The Mussel Watch California Pilot Study on contaminants of emerging concern (CECs): Synthesis and next steps

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Abstract

A multiagency pilot study on mussels (*Mytilus* spp.) collected at 68 stations in California revealed that 98% of targeted contaminants of emerging concern (CECs) were infrequently detectable at concentrations ≤1 ng/g. Selected chemicals found in commercial and consumer products were more frequently detected at mean concentrations up to 470 ng/g dry wt. The number of CECs detected and their concentrations were greatest for stations categorized as urban or influenced by stormwater discharge. Exposure to a broader suite of CECs was also characterized by passive sampling devices (PSDs), with estimated water concentrations of hydrophobic compounds correlated with *Mytilus* concentrations. The results underscore the need for focused CEC monitoring in coastal ecosystems and suggest that PSDs are complementary to bivalves in assessing water quality. Moreover, the partnership established among participating agencies led to increased spatial coverage, an expanded list of analytes and a more efficient use of available resources.

Introduction

California is the most populous (37,000,000 residents) and one of the largest (>400,000 km^2 of land area) states in the USA. With its 1,700 km of shoreline (http://resources.ca.gov/ocean/html/chapt_5c.html) along with countless rivers, lakes, and streams, California boasts one of the top-10 largest and most diverse economies in the world, based largely on agriculture, technology, services and tourism. The geography and climate are equally diverse, with central and northern coastal regions of the state receiving abundant rainfall (e.g., nearly 1700 mm/yr) compared with the largely arid southern California region, averaging 250 mm of rainfall per annum (http://cdo.ncdc.noaa.gov/climatenormals/clim20/ca/042147.pdf).

Discharges of treated municipal wastewater effluent and stormwater runoff that are currently regulated under the National Pollutant Discharge Elimination System (NPDES) represent major sources of anthropogenic contaminants to California's receiving

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waters, including thousands of chemicals that are not currently regulated and/or routinely monitored. Once discharged, these contaminants of emerging concern (CECs) can remain dissolved in the water column or can associate strongly with sediment and are subject to transformation and uptake by wildlife. Their potential for impacts to ecological and human health remains largely unknown, and depending on the route and magnitude of exposure, CECs can act through a diverse and complex network of adverse outcome pathways. With its population and economic base centered around the metropolitan San Francisco, Los Angeles and San Diego areas, the potential input of CECs into coastal waters of the state, can rival or even exceed that estimated for priority organic pollutants and metals (Lyon and Stein 2009). Thus, monitoring of the status and trends associated with CEC concentrations in areas lightly and highly impacted by regulated discharges, in parallel with studies to determine credible environmental thresholds of concern for CECs, is a high priority for coastal resource managers.

In response to changing informational needs by stakeholders about chemical stressors in the coastal and marine environment, the National Oceanic and Atmospheric Administration's National Centers for Coastal Ocean Science Mussel Watch Program (Mussel Watch) teamed with the State Water Resources Control Board (SWRCB), the Southern California Coastal Water Research Project Authority (SCCWRP) and other local, state, regional, and other federal agencies to design and carry out a two-year pilot study on CECs, focused on the state of California. A multi-agency steering committee was convened to design the pilot study to address five fundamental questions:

- What is the occurrence (i.e., frequency of detection, concentration) of CECs in the coastal California environment?
- How does CEC occurrence vary with land use?
- How does CEC occurrence vary with proximity to discharges of treated municipal wastewater effluent and stormwater runoff?
- What CECs are detectable in the water column using passive sampling devices (PSDs)?
- What is the relationship between CEC accumulation by PSDs and bivalve tissue?

In 2009, the steering committee identified a list of high priority CEC classes based on the state of the science and availability of robust methods, and designed a field-based study to address the above questions (Maruya *et al.* In press). Soft tissue from native mussels (*Mytilus* spp.) collected at stations across the state, categorized by adjacent land use and proximity to known discharges, was analyzed for hundreds of individual CECs. To characterize CECs in the water column and to determine their utility as a surrogate for bioaccumulation, PSDs were deployed at 11 stations and analyzed for both CECs and legacy pollutants. Targeted CECs were classified as pharmaceuticals and personal care products (PPCPs), current use pesticides (CUPs), industrial and commercial chemicals that included polybrominated diphenyl ether (PBDE) and other flame retardants (OFRs), perfluorinated compounds (PFCs), alkylphenols/alkylphenol ethoxylates (APs/APEs) and even single walled carbon nanotubes (SWNT). The detailed design and results of this multi-year project are summarized elsewhere (Alvarez *et al.* In press, Dodder *et al.* In press, Kimbrough *et al.* In press, Maruya *et al.* In press).

This synthesis serves to collate and synthesize the new information gleaned from the California pilot study on CECs and to recommend next steps based on these results. The synthesis will provide guidance on the types of CECs that should be targeted, how local and regional land use and the nature of regulated discharges influence the concentrations of CECs expected to occur, and where to locate monitoring stations to provide the maximum benefit. In addition, alternative approaches are presented that increase the flexibility and scope of contaminant monitoring in the coastal environment. This synthesis will be directly applicable to future monitoring efforts in California, and moreover, it will serve as a template to inform monitoring efforts for CECs in coastal aquatic systems across the nation, as well as in other regions worldwide.

