APPENDIX E - RELATED MANUSCRIPTS

Special Study on Nutrient Source Tracking and Association with Algal Blooms

Introduction

Stable isotopes offer a direct means of source identification because different sources (*e.g.* soil nitrogen, atmospheric nitrogen, chemical fertilizers, manure, and sewage) often have distinct nitrate isotopic compositions that can be traced *in situ.* Furthermore, biological cycling of nitrogen often changes isotopic ratios in predictable and recognizable ways which can be reconstructed and used to determine how nitrate is cycled within the system (Kendall and McDonnell 1998, Kendall et al. 2007). Thus utilizing the isotopic composition of nitrate in the southern California Bight (SCB) could potentially be used to identify point and non-point sources of nitrate to the bight and/or the biological transformation of nitrate (e.g. loss of nitrogen through denitrification, addition of nitrogen through nitrification and re-mineralization of organic matter).

Approach

The Offshore Water Quality component of the 2008 Southern California Bight Regional Assessment included a pilot study to determine if distinct sources of nitrate to the SCB could be identified isotopically and if the fate of those sources could then be traced into SCB coastal waters. The study had two parts: 1) determination of nitrate nitrogen and oxygen isotope ratios in specific sources (POTW effluent, river discharge, and upwelled water); and 2) field measurements of seawater to determine if source signatures were maintained in the SCB or if they were over-written by biological transformations.

The first step was to determine if the isotopic signature of disparate sources of nitrate to the SCB were isotopically distinct. To this end, we analyzed the nitrogen and oxygen stable isotopic composition ($\delta^{15}N_{NO3}$, and $\delta^{18}O_{NO3}$) of potential nitrate sources to the SCB. The effluent signature was characterized in water collected from LACSD and OCSD; the riverine signature was characterized using water from the mouths and upstream (freshwater) areas of the Los Angeles River, San Gabriel River, Santa Ana River, and San Diego Creek; the upwelling signature was characterized from mid-depth and deep water from the offshore area of the SCB; the atmospheric nitrate signature was characterized in samples of wet and dry atmospheric deposition. The utility of nitrate isotopic measurements depends on each source having a uniquely identifiable paired oxygen:nitrogen isotopic composition.

The second step was to determine if these sources can be tracked in coastal waters of the SCB and to what extent the signatures are lost due to biogeochemical transformations. To this end, water was collected from the SCB on LACSD and OCSD cruises along vertical and horizontal profiles from the POTW effluent pipes offshore and along transects from the San Gabriel and Santa Ana Rivers (Figure E-1). Salinity measurements from CTD casts were used to direct sampling of freshwater plumes. These measurements were used to assess whether the river and POTW source signatures are altered as organisms utilize and recycle nitrate in coastal waters. If so, while nitrate isotope measurements can be used to identify key biological source and loss terms for the SCB, they cannot be used for source tracking.

A. **B.**

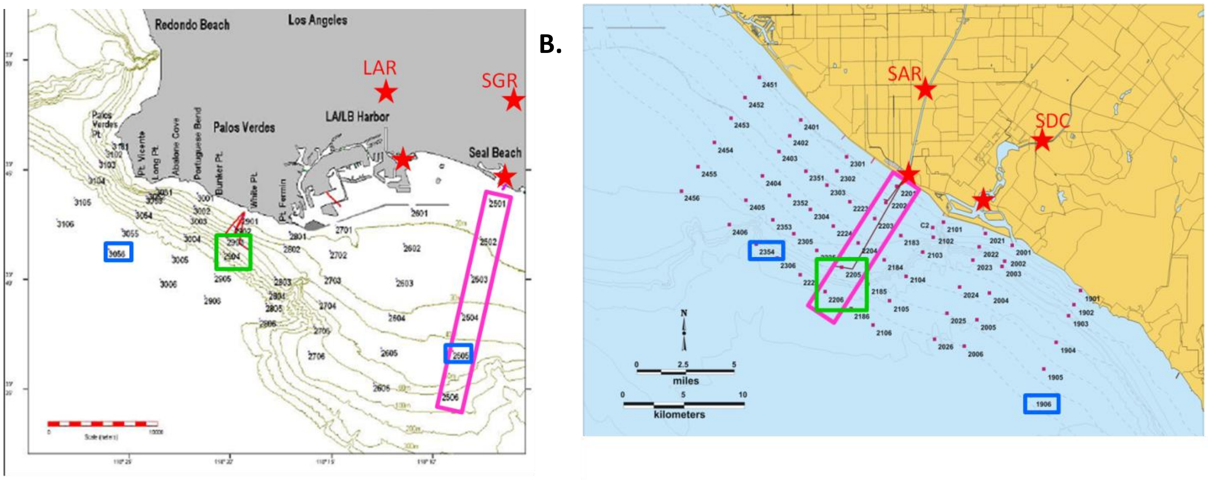

Figure E-1. Sampling sites located near the LACSD POTW outfall (A) and OCSD POTW outfall (B). Samples representing the "upwelling" end-member are from the deepest depth at each of the stations in blue squares. Samples tracing the effluent plume were taken from multiple depths at the stations in the green squares. Samples tracing the river discharge are in the purple squares. Red stars represent samples taken from distinct river systems upstream of tidal influence and at the river mouths.

Results

Results from the first component of the study indicate that upwelled nitrate is isotopically distinct from both LACSD and OCSD POTW effluent, which are also isotopically distinct from one another (Table 1, Figure 2). Nitrate concentrations were similar for LACSD and upwelled water, but OCSD effluent had an order of magnitude more nitrate compared to all other sources. The oxygen isotopic composition of water (H_2O) was used to identify plume water because effluent water had a significantly lower isotopic composition than rivers and upwelling (which could not be distinguished from one another). The isotopic composition of river nitrate was highly variable isotopically and in terms of nitrate concentration.

The second objective of the pilot study was to determine if distinct sources could be traced isotopically in waters of the SCB (Table 2). First, we attempted to trace riverine nitrate as it was discharged into surface waters of the SCB. We did this study along two lines: 1) the San Gabriel River upstream of tidal influence and at the mouth and along LACSD Cruise Line 2500 (Figure 4A) and the Santa Ana River upstream of tidal influence and at the mouth and along OCSD Cruise Line 2200 (Figure 4A). At the San Gabriel River, riverine water is isotopically distinct from upwelling water, but does not show a simple mixing relationship with that water source. Rather it seems that there is new, unknown source of nitrate or biologically altered nitrate added mid-flow path that is distinct from both upwelling and San Gabriel River water (Figure 6). Santa Ana river water was also isotopically distinct from upwelled water and water along the cruise track of line 2200 observed at the river mouth. Values for stations 2201 and 2202 indicated water might be either from a different source or biologically altered nitrate. At station 2204, characteristic isotope values indicated denitrification. At Stations 2205 and 2206 high oxygen isotopic compositions and low nitrogen isotopic compositions reflecting another source or different biological transformation (nitrification) were observed (Figure 5).

Table 1. The isotopic signature results for water and nitrate from specific nutrient sources (rivers, effluent and upwelling).

Source Type	Sampling Location	Depth	Nitrate $\delta^{15}N$	Nitrate $\delta^{18}O$	Water $\delta^{18}O$	Nitrate (µM)
Rivers (Upstream of Tidal Influence)	LA River	0	5.73	8.71	-2.88	6.3
	San Gabriel R.	0	11.45	10.81	-1.00	20.4
	Santa Ana R.	0	4.92	2.32	-0.03	0.9
	San Diego Crk	0	0.44	19.85	-0.42	2.4
Rivers (Mouth)	LA River	0	8.16	6.31	-9.32	55.0
	San Gabriel R.	0	13.73	10.69	-0.33	10.7
	Santa Ana R.	0	0.79	22.37	1.28	0.5
	San Diego Crk	0	7.57	15.23	-4.82	13.5
POTW	OCSD POTW	effluent	10.00	5.40	-8.12	157.4
	LASD POTW	effluent	-13.62	-3.28	-8.83	10.3
Upwelled Water	LACSD 2505	45	0.86	11.09	-0.07	12.3
	LACSD 3056	45	0.77	11.09	0.09	11.8
	OCSD 1906	75	0.36	10.71	0.09	12.8
	OCSD 2354	30	0.52	13.50	0.43	11.2

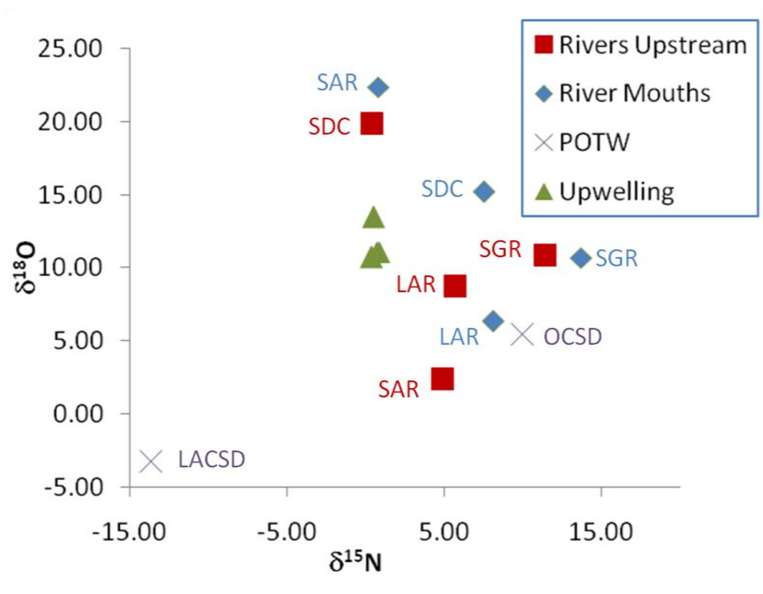

Figure 2. Stable isotope signature ($\delta^{18}O$ vs $\delta^{15}N$) of SCB nutrient sources.

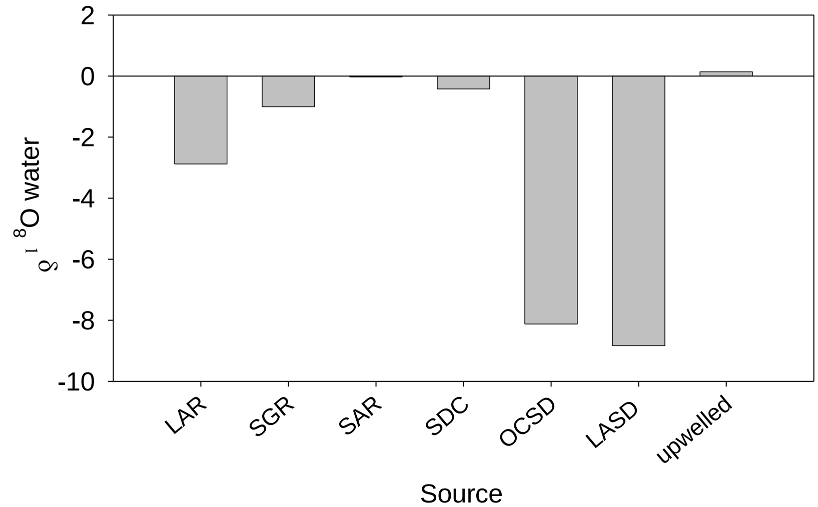

Figure 3. Oxygen isotopic composition of water from different SCB sources.

