			
W1	84	854	1534			
W2	73	335	1191			
W3	76	409	1890	127	550	2151
W4	41	354	1250			
W5	no data	no data	no data			
T11	<33	25	39	72	93	<70

Table 9. Dissolved ΣPCB concentrations determined using PE with PRC and temperature corrections (pg/L)

	PE		
Station	near-surface	mid-column	near-bottom
BA1C	13	46	138
BA3C	20	50	93
BA4C	17	38	309
BA5C	18	69	141
BA5DC	23	39	85
BA7C	13	36	125
BA7DC	15	24	62
BA8C	no data	31	27
BA8DC	10	13	72
BA9C	no data	13	32
BA9DC	12	13	24
W1	5	16	26
W2	4	7	30
W3	6	8	52
W4	4	8	38
W5			
T11	1	1	2

Figures

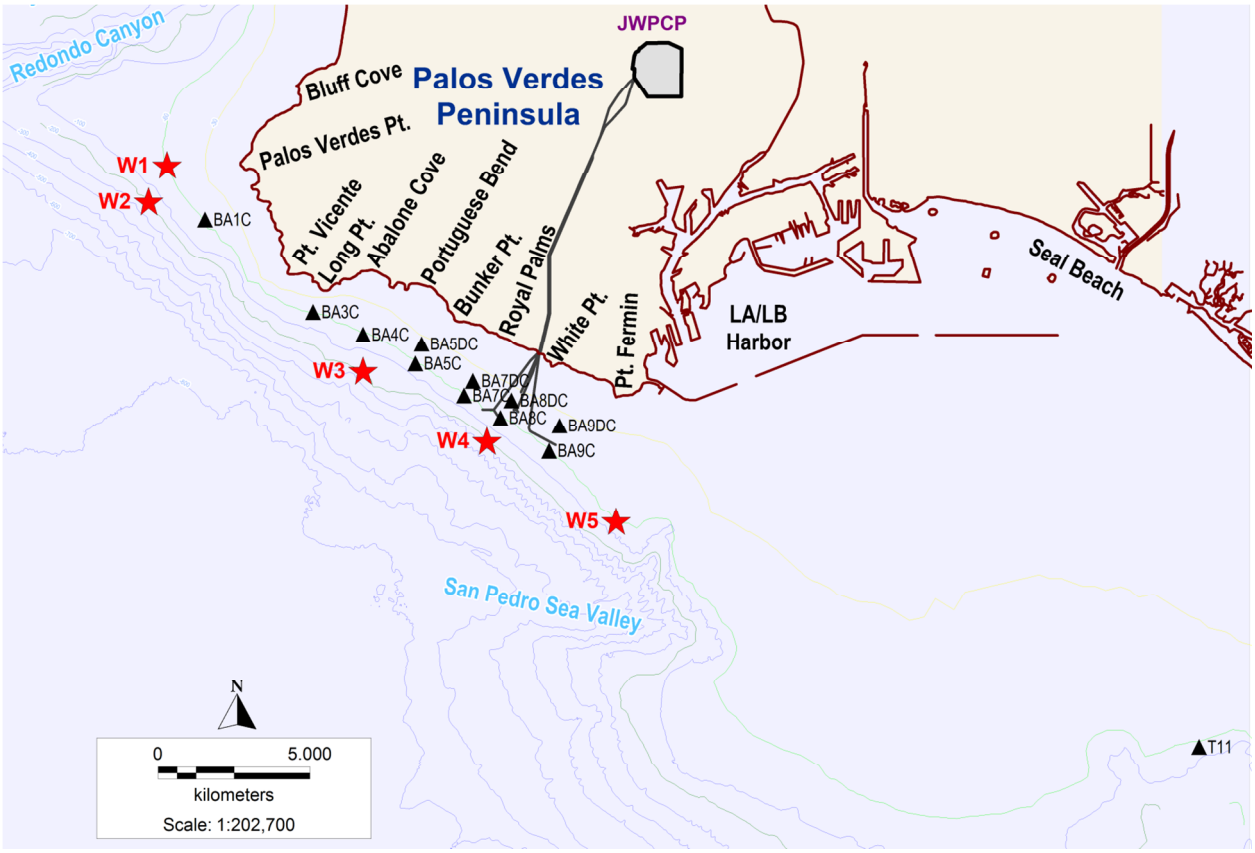

Figure 1. Sampling stations at the Palos Verdes Shelf Superfund site. Black triangles indicate stations sampled in both 2010 and 2013. Red stars are stations added for the 2013 study.

