Areas of Special Biological Significance: Northern California Bioaccumulation Monitoring

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Southern California Coastal Water Research Project

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INTRODUCTION

The California State Water Resources Control Board (SWRCB) designated Areas of Special Biological Significance (ASBSs) as marine regions that require water quality protection. Waste discharges into ASBSs, such as polluted storm water, are prohibited, but the SWRCB grants exceptions if it can be shown that the protection of marine life in receiving ocean waters is not compromised. The standard for protection is that discharges "shall not alter natural ocean water quality in an ASBS" (*1*). There are approximately 1,658 known discharges into California ASBSs, nearly all of them storm water outfalls, which have a potential to impact ASBS water quality (*2*).

Wet-weather water column contamination in ASBS receiving waters was monitored in southern California starting in 2008 (*3*), and then in northern California starting in 2012. In order to define "natural", these studies used reference sites that were minimally impacted by human activities. These studies found that water column concentrations near discharges were, on average, comparable to concentrations near reference sites. However, in some cases individual ASBS discharge sites exceeded reference-site based natural water quality guidelines. While these results were encouraging, neither study focused on bioaccumulating compounds. Bioaccumulation was first assessed in southern California ASBSs in 2013 where, with some exceptions, discharge concentrations were comparable to reference concentrations (*4*).

Based on the needs of the Northern California Regional Monitoring collaborative, which includes ASBS dischargers and the SWRCB, this survey was designed to answer the following questions: 1) What is the range of natural water quality for bioaccumulative compounds, as defined by bivalve tissue sampled near reference stations? 2) Is the water quality for bioaccumulative compounds at ASBS discharge stations similar to that at reference stations representing natural water quality? Bivalves are filter feeders that accumulate contaminants over a longer period of time compared to storm water grab samples, and may bioconcentrate contaminants resulting in potential impacts at low water column concentrations. Bivalves, including mussels, have been used for decades in NOAA's Mussel Watch Program to monitor bioaccumulative contaminants across the U.S. coastline (*5*), but have not been previously utilized to assess regional ASBS water quality along the North Coast.

METHODS

Bioaccumulative contaminants in mussels were surveyed at 10 stations within five ASBSs in northern California (Table 1 and Figure 1). Metals and synthetic organic contaminants were measured at locations representative of discharge and reference sites. The five discharge sites received ASBS storm water discharge. The five reference sites received drainage from an undeveloped watershed determined to represent natural water quality. Station locations were selected by the North Coast Regional Monitoring collaborative.

Sampling

Sample collection followed protocols established by the NOAA National Status & Trends (NS&T) Mussel Watch Program (*6,7*). Mussels were collected by hand at low tide in April 2014. Approximately 20 to 30 individuals were collected at each of three sub-stations located along a 100 m transect of shoreline (approximately 60 individuals total per station). The exception was at Hardy Creek, where a sparse local population necessitated sampling at a single sub-station. All stations were successfully sampled for *Mytilus californianus*. Duplicate field samples (two sets of approximately 60 individuals each) were collected at Shelter Cove.

Upon collection, the shells were rinsed in water at the site to remove mud and debris, drained, and placed into individual plastic bags on ice. Samples were shipped cold to the laboratory and the tissues were frozen after removal. Morphometric measurements were taken on each specimen and the individual tissues from each station were homogenized into a single sample. The sample was then split, with one portion sent for metal analysis and one portion sent for organic analysis.

Laboratory Analysis

Targeted contaminants (Table 2) were similar to those listed in the Ocean Plan and historically measured by the NOAA NS&T Mussel Watch Program: metals, legacy organochlorine pesticides, polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs). Additional contaminants of emerging concern were also measured. The polybrominated diphenyl ether (PBDE) flame retardants were recommended for monitoring in tissues by the recent expert panel on Chemical of Emerging Concern (CECs) in California marine ecosystems (*8*), and were previously observed in southern California bivalve tissue (*9*). Current use pesticides (CUP) included pyrethroids, fipronil, and fipronil degradates.

Organic contaminants were measured by gas chromatography coupled to mass spectrometry (GC/MS), and metals by inductively coupled plasma coupled to mass spectrometry (ICP/MS). The project used performance-based criteria for quality control, as follows. For metals, laboratory blanks were non-detects, blank spike recoveries were within 10% of the true value, matrix spike recoveries were within 10% of the true value, the relative percent difference between duplicate matrix spikes was <2%, certified reference material recoveries were within 20% of the true value, and the relative percent difference between replicate samples was <10%. For organics, surrogate standard recoveries were greater than 70%, blank spike recoveries were within 30% of the true value, certified reference material recoveries were within 30% of the true value, spiked matrix recoveries were within 30% of the true value, and the relative percent difference between replicate samples was <30%. All analytes passed the quality control criteria, with only minor exceedances in a single criterion. The following PBDE congeners passed the quality assurance criteria, but were unusually high in the tissue relative to the known congener distribution in the technical mixture: PBDE-17, PBDE-66, PBDE-71, PBDE-85, PBDE-138, PBDE-190. These compounds may have been natural halogenated compounds misidentified as PBDEs and were removed from the data set. The duplicate field samples taken from Shelter Cove produced consistent results, with relative percent differences of < 15% for metal analytes and <45% for organic analytes. The Shelter Cove sample "SHE-BIO-080414-1" was used for data analysis, after sensitivity analysis using both samples did not show an appreciable difference in results.

Data Analysis

Morphometric data was evaluated to compare mussel size and tissue mass among stations. Outlying morphometric parameter values at a particular station may indicate a difference in age or health of the organisms, which in turn may affect contaminant concentrations relative to other locations. Subsequent to the morphometric analysis, the contaminant concentration data was evaluated in three steps. Metals and organics were treated separately due to the higher concentration range of metals. First, the contaminant magnitudes at reference and discharge stations were compared. The non-parametric Kruskal-Wallis rank sum test was used to test for significant differences between the reference and discharge groups for each analyte. Second, a method for determining reference/discharge station equivalence was applied to each contaminant. This followed a procedure developed in the Bight '08 ASBS Study examining storm water, which used a reference-station based guideline as a proxy for distinguishing differences from natural water quality (*3*). This was also the procedure used in the 2013 southern California ASBS bioaccumulation survey (*4*). The guideline was calculated as the 85th percentile of the reference station concentrations, using a method that interpolates the value based on order (non-parametric) statistics (*10*). Exceeding discharge stations were those with concentrations greater than the guideline. Third, the northern California ASBS mussel tissue concentrations were compared to those from southern California Bight ASBSs sampled in 2013 (*4*) and from statewide sampling in 2010 as part of Mussel Watch (*9*)

In 2013, bioaccumulation at ASBSs within the southern California Bight were analyzed using similar analytical and data analysis procedures. There were, however, ten reference and ten discharge stations, which allowed for greater confidence in measurement uncertainty, in comparison to the current study with 5 reference and 5 discharge stations. In the southern California study, outlier reference concentrations were determined for each contaminant using Grubbs' test, and were excluded when determining reference guidelines. Outliers were included in the current study due to the smaller reference sample size, which resulted in weaker confidence in measurement uncertainty. However, principal components analysis was used to examine the potential for outlying reference concentrations. Also in the southern California study, individual organic contaminant concentrations (e.g., 4,4'-DDT, 4,4'-DDE, etc.) were used to assess guideline exceedance. In the current northern California study, class totals (e.g., ΣDDT) were used to assess guideline exceedance, since this reduced the uncertainty associated with lower sample size.

RESULTS

Morphometrics

Percent solids concentrations ranged from 13% to 20%, and percent lipids ranged from 0.7% to 1.3%, for all mussel samples. The mean (± standard deviation) shell length was 60 ± 7 mm, mean total mass was 21 ± 7 g, and mean tissue mass was 6.0 ± 2.3 g per individual. The mean shell length at each station varied around the total mean by < 15% (Figure 2). Shell length is a proxy for age; therefore, results indicated the mussels at each station had the same mean age, and age was likely not a confounding variable when interpreting contaminant concentrations. The relationship between shell length and tissue mass for all individual mussels (Figure 3) can be used in future studies to predict the recoverable tissue mass given the size of collected mussels.