Table 2. The isotopic signature results of water and nitrate from seawater samples collected in the SCB.

Source Type	Sampling Location	depth	nitrate $\delta^{15}N$	nitrate $\delta^{18}O$	water $\delta^{18}O$	nitrate (µM)
River Tracking	LASD 2501	0	1.39	17.80	-0.38	0.6
	LASD 2502	0	0.04	20.21	-0.59	0.2
	LASD 2503	0	-0.94	20.70	-0.56	0.5
	LASD 2504	0	0.23	16.87	-0.34	0.2
	OCSD 2201	0	-0.92	19.44	-0.47	0.3
	OCSD 2202	0	-0.03	20.33	-0.48	0.5
	OCSD 2203	0	-1.54	8.26	-0.18	0.4
	OCSD 2204	0	6.75	27.39	-0.22	0.6
	OCSD 2205	0	-6.45	27.77	-0.02	0.4
	OCSD 2206	0	-1.29	40.57	-0.18	0.4
Effluent Plume Tracking	LACSD 2903	0	47.67	35.17	0.13	0.4
	LACSD 2903	34	6.50	11.09	0.15	19.7
	LACSD 2903	45	7.27	14.24	0.05	17.7
	LACSD 2904	0	0.29	27.25	0.14	0.2
	LACSD 2904	45	5.69	15.22	0.07	12.2
	LACSD 2904	50	7.09	11.43	0.04	14.2
	OCSD 2205	0	-6.45	27.77	-0.02	0.4
	OCSD 2205	30	0.91	14.31	-0.16	19.5
	OCSD 2205	54	0.11	15.17	0.02	13.3
	OCSD 2206	0	-1.29	40.57	-0.18	0.4
	OCSD 2206	30	0.15	14.90	0.06	14.7
	OCSD 2206	45	0.37	9.69	0.05	12.6

The next step was to determine if effluent nitrate could be traced to the SCB by looking at plume waters along two depth profiles near the outfall pipes of LACSD and OCSD. The LACSD outfall plume at stations 2903 and 2904 did not fall along the expected mixing line between upwelling water and effluent waters. It did however fall along the trajectory expected for biological transformation of nitrate (denitrification and nitrification), though without more information these values cannot be attributed to this process (Figure 5). The effluent plume at OCSD stations 2205 and 2206 could not be distinguishable from upwelled water.

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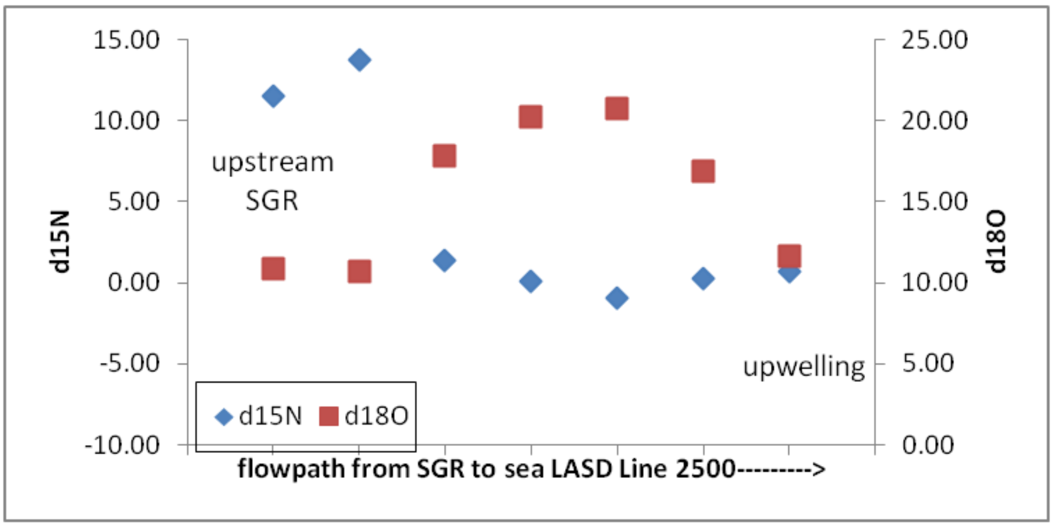

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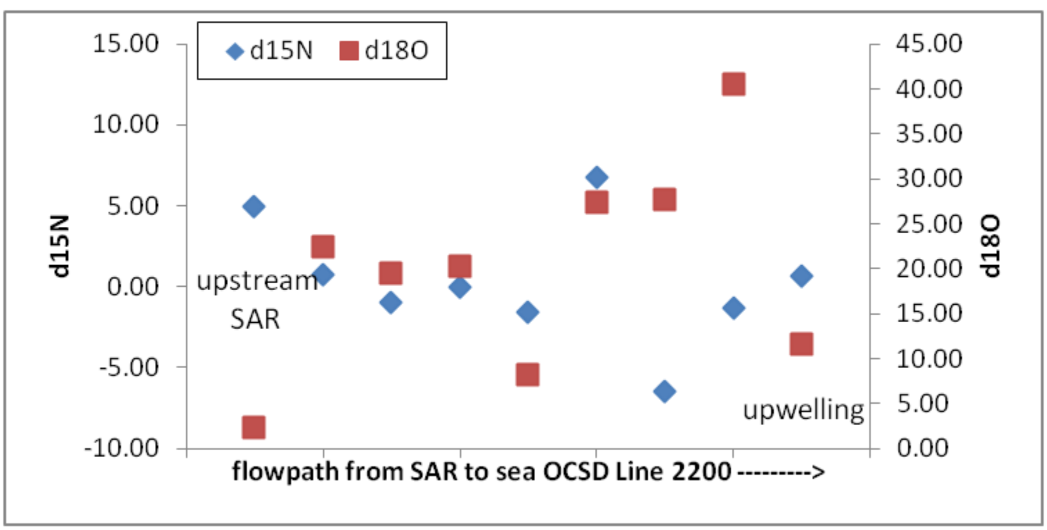

Figure 4. Surface water transect of nitrate nitrogen (δ^{15}N) and oxygen (δ^{18}O) from the San Gabriel River to offshore (line 2500) (A) and from the Santa Ana River to offshore (line 2200) (B)

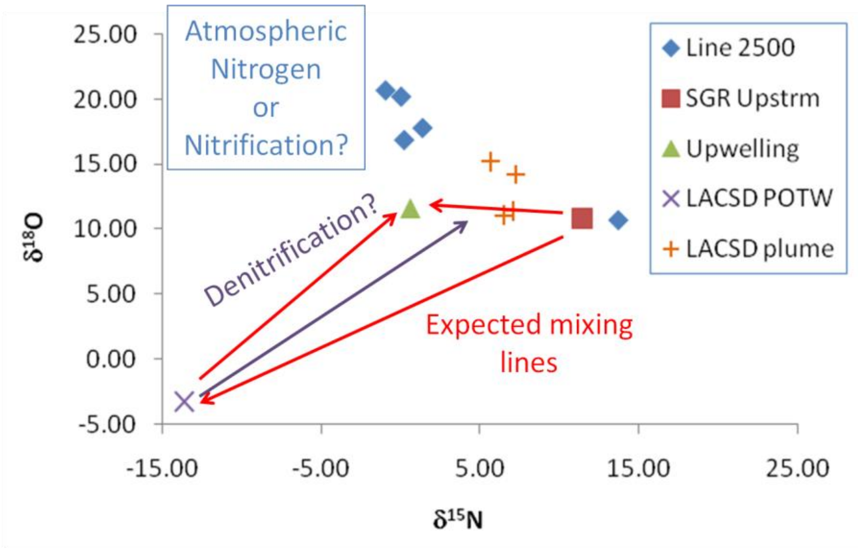

Figure 5. Comparison of isotopic compositions of surface waters from LACSD cruise line 2500 off the San Gabriel River (blue diamonds), waters from within the San Gabriel River upstream of tidal influence (red square), waters from within the effluent plume from a depth profile at LACSD 2903 and 2904 (orange crosses) and from upwelled waters (green triangle). The expected mixing between river water, effluent, and upwelling is represented by the red arrows. The trajectory of denitrification is represented by the purple line. Atmospheric nitrogen (though not measured in this study) is typically has negative δ^{15}N values and δ^{18}O values greater than 35 per million.

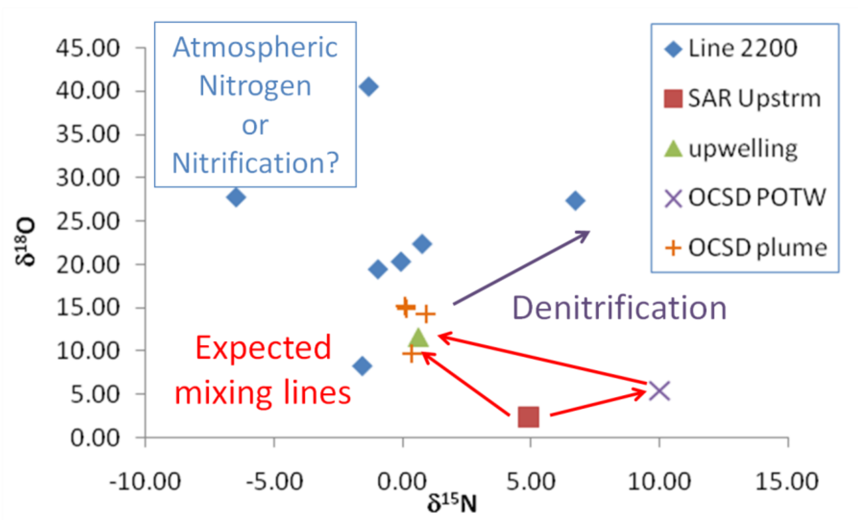

Figure 6. Comparison of isotopic compositions of surface waters from OCSD cruise line 2200 off the Santa Ana River (blue diamonds), waters from within the Santa Ana River upstream of tidal influence (red square), waters from within the effluent plume from a depth profile at OCSD 2205 and 2206 (orange crosses) and from upwelled waters (green triangle). The expected mixing between river water, effluent, and upwelling is represented by the red arrows. The trajectory of denitrification is represented by the purple line. Atmospheric nitrogen (though not measured in this study) is typically has negative δ^{15}N values and δ^{18}O values greater than 35 per mil.

