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Human Development is Linked to Multiple Water Body Impairments Along the California Coast

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ABSTRACT: To elucidate relationships between land cover and water quality along the central California coast, we collected monthly samples from 14 coastal waterway outlets representing various degrees of human development. Sites were distributed between three salinity categories, freshwater, estuarine, and marine, to better understand land cover-water quality relationships across a range of coastal aquatic ecosystems. Samples were analyzed for fecal indicator bacteria (FIB), dissolved nutrients, stable nitrogen isotopes in particulate organic matter, and chlorophyll *a* (chl *a*). Sediment samples from 11 sites were analyzed for the concentration of the anthropogenic organic contaminant perfluorooctane sulfonate and its precursors (ΣPFOS). While the data indicated impairment by nutrient, microbial, and organic contaminants at both agricultural and urban sites, the percentage of agricultural land cover was the most robust indicator of impairment, showing significant correlations ($p < 0.05$) to FIB, nutrient, chl *a*, and ΣPFOS levels. FIB densities were strongly influenced by salinity and were highest at sites dominated by agriculture and urbanization. Nutrient levels and chl *a* correlated to both agricultural and urban land use metrics as well. Positive correlations among FIB, nutrients, chl *a*, and ΣPFOS suggest a synergy between microbial, nutrient, and organic pollution. The results emphasize the importance of land management in protecting coastal water bodies and human health, and identify nutrient, microbial, and organic pollution as prevalent problems in coastal California water bodies.

Introduction

Accelerated human development in coastal areas is a serious threat to the sustainability of aquatic coastal ecosystems. Forty-four percent of the world's population lives within 150 km of the coast (Cohen et al. 1997), and this percentage is even larger in the United States. Understanding the increasing effects of the ever-growing human population on the coastal environment is critical to the development of sound management principles for the protection of both ecosystem health and the health of those who use these waters for recreation.

Surface runoff originating from a variety of anthropogenic land use practices adjacent to coastal waters is an important nonpoint source of pollution to coastal streams and rivers, as well as to marine waters. Agricultural practices can contribute excess nutrients (from fertilizers and animal waste), microbial pollution, and pesticides to coastal waters via runoff and contaminated groundwater, while also disturbing natural flow regimes through sedimentation and siltation (Wernick et al. 1998; Edwards et al. 2000). Impervious surface and storm drain systems in urbanized regions contribute to the creation of high volumes of runoff that are often enriched in microorganisms, nutrients, and organic contaminants (Osborne and Wiley 1988; Mallin et al. 2000).

In the present study, we examine relationships between human alteration of the environment and pollutant levels at study sites along the central California coast and within San Francisco Bay spanning 170 km and three salinity categories. Over a 15-mo period, monthly samples were collected at 14 fresh, estuarine, and marine waterways. We included freshwater, estuarine, and marine sites in our study to identify relationships that are relevant across a range of aquatic systems despite the potential effect of variable salinity and dilution of land-based runoff by seawater on pollutant concentrations. Indicators of microbial pollution and eutrophication, fecal indicator bacteria (FIB), dissolved nutrients, stable isotopes of nitrogen ($\delta^{15}N$), and chlorophyll *a* (chl *a*), as well as suite of perfluorinated compounds (ΣPFOS) were concurrently measured. FIB, including total coliform (TC), *Escherichia coli* (EC), and enterococci (ENT), are used worldwide as indices of water quality. Their occurrence can indicate the presence of a number of important sources of coastal pollution, including human and animal waste, partially treated sewage,

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urban runoff, and agricultural runoff (Bartram and Rees 2000). Studies report an increased human health risk associated with recreating in and consuming shellfish from FIB-contaminated waters (e.g., Balarajan et al. 1991). Nutrient levels and chl *a* provide a measure of anthropogenic nutrient enrichment and cultural eutrophication, while $\delta^{15}N$ of particulate organic matter (POM) can aid in identifying the source of nitrogen loadings (Kendall 1998; Chang et al. 2002; Costanzo et al. 2003). ΣPFOS are fluorinated organic compounds commonly used as coatings for textiles and fire fighting foams that show resistance to biological and chemical degradation (Key et al. 1998) as well as toxicological effects in laboratory animals (Giesy and Kannan 2002). The specific objectives of the present study were to identify the effects of land use on pollutant levels across a diverse set of coastal water bodies, and elucidate synergistic relationships between different pollutant groups.

Materials and Methods

Site Characterization

The central California coast provides a unique setting for our investigation because it contains a diverse set of land use practices and distinct wet and dry seasons. Fourteen sites, extending over 170 km from Monterey Bay in the south to San Pablo Bay in the north (Table 1) were chosen to represent various watershed land use practices. The sites were grouped into three salinity categories based on median salinity and salinity quartile range (75th to 25th percentile): nontidal freshwater creeks (fresh, median salinity < 5), estuarine rivers and tidal creeks (estuarine, median salinity > 5 and quartile range > 5), and marine embayments (marine, median salinity > 30 and quartile range < 5). Salinities are based on the practical salinity scale.

Watershed size, land use, percent impervious surface cover (ISC), and population size were determined for the smallest CalWater watershed delineation containing the sampling location using a combination of GIS data sets in ArcMap 9. Watershed delineations were obtained from the CalWater2.2 data set (http://cain.nbii.gov/calwater). Land use data were retrieved from the U.S. Geological Survey National Land Cover Dataset 1992 (NLCD 92), a 21-category land cover classification scheme with a resolution of 30 m. The 21 land cover categories were condensed into 6 broad categories described in Vølstad et al. (2003). Only three of these were relevant to the region of our study: agricultural (Ag), urban (Urb), and forested (Fo). We also calculated the total developed land for each watershed as the sum of Urb and Ag (UrbAg).

TABLE 1. Watershed and water body characteristics for the 14 study sites. Urban, agricultural, and forested land coverage data are from the National Land Cover Dataset (NLCD 92) and categorized based on Vølstad et al. (2003). Impervious surface data is from the NLCD 2002. The dominant land use for each site was determined using the procedure outlined in the Materials and Methods section.

