Areas of Special Biological Significance: Bioaccumulation Monitoring

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Southern California Coastal Water Research Project
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INTRODUCTION

The California Water Resources Control Board (SWRCB) has designated Areas of Special Biological Significance (ASBSs) as marine regions that require water quality protection. Discharges of waste into ASBSs, such as polluted storm water, are prohibited, but the State Water Resources Control Board (SWRCB) grants exceptions if it can be shown that the protection of marine life in ocean waters is not compromised. The standard for protection is that discharges “shall not alter natural ocean water quality in an ASBS” (SWRCB Resolution 2012-0012). In California, there are approximately 1,658 known discharges into ASBSs, nearly all of them storm water outfalls, which have a potential to impact ASBS water quality (SCCWRP 2003).

Wet-weather water column contamination in ASBS receiving waters was monitored in 2008 (Schiff et al. 2011). In order to define “natural”, the study used reference sites that were minimally impacted by human activities. The results from this survey found concentrations near discharges were, on average, similar to concentrations near reference sites. However, there were individual ASBS discharge sites that were greater than reference site based natural water quality thresholds. While these results were encouraging, the study did not focus on bioaccumulating compounds.

Driven by the needs of the SWRCB, 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 mussel 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? Mussels are filter feeders that will accumulate contaminants over a longer period of time compared to storm water grab samples, and will bioconcentrate contaminants resulting in lower analytical method detection limits. Mussels have been used for decades in NOAA’s Mussel Watch Program to monitor bioaccumulative contaminants across the U.S. coastline (Kimbrough et al. 2008), but have not been previously utilized to assess ASBS water quality.

METHODS

Bioaccumulative contaminants in mussels were surveyed at 21 stations within 10 ASBSs in the Southern California Bight (Table 1 and Figure 1). Metals and synthetic organic contaminants were measured at locations representative of discharge and reference sites. The thirteen discharge sites received ASBS storm water discharge. The eight reference sites received drainage from a watershed determined to represent natural water quality. Station locations were selected by the ASBS Technical Committee and the SWRCB.

Sampling

Sample collection followed protocols established by the NOAA NS&T Mussel Watch Program (Lauenstein and Cantillo 1998, Diehl 2007). Mussels were collected from March to May 2013 at low tide by hand. Twenty individuals were collected at each of three sub-stations located along a 100 m transect of shoreline (60 individuals total per station). All intended stations were successfully sampled except at the following two locations. On Santa Catalina Island, reference station Goat Harbor could not be sampled due to field constraints (tide/weather); instead, nearby reference station Italian Gardens was sampled. On San Clemente Island, mussels were not present at discharge station Boy Scout Camp; instead, discharge station Boy Scout camp on Santa Catalina Island was sampled. As a result, San Clemente Island did not have a discharge station, only a reference station (Eel Point). *Mytilus californianus* was collected at all stations, except at Big Fisherman Cove, Two Harbors, and Boy Scout Camp on Catalina Island, where *Mytilus galloprovincialis* was collected. These two species have similar bioaccumulation potentials (Kimbrough et al. 2008). At the latter three stations, specimens were collected on man-made surfaces, whereas at all other stations specimens were collected from native habitats.

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 Physis Laboratories 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 at Physis Laboratories and one portion sent for organic analysis at SCCWRP.

Laboratory Analysis

Targeted contaminants were similar to those listed in the Ocean Plan and historically measured by the NOAA NS&T Mussel Watch Program (Table 2): metals, legacy organochlorine pesticides (OCP), polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs). Additional contaminants of emerging concern (CECs) were also measured. The polybrominated diphenyl ether (PBDE) flame retardants were recommended for monitoring in tissues by the recent expert panel on CECs in California marine ecosystems (Anderson et al. 2012), and were previously observed in Southern California mussel tissue (Dodder et al. 2013). 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 assurance. For metals, all laboratory blanks were non-detects, blank spike recoveries were 95%-108%, matrix spike recoveries were 95%-114%, the relative percent difference between duplicate matrix spikes was 0%-3%, certified reference material recoveries were 91%-109%, and the relative percent difference between replicate samples was 0%-14%. For organics, surrogate standard recoveries were 54%-116%, certified reference material recoveries were 50%-130%, and spiked matrix recoveries were 72%-110%. The relative percent difference between replicate samples was <45% for all detected organic analytes, except for 4 that were 56%-92% in one of two batches. All analytes were determined to pass the quality assurance criteria, except PCB-153/168 and PBDE-183, which were removed due to poor accuracy in the CRM. PBDE-66 passed the quality assurance criteria, but was unusually high in the mussel tissue relative to the known congener distribution in the technical mixture. This compound may have been a natural halogenated compound misidentified as a PBDE and was removed from the data set.

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 the age or health of the organisms, which in turn may affect contaminant concentrations relative to the other locations. The contaminant concentration data was evaluated in four steps. The results from steps 1-4 were compared and used to cross-check each other. Metals and organics were treated separately due to the higher concentration range of metals. First, the magnitude of each compound class at the reference and discharge stations were compared and outliers were noted. Second, the contaminant profiles (type and abundance of all individual compounds) were compared using clustering methods. Stations that clustered into separate groups were noted. Third, outlying reference stations were determined for each contaminant using Grubbs' test, and excluded when determining the reference threshold concentration in the next step. Fourth, 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 threshold as a proxy for distinguishing differences from natural water quality (Schiff et al. 2011). The threshold was calculated as the 85th percentile of the reference station concentrations after outliers were removed. Exceeding discharge stations were those with concentrations greater than the threshold. Threshold exceedance was determined on both a dry weight and lipid weight basis.

RESULTS

Morphometrics

The mean (± standard deviation) shell length was 61 ± 10 mm, mean total mass was 20 ± 9 g, and mean tissue mass was 5.2 ± 2.9 g. The mean shell length at each station varied among the total mean by < 2%. Shell length is a proxy for age; therefore, results indicated the mussels at each station had the same mean age and age was not a confounding variable when interpreting contaminant concentrations. The relationship between shell length and tissue mass for all 1260 individual mussels (Figure 2) can be used in future studies to predict the recoverable tissue mass given the size of collected mussels.

Contaminant Magnitude

Contaminant magnitudes are shown in Figures 3a (metals) and 3b (organics). Outlying concentrations and/or discharge stations with relatively high values are labeled. For metals, discharge station Avalon Quarry, Santa Catalina Island, had copper, silver, and molybdenum concentrations that exceeded reference station levels. Discharge station Boy Scout Camp, Santa Catalina Island, had cadmium, copper, lead, and selenium concentrations that exceeded reference station levels. Reference station Thousand Springs, San Nicholas Island, had relatively high levels of arsenic and nickel that exceeded discharge station levels.

For organics, discharge station Barge Landing, San Nicholas Island, had DDT, PCB, PBDE, and Other Pesticides concentrations that exceeded reference station levels (except Thousand Springs for PCB; Figure 4). Discharge station Two Harbors, Santa Catalina Island, had PAH concentrations that exceeded reference station levels. Discharge station Muddy Canyon, Irvine Coast, had DDT and Other Pesticide concentrations that exceeded reference station concentrations. Three Orange County discharge stations, Buck Gully South, Muddy Canyon, and Heisler Park, had elevated fipronil concentrations relative to the reference stations. Reference station Thousand Springs, San Nicholas Island, had relatively high levels of PCB that exceeded discharge station levels.

Contaminant Profile Clustering

Clustering methods compare the relative abundances of the contaminants. Stations that have a shorter "distance" to one another (i.e., cluster together) have similar contaminant profiles. Stations that have a further "distance" from one another have dissimilar contaminant profiles. Clustering methods consider the relative abundances, not absolute magnitudes, of the contaminants. For the organics, individual compound concentrations were used, not the compound class concentrations. Three clustering algorithms were applied and the results are summarized in Figures 5a (metals) and 5b (organics). The methods were hierarchical analysis, *k*-means clustering, and principal components analysis (PCA). Conclusions were based on a weight of evidence approach, where the highest confidence was reached if all three algorithms had the same result.

For metals, results from the three clustering algorithms showed Eel Point and Bird Rock (reference stations on San Clemente Island and Santa Catalina Island, respectively) formed a separate cluster due to low aluminum concentrations. This is visualized in the PCA plot, where the first two principal components (PC1 and PC2) represent 73% of the variation in the data. In the PCA plot, Boy Scout Camp on Santa Catalina Island appears distinct from the other stations due to a higher cadmium concentration, but this result was not corroborated by the other clustering algorithms.

For organics, results from the three clustering algorithms showed Two Harbors and Big Fisherman Cove (discharge stations on Santa Catalina Island) formed a separate cluster due to high PAH concentrations. Thousand Springs and Barge Landing (the reference and discharge stations on San Nicholas Island, respectively) formed a second separate cluster due to high PCB concentrations. The remaining stations may be considered as one cluster. This is visualized in the PCA plot, where the first two principal components (PC1 and PC2) represent 71% of the variation in the data.

