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# Impacts of stormwater runoff in the Southern California Bight: Relationships among plume constituents

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## ABSTRACT

The effects from two winter rain storms on the coastal ocean of the Southern California Bight (SCB) were examined during February 2004 and February-March 2005. The impacts of stormwater from fecal indicator bacteria, water column toxicity, and nutrients were evaluated for five major river discharges: the Santa Clara River, Ballona Creek, the San Pedro Shelf (including the Los Angeles, San Gabriel, and Santa Ana Rivers), the San Diego River and the Tijuana River. Exceedances of bacterial standards were observed in most of the systems. However, the areas of impact were generally spatially limited, and contaminant concentrations decreased below California Ocean Plan (COP) standards typically within 2 to 3 days. The largest bacterial concentrations occurred in the Tijuana River system, where fecal indicator bacteria (FIB) exceedances were noted well away from the river mouth. Maximum nitrate concentrations (~40  $\mu\text{M}$ ) occurred in the San Pedro Shelf region near the mouth of the Los Angeles River. Based on the results of general linear models, individual sources of stormwater differ among nutrient concentrations and FIB concentration and composition. While nutrients appeared to decrease in plume waters due to simple mixing and dilution, FIB concentrations in plumes depend on more than loading and dilution rates. The relationships between contaminants (nutrients and FIB) and plume indicators (salinity and total suspended solids (TSS)) were not strong indicating the presence of other potentially important sources and/or sinks for

both nutrients and FIB. The COP standards were often exceeded in waters containing greater than 10% stormwater (<28 - 30 salinity range). Median concentration dropped below the standard 32 - 33 salinity range (1 - 4% stormwater) for total coliforms and *Enterococcus* sp., and the 28 - 30 salinity range (10 - 16% stormwater) for fecal coliforms. Nutrients showed a similar pattern with the highest median concentrations in water containing greater than 10% stormwater. Relationships between colored dissolved organic matter (CDOM) and salinity, and between TSS and beam attenuation indicated that readily measurable, optically active variables can be used as proxies to provide at least a qualitative, if not quantitative, evaluation of the distribution of dissolved, and particulate components of stormwater plumes. In this context, both CDOM absorption and the beam attenuation coefficient can be derived from satellite ocean color measurements of inherent optical properties, suggesting that remote sensing of ocean color should be useful in mapping the spatial areas and duration of impacts from these contaminants.

## INTRODUCTION

The monitoring and improvement of water quality is a major issue for local, state, and federal agencies and organizations. Coastal waters provide numerous beneficial uses including recreation, commercial and sport fisheries, marine habitat, commerce and transportation, and aesthetic enjoyment. In southern California, approximately \$9 billion of

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coastal communities' local economies come from ocean-dependent activities (Bay *et al.* 2003). A broad range of chemical and biological contaminants is discharged into coastal waters of the SCB, including: pesticides, fertilizers, trace metals, synthetic organic compounds, suspended sediments, inorganic nutrients, and human pathogens (National Research Council 1990). Reductions in water quality due to these discharges can adversely affect the beneficial uses of the receiving waters and affect the local coastal economies.

Flood events due to rain storms contribute more than 95% of the total runoff volume annually to the coastal zone (Schiff *et al.* 2000). Surface runoff, which receives no treatment prior to discharge into ocean waters, is one of the largest sources of contaminants to the SCB (Schiff *et al.* 2000). Many studies of stormwater runoff conducted in southern California have focused on public health issues, such as human pathogens and contaminants (Schiff *et al.* 2002). Beach closures due to high FIB levels and other indicators of human pathogens have been common during and immediately following rain events (Geesey 1993). Public health officials currently advise the public to avoid any contact with stormwater runoff for at least 72 hours following a significant storm event (CDPH 2006). Evidence of high levels of toxicity associated with urban runoff, especially stormwater runoff, has also been noted in several southern California regions (Bay *et al.* 2003, Gersberg *et al.* 2004). Even the high levels of sediment themselves can cause environmental damage through several mechanisms such as smothering of benthic organisms, reduction of visual clarity, irritation of fish gills, and reduction of light available for photosynthesis (Davies-Colley and Smith 2001). Proper management of these parameters is important for restoring and maintaining healthy beaches, marinas, bays, and coastal areas.

Both *in situ* and satellite remote sensing studies of stormwater plumes in the SCB have shown that plumes created from pulses of stormwater runoff can affect large areas, penetrate up to 10 m into the water column, and persist for days to weeks (Washburn *et al.* 2003, Nezlin *et al.* 2005). Although the spatial and temporal extent of stormwater plumes have begun to be examined, the extent of impact from human pathogens, nutrients, and toxicants is not well known (e.g., Nezlin *et al.* 2008). Runoff plumes have the potential, however, to disperse these constituents over large distances (Warrick *et al.* 2007),

especially small particles and dissolved materials that remain in the surface waters.

The COP and Assembly Bill 411 define the current standards required by the state of California for beach monitoring (State Water Resources Control Board 2005). Beach posting is recommended, and in some cases required, when single FIB samples exceed these standards. The accepted monitoring protocols involve collection of water samples that are evaluated for FIB using assays that require 24 to 48 hours to complete, thus limiting the number of samples that can be practically analyzed. It is impossible to adequately and routinely sample plumes by collecting water samples from a few locations limited by sampling capabilities and resources. Remotely sensed ocean color could be used as a way to track stormwater plumes over large spatial scales with high temporal frequency (e.g., Nezlin and DiGiacomo 2005; Nezlin *et al.* 2005, 2007, 2008). Knowledge of the distribution and fate of contaminants within the plumes is still limited and a focus of this study.

Based on data collected by the Sea-viewing Wide Field-of-view Sensor (SeaWiFS) and the Moderate-resolution Imaging Spectroradiometer (MODIS), remote sensing studies of stormwater plumes have used reflectance from the near-surface layer, typically measured as normalized water-leaving radiance in the range 551 to 555 nm (nLw551 for MODIS and nLw555 for SeaWiFS), as a tracer of plumes in the southern California coastal area. Remote sensing reflectance at these wavelengths is primarily a function of light backscattering from small particles, and is therefore related to turbidity. By analyzing SeaWiFS imagery, Nezlin and DiGiacomo (2005) concluded that measurements of nLw555 greater than  $1.3 \text{ mW cm}^{-2} \mu\text{m}^{-1} \text{ sr}^{-1}$  distinguished stormwater plumes from ambient water on the San Pedro Shelf. As turbidity is associated with sediment particles, the majority of which quickly sink from surface waters (Hill *et al.* 2000, Warrick *et al.* 2004), turbidity can only be used as a short-term, non-conservative tracer to follow the particulate components of stormwater plumes. The actual freshwater plume could be much more extensive than the sediment plume (Geyer *et al.* 2000). Chromophoric CDOM, defined as the light-absorbing fraction of dissolved organic matter, is a conservative tracer and not subject to sedimentation. Decreases in its concentration occur through the process of photodegradation, which takes between weeks and months to

occur (Vodacek *et al.* 1997, Opsahl and Benner 1998). Rivers constitute a major source of CDOM in the coastal ocean (Siegel *et al.* 2002, Del Castillo 2005); therefore, CDOM concentration is useful in tracking freshwater plumes and can be used to assess the impact of river-borne contaminants such as nutrients and pollutants in the coastal ocean (Coble *et al.* 2004). Like turbidity, CDOM can also be estimated from ocean color, but is more likely to be associated with dissolved plume constituents rather than particulate fractions.

In this study, two aspects of the impact of stormwater plumes on the continental shelf of the SCB were addressed. First, an attempt was made to determine the magnitude and area of impact of contaminants (nutrients and FIB) in the coastal zone based on ship-based sampling. Second, the utility of variables that can be derived from remotely sensed measurements of ocean color (e.g., CDOM and beam attenuation) to estimate the distribution and impacts of runoff plumes in the coastal area was evaluated. The correlation was examined between known contaminants and components that can be readily measured using ocean color data, to evaluate the extent to which remotely sensed ocean color can be

used to infer the magnitude and spatial extent of plume impacts.

## METHODS

### Field Collections

Seven agencies participated in field collections: City of Oxnard/ABC Labs, City of Los Angeles, Los Angeles County Sanitation District, Weston Solutions (formerly MEC Analytical Systems, Inc.), Orange County Sanitation District, City of San Diego, and Universidad Autónoma de Baja California. Shipboard sampling for this study occurred on grids offshore of five regions (including eight major river systems) in the SCB (Figure 1). Storm 1 took place on 25 February 2004, which is considered Day 0 in the following analyses. For the San Diego and Tijuana Rivers, an earlier storm that ended on 23 February was also sampled. Storm 2 occurred on 22 March 2005 (Day 0). A separate storm that ended on 12 February 2005 was sampled offshore of the San Diego and Tijuana Rivers. Stations were scheduled to be sampled on Days 1, 3, and 5 after Storm 1, and on Days 1, 2, and 3 after Storm 2. However, sampling was sometimes shifted forward or back a day depending on sampling condi-

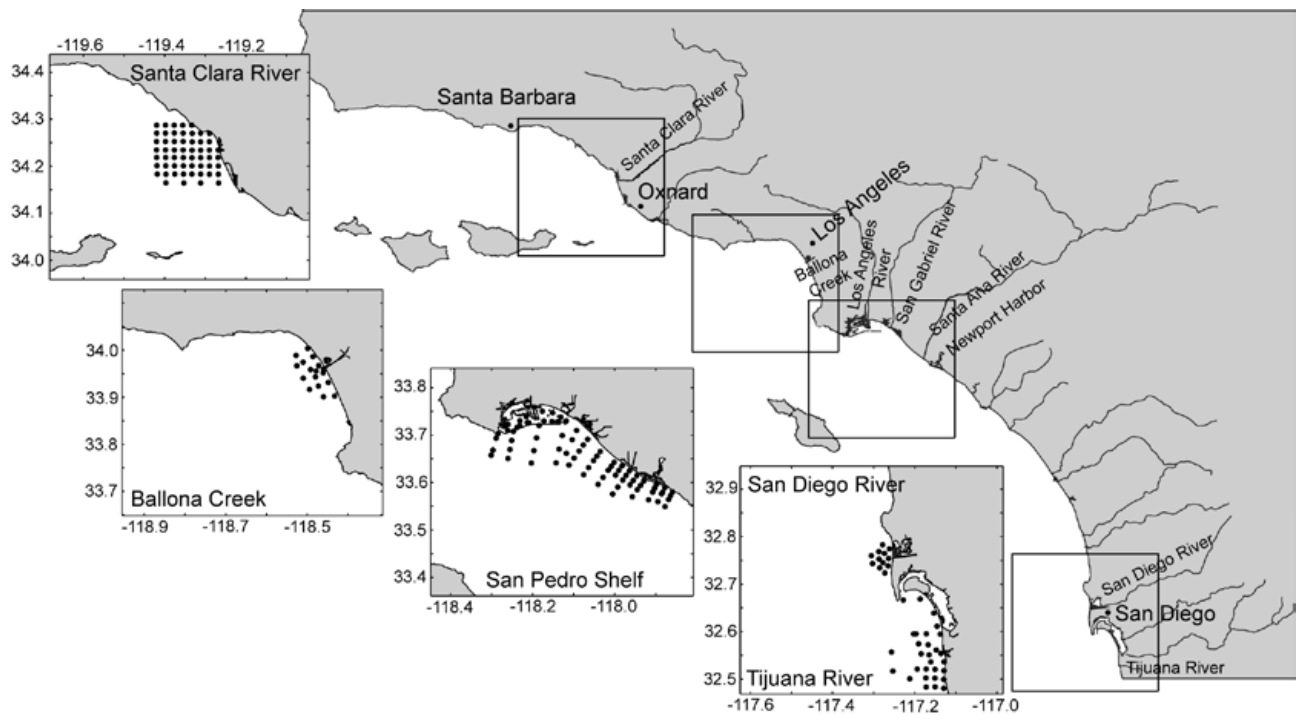


Figure 1. Map of the Southern California Bight indicating regions sampled during the study. Note that the San Pedro Shelf region was broken into the Los Angeles/San Gabriel Rivers, the Santa Ana River, and Newport Harbor for correlation analyses. Black dots indicate locations of stations sampled during the field sampling effort.

tions and vessel/crew availability. Not all sites were sampled on all days largely due to limitations from weather and sea-state.