Water Body (Site Code)	Waypoint	Salinity Category	Size (km²)	Urban %	Agricultural %	Forested %	Impervious Surface %	Population	Dominant land use category
Bolinas Lagoon (B)	37°54.52′N, 122°40.94′W	Marine	53.3	5.1	24.9	65.8	16.85	2,340	Forested
Kirby Park (K)	36°50.40′N, 121°44.61′W	Marine	30.6	4.0	55.3	9.9	19.46	1,739	Agricultural
Lagunitas Creek (L)	38°3.74′N, 122°49.00′W	Fresh	34.8	1.9	38.1	55.3	13.68	1,226	Agricultural
Moss Landing Harbor (E)	36°48.32′N, 121°47.21′W	Estuarine	30.6	4.0	55.3	9.9	19.46	1,739	Agricultural
Napa River (N)	38°5.75′N, 122°15.46′W	Estuarine	299	20.8	49.6	9.4	51.58	179,977	Agricultural
Petaluma River (Pe)	38°6.86′N, 122°30.39′W	Estuarine	105	12.4	61.8	4.3	50.51	42,786	Agricultural
Pilarcitos Creek (Pi)	37°35.73′N, 122°25.68′W	Fresh	27.7	6.3	44.7	47.1	29.22	5,202	Agricultural
Salinas River (Sa)	36°47.44′N, 121°47.41′W	Fresh	276.6	9.3	80.9	4.4	36.44	85,519	Agricultural
San Francisquito Creek (SF)	37°27.93′N, 122°6.92′W	Estuarine	31.5	59.4	20.2	16.8	37.03	171,203	Urban
San Lorenzo River (SL)	36°57.85′N, 122°0.60′W	Estuarine	25.9	72.0	13.5	10.0	46.7	61,580	Urban
San Pedro Creek (SP)	37°35.73′N, 122°30.34′W	Fresh	33.2	21.8	23.2	49.9	27.65	18,493	Agricultural
Soquel Creek (So)	36°58.35′N, 121°57.17′W	Fresh	12.1	83.4	3.4	8.0	51.68	31,079	Urban
Waddell Creek (W)	37°5.77′N, 122°16.69′W	Fresh	29.6	0.4	3.0	96.2	7.97	8	Forested
Yosemite Slough (Y)	37°43.33′N, 122°22.90′W	Estuarine	22.8	62.9	17.8	11.0	56.15	58,638	Urban

Previous studies have shown that using individual land use classes rather than broad categories does not significantly aid in resolving relationships between land use practices and water quality (Roth et al. 1998). The impervious surface portion of the NLCD 2001 data set was used to extract the percent ISC for each watershed.

Sample Collection, Preparation, and Analyses

Surface water samples (upper 5 cm) were collected on a monthly basis between June 2003 and August 2004 (except August 2003) at each site (Table 1). The Yosemite Slough (Y) and San Pedro Creek (SP) sites were not included in the study until July 2003 and October 2003, respectively. Monthly samples were collected over 2 d with 5–7 sites sampled each day. Sampling commenced in the early morning no later than 0630 h and typically ended by 1200 h.

Single samples of 500–1,000 ml were collected using clean high density polyethylene bottles that were rinsed three times with sample water prior to collection. Samples were immediately placed on ice and transported to the laboratory within at most 6 h of the first collection. At the time of collection, in situ salinity and chl *a* were recorded using a water quality probe (YSI 6600, Yellow Springs, Ohio). Samples were analyzed for FIB using Colilert-18 (TC, EC) and Enterolert (ENT) defined substrate tests (IDEXX, Westbrook, Maine, implemented in a 97-well Quanti-Tray). Ten milliliters of sample were diluted with 90 ml of Butterfield's buffer (Weber Scientific, Hamilton, New Jersey). These tests allow for the detection of organisms between 10 and 24,192 most probable number per 100 ml (MPN $(100\ ml)^{-1}$) of sample.

Thirty milliliters of 0.2-μm filtered sample water were frozen and stored for nutrient analysis. Concentrations of the combined nitrate and nitrite (nitrate + nitrite), nitrite, soluble reactive phosphate (SRP), and ammonium were determined using a 5-channel, continuous flow analyzer and standard methods (Atlas et al. 1971).

POM obtained from between 25 and 500 ml of each sample was collected on ashed Whatman GF/C filters (25-mm diameter) for isotopic analysis. After filtration, the filters were dried at 50°C and analyzed for $\delta^{15}N$ using a Carlo Erba NA1500 elemental analyzer/Conflo II device attached to a Finnigan Delta Plus mass spectrometer as described in Rowe et al. (2002).

During the March 2004 sampling, approximately 80 cm^3 of surficial sediments were collected from 11 sites: B, K, L, Pe, Sa, SF, SL, So, SP, W, and Y (see Table 1 for abbreviations). Sediment samples were analyzed for total mass of perfluorooctane sulfonate and its precursors (hereafter collectively referred to as ΣPFOS) per dry weight of sediment using a novel, sensitive technique described by Higgins et al. (2005). Sediments were subjected to hot methanol extraction, a reversed phase solid phase extraction clean-up procedure, and analyzed with liquid chromatography tandem mass spectrometry.

Statistical Analyses

All statistical analyses were carried out using Matlab v. 7.1 (Mathworks, Natick, Massachusetts). The Lilliefors test for normality was applied to each data series to determine the appropriateness of parametric analyses. The data sets were found to be predominantly nonnormal and nonlog-normal, so median values were used to characterize constituent levels at each site. The Spearman rank correlation (r_s), a distribution-independent analysis, was used to examine covariation amongst median values as well as raw data. To test for significant differences between median values, the nonparametric Wilcoxon rank sum test was employed. A significance level of $p < 0.05$ was used for all correlations and comparisons of median values.

Correlations between watershed characteristics and the various constituents were conducted at all sites, as well as separately for sites within each salinity category. The median concentration of each biological and chemical constituent over the entire study at the sites was correlated to watershed characteristics. Correlations among water quality parameters were calculated by pooling the raw data sets together. In the case of ΣPFOS, data from the single sediment sample were correlated to median values of other constituents for that site. This is justified because the persistence and accumulation of ΣPFOS in sediment reflects general water conditions, not necessarily the conditions cotemporaneous with the sediment collection.

When examining differences between results during wet and dry seasons, the wet season was defined as November through April and the dry season as between May and October. At each of 7 weather stations within our study area, at least 94.4% of the rainfall occurred during the period we defined as wet season (data not shown).