Discussion

This pilot study aimed to determine if the stable isotopic composition of nitrate could be used to trace sources and cycling of nitrate into the southern California Bight. The study was broken into two main components: 1) do the different nitrate sources have distinct isotopic compositions and 2) can these source signatures be used to trace the relative contribution of nitrate sources to the Bight. The answer to both questions is a qualified yes; however, more information is needed to fully understand the fate of nitrate in the SCB.

For source signature identification, it was initially hypothesized that source signatures could be easily assigned to coherent groups. One river signature would be similar to other river signatures; the signature of POTW effluent from OCSD would be similar to the signature of effluent from LACSD would look similar. By extension, it was also hypothesized that the source of background nitrates would be identifiable in that each source category would fall into a distinct area on a scatter plot of $\delta^{15}N$ and $\delta^{18}O$ (Kendall et al. 2007). However, upwelling was the only source for which this was true, suggesting that the "background" nitrate isotopic composition is consistent bightwide. Nitrate concentrations in effluent from OCSD were an order of magnitude higher than nitrate concentration in effluent from LACSD). This indicates different treatment of nitrate in wastewater from the two plants which is reflected in the isotopic compositions. All the rivers were also different from one another both isotopically and in terms of nitrate concentrations, which is probably reflective of the different land uses and sizes of the watersheds which may contribute disparate sources of nitrate (fertilizer, runoff, wastewater, etc.) and different levels of biological transformation within streams of different hydrology (e.g., rivers with muddy bottoms would be expected to have more denitrification than rivers with concrete bottoms). This result is important because it suggests that individual sources could potentially be distinguished from within the SCB. However, for a source tracking study to be successful in the SCB, all sources to any subregion must be fully characterized and not rely on data from similar sources in other subregions.

For isotope source tracking, it was originally hypothesized that the nitrate nitrogen and oxygen isotopic compositions of water samples in surface waters and within the effluent plumes would either fall within a three end-member mixing diagram (with upwelled water, POTW effluent, and river water representing the corners of the mixing triangle) and/or show evidence of biological alteration through either denitrification or nitrification (Kendall et al. 2007). No samples fell within the mixing diagram ranges, indicating that source signatures are either rapidly lost due to dilution with upwelled water or another source of nitrate or are rapidly biologically altered. Another uncharacterized source of nitrate to surface waters is nitrification of effluent ammonia. The ammonia concentration in effluent waters was much higher than nitrate concentrations; thus, ammonia may be converted in the water column to nitrate which could have a distinct isotopic composition from that of effluent nitrate or upwelling nitrate. Atmospheric nitrate was also unaccounted for isotopically (though it is expected to have very high $\delta^{18}O$ values and low $\delta^{15}N$ values). Either nitrified ammonia or atmospheric nitrate could account for the isotopic signatures observed in both surface waters of Lines 2200 and 2500 as well as plume tracking from the depth profiles above the discharge pipes.

Recommendations

This pilot study indicated that stable isotopes of nitrate could be used to provide some information on sources and cycling of nitrate in the SCB. However, several data gaps made interpretation of this data set difficult for source tracking, however future studies can rectify these data gaps in the following ways:

First, at least two sources were uncharacterized: atmospheric deposition and nitrate generated from nitrification of ammonia, the latter being a potentially large source given the relative concentrations of ammonia versus nitrate in POTW effluent. Data on the isotopic composition of "background" atmospheric nitrate in southern California is being assessed in a study conducted by SCCWRP during the summer and fall of 2012 (results are unavailable at the time of this writing). Data on the isotopic composition of nitrate resulting from nitrification of ammonia is currently unavailable. However, recent advances in stable isotope analytical chemistry have greatly improved the accuracy and precision of the analysis of the isotopic composition of ammonia (Hannon and Böhlke, 2008). Thus, the isotopic composition of effluent ammonia can be determined and traced into the nitrate pools.

Second, rates of denitrification and nitrification were not measured and consequently, the influence of these two processes on the data could not be quantified. Measurements of nitrogen transformations (denitrification and nitrification) have established protocols which could be applied to the SCB (Groffman et al 2006, Dore and Karl 1996).

Moving forward, studies to determine the fate of different nitrogen sources to the SCB should include the following as study components: (1) quantify the isotopic composition of nitrate-nitrogen, oxygen, and ammonia-nitrate for all potential sources, (2) measure key transformation rates (denitrification, nitrification), and (2) minimize the impact of small scale anomalies. Furthermore, measuring the isotopic composition of key food-web (microbes, phytoplankton, zooplankton) components could determine the influence of different sources on events such as algal blooms (Michener and Kaufman 2008).

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Riverine Nutrient Loads and Fluxes to the Southern California Bight (USA)

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ABSTRACT

This study presents estimates of total nitrogen and phosphorus fluxes from coastal watersheds to the Southern California Bight (SCB), USA, using a combination of field data and analytic modeling. Modeling was also used to estimate the contribution of urbanized land uses on riverine nutrient fluxes by hind-casting a pre-urbanization scenario. Total annual loads from watersheds contributed 3,900 ±130 metric tons (mt) total nitrogen (TN) and 790 ±21 mt total phosphorous (TP), yielding watershed-area normalized fluxes of 250 kg TN km^{-2} and 51 kg TP km^{-2}. Approximately 58% of the TN and 33 % of the TP loads were in the more biologically-reactive dissolved inorganic form. On average across the SCB, loading during storm events (wet weather) represented 65% of the annual TN and 77% of the TP loads to the SCB. Eight rivers constituted 70% of the TN and TP loads to the SCB: San Gabriel River, Los Angeles River, Calleguas Creek, Tijuana River, San Diego Creek (Newport Bay), and Santa Clara River-- watersheds which have heavy agricultural influences or receive discharges of treated municipal effluent. Prior to urbanization, nutrient loads were on the order of 910 mt TN and 96 mt TP. Thus relative to current day, urbanization has resulted in a four-fold increase in TN and an 8-fold increase in TP loads to the SCB from river discharge.

INTRODUCTION

Eutrophication of estuaries and coastal waters has increased globally in the last several decades (see reviews Howarth et al. 2002a, 2002b; Howarth 2008; Paerl and Piehler 2008) and many factors have been shown to contribute such as anthropogenic changes in watersheds, human population growth, increased food production which increase sewage discharges, agricultural and aquaculture runoff into the coastal oceans and burning of fossil fuels (Anderson et al. 2002; Glibert et al. 2005b; Howarth 2008). There are many ecological impacts from eutrophication such as harmful algal blooms (Anderson et al. 2008; Heisler et al. 2008), hypoxia (Rabalais and Harper 1992), impacts on aquatic food webs (Valiela et al. 1992; Kamer and Stein 2003), fish-kills and lowered fishery production (Glasgow and Burkholder 2000), loss or degradation of seagrass and kelp beds (Twilley 1985; Burkholder et al. 1992; McGlathery 2001), smothering of bivalves and other benthic organisms (Rabalais and Harper 1992), nuisance odors, and poor water quality (Bates et al. 1989, 1991; Trainer et al. 2002).

Rivers are a primary source of nutrients to coastal waters (Meybeck 1982). Increases in riverine nutrient fluxes over time are typically associated with land use changes and are strongly correlated to increasing population density (Howarth et al. 1996). In some urbanized regions, the nutrient fluxes have increased as much as 20-fold from pre-industrial times (Howarth et al. 1996). In upwelling systems such as the California Current ecosystem on the U.S. West Coast, however, there is a widely-held perception that spatial and temporal patterns of nearshore primary productivity are primarily driven by upwelled nutrients, and that nutrient fluxes of riverine or other anthropogenically-enhanced sources are insignificant in comparison. However, there is growing evidence that anthropogenic nutrients, and riverine inputs in particular can contribute to primary productivity during non-upwelling periods in California (Kudela et al. 2008; Lane et al. 2009; Quay 2011).

For the Southern California Bight (SCB), understanding of the importance of riverine nutrient loads to nearshore primary has been hampered by the lack of data. Estimating the riverine nutrient fluxes to the SCB, which drains a highly urbanized coastal region containing approximately 25% of the US coastal population (Culliton et al. 1990), will aid in discerning the relative importance of riverine inputs versus other sources in supporting the apparent increase in the extent of phytoplankton bloom in this coastal region over the last decade (Nezlin et al. 2011). This study represents the first attempts to estimate Bightwide riverine total nitrogen (TN) and total phosphorus (TP) fluxes, and to establish the extent of anthropogenic influences on those fluxes.

In general, riverine nutrient fluxes are typically quantified using two approaches: 1) direct, empirical measures, or 2) modeling. While direct measures of fluxes are understandably more accurate, for large regions such as Southern California, where discharge to the coast occurs via numerous watersheds, monitoring of riverine nutrient fluxes is patchy, because such data collection is expensive, labor intensive and plagued by the lack of long-term continuous flow and concentration data collected with standardized methods. In southern California, municipal stormwater programs are required to collect data on stormwater discharge and contaminant loads at the base of some of the SCB watersheds, but not all watersheds and storms are monitored, and data collection methods among those programs are inconsistent (Ackerman and Schiff 2003). Modeling riverine nutrient fluxes offers a complement to direct measures of riverine nutrient fluxes to extrapolate limited temporal and spatial monitoring data to make comprehensive estimates (Benard et al. 2011). In addition, unlike direct measures, models provide us with the ability to forecast trends in riverine nutrient fluxes as a function of projected land use change, or hindcast nutrient loading estimates prior to urbanization to establish an index of change.

A variety of approaches have been used to model riverine fluxes and the accuracy and precision of these models generally vary as a function of data input requirements (De Wit 2001; Proctor et al. 2003). Dynamic simulation models such as Hydrodynamic Simulation Program-Fortran (HSPF; Filoso et al. 2004) or statistical models as the SPAtially-Referenced Regression On Watershed (SPARROW; Alexander et al. 2008) are data intensive and can be costly to develop over large geographic areas. While less accurate and precise, simple spreadsheet models, such as those based on the Rational Method (Hydraulic Design Manual), can be useful in producing estimates of seasonal and annual fluxes of contaminants (Morgan 2005). The spreadsheet model utilizes a modeling paradigm similar to HSPF, in which rainfall falling on the land surface produces runoff to a stream drainage network that varies in volume and water quality as a function of the type of land cover (e.g. natural versus commercial, agricultural, residential and other land uses). Ackerman and Schiff (2003) developed the spreadsheet model to predict stormwater discharge, metal, suspended sediments and dissolved inorganic nutrient fluxes to the SCB. However, they acknowledged that data used to develop the model for dissolved inorganic nutrients were limited, and fluxes of TN and TP are widely acknowledged to be ultimately a better predictor of primary productivity in waterbodies (Howarth 1998).

The objectives of this study were two-fold: 1) Estimate wet and dry weather riverine nutrient fluxes to the SCB by a combination of empirical data and modeling, and 2) Estimate the increase in nutrients fluxes to the SCB due to urbanization of coastal watersheds.