Vertical profiles of conductivity and temperature (Sea-Bird SBE 25 or SBE 9/11), beam attenuation (WET Labs C-Star transmissometer) and CDOM fluorescence (WET Labs WETStar) were collected at each station. The instrument and manufacturer are given in parentheses; note that several different instruments were used among the seven participating agencies. Beam attenuation was computed from transmissometer observations as the beam attenuation coefficient at 660 nm (hereafter referred to as beam-c). CDOM fluorescence was converted to quinine sulfate dehydrate (QSD) concentration (in ppb) using linear calibrations provided by the manufacturer. Water samples for TSS, macronutrients ( $\text{NO}_2$ ,  $\text{NO}_3$ ,  $\text{PO}_4$ ,  $\text{SiO}_4$ ), FIB and toxicity were also collected using 5-L Niskin bottles attached to the CTD carousel or by stringing individual bottles on a line in lieu of using a rosette. These samples were collected at 1 m depth at all stations. Multiple depths were sampled at three stations for each river system. Sampling occurred on regularly spaced grids for each region (Figure 1). The primary intent of the grids was to sample the nearshore discharge areas and assess water quality there, not necessarily to fully encompass and track plumes as they advected away from the river mouth regions. Some stations were positioned further offshore and were intended to provide “non-plume” profiles for comparative purposes. Profiles were obtained to within 2 m of the seabed or to a depth of 60 m for sites deeper than 60 m. Figures of the spatial distributions of nutrients and FIB were created using Interactive Graphical Ocean Database System (IGODS; Ocean Software 2009).

Samples for the measurement of macronutrients and TSS were analyzed at the University of Southern California. The  $\text{NO}_2$ ,  $\text{NO}_3$ ,  $\text{PO}_4$ ,  $\text{SiO}_4$  concentrations were measured on an Alpkem RFA 300 Series nutrient analyzer (Sakamoto *et al.* 1990, Gordon *et al.* 1993). The bulk concentration of TSS was determined using EPA method 160.2 (USEPA 1983). Briefly, whole water samples were filtered through pre-weighed Whatman GF/F (0.7  $\mu\text{m}$ ) filters. The filters were then dried at 100°C for 2 hours and re-weighed. FIB concentrations were measured by six of the participating agencies according to each agency's standard procedures. Prior to sampling, all laboratories participated in an inter-calibration exercise to ensure comparability. The among-laboratory

variability was not significantly different from variability within each laboratory (Griffith *et al.* 2006). Samples were collected in sterile 120-ml polystyrene bottles and transported to local laboratories on ice. The concentration of total coliforms and fecal coliforms were determined using standard methods for multiple-tube fermentation - APHA methods 9221B and 9221E.1, or membrane filtration - APHA methods 9222B and 9222E (APHA 1998a, 1998b, 1998c, 1998d). *Enterococcus* spp. were enumerated using Enterolert™ (IDEXX Westbrook, ME) defined substrate kits following the manufacturer's instructions, or using membrane filtration and EPA Method 1600 (Messer and Dufour 1998). Toxicity was measured as percent fertilization in the sea urchin fertilization assay (USEPA 1995). In this method, sea urchin sperm are exposed to the sample, and the ability of the sperm to fertilize the egg is evaluated. Significant toxicity was chosen to be those values where sea urchin fertilization success was less than 84% (Bay *et al.* 2003).

## Data Analyses

To examine the fate of various contaminants in relation to stormwater plumes, relationships of contaminants to salinity and TSS were explored. The contaminants measured include nitrate ( $\text{NO}_3^-$ ), nitrite ( $\text{NO}_2^-$ ), phosphate ( $\text{PO}_4^{3-}$ ), silicate ( $\text{SiO}_4$ ), FIB (total coliforms, fecal coliforms, and *Enterococcus* spp.), and toxicity (measured as percent fertilization in the sea urchin assay). Stations were separated into regional groupings based on their proximity to major sources of inflow. For the three regions in the San Pedro Shelf area (Los Angeles/San Gabriel Rivers, Santa Ana River, and Newport Harbor), stations were grouped by examining nearshore salinity data. Note that these regions were not analyzed individually in the spatial analyses, but were grouped as the San Pedro Shelf. General linear models (GLMs) were constructed for each contaminant for each storm. Salinity or TSS (continuous), region (categorical), and day after storm (categorical) were included in the models as independent variables. Only data from the top 5 m were included as the majority of stormwater is found within this depth (Washburn *et al.* 2003). Because the number of ship-based samples was very high (250 - 376), P-values were generally low and were not always useful in distinguishing model fit. We therefore focused on improvements to other parameters such as the coefficient of determination ( $R^2$ ) when selecting the best models. The

adjusted  $R^2$  was considered to account for erroneous improvements in model fit due to the inclusion of additional independent variables. Statistical analyses were done using SYSTAT™ v. 11.0 (SSI 2004b).

Approximately 28, 56, and 59% of the total coliform, fecal coliform, and *Enterococcus* spp. data, respectively, were recorded as being below 1 of 3 detection limits (10 and 100 most probable number (MPN)/100 ml for total and fecal coliforms; 10 and 20 MPN/100 ml for *Enterococcus* spp.). An additional 7 total coliform values (approximately 1%) were reported as >80,000 MPN/100 ml. A small number of nitrite and nitrate samples were also recorded as being below a detection limit (0.1 and 0.05  $\mu\text{M}$ , respectively). Data values known only to be above or below a threshold value are referred to as censored data. Censored data cannot be analyzed using standard statistical methods. Instead, the data were analyzed using the methods of Helsel (2005) through the S-language software package NADA, an add-on package for the R environment for statistical computing (R Development Core Team 2006). These methods can be used to analyze multiply-censored data sets (data sets with multiple detection limits) with up to 80% censored data. However, the program only supports left-censored data. Therefore, the 7 total coliform data points reported as >80,000 MPN/100 ml were replaced with the value 80,000 MPN/100 ml. Though this will introduce some error, these values represent such a small proportion of the data set that this error is expected to be small. For data sets containing censored data, GLMs were constructed using the `cenreg` function in NADA. This function computes GLM parameters (e.g., slope and intercept) using maximum likelihood estimation (MLE). The MLE assumes that data above and below the detection limit follow a particular distribution. Parameters are computed that best match a fitted distribution to the observed values above each detection limit and to the percentage of data below each limit (Helsel 2005). The `cenreg` function also estimates the likelihood  $R^2$  (similar to  $R^2$  in linear regression), the log-likelihood statistic, and the associated P-value.

In addition to GLM analyses, contaminant data were examined by grouping the data into several salinity and TSS ranges, then calculating the summary statistics for each group. Box plots were created showing the median and spread of data within each group. For all uncensored data, box plots were created using SigmaPlot v. 9.01 (SSI 2004a). For

groups containing censored data, summary statistics were calculated using the censored regression on order statistics (ROS) method (Lee and Helsel 2005). ROS is a probability plotting and regression procedure that models censored distributions using a linear regression model of observed concentrations vs. their normal quantiles. This method has been evaluated as one of the most reliable procedures for developing summary statistics of multiple-censor data (Shumway *et al.* 2002). Censored box plots were created using the NADA package for R.

The relationships between *in situ* tracers of plume water and variables that can be estimated using ocean color data from satellite imagery were also explored. The best *in situ* tracer of freshwater plumes is salinity. Because evaporation will have a minimal effect over the time spans of storm events, surface salinity acts as a conservative tracer of freshwater runoff. Salinity is not currently measured using satellite imagery. Other dissolved constituents with high concentrations in stormwater, such as CDOM, can be estimated using satellite ocean color. Therefore, the *in situ* relationship between salinity and CDOM was explored to determine whether salinity could ultimately be approximated from CDOM via satellite ocean color observations (Monahan and Pybus 1978, D'Sa *et al.* 2002, Busse *et al.* 2006). Turbidity is another commonly used tracer of stormwater plumes. Turbidity can be measured *in situ* by measuring the concentration of TSS in bulk water samples or optically with a transmissometer that measures beam-c. Whereas salinity and CDOM represent the dissolved components of the plume, TSS and beam-c represent the particulate components. Again, TSS cannot be measured directly from satellites, but beam-c can be estimated from ocean color data. GLMs were constructed with salinity or TSS, region, and day after storm as independent variables and CDOM or beam-c as the dependent variable. The number of samples was very high (276 - 1030); therefore, focus was placed on adjusted  $R^2$  values when selecting the best models.

## RESULTS

The first part of this study's results evaluates the spatial and temporal extent of contaminant impacts in the SCB, specifically FIB, toxicity, and nutrients. The second part considers the use of remotely sensed ocean color for the evaluation of plume impacts based on the ability to estimate water quality param-

eters of interest from satellite ocean color observations using *in situ* satellite proxy relationships to infer spatial and temporal scales of stormwater impacts. The third part examines relationships between the contaminants and readily measured, and commonly used *in situ* water quality parameters that are considered robust tracers of stormwater plumes (salinity, TSS), and addresses the question of the extent to which these parameters can be used as a proxy for contaminants of concern.

### **Spatial and Temporal Extents of Impact**

The two sets of contaminants for which either a receiving water standard or environmental impact threshold exists are FIB and toxicity as measured by the sea urchin fertilization test. Tables 1 and 2 summarize the number of samples and exceedances of these thresholds that occurred for each of the five major river discharges that were studied (Santa Clara River, Ballona Creek, San Pedro Shelf, San Diego River, and Tijuana River). Nutrient distributions were also examined, but regulatory standards do not currently exist for these runoff constituents.

