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Relationships among catchment land use and concentrations of nutrients, algae, and dissolved oxygen in a southern California river

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Abstract. Rapid human population growth engenders landuse changes and alters nutrients, algal biomass (as chlorophyll *a* [chl *a*]), and dissolved O_2 concentrations (DO) in streams, but quantitative information on these relationships is limited in regions with a Mediterranean climate. We surveyed macroalgal % cover and chl *a* and physicochemical factors in spring and summer at 15 stream and estuarine sites in a catchment in southern California with a mosaic of undeveloped, agricultural, and urban areas to examine relationships among land use, nutrients, algae, and DO. We used nutrient diffusing substrata (NDS) at 12 sites to assess the nutrient(s) limiting algal growth. Algal chl *a* and pH often exceeded suggested or mandated water-quality impairment thresholds at sites affected by human activity, particularly those downstream from a wastewater treatment plant. Total N (TN) affected total and benthic algal chl *a* in spring and summer, total P (TP) affected benthic algal chl *a* in summer, and light influenced algae in summer. N was the sole or primary limiting nutrient at ½ of the sites and was colimiting with P at another ⅓ of the sites. Nutrient ratios (molar TN:TP) were poor predictors of algal responses to nutrient enrichment. Diel changes in dissolved O_2 were related positively to discharge and negatively to algal chl *a*, particularly when floating macroalgae were present. In June, N and chl *a* and macroalgal % cover were positively related to human landuse patterns at the subcatchment scale, whereas in September, P and chl *a* were related to landuse patterns at more local scales (500 m, 1000 m). Mediterranean streams present a variety of challenges for water-quality managers because of high seasonal and interannual variation in discharge and nutrient flux, high accumulations of algae during the dry season, low nutrient thresholds that generate nuisance algal blooms, and human population growth and associated changes in landuse patterns.

Key words: nutrients, streams, land use, Mediterranean, algae, dissolved oxygen, nutrient diffusing substrata.

Increasing human use of lands has been associated with increased nutrient loads and freshwater and marine eutrophication (Walsh et al. 2005, Kaushal et al. 2008). In particular, nutrient enrichment caused by N and P inputs from agricultural and urban runoff, atmospheric deposition, industrial activity, and wastewater discharge can increase algal biomass, reduce nighttime O_2 levels, and alter invertebrate and vertebrate communities (Peterson et al. 1993, Borchardt 1996, Dodds 2006). Other human-induced changes, such as the removal of riparian vegetation, can increase light levels and temperatures in streams, facilitating algal growth and causing nighttime depressions in dissolved O_2 (DO) concentrations that can be deleterious or fatal to fish, invertebrates, and other stream organisms (Hill et al. 1995, DeNicola 1996, Stevenson 1996, Carpenter et al. 1998). The largest effects of eutrophication on stream animals probably are mediated through altered dissolved O_2 (DO) concentrations, but few investigators have examined the entire suite of linkages from landuse change to increased nutrient

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loading to algal blooms to low nighttime DO concentrations (Mulholland et al. 2001, Bernot et al. 2010).

Many investigators have examined the effects of landuse changes, such as agricultural or urban development, on stream ecosystems (Paul and Meyer 2001, Allan 2004, Taylor et al. 2004, Black et al. 2011), but knowledge of human impacts on stream systems in Mediterranean climates (e.g., the Mediterranean Basin, southwestern and southern Australia, tip of South Africa, central Chile, and southern California/ Baja California) is limited (Martí et al. 2004, Busse et al. 2006, Von Schiller et al. 2007, Merseburger et al. 2011). Rapid human population growth in coastal regions of southern California has caused alterations to many streams and riparian zones via landuse changes (i.e., agricultural, industrial, residential, urban development), water diversions, channelization, dams, groundwater pumping, and pollution. For example, recent expanded human development in the Ventura River catchment of southern California has led to stream and river eutrophication and growth of nuisance algae (California EPA 2003).

We collected and analyzed landuse, physicochemical, and algal data from 15 stream and estuarine sites, including impaired and reference sites, in the Ventura River catchment in late spring and late summer of 2008 (similar to Busse et al. 2006). We used multiple regression techniques to examine relationships among physical (e.g., light, current, substratum sizes), chemical (nutrient concentrations), biological (algal biomass as chlorophyll a [chl a], ash-free dry mass [AFDM], % cover), and landuse variables. We used nutrient diffusing substrata (NDS) to determine the nature (N, P, both, or neither) and degree of nutrient limitation of algal chl a because predictions of nutrient limitation of algal chl a based on stream molar N:P ratios do not forecast accurately algal responses to nutrient enrichment in stream experiments (Francoeur et al. 1999, Johnson et al. 2009). We hypothesized that stream sites affected by human activity would have high levels of N, P, and light that would stimulate primary production, resulting in high algal chl a and low nighttime DO. Land use and values of chemical and biological variables can be correlated at small (<100 m) (Sonoda et al. 2001), intermediate (300–500 m) (Strayer et al. 2003, Busse et al. 2006), and larger spatial scales (Carr et al. 2005). We analyzed landuse patterns (proportion of drainage areas covered by human land uses or impervious surfaces) at different spatial scales (100 m, 250 m, 500 m, 1000 m, and entire subcatchments). We predicted that the scale of relationships between landuse patterns in upstream catchment areas and nutrient or algal levels would decrease during the summer dry season as runoff
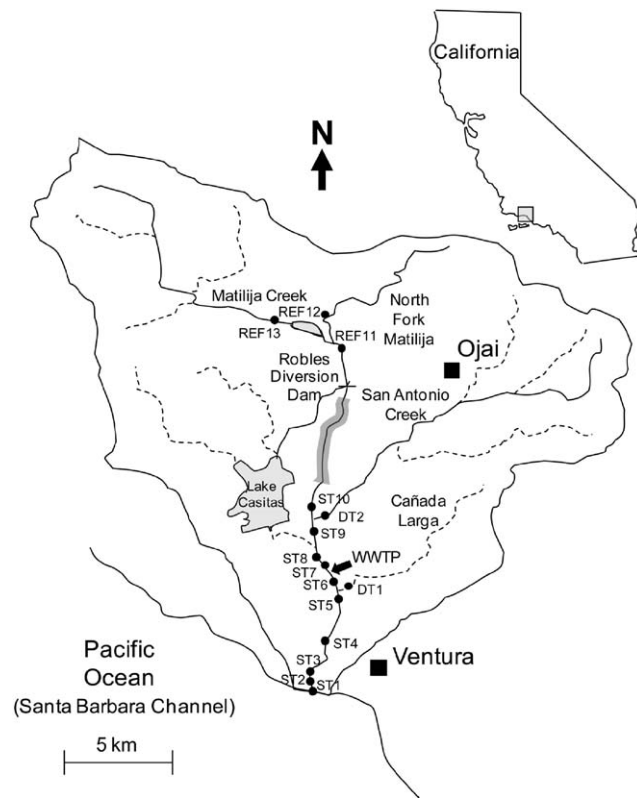

FIG. 1.   Map of the Ventura River catchment and study sites (inset shows location in California, USA). See Table 1 for site names.

and river discharge decreased, that observed molar N:P ratios would accurately forecast the nutrient limiting algal chl a, and that the degree of nutrient limitation of algal chl a would decrease as ambient nutrient concentrations increased and light levels decreased.

Methods

Catchment description and sites

The Ventura River drains a 590-km^2 catchment in coastal southern California's Transverse Range in western Ventura County, California, USA (lat 34.27–34.62°N, long 119.10–119.48°W; Fig. 1). Its headwaters originate at 1850 m asl in the San Rafael, Topatopa, Santa Ynez, and Sulphur Mountains and the river flows south for 26.5 km to the Pacific Ocean. The Ventura River catchment has a Mediterranean climate with wet cool winters and dry warm summers. Average annual rainfall ranges from 100 cm/y in the headwaters to 40 cm/y at sea level. Native vegetation includes chaparral, scrub, grassland, oak woodland, and coniferous forest, and streamside vegetation is dominated by willow (*Salix* spp.), western sycamore (*Platanus*

racemosa), coast live oak (*Quercus agrifolia*), and giant reed (*Arundo donax*).

We selected sites along a gradient of % human land use in the catchment for stream surveys and nutrient diffusing substrata (NDS) experiments (Table 1). We chose 15 sites for algal and nutrient surveys, 10 on the main stem of the Ventura River (ST1–10), 3 reference sites above most human influences in the upper catchment (REF11–13), and 2 sites on downstream tributaries (DT1–2). Six mainstem sites (ST1–6) were below the Ojai Valley Wastewater Treatment Plant (WWTP), and 4 mainstem sites (ST7–10) were above the WWTP (Fig. 1, Table 1).

Land use

We compared our field assessments of land use with published landuse data from the National Land Cover Database (NLCD) generated from 2001 Landsat satellite imagery. Land use changes from 2001 to the time of the study were limited, but we updated NLCD geographical information system (GIS) layers via manual classification based on Google Earth® (2004) images and direct observation. Correlations between landuse patterns and stream nutrient concentrations or biological characteristics vary with scale, so we analyzed relationships between land use and nutrient and algal variables over a range of spatial scales (Sonoda et al. 2001, Strayer et al. 2003, Carr et al. 2005). We calculated % upstream catchment areas affected by human development (% human land use), including urban, residential, open space (parks, golf courses, other human-maintained space), agricultural (row crops, vineyards), and grazing lands (Busse et al. 2006). Wildlands consisted of wild grasslands; deciduous, evergreen, and mixed woodlands or forests; shrub and scrub lands; and woody and emergent wetlands. We used the ArcHydro routine in ArcGIS (version 9.3; Environmental Systems Research Institute, Redlands, California) with a 30-m US Geographical Survey (USGS) digital elevation model (DEM; from the Shuttle Radar Topography Mission) to delineate subcatchment boundaries. We used GIS landuse layers to estimate % catchment area in human land uses and % cover by impermeable surfaces draining to each site. We assessed human landuse patterns at different scales by superimposing circles with radii of 100, 250, 500, or 1000 m centered on each site and delineating the upstream catchment areas circumscribed by the radii for each site. We also assessed landuse patterns at the scale of the entire subcatchment area draining to each site. DEM, landuse, and impervious surface data were downloaded from USGS databases (seamless.usgs.gov).

