Passive sampling to measure background dissolved persistent organic pollutant concentrations in the water column of the Palos Verdes Shelf Superfund site

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Abstract

Passive sampling was used to deduce water concentrations of persistent organic pollutants (POPs) in the vicinity of a marine Superfund site on the Palos Verdes Shelf, California, USA. Pre-calibrated solid phase microextraction (SPME) fibers and polyethylene (PE) strips that were pre-loaded with performance reference compounds (PRCs) were co-deployed for 32 days along an 11 station gradient at bottom, surface and mid-water depths. Retrieved samplers were analyzed for DDT congeners and their transformation products (DDE, DDD, DDMU, and DDNU) and 43 PCB congeners using GC-EI- and NCI-MS. PRCs were used to calculate compound-specific fractional equilibration achieved *in situ* for the PE samplers, using both an exponential approach to equilibrium model (EAE) and numerical integration of Fickian diffusion (NI) model. The highest observed concentrations were for p,p'-DDE, 2200 pg/L and 990 pg/L deduced from PE and SPME, respectively. The difference in these estimates could be largely attributed to uncertainty in equilibrium partition coefficients, unaccounted for disequilibrium between samplers and water, or different time scales over which the samplers average. The concordance between PE and SPME estimated concentrations for DDE was high ($R^2 = 0.95$). PCBs were only detected in PE samplers, due to their much larger size. Near-bottom waters adjacent to and down current from sediments with the highest bulk concentrations exhibited aqueous concentrations of DDTs and PCBs that exceeded Ambient Water Quality Criteria (AWQC) for human and aquatic health, indicating the need for future monitoring to determine the effectiveness of remedial activities taken against the most highly contaminated surface sediments at this site.

Introduction

Sediments of the Palos Verdes Shelf (PVS) off the coast of California are heavily contaminated with persistent organic pollutants (POPs), specifically, organochlorine pesticides (including dichlorodiphenyltrichloroethane (DDT) and its transformation products) and polychlorinated biphenyls (PCBs; Venkatesan *et al*. 1996, Quensen *et al*. 1998, Eganhouse and Pontolillo 2000, Eganhouse *et al*. 2000, Quensen *et al*. 2001, Eganhouse and Pontolillo 2008). Swartz *et al*. (1991) found the presence of these contaminants likely contributed to elevated whole sediment acute toxicity to marine amphipods exposed to sediments from PVS. These contaminants are primarily the legacy of industrial wastes released to the shelf through the outfall of the Joint Water Pollution Control Plant (JWPCP),

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a wastewater treatment facility operated by the Los Angeles County Sanitation Districts (LACSD; USEPA 2009). The prevailing coastal currents and wave activity carry remnants of the discharge in a northwesterly direction from the outfall, located off White Point (Figure 1; Ferre *et al*. 2010). As for many contaminated sites, sediments on the shelf continue be a source of chemicals to the water column, and biota living within and above them, long after the most polluted industrial releases have ended. (Young *et al*. 1976, Larsson 1985, Zeng *et al*. 1999, Friedman *et al*. 2011). In order to protect human and ecological health, the U.S. Environmental Protection Agency has explored remedial alternatives for the site (USEPA 2009).

Capping of the most contaminated sediments near the outfall has been selected as the preferred remedial alternative (USEPA 2009). Monitoring of POP concentrations in the water column before (i.e., baseline conditions), during, and after the capping is necessary to evaluate the effectiveness of the remediation as well as any adverse side effects (e.g., resuspension caused contaminant release). Measurement of dissolved concentrations ranging from femtograms per liter to tens of nanograms per liter for individual compounds, however, is technically challenging and time-consuming using traditional techniques, requiring pumping and filtering of large volumes of water (hundreds to thousands of liters) in order to collect analytically detectable contaminant

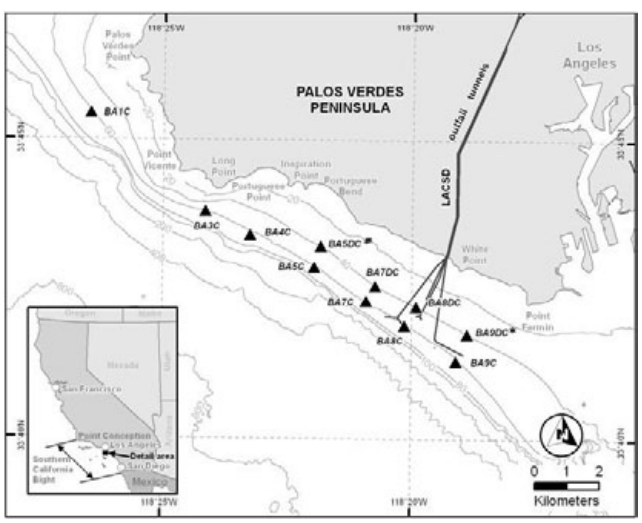


Figure 1. Black triangles indicate sampling stations off Palos Verdes, California (USA). PE and SPME were co-deployed at station BA1C, BA3C, BA4C, BA5C, BA7C, BA7DC, BA8C, BA8DC, BA9C, and T11 (not shown). *Only PE samplers were deployed at stations BA5DC, and BA9DC.

masses on absorptive material (e.g., octadecyl resin or polyurethane foam; Zeng *et al*. 1999, Zeng *et al*. 2002, Sobek and Gustafsson 2004).