#### *Fecal Indicator Bacteria*

Over 2000 water samples were analyzed for FIB from all surveys and river systems combined. Elevated FIB concentrations were found offshore of every major river system following both storm events, although the COP standards were not always exceeded (Figure 2). Nearly all of the FIB exceedances occurred in the top 10 m of the water column and in the very nearshore region of the discharge. In 2004, less than 10% of the samples exceeded the COP standards offshore each of the river systems (Table 1). Exceedances tended to be highest during the first day after the storm, but were sometimes higher on Day 2, especially near the Tijuana River during Storm 2 (2005). The extent of FIB impact was greatly reduced or absent by the third or fourth day of sampling. Of the three FIB examined, the *Enterococcus* spp. threshold was most often exceeded. During 2005, the total number of exceedances across all river systems increased (from 7.2% in 2004 to 13% in 2005). However, this was the result of a large increase in exceedances of all FIB thresholds offshore of the Tijuana River, where the standards were exceeded in 49% of the samples. Exceedances offshore of the Santa Clara River, Ballona Creek, and the San

Pedro Shelf in 2005 were similar or less than those in 2004.

The extent of impacts due to FIB varied among regions. The San Pedro Shelf region and the Tijuana River regions showed the largest areas of impact. During both storms, a large proportion of stations sampled offshore of the Tijuana River (up to 78%) exceeded the single sample standard on at least one day for each FIB group (Table 1; Figure 2). This suggests that the sampling area may not have been large enough to encompass the entire affected area. Whereas exceedances in all other regions were confined near major inflows, exceedances near the Tijuana River spanned a large area (Figure 2). Coastal areas near the Santa Clara and San Diego Rivers appeared to be the least affected during both storms (Table 1). However, it is conceivable that by the time of sampling, the plumes had advected away from the sampling areas, especially in the Santa Clara River region.

#### *Nutrients*

The distributions of nutrients offshore of the major regions after each storm tended to mirror FIB distributions. High concentrations were typically found near the river mouths, and nutrient concentrations tended to decrease and disperse over time (Figure 3). Maximum  $\text{NO}_3^-$  concentrations ( $\sim 40 \mu\text{M}$ ) were found in the San Pedro Shelf region at the mouth of the Los Angeles River. Concentrations of 10 - 15  $\mu\text{M}$  were also observed off the mouths of Ballona Creek and the Santa Clara River. In the San Diego region, concentrations were elevated less than 10  $\mu\text{M}$ . The maximum near-surface nutrient concentrations were greater in 2004 than in 2005. Storm sampling in 2004 occurred one month earlier than in 2005. It is possible that many watersheds had been flushed out by earlier storm events prior to sampling in 2005 resulting in an overall decrease in nutrient loading from that storm. Another apparent difference between the two years was the higher concentrations of nutrients below 10 m in 2005. These higher concentrations may be due to upwelling occurring along the coast, which usually begins in mid to late March in this region.

#### **Toxicity**

Of the over 700 water samples that were analyzed for toxicity by the sea urchin fertilization assay from all surveys and river systems combined, very few exhibited toxicity (Table 2). Only 30 samples

**Table 1. Summary of the number of single sample FIB exceedances by day for the first (Storm 1 = 2004) and second (Storm 2 = 2005) storm events. Numbers in parentheses indicate total number of stations sampled. n.d. = no data.**

	Santa Clara River	Ballona Creek	San Pedro Shelf	San Diego River	Tijuana River	Total
<b>Storm 1</b>						
Total Coliforms <sup>a</sup>						
Day 1	n.d.	2 (8)	4 (38)	0 (18)	7 (18)	13 (82)
Day 2	n.d.	0 (23)	4 (74)	n.d.	0 (16)	4 (113)
Day 3	0 (18)	n.d.	n.d.	0 (18)	1 (37)	1 (73)
Day 4	n.d.	0 (23)	0 (78)	0 (18)	2 (35)	2 (154)
Fecal Coliforms <sup>b</sup>						
Day 1	n.d.	2 (8)	1 (14)	0 (18)	8 (18)	11 (58)
Day 2	n.d.	0 (23)	1 (50)	n.d.	0 (16)	1 (89)
Day 3	0 (18)	n.d.	n.d.	0 (18)	3 (37)	3 (73)
Day 4	n.d.	0 (23)	0 (54)	0 (18)	1 (35)	1 (130)
<i>Enterococcus</i> spp. <sup>c</sup>						
Day 1	n.d.	2 (8)	10 (38)	0 (18)	14 (18)	26 (82)
Day 2	n.d.	3 (23)	6 (74)	n.d.	6 (16)	15 (113)
Day 3	0 (18)	n.d.	n.d.	0 (18)	4 (37)	7 (73)
Day 4	n.d.	0 (23)	2 (78)	1 (18)	2 (35)	2 (154)
TOTAL	0 (54)	9 (162)	28 (498)	1 (162)	48 (318)	86 (1194)
% of samples	0%	5.60%	5.60%	0.60%	15%	7.20%
<b>Storm 2</b>						
Total Coliforms <sup>a</sup>						
Day 1	n.d.	3 (10)	0 (26)	n.d.	9 (18)	12 (54)
Day 2	0 (20)	0 (23)	1 (28)	n.d.	11 (18)	12 (89)
Day 3	0 (20)	0 (23)	0 (80)	n.d.	4 (18)	4 (141)
Day 4	0 (20)	n.d.	n.d.	n.d.	n.d.	0 (20)
Fecal Coliforms <sup>b</sup>						
Day 1	n.d.	3 (10)	n.d.	n.d.	14 (30)	17 (40)
Day 2	0 (20)	0 (23)	0 (28)	n.d.	16 (30)	16 (101)
Day 3	0 (20)	0 (23)	0 (54)	n.d.	1 (18)	1 (115)
Day 4	0 (20)	n.d.	n.d.	n.d.	n.d.	0 (20)
<i>Enterococcus</i> spp. <sup>c</sup>						
Day 1	n.d.	3 (10)	3 (26)	n.d.	17 (30)	23 (66)
Day 2	0 (20)	0 (23)	0 (28)	n.d.	23 (30)	23 (101)
Day 3	1 (20)	0 (23)	1 (80)	n.d.	7 (18)	9 (141)
Day 4	1 (20)	n.d.	n.d.	n.d.	n.d.	1 (20)
TOTAL	2 (180)	9 (168)	5 (350)	n.d.	102 (210)	118 (808)
% of samples	1.10%	5.40%	1.40%	n.d.	49%	13%

<sup>a</sup>Total coliform COP single sample standard = 10,000 MPN/100 ml  
<sup>b</sup>Fecal coliform COP single sample standard = 400 MPN/100 ml  
<sup>c</sup>*Enterococcus* spp COP single sample standard = 104 MPN/100 ml

were considered toxic (<84% fertilization), and only 2 samples exhibited highly toxic effects (<50% fertilization). All of these were located in the top 10 m of the water column. The greatest number of toxic samples was observed in the Tijuana River plume on the first day of sampling during the February 2004

event, when the fertilization rate for 13 out of 18 samples (72%) was less than 84%. In contrast, during February 2005 when high bacteria concentrations were observed in the Tijuana River plume, no toxicity values less than 84% fertilization were observed in the plume.

**Table 2. Summary of toxicity evaluation (as percent fertilization in the sea urchin assay) by day and sampling region for the first (Storm 1 = 2004) and second (Storm 2 = 2005) storm events. Significant toxicity was chosen to be samples for which fertilization was less than 84% (Bay et al. 2003). n.d. = no data.**

	Santa Clara River			Battiona Creek			San Pedro Shelf			San Diego			Tijuana River			Total		
	>84	84-50		>84	84-50		>84	84-50		>84	84-50		>84	84-50		>84	84-50	
		<50	n.d.		n.d.	<50		n.d.	<50		n.d.	<50		n.d.	<50		n.d.	<50
<b>Storm 1</b>																		
Day 1	n.d.	n.d.	n.d.	8	0	0	37	1	0	15	2	1	5	13	0	65	16	1
Day 2	n.d.	n.d.	n.d.	22	1	0	72	2	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	94	3	1
Day 3	18	0	0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	18	0	0	18	0	0	54	0	0
Day 4	n.d.	n.d.	n.d.	21	2	0	74	4	0	18	0	0	17	1	0	130	7	0
TOTAL	18	0	0	51	3	0	183	7	1	51	2	1	40	14	0	343	26	2
% of samples	100	0	0	94.5	5.5	0	96	3.5	0.5	94.4	3.6	2	74	26	0	92.5	7	0.5
<b>Storm 2</b>																		
Day 1	n.d.	n.d.	n.d.	11	0	0	52	2	0	n.d.	n.d.	n.d.	16	0	0	81	2	0
Day 2	20	0	0	23	0	0	28	0	0	n.d.	n.d.	n.d.	18	0	0	89	0	0
Day 3	20	0	0	23	0	0	80	0	0	n.d.	n.d.	n.d.	18	0	0	141	0	0
Day 4	20	0	0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	20	0	0
TOTAL	60	0	0	57	0	0	160	2	0	n.d.	n.d.	n.d.	54	0	0	331	2	0
% of samples	100	0	0	100	0	0	99	1	0	n.d.	n.d.	n.d.	100	0	0	99.4	0.6	0