Contaminant Magnitudes

Measured contaminant concentrations are shown in Figures 4 (metals) and 5 (organics). Stations with relatively high concentrations that could be potentially outlying values are labeled. There were no significant differences in tissue concentration between the reference station group and the discharge station group for either metal or organic analytes (all p-values were greater than 0.1). Appendix tables A1 (metals), A2 (individual organics), and A3 (total organics) provide the concentration values for all samples and analytes.

Reference Station Suitability

Compared to the other reference stations, Enderts Beach had relatively high levels of DDTs, PCBs and Other Pesticides (Figure 5). The specific contaminants with high concentrations were 4,4'-DDE, PCB-138, PCB-153, and trans-nonachlor. This difference was verified using principal components analysis, a clustering method that compares the relative abundance of contaminants. Stations with a shorter "distance" to one another (i.e., clustering together) have similar contaminant profiles. Stations with a further "distance" from one another have dissimilar contaminant profiles. As shown in Figure 6, Enderts Beach has an organic contaminant profile that is distinct from all other reference and discharge stations. This suggests it may not be a suitable reference station. However, due to low sample size, there is uncertainty in this assessment and Enderts Beach was not excluded when determining reference guidelines.

Reference Guideline Exceedance

Tables 3 (metals) and 4 (organics) show the relatively few guidance exceedences of the 85th percentile. Stations with metal exceedances were Shelter Cove (5 metals exceeded), Saunders Reef (3), Del Mar Point (1), and Trinidad Bay (1). Stations with organic exceedances were Shelter Cove (2 organics exceeded), Trinidad Bay (2), Saunders Reef (1), and Del Mar Point (1). False Klamath Cove had zero exceedances. Ssilver was not detected at the reference stations.

As a measure of the magnitude of exceedance, the exceeding concentration as a percentage of the guideline value was calculated. The magnitudes were generally low, with no exceedances greater than 50% of the guideline. The single exception was cadmium at Del Mar Point, which was slightly over twice the guideline value.

Sensitivity Analysis

The 85th percentile was set as the reference guideline at the beginning of the project. To test the sensitivity of the results against this definition, exceedances were also determined using the 80th percentile and maximum of the reference concentrations. Metal results (Tables 5 and 6) were somewhat dependent on the guideline definition, with the total number of exceedances increasing with decreasing guideline (n=12 using the 80th percentile, n=10 using the 85th percentile, and n=6 using the maximum reference concentration. Organics (Tables 7 and 8) were less dependent on the guideline definition, with the total number of exceedances (n=6) using the 80th percentile being the same (n=6) using the 85th percentile, and nearly the same (n=5) using the maximum reference concentration.

For organic contaminants, the concentration basis can be expressed on either a dry weight or lipid weight basis, and is a potentially confounding factor in the interpretation of the organic contaminant results. We reported concentrations on a dry weight basis because this is the more common format for bivalve tissue data (*3,4,5,9*), but many bioaccumulative contaminants are known to be positively correlated with increasing lipid mass. Therefore, the reference guideline exceedance (using the 85th percentile) was also calculated with concentrations expressed on a lipid weight basis (Table 9). The results had only a minor dependence on the concentration basis. The only differences were 1) Saunders Reef exceeded the ΣPBDE guideline on a lipid weight basis, but not on a dry weight basis, and 2) Trinidad Bay exceeded the ΣPyrethroid/Fipronil guideline on a dry weight basis but not on a lipid weight basis.

Survey Comparison

To put the northern California bivalve data in to a statewide context, comparisons were made to the 2013 southern California ASBS bioaccumulation survey (*3*) and the 2010 statewide Mussel Watch survey (*9*). The southern California ASBS survey had a design similar to the current survey. The Mussel Watch survey, the most recent statewide Mussel Watch survey in California, measured contaminants at 68 stations statewide from a variety of agricultural, urbanization, and low development settings. Stations had exposure to wastewater treatment plant effluent, and/or stormwater discharge, or neither. The majority of stations were located outside ASBSs. Figures 7 and 8 compare results for metals and organics, respectively, among the three surveys. For the organics comparison, only individual analytes common among all three studies were included. Therefore in some cases, the summed values for northern California are slightly lower than in Figure 5.

For metals, the comparison among surveys may not be informative due to either regional background or analytical differences. For example, aluminum, chromium, and nickel had higher reference values in northern California ASBSs compared to southern California ASBSs and the statewide Mussel Watch survey. We expected the statewide survey concentrations to encompass the ASBS results, since the statewide survey included stations known to have high levels of contamination from exposure to urbanization, wastewater treatment plant effluent, and/or stormwater. As a second example, arsenic, lead, and zinc had higher levels in southern California ASBSs compared to northern California ASBSs and the statewide results. Again, we expected the statewide results to encompass the ASBS results. For metals, the same laboratory performed the northern and southern ASBS measurements, and a different laboratory performed the Mussel Watch measurements.

For organics, the statewide results encompass the ASBS results, showing that within ASBSs, the organic contaminants are 1 to 2 orders of magnitude lower that the maximum statewide concentrations. These maximum statewide concentrations occur outside ASBSs near urbanized areas. For organics, different laboratories performed the measurements for the three surveys. In some cases, (PCBs, PAHs, and Other Pesticides) the statewide Mussel Watch results do not extend as low as the northern and southern ASBS results. This was due to higher reporting levels in the Mussel Watch survey. Northern California ASBSs also had lower median concentrations than southern California ASBSs.

Conclusions and Recommendations

The goal of this project was to answer the following questions for bioaccumulative contaminants: 1) What is the range of natural water quality for bioaccumulative compounds, as defined by bivalve tissue sampled near reference stations? 2) Is the water quality for bioaccumulative compounds at ASBS discharge stations similar to that at reference stations representing natural water quality? The conclusions were:

- **Substantial differences in the concentration distributions at reference stations and discharge stations were not observed.**

  Differences in the range of concentrations between reference and discharge stations were small, as were the median contaminant concentrations. Moreover, there was no statistically significant differences between the reference and discharge populations of samples. Finally, there was no discharge site that had higher concentrations for most constituents compared to reference sites.

- **The frequency and magnitude of reference guideline exceedances were minimal**

  In some cases, discharge stations exceeded the 85^{th} percentile reference guidelines. Shelter Cove had the most exceedances, with 5 metals and 2 organics above reference guidelines. Consistent with the previous conclusion that reference and discharge sample distributions were comparable, exceedances of the reference guideline were small, never exceeding the guideline value by more than 50%. The single exception was cadmium at Del Mar Point, which was slightly over twice the guideline value. Sensitivity analysis using different guidelines or normalizing factors such as lipid content did not alter the conclusion.

- **The suitability of Enderts Beach as a reference station should be investigated for future regional monitoring.**

  Due to relatively high concentrations of 4,4'-DDE, PCB-138, PCB-153, and trans-nonachlor, Enderts Beach had a contaminant profile that was different from the other reference stations. Because of small sample size and our inability to verify that Enderts Beach was anthropogenically influenced, this site was included when establishing reference guideline values.

- **Northern California ASBS discharge stations had lower organic concentrations than southern California ASBS discharge stations and non-ASBS values observed statewide.**

  Organic concentrations within northern California ASBSs were generally lower in comparison to the 2013 southern California ASBS survey of similar design, or the 2010 statewide Mussel Watch survey.

References

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(9) Dodder NG, Maruya KA, Lee Ferguson P, Grace R, Klosterhaus S, La Guardia MJ, Lauenstein GG, Ramirez J. 2014. Occurrence of contaminants of emerging concern in mussels (Mytilus spp.) along the California coast and the influence of land use, storm water discharge, and treated wastewater effluent. *Marine Pollution Bulletin*, 81, 340-346.

(10) The command `quantile(x, probs = 0.85, type = 7)` in the R statistical programming language was used, where `x` was the vector of reference concentrations, `probs` specified the quantile probability (e.g., a percentile of 85% is a quantile of 0.85), and `type` specified the algorithm defined at https://stat.ethz.ch/R-manual/R-patched/library/stats/html/quantile.html.

Table 1. ASBS reference and discharge bioaccumulation samples and target latitude/longitudes collected in April 2014 in northern California.

