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Using performance reference compound-corrected polyethylene passive samplers and caged bivalves to measure hydrophobic contaminants of concern in urban coastal seawaters

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HIGHLIGHTS

- Hydrophobic organic contaminants were measured with polyethylene passive samplers.
- Seawater concentrations measured up to 1000 pg L^{-1} (p,p′-DDE) & 300 pg L^{-1} (DDNU).
- Seawater measurements with depth suggest bed sediments were a source of DDTs & PCBs.
- Co-deployed mussel- and polyethylene-measured concentrations correlated strongly.

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ABSTRACT

Low-density polyethylene (PE) passive samplers containing performance reference compounds (PRCs) were deployed at multiple depths in two urban coastal marine locations to estimate dissolved concentrations of hydrophobic organic contaminants (HOCs), including dichlorodiphenyltrichloroethane (DDT) and its metabolites, polychlorinated biphenyl (PCB) congeners, and polybrominated flame retardants. PE samplers pre-loaded with PRCs were deployed at the surface, mid-column, and near bottom at sites representing the nearshore continental shelf off southern California (Santa Monica Bay, USA) and a mega commercial port (Los Angeles Harbor). After correcting for fractional equilibration using PRCs, concentrations ranged up to 100 pg L^{-1} for PCBs and polybrominated diphenyl ethers (PBDEs), 500 pg L^{-1} for DDMU and 300 pg L^{-1} for DDNU, and to 1000 pg L^{-1} for p,p′-DDE. Seawater concentrations of DDTs and PCBs increased with depth, suggesting that bed sediments serve as the source of water column HOCs in Santa Monica Bay. In contrast, no discernable pattern between surface and near-bottom concentrations in Los Angeles Harbor was observed, which were also several-fold lower (DDTs: 45–300 pg L^{-1}, PCBs: 5–50 pg L^{-1}) than those in Santa Monica Bay (DDTs: 2–1100 pg L^{-1}, PCBs: 2–250 pg L^{-1}). Accumulation by mussels co-deployed with the PE samplers at select sites was strongly correlated with PE-estimated seawater concentrations, providing further evidence that these samplers are a viable alternative for monitoring of HOC exposure. Fractional equilibration observed with the PRCs increased with decreasing PRC molar volume indicating the importance of target compound physicochemical properties when estimating water column concentrations using passive samplers in situ.

1. Introduction

The southern California coastal zone is a densely populated, highly urbanized and industrialized region where the input and fate of hydrophobic organic contaminants (HOCs) in the nearshore ocean environment remains an issue of concern (Schiff, 2000). This coastal zone receives discharge of treated wastewater effluent and

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stormwater runoff from a population base of more than 10 million people. HOCs that have been deposited in bedded sediments continue to be available to biota in this marine ecosystem (Fernandez et al., 2012, 2014). Two of the most prevalent contaminants in the Southern California Bight (SCB), a system that includes Santa Monica Bay and the Palos Verdes Shelf (PVS), are remnants of technical DDT and PCB mixtures (Venkatesan et al., 1996; Eganhouse et al., 2000). In fact, the U.S. Environmental Protection Agency added the PVS to the National Priorities List and is currently evaluating remediation approaches for the site (EPA, 2009). More recently, brominated flame retardants have received attention due to their toxic potential in the aquatic environment (Darnerud, 2008). Polybrominated diphenyl ethers (PBDEs) have been detected in virtually all ecosystems and taxa (Covaci et al., 2011) and remain a concern in the SCB region and along the California coast (Dodder et al., 2012; Maruya et al., 2014). Because of their persistence and toxicity, PBDEs are being phased out of commercial use in the United States (EPA, 2009).

Monitoring to ensure that HOC concentrations are not approaching harmful levels is an essential component of protecting the integrity of the nearshore ocean environment. In addition, exposure risks and emission reduction effectiveness can be assessed by measurement of freely dissolved HOC concentrations (Lohmann and Muir, 2010). The state of California has set coastal ocean water column guidelines for the DDT metabolite dichlorodibenzoethene (DDE) at 590 pg L^{-1} and for total PCBs at 170 pg L^{-1} (EPA, 2000). However, achieving such low monitoring thresholds is difficult and costly with conventional methods, which in addition, often cannot achieve the desired detection limits (Burgess, 2012). Direct measurement of the freely dissolved water concentration has shown promise in estimating the bioavailability of HOCs (Borga et al., 2005).

Bivalves have been used to monitor water quality in the U.S. since 1975 (Farrington et al., 1983; Goldberg and Bertine, 2000). Because they are sessile and can filter hundreds of liters of seawater every day, bivalves provide time-integrated measurements of chemical concentrations in coastal waters (Goldberg and Bertine, 2000; O'Connor and Lauenstein, 2006). Polymer passive samplers that concentrate target analytes such as HOCs from the aqueous phase can serve as alternative water quality sentinels (Gorecki and Namiesnic, 2002; Mayer et al., 2003; Zabiegala et al., 2010). The utility of passive samplers is maximized when operated in equilibrium mode; i.e. when the concentrations in the water and passive sampler has reached steady-state; however, when equilibrium is not achieved, performance reference compounds (PRCs) may be used to correct for non-equilibrium (Adams et al., 2007; Booij et al., 2002). Low-density polyethylene (PE) has been successfully used to measure DDT metabolites and PCBs in seawater (Fernandez et al., 2012), and shows promise in measuring PBDEs (Sacks and Lohmann, 2012).

