MEASURING AMMONIA LOSS USING FIELD-SCALE AND LABORATORY TECHNIQUES

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ABSTRACT

Following the surface application of urea to soil, there is the potential for nitrogen (N) loss from ammonia (NH_3) volatilization until sufficient rain or irrigation has moved it into the soil. Many studies measuring NH_3 loss have used laboratory and microplot field studies. The limitation of these techniques is that they do not represent NH_3 loss under natural conditions because enclosures alter air movement, humidity, and soil and air temperature inside the chambers. However, they do allow researchers to study the individual factors controlling ammonia loss. To overcome the limitations imposed by enclosures, field-scale passive flux methods have been developed that do not change field conditions. Field and lab studies were initiated to quantify NH_3 volatilization from surface applied urea, determine if the addition of the urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT) could reduce NH_3 loss, and explore the relationship between soil properties and NH_3 volatilization. A total of three field trials were conducted 2014 and 2015, in which urea or urea + the urease inhibitor Agrotain was applied at a rate of 150 lb N/acre, and NH_3 loss measured using a passive flux method. In the lab, NH_3 loss from surface applied urea applied to six soils with varying soil properties was measured using static chambers. In the field, ≤1.6% of applied fertilizer N was lost as NH_3 within 6 to 8 days after application despite ideal conditions for loss (i.e., rapid dissolution of urea that was applied to moist, warm soil). Agrotain did not reduce ammonia loss. In the lab study, ammonia loss for soils with a CEC ≥19 cmol(+)/kg (n=5) was ≤8.4% of added urea-N, and ammonia loss from the soil with the lowest CEC (6 cmol(+)/kg) was 25.6%. The soil property that most strongly controlled NH_3 loss was CEC (which was related to soil pH buffering capacity), not pH or urease enzyme activity. This study indicates that NH_3 loss from surface applied urea is expected to be minimal for most Willamette Valley soils, which have moderate to high pH buffering capacity.

INTRODUCTION

Surface application of urea containing fertilizers can result in significant loss of N through ammonia (NH_3) volatilization when not incorporated promptly or watered into the soil with rainfall or irrigation. Research in eastern Oregon has shown cumulative NH_3-N losses to be as high as 50% of surface applied urea-N over eight days after application, and by applying 0.6 inches of water, NH_3 loss was reduced by 90% (Holocomb et al., 2011). Urea itself is not volatile, but in the presence of the enzyme urease and water it hydrolyzes and consumes H^+. This results in a temporarily rise in the soil pH around the prill, increasing the ratio of NH_3 to NH_4, which promotes volatilization loss of NH_3.

Most farmers growing sweet corn in western Oregon broadcast apply pelleted urea at growth stage V5 to V6. Due to limitations in irrigation infrastructure, especially during times of peak demand when weather is hot, the interval between urea application and irrigation to move it into the soil may be up to a week for some parts of the field. If there is sufficient moisture for the urea to dissolve and for hydrolysis to occur, there is the potential for N loss from NH_3 volatilization. Studies have shown that the urease inhibitor NBPT can significantly reduce NH_3 loss by slowing the conversion of urea to NH_4, which minimizes pH increase (Bremner, 1995).

The soil and environmental factors that contribute to ammonia loss include soil and air moisture, irrigation or rainfall rate, wind, and soil pH, CEC (related to pH buffering capacity), and urease enzyme activity (influenced by crop residues or organic matter inputs) (Jones et al., 2013). Although significant NH_3 losses have been observed from broadcast urea on some eastern Oregon soils, western Oregon soils are typically acidic and have a higher pH buffering capacity (higher clay and OM which results in a higher CEC), and little research has been done to quantify NH_3 losses from western Oregon soils.

Many studies measuring NH_3 loss have used laboratory and microplot field studies. The limitation of these laboratory and field techniques is that they do not represent NH_3 loss under natural conditions because enclosures alter air movement, humidity, soil temperature, air temperature, and solar radiation inside the chambers. To overcome these limitations, passive flux sampling methods have been developed and successfully used (e.g., Wood et al., 2000 and Holcomb et al., 2010) that measure NH_3 loss without altering field conditions.

The objectives of this study were to 1) quantify NH_3 loss in the field from surface applied urea in a worst case scenario (moist, warm soil) using a passive flux method, 2) determine if the urease inhibitor NBPT could reduce NH_3 loss, and 3) explore the relationship between soil properties and NH_3 loss under controlled conditions in the laboratory using static chambers.

