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Water quality in rice-growing watersheds in a Mediterranean climate

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A B S T R A C T

Rice (*Oryza sativa* L.) agriculture is estimated to cover 161 million ha of land on Earth, with 10% grown in temperate regions. Currently there are strong concerns about surface water nutrient pollution, and the purpose of this study was to determine the impacts of temperate rice cultivation on nutrient dynamics at the small watershed scale. Over the course of the 2008 growing season (May through September), bi-weekly grab samples were collected from outlets of 11 agricultural subwatersheds in California. Samples were analyzed for NO_3-N, NH_4-N, PO_4-P, K, and dissolved organic nitrogen (DON) concentrations, and the average values across all subwatersheds and sampling dates were 0.22, 0.031, 0.047, 1.36, and 0.32 mg L^{-1}, respectively. Linear mixed effects analysis was used to evaluate the magnitude of relationships between nutrient concentration and flux and subwatershed characteristics (i.e. percent soil clay and organic matter, percent rice area, irrigation water reuse, subwatershed discharge, irrigated area, and time, measured as the day in the growing season). For all nutrients, flux decreased over time and increased with discharge. Concentrations of K and DON were highest at the start and end of the growing season. Concentrations of NH_4-N were near non-detect levels, with the exception of a peak in mid-July, which corresponds to when many growers top-dress rice fields with N fertilizer. Nitrate-N concentration and flux decreased with percent rice area, whereas PO_4-P concentrations increased with percent rice area, indicating that rice area should be considered in future watershed-scale studies of nutrient discharge. In all subwatersheds, the discharge loads of K were smaller than surface water input loads, while NO_3-N, NH_4-N, PO_4-P, and DON discharge loads exceeded input loads when total growing season discharge was greater than 3500–6600 m^3 ha^{-1}. This implies that the management of subwatershed discharge can be used to control nutrient export from rice-growing areas.

1. Introduction

Nutrient pollution, primarily as a result of N and P loading, currently affects drinking water supplies, aquatic life, and recreational water quality, and is one of the costliest and most difficult environmental problems faced by the United States (Carpenter et al., 1998). It is generally accepted that human health impacts of nutrient pollution include toxin production by algal blooms and the risk of methemoglobinemia and stomach cancer caused by high nitrate concentrations in drinking water (USEPA, 2009). The link between high nitrate and methemoglobinemia, however, has recently been questioned (Powlson et al., 2008). Nutrient loading impacts on aquatic ecosystems include increased primary production and decomposition rates, low dissolved O_2, algal blooms, and invasion by aquatic weeds, all of which have the potential to impact food chains, species composition, and overall aquatic community function (Nijboer and Verdonschot, 2004). In response to this situation, the Clean Water Action Plan was initiated in 1998 and requires every state to develop and enforce water-body-specific N and P criteria, a process that is still currently underway in most states (USEPA, 2000).

Nutrients enter streams as direct runoff from the surrounding landscape or by infiltration into the subsurface or groundwater, followed by flow into the stream bed (Nijboer and Verdonschot, 2004). The amount of nutrients that enter a stream is dependent on a variety of factors, including the amounts of nutrients available in areas that are hydrologically connected to the stream, and nutrient retention mechanisms in the catchment area, such as uptake by vegetation or sorption onto soil. Models of nutrient levels within watersheds have used a large variety of spatial variables including land use, population density, watershed area, slope, discharge, soil type, nutrient inputs, erosion risk, and topography, and seasonal variables such as precipitation, temperature, and atmospheric deposition (Arheimer and Liden, 2000). These variables, particularly land use, soil type, and discharge, have been found to explain much of the variation occurring at the watershed scale (Allan et al., 1997; de Wit, 1999; Nijboer and Verdonschot, 2004). Once correlations are analyzed, the underlying physical,

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chemical, and biological processes can be determined based on existing literature (Arheimer and Liden, 2000; Johnston, 1991). The most influential processes have been found to be fertilization, sorption, denitrification, mineralization, stream-sediment leakage, dilution, atmospheric deposition, and uptake by microbes and vegetation (Arheimer and Liden, 2000; Johnston, 1991).

Croplands and pasture make up approximately 40% of the Earth's surface (Foley et al., 2005). One of the primary sources of nutrient pollution is agricultural fertilizer (Carpenter et al., 1998; Novotny, 1999). Only a fraction of the fertilizer applied to agricultural fields is actually utilized by crops, and excess nutrients volatilize into the air, infiltrate into the subsurface or groundwater, sorb onto soil minerals, or leave the field via drainage discharge (Nijboer and Verdonschot, 2004).

Rice (*Oryza sativa* L.) agriculture, which is estimated to cover 161 million ha, has the potential to significantly impact nutrient export dynamics in watersheds due to the combination of annual fertilizer applications onto rice fields and the production of large quantities of surface water discharge (Bouman et al., 2007). Rice has a disproportionately strong influence on drainwater flows relative to other crops because, while the evapotranspiration of rice is roughly comparable other commonly grown cereals (Hill et al., 2006; Tuong and Bouman, 2003), rice irrigation practices require more water to enter a field than is actually utilized by the crop (Bouman et al., 2007).

Temperate rice areas account for approximately 10% of the world's total rice area, and increases in the production of rice in temperate regions are raising concerns about the pollution of waterways by fertilizer nutrients (IRRI, 2010). In order to examine these concerns, this study quantified nutrient concentration and flux dynamics in rice-dominated subwatersheds in California during the rice-growing season. We hypothesized that both temporal and spatial subwatershed characteristics would be important controls on nutrient concentration and flux dynamics. The subwatershed attributes considered were sampling date, which was used as a measure of the progression of the rice-growing season, soil properties, water management, and the percent area of each subwatershed that contains rice. The specific nutrients considered were nitrate as N (NO_3-N), ammonium as N (NH_4-N), phosphate as P (PO_4-P), potassium (K), and dissolved organic nitrogen (DON), all of which are important to rice cultivation and water quality. In a separate paper (Krupa et al., in press) we presented our findings related to dissolved organic carbon from these same subwatersheds.

2. Materials and methods

2.1. Study area

In California rice is grown on approximately 230,000 ha and most of this land is located in the Sacramento Valley. The Glenn-Colusa Irrigation District (GCID) is located northwest of Sacramento and is the largest irrigation district in the Sacramento Valley, California (Fig. 1). Irrigation water in the Sacramento Valley drains from fields into small drainage canals, which drain into a series of progressively larger canals and/or natural creeks. This network of drainage canals makes up subwatersheds, similar to the concept of hydrologic watersheds (CH2MHILL, 2003).

Eleven subwatersheds are contained within the GCID ranging from 700 to 5100 ha in size (Fig. 1; Table 1). Nine of the GCID subwatersheds are rice-dominated, with more than 75% of the area in rice, while the other two subwatersheds have less than 50% rice area. The other forms of agriculture found in the GCID are diverse, and include alfalfa (*Medicago sativa* L.), almond (*Prunus dulcis* Mill.) and walnut (*Juglans regia* L.) orchards, corn (*Zea mays* L.), beans (*Phaseolus* L.), onions (*Allium cepa* L.), oats (*Avena sativa* L.), safflower (*Carthamus*

Table 1
Summary of subwatershed characteristics.

Site name[a]	Bondurant	Hunter Creek	Kuhl	Stone Corral	2047 Sidds	Salt Creek Weir	Drain 55	Section 25	Salmon Hole	Willow Creek	Logan Creek	Average
Subwatershed ID	1	2	3	4	5	6	7	8	9	10	11	
Discharge ($m^3\ ha^{-1}$)[b]	14,644	11,000	10,209	9,966	9,796	5,589	4,670	3,916	2,511	1,973	1,041	6,847
Internal reuse ($m^3\ ha^{-1}$)[b]	3,748	872	3,027	278	2,952	916	2,582	159	4,601	2,892	2,046	2,188
Reuse out ($m^3\ ha^{-1}$)[b]	1,396	0	0	1,561	0	0	0	2,829	0	3,563	0	850
Input flow ($m^3\ ha^{-1}$)[b]	24,589	13,709	17,174	16,826	20,411	9,955	18,555	19,646	10,320	12,695	13,898	16,162
Irrigated area (ha)	696	5,120	3,683	3,635	2,945	2,894	2,395	4,616	2,073	3,079	4,462	3,236
Percent irrigated[c]	100	98	96	84	99	95	99	94	99	99	46	92
Percent rice area[c]	86	78	81	47	80	42	89	84	95	94	82	78
Percent Vertisols[c]	13	69	67	59	11	82	6	78	61	35	67	50
Percent Mollisols[c]	69	7	4	12	32	18	29	2	28	16	1	20
Percent Alfisols[c]	19	23	29	29	48	0	66	20	10	48	33	30
Percent clay[d]	44	42	42	40	34	43	31	44	47	37	43	41
Percent SOM[d]	2.6	1.6	2.3	1.7	1.8	2.0	1.8	2.3	1.7	1.6	1.5	2
Net NO_3-N load ($kg\ ha^{-1}$)[b]	0.968	0.909	0.380	3.105	0.840	5.796	−0.067	−0.229	−0.060	−0.247	−0.392	1.000
Net NH_4-N load ($kg\ ha^{-1}$)[b]	0.138	0.245	0.270	0.318	0.475	0.125	−0.118	−0.111	−0.032	−0.084	−0.129	0.100
Net PO_4-P load ($kg\ ha^{-1}$)[b]	0.234	0.070	0.038	−0.103	0.602	−0.040	−0.036	−0.201	−0.037	−0.108	−0.142	0.025
Net K load ($kg\ ha^{-1}$)[b]	−18.92	−2.11	−5.07	−9.40	−12.64	−6.15	−17.34	−18.21	−8.40	−13.12	−15.20	−11.51
Net DON load ($kg\ ha^{-1}$)[b]	0.157	2.519	2.337	−0.053	0.844	−0.0002	−0.563	−0.353	0.016	−0.544	−0.770	0.326

[a] The order of the subwatersheds is from highest to lowest total discharge per hectare.
[b] Flow, reuse quantities, and net surface water NO_3-N, NH_4-N, PO_4-P, K, and DON loads represent the sum over the sampling period (May 8 through September 25 for all subwatersheds, except Salt Creek weir for which sampling began June 11), normalized by irrigated subwatershed area.
[c] Percent rice area, percent irrigated, and percent Vertisols, Mollisols, and Alfisols, indicate the fraction of the total subwatershed area containing these properties.
[d] Percent SOM and percent clay indicate the average SOM and clay contents, respectively, of the surface horizon of subwatershed soils.

