Impact of stormwater discharges to water quality in California's areas of special biological significance

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Abstract

Over 1,600 storm drain outfalls discharge untreated runoff into California's 34 marine water quality protected areas, termed Areas of Special Biological Significance (ASBS). The goal of this study was to assess the extent and magnitude of water quality impacts in California's ASBS following storm events. A stratified probabilistic design was used for sampling receiving water shorelines near (discharge) and far (non-discharge) from storm drain outfalls. In general, reasonably good water quality exists in California's ASBS following storm events. Many of the target analytes measured did not exceed the State of California's Ocean Plan water quality standards (WQS). The post-storm concentrations of most constituents in discharge and non-discharge strata of ASBS were similar. The three potentially problematic parameters identified were total PAH, chromium, and copper. Southern California, which has more intense development than elsewhere in the state, had almost twice as many target analytes exceed WQS than central or northern California.

Introduction

By their proximity, oceans adjacent to coastal land development are continually subjected to pollutant inputs. In the United States, approximately 53% of the population lives in counties bordering the coast, but comprises only 17% of the land area (Culliton *et al*. 1998). This has led to habitat alteration (Boesch *et al*. 2001), eutrophication (Bricker *et al*. 1999), contaminated sediments (EPA 2005), and accumulation of toxics in tissues of marine organisms (O'Connor 1998).

One conservation strategy used to safeguard the marine environment is the establishment of protected areas where portions of the coast are set aside for limited use. Marine protected areas exist for some of the most ecologically sensitive areas around the world including Australia's Great Barrier Reef, Fiji, the Galapagos Islands, and others. Many marine protected areas also exist within the United States including California, Hawaii, and Florida (NOAA 2008). Virtually all of these marine protected areas, however, were established based upon natural resource needs and not exclusively water quality issues. Almost in unanimity, the aforementioned marine protected areas initially have fisheries-based goals that limit recreational and/or commercial fishing. Water quality goals, if addressed, were not the primary motivation for the establishment of the marine protected area.

Unlike most other coastal conservation strategies, the State of California established 34 marine protected areas in 1974-75 specifically for the protection of water quality (SWRCB 2005). Although they are called areas of special biological significance (ASBS), not all of these marine water quality protected areas also limit harvesting (i.e., fishing). Twenty five of the ASBS occur on the mainland of California comprising 499 shoreline miles and 32% of the state coastline (Figure 1). The primacy of water quality protection is indicated

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within state policy whereby all "discharge of waste is prohibited" and "natural water quality must be maintained" in these ASBS (SWRCB 2005).

The State of California has done a remarkable job limiting point source discharges in ASBS. Less than 10 point source discharges exist statewide, and these are almost entirely discharges from marine aquaria and/or flow through seawater systems associated with research academic institutions. However, little attention has been placed on non-point source discharges, which are much more numerous. Over 1,600 outfalls have been identified along ASBS shoreline (SCCWRP 2003). The vast majority of these outfalls were storm drains that could potentially discharge urban and agricultural runoff from upstream development. Large portions of this upstream development did not exist when the ASBS were originally established in the mid-1970's.

The objective of this study was to assess the extent and magnitude of water quality impacts in ASBS following storm events. Further, the magnitude and extent of impact in ASBS was compared between areas near stormwater discharges and areas distant from discharges to determine the potential of storm drain outfalls to cause the observed impacts in water quality. Ultimately, the goal was to determine if significant water quality impacts existed within ASBS, with the results guiding managers on the need and direction of potential future intervention.