MATERIALS AND METHODS

Ammonia loss in field trials using passive flux method

Ammonia volatilized from surface applied urea in the field was measured using a modified passive flux method (Wood et al., 2000; Vaio et al., 2008) on three commercial farms growing sweet corn in 2014 and 2015. At each field site, circular plots (30-m diameter) were established that received one of the following treatments: no fertilizer (Control), prilled urea at 150 lb N/ac (Urea), and urea plus the urease inhibitor NBPT at 150 lb N/ac (Agrotain). Fertilizer was evenly applied by hand in these plots. Normally farmers fertilize their corn around V6 when N uptake begins to increase rapidly. It was necessary for us to apply the fertilizer as early as preemergence to be able to work around the farmer's field management schedule. All fields were irrigated with traveling sprinkler that contained a single high capacity nozzle with an effective coverage of 200 ft. At all sites, the fertilizer was applied to moist soil. Treatments were arranged in a randomized complete block design with three (sites 2 and 3) or four (site 1) replications. Each circular plot was separated by at least 330 ft to avoid contamination of NH3 between treatments (Vaio et al., 2008). During the field trials, none of the surrounding fields received urea applications. Soil characteristics for each field site (0-2 inches) are given in Table 1.

To collect volatilized ammonia, a rotating mast containing passive flux samplers was placed at the center of each circular plot with a tripod to stabilize the mast during high wind events. The passive flux samplers were placed at five heights (0.45, 0.75, 1.50, 2.25, and 3.00 m; Leuning et al., 1985). Each passive flux sampler consisted of a glass tube (0.7-cm i.d. by 20 cm long) with the inside surface coated with 3% (w/v) oxalic acid in acetone to scrub the NH_3 in the air flowing through the tube. Each tube had an attached nozzle with a 1-mm hole to restrict incoming air flow to prevent NH3 saturation of the oxalic acid. Flux samplers were sealed in a Ziploc bag after being coated to ensure an NH3–free environment and were only removed when being placed on the masts. In 2014, flux samplers were collected and replaced every day, but in 2015, this was done every other day.

Table 1. Soil properties (0-5 cm) of field trial sites.

	pH^1	OM^2	$Clay^3$	$Sand^3$	CEC^4
		%	%	%	cmol(+)/kg
Site 1	5.6 (5.3-5.8)	2.1 (1.5-2.5)	23 (16-28)	38 (26-58)	26 (22-28)
Site 2	6.3 (5.9-6.9)	NA	22 (16-29)	19 (10-32)	30 (27-34)
Site 3	5.7 (5.5-5.8)	NA	22 (20-24)	28 (18-36)	24 (22-26)

1- 1:2 soil to water; 2- 1.7 x total C by combustion; 3- hydrometer method; 4- by displacement

Immediately after collection of the flux samplers, they were capped at both ends, placed in a sealed Ziploc bag, and stored in a refrigerator. The samples were extracted within 3 wks of being collected. Flux samplers were extracted by adding 2 mL of deionized water and shaking for five minutes. The extracts were analyzed colorimetrically for NH4-N. The horizontal and vertical NH3 flux (Fx, μg N m−2 s−1) for each flux sampler was calculated using the equations given by Schjoerring et al. (1992), Wood et al. (2000), and Vaio et al. (2008). A weather station (Onset Computer Corp model Hobo U30-NRC) was installed at each site to measure wind speed, air and soil temperature (at 1-inch depth), and relative humidity.

Site 1 was conducted on a farm near Independence, OR in an 80 acre field located in the seasonal floodplain of the Willamette River. The field was planted to sweet corn on June 1, 2014, and on June 17, fertilizer was applied and collection towers installed. In this trial, the fertilizer containing the urease inhibitor NBPT was SuperU (Agrotain International), which also contained a nitrification inhibitor. The trial ran for eight days, after which the study was terminated when the farmer began irrigating his field.

Site 2 was conducted on a farm near Talbot, OR located at the confluence of the South Santiam and Willamette River. Due to the irrigation system which applied water in long strips across the field, each of the three replicates were set-up on different days shortly after an irrigation when soils were moist. The start date for replicates 1, 2, and 3 was June 23, June 25, and July 1, 2015, respectively. The fertilizer was applied when corn growth stage was between emergence and V2, which varied depending on the start date. The duration of the experiment was dictated by the irrigation interval, lasting 8 days for rep 1, and 6 days for reps 2, and 3. Over the entire collection period, the soil temperatures at 1 inch routinely topped out >38°C. The fertilizer containing the urease inhibitor NBPT used at this site was Agrotain Ultra.

