

# Light-mediated thresholds in stream-water nutrient composition in a river network

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**Abstract.** The elemental composition of solutes transported by rivers reflects combined influences of surrounding watersheds and transformations within stream networks, yet comparatively little is known about downstream changes in effects of watershed loading vs. in-channel processes. In the forested watershed of a river under a mediterranean hydrologic regime, we examined the influence of longitudinal changes in environmental conditions on water-column nutrient composition during summer base flow across a network of sites ranging from strongly heterotrophic headwater streams to larger, more autotrophic sites downstream. Small streams (0.1–10 km<sup>2</sup> watershed area) had longitudinally similar nutrient concentration and composition with low (~2) dissolved nitrogen (N) to phosphorus (P) ratios. Abrupt deviations from this pattern were observed in larger streams with watershed areas >100 km<sup>2</sup> where insolation and algal abundance and production rapidly increased. Downstream, phosphorus and silica concentrations decreased by >50% compared to headwater streams, and dissolved organic carbon and nitrogen increased by ~3–6 times. Decreasing dissolved P and increasing dissolved N raised stream-water N:P to 46 at the most downstream sites, suggesting a transition from N limitation in headwaters to potential P limitation in larger channels. We hypothesize that these changes were mediated by increasing algal photosynthesis and N fixation by benthic algal assemblages, which, in response to increasing light availability, strongly altered stream-water nutrient concentration and stoichiometry in larger streams and rivers.

**Key words:** *Angelo Coast Range Reserve, California, USA; autotrophy; elemental stoichiometry; geomorphology; heterotrophy; N fixation; nitrogen; phosphorus; primary production; South Fork Eel River watershed, California, USA; stream network.*

## INTRODUCTION

Longitudinal gradients in physical conditions are a central feature of stream networks. As water moves downstream from headwaters, most if not all important environmental variables change: light irradiating the stream increases as channels widen, reducing shading from trees and banks; summer temperatures rise as cool groundwater is warmed by surface heat transfer; and benthic sediment particle size decreases (Allan 1995). The influence of these gradients in temperature, light, and geomorphology on stream ecosystems has been at the foundation of many subsequent studies of streams since the introduction of the River Continuum Concept (Vannote et al. 1980).

While the presence of longitudinal environmental gradients is clear, their influences on ecological processes are less well understood. Changes in physical conditions

often elicit nonlinear responses in species distributions and interactions that could lead to rapid spatial alterations of biological processes in river networks (Power and Dietrich 2002, Woodward and Hildrew 2002, Power 2006). Such environmental transitions or thresholds in processes are inherently difficult to detect in stream networks because of stochastic variability, natural and human-induced spatial heterogeneity, and the logistical challenges of working across multiple sites.

Consideration of effects of variable environmental conditions across sites is especially relevant for improving understanding of the fate and transport of nutrients in stream networks. While the influence of surrounding watersheds has long been recognized as a major factor controlling concentration and composition of nutrients in streams (e.g., Meybeck 1982, Likens and Bormann 1995, Green and Finlay 2010), there is increasing focus on the role of in-stream processes in mediating the downstream transport and fate of important nutrient species. Many studies have demonstrated substantial rates of inorganic-nutrient removal from the water column (reviewed by Ensign and Doyle [2006]), but

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there is little consensus on when, where, or how the relative importance of internal processes vs. effects of surrounding watersheds changes in drainage networks. A network perspective, with the focus on physical gradients and stream responses to these gradients, has the potential to provide insight into these issues (see Power and Dietrich 2002, Battin et al. 2008).

Rates of key processes in stream nutrient cycles should change longitudinally in stream networks because of strong gradients in environmental conditions with stream size. Small streams with forested headwaters are rich in organic carbon from terrestrial ecosystems, have maximum sediment–water contact, and are thus thought to be key locations in the watershed network for in-stream nutrient removal. Two recent studies, for example, measured greater rates of nitrogen (N) removal in small streams compared to larger, downstream reaches (Alexander et al. 2000, Peterson et al. 2001). Larger streams and rivers may, however, also function as hotspots for nutrient cycling in stream networks. As channels widen, higher light availability and warmer temperatures stimulate autotrophic production (Webster and Meyer 1997, Battin et al. 2008). In contrast to heterotrophic bacteria and fungi that dominate biofilms in forested headwater streams, many autotrophs can store phosphorus (P), and some taxa assimilate atmospheric N via fixation. Algae also produce organic matter of higher quality and edibility compared to terrestrial inputs (Mayer and Likens 1986, Kupferberg et al. 1994). Thus, while benthic organic-carbon availability could limit nutrient cycling rates in larger streams compared to headwater channels, increases in algal biomass, nutrient demand, and N fixation may stimulate biogeochemical transformations (Webster et al. 2003, Fellows et al. 2006, Mulholland et al. 2006).

While it seems reasonable to expect longitudinal shifts in processes influencing nutrient transport and fate, we know little about the specific nature of changes in stream networks and how they affect multiple, interacting elements (Ensign and Doyle 2006, Wollheim et al. 2006). Many past studies have focused on dynamics of a single site and those that have included longitudinal comparisons have typically considered small scales, typically encompassing between 10 to 300 m of stream length (Brookshire et al. 2009), or for a small number of sites (2–4) across a large size gradient (e.g., Wollheim et al. 2001, Ensign and Doyle 2006). Moreover, most studies have focused on one or two nutrient species, without attention to effects of their relative availability (but see Von Schiller et al. 2007). While there is evidence that both small, heterotrophic streams and larger, more autotrophic channels are highly active sites for nutrient cycling, we know relatively little about the interaction of N and P cycles within stream networks.

In this study we examined evidence for changes in biological mediation of stream-water nutrient concentration, flux, and stoichiometry during base flow conditions across a gradient in stream size and organic-carbon

sources within a single watershed. We focused on two questions: (1) Given contrasts in ecosystem metabolism and organic-matter characteristics, do detrital rich, largely heterotrophic streams affect nutrient concentrations and stoichiometry differently than those more highly influenced by autotrophic metabolism? (2) Do in-channel effects operate consistently throughout watershed networks, or are there strong transitions in environmental conditions that shift processes affecting stream-water nutrient composition and flux? In a largely pristine system with low background nutrient levels set in a mediterranean climate, our work demonstrates an apparent threshold in stream size and light availability that increased autotrophic activity, inducing strong, nonlinear changes in stream nutrient composition, with consequences for both local and downstream ecosystem processes.