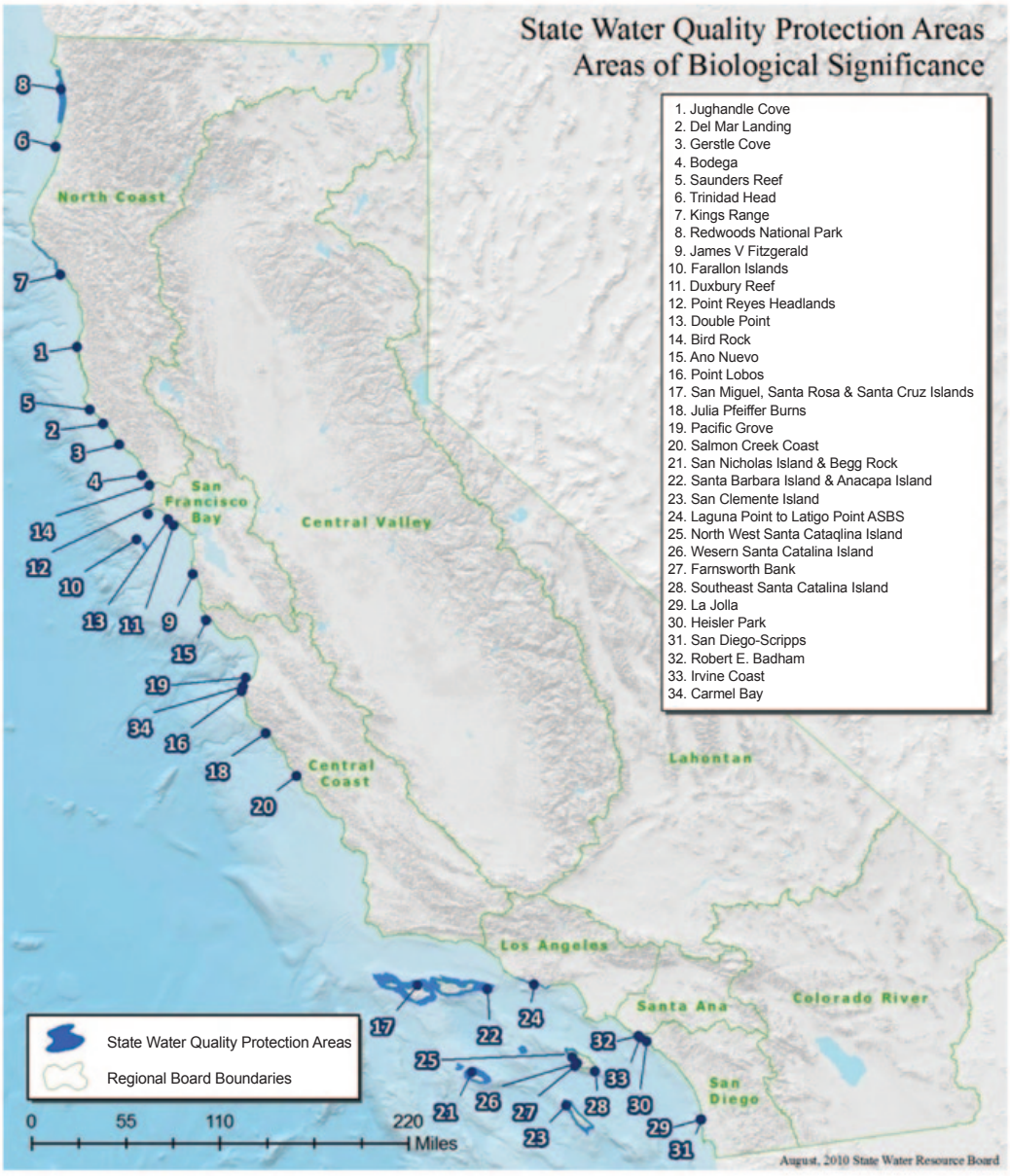

Figure 1. California's water quality protected areas termed "Areas of Special Biological Significance".

Methods

This study utilized a probabilistic-based design to estimate the shoreline-miles or percent of total shoreline-miles with observed impacts to water quality. Probabilistic designs, wherein sample sites are selected randomly, enable unbiased estimates of extent (Stevens 1997). For the current study design, the sampling frame consisted of all mainland ASBS shoreline, divided into two groups: 1) areas near direct discharges defined as less than 500m from a pipe, drain, or other surface discharge greater than 18 inches diameter; and 2) non-discharge areas defined as more than 500m distant from direct discharges. The 500m cutoff was selected based on nearshore modeling studies by Jenkins and Wasyl (2007). All sites were collected from shoreline receiving water. No effluent samples were collected as part of this study. All sites were sampled for only a single storm event between February and April, 2009.

A total of 33 sites were selected for sampling. Twenty-one sites were from the discharge stratum and 12 sites were from the non-discharge stratum (Table 1). At each site, samples were collected immediately prior to (<48 hours), then immediately following (<24 hours), significant storm events. Sampling criteria included: 1) all post-storm samples must be collected as soon after the storm event as possible (nearly all were collected less than six hours following cessation of rainfall); 2) at discharge sites, stormwater flows must reach the ocean; and 3) all ocean receiving water samples must be collected by hand from the shore (no boats). These criteria helped ensure that the focus was on receiving waters, that recent stormwater inputs had occurred, and examining the area closest to shore where potentially the least mixing occurs.

All water samples were analyzed for 98 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-phophate (PO4-P); 3) dissolved and total trace metals (As, Cd, Cr, Cu, Ni, Pb, Ag, Se, Zn); 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, 206) and total DDT (sum of o,p'- and p,p'-DDT, DDE, and DDD); 4) total polycyclic aromatic hydrocarbons (28 PAH); and 5) short-term chronic toxicity using an early life stage of an endemic species. 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). Fertilization success of the purple sea urchin, *Strongylocentrotus purpuratus*, was used for toxicity testing (USEPA 1995).

The project focused on performance-based measures of quality assurance. In general, laboratory data quality was quite good: no laboratory blank samples greater than the method detection limit; 96% success meeting data quality objectives (DQOs) for precision using laboratory duplicates; 91 % success meeting DQOs for accuracy using spiked samples. The lowest accuracy success rate was for cadmium (12 of 15 batches) and zinc (8 of 16 batches) where the requirement of 75 to 125% recovery from seawater was not met. This was due, in part, to the APDC chelation method that has lower affinities for extracting cadmium and zinc.

Data Analysis

Based on the study design, two data analysis approaches were utilized to compare spatial (discharge vs. non-discharge strata) and temporal (pre-storm vs. post-storm) relationships. The first approach examined the magnitude of changes in space and time. To do this, area-weighted geometric means were calculated for total ASBS shoreline and for each stratum and time period using a ratio estimator approach following Thompson (1992):

$$m = \frac{\sum_{i=1}^{n} (p_i * w_i)}{\sum_{i=1}^{n} w_i},$$

Where:

m = Log_{10} of the area-weighted mean concentration for population j.

p_i = Log_{10} of the parameter value (e.g., concentration) at station i.

w_i = Area weight for station i.

n = Number of stations in population j.

The standard error of the mean is calculated using the following equation where the 95%

Table 1. Sample site locations.

