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Influences of climate, hydrology, and land use on input and export of nitrogen in California watersheds

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Abstract Human activities have greatly increased the input of biologically available nitrogen (N) from land-based sources to aquatic ecosystems; yet few studies have examined how human actions influence N export in regions with a strong seasonality in water availability. In this study, we quantified N inputs and outputs for 23 California watersheds and examined how climate, hydrology, and land use practices influenced watershed N export. N inputs ranged from 581 to 11,234 kg N km^{-2} year^{-1} among watersheds, with 80% of total input for the region originating from agriculture (inorganic fertilizer, manure, and legumes). Of the potential N sources examined, mean annual concentrations of dissolved organic N and dissolved inorganic N in study rivers correlated most strongly with manure N input ($r^2 = 0.54$ and 0.53, respectively). Seasonal N export varied by basin and was correlated with climate, anthropogenic N inputs, and reservoir releases. Fractional export of watershed N inputs by study rivers annually was small (median of 8%) and scaled exponentially with runoff ($r = 0.66$). Collectively, our results show that anthropogenic activities have altered both the magnitude and timing of watershed N export in California and suggest that targeted management in specific locations and times of the year could reduce N export to downstream systems in the region.

Keywords Agriculture · California · Denitrification · Nitrogen · Nutrient budget · Watershed · Mediterranean climate

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Introduction

Input of biologically available N to terrestrial ecosystems globally has more than doubled in the past century due to N fixation associated with food production and energy consumption (Eickhout et al. 2006; Gruber and Galloway 2008). This mobilization of anthropogenic N has been connected with increased N loading to aquatic ecosystems and associated ecosystem and human health effects (Bricker et al. 1999; Mulholland et al. 2008). Several studies addressing watershed N dynamics at regional scales have been conducted in temperate deciduous forests in mesic-humid continental and subtropical watersheds of the eastern United States (Boyer et al. 2002; Howarth et al. 2006; Schaefer and Alber 2007). Rivers in these studies export 10–40% of their watershed's annual terrestrial N inputs and both temperature and hydrology have been considered important factors influencing watershed N retention and removal (Howarth et al. 2006; Schaefer and Alber 2007).

There have been fewer regional assessments of watershed N dynamics in regions with Mediterranean climates despite the fact that many of these systems are being subjected to unprecedented rates of N loading to which they may be quite sensitive (Kratzer and Shelton 1998; USDA-NASS 2002; USBoC 2005a). Mediterranean climates are characterized by hot, dry summers—during which terrestrial primary production is low—followed by cool, wet winters dominated by rain at low elevations and snow at high elevations. This climate regime allows N to naturally accumulate in dry soils via organic matter mineralization during the summer and be progressively flushed out into rivers during the wet season or immediately following snowmelt (Holloway and Dahlgren 2001). This contrasts with the climates of the eastern United States, where precipitation is more evenly distributed throughout the year (McKnight and Hess 2000). Moist soil conditions coupled with warm temperatures during the growing season in the eastern United States likely result in substantial plant N uptake, N sequestration in soil organic matter via microbial processing, or denitrification, a microbially mediated process in which nitrate (NO_3^-) is converted to dinitrogen gas (N_2) and, to a lesser extent, nitrous oxide (N_2O; a greenhouse gas; Schaefer and Alber 2007).

Land use changes influencing N input and watershed hydrology have occurred in many Mediterranean climatic regions (e.g., Kratzer et al. 2004; Salvati and Zitti 2009), suggesting changes to internal watershed N processing and hydrologic loss of N in these regions. As in other climatic regions, the development of intensive agriculture and concurrent increase in N fertilizer application rates has altered the magnitude and timing of N export for individual watersheds in these regions (e.g., Ventura et al. 2008). Modifications to hydrology for agricultural and urban water use also have altered annual and seasonal patterns of watershed N export, which in turn may alter ecosystem dynamics in downstream systems. For example, releases of water stored in reservoirs may increase the amount of N exported during summer months in rivers draining to California's Central Valley, a major agricultural region in the Mediterranean zone of the western United States, potentially facilitating algal growth in downstream ecosystems (Ahearn et al. 2005a). While these studies have shown the individual effects of land use, a regional analysis examining how climate, hydrology, and land use interact to influence watershed N export in Mediterranean climates has not been conducted.

In this paper, we analyzed N input and export for 23 watersheds in a Mediterranean climatic zone (the Central Valley, CA, US). These watersheds vary widely with respect to temperature, precipitation, land use, and hydrologic modification, allowing us to identify large-scale environmental and anthropogenic factors correlating with observed annual and seasonal patterns of N export by Central Valley (CV) rivers. Our objectives were: (1) estimate N sources in CV watersheds in a spatially explicit manner, (2) compare N sources with annual and seasonal N export, including different forms of N [i.e., dissolved organic N (DON) and dissolved inorganic N (DIN)], and (3) examine how different characteristics of climate, hydrology, and land use correspond to annual and seasonal patterns of N export in these Mediterranean watersheds. Based on the prevalence of intensive agricultural and large urban populations in portions of the region, we hypothesized that N from agricultural sources (inorganic fertilizers, manure, and legume cultivation) and sewage would dominate watershed N inputs, with atmospheric N deposition and natural N-fixation playing lesser roles in all but the least human-influenced systems. Mean annual concentrations of total N (TN), DON, and DIN in CV rivers were expected to increase with calculated watershed N inputs, with DIN showing the strongest response to variation in agricultural sources. Seasonally, we expected the magnitude of N export in CV rivers to be controlled by climate (Holloway and Dahlgren 2001) or a combination of the timing of fertilizer application (King Jr et al. 1999) and the release of water stored in upstream reservoirs (Ahearn et al. 2005a). Lastly, we expected that precipitation and runoff would correspond most strongly with the fractional export of watershed N inputs at the annual scale since we expected water availability to vary more widely among CV watersheds than other climate variables like temperature.

Site descriptions

California's CV (between 118.75°W and 123.07°W and 34.87°N and 40.74°N) is a highly productive agricultural region drained by two major rivers and several tributaries. The CV is home to over six million people and supplies nearly half of the domestic produce in the United States (USBoC 2005a; USDA-NASS 2002). The Sacramento River drains 61,721 km^2 (upstream of Freeport, CA) in the northern half of the CV as well as portions of the California Coast Range, southern Cascades Range, and northern Sierra Nevada (Fig. 1). The San Joaquin River drains 19,030 km^2 (upstream of Vernalis, CA) from the south-central CV, including portions of the Coast Range and Sierra Nevada (Fig. 1). Additionally, three rivers (Cosumnes, Mokelumne, and Calaveras) totaling 6,367 km^2 drain directly to the San Francisco Bay-Delta complex where the Sacramento and San Joaquin join (Fig. 1). Watershed elevations in the CV and adjacent mountains range from sea level to over 4,000 m. The climate is Mediterranean with cool, wet winters and hot, dry summers. Mean annual temperatures in the Sacramento basin are generally cooler than the Bay-Delta drainages and San Joaquin basins, but there also is considerable variation among individual watersheds related to differences in elevation. Precipitation falls mainly between November and May, with watersheds in the Sacramento basin generally wetter than those in the Bay-Delta Drainages and the San Joaquin Basin.

Methods

Watershed characteristics

The 23 watersheds included in this analysis were sampled for water quality by the University of California, Davis (UCD) from 2000 to 2003 and include watersheds that have previously been part of the US Geological Survey (USGS) National Water Quality Assessment (NAWQA) program (Domagalski et al. 2000; Kratzer et al. 2004).

Vegetation types and land cover were quantified at a 1 ha resolution using data collected by the California Land Cover Mapping and Monitoring program (California Department of Forestry and Fire Protection 2005). Population within each watershed was calculated from the 2000 United States census data (USBoC 2005a). We designated urban areas as those with a density >1,300 individuals km^{-2} (USBoC 2005b) to estimate the fraction of the population connected to a centralized sewer system (WHO 2008).

Climatic, geomorphic, and hydrologic characteristics were calculated for each watershed by averaging gridded data (mean annual temperature and precipitation, elevation, and slope), or using shape files (surface water area). Mean annual temperature and precipitation for each watershed was calculated using data from 2000–2003 (2.5 arcminute resolution) and compared to the 30 year mean for 1971–2000 (30 arcsecond resolution; PRISM 2008). Mean watershed elevation and slope were calculated from 30 m by 30 m resolution data from the National Elevation Dataset (USGS 1999). The surface areas of rivers, lakes, reservoirs, and wetlands in watersheds were determined from shape files assembled from USGS Digital Line Graphs at the 1:100,000 scale (USGS DLG-3 1993). Seasonal and annual discharge for each watershed during the study period and long-term (1971–2000 except where noted) were calculated from daily measurements collected by the USGS (USGS Annual Statistics for California, http://waterdata.usgs.gov/ca/nwis/annual) or by the California Department of Water Resources (California Department of Water Resources California Data Exchange Center, http://136.200.137.25/riv_flows.html). These data are summarized in Tables 1, 2, and 3.

