Occurrence of contaminants of emerging concern in mussels (*Mytilus* spp.) along the California coast and the influence of land use, stormwater discharge, and treated wastewater effluent

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Abstract

Contaminants of emerging concern were measured in mussels collected along the California coast in 2009-2010. The seven classes were alkylphenols, pharmaceuticals and personal care products, polybrominated diphenyl ethers (PBDE), other flame retardants, current use pesticides, perfluorinated compounds (PFC), and single walled carbon nanotubes. At least one contaminant was detected at 67 of the 68 stations (98%), and 67 of the 167 analytes had at least one detect (40%). Alkylphenol, PBDE, and PFC concentrations increased with urbanization and proximity to stormwater discharge; pesticides had higher concentrations at agricultural stations. These results suggest that certain compounds; for example, alkylphenols, lomefloxacin, and PBDE, are appropriate for inclusion in future coastal bivalve monitoring efforts based on maximum concentrations >50 ng/g dry weight and detection frequencies >50%. Other compounds, for example PFC and hexabromocyclododecane (HBCD), may also be suggested for inclusion due to their >25% detection frequency and potential for biomagnification.

Introduction

The National Oceanic and Atmospheric Administration's National Status and Trends (NOAA NS&T) Mussel Watch Program measures the

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concentrations of coastal contaminants in bivalves and sediments to determine their spatial distribution and temporal trends, and to provide information to assess the risk posed to marine wildlife and humans through the use of coastal resources (Kimbrough *et al.* 2008). Bivalves are mobility-limited filter feeders which draw in water and particulates from their surrounding environment and subsequently bioaccumulate contaminants in their tissues. Their tissue concentrations are indicators of local water contamination. In contrast to legacy contaminants and trace metals which have been monitored by NS&T for more than 25 years (Kimbrough *et al.* 2008), contaminants of emerging concern (CECs) are anthropogenic compounds which are released into the environment and may pose a risk, but at present are largely unregulated and thus unmonitored within the Mussel Watch Program. Due to their potential risk, CECs have received attention from regulatory bodies. For example, the US EPA has produced action plans for several classes of CECs (http://www.epa.gov/oppt/existingchemicals/index.html) and the California State Water Resources Control Board is developing a process for monitoring for CECs in the coastal environment (Anderson *et al.* 2012). In response, a multiagency California pilot study was initiated to begin to fill the CEC data gap and assess the feasibility of incorporating CECs into the Mussel Watch Program. For this pilot study, details of the study design and station selection are described in Maruya *et al.* In press a, the spatial distribution of legacy contaminants are described in Edwards *et al.* In press, and incorporation of passive samplers as mussel tissue surrogates are provided in Alvarez *et al.* In press; a synthesis of each of these components can be found in Maruya *et al.* In press b.

Analyte selection was based primarily on two criteria. First, the compound was known or suspected to bioaccumulate from previous surveys in California or other regions. Second, robust analytical methods capable of processing the relatively large sample set were available. The seven CEC classes were as follows. Alkylphenols (AP) are nonionic surfactants (David *et al.* 2009); polybrominated diphenyl ethers (PBDE) are flame retardants (Shaw *et al.* 2009); perfluorinated compounds (PFC) are polymers used in a variety of products (Houde *et al.* 2006); pharmaceuticals and personal care products (PPCP) include antibiotics, antidepressants, and stimulants; current use pesticides (CUP) include insecticides, fungicides, and herbicides, and single walled carbon nanotubes (SWNT) are additives to a variety of materials (Schierz *et al.* 2012). Other flame retardants (OFR), besides PBDE, include three sub-classes: alternatives to PBDE flame retardants, hexabromocyclododecane (HBCD) isomers, and chlorinated organophosphate flame retardants (Klosterhaus *et al.* 2012).

The data analysis is structured to address the questions posed in the overall study design (Maruya *et al.* In press a). First, the occurrence of individual CECs along the entire California coast is summarized. Second, the effect of station proximity to varying land cover, such as urban or agricultural, on the contaminant concentrations is investigated. Third, the effect of station proximity to stormwater and municipal wastewater discharge on the contaminant concentrations is investigated.