In situ passive sampling methods, including solid-phase microextraction (SPME) and low-density polyethylene (PE) strips reduce the labor involved in sampling and post-collection processing, while allowing for dissolved POP measurement at very low concentrations. Further, passive sampling avoids many of the artifacts associated with traditional methods that result in over- and under-estimating dissolved concentrations. In general, passive samplers allow dissolved concentrations to be deduced from concentrations in equilibrated polymeric phases using polymer-water partition coefficients (e.g., K_{PEW} and K_f; Zeng *et al*. 2004, Adams *et al*. 2007). For example, Zeng *et al*. (2004) applied SPMEs, polydimethylsiloxane (PDMS) coated glass fibers, to measure DDT transformation products (p,p'-DDE, o,p'-DDE, and p,p'-DDD) dissolved in the water column of the PVS. Concentrations in the range of tens of picograms per liter to nanograms per liter matched those measured using the traditional pumping, filtering, and solid phase extraction of 999 L of seawater. SPME were believed to be equilibrated with the PVS water DDTs after 18-day deployments, as no statistically significant differences in concentration were seen in SPME exposed for 18 and 30 days. Similarly, Adams (2003) and Adams *et al*. (2007) used PE strips, exposed for 15 days and assuming sampler/water equilibration, to sample PCB congener #52 in Boston Harbor and lower Hudson River estuary in the range of pictograms per liter. In order to monitor the effectiveness of remedial effort on the PVS, water concentrations for individual PCB congeners will have to be detectable to the range of tens of femtograms per liter.

In this work, both SPME and PE passive samplers are used simultaneously to measure selected DDT and PCB concentrations at eleven stations along the PVS and at a background station with historically lower detectable POP concentrations. By using large strips of PE, it is expected that even highly chlorinated PCBs, which have previously been measured in the sediments, but not detectable in the water column due to extremely low solubility, could be measured (expected range of tens to hundreds of femtograms per liter). These data will allow benchmark, time-averaged concentrations to be set for the PVS, to which water column concentrations, measured using similar methods during and after remedial activity

at the site, may be compared. Co-deployment of the two types of samplers will allow for a direct comparison of estimated concentrations providing confidence in the techniques where results are consistent, and highlighting necessary adjustments to their methods of use where results are inconsistent. Finally, an alternative method for calibrating the fractional equilibration of membrane samplers is presented and compared with a frequently-used, existing method. This alternative method may be used with any sampler material and thickness and may be useful in predicting fractional equilibrations before deployment, helping to improve the design of sampling campaigns.

Theory

Dissolved concentrations, C_W, may be deduced using data from both types of passive samplers. First, SPME-water partition coefficients, K_f (L_W/L_{PDMS}), may be used to calculate C_W (ng/L) from the mass of analyte sorbed to the fiber, N_f(ng), assuming the fibers and water are fully equilibrated:

$$C_W = N_f / (K_f V_f) \qquad \text{Eq. 1}$$

where V_f (L_{PDMS}) is the volume of the sorptive coating.

Because equilibrium between PE samplers and water cannot always be assumed for very hydrophobic compounds, such as some DDTs (e.g., DDD, DDE and DDT) and highly chlorinated PCBs, following short deployments (days to weeks), performance reference compounds (PRCs) are used to correct for non-attainment of equilibrium conditions. (Booij *et al*. 2002, Adams *et al*. 2007) Similarly to SPME, C_W may be calculated from the concentration of analyte taken up by the PE strips, while accounting for disequilibrium using PRCs that are similar to the analyte in terms of diffusivities and partitioning coefficient:

$$C_W = C^{\infty}_{PE} / K_{PEW} \qquad \text{Eq. 2}$$

$$C^{\infty}_{PE} = C_{PE,t} / f_{eq} \qquad \text{Eq. 3}$$

and $$f_{eq} = (C^0_{PRC} - C_{PRC,t}) / C^0_{PRC} \qquad \text{Eq. 4}$$

where, C^{∞}_{PE} is the equilibrium analyte concentration in the PE in ng/kg_{PE}, K_{PEW} is the compound-specific polyethylene-water partition coefficient (L_W/kg_{PE}), $C_{PE,t}$ is the concentration in the PE after deployment, C^0_{PRC} is the initial concentration of PRC in the sampler, $C_{PRC,t}$ is the concentration of PRC in the sampler after deployment, and f_{eq} is the fractional equilibration of the sampler to the water.

Challenges to using PRCs are encountered when wishing to interpolate between, or extrapolate from, PRCs to compounds that differ in terms of diffusivity and partitioning behavior. Existing methods are based on exponential approach to equilibrium (EAE) models that were originally developed for semi-permeable membrane devices (SPMDs; Booij *et al*. 1998, Huckins *et al*. 2002). Constant mass transfer coefficients are assumed and uptake/release by polymeric passive samplers is often described as being either polymer-side controlled, or water-side boundary layer controlled, depending on the diffusion rates across each layer. While semi-empirical models for specific samplers have been developed to predict the contributions to mass-transfer resistance of the polymer and water-side boundary layers (Booij *et al*. 2003, Booij and Smedes 2010), a more generic method, which could be used with any sampler material and thickness, may simplify the application of polymer films as passive water samplers.

An alternative to using EAE models may be found by using explicit, finite-difference modeling of Fickian, mass diffusion across both polymer and water layers, while accounting for the no flux boundary at the center of the polymer film (NI method). Using a stagnant film model to describe the water-side boundary layer (BL), one-dimensional Fickian diffusion in a system consisting of a PE sheet, BL, and a well-mixed infinite bath is described in the Supplemental Information (SI) available at ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/AnnualReports/2012AnnualReport/ar12_04SI.pdf (following Crank 1975). While polymer membrane thicknesses are known, BL thicknesses are unknown for any given deployment, and can change with flowrates and turbulence (Booij *et al*. 1998, Huckins *et al*. 2002). However, data from multiple PRCs may be used to find the best fit modeled BL. The same model, with a best-fit BL, may then be used to find f_{eq} for compounds which do not have matching PRCs (complete description of model in Supplemental Information; Crank (1975). For the purposes of this work, BL dependence on a compound's diffusivity in water is neglected.

Methods

Passive Sampler Preparation

PE strips (10 cm x 100 cm) were prepared from low-density polyethylene sheets (25 µm, ACE Hardware Corp., Oak Brook, IL, USA) and solvent cleaned as described previously (Fernandez *et al*. 2009). Each sampler was then soaked in an aqueous PRC solution (^{13}C-labeled p,p'-DDT, p,p'-DDE, p,p'-DDD, PCB#28, PCB#52, PCB#118, and PCB#128 (Cambridge Isotope, Andover, MA, USA)) in a 1-L amber glass jar for at least 20 weeks before deployment. In order to streamline analysis, target PRC concentrations in PE were approximately ten times the expected concentrations of target chemicals so that all concentrations would fall within the same range, assuming up to 90% loss of PRC during deployment. Finally, samplers were threaded onto solvent rinsed aluminum wires, wrapped in aluminum foil, and stored at -20ºC or on ice until deployed.