Reference Outlier Detection

Outlier reference concentrations are shown in Table 3. Thousand Springs, San Nicholas Island, was found to have multiple outlying contaminants and may not be suitable as a reference station in future surveys. For some contaminants, the normality assumption of Grubbs' test was questionable due to only one or two detects among the reference stations. In this case, if the detect was at Thousand Springs, it was considered an outlier since multiple lines of evidence (contaminant magnitudes and clustering) indicated it may not have reference conditions. Otherwise, the station was not considered an outlier.

Reference Threshold Exceedance

The 85th percentile of the reference station concentrations for a given analyte, with outliers removed, was used to set the exceedance threshold. This threshold concentration was applied to each discharge station, and the number of exceeding contaminants at each station was determined. Figures 6a (metals) and 6b (organics) show the frequency of exceeding contaminants at each station. Fifteen percent exceedance was expected due to the 85th percentile threshold that was applied. Stations close to or below 15% exceedance were determined to have natural water quality.

For metals, stations on Santa Catalina Island with a greater than 15% exceedance frequency were Avalon Quarry (50%), Boy Scout Camp (42%), Big Fisherman Cove (25%), and Two Harbors (25%). Other exceeding stations were Buck Gully South (42%), and Scripps Reef (25%). There is a greater uncertainty in the exceedance of Big Fisherman Cove, Two Harbors, and Scripps Reef because their values are closer to the 15% threshold. The metals responsible for exceeding stations are described in Table 4a. Copper was responsible for all 6 exceeding stations and manganese for 4 of the 6 stations.

For organics, island stations with a greater than 15% exceedance frequency were Barge Landing on San Nicolas (36%), and Two Harbors (36%) and Big Fisherman Cove (32%) on Santa Catalina. Mainland stations were Buck Gully South (33%) and Crystal Cove (33%). Other stations had an exceedance frequency of 15%-25% and therefore a greater uncertainty in the result. The organic contaminants responsible for the five highest exceeding stations are described in Table 4b. PAHs were primarily responsible for exceedances on Santa Catalina Island. PCBs and PBDEs were primarily responsible for exceedances on San Nicholas Island.

Tables 5a, 5b, 6a and 6b give the full set of concentrations for each contaminant at both reference and discharge stations.

DISCUSSION

All reference stations were determined to be suitable except for Thousand Springs on San Nicholas Island. This station had a similar contaminant profile to its paired discharge station, Barge Landing, and had unusually high PCB concentrations relative to the other reference stations. In this study, outlying reference concentrations for individual contaminants were removed. Future surveys should consider excluding Thousand Springs as a reference location.

Three methods were used to analyze the contaminant data: 1) compare the concentration magnitudes at reference and discharge locations, 2) compare the relative profiles using clustering algorithms, and 3) determine if the discharge station concentration exceeds a reference threshold. These three methods generally agreed on both the discharge stations that were different from reference conditions, and on the contaminants responsible for the differences. Agreement among the methods increased the confidence in the results. The exception was the clustering results for metals, which did not identify exceeding stations observed by the other methods. For example, Avalon Quarry, Santa Catalina Island, had the highest exceedance frequency at 50% (Figure 6a), but was not identified as different from reference conditions by the clustering methods. This is because the clustering algorithms compare abundances of contaminants relative to one another, not the absolute magnitudes, and can miss magnitude differences if the relative abundances of contaminants are similar.

The concentration basis is a potentially confounding factor in the interpretation of the organic contaminant results. Organic contaminant concentrations may be calculated on either a dry weight basis or a lipid weight basis. We reported concentrations on a dry weight basis because this is the more common format for mussel tissue data (Lauenstein and Cantillo 1998, Kimbrough et al. 2008, Dodder et al. 2013), but many of the bioaccumulative contaminants are known to be positively correlated with increasing lipid mass. Therefore, the reference threshold exceedance was also calculated with concentrations on a lipid weight basis. Table 7 compares the results using both normalization methods. There was agreement that Barge Landing (San Nicholas Island), Two Harbors and Big Fisherman Cove (Santa Catalina Island), and Buck Gully South (mainland) are different than reference conditions. Other stations that exceeded on a dry weight basis did not exceed on a lipid weight basis.

Taking into account the results from the three data analysis methods, with preference given to the reference threshold exceedance method, and the dry weight/lipid weight comparison for organics, the following stations were determined to be different from natural water quality. 1) Barge Landing in the San Nicholas Island ASBS (due to organics); 2) Two Harbors (organics), Big Fisherman Cove (organics), and Boy Scout Camp (metals) in the NW Santa Catalina Island ASBS; 3) Avalon Quarry (metals) in the SE Santa Catalina ASBS; and 4) Buck Gully South (metals and organics) in the Robert Badham ASBS. Note that mussels at Two Harbors and Big Fisherman Cove were collected on man-made structures (see Table 1 for the types of structures) and had relatively high PAH concentrations. Boy Scout Camp was also collected on a man-made structure and had relatively high metal concentrations. The results for these three stations may have been influenced by their close proximity to boating activity in addition to possible storm water influence.

In 2010, NOAA, the State Water Resources Control Board, and SCCWRP collaborated to sample mussel tissues across the California coast (Dodder et al. 2013). This was in part a continuation of NOAA's Mussel Watch program, but was exclusive to California, included more stations within the state, and expanded the list of measured compounds to include contaminants of emerging concern. This data set, which includes stations intentionally selected to have the highest contaminant loads in California, can be used to put the ASBS contaminant concentrations in perspective; see Table 8 for a list of representative compounds. ASBS stations measured in the present study were lower than the maximum concentrations observed at non-ASBS stations in the 2010 study. Maximum metal concentrations in the present study were within an order of magnitude of the maximum concentration at non-ASBS stations. However, maximum organic contaminant concentrations were one to two orders of magnitude higher in the non-ASBS stations.

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 mussel 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:

- **Cumulatively, the differences between reference and discharge stations were small.** Median contaminant concentrations were similar between reference stations and discharge stations for both metals and organic contaminants. Contaminant profiles (types and relative abundances) among all stations were also similar based on cluster analysis.

- **Despite the similarity in average concentrations between reference and discharge stations, there were differences in concentrations at individual sites.** For organic contaminants, the four discharge stations determined to be different from natural water quality were Barge Landing (San Nicholas Island ASBS), Two Harbors and Big Fisherman Cove (NW Santa Catalina Island ASBS), and Buck Gully South (Robert Badham ASBS). For metals, the three discharge stations determined to be different from natural water quality were Avalon Quarry (SE Santa Catalina Island ASBS), Boy Scout Camp (NW Santa Catalina Island ASBS), and Buck Gully South (Robert Badham ASBS)

- **The compounds that exceeded natural water quality thresholds most frequently were copper and PAHs.** Of those discharge stations that exceeded natural water quality thresholds, copper was the only metal of concern at every station. Similarly, PAHs were the only organic compound of concern at every station that exceeded natural water quality thresholds. While this survey was intended to examine storm water discharges, proximity to boating activity may be a contributing factor for PAH and/or copper concentrations observed in the NW Santa Catalina Island ASBS.

- **Thousand Springs on San Nicholas Island may not be a suitable reference station.** The Thousand Springs reference site had high PCB concentrations relative to the other reference stations, and also had a contaminant profile similar to the discharge station on San Nicholas Island (Barge Landing). As a result, multiple PCB congeners from Thousand Springs were removed as outliers prior to establishing reference threshold values.

- **Concentrations at ASBS discharge stations were lower than maximum values observed at non-ASBS stations in the 2010 California Mussel Watch survey.** The most recent Mussel Watch survey in California occurred in 2010. Compared to concentrations of representative compounds in the current survey, median ASBS concentrations are lower for PAH, PCB, DDT, and PBDE.

Future recommendations include:

- **Bioaccumulation results should be connected to the other concurrent ASBS surveys on aqueous-phase storm water contaminants and biodiversity.** The bioaccumulation results in this report are not the only indicator of natural water quality being measured near ASBS discharges. Storm water discharges and adjacent receiving waters are being measured for pollutant concentrations and toxicity. Also, biodiversity surveys that identify and enumerate rocky intertidal biological communities are being conducted at many of the same discharge and reference stations sampled for bioaccumulation. These different indicators of environmental stress and biological response should be integrated in a synthesis report of ASBS condition.

- **Resample San Nicholas and NW Santa Catalina Island ASBSs to confirm the contaminant concentrations observed in this study.**
  While mussels are a valuable indicator because they integrate pollutant concentrations over time, re-sampling at these sites is recommended as a confirmation step. Re-sampling efforts should investigate the use of an alternate San Nicholas Island reference station. Additionally, the NW Santa Catalina Island discharge stations should be collected at locations near the storm water discharge, but away from boating activity and on non-anthropogenic substrates in an effort to isolate the different sources of potential pollutants.

