

Nitrate Leaching in Californian Rice Fields: A Field- and Regional-Scale Assessment

X. Q. Liang,* T. Harter, L. Porta, C. van Kessel, and B. A. Linquist

Irrigated croplands can be a major source of nitrate-N ($\text{NO}_3\text{-N}$) in groundwater due to leaching. In California, where high $\text{NO}_3\text{-N}$ levels have been found in some areas of the Central Valley aquifer, the contribution from rice systems has not been determined. Nitrate leaching from rice systems was evaluated from soil cores (0–2 m), from the fate of ^{15}N fertilizer in replicated microplots, and from about 145 regional groundwater wells. Soil $\text{NO}_3\text{-N}$ concentrations were $\leq 3.3 \text{ mg kg}^{-1}$ (usually $< 1 \text{ mg kg}^{-1}$) below the root zone (below 33 cm depth). In pore-water samples, $\text{NO}_3\text{-N}$ was observed only below the root zone during the first 2 wk after the onset of flooding in either the growing season or the winter fallow period and was always $\leq 8.4 \text{ mg L}^{-1}$. Fertilizer ^{15}N accounted for 0 to 11.8% of $\text{NO}_3\text{-N}$ in pore-water samples below the root zone. One year after application, based on an analysis of soil core samples, on average 2.5% of fertilizer N was recovered as ^{15}N below the root zone (33–100 cm), possibly due to leaching in permeable soils or via preferential flow through cracks in heavy clay soils. Based on a regional assessment, groundwater samples from wells that are located in proximity to rice fields all had measured median $\text{NO}_2\text{-N}$ and $\text{NO}_3\text{-N}$ levels below 1 mg L^{-1} . These results indicate that $\text{NO}_3\text{-N}$ leaching from the majority of California rice systems poses little risk to groundwater under current crop management practices.

NITRATE ($\text{NO}_3\text{-N}$) has been well documented as the most widespread contaminant in the Earth's surface waters caused by anthropogenic activities, posing a threat to drinking water supplies and promoting eutrophication (Burns et al., 2009; McIsaac et al., 2001). High $\text{NO}_3\text{-N}$ concentration is believed to be a health hazard because it may cause methemoglobinemia in infants and may be responsible for increases in stomach cancer in other humans (Comly, 1945; Mancas et al., 2001; Powlson et al., 2008). Given this, the USEPA (2012) has set the maximum contaminant level for $\text{NO}_3\text{-N}$ in drinking water at 10 mg L^{-1} . Agriculture increases the amount of biologically available N through fertilizer applications, and leaching of $\text{NO}_3\text{-N}$ from croplands is suspected to contribute to the deterioration of surrounding water systems (Galloway et al., 2003).

Rice (*Oryza sativa* L.) is grown globally on approximately 164 million ha (FAO, 2011). Because most rice systems are flooded for much of the season (in this study we only considered flooded rice systems, not upland rice systems), there is the potential to significantly affect N export dynamics in watersheds via downward leaching (Bouman et al., 2007). However, despite this potential, $\text{NO}_3\text{-N}$ leaching is generally not considered to be an important N loss mechanism in most flooded rice soils due to the low water infiltration and high denitrification capacity of these systems (Buresh et al., 2008). Field studies also report $\text{NO}_3\text{-N}$ values below the root zone from near 0 to $< 1 \text{ mg L}^{-1}$ (Tian et al., 2007; Luo et al., 2011). However, $\text{NO}_3\text{-N}$ leaching from rice systems can be significant under certain conditions. First, in highly permeable soils, relatively high $\text{NO}_3\text{-N}$ levels in the soil pore water below the rice root zone have been reported (Zhou et al., 2009; Liang et al., 2007; Yoon et al., 2006); however, Yoon et al. (2006) did not report $\text{NO}_3\text{-N}$ levels in soil pore-water above 9 mg L^{-1} at any time during the rice growing period. Second, alternate wetting and drying of fields can promote nitrification when the soil profile becomes aerobic (Zhou et al., 2012), and leaching may occur when fields are re-flooded (Zhu et al., 2000). When soils dry, this can promote cracking within the dried layers (especially on heavy clay soils). When cracks develop to sufficient

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Abbreviations: DON, dissolved organic N; NRE, ^{15}N recovery efficiency; $\text{NO}_3\text{-N}_f$, fertilizer-induced $\text{NO}_3\text{-N}$; TDN, total dissolved N.

depth due to extensive drying, they can become preferential flow pathways for $\text{NO}_3\text{-N}$ and other forms of N to move below the root zone (Oostindie and Bronswijk, 1995). Third, when rice is rotated with other crops (such as the rice–wheat system common in India and China), researchers have found that $\text{NO}_3\text{-N}$ leaching is much higher during the wheat growing season than during the rice growing season (Zhao et al., 2012; Tian et al., 2007; Zhu et al., 2000).

A recent study in California has brought renewed attention to the problem of $\text{NO}_3\text{-N}$ leaching from California's agricultural systems in certain regions of the state (Harter et al., 2012). Groundwater contamination is a particular health risk because 85% of the California's urban population relies, at least partially, on groundwater for drinking (CDPH, 2008; SWRCB 2013), and rural households rely almost exclusively on groundwater. The contribution of rice systems to groundwater $\text{NO}_3\text{-N}$ in California is not known and has not been previously investigated. Rice is grown on approximately 230,000 ha in California, with most of the production area located in the Sacramento Valley. The objective of this study was to evaluate and quantify $\text{NO}_3\text{-N}$ leaching in Californian rice systems. This objective was accomplished using three approaches: (i) an

examination of $\text{NO}_3\text{-N}$ in the soil profile, (ii) a ^{15}N isotope tracer study, and (iii) a regional review of groundwater quality records from relatively shallow monitoring wells and deeper production wells that might be influenced by recharge from rice fields.

Materials and Methods

Site Description

All studies were located in the Sacramento Valley (Fig. 1), which occupies the northern third of California's Central Valley. Annual precipitation is typical of Mediterranean climates, with an average of 541 mm of rainfall occurring primarily from late fall to early spring, which is outside the rice growing season. The underlying aquifer system is located within the uppermost 400 to 600 m of a sediment-filled structural trough between the Sierra Nevada and Cascade Range (to the east) and the Coastal Range (to the west). The most important regional aquifer is the shallowest, unconfined aquifer, which consists of variably thick (a few meters to 200 m) Pleistocene to Holocene alluvial sediments (Fulton et al., 2003). The alluvial aquifer is divided into three regions (Olmsted and Davis, 1961): the western alluvial fans, plains, and terraces; the central floodplain

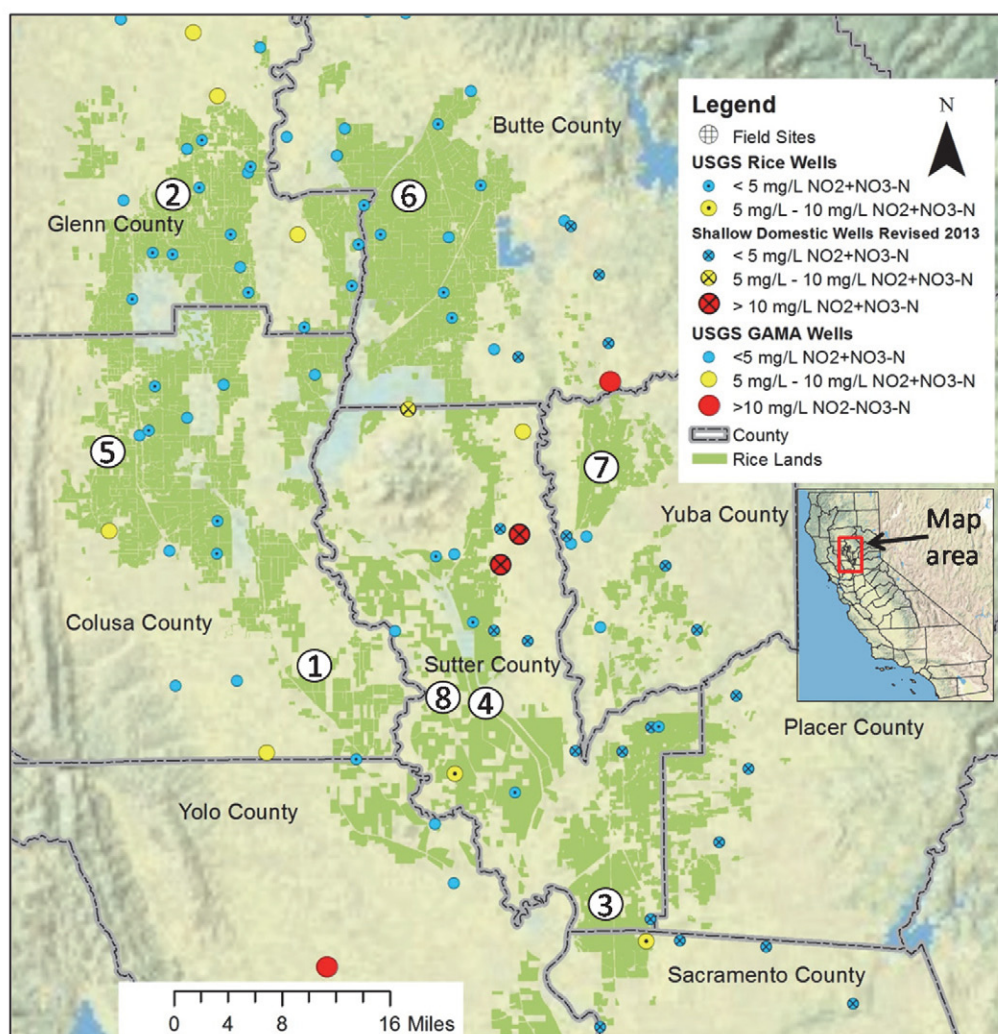


Fig. 1. Map of the Sacramento Valley delineating rice production areas, location of field studies, and locations and types of wells selected to assess groundwater impacts within and near rice lands. Concentrations indicate the maximum measured value over the monitoring period.