ASBS Number	Station Name	Type	Latitude	Longitude
ASBS 2	Del Mar Point	Discharge	-38.74113	-123.50974
ASBS 5	Saunders Reef	Discharge	-38.861	-123.65389
ASBS 6	Trinidad Bay	Discharge	-41.05661	-124.14658
ASBS 7	Shelter Cove	Discharge	-40.0225	-124.07333
ASBS 8	False Klamath Cove	Discharge	-41.59539	-124.10567
ASBS 2	Kruse Creek	Reference	-38.59722	-123.35069
ASBS 5	Point Arena Lighthouse	Reference	-38.953	-123.743
ASBS 6	Martin Creek	Reference	-41.07756	-124.15508
ASBS 7	Hardy Creek	Reference	-39.71075	-123.80819
ASBS 8	Enderts Beach	Reference	-41.70642	-124.14494

Table 2. Bioaccumulative contaminants measured in the mussel tissues. The reporting level range for each class is given in parenthesis.

Metal	PAH	PCB		Pesticides	PBDE	Pyrethroid/Fipronil Pesticides
(0.05 µg/g dw)	(0.1 ng/g dw)	(0.1 ng/g dw)		(0.1 ng/g dw)	(0.1 ng/g dw)	(0.5 ng/g dw)
Aluminum*	11H-Benzo[b]fluorene	PCB003	PCB123	Chloropyrifos*	PBDE015	Fipronil
Antimony	1-Methylnaphthalene	PCB008	PCB126	Diazinon*	PBDE017*	Fipronil desulfinyl
Arsenic	1-Methylphenanthrene	PCB018	PCB128	2,4'-DDD	PBDE028+033	Fipronil sulfide
Beryllium	2,3,5-Trimethylnaphthalene	PCB028	PCB138	2,4'-DDE	PBDE047*	Fipronil sulfone
Cadmium	2,6-Dimethylnaphthalene	PCB031	PCB141	2,4'-DDT	PBDE049*	Bifenthrin
Chromium	2-Methylnaphthalene	PCB033	PCB149	4,4'-DDD	PBDE066	Cyfluthrin
Copper	2-Methylphenanthrene	PCB037	PCB151	4,4'-DDE	PBDE071	Cyhalothrin-lambda
Lead	3,6-Dimethylphenanthrene	PCB044	PCB153	4,4'-DDMU	PBDE075	Cypermethrin
Manganese	9,10-Diphenylanthracene	PCB049	PCB156	4,4'-DDNU	PBDE085	Danitol (Fenpropathrin)
Molybdenum	Acenaphthene	PCB052	PCB157	4,4'-DDT	PBDE099*	Deltamethrin/Tralomethrin
Nickel	Acenaphthylene	PCB056	PCB158	Aldrin	PBDE100	Esfenvalerate
Selenium	Anthracene	PCB066	PCB167	Chlordane-alpha	PBDE119	Permethrin, cis-*
Silver	Benz[a]anthracene	PCB070	PCB168+132	Chlordane-gamma	PBDE138	Permethrin, trans-*
Thallium	Benzo[a]pyrene	PCB074	PCB169	Chlordene	PBDE153	
Zinc	Benzo[b]fluoranthene	PCB077	PCB170	cis-Nonachlor	PBDE154	
	Benzo[e]pyrene	PCB081	PCB174	Dieldrin	PBDE155	
	Benzo[g,h,i]perylene	PCB087	PCB177	Endrin	PBDE183	
	Benzo[k]fluoranthene	PCB095	PCB180	Heptachlor epoxide	PBDE 109	
	Biphenyl	PCB097	PCB183	Oxychlordane		
	Chrysene	PCB099	PCB187	trans-Nonachlor		
	Dibenz[a,h]anthracene	PCB101	PCB189			
	Dibenzothiophene	PCB105	PCB194			
	Fluoranthene	PCB110	PCB195			
	Fluorene	PCB114	PCB199			
	Naphthalene	PCB118	PCB201			
	Perylene	PCB119	PCB206			
	Phenanthrene		PCB209			
	Pyrene					

* RL for aluminum was 5 µg/g dw; RL for chlorpyrifos and diazinon was 5 ng/g dw; RL for BDE 17, 47, 49, and 99 was 5 ng/g dw; RL for cis- and trans-permethrin was 2 ng/g dw. DW means dry weight.

Table 3. Discharge stations exceeding metal guidance based on the 85th percentile of the reference station concentrations. Shown are the exceeding discharge stations, the measured concentration at the station, and the relative percent by which the reference guideline was exceeded. ND = non-detected concentration (silver was not detected at the reference stations).

Parameter	Reference Guideline 85th Percentile (µg/g dw)	Exceeding Discharge Stations		
		Station	Concentration (µg/g dw)	Percent Exceeding
Aluminum	640	Shelter Cove	758	18%
Arsenic	13	-	-	-
Cadmium	7.5	Del Mar Point Shelter Cove Trinidad Bay	18 9.1 7.7	134% 21% 3%
Chromium	3.5	-	-	-
Copper	14	-	-	-
Lead	1.7	-	-	-
Manganese	10	Shelter Cove	11	12%
Molybdenum	0.74	Shelter Cove	0.78	6%
Nickel	3.9	-	-	-
Selenium	2.7	Saunders Reef	2.7	<1%
Silver	ND	Shelter Cove Saunders Reef	0.22 0.13	- -
Zinc	132	Saunders Reef	159	20%

Table 4. Discharge stations exceeding organic contaminant guidelines based on the 85th percentile of the reference station concentrations. Shown are the exceeding discharge stations, the measured concentration at the station, and the relative percent by which the reference guideline was exceeded. DW=dry weight.

Parameter	Reference Guideline 85th Percentile (ng/g dw)	Exceeding Discharge Stations		
		Station	Concentration (ng/g dw)	Percent Exceeding
ΣDDT	18	-	-	-
ΣPCB	6.6	-	-	-
ΣOther Pesticides	1.3	-	-	-
ΣPAH	60	Trinidad Bay	69	15%
ΣPBDE	6.5	Shelter Cove	9.0	37%
ΣPyrethorids/Fipronil	0.81	Shelter Cove Del Mar Point Saunders Reef Trinidad Bay	1.0 0.97 0.93 0.82	25% 21% 15% 1%

Table 5. Metals sensitivity analysis using the 80th percentile reference guideline. Shown are the exceeding discharge stations, the measured concentration at the station, and the relative percent by which the reference guideline was exceeded.

Parameter	Reference Guideline 80th Percentile (µg/g dw)	Exceeding Discharge Stations		
		Station	Concentration (µg/g dw)	Percent Exceeding
Aluminum	630	Shelter Cove	758	20%
Arsenic	13	-	-	-
Cadmium	7.1	Del Mar Point Shelter Cove Trinidad Bay	18 9.1 7.7	148% 29% 9%
Chromium	3.5	-	-	-
Copper	11	-	-	-
Lead	1.7	-	-	-
Manganese	9.5	Shelter Cove Trinidad Bay False K. Cove	11 10 9.8	20% 5% 3%
Molybdenum	0.70	Shelter Cove	0.78	11%
Nickel	3.8	-	-	-
Selenium	2.7	Saunders Reef	2.7	1%
Silver	0	Shelter Cove Saunders Reef	0.22 0.13	- -
Zinc	131	Saunders Reef	159	21%

Table 6. Metals sensitivity analysis using the maximum concentration reference guideline. Shown are the exceeding discharge stations, the measured concentration at the station, and the relative percent by which the reference guideline was exceeded.

Parameter	Reference Guideline Max. Conc. (µg/g dw)	Exceeding Discharge Stations		
		Station	Concentration (µg/g dw)	Percent Exceeding
Aluminum	672	Shelter Cove	758	12%
Arsenic	15	-	-	-
Cadmium	8.9	Del Mar Point Shelter Cove	18 9.1	98% 3%
Chromium	3.8	-	-	-
Copper	23	-	-	-
Lead	1.8	-	-	-
Manganese	12	-	-	-
Molybdenum	0.86	-	-	-
Nickel	4.0	-	-	-
Selenium	2.7	-	-	-
Silver	0	Shelter Cove Saunders Reef	0.22 0.13	- -
Zinc	132	Saunders Reef	159	20%

Table 7. Organics sensitivity analysis using the 80th percentile reference guideline. Shown are the exceeding discharge stations, the measured concentration at the station, and the relative percent by which the reference guideline was exceeded.