Stratum	SiteID	Longitude	Latitude	ASBS No.	Location
Non-Discharge	N018	-124.0858	41.3196	7	Redwood National and State Parks ASBS
Discharge	D055	-124.0941	41.2799	7	Redwood National and State Parks ASBS
Discharge	D027	-124.1486	41.0608	5	Kelp Beds at Trinidad Head ASBS
Non-Discharge	N043	-124.1441	41.0573	5	Kelp Beds at Trinidad Head ASBS
Non-Discharge	N243	-124.0796	40.0584	6	Kings Range National Conservation Area ASBS
Discharge	D119	-124.0798	40.0388	6	Kings Range National Conservation Area ASBS
Non-Discharge	N035	-123.8216	39.3808	1	Pygmy Forest Ecological Staircase ASBS
Discharge	D037	-123.8188	39.3764	1	Pygmy Forest Ecological Staircase ASBS
Discharge	D050	-123.6487	38.8519	5	Kelp Beds at Saunders Reef ASBS
Discharge	D042	-123.5116	38.7408	2	Del Mar Landing Ecological Reserve ASBS
Discharge	D043	-123.3315	38.5663	3	Grestle Cove ASBS
Non-Discharge	N038	-123.0742	38.3190	4	Bodega Marine Life Refuge ASBS
Discharge	D046	-123.0704	38.3171	4	Bodega Marine Life Refuge ASBS
Non-Discharge	N051	-122.7192	37.9017	10	Duxbury Reef Reserve and Extension ASBS
Discharge	D067	-122.7111	37.8972	10	Duxbury Reef Reserve and Extension ASBS
Discharge	D058	-122.4986	37.5011	8	James V. Fitzgerald Marine Reserve ASBS
Non-Discharge	N042	-122.4958	37.4956	8	James V. Fitzgerald Marine Reserve ASBS
Discharge	D001	-122.3381	37.1361	15	Ano Nuevo Point and Island ASBS
Non-Discharge	N064	-122.3042	37.1153	15	Ano Nuevo Point and Island ASBS
Discharge	D035	-121.9135	36.6230	19	Pacific Grove Marine Gardens Fish Refuge and Hopkins Marine Life Refuge ASBS
Discharge	D220	-121.9316	36.5396	34	Carmel Bay ASBS
Non-Discharge	N055	-121.9298	36.5232	34	Carmel Bay ASBS
Non-Discharge	N002	-121.9528	36.5183	16	Point Lobos Ecological Reserve ASBS
Discharge	D030	-121.9439	36.5128	16	Point Lobos Ecological Reserve ASBS
Discharge	D031	-121.6973	36.1754	18	Julia Pfieffer Burns Underwater Park ASBS
Non-Discharge	N022	-121.6960	36.1743	18	Julia Pfieffer Burns Underwater Park ASBS
Discharge	D016	-118.8727	34.0373	24	Mugu Lagoon to Latigo Point ASBS
Non-Discharge	N006	-118.8076	34.0008	24	Mugu Lagoon to Latigo Point ASBS
Discharge	NWPT	-117.8675	33.5887	32	Newport Beach Marine Life Refuge ASBS
Discharge	D087	-117.8480	33.5774	33	Irvine Coast Marine Life Refuge ASBS
Discharge	D076	-117.7897	33.5428	30	Heisler Park Ecological Reserve ASBS
Discharge	D080	-117.2535	32.8693	31	San Diego Marine Life Refuge ASBS
Discharge	D074	-117.2637	32.8498	29	San Diego-La Jolla Ecological Reserve ASBS

21	**Total No. Sites in Discharge Stratum**
12	**Total No. Sites in NonDischarge Stratum**
33	**Total No. Sites**

confidence intervals about the mean were calculated as 1.96 times the standard error.

$$\text{Standard error (SE)} = \sqrt{\frac{\sum_{i=1}^{n}((p_i - m) * w_i)^2}{\left(\sum_{i=1}^{n} w_i\right)^2}},$$

where:

m = Log_{10} of the area-weighted mean concentration for population j.

p_i = Log_{10} of the parameter value (e.g., concentration) at station i.

w_i = Area weight for station i.

n = Number of stations in population j.

All concentrations below detection limits were treated as zero. Area-weighted geometric means and confidence interval were back-transformed for tables and graphs.

The second data analysis approach focused on estimating the areal extent of impact. To accomplish this, area weights for each sample that exceeded State of California water quality standards (WQS) were summed and divided by the total area-weight for the stratum and time period of interest. The WQS are defined in Table B of the California Ocean Plan (SWRCB 2005). Four WQS exist including six-month median, 30-day average, daily maximum, and instantaneous maximum thresholds.

Results

The post-storm concentrations of most constituents in discharge and non-discharge strata of ASBS were similar (Table 2). Except for DOC and dissolved copper, there was no statistical difference in area-weighted geomean concentrations between post-storm discharge and non-discharge strata. In the case of post-storm copper geomean concentrations, the discharge stratum was greater than the non-discharge stratum. The case was reversed for DOC; the non-discharge was greater than the discharge stratum. Although not statistically different, the area-weighted geometric mean concentration in the discharge stratum was greater for 14 of the remaining 24 parameters compared to the post-storm non-discharge stratum. Post-storm concentrations of chlorinated hydrocarbons, such as total DDT and total PCB, were uniformly non-detectable in both strata.