Sampling design

We sampled twice at each site (16 May–5 June [June] and 31 August–6 September [September] 2008). We established 10 equally spaced (10 m apart) cross-stream transects at each site and measured macroalgal % cover and chl *a*, water depth, substratum size, % open canopy, and water velocity along each transect (modified SWAMP Bioassessment Procedures 2007; http://www.swrcb.ca.gov/water_issues/programs/swamp/docs/phab_sopr6.pdf).

Physical measurements

We measured water depth, maximum reach depth, and transect width with a meter stick; water velocity with a model 210D current meter (Marsh–McBirney, Frederick, Maryland); % open canopy with a spherical densiometer; DO, conductivity, pH, and water temperature with YSI model 55 (Yellow Springs Instruments, Yellow Springs, Ohio) and Oakton CON 410 DO/conductivity and pH meters (Oakton Instruments, Vernon Hills, Illinois); and substratum size visually at each site. We took depth, substratum size, and water velocity measurements at 3 equally spaced locations along each cross-stream transect at each site ($n = 30$), canopy cover measurements in 4 directions (upstream and downstream in the river center, facing each bank at the river edges) along each transect, and all other measurements once at the top of each study reach. We measured DO, pH, and water temperature at 12 study reaches before dawn and in the afternoon 5 times (9 April, 15 May, 17 June, 25 July, 12 September).

Water chemistry

We collected water samples for NH_4-N, NO_2-N, NO_3-N, soluble reactive P (SRP), total N (TN), and total P (TP) concentrations from each study reach. TN and TP samples were unfiltered, and dissolved inorganic nutrient samples were filtered through 0.45-μm polycarbonate filters. We measured dissolved nutrient concentrations spectrophotometrically on a Lachat QuikChem 8000 flow injection analyzer (Lachat Instruments, Milwaukee, Wisconsin) with standard methods (SRP: reaction with ammonium molybdate and ascorbic acid; NO_2^- and NO_3^-: reduction of NO_3^- to NO_2^-, diazotization of NO_2^- with sulfanilamide coupled with ethylenediamine dihydrochloride; NH_4^+: QuickChem Gas Diffusion Method 31-107-06-5-A). We measured TN by injection into a Skalar Formacs HT TOC/TN Analyzer equipped with a ND20 Chemiluminescence Nitrogen Detector (Skalar Incorporated, Buford, Georgia) and combustion at 850°C in the

TABLE 1. Site names, land uses, and means for selected physicochemical variables for study sites in the Ventura River catchment sampled between 16 May and 5 June (Jun) and between 31 August and 6 September (Sept) 2008. Estuarine site ST1 was sampled 5 June 2008, but the estuary's sand bar breached on the night of 4 June 2008, so the estuary (especially lower estuary) received an influx of seawater on June 5. Site DT1 was dry during September surveys and no data were collected. DO = dissolved O_2, Cond = conductivity, Temp = temperature. – = no data available.

Site name	Site code	Surrounding land use	Month	Maximum depth (m)	Velocity (m/s)	% open canopy	Cond (µS/cm)	pH	DO (mg/L)	Temp (°C)
Estuary Bridge	ST1	Open space, agricultural, industrial, wildlands, city park, major roads, bike path, railroad tracks	Jun	2.40	0.01	100	4390	8.38	11.97	22.8
			Sept	3.70	–	100	10920	7.94	13.97	26.0
Estuary Reach	ST2	Same as above	Jun	0.44	–	77.1	1493	8.48	11.74	23.1
			Sept	0.93	0.03	75.0	1364	8.07	17.54	25.4
Main Street	ST3	Open space, agricultural, some wildlands	Jun	0.56	0.16	74.3	1129	8.53	11.96	18.7
			Sept	0.47	0.06	50.0	1117	8.06	13.81	24.6
Stanley Drain	ST4	Agricultural, some wildlands	Jun	0.59	0.20	76.4	981	8.89	12.80	26.4
			Sept	0.47	0.13	72.3	1193	8.28	15.00	25.2
Shell Road	ST5	Mixed industrial (oil facilities), agricultural	Jun	0.56	0.21	76.4	998	8.91	16.23	23.3
			Sept	0.47	0.16	68.9	1043	8.06	9.94	25.9
Cañada Larga tributary	DT1	Mixed commercial, industrial, rangelands	Jun	0.15	0.06	54.1	3220	8.22	9.76	29.4
			Sept	–	–	–	–	–	–	–
Below wastewater treatment plant	ST6	Mixed residential, industrial, institutional	Jun	0.66	0.10	64.9	964	8.33	10.43	22.9
			Sep	0.64	0.07	54.1	1009	7.66	9.76	24.3
Above wastewater treatment plant	ST7	Mixed residential, industrial	Jun	0.92	0.13	75.0	915	8.17	10.77	21.5
			Sept	0.94	0.09	66.9	915	8.03	14.13	24.2
Foster Park	ST8	County park, agricultural, residential	Jun	0.94	0.21	97.3	897	8.40	13.27	21.0
			Sept	0.79	0.10	68.9	874	7.87	12.04	27.9
Below San Antonio Creek confluence	ST9	Open space, wildlands	Jun	1.10	0.14	76.4	929	7.74	10.80	19.1
			Sept	1.06	0.09	69.6	879	7.28	11.86	21.2
San Antonio Creek tributary	DT2	Mixed residential, open space, horse stables and wineries	Jun	0.49	0.08	59.5	1213	7.90	12.19	22.0
			Sept	0.56	0.02	30.4	1279	7.48	11.50	24.4
Above San Antonio Creek confluence	ST10	Open space, some wildlands	Jun	0.54	0.19	68.9	864	7.84	12.02	21.6
			Sept	0.5	0.23	53.4	832	7.33	11.11	23.9
Ventura River below the confluence of the North Fork and Upper Matilija Creeks	REF11	Open space, wildlands	Jun	0.92	0.22	57.4	853	8.21	8.53	21.5
			Sept	0.68	0.13	45.9	867	7.97	11.30	27.5
North Fork Matilija Creek	REF12	Wildlands, limited upstream residential housing	Jun	1.22	0.14	16.9	842	8.07	8.45	19.2
			Sept	0.81	0.06	10.1	904	7.75	10.71	23.0
Upper Matilija Creek	REF13	Wildlands, limited upstream residential housing	Jun	0.95	0.21	73.6	853	8.19	8.48	22.9
			Sept	0.88	0.11	68.9	911	8.21	13.25	27.5

presence of an oxidative catalyst, converting all forms of N to nitric oxide. We measured TP after digestion of samples in nitric acid in a CEM MDS2000 microwave (CEM, Matthews, North Carolina). We analyzed digested samples at 185.9 nm with Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) with a vacuum spectrometer (Thermo Jarrell Ash Corporation, Franklin, Massachusetts).

Algal sampling and analysis

We assessed % cover of different algal types and plant genera visually with the US Environmental Protection Agency (EPA) rapid bioassessment protocol for use in streams and wadeable rivers (Barbour et al. 1999). We identified macroalgae and vascular plants to genus and classified diatom films as thin (<0.5 mm in height), medium (0.5–2.0 mm), or thick (>2.0 mm). We collected % cover data from 3 evenly spaced points along 10 transects per site, and we used methods described by Davies and Gee (1993) to collect algal chl a samples from the same points. When floating macroalgae were present, we used the outer part of a 26-mm syringe to bore a hole through the floating mat and sampled the algae on underlying benthic substrata (Davies and Gee 1993). We froze samples and stored them independently for analysis. We collected benthic and floating algae from 3 points along each transect then combined them to make 1 composite benthic sample and 1 composite floating algae sample/transect. We collected planktonic algae at the estuary site by taking 3 depth-integrated samples from the surface to 2-m depth with a flexible plastic tube. We filtered subsamples through GF/C filters for measurement of chl a and ash-free dry mass (AFDM). Filters for AFDM were precombusted at 500°C and preweighed, and we froze all filtered subsamples for later analyses.

We extracted chl a in 90% acetone at −20°C for 24 h and measured solutions fluorometrically (USEPA 1992). We measured AFDM of subsamples collected on GF/C filters by drying subsamples at 60°C for 24 h, weighing, combusting for 2 h at 500°C, and reweighing them. We averaged AFDM and chl a concentrations in benthic and floating algae samples across the 10 transects to provide estimates of floating, benthic, and total algal (floating + benthic) chl a for each site.

Nutrient limitation experiment

We used nutrient diffusing substrata (NDS) to study limitation of periphyton chl a by nutrients (Tank et al. 2006, Johnson et al. 2009). We filled 30-mL plastic containers with 3% agar, and covered them with fritted glass disks (2.7-cm diameter) set on agar surfaces. The glass discs acted as a surface for algal colonization and growth. We added N or P to the agar to create 4 experimental treatments: N addition (+N) treatments contained 0.5 M NaNO$_3$; P addition (+P) treatments contained 0.5 M KH$_2$PO$_4$; N and P addition (N+P) treatments contained 0.5 M concentrations of NaNO$_3$ and KH$_2$PO$_4$; and controls (C) contained no added nutrients. We protected NDS containers from interference by benthic animals by securing 20 diffusers (4 treatments × 5 NDS replicates/treatment) to a Plexiglas® L-bar (5 cm on a side), securing the L-bar to rebar stakes driven into the stream bottom, and elevating the L-bar above the stream bottom. We deployed NDS units at an average depth of 9 cm below the water surface for 19 d to allow adequate time for algal accrual (Tank et al. 2006).

