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Fertilizer source and placement influence ammonia volatilization losses from water-seeded rice systems

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Abstract

Ammonia volatilization, a primary N loss pathway from rice (*Oryza sativa* L.) production systems, leads to a reduction in N use efficiency and environmental problems. Ammonia volatilization has not been studied in water-seeded rice systems or where aqueous NH_3 is the primary fertilizer N source. Our objective was to quantify NH_3 volatilization from preplant aqueous NH_3 and compare it with drilled or broadcast urea. In addition, NH_3 volatilization from a topdress N application applied midseason was quantified. This was accomplished with 10 field experiments representing a range of soil types. Preplant N treatments were a zero-N control, injected aqueous NH_3, broadcast urea, and drilled urea all applied at the farmer application rate to a dry soil. For the topdress experiment, the treatments were a zero-N control and urea or $(NH_4)_2SO_4$ applied at 34 kg N ha^{-1}. Ammonia volatilization was measured up to 3 and 1 wk after the preplant and topdress N was applied, respectively, using a semi-open static chamber. Losses due to NH_3 volatilization from preplant broadcast urea were significantly higher than from the other other treatments but accounted for <2% of applied N. Losses from aqueous NH_3 and banded urea were lower but were significantly greater than from the control. The losses occurred in the first week after flooding. When N was topdressed, 1.5 and 2.6% of applied N were lost via volatilization from urea and $(NH_4)_2SO_4$, respectively.

1 | INTRODUCTION

Rice (*Oryza sativa* L.) is one of the most important staple crops and feeds almost half of the world's population (Wei & Huang, 2019). It is estimated that rice production must increase by 42% by 2050 to meet the demand of an increasing population (Ray, Mueller, West, & Foley, 2013). To obtain optimal yields in rice systems, N—the nutrient most often limiting—is applied in the largest quantities. Globally, approximately 16 million Mg of N fertilizer was used in rice production in 2017 (International Fertilizer Association, 2017). Nitrogen recovery efficiency (NRE) in rice production systems worldwide averages 46% and is lower than what is reported for maize (*Zea mays* L.) and wheat (*Triticum aestivum* L.) systems (Ladha, Pathak, Krupnick, Six, & van Kessel, 2005).

Ammonia volatilization is recognized as one of the main N loss pathways and is at least partially responsible for lower NRE in rice systems (Freney, Trevitt, De Datta, Obcemea, & Real, 1990), especially in many developing countries with higher growing season temperatures (Bouwman, Boumans, & Batjes, 2002). In addition, NH_3 volatilization can lead to a range of environmental problems including

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Abbreviations: 0N, zero-nitrogen control; Aq-D, drilled aqueous ammonia; AS, ammonium sulfate; DAA, days after application; DAF, days after flooding; FL, flood; NRE, nitrogen recovery efficiency; TD, topdress; Ur-B, broadcast urea; Ur-D, drilled urea.

acidification of soils, eutrophication (Bouwman, Van Vuuren, Derwent, & Posch, 2002; Chen et al., 2018), biodiversity reduction (Bowman, Cleveland, Halada, Hresko, & Baron, 2008; Emmett, 2007), formation of fine particulate matter ($PM_{2.5}$) (Behera, Sharma, Aneja, & Balasubramanian, 2013; Wu et al., 2016), and alteration of the global greenhouse balance (Cameron, Di, & Moir, 2013; Sutton, Erisman, Dentener, & Moller, 2008).

The amount of NH_3 volatilization is directly related to the content of aqueous NH_3 in water at the water–atmosphere interface (Buresh, Reddy, & van Kessel, 2008). The ratio of aqueous NH_3 to ammoniacal N is directly related to the water pH and temperature, with higher pH and temperatures favoring higher concentrations of aqueous NH_3 and consequently NH_3 volatilization losses (Vlek & Craswell, 1981). Additionally, wind speed, soil temperature, pH, and electrical conductivity are positively correlated with NH_3 volatilization (Liu et al., 2015; Rochette et al., 2013), while clay content, soil organic matter, and cation exchange capacity are negatively correlated with NH_3 volatilization (Liu et al., 2015).

A considerable amount of research has focused on mitigating NH_3 volatilization losses from fertilizers applied to rice systems. In general, findings suggest the following: Ammonia volatilization following urea applications is higher than that following $(NH_4)_2SO_4$ (Dillon et al., 2012; Griggs, Norman, Wilson, & Slaton, 2007; Vlek & Craswell, 1979). Second, enhanced efficiency fertilizers such as slow-release, S-coated, or those containing urease inhibitors have been shown to reduce NH_3 volatilization (Beyrouty, Sommers, & Nelson, 1988; Dillon et al., 2012; Fillery & De Datta, 1986; Norman et al., 2009; Xu et al., 2013). For example, Norman et al. (2009) reported that NH_3 volatilization losses were reduced to 2–10% of applied N when urea containing the urease inhibitor *N*-(*n*-butyl)thiophosphoric triamide (NBPT) was used compared with urea alone (17–24% of applied N lost) in dry-seeded rice systems. Third, deep placement of fertilizer (by either direct placement, banding, or incorporating by mechanically mixing with the plow layer) reduces NH_3 volatilization losses (Griggs et al., 2007; Hayashi, Nishimura, & Yagi, 2006; Liu et al., 2015; Norman et al., 2009). Liu et al. (2015), for example, reported a 62% reduction in NH_3 volatilization losses due to deep placement (10 cm) of urea compared with surface-broadcast urea. Fourth, in dry-seeded rice systems, where N fertilizer is broadcast onto the soil surface before a permanent flood, the timing and soil moisture conditions at the time of application are important. In these systems, urea must be broadcast onto a dry soil and the field must be flooded within a few days of application (Dillon et al., 2012; Griggs et al., 2007).