region; and the eastern alluvial fans, plains, and terraces. Rice fields are found throughout these three geomorphic regions, predominantly on fine-textured alluvial basin soils of clay and silty clay, sometimes underlain by low permeable hardpans or clay pans (Hill et al., 1997). Groundwater flow is generally from the valley flanks toward the Sacramento River along the valley's generally north–south, long axis, or—south of Colusa and Sutter Buttes—into areas of greatest groundwater extraction east and west of the Sacramento River (Hull, 1984). Approximately 30% of the region's water supply is provided by groundwater pumping (CDWR, 2003).

Nitrate in the Soil Profile

Eight rice fields were selected for this study to represent typical fields in California, with the exception of Site 4, which was selected to represent a soil with high leaching potential (Fig. 1; Table 1). Study locations within each field site were at least 25 m from any field border or levee. In the spring of 2010, before tillage, soils were sampled from two locations in each field (about 10 m apart) to a depth of 2 m using a Giddings soil probe with a 5-cm-diameter probe. At Sites 1 to 4, additional soil samples were taken before tillage in the spring of 2012 and 2013 to a 1-m depth as part of the ^{15}N tracer study discussed below. The soil sample at the beginning of the tracer study (spring 2012) was taken from outside the treatment rings, and the sample at the

Table 1. Cropping system and soil properties of the 2010 field sites.

	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8
Depth	Cropping system†							
	Rotated	Rice	Rice	Rotated	Rice	Rice	Rice	Rotated
	Soil order							
	Vertisol	Mollisol	Vertisol	Entisol	Alfisol	Vertisol	Alfisol	Vertisol
cm	Sand content (g kg ⁻¹)							
0–15	300	220	270	630	340	130	470	100
15–33	190	220	270	680	280	180	340	80
33–66	100	240	260	580	230	170	290	80
66–100	120	280	280	200	250	560	370	100
100–133	90	290	470	170	270	390	490	220
133–167	110	290	350	120	160	570	640	330
167–200	130	160	460	140	140	690	710	220
	Clay content (g kg ⁻¹)							
0–15	570	330	470	110	360	600	260	560
15–33	520	330	420	100	410	620	300	570
33–66	560	320	480	110	420	590	400	570
66–100	530	280	490	190	390	210	280	540
100–133	480	210	310	220	350	300	210	490
133–167	480	200	250	440	360	190	120	420
167–200	500	270	210	420	350	130	70	460
	Total C (g kg ⁻¹)							
0–15	20.5	16.6	14.6	9.8	7.8	10.2	10.6	12.0
15–33	14.6	6.7	5.5	5.9	2.8	6.8	4.0	9.7
33–66	9.1	5.2	4.2	3.8	2.4	6.1	2.2	6.9
66–100	8.1	5.6	3.7	3.0	2.2	17.4	1.0	4.0
100–133	6.3	6.5	4.3	4.7	2.5	4.8	0.8	5.5
133–167	5.9	4.2	2.0	10.4	3.3	0.9	5.5	3.2
167–200	6.5	4.7	1.1	6.2	2.6	0.8	3.1	5.3
	Total N (g kg ⁻¹)							
0–15	1.8	1.5	1.3	0.9	0.9	0.8	0.9	1.0
15–33	1.4	0.6	0.7	0.6	0.5	0.6	0.5	0.8
33–66	0.9	0.6	0.5	0.4	0.5	0.5	0.5	0.6
66–100	0.7	0.5	0.5	0.4	0.4	0.4	0.3	0.3
100–133	0.7	0.5	0.4	0.6	0.5	0.2	0.1	0.4
133–167	0.7	0.5	0.4	0.9	0.4	0.2	0.2	0.3
167–200	0.6	0.5	0.4	0.7	0.5	0.2	0.3	0.5
	Soil bulk density‡ (g cm ⁻³)							
20–25	1.21	1.58	1.56	1.49	1.46	1.15	1.64	1.22
	Hydraulic conductivity‡ (cm d ⁻¹)							
20–25	0.011	0.027	0.007	1.741	0.003	0.074	0.062	0.037

† Cropping system indicates sites that are grown continuously with rice versus sites where rice is rotated with upland crops on a periodic basis.

‡ The bulk density and hydraulic conductivity are taken from soil just below the root zone (~20–25 cm deep).

end of the study (spring 2013) was taken from within the rings. Soil cores were stored in a refrigerated room, and within 48 h the cores were divided up by depth (0–15, 15–33, 33–67, 67–100, 100–133, 133–167, and 167–200 cm) and analyzed for $\text{NO}_3\text{-N}$ in 2010 and for $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, and total dissolved N (TDN) in 2012 and 2013 after extraction with 2 mol L^{-1} KCl (Keeney and Nelson, 1982).

The rooting zone of rice is primarily in the plow layer, below which a plow pan often develops that restricts root growth and water percolation (DeDatta, 1981). Simmonds et al. (2013) found that the plow layer ranges from 7 to 22 cm depth (average, 14 cm) in Californian rice fields. In 2010, the bulk density and hydraulic conductivity of the soil just below the root zone (20–30 cm) was determined at each of the eight sites to examine the potential for water percolation. To accomplish this, the tilled soil layer (roughly the top 20 cm) was removed with a shovel. Brass rings (8.25 cm in diameter and 6 cm deep) were pushed into the soil, and the ring with the soil was removed and taken to the laboratory. Five rings per site were taken. Soils within each ring were saturated with 0.01 mol L^{-1} CaCl_2 in preparation for determination of hydraulic conductivity, which was determined by the saturated falling head method (Klute and Dirksen, 1986). After determination of hydraulic conductivity, the soil samples in the brass rings were oven dried to a constant weight at 110°C and weighed to determine bulk density.

Pore-Water Sampling and ^{15}N Tracer Study

From April 2012 through March 2013, a ^{15}N tracer field study was conducted at Sites 1 to 4 in the approximate location where the 2010 soil samples were taken. In each field, three circular iron rings (75 cm in diameter) representing triplicate microplots were inserted several meters apart from each other into the soil to the depth of the plow pan (roughly 15–20 cm)

(Fig. 2). A hole in the side of each ring ensured that the water height in the ring was the same as on the outside; however, for much of the growing season the floodwater in the field was above the height of the ring.

Pore-water samplers were set up to collect water from within (7.5 cm depth) and below (45 cm depth) the root zone within each ring (Fig. 2). The 45-cm-deep sampler was installed by removing the tilled soil within each ring and then boring a hole to 50 cm deep with an auger. Silica flour (200 mesh) was poured into the hole to fill 2 to 3 cm at the bottom of the hole, after which a porous ceramic pore-water sampler (product #1911, Soil Moisture Equipment Corp.) was inserted into the hole with an attached length of access tubing, and additional silica was poured in to cover the sampler. Bentonite was added to the hole until full to prevent preferential water flow to the sampler. The tilled soil was returned to the ring, and another pore-water sampler (10 cm porous; Rhizon MOM, Rhizosphere Research Products) was laid horizontally in the soil at a depth of 7.5 cm. A Rhizon MOM was also placed above ground and outside the ring at each site to monitor surface water N concentration.