METHODS

Study Area

The SCB is typically defined as an area from Point Conception (34.45°N) to the U.S. - Mexico border (32.53°N). The climate of this region is Mediterranean, with an average annual rainfall range of 10 to 100 cm, concentrated largely over the winter months of December-March, with an annual average of 15 rain events (Schiff et al. 2003). The majority of runoff to the SCB occurs during storm events (hereto referred to as “wet weather”). Baseflow during non-storm conditions (hereto referred to as “dry weather” runoff) have been elevated by the discharge of point and non-point source runoff from an urbanized land uses, as regional imports of water from the Colorado River and northern California have subsidized local water sources and have greatly altered the hydrological budgets of southern California coastal watersheds.

Conceptual Approach to Estimating Nutrient Loads

Total riverine nutrient fluxes to the SCB were estimated using empirical wet and dry weather data for monitored watersheds in combination with modeled wet weather fluxes for unmonitored watersheds. Continuous discharge data along with nitrogen (N) and phosphorus (P) concentrations and forms were collected for wet and dry weather (October 2008-2009) through the Southern California Bight Regional Monitoring Program (www.sccwrp.org). The spreadsheet model originally developed by Ackerman and Schiff (2003) was updated and modified to predict nutrient loads and fluxes to the SCB. The Ackerman and Schiff (2003) version, based on the Rational Method, estimated discharge, metal loads and along with dissolved inorganic nutrient loads (ammonium, nitrate, and phosphate). However, estimates of the total loads of TN and TP were not made. The model was modified to estimate TN and TP as well as dissolved inorganic nutrients, using updated land use-specific runoff concentrations for nutrients.

Field Sampling and Laboratory Methods

Discharge and water quality samples were collected at 34 wet weather and 57 dry weather mass emission stations by Ventura, Los Angeles, Orange and San Diego Counties under their National Pollution Discharge Elimination System (NPDES) permits or by SCB Regional Monitoring Program partners during the period of November 2007- October 2009 (Table 1). County NPDES reports were also reviewed for data on wet or dry weather runoff nutrient concentrations to supplement these data. Precipitation in this region has a strong interannual variation; total rainfall in 2008-2009 represents the 38th percentile of a comparative 13-year period (1997-2010).

Water quality samples of contaminants during storm events were collected as time-weighted (Orange County) or flow-weighted (other counties) composite and reported as event mean concentrations. Dry weather water quality was determined from single grab samples. The stormwater agencies routinely analyze nitrite+nitrate (NO_x), ammonium (NH_4), and soluble reactive phosphorus (PO_4) using automated colorimetry via an autoanalyzer (APHA 1992). Constituents of interest not routinely analyzed by the all the stormwater agencies included particulate nitrogen (PN) and particulate phosphorus (PP), TN and TP, silicate (Si), and urea. These additional constituents were analyzed on a split sample for all wet weather samples and on selected dry weather samples. Silicate was measured by automated colorimetry (APHA 1992). TP and TN were digested using the persulfate method (Valderrama 1981), then analyzed as PO_4 and nitrite (NO_2) by autoanalyzer (APHA 1992). Suspended matter particulate collected on a 0.7 µm glass fiber filter samples analyzed for PN and PP. Particulate P samples were digested by combustion and hydrolysis as in Solorzano and Sharp (1980) then analyzed as PO_4 by autoanalyzer (APHA 1992). Total suspended solids (TSS) were measured using a gravimetric technique (Banse et al. 1963).

Estimation of Wet Weather and Dry Weather Nutrient Flux from Field Data

Flow data available to calculate fluxes included: 1) continuous flow data from USGS or County-maintained gauges and 2) wet weather event monitoring, in which flow data is available only for the duration of the storm event.

Using continuous flow data, days representing wet weather events versus dry weather baseflow was categorized by plotting a hydrograph for November 2008-March 2009. The median flow was nominally assigned as the base flow and the 90th percentile represented a storm event. Thus the beginning of the wet weather event was determined when the total flow reached at least 120% of base-flow, and ended when the flow dropped below a threshold of 150% of baseflow. This was matched to the hydrograph to ensure accuracy.

Wet, dry weather, or total nutrient loads (L), given as daily loads (kg day^{-1}) or annual mass (kg) were estimated using nutrient concentrations (c, mg L^{-1}), flow - Q (m^3 day^{-1}), and a conversion constant k:

$$L = kcQ \qquad \textbf{Eq. 1}$$

Annual or daily flux, defined as watershed area-normalized load and expressed as kg km^{-1} day^{-1}, was calculated using L and watershed area (A_w)

$$F = LA_w^{-1} \qquad \textbf{Eq. 2}$$

Modeling Methods

A spreadsheet model based on the Rational Method (O'Loughlin et al. 1996) was used to generate freshwater runoff Q (m^3 day^{-1}) and the nutrient loads (N and P) associated with wet weather events. The general model set up, derivation of runoff coefficients for stormwater discharge volumes and land use specific runoff concentrations for TSS loads, metals and dissolved inorganic nutrients is described in detail by Ackerman and Schiff (2003), but is briefly presented here.

Modeled storm discharge (Q) is calculated as a function of drainage area (A, km^2), mean rainfall intensity (I, mm day^{-1}), hydraulic runoff coefficient (C), and conversion constant (k):

$$Q = AICk \qquad \textbf{Eq. 3}$$

Hydraulic runoff coefficient (C) varies as a function of land use/cover type (Table 2). Within each watershed, total discharge (Q) is then calculated as the sum of discharge from each of six land use categories: agriculture, commercial, industrial, open space (natural), residential, and other urban. The daily nutrient loads (L) and fluxes (F) were estimated as the sum of the product of the runoff concentration (c) and Q for each land use, using Equations 1 and 2.

The drainage area (A) is delineated for each watershed based on hydraulic unit code (HUC) Boundaries. The model domain includes all southern California coastal watersheds in San Diego, Orange, Riverside, Los Angeles, San Bernardino, Ventura and Santa Barbara counties with an initial total watershed area of 27,380 km^2 (Figure 1). Watershed areas larger than 52 km^2 upstream of dams were excluded in the model domain, in order to mimic the retention of water by dams (Ackerman and Schiff 2003). The final model domain comprised of 98 watersheds with a total of 14,652 km^2. Each of the watersheds was populated with land cover data from Stein et al. (2007), and aggregated into the six land use categories.

Daily precipitation data for approximately 200 rain gauge stations was obtained from the National Oceanic and Atmospheric Administration (NOAA), National Environmental Satellite, Data and Information Service (NESDIS), National Climatic Data Center (NCDC) and Climate Data Online (CDO) database. The data from the 200 rain gage station was transformed to estimate mean precipitation over the 98 watersheds relevant to the study. The precipitation data was interpolated within each watershed on a regular grid using a Biharmonic Spline Interpolation method (Sandwell 1987).

Model Refinement and Application to Predict Total Nutrient Loads

The model domain and set up developed by Ackerman and Schiff is identical to this study and no significant change has occurred in the land use cover since 2003. Therefore, existing model domain and hydraulic runoff coefficients (Table 2) were used to predict wet weather discharges. The Ackerman and Schiff model (2003) was improved by refining land use-specific runoff concentrations for NO_x, NH_4, and PO_4, based on values from recently published studies (Table 2; Yoon and Stein 2008; Stein et al. 2007).

Regionally, little literature is available to predict TN, TP, PN, and PP in runoff from specific land uses. In addition, the concentrations of PN and PP associated with suspended solids can be highly variable during a storm (Udiegwe et al. 2007) and often heavily dependent on watershed characteristics outside of land use (e.g. watershed geology, slope, size, storm volume; Yoon and Stein 2008). In this study, runoff concentrations for TN, PN, TP, and PP were estimated using a least squares regression model with dissolved inorganic nutrients and TSS from 29 storms (Table 3). A strong correlation between the concentrations of TN with $NO_{x,}$ and the concentrations of TP with PO_4 was observed; therefore, land use specific concentrations of TN and TP were derived from these dissolved inorganic forms to determine the total fluxes. Concentrations of PN had a low correlation with TSS, whereas PP had a high correlation with the TSS concentration.

Error Analysis and Interannual Variability in TN and TP Loads

Wet and dry weather nutrient load error estimates were based on 10 major watersheds that represent 80% of the wet weather flow and 90% of the dry weather flow. These watersheds were continuously monitored for flow, and it was assumed that the variability in nutrient concentrations was the major source of error or variability in the loading estimate. Error in the total load estimates for TN, TP and their dissolved inorganic forms was estimated as follows.

Standard deviations of nutrient concentration data were estimated for available site events in each watershed for wet and dry weather events and multiplied the standard deviation by the total wet or dry weather discharge for the watershed. The total error for wet or dry weather loads of TN or TP is the square root of the squared sums of each of the individual estimates, as shown in Equation 4.

$$\text{Total Load Standard Deviation} = \left(\sum_{1}^{10} (C_e Q)^2\right)^{1/2} \qquad \textbf{Eq. 4}$$

where C_e is the standard deviation in nutrient concentration for available wet or dry sampling events for that watershed. Q is the total annual wet or dry weather discharge.

To understand the 2008-2009 nutrient loads into a broader context, interannual variability in TN and TP loads over the comparative 13-year period (1997-2010) were examined. Interannual variability for this period correlated well with the land use data from 1997-1998 used in this study (Ackerman and Schiff 2003, Project 1998). Extensive land use data required to estimate modeled load is unavailable for periods earlier than 1997. Wet weather loads were modeled in this study, and it was assumed that dry weather loads remain relatively constant over the comparative 13-year period.

Use of the Model to Predict Anthropogenic Influence on Riverine Nutrient Fluxes

To estimate the anthropogenic influence on nutrient fluxes to the SCB, a model scenario with 100% open space land use for the entire Bight, representing a "pre-urbanization" baseline, was run. Because there were no dams withholding potential runoff in the modeled pre-urbanized state, the model domain was expanded to include areas above existing dams. Rainfall data is not available for the period representing the pre-urbanized state; therefore, current rainfall data (2008-2009) were used to estimate loads. This enables a comparison of pre- and post-urbanization loads without any bias due to differences in precipitation.

RESULTS

Nitrogen, Phosphorus and Silica Concentrations, Form, and Ratios in Measured Riverine Wet and Dry Weather Discharge

On average, mean TN concentrations in wet weather runoff to the SCB were not significantly different than the dry weather riverine mass emission stations runoff concentrations (Table 4). NO_x represented 39% of TN in wet weather and 36% in dry weather, while NH_4 represented 6% of TN in wet weather and 3% in dry weather. The greatest differences in N form across wet and dry weather were in the relative distribution of PN and dissolved organic nitrogen (DON). During wet weather, DON approximately equal to PN, while during dry weather DON was 3 to 4 times higher than PN. Urea was a minor component of total DON (10 %), with average concentrations of 0.17 to 0.1 mg urea-N L^{-1} for wet and dry weather, respectively.