Nitrogen input

Inputs of N to CV watersheds were estimated for the early 2000s using an approach similar to the one used by the DIN and dissolved organic matter (DOM) modules of the nutrient export from watersheds (NEWS) models (Dumont et al. 2005; Harrison et al. 2005). N inputs included atmospheric N deposition, natural N-fixation, N-fixation associated with agriculture, inorganic N fertilizer application, manure N application and deposition, and human sewage. Export of N in food, feed, commercial crops, and consumptive water use was estimated for individual grid cells within watersheds (Bouwman et al. 2005a). This estimate was subtracted from the sum of

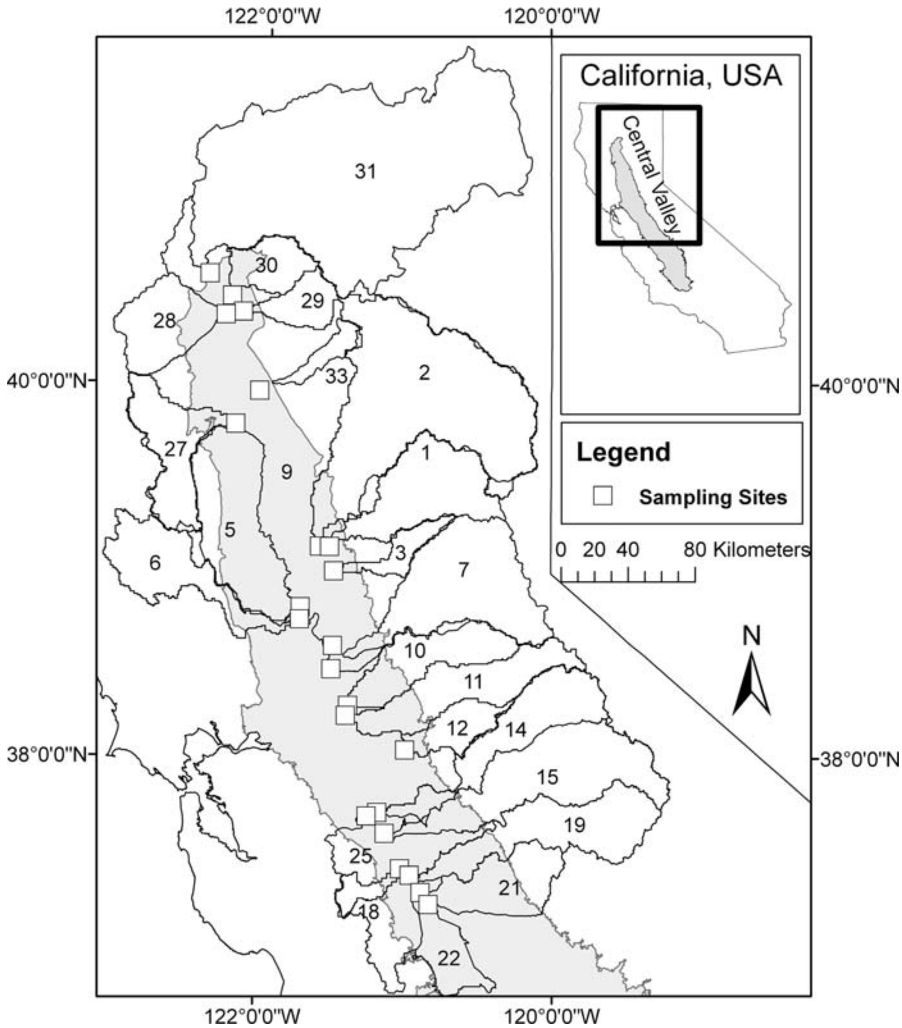

Fig. 1 Map of study watersheds in California. *Numbers* correspond to the "UCD ID" column in Table 1. *Circles* are location of sites where biweekly samples of N concentrations were collected from 2000 to 2003. Area shaded in *grey* is the Central Valley lowland. The Sacramento (*9*) and the San Joaquin (*25*) watersheds include smaller watersheds upstream from their respective sampling sites

natural and anthropogenic N inputs to calculate total net N inputs to CV watersheds.

Atmospheric deposition

Total atmospheric N deposition was estimated from data collected from 1997–2004 (NADP 2007; USEPA 2008). We interpolated inorganic N deposition (NH_4^+ and NO_3^-) in CV watersheds from California sampling stations (11 NADP sites; 7 EPA sites) using ordinary Kriging to estimate total N deposition in individual watersheds (ArcMap 9.2, ESRI Inc., Redlands, CA). Deposition of organic N was assumed to be an additional 15% on top of inorganic N deposition (Neff et al. 2002; Schaefer and Alber 2007).

N-fixation

Natural N-fixation was calculated in two ways to provide upper and lower bounds on the potential magnitude of this source. The lower bound estimate was made by assuming a non-symbiotic natural N-fixation rate of 40 kg N km^{-2} $year^{-1}$ in soils (Boyer et al. 2002) with an additional 400 kg km^{-2} $year^{-1}$ supplied from *Ceanothus* spp. in coniferous forests assuming 23% vegetation coverage by these species (Busse 2000). The upper bound estimate was made by multiplying vegetation-specific estimates of N-fixation (Cleveland et al. 1999) by surface area of the vegetation type in each watershed. We used the lowest estimated N-fixation rate for each of temperate forest (659 kg N km^{-2} $year^{-1}$), temperate

Table 1 Physiographic characteristics, land use, and population density of study watersheds in California

Watersheds	UCD (ID)[a]	Area (km^2)	Elevation[b] (m)	Slope[b] (°)	Land use (% of watershed area)				Population
					Natural	Agriculture	Urban	Water	(ind km^{-2})
Upper Sacramento River (USA)	31	17,156	1,394	7.6	92.4	4.4	0.3	2.9	4
Cow Creek (COW)	30	1,270	702	7.3	96.1	3.0	0.4	0.4	19
Battle Creek (BAT)	29	1,051	1,258	7.9	98.0	0.5	0.3	1.2	3
Cottonwood Creek (COT)	28	2,312	695	11.4	98.3	1.0	0.4	0.2	13
Deer Creek (DEE)	33	540	1,290	12.7	98.8	0.0	0.0	1.2	<1
Stony Creek (STO)	27	2,572	815	12.5	96.3	1.9	0.2	1.6	5
Feather River (FEA)	2	9,849	1,442	10.5	89.1	6.3	1.0	3.7	6
Yuba River (YUB)	1	3,475	1,285	12.6	95.9	0.6	1.2	2.2	11
Bear River (BEA)	3	736	656	7.9	85.9	5.8	6.3	2.0	39
Colousa Drain (COL)	5	4,258	103	3.0	41.9	54.1	1.7	2.2	7
Cache Creek (CAC)	6	2,736	556	10.1	78.4	12.0	2.5	7.0	19
American River (AME)	7	5,048	1,292	11.9	91.5	0.5	5.2	2.8	19
Lower Sacramento River (SAC)	9	61,721	988	8.1	82.2	12.6	2.7	2.6	9
Cosumnes River (COS)	10	2,301	587	6.2	87.1	9.4	2.6	0.8	22
Mokelumne River (MOK)	11	2,922	946	8.7	85.8	9.8	2.0	2.5	24
Calaveras River (CAL)	12	1,143	506	8.3	96.9	0.9	0.6	1.3	31
Lower San Joaquin River (SJR)	25	19,030	909	8.4	72.5	21.8	2.5	3.2	19
Stanislaus River (STA)	14	2,949	1,409	11.2	87.3	7.4	2.1	3.2	24
Tuolumne River (TUO)	15	4,810	1,496	11.5	90.2	4.4	2.0	3.5	10
Orestimba Creek (ORE)	18	461	394	10.6	86.2	13.5	0.9	0.0	2
Merced River (MER)	19	3,550	1,288	11.4	85.3	12.1	1.1	1.6	41
Salt/Mud Slough (M/S)[c]	22	1,274	49	0.6	12.6	74.3	2.4	10.7	6
Upper San Joaquin River (USJ)[d]	21	2,243	198	3.1	65.8	30.0	3.5	0.8	17

[a] Sampling site ID used by the California Department of Water Resources' California Data Exchange Center (CDEC; http://136.200.137.25/). IDs correspond to basin numbers in Fig. 1

[b] Mean for the watershed

[c] Mud and Salt Slough watersheds were considered together because of indistinct watershed boundaries

[d] Only includes the area of perennial flow in the upper San Joaquin River (Kratzer et al. 2004)

woodlands and grasslands (235 kg N km^{-2} $year^{-1}$), and chaparral-arid shrublands (152 kg N km^{-2} $year^{-1}$) types from a global synthesis of terrestrial N-fixation (Cleveland et al. 1999). For both methods, background N-fixation in agricultural areas and urban areas was assumed to be similar to the rate of non-symbiotic fixation in soils (40 kg N km^{-2} $year^{-1}$; Boyer et al. 2002). To compare natural N-fixation with other N sources in watersheds, we used the average N-fixation value between the two methods.