### ***In situ* Relationships: CDOM vs. Salinity and Beam-c vs. TSS**

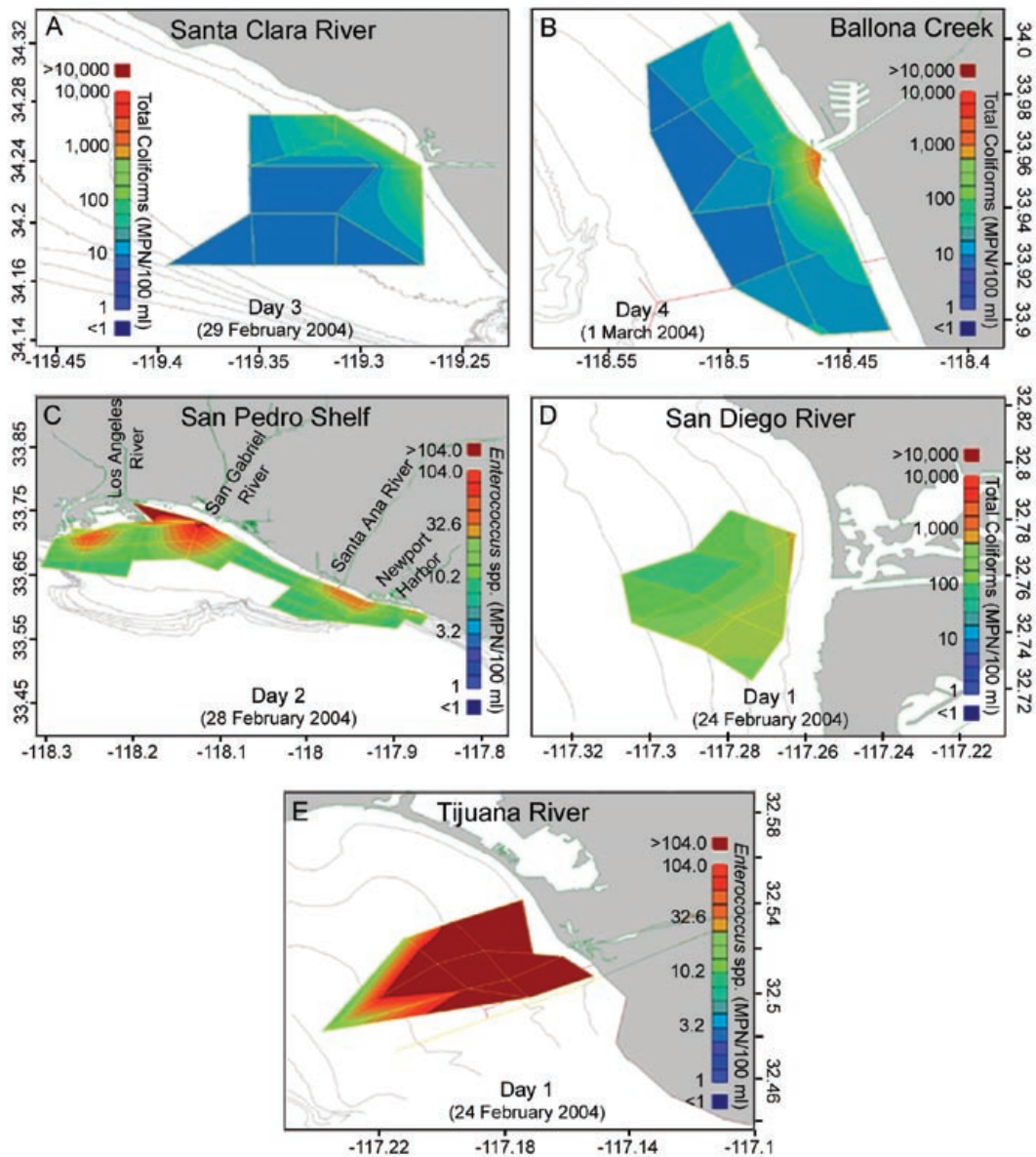
CDOM concentration generally increased linearly with decreasing salinity or increased freshwater content (Figure 4). The opposite trend was observed in the beam-c vs. TSS relationship. Beam-c generally increased with increasing TSS concentration, with some scatter around the best-fit lines (Figure 5). The addition of regions as an independent variable greatly improved the CDOM/salinity models (increase in adjusted R<sup>2</sup> of ~0.1), and the addition of day after storm resulted in a slight further improvement (increase in adjusted R<sup>2</sup> of 0.01 to 0.04; Table 3). The addition of both region and day after storm improved the beam-c vs. TSS relationships (increase in adjusted R<sup>2</sup> of 0.04 to 0.06 and 0.03 to 0.05, respectively; Table 3). The CDOM vs. salinity relationship was consistently strong (adjusted R<sup>2</sup> ~0.6 for both storms; Table 3). The relationship between beam-c and TSS, however, varied considerably between the two storm events (adjusted R<sup>2</sup> ranged from 0.4 to 0.7; Table 3).

In analyzing the CDOM vs. salinity relationship, a subset of the samples demonstrated increased CDOM fluorescence with little to no change in salinity (river mouth subset; Figure 4). Samples within this subset were collected at three stations in the Los Angeles/San Gabriel River region and three stations near Newport Harbor during the 2004 storm event. Four of the six stations were only sampled in 2004. These stations were relatively shallow and were located either just inside or just outside major river mouths. At these stations, CDOM fluorescence was generally high at all depths even though low-salinity waters indicative of stormwater runoff were noted only in surface waters (the top 1 or 2 m).

### ***In situ* Contaminant Relationships with Salinity and TSS**

Relationships of nutrients and salinity were variable but were generally negative, i.e., increasing nutrient concentrations with decreasing salinity (Table 4). The addition of region as an independent variable again greatly improved most relationships. The addition of day after storm also improved the models, but in many cases only slightly. Even when both region and day after storm were included; however, the models only explained up to half of the variation in the nutrient data (adjusted R<sup>2</sup> or likelihood R<sup>2</sup> = 0.26 to 0.55; Table 4). Although the data were variable, nutrient concentrations appeared to





**Figure 2. Spatial distributions of FIB for each of the five major regions following Storm 1 (2004). Similar patterns were observed during Storm 2 (2005). Dark red represent areas where a California Ocean Plan standard was exceeded. Note that color bars are plotted on log scale.**

decrease as the fraction of stormwater decreased (Figure 6 A through D). The largest decrease in all nutrients occurred in the 32 to 33 psu (1 - 4% stormwater) salinity range where median nutrient concentrations were 2 to 3 times lower than in the next lower salinity range (30 to 32 psu; 4 - 10% stormwater). Not surprisingly, the relationships between nutrients and TSS, an index of turbidity, were not as strong as the nutrient vs. salinity relationships. GLMs that included region and day after storm as independent variables again explained only up to half of the variation (adjusted  $R^2$  or likelihood

$R^2 = 0.19$  to  $0.52$ ; Table 4). When grouped into TSS ranges, higher nutrient concentrations tended to occur at very high concentrations of TSS ( $>30$  mg  $L^{-1}$ ; Figure 6 E through H).

Relationships between salinity and FIB were generally negative (Table 4). Unlike the nutrient relationships, the addition of day after storm as well as region improved the models. When both variables were included, the models explained less than half of the variation in the FIB data (likelihood  $R^2 = 0.35$  to  $0.48$ ; Table 4). The median FIB concentration dropped below COP standards in the 32 to 33 psu

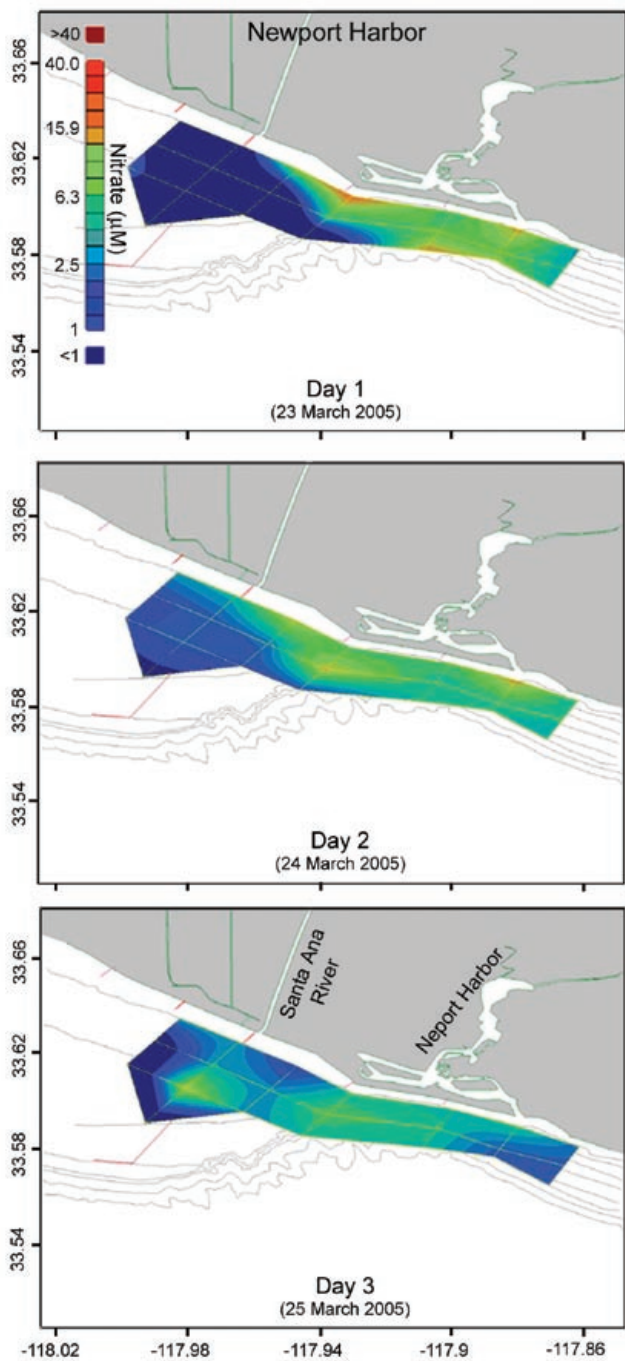


Figure 3. Surface distributions of nitrate for the Newport Harbor area (including the Santa Ana River and Newport Harbor) for Storm 2 (2005) showing the dispersion and dilution of nitrate over time after the storm. Note that color bar is plotted on log scale.

salinity range (1 - 4% stormwater) for total coliforms and *Enterococcus* spp. and in the 28 to 30 psu salinity range (10 - 16% stormwater) for fecal coliforms (Figure 7 A through D). When salinity values indicated that greater than 10% stormwater was present (<28 psu and 28 - 30 psu ranges), the median FIB

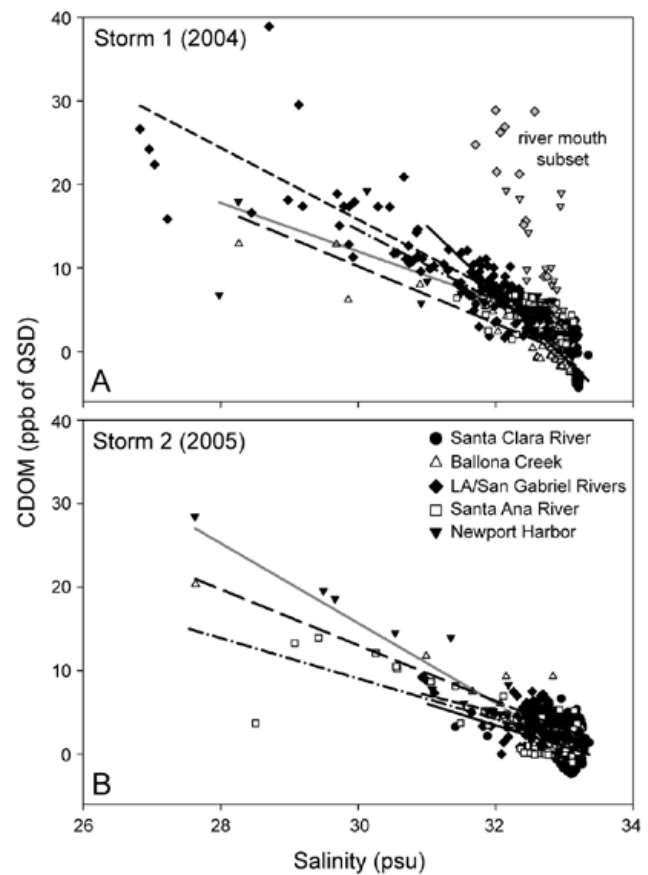


Figure 4. Relationships between CDOM and salinity separated by region for the 2004 (A) and 2005 (B) storm events. Linear regressions are plotted for the Santa Clara River (solid line), Ballona Creek (long dashed line), Los Angeles/San Gabriel Rivers (short dashed line), Santa Ana River (dot dashed line), and Newport Harbor (grey line). These lines are plotted for visual purposes and were not used for statistical analyses. CDOM data were not available for the San Diego and Tijuana Rivers. The river mouth subset for the 2004 storm event (A, grey points) consists of three stations in the Los Angeles/San Gabriel Rivers region and three stations near Newport Harbor, all located inside or just outside major river mouths.

concentrations often exceeded COP standards. Fecal indicator bacteria concentrations were generally very low, often below the maximum detection limit, in water for which salinity was greater than 32 to 33 psu. Median FIB concentrations in the greater than 33 psu salinity range were 7 to 16 times lower than those in the next lower salinity range (32 - 33 psu).