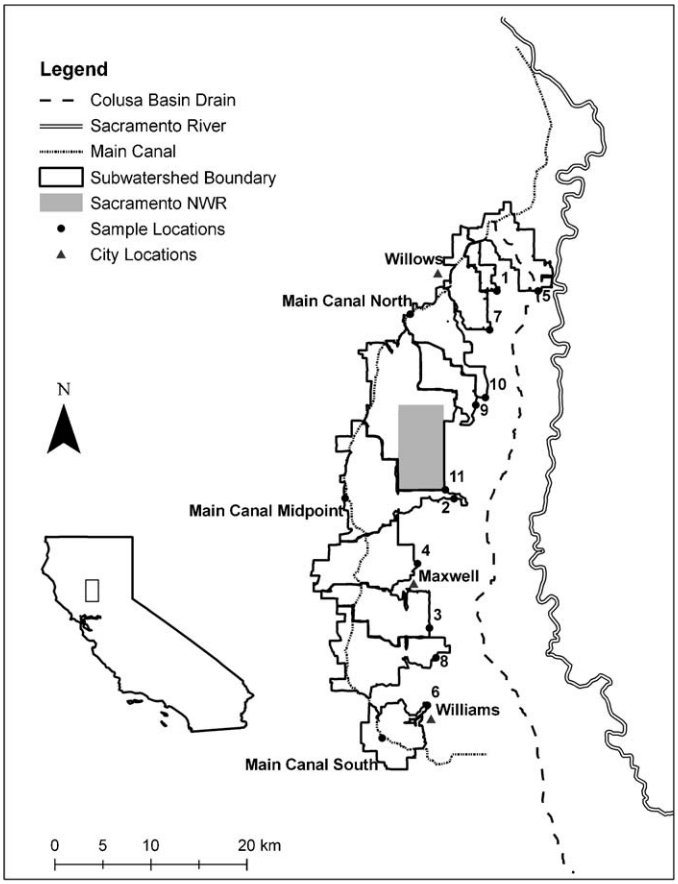

Fig. 1. Glenn-Colusa Irrigation District (GCID) subwatersheds and sampling locations (black dots). Water travels from north to south in the Sacramento River, in the Main Canal, and in the Colusa Basin Drain. GCID water is pumped into the northernmost section of the Main Canal from the Sacramento River and is delivered to subwatersheds via the Main Canal as it travels south. Drains within each subwatershed carry water from west to east to primary outlet points. Subwatershed discharge then enters the Colusa Basin Drain and is discharged back to the Sacramento River. The Sacramento National Wildlife Refuge (NWR) is located within the Logan Creek subwatershed. The numbers at the sample locations correspond to the Subwatershed IDs in Table 1. Subwatersheds 4 and 6 are low-rice subwatersheds.

tinctorius L.), sunflower (*Helianthus annuus* L.), tomatoes (*Solanum lycopersicum* L.), wheat (*Triticum aestivum* L.), and pasture (GCID, 2009). Subwatershed soils are dominated by Alfisols and Mollisols in the north and Vertisols in the south. The percent clay and percent soil organic matter of the top soil horizons range from 31 to 47%, and from 1.5 to 2.6%, respectively. Due to the high clay content, the rate of seepage and percolation is generally low, which causes surface flow paths to dominate in these rice fields, and surface drainage to account for the majority of water loss that is not lost to evapotranspiration (Hill et al., 2006). Additionally, the poor drainage of the soils makes them ill suited for non-rice crops, which limits the occurrence of crop rotation within these systems.

The climate is Mediterranean, with a mean annual precipitation of 45 cm that occurs from November through April (Glenn County, 1993). As a result of the dry summers, irrigation practices are the dominant influence on water dynamics throughout the growing season (Hernes et al., 2008); groundwater, natural stream inputs, and inputs from neighboring irrigation districts are negligible (CH2MHILL, 2003). Water from the Sacramento River is pumped into the Main Canal, which moves water north to south along the western edge of the GCID (Fig. 1). Main Canal water is delivered throughout the subwatersheds by means of a network of lateral canals. Once the water is used in an agricultural field, it enters subwatershed drainage canals, from which the drainwater can be reused, before eventually emptying into the Colusa Basin Drain (Fig. 1). The GCID is located between the California Coast Range and the Sacramento River, which results in a west to east drainage pattern across subwatersheds.

Flow-through irrigation is used in California rice agriculture. In this system, earthen berms divide a rice field into several basins. Irrigation water enters the field through one or two inlet points at the top basin and then flows through the basins sequentially. Excess water leaves the field at the bottom basin. At the start of the growing season in late April/early May, the fields are fertilized. Aqua-ammonia is the primary N source and it is injected into the soil to a depth of 5–10 cm. In addition P and K are typically added by broadcasting to the soil surface, and may or may not be lightly incorporated. Following fertilizer application fields are flooded and then seeded by airplane. For about 40 days after the initial flooding, fields may be drained and reflooded to promote seedling establishment and/or to allow for herbicide application. After this establishment period, maintenance flow begins and water levels are maintained at a depth of 10–15 cm. Between 40 and 55 days after seeding, some growers apply additional N fertilizer by air. Beginning in mid-August, fields are drained completely to allow for harvest. Due to variations in individual grower practices and rice varieties, the exact timing of these practices can vary by up to a month between rice fields.

2.2. Sample collection and analyses

Grab samples were collected every one–two weeks at about 20 cm below the water surface from the 11 GCID subwatershed outlets and from a northern, midpoint, and southern location along the Main Canal (Fig. 1). Also, a field blank of DI water and a replicate sample from a randomly chosen sample site were collected on each day that sampling took place. Sampling occurred from May 8 through September 25, 2008. A total of 15 samples were collected from each subwatershed outlet and from each Main Canal location, with the exception of the midpoint Main Canal location, from which 11 samples were collected due to site inaccessibility, and with the exception of Salt Creek Weir, from which 11 samples were collected due to sampling at this site starting in June as a result of new information being obtained from the GCID (GCID staff, personal communication). A given sampling day would begin in the morning of and end in the evening.

Water samples were stored on ice and in the dark, filtered within 24 h of collection through a 0.45 μm filter (Millipore), and stored frozen ($-20\,^{\circ}C$) in the dark until analysis. A portion of each sample was analyzed for total dissolved nitrogen (TDN) concentration using a Shimadzu TOC-V_{CSH} analyzer with a TNM-1 total nitrogen measuring unit (Shimadzu Corp., Kyoto, Japan). All TDN data are the mean of 2–3 replicate injections for which the coefficient of variance (c.v.) was always less than 2%. The remaining sample was again stored frozen ($-20\,^{\circ}C$) in the dark until analysis for NO_3-N, NH_4-N, PO_4-P, and K. The concentrations of NO_3-N, NH_4-N, and PO_4-P were determined colorimetrically using the vanadium (III) chloride reduction method for NO_3-N (Doane and Horwath, 2003), which measures total nitrate plus nitrite as N, the Berthelot reaction for NH_4-N (Forster, 1995), which measures total ammonia plus ammonium as N, and the antimony potassium tartrate reaction for PO_4-P (Murphy and Riley, 1962). The absorbance of samples was read at 540 nm for NO_3-N, 650 nm for NH_4-N, and 882 nm for PO_4-P, using a UV–Vis spectrophotometer (UV-160, Shimadzu, Japan). Concentrations of DON were calculated by subtracting the sum of the NO_3-N and NH_4-N concentrations from TDN concentrations. A portion of each sample was analyzed for K concentrations using US EPA Method 258.1 at the University of California Davis Analytical Laboratory. In the analysis of all constituents, spike samples were analyzed at a minimum once with every run, and at least 10% of samples were analyzed in duplicate.

2.3. Subwatershed characteristics data

Using ArcGIS 8.3 Desktop GIS software (ESRI, 2002) and GCID data, we calculated daily subwatershed discharge, input, and reuse rates (Figs. 2–3), total subwatershed area, total irrigated subwatershed area, and the percent of irrigated subwatershed area that was used for the various forms of agriculture during the 2008 growing season (Table 1). The GCID provided the following: (1) GIS data that delineated all of the agricultural fields within each subwatershed, the type of agriculture occurring on each field, the area of each field, and whether or not the field was irrigated; (2) daily measurements of lateral inputs, subwatershed discharge, and water reuse; and (3) ArcGIS maps of lateral and drain locations and layouts, and of pump and weir locations.

Daily subwatershed discharge was measured by the GCID using weirs at 10 sites and a staff gauge at one site. Daily inputs from the Main Canal into each lateral canal were measured by the GCID using meters located on the laterals. Daily subwatershed inputs were then calculated using the GCID lateral input measurements and using spatial data regarding the location and layout of each lateral canal within each subwatershed. Because lateral canals cross subwatershed boundaries, estimates of the amount of water delivered by a lateral to a particular subwatershed were made by estimating the fraction of the total length of a lateral that is located within a given subwatershed and multiplying this by the total daily input of water into that lateral.