Recently, Fernandez et al. (2012, 2014) measured PCBs and DDT metabolites in PVS seawater using PE and SPME passive samplers and reported a gradient emanating from bottom sediments and also away from a known area of elevated contamination (a marine Superfund site). In this study we used PE passive samplers, preloaded with PRCs, to measure DDT and its metabolites, PCBs, and PBDEs in the coastal ocean and a semi-enclosed embayment (Los Angeles Harbor) to allow for a comparison of PRC kinetics over a wider range of hydrodynamic conditions. The PE samplers were deployed at stations with increasing distances from wastewater outfalls and at varying depths within the water column. The PE-estimated seawater concentrations were analyzed to elucidate possible HOC sources (e.g., sediments, large marine wastewater treatment plant outfalls, and PVS). In addition, caged mussels were co-deployed with PE samplers to further investigate PE as a surrogate for bioaccumulation measurements in the water column.

2. Theory

At equilibrium, the concentration of a HOC dissolved in water, C_W (pg L^{-1}), can be estimated from the mass of the HOC sorbed by the PE sampler and the chemical-specific PE-water partition coefficient (K_{PEW}; L_{water} kg_{PE}^{-1}). C_W is calculated under equilibrium conditions:

$$C_W = \frac{C_{PE}^{\infty}}{K_{PEW}} \quad (1)$$

where C_{PE}^{∞} (pg kg_{PE}^{-1}) is the HOC concentration sorbed by the PE at equilibrium. PRCs can be added to the PE prior to deployment to assess (and if necessary, to correct for) the extent of equilibrium achieved (Adams et al., 2007). The PRC will allow for equilibrium to be assessed under varying ambient conditions (Booij et al., 2003). The fractional equilibration (f) achieved by a PRC can be calculated as (Fernandez et al., 2012; Friedman et al., 2012):

$$f = 1 - \frac{C_{PRC}^{t}}{C_{PRC}^{0}} \quad (2)$$

where C_{PRC}^{0} and C_{PRC}^{t} represent the concentration of the PRC prior to and after deployment, respectively. Note that this is a first-order, exponential model (Adams et al., 2007) as $1 - \frac{C_{PRC}^{t}}{C_{PRC}^{0}} = 1 - e^{-k_e t}$ where k_e is a first-order exchange rate coefficient. PRCs are matched to analytes with comparable physiochemical properties (e.g., molar volume, diffusivity, partitioning coefficient). Equation (3) below is thus used to estimate C_{PE}^{∞} so that C_W may be calculated in Eq. (1),

$$C_{PE}^{\infty} = \frac{C_{PE}^{t}}{f} \quad (3)$$

where C_{PE}^{t}, is the target analyte concentration after deployment. The surface area of the PE deployed can be increased in order to allow for very low concentrations (e.g., pg L^{-1}) to be detected by the large sorbing capacity.

If tissue concentration data are available for sentinel organisms exposed to HOCs in seawater (e.g. sessile bivalves), the bioconcentration factor (BCF, L kg^{-1}) is defined as

$$BCF = \frac{C_b}{C_W} \quad (4)$$

where C_b (ng kg^{-1}) is the biota tissue concentration and C_W (ng L^{-1}) is defined above (Arnot and Gobas, 2006).

3. Materials and methods

3.1. Materials

Low-density PE sheeting (Covalence, Minneapolis, MN; 25 μm thick) was cut into strips (5 cm × 100 cm, ~2 g) and pre-cleaned in dichloromethane (DCM; 1 day) and methanol (MeOH; 3 days) prior to loading PRCs. PRCs were loaded into cleaned PE in 1.8 L of a 4:1 MeOH:water spiking solution containing PCB congeners: 50, 155, and 184 (Ultra Scientific, N. Kingston, RI, USA) and $^{13}C_{12}$-p,p′-DDE (99%, Cambridge Isotope Laboratories, Inc., Andover, MA, USA) for 20 days (Booij et al., 2002). The nominal concentration of each PRC in the spiking solution was 100 μg L^{-1}. PRC-loaded PE strips were woven on 12 gauge copper wire and shaped into rings. Samplers were stored at −20 °C or on ice until deployment. Mussels (*Mytilus californianus*), with an average length of 7.0 ± 0.9 cm and average total mass (including shell) of 38.8 ± 10.8 g, were collected from Bodega Bay in Sonoma County, CA, USA, and maintained in flowing seawater for two weeks. They were shipped overnight on ice the day prior to deployment. Approximately ten mussels were set aside from the experiment

stock at the time of deployment and extracted to determine pre-deployment concentrations of target analytes.