After the installation of pore-water samplers, granular ^{15}N -labeled ammonium sulfate (10 atom %) was evenly applied at a rate of 150 kg N ha^{-1} and raked into the soil surface. At all sites, with the exception of Site 4, the soils were very cloddy, resulting in most of the fertilizer falling to greater depths within the plow layer. Although the N rate is typical for California, the method of application differs. In most cases, 70 to 80% of the N is applied as aqua-ammonia about 7.5 cm below the soil surface (Liquist et al., 2009). The remaining fertilizer N is usually applied to the soil surface before planting as a blended fertilizer containing P and K as well as some N (usually as ammonium sulfate or ammonium phosphate). It is unlikely that the difference in N source or application method would have a large influence on

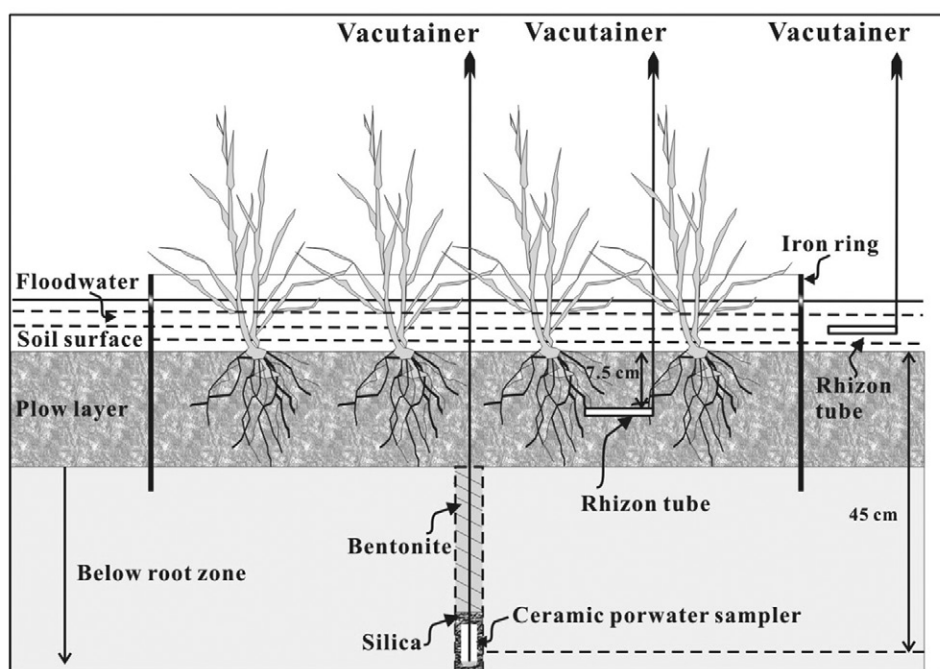


Fig. 2. Sampling equipment and setup to monitor fate of ^{15}N fertilizer in rice fields. These plots were replicated three times in each field. Due to variable plow layer depth, we assumed that soils below 33 cm were below the root zone.

leaching potential because (i) in both cases the N fertilizer is either NH_4 or in a form that rapidly converts to NH_4 and (ii) in both cases the N fertilizer applied ended up being distributed throughout the soil plow layer. Outside the rings, nonlabeled fertilizer N was applied at the same rate. All fields were flooded within 11 d of applying the fertilizer. The soil remained dry, and there was no rain during this period. The area remained flooded until the fields were drained for harvest. Irrigation, rice variety, plant density, and weed control practices in the study plots were otherwise similar to the rest of the field.

At maturity, plants in the microplots were harvested by hand, threshed, and dried, and subsamples were taken for dry matter, grain yield, total N, and ^{15}N analysis. The straw from each plot was returned and incorporated into the soil within each ring before winter flooding or rains. After rice harvest and before returning rice straw to the rings, soil samples were taken from depths of 0 to 15 cm, 15 to 30 cm, and 30 to 45 cm from within each ring. The holes left in soil from sampling were filled with bentonite below 15 cm to avoid surface soil from falling to deeper depths and flagged to avoid sampling near them at the end of the season. This sample (fall 2012) was in addition to the other samples taken in the spring of 2012 and 2013 to a depth of 1 m, as described above.

To facilitate straw decomposition during the winter, the fields were re-flooded at Sites 1 and 2 (Linguist et al., 2006), as is the common practice. Site 3 was not re-flooded. Site 4 was also flooded in winter; however, this field is located in a flood control zone, and flood water depth exceeded 3 m deep, making it impossible to sample during the winter fallow period.

Pore-water samples were taken once a week during the rice growing season in the first month after ^{15}N -labeled fertilizer input and once a month thereafter until rice harvest. During the winter fallow period, pore-water samples were taken twice in the first week after re-flooding or the first winter rain and every 2 wk thereafter, with the exception of Site 4 due to the deep flood noted above. At each sampling event, surface water samples were also taken. Before samples were taken for analysis, at least 10 mL was drawn from the system and discarded to ensure collection of fresh pore-water for analysis. Three water samples were taken consecutively from each sampler at each sampling event in 15-mL vacutainers that were under vacuum. One sample was for $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ analysis and contained 0.2 mL HCl solution (1 mol L^{-1}) to inhibit microbial activity. The other two samples were used for the determination of $^{15}\text{N}\text{-NO}_3$ and did not contain a preservative. All samples were kept in a cooler until returning to the laboratory. The $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ concentrations were determined within 24 h, and the samples for $^{15}\text{N}\text{-NO}_3$ analysis were stored in a freezer until analysis.

Water, Soil, and Plant Analysis

For water samples and soil extracts, the concentrations of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ were determined colorimetrically using the method by Doane and Horwath (2003) and Forster (1995). The TDN concentration was determined as $\text{NO}_3\text{-N}$ after alkaline persulfate oxidation (Cabrera and Beare, 1993). Dissolved organic N (DON) was calculated as TDN minus inorganic N ($\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$). Soils were also analyzed for organic C and N (Nelson and Sommers, 1996) and soil texture (Sheldrick

and Wang, 1993). The ^{15}N abundance of soil and plant samples was analyzed with a Micro Cube elemental analyzer (Elementar Analysensysteme GmbH) interfaced to a PDZ Europa 20–20 isotope ratio mass spectrometer (Sercon Ltd.) at the Stable Isotope Laboratory at UC-Davis. The ^{15}N abundance of $\text{NO}_3\text{-N}$ (detection limit = 0.014 mg L^{-1}) in water samples was determined by the bacteria denitrification method (Sigman et al., 2001) and measured with a Thermofinfinigan GasBench + PreCon trace gas concentration system interfaced to a ThermoScientific Delta V Plus isotope-ratio mass spectrometer.

Data Analysis

The fertilizer-induced $\text{NO}_3\text{-N}$ ($\text{NO}_3\text{-N}_f$) concentration in pore-water was calculated using Eq. [1], where C_s is the total $\text{NO}_3\text{-N}$ detected in pore-water.

$$\text{NO}_3 - \text{N}_f (\text{mg} \times \text{N} \times \text{L}^{-1}) = \frac{\text{Atom \% } ^{15}\text{N}_{\text{excess in soil solution}}}{\text{Atom \% } ^{15}\text{N}_{\text{excess in fertilizer}}} \times C_s \quad [1]$$

The amount of fertilizer N taken up by a plant (or left in the soil) is calculated from the total N in the plant (or soil) and the N isotope ratio in the micro-plots. The N recovery efficiency (NRE) into rice grain, straw, and soil was expressed by Eq. [2] (Rao et al., 1992).

$$\text{NRE}(\%) = \frac{\text{Atom \% } ^{15}\text{N}_{\text{excess in plant or soil}}}{\text{Atom \% } ^{15}\text{N}_{\text{excess in fertilizer}}} \times \frac{\text{NF}}{\text{NR}} \times 100\% \quad [2]$$

where NF is N uptake by the plant or left in one soil layer in the microplot (kg N ha^{-1}). The NF for each soil layer is concentration of N multiplied by the soil layer depth and bulk density (http://www.pedosphere.ca/resources/bulkdensity/triangle_us.cfm); NR is the N rate applied (150 kg N ha^{-1}); and NRE by the whole plant (or soil) is the sum of N recoveries in grain and straw (or in different soil layers).

Groundwater Well Assessment

Datasets from three separate United States Geological Survey (USGS) investigations documenting groundwater quality in the Sacramento Valley, which provide the best available data for this study, were summarized: USGS rice monitoring wells (Dawson, 2001a), USGS National Water-Quality Assessment (NAWQA) Program (Dawson, 2001b), and USGS Groundwater Ambient Monitoring and Assessment (GAMA) Program (Schmitt et al., 2008) (Fig. 1). The rice monitoring wells were established as a randomized, declustered monitoring well network with 10 sites in each of the three hydrogeologic regions (western alluvial plains, central basin, and eastern alluvial plains) to assess groundwater quality in the shallowest aquifer (up to 30 m below ground surface). The network was established and sampled during the 1990s (Dawson, 2001a) and was resampled about every other year in the 2000s. All sites are located within or adjacent to rice fields (at least 75% of the land area within 500 m of each well at the time of construction). The shallow rice monitoring wells are screened within the upper 15 m of the aquifer. If any

recharge to shallow groundwater occurs from rice fields, these monitoring wells are likely to intercept that recharge (e.g., Harter et al., 2002).

As part of the USGS NAWQA Program, a network of 29 domestic wells and two monitoring wells, with depths ranging from 15 to 90 m, was sampled in 1996 and in 2008 in the southeastern part of the study area (Dawson, 2001b). We obtained follow-up datasets for the 2000s to complement the datasets reported by Dawson (2001a,b) from the USGS NWIS data portal.

The USGS GAMA project monitored production and flow path wells in 2006, some of which were in proximity to rice-producing areas. Well location is only accurate to within 1.6 km, and the depth is unknown; however, municipal production wells are typically completed at greater depth than the monitoring and domestic wells and have much higher production rates. These wells were sampled as part of a spatially unbiased random sampling procedure (Schmitt et al., 2008). Of these wells, three were part of USGS flow path studies and were located near rice fields, and 14 public supply and irrigation wells were selected that were located within 1.6 km of rice fields.