Water reuse is the practice of diverting water from a drainage canal into a lateral canal, which allows drainwater to be reused by growers. Water reuse activities within GCID subwatersheds take three forms: (i) drainwater is reused within the subwatershed from which it came, (ii) drainwater is added to a lateral within one subwatershed from the drain of another subwatershed, and (iii) drainwater is sent to areas outside the subwatershed from which it came. The estimates of reuse that fell under categories (i) and (ii) were added together for each subwatershed to form a variable called internal reuse. The estimate of reuse that fell under category (iii) was called reuse out. Similarly to the daily input estimates, reuse estimates were made by calculating the fraction of the total length of a lateral downstream of a reuse pump or weir that is located within a given subwatershed, and multiplying this by the total daily reuse measured at the pump or weir.

Input and discharge fluxes of nutrients occurring in each subwatershed on a given sampling day were calculated by multiplying the subwatershed input and discharge measurements for that day by the corresponding input and discharge NO_3-N, NH_4-N, PO_4-P, K, and DON concentrations. Because of the low variation in nutrient concentrations across Main Canal sampling locations (Fig. 3), input concentrations for a given sampling event were estimated by averaging the values of the Main Canal samples collected during that event. Flux values were then normalized by dividing absolute flux by the irrigated area of each subwatershed.

Net input and discharge loads of NO_3-N, NH_4-N, PO_4-P, K, and DON were calculated for each subwatershed using the trapezoidal rule algorithm, AREA.XFM, in SigmaPlot 10.0 (Systat Software, 2006). The *x*-data used in the algorithm was sampling event date, and the *y*-data used were the measurements of input and discharge flux per irrigated area. The entry loads were then subtracted from the discharge loads to obtain an estimate of the net surface water growing season NO_3-N, NH_4-N, PO_4-P, K, and DON loads per irrigated area produced by each subwatershed (Table 1).

The towns of Maxwell, Williams, and Willows are located within the GCID (Fig. 1), but towns were not included in irrigated subwatershed areas because there were no storm events during the growing season, and therefore runoff from the towns to the subwatersheds was negligible. The only potential influence of the towns was through treated wastewater inputs. Williams wastewater is not discharged into any of the subwatersheds after treatment. Maxwell wastewater enters the drainage system in the middle of the Kuhl subwatershed. Willows wastewater goes through tertiary treatment and is added to a lateral for agricultural use within the Willow Creek subwatershed.

The Sacramento National Wildlife Refuge, which consists of manmade wetlands managed by the U.S. Fish and Wildlife Service, is located within the Logan Creek subwatershed (Fig. 1). It obtains its water through the Main Canal, however it does not receive a significant amount of water during the rice-growing season (U.S. Fish and Wildlife Service, personal communication), and was therefore not considered part of the Logan Creek irrigated subwatershed area (Table 1).

Soils data was obtained from the Soil Survey Geographic (SSURGO) database (Soil Survey Staff, 2009). R statistical software (R Development Core Team, 2009) and GIS tools (ESRI, 2002) were utilized to estimate the percent area of each soil order within a subwatershed. The average percent clay and percent organic matter contents in the top subwatershed soil horizons were also estimated. This was done by taking the area weighted average of the surface horizon clay and organic matter values of all the soil map units located within each subwatershed.

2.4. Statistical analyses

Linear mixed effects regression analysis (LME) (Pinheiro and Bates, 2000; Zuur et al., 2009) was used to identify and quantify relationships between independent variables (e.g. subwatershed characteristics and sampling date) and the response variables (e.g. nutrient concentration and flux) (Table 2). Analysis was conducted with Stata/SE software (StataCorp, 2009). Separate statistical analyses were performed for NO_3-N, NH_4-N, PO_4-P, K, and DON concentration and for NO_3-N, NH_4-N, PO_4-P, K, and DON flux normalized by irrigated subwatershed area (Table 2). For all analyses, sample site (subwatershed) identity was treated as a random intercept to account for autocorrelation introduced by repeated measures at each sampling location.

Fixed effect independent variables for all initial LME models were time (sampling date, measured as Julian day), discharge, percent rice area, percent surface horizon soil organic matter, percent surface horizon clay, irrigated area, internal reuse, and reuse out. In the case of the LME models of nutrient flux, the internal reuse, reuse out, and discharge variables were normalized by irrigated area in order to be consistent with the nutrient flux units. Additionally, irrigated area was removed from initial nutrient flux models because nutrient flux was already normalized by this factor. The quadratic forms of independent variables were included whenever evaluations of graphs of the relationship between response and environmental factors was potentially not a straight line. Lastly, a discharge × time interaction was included in every initial model, to determine if the effects of discharge varied over the course of the growing season. Input data was not included in the initial models because this factor was collinear with discharge (Pearson $r = 0.50$). Measurement of percent Vertisols, Alfisols, and Mollisols were not included in the initial models because each of these factors was collinear with either percent clay and percent organic matter, or both.

Final significant LME models were created using a backwards stepping approach, in which insignificant variables ($p > 0.05$) were removed from the initial model unless they were part of a significant interaction. The r^2, slope, and intercept values obtained from the simple linear regression of the observed data versus the values

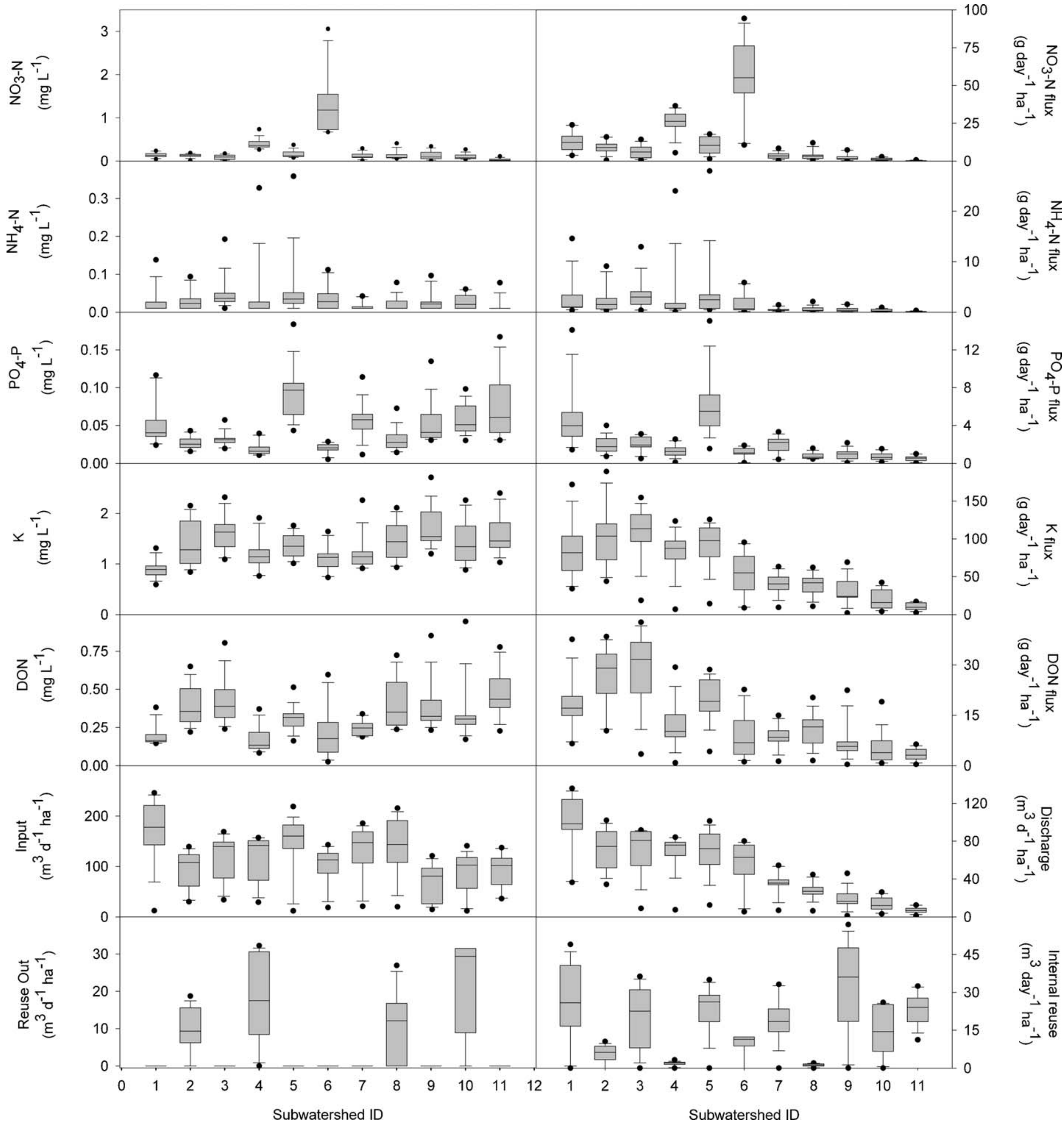

Fig. 2. Boxplots representing the distributions of nutrient concentration and flux, input and discharge flow, and reuse quantity, measured for each subwatershed. The whiskers are the upper 90% and lower 10%, the boxes are the upper 75% and lower 25%, and the line is the median value. Subwatersheds are ordered from the most to the least total growing season discharge per ha. Subwatersheds 4 and 6 are low-rice subwatersheds.

predicted by the LME models were used as indicators of goodness-of-fit (Table 2).

The assumptions of homogeneity of variance and normality were checked by evaluation of standard diagnostic graphs. Response variables that did not meet these assumptions were transformed according to the functions indicated in Table 2, and an independent variance function was used to correct heteroscedasticity (Zuur et al., 2009).