Synthesis

Expansion of Sampling Locations

A total of 68 stations (32 existing; 36 newly established) categorized by land use (urban; mixed development; low development; agricultural) and by proximity to NPDES permitted discharge from publicly owned treatment works (POTWs) and stormwater management zones were sampled in this pilot

study (Maruya *et al.* In press). Among the 36 new stations (Figure 1 and in Supplemental Information (SI) Table SI-1; ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/AnnualReports/2013AnnualReport/ar13_061_073SI.pdf), five each were located in close proximity to POTW outfalls – Carpinteria State Beach (CPSB), Farallon Islands (FIEL), Point Lobos State Reserve (PLSR), Santa Clara River – North Jetty (SCRJ), and San Francisco Bay Emeryville (SFEM) and in watersheds with major agricultural influence – Monterey Bay Salinas River (MBSR), Mugu Lagoon (MULG), SCRJ, Santa Maria Point Sal (SMPS), and San Pablo Bay Napa River (SPNR). Thirteen new stations were established at the mouths of rivers, estuaries and channels that are impacted by stormwater and agricultural runoff; e.g., the Los Angeles River (LARM), Calleguas Creek in Ventura County (MULG), and the mouth of the Salinas River in Monterey County (MBSR). The greatest number of new stations (14) was placed in close proximity to areas of special biological significance (ASBS), a network of 34 reserves managed by the state to preserve natural history. An additional station was established within the NOAA Tijuana River National Estuarine Research Reserve (TJRE) near the international border with Mexico.

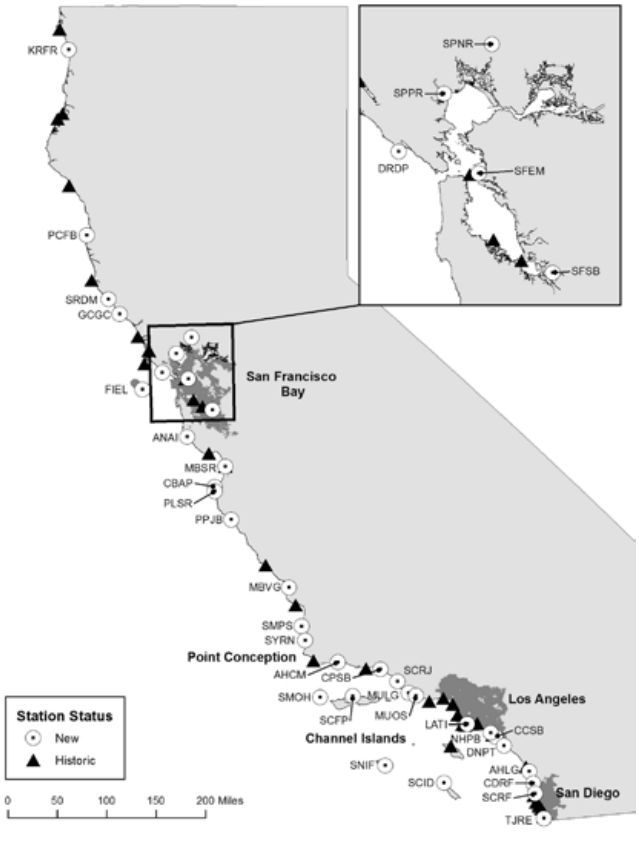

Figure 1. The 2009-10 National Status and Trends Mussel Watch California Pilot Study on contaminants of emerging concern (CECs) doubled spatial coverage along the coast by establishing 36 new stations.

PSDs that target water soluble and hydrophobic analytes were deployed (Table SI-1) at 7 of the 68 stations where native *Mytilus* were collected and analyzed. Passive samplers were co-deployed with caged *Mytilus* at four additional stations, two of which were located in urban watersheds in close proximity to POTW outfalls (Los Angeles Harbor (LATI) and San Francisco South Bay (SFSB)). The two remaining stations (SPNR, SPPR) were located at the mouths of the Napa and Petaluma Rivers in San Pablo Bay, the northern arm of the San Francisco Bay complex. The Napa River drains a watershed with a large agricultural land use component.

Nearly doubling the number of stations available for future assessment of coastal water quality in California was made possible by the unique partnership formed among federal (NOAA, USGS), State (SWRCB), and regional agencies (SCCWRP, San Francisco Estuary Institute (SFEI)). By incorporating locations that directly address the quality of regulated discharges, the information gleaned will be of great value to the water and environmental quality communities. Moreover, leveraging of resources available for environmental monitoring is maximized by co-locating Mussel Watch stations with those that are part of existing monitoring programs, e.g., the State Water Ambient Monitoring Program (SWAMP) (http://www.waterboards.ca.gov/water_issues/programs/swamp/), the Southern California Bight survey (http://www.sccwrp.org/ResearchAreas/RegionalMonitoring/) and the San Francisco Estuary Regional Monitoring Program (http://www.sfei.org/rmp/).

