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Assessing water quality in Marine Protected Areas from Southern California, USA

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ABSTRACT

Despite the regulatory mandate to maintain “natural water quality”, there are ≥ 271 storm drain discharges that potentially threaten the 14 designated marine water quality protected areas in Southern California called Areas of Special Biological Significance (ASBS). After sampling 35 site-events, the geo-mean concentrations of total suspended solids, nutrients, total and dissolved trace metals, and polycyclic aromatic hydrocarbons in the ocean following storm events were similar between reference drainages and ASBS discharge sites. Concentrations of chlorinated hydrocarbons were nondetectable and no post-storm sample exhibited significant toxicity to the endemic purple sea urchin (*Strongylocentrotus purpuratus*) near ASBS discharge sites. A reference-based threshold was developed and, despite the similarities in average concentrations, there were some individual ASBS discharge sites that were greater than reference background. Cumulatively across all ASBS, the constituents that were most frequently greater than the reference-based threshold were nutrients and general constituents, followed by dissolved and total trace metals.

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1. Introduction

Coastal municipalities and other agencies subjected to near-shore water quality regulation face a difficult task. The public demands equal access to the shoreline and, at the same time, mandates protection of water quality to maintain the integrity of marine ecosystems. Public access, especially in highly populated urban centers is almost always to the detriment of coastal marine life. This is routinely observed in terms of habitat loss (Boesch et al., 2001), harvesting of seafood and other marine resources (Cohen, 1997), and the introduction of pollutants (Daskalakis and O'Connor, 1995; Schiff et al., 2000). Almost by definition, natural water quality is in the absence of coastal development and public access (Halpern et al., 2008).

Southern California epitomizes this conundrum. Approximately 17.5 million people live within an hour's automobile drive to the beach and is home to the sprawling urban centers of Los Angeles and San Diego, two of the nation's eight largest cities (US Census Bureau, 2009). Over 1.5 billion gallons of treated wastewater are discharged to the ocean every day (Lyon and Stein, 2009). In a typical rainy season, over double this volume is discharged via surface runoff (Ackerman and Schiff, 2003). Surface runoff following storm events will carry the accumulated anthropogenic pollutants from

urban activities such as residential application of fertilizers and pesticides (Schiff and Sutula, 2004), trace metals from brake and tire wear (Davis et al., 2001), and atmospheric fallout from mobile and non-mobile sources (Sabin et al., 2006). Exacerbating these potential threats to the environment, sanitary and storm water systems are separate in Southern California. Therefore, storm water runoff receives virtually no treatment prior to entering the ocean (Lyon and Stein, 2009).

The dilemma between water quality protection and urbanization reaches a climax in Southern California at Areas of Special Biological Significance (ASBS). The ASBS are marine water quality protected areas whose standard is “no discharge of waste” and maintenance of “natural water quality” (SWRCB, 2005). Over 2800 km of shoreline in Southern California are designated as ASBS. While state regulatory agencies have been effective at minimizing point source discharges, there are at least 271 storm drain outfalls (SCCWRP, 2003). These storm drains can discharge urban runoff, but also natural runoff from undeveloped portions of their respective watersheds. Nutrients, trace metals, and some organic constituents found in urban runoff are also natural components of the ecosystem (Yoon and Stein, 2008). The dichotomy between natural versus anthropogenic inputs ultimately clashes because the state regulatory structure does not numerically define natural water quality.

In order to address the dilemma between water quality protected areas and development in the coastal zone, the goal of this study was to assess the water quality in Southern California ASBS. Specifically, the study was designed to answer two questions: (1) what is the range of natural water quality near reference drainage

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Fig. 1. Map of Areas of Special Biological Significance (ASBS) in Southern California.

locations? and (2) how does water quality near ASBS discharges compare to the natural water quality at reference drainage locations? These two questions address the primary lack of information faced by both ASBS dischargers and regulators that stymies management actions, if they are necessary. The first question aims to quantify what is meant by “natural water quality” by visiting locations presumptively free of anthropogenic contributions. The second question compares the natural water quality levels derived from the first question to water quality near ASBS discharges to determine the level of existing water quality protection.

2. Methods

There are 34 ASBS in California, 14 of which occur in Southern California (Fig. 1). The majority (78%) of ASBS shoreline in Southern California surrounds the offshore Channel Islands, but a significant fraction (35 km) occur along the six mainland ASBS.

This study had two primary design elements. The first design element was a focus on receiving water. All samples were collected in receiving waters near reference drainage or ASBS discharges; no

effluent discharge samples were collected as part of this study. The second design element was a focus on wet weather. Dry weather was not addressed in this study.