Methods

A complete description of the study design is provided in Maruya *et al.* In press a. Briefly, 68 mussel sampling stations were selected along the coast of California. Native mussels (*Mytilus* spp.) were collected from these stations between November 2009 and April 2010. Land use within 10 km was used to sort stations into four mutually exclusive categories (urban, mixed development, low development, and agricultural). Stormwater receiving stations were defined as within 1 km of a permitted stormwater discharge region. Stations receiving POTW discharge were within 2 km of small (<100 MGD) or 5 km of large (>100 MGD) outfalls. Stations could have one of four categories (stormwater only, stormwater and POTW, POTW only, or no discharge).

A total of 166 contaminants plus SWNTs were analyzed in the mussel tissue. Some contaminant classes were measured at a subset of the 68 sampling stations. The individual analytes are listed in the Supplemental Information (SI) Table SI-1 (ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/AnnualReports/2013AnnualReport/ar13_037_047SI.pdf) and were measured by positive or negative mode electrospray ionization (+/-ESI) liquid chromatography tandem mass spectrometry (LC/MS/MS), or electron impact (EI) or electron capture negative chemical ionization (ECNI) mode gas chromatography mass spectrometry (GC/MS). APs and PPCPs were measured by +/-ESI LC/MS/MS (a modified version of EPA Method 1694), PFCs by -ESI LC/MS/MS (Kannan *et al.* 2001), CUPs by EI

GC/MS (a modified version of EPA Method 1699), PBDEs by ECNI GC/MS, and OFRs by EI/ECNI GC/MS and -ESI LC/MS/MS (La Guardia *et al.* 2012). SWNTs were measured by both near infrared fluorescence spectroscopy (NIRF; Schierz *et al.* 2012) and inductively-coupled plasma mass spectrometry (ICP-MS). Descriptions of each extraction and instrumental method are provided in the SI.

Quality Control

Analytical precision and accuracy were evaluated using a performance based approach beginning with a comprehensive set of data quality objectives (DQO; Maruya *et al.* In press a). The performance of each analytical method was compared against initial project-wide thresholds, and then the DQOs were adjusted to account for actual method performance (Tables SI-2 and SI-3). The adjustment required satisfactory matrix spike/matrix spike duplicate (MS/MSD) recovery for all accepted data. MS/MSD performance directly tests the accuracy of the method, and was therefore considered more important than the recovery of the surrogate standards. Threshold adjustments were reviewed by the laboratories to ensure they conformed to known past performance. If the DQOs for a particular analyte and sample were not met, that analyte-sample pair was treated in the subsequent data analysis as not sampled. The reported concentrations were blank subtracted and non-detects were set to zero. APs were the most analytically challenging compound class; for a prior example see Loos *et al.* (2001). Table 1 shows more than 50% of the 4-nonylphenol, 4-nonylphenol monoethoxylate, and 4-nonylphenol diethoxylate measurements in this study were discarded, primarily due to high blank concentrations.

Reporting limits (RL) for individual analytes varied by site due to fluctuations in sample size. Reporting limits for each analyte was determined in one of two ways: concentrations were not reported below the RL; or, concentrations were reported below the assigned RL with recognition that there may be a greater uncertainty in the accuracy of these values. All reported concentrations, including those below the assigned RL, were used in the following data analysis. The range of reporting limits for all detected analytes is given in the Supporting Information Analyte Report.

Statistical Analysis

Plotted tissue concentrations (dry weight) were transformed as $log_{10}(x+1)$, where x is the concentration. The tick marks on the y-axes of the box and whisker plots were adjusted for this transformation. Non-parametric Kruskal-Wallis tests followed by pairwise Wilcoxon tests were used to compare tissue concentrations among the different land use and discharge categories. The statistical analysis was performed using R (R Core Team 2012).