Agricultural N-fixation was estimated by multiplying published rates of N-fixation associated with various crop types (Smil 1999) by the surface area dedicated to each crop type in each watershed. N-fixing crops included alfalfa (20,000 kg N km^{-2} $year^{-1}$), clover (15,000 kg N km^{-2} $year^{-1}$), beans and peas (4,000 kg N km^{-2} $year^{-1}$), and lima beans (6,000 kg N km^{-2} $year^{-1}$; USDA-NASS 2002). We also applied a published rate of N-fixation (2,500 kg N km^{-2} $year^{-1}$) to lands used for rice cultivation because rice paddies provide an optimal environment for N-fixation by cyanobacteria (Smil 1999). We assumed no interannual variation in the extent and composition of crops in watersheds from 2000 to 2003, which is consistent with a lack of detectable change between 1997 and 2002 USDA National Agricultural Surveys (USDA-NASS 2002).

Table 2 Reservoir storage capacity and surface water removal for the year 2000 in study watersheds in California

Watershed	Reservoir storage capacity (km^3)	Year 2000 surface water removal for irrigation (mm)[a]	Year 2000 surface water removal for urban uses (mm)[b]	Year 2000 surface water removal total (mm)
USA	5.65	23	0	23
COW	0	35	1	36
BAT	0	5	0	5
COT	0.01	10	1	11
DEE	0	0	0	0
STO	0.30	11	0	11
FEA	6.69	33	1	34
YUB	1.87	7	2	9
BEA	0.23	64	11	75
COL	0	328	0	328
CAC	0.85	47	2	49
AME	6.10	3	16	19
SAC	21.70	84	6	90
COS	0	45	7	52
MOK	1.10	48	4	52
CAL	0.39	9	3	12
SJR	10.84	59	3	62
STA	3.62	41	4	45
TUO	3.39	161	3	164
ORE	0	110	1	111
MER	1.30	89	0	89
M/S	0	435	0	435
USJ	0.05	221	0	221

[a] Based on county-level data on surface water removal for irrigation and other agricultural uses compiled by the USGS (http://water.usgs.gov/watuse/) and the spatially explicit distribution of agricultural lands in study watersheds

[b] Based on county-level data on surface water removal for municipal uses compiled by the USGS (http://water.usgs.gov/watuse/) and the spatially explicit distribution of urban lands in study watersheds

Inorganic fertilizer and manure application

Inorganic N fertilizer input was estimated by distributing county-level sales of inorganic fertilizer in 1991 (Battaglin and Goolsby 1994) across agricultural lands in watersheds. While these data are not within the time frame for other N source estimates, surveys suggest that there has not been an appreciable change in fertilizer application or agricultural land cover in the CV since the early 1990s (ERS/USDA 2008). Estimated emission losses of NH_3 (average of 5%) were subtracted from fertilizer application rates.

Manure N input was calculated by multiplying per animal manure production rate by the number of cattle, poultry, and other livestock in watersheds based on the national agricultural census in 2002 (Van der Hoek 1998; USDA-NASS 2002). Various sub-groupings of livestock types (e.g., free range cattle, feedlot cattle, and dairy cows) were distinguished to account for differences among manure production and application practices (Van der Hoek 1998). Manure was distributed on the landscape either as local deposition during grazing or as fertilizer applied to crops. First, we estimated manure locally deposited by cattle (60%), sheep (90%), and goats (90%) and distributed this amount of N on pastures and woodlands (Bouwman et al. 2004). The remainder of manure produced by cattle, sheep, and goats and all manure produced by dairy cows, pigs, and poultry was assumed to be collected and distributed as fertilizer on agricultural and pasture lands (Bouwman et al. 2004). For all estimates, we subtracted the amount of N emitted as

Table 3 Measurement period and annual climate/hydrologic characteristics of study watersheds in California

Watershed	N export period	Temperature (°C)		Precipitation (mm)		Runoff (mm)	
		Mean (min–max)	Long-term[a]	Mean (min–max)	Long-term[a]	Mean (min–max)	Long-term[a]
USA	2003	9.7[b]	12.8	964[b]	922	511[b]	535
COW	2003	14.5[b]	12.1	1234[b]	1,172	530[b]	498
BAT	2003	10.9[b]	10.1	1357[b]	1,205	476[b]	441
COT	2003	14.9[b]	15.3	1037[b]	975	439[b]	363
DEE	2003	10.2[b]	10.8	1377[b]	1,493	685[b]	566
STO	2003	13.6[b]	14.1	858[b]	815	203[b]	316[c]
FEA	2000–2003	9.8 (9.4–10.0)	12.6	1,017 (982–1,095)	1,146	255 (152–371)	518[c]
YUB	2000–2003	11.2 (10.8–11.5)	13.0	1,527 (1,477–1,645)	1,605	399 (201–526)	638
BEA	2000–2003	14.1 (13.5–14.4)	14.0	1,144 (1,072–1,328)	1,170	338 (31–589)	519
COL	2000–2003	16.2 (15.8–16.4)	12.6	551 (449–663)	506	127 (82–166)	300[d]
CAC	2000–2003	14.3 (13.9–14.6)	12.2	895 (808–1,025)	893	100 (33–185)	196
AME	2000–2003	11.5 (11.1–11.9)	10.7	1,179 (1,105–1,354)	1,324	460 (332–638)	683
SAC	2000–2003	12.1 (11.6–12.3)	11.5	967 (887–1,015)	1,001	301 (210–366)	352
COS	2000–2003	14.7 (14.3–15.0)	13.8	817 (733–978)	862	121 (62–199)	212
MOK	2000–2003	12.9 (12.5–13.2)	12.2	886 (783–1,042)	948	86 (46–152)	169
CAL	2000–2003	14.8 (14.5–15.2)	14.6	827 (733–1,010)	789	110 (71–202)	258
SJR	2001–2003	13.2 (12.9–13.5)	12.4	602 (571–722)	713	119 (88–184)	223
STA	2000–2003	10.0 (9.7–10.4)	11.7	937 (820–1,075)	1,015	186 (159–262)	283
TUO	2000–2003	10.4 (10.2–10.7)	9.7	911 (803–1,042)	981	123 (68–241)	251
ORE	2000–2003	16.5 (16.3–16.8)	12.7	339 (276–398)	420	52 (30–69)	120[d]
MER	2000–2003	11.8 (11.5–12.1)	9.8	832 (731–930)	882	98 (64–157)	162
M/S	2000–2003	16.7 (16.6–17.1)	14.3	244 (195–288)	249	207 (176–227)	216[e]
USJ	2000–2003	16.2 (15.9–16.4)	14.1	463 (311–765)	409	339 (272–490)	814

Minimum and maximum annual means for the period of record for N export measurements are in parentheses where applicable

[a] Mean from 1971–2000 except where noted

[b] Values only for 2003

[c] Long-term values from 1993–2000

[d] Long-term values from 1971–1980

[e] Long-term values from 1986–2000

NH_3 from grazing deposits (4–8% depending on livestock type) and stored manure fertilizer (28–36% during storage and 4–8% during application). We account for the possibility of inorganic N fertilizers entering livestock feed in the "Anthropogenic N Removal" section below.

Sewage input

Total net sewage N input was calculated by multiplying the 2000 United States census data (USBoC 2005a, b) by an estimated per capita excretion rate of 2.28 kg N individual^{-1} year^{-1} and subjecting this input to removal by treatment (Bouwman et al. 2005b). We assumed that on average 51% of N was removed during sewage treatment (Dumont et al. 2005) and that 95% of urban zones were connected to a centralized sewer system while only 33% of rural areas were connected (WHO 2008). We assumed sewage N not entering centralized sewer systems was stored in septic systems and therefore was not included in N input estimates.

Anthropogenic N removal

We estimated the harvest export of food, feed, and fiber crops by multiplying by N content of general crop classifications by the amount of harvested grain, vegetables, fruit, berries and fiber crops in 2002 (USDA-NASS 2002) as in Bouwman et al. (2005a). We assumed that all food, feed, and fiber crops were exported from study basins except those that ended up in sewage and manure. Using this approach, net import of N in food and feed crops is reflected in sewage and manure inputs.

Water extraction for irrigation or urban water supply also removes N before it can be transported in streams and rivers of CV watersheds. To account for this, we calculated the amount of N removed with irrigation and urban water supply. First, we calculated the amount of surface water withdrawn from each watershed using county-level data on agricultural and urban water in 2000 (Table 3). We then multiplied these values by the average annual N concentration exported by the watershed. This approach provides initial estimates of N removed by water withdrawals.

Total net watershed N input

Total net N input (kg N km^{-2} $year^{-1}$) for each watershed was calculated as: total atmospheric N deposition + natural N-fixation + agricultural N-fixation + inorganic N fertilizer input + manure N input + total net sewage N input − crop N harvest − N removed in consumptive water use.

Sensitivity analysis of N inputs

We altered N inputs and anthropogenic N removal (e.g., atmospheric N deposition, natural N-fixation, manure N input, and crop harvest) by ±20% to assess how sensitive total net N inputs were to variations in individual N input or anthropogenic removal components. Changes to total net N inputs for individual watersheds following alterations were calculated as $100\times[(\text{total net N input}_{\text{altered}} - \text{total net N input}_{\text{mean}})/\text{total net N input}_{\text{mean}}]$.