Results

Soil Texture and Hydraulic Conductivity

The soils had significant textural variability among sites and throughout the 2-m soil profile (Table 1). In general, with the exception of Site 4, the soils had high clay contents (26–62%) in the 0- to 33-cm layer; however, at deeper depths the texture varied considerably. The hydraulic conductivity below the root zone (except Site 4) ranged from 0.007 to 0.074 cm d⁻¹ (Table 1), which is classified as practically impermeable (Klute and Dirksen, 1986). At Site 4 the hydraulic conductivity was 1.74 cm d⁻¹ (very low

permeability). The bulk density of the soil in this soil layer ranged from 1.2 to 1.6 g cm⁻³.

N in the Soil Profile

In the eight soils sampled in 2010, total soil C and N tended to be highest in the 0- to 15-cm layer and tended to decrease with depth; however, in some soils there were deeper soil layers with relatively high soil C and N contents (i.e., Sites 4 and 6) (Table 1), perhaps due to the alluvial properties of these soils. At the four sites sampled in 2012 and 2013, TDN tended to be highest in the top 15 cm of soil (range, 3.9–12.3 mg N kg⁻¹) and declined with depth (range, 1.5–8.7 mg N kg⁻¹) (Table 2). Dissolved organic N (DON) ranged from 0.3 to 4.6 mg N kg⁻¹ and accounted for 30 to 70% of TDN and changed relatively little with depth (Table 2). As with DON, NH₄-N did not vary much with depth and was low (never exceeding 3.8 mg N kg⁻¹) (Table 2).

Maximum soil NO₃-N concentrations are most likely to be observed in the spring before planting rice. During this period, in the top 33 cm soil NO₃-N ranged from 0.2 to 4.2 mg kg⁻¹ (Table 3). Below the root zone (deeper than 33 cm), soil NO₃-N was below 3 mg kg⁻¹, and, with the exception of Sites 4 and 8, it was below 0.5 mg kg⁻¹. Two years later, in four of the same rice fields (Sites 1–4), preseason (spring 2012) soil NO₃-N contents below the rice root zone were ≤1.1 mg kg⁻¹ at three sites (Table 2). Site 1 had relatively high soil NO₃-N contents in the 1-m soil profile, with values of 7.4 to 8.9 mg kg⁻¹ above 33 cm depth, and relatively low soil NO₃-N (<4 mg kg⁻¹) between 33 and 100 cm (Table 2). The following year (spring 2013), soil NO₃-N contents below the root zone were all <2.0 mg kg⁻¹.

Concentrations of N in Soil Pore-water

Throughout the 1-yr sampling period, NO₃-N concentrations in the surface floodwater were below 0.3 mg L⁻¹ (mostly under

Table 2. Nitrate-N, ammonium-N, dissolved organic N, and total dissolved N within the 1-m soil profile at four sites in 2012 and 2013.

Soil parameters	Soil depth	Spring 2012				Spring 2013			
		Site 1	Site 2	Site 3	Site 4	Site 1	Site 2	Site 3	Site 4
	cm								
NO ₃ -N	0–15	8.9 (1.4)†	1.5 (0.1)	0.0 (0.3)	0.3 (0.2)	2.9 (0.2)	2.3 (0.7)	0.6 (0.1)	3.1 (0.9)
	15–33	7.4 (0.5)	0.3 (0.2)	0.2 (0.1)	0.7 (0.2)	1.8 (0.4)	0.6 (0.4)	0.7 (0.2)	1.4 (0.3)
	33–66	3.3 (0.6)	0.0 (0.1)	0.0 (0.1)	1.1 (0.3)	0.8 (0.1)	0.5 (0.4)	0.9 (0.2)	1.8 (1.4)
	66–100	1.4 (0.6)	0.0 (0.0)	0.0 (0.1)	1.0 (0.8)	0.7 (0.1)	0.3 (0.2)	0.8 (0.2)	1.9 (1.2)
NH ₄ -N	0–15	0.1 (0.4)	1.6 (0.3)	0.3 (0.1)	0.5 (0.1)	0.4 (0.2)	1.9 (0.6)	3.8 (0.1)	2.7 (0.5)
	15–33	0.5 (0.5)	1.8 (1.3)	0.1 (0.1)	0.2 (0.1)	0.6 (0.5)	1.0 (0.3)	3.4 (0.2)	1.0 (0.1)
	33–66	0.2 (0.2)	0.5 (0.1)	0.3 (0.3)	0.3 (0.2)	0.4 (0.0)	0.4 (0.2)	3.4 (0.7)	2.3 (0.3)
	66–100	0.5 (0.3)	1.0 (0.5)	0.1 (0.1)	0.2 (0.2)	0.4 (0.0)	1.1 (0.6)	2.5 (0.4)	2.0 (0.6)
DON‡	0–15	3.3 (0.9)	3.4 (0.3)	3.7 (0.7)	4.0 (0.6)	2.9 (0.8)	1.0 (0.5)	4.6 (2.0)	1.9 (1.1)
	15–33	3.3 (0.0)	2.3 (0.9)	2.3 (0.1)	2.8 (0.5)	2.9 (1.2)	0.9 (0.2)	2.1 (1.6)	2.4 (0.3)
	33–66	3.1 (0.3)	2.0 (0.4)	1.5 (0.5)	2.3 (0.3)	1.9 (0.8)	0.7 (0.7)	3.2 (4.3)	4.6 (2.8)
	66–100	3.1 (0.3)	2.0 (0.3)	1.5 (0.2)	2.7 (0.1)	3.8 (1.3)	0.3 (0.7)	2.6 (2.3)	1.8 (0.9)
TDN§	0–15	12.3 (2.2)	6.4 (0.7)	3.9 (1.0)	4.8 (0.8)	6.3 (0.9)	5.2 (0.5)	8.9 (2.1)	7.7 (2.3)
	15–33	11.2 (0.8)	4.4 (0.6)	2.6 (0.2)	3.7 (0.7)	5.2 (1.9)	2.5 (0.3)	6.2 (1.8)	4.8 (0.1)
	33–66	6.6 (0.9)	2.5 (0.4)	1.7 (0.5)	3.7 (0.2)	3.1 (0.6)	1.5 (0.6)	7.4 (5.1)	8.7 (3.0)
	66–100	4.9 (0.9)	2.9 (0.8)	1.5 (0.3)	3.8 (0.7)	5.0 (1.4)	1.7 (0.5)	6.0 (2.2)	5.6 (1.9)

† Values in parentheses are SEM.

‡ Dissolved organic N: DON = TDN – (NO₃-N + NH₄-N).

§ Total dissolved N.

Table 3. Soil NO₃-N content in the 2-m soil profile at eight rice field sites in 2010.

Depth	Soil NO ₃ -N							
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8
cm	mg kg ⁻¹							
0–15	2.1 (1.2)†	2.0 (2.1)	0.4 (0.1)	1.9 (1.4)	2.2 (0.2)	4.2 (1.1)	0.9 (0.7)	1.9 (1.0)
15–33	1.3 (0.7)	0.2 (0.2)	0.3 (0.1)	1.4 (0.3)	0.3 (0.2)	0.2 (0.1)	0.5 (0.0)	2.7 (0.2)
33–66	0.5 (0.4)	0.2 (0.2)	0.1 (0.1)	2.9 (0.7)	0.1 (0.0)	0.1 (0.1)	0.1 (0.0)	2.4 (0.9)
66–100	0.5 (0.3)	0.1 (0.1)	0.0 (0.0)	2.4 (0.4)	0.1 (0.0)	0.1 (0.1)	0.1 (0.0)	1.3 (0.4)
100–133	0.4 (0.4)	0.0 (0.0)	0.1 (0.0)	2.1 (0.0)	0.0 (0.0)	0.2 (0.1)	0.1 (0.0)	0.5 (0.2)
133–167	0.1 (0.2)	0.0 (0.0)	0.2 (0.0)	0.6 (0.6)	0.0 (0.0)	0.2 (0.0)	0.0 (0.0)	0.2 (0.0)
167–200	0.0 (0.0)	0.0 (0.0)	0.2 (0.0)	0.1 (0.2)	0.0 (0.0)	0.2 (0.0)	0.1 (0.1)	0.1 (0.0)

† Values in parentheses are SEM.

0.1 mg L⁻¹) at all sites, with relatively little change during the growing or fallow seasons (data not shown). Similarly, NH₄-N and TDN were <1.0 and 2.0 mg L⁻¹, respectively, and changed little over time (data not shown).

In the root zone (7.5 cm deep), NO₃-N in the pore-water during the growing season was <0.1 mg L⁻¹ for most sites (Fig. 3). Only at Site 1 (which also had high soil NO₃-N in the top 15 cm) (Table 2) was NO₃-N higher, being 4 mg L⁻¹ during the week after flooding but decreasing to <1 mg L⁻¹ after 1 wk. From the second week until the end of rice season, NO₃-N concentrations in root zone pore-water ranged from 0 to 0.75 mg L⁻¹ at Site 1 and from 0 to 0.2 mg L⁻¹ at other three sites. During the winter fallow, NO₃-N in the root zone

pore-water was highest after draining (range, 0–6.0 mg L⁻¹). Within 2 wk after flooding in late fall, NO₃-N decreased to undetectable levels.