Parameter	Reference Guideline 80th Percentile (ng/g dw)	Exceeding Discharge Stations		
		Station	Concentration (ng/g dw)	Percent Exceeding
ΣDDT	14	-	-	-
ΣPCB	4.2	-	-	-
ΣOther Pesticides	0.67	-	-	-
ΣPAH	57	Trinidad Bay	69	20%
ΣPBDE	6.4	Shelter Cove	9.0	41%
ΣPyrethorids/Fipronil	0.79	Shelter Cove Del Mar Point Saunders Reef Trinidad Bay	1.0 0.97 0.93 0.82	28% 23% 17% 3%

Table 8. Organics sensitivity analysis using the maximum concentration reference guideline. Shown are the exceeding discharge stations, the measured concentration at the station, and the relative percent by which the reference guideline was exceeded.

Parameter	Reference Guideline Max. Conc. (ng/g dw)	Exceeding Discharge Stations		
		Station	Concentration (ng/g dw)	Percent Exceeding
ΣDDT	30	-	-	-
ΣPCB	14	-	-	-
ΣOther Pesticides	3.3	-	-	-
ΣPAH	68	Trinidad Bay	69	1%
ΣPBDE	7.1	Shelter Cove	9.0	26%
ΣPyrethorids/Fipronil	0.81	Shelter Cove Del Mar Point Saunders Reef	1.0 0.97 0.93	18% 14% 9%

Table 9. Organics sensitivity analysis with concentrations on a lipid weight basis and using the 85th percentile reference guideline. Shown are the exceeding discharge stations, the measured concentration at the station, and the relative percent by which the reference guideline was exceeded.

Parameter	Reference Guideline 85th Percentile (ng/g lw)	Exceeding Discharge Stations		
		Station	Concentration (ng/g lw)	Percent Exceeding
ΣDDT	353	-	-	-
ΣPCB	135	-	-	-
ΣOther Pesticides	29	-	-	-
ΣPAH	1010	Trinidad Bay	1080	7%
ΣPBDE	128	Shelter Cove Saunders Reef	177 129	37% <1%
ΣPyrethorids/Fipronil	15	Saunders Reef Shelter Cove Del Mar Point	21 20 20	34% 29% 27%

Figure 1. Bioaccumulation stations in northern California.

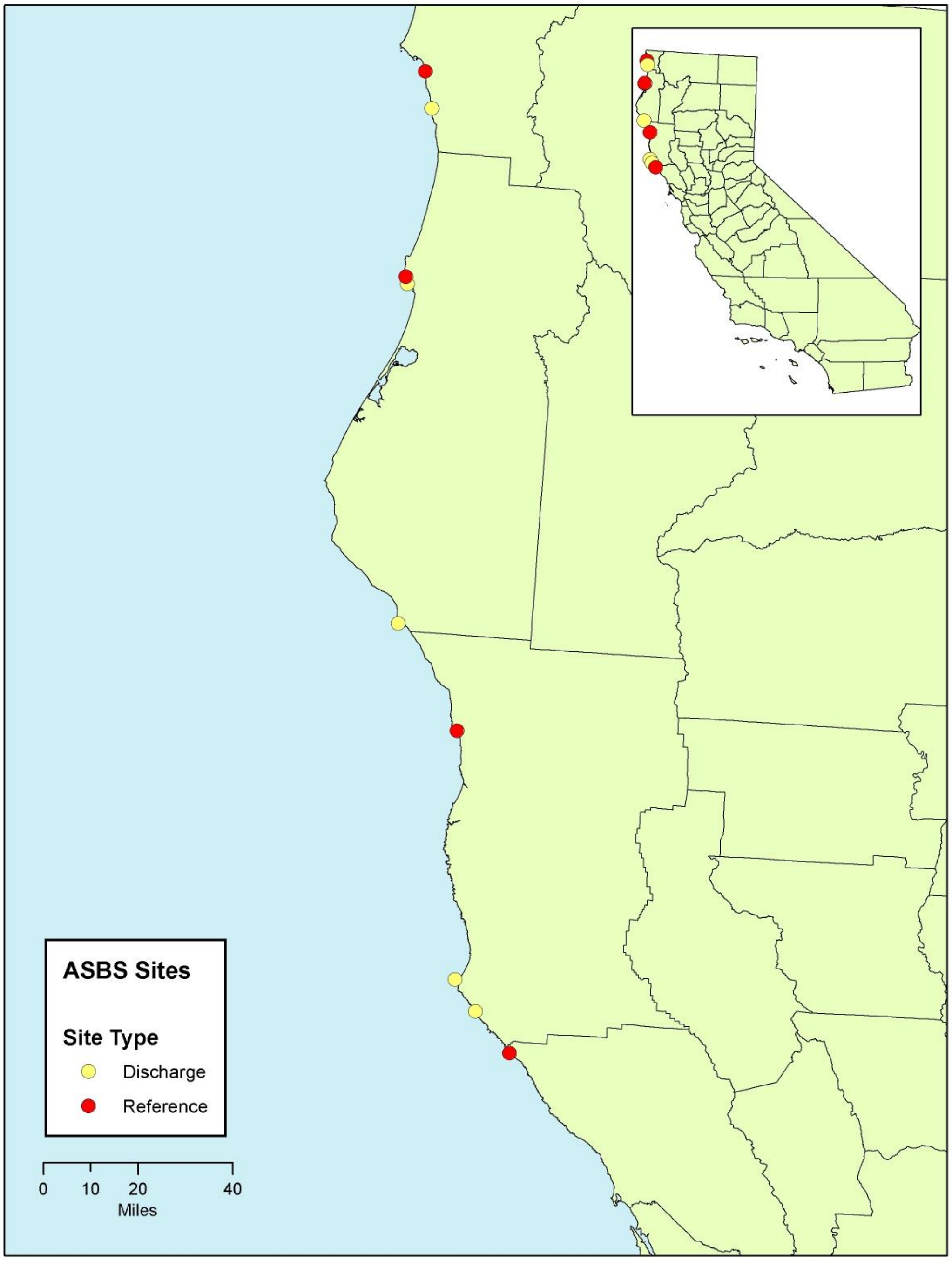


Figure 2. Variation in shell length, as a proxy for age, among stations.