Occurrence and Distribution of CECs in Native *Mytilus*

The frequency of detection for PPCPs was nearly 100% for all four land use categories, similar to that for historic Mussel Watch ("legacy") organic constituents (Table 1). The frequency of detection for other commercial chemicals (as illustrated by PFCs) increases from 13 to 71% with increasing urbanization. This general trend also holds true for CUPs (24 to 73%), with (as expected) relatively high frequencies observed for the agricultural (63%) and urban (73%) land use categories. The frequency of detection ranged from 13 to 100% and was

highest for all CEC classes at stations in proximity to stormwater discharge (64 to 100%), compared to those located in proximity to POTWs, ASBS or with no known discharge (Table 1). As with land use, PPCPs and legacy contaminants were ubiquitous across the discharge scenarios. In contrast, PFCs were infrequently detected (<20%) for the three non-stormwater impacted scenarios. As expected, the detection frequency was lowest for stations in proximity to ASBS or with no known discharges.

Polybrominated diphenyl ether congeners 47 and 99, and lomefloxacin (a fluoroquinoline antibiotic) were the only target CECs detected in more than 50 percent of the full complement of stations where native *Mytilus* tissue were collected (Table 2). The mean and maximum dry weight tissue concentrations for these CECs were ≤29 ng/g and ≤170 ng/g), respectively. Alkylphenols/ alkylphenol ethoxylates (APs/APEs), which include 4-nonylphenol, 4-n-octylphenol and its mono- and di-ethoxylates in a family of surfactants that are widely used in detergents and other consumer products, were detected in all samples that passed QA/QC acceptance criteria (Dodder *et al.* In press) and were present at higher maximum concentrations (up to 3000, 300 and 140 ng/g, respectively). However, the number of samples that passed QA/ QC screening for APs/APEs was less than 50% of available samples, suggesting that additional work is necessary to increase the robustness of methods for these analytes in bivalve tissue. The mean/maximum concentrations observed for other detectable CECs were <10 ng/g and in many cases <1 ng/g (Table 2). For example, 4,4'-DDMU (2-chloro-1,1-bis(p-chlorophenyl)-ethylene; a breakdown product of 4,4'-DDE), sertraline and hexabromocyclododecane (HBCD, a replacement flame retardant for PBDEs), were detected in more than half of the 20 stations for which data is available. The maximum concentrations of these CECs, however, were relatively low (≤18 ng/g).

A clear trend in both the number and median concentrations of detectable CECs is apparent for stations stratified by land use (Figure 2). Detailed statistical comparisons are published elsewhere (Dodder *et al.* In press). Nearly double the number of CECs was detected above the median threshold for urban stations compared to the low development stations (13 vs. 6), with stations categorized as mixed development exhibiting an intermediate number of detectable CECs. For individual analytes, the median concentrations for BDE-47 and -99 decreased from urban to mixed development and were lowest for low development and agricultural stations, illustrating their potential utility as indicators of anthropogenic discharge.

Table 1. Percent frequency of detection of CECs in *Mytilus* spp. by chemical class, land use category, and discharge scenario.

Land Use Category	Urban	Mixed Development	Low Development	Agricultural
PPCPs	100	100	87	100
PFCs	71	38	14	13
CUPs	73	33	24	63
Legacy	100	100	100	100
Discharge Scenario	**Stormwater**	**POTW**	**ASBS**	**None**
PPCPs	100	100	100	75
PFCs	64	13	19	13
CUPs	64	57	15	45
Legacy	100	100	100	100

PPCPs – pharmaceuticals and personal care products
PFCs – perfluorinated compounds
CUPs – current use pesticides
POTW – publicly owned treatment works discharging treated municipal wastewater
ASBS – areas of special biological significance

Table 2. Mean, minimum, and maximum tissue concentrations of CEC analytes detected at 10 percent or more of stations where native *Mytilus* was collected. ND = not detected.

Analyte	No. of Stations	Detection Frequency (%)	Tissue Concentration (ng/g dry wt)		
			Mean	Min	Max
4-Nonylphenol (4-NP)	14	100	470	96	3000
4-NP monoethoxylates (NPE1O)	32	100	91	6	300
4-NP diethoxylates (NPE2O)	25	88	25	ND	140
BDE-47	66	83	6.6	ND	68
DDMU	23	65	4.8	ND	18
Sertraline	22	64	1.4	ND	5.5
Lomefloxacin	66	62	29	ND	170
BDE-99	66	61	3.4	ND	38.4
HBCD, gamma	19	58	0.69	ND	2.5
HBCD, alpha	19	42	0.27	ND	1.5
BDE-100	66	39	1.3	ND	15
Dacthal	35	37	2.7	ND	47
Sulfamethazine	66	36	24	ND	430
Cocaine	58	36	0.28	ND	1.7
HBCD, beta	19	32	0.068	ND	0.4
Chlorpyrifos	45	27	1.4	ND	36
Caffeine	68	19	14	ND	140
Diphenhydramine	68	16	0.87	ND	11
Methylprednisolone	67	15	18	ND	210
Enrofloxacin	66	14	1.3	ND	12
Amphetamine	42	14	2.3	ND	20
Amitriptyline	68	13	0.4	ND	6.2
Chlorpyrifos, oxy	33	12	0.11	ND	1.8
BDE-66	66	11	0.42	ND	17
Erythromycin-H2O	56	11	0.14	ND	2
Terbufos	35	11	0.19	ND	2.3
BTBPE	19	11	0.21	ND	2
Ofloxacin	52	10	1.2	ND	18

The median and range of concentrations for APs/APEs (designated as 4-NP, -E1O and -E2O in Figure 1) also suggested a strong anthropogenic link, however, methodological issues due to the concentrations observed temper our confidence in this conclusion. Interestingly, the median concentration for perfluorododecanoic acid (PFDoDA), a PFC that is associated with stain- and grease-proof coatings on various consumer products, is elevated for urban stations. In contrast to the above CECs that exhibit an urban signature, the median concentration for lomefloxacin was highest for the agricultural stations, with no apparent trend among the land use categories (Figure 2). The occurrence of antibiotics such as lomefloxacin in agricultural lands that may also house livestock operations is not surprising as the US Food and Drug Administration estimates that 60% of antibiotic use in the US is in agriculture (Anderson *et al.* 2012).