There were several instances where the FIB densities were below or above the detection limits of the assays. In these instances, values below the detection limit were replaced with half of the detection limit (5 MPN $(100\ ml)^{-1}$), and values above the upper detection limit (24,192 MPN $(100\ ml)^{-1}$) were replaced with 25,000 MPN $(100\ ml)^{-1}$. These quantitative replacements were made to allow for the calculation of medians and geometric means.

We developed a FIB impairment index for each site as follows. We calculated the geometric mean of

TABLE 2. California fecal indicator bacteria (FIB) standards for recreational contact. The fecal coliform group includes *E. coli* (EC), and is the standard used for evaluation of EC measurements. MPN is most probable number.

Indicator Bacteria Group	Single Sample MPN(100 ml)$^{-1}$	30-d Geometric Mean MPN(100 ml)$^{-1}$
Total coliform (TC)	10,000	1,000
Fecal coliform (FC)	400	200
Enterococci (ENT)	104	35

each indicator (TC, EC, and ENT) over the entire 15 mo. The means were subsequently normalized by the California 30-d geometric mean standard for TC, FC, and ENT, respectively (Table 2; EC geometric means were compared to the fecal coliform [FC] standard; because EC is a subset of FC, an exceedance of the FC standard by EC guarantees an exceedance by FC). The highest of the three normalized values was chosen as an FIB impairment index. A value less than one suggests that the site is not impaired with elevated densities of FIB relative to California standards, a value between 1 and 1.5 indicates moderate impairment, and a value greater than 1.5 indicates severe FIB impairment.

Results

The size of the watersheds where the sampling sites are located varies from 12.1 km^2 (site So) to 276.6 km^2 (site Sa; median for all sites = 72.3 km^2). The population size in the watershed outlets varies from 8 (site W) to 179,997 people (site N; median = 24,786 people; Table 1).

The watershed outlets are composed of between 0.4–83.4% Urb land use (median = 10.8%), 3.0–80.9% Ag land use (median = 31.5%), and 4.3–96.2% Fo land cover (median = 10.5%; Table 1). Sites with more than two-thirds Fo (B, W) were considered undeveloped and categorized as forested. All other sites were determined to be either urban or agricultural by the land use category comprising the larger percentage of the watershed. Four sites were classified as Urb (SF, SL, So, Y) and 8 sites as Ag (E, K, L, N, Pe, Pi, Sa, SP). ISC ranges from 7.97% at site W to 56.15% at site Y (median = 32.83%). Sites W and Y also have the lowest and highest Urb land cover of all the sites, respectively, reflecting the close relationship between Urb and ISC ($r_s = 0.87$, $p < 0.00006$).

Using the classification scheme defined in the methods section, 2 sites (B, K) were classified as marine, 6 sites (L, Pi, Sa, SP, So, W) as fresh, and 6 sites (E, N, Pe, SF, SL, Y) as estuarine (Table 1). The salinity category was used to examine how dilution of terrestrial runoff with varying amounts of seawater influences the relationships between watershed characteristics and pollutant concentration, as well as correlations between various pollutants.

Eleven of the fourteen waterways showed moderate or significant FIB impairment relative to the California standards (Table 2), suggesting potential human health risks from contact recreation and shellfish harvesting in these water bodies or their receiving waters. TC medians ranged from 74 MPN (100 ml)$^{-1}$ at site Y to 25,000 MPN (100 ml)$^{-1}$ at site Sa (Table 3). EC medians ranged from 10 MPN (100 ml)$^{-1}$ at sites Y and K to 384 MPN (100 ml)$^{-1}$ at site Pi. ENT medians ranged from 5 MPN (100 ml)$^{-1}$ at sites Y and W to 464 MPN (100 ml)$^{-1}$ at site Pi.

Site Y had the lowest FIB impairment index at 0.2, indicating it was not impaired relative to the

TABLE 3. Summary of median parameter values for the 14 sites over the entire study period. ΣPFOS values are from the sediment samples collected in March 2004. For site abbreviations see Table 1. nd = not detected. — indicates no sample collected. MPN is most probable number. n = 14 for all sites except for Y (n = 13) and SP (n = 11).

Parameter	B	E	K	L	N	Pe	Pi	Sa	SF	SL	So	SP	W	Y
Salinity	32.53	29.41	34.38	0.98	15.86	21.13	0.32	4.89	20.42	7.96	0.49	0.21	0.41	30.32
TC (MPN(100 ml)$^{-1}$)	80	11107	148	3727	1107	948	5475	25000	4352	7615	3193	4611	1114	74
EC (MPN(100 ml)$^{-1}$)	25	98	10	378	41	69	384	200	160	336	377	186	41	10
ENT (MPN(100 ml)$^{-1}$)	7	97	10	74	31	20	464	167	63	74	74	74	5	5
FIB impairment index	0.3	7.2	0.4	3.7	1.4	1.1	10.7	14.8	3.3	7.8	3.9	4.7	1.8	0.2
Ammonium (μM)	4.58	11.65	4.94	1.91	6.66	9.10	2.86	17.59	11.19	3.11	1.55	1.91	1.40	5.57
SRP (μM)	1.91	4.69	2.24	0.61	2.62	5.52	2.24	10.36	14.23	2.77	2.20	0.57	0.69	3.96
Nitrate + nitrite (μM)	11.92	415.06	4.49	9.73	23.40	16.06	144.84	1720.1	101.66	8.20	8.26	12.38	2.52	14.52
Nitrite (μM)	0.47	4.72	0.52	0.10	0.72	0.92	0.59	11.23	1.82	0.25	0.08	0.48	0.06	0.69
Chl *a* (μg l^{-1})	2.9	7.2	5.35	2.9	3.7	9.35	3.9	29.2	9.45	2.45	3.2	2.1	2.4	4
$\delta^{15}N$ (‰)	7.75	8.31	8.65	6.04	6.33	9.53	4.89	9.30	11.63	7.75	4.44	6.26	4.54	8.65
ΣPFOS (ng g^{-1})	0.811	—	0.201	0.312	—	1.92	—	3.69	4.65	0.124	nd	0.43	nd	0.288

California state geometric mean standards. At the other extreme, site Sa had the highest impairment index at 14.8. With the exception of marine sites B and K and estuarine site Y, all of the sites had FIB impairment indices greater than one; 8 sites, including both Urb and Ag sites, had impairment indices greater than 1.5, indicating severe impairment of microbial water quality (Table 3). The FIB impairment index was driven by high TC densities, with 10 of the 14 sites exhibiting the most impairment by TC.