When we collected the NDS containers, we removed the fritted glass discs and froze them prior to chl a analysis. At each site, we collected and processed benthic algae from natural substrata and water samples for nutrient concentrations with the methods described above. In the laboratory, we added 50 mL of 90% acetone to a test tube containing a fritted glass disc and extracted and measured chl a with the methods previously described. We tested whether N and P were still diffusing from enriched NDS units at the end of the experiment by placing 1 NDS unit fitted with a new, clean glass disc from each treatment from each of 4 sites in a jar containing double-deionized (DDI) water. Water containing enriched NDS containers had targeted nutrient concentrations that were 2 orders of magnitude higher than those in water containing control NDS units after 48 h.

Data analysis

We used chl a and macroalgal % cover as indices of algal biomass because regression analyses showed strong positive relationships between AFDM and chl a for both benthic ($r^2 = 0.69$) and floating ($r^2 = 0.96$) algae, between benthic algal chl a concentrations and % cover by medium and thick diatom films ($r^2 = 0.40$), and between floating algal chl a and macroalgal % cover ($r^2 = 0.44$) (for all regressions $p < 0.001$). We ran regression analyses to examine relationships between algal chl a and physicochemical variables, among physicochemical and algal variables and land-use patterns, and among predawn DO and ΔDO (difference between predawn and afternoon DO) and algal chl a and discharge. For relationships between algal chl a and physicochemical variables, our initial regression models included TN and TP concentrations

(µg/L), water velocity (m/s), % open canopy, and substratum size ($\varphi = -\log_2$[substratum particle diameter]) as independent variables. We removed nonsignificant ($p > 0.1$) variables via backward, stepwise elimination. We applied $\ln(x)$-transformations to chl a, nutrient, and water velocity data ($\ln[n + 1]$ or $\ln[n + 0.1]$ where 0 values were present) and $\arcsin\sqrt{(x)}$-transformations to proportionate open canopy and landuse variables to normalize data.

We used 2-way analyses of variance (ANOVAs) to test the main and interactive effects of N and P additions on algal chl a in the NDS experiment. When the ANOVA was significant, we used post hoc Tukey–Kramer multiple comparison tests to identify significant differences in chl a among all pairs of treatments. We calculated log response ratios (LRR) for algal chl a responses to nutrient amendments at each site (LRR = ln[chl a in nutrient amendment treatment/chl a in control], calculated separately for +N, +P, and N+P treatments) and examined LRR relationships with environmental variables (water velocity, % open canopy, nutrient concentrations). We ran all statistical analyses in JMP (version 7.0 for Windows™; SAS Institute, Cary, North Carolina).

Results

Physicochemical variables

Mean water velocity ranged from ~0 to 0.23 m/s, pH from ~7.3 to 8.9, and conductivity from 832 to 10,920 µS/cm with highest values (4390–10,920 µS/cm) at the brackish, estuarine site (ST1). Conductivity generally was higher at sites with human activity, and 2 lower Ventura River tributaries (DT1, DT2) with extensive upstream development had the highest values (3220 and 1279 µS/cm, respectively) among nonestuarine sites (Table 1). Percent open canopy ranged from 10.1% at REF12 to 100% at ST1. In June, DO during the day was lowest at reference sites (REF11–13) and highest at developed sites (e.g., ST5) (means = 8.5 and 16.2 mg/L, respectively). In September, daytime DO was lowest (minimum value = ~9.8 mg/L) at ST6, which was just below the WWTP, and highest at ST2 (maximum = ~17.5 mg/L).

Diel changes in temperature, DO, and pH

Diel measurements of water temperature, pH, and DO over 5 dates in the spring and summer yielded temperatures ranging from 11.5 to 29.5°C, pH from 7.1 to 8.9, and DO from 4.9 to 17.6 mg/L (Fig. 2A–C). Water temperatures tended to show the greatest diel
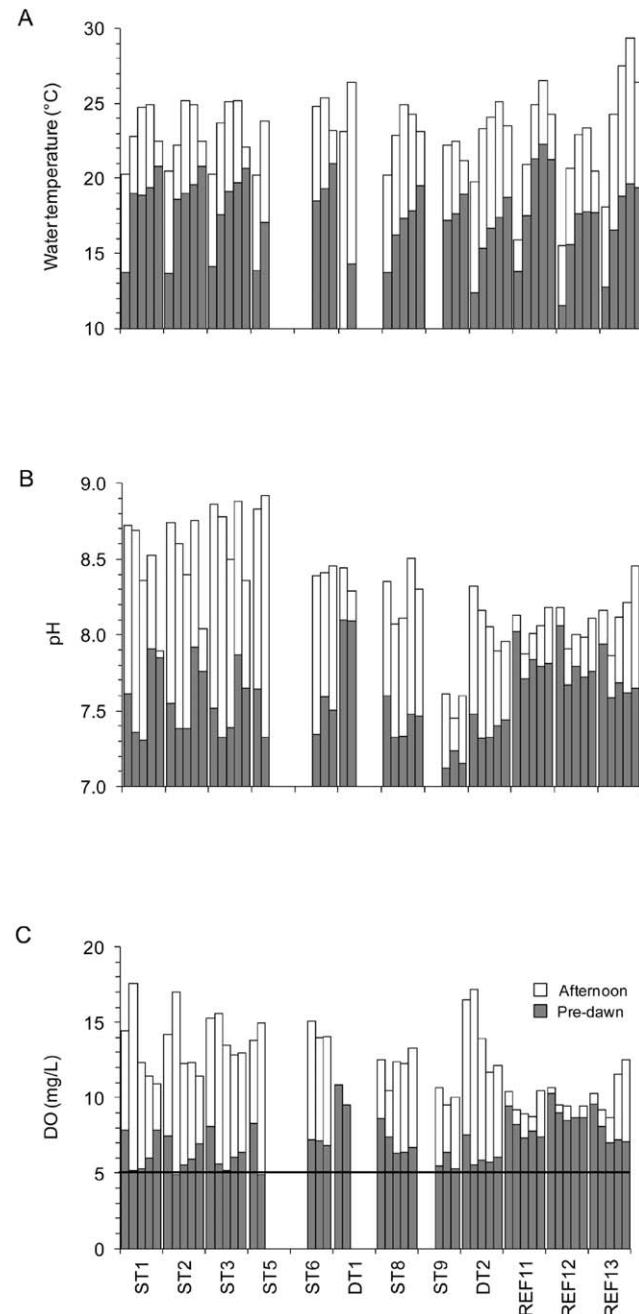

FIG. 2. Diel (24-h) changes in stream temperature (A), pH (B), and dissolved O_2 (DO) (C) at sites in the Ventura River. For most sites, data were collected on 9 April, 15 May, 17 June, 25 July, and 12 September 2008 (shown from left to right). Measurement gaps are shown as blanks. In panel C, the line indicates the minimum DO threshold (5 mg/L) set by the Los Angeles Regional Water Quality Control Board (1994) for this region.

variation in smaller tributaries, and the maximum diel temperature changes occurred at DT1 (12°C on May 15) and REF13 (10°C on July 25) (Fig. 2A). Diel changes in pH and DO were greatest at sites affected

by development and lowest at reference sites. The maximum diel change in pH was 1.6 units at ST5 (May 15) (Fig. 2B), and the maximum diel ΔDOs were at estuarine site ST1 (11–12 mg/L change), lower Ventura River sites (up to 10 mg/L change), and DT2 (12 mg/L change) in May (Fig. 2C). Nighttime DO concentrations approached or fell below the recommended 5 mg/L minimum threshold for this basin (see Discussion) at sites ST1–5 in May and June.

Nutrient concentrations

Concentrations of most forms of N (TN, dissolved inorganic N [DIN], NO_3-N, NO_2-N) were much higher at sites affected by human activity than at reference sites (Fig. 3A–E). TN concentrations were highest at the site below the WWTP (ST6) (mean = 1.54 mg/L), then declined downstream to the mouth (Fig. 3A). Differences in NH_4-N concentrations between reference and developed sites were less pronounced and NH_4-N contributed an average of 19% to TN concentrations at reference sites, but only 4% at all other sites (Fig. 3E). NO_3-N contributed an average of 92% to DIN concentrations at developed sites but only 31% at reference sites. DIN concentrations averaged 59% of TN concentrations at developed sites but only 30% of TN concentrations at REF11–13 through time.

Average TP and SRP concentrations over time were lowest at reference sites (0.029 and 0.005 mg/L, respectively), and ranged from 0.029 to 0.207 and 0.006 to 0.073 mg/L, respectively, at sites below the WWTP (Fig. 3F, G). SRP contributed 21% to TP concentrations at reference sites and 32% at all other sites, and SRP concentrations declined from peak levels below the WWTP (ST6) downstream to site ST3 (Fig. 3G).

In June and September, NO_3-N, DIN, and TN concentrations were tightly correlated (all $r > 0.96$, $p < 0.001$) across sites, whereas SRP and TP concentrations were positively correlated only in September ($r = 0.72$, $p = 0.004$). Concentrations of N and P species were not correlated across sites in June. However, N and P concentrations were correlated in September (all $r > 0.58$, $p = 0.03-0.004$ for correlations between all combinations of SRP and TP concentrations vs NO_3-N, DIN, and TN concentrations).

Molar TN:TP was consistently high in intermediate sections (ST7–10) of the mainstem Ventura River and ranged from 31 to 159 in June, 44 to 116 in July, and 22 to 162 in September. In general, sites REF11–13 had lower molar TN:TP (average = 14, range = 1.4–28) during spring and summer, whereas molar TN:TP at

sites ST3–6 ranged from 7 to 28 in June, 10 to 13 in July, and 15 to 47 in September (Fig. 3H).