Rice production in California is relatively unique compared with other rice systems in the United States and globally. In California, rice is primarily established using a water-seeded system. Typical practices include the following: After harvest, the rice straw residue is incorporated into the soil and flooded during the winter fallow period to promote straw decomposition (Linquist, Brouder, & Hill, 2006). Tillage usually begins in March, and in late April to early May the seedbed is prepared. One of the last operations in seedbed preparation is the application of fertilizer N. Aqueous NH_3 (NH_3 dissolved in water; 20–25% N) is the most common fertilizer source (Linquist et al., 2009) and is applied by injecting the liquid 7–10 cm below the soil surface in bands. After this, the field is "rolled" using a heavy corrugated roller to break large clods, pack the soil, provide a uniform surface, and create shallow furrows for seeds to fall into. This is followed by flooding the field and aerial seeding. A starter fertilizer of N–P–K is applied either before flooding or delayed and aerially applied 20 to 30 d after seeding to avoid algae buildup (Lundy, Spencer, van Kessel, Hill, & Linquist, 2012). At midseason (panicle initiation), farmers assess the crop N status and may aerially apply a topdress N application as urea or $(NH_4)_2SO_4$ if deficiency symptoms are apparent (Rehman, Borja Reis, Akbar, & Linquist, 2019).

Typical application rates of aqueous NH_3 range from 100 to 160 kg N ha^{-1} (Linquist et al., 2009). While aqueous NH_3 is the most common N source used in California rice systems, it is not uncommon for farmers to use prilled urea instead. In this case, farmers broadcast the urea onto dry soil before the field is flooded. The urea may or may not be mechanically mixed into the soil surface before flooding. Losses due to NH_3 volatilization from aqueous NH_3 applied to rice systems have not been studied in California or elsewhere. Also, relatively few studies have quantified NH_3 volatilization losses following urea being applied to a recently tilled and dry soil. Therefore, the objective of this study was to quantify NH_3 volatilization losses as affected by N source and placement in water-seeded rice systems. In addition, NH_3 volatilization losses from topdress N applications of urea and $(NH_4)_2SO_4$ were quantified.

Core Ideas

- The effect of N fertilizer source, placement, and timing on NH_3 volatilization were quantified.
- In all cases, NH_3 volatilization was <3% of applied N.
- Buried or injected preplant N resulted in lower NH_3 volatilization.
- NH_3 volatilization of preplant N fertilizer occurred during the week after flooding.
- NH_3 volatilization following topdressed $(NH_4)_2SO_4$ was greater than following urea.

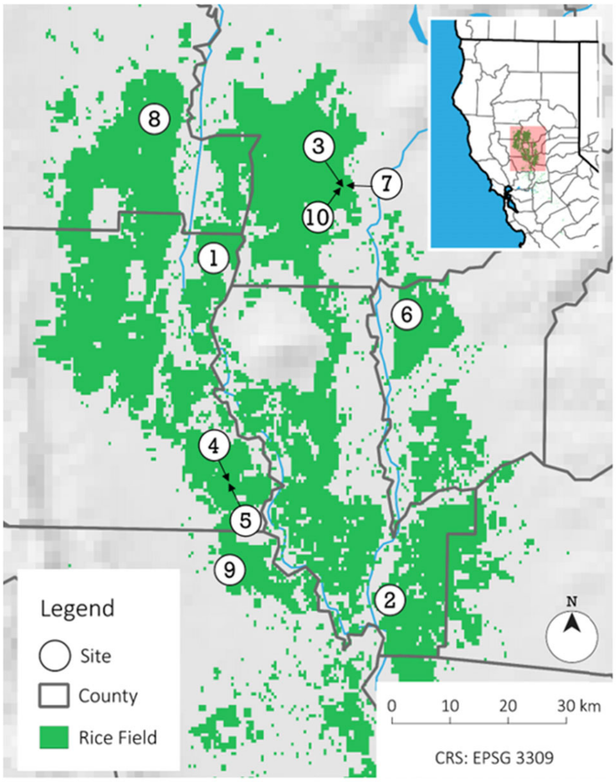

FIGURE 1 Map of site locations and the rice growing area in the Sacramento Valley of California. The rice cropping area is from the National Agricultural Statistics Service (2016), county boundaries are from the State of California (2016), and the base imagery is from ESRI (2009). The map was produced with QGIS Version 3.6 (QGIS Development Team, 2019)

2 | MATERIALS AND METHODS

2.1 | Experimental sites

Field experiments were conducted during the 2017 and 2018 growing seasons at 10 sites in California (Figure 1). Two of the sites (3 and 10) were at the Rice Experiment Station (on different fields) located near Biggs, and the other sites were on commercial rice fields in the Sacramento Valley. Sites were chosen to be a geographic representation of the rice growing region.

The Sacramento Valley has a Mediterranean climate with warm, dry growing conditions. During the two study years, precipitation and air temperature during the growing season (May–October) averaged 2.8 mm and 24.2 °C, respectively (California Irrigation Management Information System, 2019, centrally located Biggs weather station).

2.2 | Experimental design

In 2017, field trials were set up at three sites to quantify NH_3 volatilization from two treatments: drilled aqueous NH_3 (Aq-D) and a zero-N control (0N). In 2018, field experiments were conducted at seven sites and included additional treatments: a broadcast urea (Ur-B) treatment was added to all sites and a drilled urea (Ur-D) treatment to four of those sites (Site 5, 6, 7 and 10) (Table 1). Prilled urea was used in all studies. In all years and fields, treatments were set up in a randomized complete block design with four replications.

For the treatments where fertilizer N was applied, the rate applied was the same as used by the grower in the field at large, and rates ranged from 134 to 177 kg N ha^{-1} (Table 1). All preplant fertilizer N was applied to dry soils, and the fields remained dry (no rain) until they were flooded in preparation for planting. In the Aq-D treatment, the aqueous NH_3 was mechanically injected by the farmer to a depth of 7 to 10 cm using commercial equipment and a band spacing of 13 cm. Microplots (4 m^2) for Ur-D and Ur-B were established in designated areas where the farmer did not apply aqueous NH_3. In the Ur-D treatment, the urea was manually banded to the same depth and spacing as the Aq-D treatment. In the Ur-B treatment, the urea was hand broadcast to the soil surface. Plexiglas cylinders (described below) were inserted into the soil in each plot to quantify NH_3 volatilization. In the Aq-D and Ur-D treatments, these cylinders were positioned over the fertilizer band. In the Ur-B treatment, the cylinders were put in place before broadcasting the urea and an exact amount of urea, corresponding to the area covered by the cylinder, was put inside the tube.