3. Results

3.1. Rice-growing season nutrient dynamics

The soil and agricultural characteristics and water management practices investigated in this study are presented in Table 1. Climate, crop distributions, and water management and irrigation practices during the 2008 growing season showed no substantial

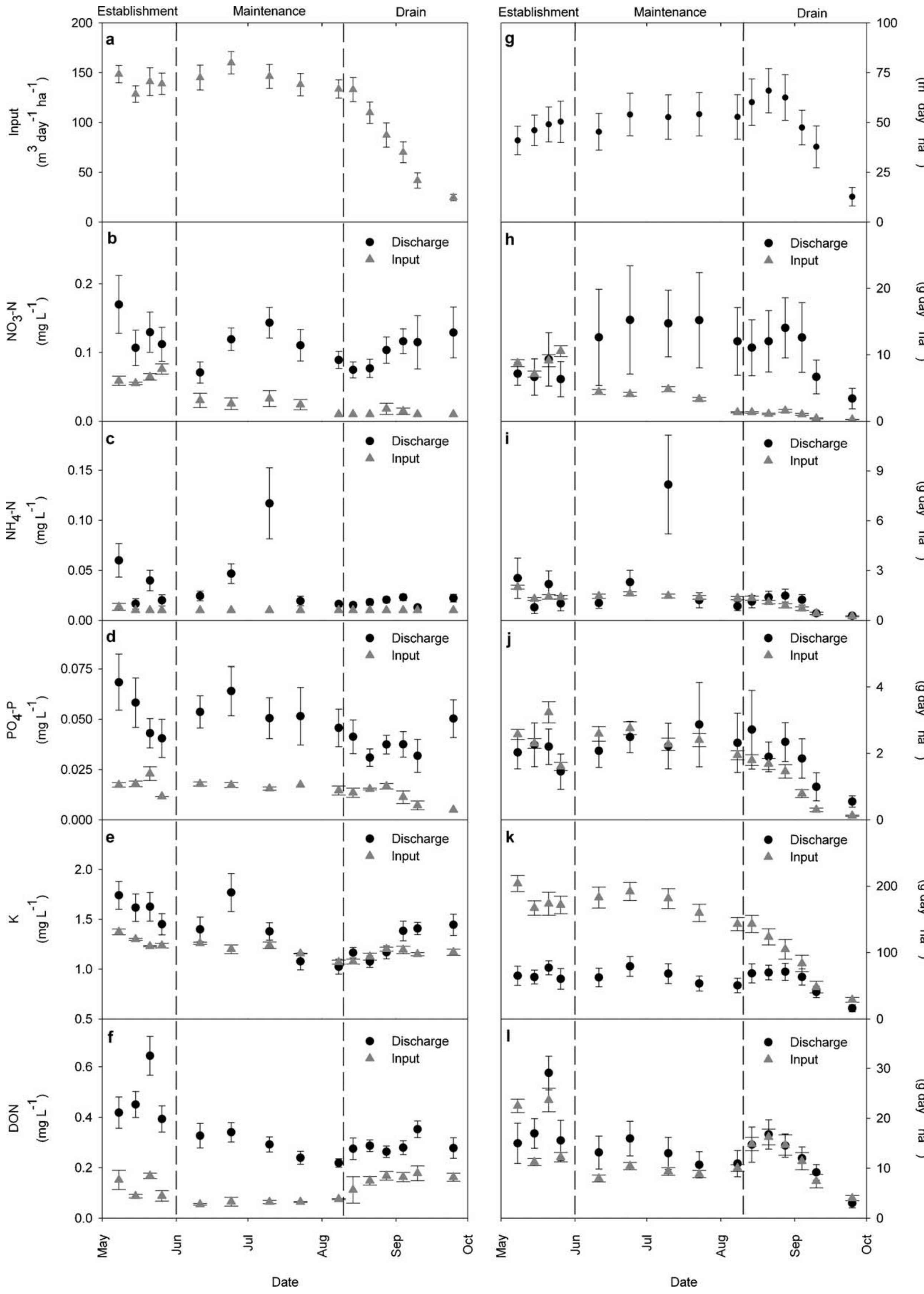

Fig. 3. (a) Average input flow and (g) average discharge flow measured during each sampling event in the eleven subwatersheds. (b–f) Average nutrient concentration measured during each sampling event in the three Main Canal locations (Input), and in the eleven subwatershed outlets (Discharge). (h–l) Average nutrient input flux (Input) and discharge flux (Discharge) measured during each sampling event in the eleven subwatersheds. Bars represent the standard error of the measurements. The dashed vertical lines indicate the approximate establishment, maintenance, and drain periods occurring within the rice-growing season in 2008.

Table 2
Results of linear mixed effects (LME) analyses for K, DON, PO_4-P, NO_3-N and NH_4-N concentrations and fluxes.

Response variable[a]	Trans form[b]	LME model coefficients ± standard error[e]					Goodness-of-fit[f]				
		Time[c]	Time^2	Discharge[d]	Rice area (%)	Rice area (%)^2	Intercept	AIC	r^2	Slope	Intercept
NO_3-N (mg L^{-1})	P(0.34)	–	–	–	−3.99e-2 ± 1.43e-2	2.37e-4 ± 1.05e-4	2.23 ± 0.453	−244	0.74	0.72	0.17
PO_4-P (mg L^{-1})	ln	−3.04e−3 ± 6.15e−4	–	–	2.12e−2 ± 7.00e−3	–	−4.31 ± 0.575	213	0.65	0.63	−1.2
K (mg L^{-1})	ln	−2.70e−2 ± 3.79e−3	6.39e−5 ± 9.59e−6	–	–	–	2.98 ± 0.363	30.9	0.53	0.52	0.13
DON (mg L^{-1})	P(0.34)	−6.30e−3 ± 1.08e−3	1.37e−5 ± 2.74e−6	–	–	–	1.35 ± 0.104	−329	0.64	0.61	0.26
NO_3-N flux (g day^{-1} ha^{-1})	P(0.26)	−7.99e−4 ± 3.26e−4	–	9.90e−3 ± 8.83e−4	−1.10e−1 ± 3.70e−2	6.57e−4 ± 2.73e−4	5.69 ± 1.16	53	0.88	0.88	0.19
NH_4-N flux (g day^{-1} ha^{-1})	ln	−6.78e−3 ± 1.25e−3	–	2.90e−2 ± 2.84e−3	–	–	−0.42 ± 0.33	424	0.70	0.70	−0.12
PO_4-P flux (g day^{-1} ha^{-1})	P(0.24)	−9.47e−4 ± 1.70e−4	–	5.34e−3 ± 4.05e−4	–	–	1.03 ± 0.058	−168	0.83	0.80	0.22
K flux (g day^{-1} ha^{-1})	P(0.5)	−9.25e−3 ± 1.40e−3	–	7.79e−2 ± 3.79e−3	–	–	5.35 ± 0.426	477	0.90	0.91	0.65
DON flux (g day^{-1} ha^{-1})	P(0.5)	−7.78e−3 ± 9.01e−4	–	3.17e−2 ± 2.41e−3	–	–	3.46 ± 0.291	343	0.84	0.83	0.58

[a] NH_4-N concentration model failed to converge due to zero-inflated data.
[b] Data was transformed to meet the assumptions of normality and homogeneity of variance according to the function indicated. *P*(*x*) indicates data was raised to the power of *x*.
[c] Time is the day in the growing season measured as Julian day.
[d] DOC flux per ha and THM flux per ha analyses were performed using discharge values that were normalized by area with units of (m^3 day^{-1} ha^{-1}). For all other analyses, discharge units were (m^3 s^{-1}).
[e] Only significant variables are shown ($p > 0.05$).
[f] Results of the linear regression of the observed data versus the values predicted by the LME model. The goodness-of-fit of an ideal model would have an r^2 and slope equal to 1, and an intercept equal to zero.

variations from typical conditions within the GCID (GCID staff, personal communication).

Subwatersheds 4 and 6, which are the two low-rice subwatersheds, showed the highest NO_3-N concentration and flux and the lowest PO_4-P concentration (Fig. 2). Variations in nutrient concentrations, flows, and fluxes over the progression of the growing season are presented in Fig. 3. There is a peak in the concentration and flux of NH_4-N during July 10 sampling event. Discharge NO_3-N flux is consistently higher than input NO_3-N flux. Conversely, discharge K flux is consistently lower than input K flux.

The means and standard errors of the NO_3-N, NH_4-N, PO_4-P, K, and DON concentrations measured across all subwatersheds and sampling dates were 0.22 ± 0.03 mg L^{-1}, 0.031 ± 0.004 mg L^{-1}, 0.047 ± 0.003 mg L^{-1}, 1.36 ± 0.03 mg L^{-1}, and 0.32 ± 0.01 mg L^{-1}, respectively (Fig. 2). The means and standard errors of the NO_3-N, NH_4-N, PO_4-P, K, and DON concentrations measured across all Main Canal locations and sampling dates were 0.032 ± 0.004 mg L^{-1}, 0.010 ± 0.0003 mg L^{-1}, 0.015 ± 0.0008 mg L^{-1}, 1.21 ± 0.01 mg L^{-1}, and 0.12 ± 0.008 mg L^{-1}, respectively (Fig. 2).

The relationship between total discharge per ha and net surface water nutrient load per ha produced by each subwatershed over the entire growing season was investigated using simple linear regression (Table 3). The strongest correlation between discharge and net load occurred for NO_3-N in the rice-dominated subwatersheds ($r^2 = 0.90$; $p < 0.001$). This relationship was much less significant when linear regression was performed including the low-rice subwatersheds ($r^2 = 0.40$; $p = 0.036$). Net NH_4-N, PO_4-P, and DON surface water loads were also significantly correlated with discharge (Table 3). The discharge levels at which the linear regressions indicated that the net load of a nutrient was equal to zero ranged from 3500 to 6600 m^3 ha^{-1} (Table 3). Net surface water K loads did not have a significant relationship with discharge ($r^2 = 0.40$; $p = 0.58$), and all subwatershed net K loads were negative (Table 1).