The relationships between FIB and TSS were quite weak (Table 4). Similar to the FIB vs. salinity relationships, the strongest models included both region and day after storm as independent variables.

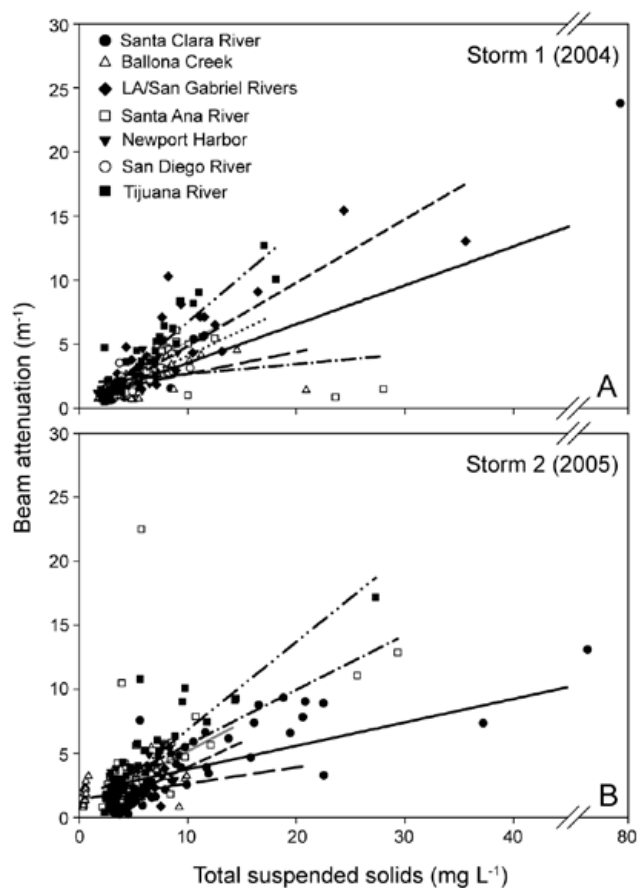


Figure 5. Relationships between beam attenuation coefficient and total suspended solids separated by region for the 2004 (A) and 2005 (B) storm events. Linear regressions are plotted for the Santa Clara River (solid line) Ballona Creek (long dashed line), Los Angeles/San Gabriel Rivers (short dashed line), Santa Ana River (dot dashed line), Newport Harbor (grey line), San Diego River (dotted line), and Tijuana River (dot dot dashed line). These lines are plotted for visual purposes and were not used for statistical analyses. No data were available for the San Diego River for Storm 2.

However, these models explained only a small amount of the variation in the FIB data (likelihood  $R^2 = 0.28 - 0.40$ ; Table 4). Similar to what was observed with nutrient concentrations, FIB concentrations were characteristically higher in waters with higher TSS loadings ( $>30 \text{ mg L}^{-1}$ ; Figure 7 E through H). This result is somewhat surprising as we generally find that human pathogenic bacteria are associated with smallest size fractions, not with larger particulate size fractions (i.e.,  $<1 \mu\text{m}$ ). At lower TSS concentrations, FIB concentrations were generally below COP standards; fecal coliforms and *Enterococcus* spp. were often below detection limits.

Toxicity showed no patterns with salinity or with TSS (Figures 6 and 7). The median percent fertilization was around 100% for all salinity and TSS ranges and never fell below 84%.

## DISCUSSION

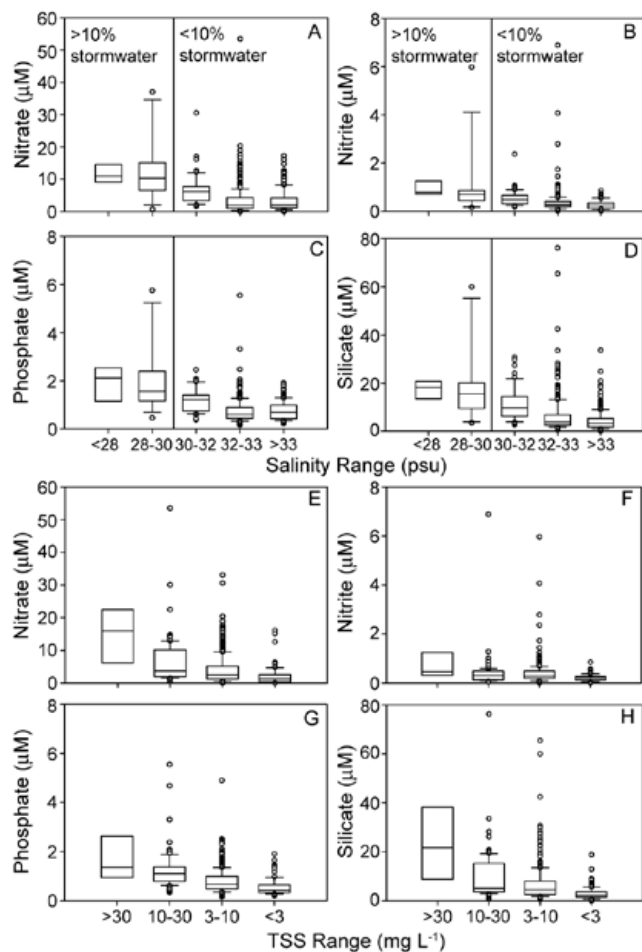
This study shows that optical signatures of stormwater plumes in southern California can be used to assess plume size and direction (see also Warrick *et al.* 2007, Nezlin *et al.* 2008, Reifel *et al.* 2009). However, contaminated parts of plumes were too small to be accurately resolved by satellite remote sensing (spatial resolution  $\sim 1 \text{ km}$ ). The *in situ* measurement of contaminants requires significant effort to both acquire and analyze (especially in a timely manner) samples, thereby limiting the ability to make frequent offshore measurements for FIB concentrations, water column toxicity, and nutrients. The results presented above indicate that impacts from contaminants, such as nutrients and FIB, after storm events were generally brief and tended to occur near major sources of stormwater in the SCB. However, important exceptions to this, such as stormwater from the Tijuana River, do occur.

### How Problematic is Stormwater?

Relationships of nutrient concentrations with salinity and TSS varied among regions, but not between the days sampled. Therefore, individual sources of stormwater probably differ in nutrient composition, but nutrients seem to decrease in plume waters due to simple mixing and dilution. The lack of a strong linear relationship indicates that other sources of nutrients, such as upwelling, were likely present in the coastal ocean creating variability in ambient nutrient concentrations. Unlike nutrients, relationships of FIB with salinity and TSS depended on both region and the number of days after the storm. This indicates that the composition and FIB concentrations in stormwater runoff vary among regions, and that their concentration within stormwater plumes is dependent on more than just loading and dilution rates. Fecal indicator bacteria cannot survive for long periods of time in the surface ocean, and mortality is increased by exposure to ultraviolet radiation (Fujioka *et al.* 1981, Sinton *et al.* 2002, Anderson *et al.* 2005). Therefore, FIB are likely lost from plume waters faster than they would be through simple mixing with ambient coastal water. Some studies have found relationships between salinity and

**Table 3. Results of general linear models for CDOM vs. salinity and beam-c vs. TSS, with region and day after storm included as additional independent variables. n/a = not applicable.**

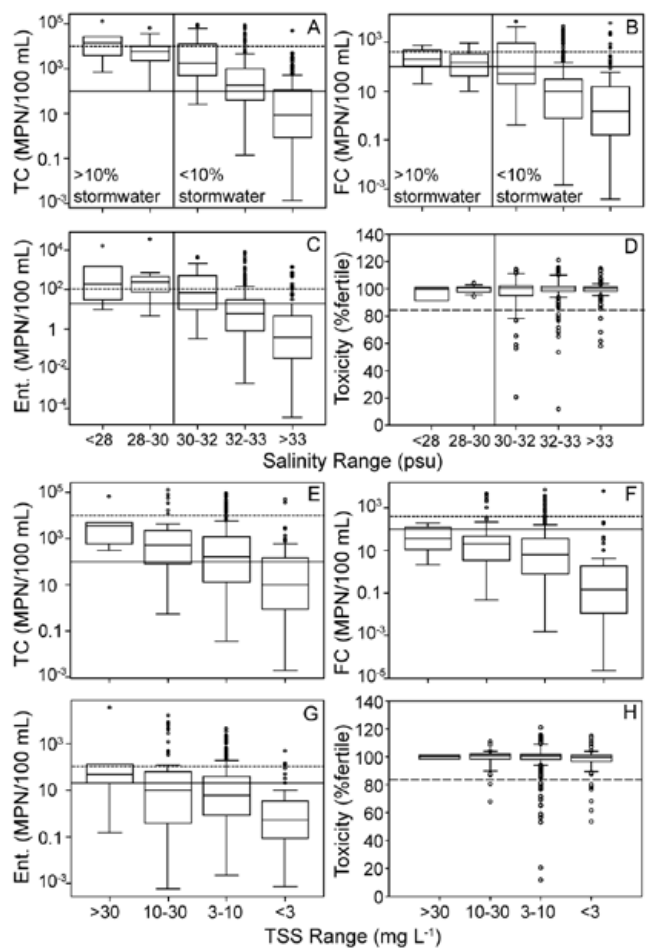
Independent Variable(s)	n	Slope	y-Intercept	Adjusted R <sup>2</sup>	Independent Variable P-Value		
					Salinity/TSS	Region	Day
<b>CDOM vs. Salinity</b>							
Storm 1 - 2004							
salinity	816	-4.576	152.622	0.567	<0.0005	n/a	n/a
salinity + region	816	-4.021	133.941	0.660	<0.0005	<0.0005	n/a
salinity + region + day	816	-3.984	132.082	0.664	<0.0005	<0.0005	0.004
Storm 2 - 2005							
salinity	1030	-3.416	114.763	0.470	<0.0005	n/a	n/a
salinity + region	1030	-3.198	107.596	0.569	<0.0005	<0.0005	n/a
salinity + region + day	1030	-3.169	106.633	0.608	<0.0005	<0.0005	<0.0005
<b>Beam-c vs. TSS</b>							
Storm 1 - 2004							
TSS	323	0.335	0.609	0.635	<0.0005	n/a	n/a
TSS + region	323	0.339	0.552	0.675	<0.0005	<0.0005	n/a
TSS + region + day	323	0.329	0.545	0.702	<0.0005	<0.0005	<0.0005
Storm 2 - 2005							
TSS	276	0.258	1.453	0.386	<0.0005	n/a	n/a
TSS + region	276	0.263	1.460	0.451	<0.0005	<0.0005	n/a
TSS + region + day	276	0.237	1.590	0.499	<0.0005	<0.0005	<0.0005



**Figure 6.** Box plots showing the medians and quartiles of nutrient concentrations in five salinity ranges (A through D) and four ranges of total suspended solids (E through H). Vertical lines in plots A through D indicate 10% stormwater salinity level. Whiskers on box plots extend to the 10th and 90th percentiles. Points outside this range are shown as open circles.

various contaminants, such as nutrients or toxicity (Bay *et al.* 2003, Ragan 2003). However, others have found no consistent relationship between FIB and plume tracers (Ahn *et al.* 2005). Concentrations of contaminants seem to be highly variable, especially when the proportion of stormwater is  $\sim 1 - 4\%$  (see Figures 6 and 7). However, it is possible to determine when and where contaminants are likely to exceed COP standards through quick and easy measurements such as salinity and TSS concentration by using the median values as a guideline.