Results and Discussion

CECs as a group were detected at 67 of 68 stations (98%); the exception was station SSSS\ San Simeon Point-San Simeon Point, located in an undeveloped region of the central coast that is approximately equidistant (350 km) between the Los Angeles and San Francisco Bay metropolitan areas. Figure 1 shows the total concentration at each station for each compound class. The order by mean concentration was PPCP > AP > PBDE > CUP > OFR > PFC. The variation in concentration within each class spanned between approximately 1 and >3 orders of magnitude. Table 1 summarizes the occurrence of individual CECs across all stations. The total number of stations analyzed per compound varied because some compound classes were measured at fewer stations: CUPs were measured at 45 stations and OFRs were measured at 19 stations. Additionally, some individual analytes were eliminated at specific stations because they did not pass the DQOs.

Percent dry weight in analyzed tissue samples ranged between 9 and 22% (mean 15%); and the percent lipid (based on the wet weight) was 0.5 to 2.2% (mean 1.3%). Target analytes ranged in polarity from hydrophilic (for example pharmaceuticals) to lipophilic (for example PBDEs); therefore, the concentrations of all analytes are presented on a dry weight basis since hydrophilic contaminants do not correlate well with lipid content (Ramirez *et al.* 2009). For reference, Table SI-1 is an extended version of Table 1 listing the summary statistics for all analytes (including those not detected) on a dry weight, wet weight, and lipid weight basis.

The number of analytes detected within each class was as follows (number detected/total in class): AP (4/4 = 100%), PBDE (16/26 = 61%), PFC (5/12 = 42%), CUP (8/27 = 30%), PPCP (30/88 = 34%), and OFR (4/9 = 44%). The seventh compound class, SWNT, was not detected at the 10 stations at which

Table 1. *Mytilus* spp. tissue concentrations for target compounds with a detection frequency >5%, in decreasing order of the 75th quantile concentration. 'Passing' refers to the percentage of stations that met QA/QC guidelines. 'Stations' refers to the number that passed QA/QC guidelines and were used in the subsequent data analysis. 'Detects' refers to the percentage of QA/QC passing stations with detectable concentrations of the contaminant. NP1EO: 4-nonylphenol monoethoxylate, NP2EO: 4-nonylphenol diethoxylate, BDE: brominated diphenyl ether, PFDoDA: perfluorododecanoic acid, HBCD: hexabromocyclododecane, PFUnDA: perfluoroundecanoic acid, BTBPE: 1,2-Bis(2,4,6-tribromophenoxy)ethane.

Contaminant	Class	Passing (%)	Stations	Detects (%)	Tissue Concentration (ng/g dry wt)				
					Min	Mean	Median	75th Quantile	Max
4-Nonylphenol	AP	21	14	100	96	470	200	290	3000
4-NP1EO	AP	47	32	100	6.3	91	45	150	300
Lomefloxacin	PPCP	97	66	62	0	29	18	55	170
4-NP2EO	AP	37	25	88	0	25	7.4	24	140
Sulfamethazine	PPCP	97	66	36	0	24	0	17	430
BDE-47	PBDE	99	66	83	0	6.6	3.2	6.6	68
BDE-99	PBDE	99	66	61	0	3.4	1.6	3.2	38
Sertraline	PPCP	32	22	64	0	1.4	1.3	1.9	5.5
BDE-100	PBDE	99	66	39	0	1.3	0	1.5	15
PFDoDA	PFC	99	67	28	0	1.8	0	1.4	29
HBCD, gamma	OFR	100	19	58	0	0.69	0.4	0.95	2.5
Cocaine	PPCP	85	58	36	0	0.28	0	0.58	1.7
Chlorpyrifos	CUP	100	45	27	0	1.4	0	0.45	36
HBCD, alpha	OFR	100	19	42	0	0.27	0	0.4	1.5
Dacthal	CUP	100	35	37	0	2.7	0	0.2	47
HBCD, beta	OFR	100	19	32	0	0.068	0	0.1	0.4
Caffeine	PPCP	100	68	19	0	14	0	0	140
Diphenhydramine	PPCP	100	68	16	0	0.87	0	0	11
Methylprednisolone	PPCP	99	67	15	0	18	0	0	210
Amphetamine	PPCP	62	42	14	0	2.3	0	0	20
Enrofloxacin	PPCP	97	66	14	0	1.3	0	0	12
Amitriptyline	PPCP	100	68	13	0	0.4	0	0	6.2
PFUnDA	PFC	99	67	12	0	0.23	0	0	2.8
BDE-66	PBDE	99	66	11	0	0.42	0	0	17
Terbufos	CUP	100	35	11	0	0.19	0	0	2.3
Erythromycin-H2O	PPCP	82	56	11	0	0.14	0	0	2
BTBPE	OFR	100	19	11	0	0.21	0	0	2
Ofloxacin	PPCP	76	52	10	0	1.2	0	0	18
BDE-49/71	PBDE	99	66	9	0	0.57	0	0	9.5
BDE-28	PBDE	99	66	8	0	0.17	0	0	4.2
BDE-17	PBDE	99	66	8	0	0.18	0	0	3.7
BDE-153	PBDE	99	66	8	0	0.16	0	0	2.8
BDE-183	PBDE	99	66	8	0	0.085	0	0	2.3
Quintozene	CUP	80	28	7	0	0.098	0	0	1.7
Atenolol	PPCP	100	68	6	0	0.45	0	0	13
BDE-75	PBDE	99	66	6	0	0.22	0	0	5.2
BDE-154	PBDE	99	66	6	0	0.067	0	0	1.3