The target compounds of interest included: p,p′-DDT; o,p′-DDT; p,p′-DDD; o,p′-DDD; o,p′-DDE; p,p′-DDE and its metabolites DDMU and DDNU; PCBs: 28, 49, 52, 99, 101, 118, 138, 149, 153/168, and 187; and PBDEs: 47, 99, and 100. Standard solutions for DDMU, PCBs, and PBDEs were purchased from Accustandard (New Haven, CT). Neat DDNU (50 mg) was purchased from Sigma–Aldrich (St. Louis, MO). Each standard was dissolved and/or transferred into hexanes and diluted to 50 μg mL^{-1}. Pesticide-grade DCM, MeOH, acetone, and hexanes were purchased from Fisher Scientific (Fairlawn, NJ) and used without further purification.

3.2. Field studies

In June 2011, PE passive samplers were deployed at three stations each in Santa Monica Bay (SMB) and Los Angeles Harbor (LAH) for a period of 28–30 days (Fig. 1). Mussels were co-deployed at the same time, but left in situ for a period of 90 days. The SMB sites were located near the marine outfall of the Hyperion Wastewater Treatment Plant (HTP), which processes 250–300 million gal per day (mgd) of domestic wastewater using full-secondary treatment and discharges its effluent at 60 m near the seafloor. The LAH sites are located near the Terminal Island Water Reclamation Plant (TIWRP), which processes ~20–40 mgd of domestic wastewater using tertiary treatment and discharges its effluent at 10-m depth near the bottom inside the harbor. The LAH and SMB sites are located ~10 km east and 30–40 km northwest, respectively, of the Palos Verdes Superfund (PVS) site. In LAH, caged mussels and triplicate PE were deployed at two depths at each station: 2 m below the surface and 1 m above the sediment–water interface (~9 m depth; Fig. S1). Triplicate PE samplers were co-deployed on the same moorings in SMB along the 60-m isobath at three depths per station: 2 m and 45 m below the sur-