On average, the increase in concentration across all target analytes from pre- to post-storm samples was less than 3-fold in the discharge stratum (Table 2; Figure 2). In fact, none of the target analyte concentrations were significantly greater post-storm compared to pre-storm. Average concentrations for 12 of the 25 target analytes actually decreased from pre- to post-storm in the discharge stratum. Of the remaining 13 target analytes, the most substantial concentration increases were for dissolved iron (26-fold) and DOC (15-fold).

In general, exceedence of WQS such as instantaneous maxima, daily maxima, and six-month medians, were infrequent for ammonia and trace metals following storm events (Table 3). None of the target analytes collected post-storm exceeded WQS based on instantaneous maxima. Only a single target analyte collected post-storm exceeded the WQS based on the daily maximum. This analyte, total chromium, exceeded 2% of the post-storm shoreline-miles across all ASBS. Ten of 18 parameters collected post-storm exceeded the WQS based on six-month median objectives. Three parameters were dissolved metals (cadmium, copper, and nickel); none of these dissolved metals exceeded the six-month median in more than 2% of the ASBS shoreline-miles. Seven of the parameters exceeding the six-month median were for total metals. The parameter that exceeded the six-month median WQS most frequently (50% of ASBS shoreline-miles) was total chromium. Total nickel exceeded the six-month median WQS second most frequently (15% of ASBS shoreline-miles). Total arsenic, cadmium, copper, lead and zinc exceeded six-month median WQS between 2 and 7% of the ASBS shoreline-miles.

In contrast to ammonia and trace metals, exceedence of state WQS for trace organic parameters was much more frequent (Table 4). Of the six target organic analytes collected post-storm, only total PAH exceeded the 30-day average WQS. However, total PAH exceeded the 30-day average WQS an estimated 87% of the ASBS shoreline-miles. Other trace organic parameters including total DDTs, total PCBs, chlordane, and dieldrin did not exceed the 30-day average WQS.

Except for total chromium and total nickel, there was no dramatic difference in the extent of post-storm WQS exceedences between discharge and non-discharge strata (Tables 3 and 4). The difference in exceedence of the six-month median WQS following storm events was nearly two-fold for total chromium

Table 2. Area weighted geomean concentrations (+95% confidence intervals) for receiving water strata near (discharge) and far (nondischarge) from outfalls in areas of special biological significance <48 hours before (pre-storm) and <24 hours following (post-storm) wet weather events. '--' indicates no detectable quantities.

Parameter	Units	Nondischarge				Discharge			
		Pre-storm		Post-storm		Pre-storm		Post-storm	
		Geomean	(±) 95% CI	Geomean	(±) 95% CI	Geomean	(±) 95% CI	Geomean	(±) 95% CI
Ammonia-N	mg/L	0.001	0.002	0.004	0.008	0.017	0.031	0.009	0.009
Nitrate+Nitrite-N	mg/L	0.13	0.10	0.14	0.10	0.11	0.07	0.12	0.0559
Total P	mg/L	0.41	0.24	0.19	0.09	0.21	0.20	0.07	0.03
Total N	mg/L	0.76	1.22	0.82	1.03	0.37	0.56	1.25	1.44
TSS	mg/L	95.7	145.3	78.5	52.3	91.7	69.2	95.5	75.4
DOC	mg/L	--	--	--	--	0.03	0.06	0.89	1.03
Arsenic-Total	ug/L	1.69	0.35	1.72	0.30	1.96	0.42	1.87	0.40
Cadmium-Total	ug/L	0.05	0.02	0.05	0.02	0.08	0.02	0.11	0.10
Chromium-Total	ug/L	1.61	0.49	2.17	0.74	2.85	1.48	2.59	0.96
Copper-Total	ug/L	0.99	0.32	1.43	0.70	1.09	0.37	1.19	0.43
Iron-Total	ug/L	761	539	1301	1098	1288	919	994	474
Lead-Total	ug/L	0.71	0.82	0.60	0.49	0.89	0.61	0.50	0.13
Nickel-Total	ug/L	2.07	0.84	2.91	0.88	2.87	1.28	2.90	0.95
Silver-Total	ug/L	0.002	0.004	--	--	0.007	0.010	--	--
Zinc-Total	ug/L	1.91	1.76	1.10	1.20	3.39	0.91	4.59	2.86
Arsenic-Dissolved	ug/L	1.43	0.07	1.32	0.16	1.35	0.07	1.29	0.13
Cadmium-Dissolved	ug/L	0.02	0.02	0.03	0.02	0.20	0.27	0.05	0.03
Chromium-Dissolved	ug/L	0.18	0.02	0.18	0.04	0.16	0.01	0.21	0.02
Copper-Dissolved	ug/L	0.17	0.03	0.21	0.05	0.23	0.10	0.54	0.24
Iron-Dissolved	ug/L	0.07	0.12	0.15	0.21	0.36	0.24	5.33	4.90
Lead-Dissolved	ug/L	0.002	0.003	0.003	0.003	0.009	0.006	0.018	0.019
Nickel-Dissolved	ug/L	0.39	0.13	0.47	0.27	0.37	0.15	0.93	0.65
Silver-Dissolved	ug/L	--	--	--	--	--	--	--	--
Zinc-Dissolved	ug/L	0.24	0.34	0.26	0.33	1.53	1.63	1.44	1.84
Total PAH	ug/L	0.020	0.017	0.038	0.033	0.106	0.117	0.015	0.005

(35% of shoreline-miles for the non-discharge stratum compared to 61% of shoreline-miles for the discharge stratum) and a factor of eight for total nickel (3% of shoreline-miles for the non-discharge stratum compared to 24% of shoreline-miles for the discharge stratum).