To evaluate NH_3 volatilization losses from topdress N applications, three treatments set up in a randomized complete block design with four replications were evaluated: a zero-N control (TD-0N), urea (TD-Urea), and $(NH_4)_2SO_4$ (TD-AS). This was only done in 2018 at Sites 4 through 10. The experiment was set up in the preplant experiment in the treatment that had received aqueous NH_3 as the preplant treatment (Aq-D). Cylinders were set up in each plot at the panicle initiation stage when growers typically apply topdress N fertilizer. The cylinders were placed between plants (no plants inside the cylinder) with the base of the cylinder being pushed only 2 cm into the ground to avoid root damage. The objective was to quantify NH_3 volatilization losses from the topdress N applications (we were not interested in quantifying plant N uptake and NRE from these treatments). In each cylinder receiving fertilizer N, both the urea and $(NH_4)_2SO_4$ was applied at a rate equivalent to 34 kg N ha^{-1}. No topdress fertilizer was applied outside of the cylinder to the rest of the plot.

2.3 | Ammonia volatilization measurements

The volatilization of NH_3 was quantified using a modification of the semi-open static system described by Beyrouty et al. (1988). This system has been modified by others for use in rice systems (Dillon et al., 2012; Griggs et al., 2007; Norman

TABLE 1 Nitrogen rates and key dates for the preplant NH_3 volatilization trial

Year	Site	N-application date	Flood date	Preplant N rate	Treatments at site[a]	NH_3 volatilization measured for each period[b]			
						Pre-FL	FL	Early-FL	Late-FL
				kg ha^{-1}		d			
2017	1	3 May	8 May	176	0N, Aq-D	4.7	1.2	7.8	6.2
	2	16 May	18 May	134	0N, Aq-D	1.9	1.0	7.0	5.1
	3	1 June	2 June	168	0N, Aq-D	0.9	3.1	6.9	7.3
2018	4	1 May	3 May	168	0N, Aq-D, Ur-B	1.9	1.1	4.1	3.8
	5[c]	3 May	6 May	168	0N, Aq-D, Ur-B, Ur-D	1.3	2.2	4.3	4.2
	6[c]	9 May	13 May	168	0N, Aq-D, Ur-B, Ur-D	2.9	2.1	3.8	4.2
	7[c]	10 May	13 May	168	0N, Aq-D, Ur-B, Ur-D	2.8	1.0	4.2	4.1
	8	14 May	22 May	151	0N, Aq-D, Ur-B	6.9	1.9	4.2	3.6
	9	16 May	20 May	177	0N, Aq-D, Ur-B	2.6	3.1	3.7	5.0
	10[c]	23 May	27 May	168	0N, Aq-D, Ur-B, Ur-D	3.7	1.2	4.0	5.0

[a] 0N, zero-N control; Aq-D, drilled aqueous NH_3; Ur-B, broadcast urea; Ur-D, drilled urea. [b] Pre-FL (from the time the fertilizer was applied until just before the treatment plots were flooded); FL (the time the treatment plots were flooded up to 1 d after flooding); Early-FL (early part of when the field was flooded); Late-FL (late post-flood period). [c] Grain yield and N uptake were quantified from all treatments at these sites.

et al., 2009). While details of the system were reported by Dillon et al. (2012), the system is briefly described here. Transparent Plexiglas cylinders (14.52-cm diameter, 76-cm height) were driven 10 to 15 cm deep into the soil (2 cm deep in the topdress experiment to avoid root damage) either before (Ur-B) or after N application and over the fertilizer bands (Aq-D and Ur-D). Each cylinder contained two circular pieces of polyurethane foam (American Excelsior Company), cut to fit tightly inside the cylinder (referred to as *sorbers*). These sorbers were 2.5 cm thick and were impregnated with 20 ml of a 0.73 M H_3PO_4 and 33% glycerol solution. The lower sorber, placed 15 cm below the top of the cylinder, trapped NH_3 volatilizing from the soil or water surface. The other sorber was placed at the top of the tube and prevented contamination by capturing atmospheric NH_3. White 20-L buckets were placed on top of each cylinder to protect it from rainfall. Airflow between the bucket and the top of the cylinder was maintained by placing a polyvinyl chloride cross-shaped structure between them.

2.4 | Sampling and analysis

Ammonia volatilization was determined for various periods. The duration of the periods varied among sites due to working in commercial farm fields where the desired timing could not always be achieved for various reasons including not knowing when irrigation water would become available and because of pesticide operations preventing access to sites. However, four general periods were defined based on soil flooding and the time of flooding (Table 1). Sorbers were removed and replaced with new ones at the end of each period. The first period extended from the time the fertilizer was applied until just before the treatment plots were flooded, which we defined as preflood (Pre-FL). The timing of this period varied considerably among the sites, but in all cases the soil was dry during this period (no rain). The second period, denoted as flooding (FL), covered the time the treatment plots were flooded up to 1 d after flooding (DAF). This period varied in duration from 1 to 3 d, but the variation in time was always due to longer dry periods before flooding as the period always ended within 1 d after the treatment area was flooded. During the third period, the fields remained flooded and the period ended at 8–10 DAF in 2017 and 5–7 DAF in 2018 (this early post-flood period is denoted as Early-FL). The fourth period, the late post-flood period (Late-FL), ended at 13–17 DAF in 2017 and 9–12 DAF in 2018. For the topdress experiment, two periods were evaluated: from the time of N-fertilizer application to 3 d after application (DAA) and from 3 to 7 DAA, after which the experiment was terminated.

In 2017, the cylinders used to evaluate preplant N remained in one place for the whole monitoring period; however, in 2018, the cylinders were repositioned at the end of the third period to another location within each treatment plot. This was done to alleviate concerns that the soil–water environment within the cylinder was different than what may be expected in the field (Beyrouty et al., 1988). At each experimental site in 2018, a datalogger (HOBO U23 Pro v2; Onset) with temperature sensors was installed on one of the cylinders to measure the water temperature every hour both inside and outside of the cylinder. This was also done in the topdress experiment.

When a sorber was removed, it was placed immediately in a Zip-Lock plastic bag and placed in a cooler. Upon returning to the laboratory, 100 ml of 2 M KCl was added to the bag and the sorber was manually squeezed several times to assure that the KCl was uniformly mixed throughout the sorber. The sorber was stored in a cold room until analysis. To analyze the amount of NH_3–N captured by the sorber, it was manually squeezed 10 times again before squeezing out an aliquot for NH_4^+ analysis. The aliquot was removed from the bag and the NH_4^+ concentration was determined by colorimetric analysis using a spectrophotometer with 650-nm wavelength (Forster, 1995).