Median nutrient concentrations ranged from 1.40 μM at site W to 17.59 μM at site Sa for ammonium, 0.57 μM at site SP to 14.23 μM at site SF for SRP, 2.52 μM at site W to 1,720.1 μM at site Sa for the combined nitrate + nitrite, and 0.06 μM at site W to 11.23 μM at site Sa for nitrite (Table 3). Chl *a* median values ranged from 2.1 $\mu g\ l^{-1}$ at site SP to 29.2 $\mu g\ l^{-1}$ at site Sa.

There are presently no set regulatory standards for nutrient concentrations in waterways. Still, it is helpful to place measured concentrations in context by comparing them to typical coastal concentrations. Coastal nearshore nutrient levels outside of San Francisco Bay and Monterey Bay typically range from 12 to 20 μM for nitrate + nitrite (Pennington and Chavez 2000; Wilkerson et al. 2002), indicating that the nitrate + nitrite-enriched sites E, Pi, Sa, and SF might be significant nutrient sources to nearshore coastal waters (Table 3).

Though California has not yet developed numeric criteria for chl *a*, the parameter is recognized as an effective primary response variable to assess the effect of nutrient loading in coastal aquatic systems (Clement et al. 2001). Previous studies have proposed mean chl *a* ranges describing eutrophic conditions for fresh (6.7–31 $\mu g\ l^{-1}$; Ryding and Rast 1989), estuarine ($>11.1\ \mu g\ l^{-1}$; USEPA 2003), and marine waters (3–5 $\mu g\ l^{-1}$; $>7\ \mu g\ l^{-1}$; Molvaer et al. 1997; Smith 1998). Based on these criteria, sites Sa, Pe, and E, all primarily Ag (>55%), are considered eutrophic during either the wet season, dry season, or both. Adopting criteria used in other states, we chose 15 $\mu g\ l^{-1}$ as a moderate cutoff above which a single chl *a* measurement would be considered symptomatic of eutrophication; samples exceeding this concentration were found at sites Sa, SF, K, E, and Pe.

At our sites, $\delta^{15}N$ values of POM ranged from 4.44‰ at site So to 11.63‰ at site SF (Table 3). Compared to an average $\delta^{15}N$ value of 4.4 ± 3.4‰ measured in four large U.S. river systems (Kendall et al. 2001), the values in this study are elevated. Eight sites in our study (B, E, K, Pe, Pi, Sa, SF, and Y) contained single $\delta^{15}N$ of POM values greater than 10‰, suggesting that at least some sites are receiving significant nitrogen from wastewater, untreated sewage, or manure (Costanzo et al. 2001). The $\delta^{15}N$ signature of POM is a useful tool for detecting anthropogenic effects on hydrosphere nitrogen cycles (Kendall 1998; Costanzo et al. 2001). The presence of nitrogen from manure (nitrate $\delta^{15}N \approx$ 10–22‰), treated sewage (nitrate $\delta^{15}N \approx$ 10‰), or fertilizer (nitrate and ammonium $\delta^{15}N \approx$ 0–2‰) can be inferred from the $\delta^{15}N$ values in the organisms using that nitrate, assuming the isotopic signature has not been substantially altered by denitrification or preferential nitrate uptake. All of our sites were oxic and there was no negative correlation between $\delta^{15}N$ and nitrate concentrations (data not shown), suggesting that our elevated $\delta^{15}N$ values are good representations of source values.

ΣPFOS in the sediments ranged from undetectable levels at sites So and W to 4.65 ng g^{-1} sediment at site SF (Table 3). For reference, sediments immediately adjacent to a wastewater treatment plant outfall in south San Francisco Bay contained ΣPFOS levels of 9.60 ng g^{-1} (Higgins et al. 2005). Detection of ΣPFOS at 9 out of 11 sites indicates widespread contamination in this region. This is of particular concern because this emerging class of organic contaminants is resistant to biological and chemical degradation (Key et al. 1998) and exhibits toxicological effects in laboratory animals (Giesy and Kannan 2002).

Discussion

FIB densities exhibited no significant correlations to watershed development metrics when sites in all salinity categories were pooled together (Table 4). If only the 6 fresh sites are considered, a significant correlation is observed between TC densities and Ag ($r_s = 0.94$, $p = 0.0048$). The fact that significant relationships between land use and FIB densities were not observed across all sites but only for sites within the fresh salinity category suggests that

TABLE 4. Spearman rank correlation coefficients (r_s) between land use metrics and median parameter values at all 14 sites. Significant level: * $p < 0.05$, ** $p < 0.01$.

Parameter	Fo (%)	Urb (%)	Ag (%)	UrbAg (%)	ISC (%)	Population size	Population density
TC	−0.12	0.03	0.16	0.24	−0.13	0.11	0.07
EC	−0.01	0.16	−0.06	0.17	0.01	0.03	0.07
ENT	−0.29	0.12	0.30	0.31	0.06	0.12	0.07
Ammonium	−0.57*	0.05	0.69*	0.46	0.28	0.51	0.23
SRP	−0.62*	0.31	0.39	0.69**	0.51	0.64*	0.46
Nitrate + nitrite	−0.37	0.09	0.59*	0.30	0.26	0.46	0.23
Nitrite	−0.54*	0.08	0.71**	0.42	0.31	0.52	0.30
Chl *a*	−0.64*	0.04	0.64*	0.53	0.32	0.39	0.19
$\delta^{15}N$	−0.43	0.17	0.48	0.45	0.28	0.48	0.39
ΣPFOS (n = 11)	−0.16	−0.05	0.68*	0.10	0.04	0.51	0.24

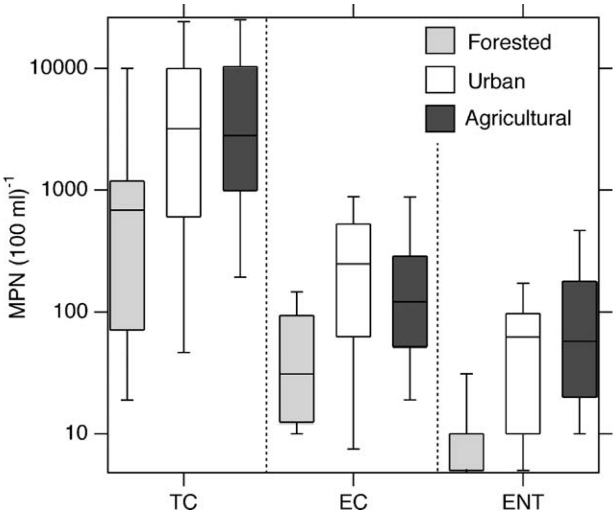

Fig. 1. Median indicator levels for forested, urban, and agricultural sites across all salinity categories. Upper and lower bounds of the box represent the 75th and 25th percentiles, respectively, and the whiskers are the 90th and 10th percentiles.

dilution of land-based flow by seawater or salinity-induced die-off (Bordalo et al. 2002; Kirschner et al. 2004) are important in controlling FIB densities in these waterways.