Watershed N export

At sampling sites in the watersheds (Table 1; Fig. 1), water samples were collected at biweekly intervals. Samples were passed through a 0.2 μm filter (Millipore polycarbonate membrane) and analyzed for total dissolved nitrogen (TDN), nitrate (NO_3–N), and ammonium (NH_4–N). Nitrate and ammonium were determined using a conductimetric autoanalyzer (minimum detection limit = 0.005 mg L^{-1}; Carlson 1978, 1986). Total N (non-filtered) and total dissolved N (filtered) were determined conductimetrically following oxidization with 1% potassium persulfate. DIN was calculated as the sum of NH_4–N and NO_3–N. Dissolved organic N (DON) was calculated as: DON = TDN − DIN).

Average annual concentrations of TN, DIN, and DON were calculated by flow-weighting the average N concentrations between sampling events. Annual yields of TN (kg N km^{-2} $year^{-1}$) for each watershed and for each year were calculated by multiplying the flow-weighted average TN concentration by total volume of river flow for the corresponding year and dividing this load value by watershed area. Average annual yield was calculated by averaging calculated annual yields for each year on record. Lastly, we estimated fractional watershed N export by dividing measured mean annual N yield by the calculated mean annual per-area watershed N input (Schaefer and Alber 2007).

Seasonal pattern of N export

We also examined seasonal export of individual N forms (DIN, DON, and TN) in CV rivers to investigate the relationship among N inputs, land use patterns, and watershed hydrology. We analyzed the patterns of TN, DIN, and DON concentrations with river discharge in each watershed and compared them with information on land use characteristics in the watershed, reservoir management (CDWR 2008), and the timing of spring/summer fertilizer application in the CV (King Jr et al. 1999). We used data from the 2003 water year for these comparisons because it was the only period for which there was a complete data set on N export for all 23 watersheds in the study. This year was classified as a slightly-above-average (119%) precipitation year (CDWR 2008), though there was considerable variation among watersheds (Table 3). While interannual differences in precipitation and discharge can influence N export in rivers (Donner et al. 2002), an analysis of a subset of seven watersheds (BAT, SAC, COS, MOK, SJR, STA, M/S, and USJ) in the water years 2000 and 2001 (Ahearn et al. 2005a) suggested that seasonal patterns of N export did not differ substantially from 2003.

Factors influencing annual patterns of N export

We compared annual concentrations of TN, DIN, and DON as well as N yields in rivers with per area N input rates for their corresponding watershed using linear regression and nonlinear regression (depending on normality of data). We then assessed the correlation strength between explanatory variables for annual averages of TN, DIN, and DON concentrations, TN yield, and fractional N export using Pearson's correlation coefficient (r). Concentrations, yield, and fractional N export were natural log-transformed to improve normality; all other remaining variables were either natural-log transformed (right-positive skewed variables) or arcsine square root-transformed (land use percents) if the transformation improved normality. All statistics were performed in R version 2.6 (R Core Development Team 2007).

Results and discussion

N inputs in the CV

As expected, total net N input in the CV was heavily influenced by the extent and intensity of agricultural activities in watersheds (Table 4; Fig. 2). Approximately 80% of N entering the entire study area originated from fertilizers, manure, or legume cultivation. Per area input of N (with anthropogenic removals taken into account) ranged from 581 to 11,234 kg N km^{-2} year^{-1} for individual watersheds, falling within the range of estimates for watershed N inputs in the midwestern, northeastern, and southeastern United States (Boyer et al. 2002; McIsaac and Hu 2004; Brookshire et al. 2007; Schaefer and Alber 2007). Estimates of per area N inputs to individual CV watersheds increased significantly from north to south ($p = 0.001$; $r^2 = 0.36$; Fig. 2), corresponding to more agricultural land and larger livestock populations in watershed from the southern CV versus those in the northern CV (USDA-NASS 2002; Table 1).

Inorganic fertilizer and manure were the largest N inputs to 15 of the 23 CV watersheds in this study and made up 49 and 25% of N input to the entire study area, respectively. However, there was considerable variation among individual watersheds (Table 4). Estimates of per area input rates of inorganic fertilizer (254–7,528 kg N km^{-2} year^{-1}) and manure (105–3,654 kg N km^{-2} year^{-1}) in watersheds with >5% agriculture were similar to estimates for most other agricultural regions in the United States (Puckett 1994; McIsaac and Hu 2004; Alexander et al. 2008). However, they were two-to-five times greater than in northeastern and southeastern United States watersheds despite similar percents of agricultural land cover (Boyer et al. 2002; Schaefer and Alber 2007). One other agricultural N source, N-fixation by legumes and cover crops, contributed only 4% of N input to the entire study area and never exceeded more than 10% of total N input in individual watersheds (Table 4). Rates of agricultural N-fixation ranged from 0 to 745 kg N km^{-2} year^{-1} and were similar to previous estimates in other United States watersheds with comparable agricultural land cover (Boyer et al. 2002; Schaefer and Alber 2007).

Atmospheric N deposition and natural N-fixation were more important in the northern CV compared to those in the southern portion of the study area (Fig. 1; Table 4). Watershed estimates of atmospheric deposition rates ranged from 173 to 318 kg N km^{-2} year^{-1} (Table 4). In comparison, N deposition rates in the northeastern and southeastern United States, where air pollution is a more important component of watershed N input, can range from 510 to over 4,000 kg N km^{-2} year^{-1} (Boyer et al. 2002; Brookshire et al. 2007). Our estimates for CV watersheds fall within the range of previous estimates for the Sierra Nevada (50–467 kg N km^{-2} year^{-1}) and probably reflect emission of NH_3 from livestock waste and fertilizers as well as NO_x emissions from urban areas (Jassby et al. 1994; Bytnerowicz and Fenn 1996; USDA-NASS 2002).

Our two methods for estimating natural N-fixation produced a lower range of 41–287 kg N km^{-2} year^{-1} and a higher range of 240–491 kg N km^{-2} year^{-1} for this source (Table 4). The mean N-fixation rate for each watershed based on these methods ranged from 140 to 390 kg N km^{-2} year^{-1} (Table 4). Estimates of natural N-fixation were generally higher than those in northeastern and southeastern United States watersheds (Boyer et al. 2002; Schaefer and Alber 2007). However, they fell within the range of previous estimates for the western United States (Busse 2000) and are consistent with the abundance of native N-fixing plants such as *Ceanothus* spp. in CV watersheds and high prevalence of disturbed land, which is associated

Table 4 Summary of inputs and anthropogenic basin transfers of N calculated for watersheds in California during the early 2000s

Watershed	Atmospheric deposition	Natural fixation (low–high)[a]	Crop fixation	Inorganic fertilizer	Manure	Sewage	Harvest	Water removal	Total net N inputs[b]
USA	183	314 (221–406)	11	101	98	1	−2	−4	702
COW	176	265 (172–359)	2	92	148	3	0	−9	677
BAT	166	366 (259–474)	0	21	51	1	0	−2	603
COT	198	299 (202–396)	1	36	97	1	0	−3	629
DEE	173	387 (282–491)	0	0	21	0	0	0	581
STO	189	216 (136–295)	12	149	162	0	−31	−3	694
FEA	174	390 (284–497)	11	254	106	2	−37	−9	891
YUB	176	388 (287–489)	1	47	63	3	−5	−1	672
BEA	204	274 (188–360)	9	431	262	14	−39	−22	1,133
COL	226	147 (44–250)	542	4,658	518	1	−1,388	−345	4,359
CAC	196	161 (90–232)	137	810	133	3	−155	−126	1,159
AME	189	352 (257–448)	0	20	53	4	0	−5	613
SAC	192	291 (193–389)	83	941	193	2	−243	−36	1,423
COS	233	241 (150–332)	31	673	532	6	−95	−19	1,602
MOK	238	283 (189–377)	130	926	621	5	−156	−12	2,035
CAL	244	223 (146–300)	12	97	355	5	−14	−5	917
SJR	299	245 (147–343)	275	2,247	1,987	3	−147	−163	4,746
STA	266	313 (216–410)	84	805	701	3	−51	−113	2,008
TUO	303	303 (208–399)	45	501	645	2	−20	−77	1,702
ORE	229	218 (123–314)	138	1,430	2,214	1	−62	−421	3,747
MER	318	297 (199–395)	195	1,198	1,070	1	−94	−202	2,783
M/S	241	140 (41–240)	745	7,528	3,654	2	−562	−514	11,234
USJ	296	146 (49–244)	489	2,972	2,900	3	−235	−1,036	5,535

Units are kg N km^{-2} year^{-1} except where noted

[a] Values are the means of low and high estimates (with range in parentheses); see text for description of methods used

[b] Total net input values include only the mean of natural N-fixation inputs to watersheds

with elevated N-fixation (Casals et al. 2005; Lagerstrom et al. 2007).