SPME (100 µm PDMS coated silica fibers, Supelco, Bellefonte, PA, USA) were prepared and handled as described previously.(Zeng *et al*. 2004) Briefly, newly purchased SPME fibers were pre-conditioned at 250°C for 0.5 hours prior to assembly into individual perforated copper casings for protection during deployment. Each fiber/casing assembly was kept in a sealed glass vial in a freezer at -20ºC and shipped on ice until deployment.

Field Deployment and Retrieval

In September 2010, PE and SPME samplers, prepared as described above, were co-deployed at multiple stations along the 40 and 60 m isobaths of the PVS, from just up current of the JWPCP outfall, to approximately 10 km down current (Figure 1), and at a background station (T11) approximately 24 km SE of the outfall (station labels reflect those used in previous monitoring of PVS sediment and water). Samplers were co-deployed at three depths per station: 5 m below the surface ("surface"); 5 m above the bottom ("near bottom") and 30 to 35 m below the surface ("mid-depth"). PE samplers were deployed in triplicate at each depth for all 12 stations shown in Figure 1. SPME samplers were deployed in quadruplicate at each depth for 10 of the 12 stations (excluding BA5DC and BA9DC). Both types of samplers were retrieved after 32 days. Because the aluminum wire on which PE were threaded broke for the shallower samplers, only PEs from the near bottom depth were recovered from eight stations, with the addition of the mid-depth samplers at stations BA4C and BA5DC. Copper or stainless steel wire would have been more appropriate for this application. All SPME samplers were recovered. Water temperature and salinity were measured using conductivity, temperature, and depth meter (CTD) casts at time of deployment. Dissolved organic carbon (DOC) was determined on discrete water samples collected at depth using a Niskin bottle. Analyses for DOC were performed on a Shimadzu TOC-VCSH analyzer (Kyoto, Japan). All samplers were returned to the laboratory on ice and remained frozen until analyzed.

Sampler Analysis and Partition Coefficients

SPME fibers were manually injected on the GC/MSD (see SI for details), and two fibers from each station/depth were analyzed using EI and NCI ionization modes. PE strips were wiped with laboratory tissues to remove adhering particles and biofilms, cut with clean scissors into small pieces, placed in solvent rinsed 500 ml amber glass bottles, and spiked with recovery surrogates, dibromooctafluorobiphenyl (DBOFB) and PCB208. PE were then extracted three times by sonicating in 300 ml dichloromethane (DCM) for 15 minutes. The combined extract was dried with pre-combusted Na_2SO_4 and concentrated to ~5 ml using a TurboVap II Concentration Workstation (Caliper Life Sciences, Hopkinton, MA, USA). Extracts were then solvent exchanged into hexane and concentrated to 0.5 ml. After the addition of internal standards, PCB 30 and PCB 205, extracts were analyzed by GC/MSD. Target compounds included p,p'- and o,p'- congeners of DDT, DDE and DDD, p,p'-DDMU, p,p'-DDNU, and 43 PCB congeners (Table 1).

The polyethylene-water partition coefficients (K_{PEW}) used in this work were based on laboratory measurements (in seawater) and published values (Supplemental Information). For this study, PRCs in PE samplers were assumed to have equivalent K_{PEW} and diffusivities to the non-^{13}C-labeled compounds. Compound-specific SPME-water partition coefficients (K_f) were also measured in seawater, for DDTs and their transformation products (M. Pirogovsky, unpublished data). Calculation of temperature effects on partition coefficients indicated only small (<20%) differences were expected, thus no site-specific temperature corrections were made in this work (Lohmann 2012).

Table 1. PE derived C_w 5 m above bottom in pg/L measured in this work, and bulk sediment concentrations (ug/kg) of total PCB and total DDTs measured by USEPA in 2009 (average for top 6 cm). Uncertainty reflects the propagated error of initial and post-deployment PE concentrations expressed as one standard deviation (1 s.d.).