In a coarser measure of the effect of land use on indicator levels, median FIB densities at Urb and Ag sites were found to be significantly elevated ($p = 0.0012$) compared to Fo sites, though there were no significant differences between the Urb and Ag sites (Fig. 1). Within the estuarine salinity category, the Urb sites (SF, SL, Y; average Urb = 64.8%) had significantly higher EC levels ($p = 0.033$) than the Ag sites (E, N, Pe; average Ag = 55.6%). These findings support previous work identifying both Urb and Ag land cover as sources of microbial pollution (Edwards et al. 2000; Mallin et al. 2000), but are particularly important considering the spatial range and salinity gradient of the sites included.

A correlation analysis between land use and FIB with wet and dry season data alone did not reveal any significant seasonally-dependent correlations. It is interesting to note that FIB densities do exhibit strong seasonality (Fig. 2). Significantly ($p < 0.014$) elevated TC and EC densities were observed during the dry season relative to the wet season across all sites and within salinity categories, despite water temperature, salinity, and solar radiation conditions unfavorable for FIB persistence during that time of year. These findings are in agreement with previous studies conducted in Arkansas streams (Edwards et al. 1997). No significant seasonal patterns were observed for ENT. Elevated dry-season indicator densities imply there is both a significant generation rate and a source of runoff delivering the fecal

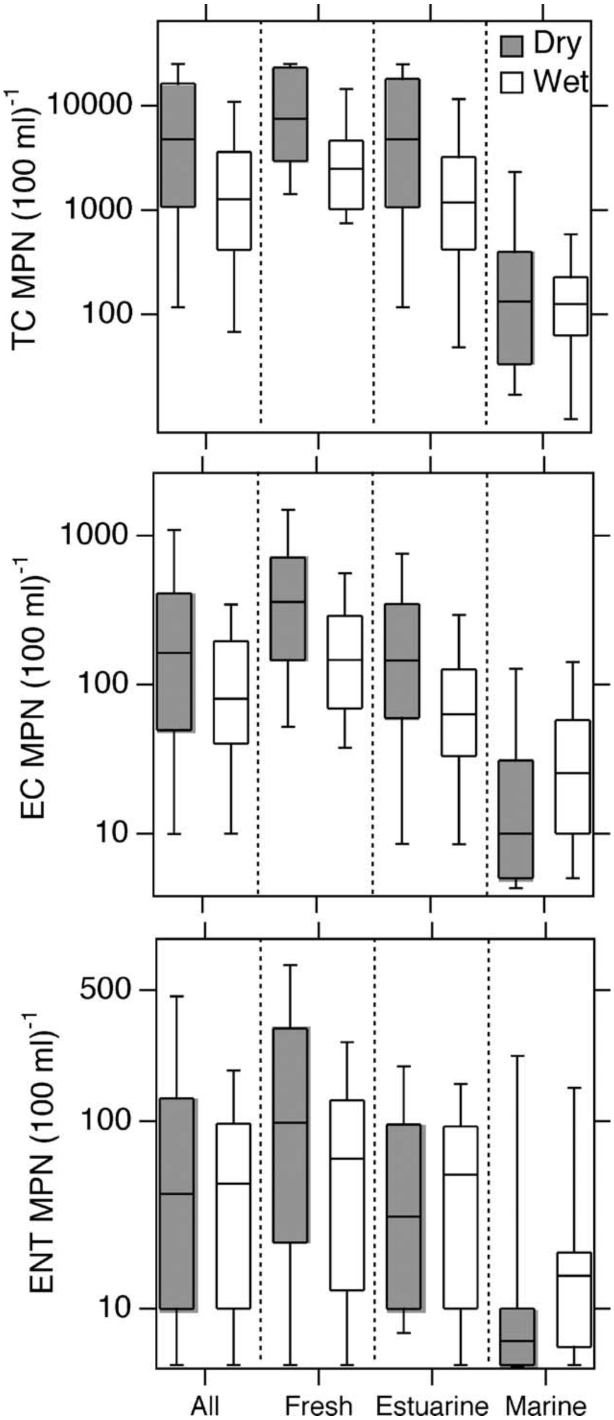

Fig. 2. Median levels of total coliform (TC), *E. coli* (EC) and enterococci (ENT) measured during wet seasons compared to dry seasons at fresh, marine, estuarine, and all sites. The wet season is defined as Nov–April. Upper and lower bounds of the box represent the 75th and 25th percentiles, respectively, and the whiskers are the 90th and 10th percentiles.

pollution during the dry season. An increased generation of fecal contamination by grazing animals during the summer could provide a FIB source at livestock affected waterways such as sites L, Pe, Pi, and Sa (Tian et al. 2002). Runoff to deliver the fecal pollution was likely generated by intensive dry season irrigation in agricultural areas and nuisance runoff from urbanized watersheds. These two factors, combined with reduced dilution by FIB-free rainwater during low flow conditions, could explain the elevated dry season FIB levels.

When sites were considered in aggregate (regardless of salinity category), ammonium ($r_s = 0.69$, $p = 0.0067$), nitrate + nitrite ($r_s = 0.59$, $p = 0.025$), and nitrite concentrations ($r_s = 0.71$, $p = 0.0044$) were positively correlated to Ag land use, while SRP was positively correlated to the sum of Urb and Ag land (UrbAg) and population size (Fig. 3 and Table 4). Fo land use exhibited negative relationships to ammonium ($r_s = -0.57$, $p = 0.034$), SRP ($r_s = -0.62$, $p = 0.018$), and nitrite ($r_s = -0.54$, $p = 0.045$). Chl *a* concentrations showed a significant correlation to Ag ($r_s = 0.64$, $p = 0.014$, Fig. 4) and Fo ($r_s = -0.64$, $p = 0.014$). When performing the same analyses on wet and dry season data separately, the significant correlations were found to be stronger during the wet season (data not shown).