2.1. Sampling

Sixteen sites were selected for wet weather sampling in this study (Table 1). Six of the sampling locations were reference drainage sites (representing natural water quality) and 10 were ASBS discharge sites. Reference site selection followed five criteria: (1) the site must be an open beach with breaking waves (i.e., no embayments); (2) the beach must have drainage from a watershed that produces flowing surface waters during storm events; (3) the reference watershed should be similar in size to the watersheds that discharge to ASBS; (4) the watershed must be comprised of primarily (>90%) open space; and (5) neither the shoreline nor any segment within the contributing watershed can be on the State's 2006 list of impaired waterbodies (e.g., §303d list). All but one of the reference drainage sites was located within an ASBS.

A total of 35 site-events were sampled (Table 1). Twelve site-events were sampled near reference drainage locations, and another 23 site-events were sampled near ASBS discharge locations. Up to three storm events were sampled per site. A storm was defined as any wet weather event that resulted in surface flow across the beach into the ocean receiving water. Rainfall during sampled events ranged from 0.1 to 9.8 cm. Pre-storm samples were collected prior to (<48 h) rainfall, and post-storm samples were collected immediately following (<24 h) rainfall, with most post-storm samples collected less than 6 h after rainfall cessation. Approximately 89% of all post-storm samples also had a pre-storm sample collected. Samples were collected in the ocean at the initial mixing location in the receiving water. Both pre- and post-storm samples were collected by direct filling of pre-cleaned sample containers just below the water surface.

2.2. Laboratory analysis

All water samples were analyzed for 93 parameters: (1) general constituents including total suspended solids (TSS), dissolved organic carbon (DOC), and salinity; (2) nutrients including nitrate (NO₃-N), nitrite (NO₂-N), ammonia (NH₃-N), total nitrogen (TN), total phosphorus (TP), and ortho-phosphate (PO₄-P); (3) dissolved

Table 1
Reference drainage and ASBS discharge sites, and their respective sampling effort, collected immediately prior to and immediately following storm events in Southern California.

ASBS number	ASBS name	Site name	Latitude	Longitude	Reference or discharge	Number pre-storm samples	Number post-storm samples
ASBS 21	San Nicolas Island	Barge Landing	33.21967	-119.44728	Discharge	2	2
ASBS 21	San Nicolas Island	Cissy Cove	33.21448	-119.48459	Discharge	1	1
ASBS 21	San Nicolas Island	Reference Site	37.26600	-119.49828	Reference	2	2
ASBS 21	San Nicolas Island	Reverse Osmosis site	33.24281	-119.44433	Discharge	1	1
ASBS 24	Malibu	Solstice Beach	34.03255	-118.74216	Reference	1	1
ASBS 24	Malibu	Arroyo Sequit	34.04441	-118.93393	Reference	1	1
ASBS 24	Malibu	Broad Beach	34.03339	-118.85090	Discharge	3	3
ASBS 24	Malibu	Nicholas Canyon	34.04172	-118.91574	Reference	3	3
ASBS 24	Malibu	Westward Beach	34.01030	-118.81721	Discharge	2	2
ASBS 25	Santa Catalina island	Two Harbors Pier	33.44194	-118.49821	Discharge	1	2
-	-	Italian gardens	33.41011	-118.38176	Reference	1	2
ASBS 29	San Diego	Avienda de la Playa	32.85466	-117.25899	Discharge	3	3
ASBS 31	La Jolla	San Diego Marine Life Refuge	32.86632	-117.25469	Discharge	1	3
ASBS 32	Newport Coast/Crystal Cove	Newport Coast/Crystal Cove	33.58867	-117.86759	Discharge	3	3
ASBS 33	Heisler Park	El Moro Canyon	33.56033	-117.82205	Reference	3	3
ASBS 33	Heisler Park	Heisler Park	33.54301	-117.78958	Discharge	3	3
					Discharge	20	23
					Reference	11	12
					Total	31	35

and total trace metals (arsenic, cadmium, chromium, copper, nickel, lead, silver and zinc); (3) chlorinated hydrocarbons including total PCB (sum of congeners 18, 28, 37, 44, 49, 52, 66, 70, 74, 77, 81, 87, 99, 101, 105, 110, 114, 118, 119, 123, 126, 128, 138, 149, 151, 153, 156, 157, 158, 167, 168, 169, 170, 177, 180, 183, 187, 189, 194, 201 and 206) and total DDT (sum of *o,p'*- and *p,p'*-DDT, DDE, and DDD); (4) total polycyclic aromatic hydrocarbons (28 PAHs); and (5) short-term chronic toxicity. All sample analysis followed standard methods and/or EPA approved procedures (APHA, 2006). Trace metals were prepared for analysis using ammonium pyrrolidine dithiocarbamate (APDC), a chelation method that concentrates trace metals and removes matrix interferences (USEPA, 1996). Toxicity of the receiving water was evaluated by performing an egg fertilization test using the endemic purple sea urchin *Strongylocentrotus purpuratus* (USEPA, 1995).