Contrary to expectations, there was little change in the extent of WQS exceedences from pre- to post-storm in the discharge stratum (Tables 3 and 4). For example, the percent of shoreline-miles that exceeded WQS for chromium and total PAH changed by less than 10% (Figure 3). On the other hand, there were substantial changes in the extent of WQS exceedence from pre- to post-storm in the non-discharge stratum, particularly for these same two target analytes. The extent of shoreline-miles approximately doubled pre- to post-storm for total chromium and total PAH. In fact, the extent of post-storm WQS exceedences of total PAH in the non-discharge stratum looked very much like the extent in the discharge stratum (89% vs. 86% of shoreline-miles, respectively).

Exceedences of the WQS occurred most frequently in southern California compared to northern or central California (Figure 4). The Irvine Coast ASBS in southern California had the greatest number of target analytes (six) sampled post-storm that exceeded WQS and had concentrations that increased from pre- to post-storm. The Robert Badham ASBS followed with four target analytes sampled post-storm that exceeded WQS. No ASBS in Central and Northern California exceeded these same criteria by more than three target analytes. Only a single ASBS in southern California (San Diego-Scripps ASBS) had no exceedences of the WQS for any analyte. There were six ASBS in Central and Northern California that had no analytes exceeding the WQS.

The occurrence of toxicity in post-discharge samples from ASBS was rare. Roughly 3% of the shoreline miles observed post-storm toxicity. This was relatively evenly split between non-discharge and discharge strata.

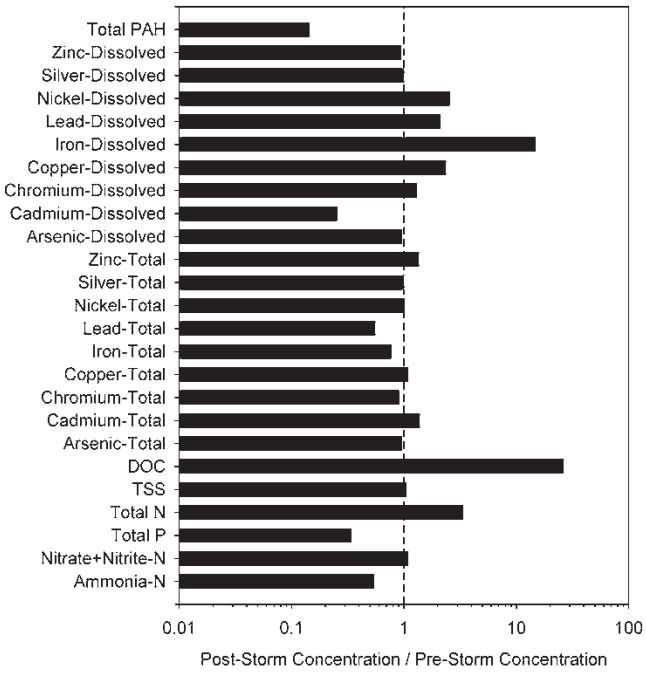

Figure 2. Relative increase of target analyte concentrations in Areas of Special Biological Significance (ASBS) collected <48 hours prior to a storm (pre-) compared to concentrations collected <24 hours following a storm (post-). Unity indicates pre- and post-storm concentrations were the same. Values greater than 1 indicate a post-storm increase in concentration.

Discussion

Based on the results from this study, generally good water quality exists in California's ASBS following storm events. Most target analytes measured did not exceed the State of California's WQS and, for the majority of analytes that did exceed the WQS, the relative extent of impact was small (<7% of ASBS shoreline-miles). All of the target analytes that exceeded WQS have natural as well as anthropogenic sources (e.g., trace metals), but synthetic pesticides (e.g., total DDTs, total PCBs, chlordane and dieldrin) never exceeded WQS and were rarely detected. Additionally, toxicity using an endemic species (sea urchin fertilization test) was infrequent indicating unmeasured analytes were likely not problematic. Finally, average receiving water concentrations of most common stormwater constituents (i.e., lead, zinc, etc.) were statistically similar between the discharge and non-discharge stratum, and average concentrations measured pre-storm were statistically similar to post-storm concentrations in discharge stratum. The lack of demonstrative impact following storm events is an important finding because the greatest perceived risk to ASBS water quality is from stormwater runoff generated by urban, agricultural, and other nonpoint source activities.

While the summary of post-storm water quality in ASBS can be described as good, there were three parameters that stand out as potentially problematic. These include total PAH, chromium, and copper. Total PAH is a known stormwater contaminant from studies not only in California (Stein *et al*. 2006), but around the United States (Hoffman *et al*. 1984). Total PAH concentrations in ASBS were generally low, never exceeding 186 ng/L. Unlike all the other analytes that indicated impairment, the WQS for PAH is based on risk to human health through bioaccumulation in seafood. Hence, the total PAH WQS may be marginally applicable for the protection of marine aquatic life. Interestingly, the frequency of WQS exceedence for total PAH was similar between pre- and post-storm in the discharge stratum so non-storm sources may be at play. Other potential sources could be numerous including dry weather runoff (Stein *et al*. 2006), atmospheric deposition (Sabin *et al*. 2009), or natural seeps (Leifer *et al*. 2006). Clearly, future work on source attribution of total PAH and its potential for biological effects, should be evaluated.