The correlations between Ag and nutrient and chl *a* concentrations found in this study are important because they were observed for all sites, including fresh, estuarine, and marine waterways. Varying amounts of Urb and Fo land uses and seawater dilution at each site were not strong enough factors to mask the deleterious effect of Ag land use. The strong correlation between chl *a* and Ag indicates a potentially harmful biological response to nutrient loading in coastal waterways of varying salinities.

The strong positive correlations between SRP concentrations and measures of Urb development ($r_s = 0.64$ and 0.69, $p < 0.014$ with population size and UrbAg, respectively) point to widespread anthropogenic sources of SRP to coastal waterways. In contrast to the Ag-dominated nutrients (nitrate + nitrite and ammonium), SRP is significantly correlated only to UrbAg and population size. These findings agree with previous work in an Illinois river (Osborne and Wiley 1988), which found that urban land cover was the dominant factor controlling in-stream SRP concentrations. In urbanized areas, runoff can deliver fertilizer, detergents, and waste from domesticated animals, municipal waste streams, and failed septic systems, all of which are enriched in SRP. Precipitation-generated and irrigation-generated agricultural runoff contains fertilizer-derived SRP. Water bodies affected by significant levels of both Urb and Ag land use practices are the most affected by SRP loading.

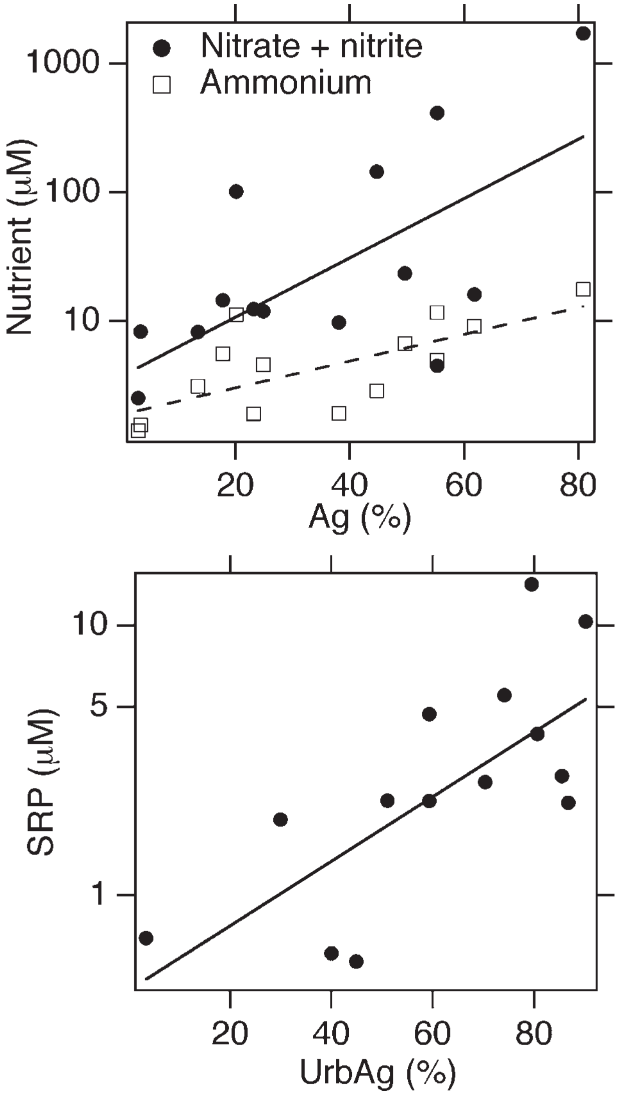

Fig. 3. Median concentrations of nitrate + nitrite and ammonium measured at all the sites as a function of percent of watershed that is comprised of agricultural land use (Ag). The lines represent a linear curve fit through the points. The Spearman correlation coefficients between the values are $r_s = 0.59$ ($p = 0.025$) for nitrate + nitrite and $r_s = 0.69$ ($p = 0.0067$) for ammonium. The median concentrations of soluble reactive phosphate (SRP) measured at all the sites as a function of percent of watershed that is comprised of urban and agricultural land use (UrbAg). The line represents a linear curve fit through the points. The Spearman correlation coefficient between the values is $r_s = 0.69$ ($p = 0.0067$).

Stronger correlations between land use and nutrient concentrations during the wet season (data not shown) suggest rain-generated runoff is a dominant pathway in delivering terrestrial nutrient sources to the aqueous environment. Nutrient concentrations themselves were not found to be consistently higher during the wet season. Dry season irrigation, which targets the agricultural

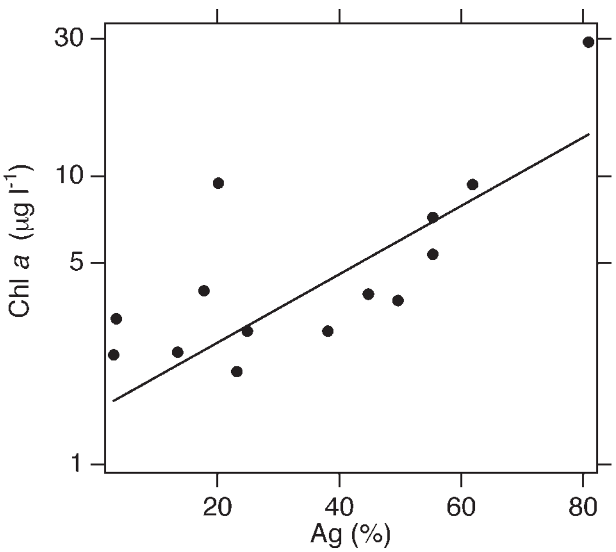

Fig. 4. Median chl *a* at all sites as a function of percent of watershed that is comprised of agricultural land use (Ag). The line is a linear curve fit through the points. The Spearman correlation coefficient between the values is $r_s = 0.74$ ($p = 0.014$).

areas where fertilizers have been applied, could be delivering extremely nutrient-rich runoff to coastal waterways during low flow conditions and causing significant nutrient pollution when there is no rain-generated runoff. Similar seasonal patterns were observed in agriculturally affected watersheds by Wernick et al. (1998).