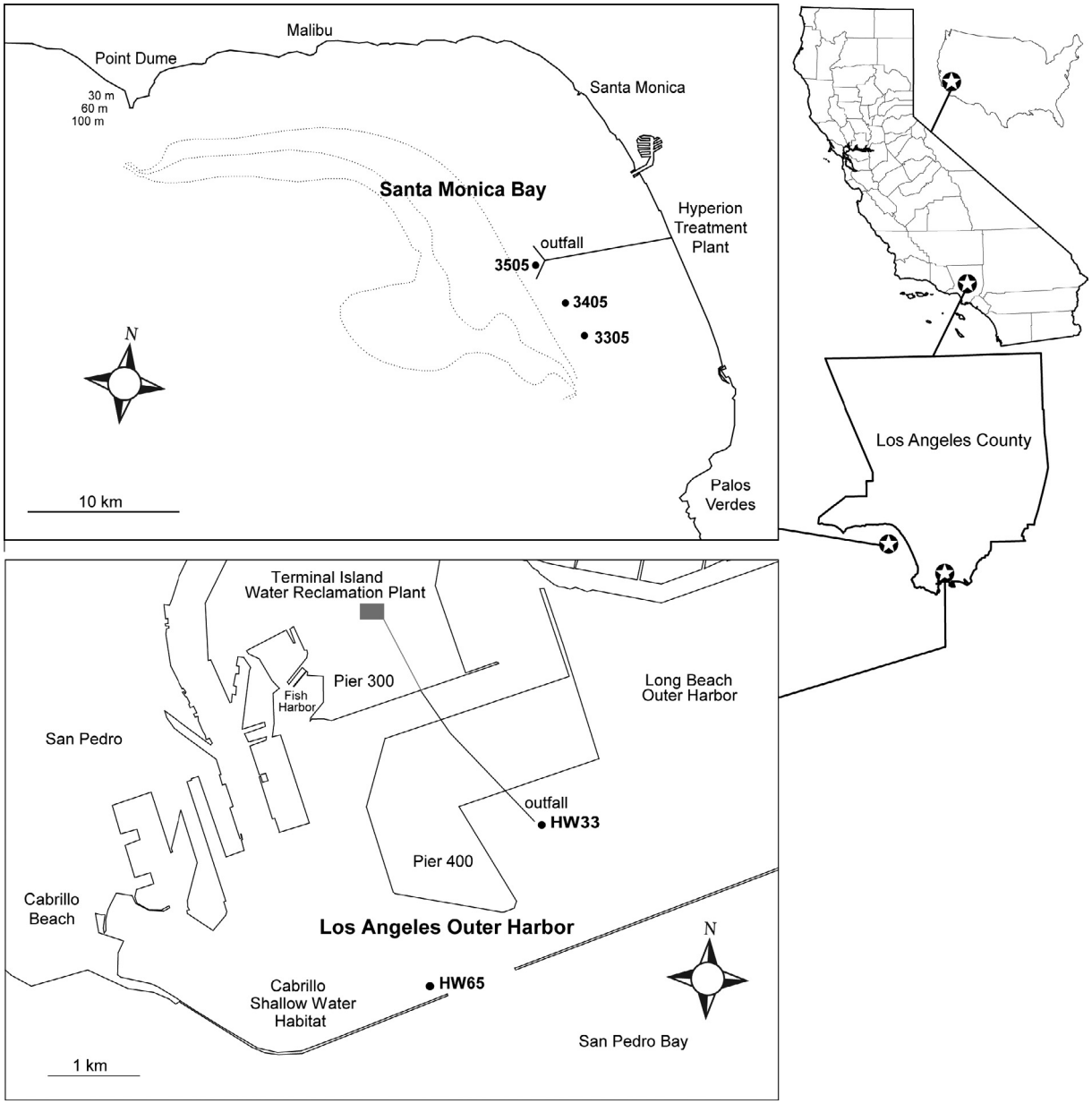

Fig. 1. PE passive samplers were co-deployed with caged mussels (*Mytilus californianus*) at three stations in Santa Monica Bay near the outfall of the Hyperion Wastewater Treatment Plant; and at two stations in Los Angeles Harbor (LAH) near the outfall of the Terminal Island Water Reclamation Plant. Distances from nearest outfall diffusers are: SMB 3505: 0.16 km; SMB 3405: 2.4 km; SMB 3305: 4.7 km; LAH 33: 0.002 km; LAH 65: 1.7 km. Southern California countercurrent flow in SMB is northwest.

face, and 1 m above the sediment–water interface (~60 m depth; Fig. S1). Caged mussels were deployed at 2 and 45 m below the surface at each station. PRC-loaded PE samplers exposed during deployment served as travel/field blanks. Conductivity-temperature-depth (CTD) multi-instrument profiler casts were also collected during sampler deployment and recovery (Table S1).

Upon retrieval, PE samplers were placed in pre-cleaned amber glass jars and stored on ice during transit. Once at the laboratory, PE samplers were wiped clean of visible residue/biological growth using a Kimwipe and rinsed with de-ionized water. Samplers were stored in pre-cleaned glass vials at −20 °C until analysis. Mussels were removed from mesh caging, rinsed with tap water, wrapped in aluminum foil, and stored at −20 °C until analysis.

3.3. Sample processing and analysis

PE samples were extracted as reported by Fernandez et al. (2012). Briefly PE were spiked with dibromooctafluorobiphenyl (DBOFB) and PCB 205 as recovery surrogates, and extracted by sonication in DCM (100 mL, 15 min, 3×). The combined DCM extract was dried over sodium sulfate, concentrated using a TurboVap II (Caliper Life Sciences, Hopkinton, MA, USA; 5–8 psi, 34 °C), exchanged to hexane, and concentrated to 0.5 mL under a gentle stream of high purity nitrogen. DCM extracts from LAH were further purified through a plug of silica gel and alumina, eluting with 15 mL hexane, followed by 65 mL 70:30 hexane:DCM. The eluent volume was reduced, exchanged to hexane, and re-concentrated to 0.5 mL. Once all samples were brought to 0.5 mL, they were spiked with internal standards PCB 30 and PCB 208 and stored in amber glass, crimp cap vials at −20 °C until analysis by GC–MS (details in Section S1, Tables S2–S3).

Retrieved mussels were shucked and soft tissue was freeze-dried, homogenized, and pulverized into a powder using a mortar and pestle. Approximately 2 g of dry tissue was then spiked with recovery surrogates DBOFB and PCB 205 and extracted with DCM at 100 °C and 1500 psi (35 mL × 4) using a Dionex 300 Accelerated Solvent Extraction system (ThermoScientific, Sunnyvale, CA, USA). Organism lipid content was analyzed gravimetrically by evaporating a small sample of concentrated extracted mussel tissue to dryness. Raw extracts were concentrated and purified by gel permeation chromatography (GPC) with a mobile phase of 1:1 DCM:hexane. Two fractions were collected; the first 75 mL was discarded and the following 125 mL was kept and further purified. The collected GPC fraction was then processed as described above for PE samplers from LAH. Mussels from SMB Station 3305 could not be retrieved and thus do not appear in the subsequent data analysis.

3.4. Data analysis and quality control

Each chromatogram was integrated using MSD Chem Station (E.02.01117, Santa Clara, CA, USA). PE and mussel samples were quantified by the internal standard method using a seven-point calibration curve. Analysis of pre-cleaned, virgin PE showed that no target analytes were detectable prior to deployment. Six non-deployed, PRC-loaded PE samplers were extracted to determine C^0_{PRC}, these values for each PRC agreed within 15%. Pre-deployment mussel tissue showed no detectable target analytes except for p,p′-DDE and DDMU (2.9 and 2.5 ng g^{-1} dry mass, respectively). Two measured concentrations of DDMU that were within 20% of the pre-deployment concentrations were reported as below the limit of quantitation. Recoveries (mean ± one standard deviation) of DBOFB and PCB 205 were 65 ± 16% and 100 ± 23% for SMB PE, 51 ± 8% and 87 ± 7% for LAH PE, and 51 ± 20% and 83 ± 20% for mussel tissues, respectively. No targeted analytes were corrected for surrogate recovery.