	Station									
Compound	BA1C	BA4C	BA5C	BA5DC	BA7DC	BA8C	BA8DC	BA9C	BA9DC	T11
DDNU	120 ± 20	230 ± 50	190 ± 40	220 ± 50	180 ± 40	140 ± 30	160 ± 30	98 ± 21	120 ± 20	< 60
o,p-DDE	130 ± 30	350 ± 70	310 ± 60	230 ± 50	230 ± 50	200 ± 40	160 ± 30	79 ± 16	130 ± 30	4.3 ± 0.9
DDMU	230 ± 50	410 ± 80	410 ± 80	290 ± 60	280 ± 60	310 ± 60	250 ± 50	130 ± 30	180 ± 40	< 5
p-p'-DDE	970 ± 170	2200 ± 400	2100 ± 400	1500 ± 300	1600 ± 300	1400 ± 200	1300 ± 200	650 ± 120	950 ± 170	37 ± 7
o,p'-DDD	9.3 ± 2.1	21 ± 5	13 ± 3	11 ± 2	11 ± 2	14 ± 3	11 ± 2	5.4 ± 1.2	7.8 ± 1.8	< 2
o,p'-DDT	< 7	< 7	< 7	< 7	< 7	< 7	< 7	< 7	< 7	< 7
p,p'-DDD	20 ± 4	42 ± 8	34 ± 7	24 ± 5	27 ± 5	33 ± 6	29 ± 5	11 ± 2	18 ± 3	< 6
p,p'-DDT	< 8	< 8	< 8	< 8	< 8	< 8	< 8	< 8	< 8	< 8
Total PCB[a]	156	316	217	198	174	163	158	90	119	50
PCB8	< 17	< 17	< 17	< 17	< 17	< 17	< 17	< 17	< 17	< 17
PCB18	< 13	< 13	< 13	< 13	< 13	< 13	< 13	< 13	< 13	< 13
PCB28	< 6	< 6	< 6	< 6	< 6	< 6	< 6	< 6	< 6	< 6
PCB52	6.4 ± 1.1	14 ± 3	14 ± 2	16 ± 3	15 ± 3	9.3 ± 1.7	15 ± 3	8.1 ± 1.5	12 ± 2	5.9 ± 1.1
PCB49	7.1 ± 0.9	7.9 ± 1.0	12 ± 2	19 ± 2	15 ± 2	9.7 ± 1.3	8.6 ± 1.1	9.2 ± 1.2	7.8 ± 1.0	< 6
PCB44	8.7 ± 1.0	9.7 ± 1.2	14 ± 2	16 ± 2	< 4	< 4	< 4	< 4	< 4	< 4
PCB37	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3
PCB74	4.1 ± 0.7	7.4 ± 1.3	7.2 ± 1.3	5.8 ± 1.0	5.1 ± 1.0	3.9 ± 0.7	4.6 ± 0.8	< 1.5	2.3 ± 0.4	< 1.5
PCB70	7.0 ± 1.2	16 ± 3	14 ± 3	9.5 ± 1.7	9.1 ± 1.7	11 ± 2	8.5 ± 1.5	3.9 ± 0.7	6.0 ± 1.1	< 1.3
PCB66	6.0 ± 3.0	15 ± 8	11 ± 5	8.0 ± 3.9	7.1 ± 3.9	8.0 ± 3.5	6.3 ± 3.0	1.3 ± 1.4	4.9 ± 2.1	< 1.8
PCB101	15 ± 4	35 ± 9	22 ± 6	18 ± 5	17 ± 5	17 ± 4	14 ± 4	6.7 ± 1.7	10 ± 3	< 2
PCB99	8.1 ± 3.0	18 ± 7	11 ± 4	9.1 ± 3.4	9.3 ± 3.5	8.7 ± 3.2	15 ± 6	3.5 ± 1.3	5.9 ± 2.2	< 3
PCB119	1.1 ± 0.4	1.7 ± 0.6	1.1 ± 0.4	< 1	< 1	< 1	< 1	< 1	< 1	< 1
PCB87	5.3 ± 1.5	14 ± 4	8.2 ± 2.3	6.4 ± 1.8	6.7 ± 1.9	6.9 ± 1.9	5.6 ± 1.6	0.94 ± 0.26	3.8 ± 1.1	< 0.34
PCB110	13 ± 4	32 ± 9	19 ± 6	15 ± 5	15 ± 5	15 ± 5	11 ± 3	5.9 ± 1.8	7.7 ± 2.4	< 2
PCB81	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
PCB151	1.3 ± 0.4	2.0 ± 0.5	1.4 ± 0.4	1.2 ± 0.4	1.1 ± 0.4	1.1 ± 0.31	0.88 ± 0.24	0.47 ± 0.15	0.70 ± 0.20	0.13 ± 0.04
PCB77	0.71 ± 0.33	1.2 ± 0.6	1.0 ± 0.5	0.81 ± 0.38	2.5 ± 0.4	0.86 ± 0.41	3.3 ± 1.5	0.15 ± 0.07	0.58 ± 0.27	< 0.06
PCB149	1.2 ± 0.4	2.8 ± 1.5	1.4 ± 0.6	1.2 ± 0.4	1.1 ± 0.4	1.2 ± 0.4	0.94 ± 0.32	0.47 ± 0.19	0.68 ± 0.24	0.13 ± 0.05
PCB123	1.9 ± 0.6	6.7 ± 2.1	2.4 ± 0.8	2.0 ± 0.7	2.0 ± 0.7	1.9 ± 0.6	1.6 ± 0.5	0.81 ± 0.26	1.2 ± 0.4	< 0.2
PCB118	14 ± 5	53 ± 17	19 ± 6	16 ± 5	15 ± 5	15 ± 5	13 ± 4	6.2 ± 2.0	9.1 ± 2.9	< 0.2
PCB114	0.58 ± 0.14	1.1 ± 0.3	0.70 ± 0.17	0.61 ± 0.15	0.58 ± 0.14	0.56 ± 0.13	0.46 ± 0.11	0.22 ± 0.05	0.34 ± 0.08	< 0.07
PCB153/168	5.2 ± 1.5	6.8 ± 1.7	5.3 ± 1.7	5.1 ± 1.3	4.2 ± 1.1	4.2 ± 1.3	3.4 ± 1.0	1.9 ± 0.6	2.8 ± 0.8	0.67 ± 0.19
PCB105	5.7 ± 1.5	13 ± 4	7.9 ± 2.1	6.4 ± 1.7	6.2 ± 1.7	6.3 ± 1.7	5.2 ± 1.4	2.4 ± 0.7	3.6 ± 1.0	0.51 ± 0.14
PCB138	4.6 ± 1.3	6.7 ± 1.8	4.8 ± 1.5	4.1 ± 1.1	3.6 ± 0.9	3.6 ± 1.0	2.9 ± 0.8	1.6 ± 0.5	2.2 ± 0.6	0.47 ± 0.14
PCB158	0.59 ± 0.16	0.83 ± 0.21	0.68 ± 0.19	0 .54 ± 0.14	0.45 ± 0.12	0.47 ± 0.13	0.36 ± 0.10	0.20 ± 0.06	0.29 ± 0.09	0.056 ± 0.008
PCB187	1.6 ± 0.4	2.0 ± 0.5	1.7 ± 0.4	1.4 ± 0.4	1.1 ± 0.3	1.3 ± 0.3	1.1 ± 0.3	0.77 ± 0.19	0.93 ± 0.23	0.23 ± 0.06
PCB183	0.59 ± 0.14	0.75 ± 0.19	0.64 ± 0.16	0.50 ± 0.13	0.42 ± 0.11	0.45 ± 0.11	0.36 ± 0.09	0.27 ± 0.07	0.31 ± 0.09	0.063 ± 0.015
PCB126	0.16± 0.06	0.60 ± 0.24	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
PCB128	1.2 ± 0.5	3.4 ± 0.9	1.2 ± 0.4	1.1 ± 0.35	0.93 ± 0.31	0.93 ± 0.34	0.75 ± 0.26	0.43 ± 0.18	0.64 ± 0.23	0.22 ± 0.07
PCB167	0.30 ± 0.08	3.7 ± 0.9	0.26 ± 0.08	0.24 ± 0.07	0.22 ± 0.05	0.21 ± 0.06	0.17 ± 0.05	0.095 ± 0.031	0.14 ± 0.04	< 0.03
PCB177	0.64 ± 0.16	2.0 ± 0.5	0.66 ± 0.17	0.51 ± 0.12	0.42 ± 0.11	0.47 ± 0.12	0.38 ± 0.10	0.28 ± 0.07	0.33 ± 0.08	0.074 ± 0.019
PCB200	0.081 ± 0.020	0.18 ± 0.05	0.065 ± 0.016	0.049 ± 0.012	0.048 ± 0.012	0.057 ± 0.014	< 0.04	< 0.04	< 0.04	< 0.04
PCB156	0.58 ± 0.18	0.84 ± 0.21	0.57 ± 0.19	0.50 ± 0.14	0.43 ± 0.12	0.46 ± 0.14	0.35 ± 0.10	0.19 ± 0.06	0.27 ± 0.08	0.053 ± 0.015
PCB157	0.21 ± 0.06	0.22 ± 0.06	0.17 ± 0.06	0.13 ± 0.04	0.13 ± 0.04	0.14 ± 0.05	0.11 ± 0.04	0.044 ± 0.011	0.067 ± 0.023	0.062 ± 0.020
PCB180	1.7 ± 0.4	5.8 ± 1.5	2.0 ± 0.5	1.5 ± 0.4	1.3 ± 0.32	1.4 ± 0.4	1.2 ± 0.3	0.83 ± 0.21	0.98 ± 0.25	0.16 ± 0.04
PCB170	0.76 ± 0.19	0.96 ± 0.31	0.82 ± 0.20	0.61 ± 0.15	0.51 ± 0.13	0.58 ± 0.15	0.46 ± 0.12	0.33 ± 0.08	0.39 ± 0.10	0.083 ± 0.021
PCB201	0.56 ± 0.14	0.65 ± 0.15	0.56 ± 0.14	0.42 ± 0.11	0.36 ± 0.09	0.40 ± 0.10	0.32 ± 0.08	0.26 ± 0.07	0.30 ± 0.08	0.11 ± 0.03
PCB169	0.17 ± 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05
PCB189	0.14 ± 0.04	0.071 ± 0.018	0.063 ± 0.015	0.054 ± 0.014	0.081 ± 0.020	0.063 ± 0.016	0.063 ± 0.016	0.075 ± 0.019	< 0.05	< 0.05
PCB194	0.39 ± 0.10	0.77 ± 0.19	0.30 ± 0.08	0.20 ± 0.05	0.23 ± 0.06	0.25 ± 0.06	0.17 ± 0.04	0.16 ± 0.04	0.16 ± 0.04	0.099 ± 0.025
PCB206	0.46 ± 0.11	0.33 ± 0.08	0.37 ± 0.09	0.30 ± 0.10	0.34 ± 0.09	0.34 ± 0.09	0.30 ± 0.08	0.29 ± 0.06	0.30 ± 0.08	0.27 ± 0.07
PCB209	< 18	< 18	< 18	< 18	< 18	< 18	< 18	< 18	< 18	< 18
Bulk sediment concentrations (ug/kg)[b]										
Total DDTs[c]	2400	2100	2100	540	330	100000	2200	1100	710	
Total PCBs[d]	100	120	110	35	3.8	2100	52	71	42	