ΣPFOS levels in sediments correlated strongly to Ag across the 11 sites where sediment samples were collected ($r_s = 0.68$, $p = 0.022$). While ΣPFOS levels did not correlate to Urb, UrbAg, ISC, and population size, the site most contaminated by ΣPFOS was the highly urbanized site SF. The 3 sites containing the most ΣPFOS (SF, Sa, and Pe) all receive water from wastewater treatment plants, either through direct discharge (sites Sa and Pe) or though tidal intrusion of water from San Francisco Bay (site SF). San Francisco Bay receives nearly 3 million cubic meters of treated wastewater per day, as well as untreated sewage during large storms due to combined sewer overflow (http://water.usgs.gov/wid/html/sfb.html). Sewage sludge, with ΣPFOS concentrations exceeding those typically found in sediments by more than three orders of magnitude (Higgins et al. 2005), is commonly used as soil treatment for agricultural land and could be a source of ΣPFOS to the agriculturally affected waterways examined in this study.

Consistent positive correlations were observed between FIB, nutrient concentrations (ammonium, SRP, and nitrate + nitrite), and chl *a* (Table 5). Chl *a* levels showed a strong positive response to increased nutrient concentrations, especially nitrate + nitrite, nitrite, and SRP, across all sites (Fig. 5) and within salinity categories. $\delta^{15}N$ correlated positively to ammonium ($r_s = 0.22$, $p = 0.0023$), SRP ($r_s = 0.28$, $p = 0.0001$), and nitrate + nitrite ($r_s = 0.18$, $p = 0.013$).

The positive correlations between FIB and nutrient levels (ammonium, SRP, and nitrate + nitrite) across all sites either indicate a common anthropogenic source of these constituents or imply that these nutrients influence the persistence of FIB. The latter has not been illustrated in laboratory mesocosm studies to date; Urb and Ag runoff are known to contain both FIB and nutrients, making them potential common sources of FIB and nutrient impairment. These correlations indicate that, even across a broad range of watershed development and a large salinity gradient, we can observe coupling between multiple ecosystem impairments derived from anthropogenic pollutant sources. The relationships between $\delta^{15}N$, nutrients, and chl *a* concentrations support the idea that $\delta^{15}N$ of POM and chl *a* can be used as indicators of anthropogenic nutrient enrichment across a range of aquatic systems (Costanzo et al. 2003).

In addition to these correlations, 20 of the 191 samples were found to be eutrophic by the chl *a* criteria (chl $a > 15$ μg l^{-1}). These samples were collected from sites Sa (n = 13), SF (n = 4), E (n = 1), K (n = 1), and Pe (n = 1). The eutrophic samples were extremely enriched in TC, EC, ENT, dissolved nutrients, and $\delta^{15}N$ of POM (Fig. 6), suggesting a synergistic relationship between a nutrient-rich environment and the presence or persistence of FIB. Evidence pointing towards the coupling of these two anthropogenic effects, eutrophication and microbial pollution, has important implications for land management adjacent to our

TABLE 5. Spearman correlation coefficients between a subset of measured constituents across all sites. Raw data were used in all calculations. Significance: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$.

Parameter	Ammonium (n = 190)	SRP (n = 190)	Nitrate + nitrite (n = 190)	Nitrite (n = 163)	Chl *a* (n = 191)
TC (n = 190)	0.31***	0.22**	0.33***	0.08	0.17*
EC (n = 190)	0.20**	0.16*	0.24***	−0.02	−0.01
ENT (n = 190)	0.26***	0.18*	0.34***	0.14	0.20**
Chl *a* (n = 191)	0.42***	0.58**	0.42***	0.36**	—
$\delta^{15}N$ (n = 190)	0.22**	0.28**	0.18*	0.10	0.26***

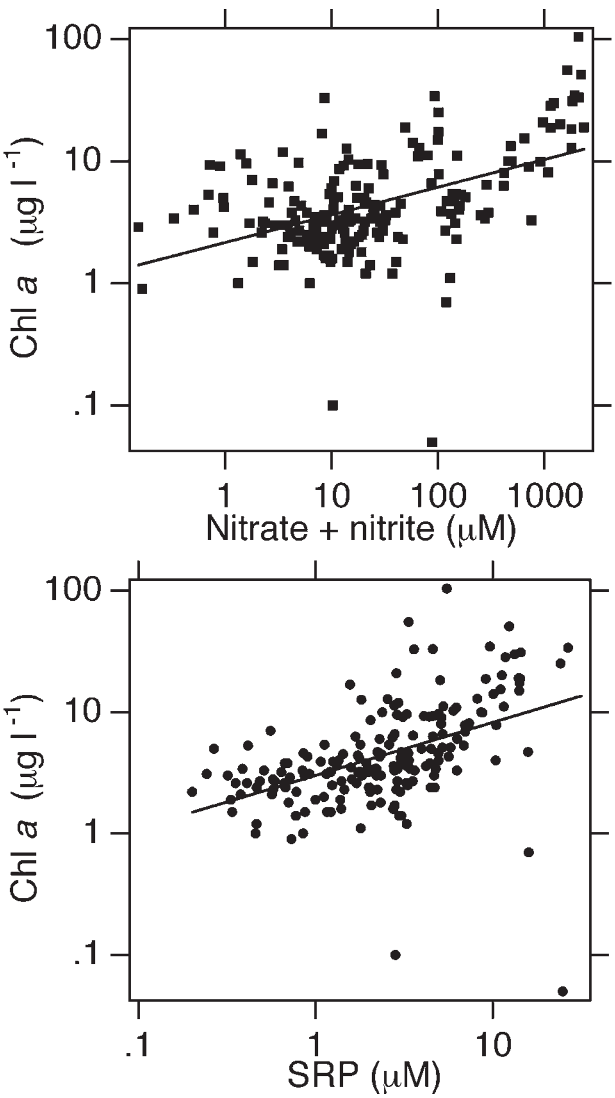

Fig. 5. Measured chl *a* as a function of nitrate + nitrite for each water sample collected. The line shows the best fit between the log transformed data. The Spearman correlation coefficient between the log-transformed variables is $r_s = 0.42$ ($p < 0.0001$). Measured chl *a* as a function of soluble reactive phosphate (SRP) for each water sample collected. The line shows the best fit between the log transformed data. The Spearman correlation coefficient between the variables is $r_s = 0.58$ ($p < 0.0001$).