PE-derived water concentrations were calculated (Eq. (1)) using a compound specific K_{PEW} (Fig. S2 and Table S4) and corrected for non-equilibrium deployment conditions (Eqs. (2) and (3)). Briefly, a fractional equilibration correction factor (i.e. $1/f$) for each target compound was referenced to the PRC with the most similar molecular volume (Section S2 and Table S4). More specifically target analytes were matched to a PRC where the corresponding molecular volume was within 3% (Table S4). Exceptions to this criteria were PCB 28 (6% smaller than corresponding PRC), as PCB 50 reached equilibrium, it was assumed that PCB 28 did as well; PCB 209 (13% larger than corresponding PRC), however PCB 209 was not detected in any samples; and o,p′- and p,p′-DDT (6% and 7% larger than corresponding PRC, respectively), again these compounds were not detected in any samples. Concentrations for pentachlorinated PCB congeners were reported as a range using correction factors referenced to both PCB 50 and PCB 155. Based on an estimated analytical error of 10%, compounds with the corresponding PRC resulting in $f < 0.1$ was adjusted using $f = 0.10$ while compounds with a PRC exhibiting $f > 0.85$ were not corrected (i.e. f was assumed to be unity).

The uncertainty in estimated water column concentrations was characterized by propagating error associated with passive sampler measurements (C^t_{PE}) and estimation of f values (see Eq. (3)). A propagated error of 40% was calculated for target analytes that were corrected using $f > 0.1$ or that exhibited quantitative extraction based on surrogate recovery. The uncertainty for target analytes subject to non-equilibrium correction of $f = 0.1$ and/or that were represented by lower DBOFB surrogate recoveries (e.g. the most volatile target compounds) were estimated at 80%. Statistical comparisons for PRCs and DDT metabolites were done using a pooled t-test or an ANOVA (comparison of more than two; e.g., 3 depths) at the 95% confidence interval.

4. Results and discussion

4.1. PRC-measured fractional equilibration in PE samplers

The fractional equilibration f for PRCs generally decreased with increasing molar volume (V_m; Fig. 2 and Table S5). In Santa Monica Bay (SMB), site 3405 at 58-m depth, f decreased from 0.88 ± 0.04 (PCB 50; V_m = 200.3 cm^3 mol^{-1}; 4 Cl) to 0.17 ± 0.09 (PCB 184; V_m = 235.1 cm^3 mol^{-1}; 7 Cl). Because larger molecules diffuse more slowly through the polymer and water boundary layers, the times to equilibrium are longer. The smaller fractional equilibration for larger molecules is in agreement with laboratory studies that found larger molecules take longer times to diffuse (Adams et al., 2007) and point to the importance of using PRCs of varying molecular size for fractional equilibration correction.

For some PRCs, a trend of decreasing f values with increasing water depth was observed. For example, for PCB 184 at SMB 3405, f was 0.47 ± 0.19 at the surface and decreased to 0.17 ± 0.09 in bottom waters (Fig. 2), however, an ANOVA of the f values for three depths found that they did not significantly change with increasing depth ($p = 0.16$). These small variations with depth, though not statistically significant, may be, in part, due to differences in water velocities. Previous studies in Santa Monica Bay have measured slightly larger surface velocities (1–9 cm s^{-1}) and smaller bottom water velocities (1–3 cm s^{-1}; Hickey et al., 2003). These small decreases in f with decreasing water velocities are consistent with previous studies (Estoppey, 2014). However, as Estoppey et al. tested PE in river-like flow conditions with larger velocity variation, this trend is evident, while in the coastal ocean studied here, where water current is multidirectional and slower, f trends with depth are less apparent. Fractional equilibration variations with depth were even less apparent in LAH (Fig. 2). These smaller variations are likely due to the more shallow, uniform water col-