Below the root zone (at 45 cm depth), NO₃-N concentrations in the pore-water during the growing season were highest (0.5–8.4 mg L⁻¹) immediately after flooding the field (Fig. 4). Nitrate-N concentrations decreased during the first month after flooding, after which they were nondetectable for the rest of the growing season. During the winter fallow period, NO₃-N concentrations below the root zone ranged from 0 to 8.0 mg L⁻¹ and were highest between harvest and the onset of winter flooding or rainfall.

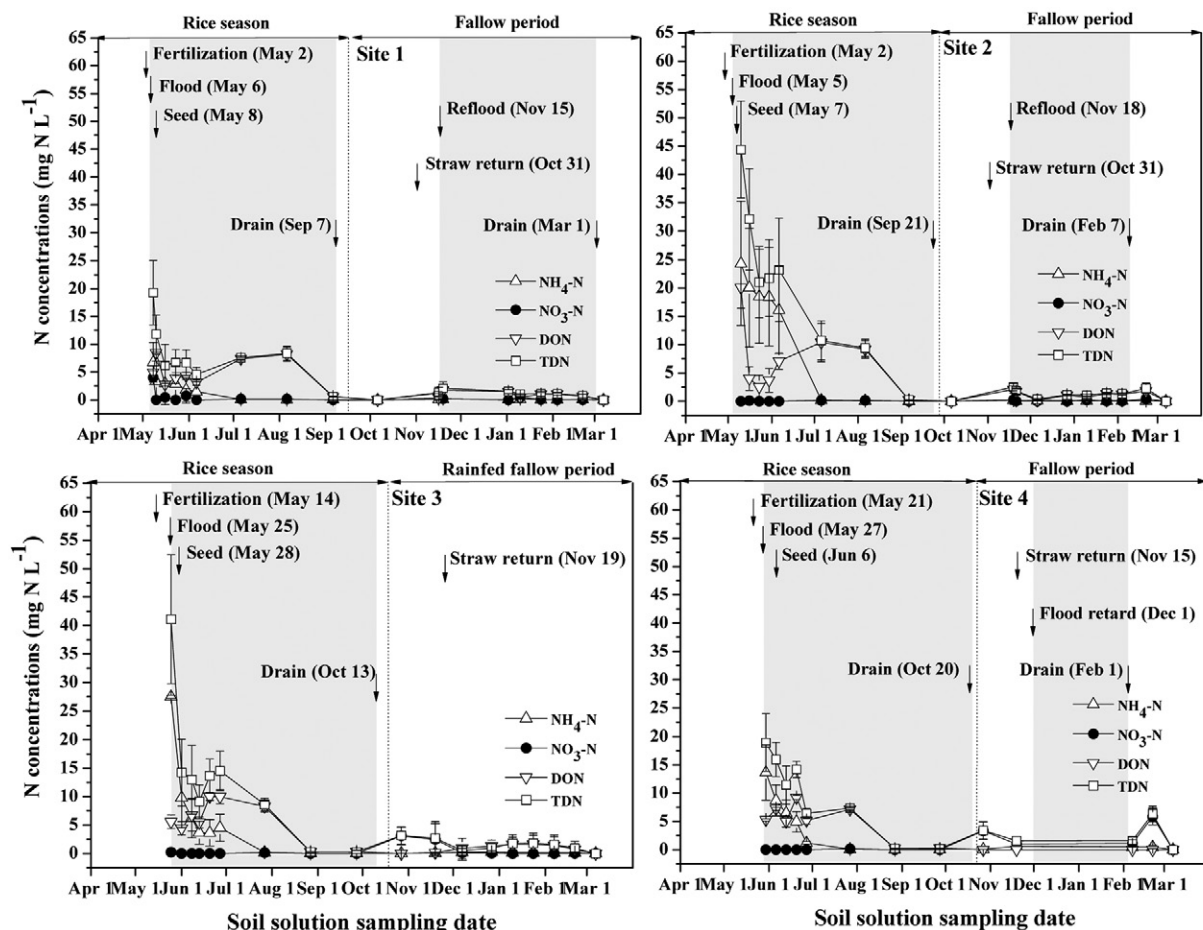


Fig. 3. Total dissolved N (TDN), NH₄-N, NO₃-N, and dissolved organic N (DON = TDN – [NH₄-N + NO₃-N]) in 7.5-cm pore-water at four field sites. Water was sampled from April 2012 to March 2013. Shaded area denotes period when field was flooded. Site 3 was not flooded during the winter.

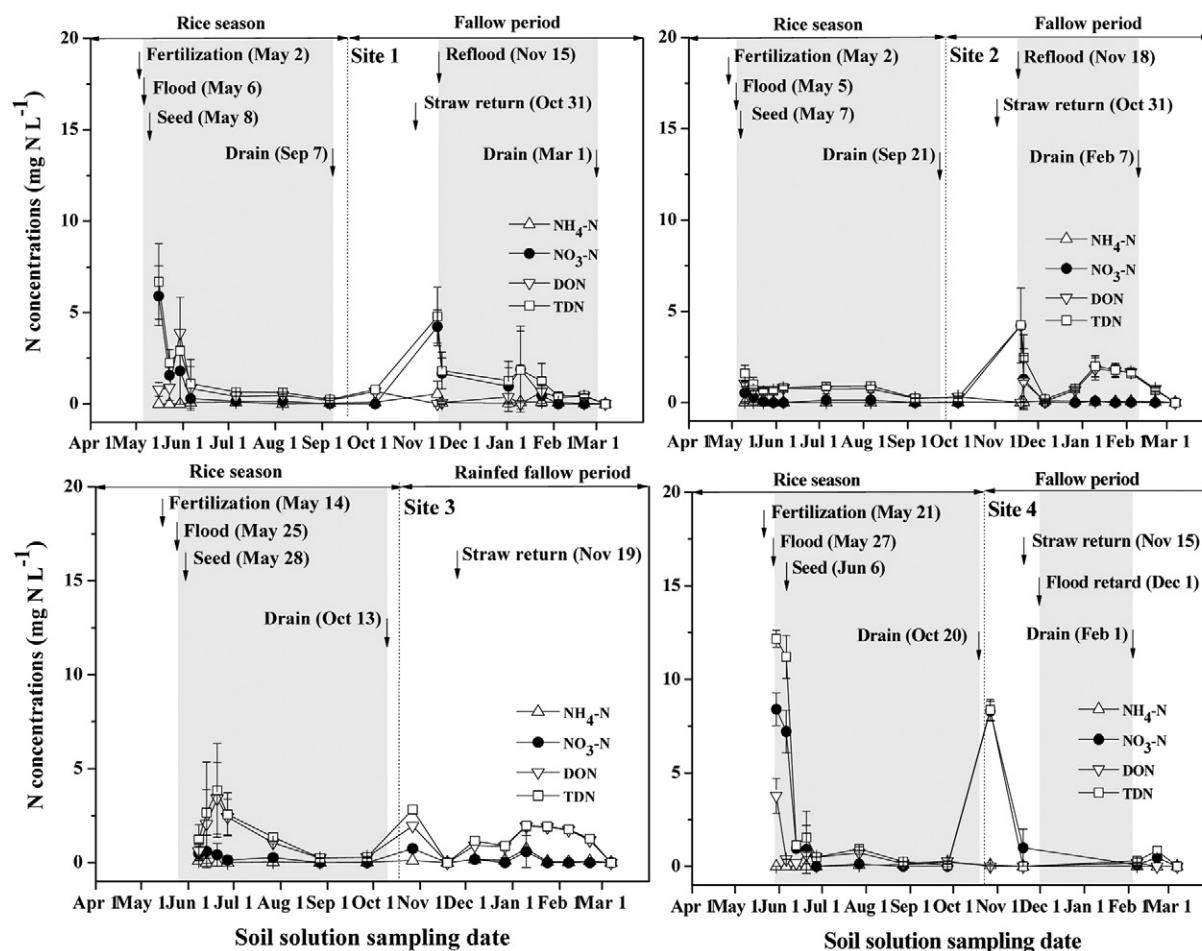


Fig. 4. Total dissolved N (TDN), $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, and dissolved organic N (DON = $\text{TDN} - [\text{NH}_4\text{-N} + \text{NO}_3\text{-N}]$) in 45-cm pore-water at four field sites. Water was sampled from April 2012 to March 2013. Shaded area denotes period when field was flooded. Site 3 was not flooded during the winter.

Ammonium-N was the main form of dissolved N found in the root zone pore-water (Fig. 3) due to fertilizer applications, ranging from 7 to 28 mg N L^{-1} at the beginning of the growing season. During the growing season, $\text{NH}_4\text{-N}$ declined due to plant uptake and possibly other forms of N loss. Below the root zone, $\text{NH}_4\text{-N}$ was always $<0.1 \text{ mg N L}^{-1}$ (Fig. 4). During the winter, $\text{NH}_4\text{-N}$ was low ($<0.8 \text{ mg N L}^{-1}$) in and below the root zone.

Dissolved organic N in pore-water at 7.5 cm depth ranged from 0 to 20.1 mg N L^{-1} . It was generally high at the beginning of the season ($>5 \text{ mg N L}^{-1}$), decreased to nondetectable levels by the end of the growing season, and remained low during the winter fallow period (Fig. 3). Below the root zone, DON was $<4.0 \text{ mg N L}^{-1}$ during the growing season and winter fallow period (Fig. 4).