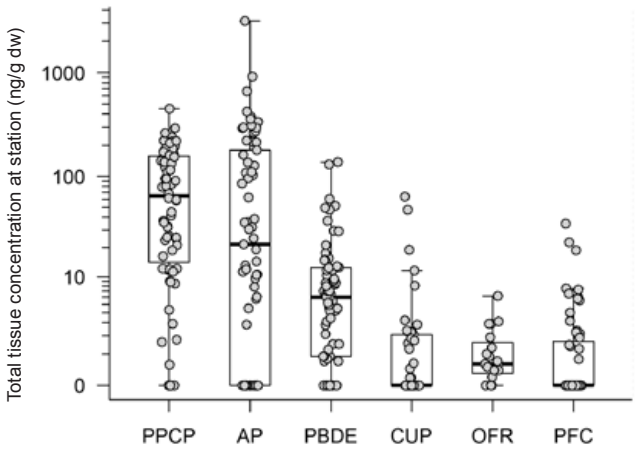

Figure 1. Total concentrations for target compound classes at each station. The median is represented by the horizontal line, the box shows the interquartile range (IQR), and the whiskers flag potential outliers and extend to the furthest data point that is <1.5 × IQR from the box. PPCP: pharmaceuticals and personal care products, AP: alkylphenols, PBDE: polybrominated diphenyl ethers, CUP: current use pesticides, OFR: other flame retardants, PFC: perfluorinated compounds.

it was analyzed. However, the applied analytical method was not optimized to detect multi-walled carbon nanotubes or fullerene nanoparticles, and thus it is not possible to rule out the presence of those species. Within the six detected classes, individual compounds had a range of detection frequencies (Table 1). Note that some compounds such as the HBCD isomers had relatively low concentrations, but relatively high detection frequencies. However, HBCD was measured at a subset of 19 stations, making a direct comparison of detection frequencies with other compounds difficult. Two reports provided in the Supplemental Information show individual contaminant and station specific information. The Analyte Report is organized by contaminant and shows the concentration and detection limit at each station. The Station Report is organized by location and shows the contaminant profile (type and abundance), land use, and discharge information at each station.

Contaminant Variation with Land Use

Figure 2 shows the variation in contaminant class abundance with nearby land use. Table SI-4 shows the results of statistical significance tests used to compare the contaminant concentrations. Figure SI-1 shows the abundance of individual contaminants in each of the land use categories. APs, PBDEs, and PFCs show a trend of increasing concentrations with increasing urbanization. There were statistically significant differences (p <0.05) in concentration between agricultural versus urban, and low development versus urban categories for these classes. APs, PBDEs, and PFCs are used in a wide variety of industrial and consumer products and their occurrence was expected to correlate with proximity to urban centers (Bennett *et al.* 1998; Hoh and Hites, 2005; Murakami *et al.* 2008). Figure SI-2 ranks the total AP, PBDE, and PFC concentration at all 68 stations. The five stations with the highest median concentrations across these three classes were located at the mouths of urban embayments or waterways: TJRE/Tijuana River Estuary (influenced by the San Diego/Tijuana metropolitan region), LARM/LA River-Queen Mary (influenced by Los Angeles), MDSJ/Marina Del Rey-South Jetty (influenced by Los Angeles), IBNJ/Imperial Beach-North Jetty (influenced by San Diego), and SFEM/San Francisco Bay-Emeryville (influenced by the Oakland/Berkeley region).