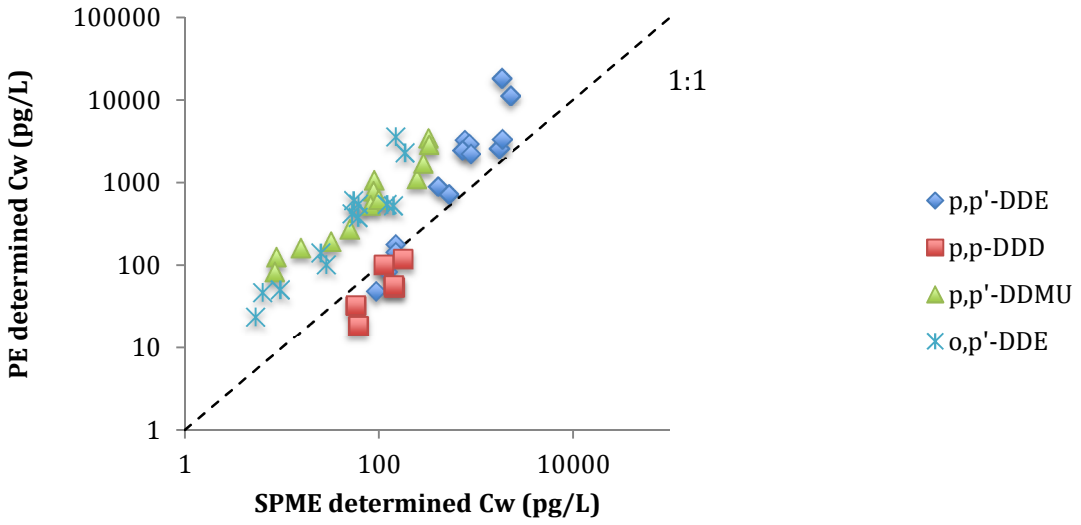

Figure 2. PE determined C_W vs. SPME determined C_W using 2010 K_{PEW} values

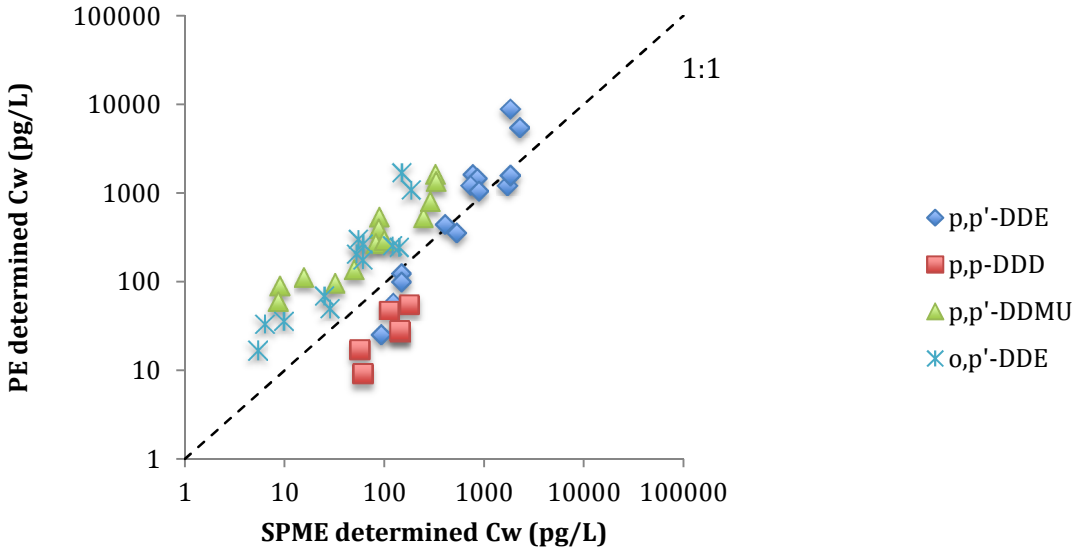

Figure 3. PE determined C_W vs. SPME determined C_W using temperature corrected K_{PEW} values (Table 1).