Site 3 was conducted on a farm located east of Monroe, OR. Initially, three replicates were set up on July 23, 2015, however, one replicate was compromised due to wind drift of irrigation water into the plots. Agrotain Ultra was also used at this site. The experiment was terminated on July 29. Soil temperatures at 1 inch were similar to those at site 2, with daily temperatures often exceeding 38°C. The field received 1 mm of rain between 7/25 and 7/26, which was enough to dissolve most of the prills.

Ammonia loss in laboratory using static chambers

A total of six soils were collected in the Spring of 2016; five from Oregon and one from Idaho (Table 2). All soils were collected from cultivated fields except for Site 6, which was forested. The soils were sieved in the field to pass a 4.8 mm screen, and were stored for no more than four weeks at 4°C before being used.

Physical and chemical characteristics of the soils used in the lab study are given in Table 2. The buffer capacity was measured by adding three rates of a 0.022M calcium hydroxide ($Ca(OH)_2$) solution to 15 g of air-dried soil, adding DI water to achieve a final ratio of 1:2 soil to solution, adding chloroform to inhibit microbial activity, and incubating for 3 days in the dark. The buffer capacity was then calculated using a linear regression of the pH response to added $Ca(OH)_2$. Urease enzyme activity assay was conducted using the methods given by Kandeler and Gerber (1988) on soils that had been frozen for six months.

Table 2. Properties of soils used in the static chamber ammonia loss experiment

Site	Collection location	Soil mapping and texture	pH[1]	CEC[2]	OM[3]	Clay[4]	Sand[4]	Buffer capacity	Urease activity
				cmol(+)/kg	%	%	%	Mg lime per unit pH increase	μg urea-N/g OD soil/2 hr
1	Western, OR	Camas gr sl	5.6	19	2.5	16	57	3.3	8
2	Eastern, OR	Adkins fsl	6.7	6	0.9	4	89	0.8	7
3	Western, OR	Woodburn sil	5.8	21	2.7	25	13	3.8	11
4	Western, OR	Cloquato sil	5.7	33	4.3	28	17	4.6	27
5	Twin Falls, ID	Portneuf sil	8.1	20	1.7	24	18	NA	10
6	Western, OR	Jory sicl	5.9	33	9.5	38	30	6.3	134

1- 1:2 soil to water; 2- by displacement; 3- loss on ignition; 4- hydrometer method

Ammonia loss following addition of prilled urea was measured using static chambers and methods similar to those used by Goos (2013). Most soils were considered to be close to field capacity as they were collected in the spring several days after rain. DI water was added to soils from sites 3 and 5 by laying the soil on a tarp, spraying with DI water, and mixing by lifting up edges of the tarp. Moist soil was added to PVC cylinders (10 cm diameter by 15 cm height) with a closed bottom at an equivalent rate of 400 g oven dry soil. The cylinder with soil was lightly tamped to consolidate the soil. The final soil depth was 5 to 6 cm. This depth was chosen because in previous studies using this method maximum urea diffusion was < 1 inch cm, and at this depth the capacity of soil to buffer change was not maxed out (unpublished data). The trial consisted of two treatments, 1) Control (no fertilizer) and 2) Urea (150 lb N/ac) replicated three times. Urea prills were evenly dispersed over the soil surface. The average number of prills added to each chamber was 10 (range 8-12). For each soil, a total of 24 cylinders were created (2 treatments x 3 replicates x 4 sampling dates).

Ammonia volatilization was measured using acid-treated foam traps using the methods given by Goos (2013). After fertilizer application, a 2.5 cm thick polyurethane foam sponge containing phosphoric acid was placed so that the sponge was level with the top of the cylinder. The sponges were prepared by soaking in 1% (vol/vol) hydrochloric acid (HCl), followed by rinsing with distilled water and then soaking in a solution of phosphoric acid and glycerol (100 mL phosphoric acid and 150 mL glycerol, diluted to 2.5 L with water), followed by squeezing the sponges to remove excess acid solution.

At each sampling date (4, 8, 12 and 16 days after application), the sponges were removed and one set of cylinders was destructively sampled. The sponges were extracted with 200 mL of 1% HCl, and an aliquot was analyzed colorimetrically for NH_4-N. Fresh phosphoric acid–treated sponges were then installed in the remaining cylinders. For the destructively sampled cylinders, the soil was thoroughly mixed, a subsample taken for moisture content, and a 15 g subsample was extracted with 2M KCl. Following 30 minutes of shaking and filtering, the extracts were immediately frozen until the end of the trial, at which time they were thawed and analyzed for ammonium, nitrate (Doane and Horwath, 2003), and urea (Greenan et al., 1995).

