Occurrence of contaminants of emerging concern along the California coast (2009-10) using passive sampling devices

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Abstract

Three passive sampling devices (PSDs), polar organic chemical integrative samplers (POCIS), polyethylene devices (PEDs), and solid-phase microextraction (SPME) samplers were used to sample a diverse set of chemicals in the coastal waters of San Francisco Bay and the Southern California Bight. Seventy-one chemicals (including fragrances, phosphate flame retardants, pharmaceuticals, PAHs, PCBs, PBDEs, and pesticides) were measured in at least 50% of the sites. The chemical profile from the San Francisco Bay sites was distinct from profiles from the sites in the Southern California Bight. This distinction was not due to a single compound or class, but by the relative abundances/concentrations of the chemicals. Comparing the PSDs to mussel (*Mytilus* spp.) tissues, a positive correlation exists for the 25 and 26 chemicals in common for the PEDs and SPME, respectively. Diphenhydramine was the only common chemical out of 40 analyzed in both POCIS and tissues detected at a common site.

Introduction

The National Oceanic and Atmospheric Administration's National Status and Trends Mussel Watch Program has analyzed bivalves since 1986 to characterize spatial and temporal trends of contaminants in the coastal areas of the United States. Bivalves can be a useful sentinel species for contaminant monitoring programs as they remain in fixed locations and are good accumulators of persistent, bioaccumulative, and toxic (PBT) organics. This long-term monitoring program has shown that levels of the banned or restricted chlorinated organics such as polychlorinated biphenyls (PCBs) and organochlorine pesticides have decreased compared to historical values (Kimbrough *et al.* 2008).

With the levels of many PBTs decreasing, the research focus is beginning to shift to ''contaminants of emerging concern'' (or CECs). CECs is a term encompassing a broad range of chemicals not traditionally part of monitoring studies such as pharmaceuticals, fragrances, flame retardants, and current-use pesticides. These CECs sometimes lack the persistence of traditional chlorinated organics, but due to their continual input into the environment from industrial, agricultural, and urban sources, they maintain a pseudo-persistence (Daughton and Ternes 1999). Long-term exposure to some CECs has been shown to cause sub-lethal effects such as endocrine disruption in aquatic species including mussels (Gagné *et al.* 2004, Porte *et al.* 2006, Matthiessen 2008).

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The measurement of PBTs and CECs in open waters can be difficult using traditional grab sampling techniques as the concentrations of these chemicals are often at levels below the method detection limits achievable with a standard 1 L water sample (Alvarez and Jones-Lepp 2011). The use of passive sampling techniques can overcome the volume limitations of grab samples and be used to sample CECs which do not bioaccumulate in typical biomonitoring organisms. In this work, three types of passive sampling devices (PSDs), the polar organic chemical integrative sampler (POCIS), low density polyethylene film devices (PEDs), and solid phase microextraction (SPME) fibers were co-deployed in arrays to measure concentrations of PBTs and CECs along the California coast.

Methods

Sampling Locations

The PSD arrays were deployed at 11 stations for periods of 28 to 30 days along California's San Francisco Bay and the Southern California Bight (Table 1; Figure 1). These stations comprised a mixture of land-use from highly urban (number of sites, 6), mixed development (1), low development (2) to largely agricultural (2). Four of the stations received permitted stormwater discharges, one received discharge from a publicly owned treatment works (POTWs) only, three received discharges from both stormwater and POTWs, and three were not within proximity to regulated discharges. Details on how the land-use categories were determined and discharge identification are given by Maruya *et al*. (In press).

Passive Sampling Devices

At each station, POCIS, PEDs, and SPME fibers were deployed subtidally within 500 m of a corresponding mussel sampling location. At four of the PSD stations (LATI; SFSB; SPNR; and SPPR), no native mussels were available for collection therefore caged mussels (*Mytilus* spp.) were co-deployed with the PSDs. A complete list of the chemicals analyzed from each PSD (166 in POCIS, 95 in PEDs, and 99

Table 1. Passive sampler deployment stations for the California pilot study on contaminants of emerging concern (CECs) in 2009-10 (arranged north to south). Mussel sampling locations are described in Dodder *et al*. (In press).

Station Name	Latitude / Longitude	Land-Use Category	Mussel Sampling Location (Lat / Long)
SPPR / San Pablo Bay - Petaluma River	38.13378 / -122.501	Low Dev	None
SFYB / San Francisco - Yerba Buena	37.81375 / -122.359	Urban	Nearby 37.8152 / -122.371
SPNR / San Pablo Bay - Napa River	38.29931 / -122.283	Ag	None
SFSB / San Francisco Bay - South Bay	37.46053 / -121.975	Urban	None
CPSB / Carpenteria State Beach	34.38693 / -119.514	Low Dev	Nearby 34.38712 / -119.514
MULG / Mugu Lagoon	34.10212 / -119.104	Ag	Nearby 34.1023 / -119.104
LATI / Los Angeles Harbor Terminal Island	33.722 / -118.243	Urban	Co-Deployed
LARM / LA River - Queen Mary	33.75523 / -118.195	Urban	Nearby 33.75525 / -118.195
NHPB / Newport Harbor PCH Bridge	33.61695 / -117.904	Mixed Dev	Nearby 33.6166 / -117.905
SDHI / San Diego - Harbor Island	32.7248 / -117.195	Urban	Nearby 32.72478 / -117.195
TJRE / Tijuana River Estuary	32.56988 / -117.127	Urban	Nearby 32.56982 / -117.127