Unlike total PAH, the WQS for chromium is based on the predicted marine life toxicity of its most harmful state, hexavalent chromium. While total chromium is the accepted surrogate for hexavalent chromium in most regulatory applications, no analysis was done in this study to evaluate the relative contribution of hexavalent chromium. Since toxicity was infrequently observed, one can hypothesize that hexavalent chromium was often below the WQS. However, the disparity in the extent of total chromium exceeding WQS between the discharge stratum and non-discharge stratum was sizeable (61 vs. 35% of ASBS shoreline-miles, respectively). Therefore, total chromium in stormwater discharges likely has some influence on ASBS receiving water concentrations. Adding to the concern, total chromium is a commonly found analyte in urban stormwater discharges, with industrial land uses having amongst the greatest concentrations in southern California (Tiefenthaler *et al*. 2008). Chromium is also a naturally occurring component of serpentine rock in many coastal California locations (Caillaud *et al*. 2009). Because of the issues associated with natural versus anthropogenic sources of chromium, surveys focused

Table 3. Percent of shoreline-miles exceeding daily maximum or six-month median water quality standards (WQS) in receiving water either near outfalls (discharge), far from outfalls (nondischarge), or combined (statewide) in areas of special biological significance <48 hours before (pre-storm) and <24 hours following (post-storm) wet weather events. '--' indicates no detectable quantities.

Parameter	Units	Shoreline-Miles (%) Exceeding Daily Maximum WQS						
		WQS	Pre-Storm			Post-Storm		
			Statewide	Discharge	Non-Discharge	Statewide	Discharge	Non-Discharge
Ammonia-N	mg/L	2.4	--	--	--	--	--	--
Arsenic-Dissolved	ug/L	32	--	--	--	--	--	--
Cadmium-Dissolved	ug/L	4	--	--	--	--	--	--
Chromium-Dissolved	ug/L	8	--	--	--	--	--	--
Copper-Dissolved	ug/L	12	--	--	--	--	--	--
Lead-Dissolved	ug/L	8	--	--	--	--	--	--
Nickel-Dissolved	ug/L	20	--	--	--	--	--	--
Silver-Dissolved	ug/L	2.8	--	--	--	--	--	--
Zinc-Dissolved	ug/L	80	--	--	--	--	--	--
Arsenic-Total	ug/L	32	--	--	--	--	--	--
Cadmium-Total	ug/L	4	--	--	--	2	3	--
Chromium-Total	ug/L	8	--	--	--	--	--	--
Copper-Total	ug/L	12	--	--	--	--	--	--
Lead-Total	ug/L	8	--	--	--	--	--	--
Nickel-Total	ug/L	20	--	--	--	--	--	--
Silver-Total	ug/L	2.8	--	--	--	--	--	--
Zinc-Total	ug/L	80	--	--	--	--	--	--

Parameter	Units	Shoreline-Miles (%) Exceeding 6-Month Median WQS						
		WQS	Pre-Storm			Post-Storm		
			Statewide	Discharge	Non-Discharge	Statewide	Discharge	Non-Discharge
Ammonia-N	mg/L	0.6	--	--	--	--	--	--
Arsenic-Dissolved	ug/L	8	--	--	--	--	--	--
Cadmium-Dissolved	ug/L	1	--	--	--	<1	<1	--
Chromium-Dissolved	ug/L	2	--	--	--	--	--	--
Copper-Dissolved	ug/L	3	--	--	--	<1	<1	--
Lead-Dissolved	ug/L	2	--	--	--	--	--	--
Nickel-Dissolved	ug/L	5	--	--	--	2	3	--
Silver-Dissolved	ug/L	0.7	--	--	--	--	--	--
Zinc-Dissolved	ug/L	20	--	--	--	--	--	--
Arsenic-Total	ug/L	8	--	--	--	2	3	--
Cadmium-Total	ug/L	1	--	--	--	2	4	--
Chromium-Total	ug/L	2	41	62	12	50	61	35
Copper-Total	ug/L	3	--	--	--	7	5	10
Lead-Total	ug/L	2	11	6	18	5	--	11
Nickel-Total	ug/L	5	3	6	--	15	24	3
Silver-Total	ug/L	0.7	--	--	--	--	--	--
Zinc-Total	ug/L	20	--	--	--	4	7	--

Table 4. Percent of shoreline-miles exceeding 30-day average water quality standards (WQS) in receiving water either near outfalls (discharge), far from outfalls (nondischarge), or combined (statewide) in areas of special biological significance <48 hours before (pre-storm) and <24 hours following (post-storm) wet weather events. '--' indicates no detectable quantities.

Parameter	Units	Shoreline-Miles (%) Exceeding 30-Day Average WQS						
		WQS	Pre-Storm			Post-Storm		
			Statewide	Discharge	Non-Discharge	Statewide	Discharge	Non-Discharge
Fluoranthene	ng/L	150	--	--	--	--	--	--
Chlordane	ng/L	0.023	--	--	--	--	--	--
DDT	ng/L	0.17	<1	1	--	--	--	--
Dieldrin	ng/L	0.04	--	--	--	--	--	--
PAHs	ng/L	8.8	66	76	54	87	86	89
PCBs	ng/L	0.019	--	--	--	--	--	--

on chromium and the relationship between total and hexavalent chromium at problematic ASBS may be warranted.