Mytilus collected at stormwater impacted stations clearly contain both a greater number and higher overall concentrations of individual CECs than those collected near POTWs and at stations with no known discharge (Figure 3). Detailed statistical comparisons are published elsewhere (Dodder *et al.* In press). Similarity between the box plots for stormwater, POTW and no discharge (designated as "none" in Figure 3) suggest that diffuse and/or unknown sources, e.g., atmospheric input, maybe important for several CECs that were detectable in this study. The discharge category showing the lowest relative impact in terms of CEC concentrations is POTWs. Interestingly, CECs such as caffeine that have

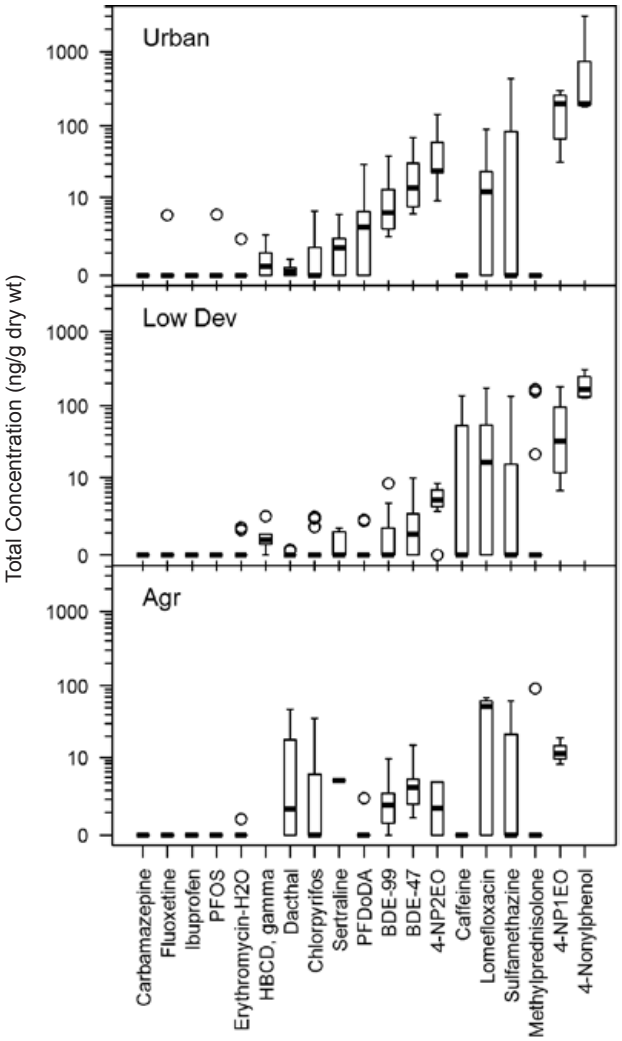

Figure 2. ***Mytilus*** **spp. tissue concentration box plots for selected CECs based on land use categorization (urban, low development and agricultural) of 68 stations along the California coast. The rectangle, horizontal bar and error bars represent the interquartile range (IQR), median, and minimum and maximum concentrations, respectively. The median concentration was assigned as zero for analytes that were not detected. Concentrations greater than 1.5 times the IQR are shown individual circles. No data was available for 4-nonylphenol at agricultural stations.**