In past studies of the SCB, high FIB concentrations and/or toxicity were found in stormwater itself, near sewage outfalls and stormdrains/river outlets, and at sites very nearshore (e.g., beaches and surf-zone areas; Geesey 1993, Bay *et al.* 2003, Gersberg



**Figure 7.** Box plots showing the medians and quartiles of concentrations of fecal indicator bacteria and toxicity in five salinity ranges (A through D) and four ranges of total suspended solids (E through H). The solid horizontal lines indicate maximum detection limit. Below this level, distributions are estimated. The dashed lines indicate single sample California Ocean Plan standards. Dashed lines in toxicity plots indicate 84% toxicity. Vertical lines in plots A through D indicate 10% stormwater salinity level. Whiskers on box plots extend to four times the interquartile range, except in plots in D and H where they extend to the 10th and 90th percentiles. Points outside these ranges are shown as open circles. TC = total coliforms, FC = fecal coliforms, and Ent. = *Enterococcus* spp.

*et al.* 2004). The few studies that have attempted to examine FIB in offshore waters have found that they tend to occur in low concentrations, but can exceed California standards offshore of major rivers after storm events (ZoBell 1941, Ahn *et al.* 2005). During this study, with few exceptions, exceedances of COP standards occurred near areas of stormwater discharge during the first day or two after a storm event, similar to what was found in these past studies.

**Table 4. Results of general linear models for contaminants vs. salinity and contaminants vs. TSS, with region and day after storm included as additional independent variables. n/a = not applicable.**

Dependent Variable Contaminants vs. Salinity	n	Slope	y-Intercept	Adjusted R <sup>2</sup>	Independent Variable P-Value*		
					Salinity/TSS	Region	Day
<b>Storm 1 - 2004</b>							
nitrite	339	-0.46	13.355	0.211**	<0.0005	n/a	n/a
nitrite+region	339	-0.356	10.391	0.423**	<0.0005	n/a	n/a
nitrite+region+day	339	-0.352	10.159	0.484**	<0.0005	n/a	n/a
nitrate	339	-2.663	90.201	0.281	<0.0005	n/a	n/a
nitrate+region	339	-2.632	88.909	0.337	<0.0005	<0.0005	n/a
nitrate+region+day	339	-2.733	91.989	0.338	<0.0005	<0.0005	0.383
phosphate (PO <sub>4</sub> )	339	-0.374	13.005	0.327	<0.0005	n/a	n/a
PO <sub>4</sub> +region	339	-0.369	12.765	0.435	<0.0005	<0.0005	n/a
PO <sub>4</sub> +region+day	339	-0.347	11.989	0.446	<0.0005	<0.0005	0.037
silicate	339	-3.931	133.361	0.305	<0.0005	n/a	n/a
silicate+region	339	-3.771	127.709	0.345	<0.0005	<0.0005	n/a
silicate+region+day	339	-4.014	135.626	0.352	<0.0005	<0.0005	0.112
total coliforms (TC)	335	-1.542	54.404	0.255**	<0.0005	n/a	n/a
TC+region	335	-1.708	59.793	0.316**	<0.0005	n/a	n/a
TC+region+day	335	-1.507	54.71	0.394**	<0.0005	n/a	n/a
fecal coliforms (FC)	269	-0.98	33.762	0.092**	<0.0005	n/a	n/a
FC+region	269	-1.162	39.705	0.237**	<0.0005	n/a	n/a
FC+region+day	269	-0.744	28.244	0.355**	<0.0005	n/a	n/a
<i>Enterococcus</i> spp. (ent)	335	-1.26	42.321	0.195**	<0.0005	n/a	n/a
ent+region	335	-1.37	46.124	0.252**	<0.0005	n/a	n/a
ent+region+day	335	-1.071	38.513	0.346**	<0.0005	n/a	n/a
<b>Storm 2 - 2005</b>							
nitrite	250	-0.038	1.632	0.003	0.176	n/a	n/a
nitrate+region	250	-0.075	2.848	0.225	0.004	<0.0005	n/a
nitrate+region+day	250	-0.102	3.719	0.265	<0.0005	<0.0005	0.001
nitrate	250	-0.372	12.831	0.027**	0.002	n/a	n/a
nitrate+region	250	-0.505	15.225	0.526**	<0.0005	n/a	n/a
nitrate+region+day	250	-0.518	15.767	0.553**	<0.0005	n/a	n/a
phosphate (PO <sub>4</sub> )	250	-0.14	5.368	0.064	<0.0005	n/a	n/a
PO <sub>4</sub> +region	250	-0.171	6.387	0.431	<0.0005	<0.0005	n/a
PO <sub>4</sub> +region+day	250	-0.159	5.975	0.448	<0.0005	<0.0005	0.015
silicate	250	-2.439	87.454	0.059	<0.0005	n/a	n/a
silicate+region	250	-3.376	118.136	0.374	<0.0005	<0.0005	n/a
silicate+region+day	250	-3.59	124.777	0.387	<0.0005	<0.0005	0.04
total coliforms (TC)	252	-1.83	64.9	0.110**	<0.0005	n/a	n/a
TC+region	252	-1.824	64.513	0.301**	<0.0005	n/a	n/a
TC+region+day	252	-1.684	60.837	0.382**	<0.0005	n/a	n/a
fecal coliforms (FC)	232	-1.07	37.52	0.040**	0.0002	n/a	n/a
FC+region	232	-1.316	44.842	0.370**	<0.0005	n/a	n/a
FC+region+day	232	-1.208	42.244	0.434**	<0.0005	n/a	n/a
<i>Enterococcus</i> spp. (ent)	276	-1.157	40.116	0.055**	<0.0005	n/a	n/a
ent+region	276	-1.403	47.873	0.421**	<0.0005	n/a	n/a
ent+region+day	276	-1.303	45.294	0.468**	<0.0005	n/a	n/a

\*Note that cenreg calculates one P-value for the entire model and does not calculate P-values for each independent variable.  
 \*\*These are likelihood R<sup>2</sup> values estimated using the cenreg function in NADA.

**Table 4. Continued**

Dependent Variable Contaminants vs. Salinity	n	Slope	y-Intercept	Adjusted R <sup>2</sup>	Independent Variable P-Value*		
					Salinity/TSS	Region	Day
<b>Storm 1 - 2004</b>							
nitrite	376	0.012	-1.713	0.006**	0.13	n/a	n/a
nitrite+region	376	0.035	-1.385	0.383**	<0.0005	n/a	n/a
nitrite+region+day	376	0.033	-1.328	0.425**	<0.0005	n/a	n/a
nitrate	376	0.193	1.982	0.061	<0.0005	n/a	n/a
nitrate+region	376	0.241	1.354	0.204	<0.0005	<0.0005	n/a
nitrate+region+day	376	0.24	1.241	0.201	<0.0005	<0.0005	0.652
phosphate (PO <sub>4</sub> )	376	0.034	0.582	0.112	<0.0005	n/a	n/a
PO <sub>4</sub> +region	376	0.039	0.45	0.306	<0.0005	<0.0005	n/a
PO <sub>4</sub> +region+day	376	0.038	0.473	0.343	<0.0005	<0.0005	<0.0005
silicate	376	0.248	3.589	0.049	<0.0005	n/a	n/a
silicate+region	376	0.352	2.299	0.196	<0.0005	<0.0005	n/a
silicate+region+day	376	0.358	2.252	0.188	<0.0005	<0.0005	0.636
total coliforms (TC)	372	0.138	3.124	0.085**	<0.0005	n/a	n/a
TC+region	372	0.166	3.289	0.156**	<0.0005	n/a	n/a
TC+region+day	372	0.147	5.74	0.296**	<0.0005	n/a	n/a
fecal coliforms (FC)	306	0.091	1.004	0.049**	<0.0005	n/a	n/a
FC+region	306	0.134	1.159	0.189**	<0.0005	n/a	n/a
FC+region+day	306	0.126	4.075	0.396**	<0.0005	n/a	n/a
<i>Enterococcus</i> spp. (ent)	372	0.108	0.303	0.050**	<0.0005	n/a	n/a
ent+region	372	0.127	0.767	0.123**	<0.0005	n/a	n/a
ent+region+day	372	0.108	3.55	0.275**	<0.0005	n/a	n/a
<b>Storm 2 - 2005</b>							
nitrite	250	0.006	0.363	0.01	0.06	n/a	n/a
nitrite+region	250	0.004	0.375	0.202	0.268	<0.0005	n/a
nitrite+region+day	250	0.006	0.357	0.227	0.093	<0.0005	0.012
nitrate	250	0.092	0.151	0.123**	<0.0005	n/a	n/a
nitrate+region	250	0.044	-1.401	0.494**	<0.0005	n/a	n/a
nitrate+region+day	250	0.041	-1.127	0.518**	<0.0005	n/a	n/a
phosphate (PO <sub>4</sub> )	250	0.029	0.62	0.208	<0.0005	n/a	n/a
PO <sub>4</sub> +region	250	0.02	0.697	0.418	<0.0005	<0.0005	n/a
PO <sub>4</sub> +region+day	250	0.018	0.683	0.436	<0.0005	<0.0005	0.014
silicate	250	0.538	4.657	0.223	<0.0005	n/a	n/a
silicate+region	250	0.369	5.885	0.345	<0.0005	<0.0005	n/a
silicate+region+day	250	0.39	5.425	0.358	<0.0005	<0.0005	0.049
total coliforms (TC)	252	0.134	4.532	0.062**	<0.0005	n/a	n/a
TC+region	252	0.144	4.53	0.241**	<0.0005	n/a	n/a
TC+region+day	252	0.118	5.895	0.317**	<0.0005	n/a	n/a
fecal coliforms (FC)	208	0.111	1.596	0.053**	<0.0005	n/a	n/a
FC+region	208	0.113	1.585	0.269**	<0.0005	n/a	n/a
FC+region+day	208	0.087	3.443	0.351**	<0.0005	n/a	n/a
<i>Enterococcus</i> spp. (ent)	252	0.115	1.282	0.060**	<0.0005	n/a	n/a
ent+ region	252	0.121	1.724	0.306**	<0.0005	n/a	n/a
ent+region+day	252	0.098	3.192	0.366**	<0.0005	n/a	n/a

\*Note that cenreg calculates one P-value for the entire model and does not calculate P-values for each independent variable.