3.2. LME analysis of significant factors driving nutrient dynamics

The NH_4-N concentration data was highly zero inflated, with 48% of the 157 measurements below the 0.02 mg L^{-1} detection limit. Furthermore, only 16% of NH_4-N concentration measurements were above 0.05 mg L^{-1}. Because of this highly skewed data distribution, the data could not be transformed to meet the normality and homogeneity assumptions of LME analysis. Furthermore, LME analyses based on Poisson and negative binomial distributions consistently failed to converge. Since the peak on the July 10th sampling event appears to be the only time in which NH_4-N concentrations exhibit substantial variation, NH_4-N concentration patterns are treated qualitatively in the discussion.

The results of the LME analysis for all other independent variables are presented in Table 2. As in simple linear regression, the coefficients represent the magnitude of the relationship between the independent and response variables and whether the relationship is a positive or negative correlation.

There is a significant quadratic relationship between NO_3-N concentration and flux and rice (Fig. 4a and b; Table 2). Additionally, NO_3-N flux is negatively correlated with time, and positively correlated with discharge (Table 2). Because the nature of a quadratic relationship is difficult to discern by considering only the coefficients, the NO_3-N concentration and flux data and corresponding LME models, are presented in Fig. 4a and b, respectively. The two low-rice subwatersheds have high NO_3-N concentrations and fluxes relative to the nine rice-dominated systems, which show similar NO_3-N concentration and flux levels across their entire percent rice area range (Fig. 4a and b).

Table 3
Results of the linear regression of total discharge versus net surface water NO_3-N, NH_4-N, PO_4-P, K, and DON loads estimated for each subwatershed during the growing season sampling period beginning May 8 and ending September 25, 2008.

Net load[a] (kg ha^{-1})	Slope[e]	Intercept[e]	r^2	p-value	Discharge at net load equal to zero[f] (m^3 ha^{-1})
NO_3-N [b]	0.567 ± 0.231	−4.46 ± 1.99	0.40	0.036	2600
NO_3-N [c]	1.07e−4 ± 1.37e−5	−0.478 ± 0.110	0.90	<0.001	4500
NH_4-N	0.180 ± 0.045	−1.47 ± 0.389	0.64	0.003	3500
PO_4-P	2.75e−5 ± 1.11e−5	−0.181 ± 0.089	0.41	0.035	6600
K[d]	2.39e−4 ± 4.18e−4	−13.1 ± 3.37	0.04	0.58	–
DON	0.793 ± 0.205	−6.83 ± 1.76	0.63	0.004	5500

[a] The linear regression for each nutrient was performed using 11 discharge and 11 net load values, unless otherwise noted. Data was transformed to meet homogeneity of variance and normality assumptions.
[b] Linear regression results of net NO_3-N load versus discharge for data from all 11 subwatersheds.
[c] Linear regression results of net NO_3-N load versus discharge for data from only the nine rice-dominated subwatersheds.
[d] There was no significant model for net K loads and the linear regression line did not cross the point of zero net load within the range of discharge values measured over the entire growing season across all subwatersheds.
[e] '±' sign indicates the standard error of the parameter.
[f] The discharge at which subwatersheds are predicted to have a net load of zero was calculated for each constituent.

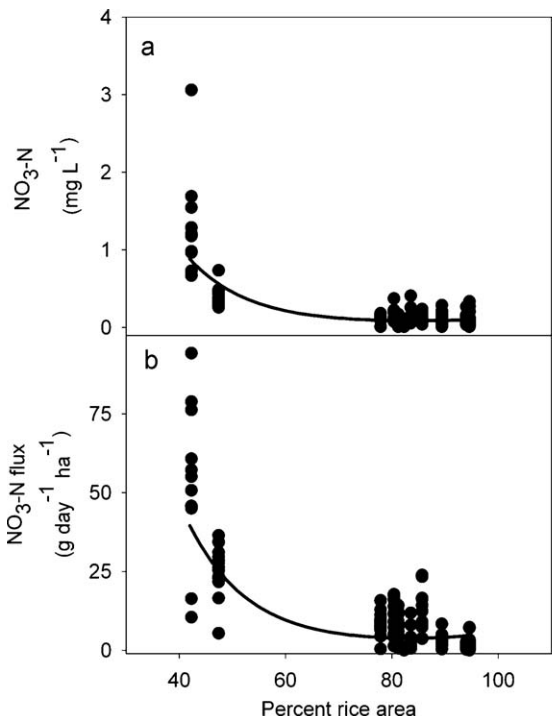

Fig. 4. Graphical depictions of the quadratic response of (a) NO_3-N concentration to changes in percent rice area estimated by the linear mixed effects (LME) model: $[NO_3\text{-N}] = 2.23–3.99e^{-2} \times \text{rice} + 2.37e^{-4} \times \text{rice}^2$ and (b) NO_3-N flux to changes in percent rice area, estimated by the LME model: NO_3-N flux $= 5.69–1.10e^{-1} \times \text{rice} + 6.57e^{-4} \times \text{rice}^2–7.99e^{-4} \times 200 + 9.90e^{-3} \times 49$; average values of Julian day equal to 200 and discharge equal to 49 m^3 day^{-1} ha^{-1} were used as hypothetical values in the equation. The goodness-of-fit parameters of both LME models are presented in Table 2.

The equation for NO_3-N flux developed based on the coefficients in Table 2 is:

$$NO_3 - \text{N flux} = 5.69 - 7.99e - 4 \times \text{time} + 9.90e - 3 \times \text{discharge} - 1.10e - 1 \times \text{rice} + 6.57e - 4 \times \text{rice}^2$$

The goodness-of-fit parameters show that this model has an r^2 and slope close to 1, and an intercept value that is relatively small compared to the magnitude of the range in NO_3-N flux per ha (Fig. 3). This indicates that the LME model explains a large portion of the variation in NO_3-N flux per ha leaving each subwatershed.

The concentration of PO_4-P was negatively correlated with time and positively correlated with rice. The K and DON concentrations were significantly correlated with the time and time^2 terms, showing relatively elevated values during the establishment and drain periods, and lower values during the maintenance flow period (Fig. 3). The fluxes of NH_4-N, PO_4-P, K, and DON were all negatively correlated with time and positively correlated with discharge.

4. Discussion

4.1. Nutrient concentration comparison to existing water quality standards

The national drinking water standard for NO_3-N is 10 mg L^{-1} (Powlson et al., 2008). There is no NO_3-N standard for the protection of aquatic life, however the average level of NO_3-N in undeveloped United States streams is 0.24 mg L^{-1} (Dubrovsky et al., 2010). The NO_3-N concentrations across the nine rice-dominated subwatersheds were on average 0.12 mg L^{-1}, with a maximum of 0.41 mg L^{-1}, and in the two low-rice subwatersheds were on average 0.76 mg L^{-1}, with a maximum of 3.06 mg L^{-1}. These concentrations are unlikely to impact drinking water quality, but low-rice subwatersheds have the potential to degrade downstream aquatic ecosystems.

Ammonia can be toxic to aquatic life (Ip et al., 2001), and under current regulations, the water quality standard for NH_4-N in subwatershed discharge is 1.02 mg L^{-1} (RWQCB, 2008). This estimate is based on a maximum pH of 7.93 and a maximum temperature of 27.09 °C measured in Section 25 discharge in 2010 (unpublished results). The highest NH_4-N concentration measured across all subwatersheds was 0.36 mg L^{-1}, which is well below levels that could threaten aquatic life.

The recommended PO_4-P level to protect drinking water quality and prevent aquatic ecosystem degradation in streams that do not flow into a reservoir is 0.10 mg L^{-1} (MacDonald, 1991). Approximately 8% of PO_4-P samples had concentrations greater than 0.10 mg L^{-1}, with a maximum concentration of 0.18 mg L^{-1}, which indicates that the PO_4-P in discharge is unlikely to degrade downstream water quality.

Concentrations of DON will come under indirect regulation when water quality standards for total N are adopted (USEPA, 2000). The relative contribution of DON to total N loss varies across watersheds (Hedin et al., 1995; Jordan et al., 1997; McDowell and Asbury, 1994). In our study, the average concentration and flux of DON (0.32 mg L^{-1} and 13.7 g day^{-1} ha^{-1}, respectively) was similar to average mineral N (NO_3-N + NH_4-N) concentration and flux (0.25 mg L^{-1} and 12.3 g day^{-1} ha^{-1}, respectively) (Fig. 2). These results are consistent with Zhao et al. (2009), which found that DON makes up a large part (64–77%) of total N loss from rice fields via leaching and runoff.

4.2. Influence of rice area and water management and fertilization practices on nutrient dynamics

The high NO_3-N flux and concentration in discharge from low-rice systems (Table 2) has been commonly observed in non-rice agricultural watersheds (Boyer et al., 2002; Dukes and Evans, 2006; Johnson et al., 1997), and is likely due to aerobic conditions limiting the nitrification/denitrification N loss mechanism (Di and Cameron, 2002; Gambrell et al., 1975; Skaggs et al., 1994), which dominates in rice fields (Feng et al., 2004; Gambrell et al., 1975). As a result of this difference, the linear regression of net growing season load versus total growing season discharge is much weaker when both rice-dominated and low-rice subwatershed data is included (Table 3).