At each site, a preplant soil sample (0–15 cm) was taken before any fertilizer was applied. Soils samples were air dried and passed through a 2-mm sieve before analysis. Soils were analyzed for pH (saturated paste extract, U.S. Salinity Laboratory Staff, 1954), cation exchange capacity (Rible & Quick, 1960), electrical conductivity (saturated paste extract; Rhoades, 1982), total N (AOAC International, 1997), soil organic matter (Nelson & Sommers, 1982) and soil texture (Sheldrick & Wang, 1993).

Yield and N uptake were determined from plant samples taken at physiological maturity from Sites 5, 6, 7, and 10 by cutting all aboveground biomass from a 1-m^2 area at ground level. After drying, the rice grain was manually removed from the panicles, cleaned using a seed blower, and dried to constant weight at 60 °C. Grain yields are reported at 14% moisture (standard moisture content for reporting grain yields in California). Grain and straw fractions were ground and analyzed for N concentration.

2.5 | Data analysis

Fertilizer-induced NH_3 volatilization losses were determined from the cumulative emissions across all time periods and calculated as the volatilization from a treatment receiving N minus the volatilization from the 0N control plot. The N recovery efficiency (NRE) was calculated as (Mueller et al., 2017)

$$\frac{N_{\mathrm{fert}}\,\mathrm{uptake} - N_{\mathrm{unfert}}\,\mathrm{uptake}}{\mathrm{Fertilizer\ N\ applied}} \times 100$$

where N_{fert} refers to fertilized plots (kg ha^{-1}), N_{unfert} refers to unfertilized plots (kg ha^{-1}), and fertilizer N is in the same units.

Statistical analyses of the data were performed using R Studio version 1.2 (RStudio Team 2018). The package ggplot2 (Wickham, 2016) was used to visualize the data and construct plots. The data from the preplant experiment were analyzed separately by year. In 2017, a two-sample *t*-test with equal variances was used to detect cumulative NH_3 volatilization differences between the 0N and Aq-D treatments. In 2018, the cumulative NH_3 volatilization data from all locations and treatments were analyzed together using a linear mixed-effects model developed with the lme function of the nlme package (Pinheiro, Bates, DebRoy, & Sarkar, 2019) for both the preplant and topdressing experiments, with treatments as a fixed effect, and site and block as random effects. The 2018 preplant data are unbalanced because not all treatments were implemented at all sites (seven sites total in 2018). The treatment Ur-D was implemented at only four of the seven sites. Results of the mixed effects model analyses returned by the function lme are robust to the effects of unbalanced design (Pinhiero & Bates, 2000). A one-way analysis of variance (ANOVA) was performed on NH_3 volatilization losses and followed by pairwise mean comparisons using Tukey's test. To meet the assumptions of homogeneity of variance and normally distributed residuals for the ANOVA, the cumulative NH_3 volatilization data from the preplant experiment had to be logarithmically transformed. This was not necessary for the topdress experiment.

The grain yield and N uptake data from the four sites that had all four treatments (Table 1) were also analyzed using a linear mixed-effects model developed with the lme function of the nlme package (Pinheiro et al., 2019), with treatments as a fixed effect and site and block as random effects. A one-way ANOVA was performed on grain yield and N uptake and followed by pairwise mean comparisons using Tukey's test. Pearson's correlation analysis was used to evaluate the effect of soil properties on cumulative NH_3 volatilization losses from the Ur-B treatment. For all analyses, the level at which the results were considered significant was $P \leq .05$.

3 | RESULTS

Soil details from each site, including taxonomy and chemical and physical properties, are shown in Table 2. The soil clay content was high (40–54%) at most sites, which is typical for the rice-growing region in the Sacramento Valley, although some sites (1, 6, and 7) were coarser textured. Most soils were slightly acidic, but soil pH was >7 at two sites. Cation exchange capacity ranged from 13 to 49.2 cmol kg^{-1}, electrical conductivity ranged from 0.29 to 1.07 dS m^{-1}, soil organic matter ranged from 12.0 to 21.2 g kg^{-1}, and total soil N content ranged from 0.90 to 1.75 g kg^{-1}.

3.1 | Volatilization from preplant fertilizer nitrogen applications

In 2018, the water temperature inside and outside of the cylinders was measured during the period when NH_3 volatilization was being quantified. Water temperature was similar both inside and outside of the cylinder and

TABLE 2 Selected soil propert0069es (0–15 cm) at each study site

Site	Series	Taxonomic classification	pH	Cation exchange capacity	Electrical conductivity	Total N	Organic matter	Texture		
								Sand	Silt	Clay
				cmol kg^{-1}	dS m^{-1}	——g kg^{-1}——		————%————		
1	Nueva loam	fine-loamy, mixed, superactive, thermic Fluventic Haploxeroll	6.2	24.4	0.31	1.06	12.40	47	32	21
2	Capay silty clay	fine, smectitic, thermic Typic Haploxerert	5.5	38.0	0.49	1.30	15.20	26	32	42
3[a]	Esquon–Neerdobe	fine, smectitic, thermic Xeric Epiaquerts	5.1	24.5	NA	0.90	10.60	29	26	45
4	Scribner clay loam	fine-loamy, mixed, superactive, thermic Cumulic Endoaquoll	7.1	38.5	1.07	1.31	14.10	20	40	40
5	Clear Lake clay	fine, smectitic, thermic Xeric Endoaquert	6.3	49.2	0.46	1.75	21.20	30	21	49
6	San Joaquin loam	fine, mixed, active, thermic Abruptic Durixeralf	4.6	13.0	0.23	1.46	19.10	39	39	22
7	Duric Xerarents–Eastbiggs	thermic Duric Xerarents	4.9	18.2	0.59	1.24	15.20	50	30	20
8	Castro clay	fine, thermic Typic Calciaquoll	7.7	33.0	0.51	1.54	14.60	31	27	42
9	Capay silty clay	fine, smectitic, thermic Typic Haploxerert	6.8	43.5	0.95	1.73	18.00	13	33	54
10	Esquon–Neerdobe	fine, smectitic, thermic Xeric Epiaquerts	4.9	35.4	0.29	1.00	12.00	31	24	45

[a] A preplant soil sample was not taken at this location. Data are from an earlier year, but electrical conductivity data were not available (NA).