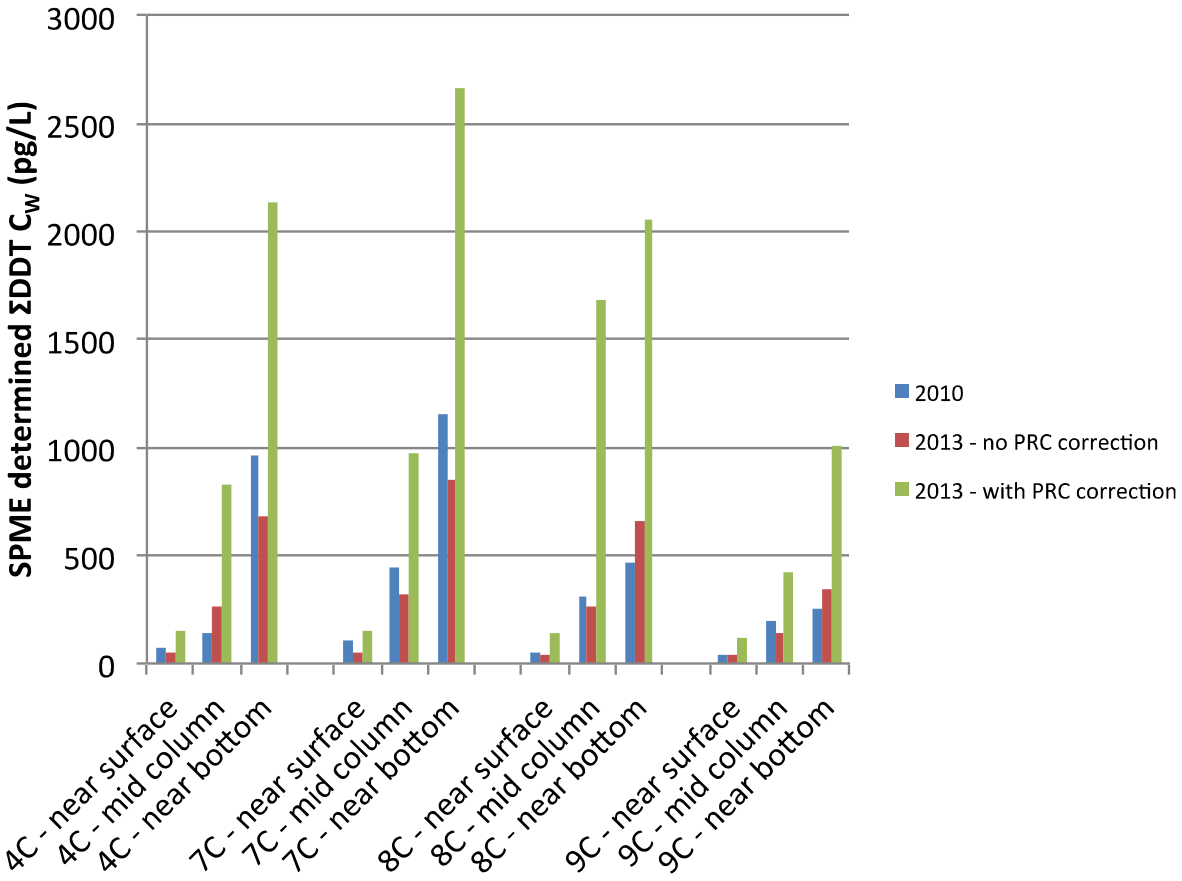

Figure 4. Comparison of SPME determined ΣDDT C_W from 2010 sampling event and this work (2013). Comparison is made between SPME determined values with and without PRC corrections. PRCs were not used with SPME in the 2010 study. ΣDDT includes concentrations of *p,p*'- and *o,p*'- congeners of DDE, and DDD where non-detects were not included in the sum. Parent DDTs were below detection limits in 2010 study and were not analyzed in 2013 work.