\*\*These are likelihood R<sup>2</sup> values estimated using the cenreg function in NADA.

In 2004, waters offshore of the Tijuana River consistently exceeded COP standards for multiple FIB species; in 2005, the area of exceedance was even larger than what could be mapped based on the fixed sampling grid. Gersberg *et al.* (2004) found marked increases in toxicity in the Tijuana River during storm events. The Tijuana River, with a discharge rate of 5 to 10 m<sup>3</sup> s<sup>-1</sup>, does not have a large flow volume compared to the Los Angeles or San Gabriel River systems, whose storm discharge rates often exceed 1000 m<sup>3</sup> s<sup>-1</sup> (see Warrick *et al.* 2007). This implies that FIB in the Tijuana River are highly concentrated and not always rapidly diluted or advected from the region in the three to four days following the storm.

Contrary to prior studies, very few samples collected during the survey showed high levels of toxicity, and toxicity was not related to the variables used to track plume location (salinity and TSS). Bay *et al.* (2003) detected toxicity in samples collected in the Ballona Creek discharge plume when the proportion of stormwater exceeded 10%. Samples outside the Ballona Creek plume were not toxic. In Bay *et al.*, the authors did not use a fixed grid of samples, but adapted stations based on salinity levels always collecting samples both inside and outside the plume. The present study was designed to monitor specific locations around major river discharges and, in most cases, not to adaptively track and sample plumes. This design likely missed much of the plume, as evidenced by the small proportion of sites located in low-salinity water. Runoff plumes can be advected through the area of a given sampling grid in as little as a day and are often advected up or downcoast (Warrick *et al.* 2007, Nezlin *et al.* 2008). Because the plume was moving while the sampling grid remained stationary, it is likely that even though the sampling was distributed over several days, the evolving discharge plume was not adequately sampled. Relationships between toxicity and variables indicative of plumes may have been detected under a different sampling scheme.

Other differences between the results from this and other studies may be due to differences in the time spans over which sampling took place. In a project of this type, it is difficult to obtain a good series of observations that span the time from initial discharge to thorough dilution and/or dispersion in the coastal receiving waters. First, the exact timing of storms is not known in advance, and it is difficult to guarantee the availability of the boat and crew

during the event. Second, even if resources are available, the sea state often prevents operations by the vessels typically used for this type of sampling (Nezlin *et al.* 2007). Third, it is hard to maintain a sufficiently long time series to follow the evolution of these systems because of the commitments of the technical and scientific crews and vessels to other projects. During this study, no sampling occurred during the initial portions of the runoff events, so the effects of the initial mixing of the stormwater into the coastal ocean were missed. Bay *et al.* (2003) were able to sample both during and immediately after storm events, which may also explain the differences in their findings.

### **Feasibility of Using CDOM and Beam-c to Map Plumes**

Strong correlations between CDOM and salinity, and between beam-c and TSS indicate that satellite ocean color data can be used to assess stormwater plumes based on the gradients in salinity and turbidity. Beam-c and TSS represent two different ways to examine the particulate component of seawater. TSS is a measurement of the concentration, by weight, of particles whereas beam-c is an optical measurement related to both the size and concentration of particles. Because of the dependence of light attenuation on particle size, beam-c depends on the geometrical cross-section of particles per unit volume, not necessarily on TSS concentration alone (Davies-Colley and Smith 2001). Therefore, changes in particle size and composition (i.e., inorganic vs. organic) can result in a change in beam-c without a corresponding change in TSS. The relationship between beam-c and TSS may be expected to change over space and time as the particle composition may be quite different just after a storm versus several days later due to the rapid sinking of large particles and flocs (Hill *et al.* 2000, Warrick *et al.* 2004). Particle composition might also vary among regions. Analysis of the present study data confirms that the relationship between beam-c and TSS varies among regions and over time after a storm event.

Salinity and CDOM both represent concentrations of dissolved constituents. River and runoff systems typically have elevated levels of CDOM that can correlate with salinity, such that CDOM concentration increases with decreasing salinity (Twardowski and Donaghay 2001, D'Sa *et al.* 2002). In theory, salinity and CDOM could be used interchangeably as tracers of the dissolved portion of a



runoff plume. In the SCB, the composition and concentration of CDOM likely varies among sources of stormwater runoff. However, it appears that over at least the first few days, CDOM concentration decreases in plume waters through simple mixing processes.

In contrast, for some shallow regions near major river mouths, increased CDOM fluorescence was uncorrelated with salinity. Twardowski and Donaghay (2001) reported that deviations from the typical inverse linear relationship between CDOM and salinity could arise even in coastal waters due to *in situ* CDOM production processes, including sediment resuspension and reworking of the products of primary production. Chen and Bada (1992) noticed that CDOM fluorescence decreased by about 20% after filtration in nearshore samples. However, in a more recent study, Belzile *et al.* (2006) observed little to no difference in CDOM fluorescence in filtered vs. unfiltered samples. The rapid formation of CDOM from dissolved organic matter precursors exuded by phytoplankton has been observed in several studies (reviewed in Twardowski and Donaghay 2001). Localized phytoplankton blooms tend to persist near the mouth of the Los Angeles River (Hardy 1993, Gregorio and Pieper 2000), and elevated concentrations of chlorophyll *a* were observed at stations within the Los Angeles Harbor. Although chlorophyll *a* concentrations were not high at stations near Newport Harbor at the time of sampling, it cannot be ruled out as contributing to the production of CDOM from a past localized bloom in that area. Further research is needed to determine whether *in situ* production of CDOM occurs due to processes such as sediment resuspension, or due to production of algal exudates in the Southern California Bight, and whether these processes contribute to deviations in the CDOM/salinity relationship.

In previous studies, detection of stormwater plumes off southern California using ocean color has generally relied on increases in nLw in the 531 to 551 nm range for MODIS (e.g., Nezlin *et al.* 2008) and 555 nm for SeaWiFS (e.g. Otero and Siegel 2004, Nezlin and DiGiacomo 2005, Nezlin *et al.* 2005). The increase in nLw at these wavelengths is likely due to increased concentrations of suspended sediments within plumes, which increase backscattering. This signal is an indication of only the particulate portion of the plume. MODIS ocean color data analyzed as part of the present project showed both an increase in nLw within the plume waters at longer wavelengths (primarily 531 to 551 nm) and a

decrease in nLw at short wavelengths (primarily 412 nm), the latter potentially explained by light absorption by CDOM (Nezlin *et al.* 2008). In this manner, it should be possible to use satellite ocean color-derived estimates of CDOM absorption and increased backscatter (increased nLw) at long wavelengths as fairly conservative tracers of stormwater runoff plumes off southern California, representing the dissolved and particulate constituents of the plumes, respectively, as described above.

Analogous for CDOM and beam-c can be derived from the inherent optical properties of the water column, which in turn can be derived from the remote sensing reflectance obtained by satellite ocean color sensors. In this context, methods such as the Quasi-Analytical Algorithm (QAA), developed for deriving inherent optical properties (IOPs) from remotely sensed ocean color measurements (Lee *et al.* 2002, 2006), are available to do this in complex nearshore waters such as those off southern California, which derive potentially informative properties such as  $a_{dg}(412)$  and  $b_b(551)$ . Strong correlations between CDOM and salinity, and between beam-c and TSS, indicate that satellite ocean color data can potentially be used to infer and perhaps accurately assess gradients in salinity and turbidity. However, these remotely-sensed measurements may be limited by spatial resolution of satellite sensors (~1 km), which in southern California is comparable with the spatial extent of the impacted areas. The actual CDOM/salinity and beam-c/TSS relationships differ among regions and between storm events. Therefore, quantitative estimations of salinity or TSS via satellite ocean color measurements would require building empirical relationships specific to each region. Regardless, ocean color imagery can, and should, be built into regional monitoring programs to provide qualitative information on the locations of plumes and areas likely impacted by contaminants, and to guide ship-based monitoring efforts.

## LITERATURE CITED

- Ahn, J.H., S.B. Grant, C.Q. Surbeck, P.M. DiGiacomo, N.P. Nezlin and S. Jiang. 2005. Coastal water quality impact of stormwater runoff from an urban watershed in southern California. *Environmental Science & Technology* 39:5940-5953.
- Anderson, K.L., J.E. Whitlock and V.J. Harwood. 2005. Persistence and differential survival of fecal indicator bacteria in subtropical waters and sedi-