The elevated PO_4-P concentrations in rice-dominated subwatersheds (Table 2) are likely the result of several processes. First, P fertilizer is generally surface applied in these systems, causing high concentrations early in the growing season. These concentrations then decrease over time (Table 2; Fig. 3) due to plant uptake and the binding of PO_4-P onto soil minerals (McDowell et al., 2001). Second, flooded conditions make P more soluble due to a variety of mechanisms, including the hydrolysis of Al and Fe phosphate, dissolution of P containing minerals, desorption of P from clay, and the reduction of ferric PO_4 to the more soluble ferrous forms (De Datta, 1981; Patrick and Khalid, 1974). This makes the P more available to be taken up by plants, but also more prone to removal from fields via runoff. Third, surface flow path dominance in rice fields likely limits the sorption of P onto soil minerals (McDowell et al., 2001; Meyer and Likens, 1979).

Nutrient concentrations and fluxes were highest early in the growing season, with the exception of NO_3-N and NH_4-N concentrations. Most NH_4-N concentration measurements were at or near the average national background level of 0.025 mg L^{-1} (Dubrovsky et al., 2010). The most likely cause of the peak in NH_4-N concentration during the July 10 sampling event (Fig. 3) is the top-dressing of N fertilizer that many growers apply during this period. This N is applied aerially onto the flood water, thus causing it to be prone to removal through surface flow.

Both K and DON concentrations exhibited a quadratic trend over the course of the growing season (Table 2; Fig. 3), with higher values during the periods of flooding and draining. Also, both K and DON fluxes decreased over the course of the growing season. The decrease in K concentration and flux from the establishment through the maintenance flow periods is likely driven by high initial concentrations due to fertilizer application, followed by K reductions due to rice and weed uptake (Lowrance et al., 1985). The rise in K concentrations in September occurs at the end of the growing season when draining in most fields is almost complete and discharge flow rates and K fluxes are small (Fig. 3). This implies that K is being concentrated due to the low drainwater flow.

Dissolved organic nitrogen is the N component of dissolved organic matter (DOM), and the primary sources of DON in rice field discharge are input waters, soil organic matter, and fresh and decomposing rice straw (Aitkenhead-Peterson et al., 2003; Caraco and Cole, 2003; Williams, 2010). The high DON concentration and flux in the early growing season coincides with the onset of flooding. Peaks in DOM in general have been observed in systems when dry areas are first wetted (Ruark et al., 2010; Tipping et al., 1999). This is likely due to the combination of decreased microbial utilization limiting the depletion of organic matter, and the disruption of soil structure by the rewetting of fields, which releases previously sorbed and protected organic matter (Tipping et al., 1999). The decline in DON concentration and flux that occurs from the establishment through the maintenance flow periods is likely caused by the depletion of organic matter source pools due to the constant outflow of water over time (Chow et al., 2009; Sanderman et al., 2009; Spencer et al., 2010). The small rise in DON concentrations that coincides with the beginning of the onset of draining is potentially due to higher discharge flows during the drain period in August (Fig. 3) (Hood et al., 2006; Jardine et al., 1990; Kalbitz et al., 2000). Similar trends in dissolved organic carbon concentration and flux during the growing season were also found in this study (Krupa et al., in press).

Nutrient concentrations did not respond to changes in discharge, however, nutrient fluxes increased with discharge (Fig. 3; Table 2). The most likely causes of this relationship are that higher discharge flows (i) have the capacity to carry more nutrients and the sediments to which nutrients are bound (Evans et al., 1995; McDowell et al., 2001), (ii) reduce the time for nutrient retention processes, such as biological uptake and sorption mechanisms, to occur (Johnston et al., 1990; Kalbitz et al., 2000; Royer et al., 2006), and (iii) in the case of DON, are able to flush more of the DOM adsorbed on soil aggregate surfaces and contained in soil micropores (Hood et al., 2006; Jardine et al., 1990; Kalbitz et al., 2000). This correlation is commonly seen in both agricultural and natural systems (Hill, 1981; Lewis et al., 2006; Royer et al., 2006).

In contrast to several other studies linking soil properties to nutrient dynamics in agricultural watersheds (Dukes and Evans, 2006; Norton and Fisher, 2000; Sliva and Williams, 2001), in this study, soil properties were not significantly correlated with nutrient concentration or flux. This is potentially due to rice field management causing such an intense change in the soil, that soil differences prior to rice cultivation are masked by the strength of anthropogenic management effects (Kogel-Knabner et al., 2010). Another potential cause is that percent clay and percent soil organic matter may not have varied enough across subwatersheds to significantly influence nutrient dynamics (Table 1).

The reason for the relatively high unexplained variation in nutrient concentration models is likely linked to complex nutrient cycling processes occurring within streams and within fields that cause short-term variability which cannot be captured by subwatershed and growing season scale characteristics (Johnson et al., 1997; Nijboer and Verdonschot, 2004; Prior and Johnes, 2002). In future studies, it would be helpful to include measurements of critical biogeochemical processes, particularly sorption onto sediments, spiraling, and uptake of nutrients by algae and aquatic plants (Johnston, 1991; Kroeze et al., 2003; Nijboer and Verdonschot, 2004). This would help to explain the remaining variation of nutrient dynamics in rice-growing areas.

4.3. Total net growing season loads

The significant correlations of net surface water NO_3-N, NH_4-N, PO_4-P, and DON loads with total growing season discharge (Table 3) indicate that discharge plays a critical role in determining whether surface water nutrient exports exceed inputs. The discharge at which net surface water nutrient loads equal zero ranged from 3500 to 6600 m^3 ha^{-1} (Table 3). In this study, six subwatersheds had total discharge of less than 6600 m^3 ha^{-1} and three subwatersheds had total discharge of less than 3500 m^3 ha^{-1}, and in most cases these subwatersheds behaved as sinks of surface water NO_3-N, NH_4-N, PO_4-P, and DON (Table 1). This indicates that it is feasible to manage discharge rates within subwatersheds in order to control nutrient export. Potential water management strategies include allowing no discharge from a field, or reusing water at the field, farm, subwatershed, and/or irrigation district scale (Bouman and Tuong, 2001; Hafeez et al., 2007; Zulu et al., 1996). The costs of implementing these practices can be minor, as in the case of simply reducing input flows, or they can be substantial, as in the case of building and maintaining infrastructure for water reuse

Table 4
Average growing season nutrient loads within rice-dominated subwatersheds.

Nutrient	Fertilizer[b] (kg ha^{-1})	Input load[c,d] (kg ha^{-1})	Discharge[c,d] load (kg ha^{-1})
Mineral N[a]	165	0.71 ± 0.19	1.02 ± 0.85
PO_4-P	22	0.27 ± 0.07	0.32 ± 0.29
K	34	20.6 ± 5.65	8.27 ± 5.52
DON	na	1.56 ± 0.46	1.97 ± 1.33

[a] Mineral N is the sum of NO_3-N and NH_4-N.
[b] The average fertilizer loads were taken from a survey of California rice growers (unpublished results).
[c] The average surface water input and discharge loads were calculated using the total nutrient loads measured in the nine rice-dominated subwatersheds during the sampling period (May 8 through September 25).
[d] The '±' indicates standard error.

at larger scales. Before embarking on the control nutrient export from rice systems however, it should be considered whether or not the concentrations and loads are high enough to warrant management.

4.4. Nutrient loads relative to fertilizer nutrient inputs

When compared to fertilizer use, the growing season input and discharge loads of mineral N and PO_4-P are extremely small (Table 4). The low mineral N discharge loads are consistent with many studies which reported that discharge accounts for only a fraction of total N inputs into watersheds (Boyer et al., 2002; Liang et al., 2007; Peterjohn and Correll, 1984). Rice systems and wetlands in particular tend to decrease N loads in surface runoff (Feng et al., 2004; Liang et al., 2007; Prior and Johnes, 2002). The most likely mechanisms of N loss in rice fields are N removal through plant harvesting (Liang et al., 2007; Patrick and Reddy, 1976; Zhao et al., 2009), and N loss as gas through nitrification/denitrification (Bouman et al., 2002; Feng et al., 2004). Leaching is not an important N loss mechanism in high clay rice fields because the injected ammonium binds strongly to the cation exchange complex of soil minerals (Bajwa, 1982, 1987) and because the downward movement of water is limited by the presence of high clay soils (Kroeze et al., 2003; Tsubo et al., 2007).

Similar to mineral N, the flux of PO_4-P was low relative to fertilizer use (Table 4), which is consistent with the low export of P via surface flow found in other systems (Carpenter et al., 1998; McDowell et al., 2001; Peterjohn and Correll, 1984). Wetland and rice systems often act as sinks of PO_4-P (Feng et al., 2004; Kao and Wu, 2001; Prior and Johnes, 2002) due to (i) the formation of stable complexes between P and Ca, Al, and Fe minerals in the soil, (ii) the incorporation of P into soil organic matter (Carpenter et al., 1998; McDowell et al., 2001), and (iii) the uptake of P by rice (Carpenter et al., 1998; McDowell et al., 2001; Peterjohn and Correll, 1984).

In contrast, the average net surface water input load of K into these systems was 12.33 kg ha^{-1}, which is equal to 36% of the average amount of fertilizer added by growers (Table 4). Rice requires large amounts of K, and the removal of large loads of K through plant uptake has been observed in many rice systems (Dobermann et al., 1996, 1998). The relatively low discharge of K (Table 1), despite substantial K additions via input waters, implies that input waters acts act as a crucial source of K to rice plants.

5. Conclusions

Across all subwatersheds, NO_3-N, PO_4-P, and NH4-N were generally below levels that could degrade drinking water quality or harm aquatic life. In low-rice subwatersheds, NO_3-N concentrations do have the potential to impact downstream aquatic ecosystems. DON contributed approximately half of the total N concentration and flux leaving these systems. Total growing season input and discharge loads of mineral N and PO_4-P were small compared to fertilizer inputs, while K surface water input loads were substantial and likely act as a significant source of this nutrient to rice plants.