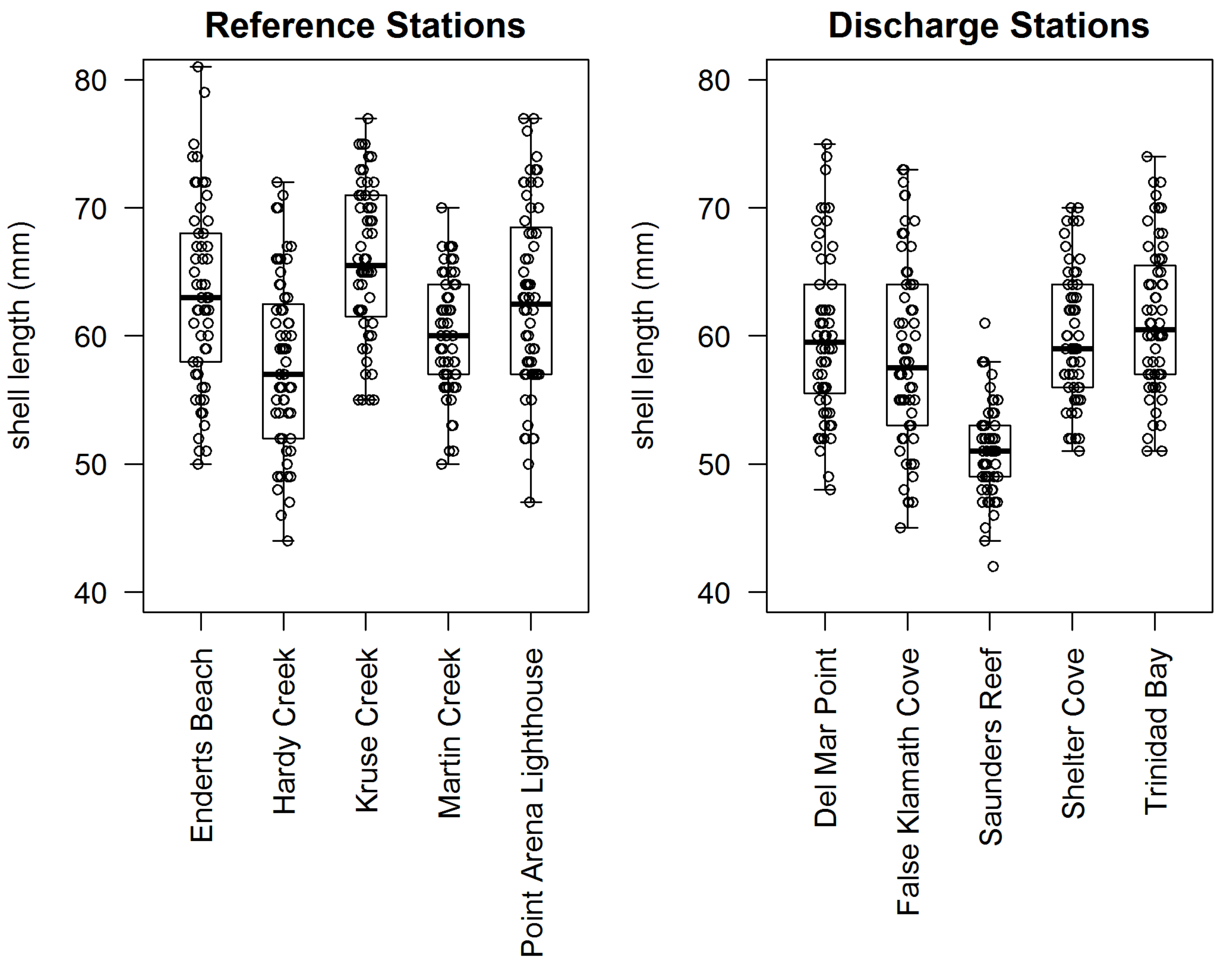


Figure 3. Shell length as a predictor of tissue mass (*Mytilus californianus*). The fitted line is a cubic smoothing spline.

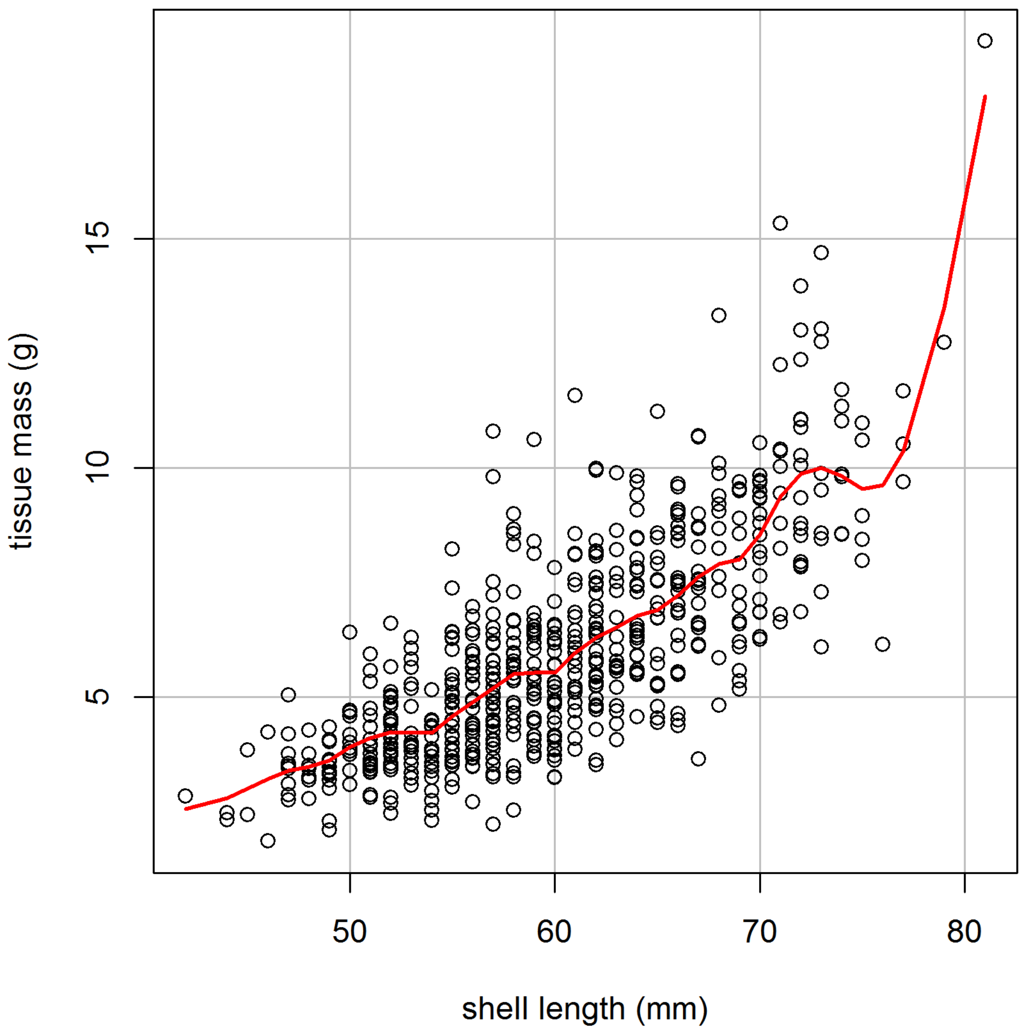


Figure 4. Metal concentrations in northern California ASBS stations. Stations with the highest concentration are labeled.

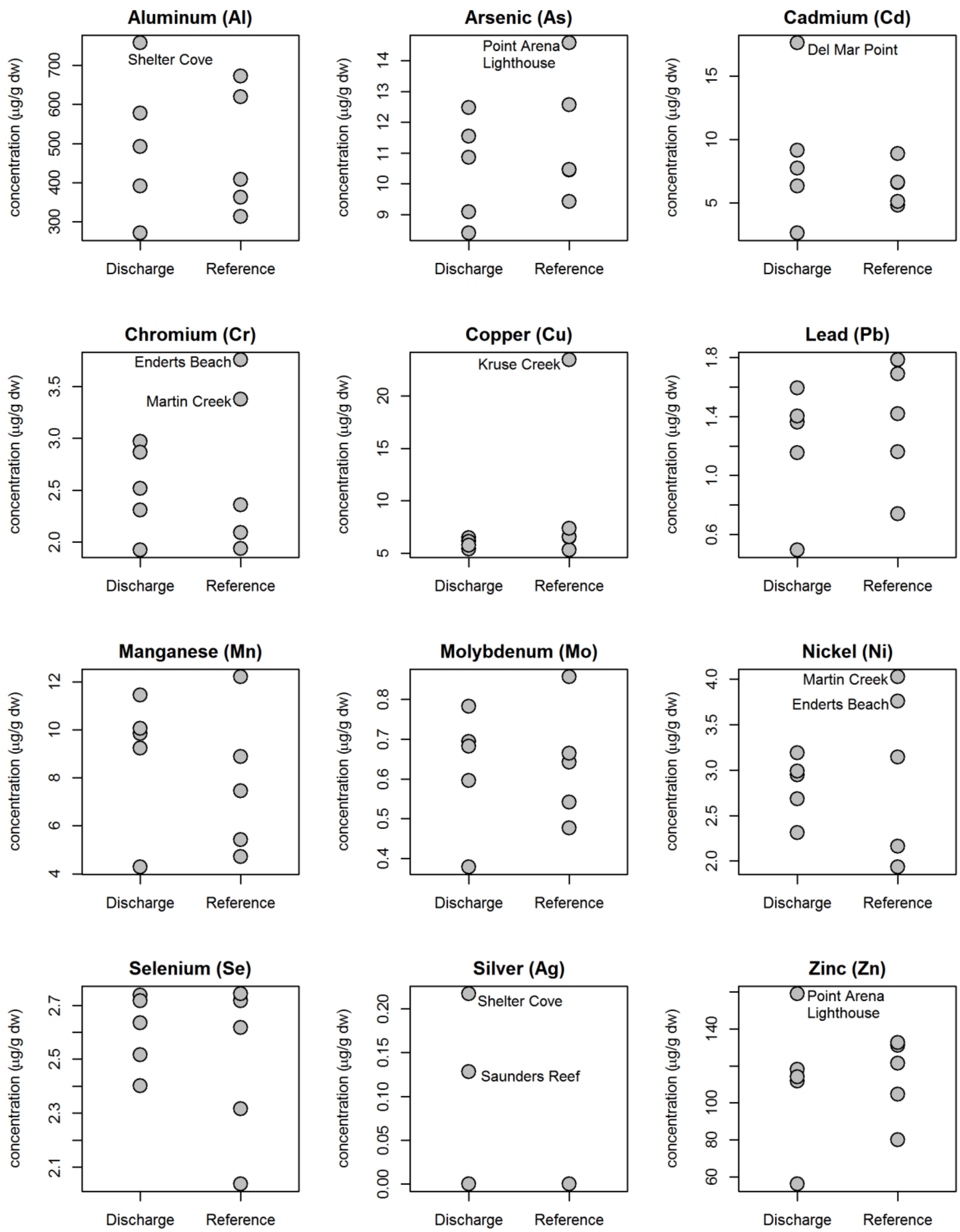


Figure 5. Organic contaminant concentrations in northern California ASBS stations. Stations with the highest concentrations are labeled.