Fate of ^{15}N Fertilizer

^{15}N in Pore-Water Samples

In the pore-water samples from 7.5 and 45 cm depths at each site, $\text{NO}_3\text{-N}_f$ concentrations were $<1 \text{ mg N L}^{-1}$ throughout the 1-yr sampling period at all sites (Fig. 5). Like total $\text{NO}_3\text{-N}$, the peak values of $\text{NO}_3\text{-N}_f$ concentrations in pore-water appeared only for a short time after the fields were flooded (either for the growing season or for the winter fallow period) or during drain periods. Fertilizer-induced $\text{NO}_3\text{-N}$ accounted for 0 to 28.8% of

total $\text{NO}_3\text{-N}$ in the pore-water samples at 7.5 cm depth and for 0 to 11% at 45 cm depth.

^{15}N Recovery in Plant and Soil

Grain yields ranged from 6.8 to 11.8 Mg ha^{-1} (Table 4). At harvest, the ^{15}N recovered in the grain and straw ranged from 18.5 to 31.8% and from 10.8 to 20.3% of total ^{15}N applied, respectively. In the soil, 39.7 to 42% of the ^{15}N was recovered throughout the soil profile. Based on these recoveries, 11.7 to 27.6% of the fertilizer N was lost (unrecovered) during the growing season.

Before the winter fallow, the straw was incorporated into the soil at each site. At the end of the winter fallow, ^{15}N recovered in the soil ranged from 31.7 to 44.3%, and fertilizer N losses during the winter fallow ranged from 9.5 to 27.3%. In general, the sites where N losses were highest in the growing season (i.e., Site 4) had lower N losses during the winter fallow, and vice versa (i.e., Site 1). Therefore, total annual ^{15}N losses among sites were similar and ranged from 37.1 to 39.0%.

After harvest, 29 to 38.2% of the ^{15}N was recovered in the plow layer soil where the fertilizer was added (Table 5). At the more typical rice fields (Sites 1–3), ^{15}N recovery ranged from 0.8 to 1.4% below the root zone, whereas at Site 4 (a sandy soil) 3.8% of N was recovered in the 30- to 45-cm layer. After the winter fallow, the ^{15}N recovery throughout the profile remained

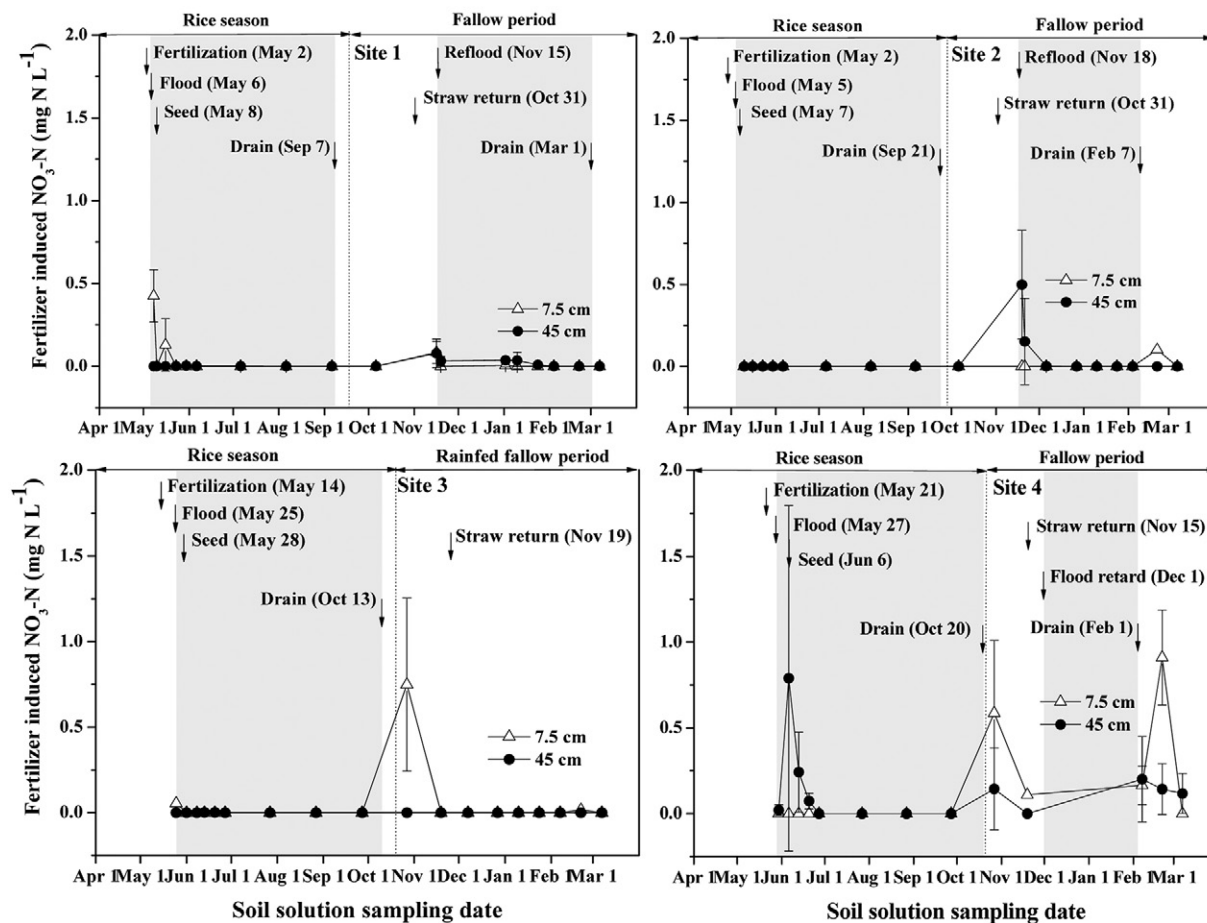


Fig. 5. Temporal changes of fertilizer induced $\text{NO}_3\text{-N}$ concentrations in 7.5-cm (root zone) and 45-cm (below root zone) pore-water at four sites. Site 3 was not flooded during the winter.

Table 4. Yield and N uptake in grain and straw and ^{15}N recovery in grain, straw, and soil after rice harvest (fall 2012) and winter fallow (spring 2013).

	Site 1	Site 2	Site 3	Site 4
Yield (Mg ha^{-1})				
Grain	10.1 (0.2)†	11.8 (0.5)	10.0 (0.8)	6.8 (0.4)
Straw	11.7 (0.6)	10.4 (0.3)	9.2 (0.5)	9.1 (0.9)
N uptake (kg N ha^{-1})				
Grain	90 (3)	150 (21)	115 (9)	100 (7)
Straw	64 (3)	65 (5)	57 (3)	63 (16)
^{15}N recovery (%), fall 2012				
Grain	31.8 (0.9)	29.5 (4.1)	24.2 (1.8)	18.5 (0.8)
Straw	20.4 (0.1)	12.8 (1.7)	10.8 (1.0)	12.7 (3.4)
Soil, 2012	42.0 (9.7)	39.7 (9.0)	40.2 (10.8)	41.0 (5.0)
Total, 2012‡	94.2 (3.4)	82.1 (6.9)	75.3 (12)	72.4 (2.7)
^{15}N recovery (%), spring 2013				
Soil, 2013	31.7 (6.5)	32.4 (4.0)	41.6 (6.3)	44.3 (4.6)
Total, 2013	63.5 (6.9)	62.0 (7.9)	65.9 (5.2)	62.9 (4.5)
Fertilizer N lost§				
Growing season	5.8 (3.4)	17.9 (6.9)	24.7 (12)	27.6 (2.7)
Winter fallow	30.7 (10.8)	20.1 (11.4)	19.0 (4.4)	9.5 (5.7)
Full year	36.5 (7.4)	38.0 (7.9)	37.4 (2.5)	37.1 (4.5)

† Values in parentheses are SEM.

‡ Total ^{15}N recovery in 2012 is calculated as the sum of straw, grain, and soil. In 2013 it was calculated as the sum of grain and soil because the straw was incorporated into the soil after harvest in the fall of 2012.

§ Fertilizer N lost in rice season is calculated by 100% ^{15}N recovery of total 2012; in the fallow period it is calculated as the difference in ^{15}N recovery between total 2012 and total 2013.

largely the same as after harvest despite the residue straw being added to plow layer. In the 0- to 15-cm layer, 28.1 to 38.6%

of the N was recovered, and at the deepest layer (66–100 cm), <1.6% of the N was recovered.

Table 5. Soil ^{15}N background, ^{15}N enrichment, and fertilizer N recovery after rice harvest (fall 2012) and after the winter fallow (spring 2013).