## METHODS

### *Site characteristics*

The study watershed is in the Coast Range of northern California, USA, ~12 km from the Pacific Ocean (Fig. 1). The watershed is steep, underlain by marine sandstone, mudstone, and shale, and forested primarily with evergreen and drought-deciduous trees. Old-growth redwood and mixed deciduous–Douglas-fir forests dominate valley bottoms and lower slopes and chaparral occurs at higher elevations. Stream channels are deeply incised, bearing high sediment loads in winter and clear water during summer base flow.

The region has a mediterranean climate with hot dry summers and cool wet winters. Little rain falls between June and October, when sample collection occurred. Streams are typically “reset” by scouring winter floods, and during summer algal production is limited by nitrogen availability (Power 1992, Power et al. 2008). Effects of heterogeneity in land cover appear to be minimal, in part due to low human population density (<2 persons/km<sup>2</sup>) facilitating examination of in-stream processes. As in many other forested watersheds, there are strong gradients in physical and chemical conditions associated with stream size as water moves from headwater springs to streams and rivers. Most notably, solar inputs and stream temperatures increase with the widening of the active channel, and ecosystem metabolism becomes more influenced by algal production (Warnaars et al. 2007). Epilithic algae were present at all sites as a thin, heavily grazed layer consisting primarily of diatoms (McNeely and Power 2007). Algal biomass and algal-derived detritus were substantially greater in the two larger river reaches draining >100 km<sup>2</sup>, where blooms of the chlorophyte *Cladophora glomerata* usually form in June and persist through August (Power 1992, McNeely et al. 2006, Warnaars et al. 2007, Power et al. 2009).

We examined downstream changes in the form and stoichiometry of nutrients transported from terrestrial ecosystems through hydrologically connected stream reaches. The study streams ranged in size from small headwater streams to sunny downstream reaches of the