TABLE 3 Cumulative NH$_3$ volatilization from the 2017 trials. Data are the average of three sites (1–3, Table 1)

Treatment	Avg. NH$_3$ volatilization	*t*-value	*p* value
	kg NH$_3$-N ha^{-1}		
Zero-N control	0.23 (0.01)	2.34	.03
Drilled aqueous NH$_3$	0.35 (0.05)		

Note. Standard error of the mean in parentheses.

averaged 22.8 °C (data not shown) during the early part of the season when preplant fertilizer N volatilization was being quantified.

There was measurable NH$_3$ volatilization from all treatments in both years, with the amounts being dependent on treatment and site. In 2017, when only 0N and Aq-D treatments were evaluated, cumulative NH$_3$ volatilization was significantly higher in the Aq-D treatment (Table 3); however, NH$_3$ volatilization was <0.4 kg N ha^{-1} in both treatments. Similarly, in 2018, across all sites cumulative NH$_3$ volatilization from the 0N and Aq-D treatments was low, averaging <0.2 kg N ha^{-1}, and not significantly different (Figure 2). Volatilization from the Ur-D treatment was higher than from the 0N and Aq-D treatments but still averaged <0.5 kg N ha^{-1}. At Site 10, NH$_3$ volatilization was highest from Ur-D, and averaged approximately 1.0 kg N ha^{-1}. The Ur-B treatment had the highest volatilization, with cumulative volatilization ranging from 0.5 to 6.4 kg N ha^{-1} and averaging 3.0 kg N ha^{-1}. Fertilizer N lost due to NH$_3$ volatilization averaged 0.04, 1.57, and 0.18% of applied N for Aq-D, Ur-B, and Ur-D, respectively (Table 4).

The period when the majority of NH$_3$ volatilization occurred varied with time and treatment. In the 0N treatment, volatilization was low throughout the monitoring period (Figure 3). In general, when the field was dry (Pre-FL), volatilization was low; however, in the Aq-D treatment there were some observations where NH$_3$ volatilization reached about 0.5 kg N ha^{-1}. During the Early-FL period, which ranged from 5 to 7 d after the field was flooded, volatilization was the highest for both the urea treatments. This was especially the case with the Ur-B treatment where, on average, 2.8 kg N ha^{-1} volatilized. During the last period (Late-FL) volatilization was low in all treatments.

Grain yields and N uptake were higher than the 0N control in all treatments with a preplant N application (Table 5). On average, grain yields and N uptake were 5,800 kg ha^{-1} and 70 kg N ha^{-1}, respectively, in the 0N control. In treatments receiving preplant N, yields, N uptake, and NRE were similar among treatments and averaged 12,040 kg ha^{-1}, 174 kg N ha^{-1}, and 61%, respectively.

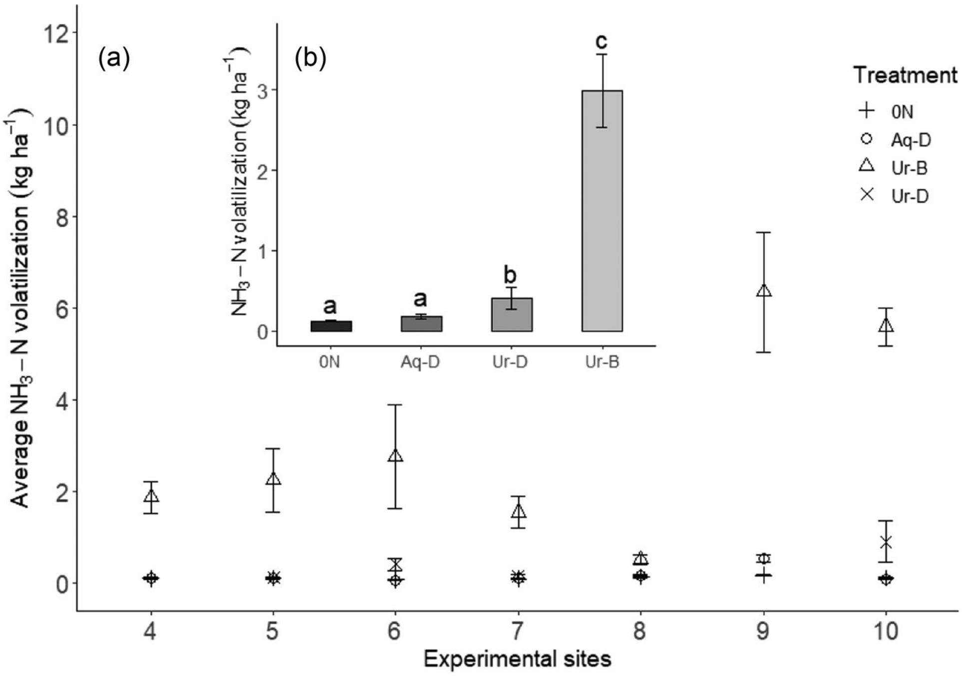

FIGURE 2 (a) The cumulative NH_3 volatilization losses of different treatments from the seven preplant sites in 2018, and (b) cumulative NH_3 volatilization across all sites. The error bars are the standard error of the mean. The lowercase letters in (b) show the statistically significant ($p < .05$) differences between treatments. Treatments are: 0N, zero-N control; Aq-D, drilled aqueous NH_3; Ur-D, drilled urea; and Ur-B, broadcast urea

TABLE 4 Cumulative NH_3 volatilization losses as a percentage of fertilizer N applied from the 2018 trials

Treatment	Fertilizer N loss due to NH_3 volatilization	
	Min. − max.	Mean
	%	
Preplant N application		
Drilled aqueous NH_3	0.00–0.29	0.04 (0.01)
Broadcast urea	0.00–4.97	1.57 (0.29)
Drilled urea	0.00–0.99	0.18 (0.08)
Topdressing N application		
Topdressed urea	0.00–3.76	1.39 (0.23)

Note. Standard error of the mean in parentheses.