≤ estimated concentration below detection limit (DL); < not detected (DL)

[a] Total PCB = sum of congeners reported. One half of the detection limit was included in sum for congeners below detection limit

[b] unpublished data from EPA have not been fully validated and are included for spatial comparison purposes only

[c] Total DDTs = sum of p,p-DDT, o,p'-DDT, p,p'-DDE, o,p'-DDE, p,p'-DDD, o,p'-DDD, p,p'-DDMU, and p,p'-DDNU

PCB170, PCB180, PCB187, PCB189, PCB195, PCB206, and PCB209

Results

Dissolved DDT and PCB Concentrations using SPME

The highest dissolved concentrations measured at each station were of p,p'-DDE, ranging from 36 pg/L in the surface waters at station BA9C, just up-current of the outfall, to 990 pg/L in near bottom water at station BA7C, just down-current of the outfall. At each station, DDE concentrations increased with depth, with the surface water concentrations averaging 16% of the concentrations measured in the bottom waters (Table 2), consistent with the trend observed using SPME water column samplers deployed in 2003-04 (Zeng *et al*. 2005). Of the remaining compounds, only o,p'-DDE and p,p'-DDMU were detected frequently, and were 10% (<1 - 170 pg/L) to 30% (<4 - 230 pg/L) of the p,p'-DDE concentration at each station and depth, respectively. If detected, a contaminant followed the same depth to concentration trend noted above for p,p'-DDE; that is, the highest concentrations were observed at the bottom

Table 2. SPME derived CW in pg/L for samplers deployed at three depths (mean of two fibers).