Algal cover and composition

In June, benthic algae assemblages were composed mainly of *Cladophora*, and the representation of diatoms and a variety of other filamentous algae increased in September (Fig. 4A, B). In June, % diatom cover was higher at REF11–13 than at other sites (*t*-test, $t = 2.70$, $p = 0.009$), but % diatom cover did not differ between reference and developed sites by September. Reference sites were dominated by diatoms and *Cladophora* in June, but the algal community shifted to greater dominance by diatoms at REF11–12 and to dominance by *Mougeotia* and diatoms at REF13 in September. Lower mainstem sites (ST3–6) were dominated by *Cladophora* and brackish sites (ST2) by *Enteromorpha* in June, but % diatom cover at both sites increased in September. ST7–10 were dominated by *Cladophora* in June, but by diatoms, *Cladophora*, and other macroalgae species (*Spirogyra*, *Enteromorpha*) in September. Over all sites, macroalgal % cover decreased significantly from spring to late summer (from 23–99% June to 1–70% in September; paired *t*-test, $t = 4.77$, $p < 0.001$). Aquatic vascular plants were absent from all sites in June and from REF11–13 in September, but covered substantial amounts of space at ST3–5 below the WWTP in September (Fig. 4A, B). In general, macroalgae were found at all stream sites, but macroalgal % cover tended to be greater at sites affected by development than at reference sites, particularly in spring.

Chl a concentrations and relationships to diel changes in DO

In June and September, total and benthic chl *a* at REF11–13 (<58 mg/m^2) were below the maximum chl *a* concentrations suggested by the USEPA (2007) for Ecoregion III to avoid impairment (43.9 mg chl a/m^2) and by Dodds et al. (1998) (150 mg chl a/m^2). However, these thresholds were often exceeded at ST2–6 in spring and summer and at ST7–10, particularly in spring (Fig. 5A–C). REF11–13 contained little or no floating algae during spring and summer, but other sites (ST3–10) had substantial floating algal chl *a* (180–746 mg/m^2), particularly in spring (Fig. 5B). Concordant with nutrient concentrations, total, benthic, and floating algal chl *a* increased from ST7 to ST6 (above to below the WWTP, respectively). However, chl *a* declined or remained relatively constant downstream to ST5 before increasing to peak levels at ST3 (June) and ST4 (September) (Fig. 5A–C). Total and floating algal chl *a* concentrations also tended to be high at
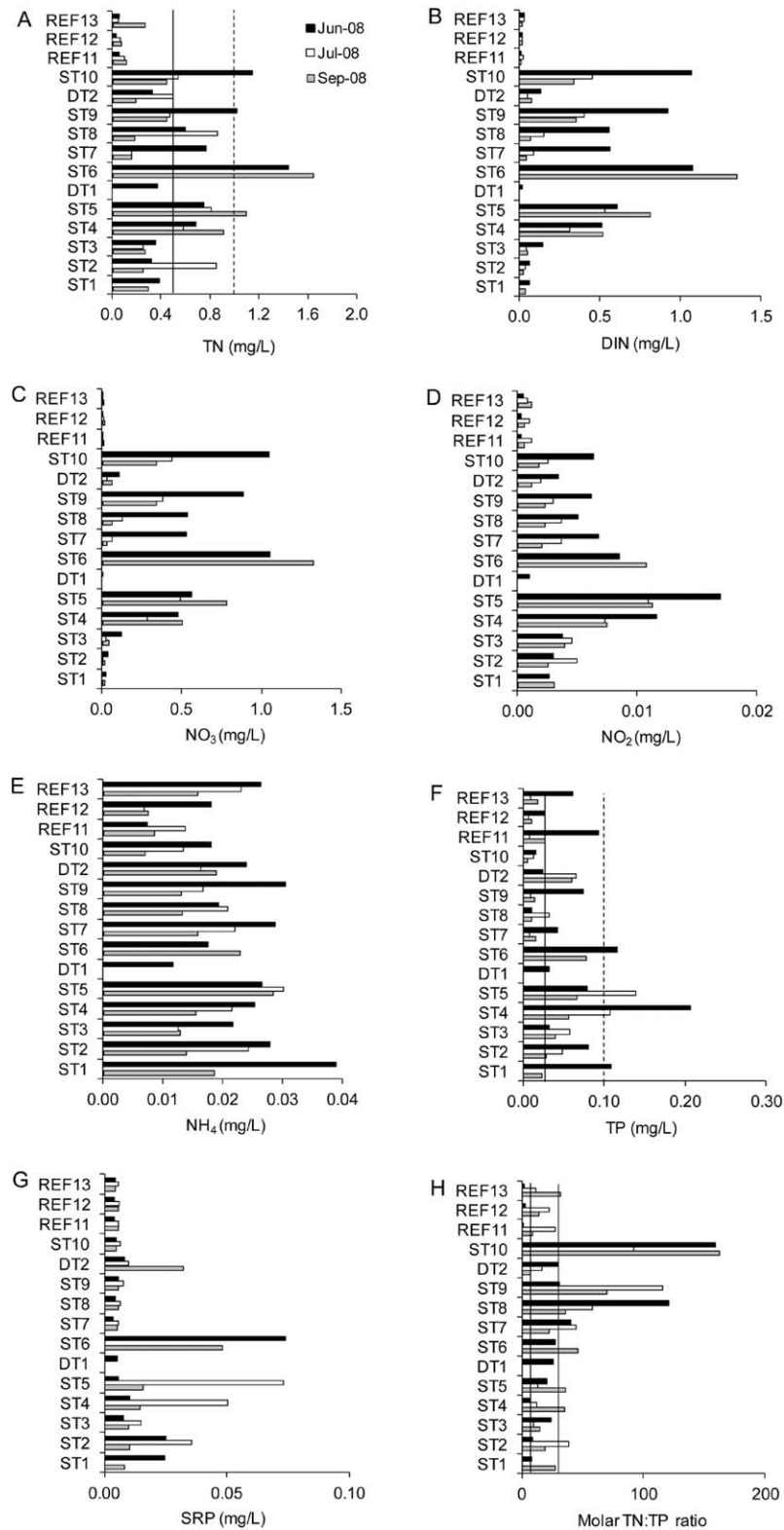
FIG. 3.   Total N (TN) (A), total dissolved inorganic N (DIN) (B), NO$_3$-N (C), NO$_2$-N (D), NH$_4$-N (E), total P (TP) (F), soluble reactive P (SRP) (G), and molar TN:TP (H) at sites in the Ventura River in June, July, and September 2008. In A and F, solid lines show the USEPA (2000) maximum TN (0.5 mg TN/L) or TP (0.03 mg TP/L) to avoid impairment for rivers and streams in Ecoregion III subecoregion VI, and broken lines show the USEPA (2007) Malibu Creek total maximum daily load for TN
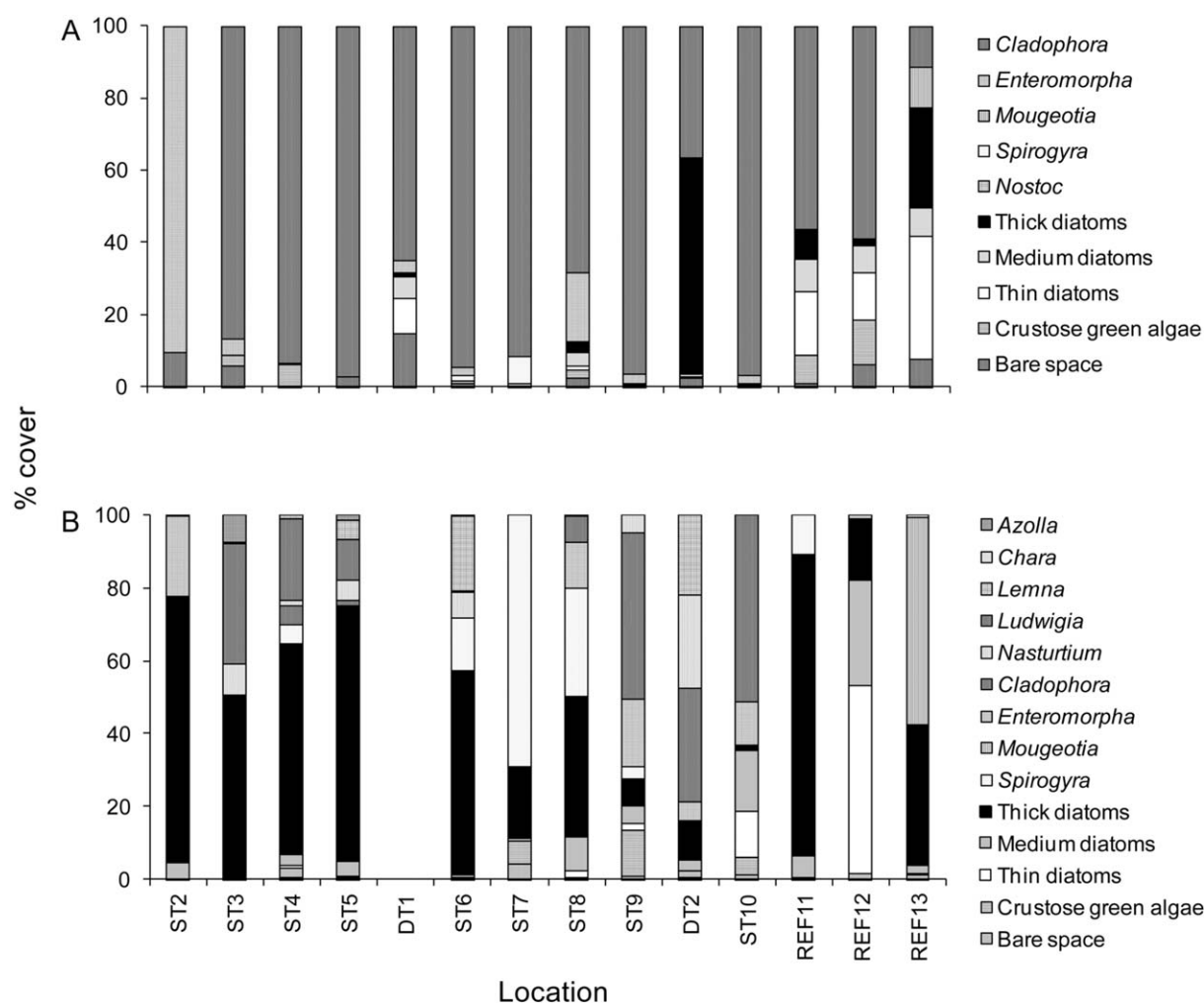
FIG. 4.   Mean % cover of macroalgae and aquatic plant types or genera at sites in the Ventura River catchment in June (A) and September (B) 2008. Macroalgal and plant % cover were averaged over all transects at a site. DT1 was dry during September.