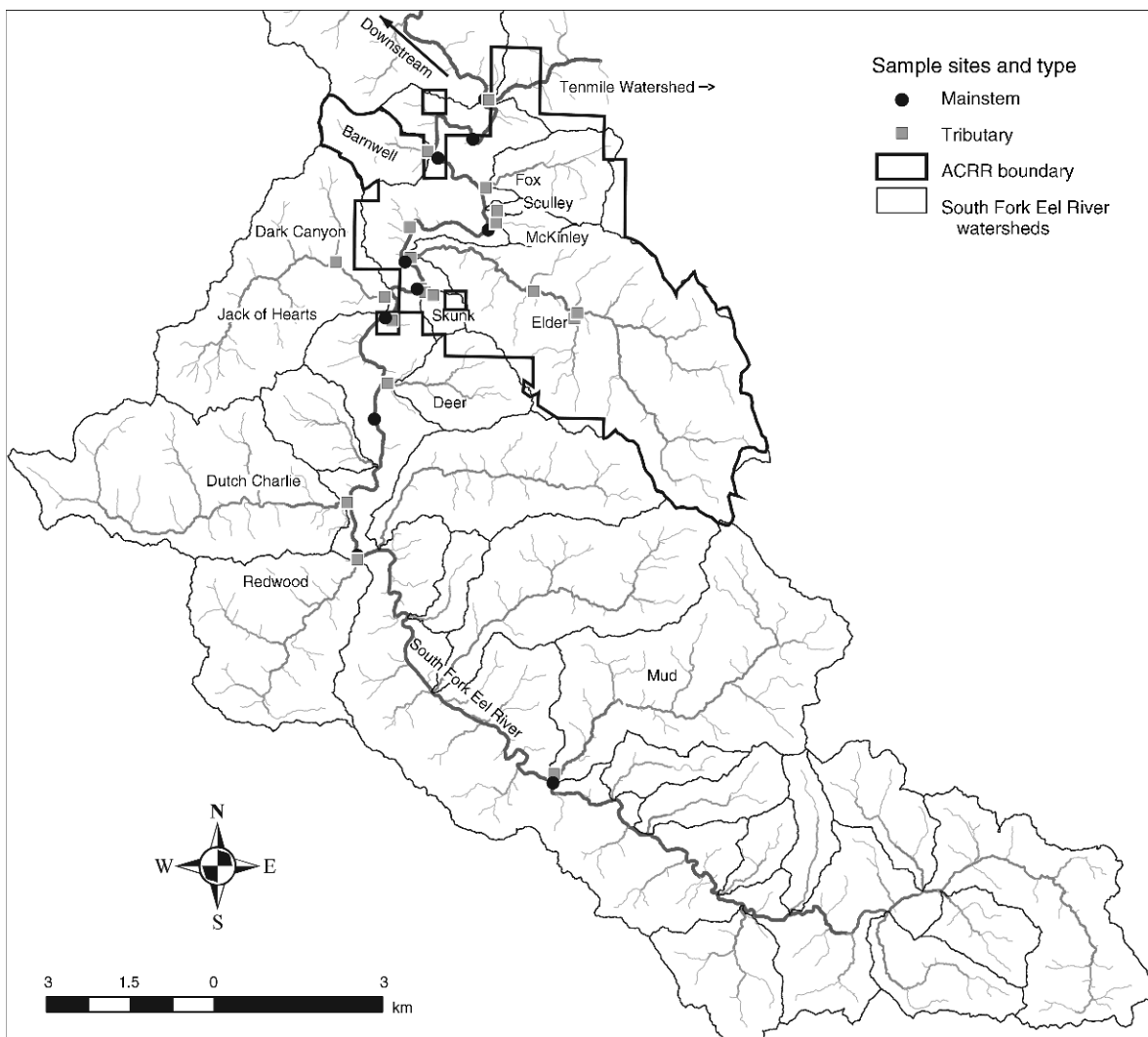


FIG. 1. Study sites in and near the Angelo Coast Range Reserve (ACRR), northern California, USA. Black lines show the boundaries of the ACRR. Most tributary streams were sampled near their confluence with the South Fork Eel River, except for Rattlesnake and Elk Creeks (not shown, located about 30 km northwest of ACRR at U.S. Highway 101). Skunk and Elder Creeks were sampled at multiple sites, including one small tributary of Elder Creek. Only subwatersheds that were sampled are labeled; their basin areas are: Barnwell, 2 km<sup>2</sup>; Dark Canyon, 1.7 km<sup>2</sup>; Jack of Hearts, 10.1 km<sup>2</sup>; Dutch Charlie, 11.6 km<sup>2</sup>; Redwood, 8.1 km<sup>2</sup>; Fox, 2.7 km<sup>2</sup>; Sculley, 0.2 km<sup>2</sup>; McKinley, 0.6 km<sup>2</sup>; Skunk, 0.2 km<sup>2</sup>; Elder, 17 km<sup>2</sup>; Deer, 2.9 km<sup>2</sup>; and Mud, 13.3 km<sup>2</sup>. Watershed areas for the 10 main-stem South Fork Eel from upstream to downstream were 40.0, 83.9, 108.1, 116, 124.9, 125.6, 144.7, 149.6, 152, and 154 km<sup>2</sup>. The thickness of lines representing streams is proportional to the relative size of the watershed.

upper South Fork Eel River (150 km<sup>2</sup> watershed area) and its tributaries near Branscomb, California (Fig. 1). Most sites were within the Angelo Coast Range Reserve (ACRR), a protected research site in the University of California Natural Reserve System. A smaller number of sites were adjacent to or near the ACRR. Parts of these watersheds were logged in the 1950s but the ACRR's forests have been protected since the early 1930s. Although atmospheric deposition of nutrients was not monitored, inputs from anthropogenic sources are likely low because the site is close to the Pacific Ocean and there are no local municipal or industrial sources of pollutants, and few roads and houses. The

closest nearby atmospheric monitoring site (<100 km away in Hopland, California) shows nitrogen deposition levels that are among the lowest reported in the United States (data available online).<sup>7</sup> Considering that Hopland is further inland than ACRR and near several large towns, N deposition rates are likely higher there than our more remote, coastal study site.

#### *Environmental conditions*

Discharge and stream temperature are monitored continuously on Elder Creek and the South Fork Eel

<sup>7</sup> <http://nadp.sws.uiuc.edu/sites/>

River (data *available online*)<sup>8</sup>; discharge, temperature, and light levels were measured less frequently at other sites to examine spatial variation in environmental parameters that potentially influence nutrient dynamics. Temperature was measured at some sites during mid-afternoon as reported in a previous study (Finlay 2003). Light intensity (i.e., illuminance) was measured immediately above the stream surface in the middle of the channel across the watershed at 22 sites for 3–7 days in mid-August 2008 using HOBO data loggers (model UA-002; Onset Computer Corporation, Bourne, Massachusetts, USA). Light intensity was measured at 10-min intervals, and mean intensities were calculated from data recorded from 06:00 to 20:00 hours. Although light intensity is correlated with photosynthetically active radiation (PAR), the relationships may be site specific. Light intensity data were therefore used for qualitative comparisons of levels of sunlight reaching the stream surface, and may not represent absolute differences in PAR. Discharge was measured at 6–8 sites on four dates to establish relationships between watershed area and water flux. These measurements were correlated with discharge measured on Elder Creek, which is monitored continuously. These correlations were used to estimate discharge at all study sites under average summer base flow conditions. Channel width (i.e., estimated bank-full width) was measured at most sites with a meter tape.

#### *Dissolved nutrients*

Concentrations of dissolved forms of phosphorus, nitrogen, and organic carbon were measured approximately every two weeks across a network of sites during basin-wide surveys. Dissolved silica (DSi) and bicarbonate ( $\text{HCO}_3$ ) were measured less frequently. All measurements occurred during base flow conditions. Data for periods of higher flows in late fall through spring, when in-stream signals are harder to detect and interpret relative to effects of storm events, are not reported here. All samples were collected during daylight hours. In larger streams with higher rates of autotrophic production, sample collection occurred between 12:00 and 18:00 hours to minimize potential effects of diel changes in water chemistry (Finlay 2003). Diel changes in inorganic nutrient chemistry were assessed on two dates in Fox Creek and the South Fork Eel River, and showed small but significant changes for  $\text{NH}_4$  only in the South Fork Eel. Concentrations of other reactive nutrient species were stable over daily cycles (J. M. Hood and J. C. Finlay, *unpublished data*).

Water samples were filtered in the field with glass-fiber filters (GF/F; Whatman, Kent, UK), and refrigerated or frozen within several hours of collection. Dissolved reactive phosphorus and ammonium were analyzed within 1–2 days after collection at the field site when possible or were frozen if they could not be analyzed

immediately. Soluble reactive phosphorus (SRP) was analyzed using molybdate colorimetric analyses on a spectrophotometer. Ammonium was analyzed using the OPA-fluorometric technique (Taylor et al. 2007) with a portable fluorometer (Turner Designs, Sunnyvale, California, USA). Because ammonium concentrations were low, difficult to measure, and did not vary consistently among sites, we analyzed a subset of the samples collected and used the average concentration of all data ( $\sim 5 \mu\text{g N/L}$ ) to calculate dissolved organic nitrogen (DON) from total dissolved nitrogen (TDN). Samples for other nutrients were preserved by freezing (total dissolved phosphorus, nitrate, and silica), acidification/refrigeration (total dissolved nitrogen and dissolved organic carbon) or refrigeration ( $\text{HCO}_3$ ) and were usually analyzed within 2–6 weeks. Total dissolved phosphorus (TDP) was measured using the colorimetric method used for SRP following persulfate oxidation, and nitrate was analyzed using cadmium reduction to  $\text{NO}_2$  followed by colorimetric analysis. Total dissolved nitrogen (TDN), dissolved organic carbon (DOC), and  $\text{HCO}_3$  were analyzed on a Shimadzu Vcpn analyzer (Shimadzu Corporation, Kyoto, Japan). DON was estimated from the difference between TDN and DIN (dissolved inorganic nitrogen) (i.e.,  $\text{NH}_4 + \text{NO}_3 + \text{NO}_2$ ). Dissolved silica (as  $\text{SiO}_2$ ) was measured using colorimetric methods using a spectrophotometer (Strickland and Parsons 1968).