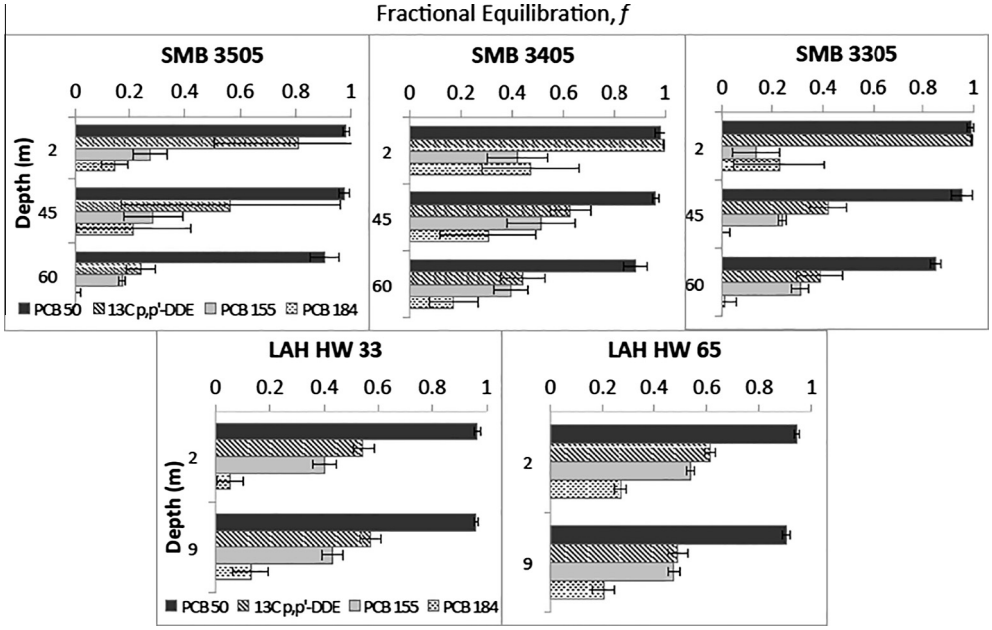

Fig. 2. Fractional equilibration, *f*, reached by performance reference compounds (PRCs) pre-loaded into polyethylene passive samplers. PRCs are listed by increasing molecular volume (V_m; PCB 50, V_m = 200.3 cm^3 mol^{-1}; p,p′-DDE, V_m = 222.4 cm^3 mol^{-1} [b]; PCB 155, V_m = 224.0 cm^3 mol^{-1}; PCB 184, V_m = 235.1 cm^3 mol^{-1})[a]. Station locations are shown in Fig. 1. [a]Molecular volume values from SPARC (Hilal et al., 2004). [b]Molecular volume for ^{12}C-p,p′-DDE; ^{13}C-p,p′-DDE value was not available.

umn (~10 m) in LAH and are further supported by the small temperature variation throughout the 10-m water column in LAH, as gathered from CTD casts collected during sampler deployment and recovery.

The measured *f* values for ^{13}C-p,p′-DDE and PCB 155 were expected to be comparable at each sampling location, based on their comparable molecular volumes. In LAH, the *f* ratios (^{13}C-p,p′-DDE: PCB 155; Fig. 2) showed no significant variability with depth with ratios all at 1. In SMB, the measured *f* for ^{13}C-p,p′-DDE were 1–2 times larger than *f* for PCB 155 at each of the 45- and 60-m depths. In contrast, *f* values for ^{13}C-p,p′-DDE exceeded PCB 155 in SMB surface waters by factors ranging from 2 to 7 suggesting that DDE may be have been eliminated by an alternative pathway at surface sites in SMB. Previously, DDE has been shown to photodegrade in aqueous environments (Wolfe et al., 1977) and in passive sampling media such as PDMS (Llompart et al., 2003). To our knowledge there have been no studies measuring the photostability of DDE in LDPE. Data collected in CTD casts (Table SI) showed increased levels of transmittance at the SMB (78–83%) surface compared to the LAH surface (62–69%), which supports the possibility of ^{13}C-p,p′-DDE photodegradation in SMB surface water. Given that *f* values for PCB 155 and 184 did not vary appreciably with depth, using the measured ^{13}C-p,p′-DDE *f* values at the surface samples instead of PCB 155 or ^{13}C-p,p′-DDE *f* values at the 45-m depth to correct for target analytes may have resulted in an underestimation of water concentration by a factor of 2 for the surface DDE analytes.

4.2. Seawater concentrations estimated by PE passive samplers

Freely dissolved water concentrations were estimated from each target analyte's concentration extracted from the PE after deployment (C_{PE}^{t}). The C_{PE}^{t} was adjusted to estimated concentration (C_{PE}^{∞}) of the analyte in the PE at equilibrium following Eq. (3). A list of each target compound and its corresponding PRC is given in Table S4 and values for *f* are given in Table S5. Each target analyte's C_{PE}^{∞} value was then divided by its partitioning coefficient (listed in Table S4) as described in Eq. (1) to yield a water concentration.

For SMB stations, the measured water concentrations for DDT-related compounds (Fig. 3) and PCBs (Fig. S3) increased with increasing depth, suggesting that sediment is the primary contaminant source. Several target analytes (p,p′-DDT, o,p′-DDT, and o,p′-DDD) were not detected in the present study (Table S6). Seawater concentrations of p,p′-DDE ranged from 4.0 to 1100 pg L^{-1} and total PCB concentrations (sum of 12 congeners measured; Fig. S3) were up to 350 pg L^{-1}. The p,p′-DDE concentrations (and the other DDT compounds) were highest at Station 3305, followed by Stations 3505 and 3405. The elevated concentrations for the 45-m and 60-m depths at Station 3305 may be due in part to proximity (~30 km northwest) to the PVS Superfund site, where DDT contamination remains elevated and the southern California countercurrent flows northwest (Hickey, Dobbins, & Allen, 2003) transporting HOCs from the water column in the PVS into Santa Monica Bay proper. Near-bottom concentrations of DDTs and PCBs at Station 3505 may be the result of historical deposition from the marine outfall of the Hyperion WWTP (Venkatesan et al., 2010).