The project achieved virtually all of its performance-based measures of quality assurance. No laboratory blank sample was greater than the method detection limit (detection limits can be found in the Supplementary Information). The data quality objective (DQO) for precision using laboratory duplicates was $\leq 25\%$ reproducible percent difference (RPD) for TSS, nutrients, and trace metals. The overall success rate for achieving precision DQOs was 96%. The DQO for accuracy was 80–120% recovery of nutrient spiked samples in seawater, and 75–125% recovery of trace metals spiked samples in seawater. The overall success rate for achieving accuracy DQOs was 91%. The accuracy DQO success rate for arsenic, chromium, and lead was 100%. The accuracy DQO success rate for copper, nickel, and silver was 93%. The accuracy DQO success rate for cadmium was 80% and for zinc was 57%. The decreased success rate for cadmium and zinc was due, in part, to the APDC chelation method that has lower affinities for extracting cadmium and zinc from seawater. The actual recovery of spiked cadmium ranged from 64% to 90% per batch, averaging 79% recovery overall. The recovery of spiked zinc ranged from 62% to 109% per batch, averaging 77% recovery overall. Since relative concentrations were being compared (i.e., pre- to post-storm) and these paired samples were analyzed in the same batch, the cadmium and zinc data were retained in the data set for analysis.

2.3. Data analysis

Data analysis followed four steps. The first step was determining the validity of reference drainage site selection. This was achieved by examining the data for known anthropogenic contamination (i.e., chlorinated hydrocarbons such as DDTs and PCBs), testing for outlier samples in the reference drainage data set, and the presence of toxicity. The second data analysis step compared the average concentration of post-storm ambient concentrations at reference drainage sites to ASBS discharge sites. Differences between these concentrations were evaluated using a studentized *T*-test. The third data analysis step examined potential relationships among parameters looking for explanatory variables that derive differences both within reference drainage sites and between reference drainage and ASBS discharge sites. Rainfall quantity, antecedent dry period, TSS and DOC concentrations were correlated with all of the post-storm chemical concentrations and with the relative change in concentration between pre- and post-storm concentrations after log-transformation for data normalization. For the final data analysis, a reference based threshold was used as a proxy for distinguishing differences from natural water quality. The reference based threshold included a two-step process: (1) was the individual chemical post-storm discharge concentration greater than the 85th percentile of the reference drainage site post-storm concentrations; and then (2) was the individual post-storm discharge concentration greater than the pre-storm concentration for the same storm event. For ASBS discharge sites that did not

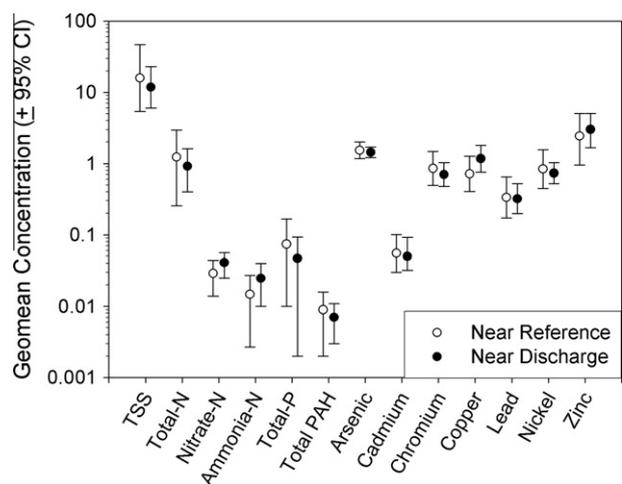


Fig. 2. Comparison of geometric mean (+95% confidence interval) concentrations in ambient near-shore receiving waters following storm events at reference drainage and ASBS discharge sites. Total suspended solids (TSS) and nutrients in mg/L; total polycyclic aromatic hydrocarbons (Total PAHs), and total trace metals in $\mu\text{g/L}$.

have a matching pre-storm concentration, the pre-storm concentration from the previous storm at that site for which data was available was used.

3. Results

Post-storm reference drainage site concentrations were similar to post-storm ASBS discharge site concentrations (Fig. 2, Supplementary Information). For 13 parameters (including TSS, nutrients, total PAH and total trace metals), none were significantly different between reference drainage and discharge sites following storm events ($p < 0.05$). Of the minor differences between reference drainage and ASBS discharge site results, post-storm geometric mean concentrations were greater for nine of 13 constituents at reference drainage sites. No detectable concentrations of total DDT or total PCB were observed at reference drainage sites. However, detectable quantities of chlorinated hydrocarbons (*p,p'*-DDE), while extremely rare, did occur at certain ASBS discharge sites. The average difference between geometric mean concentrations at reference drainage vs. ASBS discharge sites across all parameters (except chlorinated hydrocarbons) was 3%; no parameter differed by more than a factor of 70%.