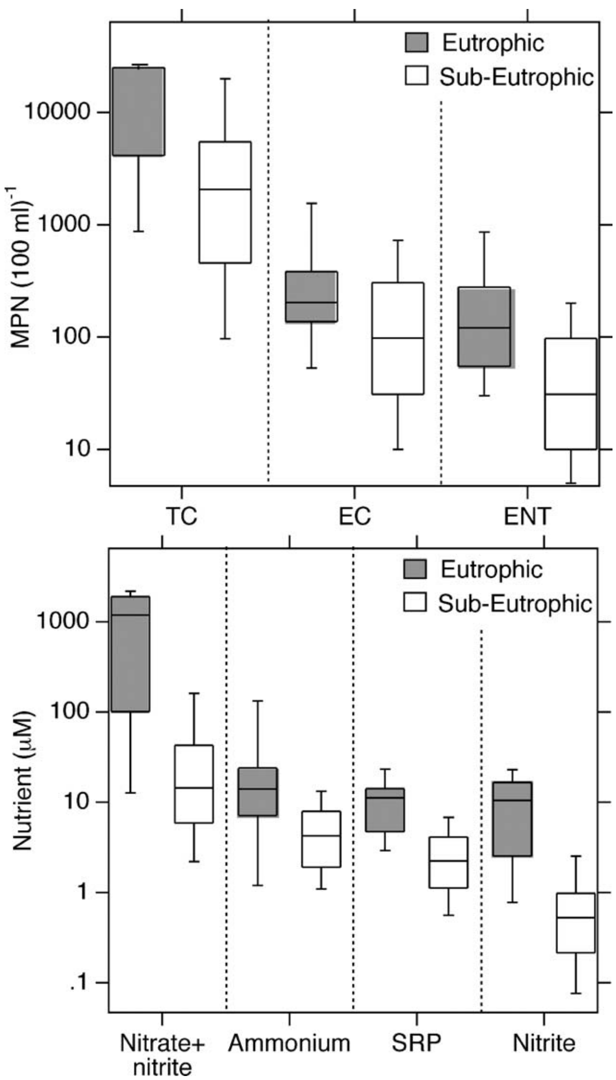

Fig. 6. Median of fecal indicator bacteria (FIB) total coliform (TC), *E. coli* (EC), and enterococci (ENT) measured in eutrophic (chl $a > 15$ μg l^{-1}) compared to subeutrophic (chl $a \leq 15$ μg l^{-1}) samples. Median concentrations of nitrate + nitrite, ammonium, soluble reactive phosphate (SRP), and nitrite measured in eutrophic compared to subeutrophic samples. Upper and lower bounds of the box represent the 75th and 25th percentiles, respectively, and the whiskers are the 90th and 10th percentiles.

coastal waterways. Because microbial pollution (more so than elevated nutrients) is a primary concern for managers aiming to protect human health, evidence linking these two pollutant categories in either origin or persistence implies that nutrient sources to coastal waterways (e.g., agriculture, water treatment plants) should be closely monitored as potential threats to humans engaging in contact recreation.

ΣPFOS concentrations were highly correlated to median concentrations of ammonium ($r_s = 0.78$, $p < 0.005$), nitrate + nitrite ($r_s = 0.88$, $p < 0.0005$), nitrite ($r_s = 0.82$, $p < 0.0023$), and $\delta^{15}N$ of POM ($r_s = 0.74$, $p < 0.009$; Fig. 7), suggesting sewage may be a source of ΣPFOS in urban sediments. While industrial and residential waste streams are suspected to be the main sources of ΣPFOS and other perfluorocarbons to the local environment (Higgins et al. 2005), correlations between ΣPFOS and nutrient concentrations, taken together with the correlations between ΣPFOS and Ag suggest land application of sewage-derived biosolids for agricul-

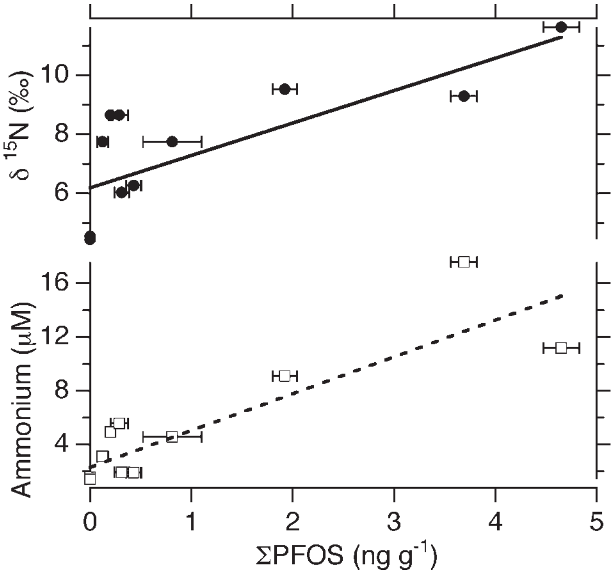

Fig. 7. Median $\delta^{15}N$ and ammonium concentrations in water as a function of ΣPFOS concentrations in sediments. Error bars represent 95% confidence intervals for the triplicate ΣPFOS measurements taken from each sediment sample. The lines show the best linear fit between the data.

tural purposes may also serve as a source of ΣPFOS to the environment.

Conclusions

Our findings highlight the importance of land management in the protection of human and ecosystem health along the California coast. Agricultural and livestock best management practices (BMPs) related to appropriate fertilizer application, crop rotation, locations of grazing and crop areas, and protection of riparian buffer regions should be used to minimize the deleterious effects of nutrient loading and associated microbial contamination. In urbanized areas, the use of structural BMPs such as detention ponds, infiltration systems, and constructed wetlands can help control the volume and intensity of runoff from rainfall. Nonstructural BMPs, which focus on educational and management strategies aimed to reduce the conversion of rainfall to runoff as well as to prevent pollutants from entering runoff, should be employed. As human populations in coastal regions continue to grow, so must our awareness of anthropogenic effects on coastal waters and our strategies to protect them.

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