The distribution of DDT metabolites was not uniform across the study depths, with a larger proportion of DDE (both the p,p′- and o,p′-isomers) near the sediment–water interface. In contrast, the aqueous phase distribution for DDMU and DDNU showed less variation across depths likely owing to their higher water solubility and greater potential to disperse throughout the water column. Measurements were made near the surface (2-m), at mid-depth (45-m) and near the bottom (60-m) in an effort to assess these vertical trends. ANOVAs comparing concentrations at each depth (2-, 45-, and 60-m) show that p,p′-DDE, DDMU and DDNU concentrations were significantly different across depth (ANOVA, $p < 0.05$) with the exception of DDNU at station 3505 (ANOVA, $p = 0.50$). DDNU was the most prevalent DDT metabolite at the surface (61–180 pg L^{-1}), and its concentrations showed smaller changes with depth as they were within factors of two (stations 3505 and 3405) to four (station 3305) throughout the water column. In contrast, p,p′-DDE concentrations varied by factors of 10 (station 3505) to 200 (stations 3405 and 3305) with depth and elevated concentrations were apparent in the bottom water (680–1100 pg L^{-1}) indicating the sediment as a possible source.

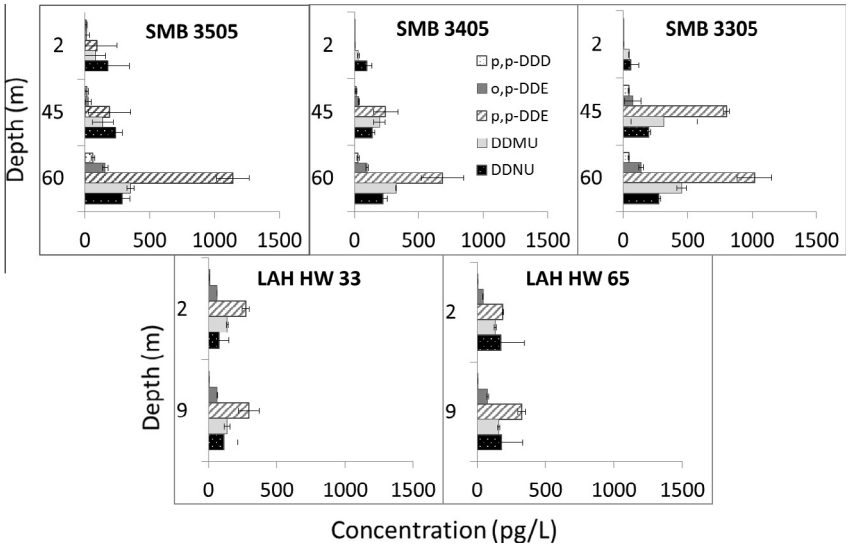

Fig. 3. Seawater concentrations of DDT related compounds estimated by polyethylene (PE) samplers for Santa Monica Bay (top) and Los Angeles Harbor (bottom). Values are the mean and error bars represent one standard deviation ($n = 3$). Station locations are shown in Fig. 1.

DDT metabolite and PCB congener analytes in LAH varied little with depth, suggesting that the relatively shallow water column (10 m) was well mixed. Concentrations of DDT metabolites were approximately three times lower at the stations in LAH compared to SMB, suggesting that the protected waters of the harbor are largely isolated from the PVS to the northwest. The lack of an apparent concentration gradient away from the TIWRP outfall suggests little contribution of DDTs in this discharge to the harbor. Seawater concentrations of PCBs in LAH were very similar to those measured in SMB. Hexachlorinated PCBs were the most abundant homolog in seawater, with PCB 138 and 149 exhibiting the highest concentrations among congeners targeted. Similar compound distributions between stations were observed for sites at the same depths. Like the DDTs, a larger percentage of higher chlorinated PCB homologs were measured with increasing water depth, i.e. approaching the sediment–water interface.

PBDE congeners 47, 99, and 100 were detected in seawater at every site/depth. PBDE 47 was found at the highest concentrations (up to 100 pg L^{-1}), followed in order by PBDE 99 and PBDE 100 (Fig. S4 and Table S6). In SMB, seawater PBDE concentrations were largest at the 45-m depth, intermediate at 60 m, and lowest near the surface. The increasing concentration profile of PBDE 47 with depth at Station 3505, nearest to the HTP outfall, suggested bedded sediment as the primary source of PBDEs being released into the water column, similar to the depth profile observed for DDTs at this station. In contrast, seawater PBDE concentrations at the surface at LAH Station HW33 appear greater than the near-bottom (9 m) concentration by a factor of about two, although the maximum concentrations observed in LAH were lower than those in SMB. These differences in observed depth profiles indicate that, unlike DDTs and PCBs, sediments may not be the only and/or major source of PBDEs to the water column. Because PBDEs are present in a wide variety of household and industrial products and production is still being phased out in the U.S. (Covaci et al., 2011), surface runoff input from Ballona Creek which drains into SMB near the HTP, and the Los Angeles River and Dominguez Channel, which both drain into LAH, are also potential sources of PBDEs (Dodder et al., 2012).

4.3. Comparison of water concentrations with previous studies

Concentrations of DDTs and PCBs measured in the present study were within the range reported previously using passive samplers deployed in 2010 on the PVS (Fernandez et al., 2012). As a further comparison, concentrations of p,p′-DDE (~1000 pg L^{-1}) at Station 3305, nearest to the PVS Superfund site, were similar in magnitude to those reported by Fernandez et al. (2012; 650–2200 pg L^{-1}). Moreover, the distribution of DDT metabolites reported by Fernandez et al. (2012) was similar to that measured in the present study (Fig. 3). Our largest measured values for DDMU and DDNU (450 and 270 pg L^{-1}, respectively) are also comparable to the DDMU (130–410 pg L^{-1}) and DDNU (98–230 pg L^{-1}) values measured by Fernandez et al. (2012). The average percent DDMU (relative to sum of p,p-DDE + DDMU) at the near-bottom depths was 29% in SMB (Table S6a) and is comparable to the 30–35% DDMU values found in Palos Verdes sediments (Eganhouse and Pontolillo, 2008).