We estimated that sewage N collected in centralized sewer systems contributed 0–14 kg N km^{-2} year^{-1}, or <1.1% of total N input to individual CV watersheds (Table 4). The fractional contribution of sewage N input to CV watersheds was much lower than in the northeastern United States (38–75%; Boyer et al. 2002; Driscoll et al. 2003). However, N from sewage enters surface waters directly and is not subject to the same landscape removal processes as non-point N, so it could be a more important source of N to CV rivers than the magnitude of this source suggests (Dumont et al. 2005). Also, our approach to calculating sewage N inputs is more conservative than those for watersheds in the northeastern United States since we do not consider N entering residential septic tanks to be part of annual watershed N inputs. Urban sewage probably has a significant (if not dominant) impact on N loading to the lower Sacramento and San Joaquin Rivers outside of our study area (Kratzer and Shelton 1998) since major sewage outflows for the cities of Sacramento and Stockton are located downstream of monitoring stations used in this study. There were only five major point sources of treated sewage in the study area, with the majority of sewage disposed of through dry land application (Kratzer and Shelton 1998; C. Kratzer, personal communication). Our estimates also did not include N stored in septic systems or sewage overflows during storm events. N stored in septic systems eventually could leach into adjacent groundwater; however, groundwater N input to CV rivers appears to be low, possibly from high denitrification

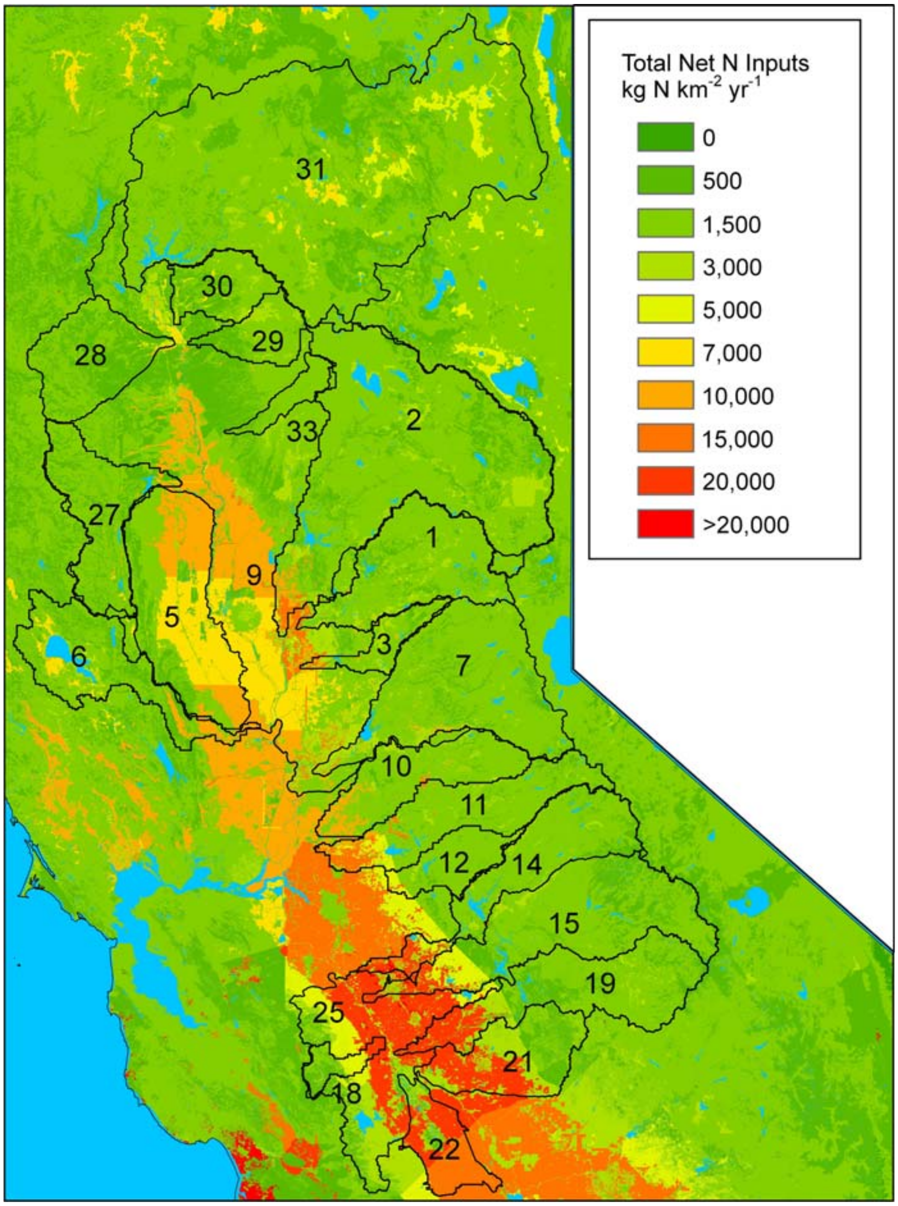

Fig. 2 Map of total net N inputs (kg N km^{-2} $year^{-1}$) in study watersheds in California. Map resolution is at the 1 ha scale

rates in these zones (Puckett et al. 2008; Dahlgren et al. 2008).

The sensitivity analysis of N input variables showed that assuming ±20% error in individual N input variables resulted in an absolute change in total net N inputs for watersheds of <1–13%, with variation in natural N-fixation rates resulting in the largest percent change (Table 5). Watersheds in the northern CV, where anthropogenic N inputs are relatively low and N-fixation composed the largest N source, were most sensitive in the analysis (Table 5). These results suggest that fairly substantial errors in individual input estimates generally have a small impact in the total estimate of total net N inputs in CV watersheds. However, they also suggest natural N-fixation in CV watersheds warrants further study in future efforts to better constrain estimates from this source, particularly in basins with low human impact.

N export

N removed from watersheds by harvest ranged from 0 to 1,388 kg N km^{-2} $year^{-1}$ (Table 4). Most of these

Table 5 Absolute percent change in total net N inputs according to a ±20% variation of individual input or anthropogenic N removal components for watersheds in California

Watershed	Atmospheric deposition	Natural fixation[a]	Crop fixation	Inorganic fertilizer	Manure	Sewage	Harvest	Water removal
USA	5	9	<1	2	3	<1	<1	<1
COW	5	8	<1	1	4	<1	<1	<1
BAT	5	11	<1	<1	2	<1	<1	<1
COT	6	9	<1	<1	3	<1	<1	<1
DEE	6	13	<1	0	1	<1	0	<1
STO	5	6	<1	1	4	<1	1	<1
FEA	3	8	<1	3	2	<1	1	<1
YUB	4	10	<1	1	2	<1	<1	<1
BEA	4	5	<1	8	5	1	1	<1
COL	1	1	2	10	2	<1	6	2
CAC	3	3	2	7	2	<1	3	2
AME	5	10	<1	<1	1	1	<1	<1
SAC	2	4	1	7	3	<1	3	<1
COS	3	3	<1	5	7	<1	1	<1
MOK	2	3	1	5	6	<1	2	<1
CAL	5	5	<1	2	7	1	<1	<1
SJR	1	1	1	4	8	<1	1	1
STA	3	3	1	3	7	<1	1	1
TUO	4	4	1	2	8	<1	<1	1
ORE	1	1	1	2	12	<1	<1	2
MER	2	2	1	5	8	<1	1	1
M/S	<1	<1	1	6	6	<1	1	1
USJ	1	1	2	5	11	<1	1	4

[a] Sensitivity values were based only on mean estimates of natural N-fixation; see text for description

values fall within the range reported for anthropogenic N removal via harvest for watersheds in the southeastern United States (Schaefer and Alber 2007), though several estimates from the most agriculturally influenced watersheds were much higher (Table 4). Harvest removal accounted for 0–24% of agricultural N inputs, depending on the basin. These values are somewhat lower than an estimated crop N removal of 35% in the United States (NRC 1993). Our estimates of N removed with consumptive water use (0–1,036 kg N km^{-2} $year^{-1}$), while preliminary, suggest that this N loss pathway could be similar in magnitude to net losses through crop harvest (Table 4), though additional research is needed to more fully constrain this estimate for CV watersheds. Lastly, variation in harvest and water removal terms by ±20% generally resulted in a small change (0–6%) in total net N inputs for watersheds (Table 5).