CUPs had higher median concentrations at the agricultural stations compared to other land uses, but this difference was not statistically significant. Chlorpyrifos (an organophosphate insecticide) and dacthal (an herbicide) were largely responsible for the occurrence of CUPs and have agricultural sources within California (Wettasinghe 1993, McConnell 1998, Hageman 2006); although chlorpyrifos was also used to treat urban structures (Pope 1999). This may explain the occurrence of the maximum chlorpyrifos concentrations at the agricultural stations, followed by urban stations. The three stations with the highest total CUP concentrations were MULG/Mugu Lagoon (located in southern California), MBSR/Monterey Bay-Salinas River, and MBES/Monterey Bay-Elkhorn Slough (the latter two in the central coast region).

As a class, PPCPs had similar concentrations across all land use categories. The Supporting Information Analyte Report shows that the spatial distribution of individual PPCPs are dissimilar, perhaps due to varying sources. Lomefloxacin (a fluoroquinolone antibiotic; Jia *et al.* 2012), sulfamethazine (a sulfonamide antibiotic; Hartig *et al.* 1999), and methylprednisolone (a synthetic glucocorticoid; Chang *et al.* 2007) are used in both livestock and human medicine, and therefore may have both non-urban and urban sources. Livestock related sources may not have been accounted for by the land use model. In contrast, a literature search