Figure 1. Map of discharge and reference stations sampled for bioaccumulative contaminants in mussels.

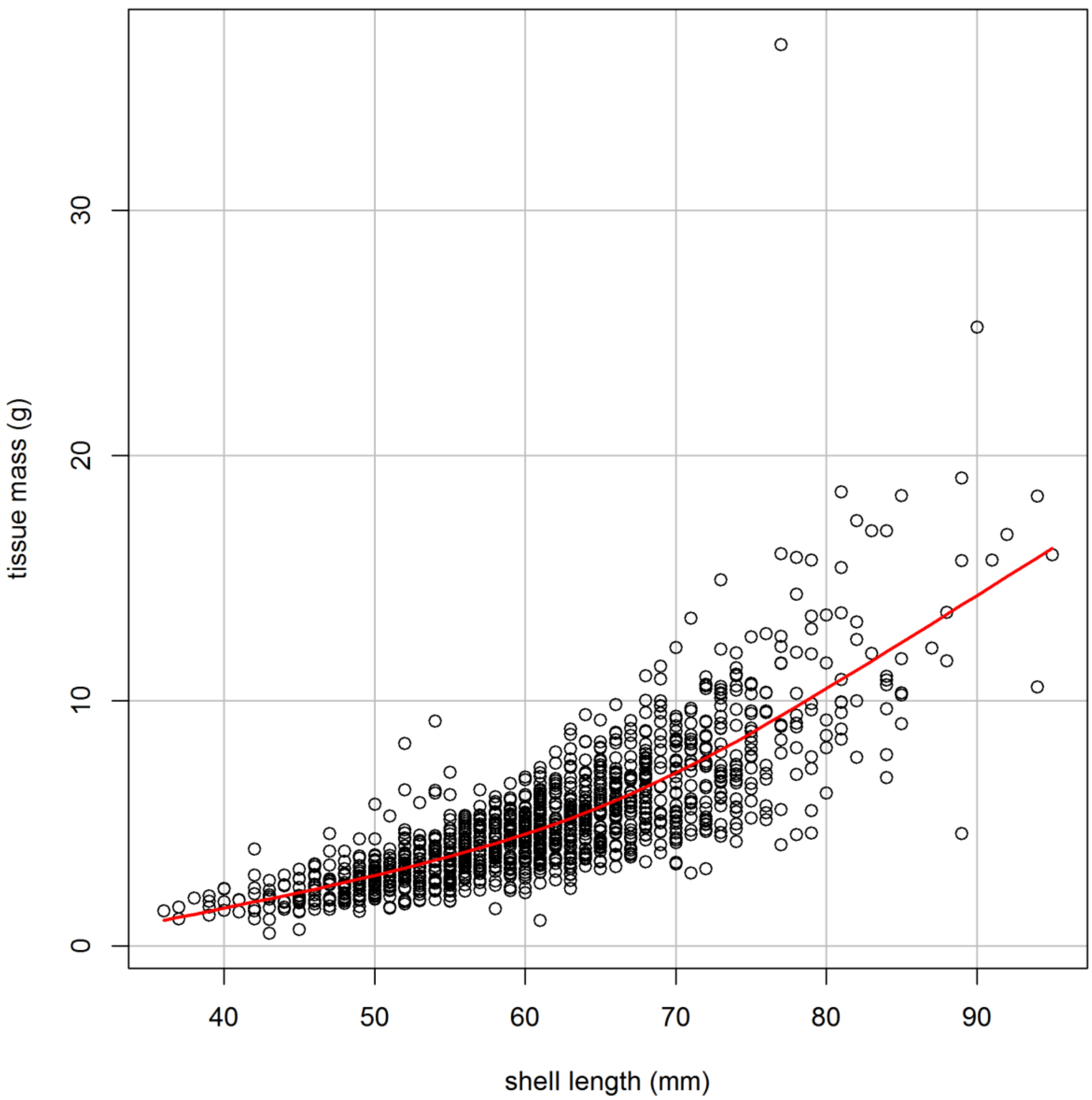

Figure 2. Shell length as a predictor of tissue mass. The data set is primarily *Mytilus californianus*, but 14% of the mussels (3 of the 21 stations) were *Mytilus galloprovincialis*. The fitted line is a cubic smoothing spline.

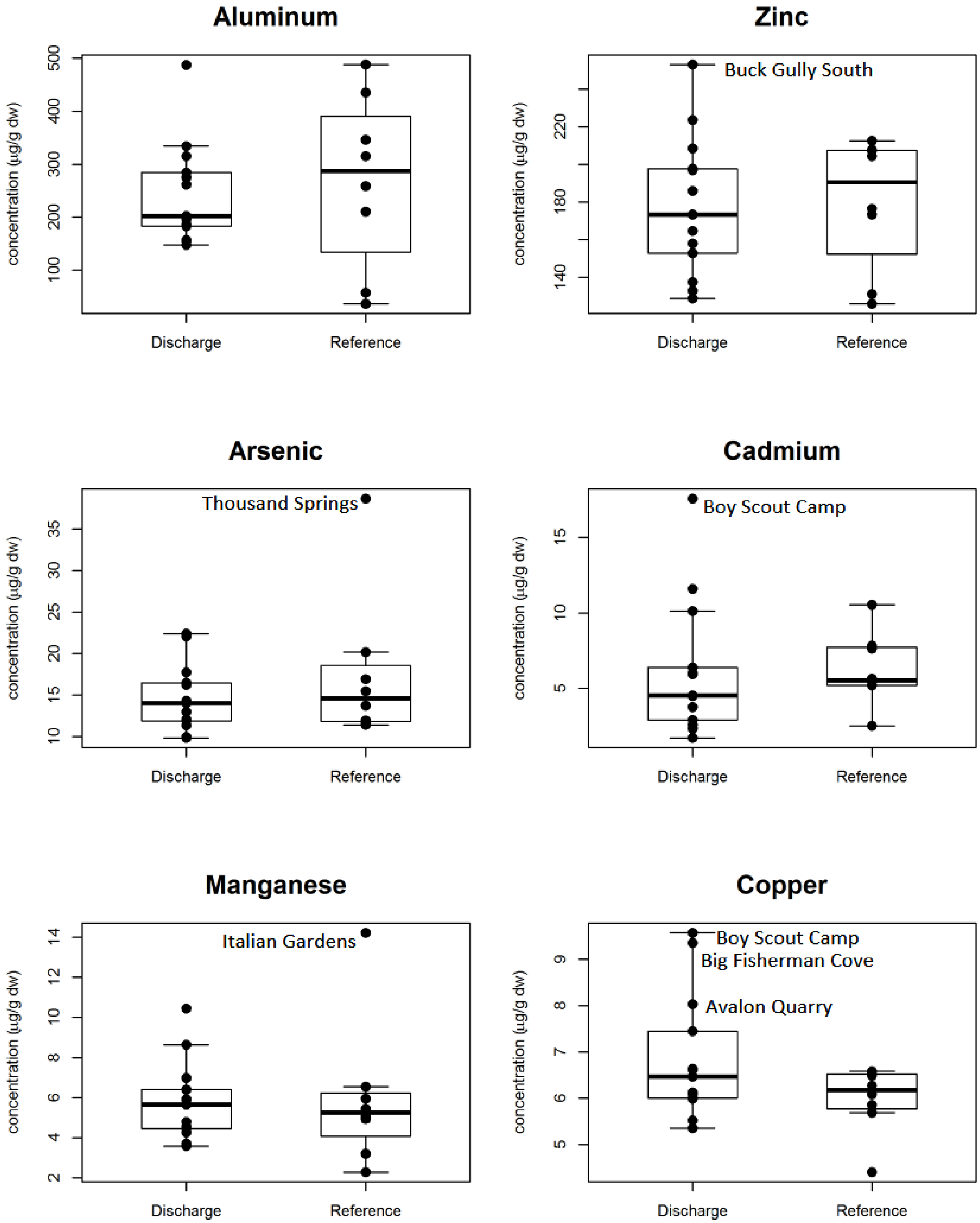

Figure 3a. Metal concentrations at discharge and reference stations.