4.4. Correlation between bivalve tissue and PE-predicted concentrations

Lipid-normalized mussel concentrations showed a positive correlation with PE-derived mussel predicted concentrations (Fig. 4). The K_{ow} for each chemical of interest was used as an estimate of the lipid-water partitioning coefficient so that PE-derived mussel/biota predicted concentrations ($C_{b,pred} = C_{W,PE} * K_{ow}$) could be directly compared to measured mussel concentrations. The mussel/biota concentration is well-predicted using a linear relationship (slope = 0.84; $R^2 = 0.88$; $n = 121$). In addition, BCF values were estimated by plotting dry mass normalized mussel concentrations (Table S7) with PRC corrected, PE-determined water concentrations for each compound (Fig. S5 and Table S8) for these analytes. Because the mussels were assumed to reach equilibration at 90 days and the PE-predicted concentrations were corrected for fractional equilibration, a one-to-one correlation was expected; however, it is of note that a few of the higher molecular weight (HMW) chemicals (corrected with PRC PCB 184) are the farthest below the one-to-one line and exhibit lower mussel concentrations than those predicted using PE (Fig. 4). It is possible that HMW chemicals may not be completely equilibrated in mussels at 90 days. Additionally, the f correction factors for the outlier HMW chemicals were ~0.10 and may have resulted in an over-correction to the PE-predicted concentrations. A similar relationship between oligochaete tissue concentrations and SPME-predicted tissue concentrations was observed in a porewater study (Lu et al., 2011). The good correlation shown here, confirms that PE

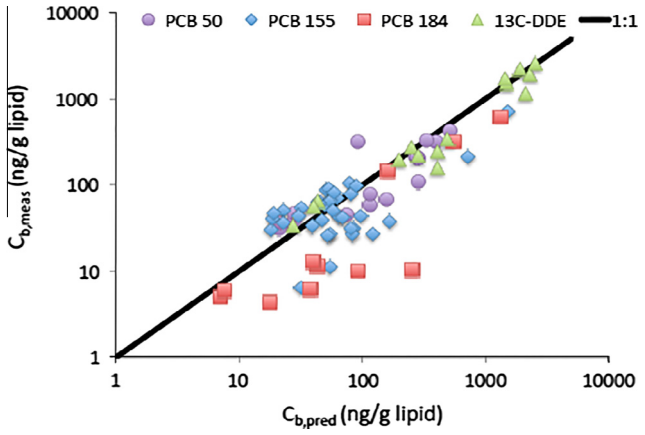

Fig. 4. Measured ($C_{b,meas}$) versus predicted ($C_{b,pred}$) concentration in mussels co-deployed with polyethylene passive samplers. $C_{b,pred} = C_{W,PE} * K_{ow}$, where $C_{W,PE}$ is corrected for fractional equilibration achieved using performance reference compounds in order of increasing molar volume: PCB 50 (circle); C13-p,p′-DDE (circle); PCB 155 (triangle); PCB 184 (square). Best-fit line: $C_{b,meas} = 0.85\ C_{b,pred} - 15$; $R^2 = 0.88$; $n = 121$.

passive samplers provide a good surrogate measure of bioaccumulation in mussels (Maruya et al., 2014) and should be considered for water quality monitoring applications for the targeted HOCs.

5. Conclusions

Several HOCs of concern were detected in the ng L^{-1} (e.g. DDTs) to pg L^{-1} (e.g. PCBs and PBDEs) range in southern California coastal marine waters using PRC-corrected PE passive samplers. The utility of analyte- and sampler-specific PRCs was demonstrated in PE where a large range of fractional equilibration was achieved due to varying PRC molecular size; no significant changes in fractional equilibrium were observed with depth. In Santa Monica Bay, a large embayment with historically contaminated sediments, seawater concentrations of DDTs and PCBs increased with depth, suggesting that bedded sediments remain a source to the water column. In contrast, there was no statistical difference between near-surface and near-bottom water concentrations of DDTs, PCBs, or PBDEs in LAH. Lipid-normalized mussel concentrations for the targeted HOCs showed a good correlation with PE-predicted mussel concentrations demonstrating that PE passive samplers provide a viable alternative measure of bioaccumulation by sentinel bivalves. Because more hydrophobic and slower-diffusing HOCs result in smaller fractional equilibration and larger correction factors, future work should focus on reducing the uncertainty associated with application of small fractional equilibration correction factors.

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Appendix A. Supplementary material

Supplementary data associated with this article including SPME- and PE-derived water concentrations for PCBs, DDTs, & PBDEs; GC/MS details; and BCF regressions can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2014.12.067.

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