Samples for particulate C, N, and P were collected onto ashed glass-fiber filters from 200–1500 mL of stream water. Filters were dried and stored in the dark until analysis. Particulate P was analyzed colorimetrically using similar methods as for TDP. Particulate N and C were measured directly with a Perkin Elmer CHN analyzer (Perkin Elmer, Waltham, Massachusetts, USA) or indirectly via calibration of near infrared spectroscopy (NIRS) as described in Hood et al. (2006).

#### *DOM source tracing*

We measured DOC stable carbon isotopes (i.e.,  $\delta^{13}\text{C}$ ) to distinguish DOM sources in the watershed.  $\delta^{13}\text{C}$  values are very similar between DOC and its particulate organic-matter source (Coffin et al. 1989). Thus,  $\delta^{13}\text{C}$  can be used to separate terrestrial vs. algal contributions to DOM (dissolved organic matter) when they are isotopically distinct. In the South Fork Eel watershed, there are three potential sources of stream DOC: marine shale in bedrock, riparian trees, and algae. DOM from these sources should have similar isotopic values. Local shale has  $\delta^{13}\text{C} -24.3\text{‰}$  (Leithold and Blair 2001, Blair et al. 2003). Senesced foliage of deciduous and evergreen trees averages  $-27.6\text{‰}$  (Finlay 2001, Leithold and Blair 2001, Blair et al. 2003).  $\delta^{13}\text{C}$  values are slightly elevated for the deciduous litter layer from the forest floor ( $-27.2\text{‰}$ ) and stream-conditioned leaves ( $-27.1\text{‰}$  for deciduous species) so a value of  $-27.1\text{‰}$  was used to represent the mean for modern terrestrial organic-carbon inputs to streams (Finlay 2001). Algal  $\delta^{13}\text{C}$

<sup>8</sup> <http://angelo.berkeley.edu/sensors/met/>



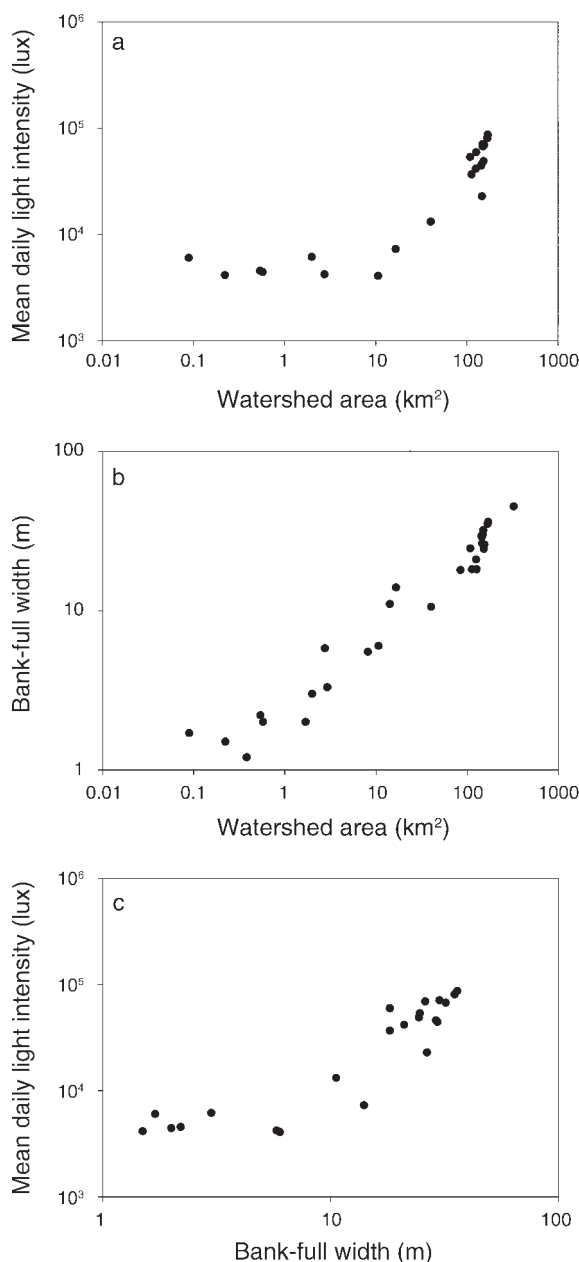


FIG. 2. Relationships between watershed area, bank-full width, and light intensity (lux = lumens/m<sup>2</sup>): (a) light intensity vs. watershed area; (b) bank-full width vs. watershed area; (c) light intensity vs. bank-full width. Note the log-log scales.

values are much more spatially variable, increasing from low (i.e., <sup>13</sup>C-depleted) values in headwater streams (−44‰ to −30‰) to <sup>13</sup>C-enriched values (up to −14‰ for benthic diatoms in pool margins) in larger downstream sites (Finlay 2004). Algal biomass is dominated by a single alga (*Cladophora glomerata*) and its epiphytes in downstream sites (Power et al. 2009). <sup>δ13</sup>C values for these taxa during the summer are fairly constant, and in pools, algae are <sup>δ13</sup>C enriched (−23‰; see Finlay

2004) relative to terrestrial detritus, facilitating analyses of DOC sources using mixing models.

DOC samples were collected for <sup>δ13</sup>C into ashed vials with Teflon-faced septa following filtration as described for nutrient samples. Samples were preserved with hydrochloric acid to pH 2, and refrigerated until analysis at the Colorado Plateau Stable Isotope Laboratory (Flagstaff, Arizona, USA) following methods of St. Jean (2003).

#### Mass-balance calculations

We used mass-balance measurements to estimate the changes in N fluxes associated with water movement through the stream network. N fluxes were calculated using discharge values (estimated as described above) and measured nutrient concentrations, including particulate N, at each sampling point.

## RESULTS

### Patterns in physical conditions

Study sites ranged from very small upland streams to small rivers with watershed areas of ~150 km<sup>2</sup> and bank-full widths of ~40 m (Fig. 2a, b). Over this gradient, tree canopy cover decreased, and light intensity and water temperature increased (Fig. 2a, c). Mean light intensity, measured over several days in August 2008, showed a threshold response, increasing with stream size only for streams with watershed areas >10 km<sup>2</sup> and widths >10 m (Fig. 2a, c). Mean light intensity observed at the largest sites was below typical instantaneous values for full sunlight (~100 000 lux) largely due to shading by surrounding ridges and trees in the morning and afternoon. Thus light intensity should be expected to continue to increase with stream size before leveling off in downstream sites with no terrestrial shading (Julian et al. 2008).