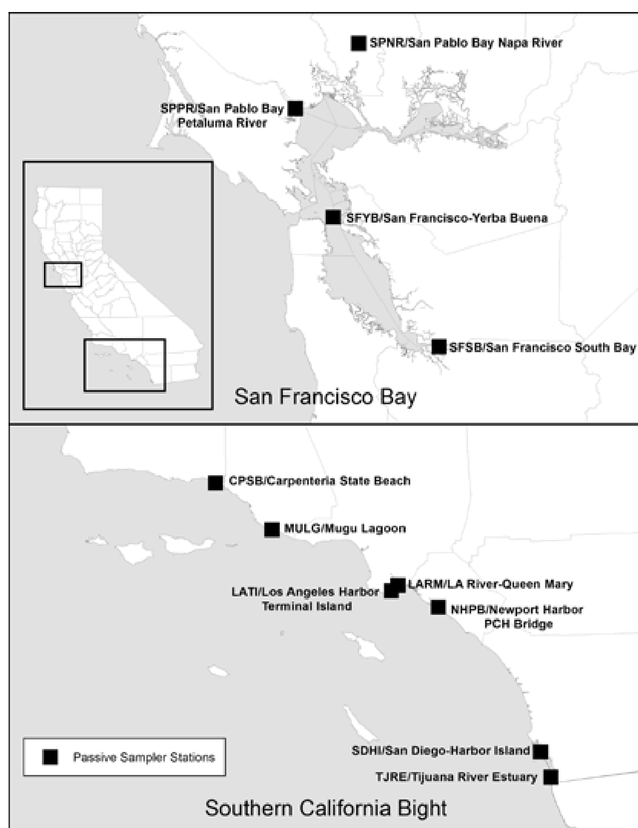

Figure 1. Passive sampler deployment locations during the 2009–10 pilot study on contaminants of emerging concern (CECs) along the California coast in San Francisco Bay and the Southern Bight.

in SPME) is given in the Supplemental Information (SI) Table SI-1 (ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/AnnualReports/2013AnnualReport/ar13_049_059SI.pdf).

POCIS

For each deployment site, a stainless steel deployment canister housing five POCIS (41 cm^2 sampling surface area, 200 mg of Oasis HLB each) was prepared according to established procedures (Alvarez *et al.* 2004). The loaded deployment canisters were shipped to the study sites on ice in airtight metal cans. At the deployment sites, they were quickly attached to the PSD arrays with nylon ropes and metal clips and secured in the water. Upon retrieval, the canisters were placed back in the metal cans and shipped to the laboratory in coolers on ice for processing.

PEDs

The low-density polyethylene strips (25.4 µm nominal thickness, 1.2 g each, Covalence, Minneapolis, MN, USA) were pre-cleaned by sonication (3 x 15 minutes) using methylene chloride, followed by methanol, and then deionized water. The pre-cleaned strips were threaded onto solvent rinsed copper wire, wrapped in aluminum foil and stored at -20°C or ice until deployment. Triplicate PEDs were attached onto polypropylene rope with stainless steel hose clamps for deployment at each site. Upon retrieval, each PED was gently wiped with a Kimwipe to remove visible residue and rinsed with deionized (DI) water. The PEDs were placed in individual pre-cleaned glass vials and transported on ice to the laboratory.

SPME

New SPME fibers coated with 100 µm polydimethylsiloxane (Supelco Inc., Bellefonte, PA, USA) were pre-conditioned by heating at 250°C for 0.5 hours prior to insertion into a perforated copper casing to protect against breakage and biofouling (Zeng *et al.* 2004, Fernandez *et al.* 2012). The SPME fibers were attached in triplicate to the PEDs at each site using metal clips and nylon rope. Following the field deployment, the SPME fibers were placed in glass vials and transported on ice to the laboratory.

Analytical Methods

POCIS

The POCIS were removed from the deployment canisters and rinsed with DI water to remove any particles that may fall into the extraction cartridges. Each POCIS was carefully opened and the sorbent transferred with DI water into pre-cleaned empty solid-phase extraction (SPE) cartridges (25 ml, Biotage, Charlotte, NC). The sorbent was dried by pulling (by vacuum) air through the sorbent bed for 10 minutes. Once dry, the sorbents were designated for analysis of waste indicator compounds (two POCIS per site), pharmaceuticals (two POCIS per site), and pesticides (one POCIS per site).

The two POCIS for the waste indicator compounds were each extracted with 25 ml of 80:20 (v:v) dichloromethane:methyltert-butyl (Optima grade, Fisher Scientific) ether prior to being combined into a single sample and reduced in volume to 2 to 3 ml by rotary evaporation. The concentrated extracts were dried by passing them through filter cartridges (Captiva 3 ml, Agilent Technologies) containing a layer of anhydrous sodium sulfate. The dried extracts were reduced in volume under nitrogen, transferred into gas chromatography (GC) vials, spiked with 500 µg of *p*-terphenyl-d_{14} as an instrumental internal

standard and adjusted to a final volume of 1 ml. Analyses were performed using an Agilent 6890 GC coupled to a 5973 N quadrupole mass selective detector (MSD) operated in full scan positive ion electron ionization (EI) mode. Details on the instrument conditions have been previously reported (Alvarez *et al.* 2009).