		Station									
Compound[1]	Depth	BA1C	BA3C	BA4C	BA5C	BA7C	BA7DC	BA8C	BA8DC	BA9C	T11
DDNU	5 m below surface	≤ 12	≤ 9	≤ 6	≤ 3	≤ 6	< 40	< 40	< 40	< 40	< 40
	mid-depth	≤ 14	≤ 14	≤ 6	≤ 9	≤ 12	< 40	< 40	< 40	≤ 6	< 40
	5 m off bottom	≤ 17	≤ 17	≤ 14	≤ 12	≤ 9	< 40	< 40	< 40	≤ 3	< 40
o,p'-DDE	5 m below surface	7	12	8	24	15	24	5	8	5	< 1
	mid-depth	21	17	16	44	53	49	33	29	21	< 1
	5 m off bottom	37	45	170	120	150	100	49	48	25	< 1
DDMU	5 m below surface	15	15	14	41	< 4	26	< 4	18	< 4	< 4
	mid-depth	27	35	22	61	69	82	39	58	28	< 4
	5 m off bottom	45	120	230	140	180	150	66	70	43	< 4
p,p'-DDE	5 m below surface	54	94	68	110	93	140	46	70	36	< 9
	mid-depth	170	130	130	300	390	280	280	160	180	< 9
	5 m off bottom	330	410	790	810	990	560	420	280	230	≤ 5
o,p'-DDD	5 m below surface	< 14	< 14	< 14	< 14	< 14	< 14	< 14	< 14	< 14	< 14
	mid-depth	< 14	< 14	< 14	< 14	< 14	< 14	< 14	< 14	< 14	< 14
	5 m off bottom	< 14	< 14	< 14	31	23	< 14	< 14	< 14	< 14	< 14
o,p'-DDT	5 m below surface	< 16	< 16	< 16	< 16	< 16	< 16	< 16	< 16	< 16	< 16
	mid-depth	< 14	< 16	< 16	< 16	< 16	< 16	< 16	< 16	< 16	< 16
	5 m off bottom	< 16	< 16	< 16	< 16	< 16	< 16	< 16	< 16	< 16	< 16
p,p'-DDD	5 m below surface	< 70	< 70	< 70	< 70	< 70	< 70	< 70	< 70	< 70	< 70
	mid-depth	< 70	< 70	< 70	< 70	< 70	< 70	< 70	< 70	< 70	< 70
	5 m off bottom	< 70	< 70	< 70	< 70	< 70	< 70	< 70	< 70	< 70	< 70
p,-p'-DDT	5 m below surface	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30
	mid-depth	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30
	5 m off bottom	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30	< 30

≤ estimated concentration below DL; < not detected (DL); [1] DDNU = 1-phenylethenylbenzene; o,p'-DDE = o,p'-dichlorodiphenyldichloroethylene ; DDMU = 1-chloro-4-[2-chloro-1-(4-chlorophenyl)ethenyl]benzene; p,p'-DDE = p,p'-dichlorodiphenyldichloroethylene; o,p'-DDD = o,p'-dichlorodiphenyl dichloroethane ; o,p'-DDT = o,p'-dichlorodiphenyltrichloroethane; p,p'-DDD = p,p'-dichlorodiphenyl dichloroethane; p,p'-DDT = p,p'-dichlorodiphenyltrichloroethane

and decreased towards the surface. The presence of DDE and DDMU reflect the process of sequential reductive dechlorination of DDT in the sediments (Eganhouse and Pontolillo 2008), and transport of the more water soluble metabolite DDMU into the water column. Due to the very low concentrations and low polymer mass on SPME, PCB concentrations were all below detection limits (DLs; 5 - 200 pg/L depending on the congener). Within the range of DOC detected, 0.2 to 2.9 mg/L, no corrections for SPME performance were necessary (Zeng *et al*. 2004).

Fractional Equilibration of PE Samplers

The fractional equilibration (Eq. 4) of ^{13}C-labeled PCB28, PCB52, PCB118, PCB128, p,p'-DDE, p,p'-DDD and p,p'-DDT in each of the samplers was used as the fractional equilibration of the 3, 4, 5, and 6 chlorine PCBs, DDE, DDD, and DDT congeners, respectively. These f_{eq} averaged 85% (± 6%), 80% (± 7%), 18% (± 20%), 12% (± 25%) for PCB28, PCB52, PCB118, and PCB128, respectively, and 31% (± 5%), 80% (± 4%), and 94% (± 6%) for DDE, DDD, and DDT, respectively (uncertainty equal to 1 s.d., N = 26). Although only two field blank samplers were analyzed for initial PRC concentrations, agreement between the two was good. Measurements agreed within 5% for all PRCs except PCB28, which agreed within 16%. For analytes without a matching PRC (i.e., p,p'-DDMU, p,p'-DDNU, and PCBs with 2, 7, 8, 9 and 10 chlorines), f_{eq} was modeled, using explicit, finite-difference numerical techniques following Crank (1975; NI method; details and sample Matlab code available in supplemental information). Diffusivities for DDTs and PCBs in polyethylene were taken from Hale *et al*. (2009) and Rusina *et al*. (2010), respectively. Diffusivities in water were estimated from their molar volume following Schwarzenbach *et al*. (2003).

As similar PRC losses were measured in the 26 PE samplers, average values were used to model an average BL, which was then used to calculate the fractional equilibration of PE and waters for compounds without a matching PRC. Modeled BL for the six PRCs, excluding ^{13}C-p,p'-DDT ranged from 190 to 340 µm. No trend with diffusivity in water was observed. The modeled BL using ^{13}C-p,p'-DDT data was only 64 µm, however. The higher than expected, but very consistent loss of most of the ^{13}C-p,p'-DDT PRC during deployment (94% on average), suggests that the compound is being transformed during deployment. For this reason, ^{13}C-p,p'-DDT was left out when finding an average BL for the samplers. An average modeled BL thickness of 230 µm (s.d. = 90 µm) was used with the NI model to estimate the fractional equilibration of p,p'-DDMU, p,p'-DDNU, and PCB congeners with 1, 2, 7, 8, 9 and 10 chlorines.

This mass-transfer modeling indicated that samplers were equilibrated (>99%) with water column for PCBs of low chlorination level (up to 2 Cl), and for DDNU. DDMU were 76% equilibrated with water column, while PCB congeners with seven or more chlorines were less than 4% equilibrated with water column, 3, 1, 0.3, and 0.1% for PCBs with 7, 8, 9, and 10 Cl, respectively.

Dissolved DDT and PCB Concentrations using PE

Due to the much larger polymer mass in the PE samplers as compared to the SPME, DLs ranged from 0.01 pg/L to 18 pg/L for individual PCBs and 0.4 pg/L to 60 pg/L for the individual DDTs (Table 1). As with SPMEs, the compound measured at the highest concentration at every station with PE samplers was p,p'-DDE, with a maximum at station BA4C (2200 ± 400 pg/L; Table 1). Similar to SPME, o,p'-DDE concentrations were observed to be 12% to 16% of the p,p'-DDE concentrations at each station (10% on average for SPME), and p,p'-DDMU concentrations are 17 to 24% of the p,p'-DDE concentrations (30% on average for SPME). Even with the large polymer mass of PE relative to the SPME, some DDT congeners remained below DLs (i.e., 7 and 8 pg/L, for o,p'-DDT and p,p'-DDT, respectively). The reported uncertainties in PE deduced C_W are the propagated uncertainties (1 SD) in the initial and post-deployment PE concentrations.