### Patterns in stream-water nutrients

Across headwater reaches of the stream network (i.e., defined as small streams 0.1–10 km<sup>2</sup> watershed area), dissolved oxygen concentration (DOC) increased slightly but there was little change in stream nutrient composition despite a large range of physical conditions (Fig. 3). During summer, dissolved silica (DSi) and TDP concentration averaged 7.5 mg Si/L and 25.0 µg P/L, respectively. Total dissolved nitrogen (TDN) and dissolved organic carbon (DOC) concentrations at base flow were very low, averaging 36 µg N/L and 423 µg C/L, respectively. Four headwater springs sampled once in 2007 had even lower concentrations for TDN and DOC (23 ± 7 µg/L and 160 ± 16 µg/L [mean ± SD], respectively), suggesting extremely low levels in groundwater. A combination of factors may be responsible for low DOC and TDN concentrations including a steep, well-drained catchment, lack of summer rainfall, and strong terrestrial N retention in the surrounding-old growth forest.

Nutrient concentrations in sites draining >100 km<sup>2</sup> departed markedly from those in headwater streams.

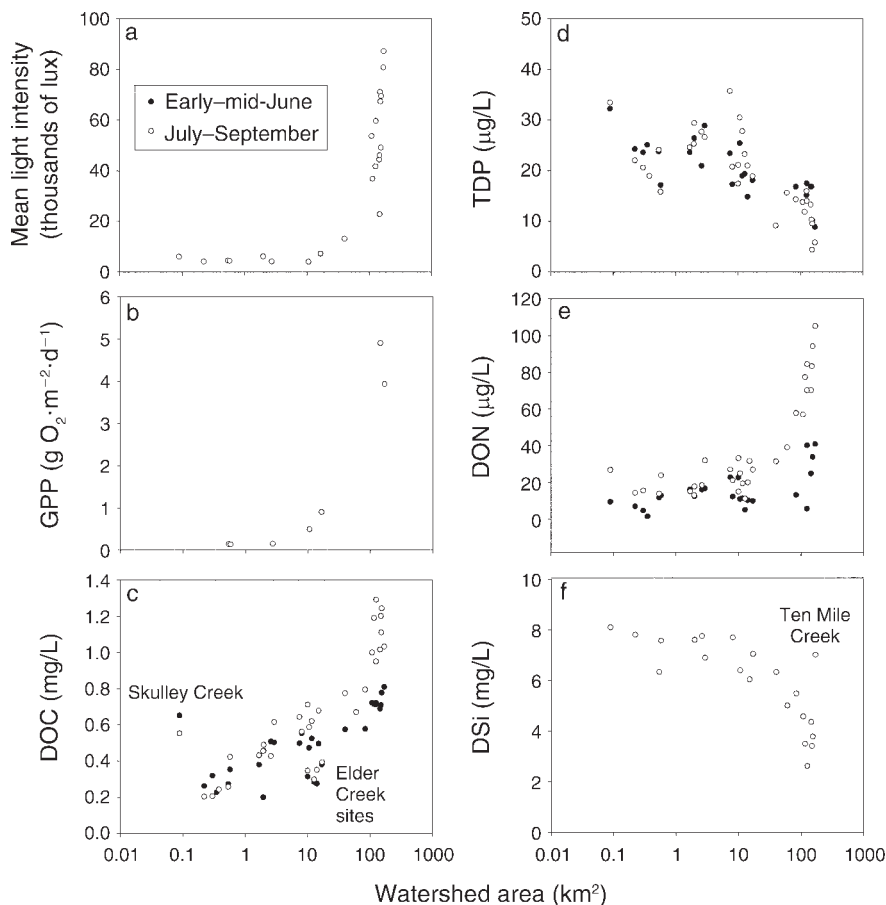


FIG. 3. Relationships between watershed area and (a) mean light intensity ( $\text{lux} = \text{lumens/m}^2$ ), (b) gross primary production (GPP), (c) dissolved organic carbon (DOC), (d) total dissolved phosphorus (TDP), (e) dissolved organic nitrogen (DON), and (f) dissolved silica (DSi). All data are from 2006–2008 except GPP, which was measured in 2003 and 2004 as reported in Warnars et al. (2007), light intensity (mid-August 2008), and DSi (July and August 2008). Each point in panels (c)–(e) represents the mean of 1–3 and 1–6 separate sampling events for early–mid-June and late June–late September, respectively, except for DSi (which represents data from two periods as noted above). Several outlier points are noted for reference. Note the x-axis logarithmic scale.

Dissolved silica and P concentrations rapidly declined, and DOC and DON concentration increased sharply (Fig. 3). DON increases were similar to TDN patterns for many of these sites reported by Power et al. (2009) for two dates in 2007. The large increases in DON were observed only for sites with  $>100 \text{ km}^2$  watershed area, and not at the sites most likely to be affected by humans such the South Fork Eel at Redwood Creek, the first site downstream of the town of Branscomb (California, USA), or Rattlesnake Creek, which borders U.S. Highway 101. The magnitude of all observed changes at downstream sites increased as base flow dropped over the summer (Fig. 3). Dissolved inorganic nitrogen concentrations were low throughout all sites (mean  $\text{NH}_4$  and  $\text{NO}_3 + \text{NO}_2$  of  $5.2$  and  $14.3 \text{ } \mu\text{g N/L}$ , respectively), and showed no trend with stream size or network position (data not shown). Virtually all P was present as soluble reactive P, with a minor dissolved organic and particulate contribution. Particulate C, N,

and P generally increased with stream size, but these increases had small to modest effects on total C, N, and P concentrations and stoichiometric relationships (J. Finlay, *unpublished data*).