ST7–10 in June, but declined in September (Fig. 5B, C). Mean benthic algal chl *a* did not differ across all sites between spring and summer (Fig. 5A), but mean floating chl *a* was greater in June than in September across all sites (paired *t*-test, $t = 2.39$, $p = 0.03$; Fig. 5B).

Predawn DO was related to both chl *a* and discharge (Q, m^3/s) ($\log[\text{DO}_{\min}] = 1.08 + 0.11 \log[Q]$ $- 0.09 \log[\text{chl } a]$; $R^2 = 0.38$, $p = 0.02$). A regression model including both chl *a* and Q as independent variables accounted for 81% of the variation in observed diel ΔDO ($\log[\Delta\text{DO}] = -0.65 + 0.54\log[\text{chl } a]$ $- 0.21\log[Q]$; $R^2 = 0.81$, $p < 0.001$).

Relationships between algal chl a, *and nutrient concentrations and light*

Total and floating chl *a* in both months and benthic chl *a* and macroalgal % cover in June were positively related to TN (Table 2; $r^2 = 0.65$, $p < 0.001$ for macroalgal % cover vs TN in June). Backward stepwise elimination of nonsignificant environmental variables during regression analysis indicated the primacy of N concentrations as a driver of chl *a* concentrations, with the exception that benthic chl *a* was positively related to TP in September (Table 2). Floating chl *a* was positively related to current velocity in the spring,

←

(1.0 mg TN/L) or TP (0.1 mg/L TP) to avoid impairment (Stevenson et al. 2006). In H, the reference lines indicate molar TN:TP threshold ratios for N vs P limitation in streams and rivers (<10 = N limitation, >30 = P limitation, 10–30 = colimitation or no limitation; Schanz and Juon 1983, Francoeur et al. 1999).
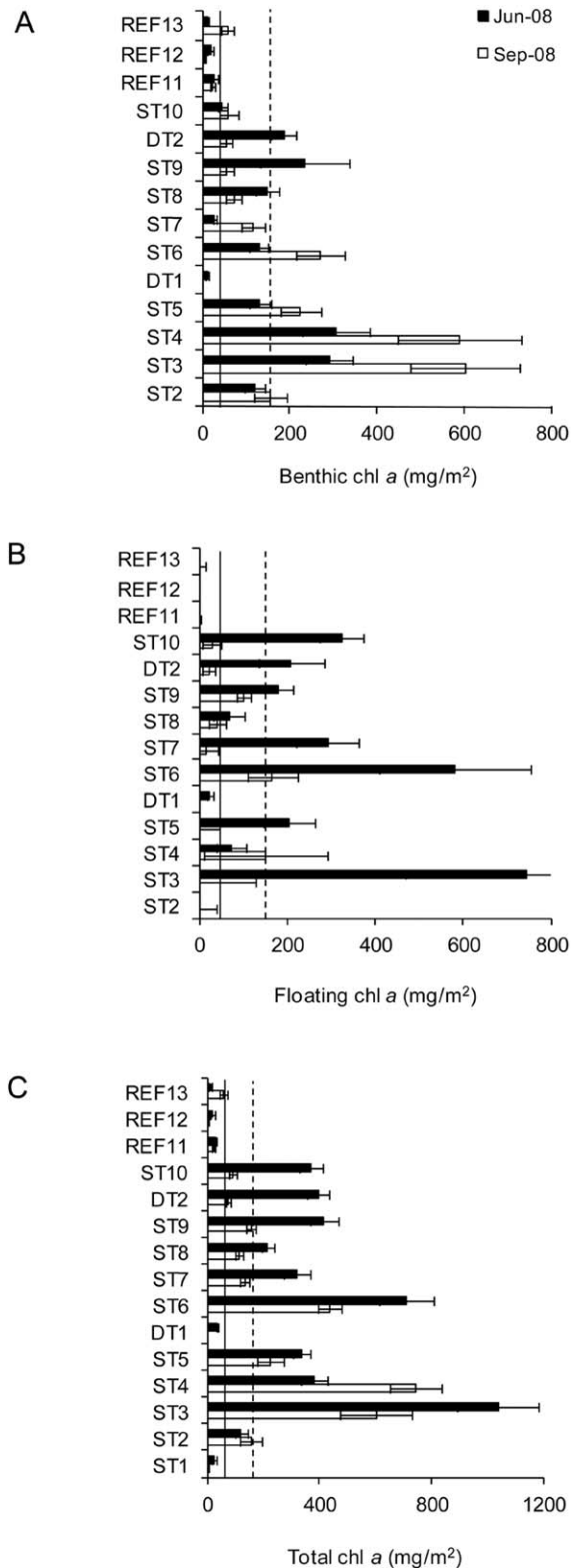
FIG. 5.   Mean (+1 SE) biomass (as chlorophyll a [chl a]) of benthic (A), floating (B), and total algae (C) at sites in the Ventura River catchment in June and September 2008. Solid lines show the recommended USEPA (2007) maximum chl a

and total and benthic chl a were positively related to % open canopy in September (univariate regressions of total and benthic chl a vs % open canopy: $r^2 = 0.45$, $p = 0.01$; $r^2 = 0.41$, $p = 0.02$, respectively; Table 2).

Nutrient diffusion experiment

Algal chl a responded positively to N additions at ST2–4, DT2, and REF12–13, whereas P enrichment had a negative effect on chl a concentrations at ST2–4 (Fig. 6). Algal chl a responded positively to P and secondarily to N enrichment at ST8, but the reverse was observed at REF12–13. In contrast, only N and P together resulted in algal chl a increases at ST7, ST9, ST10, and REF11 (Fig. 6). Nutrients were not limiting at ST5, our nearest NDS site downstream from the WWTP, and algal chl a on control treatments and averaged across all nutrient-addition treatments were significantly greater at ST5 than at all other sites (controls: ST5 mean = 393 vs 78 mg/m^2 [mean across all other sites]; all nutrient addition treatments: ST5 mean = 373 vs 111 mg/m^2 [mean across all other sites]; t-tests, t = 13.2 and 9.7, respectively, both $p < 0.001$; Fig. 6).

LRR$_{+N}$ was not related to ambient TN, but LRR$_{+P}$ was negatively related to ambient TP ($r = -0.64$, $p = 0.02$), and LRR$_{N+P}$ was negatively related to both TN and TP concentrations ($r = -0.64$ and -0.81, $p = \sim 0.02$ and 0.001, respectively). LRRs were not related to current velocity or % open canopy.

Initial multiple regression models for NDS data from this study and Busse et al. (2006, Malibu Creek basin, southern California) combined included LRRs as the dependent variables and log(TP), log(TN), log(current velocity), and arcsin$\sqrt{(x)}$-transformed % open canopy as the independent variables. Final models showed that LRR$_{+N}$ (Fig. 7A) and LRR$_{N+P}$ (Fig. 7C) were negatively related to log(TN) and log(TP), respectively (equations in Fig. 7A, C). The final model for LRR$_{+P}$ was LRR$_{+P}$ = 1.19 − 0.59log(TP) + 0.56log(current velocity) ($p_{intercept} < 0.001$, $p_{TP} = 0.0002$, $p_{current} < 0.05$; $R^2 = 0.66$). There was a significant negative univariate relationship between LRR$_{+P}$ and log(TP) (Fig. 7B).

Land use and physicochemical and biological variables

In June and September, values of physical, chemical, and algal variables were not related to landuse

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(43.9 mg chl a/m^2) to avoid impairment for rivers and streams in Ecoregion III. Broken lines show the USEPA (2007) Malibu Creek total maximum daily load for chl a (150 mg chl a/m^2) and maximum chl a levels to avoid impairment (Dodds et al. 1998).

TABLE 2.   Results of multiple regression analyses with stepwise backward elimination of nonsignificant variables (see text) for relationships between total, benthic, and floating algal chlorophyll *a* concentrations (dependent variables; mg/m^2) and physicochemical variables (independent variables; in µg/L for nutrients, m/s for current velocity, % for open canopy, and φ = $-\log_2$[substratum particle diameter] for substratum size). *p* = probability value for *t*-test examining the difference of the slope from 0, RSE = residual standard error. TN = total N, TP = total P.

Month	Algal type	Physicochemical variable	Partial coefficient	*p*	Model overall *p*	RSE	Error df	Multiple R^2
June 2008	Total	TN	1.01	<0.001	<0.001	0.82	12	0.71
	Benthic	TN	0.57	0.031	0.031	1.02	12	0.33
	Floating	TN	1.82	<0.001	<0.001	1.27	10	0.80
		Current velocity	1.01	0.038				
September 2008	Total	TN	0.85	0.020	0.003	0.84	10	0.63
		% open canopy	2.55	0.092				
	Benthic	TP	0.86	0.013	0.003	0.81	10	0.64
		% open canopy	3.89	0.007				
	Floating	TN	1.12	0.101	0.101	1.99	11	0.23

patterns at the 100-m and 250-m scales, and % open canopy, water velocity, and temperature were not related to landuse indices at any scale. N species (TN, DIN, NO_3-N, NO_2-N, NH_4-N, molar TN:TP), chl *a* variables (total, benthic, floating), and macroalgal % cover were positively related to % impervious surface at the subcatchment scale in June ($r = 0.54$–0.91, $p < 0.05$ to < 0.0001; Fig. 8B, C). In September, TN (Fig. 8E), molar TN:TP ratio, floating algae chl *a*, and macroalgal % cover were not related to indices of human land use at any scale, but DIN and TP (Fig. 8D) were related to % impervious surface at the subcatchment scale ($r = 0.56$ and 0.64, respectively, both $p < 0.05$). NO_2-N, total chl *a* (Fig. 8F), and benthic chl *a* were related to landuse indices at much smaller scales in September than in June, with all 3 variables being related to % impervious surface at the 500-m, 1000-m, and subcatchment scales ($r = 0.62$–0.82, $p < 0.02$ to < 0.005). Percent human land use was most strongly related to total and benthic chl *a* concentrations at the 1000-m scale (total chl *a*: 500-m: $r = 0.56$, $p < 0.05$; 1000-m: $r = 0.76$, $p < 0.005$; subcatchment: $r = 0.63$, $p < 0.05$; benthic chl *a*: 500-m: $r = 0.59$, $p < 0.001$; 1000-m: $r = 0.81$, $p < 0.001$; subcatchment: $r = 0.11$, $p > 0.10$). TP and SRP were not related to landuse indices at any scale in June (Fig. 8A), but in September, TP was correlated with % impervious surface at the 500-m scale (Fig. 8D), and SRP was correlated with % human land use at the 500-m ($r = 0.72$, $p < 0.005$), 1000-m ($r = 0.60$, $p < 0.05$), and subcatchment ($r = 0.60$, $p < 0.05$) scales.