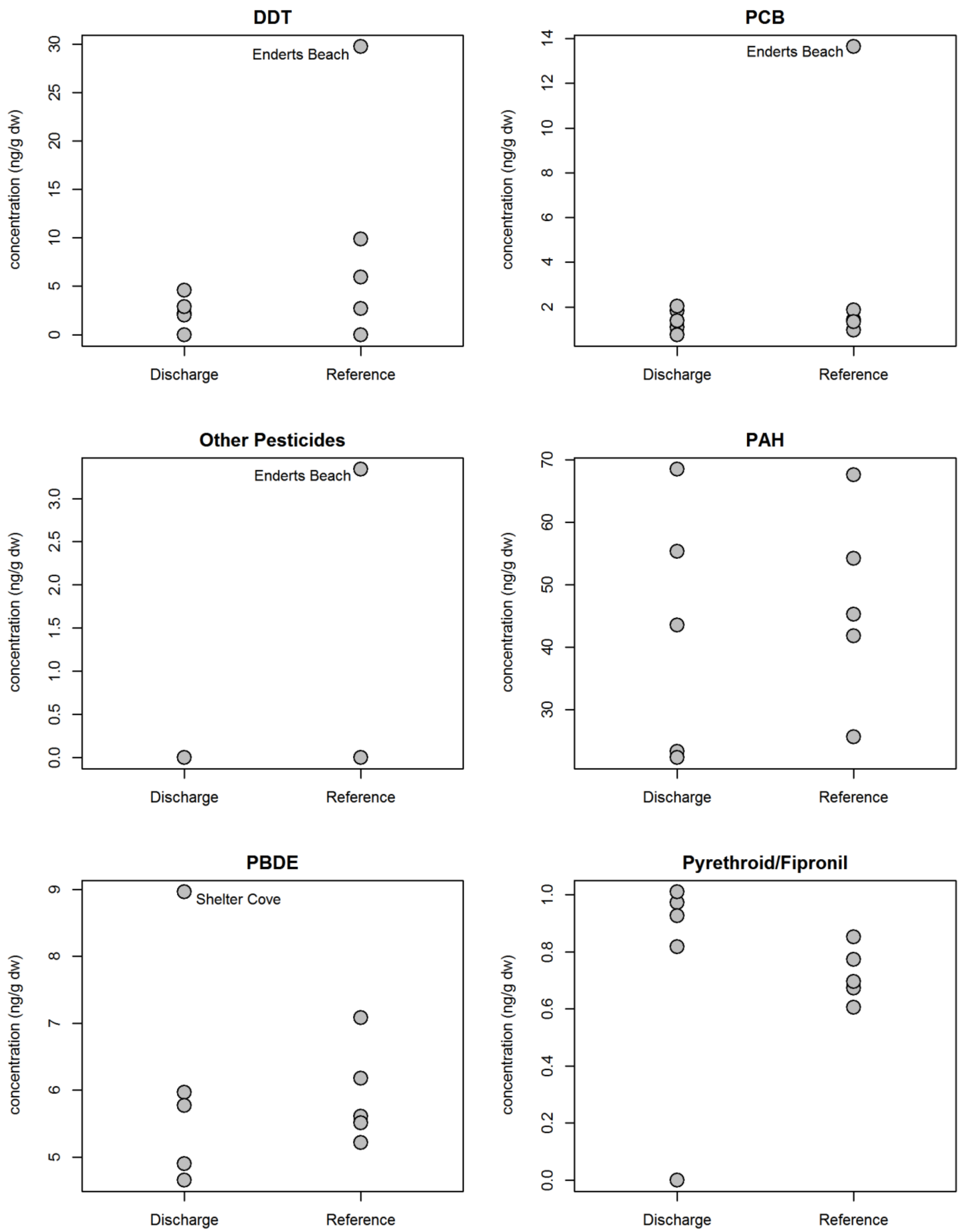


Figure 6. PCA plot of the organic contaminant profiles at each station. The first two principal components (PC1 and PC2) represent 58% of the variation in the data.

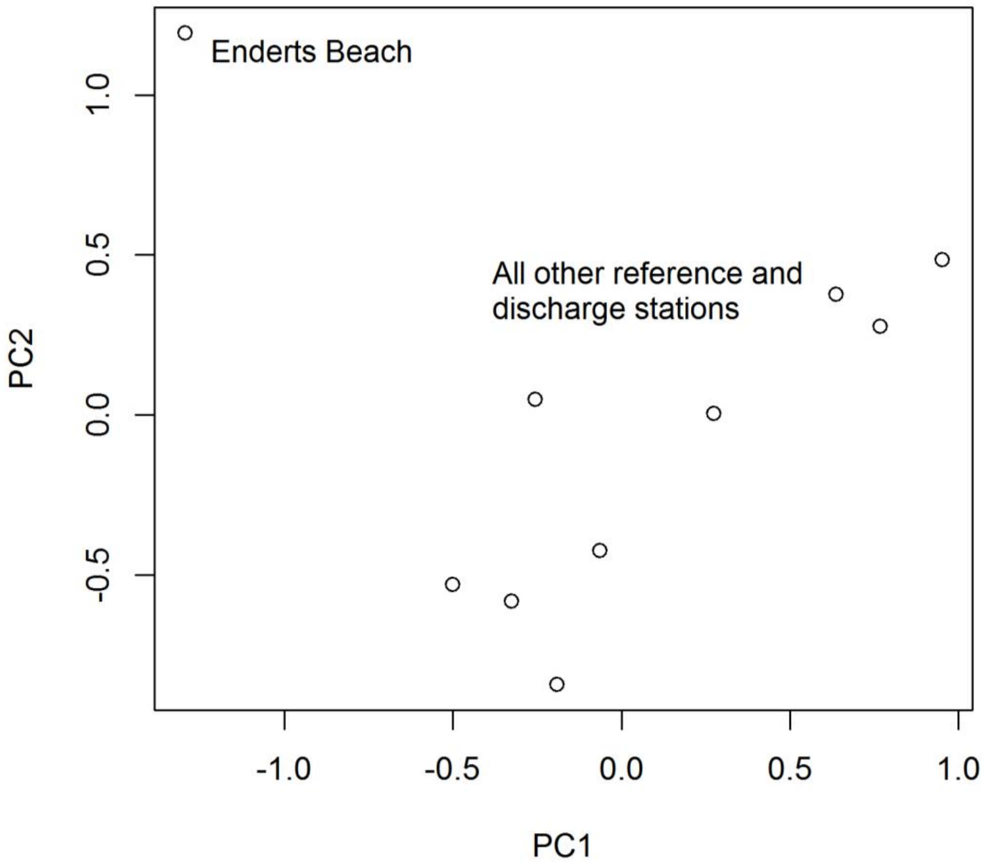


Figure 7. Comparison of metal concentrations in bivalves among the northern California 2014 ASBS survey, the southern California Bight 2013 ASBS survey, and the statewide Mussel Watch 2010 survey.