Phosphate was a minor component for both wet and dry weather, representing 17 to 23% of TP. Dissolved organic phosphorus (DOP) and PP co-dominated the wet weather distribution (45% DOP and 38% PP), while the distribution changed in the dry weather with 68% DOP and 9% PP.

Silicate concentrations in riverine runoff to the SCB were roughly 50% lower during wet weather relative to dry weather. Mean molar Si: PO_4 ratios for all rivers sampled Bightwide indicate that silicate is not limiting during wet or dry weather runoff, relative to the Redfield-Brzezinski ratio of 15:16:1. DIN:PO_4 for total loads to the SCB during both wet and dry weather events indicate that runoff is P limited (19:1 wet and 18.1: 1 dry), as was TN:TP ratio of total dry weather loads (18:1). Flow-weighted ratios of TN:TP during wet weather were slightly N-limited (9.3:1). Table 5 shows show high variability in Si:DIN:PO_4 ratios among rivers.

Model Validation - Discharge, Nitrogen and Phosphorus Loads

Validation of model hydrology based on 29 storm events during 2008-2009 shows good correspondence between modeled (562 x 10^6 m^3) versus measured stormwater volume (461 x 10^6 m^3; R^2 = 0.79, slope: 1.17) for wet weather, with the model overestimating storm volume by 17%. A time series of modeled versus measured discharge shows that the model captures the timing and magnitude of peak flows to the SCB (Figure 2).

Modeled nutrient loads were validated with measured loads from 23 watersheds that had a complete suite of measured discharge and nutrient concentration data for the 2008-2009 wet weather (Table 6). On an individual watershed level, the model tends to under-predict nutrient loads, with slopes from 0.63 to 0.14. The model performs best for TP, TN, NH_4, and PO_4 and poorest for NO_x (Table 6). Analyses indicate that the outliers had a disproportionately high representation of watersheds with POTW effluent discharges and/or heavy dominance by agricultural land uses. When aggregated across watersheds, the relative error improves, ranging from 4 to 38% for TP and TN respectively and 18 to78% for dissolved inorganic forms (Table 6).

Loads and Fluxes of Water, Nitrogen and Phosphorus to the SCB

Total discharge from the SCB during the 2008-2009 water year was estimated at 760 x 10^6 m^3; area normalized discharge was estimated at 4.90E^{-02} m yr^{-1}. Dry weather discharge represented 40% of total annual discharge (299 x 10^6 m^3), with approximately (134 x 10^6 m^3 dry weather flow occurring during the wet season October 1-April 30. Twelve of the 90 watersheds account for approximately 80% of wet weather discharge, while 10 watersheds account for 90% of the dry weather flow. Measured total and area-normalized discharges from the monitored watersheds are shown in Table 7. Though larger watersheds tend to have higher peak storm flows, the urbanized watersheds normally have higher area-normalized discharges due to contributions from municipal effluent discharges and irrigated land uses. Urbanized watersheds also have higher dry weather flow (Los Angeles River, 97 x 10^6 m^3 and San Gabriel River, 72 x 10^6 m^3).

Total annual loads from watersheds contribute 3900 ±130 metric tons (mt) TN and 790 ±21 mt TP to the SCB (Tables 8 and 9). Normalizing these annual loads by contributing area yielded mean fluxes estimates of 250 kg TN km^{-2} and 50.6 kg TP km^{-2}. Approximately 58% of TN and 33 % of TP loads were in the dissolved inorganic form, considered to be more biologically reactive than dissolved organic or particulate forms (Tables 8 and 9). Approximately 94.2% of the loads were empirically measured from the monitored watersheds, making the contribution of modeled loads fairly insignificant (5.8%) for the 2008-2009 period.

The 2008-2009 water year was relatively dry, ranking within the 16th percentile of the comparative 13-year period. Using the model to estimate the 25th median and 75th percentile of wet weather nutrient loads over the comparative 13-year period and assuming dry weather loads to be relatively constant over this period, the median TN and TP loads to the SCB was projected to be 4340 mt kg TN and 925 mt TP, respectively, with a range of 3040 to 9700 mt TN and 151 to 249 mt TP (representing the 25th and 75th percentile of the comparative period). Normalized over watershed areas, median fluxes over the comparative 13-year period were 278 kg km^{-2} TN and 59 kg km^{-2} TP.

On average, riverine TN loads were 46% higher and TP loads were 71% higher during wet weather than dry weather. The exception to this was observed in San Gabriel, Los Angeles and Santa Clara Rivers, where TN and TP loads were comparable or greater during dry weather. The San Gabriel River, Los Angeles River, Santa Clara River and Calleguas Creek watersheds represent the dry weather "hot spots" for nutrient loading to the SCB, representing 59 % of the dry weather total TN and 62% of the total TP loads to the SCB (Figure 3). During wet weather, eight watersheds (Los Angeles River, San Gabriel River, Calleguas Creek, San Diego Creek, Tijuana River and Santa Margarita River, Chollas Creek and Santa Ana River) account for 75% of the TN loads, while eight watersheds (Los Angeles River, San Gabriel River, Calleguas Creek, San Diego Creek, Tijuana River, Santa Margarita River, Santa Clara River and San Marcos River) constituted 71% of the wet weather TP loads (Table 7; Figure 3).

Among watersheds, fluxes vary over several orders of magnitude (0.9 to 2436 kg km^{-2} TN, 0.2 to 245 kg km^{-2} TP). Ranking the watersheds based on fluxes rather than absolute loads allowed us to parse out the watersheds that contribute more N and P on an areal basis; for example, many watersheds, such as Los Angeles River watershed, contribute significantly to the total nutrient load but have relatively lower nutrient fluxes,.

Anthropogenic Influence on Riverine Nutrient Fluxes

Bightwide, the model predicts that nutrient loads pre-urbanization were on the order of 910 mt TN and 96 mt TP, which represents a 4-fold increase in TN and an 8-fold increase in TP, relative to a predevelopment scenario. The effect of anthropogenic land use changes was disproportionate on nutrient forms; NH_4 loads increased 14-fold, compared to NO_3 (5-fold) and PN + DON (4-fold); for P, the model predicts a 25-fold increase for PO_4 loads, compared to 6-fold increase in the PP+DOP loads.

The degree of increase predicted by the model varies among SCB subregions: South San Diego, North San Diego/South Orange County, North Orange County/San Pedro Bay, Santa Monica Bay, Ventura and Santa Barbara (Figure 4). Binning the watersheds highlights the distribution of nutrient loads increase throughout the Bight, with more heavily urbanized area showing the greatest increase. The largest change was observed in North Orange County/San Pedro Bay and Santa Monica Bay subregions, with an approximately 9-fold increase in the TN and 14-fold increase TP loads (Figure 4). The lowest change was observed in Santa Barbara with a below the Bight average 2-fold in TN and 3-fold increase in TP.

DISCUSSION

Comparison of SCB Riverine Nutrient Fluxes and Estimated Anthropogenic Contribution with Other Regions

Nearshore eutrophication is one of the major consequences of anthropogenically-induced global change on the world's coastal oceans (Vitousek et al. 1997; Boesch et al. 2000; Scavia et al. 2002). While nutrient pollution in coastal waters is generally greatest where agricultural activity and urbanization are intense, neither the distribution of loading nor the effects on the coastal ecosystems are uniform; thus there is a critical need to better document the quantitative links between anthropogenic activities in watersheds, nutrient inputs to coastal systems, and their ecosystem effects.

This study presents the first estimates of TN and TP fluxes from riverine sources to the SCB, an ecologically important yet highly urbanized region of the California Current ecosystem. Annual median riverine nutrient fluxes to the SCB over a period of 1997-2010 were estimated at 4340 mt TN and 925 mt TP, representing Bightwide watershed area normalized fluxes of 278 kg TN km^{-2} and 59 kg TP km^{-2}. SCB TN and TP fluxes estimated in this study are roughly a one quarter those of the US Atlantic Coast and Northern Europe watersheds, recognized as having some of the highest nutrient fluxes published (Table 9). However, some heavily urbanized SCB watersheds had peak fluxes of up to 2,436 kg TN km^{-2} and 245 kg TP km^{-2}, which are double the estimates for US Atlantic and Northern Europe watersheds.

Within the continental United States, human activity has increased riverine N fluxes to the coast by an estimated 6-fold (Howarth et al. 2002b; Howarth 2003). In some areas of the world, such as in the Yellow Sea of China, human activity has increased N fluxes by 10- to 15-fold (Howarth 2003). The present study estimated that anthropogenic land use changes in SCB coastal watersheds have increased nutrient loads to the SCB by approximately 3000 mt TN and 700 mt TP, representing a 4-fold increase in N and an 8-fold increase in P from the pre-urbanization scenario. Dissolved inorganic nutrients have a disproportionate share in the increase; relative to the pre-urbanization estimates, NH_4 loads increased 14-fold, NO_3 loads increased 5-fold, while PO4 increased 25-fold. These increases can been attributed to largely to fertilizer application, treated municipal and industrial wastewater releases, human-induced increases in atmospheric deposition of oxidized forms of nitrogen, fixation by leguminous crops (Howarth et al. 1996).

Significance of Magnitude, Timing, and Spatial Patterns of Nutrient Loads to the SCB
Anthropogenic inputs of nutrients loads have a well-documented linkage with effects on coastal ecosystems (Nixon 1995; Paerl 1997; NRC 2000). However, in eastern boundary current systems such as those found in coastal California, the relative importance of this term to vertical wind-driven nutrient flux (upwelling) (Bakun et al. 2010) is still unclear (e.g. Kahru et al. 2009]. In California, there is a widely held perception among coastal resource managers that anthropogenic nutrient sources are a relatively minor factor in comparison with upwelling, even in highly urbanized coastal areas such as Southern California (Warrick et al. 2005). Yet, a rigorous source comparison has yet to be completed for this region and is now the focus of current work by the Bight 2008 Regional Monitoring Program (Howard et al. unpublished data).

In a 12-year analysis of ocean color data collected by SeaWiFS satellite imagery, Nezlin et al. (2011) found that over the last decade, the extent of phytoplankton blooms have increased significantly in the SCB coastal waters. While region-wide, nutrient loading during storm events represents 68% of the annual TN and 80% of TP delivered to the SCB, Nezlin et al. (2011) found no evidence on a regional scale that phytoplankton blooms increased significantly after storm events. However, Nezlin et al. (2011) acknowledged on a local scale that anthropogenic inputs could be more important; proximal to large river mouths, they noted that extent of algal blooms increased approximately 1 to 3 days following large storm events. Other studies in Southern California have shown that stormwater runoff can at times be the dominant source of nitrogen inputs during non-upwelling periods (Warrick et al. 2005; McPhee-Shaw et al. 2007). In Monterey Bay, a more extensive study of this dynamic has shown similar results where riverine inputs of nitrate exceeded upwelling inputs across short, daily to weekly, timescales as often as 28% of days in a given year (Quay 2011). It is important to recognize, that these short timescales are more ecologically relevant for primary productivity and HAB development.