RESULTS AND DISCUSSION

Ammonia loss in field trials using passive flux method

Ammonia loss from the three field sites are given in Fig.1. At all sites, measured NH_3 loss was minimal, accounting for ≤1.6% of applied urea-N volatilized 6 days after application. Although the duration at site 1 was 8 days, there was not much change in volatilization between 6 and 8 days, and day 6 was chosen to be able to compare results across trials. If sufficient moisture is present to cause the urea pellets to dissolve, and for hydrolysis to occur, the greatest NH_3 fluxes occur 2 to 8 days after application (e.g., Holcomb et al., 2010).

Low fluxes may be the result of a high pH buffering capacity of the soils. The soils at the field sites all had moderate to high CEC (24-30 cmol(+)/kg) and pH ≤6.3, which contribute to a large reserve acidity and high pH buffering capacity. As a result, the pH change around the pellets was buffered, and the ratio of NH_3 to NH_4 was likely small, which prevented loss. Many lab and field studies that have measured high ammonia losses (>40%) from surface applied urea fertilizers have used soils with low CEC (<10 cmol(+)/kg).

Another possible explanation of the low fluxes may be related to soil moisture. At all sites, we applied urea to moist soil, however, due to experimental constraints (i.e., irrigation method and need for large separation distances between plots), soil moisture was not always uniform in all experimental plots. This resulted in different rates of urea dissolution. Soil moisture was the most uniform at site 1, and all pellets had dissolved within 3 days. Further confounding results is the rate of soil drying following application. Despite applying pellets to moist soil, some pellets were still visible in some plots at sites 2 and 3 when the experiment was terminated. Even if the pellets had completely dissolved, rapid soil drying may have reduced surface moisture to the level at which urea hydrolysis was inhibited. Daily soil temperatures routinely reached 38^oC at 1-inch. Although experimental conditions were not uniform across experimental plots, the NH_3 loss data represents volatilization under actual field conditions.

If the urea was applied at V4 to V6, NH_3 loss may have been higher. The crop would shade the soil surface, which may have slowed surface drying, and urea pellets that land in whorls and get wet would release NH_3 because the buffering capacity of rain and irrigation water is low.

Ammonia loss in laboratory using static chambers

Changes in soil urea and ammonium concentrations, and cumulative NH_3 recovered in the acid sponges are given in Fig. 2. At 4 days after application (DAA), 44% (range 38 to 52%) of applied urea-N had not converted to ammonium for sites 1 to 5. For site 6, which was in forest and had the highest urease activity, urea was rapidly converted and only 3% of applied urea-N remained at 4 DAA. By 8 and 12 DAA, an average of 9 and 1% of applied urea-N was present, respectively.

Although urea was rapidly hydrolyzed for site 6, which would have resulted in a rapid spike in pH around the prills, cumulative NH_3 loss was 5% of applied urea-N. The high pH buffering capacity of this soil likely minimized pH change (Table 2). The soil from Idaho (site 5) had the highest pH (8.1), but NH_3 loss was only 5% of applied urea-N. This was surprising because high pH increases the potential for NH_3 volatilization. Even with a moderate CEC (20 cmol(+)/kg), the high pH indicates that there was little reserve acidity to buffer pH change. Site 1 had the second highest NH_3 volatilization losses (8%). This site had less clay and significantly more sand than the western Oregon and Idaho soils, and a slightly lower CEC (Table 2). Soil collected from Hermiston Oregon (Site 2) had the highest NH_3 volatilization losses (26%). This soil had a pH of 6.7 and the lowest CEC (6 cmol(+)/kg) of all the soils tested. Based on this small data set, the factors that appeared to be most important in controlling NH_3 volatilization losses was CEC, sand content, and buffering capacity (which are interrelated), not soil pH or urease enzyme activity.

Relating NH_3 loss from laboratory studies to field losses is difficult because many factors are controlled that otherwise affect NH_3 volatilization; however, results from this laboratory study help explain why NH_3 volatilization losses were so low in our field trials compared to studies conducted in the Hermiston area.