Site	Depth	¹⁵ N background	¹⁵ N enrichment	N recovery
	cm	atom %		%
		Fall 2012		
Site 1	0–15†	0.3671 (0.0001)	0.5369 (0.0379)	37.9 (9.1)
	15–30	0.3671 (0.0001)	0.3828 (0.0033)	2.8 (0.5)
	30–45	0.3671 (0.0001)	0.3782 (0.0020)	1.4 (0.3)
Site 2	0–15	0.3669 (0.0001)	0.5248 (0.0301)	36.0 (8.2)
	15–30	0.3672 (0.0003)	0.3913 (0.0091)	2.9 (1.2)
	30–45	0.3679 (0.0002)	0.3784 (0.0011)	0.8 (0.1)
Site 3	0–15	0.3671 (0.0001)	0.5833 (0.0563)	38.2 (10.0)
	15–30	0.3684 (0.0005)	0.3791 (0.0015)	1.0 (0.1)
	30–45	0.3685 (0.0005)	0.3839 (0.0045)	1.1 (0.4)
Site 4	0–15	0.3664 (0.0004)	0.6621 (0.0180)	29.0 (0.8)
	15–30	0.3659 (0.0009)	0.5325 (0.0221)	8.3 (1.5)
	30–45	0.3681 (0.0009)	0.4989 (0.1070)	3.8 (3.2)
		Spring 2013		
Site 1	0–15	0.3671 (0.0001)	0.4936 (0.0291)	28.1 (6.8)
	15–33	0.3671 (0.0001)	0.3755 (0.0015)	1.8 (0.3)
	33–66	0.3671 (0.0001)	0.3726 (0.0034)	1.5 (0.9)
	66–100	0.3676 (0.0004)	0.3691 (0.0011)	0.3 (0.2)
Site 2	0–15	0.3669 (0.0001)	0.5018 (0.0164)	29.7 (4.0)
	15–33	0.3672 (0.0003)	0.3776 (0.0051)	1.2 (0.6)
	33–66	0.3679 (0.0002)	0.3712 (0.0013)	0.5 (0.2)
	66–100	0.3673 (0.0000)	0.3749 (0.0057)	1.0 (0.7)
Site 3	0–15	0.3671 (0.0001)	0.5954 (0.0294)	38.6 (5.7)
	15–33	0.3684 (0.0005)	0.3855 (0.0060)	1.7 (0.6)
	33–66	0.3685 (0.0005)	0.3730 (0.0032)	0.7 (0.6)
	66–100	0.3684 (0.0003)	0.3737 (0.0066)	0.6 (0.7)
Site 4	0–15	0.3664 (0.0004)	0.6989 (0.0479)	31.8 (4.3)
	15–33	0.3659 (0.0009)	0.4812 (0.0299)	6.1 (1.5)
	33–66	0.3681 (0.0009)	0.4462 (0.0220)	4.9 (0.9)
	66–100	0.3681 (0.0001)	0.3964 (0.0068)	1.6 (0.1)

† Values in parentheses are SEM.

Table 6. Nitrogen water quality of wells in the Sacramento Valley sampled between 2006 and 2010.

Well type and nutrient†	No. of detections/ no. of samples	Min.	Lower quart.	Median	Upper quart.	Max.
USGS RICE monitoring wells, most recent available sample (2006–2010)						
$\text{NH}_4\text{-N}$, mg L^{-1}	14/21	0.01	0.01	0.01	0.02	0.52
$\text{NO}_2 + \text{NO}_3\text{-N}$, mg L^{-1}	21/21	0.036	0.06	0.36	0.88	3.8
Decadal trend, $\text{NO}_2 + \text{NO}_3\text{-N}$, $\text{mg L}^{-1} \text{ yr}^{-1}$	21/21	−0.29	−0.07	−0.0047	0.0011	0.078
Depth to water, m	20/21	0.34	0.52	0.70	1.26	1.52
USGS NAWQA shallow domestic wells, 2008						
$\text{NH}_4\text{-N}$, mg L^{-1}	27/27	0.01	0.02	0.02	0.02	0.11
$\text{NO}_2 + \text{NO}_3\text{-N}$, mg L^{-1}	28/28	0.02	0.14	1.14	3.3	18
Decadal trend, $\text{NO}_2 + \text{NO}_3\text{-N}$, $\text{mg L}^{-1} \text{ yr}^{-1}$	28/28	−0.4	−0.01	0.01	0.06	0.5
Depth to water, m	22/28	1.0	4.3	10.4	24.4	48.2
USGS GAMA production wells in rice area, 2006						
$\text{NO}_3\text{-N}$, mg L^{-1}	14/−	0.13	0.46	0.78	0.94	7.5
USGS GAMA flow path wells in rice area, 2006						
$\text{NO}_3\text{-N}$, mg L^{-1}	3/−	0.03		0.16		1.3

† GAMA, Groundwater Ambient Monitoring and Assessment; NAWQA, National Water-Quality Assessment. Production well and flow path monitoring wells are from 2006 (Schmitt et al., 2008). Trends between 1997 and the late 2000s were evaluated in wells from networks described in Dawson (2001a, b) with long-term records.

Groundwater Well Monitoring

Recent data collected between 2006 and 2010 from the rice monitoring well network indicate that the depth to water varied from 0.34 to 1.5 m below ground surface (Table 6). Depth to groundwater was significantly deeper in the domestic well network (1–48 m; median, 10 m). Ammonium-N concentrations in both networks were low (≤ 0.52 mg L⁻¹). Nitrate-N (plus NO₂-N) concentrations in the rice monitoring well network ranged from <0.04 to 3.8 mg L⁻¹ (median, 0.36 mg L⁻¹). Of the 21 monitoring wells sampled in the late 2000s, only two wells exceeded 2 mg L⁻¹, often considered a lower limit for anthropogenically influenced NO₃-N levels (Nolan et al., 2002). In the domestic well network, where the source area may not be dominated by rice due to its greater depth and greater distance from rice fields, NO₃-N concentrations were higher, with a 2008 median of 1.2 mg L⁻¹ and two well samples from 2008 in excess of the federal health standard for NO₃-N (10 mg L⁻¹). Nine of 28 wells exceeded 2 mg L⁻¹. These values present no significant change from the values reported by Dawson (2001a,b) for 1996–1997. Over the decadal observation period, a decrease in NO₃-N (plus NO₂-N) concentrations was observed in 13 of 21 rice monitoring wells and in 12 of 28 domestic wells (Table 6). No significant upward or downward trend was observed in either well network. Because the USGS GAMA wells are generally deeper and have higher production rates than the monitoring and domestic wells, they represent much larger source areas with inputs that occurred over a significantly longer time period. The median NO₃-N (plus NO₂-N) concentrations of the production wells thought to be potentially affected by rice fields was 0.78 mg L⁻¹ (maximum, 7.5 mg L⁻¹), whereas the median of the flow-path wells was 0.16 mg L⁻¹ (maximum, 1.3 mg L⁻¹). Of all wells evaluated in the region, three had levels that at some point exceeded 10 mg L⁻¹ (Fig. 1). These three wells were either outside of rice-producing areas or on the boundary between rice production and other land use systems. Furthermore, because underground water tends to flow toward the Sacramento River in the middle of the valley, these wells are located on the upstream side of rice-producing areas and are thus more likely influenced by other land uses.

Discussion

Evidence of Nitrate Leaching

Nitrate leaching from rice systems was evaluated using the following approaches: (i) evaluation of extractable soil NO₃-N in soil cores, (ii) pore-water sampling within and below the root zone for NO₃-N and ¹⁵N-NO₃, (iii) determining the fate of ¹⁵N fertilizer in the soil profile, and (iv) regional monitoring well networks that are located in close proximity to rice-producing areas. Results from this analysis show some NO₃-N below the rice root zone; however, the amounts were small, and in no instance were they above 10 mg L⁻¹, the recognized federal health standard (USEPA, 2012). In most cases values were much lower than 10 mg L⁻¹. At four sampling events NO₃-N in pore-water samples below the root zone was between 5 and 8.4 mg kg⁻¹, but these concentrations occurred during brief periods after flooding at the start of the growing season (Sites 1 and 4) or between harvest and winter flooding (Site 4) and are

thus thought to represent temporally brief maxima. Monitoring well data also support that NO₃-N leaching is limited from rice systems. No wells that were likely influenced by rice had NO₃-N levels >10 mg L⁻¹, only three had values between 5 and 10 mg L⁻¹, and the vast majority had concentrations <5 mg L⁻¹ (Fig. 1). Similar findings are reported by others who have investigated shallow well NO₃-N concentrations in relation to land use and have found NO₃-N concentrations in rice dominated landscapes to be <2.0 mg L⁻¹, whereas in landscapes dominated by upland crops it was higher (2–46 mg L⁻¹) (Bouman et al., 2002; Kumazawa, 2002).

The amount of ¹⁵N in each soil layer throughout the soil profile (Table 5) allows us to determine the net amount of fertilizer N that moved below the root zone during the 1-yr study period (it is possible that some fertilizer N leached below the root zone, where it may have denitrified and was lost as gas). It is possible that some of the ¹⁵N observed at the deeper depths is due in part to contamination from the surface soil during soil sampling (which is almost impossible to completely avoid). Nevertheless, using these values, after 1 yr, in the typical rice fields (Sites 1–3) 1.3 to 1.8% (2.1–2.7 kg N ha⁻¹) of applied fertilizer N was recovered below the root zone (33 cm depth). In contrast, at Site 4 (a sandy soil with higher permeability), 6.5% (9.8 kg N ha⁻¹) of the fertilizer was found below the root zone. Others have also found more NO₃-N leaching in highly permeable rice soils (Zhou et al., 2009; Buresh et al., 2008; Vlek et al., 1980), highlighting the importance of good N management in these soils. The amount of leaching found here (1.3–6.5% of fertilizer N) is significantly lower than the 22 and 15% of applied N that is leached from wheat and maize systems (Zhou and Butterbach-Bahl, 2013).