Although smaller relative to wet weather loading, dry weather loading may be playing a role in sustaining chronic algal blooms in certain regions of the SCB. Nezlin et al. (2011) documented that regions along the coast in which chronic phytoplankton blooms were evident year round. These "hotspots" were generally co-located near river mouths, locations of the discharges of Publically Owned Treatment Works (POTW) treated effluent to ocean outfalls, and in shallow semi-enclosed basins characterized by long water residence time (e.g. Santa Barbara Channel, Santa Monica Bay, San Pedro Bay, and South San Diego, Nezlin et al. 2011). Chronic algal blooms in observed in Santa Barbara Channel and San Pedro Bay coincide with two main areas of significant dry weather discharge from the Santa Clara River/Calleguas Creek watersheds (which drain into the southwestern boundary of the Santa Barbara Channel) and the San Gabriel River/LA River watersheds, which drain into San Pedro Bay. Together, these dry weather discharges from these four rivers represented 59 and 62% of the total dry weather loads of TN and TP, respectively, into the SCB. The dry weather discharges are driven by in-stream discharges of treated POTW effluent and, in some cases, runoff from irrigated, intensive agriculture. Together with POTW ocean outfalls, this dry weather discharge represents a chronic source of nutrients to coastal waters. Previous work by Warrick et al. (2005) indicated that riverine discharge from the Santa Clara and Ventura Rivers was negligible relative to estimates of upwelling to the Santa

Barbara Channel. However, their analysis only focused on nitrate, rather than on TN and direct discharge of POTW effluent to the Santa Clara River estuary was not considered, which represents 99.6% of the total dry weather loads from this watershed to the Santa Barbara Channel.

Comparison of SCB riverine nutrient fluxes to the outfall discharges from large and small POTWs, other major source of nutrients to the SCB, indicates that riverine nutrient loads are generally an order of magnitude lower than POTW discharge for TN and roughly two-fold lower for TP (5.1×10^4 mt TN and 2.2×10^3 mt TP; Lyons and Sutula 2011; Lyons and Stein 2009). If POTW discharges to the SCB via ocean outfalls are included in this estimate, the estimate of anthropogenic influence on nutrient loads to the SCB increase to 5.4×10^4 mt TN and 2.9×10^3 mt TP. Additional work is needed to compare these estimates to other sources of nutrients to the SCB (e.g. upwelling, atmospheric deposition), to understand the anthropogenic influences on these additional sources and to understand the relative importance of these inputs on a sub-basin scale (e.g. San Pedro Bay, Santa Barbara Channel).

It is important to quantify not only the loads of TN and TP entering coastal waters, but also the magnitude and ratios of nutrient forms (dissolved inorganic, organic, and particulate forms), because different elements and elemental ratios can have different bioreactivities and ecosystem effects. The pools of NO_3+NH_4 and PO_4 are considered to be readily bio-available, while only a portion of DON and DOP is readily available for uptake bacteria and some phytoplankton (Bronk 2002; Seitzinger et al. 2002). However, DON and particularly urea can be an important N source. Urea has been implicated in the formation of coastal harmful algal blooms and in increased toxin production in common California HAB species (Paerl 1988; Berg et al. 1997; Berg et al. 2003; Granéli et al. 1999; Kudela and Cochlan, 2000; Glibert et al. 2005a, 2005b; Howard et al. 2007; Cochlan et al. 2008; Kudela et al. 2008; Switzer 2008).

Within the SCB, riverine dissolved inorganic nutrient fluxes constituted approximately one-third to one half the TN and TP fluxes respectively, comparable to estimates by Ackerman and Schiff (2003). Urea was very low in riverine TN concentration, representing 10% of DON and 3 to 4% of TN. Mean molar Si:PO_4 ratios for all rivers sampled Bight wide indicate that silicate is not limiting during wet or dry weather runoff, relative to the Redfield-Brzezinski ratio of 15:16:1. DIN:PO_4 ratios for total loads to the SCB during both wet and dry weather events indicate that runoff is P limited (19:1 wet and 18.1:1 dry; Table 5), as is the discharge of POTW effluent to ocean outfalls (58:1 DIN:PO_4). Total annual riverine nutrient flux is somewhat N-limited, based on a TN:TP ratio of 10.8:1, while the average Redfield-Brzezinski ratio of upwelled waters in this region is 13:10:1, indicating an N-limited source. To understand the implications of these ratios, further work is required to analyze the source budgets on ecologically relevant spatial and time scales (weeks-to-months) for individual sub-basins within the SCB, factoring in oceanic circulation, composition of dominant phytoplankton communities, and importance of trace metals and other limiting factors (Ladizinsky and Smith 2000; Rue and Bruland 2001; Maldonado et al. 2002; Kudela et al. 2004; Mitrovic et al. 2004, 2005; Wells et al. 2005; Sunda 2006)

Evaluation of Methodology for Estimating Riverine Nutrient Fluxes

The present study sought to estimate riverine nutrient loads and fluxes to the SCB using a combination of empirical measurements and modeling techniques. Similar attempts have acknowledged the limitations inherent in such large-scale estimates (Meybeck et al. 1988). It is helpful to understand the limitations in methodology and possible sources of bias in these estimates in order to appropriately use them in the appropriate context. For the 2008-2009 hydrological year, the majority of loads to the Bight were estimated based on empirical data, while the model accounted for only 6% of the total loads. The absolute error for 2008-2009 estimates, calculated based on the variability in mean concentrations of wet and dry weather nutrients respectively for the top 10 watersheds discharging to the SCB, is roughly in the 25th to 75th percentile range of loads to the SCB over a 13-year period. Thus, load estimates for the present study are reliable generally within an order of magnitude. However, these estimates do not adequately capture temporal variability in wet or dry weather concentrations over a season and years, particularly with respect to well-studied watershed processes, such as first-flush phenomenon, that inherently provide tremendous variability (Bertrand-Krajewski et al. 1998). Constituent concentrations from a given land use will vary from site to site and storm to storm. This variability is magnified when the area of interest is expanded from single land use areas to watersheds because of runoff behavior and complexity. Assumptions were based on investigating long-term loading to the SCB, but understanding inter-storm and intra-site variability is critical to estimate loads on a shorter time scales.

The spreadsheet model based on Rational method predicts the volume of stormwater discharge to the SCB within acceptable degree of accuracy at this spatial scale (Ackerman and Schiff 2003), indicating that the model is hydrologically well-optimized. However, wet weather nutrient loads are generally under-predicted by 3 to 48% in TP and TN loads respectively, and at greater percentages for dissolved inorganic nutrients. One primary reason is the resolution of land use-specific runoff data; currently many diverse land uses are lumped generally within one category (e.g. agriculture includes nurseries, dry land row cropping, orchards, etc.). These predictions could improve with optimization given more extensive land use-specific runoff information (Ackerman and Schiff 2003). Another factor was limited sample size of important constituents, which limited the ability to model representative concentrations. Another factor unaccounted for is the discharge of high-nutrient groundwater, acknowledged to be a factor in watersheds such as San Diego Creek (Hibbs et al. 2007), the discharge of imported water (e.g. Santa Margarita River; Thomas et al. 2006), and treated effluent releases (e.g. San Gabriel River; Mitrovic et al. 2004) which in some watersheds can elevate the wet weather baseline well above what would be predicted based on nonpoint source runoff due to precipitation. Use of the Rational Method for this analysis also assumes that nutrients near the coast are transported with equal efficiency as those that originate in headwater regions, something that for nutrients such as nitrogen that can transform or denitrify, is not likely to be the case. To overcome these assumptions, more complex models such as HSPF (Bicknell et al. 1997), SWMM (Huber and Dickinson 1988), or SPARROW (Smith et a1. 1997) are required to incorporate additional hydraulic, hydrodynamic, and water quality processes.

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Tables

Table 1 Number of monitored watersheds with the number of wet and dry weather monitoring events

County/Partner	Wet Weather Sites	No. of Site-Events Monitored	Dry Weather Sites	No. of Site-Events Monitored
Ventura	4	8	3	9
Los Angeles	7	14	7	49
Orange	12	22	11	44
San Diego	11	22	11	11
Bight '08 Estuaries	--	--	25	150
Total	**34**	**66**	**57**	**263**

Table 2 Runoff coefficients (C) for stormwater discharge and average concentrations of ammonium, nitrate, phosphate and total suspended solids in runoff from land uses based on literature and regional stormwater studies - Values are from Ackerman and Schiff (2003) unless otherwise noted

Land Use Type	Runoff Coefficient	Ammonium (mg L^{-1})	Nitrate (mg L^{-1})	Phosphate (mg L^{-1})	Total Nitrogen (mg L^{-1})	Total Phosphorus (mg L^{-1})
Agriculture	0.10	1.34	7.31	3.27	10.41	11.30
Commercial	0.61	0.45	1.30[b]	0.09	3.56	0.56
Industrial	0.64	0.34	1.29[b]	0.32	3.55	1.33
Open	0.06	0.04[a]	0.34[a]	0.03[a]	2.46[a]	0.35
Residential	0.39	0.42	1.65[b]	0.25[b]	3.96	1.10
Other Urban	0.41	0.40	0.80	0.17	3.00	0.83

[a] Value from Yoon and Stein (2007)

[b] Value from Stein et al. (2007)

Table 3 Relationship between predicted nutrients (particulate, total, and total-dissolved N and P; PN, TN, TDN, PP, TP, and TDP, respectively) and observed total suspended solids (TSS) and inorganic nutrients (NO_x and PO_4) - $NO_x = NO_2+NO_3$

Predicted (y)	**Observed (x)**	**Relationship**	**Regression Coefficient**
PN	TSS	$y=0.23x^{0.23}$	0.11
TDN	NO_x	$y= -0.062x^2+0.65x+1.7$	0.1
TN	NO_x	$y=1.14x+2.08$	0.6
PP	TSS	$y=0.006x^{0.80}$	0.7
TDP	PO_4	$y=0.76x+0.119$	0.57
TP	PO_4	$y= 3.38x+0.25$	0.4
TP	PO_4 (x_1), TSS (x_2)	$y=1.72x_1+0.017x_2+0.08$	0.58

Table 4 Mean concentrations and standard deviations of N and P forms (total nitrogen (TN), NO_2+NO_3 (NO_x), ammonium (NH_4), dissolved organic nitrogen (DON), urea, and particulate nitrogen (PN), total phosphorous (TP), phosphate (PO_4), dissolved organic phosphorous (DOP), particulate phosphorous (PP) and silicate (Si)) in wet and dry weather discharge, and percentage of TN and TP where applicable - n = sample size (total number of wet or dry weather sampling events) and all concentrations are expressed in mg L^{-1}