Discussion

Nutrient concentrations

Nutrient concentrations increased along a gradient from sites in undeveloped to developed areas as described by Paul and Meyer (2001), Allan (2004), and Johnson et al. (2009) and were highest below a WWTP. In general, DIN and SRP at REF11–13 (DIN: 0.011–0.033 mg/L, SRP: 0.004–0.006 mg/L) were comparable to or lower than those reported from streams in other undeveloped catchments (DIN: 0.01–0.03 mg/L, SRP: 0–0.05 mg/L), whereas DIN and SRP concentrations at agricultural and urban sites were much higher (DIN: 0.017–1.36 mg/L, SRP: 0.004–0.074 mg/L) than those at reference sites and similar to or lower than those reported from streams draining developed catchments in other parts of the world (DIN: 0.022–5.06 mg/L, SRP 0.004–0.32 mg/L) (Royer et al. 2004, Taylor et al. 2004, Grimm et al. 2005, Meyer et al. 2005, Busse et al. 2006, Stein and Yoon 2007, Von Schiller et al. 2007, Arango et al. 2008). Mean NO_3-N concentrations at REF11–13 were low relative to those at developed sites (means: 0.007 vs 0.336 mg/L) and had concentrations 1 to 2 orders of magnitude lower than those reported from streams draining undeveloped lands in other Mediterranean areas (0.05–0.23 mg/L) (Stein and Yoon 2007, Von Schiller et al. 2007). Molar DIN:SRP at REF11–13 (5–13) were low relative to ratios in undeveloped stream sites in Spain (21–24). However, developed sites in the Ventura River catchment had ratios (2–500) comparable to or greater than agricultural and urbanized sites in Spain (36–124) (Martí and Sabater 1996, Von Schiller et al. 2007).

Algal data

In spring, algal chl *a* and macroalgal % cover were dominated by the filamentous green alga *Cladophora* at most sites. However, in late summer, diatoms, other macroalgal genera, and, in the lower river, macrophytes were prominent. These results are similar to
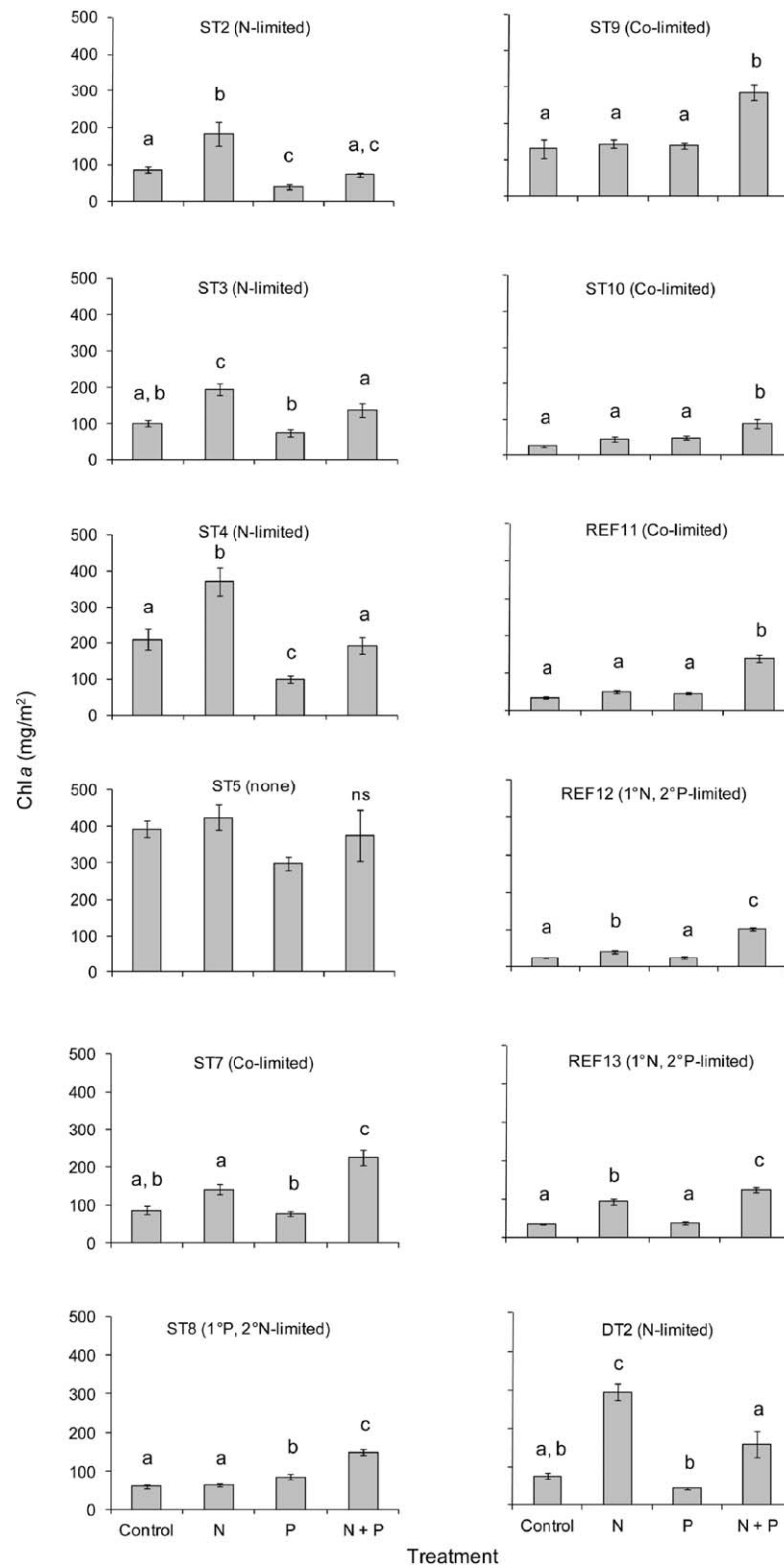
FIG. 6.   Mean (±1 SE) chlorophyll *a* (chl *a*) concentrations on nutrient diffusing substrata assigned to different experimental treatments (Control = no nutrients added, N = N added, P = P added, N+P = N and P added) and deployed at 12 sites in the Ventura River catchment from 3–21 July 2008. Bars with the same letter are not significantly different (Tukey–Kramer multiple comparisons tests, *p* > 0.05). Interpretations are shown in parentheses next to site names. 1° = primary, 2° = secondary.
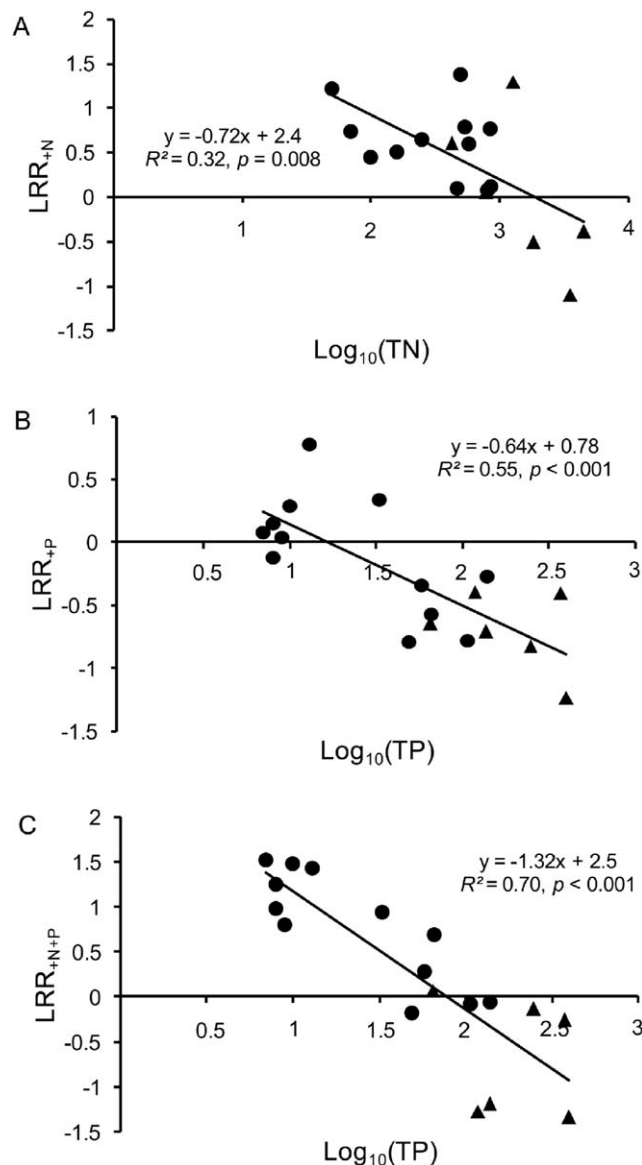
FIG. 7. Relationships between ln(chlorophyll *a* [chl *a*]) response ratios (LRR) to N addition (A), P addition (B), and N + P addition (C) vs log$_{10}$-transformed total N (TN) or total P (TP) (μg/L) in nutrient diffusing substrate experiments in the Ventura River (our study; *n* = 12, circles) and Malibu Creek (Busse et al. 2006; *n* = 6, triangles).

those obtained by Simpson (2006) for the lower Ventura River. *Cladophora* often is associated with nutrient-rich rivers, but it can form spring blooms at sites with low average nutrient concentrations, as we observed at our reference sites (Dodds and Gudder 1992). Authors of studies done in southern California, Spain, and New Zealand have reported high % cover of filamentous algae in unshaded, enriched stream sites with low flows (Sabater et al. 2000, Suren et al. 2003, Busse et al. 2006). Most of our sites in June

and half of our sites in September had % cover of filamentous macroalgae ≥20 to 30%. These values have been suggested as maximum threshold values to avoid problems associated with low DO, impaired habitat for invertebrates and fish, and limited recreational and aesthetic uses of streams (Welch et al. 1988, Biggs 2000b).