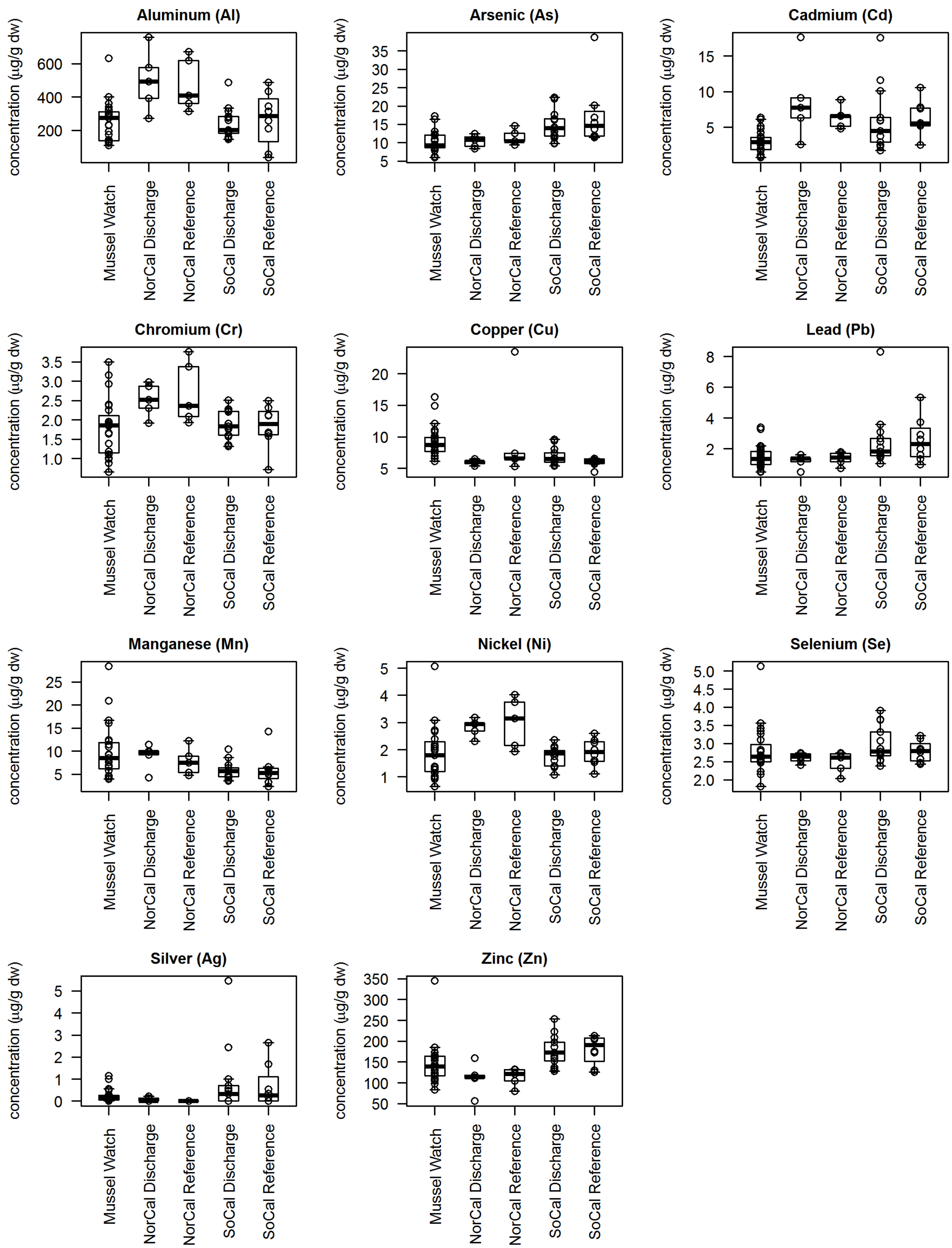
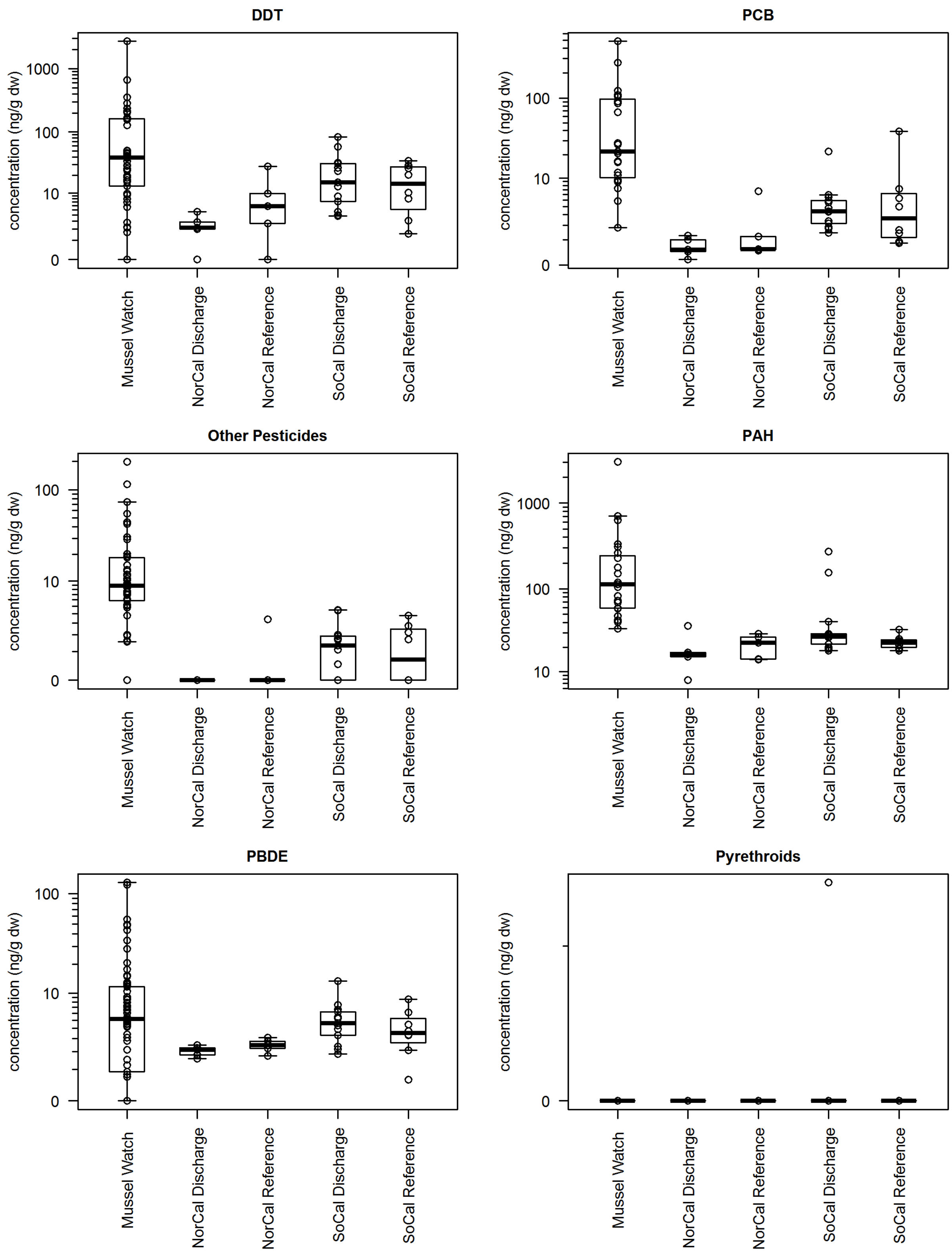


Figure 8. Comparison of organic contaminants in bivalves among the northern California 2014 ASBS survey, the southern California Bight 2013 ASBS survey, and the statewide Mussel Watch 2010 survey.



APPENDIX

Table A1. Bivalve tissue metal concentrations (µg/g dw).

Compound	Del Mar Point	Enderts Beach	Hardy Creek	False Klamath Cove	Kruse Creek	Martin Creek	Point Arena Lighthouse	Saunders Reef	Shelter Cove	Trinidad Bay
Aluminum (Al)	271	313	619	391	408	672	363	493	758	577
Antimony (Sb)	0	0	0	0	0	0	0	0	0	0
Arsenic (As)	10.9	9.43	12.6	8.4	10.5	10.5	14.6	11.5	12.5	9.09
Beryllium (Be)	0	0	0	0	0	0	0	0	0	0
Cadmium (Cd)	17.6	4.83	8.88	2.64	6.58	5.13	6.64	6.35	9.13	7.74
Chromium (Cr)	2.52	3.76	2.09	1.92	1.94	3.38	2.36	2.31	2.97	2.87
Copper (Cu)	5.37	6.51	5.30	6.15	23.5	6.56	7.36	6.47	6.09	5.73
Lead (Pb)	1.36	0.738	1.42	0.495	1.16	1.69	1.79	1.15	1.59	1.40
Manganese (Mn)	4.29	7.45	8.88	9.84	5.42	12.2	4.71	9.23	11.4	10.1
Molybdenum (Mo)	0.694	0.477	0.642	0.379	0.542	0.857	0.664	0.596	0.783	0.683
Nickel (Ni)	2.31	3.76	2.16	3.19	1.94	4.03	3.14	2.95	2.68	2.99
Selenium (Se)	2.52	2.32	2.04	2.40	2.72	2.62	2.74	2.74	2.72	2.63
Silver (Ag)	0	0	0	0	0	0	0	0.128	0.217	0
Thallium (Tl)	0	0	0	0	0	0	0	0	0	0
Zinc (Zn)	118	80.0	121	56.3	105	131	132	159	112	114

Table A2. Bivalve tissue organic contaminant concentrations (ng/g dw). Only detected analytes are shown.