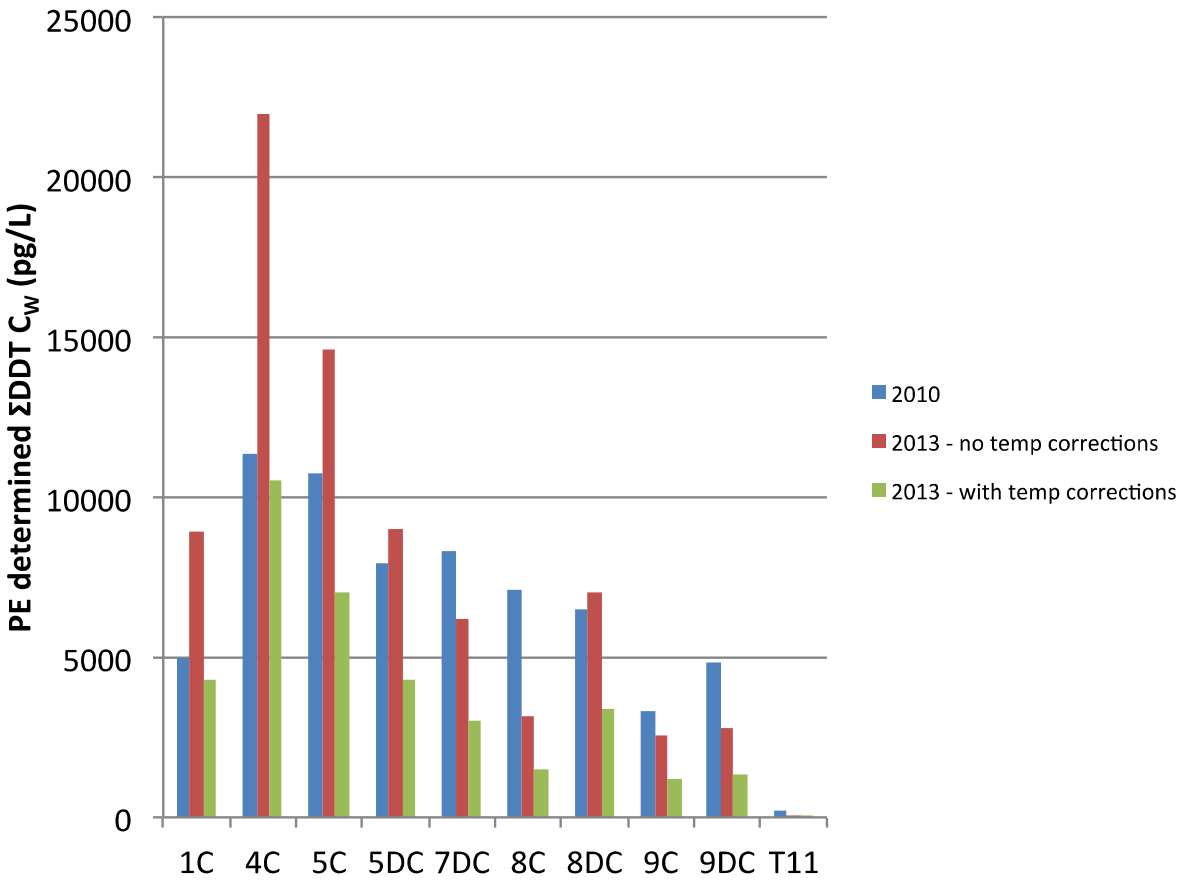

Figure 5. Comparison of PE determined ΣDDT C_W from the 2010 sampling event and this work (2013). All values are for near-bottom deployment at each station due to loss of mid-column and surface PE samplers in 2010 study. Comparisons made between PE determined values with and without corrections for temperature effects. Temperature effects were not considered in the 2010 study. ΣDDT includes concentrations of *p,p*'- and *o,p*'- congeners of DDE, and DDD where non-detects were not included in the sum. Parent DDTs were below detection limits in 2010 study and were not analyzed in 2013 work. All values are corrected by PRCs.

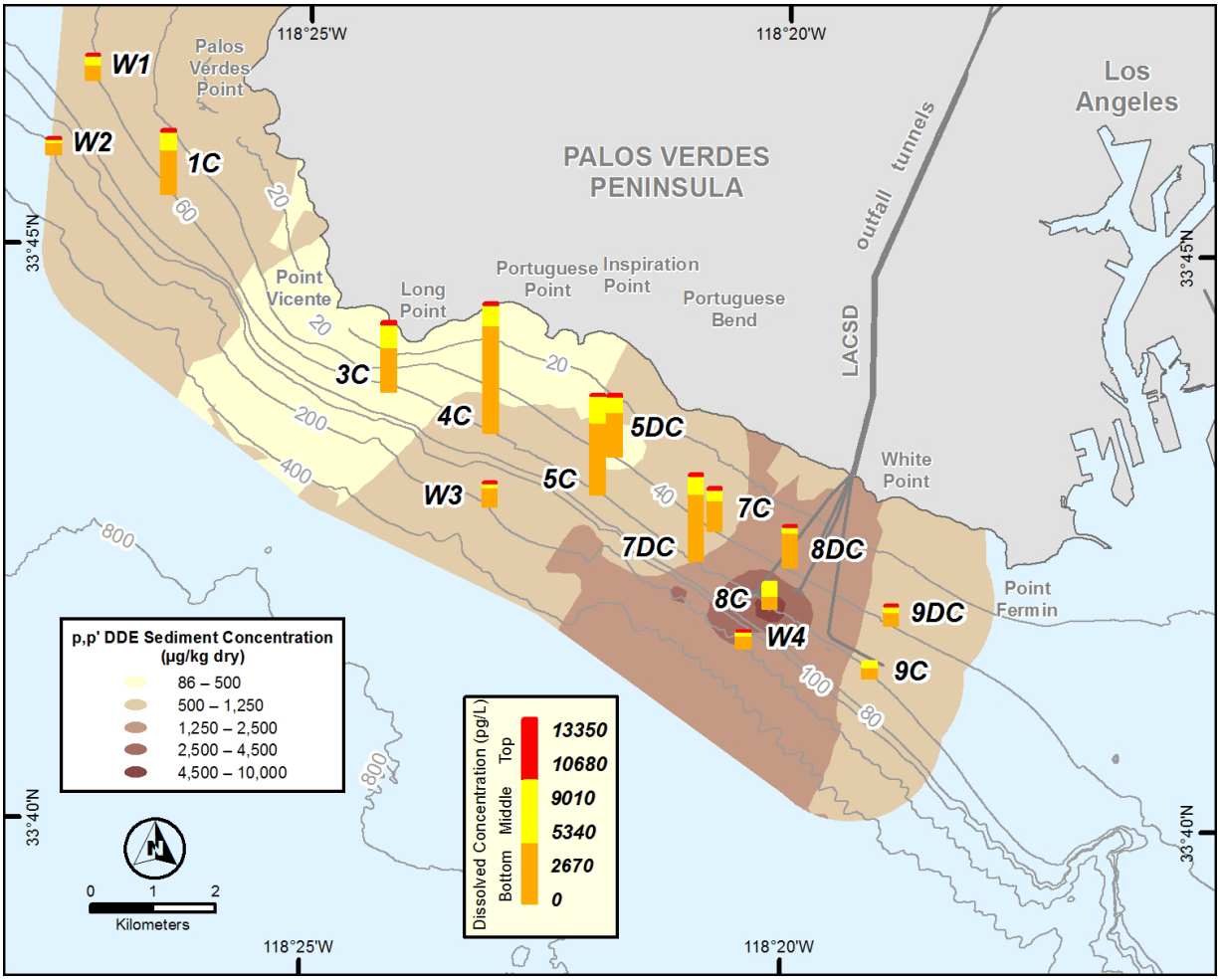

Figure 6. ΣDDT concentrations in three levels of the water column (bars) at each station, overlain on contour plot of p,p'-DDE surface sediment concentrations. Sediment surface concentrations are based on U.S. EPA (unpublished data) and interpolated using a radial basis function. All values are corrected by PRCs and for temperature effects.