3.2 | Topdress trial

As in the preplant N trial, water temperature both inside and outside the cylinder were similar but average temperatures were higher (averaged 25.6 °C, data not shown). Cumulative NH_3 volatilization was higher where topdress N was applied compared with the 0N control (Figure 4). Cumulative volatilization following the application of $(NH_4)_2SO_4$ averaged 0.9 kg N ha^{-1} and was significantly higher than from urea (0.5 kg N ha^{-1}). The NH_3 volatilization from $(NH_4)_2SO_4$ during the first 3 d after application (3 DAA; 0.6 kg N ha^{-1}) was higher than 3 to 7 d after application (7 DAA) (Figure 5). In contrast, NH_3 volatilization from urea was similar for both periods (between 0.2–0.3 kg N ha^{-1}).

4 | DISCUSSION

4.1 | Ammonia volatilization from the zero-nitrogen plots

In plots receiving no fertilizer N, cumulative NH_3 volatilization averaged 0.15 and 0.04 kg N ha^{-1} for the preplant and topdress experiments in 2018 during the course of an average 13 and 7 d, respectively (Figures 2b and 4). The topdress experiment was on plots that had received preplant N; however, LaHue, Chaney, Adviento-Borbe, and Linquist (2016) reported that by the time the topdress N fertilizer was applied in this experiment (panicle initiation) all of the preplant fertilizer N would have been taken up by the plant. Extrapolating the NH_3 volatilization from these two time periods to the whole growing season suggests that when no fertilizer N is applied, seasonal NH_3 volatilization was approximately 1.0 kg N ha^{-1}. This finding is a little lower than that found by Liu et al. (2015), who reported approximately 3.5 kg N ha^{-1} of volatilization losses per season from a zero-N plot in a no-till rice system. The main source of NH_3 in the unfertilized plots is probably the mineralized N from the decomposition of soil organic material by soil microorganisms (Beare, Hendrix, Cabrera, & Coleman, 1994).

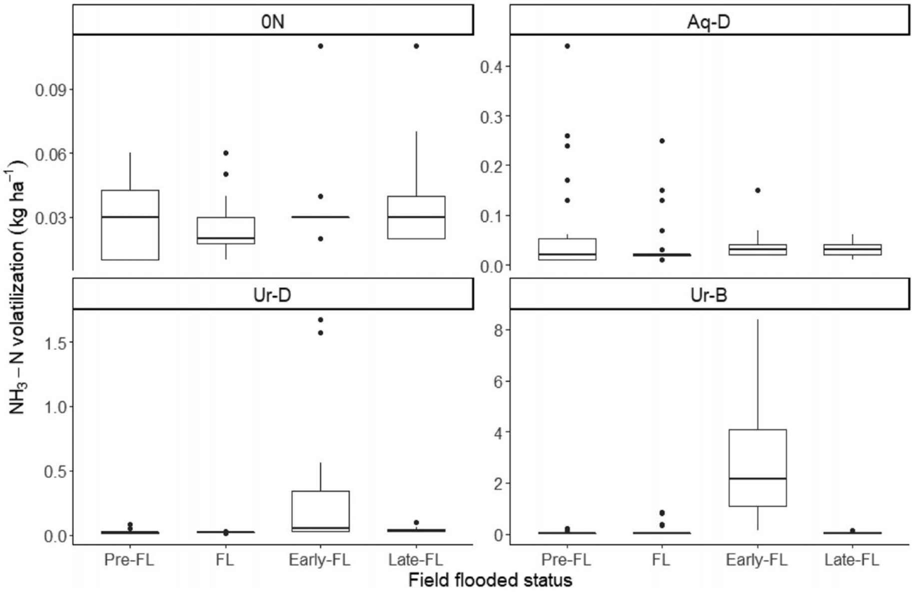

FIGURE 3 Ammonia volatilization from preplant N applications in 2018. Treatments are: 0N, zero-N control; Aq-D, drilled aqueous NH_3; Ur-D, drilled urea; and Ur-B, broadcast urea. Different measurement times include from the time the fertilizer was applied until just before the treatment plots were flooded (Pre-FL); the time the treatment plots were flooded up to 1 d after flooding (FL); the early part of when the field was flooded (Early-FL); and the late post-flood period (Late-FL). Note the different scales on the *y* axis

TABLE 5 Average rice grain yields, N uptake, and N recovery efficiency (NRE) for the different N fertilizer treatments. Data are from the four sites where all four treatments were included in 2018 (5, 6, 7, and 10, Table 1)

Treatment	Grain yield[a]	N uptake	NRE
	——kg ha^{-1}——		%
Zero-N control	5,797 (523) ba	70.4 (6.37) a	–
Drilled aqueous NH_3	12,025 (170) b	177.7 (7.89) b	62 (1.5) a
Broadcast urea	12,059 (173) b	164.3 (7.67) b	56 (3.2) a
Drilled urea	12,035 (112) b	179.5 (8.10) b	64 (5.6) a

Note. Standard error of mean in parentheses. Different lowercase letters within the same column indicate statistically significant ($P < .05$) differences between treatments.

[a] Yield adjusted to 14% moisture content.

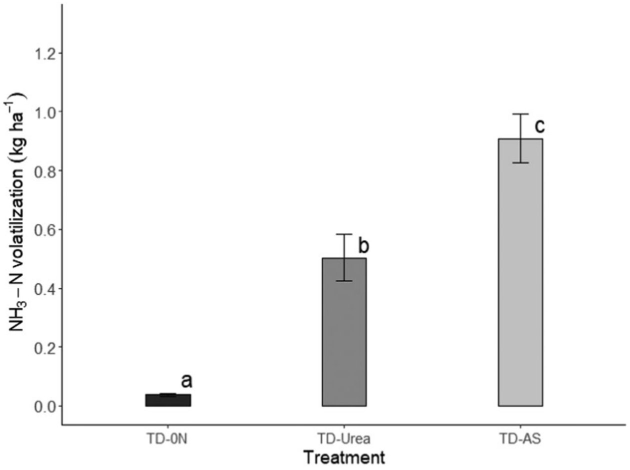

FIGURE 4 Cumulative NH_3 volatilization from a topdress (TD) N application at panicle initiation, comparing $(NH_4)_2SO_4$ (AS) and urea fertilizers with a zero-N (0N) control. The error bar is the standard error of mean. Different lowercase letters indicate statistically significant differences ($p < .05$)

4.2 | Ammonia volatilization following preplant nitrogen fertilizer applications

The addition of N fertilizer increased volatilization losses such that Ur-B ≫ Ur-D > Aq-D ≥ 0N (Figure 2; Tables 3 and 4). Drilling or burying the fertilizer led to a large reduction in NH_3 volatilization. There was an 87 and 94% reduction in NH_3 volatilization in the Ur-D and Aq-D treatments, respectively, compared with the Ur-B treatment. If the fertilizer was buried, regardless of N source, losses due to NH_3 volatilization were <0.5 kg N ha^{-1} and were a little higher than the 0N control, which was approximately 0.15 kg N ha^{-1}, on average.