Compound	Del Mar Point	Enderts Beach	Hardy Creek	False Klamath Cove	Kruse Creek	Martin Creek	Point Arena Lighthouse	Saunders Reef	Shelter Cove	Trinidad Bay
1-Methylnaphthalene	1.04	0.16	1.35	0.4	0	1.65	0	0.4	1.53	2.86
1-Methylphenanthrene	1.42	0	3.03	0	2.4	0	2.5	1.04	0	2.79
2-Methylnaphthalene	2.31	0.76	3.61	0.29	1.89	7.16	0.71	1.18	2.5	6.43
2-Methylphenanthrene	6.79	38.7	17	46.2	17	33.2	10.4	4.75	20.6	27.6
2,3,5-Trimethylnaphthalene	0	0.35	0.81	0	0	0.42	0	0.06	0.79	1.75
2,4'-DDD	0	0	0	0	3.45	0	0	0	0	0
2,4'-DDE	0	0	0	0	0	0	1.11	0	0	0.67
2,6-Dimethylnaphthalene	0	4.61	1.92	1.53	0	2.66	1.99	0	1.5	3.48
3,6-Dimethylphenanthrene	0.91	1.11	0.87	1.08	0.8	1.23	0.99	0.45	0.87	0.88
4,4'-DDE	4.59	28.3	2.71	2.18	6.4	0	4.83	2	0	2.22
4,4'-DDNU	0	1.48	0	0	0	0	0	0	0	0
Acenaphthene	1.51	0	1.23	0	1.28	0	0	1.15	0	0
Anthracene	0	0.74	0.05	0	0.21	0	0.13	0	0	0.87
Benz[a]anthracene	0	0	0	0	0	0	0	1.34	0	0
Benzo[b]fluoranthene	0	0	0	0	0	1.49	0	0	0	0
Benzo[e]pyrene	0	0	0	0	0	1.03	0	0	0	0
Benzo[g,h,i]perylene	0	0	0	1.74	5.01	0	0	0	0	0
Benzo[k]fluoranthene	0	0	0	0	0	1.4	0	0	0	0
Biphenyl	1.22	0.34	1.5	0.33	0.42	2.13	0.9	0.31	1.55	1.77
Chrysene	0.58	0	0.93	0	0.83	0.65	0.6	0.95	0	0.89
Dibenzothiophene	0.27	0.12	0.8	0.3	1.29	3.93	0	0.64	4.78	3.79
Fipronil Sulfide	0.972	0.673	0.853	0	0.696	0.774	0.606	0.926	1.01	0.817
Fluoranthene	0	0	0	0	0.31	0	0	0	0	0
Fluorene	0	1.66	0.91	0	0	1.65	0	0.09	0.91	0.8
Naphthalene	3.1	2.16	5.49	2.08	2.88	4.95	2.82	2.71	3.58	6.04
PBDE047	1.22	1.78	0.97	0.94	1.61	0.97	1.36	1.67	1.88	1.41
PBDE049	0	0.66	0.82	1.32	0.9	0.58	0.36	0.45	0.58	0.37
PBDE075	0	0	0	0	0	0	0	0	0	0
PBDE099	0.34	0	0.45	0	0.58	0	0	0	0	0
PBDE100	0	0	0.52	0	0	0	0	0	0	0
PBDE119	1.56	0.33	0.37	0.44	0	0	0	0	2.96	0.37
PBDE154	0	0	0	0	0	0.65	0	0	0	0
PBDE183	2.85	2.84	3.95	2.2	3.09	3.31	3.5	3.65	3.54	2.51
PCB018	0.14	0	0	0.35	0	0.39	0	0	0.59	0

PCB028	0.17	0.1	0.21	0.14	0.13	0.12	0.25	0.04	0.22	0.12
PCB031	0.11	0.13	0.16	0.1	0.11	0.24	0.21	0.1	0.09	0.14
PCB033	0.06	0.15	0.09	0.07	0.1	0	0.2	0.08	0.15	0
PCB037	0	0	0	0	0	0	0	0.08	0	0
PCB044	0.06	0.05	0.03	0	0.1	0.03	0.03	0.06	0.03	0
PCB049	0	0	0.02	0.02	0	0	0	0	0	0
PCB052	0	0.03	0	0	0.03	0	0	0	0	0
PCB056	0.03	0.05	0.03	0.09	0	0	0	0.04	0	0.04
PCB066	0.04	0.09	0.06	0.23	0.04	0.16	0.06	0	0.02	0.08
PCB070	0	0.05	0	0.04	0	0	0	0.01	0	0.08
PCB074	0	0.01	0.01	0.09	0.02	0	0.04	0.01	0	0.02
PCB077	0	0	0	0	0	0	0	0	0	0
PCB081	0.02	0.02	0.02	0.14	0.06	0	0	0.02	0.02	0.06
PCB087	0.21	0.19	0.26	0.25	0	0	0.17	0.16	0	0.32
PCB095	0	0	0	0	0	0	0	0	0.04	0
PCB097	0.02	0.1	0.08	0	0	0.1	0	0	0.08	0
PCB099	0.06	0.12	0.05	0	0	0.17	0	0	0.03	0
PCB105	0.04	0.17	0.03	0.06	0.12	0.11	0.03	0	0.05	0.12
PCB110	0	0.02	0.05	0.02	0	0.07	0.05	0	0.05	0.02
PCB114	0.03	0.03	0.08	0.1	0.04	0.06	0.12	0.03	0.2	0.26
PCB118	0.03	0.06	0.05	0.06	0.02	0.08	0.05	0.05	0.09	0.02
PCB119	0	0	0	0	0	0	0	0	0	0
PCB123	0.02	0.09	0.08	0.06	0.06	0.1	0.03	0.04	0.12	0
PCB126	0.05	0	0.12	0	0.1	0.2	0.09	0.04	0.11	0.07
PCB138	0	4.26	0	0	0.03	0.03	0	0	0	0
PCB153	0	6.22	0	0	0	0	0	0	0	0.03
PCB180	0	0	0	0	0	0	0	0	0.04	0
PCB187	0	1.7	0	0	0	0	0	0	0	0
PCB189	0	0	0	0	0	0	0	0	0.03	0
PCB194	0	0	0	0	0	0	0	0	0.08	0
Perylene	0	0	0	0	0.97	0	4.06	4.99	0	0
Phenanthrene	3.29	3.55	5.87	0.8	5.92	4.1	0.48	2.32	4.8	7.78
Pyrene	0.86	0	0	0.6	0.65	0	0	0	0.14	0.8
trans-Nonachlor	0	3.34	0	0	0	0	0	0	0	0

Table A3. Bivalve tissue total organic contaminant concentrations (ng/g dw).

Compound Class	Del Mar Point	Enderts Beach	False Klamath Cove	Hardy Creek	Kruse Creek	Martin Creek	Point Arena Lighthouse	Saunders Reef	Shelter Cove	Trinidad Bay
DDT	4.59	29.7	2.18	2.71	9.85	0	5.94	2	0	2.89
Other Pesticides	0	3.34	0	0	0	0	0	0	0	0
PAH	23.3	54.3	55.4	45.3	41.9	67.6	25.6	22.4	43.6	68.5
PBDE	5.97	5.61	4.90	7.08	6.18	5.51	5.22	5.77	8.96	4.66
PCB	1.09	13.6	1.82	1.43	0.960	1.86	1.33	0.76	2.04	1.38
Pyrethroid/Fipronil	0.972	0.673	0	0.853	0.696	0.774	0.606	0.926	1.01	0.817