The total growing season discharge at which net surface water NO_3-N, NH_4-N, PO_4-P, and DON loads equaled zero ranged from 3500 to 6600 m^3 ha^{-1}. Below these rates, nutrient discharge loads tended to be lower than input loads, which indicates that the control of discharge is a critical tool that can be used to manage nutrient export from rice-growing systems.

LME analysis indicated that nutrient fluxes decreased over the course of the growing season, and increased with discharge. NO_3-N concentration and flux decreased with percent rice area. PO_4-P concentration increased with percent rice area, and decreased over the progression of the growing season. Concentrations of K and DON decreased from the onset of flooding through the maintenance flow period, and increased at the end of the growing season. Concentrations of NH_4-N were at or near non-detectable levels for much of the growing season, with the exception of a peak on July 10, which is most likely due to top-dressing of flooded fields with NH_4 fertilizer. Soil characteristics were not significant predictors of nutrient concentration and flux. The results of this study show that the amount of rice in a given subwatershed, and the fertilization and irrigation practices associated with rice cultivation, have a unique impact on surface water nutrient concentration and discharge rates relative to non-rice agriculture. Currently, most models of watershed nutrient dynamics treat all forms of agriculture as one land use variable, but the distinct impacts of rice cultivation, particularly on N and P, indicate that rice-growing areas should be treated separately in future watershed studies.

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References

Aitkenhead-Peterson, J.A., McDowell, W.H., Neff, J.C., 2003. Sources, production, and regulation of allochthonous dissolved organic matter inputs to surface waters. In: Findlay, S.E.G., Sinsabaugh, R.L. (Eds.), Aquatic Ecosystems: Interactivity of Dissolved Organic Matter. Elsevier, New York, pp. 25–70.
Allan, J.D., Erickson, D.L., Fay, J., 1997. The influence of catchment land use on stream integrity across multiple spatial scales. Freshw. Biol. 37, 149–161.
Arheimer, B., Liden, R., 2000. Nitrogen and phosphorus concentrations from agricultural catchments—influence of spatial and temporal variables. J. Hydrol. 227, 140–159.

Bajwa, M.I., 1982. Soil clay mineralogies in relation to fertility management—effect of clay mineral types on ammonium fixation under conditions of wetland rice culture. Agronomy J. 74, 143–144.
Bajwa, M.I., 1987. Comparative ammonium and potassium fixation by some wetland rice soil clays as affected by mineralogical composition and treatment sequence. J. Agronomy.Crop Sci. 158, 65–68.
Bouman, B.A.M., Castaneda, A.R., Bhuiyan, S.I., 2002. Nitrate and pesticide contamination of groundwater under rice-based cropping systems: past and current evidence from the Philippines. Agric. Ecosyst. Environ. 92, 185–199.
Bouman, B.A.M., Humphreys, E., Tuong, T.P., Barker, R., 2007. Rice and water. Adv. Agron. 92, 187–237.
Boyer, E.W., Goodale, C.L., Jaworsk, N.A., Howarth, R.W., 2002. Anthropogenic nitrogen sources and relationships to riverine nitrogen export in the northeastern USA. Biogeochemistry 57, 137–169.
Caraco, N.F., Cole, J.J., 2003. The importance of organic nitrogen production in aquatic systems: a landscape perspective. In: Findlay, S.E.G., Sinsabaugh, R.L. (Eds.), Aquatic Ecosystems: Interactivity of Dissolved Organic Matter. Elsevier, New York, pp. 263–283.
Carpenter, S.R., Caraco, N.F., Correll, D.L., Howarth, R.W., Sharpley, A.N., Smith, V.H., 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecol. Appl. 8, 559–568.
CH2MHILL, 2003. GCID drainwater operations study: a CALFED water use efficiency program study. Glenn-Colusa Irrigation District, 344 East Laurel Street, Willows, CA, USA.
Chow, A.T., Lee, S.T., O'Geen, A.T., Orozco, T., Beaudette, D., Wong, P.K., Hernes, P.J., Tate, K.W., Dahlgren, R.A., 2009. Litter contributions to dissolved organic matter and disinfection byproduct precursors in California oak woodland watersheds. J. Environ. Qual. 38, 2334–2343.
De Datta, S.K., 1981. Principles and Practices of Rice Production. John Wiley & Sons, New York.
de Wit, M., 1999. Modelling nutrient fluxes from source to river load: a macroscopic analysis applied to the Rhine and Elbe basins. Hydrobiologia 410, 123–130.
Di, H.J., Cameron, K.C., 2002. Nitrate leaching in temperate agroecosystems: sources, factors and mitigating strategies. Nutr. Cycl. Agroecosyst. 64, 237–256.
Doane, T.A., Horwath, W.R., 2003. Spectrophotometric determination of nitrate with a single reagent. Anal. Lett. 36, 2713–2722.
Dobermann, A., Sta, P.C., Cassman, K.G., 1996. Fertilizer inputs, nutrient balance, and soil nutrient-supplying power in intensive, irrigated rice systems.1 Potassium uptake and K balance. Nutr. Cycl. Agroecosyst. 46, 1–10.
Dobermann, A., Cassman, K.G., Mamaril, C.P., Sheehy, J.E., 1998. Management of phosphorus, potassium, and sulfur in intensive, irrigated lowland rice. Field Crop. Res. 56, 113–138.
Dubrovsky, N.M., Burow, K.R., Clark, G.M., Gronberg, J.M., Hamilton P.A., Hitt, K.J., Mueller, D.K., Munn, M.D., Nolan, B.T., Puckett, L.J., Rupert, M.G., Short, T.M., Spahr, N.E., Sprague, L.A., Wilber, W.G., 2010. The quality of our nation's waters—nutrients in the nation's streams and groundwater, 1992–2004. United States Geological Survey Circular 1350. Available online at: http://pubs.usgs.gov/circ/1350/ (accessed May 2011).
Dukes, M.D., Evans, R.O., 2006. Impact of agriculture on water quality in the North Carolina Middle Coastal Plain. J. Irrig. Drain. Eng-ASCE 132, 250–262.
ESRI, 2002. ArcGIS: Release 8.3 software. Environmental Systems Research Institute, Redlands, CA, USA.
Evans, R.O., Skaggs, R.W., Gilliam, J.W., 1995. Controlled versus conventional drainage effects on water-quality. J. Irrig. Drain. Eng-ASCE 121, 271–276.
Feng, Y.W., Yoshinaga, I., Shiratani, E., Hitomi, T., Hasebe, H., 2004. Characteristics and behavior of nutrients in a paddy field area equipped with a recycling irrigation system. Agric. Water Manage. 68, 47–60.
Foley, J.A., DeFries, R., Asner, G.P., Barford, C., Bonan, G., Carpenter, S.R., Chapin, F.S., Coe, M.T., Daily, G.C., Gibbs, H.K., Helkowski, J.H., Holloway, T., Howard, E.A., Kucharik, C.J., Monfreda, C., Patz, J.A., Prentice, I.C., Ramankutty, N., Snyder, P.K., 2005. Global consequences of land use. Science 309, 570–574.
Forster, J.C., 1995. Soil nitrogen. In: Alef, K., Nannipieri, P. (Eds.), Methods in Applied Soil Microbiology and Biochemistry. Academic Press, San Diego, CA, USA, pp. 79–87.
Gambrell, R.P., Gilliam, J.W., Weed, S.B., 1975. Denitrification in subsoils of north-Carolina coastal-plain as affected by soil drainage. J. Environ. Qual. 4, 311–316.
GCID, 2009. Glenn-Colusa Irrigation District report on water measurement program for 2008, 47th Edition. Glenn-Colusa Irrigation District, 344 East Laurel Street, Willows, CA, USA.
Glenn County, 1993. Glenn County general plan volume III: environmental settings technical paper. Available online at: http://gcplanupdate.net/general_plan/default.asp (accessed May 2011).
Hafeez, M.M., Bouman, B.A.M., Van de Giesen, N., Vlek, P., 2007. Scale effects on water use and water productivity in a rice-based irrigation system (UPRIIS) in the Philippines. Agric. Water Manage. 92, 81–89.
Hedin, L.O., Armesto, J.J., Johnson, A.H., 1995. Patterns of nutrient loss from unpolluted, old-growth temperate forests—evaluation of biogeochemical theory. Ecology 76, 493–509.
Hernes, P.J., Spencer, R.G.M., Dyda, R.Y., Pellerin, B.A., Bachand, P.A.M., Bergamaschi, B.A., 2008. The role of hydrologic regimes on dissolved organic carbon composition in an agricultural watershed. Geochim. Cosmochim. Acta 72, 5266–5277.
Hill, A.R., 1981. Stream phosphorus exports from watersheds with contrasting land uses in southern Ontario. Water Resour. Bull. 17, 627–634.
Hill, J.E., Williams, J.F., Mutters, R.G., Greer, C.A., 2006. The California rice cropping system: agronomic and natural resource issues for long-term sustainability. Paddy Water Environ. 4, 13–19.
Hood, E., Gooseff, M.N., Johnson, S.L., 2006. Changes in the character of stream water dissolved organic carbon during flushing in three small watersheds. Oregon. J. Geophys. Res. Biogeosci. 111, G01007.
Ip, Y.K., Chew, S.F., Randall, D.J., 2001. Ammonia toxicity, tolerance, and excretion. In: Patricia, W., Paul, A. (Eds.), Fish Physiology. Academic Press, New York, pp. 109–148.
IRRI, 2010. Temperate rice consortium: about temperate rice. International Rice Research Institute. Available online at: http://beta.irri.org/index.php/Networks/Temperate-Rice-Research-Consortium/Areas-of-Production.html (accessed July 2011).
Jardine, P.M., Wilson, G.V., McCarthy, J.F., Luxmoore, R.J., Taylor, D.L., Zelazny, L.W., 1990. Hydrogeochemical processes controlling the transport of dissolved organic carbon through a forested hillslope. J. Contam. Hydrol. 6, 3–20.
Johnson, L.B., Richards, C., Host, G.E., Arthur, J.W., 1997. Landscape influences on water chemistry in Midwestern stream ecosystems. Freshw. Biol. 37, 193–208.
Johnston, C.A., Detenbeck, N.E., Niemi, G.J., 1990. The cumulative effect of wetlands on stream water-quality and quantity—a landscape approach. Biogeochemistry 10, 105–141.
Johnston, C.A., 1991. Sediment and nutrient retention by fresh-water wetlands—effects on surface-water quality. Crit. Rev. Environ. Sci. Tech. 21, 491–565.
Jordan, T.E., Correll, D.L., Weller, D.E., 1997. Effects of agriculture on discharges of nutrients from coastal plain watersheds of Chesapeake Bay. J. Environ. Qual. 26, 836–848.
Kalbitz, K., Solinger, S., Park, J.H., Michalzik, B., Matzner, E., 2000. Controls on the dynamics of dissolved organic matter in soils: a review. Soil Sci. 165, 277–304.
Kao, C.M., Wu, M.J., 2001. Control of non-point source pollution by a natural wetland. Water Sci. Technol. 43, 169–174.
Kogel-Knabner, I., Amelung, W., Cao, Z.H., Fiedler, S., Frenzel, P., Jahn, R., Kalbitz, K., Kolbl, A., Schloter, M., 2010. Biogeochemistry of paddy soils. Geoderma 157, 1–14.
Kroeze, C., Aerts, R., van Breemen, N., van Dam, D., van der Hoek, K., Hofschreuder, P., Hoosbeek, M., de Klein, J., Kros, H., van Oene, H., Oenema, O., Tietema, A., van der Veeren, R., de Vries, W., 2003. Uncertainties in the fate of nitrogen. I: an overview of sources of uncertainty illustrated with a Dutch case study. Nutr. Cycl. Agroecosyst. 66, 43–69.
Krupa, M., Spencer, R.G.M., Tate, K.W., Six, J., van Kessel, C., Linquist, B.A., Controls on dissolved organic carbon composition and export from rice-dominated systems. Biogeochemistry, in press.
Lewis, D.J., Singer, M.J., Dahlgren, R.A., Tate, K.W., 2006. Nitrate and sediment fluxes from a California rangeland watershed. J. Environ. Qual. 35, 2202–2211.
Liang, X.Q., Chen, Y.X., Li, H., Tian, G.M., Ni, W.Z., He, M.M., Zhang, Z.J., 2007. Modeling transport and fate of nitrogen from urea applied to a near-trench paddy field. Environ. Pollut. 150, 313–320.
Lowrance, R.R., Leonard, R.A., Asmussen, L.E., Todd, R.L., 1985. Nutrient budgets for agricultural watersheds in the southeastern coastal-plain. Ecology 66, 287–296.
MacDonald, L.H., 1991. Monitoring guidelines to evaluate effects of forestry activities on streams in the Pacific Northwest and Alaska. United States Environmental Protection Agency, Region 10, Nonpoint Source Section, Seattle, WA (EPA/910/9-91-001).
McDowell, W.H., Asbury, C.E., 1994. Export of carbon, nitrogen, and major ions from 3 tropical montane watersheds. Limnol. Oceanogr. 39, 111–125.
McDowell, R.W., Sharpley, A.N., Condron, L.M., Haygarth, P.M., Brookes, P.C., 2001. Processes controlling soil phosphorus release to runoff and implications for agricultural management. Nutr. Cycl. Agroecosyst. 59, 269–284.
Meyer, J.L., Likens, G.E., 1979. Transport and transformation of phosphorus in a forest stream ecosystem. Ecology 60, 1255–1269.
Murphy, J., Riley, J.P., 1962. A modified single solution method for determination of phosphate in natural waters. Anal. Chim. Acta 26, 678–681.
Nijboer, R.C., Verdonschot, P.F.M., 2004. Variable selection for modelling effects of eutrophication on stream and river ecosystems. Ecol. Model. 177, 17–39.
Norton, M.M., Fisher, T.R., 2000. The effects of forest on stream water quality in two coastal plain watersheds of the Chesapeake Bay. Ecol. Eng. 14, 337–362.
Novotny, V., 1999. Diffuse pollution from agriculture—a worldwide outlook. Water Sci. Technol. 39, 1–13.
Patrick, W.H., Khalid, R.A., 1974. Phosphate release and sorption by soils and sediments—effect of aerobic and anaerobic conditions. Science 186, 53–55.
Peterjohn, W.T., Correll, D.L., 1984. Nutrient dynamics in an agricultural watershed—observations on the role of a riparian forest. Ecology 65, 1466–1475.
Pinheiro, J.C., Bates, D.M., 2000. Mixed-Effects Models in S and S-PLUS. Springer, New York.
Powlson, D.S., Addisott, T.M., Benjamin, N., Cassman, K.G., de Kok, T.M., van Grinsven, H., L'Hirondel, J.L., Avery, A.A., van Kessel, C., 2008. When does nitrate become a risk for humans? J. Environ. Qual. 37, 291–295.
Prior, H., Johnes, P.J., 2002. Regulation of surface water quality in a Cretaceous Chalk catchment. UK: an assessment of the relative importance of instream and wetland processes. Sci. Total Environ. 282, 159–174.
R Development Core Team, 2009. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. Available online at: http://www.R-project.org (accessed May 2011).
Royer, T.V., David, M.B., Gentry, L.E., 2006. Timing of riverine export of nitrate and phosphorus from agricultural watersheds in Illinois: Implications for reducing nutrient loading to the Mississippi River. Environ. Sci. Technol. 40, 4126–4131.
Ruark, M.D., Linquist, B.A., Six, J., van Kessel, C., Greer, C.A., Mutters, R.G., Hill, J.E., 2010. Seasonal losses of dissolved organic carbon and total dissolved solids from rice production systems in Northern California. J. Environ. Qual. 39, 304–313.