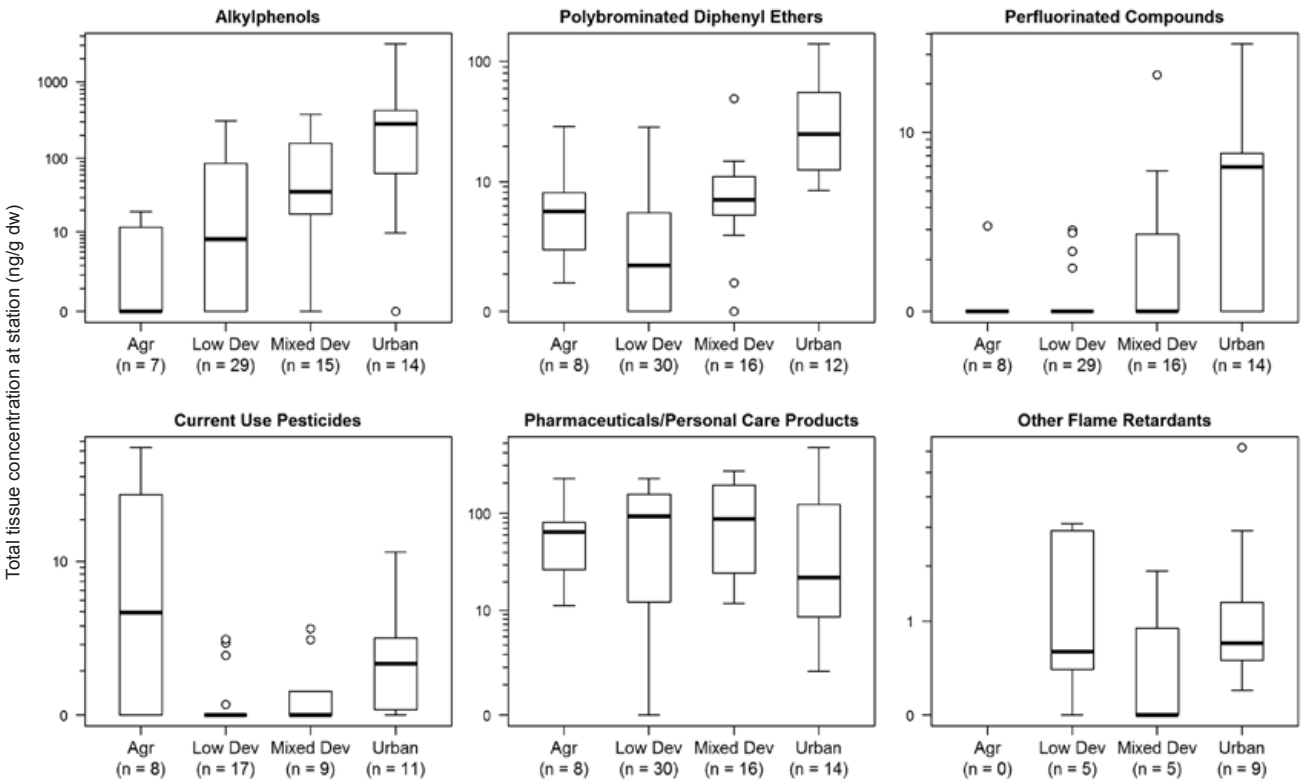

Figure 2. Variation of *Mytilus* spp. tissue contaminant concentration with land use category. Agr: agricultural, Low Dev: low development, Mixed Dev: mixed development, and *n* is the number of sites within the category. A description of the box and whiskers is in Figure 1.

did not indicate diphenhydramine (an antihistamine; Berninger *et al.* 2011) was used to treat livestock. This compound was found at higher concentrations in urban locations: 9 detects at the 30 urban and mixed development stations, and 2 detects at the low development and agricultural stations. Cocaine, sertraline, and caffeine were within a factor of 3 from the method reporting limit and may not provide reliable spatial distributions. Note the accompanying passive sampler study indicated polar organic chemical integrative samplers (POCIS) may accumulate certain PPCPs at a higher rate than mussel tissue; for example, trimethoprim, cotinine, and caffeine (Alvarez *et al.* In press).

OFRs may be expected to have urban sources, similar to the PBDE flame retardants. However, OFRs did not show increasing concentrations with increasing urbanization, possibly due to the fewer number of stations analyzed and the lower statistical power. The OFRs detected were primarily the three HBCD isomers, with two detections of the alternate to PBDE, 1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE). This result may be explained by log biota-sediment bioaccumulation factors of less than zero for BTBPE, 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB), and 2-ethylhexyl-2,3,4,5-tetrabromophthalate (TBPH), compared to greater than zero for α- and β-HBCD (La Guardia *et al.* 2012). The chlorinated organophosphate flame retardants tris(1-chloro-2-propyl)phosphate (TCPP), tris(2-chloroethyl) phosphate (TCEP), and tris(1,3-dichloro-2-propyl) phosphate (TDCPP) were not detected in mussels, but were detected in California coastal waters by POCIS in the accompanying passive sampler study (Alvarez *et al.* In press).

Contaminant Variation with Discharge

Figure 3 shows the variation in contaminant class abundance with two forms of nearby discharge. Table SI-5 shows results of the statistical significance tests used to compare contaminant concentrations. Figure SI-3 shows the abundance of individual contaminants in each discharge category.

APs, PBDEs, and PFCs tended to have higher concentrations at stations receiving stormwater, indicating this is a source of these contaminants to the coastal waters. There were statistically significant differences (p <0.05) in concentration