As expected, concentrations of TN, DIN, and DON were significantly correlated with per area N inputs to watersheds (Fig. 3a, b, c). However, only 41% of the variance in TN concentrations, 32% of the variance in DIN concentrations, and 46% of the variance in DON concentrations were explained by per-area N inputs (Fig. 3c), suggesting a complex relationship between N inputs and river N export in the CV. Though it is commonly observed that DIN is the N form most strongly correlated with anthropogenic N inputs (e.g., Driscoll et al. 2003; Gruber and Galloway 2008) and that N export in agricultural regions is most strongly related to inorganic fertilizer input (e.g., McIsaac and Hu 2004), this was not the case in the CV (Fig. 3a, b). TN, DIN, and DON

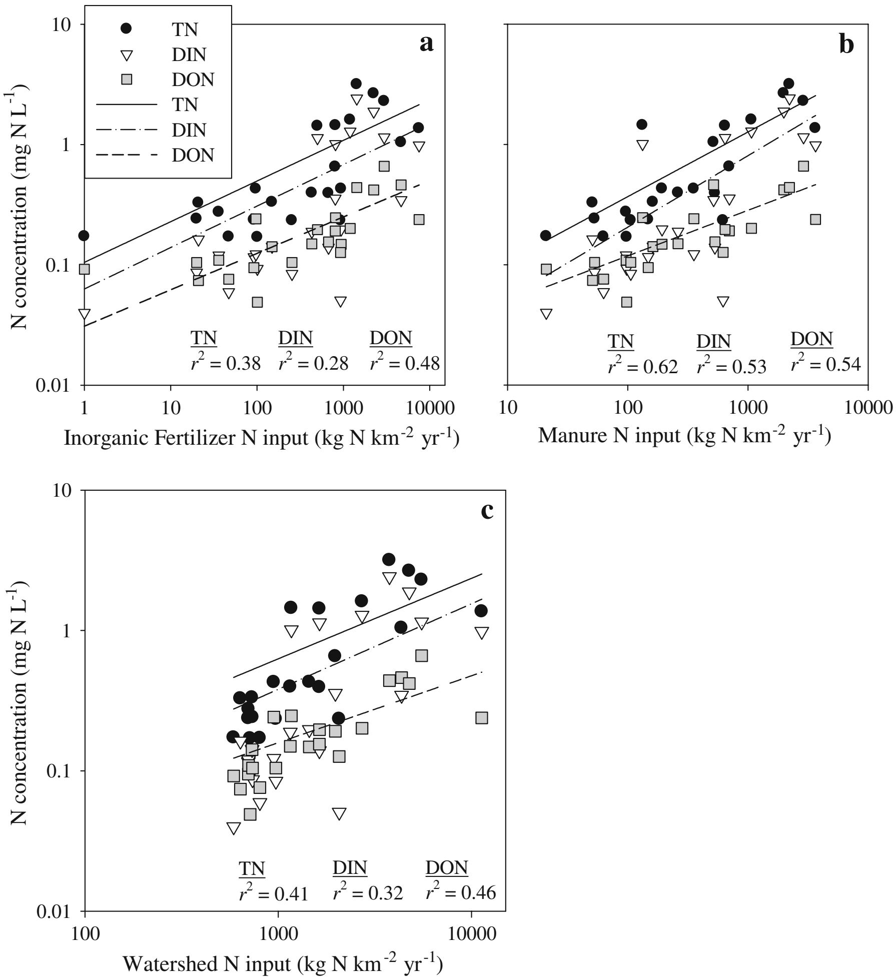

Fig. 3 Relationship between total N (*TN*), dissolved inorganic N (*DIN*), and dissolved organic N (*DON*) concentrations and per area; **a** inorganic N fertilizer inputs, **b** manure inputs, and **c** total net N inputs for study watersheds in California. In **a**, a value of 1 kg N km^{-2} year^{-1} was given to the Deer Creek (*DEE*) watershed to avoid log-transformation of zero. All correlations were statistically significant ($p < 0.05$)

concentrations correlated most strongly with per area manure input in watersheds, with DON concentrations having the strongest correlation ($r^2 = 0.54$; Fig. 3b). This suggests that manure constitutes an important source of N to CV rivers and by extension that improved manure fertilizer application or waste disposal from livestock operations could reduce the amount of N exported from CV watersheds, particularly in the San Joaquin basin where dairy operations are most dense (Gronberg et al. 1998).

On average, annual N export in CV rivers during the early 2000s was one-to-two orders of magnitude lower than annual net inputs to their watersheds (Tables 4, 6; Fig. 4). N exported by rivers ranged from 21 to 947 kg N km^{-2} year^{-1} and was significantly correlated with per area N input rates ($p < 0.0001$; $r^2 = 0.60$; Fig. 4). These per area export rates were generally lower than deciduous forest watersheds from the northeastern and southeastern United States despite similar watershed N input rates (Boyer et al. 2002; Schaefer and Alber 2007), but fell within the range for rivers draining large basins in xeric climates around the globe (Caraco and Cole 2001). Unlike per area N input rates, per area export of N from CV watersheds did not increase from north to south ($p = 0.84$). Thus, only a small fraction of N inputs (hereafter fractional N export) was exported from CV watersheds (median of 8%; range of 1–45%; Table 6). On average, our Mediterranean climate-dominated CV watersheds exported less of their N inputs in the early 2000s than those calculated for the mid-1990s in the humid continental and humid subtropical climates of the eastern United States (Boyer et al. 2002; Schaefer and Alber 2007). However, fractional N export rates in the mainstem Sacramento and San Joaquin Rivers

Table 6 Summary of mean annual river N concentrations, yields, and fractional export of N inputs for study watersheds in California

Watershed	TN (mg L^{-1})	DIN (mg L^{-1})	DON (mg L^{-1})	River TN yield (kg km^{-2} $year^{-1}$)	Fractional N export[b] (%)	Highest TN (month)	Lowest TN (month)	Seasonal pattern[b]
USA	0.17[a]	0.09[a]	0.05[a]	77[a]	11[a]	Dec/Jan	May	RD
COW	0.24[a]	0.12[a]	0.09[a]	76[a]	11[a]	Dec/Jan	May	WSD
BAT	0.33[a]	0.16[a]	0.07[a]	129[a]	21[a]	Nov	Jul	WSD
COT	0.28[a]	0.12[a]	0.11[a]	88[a]	14[a]	Dec	May	WSD
DEE	0.17[a]	0.04[a]	0.09[a]	259[a]	45[a]	Nov	Jun	WSD
STO	0.33[a]	0.14[a]	0.14[a]	54[a]	8[a]	Jan	Oct	WSD
FEA	0.23 (0.01)	0.08 (0.01)	0.10 (0.01)	57 (18)	6 (2)	Feb	Aug	RD
YUB	0.17 (0.03)	0.06 (0.01)	0.08 (0.02)	65 (22)	10 (3)	Feb	Jun	RD
BEA	0.40 (0.14)	0.19 (0.09)	0.15 (0.04)	141 (92)	12 (8)	Jan	Sep	WSD
COL	1.04 (0.09)	0.35 (0.07)	0.46 (0.05)	128 (40)	3 (1)	Apr	Sep	AD
CAC	1.44 (0.34)	1.01 (0.35)	0.25 (0.07)	114 (46)	10 (4)	Apr	Sep	AD
AME	0.24 (0.04)	0.09 (0.02)	0.10 (0.02)	108 (32)	18 (5)	Feb	Apr	WSD
SAC	0.43 (0.06)	0.20 (0.03)	0.15 (0.02)	126 (34)	9 (2)	Jan	Aug	WSD
COS	0.39 (0.03)	0.14 (0.03)	0.15 (0.02)	40 (15)	2 (1)	Dec	Jun–Oct	WSD
MOK	0.23 (0.04)	0.05 (0.02)	0.13 (0.02)	21 (16)	1 (1)	Jan	July	RD
CAL	0.43 (0.20)	0.12 (0.07)	0.24 (0.10)	72 (94)	8 (10)	Dec/Jan	Sep/Oct	WSD
SJR	2.66 (0.41)	1.88 (0.27)	0.42 (0.02)	135 (67)	5 (2)	May	Mar	RD
STA	0.65 (0.15)	0.36 (0.07)	0.19 (0.06)	120 (35)	6 (2)	Dec	May	RD
TUO	1.43 (0.48)	1.13 (0.41)	0.20 (0.70)	149 (42)	9 (2)	Jun/Dec	Mar	RD
ORE	3.17 (0.21)	2.42 (0.20)	0.44 (0.08)	134 (50)	4 (1)	Jul	Dec	AD
MER	1.61 (0.30)	1.28 (0.24)	0.20 (0.05)	144 (37)	5 (1)	Aug	May	RD
M/S	1.36 (0.40)	0.98 (0.28)	0.24 (0.09)	947 (137)	8 (1)	Dec	Aug	AD
USJ	2.29 (0.25)	1.15 (0.16)	0.66 (0.14)	64 (48)	1 (1)	Mar	Dec	AD

Standard deviations of mean annual N concentration and N yield are in parentheses where applicable

TN total N; *DIN* dissolved inorganic N; *DON* dissolved organic N

[a] Only data for the water year 2003 available

[b] Fractional N export is the average annual yield of total N for the study period in each watershed divided by the corresponding net N input calculated for 2000–2003, assuming no variation in total net N inputs among years

were similar to that for other large river basins (Caraco and Cole 2001).