RWQCB, 2008. A compilation of water quality goals. California Regional Water Quality Control Board, Central Valley Region. Available online at: http://www.swrcb.ca.gov/water_issues/programs/water_quality_goals/docs/wq_goals_2008.pdf (accessed May 2011).

Sanderman, J., Lohse, K.A., Baldock, J.A., Amundson, R., 2009. Linking soils and streams: sources and chemistry of dissolved organic matter in a small coastal watershed. Water Resour. Res., 45.

Skaggs, R.W., Breve, M.A., Gilliam, J.W., 1994. Hydrologic and water-quality impacts of agricultural drainage. Crit. Rev. Environ. Sci. Technol. 24, 1–32.

Sliva, L., Williams, D.D., 2001. Buffer zone versus whole catchment approaches to studying land use impact on river water quality. Water Res. 35, 3462–3472.

Soil Survey Staff, 2009. Soil Survey Geographic (SSURGO) Database for Glenn and Colusa counties, California. Natural Resources Conservation Service, United States Department of Agriculture. Available online at: http://soildatamart.nrcs.usda.gov (accessed May 2011).

Spencer, R.G.M., Hernes, P.J., Ruf, R., Baker, A., Dyda, R.Y., Stubbins, A., Six, J., 2010. Temporal controls on dissolved organic matter and lignin biogeochemistry in a pristine tropical river. Democratic Republic of Congo. J. Geophys. Res. Biogeosci., 115.

StataCorp, 2009. Stata/SE 11.1 for Windows. StataCorp LP, College Station, TX, USA.

Systat Software, 2006. Sigmaplot for Windows version 10.0. Systat Software, Inc., Chicago, IL, USA.

Tipping, E., Woof, C., Rigg, E., Harrison, A.F., Ineson, P., Taylor, K., Benham, D., Poskitt, J., Rowland, A.P., Bol, R., Harkness, D.D., 1999. Climatic influences on the leaching of dissolved organic matter from upland UK Moorland soils, investigated by a field manipulation experiment. Environ. Int. 25, 83–95.

Tsubo, M., Fukai, S., Basnayake, J., Tuong, T.P., Bouman, B., Harnpichitvitaya, D., 2007. Effects of soil clay content on water balance and productivity in rainfed lowland rice ecosystem in northeast Thailand. Plant. Prod. Sci. 10, 232–241.

Tuong, T.P., Bouman, B.A.M., 2003. Rice production in water-scarce environments. In: Kijne, J.W., Barker, R., Molden, D. (Eds.), Water Productivity in Agriculture: Limits and Opportunities for Improvement. CABI Publishing, Wallingford, pp. 53–67.

USEPA, 2000. Nutrient criteria technical guidance manual: rivers and streams. United States Environmental Protection Agency. Available online at: http://www.epa.gov/waterscience/criteria/nutrient/guidance/rivers/rivers-streams-full.pdf (accessed May 2011).

USEPA, 2009. An urgent call to action: report of the state-EPA nutrient innovations task group. United States Environmental Protection Agency. Available online at: http://www.epa.gov/waterscience/criteria/nutrient/nitgreport.pdf (accessed May 2011).

Williams, J.F., 2010. Rice Nutrient Management in California. University of California, Agriculture and Natural Resources, Publication 3516.

Zhao, X., Xie, Y.X., Xiong, Z.Q., Yan, X.Y., Xing, G.X., Zhu, Z.L., 2009. Nitrogen fate and environmental consequence in paddy soil under rice–wheat rotation in the Taihu lake region. China. Plant Soil 319, 225–234.

Zulu, G., Toyota, M., Misawa, S., 1996. Characteristics of water reuse and its effects on paddy irrigation system water balance and the riceland ecosystem. Agric. Water Manage. 31, 269–283.

Zuur, A.F., Ieno, E.N., Walker, N.J., Saveliev, A.A., Smith, G.M., 2009. Mixed Effects Models and Extensions in Ecology with R. Springer, New York.