The two POCIS for the pharmaceuticals were each extracted with 25 ml of methanol (Optima grade, Fisher Scientific), which was subsequently evaporated to 2 to3 ml by rotary evaporation prior to being combined into a single sample. The samples were concentrated to <1 ml under nitrogen and solvent exchanged into water for analysis by high-performance liquid chromatography/tandem mass spectrometry (HPLC/MS/MS). Details of the method are described in Tertuliani *et al*. (2008). The HPLC/MS/MS analyses used an ammonium formate-modified water:methanol gradient to separate the pharmaceuticals on a reversed-phase C-18 stationary phase column. Electrospray ionization operated in the positive-ion mode was used for identification and quantification of the target pharmaceuticals. For each pharmaceutical, a protonated pseudomolecular precursor ion was formed during ionization and subsequently fragmented in theMS/MS. At least two characteristic product fragmentions formed from the precursor ion were monitored for each pharmaceutical. Qualitative identification of each pharmaceutical was based on the HPLC retention times, relative abundances of these diagnostic precursor-product transitions; quantitation of the more abundant primary transition was used to determine individual pharmaceutical concentrations in the extracts. Quantitation was determined by the internal standard method using ethyl nicotinoate-d_4, carbamazepine-d_{10}, fluoxetine-d_5, and norfluoxetine-d_5 which were added to the extracts prior to analysis.

The remaining POCIS for current-use pesticides was also extracted with 25 ml of methanol and evaporated by rotary evaporation. Atrazine-d_{10} was added as a recovery surrogate. The extracts were exchanged into ethyl acetate, reduced to a final volume of 0.5 ml, and acenaphthene-d_{10} and pyrene-d_{10} were added as internal standards. Analyses were performed using an Agilent 7890 GC coupled to a 5975 MSD operating in EI mode. Details on the instrument conditions have been previously reported (Reilly *et al.* 2012).

PEDs and SPME

The PEDs were cut into small pieces, placed in solvent rinsed glass bottles, spiked with dibromooctafluorobiphenyl (DBOFB) and PCB 208 (as recovery surrogates), and sonicated for 15 minutes with 3 × 300 ml of dichloromethane. The combined dichloromethane extract was dried over anhydrous sodium sulfate and concentrated to about 5 ml and then exchanged to hexane to a final volume of 0.5 ml using a TurboVap II Concentration Workstation (Caliper Life Sciences, Hopkinton, MA). The extract was transferred to a GC vial and spiked with PCBs 30 and 205 as internal standards.

Polybrominated diphenyl ethers (PBDEs), PCB congeners with five or more chlorine atoms, pyrethroids, and fipronil and its three degradates (Table SI-1) were analyzed using an Agilent 7890 GC coupled to a 5975C quadrupole MSD (Wilmington, DE, USA) operating in the negative chemical ionization (NCI) mode. Polycyclic aromatic hydrocarbons (PAH) and PCB congeners with less than five chlorine atoms (18, 28, 37, 44, 49, and 52) were analyzed on a similar instrument operating in the EI mode (70 eV). Details for these analyses were published previously (Fernandez *et al.* 2012). A single quantitation ion per target compound was acquired using the selected ion monitoring (SIM) mode. SPME fibers were manually injected into the GC inlet; two fibers were analyzed in the NCI mode and a single fiber was analyzed in the EI mode. For the stations with duplicate SPME, one each was analyzed in the NCI and EI modes. Five-point external (SPME) and internal (PED) standard calibration curves were used to quantify target compounds. Analyte-specific method detection limits (MDLs) were estimated using the lowest detectable target analyte mass for a minimum signal to noise ratio of 3.

Quality Assurance/Quality Control (QA/QC)

A QA/QC approach using a comprehensive set of performance based data quality control objectives was used in this study (Maruya *et al.* In press). This included field blanks, surrogate recovery checks, replicate samples, and data validation checks (Alvarez *et al.* 2007). The results from replicate PSDs deployed at MUGU and YBI were averaged. Final concentrations were blank subtracted.

POCIS

Tetrachloroethylene (37%) and triethyl phosphate (167%) were removed from the data

set due to their low or high recovery in the spiked matrix. Cholesterol was removed from the data set due to a high duplicate sample relative percent difference (RPD) of 124%. The results for the three POCIS compound classes (wastewater compounds, pharmaceuticals, and pesticides) met the project's acceptance criteria. The recovery of the matrix spikes for all detected wastewater compounds in the data set ranged from 65% to 150%. In the set of duplicate deployments, all compounds significantly above the detection limit had RPDs ≤54%, except for diethylhexylphthalate (DEHP) at 156%. For pharmaceuticals, the solvent exchange/blowdown recovery was 25 to 32%, where negative values represent a loss of compound, and positive values represent an apparent gain of compound. In the set of duplicate deployments, all compounds significantly above the detection limit had RPDs ≤60%. For the pesticides, surrogate (atrazine-d_{10}) recoveries were between 85 and 121%. In the set of duplicate deployments, all compounds significantly above the detection limit had RPDs ≤42%.