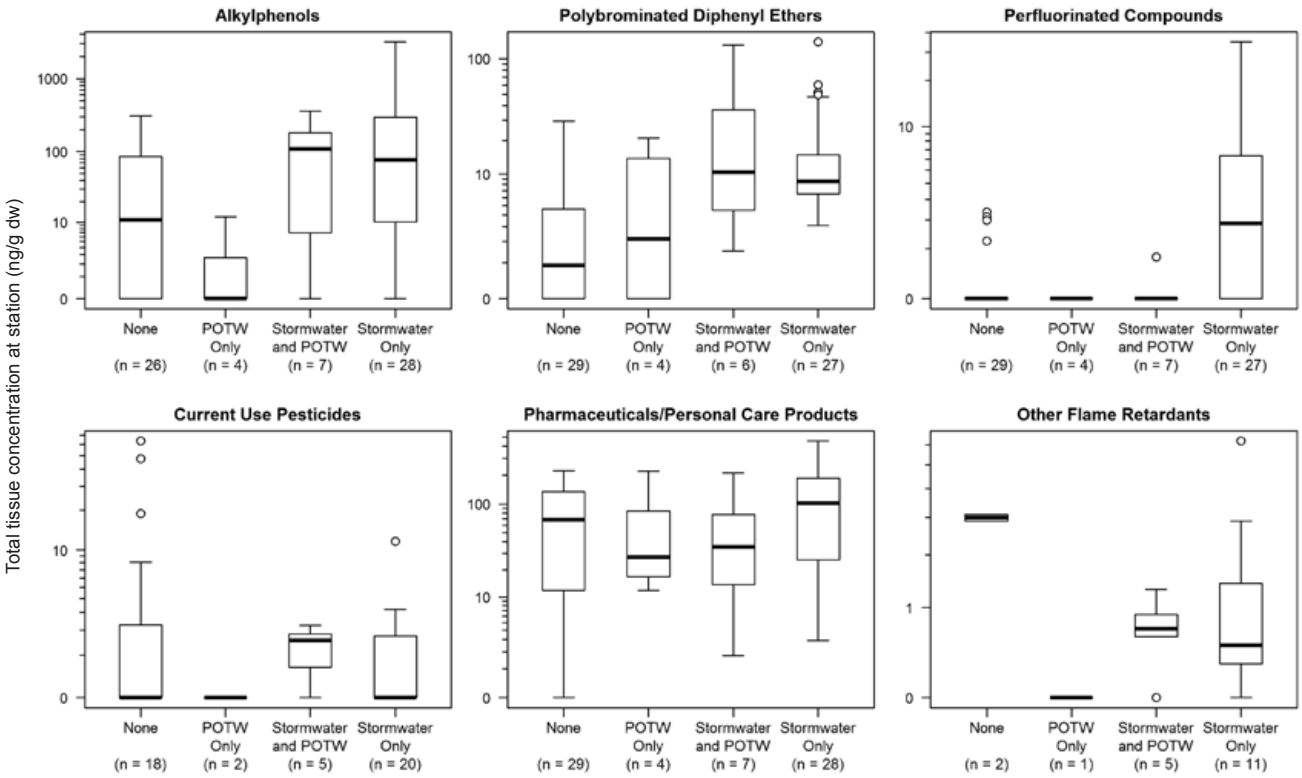

Figure 3. Variation of *Mytilus* spp. tissue contaminant concentrations by discharge category. POTW: treated effluent from publically owned treatment works, "none" refers to sites with neither stormwater nor POTW discharge, and *n* is the number of sites within the category. A description of the box and whiskers is in Figure 1.

between stormwater receiving stations versus stations receiving no discharge. The median concentration for these contaminants was higher at stations receiving stormwater than at stations receiving POTW discharge only. However, this difference was not statistically significant, perhaps due to low statistical power resulting from the small number of stations receiving POTW discharge only (n = 4). Stormwater was expected to be a larger source than POTW discharge as a previous study found that the relative contribution of stormwater related sources of legacy contaminants has increased relative to POTW sources in recent years (Lyon and Stein 2009); the present study's finding are further supported by a study on southern California coastal sediments that found stormwater to be a greater source of PBDEs than POTW effluent discharge (Dodder *et al.* 2012). CUPs and PPCPs did not show statistically significant differences among discharge categories, indicating neither POTW nor stormwater discharge dominated the input. Alternatively, other sources may be important, for example agricultural runoff. As discussed above, OFRs had a low statistical power to test for differences and were measured at relatively low concentrations. No conclusion was drawn from their distribution.