In general, there was no consistent increase or decrease in concentrations pre- to post-storm at reference drainage or ASBS discharge sites (Fig. 3, Supplementary Information). Pre:post-storm concentration ratios were not significantly different between reference drainage and ASBS discharge sites for any of the trace metals. Nearly every trace metal, whether from reference drainage or ASBS discharge sites, encompassed unity within its interquartile distribution indicating that pre- and post-storm concentrations were similar. The only exception was copper that, despite having similar reference drainage and discharge site concentrations, had roughly 75% of their respective distributions greater than unity. This would indicate that receiving water concentrations of copper increased following storm events.

Most relationships of discharge post-storm concentrations with storm characteristics were poor (Table 2). Correlation coefficients with storm size ranged from -0.2 to 0.25 across all constituents, none of which were significant. Correlation coefficients with antecedent dry days were marginally better, ranging from -0.45 to 0.34 across all constituents; only salinity and total *P* were statistically significant. Other potential explanatory variables such as

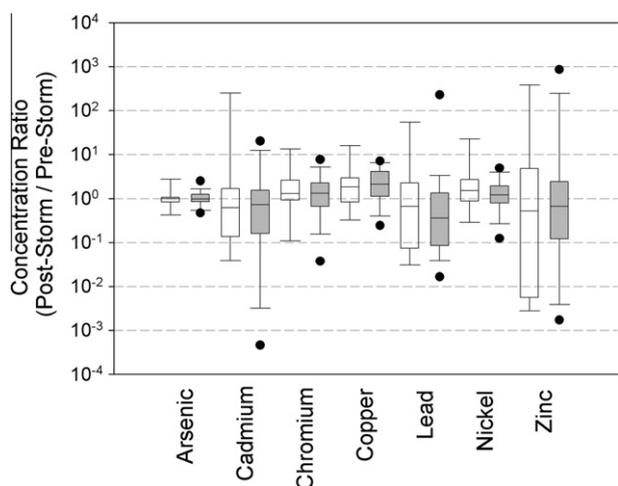


Fig. 3. Distribution of post-storm relative to pre-storm trace metal concentrations in ambient near-coastal waters at reference drainage (in white) and ASBS discharge (in grey) sites. Box plots include the 5th, 25th, 50th, 75th, and 95th percentile of the data distribution.

salinity, TSS, or DOC concentrations provided limited insight. Salinity was negatively correlated with most of the total trace metals; cadmium, chromium, and copper were statistically significant. In contrast, TSS was positively correlated with most of the total trace metals; arsenic, chromium, lead and nickel were statistically significant. Despite the statistically significant correlation for a subset of metals for both salinity and TSS, no correlation explained more than 45% of the variability in parameter concentrations observed in ASBS receiving waters. In fact, roughly one-third of the parameters had correlation coefficients less than 0.30.

Differences from natural water quality were relatively infrequent at ASBS discharge sites (Table 3, Fig. 4). ASBS 25 (Northwest Santa Catalina Island) had the greatest proportion of analyses that were greater than reference site based thresholds (35% of all analyses). ASBS 29 (La Jolla) had the smallest proportion of analyses that were greater than reference site based thresholds (5% of all analyses). Cumulatively across all ASBS, 15% of all analyses were greater than reference site based thresholds. Nutrients (24% of all analyses) and general constituents (23% of all analyses) were greater than reference site based thresholds most frequently (Table 3, Fig. 5). For both total and dissolved metals, approximately 19% of all samples were greater than reference site based thresholds. Total PAH were greater than reference site based thresholds least frequently (2% of all analyses).

Table 2
Correlation coefficients between storm characteristics: rainfall quantity, antecedent dry days (Ant Dry); or conservative tracers: total suspended solids (TSS), salinity, dissolved organic carbon (DOC) and chemical parameters of interest. Bold numbers are statistically significant at $p < 0.05$.

	Rainfall	Ant dry	Salinity	TSS	DOC
Salinity	0.20	-0.43			
TSS	0.19	0.23	0.02		
DOC	0.08	-0.11	0.50	0.05	
Ammonia-N	0.08	0.29	-0.34	-0.11	0.26
Nitrate-N	-0.05	0.05	0.00	-0.08	0.41
Total-N	-0.02	0.22	-0.07	0.15	0.09
Total-P	-0.07	0.34	0.03	0.07	-0.21
Arsenic	-0.04	-0.04	0.13	0.46	0.17
Cadmium	-0.01	-0.01	-0.34	-0.09	0.03
Chromium	0.25	0.25	-0.34	0.67	0.21
Copper	0.07	0.07	0.02	0.27	0.24
Lead	0.13	0.13	-0.06	0.37	0.15
Nickel	0.14	0.14	-0.19	0.55	0.32
Zinc	0.02	0.02	-0.44	0.31	-0.10
Total PAH	0.16	0.16	-0.03	0.03	0.11

Significant toxicity was not observed during this study. Sea urchin fertilization in all post-storm samples ranged from 88% to 100% of laboratory control responses, indicating a lack of statistically significant effect in both the reference drainage and ASBS discharge samples. However, samples from ASBS 25, the site that differed most from natural water quality, had no toxicity data.