PEDs and SPME

All analytes from the PEDs and SPME analyses passed the acceptance criteria and were included in the data set. Recovery (mean ±sd) of surrogates in PED extracts was 79 ±15 and 96 ±5.7 for DBOFB and PCB 208, respectively. Estimated concentrations for analytes that were detectable on SPME travel blanks were <10% of the reported MDLs, except for chlordane and p,p'-DDD (both 12%). Estimated concentrations for analytes detectable in PED procedural and travel blanks were in some cases comparable to the reported MDL (e.g., heptachlor epoxide, o,p'-DDT, PCB 153/168) ,but were <10% of reported sample concentrations.

Results and Discussion

Chemical Profiles Compared to Land-Use

The PSDs were deployed at eleven sites along the Southern California Bight (SCB) and San Francisco Bay (SF Bay). Seventy-one individual chemicals were measured by the PSDs in at least 50% of the sites (Table 2). The POCIS detected 17 compounds (fragrances, phosphate flame retardants, plasticizers, and pharmaceuticals) while the SPME and PEDs detected 29 and 44 compounds (PAHs, PCBs, PBDEs, and chlorinated pesticides), respectively. Due to the widespread urbanization along the California coast, only six current-use agricultural pesticides were detected at two sites (MULG/Mugu Lagoon and NHPB/Newport Harbor).

Figure 2 is a heat map showing the concentration of each analyte at each station as a color. The x- and y-axes were ordered by hierarchical clustering, resulting in the placement of stations and analytes with similar patterns near one another. Dendrograms showing the relationship information are positioned on the sides of the grid. The heat map was generated with POCIS analytes; PAH analytes from SPME; and PCB, OC, and PBDE analytes from PEDs. This combination was selected because the PAH analyte set was larger for SPME than PED, and PED was more sensitive towards PCBs, OCs, and PBDEs than SPME. All analytes detected in at least one sample were included. The abundances for POCIS and SPME/PED are in different units in order to visualize the contaminant profiles on the heat map (Figure 2). Stations LARM and LATI are absent due to incomplete data sets.

The heat map shows the SF Bay contaminant profile is distinct from the SCB profile (that is, the four SF Bay stations are clustered at the top of the heat map; the five SCB stations are clustered at the bottom). Stations are not clustered by land-use, perhaps due to the low statistical power resulting from the limited number of stations within each land-use category. The distinction between SF Bay and the SCB is tentative due to the small number of stations. The apparent distinction is not due to a single compound class; for example, the analytes making up Cluster 1 (highlighted in Figure 2) and found at higher relative abundance in SF Bay are indole, PCB-52, PCB-101, PCB-138, DEET, heptachlor epoxide B, and endrin. The analytes making up Cluster 2 and found at relatively high abundance at eight or more stations from both SF Bay and the SCB are phenanthrene, fluoranthene, pyrene, diphenyl phthalate, and tris(1-chloro-2-propyl)phosphate (TCPP). An expanded version of the heat map naming all analytes is provided in the Supporting information (Figure SI-1).

Comparison of POCIS/PEDs/SPME

Comparisons between the hydrophilic POCIS (focusing on current-use and emerging contaminants) and the hydrophobic PED and SPME (both mainly focusing on legacy contaminants) were limited as each PSD was analyzed for different suites of chemicals which were likely to be sampled by that

Table 2. Mean, minimum, and maximum concentrations of CECs and legacy analytes detected by passive sampling devices at 50% or more of the study sites.

POCIS Compound	Percent Detection	Concentration (ng/L) mean/min/max
Bromoform	100	32 / 5.3 / 77
Tris(1-chloro-2-propyl)phosphate (TCPP)	90	410 / nd / 3100
Diethyl phthalate	90	150 / nd / 600
Galaxolide (HHCB)	80	150 / nd / 1300
Diethylhexylphthalate (DEHP)	80	400 / nd / 1100
Acetophenone	80	11 / nd / 47
Cotinine	80	2.7 / nd / 6.3
d-Limonene	70	15 / nd / 46
Caffeine	70	10 / nd / 32
Tributyl phosphate	70	6.6 / nd / 25
Carbamazepine	70	2.6 / nd / 21
Trimethoprim	70	0.3 / nd / 2
N,N-diethyltoluamide (DEET)	60	10 / nd / 69
Tris(2-chloroethyl)phosphate (TCEP)	60	7.6 / nd / 56
Tris(1-chloro-2-propyl)phosphate isomer	50	930 / nd / 8900
Camphor	50	30 / nd / 92
Benzophenone	50	0.89 / nd / 5.1