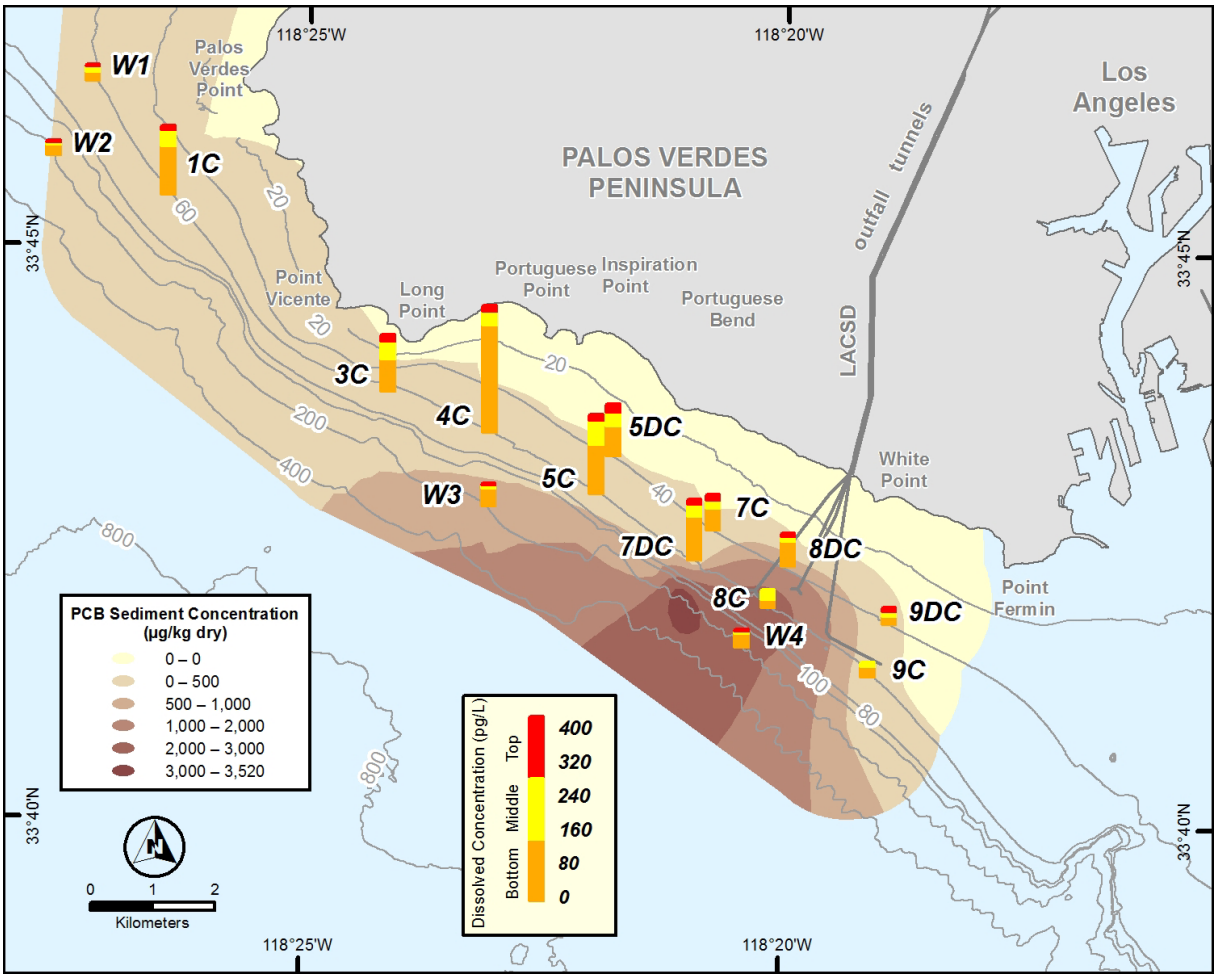

Figure 7. ΣPCB concentrations in three levels of the water column (bars) at each station, overlain on contour plot of ΣPCB surface sediment concentrations. Sediment surface concentrations are based on U.S. EPA (unpublished data) and interpolated using a radial basis function. All values are corrected by PRCs and for temperature effects.