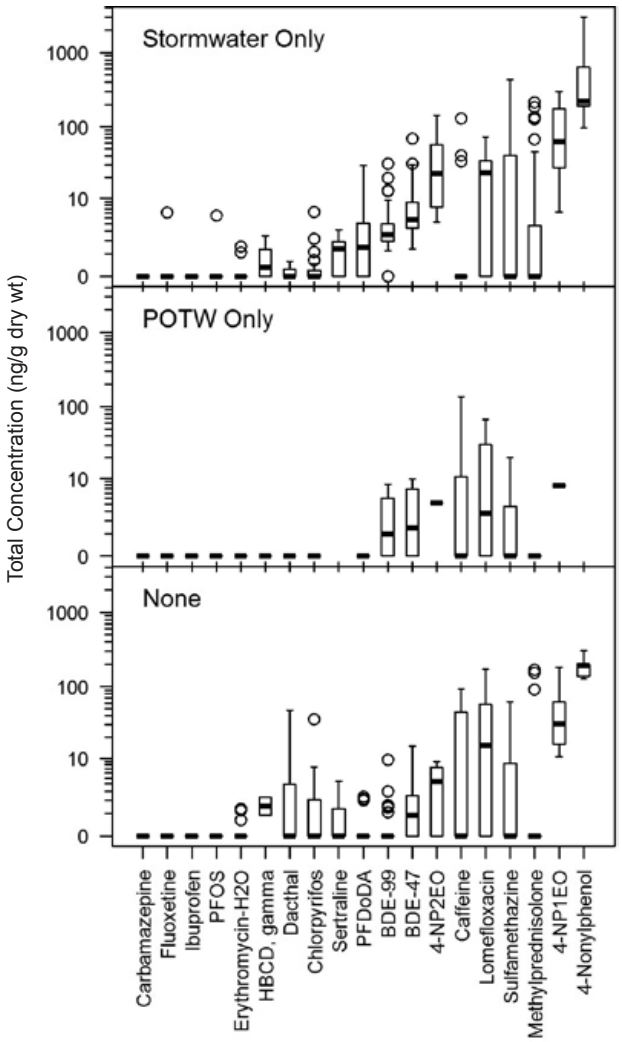

Figure 3. ***Mytilus*** **spp. tissue concentration box plots for selected CECs based on discharge scenario for 68 stations along the California coast. POTW = publicly owned treatment works discharging treated municipal wastewater effluent. The rectangle, horizontal bar and error bars represent the interquartile range (IQR), median, and minimum and maximum concentrations, respectively. The median concentration was assigned as zero for analytes that were not detected. Concentrations greater than 1.5 times the IQR are shown individual circles. No data was available for 4-nonylphenol at stations in close proximity to POTWs.**

been reported as selective indicators of wastewater impact (Buerge *et al.* 2003) were also detectable in stormwater- and no discharge stations. Only the drug amphetamine appears to be specific to POTW input (data not shown). When summed by contaminant class, the median concentrations of measured analytes, including legacy organics, were higher in non-ASBS stations compared to those in close proximity to ASBS (e.g., HBCD; Figure SI-1). The two exceptions were PPCPs and the other, non-PBDE flame retardants, which suggest non-urban sources (e.g., atmospheric deposition for HBCD) may be responsible for their input. Although lomefloxacin has been reported in sediments near POTW outfalls (Zhou *et al.* 2011) and may result from veterinary application to livestock (Anderson *et al.* 2012, Dodder *et al.* In press), its sources along the California coast remain unknown. Significantly lower median concentrations for ASBS stations were noted for

polycyclic aromatic hydrocarbons (PAH), legacy organochlorine pesticides (e.g., DDTs, chlordanes), PBDEs and CUPs (Figure SI-1). Although both documented and undocumented discharge sources occur within ASBS, contaminant concentrations are for the most part lower for ASBS vs. non-ASBS stations, suggesting that existing regulations are effective in maintaining contaminants to near background levels.

Waterborne CECs using Passive Sampling Devices (PSDs)

The flame retarding chemical tris(1-chloro-2-propyl)phosphate (TCPP), the plasticizers diethyl- and diethylhexyl-phthalate, and the synthetic fragrance galaxolide (HHCB) were among the most frequently detected CECs in extracts of polar organic chemical integrated samplers (POCIS; Alvarez *et al.* In press). Moreover, the mean and maximum concentrations for these CECs (averaging 410 and as high as 3100 ng/L for TCPP) far exceeded those of other frequently detected CECs (Table 3). These results are consistent with recently determined concentrations in samples from treated wastewater effluent dominated coastal waterways in southern California (K. Maruya unpublished results). Concentrations estimated by POCIS varied by more than two orders of magnitude for the aforementioned CECs, with the highest concentrations observed at stations (e.g., SFSB, SFYB, TJRE) that were in close proximity to POTWs and/or stormwater discharge (Alvarez *et al.* In press).

Dozens of legacy pollutants were detectable by low density polyethylene devices and solid phase microextraction samplers (PED and SPME, respectively) that target hydrophobic organic chemicals. Polycyclic aromatic hydrocarbons (e.g., phenanthrene, fluoranthene, chrysene) were detected at estimated concentrations in the ng/L range, whereas legacy chlorinated hydrocarbons (e.g., PCB congeners; DDTs and chlordanes) were an order of magnitude lower (pg/L range). Agreement between concentrations for various legacy chemicals estimated by PED and SPME was excellent (Alvarez *et al.* In press), indicating that either and/or both of these PSDs, once properly calibrated and deployed, can be used to estimate aqueous concentrations of hydrophobic chemicals (Fernandez *et al.* 2012). Compared with the water soluble CECs detected by POCIS, the difference in legacy pollutant concentrations among stations was not as pronounced, and were highest at stormwater (as opposed to POTW) impacted locations (Alvarez *et al.* In press). Although several factors (including time-varying exposure due to episodic events and uncertainty in

Table 3. Mean, minimum, and maximum concentrations of CEC analytes detected by 50 percent or more of the polar chemical integrative samplers (POCIS). ND = not detected.

Analyte	Detection Frequency (%)	Estimated 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
Diethylhexylphthalate (DEHP)	80	400	ND	1105
Galaxolide (HHCB)	80	150	ND	1300
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

PSD measurements at very low concentrations) may influence the correspondence between PSD and tissue concentrations of sentinel bivalve species, statistically significant correlations (p <0.05) among tissue and PSD-estimated waterborne concentrations (Figure 4) for most classes of legacy organic pollutants (Alvarez *et al.* In press) also suggests that these PSDs are a good proxy for exposure and/or bioaccumulation by *Mytilus*.