SPME Compound	Percent Detection	Concentration (pg/L) mean/min/max
Fluoranthene	100	3000 / 410 / 14000
Phenanthrene	100	2000 / 8.4 / 7800
Pyrene	100	1100 / 96 / 2400
Chlordane, alpha	100	33 / 2.1 / 120
Chlordane, gamma	100	11 / 0.67 / 40
Nonchlor, trans	100	8 / 0.55 / 26
BDE-47	100	4.5 / 0.56 / 22
Nonachlor, cis	100	5.9 / 0.53 / 20
PCB-153/168	100	1.4 / 0.09 / 8.4
BDE-99	93	0.98 / nd / 6.2 pg/fiber
BDE-49	93	0.48 / nd / 2.2 pg/fiber
Fluorene	85	1300 / nd / 5500
p,p'-DDE	79	44 / nd / 250
PCB-187	79	4.2 / nd / 26
Acenaphthene	77	1600 / nd / 8800
Anthracene	77	1400 / nd / 6000
PCB-118	71	3.7 / nd / 20
BDE-100	71	0.38 / nd / 2.3 pg/fiber
Chrysene	69	230 / nd / 810
Benzo[k]fluoranthene	69	72 / nd / 360
PCB-151	64	1.8 / nd / 13
Benz[a]anthracene	62	160 / nd / 590
Benzo[b]fluoranthene	62	110 / nd / 570
Dieldrin	57	51 / nd / 200
PCB-138	57	4.5 / nd / 31
PCB-170	50	1.8 / nd / 11
PCB-183	50	1.5 / nd / 11
PCB-201	50	2 / nd / 11
BDE-28	50	0.32 / nd / 1.4 pg/fiber

PED Compound	Percent Detection	Concentration (pg/L) mean/min/max
p,p'-DDE	100	48 / 2.2 / 190
Dibenzo[a,h]anthracene + Indeno[1,2,3-cd]pyrene	100	34 / 3 / 160
Benzo[g,h,i]perylene	100	13 / 0.9 / 67
Chlordane, alpha	100	14 / 2.5 / 45
Chlordane, gamma	100	6.2 / 1.2 / 22
BDE-49	100	4.3 / 0.47 / 17
BDE-47	100	2 / 0.31 / 9.4
Nonchlor, trans	100	3 / 0.59 / 9.2
Nonachlor, cis	100	2.6 / 0.49 / 8.2
PCB-153/168	100	0.68 / 0.04 / 3.3
BDE-99	100	0.44 / 0.06 / 2.6
BDE-100	100	0.14 / 0.02 / 0.6
Chrysene	92	640 / nd / 6400
Benzo[a]pyrene	92	54 / nd / 220
PCB-52	92	26 / nd / 94
PCB-101	92	21 / nd / 55
PCB-138	92	13 / nd / 55
PCB-149	92	1.4 / nd / 7.9
PCB-118	92	0.6 / nd / 2.4
PCB-187	92	0.16 / nd / 0.79
PCB-180	92	0.15 / nd / 0.72
PCB-201	92	0.038 / nd / 0.16
PCB-110	85	2 / nd / 10
PCB-151	85	0.3 / nd / 1.7
PCB-128	85	0.15 / nd / 0.65
PCB-177	85	0.11 / nd / 0.58
PCB-123	85	0.099 / nd / 0.42
PCB-183	85	0.066 / nd / 0.37
PCB-158	85	0.042 / nd / 0.20
PCB-194	85	0.013 / nd / 0.057
BDE-154	85	0.008 / nd / 0.043
Dieldrin	77	28 / nd / 92
PCB-105	77	0.23 / nd / 0.90
BDE-66	77	0.14 / nd / 0.46
PCB-114	77	0.061 / nd / 0.31
PCB-156	77	0.046 / nd / 0.19
BDE-28	69	1.2 / nd / 5.6
PCB-170	69	0.076 / nd / 0.43
BDE-153	69	0.011 / nd / 0.05
p,p'-DDD	62	30 / nd / 190
o,p'-DDE	54	4 / nd / 16
Bifenthrin	54	1.9 / nd / 12
PCB-99	54	1 / nd / 5.5
PCB-206	54	0.003 / nd / 0.014