Seasonal N export

Seasonal patterns of N export provide insight into internal processes governing N retention/removal and, conversely, N mobilization in watersheds. In CV watersheds, seasonal patterns of N export showed a clear relationship with seasonal precipitation in 10 wet-season dominated (WSD) watersheds (Table 6; Fig. 5a, b, c). In five agricultural-dominated (AD) watersheds, the application of N fertilizers during the growing season dominated the seasonal pattern of N export (Table 6; Fig. 5d, e, f). And in eight reservoir-dominated (RD) watersheds, reservoir releases appeared to influence seasonal concentrations of N (Table 6; Fig. 5g, h, i). These classifications originated from an examination of seasonal precipitation and discharge (precipitation data: PRISM (2008); discharge data: CWR (2008)), information on application of N fertilizers during the year (King Jr et al. 1999), and data on reservoir releases in watersheds (CWR 2008).

We calculated that the 10 WSD watersheds received the lowest watershed N inputs (887 ± 125 kg N km^2 $year^{-1}$; mean ± SE) yet had the highest fractional N export (15 ± 4%). The Cosumnes River represented an endpoint for WSD watersheds because

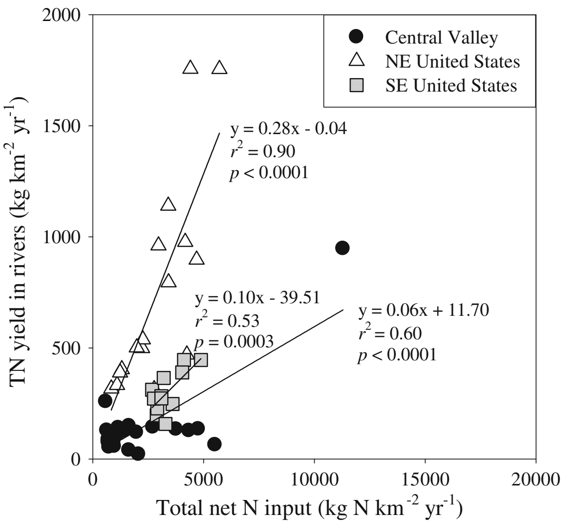

Fig. 4 Relationship between N yield and per area N input for California watersheds (*filled circles*), northeastern United States watersheds (*open triangles*; Boyer et al. 2002), and southeastern United States watersheds (*grey* squares; Schaefer and Alber 2007)

it contains relatively low agricultural land cover (9%; Table 1) and is the last large un-dammed CV river draining the Sierra Nevada (Ahearn et al. 2005b). In 2003, concentrations of DIN and DON in the Cosumnes River were 10- to 56-fold greater during the wet season (October through December) than during summer and spring months (excluding periods when the main channel had gone dry after June 25th; Fig. 5b, c). This is a common pattern seen in Mediterranean climates and is probably due to the flushing of mobile inorganic and organic forms of N that have built up in watershed soils during the dry season (Holloway and Dahlgren 2001). Previous research has shown that asynchrony in biological processes and California's Mediterranean climate causes marked spikes in NO_3^- concentrations in surface waters during the onset of the wet season (Holloway and Dahlgren 2001). Winter storms progressively flush the soil nitrogen pool so that by March there is substantially less N mobilized during storm flows.

The five AD watersheds possessed the highest watershed N inputs (5,206 ± 1,865 kg N km^{-2} year^{-1}), but also the lowest annual fractional N export (5 ± 2%). These watersheds displayed a peak in N concentrations that coincided with the average start date (March 1st) for spring/summer fertilizer application of major crop types in the CV (King Jr et al. 1999). Mud/Salt Slough is a representative watershed for this category (Fig. 5d, e, f). Beginning in late February through April, DIN concentrations increased markedly. For example, DIN concentrations increased from 0.78 to 4.12 mg N L^{-1} between February 5th and the 19th in M/S (Fig. 5e). Concentrations of N remained elevated during the spring and summer relative to fall and winter months. In Mud/Salt Slough, the second- and fourth-highest instantaneous estimates of N export from the system occurred when discharge was low and stable in late summer (Fig. 5d, e), possibly reflecting the combined influence of fertilizers, irrigation, and shifting flowpaths in the watershed's tile drainage network (Kratzer et al. 2004). In contrast to WSD watersheds, increased N inputs during the growing season coupled with high temperatures, labile carbon in topsoil, and moist (and possibly anoxic) conditions resulting from irrigation may prime watersheds for high rates of denitrification. However, these practices may also be facilitating long-term storage of N in watersheds by increasing sequestration of N in soil organic matter, storage in deep groundwater pools, or uptake into plant biomass, all of which could contribute to a long-term build up of N in CV watersheds. Additional work investigating soil characteristics, biological activity, and water residence times in these watersheds is needed to investigate the relative role of denitrification and N storage processes in these watersheds.

The seven RD watersheds were intermediate to WSD and AD watersheds, both with respect to N input (1,942 ± 513 kg N km^{-2} year^{-1}) and annual fractional N export (7 ± 1%). The seasonal pattern of N concentrations for the Tuolumne River (TUO) was typical of RD systems (Fig. 5g, h, i). DIN, DON, and TN concentrations were highest from late summer through early spring, with reservoir releases diluting N concentrations beginning in March and lasting through July (Fig. 5h). However, the load of DIN, DON, and TN exported from these systems remained relatively constant throughout the year. These watersheds contained variable amounts of agricultural land (7–54%) primarily located in the lowland portions of watersheds downstream of the reservoirs. The upland portions of these individual watersheds, the Sierra Nevada, are primarily dominated by snowmelt with much lower N concentrations (Sickman et al. 2003; Ahearn et al. 2005a). Thus, while reservoirs often

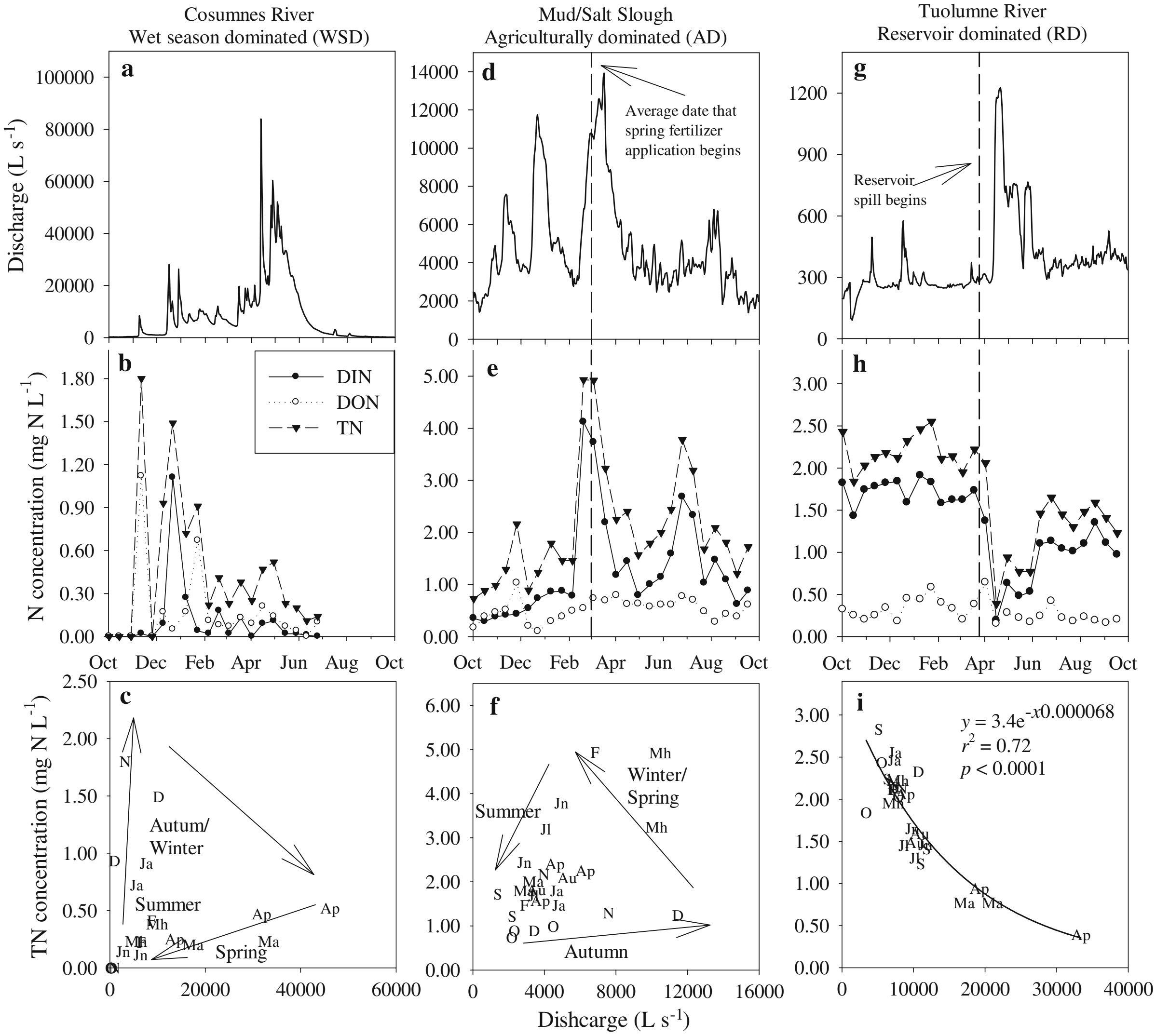

Fig. 5 Stream flow and N concentration data for representative watersheds during the 2003 water year in California. Panels **a**, **b**, and **c** display a wet-season dominated watershed (Cosumnes River); panels **d**, **e**, and **f** show an agriculturally dominated watershed (Salt Slough); and panels **g**, **h**, and **i** illustrate a reservoir dominated watershed (Tuolumne River). Panels are for discharge (**a**, **d**, and **g**), N concentrations of N (**b**, **e**, and **h**), and the relationship of TN concentrations with discharge in 2003 (**c**, **f**, and **i**). In panels **c**, **f**, and **i**, data are represented with letters to indicate the month of sample collection: *Ja*, January; *F*, February; *Mh*, March; *Ap*, April; *Ma*, May; *Jn*, June; *Jl*, July; *Au*, August; *S*, September; *O*, October; *N*, November; and *D*, December. See text for details on watershed conditions. Discharge data are daily mean flows for the 2003 water year (CDWR 2008). Water samples were not collected after 25 June for Cosumnes River because the main channel had gone dry