4. Discussion

Based on the data collected during this study, ASBS in Southern California are consistently protective of natural water quality following storm events. On average, the range of post-storm pollutant concentrations in receiving waters sampled near ASBS discharge sites were not significantly different from post-storm concentrations at reference drainage sites, which included storm water inputs free of (or minimally influenced by) anthropogenic sources. No conservative tracer could be used to track natural constituents such as salinity, TSS, or DOC, in large part because pollutant concentrations were so low. Furthermore, synthetic anthropogenic contaminants such as total DDT or total PCB were not detectable across the wide variety of reference drainage sample locations in ASBS, and were rarely detectable at discharge sites in ASBS. Moreover, no post-storm samples collected near ASBS discharges exhibited toxicity.

Although ASBS on average were maintaining natural water quality, there were some individual ASBS sites that appeared to have anthropogenic contributions. ASBS 25 (Catalina Island) had an unusually large proportion of analyses that were greater than reference site based thresholds. This is not wholly unexpected as this site is subject to pollutant inputs via storm water runoff from a developed community as well as a vessel mooring field. ASBS 21 (San Nicolas Island), 32 (Newport Coast), and 33 (Heisler Park), all of which receive discharges from municipal and/or industrial (military) storm water runoff, were the next three water quality protected areas to exceed reference site based thresholds. While no storm water discharge information was collected just upstream of the ASBS during our storm events, other studies have identified pollutants such as nutrients and trace metals widespread in municipal (Tiefenthaler et al., 2008) and industrial (Lee et al., 2007) storm water. Trace metals and nutrients were also two groups of constituents that had the greatest proportion of samples greater than the reference site based thresholds in this study.

The reference drainage sites in this study were used to as a proxy for establishing natural water quality thresholds. The algorithm selected for this natural water quality threshold, while not arbitrary, is not an exclusive approach to utilizing the reference drainage site information. In this case, the 85th percentile of the reference site distribution was selected as a primary threshold. Because of the similarities to the reference site data, approximately 15% of the ASBS discharge data distribution also exceeded this threshold. As a test of sensitivity, differing reference thresholds were used to assess the ASBS discharge site information. Regardless of whether the thresholds were empirically based (i.e., 95th percentile) or statistically based (i.e., 95th prediction interval), a concomitant decrease in ASBS discharge site difference from natural water quality followed (i.e., 5%). This once again emphasizes that, despite a few samples with high magnitude concentrations that exceeded reference site maxima, the reference and discharge data were similar in their distribution.

Turbulent mixing and advection associated with breaking waves likely plays a large role in reducing concentrations in coastal storm water plumes. Mixing and advection were the primary forces associated with shoreline dilution of dye and bacteria near flowing storm drains in Santa Monica Bay (Clarke et al., 2007). In these examples, dilution factors of 10^3 – 10^6 were observed at

Table 3
Reference site based threshold exceedence frequency near discharges into Areas of Special Biological Significance (ASBS) following storm events in Southern California.

Parameter	Reference site based threshold		Discharge site comparison		
	85th percentile of reference data	Units	Total no. post-storm Samples	Pct samples > reference 85th percentile	Pct of samples > reference 85th percentile and greater than pre-storm concentration
Total suspended solids	16.5	mg/L	23	35	22
Dissolved organic carbon	0.08	mg/L	21	24	19
Ammonia-N	0.03	mg/L	23	30	26
Nitrate-N	0.05	mg/L	23	26	13
Nitrite-N	0.01	mg/L	23	0	0
Total nitrogen	4.0	mg/L	21	10	5
Total phosphorus	0.10	mg/L	23	9	9
Arsenic-dissolved	1.48	µg/L	19	32	32
Arsenic-total	1.9	µg/L	23	13	4
Cadmium-dissolved	0.05	µg/L	19	21	16
Cadmium-total	0.14	µg/L	23	26	17
Chromium-dissolved	0.21	µg/L	19	5	5
Chromium-total	1.6	µg/L	23	17	13
Copper-dissolved	0.45	µg/L	19	47	42
Copper-total	2.2	µg/L	23	26	26
Iron-dissolved	1.7	µg/L	19	11	11
Iron-total	8.13	µg/L	23	13	13
Lead-dissolved	0.02	µg/L	19	26	21
Lead-total	1.1	µg/L	23	13	17
Nickel-dissolved	0.32	µg/L	19	32	26
Nickel-total	1.5	µg/L	23	17	17
Silver-dissolved	ND	µg/L	19	0	0
Silver-total	0.0	µg/L	23	13	9
Zinc-dissolved	2.88	µg/L	19	5	5
Zinc-total	8.6	µg/L	23	30	30
Total PAH	19.6	µg/L	23	9	9