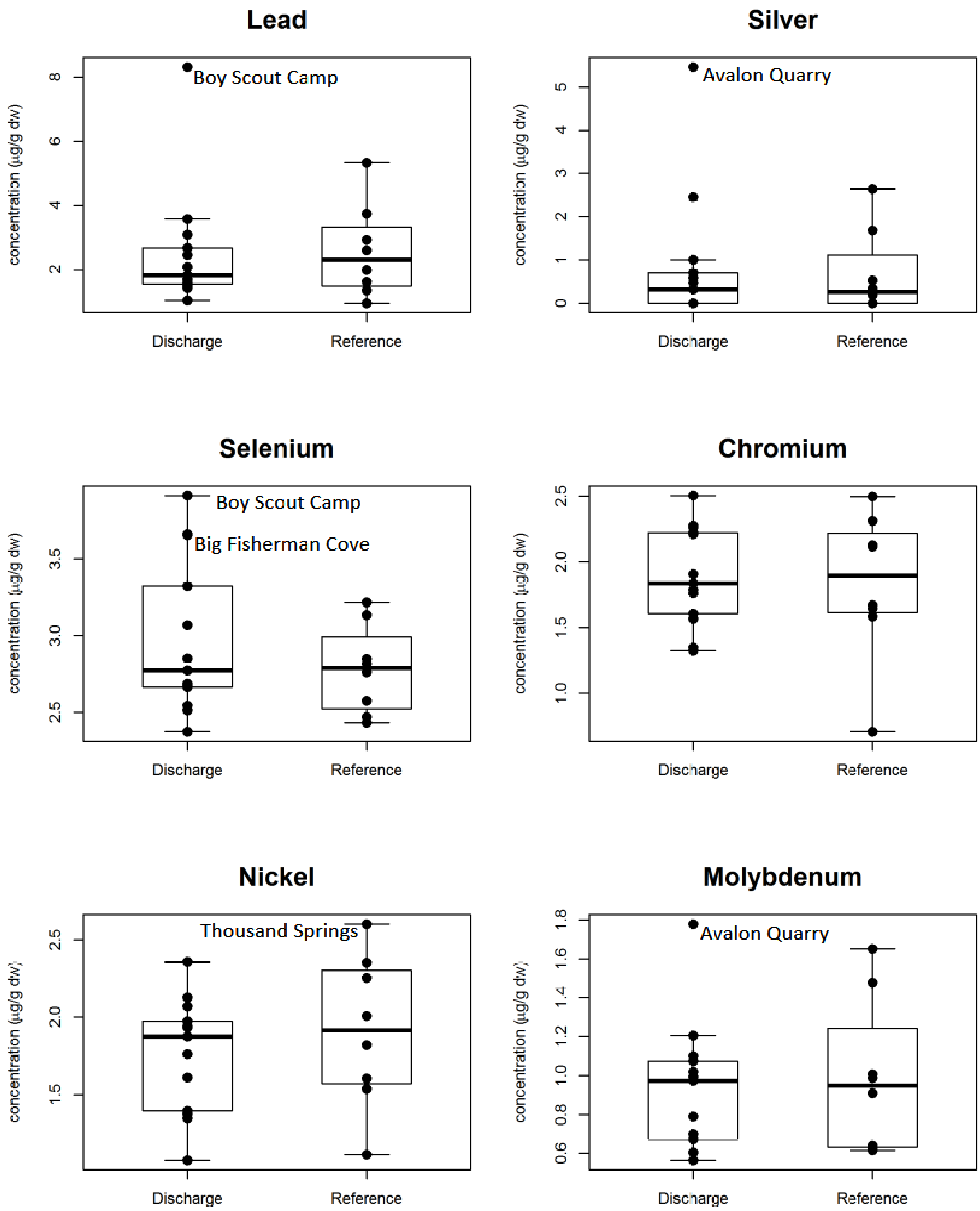

Figure 3b. Metal concentrations at discharge and reference stations.

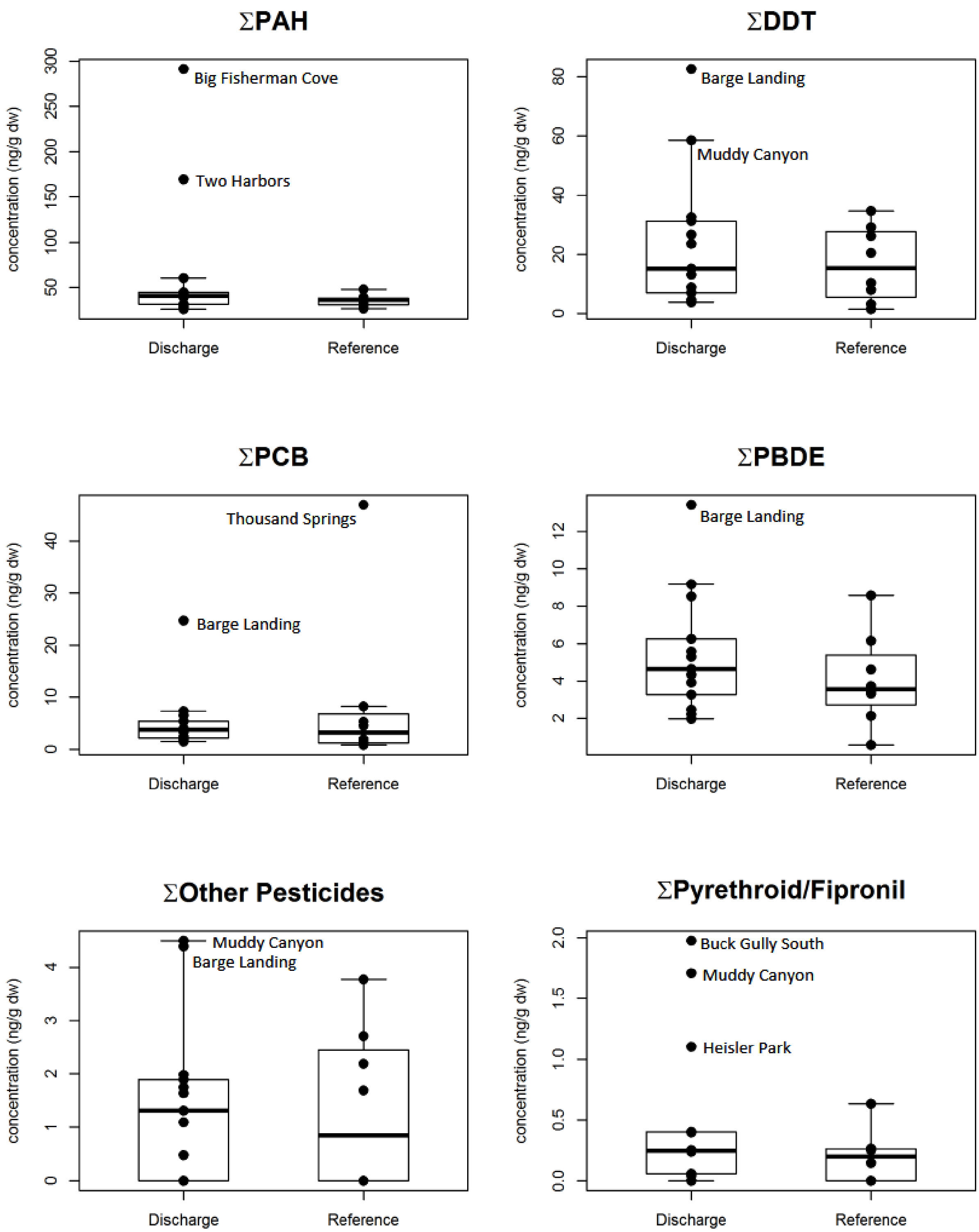

Figure 4. Organic contaminant concentrations at discharge and reference stations. The total concentration for the compound class is shown.

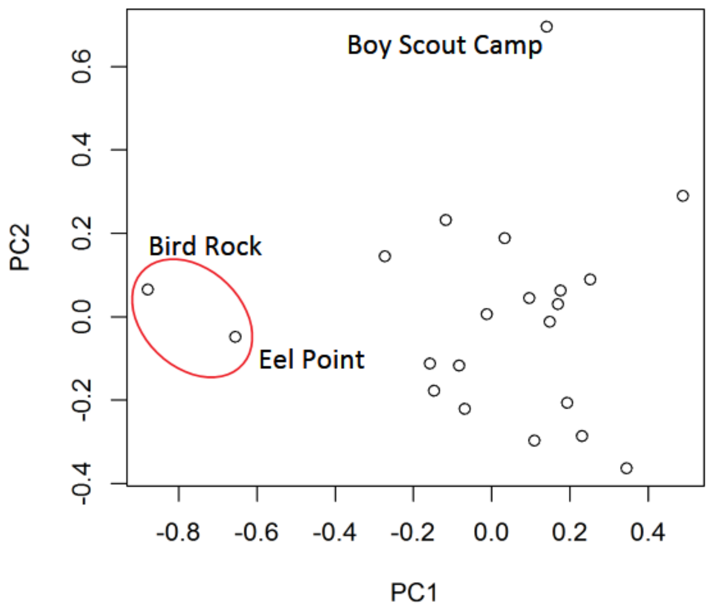

Figure 5a. PCA plot of the metal profiles at each station. Each point represents a station, and points closer in space have more similar profiles. The red circle identifies a separate PCA cluster (i.e., stations that are different from the others). These stations were also identified as a separate cluster by the *k*-means and hierarchical clustering algorithms.