Constituent	**Wet Weather (n = 66)**		**Dry Weather (n = 263)**	
	Mean ±Std Dev	**% of TN**	**Mean ±Std Dev**	**% of TN**
TN	4.16±2.18	--	3.38±3.57	--
NO_x	1.61±1.17	39%	1.33±2.25	36%
NH_4	0.26±0.29	6%	0.11±0.12	3%
DON	1.18±0.82	28%	1.74±2.32	48%
- Urea	0.17±0.13	4%	0.10±0.11	3%
- Other DON	1.01±0.69	24%	1.64±2.21	45%
PN	1.10±1.26	27%	0.48±0.74	13%
	Mean ±Std Dev	**% of TP**	**Mean ±Std Dev**	**% of TP**
TP	1.52±1.93	--	0.60±1.02	--
PO_4	0.26±0.23	17%	0.15±0.32	23%
DOP	0.68±0.93	45%	0.43±0.86	68%
PP	0.58±0.93	38%	0.06±0.09	9%
	Mean ±Std Dev		**Mean ±Std Dev**	
Si	4.0±2.8	--	7.3±2.7	--

Table 5 Silicate, dissolved inorganic nitrogen, and phosphate ratios (Si:DIN:PO_4) during wet and dry weather for Southern California Bight rivers sampled during study

Watershed Name	Wet Weather	Dry Weather	Watershed Name	Wet Weather	Dry Weather
Tijuana River	4: 10:1	ND	Laguna Canyon Wash	32:34:1	115:3:1
Sweetwater River	16:2:1	10:2:1	Costa Mesa Channel	5:42:1	21:5:1
Chollas Creek	4:17:1	ND	San Diego Creek	9:78:1	ND
San Diego River	118:18:1	59:3:1	Santa Ana Delhi Channel	19:172:1	462:24:1
Tecolote Creek	64:40:1	1408:5:1	Bolsa Chica Channel	ND	886:9:1
Los Penasquitos Creek	66:8:1	345:42:1	Coyote Creek	8:15:1	703:248:1
San Dieguito River	176:12:1	ND	Los Angeles River	8:13:1	28:12:1
Escondido Creek	93:71:1	75:23:1	Dominguez Channel	4:12:1	37:12:1
Agua Hedionda Creek	165:65:1	1665:151:1	Ballona Creek	10:12:1	131:31:1
San Luis Rey River	10:7:1	ND	San Gabriel River	19:24:1	23:28:1
Santa Margarita River	18:27:1	8:0.5:1	Malibu Creek	22:ND:1	194:4:1
Secunda Deschecha	ND	39:194:1	Santa Clara River	7:10:1	98:27:1
Prima Deschecha	31:120:1	23:127	Calleguas Creek	9:12:1	7:10:1
Arroyo Trabuco Creek	20:27:1	274:ND:1	Santa Clara River	146:85:1	130:53:1
San Juan Creek	24:34:1	999:22:1	Ventura River	521:68:1	876:42:1
Aliso Creek	26:45:1	43:69:1			
Average All Rivers	56:36:1	333:46:1			
Std. Error All Rivers	35:13:1	114:32:1			

Table 6 Results of model validation of nutrient loads where slope represents the accuracy of the prediction modeled load = Slope(measured load) *at a watershed scale*, R^2 represents precision, and relative error represents the difference between modeled and measured wet weather loads *summing across watersheds*

Nutrient Form	Slope	R^2	Relative Error in Total Loads Aggregated Across Watersheds
TN	0.50	0.63	38%
TP	0.63	0.30	4%
NH_4	0.63	0.71	18%
NO_2+NO_3	0.14	0.29	78%
PO_4	0.50	0.56	30%

Table 7 Watershed area (m^2), total nitrogen (TN) and total phosphorous (TP) fluxes (kg km^{-2} yr^{-1}); total and annual wet weather (WW) and dry weather (DW) discharge (m^3) derived from monitoring data

Watershed	Watershed Area	Total Annual Flux		Total WW Discharge	Annual WW Load		Total DW Discharge	Annual DW Load	
		TN	TP		TN	TP		TN	TP
San Gabriel River	3.0E+08	2436.1	245.0	8.1E+07	798.1	139.8	7.2E+07	1637.9	105.2
Chollas Creek	8.7E+07	1243.9	154.4	8.1E+06	1220.9	150.7	4.1E+05	22.9	3.7
Agua Hedionda Creek	7.9E+07	958.1	52.6	8.7E+06	705.2	41.8	1.2E+07	252.9	10.8
Los Penasquitos Creek	3.4E+07	846.5	173.1	9.7E+06	812.6	166.7	2.1E+06	33.9	6.3
Newport Bay	3.7E+08	741.2	188.7	2.2E+07	671.2	186.1	5.3E+06	69.9	2.6
Tecolote Creek	2.5E+07	613.5	69.0	3.8E+06	612.2	68.8	1.2E+05	1.3	0.2
Tijuana River	5.7E+08	605.9	154.9	2.6E+07	565.2	144.5	1.3E+06	40.7	10.4
Secunda Deschecha	2.8E+07	495.3	46.0	2.6E+06	195.6	38.1	5.8E+05	299.7	7.9
Calleguas Creek	8.7E+08	413.8	115.7	2.4E+07	249.6	90.0	1.3E+07	164.2	25.7
San Marcos Creek	1.5E+08	399.1	311.5	1.1E+07	391.4	310.2	1.7E+06	7.7	1.3
Los Angeles River	1.4E+09	383.2	57.7	8.7E+07	235.7	31.0	9.7E+07	147.5	26.7
Malibu Creek	1.2E+08	324.2	36.3	5.4E+06	190.4	28.7	6.6E+06	133.8	7.6
San Dieguito River	1.4E+08	310.3	101.8	4.2E+06	167.0	92.8	6.6E+06	143.3	8.9
Ballona Creek	3.2E+08	293.3	52.1	2.7E+07	240.0	43.0	9.3E+06	53.3	9.1
Escondido Creek	2.2E+08	289.3	11.4	9.5E+06	215.9	9.5	4.1E+06	73.4	1.9
Prima Deschecha	2.1E+07	282.7	9.8	4.7E+05	232.4	4.5	3.3E+05	50.2	5.3
Goleta Slough	1.3E+08	221.7	95.4	3.9E+06	212.8	94.1	6.2E+05	8.9	1.3
Dominguez Channel	1.7E+08	196.5	74.0	1.8E+07	127.6	63.8	4.1E+06	68.9	10.2
Bolsa Chica Channel	5.8E+08	189.8	31.5	4.1E+07	188.4	31.4	2.8E+05	1.4	0.0
Buena Vista Creek	5.8E+07	157.7	21.8	4.4E+06	144.5	21.2	4.3E+05	13.2	0.6
Santa Margarita River	9.8E+08	140.3	20.6	1.7E+07	137.6	19.5	7.6E+06	2.7	1.1
San Diego River	4.5E+08	121.2	11.5	1.9E+07	114.3	10.4	4.9E+06	6.8	1.1
Carpenteria Creek	9.4E+07	81.6	30.8	2.6E+06	81.6	30.8	3.4E+03	NA	NA
Santa Clara River	3.1E+09	76.5	18.8	1.8E+07	19.3	7.2	5.6E+05	57.2	11.6
Sweetwater Creek	1.2E+08	76.4	7.8	1.1E+06	23.3	1.8	2.3E+06	53.1	6.0
San Juan Creek	4.5E+08	66.3	17.1	1.1E+07	62.2	17.0	2.9E+06	4.1	0.2

San Luis Rey River	9.2E+08	47.2	8.9	5.9E+06	24.1	4.2	8.4E+06	23.1	4.6
San Mateo Creek	3.4E+08	26.3	2.2	2.5E+06	13.4	2.1	9.5E+05	12.9	0.1
Zuma Creek	2.6E+07	22.5	6.0	1.0E+05	21.9	6.0	2.0E+04	0.6	0.0
Laguna Creek	2.7E+07	15.8	1.2	6.7E+04	10.3	1.1	1.8E+04	5.5	0.1
Ventura River	7.8E+08	5.0	0.4	1.4E+06	0.8	0.1	5.4E+06	4.2	0.3
Topanga Creek	5.1E+07	3.7	0.8	6.2E+05	0.6	0.5	4.7E+05	3.0	0.3
Las Flores Creek	7.8E+07	1.0	0.7	2.0E+04	1.0	0.7	3.7E+03	NA	NA
San Onofre Creek	1.5E+08	0.9	0.2	9.3E+04	0.9	0.2	NA	NA	NA

Table 8 Total annual, wet and dry weather riverine loads (kg yr^{-1}) and fluxes (kg km^{-2} yr^{-1}) to the Southern California Bight by nutrient form

Nutrient Form	Wet Weather		Dry Weather		Total	
	Annual Load	Annual Flux	Annual Load	Annual Flux	Annual Load	Annual Flux
TN	2.67E+06	171.0	1.23E+06	78.8	3.90E+06	249.8
NH_4	2.71E+05	17.4	7.05E+04	4.5	3.36E+05	21.5
NO_3	1.15E+06	73.8	8.02E+05	51.4	1.95E+06	125.2
DON+PN	1.26E+06	80.5	3.54E+05	22.7	1.62E+06	103.2
TP	6.38E+05	40.9	1.51E+05	9.7	7.89E+05	50.6
PO_4	1.66E+05	10.6	1.07E+05	6.9	2.73E+05	17.5
DOP+PP	4.72E+05	30.3	4.42E+04	2.8	5.17E+05	33.2

Table 9 Absolute (kg yr^{-1}) and relative percent error of monitored total nutrient loads estimates to the Southern California Bight

Constituent	Wet Weather		Dry Weather	
	Absolute Error	% Error	Absolute Error	% Error
TN	2.24E+05	9	3.08E+04	2
NO_3+NO_2	8.45E+04	8	2.71E+04	4
NH_4	9.44E+04	38	8.17E+03	12
TP	3.76E+04	6	5.29E+04	3.5
PO_4	5.24E+03	3	1.96E+03	1.8

Table 10 Comparison of riverine nutrient fluxes from SCB watersheds to fluxes cited in similar studies - All estimates are in kg km^{-2} yr^{-1}

Source	Region	TN	TP
Howarth et al. 1996	North Canadian River	76	4.5
	Northeast Coast (U.S)	1,070	139
	North Sea	1,450	117
	Northwest European Coast	1,300	82
	Amazon & Tocatins	505	236
Ludwig et al. 2009	Mediterranean Sea	707	32
	Black Sea	422	21
This Study	Southern California Bight	355	63
	Southern California Bight (Top 10 Watersheds)	875	151