The PCB congeners measured at the highest concentrations at each station were the pentachlorobiphenyls PCB101, PCB110, and PCB118, with a maximum of 53 ± 17 pg/L for PCB118 in the bottom waters at station BA4C (Table 1). Summing the congeners measured in this study (counting one half of the DL for compounds below the DL), ΣPCBs in the bottom waters ranged from 90 pg/L at station BA9C to 316 pg/L at station BA4C. At the two stations where mid-depth PE samplers were recovered, ΣPCB concentrations were lower than those observed at the near bottom depth as demonstrated earlier by the SPME results for the detectable DDTs. At the background station, T11 (near bottom), ΣPCB concentrations were 50 pg/L, and the only detectable

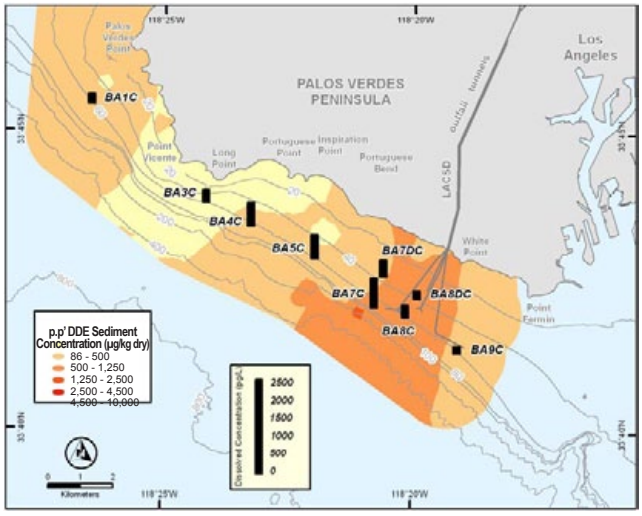
DDT compounds were p,p'- and o,p'-DDE, at 37 and 4 pg/L, respectively.

Discussion

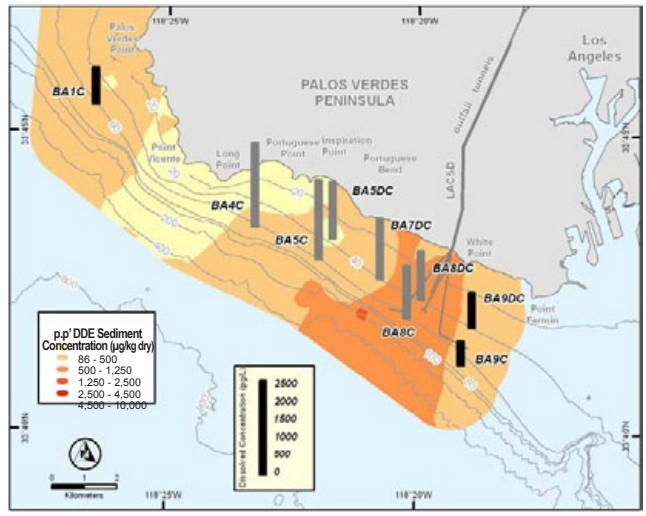
Dissolved concentrations measured in this work are similar to those measured in previous studies. For example, Zeng *et al*. (2004) first measured p,p'-DDE at 2 m above the sediment-water interface at station BA6C (between stations BA5C and BA7C in this work) in 2003 and reported concentrations of 2.8 to 4.5 ng/L using SPME and 3.2 ng/L using a method of high-volume pumping and solid phase extraction. Dissolved p,p'-DDE measured in this work 5 m above the sediment-water interface at station BA5C were 2.1 and 0.81 ng/L using PE and SPME, respectively.

Without the influence of horizontal advection, we may expect samplers above the most contaminated sediments to have the highest contaminant concentrations. However, it is interesting to note that with both types of passive samplers DDTs and ΣPCBs were at the highest water concentrations downcurrent of the most contaminated sediments (BA8C; USEPA unpublished data): station BA4C for PE and station BA7C for SPME (Table 1; Figure 2). It should be noted that the sediment concentrations in Table 1 have not been fully validated and are presented to compare the spatial variability within the study area, and not for their absolute accuracy. As demonstrated previously by Zeng *et al*. (2005), the plume of DDT- and PCB-contaminated waters are carried north-westward by the current, resulting in the highest detected concentrations just downcurrent of the outfall station (i.e., BA8C) and a subsequent decrease with increasing distance away from the Palos Verdes peninsula and into Santa Monica Bay proper.

a)



b)



c)

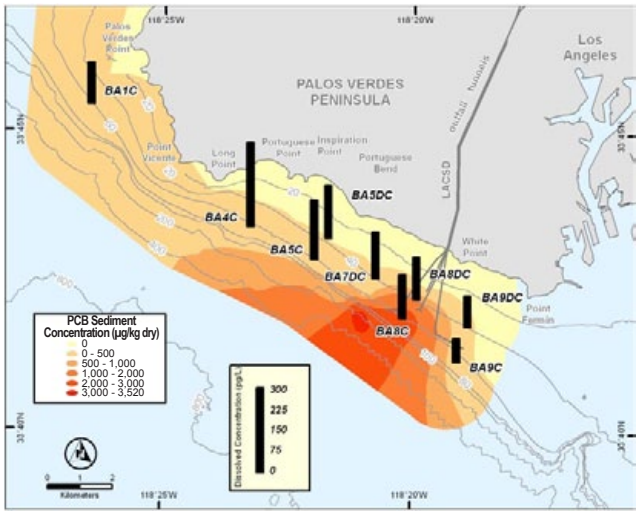


Figure 2. Dissolved concentrations (pg/L) five meters above the sediment surface: SPME-based p,p'-DDE dissolved concentrations* (a), PE-based p,p'-DDE concentrations with gray columns and black columns* (b), and PE-based ΣPCB concentrations* (c). Sediment response surface concentrations are based on USEPA (unpublished data to be used for spatial comparative purposes only) using a radial basis function. *concentration exceeded the human health ambient water quality criteria (AWQC); **concentration exceeded both human health and aquatic life AWQC.**