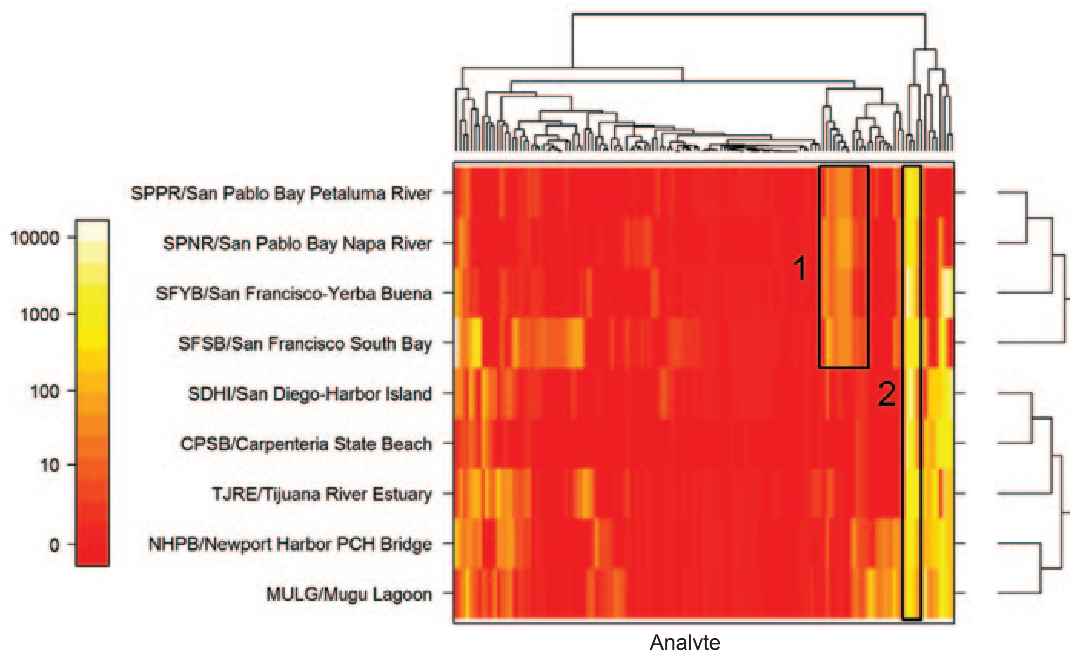

Figure 2. Heat map showing hierarchical clustering of stations and analytes. The abundance key is shown on the left, with the abundance for calibrated POCIS analytes corresponding to ng/L and for calibrated SPME/PED analytes corresponding to pg/L. For non-calibrated analytes the abundance corresponds to ng/sampler matrix for POCIS and pg/sampler matrix for SPME/PED.

device. However, there was some overlap between PSDs as many of the analytical methods contained chemicals with a broad range of polarities. None of the 15 chemicals in common between the POCIS and SPME or the nine chemicals in common between the POCIS and PED were detected in both samplers. Nearly all of the common chemicals, with the exception of diazinon (not detected by any sampler) and the fipronil degradation products, have $\log K_{ow}$ values greater than 4 and therefore have a much lower affinity for the POCIS.

There were 71 common chemicals measured in both the PED and SPME. Overall, there was good agreement between these two samplers in terms of chemicals detected and estimated water concentrations (Tables SI-2, SI-3, SI-4). The PED did have a higher number of detections, all of which were at a lower estimated water concentration compared to the SPME, suggesting the PED may be more useful in trace level applications.

The amount of chemical sampled is related to the volume of the receiving phase in the PSD. In this study, the volume of the PDMS sorptive layer coated on the SPME fiber was approximately 0.612 µl compared to a PED volume of 1300 µl. At equilibrium, the freely dissolved aqueous phase concentration (C_w) for a hydrophobic chemical sampled by both devices is represented using the equation:

$$C_w = \frac{N_{PSD}}{K_{PSD} V_{PSD}}$$

where N_{PSD} is mass of the chemical taken up by the receiving phase; K_{PSD} is the PSD-water partition coefficient, and V_{PSD} is the volume of the receiving phase.

Using PCB congener 52 as an example, the PED was able to detect much lower concentrations of chemicals in the water even though its K_{PSD} was somewhat less compared to SPME (250,000 vs. 330,000; Booij *et al.* 2003, Zeng *et al.* 2004). This is due to the much larger sorptive volume of PEDs compared to the SPME fibers used in the present study. It follows that PEDs may be more useful when targeting ultra-trace level (i.e., pg/L range) concentrations. However, the application of PEDs comes at a cost of additional post-sampling processing effort that is eliminated when utilizing SPME. Thus, practitioners are encouraged to carefully consider the measurement objectives when targeting PBT contaminants prior to selecting the appropriate PSD.

The POCIS hold a unique position among the PSDs used in this study. The use of a polyfunctional

sorbent matrix, such as the Oasis HLB used in the POCIS in this study, provides different means of retaining more polar chemicals (Alvarez *et al.* 2007) than the basic partitioning of hydrophobic chemicals into SPME or PED. This means the POCIS is better considered as a complementary passive sampling technique to SPME and PEDs, rather than evaluating it directly via a common set of analyses.

Comparison of PSDs to Tissue

A series of hydrophobic chemicals including PAHs, PCBs, and chlorinated pesticides covering a range of logK_{ow} values from 4.1 to 8.1 were found to bioaccumulate in mussel tissues and also sampled by the SPME and PED (Dodder *et al.* In press). Twenty-six compounds were measured in both the SPME and tissues including 12 PAHs, 10 PCB congeners, and four chlorinated pesticides. The PED and tissues had 25 compounds in common with three PAHs, 16 PCB congeners, and six chlorinated pesticides. Water concentrations estimated by the PSDs were positively correlated ($p < 0.05$) with mussel tissue concentrations for PAHs (both SPME and PED); for PCBs by PED; and for OC pesticides by SPME (Figure 3). The Pearson correlation coefficients (r^2) for these relationships ranged between 0.12 and 0.40. In contrast, the relationships for the PCBs by SPME ($p = 0.44$; $r^2 = 0.21$; $n = 30$) and OCs by PED ($p = 0.067$; $r^2 = 0.12$; $n = 29$) were not statistically significant. The detectability of PCBs at sub ng/L concentrations by SPME is limited, resulting in a lower number of matched data points and a likely higher uncertainty in the aqueous concentrations reported near/ at the congener-specific MDL. The estimated aqueous concentrations for dieldrin fell well below the trend lines for both PSDs (more so for PEDs), suggesting a lower bioaccumulative potential compared with the other OC analytes. Even so, the PED-tissue relationship for OCs was marginally significant. PBDEs were observed in extremely low concentrations over a relatively narrow concentration range and thus are not shown. Taken together, these results indicate that