There are a number of reasons why N leaching is low in Sacramento Valley rice fields. First, most rice soils have low hydraulic conductivity. The hydraulic conductivity of the soils below the root zone is classified as practically impermeable, with the exception of Site 4 (very low permeability) (Klute and Dirksen, 1986). It is in part due to this soil characteristic that rice is grown on these soils (Hill et al., 2006). Second, surface soil NO₃-N levels are low. Based on soil core samples from the three sampling events in the spring of 2010, 2012, and 2013, the amount of NO₃-N in the surface soils (0–15 cm) never exceeded 8.9 mg kg⁻¹ and in most cases (88%) was below 3.1 mg kg⁻¹. In other studies of Californian rice systems, NO₃-N levels before planting were also shown to be low, ranging from <1 to 12 mg kg⁻¹ (Linquist et al., 2006). Low soil NO₃-N levels before planting may in part be attributed to weed uptake during early spring (George et al., 1995). Third, fertilizers containing NO₃-N are not applied to rice, and fields are flooded soon after fertilizer application, which limits the nitrification potential during the periods when soils remain flooded (most of the growing period and the winter fallow period). This is evidenced by the low NO₃-N contents (<4 mg L⁻¹) of the soil pore-water samples in the 0- to 15-cm layer where fertilizer N was applied (Fig. 3 and 5). Fourth, much of the NO₃-N in the root zone likely denitrifies shortly after flooding due to anaerobic conditions (Buresh et al., 2008), as seen by the low (usually undetectable) NO₃-N concentrations in the pore-water shortly after flooding (Fig. 3 and 5).

Although there is limited $\text{NO}_3\text{-N}$ leaching at these sites, $\text{NO}_3\text{-N}$ does not appear to accumulate below the root zone. This is evidenced by low $\text{NO}_3\text{-N}$ levels in soil profile samples down to 2 m (Tables 2 and 3) and low $\text{NO}_3\text{-N}$ levels in monitoring wells that are associated with rice systems (Fig. 1). Although many studies have shown that denitrification can be a major loss pathway for N in the plow layer of rice soils (Buresh et al., 2008), denitrification also occurs below the root zone and is a major loss pathway of N below the root zone in saturated soils in rice (Zhu et al., 2003; Xing et al., 2002), riparian (Flynn et al., 1999), and upland systems (Farrell et al., 1996). In Californian rice systems, the water table is often within or just below the root zone (Table 6). Provided there is adequate carbon for microbial activity, it is likely that $\text{NO}_3\text{-N}$ below the root zone denitrifies (Rivett et al., 2008).

The groundwater $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ observations obtained from sampling campaigns in 1996–1997 and in the late 2000s are consistent with the magnitudes of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ leaching found in soil pore-water, confirming that the site-specific data at the field plots are likely representative of the larger-scale impacts of rice farming. Although groundwater data are not available to confirm the potential impacts of short-term, seasonal $\text{NO}_3\text{-N}$ flushing on groundwater quality, the monitoring, domestic, and production wells capture a vertical mixture of water along their respective intake screens. Even the relatively short-screened monitoring wells by Dawson (2001a) represent a vertical mix of recharge water and quality over a period exceeding 1 yr or longer. Domestic and large-scale production well samples consist of mixed groundwater along much longer vertical well screens than shallow monitoring wells and represent average impacts across decadal and longer recharge periods and on a more regional scale (Horn and Harter, 2009).

Mechanisms of Leaching

Although N leaching was minimal in this study, the data do show temporal and spatial variation. In 2010, Sites 4 and 8 had higher soil-extractable $\text{NO}_3\text{-N}$ levels ($2\text{--}3\text{ mg kg}^{-1}$) between 15 and 100 cm depth than in the surface soil (Table 3). Also, in the spring of 2012, Site 1 had relatively high soil $\text{NO}_3\text{-N}$ levels ($1.4\text{--}3.3\text{ mg kg}^{-1}$) below the root zone (Table 2). At all these sites rice is rotated with upland crops (Table 1). Where rice is rotated, the time between rice crops varies from rice being grown 3 to 4 yr out of 5 to being grown once every 5 yr. Similarly, the rotational crops (and their N management) vary considerably, but common crops are tomatoes, beans, melons, and crops grown for the seed industry. Bouman et al. (2002) also reported that $\text{NO}_3\text{-N}$ in shallow groundwater wells was higher ($5\text{--}12\text{ mg L}^{-1}$) in regions where rice was rotated with other crops (vegetables in this case) compared with where rice was grown continuously ($0\text{--}2\text{ mg L}^{-1}$). Where rice is grown continuously (in the northern part of the Sacramento Valley), $\text{NO}_3\text{-N}$ in well water was always below 5 mg L^{-1} , whereas in areas where rice is rotated with other crops (in the southern part of Sacramento Valley), there were a limited number of wells showing 5 to 10 mg L^{-1} of $\text{NO}_3\text{-N}$ in groundwater (Fig. 1). Similar observations have been reported in systems where rice is grown in rotation with other crops. For example, Zhu et al. (2000) reported from rice–wheat rotation in China that $\text{NO}_3\text{-N}$ in the leachate below the root zone exceeded

50 mg L^{-1} when wheat was grown, compared with $<5\text{ mg L}^{-1}$ during the entire rice season and $<1.5\text{ mg L}^{-1}$ when rice was flooded. This pattern persisted even though more fertilizer N was applied to the rice. In another study of a rice–wheat system, Tian et al. (2007) reported that during the rice season $\text{NO}_3\text{-N}$ in leachates never exceeded 1 mg L^{-1} , whereas values up to 8.2 mg L^{-1} were observed during the wheat season.

Site 4 stands out from the others as having higher extractable soil N below the root zone (Tables 2 and 3), more $\text{NO}_3\text{-N}$ in the pore-water below the root zone (Fig. 4 and 5), and the greatest percentage of ^{15}N fertilizer recovered below the root zone (6.5%, compared with 1.5% average for other sites) (Table 5). This site is unusual for Sacramento Valley rice fields in that it is a sandy soil with higher hydraulic conductivity than the other sites (Table 1). However, even at this site, $\text{NO}_3\text{-N}$ values below the root zone never exceeded 8.4 mg L^{-1} (Fig. 4). Other studies have also found $\text{NO}_3\text{-N}$ leaching to be relatively higher on more permeable rice soils (Zhou et al., 2009; Yoon et al., 2006).

Even in the practically impermeable rice soils (Sites 1–3), the amount of N varied over time in the soil profile. At Site 1, for example, in 2010 soil $\text{NO}_3\text{-N}$ was $\leq 2.1\text{ mg kg}^{-1}$ (Table 3), and in 2012 it ranged from 3.3 to 8.9 mg kg^{-1} in the top 66 cm of soil (Table 2). Also, at all sites a small fraction of the ^{15}N was found below the root zone. Given the low permeability of these soils, the downward movement of N in the soil profile may be due to the potential for shrinking and swelling of these clay soils resulting in cracks. Such cracks can be a pathway of N to deeper soil levels through preferential flow as the field is being flooded or through surface soil falling into the cracks (Oostindie and Bronswijk, 1995).

N Budget and Fate of N

By the end of the growing season, 72 to 94% of the applied fertilizer N was accounted for in the plant and soil (Table 4), similar to reports by others (e.g., Patrick and Reddy, 1976). On average, 40% (range, 31–52%) of fertilizer N was taken up by the rice crop, similar to what has been reported for rice by others (Ladha et al., 2005). Based on the N difference method, Linquist et al. (2009) found that 49% of the N applied was recovered in California rice systems; however, N recovery based on the ^{15}N -dilution method is on average 11% higher than that suggested by the N difference method (Ladha et al., 2005). During the course of the year, 36.5 to 38% of the applied fertilizer N was lost. Because leaching losses are accounted for (Table 5), N losses are likely the result of runoff, ammonia volatilization, or denitrification. Surface runoff was not directly measured in this study; however, Krupa et al. (2011) found low $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ levels in California rice drainage waters and reported that average mineral N losses during the growing season were only 1 kg N ha^{-1} . Our study supports those findings in that surface flood water $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$, and TDN were always low, being less than 0.3, 1.0, and 2.0 mg L^{-1} , respectively. Therefore, most N losses can be attributed to denitrification and ammonia volatilization, which are considered the main N loss pathways in most rice systems (Buresh et al., 2008).

Conclusion

This study suggests that under current rice management practices $\text{NO}_3\text{-N}$ leaching under rice fields poses little risk to

groundwater quality in California's Sacramento Valley. Although $\text{NO}_3\text{-N}$ was observed below the root zone of some rice systems it was often below maximum levels considered to evidence anthropogenic influence, with highest measured values typically well below the federal health standard. The highest $\text{NO}_3\text{-N}$ levels were found where rice is rotated with upland crops, during flooding and draining events, and in highly permeable soils with low nutrient retention. Altering management practices, such as introducing upland crop rotations or the use of intermittent flooding (which increases the number of flood/drain events), may increase $\text{NO}_3\text{-N}$ leaching in these systems.

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