Copper was the final target analyte of concern. The concern was generated by four factors that individually aren't alarming, but collectively may indicate stormwater influences. First, total copper exceeded WQS, although not extensively (7% of ASBS shoreline-miles). However, the extent of impact occurred exclusively in the discharge stratum while the non-discharge stratum was free of copper WQS exceedences. Second, the copper WQS exceedence in the discharge stratum occurred post-storm, but was absent in pre-storm samples. Third, the WQS exceedence occurred not just for total copper, but also for dissolved copper. Fourth, the average dissolved copper concentration was significantly greater post-storm than pre-storm. The third and fourth factors are relevant to stormwater inputs because dissolved copper is more bio-available, and an inherently greater toxicological risk to marine life, compared to total copper (Arnold *et al*. 2005). Moreover, copper is consistently observed in stormwater discharges (Tiefenthaler 2008). Further, copper has been identified as the primary toxicant of concern for failed toxicity tests using the sea urchin fertilization test in near coastal water influenced by stormwater runoff (Bay *et al*. 2003)

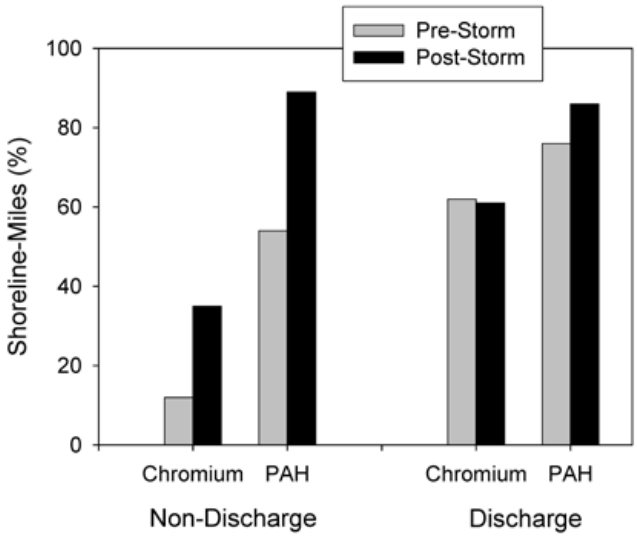

Figure 3. Comparison of the percent shoreline-miles in Areas of Special Biological Significance (ASBS) that exceeded State of California 30-day water quality standards for total chromium and total PAH from pre- and post-storm samples in discharge and non-discharge strata.

The larger concern for total PAH and total chromium may actually be in the non-discharge stratum. It was in the non-discharge stratum that WQS exceedences rose dramatically from pre- to post-storm. While average concentrations did not dramatically increase, they were very near the state's WQS and the extent of ASBS shoreline-miles exceeding WQS doubled or tripled. In fact, the extent of WQS exceedence in non-discharge areas post-storm looked very similar to the extent observed in the discharge stratum. This study design element was intentional; we wanted to see if discharges either

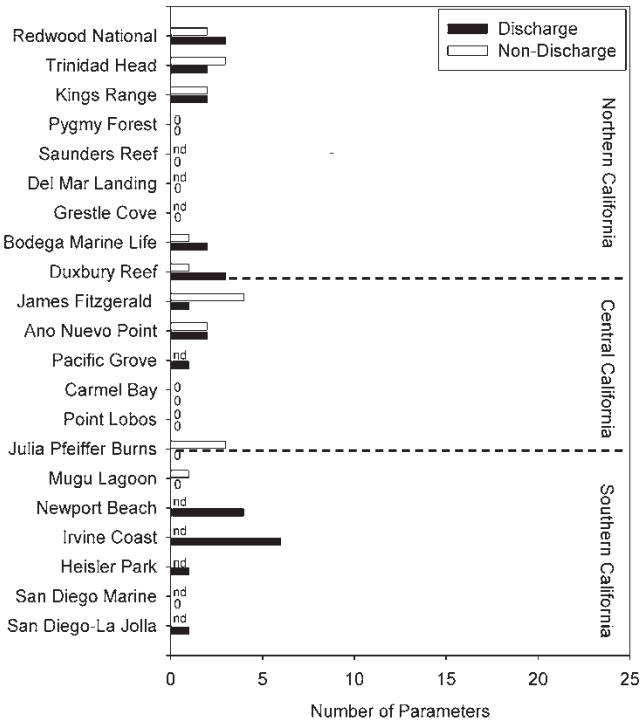

Figure 4. Number of parameters (out of 25) that exceeded State Water Quality Standards (six month median for ammonia and trace metals, 30-day average for trace organics, SWRCB 2005), and had post-storm concentrations greater than pre-storm concentrations, in each of the sampled Areas of Special Biological Significance (ASBS). Data are presented for both the discharge and non-discharge strata. '0' = no parameters exceeded water quality standard (WQS); 'nd' = no data.

inside or outside of ASBS may impact non-discharge shoreline. The influence of distant sources, at least for these two target analytes, was obvious.

An alternative hypothesis is that applying long-term WQS to short-term events, like storm events, are not appropriate in the nearshore zone. California has several short-term thresholds including instantaneous maximum, daily maximum, and additional long-term thresholds such as the 30-day average (for trace organics) or six-month median (for ammonia and trace metals). However, it is standard regulatory practice to use even single samples to evaluate the long-term thresholds when additional data are not available. In the case of this study, even the most problematic target analytes (total PAH and total chromium, both of which have natural and anthropogenic sources) did not exceed the short-term thresholds. It was application of the long-term thresholds, whose benchmark concentrations are much lower, when WQS exceedences became problematic. For this reason, a more appropriate measure might be "natural water quality" as designated in state policy. Natural water quality, while attractive, has its own set of technical and political challenges. Since no statewide data exists from natural (e.g., reference) sites, additional data collection would be necessary.