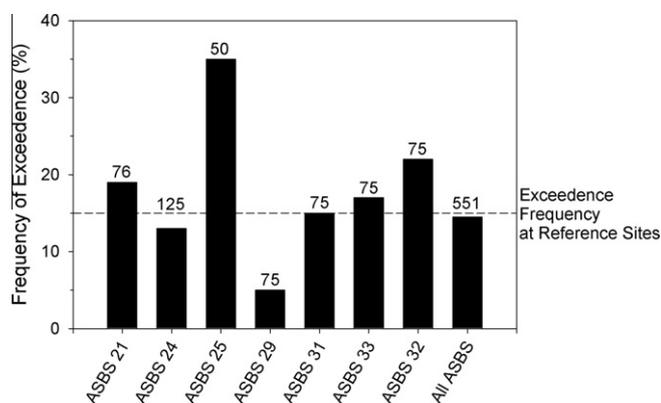


Fig. 4. Frequency of reference site based threshold exceedences for all parameters during all storm events at each Area of Special Biological Significance (ASBS) in Southern California. Number above bar is total sample size.

distances of 25 m from the discharge mixing zone during dry weather. While the increased flows from dry to wet weather could overwhelm nearshore mixing and advection, wave energy also increases during storm events. Similarly detailed studies at the shoreline during wet weather have not been conducted.

Although a handful of other studies have reported water column trace metal concentrations in the Southern California Bight, the data in this study represent some of the first near-shore seawater concentrations at reference drainage sites that are influenced by storm water inputs (Table 4). Probably the closest analogy was reported by Sanudo-Wilhelmy and Flegal (1996) who measured filtered water column concentrations in samples approximately 100 m from shore (compared to at the shoreline in this study) at sites between San Diego and Baja California, Mexico. These nearshore samples, collected during dry weather, were similar to the average post-storm

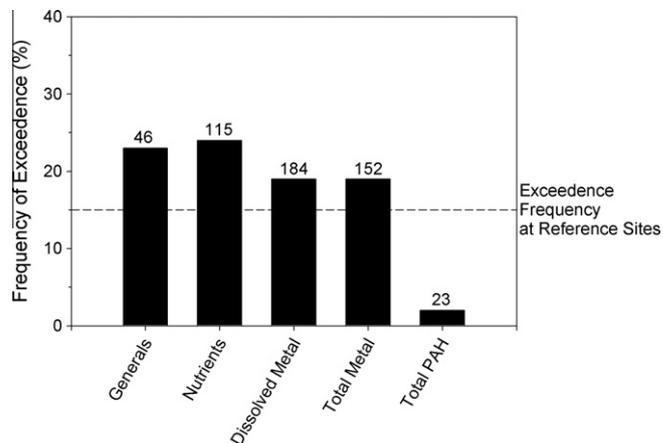


Fig. 5. Frequency of reference site based threshold exceedences by parameter group for all storm events and all Areas of Special Biological Significance (ASBS) in Southern California. Number above bar is total sample size.

concentrations at reference discharge sites measured herein. This is not surprising since pre-storm sample concentrations were not significantly different from post-storm sample concentrations at reference discharge sites during the present study. In contrast, water column concentrations collected at offshore reference sites in the Southern California Bight (Sanudo-Wilhelmy and Flegal, 1996; Young and Jan, 1975) were generally lower than the average post-storm reference discharge sites sampled in at the shoreline this study. These open ocean sites were characterized as having lower suspended solids, less influenced by coastal upwelling, and subject to more biological scavenging and greater dilution by oceanic waters than nearshore sites. Both offshore open ocean studies were conducted during dry weather. The last comparison focused not on

Table 4

Comparison of water column trace metal concentrations from this study to other studies in Southern California.