Because they target aqueous phase chemicals at ultratrace levels, the three types of PSDs utilized in this study provide exposure information above and beyond what accumulates in bivalve tissue. For example, waterborne concentrations determined by PSDs can be compared to various numeric water quality goals/standards, including aquatic life criteria for estrogenic chemicals (USEPA 2005, 2008) and those specified in the California Ocean Plan (SWRCB 2009) and in total maximum daily load (TMDL) regulations for coastal waterbodies. These devices also afford greater flexibility than native bivalves in targeting suspected sources of CEC discharge, as evidenced by the detection of analytes associated with POTW effluent (e.g., galaxolide), stormwater (e.g., permethrin and other pyrethroid insecticides) or agricultural activity (e.g., boscalid and other fungicides; Alvarez *et al.* in press) of toxicological concern but that do not bioaccumulate in *Mytilus* or other sentinel organisms. Passive samplers may be deployed at multiple fixed depths using anchored moorings (Zeng *et al.* 2004, Fernandez *et al.* 2012) and/or existing structures in place of/or in addition to caged bivalves. Moreover, properly calibrated and deployed PSDs are immune to predation and physiological changes that complicate interpretation of bioaccumulation data obtained using native and/or caged bivalves. Biofouling of unprotected PSDs remains a concern in certain scenarios, however, corrections for attenuated exchange between the water column and the PSD sorbing phase can be made by incorporating performance reference compounds (Fernandez *et al.* 2012).

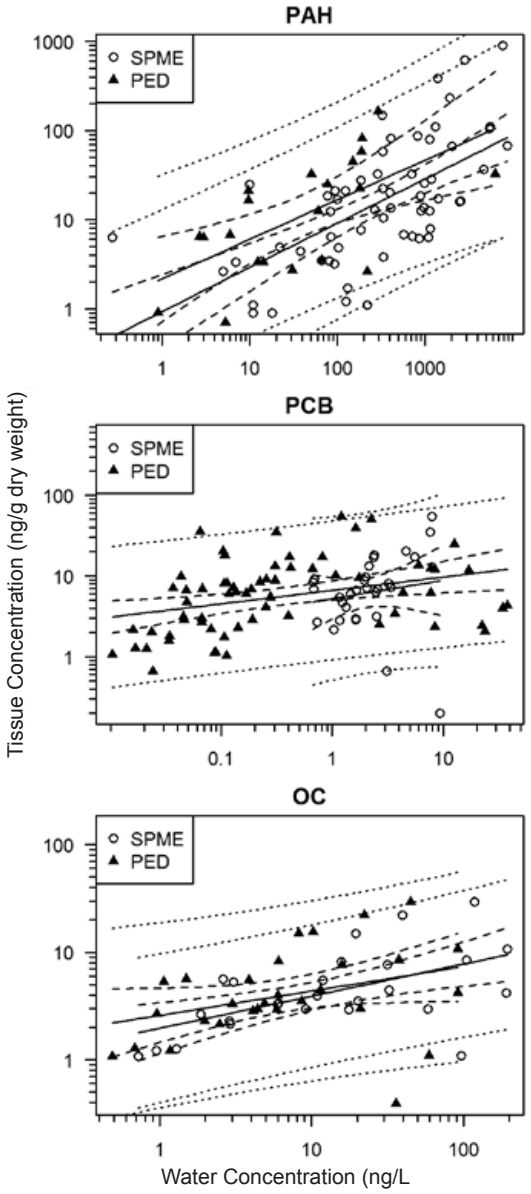

Figure 4. Mussel (*Mytilus* spp.) tissue concentrations of hydrophobic organic contaminants were correlated (p <0.05; R^2 = 0.12 - 0.40) with water column concentrations estimated using solid phase microextraction (SPME) and low density polyethylene film (PED) passive samplers for polycyclic aromatic hydrocarbons (PAH); polychlorinated biphenyls (PCBs) – PED only; and organochlorine pesticides (OCs including DDTs and chlordanes) – SPME only. The regressions for OCs by PEDs (p = 0.067; R^2 = 0.12) and PCBs by SPME (p = 0.44; R^2 = 0.21) were not statistically significant.

Recommendations and Future Challenges

Other efforts in California have identified CECs for potential future monitoring and assessment in ambient receiving waters. The San Francisco Estuary Regional Monitoring Program has performed pilot studies on various classes of CECs since 2000, starting with PBDEs (Oros *et al.* 2005) and more recently focusing on the occurrence of other halogenated flame retardants (Klosterhaus *et al.* 2012) as well as bioaccumulation of PFCs (Sedlak and Greig 2012). On a statewide level, a panel of

experts recently identified 16 individual CECs for future monitoring in coastal embayments and oceanic stations that receive POTW effluent and stormwater discharge, using a risk-based framework and available occurrence and toxicity data (Anderson *et al*. 2012). Among the CECs identified by this panel were many of those highlighted in the present study, including PBDEs, PFCs, phthalates, 4-nonylphenol and galaxolide. These experts also recommended data collection for CECs that lack either occurrence and/or toxicity data. Included in this "second tier" of CECs were the pesticides diuron and fipronil and degradates; chlorinated phosphate flame retardants (e.g., TCEP, TCDD, TDCPP) and synthetic hormones used increasingly as pharmaceuticals (e.g., levonorgestrel). To circumvent the never-ending pursuit of analytical methods for "new" CECs as future chemical production and use patterns change, the panel strongly recommended the development of bioanalytical techniques that incorporate both potential exposure and the likelihood of deleterious effect due to chemicals acting with common modes of biological action (Anderson *et al.* 2012).