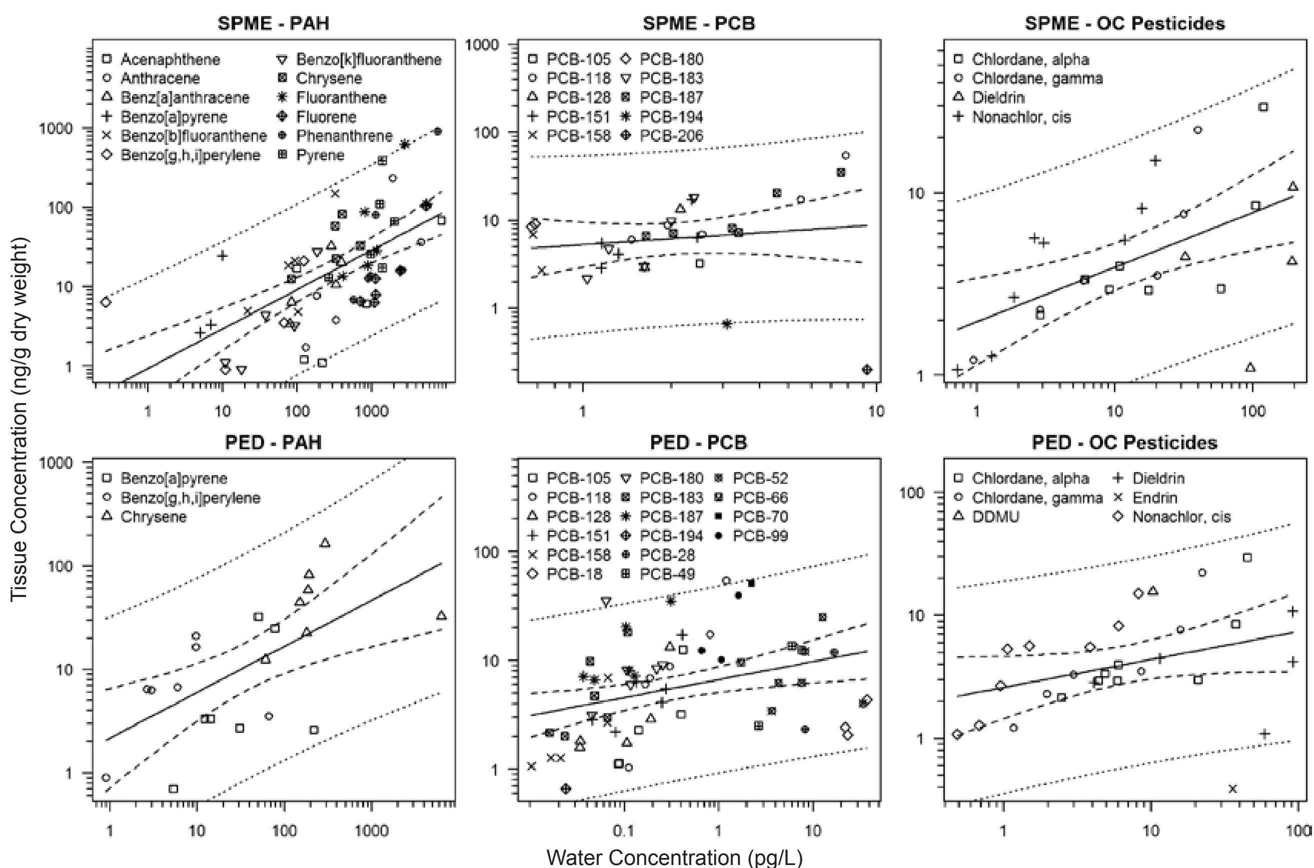

Figure 3. Comparison of mussel (*Mytilus* spp.) tissue concentrations of persistent, bioaccumulative and toxic (PBT) organics (Dodder *et al.* In press) and ambient water concentrations estimated from SPME and PED measurements. The solid line is the best-fit regression, the dashed lines are the confidence band, and dotted lines are the prediction band.

both types of PSDs represent the bioaccumulation potential of the targeted hydrophobic chemicals.

Of the 40 common analytes measured in both tissues and POCIS, only diphenhydramine was detected in both matrices at a common site (Figure 4). Concentrations of diphenhydramine ranged from 0.1 and 0.03 ng/L at SFYB and LARM, respectively, compared to mussel concentrations of 0.24 and 0.25 ng/g (dry weight). In most cases, the chemicals detected in the mussels had log K_{ow} values >3 indicating a greater potential to bioconcentrate whereas chemicals detected in the POCIS had logK_{ow} values <3 which is consistent with the predicted performance of the sampler (Alvarez *et al.* 2007).

Phosphate flame retardants (PFRs) were detected in high concentrations in POCIS ranging from a mean of 1.2 ng/L (triphenyl phosphate) to 930 ng/L (TDCPP), but were not detected in tissues from any site. Information on the accumulation of PFRs in mussel tissue is limited. Green *et al*. (2008) reported measuring TCEP (23 µg/kg wet weight) in blue mussels from only one site in Norwegian waters compared to relatively high concentrations in all sediment samples collected during the study. Bioconcentration factors (BCFs) of PFRs in mussels are unknown; however, measurements have been made in common carp (*Cyprinus carpio*) for TCEP (0.6 - 0.8 L/kg), TDCPP (0.3 - 3.3 L/kg), and TCPP (0.8 - 2.8 L/kg) indicating the potential for bioconcentration albeit low in many cases (Verbruggen *et al.* 2005). Potentially lower lipid levels in mussels than in carp may also result in lower BCF values, thereby reducing the likelihood of detecting PFRs in mussel tissue.