	Units	Surf zone		Open coastal		Near anthropogenic sources			
		Reference site post storm geomean (95% conf interval) ¹	Dry weather 100 m from shore ²	Southern California Bight ²	Southern California Bight ⁴	Santa Monica Bay ³	San Diego Bay ⁵	Marinas ⁶	Near wastewater outfall ⁴
Arsenic-total	µg/L	1.53 (1.17, 2.00)							
Cadmium-dissolved	µg/L	0.04 (0.02, 0.06)	0.02–0.03		0.05				nd–0.08
Cadmium-total	µg/L	0.06 (0.03, 0.10)		0.004–0.02	0.02	1.1–2.5			0.09–0.18
Chromium-dissolved	µg/L	0.18 (0.16, 0.22)			0.23				0.18–0.50
Chromium-total	µg/L	0.85 (0.49, 1.47)			0.03				1.3–2.0
Copper-dissolved	µg/L	0.23 (0.13, 0.42)	0.2–0.4		0.1			<0.16–21.0	0.26–0.61
Copper-total	µg/L	0.71 (0.40, 1.26)		0.02	0.02	<0.2–7.2	<0.2–4		0.89–1.4
Lead-dissolved	µg/L	0.02 (0.01, 0.03)							
Lead-total	µg/L	0.33 (0.17, 0.65)						1.1–4.0	
Nickel-dissolved	µg/L	0.25 (0.20, 0.31)	0.2–0.4		0.29				0.72–1.2
Nickel-total	µg/L	0.83 (0.45, 1.56)		0.2–0.3	0.02	1.4–15.0			0.18–0.26
Zinc-dissolved	µg/L	0.92 (0.13, 2.27)							
Zinc-total	µg/L	2.43 (0.95, 5.03)						2.6–41.8	

¹ Present study.² Sanudo-Wilhelmy and Flegal (1996).³ Cross et al. (1987).⁴ Young and Chan (1975).⁵ Rivera-Duarte et al. (2005).⁶ Schiff et al. (2004).

reference sites, but sampling sites near known anthropogenic sources of trace metal inputs such as marinas (Schiff et al., 2004), treated wastewater outfalls (Young and Jan, 1975), and adjacent to highly developed urban centers including Santa Monica or San Diego Bays (Cross et al., 1987; Rivera-Duarte et al., 2005). Trace metal concentrations near anthropogenic sources, even though they were collected during dry weather, were frequently greater than the concentrations measured at post-storm reference discharge sites in this study.

Despite this new source of information, many data gaps remain in regards to natural water quality and these data gaps limit our ability to definitively assess water quality in ASBS. The data gaps fall into five categories. First, the reference data set that was used to derive natural water quality is limited. While this study produced one of the most complete data sets to date on ambient seawater concentrations near reference drainages during wet weather, it was only comprised of 12 site-events. Undoubtedly, this is insufficient to capture the wide range of natural conditions associated with watershed size and composition, storm size and intensity, or receiving water dynamics associated with waves and currents. Without a good grasp of natural water quality following storm events, it will be uncertain whether those ASBS discharges that were similar to reference drainage conditions actually lacked measurable anthropogenic enhancements. The second data gap is associated with those ASBS discharges that were dissimilar from reference drainage sites. While it appeared clear, even from our limited reference data set, that some ASBS discharge sites contained anthropogenic contributions, the thresholds we evaluated are not currently regulatory compliance measures. Additional information on the magnitude and duration of anthropogenic contributions is crucial before state regulators or regulated ASBS managers can rank or prioritize discharges for remediation. The third data gap addresses sources of anthropogenic inputs to ASBS discharges. Sites that appeared dissimilar from natural water quality may be attributable to non-anthropogenic site-specific causes (i.e., marine mammal defecation of nutrients). This gap is best addressed through follow-on site-specific investigations. The fourth data gap addresses all of the non-sampled ASBS discharges. Only 10 ASBS discharges were targeted in this study and, while these may have been the largest and perceived greatest risk to the ASBS, they are only a small fraction of the 271 discharges to the Southern Cali-

fornia ASBS. The last data gap to evaluate for natural water quality is non-water quality threats. Risks posed by poaching, trampling, or invasive species are equally, or perhaps even more, threatening to the health of ASBS. To compliment this chemical and toxicity testing effort, the State of California and stakeholders are currently addressing this data gap by conducting intertidal and subtidal biological surveys of ASBS.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.marpolbul.2011.09.009](https://doi.org/10.1016/j.marpolbul.2011.09.009).

References

- Ackerman, D., Schiff, K., 2003. Modeling storm water mass emissions to the Southern California Bight. *Journal of Environmental Engineering* 129, 308–317.
- American Public Health Association (APHA), 2006. *Standard Methods for the Examination of Water and Wastewater*, 19th ed. APHA, Washington, DC.
- Boesch, D.F., Burroughs, R.H., Baker, J.E., Mason, R.P., Rowe, C.L., Siefert, R.L., 2001. *Marine Pollution in the United States*. Pew Oceans Commission, Arlington, Virginia.
- Clarke, L.B., Ackerman, D., Largier, J., 2007. Dye dispersion in the surf zone: measurements and simple models. *Continental Shelf Research* 27, 650–669.
- Cohen, A., 1997. Sturgeon poaching and black market caviar: a case study. *Environmental Biology of Fishes* 48, 423–426.
- Cross, J.N., Hardy, J.T., Hose, J.E., Herschelman, G.P., Antrim, L.D., Gossett, R.W., Crecelius, E.A., 1987. Contaminant concentrations and toxicity of sea-surface microlayer near Los Angeles, California. *Marine Environmental Research* 23, 307–323.