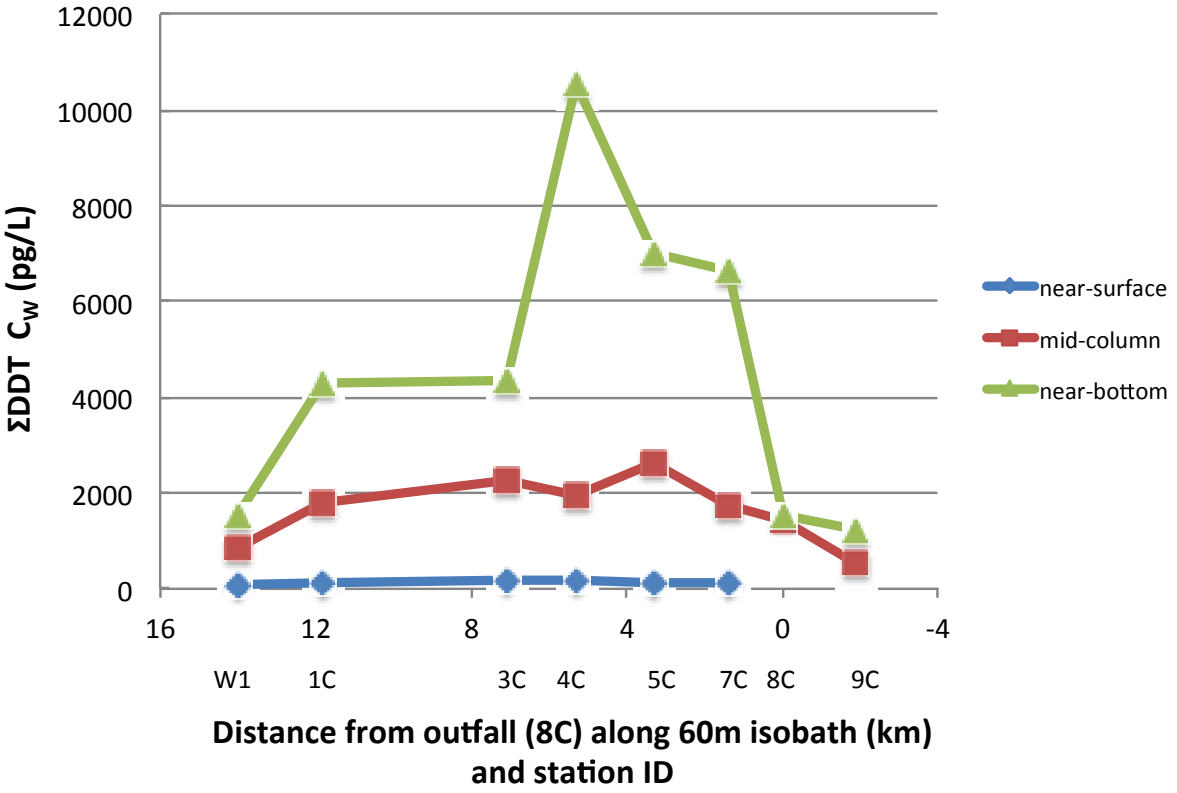

Figure 8. ΣDDT concentrations at three depths along the 60m isobath. All values are corrected by PRCs and for temperature effects.

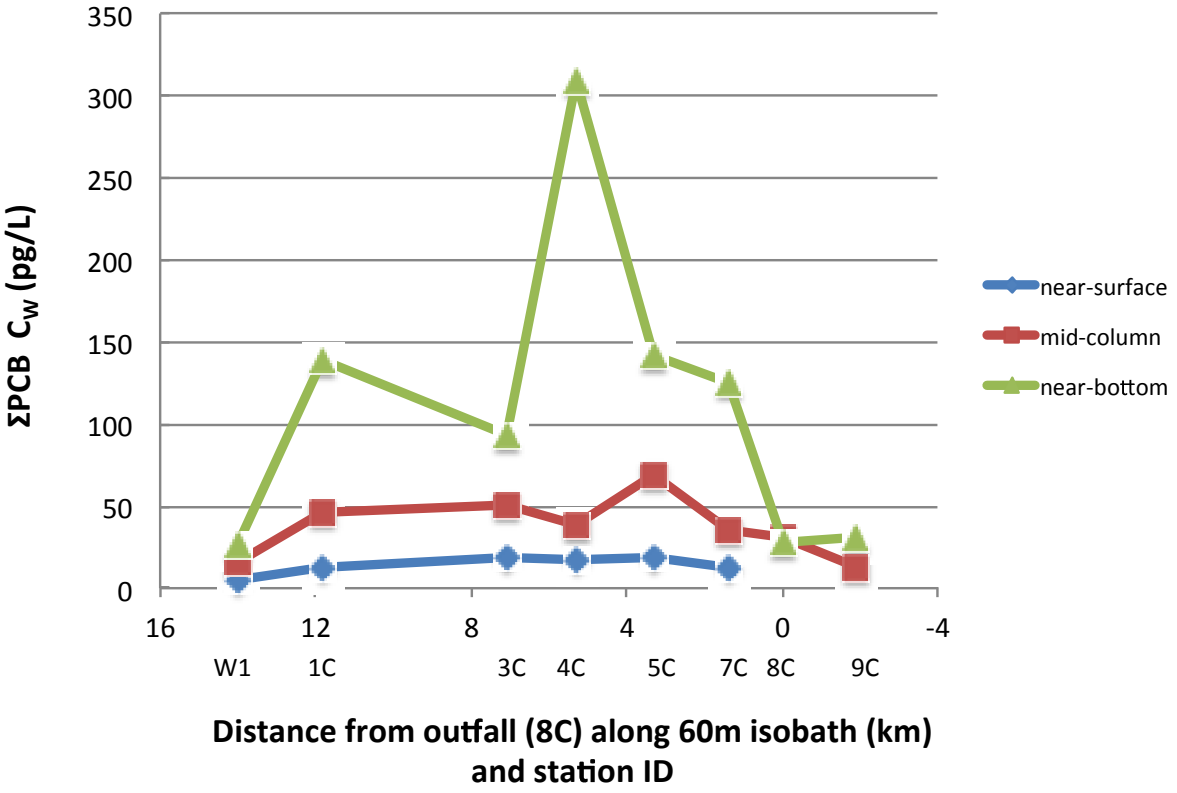

Figure 9. ΣPCB concentrations at three depths along the 60m isobath. All values are corrected by PRCs and for temperature effects.