Inclusion of PBDEs in statewide coastal monitoring efforts was first instituted in a Mussel Watch pilot study (Kimbrough *et al.* 2008a). This action is further supported by recent investigations reporting widespread occurrence of PBDEs in southern California embayment sediments (Dodder *et al.* 2012), and among the highest ever reported concentrations in marine mammals stranded along the southern California coast (Meng *et al.* 2009) as well as in predatory birds inhabiting urban landscapes (Newsome *et al.* 2010). Instrumental technology and methodological development has advanced to the point where routine analysis of many PBDE congeners in environmental matrices, including bivalve tissue, is easily attainable. A possible exception is the decabromo formulation -- still approved for use in California and in many other parts of the world -- where discharge of its main constituent (BDE 209) and its transformation products present the potential for continued input of PBDEs into coastal ecosystems. Thus, bivalves and other coastal/marine sentinel species remain viable and highly relevant indicators of persistent and bioaccumulative CECs.

The results of this study clearly show the effect of land use on the occurrence of CECs. For example, PBDEs that have in the past been linked to human population centers (Kimbrough *et al.* 2008b) were ubiquitous at locations classified as urban and mixed land use in California. The occurrence of targeted CECs at stations classified as low development and agricultural was less frequent, and typically at lower concentrations. However, it should be noted that the number of agricultural stations and pesticide analytes currently used in California in this study was limited. The occurrence of targeted CECs was also greater (both frequency of detection and concentrations) for stations impacted by stormwater discharge compared with those influenced by POTW discharge, which in California are mostly conveyed and treated separately. As significant improvements in the quality of POTW effluent have been realized since the inception of the Clean Water Act of the 1970s (e.g., SCCWRP 2012), reduction of pollutant discharge and loading associated with stormwater presents the next challenge for the environmental managers. It follows that local, regional and statewide monitoring programs in California should focus on areas of high population density, the occurrence and loading of CECs associated with stormwater discharge, and in filling data gaps associated with specialty land use and treated non-domestic waste streams (e.g., from concentrated agricultural feed operations).

The concentrations of chlorinated phosphates (e.g., TCPP) detected by PSDs in this effort is also noteworthy. While not a bioaccumulative threat, compounds in this class of "replacement" flame retardant are among the highest occurring CECs in both POTW effluent and in stormwater runoff (K. Maruya unpublished results). This is not surprising based on recent reports of its high parts per million concentrations in association with household dust, even higher than is found for PBDEs (Dodson *et al.* 2012). Thus, it is reasonable to anticipate an increase in the occurrence of such high production volume replacement chemicals, particularly those with documented sources and pathways into the coastal aquatic environment. Passive samplers now offer the robust performance characteristics to sample for a wide range of both hydrophobic and water soluble constituents (Fernandez *et al.* 2012, Alvarez *et al.* In press), that when employed in concert with bivalve accumulation, provide a more comprehensive picture of coastal water quality.

Current analytical methodology for some CECs targeted in this study (e.g., APs/APEs) was found to be marginally adequate to meet current measurement goals. Other priority CECs (e.g., phthalates) were not included due to a lack of confidence in

the performance of currently available methods. In the short term, improvements in the robustness and cost-efficiency of analytical methods for these high priority CECs are needed. Over the long run, development of a more efficient monitoring paradigm is needed to keep up with the rapid pace of change in chemical production, usage and discharge to the environment.

The recent focus on CECs in the environment also creates a competition for resources slated for monitoring and assessment. The aforementioned expert panel acknowledged this issue and recommended the determination of relative risk posed by CECs compared with currently monitored "priority or legacy pollutants", such as trace metals, PAH and PCBs and organochlorine pesticides (Anderson *et al.* 2012). The concentrations of APs/APEs, PBDEs and a select number of PPCPs observed in *Mytilus* tissue in this study were of the same order of magnitude as legacy organochlorines (i.e., PCBs, DDTs and chlordanes; Kimbrough *et al.* In press), whereas the vast majority of CECs targeted in this study were not detectable or were observed at extremely low (<10 ng/g) concentrations (Figure 5). While these data do not factor in toxic potency or represent accumulation by higher trophic level species such as birds, marine or terrestrial mammals, they suggest that most CECs are not accumulating to an extent greater than is observed for legacy pollutants (e.g., DDTs, PCBs). Moreover, these results are a much needed first step in determining the relative risk of legacy vs. emerging chemicals.