Due to rising DON and decreasing TDP, total dissolved N:P increased from between 1.5 and 4, indicative of strong N limitation, up to 46 (Fig. 4a), a value suggesting P limitation. Similar patterns were observed when ratios of inorganic N:P were assessed (data not shown), primarily due to decreasing SRP concentrations. Fluxes of dissolved nutrients and organic carbon from the study watershed strongly depended on network position. For example, stream nitrogen fluxes increased from an average of  $1.3 \text{ mg N} \cdot \text{s}^{-1} \cdot \text{km}^{-2}$  watershed area in the headwater streams  $<1 \text{ km}^2$  up to  $5 \text{ mg N} \cdot \text{s}^{-1} \cdot \text{km}^{-2}$  at the two most downstream sites (Fig. 4b). Changes of similar magnitude were observed for DOC and TDP (data not shown).

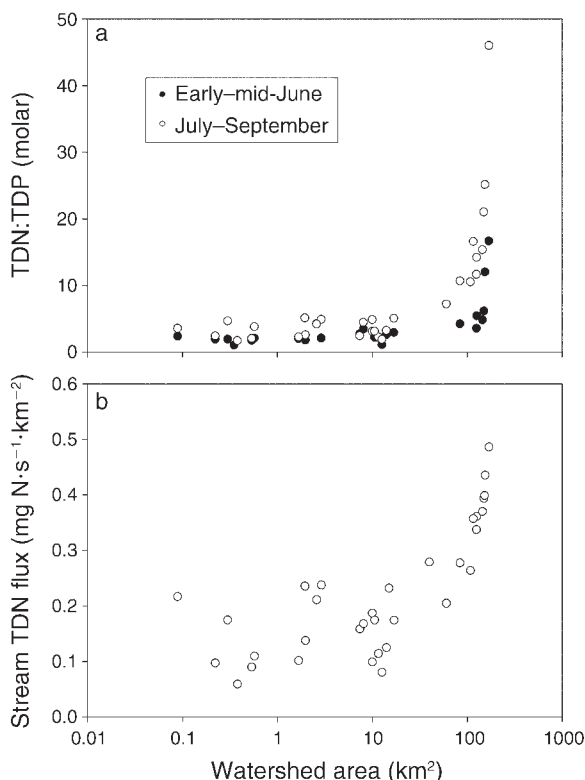


FIG. 4. Two effects of thresholds in in-stream nutrient cycling. (a) Opposite trends in TDN (total dissolved nitrogen) vs. TDP (total dissolved phosphorus) resulted in increasing dissolved N:P with watershed area. (b) Stream TDN flux estimates (expressed per unit of watershed area for typical summer conditions) depend on the network position. Note the x-axis logarithmic scale.

#### Sources and controls of dissolved nutrients in the network

Changes in stream nutrient concentration, flux, and stoichiometry corresponded to increasing insolation of the stream channel (Fig. 3a) due to widening of the active channel. Increasing sunlight stimulated autotrophic metabolism and increased algal biomass (Fig. 3b; see also Finlay 2004, McNeely et al. 2006, Warnars et al. 2007), especially of the macroalga *Cladophora glomerata* and its epiphytes (Power 1992). Mean light intensity in August 2008 was strongly correlated to average concentrations of biologically active elements such as DON, DOC, and TDP, but unrelated to bicarbonate ( $\text{HCO}_3$ ) (Table 1).

Aside from increasing algal production, there were no other changes in watershed or stream characteristics that could explain the changes in nutrient concentration. Less biologically reactive solutes such as  $\text{HCO}_3$  showed no trend with stream size and stream productivity (Finlay 2003, *unpublished data*). Human population density is low in the study area, and is concentrated in the town of Branscomb ( $\sim 60 \text{ km}^2$  watershed area) on the South Fork Eel River well upstream of the strong changes in stream chemistry. White alders (*Alnus*

*rhombifolia*) increase in abundance along riparian margins of channels draining  $>100 \text{ km}^2$ , but do not elevate TDN concentrations in shallow groundwater over ambient levels during summer (T. Heatherly and S. Thomas [University of Nebraska], *unpublished data*), perhaps because of limited hydrological connectivity between riparian soils and riparian groundwater under base flow conditions. Together this suggests that the observed patterns in stream nutrient chemistry were not related to spatial heterogeneity in watershed inputs or human activities.

DOC and DON were tightly correlated in our study (for July–September data,  $r^2 = 0.82$ ), suggesting similar sources. In headwater streams,  $\delta^{13}\text{C}$  DOC values around  $-27\text{‰}$  indicated modern terrestrial origin of DOM; higher values in the smallest streams suggested inputs of older soil carbon were significant, although the DOC concentrations were extremely low at these sites (Fig. 3c). As DOC increased with stream size from as low as  $0.2 \text{ mg/L}$  up to  $1.3 \text{ mg/L}$ ,  $\delta^{13}\text{C}$  DOC increased from  $-27\text{‰}$  toward similarity with biomass of *Cladophora* ( $-22.8\text{‰}$  at the two most downstream sites during late summer; Fig. 5). A two-source mixing model (Phillips and Gregg 2001) considering terrestrial vegetation and *Cladophora* as end members for DOC in the most downstream sites in the South Fork Eel River and Ten Mile Creek indicated that *Cladophora* was a large source for DOC ( $87\% \pm 18\%$  [mean  $\pm$  SE]) with a smaller (13%) contribution from modern terrestrial plants.

#### DISCUSSION

Nutrient inputs from surrounding forested watersheds were low and not greatly modified across small, detrital-dominated headwater streams. Downstream, striking changes in nutrient concentrations and stoichiometry occurred with relatively small increases in stream size in the undisturbed forested watershed we examined. Organic carbon and nitrogen concentrations increased strongly downstream relative to headwater streams, while phosphorus and silica concentrations declined substantially. These changes altered elemental ratios and, in particular, increased stream water N:P from 2 up to 46, suggesting a shift from N to P limitation at sites draining  $>100 \text{ km}^2$  where light, temperature, and rates of algal metabolism increased rapidly. Autotrophs strongly altered stream-water nutrient concentration,

TABLE 1. Summary of linear regression analyses of light (mid-August 2008) and nutrients (data for mid to late summer).