SUMMARY

The field-scale passive flux method and the laboratory static chamber method were complimentary. The passive flux method allowed us to measure NH_3 under field conditions, while the static chambers allowed us to understand the soil properties controlling ammonia loss. Using the passive flux method, cumulative NH_3 loss over 6 days in three field trials was ≤1.6% of surface applied urea-N, and Agrotain did not reduce NH_3 loss. Results from the laboratory study using static chambers indicated that the soil property that most strongly controlled NH_3 loss was CEC (which is correlated to soil pH buffering capacity), not pH or urease enzyme activity. The laboratory results help explain why NH_3 loss in the field was so low; the CEC at all field sites were moderate to high (22 to 34 cmol(+)/kg). Rapid drying of soil surface may have also contributed to low NH_3 loss in the field by preventing complete dissolution of urea pellets and inhibiting urea hydrolysis due to insufficient moisture. Results from this study indicate that NH_3 volatilization from surface applied urea is expected to be minimal in western Oregon sweet corn production systems, and use of the urease inhibitor NBPT is unlikely to increase nitrogen use efficiency.

REFERENCES

Bremner, J.M. 1995. Recent research on problems in the use of urea as a nitrogen fertilizer nutrient cycling in Agroecosystems. 42:21-329

Doane, T.A., and W.R. Horwáth. 2003. Spectrophotometric determination of nitrate with a single reagent. Analytical Letters 36:2713-2722.

Goos, J. 2013. Effects of Fertilizer Additives on Ammonia Loss after Surface Application of Urea–Ammonium Nitrate Fertilizer. Comm. in Soil Sci. and Plant Anal. 44:1909-1917

Greenan, N., R. Mulvaney, and G. Sims. 1995. A microscale method for colorimetric determination of urea in soil extracts. Comm. in Soil Sci. and Plant Anal. 26:2519-2529.

Holcomb, J.C., D.M. Sullivan, D.A. Horneck, and G.H. Clough. 2011. Effect of Irrigation Rate on Ammonia Volatilization. Soil Sci. Soc. of Am. Journal. 75:2341-2347

Jones, C., B. Brown, R. Engel, D. Horneck, and K. Olsen-Rutz. 2013. Factors Affecting Nitrogen Fertilizer Volatilization. Montana State Extension Publication EB0208.

Kandeler, E. and H. Gerber. 1988. Short-term assay of soil urease activity using colorimetric determination of ammonium. Biology and Fertility of Soils. 6:68-72

Leuning, R., J.R. Freney, O.T. Denmead, and J.R. Simpson. 1985. A sampler for measuring atmospheric ammonia flux. Atmos. Environ. 19:1117–1124

Schjoerring, J.K., S.G. Sommer, and M. Ferm. 1992. A simple passive sampler for measuring ammonia emission in the field. Water Air Soil Pollut. 62:13–24

Vaio, N., M.L. Cabrera, D.E. Kissel, J.A. Rema, J.F. Newsome, and V.H. Calvert III. 2008. Ammonia volatilization from urea-based fertilizers applied to tall fescue pastures in Georgia, USA. Soil Sci. Soc. Am. J. 72:1665–1671

Wood, C.W., S.B. Marshall, and M.L. Cabrera. 2000. Improved method for field-scale measurement of ammonia volatilization. Commun. Soil Sci. Plant Anal. 31:581–590.

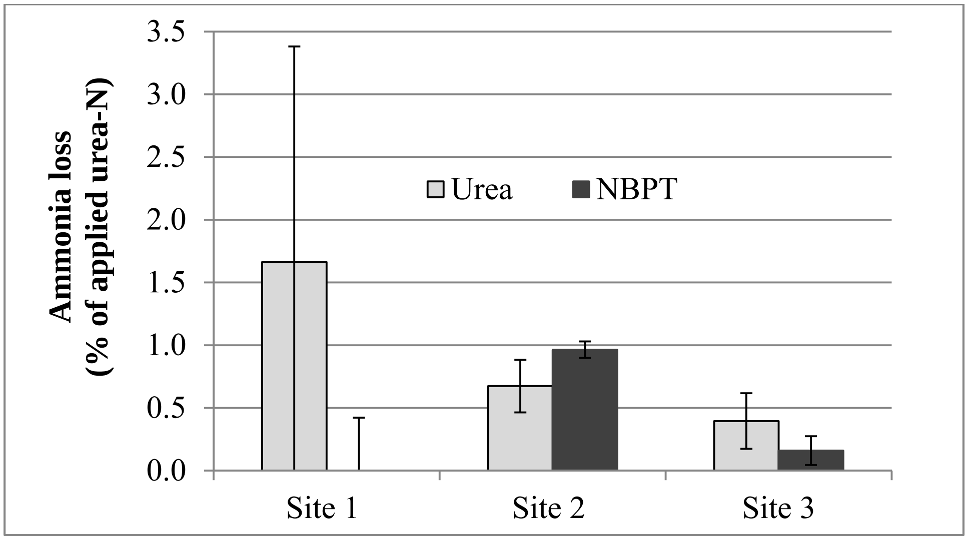

Figure 1. Cumulative ammonia loss from three field sites 6 days after application as measured using a passive flux method. Error bars represent the SEM.