- ments. *Applied and Environmental Microbiology* 71:3041-3048.
- American Public Health Association (APHA). 1998a. 9221B. Standard total coliform fermentation technique. pp. 48-51 *in*: M.A.H. Franson, L.S. Clesceri, A.E. Greenberg and A.D. Eaton (eds.), Standard Methods for the Examination of Water and Wastewater, 20th edition. APHA, American Water Works Association, Water Environment Federation. Washington, DC.
- APHA. 1998b. 9221E. Fecal coliform procedure. pp. 54-55 *in*: M.A.H. Franson, L.S. Clesceri, A.E. Greenberg and A.D. Eaton (eds.), Standard Methods for the Examination of Water and Wastewater, 20th edition. APHA, American Water Works Association, Water Environment Federation. Washington, DC.
- APHA. 1998c. 9222B. Standard total coliform membrane filter procedure. pp. 57-62 *in*: M.A.H. Franson, L.S. Clesceri, A.E. Greenberg and A.D. Eaton (eds.), Standard Methods for the Examination of Water and Wastewater, 20th edition. APHA, American Water Works Association, Water Environment Federation. Washington, DC.
- APHA. 1998d. 9222D. Fecal coliform membrane filter procedure. pp. 63-65 *in*: M.A.H. Franson, L.S. Clesceri, A.E. Greenberg and A.D. Eaton (eds.), Standard Methods for the Examination of Water and Wastewater, 20th edition. APHA, American Water Works Association, Water Environment Federation. Washington, DC.
- Bay, S., B.H. Jones, K. Schiff and L. Washburn. 2003. Water quality impacts of stormwater discharges to Santa Monica Bay. *Marine Environmental Research* 56:205-223.
- Belzile, C., C.S. Roesler, J.P. Christensen, N. Shakhova and I.P. Semiletov. 2006. Fluorescence measured using the WETStar DOM fluorimeter as a proxy for dissolved matter absorption. *Estuarine Coastal and Shelf Science* 67:441-449.
- Busse, L.B., E.L. Venrick, R. Antrobus, P.E. Miller, V. Vigilant, M.W. Silver, C. Mengelt, L. Mydlarz and B.B. Prezelin. 2006. Domoic acid in phytoplankton and fish in San Diego. *Harmful Algae* 5:91-101.
- California Department of Public Health (CDPH). 2006. Draft guidance for salt water beaches. CDHP, Division of Drinking Water and Environmental Management. Sacramento, CA.
- Chen, R.F. and J.L. Bada. 1992. The fluorescence of dissolved organic matter. *Marine Chemistry* 37:191-221.
- Coble, P.G., C. Hu, R.W. Gould, G. Chang and A.M. Wood. 2004. Colored dissolved organic matter in the coastal ocean: An optical tool for coastal zone environmental assessment and management. *Oceanography* 17:51-59.
- D'Sa, E.J., C. Hu, F.E. Muller-Karger and K.L. Carder. 2002. Estimation of colored dissolved organic matter and salinity fields in case 2 waters using SeaWiFS: Examples from Florida Bay and Florida Shelf. *Proceedings of the Indian Academy of Sciences-Earth and Planetary Sciences* 111:197-207.
- Davies-Colley, R.J. and D.G. Smith. 2001. Turbidity, suspended sediment, and water clarity: a review. *Journal of the American Water Resources Association* 37:1085-1101.
- Del Castillo, C.E. 2005. Remote sensing of organic matter in coastal waters. pp. 157-180 *in*: R.L. Miller, C.E. Del Castillo and B.A. McKee (eds.), Remote Sensing of Coastal Aquatic Environments: Technologies, Techniques and Applications. Springer. Dordrecht, the Netherlands.
- Fujioka, R.S., H.H. Hashimoto, E.B. Siwak and R.H. Young. 1981. Effect of sunlight on survival of indicator bacteria in seawater. *Applied and Environmental Microbiology* 41:690-696.
- Geesey, G.G. 1993. Microbiology. pp. 190-232 *in*: M.D. Dailey, D.J. Reish and J.W. Anderson (eds.), Ecology of the Southern California Bight. University of California Press. Los Angeles, CA.
- Gersberg, R.M., D. Daft and D. Yorkey. 2004. Temporal pattern of toxicity in runoff from the Tijuana River Watershed. *Water Research* 38:559-568.
- Geyer, W.R., P. Hill, T. Milligan and P. Traykovski. 2000. The structure of the Eel River plume during floods. *Continental Shelf Research* 20:2067-2093.
- Gordon, L.I., J.C.J. Jennings, A.A. Ross and J.M. Krest. 1993. A suggested protocol for continuous flow automated analysis of seawater nutrients (phosphate, nitrate, nitrite and silicic acid) in the WOCE

- Hydrographic Program and the Joint Global Ocean Fluxes Study. WHP Operation and Methods. WOCE Hydrographic Program Office. Corvallis, OR.
- Gregorio, D.E. and R.E. Pieper. 2000. Investigations of red tides along the southern California coast. *Bulletin of the Southern California Academy of Sciences* 99:147-160.
- Griffith, J.F., L.A. Aumand, I.M. Lee, C.D. McGee, L.L. Othman, K.J. Ritter, K.O. Walker and S.B. Weisberg. 2006. Comparison and verification of bacterial water quality indicator measurement methods using ambient coastal water samples. *Environmental Monitoring and Assessment* 116:335-344.
- Hardy, J.T. 1993. Phytoplankton. pp. 233-265 in: M.D. Dailey, D.J. Reish and J.W. Anderson (eds.), *Ecology of the Southern California Bight*. University of California Press. Berkeley, CA.
- Helsel, D.R. 2005. *Nondetects and Data Analysis*. Wiley. New York, NY.
- Hill, P.S., T.G. Milligan and W.R. Geyer. 2000. Controls on effective settling velocity of suspended sediment in the Eel River flood plume. *Continental Shelf Research* 20:2095-2111.
- Lee, L. and D.R. Helsel. 2005. Statistical analysis of water-quality data containing multiple detection limits: S-language software for regression on order statistics. *Computers and Geosciences* 31:1241-1248.
- Lee, Z., K.L. Carder and R.A. Arnone. 2002. Deriving inherent optical properties from water color: a multiband quasi-analytical algorithm for optically deep waters. *Applied Optics* 41:5755-5772.
- Lee, Z., K.L. Carder and R.A. Arnone. 2006. The Quasi-Analytical Algorithm. pp. 73-79 in: Z. Lee (ed.), *Remote Sensing of Inherent Optical Properties: Fundamentals, Tests of Algorithms and Applications*, Vol. 5. IOCCG. Dartmouth, Canada.
- Messer, J.W. and A.P. Dufour. 1998. A rapid, specific membrane filtration procedure for enumeration of Enterococci in recreational water. *Applied and Environmental Microbiology* 64:678-680.
- Monahan, E.C. and M.J. Pybus. 1978. Colour, UV absorbance and salinity of the surface waters off the west coast of Ireland. *Nature* 274:782-784.
- National Research Council. 1990. *Monitoring Southern California's Coastal Waters*. National Academy Press. Washington, DC.
- Nezlin, N.P. and P.M. DiGiacomo. 2005. Satellite ocean color observations of stormwater runoff plumes along the San Pedro Shelf (southern California) during 1997 to 2003. *Continental Shelf Research* 25:1692-1711.
- Nezlin, N.P., P.M. DiGiacomo, D.W. Diehl, B.H. Jones, S.C. Johnson, M.J. Mengel, K.M. Reifel, J.A. Warrick and M. Wang. 2008. Stormwater plume detection by MODIS imagery in the southern California coastal ocean. *Estuarine, Coastal and Shelf Science* 80:141-152.
- Nezlin, N.P., P.M. DiGiacomo, E.D. Stein and D. Ackerman. 2005. Stormwater runoff plumes observed by SeaWiFS radiometer in the Southern California Bight. *Remote Sensing of Environment* 98:494-510.
- Nezlin, N.P., S.B. Weisberg and D.W. Diehl. 2007. Relative availability of satellite imagery and ship-based sampling for assessment of stormwater runoff plumes in coastal southern California. *Estuarine, Coastal and Shelf Science* 71:250-258.
- Ocean Software. 2009. *Interactive Graphical Ocean Database System (IGODS)*. OceanSoftware. Long Beach, CA.
- Opsahl, S. and R. Benner. 1998. Photochemical reactivity of dissolved lignin in river and ocean waters. *Limnology and Oceanography* 43:1297-1304.
- Otero, M.P. and D.A. Siegel. 2004. Spatial and temporal characteristics of sediment plumes and phytoplankton blooms in the Santa Barbara Channel. *Deep-Sea Research II* 51:1129-1149.
- R Development Core Team. 2006. *R: A Language and Environment for Statistical Computing*. R Foundation for Statistical Computing. Vienna, Austria.
- Ragan, M.A. 2003. *Response of inherent optical properties to stormwater runoff in Santa Monica Bay, California*. Unpublished Master of Science Thesis, University of Southern California. Los Angeles, CA.
- Reifel, K.M., S.C. Johnson, P.M. DiGiacomo, M.J. Mengel, N.P. Nezlin, J.A. Warrick and B.H. Jones. 2009. Impacts of stormwater runoff in the Southern

- California Bight: Relationships among plume constituents. *Continental Shelf Research* 29:1821-1835.
- Sakamoto, C.M., G.E. Friederich and L.A. Codispoti. 1990. MBARI procedures for automated nutrient analyses using a modified Alpkem series 300 rapid flow analyzer. Monterey Bay Aquarium Research Institute. Moss Landing, CA.
- Schiff, K.C., M.J. Allen, E.Y. Zeng and S.M. Bay. 2000. Southern California. *Marine Pollution Bulletin* 41:76-93.
- Schiff, K.C., S.B. Weisberg and V.E. Raco-Rands. 2002. Inventory of Ocean Monitoring in the Southern California Bight. *Environmental Management* 29:871-876.
- Shumway, R.H., R.S. Azari and M. Kayhanian. 2002. Statistical approaches to estimating mean water quality concentrations with detection limits. *Environmental Science & Technology* 36:3345-3353.
- Siegel, D.A., S. Maritorea, N.B. Nelson, D.A. Hansell and M. Lorenzi-Kayser. 2002. Global distribution and dynamics of colored dissolved and detrital organic materials. *Journal of Geophysical Research-Oceans* 107:3228, doi:3210.1029/2001JC000965.
- Sinton, L.W., C.H. Hall, P.A. Lynch and R.J. Davies-Colley. 2002. Sunlight inactivation of fecal indicator bacteria and bacteriophages from waste stabilization pond effluent in fresh and saline waters. *Applied and Environmental Microbiology* 68:1122-1131.
- State Water Resources Control Board. 2005. California Ocean Plan. State Water Resources Control Board. Sacramento, CA.
- Systat Software, Inc. (SSI). 2004a. SigmaPlot. SSI. Richmond, CA.
- SSI. 2004b. SYSTAT for Windows. SSI. Richmond, CA.
- Twardowski, M.S. and P.L. Donaghay. 2001. Separating *in situ* and terrigenous sources of absorption by dissolved materials in coastal waters. *Journal of Geophysical Research-Oceans* 106:2545-2560.
- United States Environmental Protection Agency (USEPA). 1983. Method 160.2: residue, non-filterable (gravimetric, dried at 103-105°C). pp. 1602-1601, 1602-1603 in: Methods for Chemical Analysis of Water and Wastes. USEPA, Office of Research and Development. Cincinnati, OH.
- USEPA. 1995. Short-term methods for estimating the chronic toxicity of effluents and receiving waters to West Coast marine and estuarine organisms (1st edition). USEPA, Office of Research and Development. Cincinnati, OH.
- Vodacek, A., N.V. Blough, M.D. DeGrandpe, E.T. Peltzer and R.K. Nelson. 1997. Seasonal variation of CDOM and DOC in the Middle Atlantic Bight: Terrestrial inputs and photooxidation. *Limnology and Oceanography* 42:674-686.
- Warrick, J.A., P.M. DiGiacomo, S.B. Weisberg, N.P. Nezlin, M.J. Mengel, B.H. Jones, J.C. Ohlmann, L. Washburn, E.J. Terrill and K.L. Farnsworth. 2007. River plume patterns and dynamics within the Southern California Bight. *Continental Shelf Research* 27:2427-2448.
- Warrick, J.A., L.A.K. Mertes, L. Washburn and D.A. Siegel. 2004. A conceptual model for river water and sediment dispersal in the Santa Barbara Channel, California. *Continental Shelf Research* 24:2029-2043.
- Warrick, J.A., L. Washburn, M.A. Brzezinski and D.A. Siegel. 2005. Nutrient contributions to the Santa Barbara Channel, California, from the ephemeral Santa Clara River. *Estuarine, Coastal and Shelf Science* 62:559-574.
- Washburn, L., K.A. McClure, B.H. Jones and S.M. Bay. 2003. Spatial scales and evolution of stormwater plumes in Santa Monica Bay. *Marine Environmental Research* 56:103-125.
- ZoBell, C.E. 1941. The occurrence of coliform bacteria in oceanic water. *Journal of Bacteriology* 42:284.

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