Figures

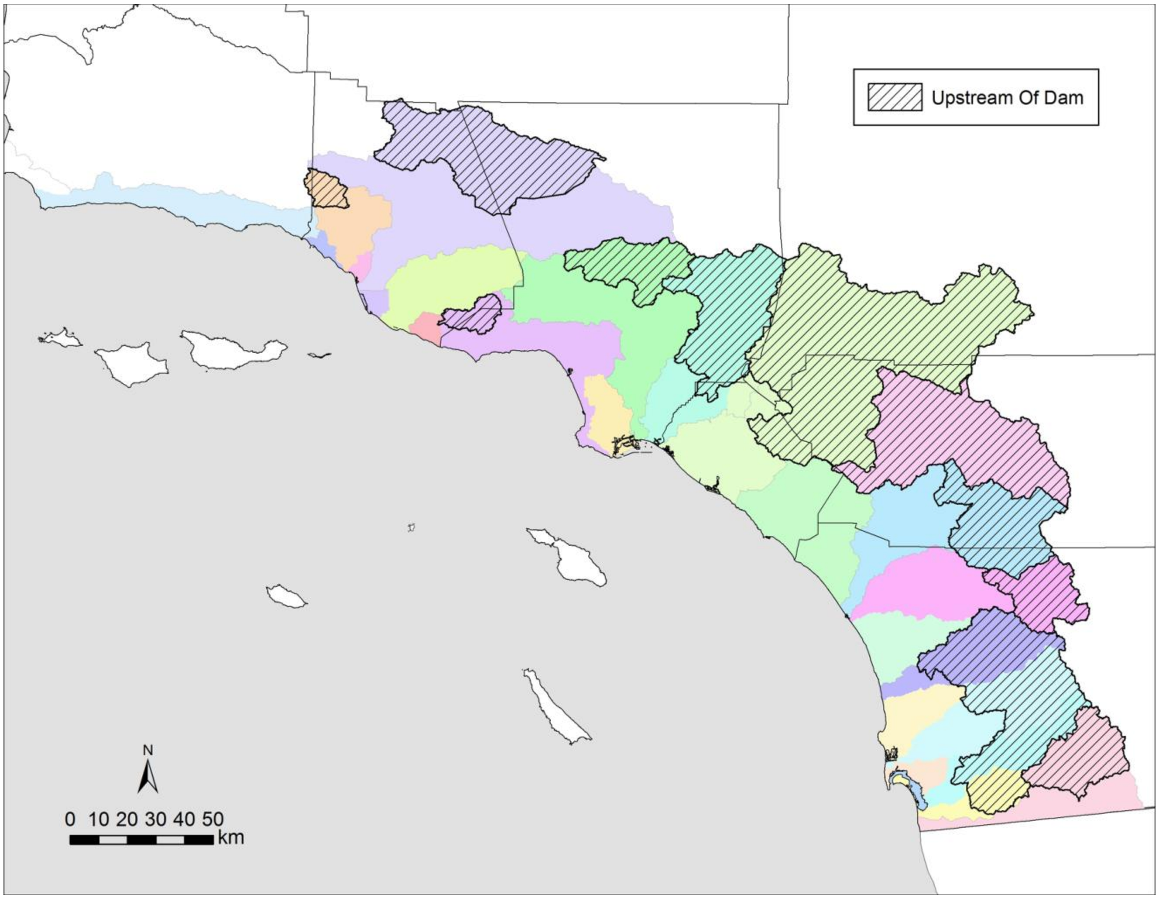

Figure 1 Map of the coastal watersheds draining to the Southern California Bight (colored areas), the geographic scope of the study - Hashed lines indicate areas behind major dams that were excluded from the model domain (see modeling methods)

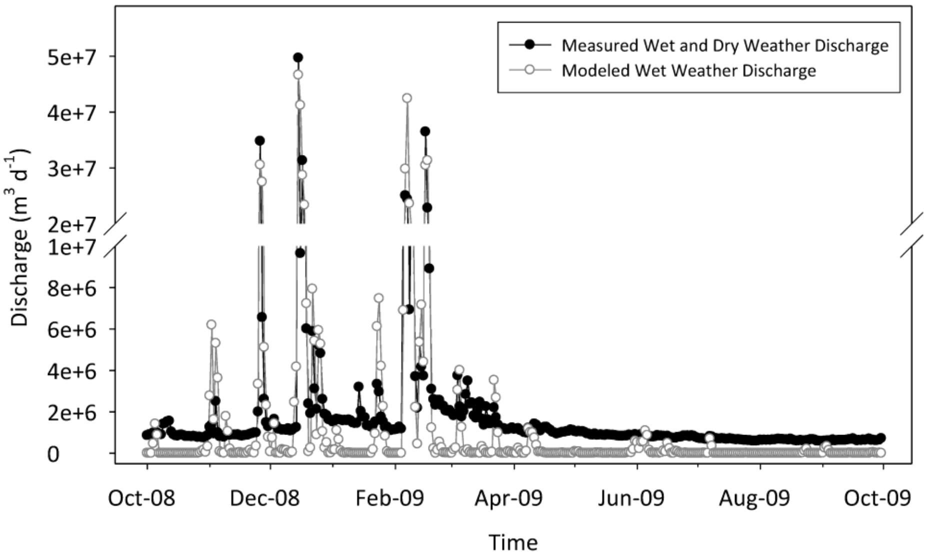

Figure 2 Comparison of total wet and dry weather measured versus modeled wet discharge (m^3 day^{-1}) to the Southern California Bight for October 2008-2009

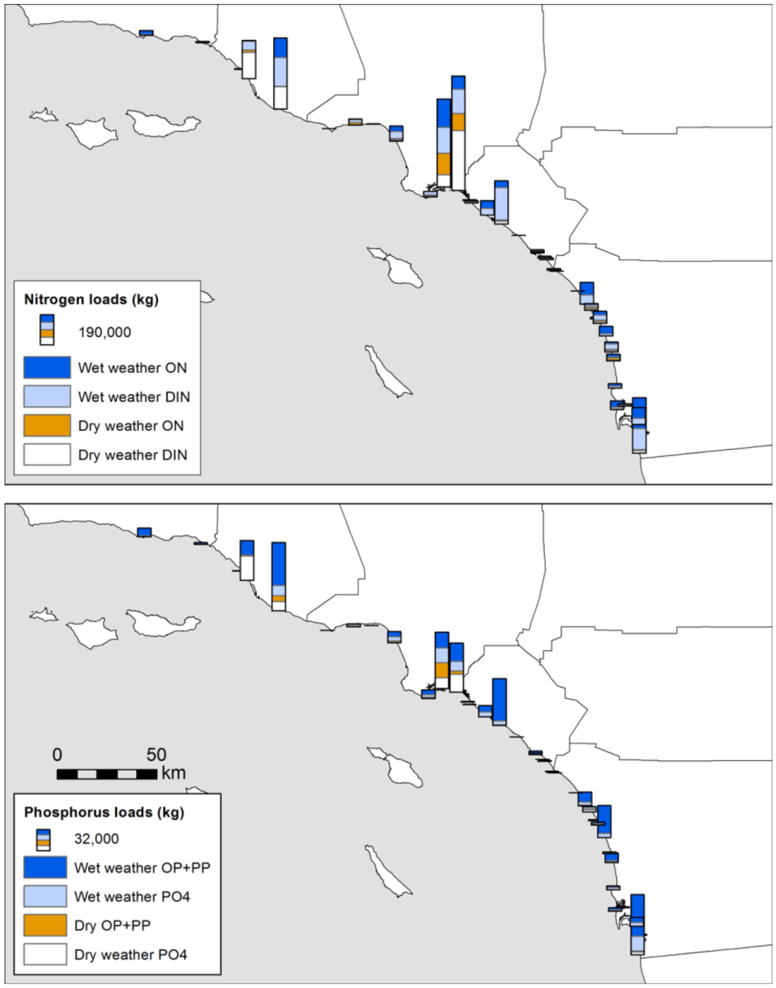

Figure 3 Relative magnitude of wet and dry weather Nitrogen and Phosphorus loading among SCB watersheds during 2008-2009

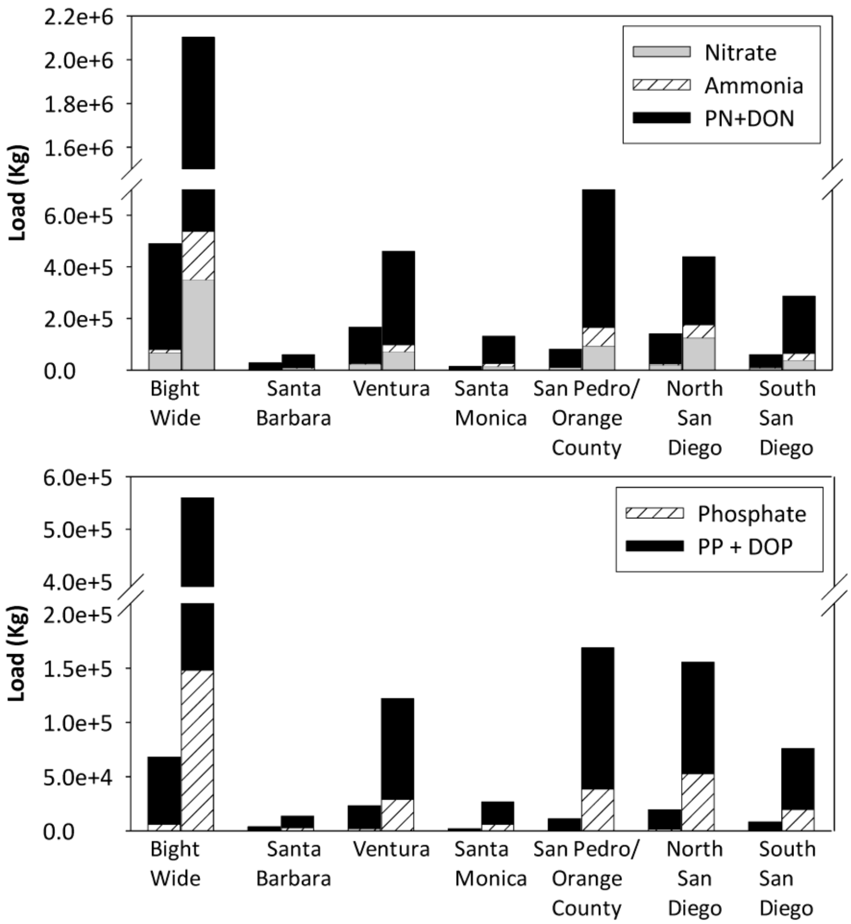

Figure 4 Estimated change in nutrient loads to the SCB as a result of anthropogenic changes in land use, with left bar representing a "pre-development" scenario and right bar representing a "post-development" scenario for each region – Pre-development represents a 100% open land use scenario under 2008-2009 rainfall amounts, while post-development represents the estimated loads during the 2008-2009 rainfall year