Others have also reported that burying fertilizer concentrates the NH_4^+ below the soil surface and reduces NH_3 volatilization losses (Kapoor et al., 2008; Koudjega et al., 2019; Liu et al., 2015; Mohanty, Singh, Balasubramanian, & Jha, 1999) for a couple of reasons. First, the NH_4^+ concentration of the soil–water solution determines the potential for NH_3 volatilization losses. Liu et al. (2015) reported that urea hydrolysis by urease was slower when urea was buried in the soil compared with being broadcast on the soil surface, resulting in less NH_4^+ in the soil–water solution. Second, burying the fertilizer increases contact and adsorption of the NH_4^+

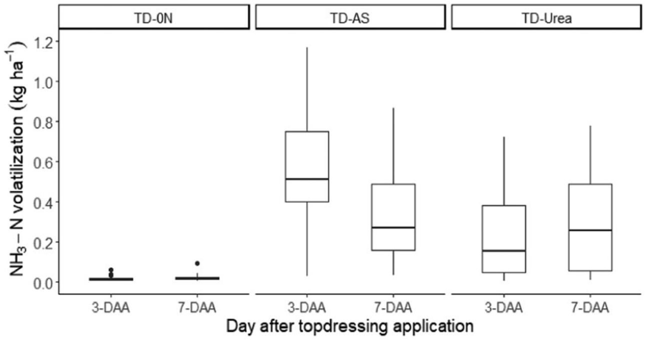

FIGURE 5 Ammonia volatilization from topdress (TD) applications of $(NH_4)_2SO_4$ (AS) and urea relative to a zero-N control (0N). Ammonia volatilization was quantified during two periods: 0–3 d after application (3-DAA) and 3–7 DAA (7-DAA)

(a product of the urea hydrolysis) on the negatively charged soil exchange complex sites. This limits its movement to the floodwater's surface, thus minimizing the NH_4^+/NH_3 ratio in the floodwater, and consequently decreases the potential for NH_3 volatilization (Hayashi et al., 2006; Sommer, Schjoerring, & Denmead, 2004). Furthermore, in support of the findings here, Smith and Chalk (1980) compared the efficiency of urea and aqueous NH_3 that had been injected in solution form to a 3.5-cm depth below the soil surface. While they did not measure volatilization directly, they reported that total ^{15}N recovery from both plant and soil was 94–100% for both fertilizers, suggesting that there was limited volatilization of either fertilizer if buried below the soil surface.

Interestingly, NH_3 volatilization following the application of aqueous NH_3 was very low, despite this fertilizer being highly volatile. While volatilization before the fields were flooded was not significantly higher for Aq-D than for the other fertilizer sources, it is clear that, at least at some sites, volatilization was higher than when urea was applied (either drilled or broadcast) (Figure 3). However, even when NH_3 volatilization was greatest, there was <0.5 kg N ha^{-1} volatilized before flooding from the Aq-D treatment. This indicates that burying the fertilizer and applying it to a dry soil has the potential to significantly reduce the volatilization even from a highly volatile N fertilizer.

It is known that broadcasting urea on the soil surface greatly increases the potential for volatilization losses. Surface-applied urea increases the NH_4^+ concentration in the soil solution and pH around the urea microsite as a result of urea hydrolysis. The positive correlation between NH_4^+ concentration and pH in soil–water solution and NH_3 volatilization has been reported by others (Bouwmeester, Vlek, & Stumpe, 1985; Jayaweera, Mikkelsen, & Paw U, 1990; Liu et al., 2015; Mikkelsen, De Datta, & Obcemea, 1978; Rochette et al., 2013; Vlek & Craswell, 1979). However, in this study, volatilization losses from broadcast urea averaged 3.0 kg N ha^{-1} (range 0.2–9.0 kg N ha^{-1}) and was generally lower than what has been reported in other studies. In transplanted systems, losses from 10 to 56% of applied N have been reported when urea is broadcast into floodwater (De Datta et al., 1989; Freney et al., 1990; Koudjega et al., 2019). De Datta et al. (1989) found that up to 56% of N applied was lost via NH_3 volatilization during the first 8 d after broadcasting urea into floodwater 10 d after transplanting. In dry-seeded or delayed-flood systems in the southern United States, losses of 6 to 33% of applied urea N have been reported (Dillon et al., 2012; Griggs et al., 2007; Norman et al., 2009).

There are several reasons why we may have observed lower volatilization losses from broadcast urea than what was found in other studies. First, in this study, the urea was broadcast onto dry soil. In contrast, in many other studies the urea has been broadcast into floodwater, as in the case of transplanted rice systems (Freney et al., 1990; Obcemea, Real, & De Datta, 1988; Watanabe et al., 2009; Zhu et al., 1989), or onto a soil that may be wet (or becomes wet from rainfall after fertilizer application), as in the case with some dry-seeded systems (Dillon et al., 2012; Griggs et al., 2007; Norman et al., 2009). Second, in addition to being dry, the seedbed was cloddy; therefore, much of the urea that was broadcast on the soil surface fell deeper into the soil between the soil clods, effectively burying a portion of the applied fertilizer (Pelster et al., 2019). When the soil was then flooded, the soil clods broke down and sealed the urea below the soil surface. Third, when a dry field is being flooded, the water transports the urea compound deeper into the soil via water percolation (Broadbent, Hill, & Tyler, 1958; De Datta and Patrick, 1986; Savin, Miller, Tomlinson, Brye, & Norman, 2007). Finally, higher temperatures favor higher rates of hydrolysis and volatilization (Jayaweera et al., 1990; Sommer et al., 2004; Vahed, Shahinrokhsar, & Rezaei, 2011). In our study, average water temperatures were generally lower (22.8°C) than reported in other studies due to the low nighttime temperatures that are common in this region during the early part of the growing season.