Mean algal chl *a* was higher at sites below the WWTP (mean = 475 mg chl *a*/m^2) than at sites above the WWTP (ST7–10) (mean = 226 mg chl *a*/m^2), which were higher than the mean algal chl *a* at REF11–13 (23 mg chl *a*/m^2). Busse et al. (2006) reported mean total chl *a* values of 218 to 322 mg/m^2 from urban sites with no WWTP inputs and 2 to 26 mg/m^2 from reference and rural sites in the Malibu Creek basin of southern California. In our study, algal chl *a* at most developed sites exceeded the highest impairment thresholds recommended in the literature, whereas reference-site chl *a* was similar to that reported from other undisturbed sites throughout the world (Nordin 1985, Welch et al. 1989, Dodds et al. 1998, Biggs 2000b, Busse et al. 2006).

Chl *a* levels as high as those observed at our developed sites have rarely been reported in the literature and typically were associated with floating filamentous algae, which can reach levels ≥1000 mg chl *a*/m^2 (Biggs 2000b, Taylor et al. 2004, Busse et al. 2006). Large floating algal mats made up an average of 62 and 19% of total algal chl *a* at sites affected by human activity during June and September, respectively, but were consistently absent at reference sites. Busse et al. (2006) reported that floating algae made significant contributions to total algal biomass in southern California streams during the summer months, and Biggs and Price (1987) found that the biomass of floating algae was substantial at some New Zealand sites during prolonged periods of low flow and was positively correlated with conductivity.

Relationships between algal chl a and physicochemical factors

In June, total, benthic, and floating algal chl *a* were strongly related to TN. In September, total algal chl *a* was strongly and floating algal chl *a* was weakly related to TN. In September, lower reaches of the Ventura River had substantial stands of aquatic vascular plants (*Ludwigia*), which may have confounded or obscured relationships between algal and nutrient levels if plants and benthic algae were competing for space, light, or nutrients (Simpson 2006). However, algal chl *a* samples were taken from
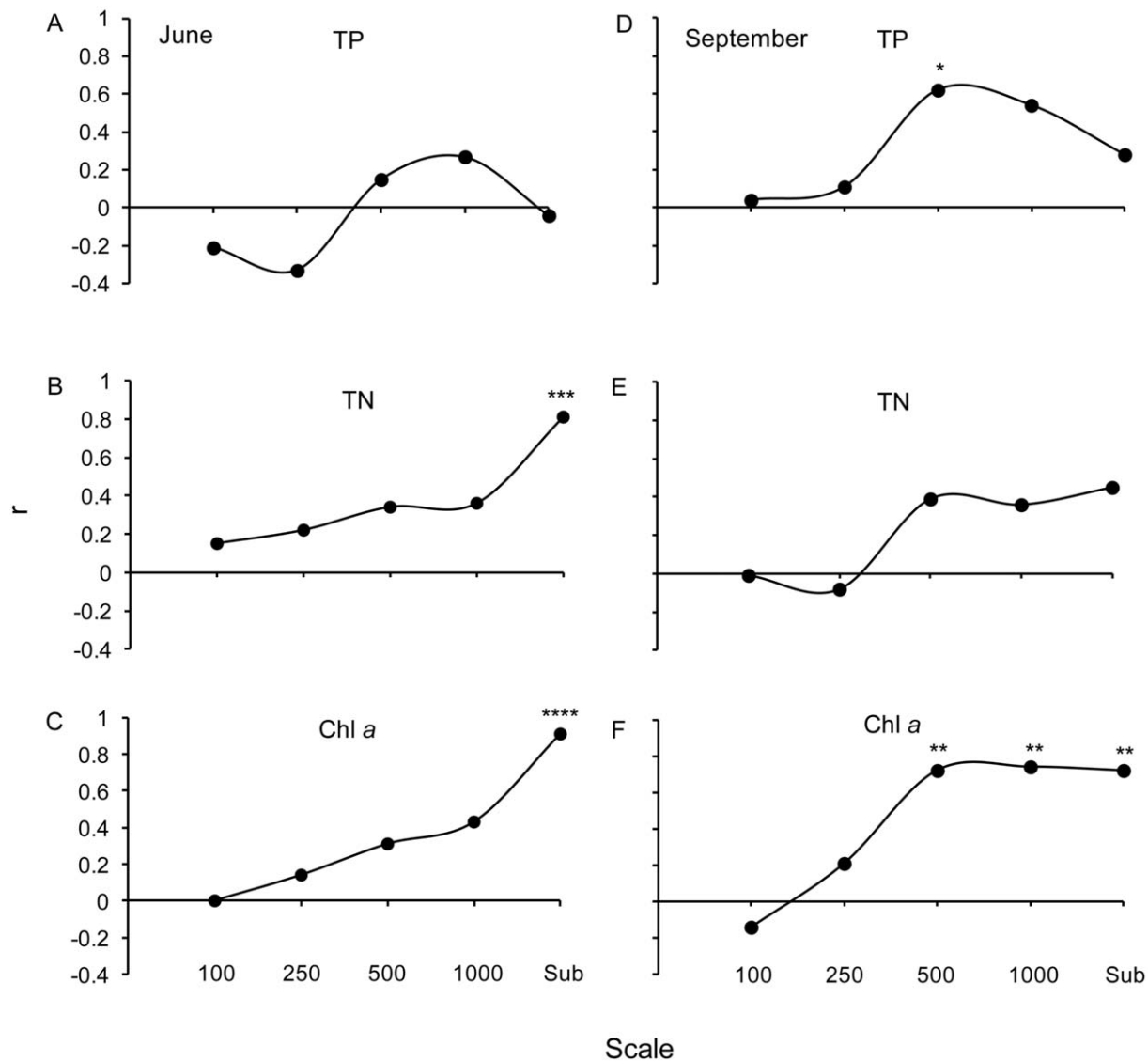
FIG. 8. Pearson's correlations (r) between total P (TP) (A, D), total N (TN) (B, E), and total chlorophyll a (chl a) (C, F) concentrations vs arcsin$\sqrt{(x)}$-transformed % catchment area covered by impervious surface at different scales of analysis (in m) including the subcatchment (Sub) scale during June (A, B, C) and September (D, E, F). Units for TP and TN were µg/L and for chl a were mg/m². Asterisks denote significant correlations as follows: * = $p < 0.05$, ** = $p < 0.01$, *** = $p < 0.001$, and **** = $p < 0.0001$.

points unshaded by vascular plants, and plants occupied river margins, whereas mainstream areas were dominated by algae in September.

Analyses of the survey data suggested that N was the primary driver of algal chl a in the Ventura River system, but benthic chl a concentration was more tightly related to TP than to TN in September, a result suggesting that the relative importance of N vs P limitation of benthic algal chl a may have shifted between late spring and late summer. These relationships are difficult to disentangle because TN and TP were correlated in September ($r^2 = 0.62$, $p < 0.02$) and

benthic algal chl a and TN were significantly related in September ($r^2 = 0.58$, $p = 0.002$). Based on the results of NDS experiments, Grimm et al. (2005) reported that algal chl a was limited by N in spring but not summer or autumn in a suburban stream in New Mexico. The results of our NDS experiments indicated that N or N and P together limited benthic algal chl a in early summer, whereas the relationship between benthic algal chl a and P in late summer was consistent with relationships between algal chl a and P in another southern California catchment in late summer and autumn (Busse et al. 2006). Thus, our

results suggest that the identity of the limiting nutrient may depend on the time of year and inputs from different anthropogenic sources (Johnson et al. 2009, Sanderson et al. 2009).

Our regression analyses indicated that factors other than nutrients, such as current velocity and light levels, affected algal chl *a*. Winter floods, which are common in southern California, scour and remove algae but may ultimately benefit algae during the early dry season by increasing nutrient delivery rates (Biggs and Close 1989, Biggs 2000a). Mean current velocities were higher in June than in September (0.15 vs 0.10 m/s, respectively; *t*-test, $p = 0.006$), but mean total chl *a* did not differ between June and September (314 vs 217 mg chl a/m^2, respectively), and total and benthic chl *a* were not related to current velocity in June or September. In contrast, floating chl *a* was related positively to current velocity during spring, but not summer, apparently because floating algal mats were intercepted and retained by protruding rocks in fast-flowing areas in spring. Perennial rivers in Mediterranean areas undergo long periods of low flow during the dry season, which allow succession and accumulation of algae undisturbed by floods. Dry-season current velocities probably are not sufficient to scour substrata or dislodge benthic algae, but may transport and distribute detached mats.

Total and benthic chl *a* were positively related to % open canopy in September. Percent open canopy was associated with growth of riparian vegetation, which increased from June to September across sites. Thus, light might have been more limiting in September than in June. In other Mediterranean streams with land uses similar to those in the Ventura River catchment, light was more important than nutrients in controlling algal chl *a* (Von Schiller et al. 2008).