Solute	Equation	$r^2$	P
DON ( $\mu\text{g/L}$ )	$16.95 + 1.12 \times 10^{-3}(\text{light})$	0.95	<0.0001
DOC ( $\text{mg/L}$ )	$0.42 + 1.18 \times 10^{-5}(\text{light})$	0.77	<0.0001
SRP ( $\mu\text{g/L}$ )	$26.38 - 3.16 \times 10^{-4}(\text{light})$	0.75	<0.0001
TDP ( $\mu\text{g/L}$ )	$24.37 - 1.65 \times 10^{-4}(\text{light})$	0.58	0.0008
Si ( $\text{mg/L}$ )	$7.20 - 4.44 \times 10^{-5}(\text{light})$	0.44	0.0043
$\text{HCO}_3$ ( $\text{mg C/L}$ )	$17.20 - 6.59 \times 10^{-5}(\text{light})$	0.15	0.0924

Note: Source data for these analyses are shown in Fig. 3; light is measured in lux (i.e., lumens/ $\text{m}^2$ ).

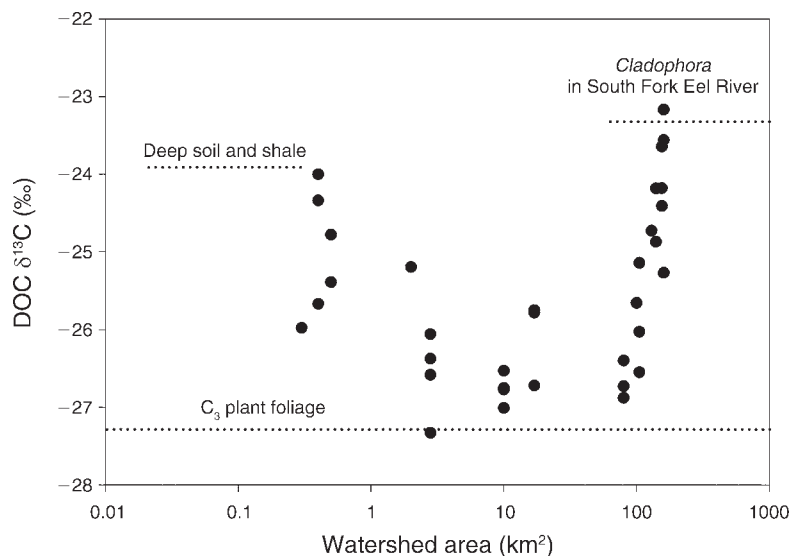


FIG. 5. Spatial patterns of stable carbon isotopes ( $\delta^{13}\text{C}$ ) DOC. End members are shown with dotted lines. Values were taken from the literature or from published data as follows: deep soil (Leithold and Blair 2001, Blair et al. 2003), terrestrial  $\text{C}_3$  plants (Finlay 2001), and the macroalgae *Cladophora* (J. C. Finlay, unpublished data). Note the x-axis logarithmic scale.

stoichiometry, and flux in lower portions of the river network due to the large standing stock and rapid metabolism allowed by the high-light and stable flow of this mediterranean system, coupled with effects of increasing N fixation.

#### *Thresholds in stream nutrient chemistry*

Strong changes in dissolved N and P, DSI, and DOC concentration and stoichiometry were observed at the same stream-size threshold of  $\sim 100 \text{ km}^2$  watershed area. What factors lead to the nonlinear behavior of dissolved nutrient concentrations in the watershed? The most obvious spatial changes accompanying the observed patterns were those in light inputs and rates of algal production. Stream nutrient concentrations changed where streams widened and riparian vegetation was set far back from the summer-inundated channel by scouring winter floods. Although watershed size and channel width increased predictably downstream (Leopold et al. 1964), light and nutrients showed nonlinear responses so that shifts from upstream conditions only were evident above  $10 \text{ km}^2$  and  $10 \text{ m}$  channel width.

Light limits algal production in forest streams, and release from light limitation increased autotrophic production  $\sim 10$  to  $30$  times from the smallest streams to the two largest sites examined here (Finlay 2004, Warnars et al. 2007). The increase in primary production was due to both increased photosynthetic activity by epilithic diatoms (Finlay 2004) and appearance of large aggregations and mats of *Cladophora glomerata* (Power et al. 2009), a species with high light demands (Robinson and Hawkes 1986, Lorenz et al. 1991). Increasing autotrophic production and biomass stimulates demand for nutrients, and this likely explains the sharp decrease in dissolved P concentrations

observed. Decreases in DSI concentrations were consistent with increased diatom growth because diatoms have a high Si requirement and dominate both epilithic assemblages (McNeely et al. 2006) and epiphytes of *Cladophora* (Power et al. 2009). Increasing algal production cannot, however, solely explain increased N concentrations in lower reaches. Since N availability strongly limits autotrophic production in streams of the western United States (Grimm 1987), including in northern California (Hill and Knight 1988, Ambrose et al. 2004), strong N retention is expected. Rising production by N-limited algal assemblage should further depress stream-water N concentrations. The observed increase in DON concentration is contrary to this expectation and suggests an additional source of N was available to support increased primary production. For example, given the  $10$ – $30$  times increase in autotrophic production between small streams and the larger sites, algal N demand must also have increased by a similar magnitude; there was no evidence that external (i.e., watershed) supply increased to provide it.

Where did the additional N come from? There is no evidence that terrestrial or watershed inputs of N could account for the observed patterns of N in the area. As described previously, human sources of N are not likely since the watershed has a low population density, and patterns of dissolved N concentrations did not correspond with human activities. Although N from geologic sources has been observed in streams, including some in California (Holloway et al. 1998), low concentrations in springs and tributary streams discount deep bedrock sources in the South Fork Eel River watershed. Alders are common in the region, yet stream-water N increased at a time when riparian zones are least connected to groundwater and stream water, and no increase in



groundwater TDN associated with alder stands has been detected during summer (T. Heatherly and S. Thomas [University of Nebraska], *unpublished data*).