Summary

In this study, three PSDs were used to sample a diverse set of anthropogenic organic chemicals in the coastal waters of San Francisco Bay and the Southern California Bight. The distribution of chemicals across sites was broad preventing linking chemical occurrence to the land-use characteristics of the site.

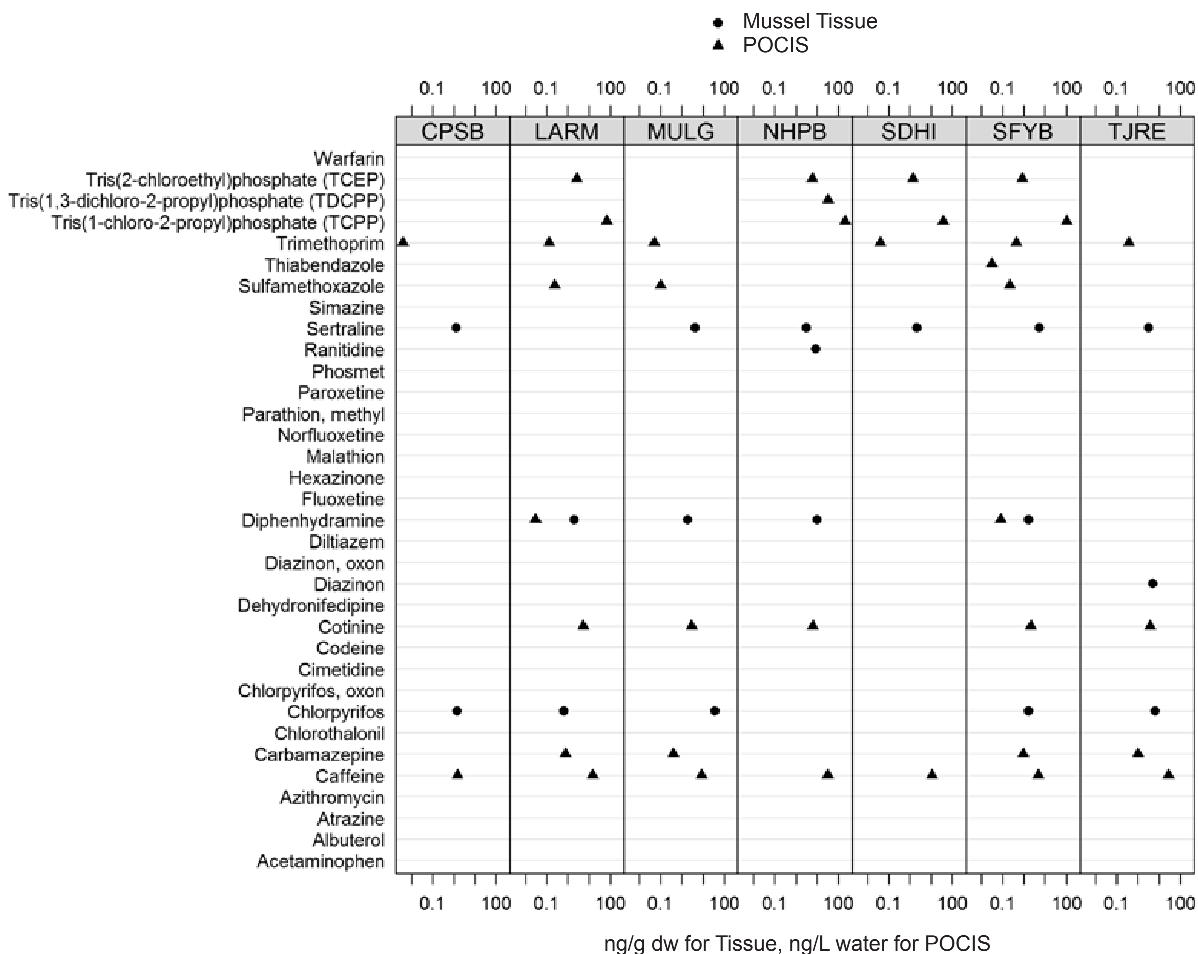

Figure 4. Comparison of mussel (*Mytilus* spp.) tissue concentrations of contaminants of emerging concern (CECs; Dodder *et al.* In press) and ambient water concentrations estimated from POCIS measurements.

However, when comparing the abundance of individual chemicals at each site, there was a distinction between the sites located in the SF Bay area and the SCB.

Comparison of the three PSDs used in this study indicated that the most information on the presence of organic contaminants in the watershed would be obtained by using a combination of the samplers. Differences between the PED and SPME were minor with the exception of the amount of chemical sampled for detection. Combined with the POCIS, data on chemicals with a wide range of K_{ow} values can be measured.

The data from the PSD/mussel tissue comparison clearly shows that while use of biota for contaminant monitoring programs is useful for PBTs, it can be extremely limited in the ability to detect most of the hydrophilic CECs. PSDs such as the POCIS provide a means of measuring CECs at low, but potentially toxicologically relevant concentrations. The data does not suggest that one monitoring technique should be used exclusively. Instead, the different types of PSDs and incorporation of tissue analyses should be considered as complementary techniques, each providing a unique picture of chemical occurrence in the environment.

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Supplemental Information

Supplemental Information is available at ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/AnnualReports/2013AnnualReport/ar13_049_059SI.pdf.