Nutrient limitation of algal chl a

Based on the NDS results, we predicted a relationship between the identity and magnitude of nutrient limitation of chl *a* and molar N:P ratios measured in the field (Schanz and Juon 1983, Francoeur et al. 1999). However, algal responses were not related to N or P enrichment, molar TN:TP, water velocity, or % open canopy. Excluding ST5 (below the WWTP) where ambient nutrient concentrations and control NDS algal chl *a* were high and algal chl *a* did not respond to nutrient enrichment, molar TN:TP correctly predicted the identity of the limiting nutrient at only 3 (ST3: N-limited, ST8: P-limited, REF11: co-limited) of the 11 remaining NDS sites. These results corroborate other studies showing that molar N:P is an inadequate predictor of algal response to enrichment (Francoeur

et al. 1999, Dodds 2003, Tank and Dodds 2003, Busse et al. 2006). Concentrations of dissolved inorganic nutrients may be poor indicators of the nutrients available to primary producers (including emergent or floating plants, such as *Ludwigia*) because of high levels of nutrient uptake (including luxury uptake and storage) and water-column depression by primary producers (Francoeur et al. 1999, Dodds 2003). In enriched Mediterranean rivers, algae accumulate to high levels during the dry season, resulting in high nutrient uptake and reduction of nutrients at low flows, as indicated by the decline in nutrient concentrations from the WWTP downstream (Fig. 3A–H) (Gasith and Resh 1999).

Early studies identified P as the primary nutrient driving eutrophication in freshwater systems, but more recent experimental work has shown that algal chl *a* can respond as strongly to N as to P additions and that adding both N and P often results in the highest response (Elser et al. 2007). In a meta-analysis of NDS results from lotic systems, 43% of the experiments showed no benthic algal response, 16% indicated that N was the primary or sole limiting nutrient, 18% indicated that P was the primary or sole limiting nutrient, and 23% showed algal responses only to the joint addition of N and P ($n = 237$; Francoeur 2001). In other studies of results from multiple lotic NDS experiments ($n = 10$–72), the percentages of no, N, P, and colimitation were 32 to 75%, 14 to 30%, 0 to 3%, and 8 to 39%, respectively (Tank and Dodds 2003, Johnson et al. 2009, Sanderson et al. 2009). In our study, the percentages were 8%, 50%, 8%, and 33%, respectively. These collective results indicate that P is very rarely the sole or primary limiting nutrient in streams and that colimitation by N and P may be common.

Light can account for variation in algal responses to nutrient amendments (Tank and Dodds 2003, Johnson et al. 2009, Sanderson et al. 2009), but we and Busse et al. (2006) found no relationship between algal response ratios and % open canopy, perhaps because most sites were open (78% in our study, >50% in Busse et al. 2006). Our results and those of Busse et al. (2006) showed negative relationships between algal LRRs and ambient nutrient concentrations, results indicating that the degree of nutrient limitation was inversely related to ambient nutrient concentrations and that nutrients become saturating for algal growth at high nutrient levels (Fig. 7A–C; Sanderson et al. 2009). Thus, the absence of algal responses to nutrient amendments at sites in the Malibu Creek catchment and at the site below the WWTP in the Ventura River probably can be attributed to saturating nutrient levels. We also observed that P additions sometimes

led to decreases in algal chl *a* relative to unenriched controls, particularly at sites with high nutrient concentrations (Fig. 7B), but explanations for this phenomenon are elusive (Francoeur 2001, Tank and Dodds 2003, Sanderson et al. 2009). Last, our NDS results indicating N or colimitation at most sites in the Ventura River catchment were generally congruent with survey results showing relationships between algal chl *a* and TN.

Diel changes in pH, DO, and temperature

During summer low-flow periods, rivers and streams in Mediterranean climates have elevated temperatures, high rates of photosynthesis during the day and respiration at night, and increased algal and microbial production (Gasith and Resh 1999). Many stream organisms are sensitive to high temperatures, low DO, and large changes in pH, so the effect of high nutrient concentrations on algal chl *a* and, in turn, diel changes in DO, temperature, and pH should be evaluated. As expected, levels of DO, temperature, and pH were lowest just before dawn and highest in the afternoon at Ventura River sites. Temperatures at most sites were >21 to 25°C during the day, exceeding the maximum threshold recommended for survival of steelhead (*Oncorhynchus mykiss*) (USEPA 1999), which were common at some Ventura River sites. Steelhead show considerable behavioral flexibility and seek sites that have lower temperatures, such as groundwater springs or seeps (Matthews and Berg 1997, Richter and Kolmes 2005). Diel pH changes in the lower Ventura River (pH 7.5 [night] to 8.8 [day]) exceeded those at reference sites (pH 7.7 [night] to 8.0 [day]) by ~0.5 to 1 pH unit. However, how diel pH changes within the range of 6 to 9 pH units affect riverine organisms is not known. The Los Angeles Regional Water Quality Control Board (LARWQCB 1994) recommends that stream pH should not be <6.5 or >8.5 and should not deviate >0.5 units from natural conditions as a result of wastewater discharge, but pH at ST1–6 often exceeded recommended upper pH limits.

Nighttime DO concentrations approached or were <5 mg/L at sites ST1–5 in May and June. DO concentrations that cause physiological impairment or death for aquatic species are relatively well known, but they vary considerably across species and life-history stages (Pollock et al. 2007). Embryos and larvae of steelhead or rainbow trout require >8 mg DO/L for high survivorship, whereas adults and juveniles show high mortality at <3 mg DO/L with diminished feeding and growth rates at <6 to 8 mg DO/L (Carter 2005). The impairment threshold for mean annual DO in the Ventura River catchment is 7 mg/L, with no values <5 mg DO/L (LARWQCB 1994). Thus, some of the Ventura River sites affected by human activity approached nighttime minimum DO thresholds. In contrast, reference sites always had predawn DO > 7 mg/L.

ΔDO was greatest at ST1–6 (10–12 mg/L) and lowest at REF11–13 sites (0.4 to 5 mg/L). Minimum DO and ΔDO are influenced by many factors, including flow rates or volumes, temperature, turbulence, the decomposition of organic material, algal photosynthesis, and community respiration (Cox 2003). We found that 38% of the variation in predawn DO and 81% of the variation in ΔDO could be attributed to chl *a* and *Q*.

Landuse patterns

Landuse changes, particularly urban and agricultural development, strongly affect stream ecosystems by altering hydrographs and geomorphology, and increasing nutrients, other contaminants, fine sediment, light, and water temperature, with many repercussions for the stream biota (Carpenter et al. 1998, Paul and Meyer 2001, Allan 2004, Pan et al. 2004, Walsh et al. 2005, Johnson and Host 2010). As expected, TN, TP, molar TN:TP, macroalgal % cover, and total, benthic, and floating chl *a* increased with development in our study, similar to results of others (Busse et al. 2006, Merseburger et al. 2011).

In June, values of all N and chl *a* variables in the Ventura River catchment were related to indices of human land use at the subcatchment scale. High levels of N delivery and availability caused by high runoff and *Q* during spring strongly affected algal chl *a* and macroalgal % cover at sites draining areas with substantial development. Our results agree with those of other studies of relationships among urban and agricultural land uses, N concentrations, and algal chl *a*. During spring runoff, high-flow conditions flush accumulated N from soils and groundwater in the entire catchment (Strayer et al. 2003, Carr et al. 2005, Kaushal et al. 2008).

In contrast, in September, total and benthic chl *a* levels were positively associated with indices of human land use at scales from 500 m to subcatchments. However, the strongest relationships were observed at 500-m and 1000-m scales. TP was significantly positively related to % human land use at the 500-m and 1000-m scales and to % impervious surface at the 500-m scale, whereas SRP concentrations were most strongly related to % human land use at the 500-m scale. These results suggest that the local effect of human activity on P and algal chl *a* is greater when runoff and river flows are low and inputs from point

sources (WWTP, agricultural operations) dominate flows (i.e., in late summer). Relationships between algal and nutrient variables vs landuse indices were observed at much smaller scales in September than in June, but some of these variables also were significantly correlated at the subcatchment scale in September, as might be expected when nutrients from point sources move downstream. Algal biomass was most strongly influenced by residential and urban landuse patterns in the Malibu Creek catchment of southern California at intermediate scales (500 m) in summer (Busse et al. 2006).

Concluding remarks

Streams and rivers in Mediterranean regions have distinctive hydrographic signatures characterized by intense flashy winter floods and low or nonexistent dry-season flows and are prone to erosion, debris flows, and mud slides in steep terrain (Gasith and Resh 1999). Mediterranean climates are relatively benign, so they attract human settlement and trigger population growth which modify natural hydrologic, biogeochemical, and geomorphologic cycles by replacing native vegetation with impervious surfaces and introduced species that often require fertilizer inputs (Underwood et al. 2009). High annual and interannual variation in precipitation and the steep terrains of many Mediterranean regions combined with landuse change engender increased flows, sediment erosion and transport, and nutrient inputs during winter storms and reduced flows and enhanced nutrient inputs, temperature, algal levels and production, and community respiration during the dry season (Gasith and Resh 1999, Paul and Meyer 2001, Allan 2004, Wenger et al. 2009, Johnson and Host 2010). Natural Mediterranean streams have distinctive abiotic and biotic characteristics, but the effects of human population growth and associated landuse changes on Mediterranean stream ecosystems are similar to their effects on streams in other regions, contributing to the global homogenization of ecosystem characteristics. The unique characteristics of Mediterranean streams, such as prolonged low flows in the dry season, may exacerbate the impacts of increased nutrient loading by reducing contaminant dilution, increasing temperatures, and allowing the extended accumulation of algal and plant biomass, which, in turn, engenders pronounced diel ΔDO, sometimes below lethal thresholds. Much of the dry-season discharge in Mediterranean streams and rivers surrounded by developed land comes from WWTPs, which contribute high nutrient loads (Martí et al. 2004) and foster nuisance algal blooms (Klose et al. 2009).

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