Three observations suggest that increasing production and N levels in the system are a result of increasing autotrophic N fixation. First, the abundance of N-fixing algae (i.e., the cyanobacteria *Nostoc parmeloides*, and *Rivularia* spp., the diatoms *Epithemia turgid*, *E. sorex*, *E. adnata*, and *Rhopalodia* sp.) increase at approximately the same point as increased dissolved N in the watershed (Power et al. 2009). Second, nitrogen stable-isotope ratios ( $\delta^{15}\text{N}$ ) in algae and grazers decrease with increasing stream size from elevated levels (3–6‰) in small streams to –1‰ to 0‰ (J. C. Finlay, *unpublished data*), values consistent with fixed nitrogen sources for algae (Gu and Alexander 1993, Scott et al. 2007). Finally, direct measurements of N fixation in 2008 and 2009 showed significantly higher rates of N fixation in the South Fork Eel River compared to two small headwater streams (J. R. Welter, *unpublished data*). These data indicate that with alleviation of light limitation, N-limited primary producers can rapidly bring in new nitrogen to stream systems to meet nutritional demands associated with increased potential for photosynthetic carbon fixation. Greater algal production resulted in lower P and DSi availability and increased production or loss of DOC and DON, substantially altering flux and stoichiometry of transported nutrients in the watershed.

Increasing stream-water N levels present a paradox under strong N limitation of autotrophic production given that DOC tracer data suggest that dissolved organic matter (DOM) at downstream sites was derived from algae and not terrestrial plants. Assuming that DOC and DON share a common source, the DOC  $\delta^{13}\text{C}$  suggests that while N fixation can add large amounts of N to local algal communities, losses of N (as DON) may be substantial. To further support our conclusion of algal sources for N at downstream sites, we estimated the N flux from the streambed during midsummer conditions and compare that to the N demand associated with previously measured rates of primary production. For the reach of the South Fork Eel River where increases in N concentration were strongest (i.e., watershed area between 100 and 150 km<sup>2</sup>), we estimate an approximate wetted streambed area of 137 000 m<sup>2</sup>. Assuming typical late-summer discharge conditions (750 L/s at the most downstream site) and accounting for tributary inputs of N, we estimate total N loss from this reach of the South Fork Eel River of ~3.9 kg N/d or 29 mg N·m<sup>-2</sup>·d<sup>-1</sup>. Assuming a photosynthesis rate of 1.5 g C·m<sup>-2</sup>·d<sup>-1</sup> with Redfield C:N stoichiometry, assimilation of 109 mg of N is needed to balance C fixation. Thus, these rough estimates show that N loss from the stream bottom represents ~26% of the N amount required for algal metabolism in the reach. This loss rate, while surprisingly high for a nitrogen-limited ecosystem, is plausible and could be explained by

inefficiencies in N cycling (see Neff et al. 2003) or other loss pathways. Although the specific mechanisms leading to N losses are unknown, we speculate that herbivory, cell leakage and lysis, or UV damage may lead to loss of N from algal cells, as observed elsewhere (Kaplan and Bott 1982, Baines and Pace 1991, Nagao and Miyazaki 2002).

The mediterranean climate, and in particular the low-summer-flow conditions within the South Fork Eel River watershed, likely played a key role in allowing autotrophs to drive the changes in stream nutrient conditions observed in this study. Steady summer stream flows in the region allow accrual of algal biomass in larger sunlit channels, and the low water fluxes amplify effects of in-stream nutrient uptake and release. Increasing stream metabolism with stream size is a common feature of forested stream networks (Webster and Meyer 1997), suggesting that similar changes in nutrient concentrations and flux may occur in other watersheds at base flow. The potential for downstream changes like those observed here thus appears greatest for forested watersheds with low to modest summer rainfall. Within such watersheds, strong spatial changes in algal productivity and nutrient chemistry may not necessarily occur at the same position (drainage area or stream-width thresholds) in the stream network due to variation in stream geomorphology, riparian forest cover, and climate. It is less likely that effects of in-stream processes would be as apparent within non-forested watersheds, where light conditions may be more similar longitudinally, or within watersheds with summer high flows or extensive watershed heterogeneity. These factors may reduce variation in algal production or override the influence of autotrophic activity on stream nutrient composition.

#### *Consequences for downstream ecosystems*

Longitudinal changes in stream-water nutrient concentration have implications for downstream ecosystems. During periods of peak biological activity, production in downstream reaches and nearshore marine environments may be strongly affected by upstream processes that modify the form and concentration of nutrients (see also (Mulholland and Rosemond 1992, Scott et al. 2007)). Increasing light and N availability in stream channels substantially alters the availability and stoichiometry of N, P, and Si for downstream food webs in the watershed. As an illustration, we use data for total N export (including particulate N, which showed a small increase downstream), to estimate the instantaneous flux of N per unit of watershed area at different locations in the watershed during summer base flow. This analysis shows a substantial increase in the transport of N from the watershed with increasing stream size (Fig. 4b), with fluxes at largest sites 2–10 times old higher than those for headwater streams. It is likely that algal-derived DON produced in small rivers is labile (Berman and Bronk 2003). If so, mineralization of DON or direct DON

uptake could alleviate N limitation in downstream reaches, and possibly induce P limitation. However, if denitrification also increases with algal production and stream size, as suggested by a recent study in the watershed (O'Connor et al. 2006), N limitation may be sustained throughout river networks despite increasing N fixation. Because of the low summer base flows associated with the mediterranean climate of the region, the influence of in-channel modification of nutrient concentrations on annual fluxes of dissolved nutrients to the ocean may be modest relative to transport during winter and spring but highly important to the functioning of ecosystems during the most productive summer periods.

### Conclusions

Stream ecosystems in forested watersheds are dominated by longitudinal changes in physical factors that have strong influences on biological processes. In particular, light inputs increase as channels widen, allowing increased primary production while terrestrial carbon inputs decline. While stream-water nutrient composition appears to be fairly stable longitudinally in small detrital-based streams, increases in algal metabolism and biomass can drive changes in stream nutrient concentrations and stoichiometry. Stoichiometric flexibility of algae (Sterner and Elser 2002), increasing availability of high-quality organic carbon to drive biogeochemical transformations (Finlay 2004, O'Connor et al. 2006, Warnars et al. 2007), and increased rates of N fixation (Power et al. 2009) all likely contribute to the observed abrupt change in N:P stoichiometry with increasing stream size at our study site. Similar longitudinal patterns of light availability and autotrophic metabolism in other stream networks (Webster 2007, Battin et al. 2008, Julian et al. 2008) suggest that such responses could be common, although possibly less evident in watersheds with greater summertime precipitation and flows, anthropogenic disruption of nutrient cycles, or within non-forested landscapes.

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