To effectively address the potential impact of waterborne CECs as well as legacy pollutants using the current risk-based paradigm, credible environmental thresholds of concern that target the appropriate mode of biological action and coastal sentinel species are needed. For the ever-growing list of CECs, only a handful of such values are widely accepted, and of these, most are relevant only to aqueous phase exposure and ambient concentrations (USEPA 2005, 2008). Moreover, screening level threshold concentrations for tissue are virtually non-existent. Thus, new monitoring and assessment tools for the enormous number of potential environmental chemicals and mixtures thereof that integrate exposure and address effects are sorely needed. The ability to screen for both exposure and effects using a battery of bioanalytical assays, compared to determination of an expansive list of individual chemicals by the current analytical approach, is potentially a much more cost-effective paradigm for environmental monitoring (Anderson *et al.* 2012, Scott *et al.* 2012). To that end, efforts are underway to develop rapid, high throughput *in vitro* bioassays that target chemicals by mode of biological activity. Screening bioassays that target relevant biological endpoints and that respond in a robust and predictable fashion can then be further evaluated to characterize their ability to predict higher order effects, e.g., at the

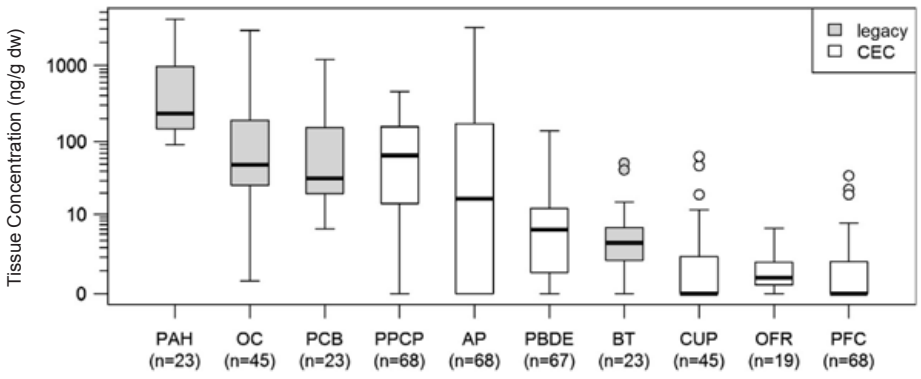

Figure 5. *Mytilus* spp. tissue concentration box plots for all analyte classes measured in this study. The rectangle, horizontal bar and error bars represent the interquartile range (IQR), median, and minimum and maximum concentrations, respectively. The median concentration was assigned as zero for analytes that were not detected. Concentrations greater than 1.5 times the IQR are shown individual circles. Historic Mussel Watch ("legacy") pollutants include polycyclic aromatic hydrocarbons (PAH); organochlorine pesticides (OC); polychlorinated biphenyls (PCB); and butyltins (BT). Pilot study contaminants of emerging concern (CECs) include pharmaceuticals and personal care products (PPCP); alkylphenols/alkylphenol ethoxylates (AP); polybrominated diphenyl ethers (PBDE); current use pesticides (CUP); other (non-PBDE) flame retardants (OFR); and perfluorinated chemicals (PFC).

organism or population scale. The Mussel Watch program in collaboration with regional monitoring and focused pilot studies provide an excellent platform to evaluate new bioanalytical tools and to investigate their linkage to higher biological effects.

The successes resulting from this study were predicated on multi-agency collaboration and leveraging of monitoring and assessment expertise, effort and funds. This level of cooperation among the five primary agencies (NOAA, State of California, SCCWRP, SFEI and USGS) with contributions from many more local and regional entities essentially tripled the allocated Mussel Watch single year budget dedicated to this pilot study. As a result, data for more than 300 analytes in *Mytilus* tissue as well as in PSDs were generated and compiled. New analytes (CECs) constituted more than half of all target analytes, and spatial coverage was doubled to create a comprehensive network of monitoring stations coast-wide. Passive samplers were incorporated to expand the monitoring effort, allowing assessment of locations void of native mussels and inclusion of water soluble CECs. In all of the above ways, the Mussel Watch California pilot for CECs serves as a template for collaboration among multiple agencies to achieve common goals relevant to water quality assessment and management at the local, regional, state and federal levels.

Summary

- Most of the 167 CECs targeted in *Mytilus* were infrequently detected. When detectable, concentrations were typically low (<10 ng/g dry wt).
- Some CECs were detected at a frequency and at concentrations that warrant monitoring to determine future status and trends in *Mytilus*. These include nonylphenol (and its derivatives), PFCs, flame retarding chemicals (e.g., PBDEs, HBCD and chlorinated phosphates), and the antibiotic lomefloxacin.
- Concentrations of most CECs in *Mytilus* were highest at stations in urbanized areas and in close proximity to NPDES stormwater management zones. Attention to these areas/zones in future monitoring efforts is recommended.
- Passive samplers were successful in sampling a broad range of analytes in coastal water. Water concentrations of persistent and bioaccumulative compounds estimated using PSDs were positively correlated with *Mytilus* concentrations. PSDs can be used to monitor the occurrence of water soluble CECs, as surrogates for bivalves when assessing bioaccumulation of persistent contaminants, and at locations where sentinel species are non-existent and/or scarce. Future studies should compare PSD and tissue measurements for bioaccumulative CECs identified by on-going prioritization and monitoring efforts.
- New monitoring and assessment tools are needed to effectively address the potential impact of the ever-growing number and ever-changing composition of environmental chemicals. Improvements in and standardization of analytical methods for "difficult to measure" CECs (e.g., APs/APEs, phthalates) are needed. Promising bioanalytical techniques that integrate exposure of multiple classes of CECs (and mixtures thereof) and provide relevant response information should be adapted for environmental monitoring and water quality assessment applications.
- Partnerships among local, regional, state and federal agencies tasked with coastal monitoring can effectively address management questions while maximizing efficient use of available resources.

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Supplemental Information

Supplemental Information is available at ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/AnnualReports/2013AnnualReport/ar13_061_073SI.pdf.