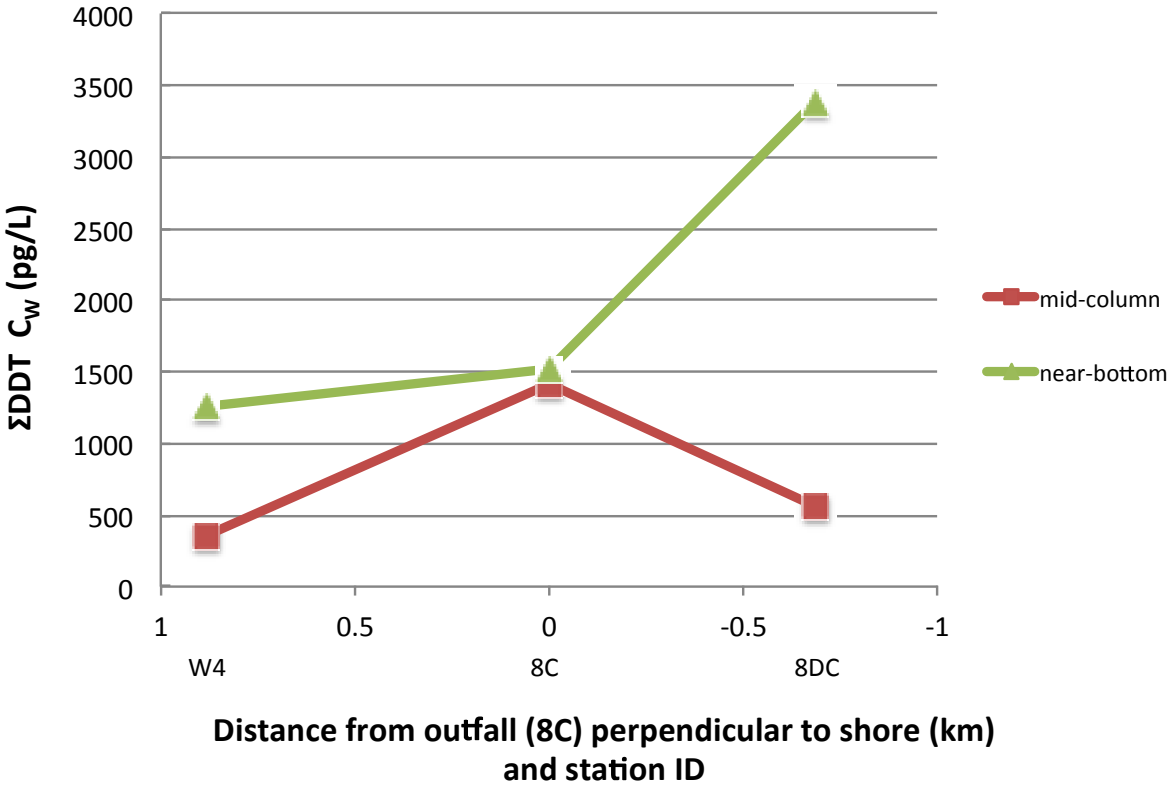

Figure 10. ΣDDT concentrations at mid-column and near-bottom along a transect perpendicular to shore nearest the LACSD outfalls. All values are corrected by PRCs and for temperature effects.