Relationship of Measured Dissolved Concentrations to Ambient Water Quality Criteria (AWQC)

Human and aquatic life AWQC values for DDT are 220 pg/L and 1000 pg/L, respectively, and for ΣPCB are 64 pg/L and 30,000 pg/L, respectively (http://water.epa.gov/scitech/swguidance/standards/current/index.cfm). To capture the worst case scenario, stations located five meters above the bottom that exceeded these criteria are shown in Figure 2 (assuming similar toxicity values for p,p' DDE, the predominant compound in ΣDDT at this site). Dissolved concentrations of p,p' DDE based on SPME and PE show that all stations where samplers were deployed, except the background station (T11), exceeded the human health AWQC (Figure 2a,b). Based on the PE, dissolved concentrations of p,p' DDE also exceeded both human health and aquatic life AWQC at several stations (Figure 2b). Further, based on SPME, many stations, exceeded the AWQC for p,p' DDE up into mid-water-column depth (Table 2).

PE estimates of dissolved ΣPCB concentrations indicated that all stations, except the background station (T11), exceeded the human health AWQC but none exceeded the aquatic life AWQC (Figure 2c). As noted above, and in agreement with the hypothesis that the sediments serve as the primary source of water column PCBs and DDTs, most AWQC exceedances were associated with samplers close to the sediment water interface. Future efforts in this project will follow the concentrations of DDTs and PCBs in the water column during and after remediation to assess how effective capping is on decreasing the types of exceedances reported above.

Comparison of PE and SPME Samplers

With the aim of assessing the performance of numerical integration techniques for interpreting PRC data, both NI and EAE methods were used to predict the average fractional equilibration of the PRCs. In general, both methods predicted the measured f_{eq} well (within a factor of 2 for all PRCs; Figure SI-2, supplemental information). As mentioned above, the f_{eq} of ^{13}C-p,p'-DDT was not included in the analysis due to very high loss of the PRC, suggesting transformation of the compound during deployment. Either EAE or NI method would have yielded similar results in this investigation. However, using a reasonable range of BL values, f_{eq} for the target compounds could have been predicted before deployment began informing the design of the sampling campaign in terms of the thickness of PE used or duration of deployment.

PE deduced dissolved o,p'- and p,p'-DDE water concentrations (the compounds for which the most comparable data are available) averaged three times greater than the SPME deduced water concentrations (Figure 3). Part of this difference is likely due to PE data being PRC corrected (by factors ranging from 2.4 to 4.5) while SPME are assumed to be equilibrated (no correction). Using the NI method to model diffusion of DDE between a PDMS layer (100 μm thickness with no-flux boundary on one side) and water across a 200 μm thick BL for 32-day results in an integrated mass in the PDMS that is 70% of the equilibrium value (assuming D_{PDMS} of $10^{-6.9}$ (cm^2/s), extrapolated from PCB diffusivities (Rusina *et al*. 2010), and D_W of $10^{-5.3}$ (cm^2/s; Schwarzenbach *et al*. 2003), and ignoring cylindrical geometry of SPME). "Correcting" the SPME deduced C_W by this fraction has the effect of nudging the PE and SPME deduced C_W values closer together. On the other hand, if the fast equilibration assumption for SPME is correct, SPME and PE are time-averaging concentrations over different times. If concentrations of DDE vary with time in the water column, then the two methods should give different values for C_W. In addition to kinetic considerations *in situ*, the difference in concentrations may be due to uncertainties in K_{PEW} and K_f values.

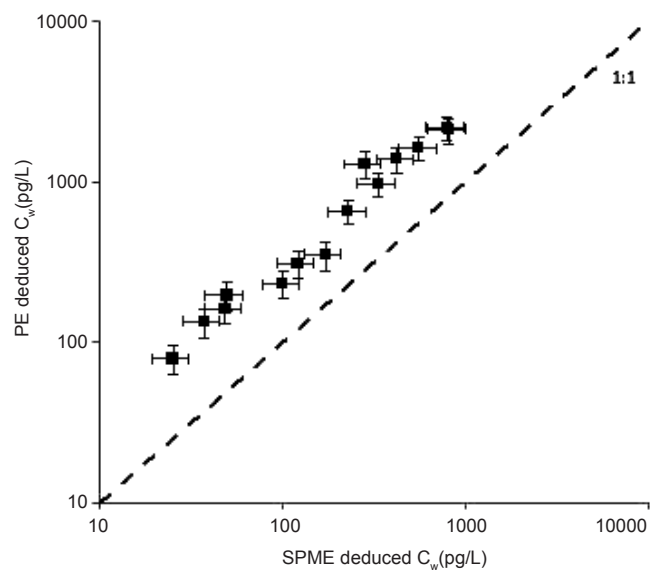


Figure 3. Comparisons of o,p'- and p,p'-DDE PE deduced, CW vs. SPME (squares), in waters near the bottom at stations BA1C, BA4C, BA5C, BA7DC, BA8C, BA8DC, and BA9C.

With or without PRC correction, the PE and SPME deduced concentrations correlate very well ($R^2 = 0.95$), indicating that with appropriate corrections, these samplers are capable of converging on *in situ* dissolved concentrations. Future work should focus on reducing the uncertainties associated with both determination of equilibrium parameters (i.e., K values) and correction factors for non-equilibrium exposure scenarios, including testing the full equilibration assumption for SPME samplers.

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Acknowledgements

We thank Dario Diehl and David Tsukada of SCCWRP and the crew of the R/V Early Bird II for their work deploying and recovering samplers. We also thank Mike Charpentier (Raytheon, Narragansett, RI, USA) for preparing Figures 1 and 2.

Supplemental Information

Supplemental Information is available at ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/AnnualReports/2012AnnualReport/ar12_04SI.pdf