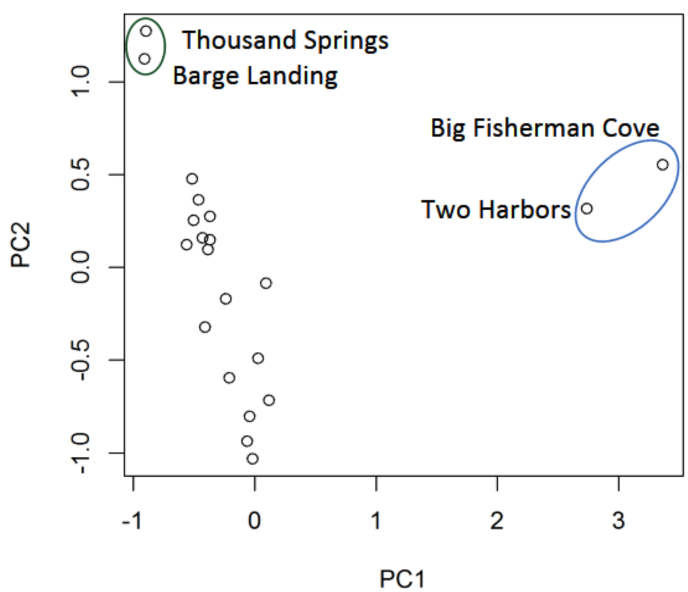

Figure 5b. PCA plot of the organic contaminant profiles at each station. The green and blue circles identify separate PCA clusters (i.e., stations that are different from the others). These stations were also identified as a separate clusters by the *k*-means and hierarchical clustering algorithms.

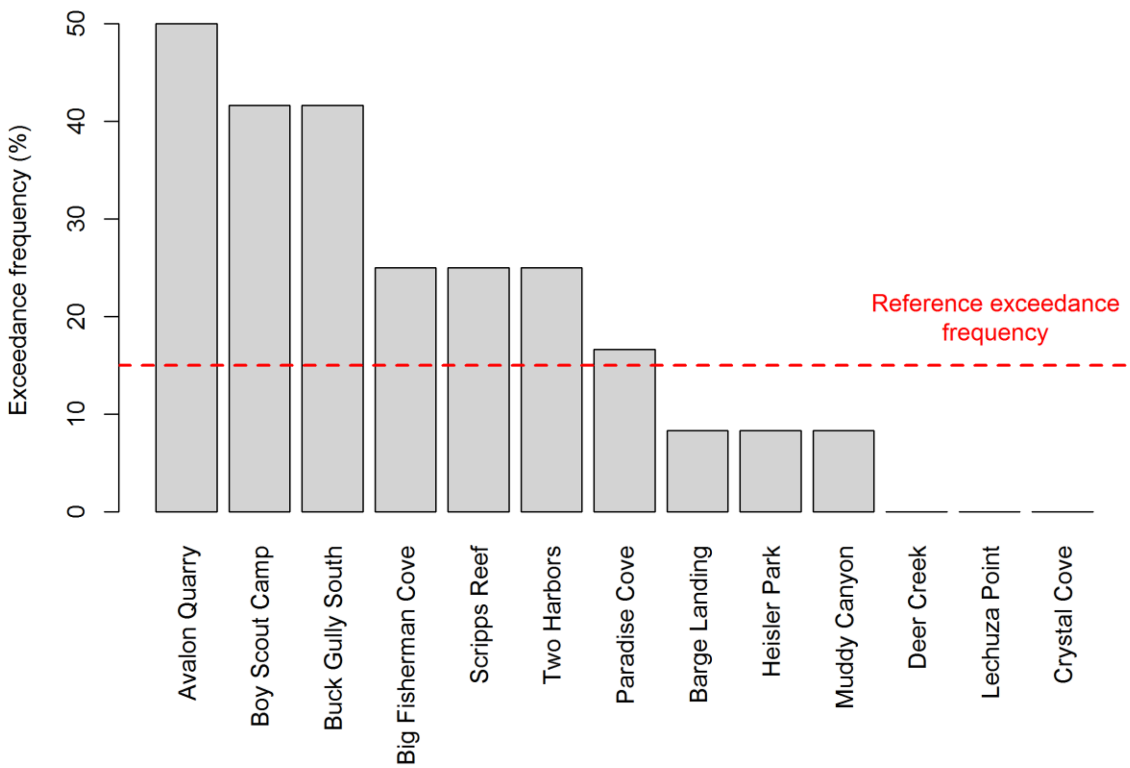

Figure 6a. Metal exceedance frequency at each station. The expected exceedance frequency (dashed line) was 15%.

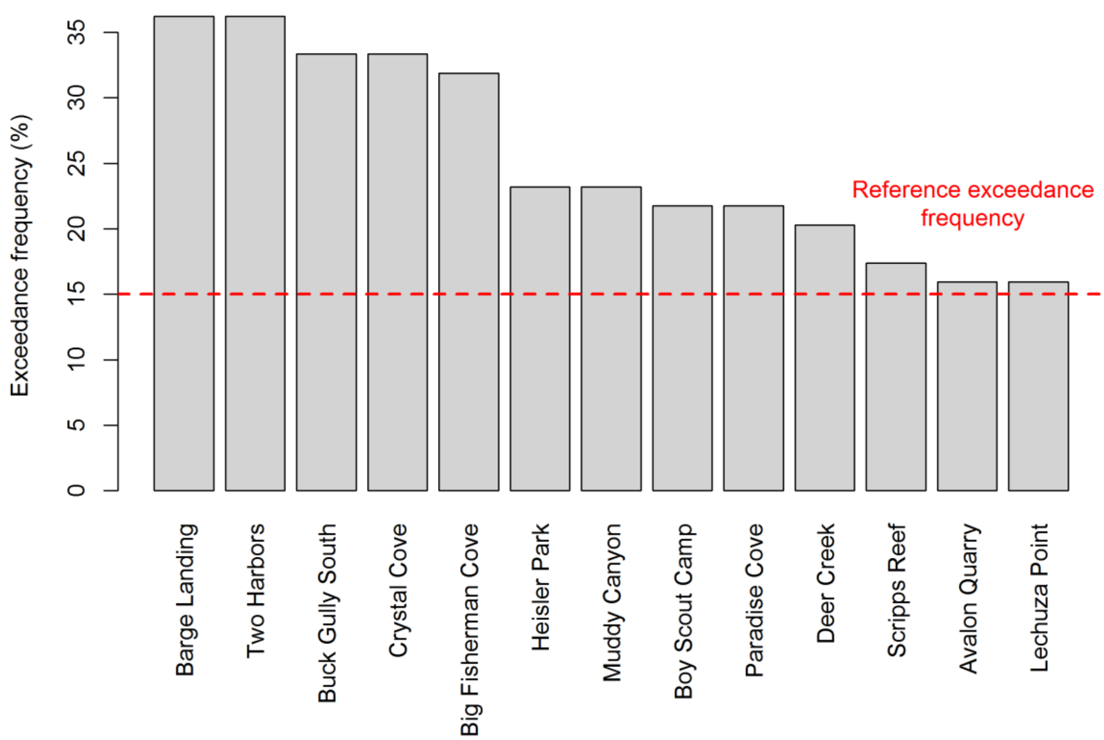

Figure 6b. Organic contaminant exceedance frequency at each station. The expected exceedance frequency (dashed line) was 15%.

Table 1. ASBS reference and discharge bioaccumulation samples collected between March and May 2013 in Southern California.