provide favorable conditions for denitrification (Harrison et al. 2008), the location of these features likely prevents them from acting as an important N sink in CV watersheds. Information from upstream of the reservoir on the Tuolumne River in the late summer of 2001 demonstrates the N-poor nature of water originating from the upper catchment, with a 1.00–1.20 mg N L^{-1} increase in TN concentration between a sampling site upstream of the reservoir and the sampling site downstream of the reservoir near the confluence with the mainstem San Joaquin River (R. Dahlgren, unpublished data). Without the reservoirs, RD systems may have shown similar seasonal patterns of N export to AD or WSD systems,

Table 7 Pearson's correlation coefficients (r) of mean annual total N (TN), dissolved inorganic N (DIN), and dissolved organic N (DON) concentrations (mg L^{-1}), TN yield (kg km^{-2} $year^{-1}$), and fractional N export with watershed level explanatory variables of climate, hydrology, and land use in California watersheds ($n = 23$)

Variable	TN[a]	DIN[a]	DON[a]	TN yield[a]	Fractional N export[a]
Watershed area[a]	NS	NS	NS	NS	NS
Mean elevation	−0.43	NS	−0.70	NS	NS
Mean slope	NS	NS	−0.50	NS	NS
Natural (% of watershed)[b]	−0.60	−0.56	−0.73	−0.57	NS
Agriculture (% of watershed)[b]	0.64	0.59	0.77	0.56	NS
Urban (% of watershed)[b]	NS	NS	NS	NS	NS
Water (% of watershed)[b]	NS	NS	NS	NS	NS
Population density	NS	NS	NS	NS	NS
Mean temperature	0.45	NS	0.70	NS	NS
Annual precipitation	−0.76	−0.70	−0.86	−0.48	0.62
Annual runoff	−0.62	−0.60	−0.62	NS	0.66
Reservoir storage capacity	NS	NS	NS	NS	NS
Surface water removal	NS	NS	NS	NS	NS

Values are based on the means from the measurement period in each watershed. Only significant ($p < 0.05$) correlations are shown; *NS* non-significant

[a] Natural-log transformed

[b] Arcsine-square root transformed

depending on the degree of agriculture in the basin. In the case of RD systems that would have been WSD systems, elevated flows during the summer season maintains a high flux, though low concentration, of N to downstream systems (Fig. 5h, i). In the case of RD systems that would have been classified as AD, irrigation from reservoir releases could be decreasing water residence time in CV watersheds, thereby decreasing the opportunity for in-river N removal, which is highly dependent on discharge (Peterson et al. 2001).

Factors influencing annual N export

Relationships between climatic, topographic, and land use characteristics of watersheds and annual N export also provide insight into processes governing regional variation in watershed N dynamics. While annual TN, DIN, and DON concentrations and annual watershed N yield exhibited significant correlations with topography, land use, and climate, fractional N export of annual N inputs was only significantly correlated with annual precipitation and runoff ($p < 0.05$; Table 7). This suggests that water availability was an important influence on the capacity of CV watersheds to remove or store N on an annual basis.

Our results were consistent with the hypothesis that fractional N export would be most strongly correlated with mean annual precipitation and runoff in CV watersheds. Our results show that fractional N export from CV watersheds was significantly ($p < 0.05$) correlated with annual precipitation ($r = 0.62$) and runoff ($r = 0.66$), but not with mean annual temperature (Table 7). This contrasts with watersheds in the eastern United States where mean annual temperature correlated more strongly with fractional N export than precipitation or runoff (Schaefer and Alber 2007). Water availability, which influences N residence time and the opportunity for biotic processing of N (Caraco and Cole 2001; Donner et al. 2002; Helliwell et al. 2007), and temperature, which influences rates of N assimilation by plants or microbes and denitrification (Schaefer and Alber 2007), have both been demonstrated to be important factors controlling the fractional export of N inputs from watersheds (Howarth et al. 2006; Schaefer and Alber 2007). In CV watersheds, variability in mean annual precipitation and runoff (coefficient of variations of 34 and 58%, respectively) was larger than variability in mean annual temperature (coefficient of variation of 18%; Table 3). This was the inverse of the pattern for watersheds in the eastern United States, where temperature-mediated N removal processes have been suggested to be most important (Boyer et al. 2002; Schaefer and Alber 2007). Thus, effects of temperature on controlling watershed N processing may be strongest where there is a relatively abundant water supply. An analysis of a subset of CV watersheds supports this concept: there was a significant ($p = 0.04$) negative correlation between fractional N export and mean annual temperature ($r = -0.63$) for a subset of CV watersheds with the ten highest values in mean annual runoff.

Fractional N export shows a highly significant exponential increase with increasing precipitation ($p = 0.003$) and runoff ($p < 0.0001$) when CV watersheds are combined with watersheds in the northeastern and southeastern United States (Boyer et al. 2002; Schaefer and Alber 2007). Runoff alone explains 76% of the variance in fractional N export between the two regions (Fig. 6) whereas mean annual precipitation explains only 15%. Fractional N export also correlates significantly with mean annual temperature with combined data from the two regions ($p < 0.001$; $r^2 = 0.51$); however, temperature is not significant when included with runoff in a multiple regression model ($p = 0.23$; extra-sum-of-squares F-test). Similar to results for the CV

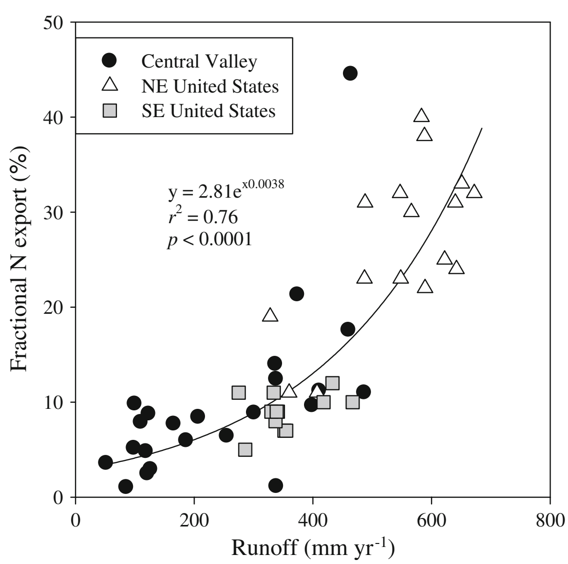

Fig. 6 Fractional N export (annual watershed N export divided by annual input; %) for 2000–2003 versus mean annual runoff for watersheds in California (*black circles*), northeastern United States (*grey triangles*; Boyer et al. 2002), and southeastern United States (Schaefer and Alber 2007)

watersheds alone, the variation in runoff among watersheds from the two regions was larger (coefficient of variation of 47%) than for mean annual temperature (coefficient of variation of 32%). Collectively, these results suggest that runoff is a strong predictor of annual fractional N export among systems with a wide moisture gradient in different climate zones.

Summary and implications

Here we have presented the first spatially explicit analysis of N inputs and export for 23 individual watersheds in California's Central Valley during the early 2000s. Collectively, our results identify portions of watersheds, times of the year, and specific human activities that are especially important for N export in the CV. For example, four major tributaries (STA, TUO, MER, and M/S) contributed nearly 50% of the annual N load to the lower San Joaquin River (LSJ). In these tributaries, inorganic fertilizers and manure contributed 61–89% of total N input; but these N inputs were only applied to a small fraction ($\sim$10%) of the land area in each of these basins (Fig. 2). Also, three of the systems (STA, TUO, and MER) possessed large reservoirs upstream of agricultural areas, altering flow regimes and elevating N export to downstream systems during summer months. Results presented here suggest that anthropogenic activities have not only altered the magnitude of N export in CV rivers, but have also changed the seasonal timing of N export in CV rivers. Hence, nutrient management in a small area and changes to reservoir release schedules could substantially reduce total N export in the SJR, which in turn could improve ecological conditions of the lower San Joaquin River (CRWCB 2004). However, more work is required to define the actual contribution of various N sources to river N export.

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