Finally, the notably good water quality on a statewide basis was not evenly distributed throughout the state. Some ASBS exceeded WQS standards at a much greater frequency and these regions should likely receive further attention. For example, sites in southern California fared worse than their northern or central California counterparts. This may be due, in part, to the intense urbanization of the southern region. More than 20 million people live in southern California and coastal development pressure is intense (Ackerman and Schiff 2003). In the statewide survey of storm drain discharges to ASBS, over 46% occurred in southern California. In fact, so much development occurs in southern California coastal watersheds that the non-discharge stratum (defined as >500 m from drain discharges 18 inches and greater) did not exist in southern California.

Literature Cited

Ackerman, D. and K. Schiff. 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 Edition. American Public Health Association. Washington, DC.

Arnold, W.R., R.C. Santore, and S. Cotsifas. 2005. Predicting copper toxicity in estuarine and marine waters using the Biotic Ligand Model. *Marine Pollution Bulletin* 50:1634-1640.

Bay, S., B. Jones, K. Schiff, and L. Washburn. 2003. Water quality impacts of stormwater discharges to Santa Monica Bay. *Marine Environmental Research* 56:205-223.

Boesch, D., R. Burroughs, J. Baker, R. Mason, C. Rowe, and R. Siefert. 2001. Marine pollution in the United States. A report to the PEW Oceans Commission. Arlington, VA.

Bricker, S., C. Clement, D. Pirhalla, S.P. Orlando, and D. Farrow. 1999. National estuarine eutrophication assessment: effects of nutrient

enrichment in the nation's estuaries. National Oceanic and Atmospheric Administration (NOAA). Silver Spring, MD.

Caillaud, J., D. Proust, S. Philippe, C. Fontaine, and M. Fialin. 2009. Trace metals distribution from a serpentinite weathering at the scales of the weathering profile and its related weathering microsystems and clay minerals. *Geoderma* 149:199-208.

Culliton, T. 1998. Population: distribution, density and growth. State of the Coast Report. National Oceanic and Atmospheric Administration (NOAA). Silver Spring, MD.

Environmental Protection Agency (EPA). 1995. Short-term methods for estimating the chronic toxicity of effluents and receiving waters to west coast marine and estuarine organisms. EPA 600/R-95/136. United States Environmental Protection Agency, Office of Research and Development. Cincinnati, OH.

Environmental Protection Agency. 1996. Method 1640: determination of trace metal elements in ambient waters by on-line chelation preconcentration and inductive coupled plasma-mass spectrometry. United States Environmental Protection Agency, Office of Water, Engineering and Analysis Division. Washington, DC.

Environmental Protection Agency. 2005. National coastal condition report. EPA 620/R-03/002. United States Environmental Protection Agency, Office of Wetlands, Oceans, and Watersheds. Washington, D.C.

Hoffman, E., G. Mills, J. Latimer, and J. Quinn. 1984. Urban runoff as a source of polycyclic aromatic hydrocarbons to coastal waters. *Environmental Science & Technology* 18:580-587.

Jenkins, S. and J. Wasyl. 2007. Hydrodynamic simulations of shoreline discharges of laboratory seawater and storm water at Scripps Beach, CA. Report to: Facilities Design and Construction, University of California, San Diego. La Jolla, CA

Leifer, I., B. Luyendyk, and K. Broderick. 2006. Tracking an oil slick from multiple natural sources, Coal Oil Point, California. *Marine Petroleum Geology* 23:621-630.

National Oceanic and Atmospheric Administration (NOAA). 2008. Framework for the national system of marine protected areas of the United State of America. Silver Spring, MD.

O'Connor, T. 1998. Mussel watch results from 1986 to 1996. *Marine Pollution Bulletin* 37:14-19.

Sabin, L.D., K.A. Maruya, W. Lao, D.W. Diehl, D. Tsukada, K.D. Stolzenbach, and K.C. Schiff. 2009. Exchange of polycyclic aromatic hydrocarbons between the atmosphere, water, and sediment in southern California coastal embayments. *Environmental Toxicology & Chemistry* 29:265-274.

Southern California Coastal Water Research Project (SCCWRP). 2003. Discharges into state water quality protected areas. Final Report to the State Water Resources Control Board. Southern California Coastal Water Research Project. Westminster, CA.

State Water Resources Control Board (SWRCB). 2005. California ocean plan. Sacramento, CA.

Stein, E.D., L.L. Tiefenthaler, and K.C. Schiff. 2006. Watershed-based sources of polycyclic aromatic hydrocarbons in urban storm water. *Environmental Toxicology & Chemistry* 25:373-385.

Stevens, D. 1997. Variable density grid-based designs for continuous spatial populations. *Envirometrics* 8:167-195.

Thompson, S.K. 1992. Sampling. John Wiley and Sons. New York, NY.

Tiefenthaler, L.L., E.D. Stein, and K.C. Schiff. 2008. Watershed and land use-based sources of trace metals in urban stormwater. *Environmental Toxicology & Chemistry* 27:277-287.

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