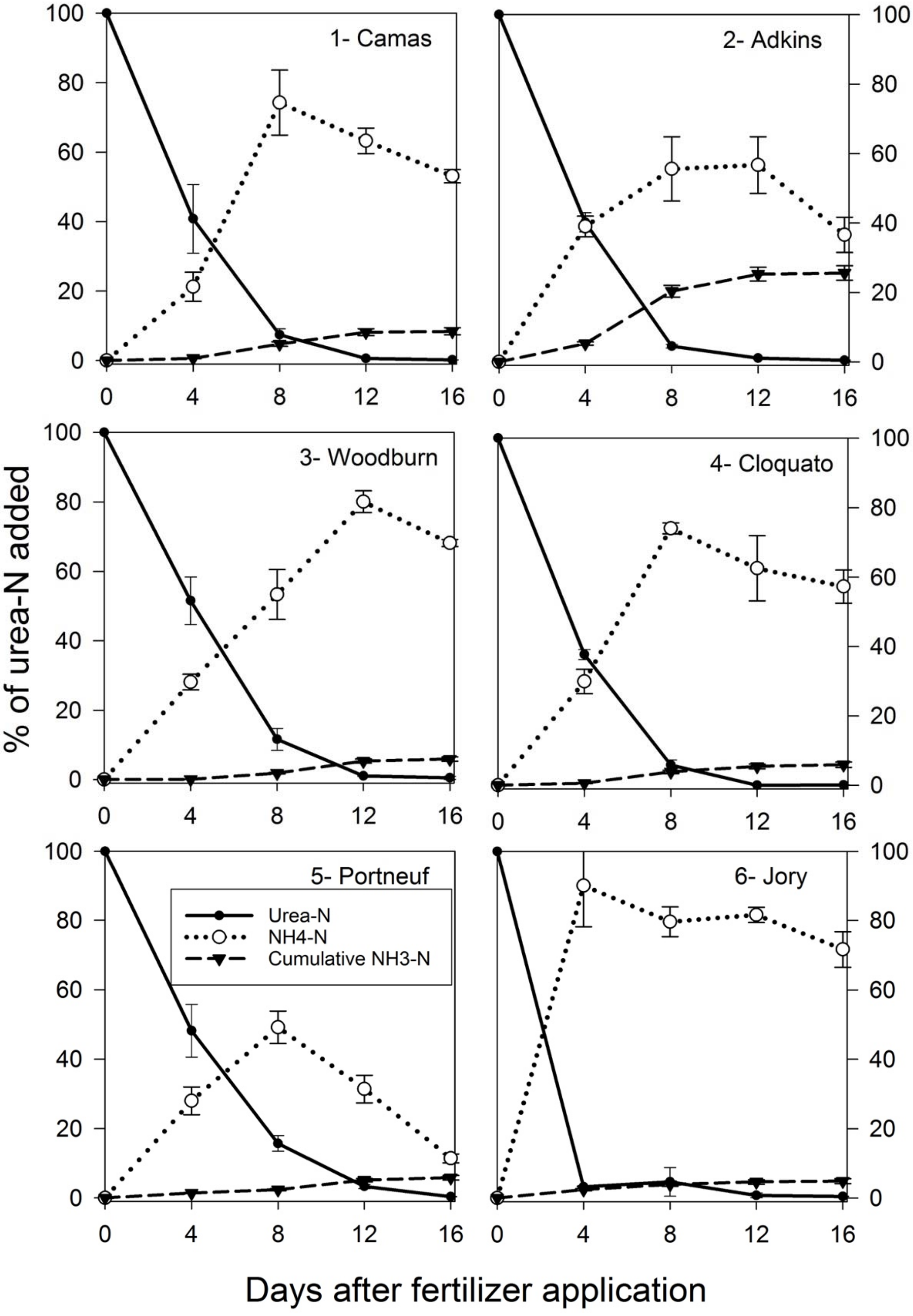

Figure 2. Soil NH_4-N and urea-N, and volatilized NH_3-N during a 16-d laboratory incubation in static chambers. Error bars represent SEM (n=3).