ASBS Number	Station Name	ASBS Name or Location	Type	Species	Collection Surface	Latitude	Longitude
ASBS 31	Scripps Reef	San Diego-Scripps	Discharge	*Mytilus californianus*	native	32.87148	-117.25327
not in ASBS	Dana Point	Orange County Coast	Reference	*Mytilus californianus*	native	33.45984	-117.71401
ASBS 33	Muddy Canyon	Irvine Coast	Discharge	*Mytilus californianus*	native	33.56572	-117.83314
ASBS 30	Heisler Park	Heisler Park	Discharge	*Mytilus californianus*	native	33.54251	-117.78942
ASBS 33	Crystal Cove	Irvine Coast	Discharge	*Mytilus californianus*	native	33.57078	-117.83778
ASBS 32	Buck Gully South	Robert E. Badham	Discharge	*Mytilus californianus*	native	33.58821	-117.86764
ASBS 24	Old Stairs	Laguna Point to Latigo Point	Reference	*Mytilus californianus*	native	34.06612	-118.99821
ASBS 24	Point Dume	Laguna Point to Latigo Point	Reference	*Mytilus californianus*	native	34.00027	-118.80706
ASBS 24	Sequit Point	Laguna Point to Latigo Point	Reference	*Mytilus californianus*	native	34.04303	-118.93689
ASBS 24	Deer Creek	Laguna Point to Latigo Point	Discharge	*Mytilus californianus*	native	34.06087	-118.98327
ASBS 24	Lechuza Point	Laguna Point to Latigo Point	Discharge	*Mytilus californianus*	native	34.0343	-118.86182
ASBS 24	Paradise Cove	Laguna Point to Latigo Point	Discharge	*Mytilus californianus*	native	34.01205	-118.79218
ASBS 28	Avalon Quarry	SE Santa Catalina Island	Discharge	*Mytilus californianus*	native	33.317361	-118.303556
not in ASBS	Italian Gardens	Santa Catalina Island	Reference	*Mytilus californianus*	native	33.412806	-118.384333
ASBS 25	Big Fisherman Cove	NW Santa Catalina Island	Discharge	*Mytilus galloprovincialis*	floating dock	33.445056	-118.4845
ASBS 25	Bird Rock	NW Santa Catalina Island	Reference	*Mytilus californianus*	native	33.451917	-118.487611
ASBS 25	Two Harbors	NW Santa Catalina Island	Discharge	*Mytilus galloprovincialis*	pier piling	33.442028	-118.49775
ASBS 25	Boy Scout Camp	NW Santa Catalina Island	Discharge	*Mytilus galloprovincialis*	mooring can	33.469056	-118.529917
ASBS 23	Eel Point	San Clemente Island	Reference	*Mytilus californianus*	native	32.91810139	-118.5470194
ASBS 21	Thousand Springs	San Nicolas Island	Reference	*Mytilus californianus*	native	33.284908	-119.534287
ASBS 21	Barge Landing	San Nicolas Island	Discharge	*Mytilus californianus*	native	33.219443	-119.442661

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

Metal	PAH	PCB		Pesticide	PBDE	Pyrethroid/Fipronil Pesticides
(0.058–2.8 µg/g dw)	(0.11–0.98 ng/g dw)	(0.25–1.6 ng/g dw)		(0.66–5.5 ng/g dw)	(0.020–0.31 ng/g dw)	(0.021–2.1 ng/g dw)
Aluminum	11H-Benzo[b]fluorene	PCB 8	PCB 156	Chloropyrifos	BDE 15	Fipronil
Antimony	1-Methylnaphthalene	PCB 18	PCB 157	Diazinon	BDE 28	Fipronil desulfinyl
Arsenic	1-Methylphenanthrene	PCB 28	PCB 158	Aldrin	BDE 33	Fipronil sulfide
Beryllium	2,3,5-Trimethylnaphthaline	PCB 37	PCB 167	Dieldrin	BDE 47	Fipronil sulfone
Cadmium	2,6-Dimethylnaphthalene	PCB 44	PCB 169	Endrin	BDE 49	Permethrin
Chromium	2-Methylnaphthalene	PCB 49	PCB 170	Chlordene	BDE 66	Lamda-Cyhalothrin
Copper	2-Methylphenanthrene	PCB 52	PCB 177	Oxychlordane	BDE 75	Fenpropathrin
Lead	3,6-Dimethylphenanthrene	PCB 66	PCB 180	Heptachlor Epoxide B	BDE 99	Esfenvalerate
Manganese	9,10-Diphenylanthracene	PCB 70	PCB 183	Cis-Chlordane (Alpha)	BDE 100	Deltamethrin
Molybdenum	Acenaphthene	PCB 74	PCB 187	Trans-Chlordane (Gamma)	BDE 119	Cypermethrin
Nickel	Acenaphthylene	PCB 77	PCB 189	Cis-Nonachlor	BDE 153	Cyfluthrin
Selenium	Anthracene	PCB 81	PCB 194	Trans-Nonchlor	BDE 154	Bifenthrin
Silver	Benz[a]anthracene	PCB 87	PCB 200	o,p'-DDT	BDE 155	
Thallium	Benzo[a]pyrene	PCB 99	PCB 201	p,p'-DDT	BDE 183	
Zinc	Benzo[b]fluoranthene	PCB 101	PCB 206	o,p'-DDD		
	Benzo[e]pyrene	PCB 105	PCB 209	p,p'-DDD		
	Benzo[g,h,i]perylene	PCB 110		o,p-DDE		
	Benzo[k]fluoranthene	PCB 114		p,p'-DDE		
	Biphenyl	PCB 118		DDMU		
	Chrysene	PCB 119		DDNU		
	Dibenzo[a,h]anthracene	PCB 123				
	Fluoranthene	PCB 126				
	Fluorene	PCB 128				
	Naphthalene	PCB 138				
	Perylene	PCB 149				
	Phenanthrene	PCB 151				
	Pyrene	PCB 153/168				

Table 3. Number of outlier concentrations detected at the reference stations.

Station	Contaminant Class	Number of Outliers
Thousand Springs	PCB	19
	PAH	2
	PBDE	2
	Metal (Arsenic)	1
Dana Point	Fipronil	4
	PAH	2
Italian Gardens	PAH	1
	Metal (Manganese)	1
Old Stairs	PAH	2
Eel Point	PAH	1
Sequit Point	PAH	1

Table 4a. Metal threshold exceedance by station. Check marks indicate metals that exceeded the reference threshold concentration.

Metal	Avalon Quarry	Boy Scout Camp	Buck Gully South	Big Fisherman Cove	Scripps Reef	Two Harbors
Copper	✓	✓	✓	✓	✓	✓
Manganese	✓	✓	✓		✓	
Selenium	✓	✓		✓		✓
Cadmium		✓		✓		✓
Zinc	✓		✓			
Molybdenum	✓					
Silver	✓					
Lead		✓				
Arsenic			✓			
Nickel			✓			

Table 4b. Organic contaminant threshold exceedance by station. Values are the number of individual compounds that exceeded the reference threshold concentrations. The value in parentheses is the percent of exceeding contaminants within the compound class.

Contaminant Class	Barge Landing	Two Harbors	Big Fisherman Cove	Crystal Cove	Buck Gully South
PAH	2	22 (81%)	19 (70%)	4	13 (48%)
PCB	12 (28%)	0	0	7 (16%)	1
PBDE	8 (57%)	2	2	8 (57%)	3
Fipronil	1	0	1	1	3 (75%)
DDT	1	0	0	4 (50%)	0
Other Pesticides	2	0	0	0	0

Table 5a. Discharge station metal concentrations (µg/g dry weight).

Metal	Reference Threshold	Avalon Quarry	Barge Landing	Big Fisherman Cove	Boy Scout Camp	Buck Gully South	Crystal Cove	Deer Creek	Heisler Park	Lechuza Point	Muddy Canyon	Paradise Cove	Scripps Reef	Two Harbors
Aluminum	431	186	183	148	284	261	275	334	154	196	157	315	487	202
Arsenic	17.3	14.0	22.4	12.0	11.4	22.0	14.3	11.8	17.7	12.9	16.5	16.2	9.8	10.0
Cadmium	7.81	6.4	5.9	10.1	17.6	4.5	2.3	6.0	2.6	4.5	3.8	2.9	1.7	11.6
Chromium	2.30	2.22	1.57	1.84	1.76	2.27	1.60	1.79	2.26	1.35	1.90	2.50	1.32	2.21
Copper	6.55	8.03	5.52	9.35	9.58	7.45	6.12	6.00	6.08	6.47	5.36	5.99	6.64	6.61
Lead	3.69	2.68	1.47	1.43	8.31	3.58	1.55	3.09	2.46	1.69	2.08	1.83	1.05	1.68
Manganese	6.01	10.4	3.7	4.3	8.6	7.0	4.8	5.9	4.5	4.6	3.6	5.7	6.4	5.9
Molybdenum	1.45	1.78	0.70	1.07	1.20	1.02	0.79	0.61	0.97	0.57	0.99	0.67	0.60	1.10
Nickel	2.35	2.07	1.61	1.35	1.87	2.36	1.40	1.93	1.97	1.37	1.76	2.13	1.08	1.94
Selenium	3.12	3.66	2.55	3.66	3.92	2.69	2.67	2.52	2.38	2.85	2.67	3.07	2.77	3.32
Silver	1.63	5.46	0	0	0	0.47	0	0.58	0.71	1.00	0.32	2.45	0	0
Zinc	208	209	186	158	133	253	164	198	197	153	224	173	129	137

Table 5b. Reference station metal concentrations (µg/g dry weight).