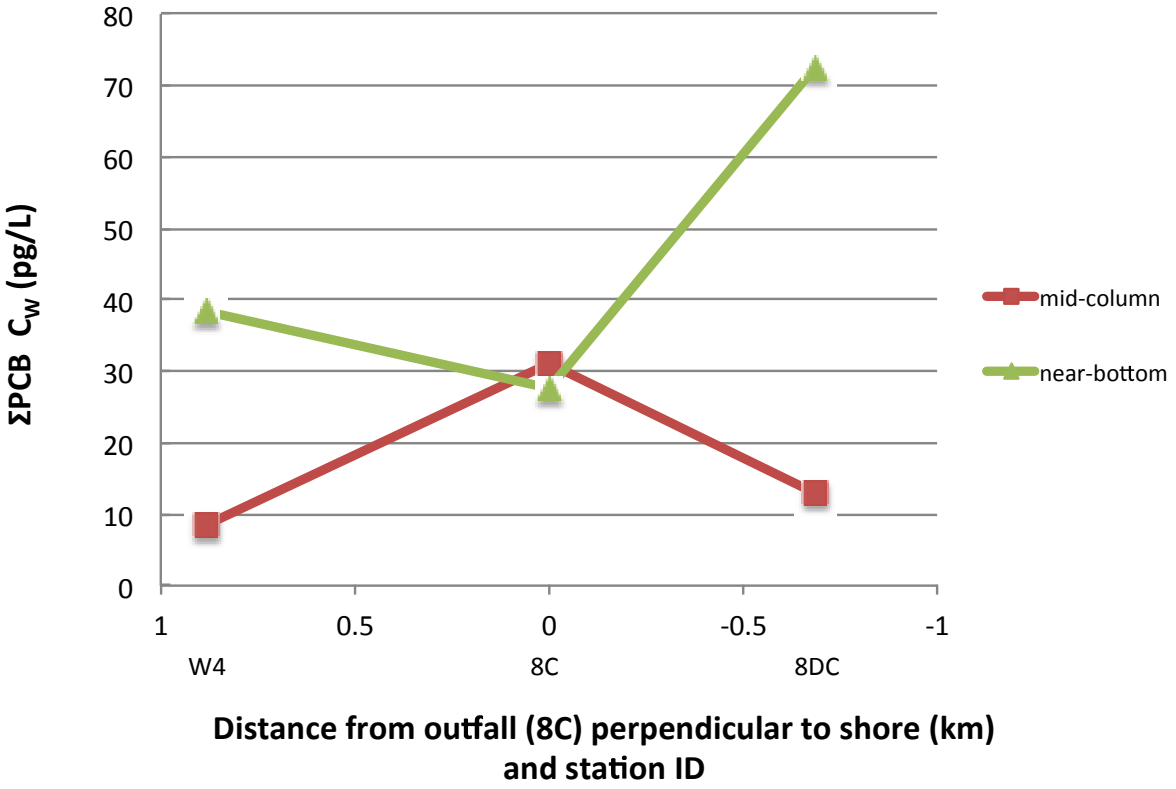

Figure 11. ΣPCB concentrations at mid-column and near-bottom along a transect perpendicular to shore nearest the LACSD outfalls. All values are corrected by PRCs and for temperature effects.

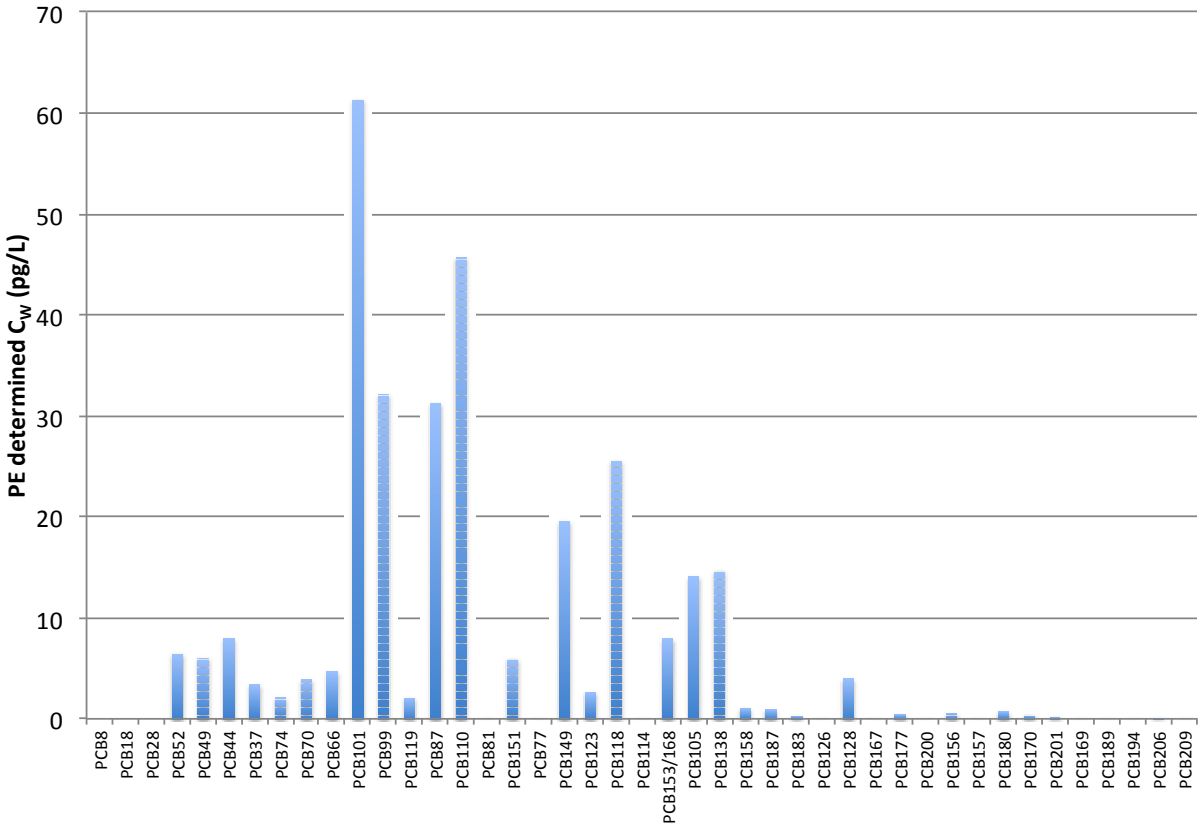

Figure 12. Dissolved PCB congener concentrations determined using PE samplers at station 4C at the near-bottom depth. All values are corrected by PRCs and for temperature effects.