As a percentage of the N applied, when urea was broadcast (Ur-B), NH_3 volatilization accounted for only 1.6% of the applied N (Table 4). The overall low losses due to NH_3 volatilization in this study are supported by similar grain yields, N uptake, and NRE among the treatments that received N regardless of placement and source (Table 5). Furthermore, in a separate study, but also in California and under similar fertilizer N application practices, Adviento-Borbe and Linquist (2016) reported yield response and NRE to be similar when urea was either buried (banded below the soil surface) or broadcast on the soil surface.

In contrast to this study, many rice-growing regions of the world consider NH_3 volatilization to be the primary N loss pathway in flooded rice systems (Fillery, Simpson, & De Datta, 1986; Griggs et al., 2007; Watanabe et al., 2009; Zhu et al., 1989). Our data suggest that in the water-seeded systems described here, volatilization is a minor loss. This may explain why NRE is often higher in California rice systems than in other rice systems. The average NRE in this study was 56 to 64% (Table 5) and in other on-farm studies in California, NRE has ranged from 50–73% (Linquist et al., 2009; Pittelkow et al., 2014). In contrast, Ladha et al. (2005) reported that the global average NRE for rice was 46%. Furthermore, the data reported in our study are largely from on-farm studies. Dobermann et al. (2004) compared NRE from on-farm and on-station (or researcher managed) studies in Asia and found that NRE from on-farm studies averaged 31% compared with 41% on research stations or researcher managed plots.

With regard to the timing of volatilization, volatilization occurred primarily during the early post-flood period of 5 to 7 d after flooding (Early-FL), after which volatilization was negligible in the two treatments where the volatilization of fertilizer N was significant (Figure 3). This finding is similar to the results of Fillery, Simpson, and De Datta (1984) and Hayashi et al. (2006). Interestingly, although the Aq-D treatment had low cumulative volatilization, before flooding (Pre-FL) there were some observations with relatively high volatilization (0.19–0.69 kg N ha^{-1}) (Figure 3). While we are not sure of the reason for this, the fertilizer N being applied in the aqueous NH_3 form may be more susceptible to immediate volatilization.

A large body of research has shown relationships between NH_3 volatilization and various soil properties such as clay content, soil pH, soil organic matter, cation exchange capacity, and electrical conductivity (Ernst & Massey, 1960; Fenn, Matocha, & Wu, 1982; Ferguson, Kissel, Koelliker, & Basel, 1984; Pelster et al., 2019; Zhenghu & Honglang, 2000). Examining the NH_3 volatilization from the Ur-B treatment, which had the highest amount of volatilization, there was no relationship between NH_3 volatilization and any of the soil properties measured (data not shown). The reason no relationships were detected might be that the magnitude of NH_3 volatilized in this study was too low to detect significant correlations. Similarly, the range in soil properties across our study sites (Table 2) may have been too small to detect relationships.

4.3 | Ammonia volatilization following topdressed nitrogen fertilizer application

The NH_3 volatilization from urea and $(NH_4)_2SO_4$ topdress applications was significantly higher than the control treatment (Figure 4). Furthermore, volatilization following the application of $(NH_4)_2SO_4$ was significantly higher than following urea. The average cumulative NH_3 volatilization from urea and $(NH_4)_2SO_4$ were 0.50 and 0.90 kg N ha^{-1} and represent 1.39 and 2.58%, respectively, of the total amount of topdress N applied. Importantly, these values are based on volatilization over a period of only 7 d. From this study, we cannot rule out that volatilization did not continue after this period as there was significant volatilization during the last measurement period (Figure 5); however, others have found volatilization to be negligible after 7 d (Fillery et al., 1984; Hayashi et al., 2006). In the preplant study we also found NH_3 volatilization to be negligible after about 7 d (Figure 3). The NH_3 volatilization of topdressed N was low overall and may be explained by the fact that by this time in the season the plants are growing rapidly and have an extensive root system near the soil surface, which is able to quickly take up applied N (Bah, Syed Omar, Anuar, & Husni, 2009; Broadbent & Mikkelsen, 1968).

There are a number of explanations as to why volatilization was higher following $(NH_4)_2SO_4$ than urea applications. First, Fillery, Roger, and De Datta (1986) found that $(NH_4)_2SO_4$ dissolves rapidly and increases the amount of $NH_4{}^+$ in the floodwater almost immediately, leading to a rapid and higher potential for volatilization. This hypothesis is supported by higher volatilization from $(NH_4)_2SO_4$ than urea during the first 3 DAA (Figure 5). Second, the rate of urea hydrolysis is affected by water temperature. Simpson et al. (1984), studying urea transformations after application to flooded rice, reported that the urease activity in the floodwater was low at 25 °C, resulting in only 4% of applied urea being hydrolyzed in the first 24 h after application. The water temperature during our study period averaged 25.6 °C (data not shown), and this may be why there was lower volatilization from urea during the first 3 DAA. Third, urea moves more readily downward into the soil via mass flow than does $NH_4{}^+$ because urea is not as readily absorbed to moist soil (Mikkelsen, 1987). Hongprayoon, Lindau, Patrick, Bouldin, and Reddy (1991) reported that urea diffused up to 2 cm below the soil surface in 12 h and up to 10 cm in 4–6 d after urea was added to the floodwater. In contrast, the $NH_4{}^+$ may have restricted movement due to its positive charge (Du Preez & Burger, 1988).

5 | CONCLUSION

In this study, we examined NH_3 volatilization losses from preplant and topdress N applications. This is the first study to look at NH_3 volatilization losses when aqueous NH_3 is used as a primary N source in rice systems, and NH_3 volatilization losses were similar to when no N had been applied. In both preplant N treatments where the fertilizer was buried, NH_3 volatilization losses were low. When urea was broadcast, NH_3 volatilization increased but was still <2% of applied preplant N. This is likely because the urea was broadcast onto dry cloddy soil and much of the fertilizer prills dropped below the soil surface, effectively burying or incorporating the fertilizer. Furthermore, water temperatures were lower than in many rice growing areas, which may further limit volatilization losses. For topdressed N, losses were <3% of applied N, regardless of source. These results are encouraging and suggest that the higher NRE often reported from California rice systems may be due to low NH_3 volatilization potential. However, if management practices change, for example to a dry-seeded system, the potential for volatilization losses will need to be reassessed.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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