Metal	Bird Rock	Dana Point	Eel Point	Italian Gardens	Old Stairs	Point Dume	Sequit Point	Thousand Springs
Aluminum	37	346	57	488	315	259	210	435
Arsenic	11.6	16.9	20.2	15.5	11.4	11.9	13.7	38.7
Cadmium	10.55	2.52	7.82	5.64	5.43	5.19	5.19	7.64
Chromium	0.71	2.50	1.67	1.65	2.13	2.12	1.58	2.31
Copper	6.08	5.86	4.41	6.55	6.58	6.27	6.49	5.69
Lead	0.96	1.35	1.62	5.33	1.99	3.73	2.92	2.60
Manganese	3.22	5.95	2.30	14.22	6.54	5.06	4.95	5.45
Molybdenum	0.99	0.91	1.01	1.48	0.63	0.64	0.62	1.65
Nickel	1.11	2.25	2.35	2.01	1.54	1.82	1.60	2.60
Selenium	3.13	2.43	2.82	3.22	2.47	2.76	2.85	2.58
Silver	0	0.180	0	2.65	0.34	1.68	0.53	0
Zinc	131	204	213	126	173	207	176	208

Table 6a. Discharge station organic concentrations (ng/g dry weight).

Organic Analyte	Reference Threshold	Avalon Quarry	Barge Landing	Big Fisherman Cove	Boy Scout Camp	Buck Gully South	Crystal Cove	Deer Creek	Heisler Park	Lechuza Point	Muddy Canyon	Paradise Cove	Scripps Reef	Two Harbors
11H-Benzo[b]fluorene	0	0	0	1.96	0	0	0	0	0	0	0	0	0	3.87
1-Methylnaphthalene	0.273	0.198	0.441	0.241	0.247	0.261	0.199	0.182	0.164	0.24	0.167	0.251	0.153	0.338
1-Methylphenanthrene	10.9	9.47	9.47	10.67	11.5	17.5	8.555	12.4	11.1	7.42	12.2	9.77	7.8	7.65
2,3,5-Trimethylnaphthalene	0.203	0.456	0	0	0.222	0	0	0	0	0	0.183	0.538	0	0.222
2,6-Dimethylnaphthalene	0	0	0	0	0	1.11	0	0	0	0	0	0	0	0
2-Methylnaphthalene	0.440	0.313	0	0.439	0.384	0.418	0.221	0.402	0.238	0.400	0.257	0.343	0.387	0.566
2-Methylphenanthrene	10.9	10.1	8.59	12.8	12	14.6	8.002	12.4	10.8	7.42	11.3	10.4	6.29	9.22
3,6-Dimethylphenanthrene	3.02	2.26	2.68	3.18	3.35	4.74	0	3.74	3.15	2.12	3.21	2.21	1.41	2.23
Acenaphthene	0	0	0	0.282	0	0	0	0	0	0	0	0	0	0.386
Acenaphthylene	0.0300	1.8	0	1.31	0	0.203	0	0	1.331	0	0	0	0.164	0.301
Anthracene	0	0.485	0	5.92	0	0	0	0.714	0	0	0	0	0	3.835
Benz[a]anthracene	0	0	0	16.8	0	0.53	0	0	0	0	0	0	0	8.67
Benzo[a]pyrene	0	0	0	3.31	0	0.669	0	0	0	0	0	0	0.419	3.72
Benzo[b]fluoranthene	0.171	0	0	24.3	0.333	0	0.218	0	0	0.154	0.152	0	0.188	11.5
Benzo[e]pyrene	0.321	0.2	0	11	0.417	1.59	0.331	0.274	0.394	0.252	0.247	0.284	0.884	7.45
Benzo[g,h,i]perylene	0	0	0	2.91	0	0.381	0	0	0	0	0	0	0	3.86
Benzo[k]fluoranthene	0	0	0	9.71	0.171	0	0	0	0	0	0	0	0	4.94
Biphenyl	0.523	0.447	0.293	0.491	0.464	0.593	0.32	0.318	0.409	0.276	0.343	0.361	0.283	0.742
Chrysene	1.06	0.528	0	52.5	1.25	1.61	0.769	0.74	1.16	0.854	1.07	0.812	0	13.6
Dibenzo[a,h]anthracene	0	0	0	3.75	0	0	0	0	0	0	0	0	0	3.4
Fluoranthene	0.792	1	0.572	50.3	1.52	1.33	1.1	1.06	1.09	0.807	1.18	0.723	0.311	33.3
Fluorene	0.486	0.689	0	0.985	0.497	0	0	0.598	0	0	0	0.944	0.515	0.972
Naphthalene	0.729	0.595	1.19	0.66	0.695	0.644	0.448	0.492	0.473	0.638	0.461	0.597	0.41	0.745
Perylene	0.0302	0	0	2.05	0	0.519	1.78	0	0	0	1.13	0.3	0	1.99
Phenanthrene	6.53	7.83	5.06	26	6.76	8.15	5.095	7.4	6.28	5.36	7.1	8.54	4.75	15.8
Pyrene	3.92	3.15	3.11	50.1	4.63	5.52	2.81	3.55	4.06	2.93	3.87	2.85	2.03	30.3
BDE 100	0.549	0.258	1.78	0.259	0.119	0.448	0.838	0.498	0.92	0.6	0.58	0.4	0.83	0.2
BDE 119	0.0371	0	0	0.12	0.158	0	0	0	0.06	0	0	0	0.04	0.08
BDE 153	0.0600	0	0.18	0.08	0	0.124	0.1	0.08	0	0.04	0.1	0.06	0	0
BDE 154	0.0771	0	0.16	0.04	0.02	0.1	0.1	0.08	0.02	0.06	0.08	0.06	0.079	0.04
BDE 155	0.0405	0.04	0.16	0	0	0.199	0.08	0	0.04	0	0.04	0.04	0	0
BDE 28	0.0790	0.06	0	0	0	0	2.59	0	0	0.1	0	0	1.05	0
BDE 33	0.278	0.06	0.36	0	0.119	0	0	0.219	0	0	0	0	0.988	0.14
BDE 47	3.29	1.55	8.1	1.49	0.968	2.34	3.59	2.21	2.9	3.26	1.92	1.7	3.81	0.84
BDE 49	0.403	0.952	0.82	0	0.277	0	0.538	0.239	0	0.34	0.26	0.28	0	0.5
BDE 75	0	1.806	0	0	0	0	0.08	0.159	0.08	0	0	0	0	0
BDE 99	1.45	0.556	1.86	0.478	0.316	1.44	1.26	0.857	2.24	1.18	0.94	0.74	1.74	0.42

Table 6a, continued. Discharge station organic concentrations (ng/g dry weight).

Organic Analyte	Reference Threshold	Avalon Quarry	Barge Landing	Big Fisherman Cove	Boy Scout Camp	Buck Gully South	Crystal Cove	Deer Creek	Heisler Park	Lechuza Point	Muddy Canyon	Paradise Cove	Scripps Reef	Two Harbors
Bifenthrin	0	0	0	0	0	1.35	0	0	0	0	0	0	0	0
Cis-Chlordane (Alpha)	1.05	0	1.09	0	0	0.615	0.74	1.01	0	1.001	4.497	0.867	0.863	0
Cypermethrin	0	0	0	0	0	0	0	0	0	0	1.66	0	0	0
DDMU	2.94	0	0	0	0	0	3.61	3.83	2.23	3.44	2.74	2.5	1.35	0
Fipronil	0.232	0.367	0	0.183	0.239	0.124	0	0	0.57	0.302	0	0.138	0	0.186
Fipronil desulfinyl	0.00320	0.034	0	0	0	0.127	0.038	0	0.094	0	0	0.026	0	0
Fipronil sulfide	0	0	0	0	0	0.05	0	0	0.038	0	0	0	0	0
Fipronil sulfone	0.0489	0	0.058	0.06	0	0.326	0	0	0.4	0.096	0.05	0.088	0	0.058
o,p'-DDD	0	0	0	0	0	0	1.51	0	0	0	0	1.34	0	0
o,p-DDE	1.95	0	0	0.456	0	1.26	2.07	1.41	0.795	2.348	1.35	1.57	0	0.474
p,p'-DDD	1.01	0	0	0	0	0	1.48	0	0	1.11	0	0	0	0
p,p'-DDE	23.8	3.8	82.7	6.66	3.99	13.98	22.6	21.5	10.1	25.6	54.5	18.2	7.47	4.16
Trans-Chlordane (Gamma)	1.17	0	0.433	0	0	0.476	0.569	0.976	0.474	0.888	0	0.773	0.882	0
Trans-Nonchlor	0.828	0	2.86	0	0	0	0	0	0	0	0	0	0	0
PCB 101	0.664	0	1.08	0	0	0.438	0.781	0.464	0.349	0.641	0.386	0.871	0.3	0.306
PCB 105	0	0.968	0	0	0	0	0	0	0	0	0	0	0	0
PCB 110	0.442	0	0	0	0	0	0.465	0.305	0.238	0.416	0.282	0.628	0	0.215
PCB 118	0.532	0	2.81	0	0	0	0.955	0.49	0.532	0.738	0	1.135	0	0.285
PCB 128	0	0	0.805	0	0	0	0	0	0	0	0	0	0	0
PCB 138	1.26	0.316	8.24	0.46	0.35	1.182	1.42	1.358	0.92	1.144	0.825	1.53	0.545	0.414
PCB 149	0.737	0	1.36	0.271	0	0.455	0.64	0.656	0.282	0.676	0.421	0.789	0.323	0
PCB 151	0.0317	0	0	0	0	0	0	0	0	0	0	0	0	0
PCB 156	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PCB 177	0.0380	0	0	0	0	0	0	0	0	0	0	0	0	0
PCB 180	0.0380	0	1.16	0	0.389	0	0	0	0	0	0.367	0	0	0
PCB 183	0.0399	0	0.963	0	0	0	0	0	0	0	0	0	0	0
PCB 187	0.637	0	2.58	0	0	0.379	0.55	0.701	0.367	0.53	0.363	0.546	0	0
PCB 200	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PCB 49	0.745	0.545	2.18	0.371	0.626	0	0.508	0.681	0.603	0.399	0.364	0.586	0.693	0.569
PCB 52	0.363	0.311	1.97	0.321	0.358	0.474	0.517	0.392	0.396	0.347	0.491	0.406	0.255	0.326
PCB 87	0	0	0	0	0	0	0	0	0	0	0	0.295	0	0
PCB 99	0.475	0	1.56	0	0	0.393	0.623	0.328	0.259	0.494	0.319	0.562	0.236	0

Table 6b. Reference station organic contaminant concentrations (ng/g dry weight).