- Daskalakis, K.D., O'Connor, T.P., 1995. Distribution of chemical concentrations in US coastal and estuarine sediment. *Marine Environmental Research* 40, 381–398.
- Davis, A.P., Shokouhian, M., Ni, S.B., 2001. Loading estimates of lead, copper, cadmium, and zinc in urban runoff from specific sources. *Chemosphere* 44, 997–1009.
- Halpern, B.S., Walbridge, S., Selkoe, K.A., Kappel, C.V., Micheli, F., D'Agrosa, C., Bruno, J.F., Casey, K.S., Ebert, C., Fox, H.E., Fujita, R., Heinemann, D., Lenihan, H.S., Madin, E.M.P., Perry, M.T., Selig, E.R., Spalding, M., Steneck, R., Watson, R., 2008. A global map of human impact on marine ecosystems. *Science* 15, 948–952.
- Lee, H., Swamikannu, X., Radulescu, D., Kim, S.J., Stenstrom, M.K., 2007. Design of storm water monitoring programs. *Water Research* 41, 4186–4196.
- Lyon, G.S., Stein, E.D., 2009. How effective has the Clean Water Act been at reducing pollutant mass emissions to the Southern California Bight over the past 35 years? *Environmental Monitoring and Assessment* 154, 413–426.
- Rivera-Duarte, I., Rosen, G., LaPota, D., Chadwick, D.B., Kear-Padilla, L., Zirino, A., 2005. Copper toxicity to larval stages of three marine invertebrates and copper complexation capacity in San Diego Bay, California. *Environmental Science & Technology* 39, 1542–1546.
- Sabin, L.D., Lim, J.H., Stolzenbach, K.D., Schiff, K.C., 2006. Atmospheric dry deposition of trace metals in the coastal region of Los Angeles, California, USA. *Environmental Toxicology and Chemistry* 25, 2334–2341.
- Sanudo-Wilhelmy, S.A., Flegal, A.R., 1996. Trace metal concentrations in the surf zone and in coastal waters off Baja California, Mexico. *Environmental Science & Technology* 30, 1575–1580.
- Schiff, K., Sutula, M., 2004. Organophosphorus pesticides in storm water runoff from Southern California (USA). *Environmental Toxicology and Chemistry* 23, 1815–1821.
- Schiff, K., Bay, S., Allen, M.J., Zeng, E., 2000. Southern California. In: Sheppard, C. (Ed.), *Seas at the Millennium*. Elsevier Press, London, UK, pp. 385–404 (Chapter 24).
- Schiff, K., Diehl, D., Valkirs, A., 2004. Copper emissions from antifouling paint on recreational vessels. *Marine Pollution Bulletin* 48, 371–377.
- Southern California Coastal Water Research Project (SCCWRP), 2003. Discharges into State Water Quality Protected Areas. Report to the State Water Resources Control Board. SCCWRP, Costa Mesa, CA.
- State Water Resources Control Board (SWRCB), 2005. California Ocean Plan. SWRCB, Sacramento, CA.
- Tiefenthaler, L.L., Stein, E.D., Schiff, K.C., 2008. Watershed and land use-based sources of trace metals in urban storm water. *Environmental Toxicology and Chemistry* 27, 277–287.
- United States Environmental Protection Agency (USEPA), 1995. Short-term methods for estimating the chronic toxicity of effluents and receiving waters to west coast marine and estuarine organisms. Report No. EPA 600/R-95/136. USEPA Office of Research and Development, Cincinnati, OH.
- US Census Bureau. 2009. Population estimates by State and County. <http://www.census.gov/>.
- USEPA, 1996. Method 1640: Determination of Trace Metal Elements in Ambient Waters by On-Line Chelation Preconcentration and Inductive Coupled Plasma-Mass Spectrometry. USEPA, Office of Water, Engineering and Analysis Division, Washington, DC.
- Yoon, V.K., Stein, E.D., 2008. Natural catchments as sources of background levels of storm-water metals, nutrients, and solids. *Journal of Environmental Engineering* 134, 961–973.
- Young, D.R., Jan, T.K., 1975. Trace metals in nearshore seawater. In: Bascom, W. (Ed.), *Southern California Coastal Water Research Project 1975 Annual Report*. Southern California Coastal Water Research Project, El Segundo, CA, pp. 143–146, ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/AnnualReports/1975AnnualReport/27_.pdf.