Literature Comparison

Tissue concentrations in this study are similar to those observed in other coastal bivalve surveys. For example, the range of total nonylphenol along the Spanish coast was non-detect to 147 ng/g ww (Bouzas *et al.* 2011) and non-detect to 7600 ng/g dw along the coast of China (Wang *et al.* 2010). The range of 4-nonylphenol in the present survey was 16 to 290 ng/g ww, or 96 to 3000 ng/g dw. Approximately 90% of technical nonylphenol is 4-nonylphenol (Eganhouse *et al.* 2009). BDE-47 was non-detect to 60 ng/g dw in an earlier study in San Francisco Bay (Oros *et al.* 2005). BDE-47 ranged from non-detect to 68 ng/g dw in the present study. The two primary PFCs detected in this survey, perfluorododecanoic acid (PFDoDA) and perfluoroundecanoic acid (PFUnDA), ranged from non-detect to 29 ng/g dw and non-detect to 2.8 ng/g dw, respectively. In China and Japan PFDoDA ranged from non-detect to 196 ng/g dw and PFUnDA was not detected (So *et al.* 2006). Note that in other organisms perfluorooctane sulfonate (PFOS) is often

the most abundant PFC (Houde *et al.* 2006). The sum of the three HBCD isomers ranged from non-detect to 3.4 ng/g ww in Asian coastal bivalves (Isobe *et al.* 2012). In the present study it was non-detect to 0.62 ng/g ww. The range of chlorpyrifos along the US coast was non-detect to 53 ng/g dw (Wade *et al.* 1998). In the present study it was non-detect to 36 ng/g dw. To the authors' knowledge, the PPCP data in the present study are among the first to be published for coastal bivalves.

Biomagnification Potential

Biomagnification is a contaminant's potential to transfer through the food web and accumulate at the highest concentrations in apex predators (Mackay *et al.* 2000). Mussels are at a low trophic level and the biomagnification potential varies among contaminants; therefore, the contaminant concentrations may not directly correlate to risk, particularly at high trophic levels. Field observations have shown APs do not biomagnify (Ahel *et al.* 1993), and laboratory experiments indicated chlorpyrifos does not biomagnify (Varo *et al.* 2002). The log K_{ow} of the detected PPCPs are generally less than 4 (data from http://pubchem.ncbi.nlm.nih.gov/), indicating these compounds do not biomagnify (Fisk *et al.* 2001). In contrast, field observations have shown that PBDEs (Johnson-Restrepo *et al.* 2005), PFCs (Houde *et al.* 2011) and HBCDs (Covaci *et al.* 2006) biomagnify, although with different potentials for the individual forms. The toxicity of individual compounds will also vary and factor into ecological risk.

Summary

Contaminant concentrations followed positively skewed distributions, with 4-nonylphenol, 4-nonylphenol monoethoxylate, 4-nonylphenol diethoxylate, lomefloxacin, sulfamethazine, setraline, cocaine, BDE-47, BDE-99, BDE-100, perfluorododecanoic acid, gamma- and alpha-HBCD, chloryprifos, and dacthal detected in greater than 25% of the mussel samples. Of these, the alkylphenols and lomefloxacin exhibited mean concentrations that exceeded 10 ng/g dw. A total of 26 compounds had maximum concentrations that exceeded 10 ng/g dw. AP, PBDE and PFC tissue concentrations were correlated with increasing urbanization and stormwater discharge. The evidence suggested that elevated CUP abundance was associated with agricultural land use. As a class, PPCPs showed no discernable trend with land use, perhaps due to varying sources of the detected antibiotics. The widespread detection of these pharmaceuticals in mussels is a novel result and should be verified. The results suggest that certain compounds are appropriate for inclusion in future coastal bivalve monitoring efforts based on their relatively high concentrations and detection frequencies alone; for example, alkylphenols, lomefloxacin, and PBDEs. Other compounds with lower concentrations may also be suggested for future monitoring due to their >25% detection frequency and potential for biomagnification through the food web; for example PFCs and HBCD.

Two analytical issues may require further investigation or improvement. First, quantification of individual APs at 53 to 79% of the stations was prevented by high blank concentrations. Therefore, improvement in blank performance should be pursued, assuming effects thresholds for APs require detection at ng/g concentrations. Second, a comparison with POCIS samplers indicated mussels may not bioaccumulate certain contaminants that are present in the water column. Therefore, the use of alternate monitoring tools such as passive samplers may complement tissue monitoring.

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Supplemental Information

Supplemental Information is available at ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/AnnualReports/2013AnnualReport/ar13_037_047SI.pdf.