Organic Analyte	Bird Rock	Dana Point	Eel Point	Italian Gardens	Old Stairs	Point Dume	Sequit Point	Thousand Springs
11H-Benzo[b]fluorene	0	0	0	0	0	0	0	0
1-Methylnaphthalene	0.302	0.222	0.151	0.247	0.207	0.15	0.27	0.515
1-Methylphenanthrene	9.9	11.6	9.89	10.9	10.4	8.21	6.07	9.11
2,3,5-Trimethylnaphthalene	0.259	0.187	0	0.204	0	0	0	0
2,6-Dimethylnaphthalene	0	0	0	0.749	0	0	0	0
2-Methylnaphthalene	0.442	0.377	0.24	0.394	0.399	0.312	0.594	0.205
2-Methylphenanthrene	10.5	11.5	10.5	10.9	10.4	7.97	6.49	8.6
3,6-Dimethylphenanthrene	2.65	3.03	3.06	2.91	2.86	1.75	1.7	2.4
Acenaphthene	0	0	0.219	0	0	0	0	0
Acenaphthylene	0	3.301	0.3	0	0	0	0	0
Anthracene	0	0	0	0	0.439	0	0	0
Benz[a]anthracene	0	0	0	0	0	0	0.444	0
Benzo[a]pyrene	0	0	0	0	0.273	0	0	0
Benzo[b]fluoranthene	0	0.183	0	0	0	0.171	0.161	0
Benzo[e]pyrene	0.25	0.309	0.239	0.207	0.578	0.322	0.25	0
Benzo[g,h,i]perylene	0	0	0	0	0	0	0	0
Benzo[k]fluoranthene	0	0	0	0	0	0	0	0
Biphenyl	0.335	0.523	0.298	0.525	0.331	0.523	0.286	0.423
Chrysene	0.459	1.34	0.676	0.686	0.687	0	1.08	0
Dibenzo[a,h]anthracene	0	0	0	0	0	0	0	0
Fluoranthene	0.602	1.11	0.73	0.791	0.708	0.749	0.8	0.66
Fluorene	0.512	0	0	0	0	0.683	0	0
Naphthalene	0.771	0.589	0.461	0.724	0.581	0.4	0.714	1.21
Perylene	0	1.79	0	0	0	0	0	0.302
Phenanthrene	6.53	7.36	4.96	6.49	6.24	5.22	5.49	5.46
Pyrene	3.25	4.2	3.94	3.55	3.35	2.47	2.24	3.22
BDE 100	0.24	0.513	0.082	0	0.768	0.551	0.42	0.438
BDE 119	0	0.045	0	0	0	0.039	0	0
BDE 153	0	0	0	0	0.079	0.039	0.06	0.06
BDE 154	0.02	0.022	0	0	0.079	0.079	0.04	0.02
BDE 155	0	0.045	0	0.04	0.039	0	0	0.159
BDE 28	0.06	0.134	0	0	0	0	0.08	0
BDE 33	0.26	0	0	0.44	0	0	0	1.116
BDE 47	1.2	2.01	0.328	0.44	3.35	2.19	1.86	4.76
BDE 49	0.08	0.402	0	2.26	0.413	0	0.2	0.219
BDE 75	0	0	0	0	0	0	0	0
BDE 99	0.28	1.45	0.184	0.16	1.42	0.846	0.74	1.81

Table 6b, continued. Reference station organic contaminant concentrations (ng/g dry weight).

Organic Analyte	Bird Rock	Dana Point	Eel Point	Italian Gardens	Old Stairs	Point Dume	Sequit Point	Thousand Springs
Bifenthrin	0	0	0	0	0	0	0	0
Cis-Chlordane (Alpha)	0	0	0	0	1.33	0.993	1.01	1.05
Cypermethrin	0	0	0	0	0	0	0	0
DDMU	0	0	0	0	2.98	3.21	2.24	0
Fipronil	0.234	0.277	0.201	0.146	0	0	0.19	0
Fipronil desulfinyl	0.032	0.071	0	0	0	0	0	0
Fipronil sulfide	0	0.022	0	0	0	0	0	0
Fipronil sulfone	0	0.264	0.047	0	0	0	0.066	0
o,p'-DDD	0	0	0	0	0	0	0	0
o,p-DDE	0.642	0.756	0	0	1.97	2.05	1.66	1.26
p,p'-DDD	0	0	0	0	1.65	0	1.06	0
PCB 101	0	0.229	0	0	0.663	0.676	0.469	3.65
PCB 105	0	0	0	0	0	0	0	1.95
PCB 110	0	0	0	0	0.438	0.48	0.314	3.38
PCB 118	0	0.273	0	0	0.677	0	0.516	5.63
PCB 128	0	0	0	0	0	0	0	1.09
PCB 138	0.335	0.517	0	0	1.621	1.22	0.971	8.18
PCB 149	0	0	0	0	1.184	0.687	0.62	3.45
PCB 151	0	0	0	0	0.317	0	0	1.15
PCB 156	0	0	0	0	0	0	0	0.787
PCB 177	0	0	0	0	0.38	0	0	1
PCB 180	0.38	0	0	0	0	0	0	2.31
PCB 183	0	0	0	0	0.399	0	0	1.32
PCB 187	0	0	0	0	0.993	0.597	0.498	3.38
PCB 200	0	0	0	0	0	0	0	0.352
PCB 49	0.364	0.501	0.625	0.563	0.866	0.731	0.46	3.19
PCB 52	0.323	0.381	0.264	0.265	0.256	0.361	0.272	2.62
PCB 87	0	0	0	0	0	0	0	1.38
PCB 99	0	0	0	0	0.468	0.536	0.378	2.15
p-p'-DDE	9.69	7.29	1.53	3.11	28.1	23.9	21.3	19.2
Trans-Chlordane (Gamma)	0	0	0	0	1.57	1.2	0.685	0.564
Trans-Nonchlor	0	0	0	0	0.872	0	0	1.09

Table 7. Exceedance frequency (%) comparison for organic contaminants. Calculations were performed on a dry weight basis and lipid weight basis. Exceedance frequencies greater than 20% are in bold text.

Discharge Station	Dry Weight Basis Exceedance Frequency (%)	Lipid Weight Basis Exceedance Frequency (%)
Barge Landing	**36**	**43**
Two Harbors	**36**	**30**
Buck Gully South	**33**	**26**
Crystal Cove	**33**	20
Big Fisherman Cove	**31**	**36**
Heisler Park	**23**	12
Muddy Canyon	**23**	17
Boy Scout Camp	**22**	9
Paradise Cove	**22**	19
Deer Creek	**20**	17
Scripps Reef	17	16
Avalon Quarry	16	14
Lechuza Point	16	**22**

Table 8. Concentrations of representative compounds in four compound classes in the present study, compared to the Mussel Watch 2010 survey (ng/g dry weight).

	Chrysene (PAH)		PCB-118 (PCB)		p,p'-DDE (DDT)		BDE-47 (PBDE)	
	This Study	**MW 2010**	**This Study**	**MW 2010**	**This Study**	**MW 2010**	**This Study**	**MW 2010**
Median	0.77	4.7	0.27	2.0	14	30	2.0	3.2
Range	0-53	1.3-160	0-5.6	0-54	1.5-83	0-1800	0.33-8.1	0-68
Number of Stations	21	23	21	23	21	45	21	66
Maximum Station	Big Fisherman Cove	Tijuana River Estuary	Thousand Springs	San Diego-Harbor Island	Barge Landing	Monterey Bay-Salinas River	Barge Landing	Imperial Beach North Jetty

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