



Ammonia volatilization following nitrogen fertilization with enhanced efficiency fertilizers and urea in loblolly pine (*Pinus taeda* L.) plantations of the southern United States



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ABSTRACT

Ammonia (NH₃) volatilization losses following surface application of urea and three enhanced efficiency nitrogen (N) containing fertilizers (EEFs) were compared in six thinned mid-rotation loblolly pine (*Pinus taeda* L.) stands across the southern United States. All fertilizer treatments were labeled with ¹⁵N (~370‰, 0.5 AP) and applied during two different seasons (spring, summer) in 2011 to open chamber microcosms. Individual microcosms were sampled 1, 15 and 30 days after fertilization to estimate remaining ¹⁵N. Losses of fertilizer N were determined using a mass balance calculation. Significantly less N loss occurred following fertilization with EEFs compared to urea after all sampling days for both seasons. Because root uptake was eliminated in the microcosms and there was no leaching of ¹⁵N below the microcosms, the most likely loss pathway of the ¹⁵N from the microcosms was NH₃ volatilization. There were generally no differences among the individual EEFs. Following spring application, the mean NH₃ volatilization during the 30 day experiment ranged from 4% to 26% for the EEFs compared to 26–40% for urea. In summer, mean NH₃ volatilization for EEFs ranged from 8% to 23% compared to 29–49% for urea. This research highlights the potential of EEFs to reduce loss of fertilizer N in forest systems, potentially increasing fertilizer N use efficiency in these pine plantations.

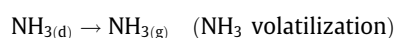
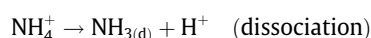
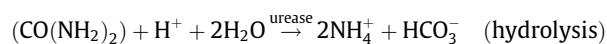
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1. Introduction

The productivity of many loblolly pine (*Pinus taeda* L.) plantations in the southern United States is limited by low levels of plant available soil nutrients, especially nitrogen (N) and phosphorous (P) (Allen, 1987). These N deficiencies are common because N is required in larger quantities compared to other nutrients for the formation of foliar tissue and photosynthetic enzymes (Miller, 1981; Chapin et al., 1986). Nitrogen deficiencies can generally be ameliorated through fertilization (Fox et al., 2007a; Carlson et al., 2014). In the South, loblolly pine plantations generally respond positively to a mid-rotation fertilization with a mean growth increase of 3 m³ ha⁻¹ over 8 years following the application of 224 kg ha⁻¹ N plus 30 kg ha⁻¹ of P (Fox et al., 2007a). Consequently, fertilization has become an important silvicultural tool to improve forest productivity (Allen, 1987; Fox et al., 2007b). Despite these systems being N deficient, less than 50% of applied N fertilizer is usually utilized by the loblolly pines, with some

studies indicating a much lower percentage (Baker et al., 1974; Mead and Pritchett, 1975; Johnson and Todd, 1988; Li et al., 1991; Albaugh et al., 1998, 2004; Blazier et al., 2006).

The most common N fertilizer used in loblolly pine plantations in the South is pelletized (granular) urea (CO(NH₂)₂) which is surface applied via aerial or ground broadcast methods (Allen, 1987). Urea is used because of its high N content (46% N) and ease of transport-storage-application, translating to the lowest overall cost per pound of applied N (Allen, 1987; Harre and Bridges, 1988; Fox et al., 2007b). In the acidic forest soils of the South that support loblolly pine plantations, urea undergoes a series of chemical reactions that can lead to ammonia (NH₃) volatilization losses (Hauck and Stephenson, 1965).



The initial reaction, urea hydrolysis, is facilitated by the extracellular enzyme urease which originates from plant and animal residues and microbial activities and is common in forest soils

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(Conrad, 1942; Pettit et al., 1976; Marsh et al., 2005). Urea hydrolysis produces ammonium carbonate which dissociates into ammonium (NH_4^+) and bicarbonate (HCO_3^-). The bicarbonate consumes hydrogen (H^+) ions near the dissolving urea granule which raises the surrounding pH ($\text{pH} > 8$). With the pH increase ($\text{pH} > 7$), a higher proportion of ammonium ions (NH_4^+) dissociate and are converted to ammonia (NH_3) which can be volatilized and lost to the atmosphere.

The losses of fertilizer N by NH_3 volatilization after application of urea in plantation forests can be rapid and significant (Nõmmik, 1973; Kissel et al., 2004; Cabrera et al., 2010; Zerpa and Fox, 2011; Elliot and Fox, 2014). Losses range from less than 10% (Boomsma and Pritchett, 1979; Craig and Wollum, 1982), 10–40% (Nõmmik, 1973; Zerpa and Fox, 2011) to >50% (Kissel et al., 2004, 2009; Elliot and Fox, 2014). The losses due to NH_3 volatilization in pine plantation systems are similar to the NH_3 volatilization losses observed in agriculture, which can range from 25% to 47% when urea is applied to the soil surface (Scharf and Alley, 1988).

The factors that influence NH_3 volatilization after urea fertilization in agricultural systems are well studied (Volk, 1959; Black et al., 1987; Kissel and Cabrera, 1988) whereas less research has focused on forested systems (Volk, 1970; Nõmmik, 1973; Kissel et al., 2004; Elliot and Fox, 2014). Ammonia volatilization is affected by soil pH (Ernst and Massey, 1960; Cabrera et al., 1991; Kissel et al., 2009), soil moisture (Clay et al., 1990; Kissel et al., 2004), mineral soil substrate (Cabrera et al., 2005; Kissel et al., 2009; Zerpa and Fox, 2011), relative humidity (Cabrera et al., 2005), soil temperature (Ernst and Massey, 1960; Clay et al., 1990; Moyo et al., 1989), surficial wind speed (Watkins et al., 1972; Kissel et al., 2004), precipitation (Craig and Wollum, 1982; Kissel et al., 2004) and air temperature (Gould et al., 1973; Craig and Wollum, 1982; Koelliker and Kissel, 1988). The organic (O) horizon (forest floor) in forest soils can also have a significant effect on NH_3 volatilization (Cabrera et al., 2005; Kissel et al., 2009; Zerpa and Fox, 2011). Soils with a high H^+ buffering capacity (high organic matter, clay, silt) generally have lower NH_3 volatilization losses of fertilizer N compared to those soils with a lower buffering capacity (sand) (Fenn and Kissel, 1976; Ferguson et al., 1984).

Urea applied under cooler, wetter conditions generally has low NH_3 volatilization losses (Ferguson and Kissel, 1986; Moyo et al., 1989; Cabrera et al., 2010) due to rapid urea dissolution and movement into the soil (Black et al., 1987; Paramasivam and Alva, 1997). Higher temperatures and relative humidity stimulate urease activity and increase NH_3 volatilization (Craig and Wollum, 1982; Ferguson and Kissel, 1986; Moyo et al., 1989). Elevated wind near the soil boundary layer (Kissel et al., 2004) can also exacerbate losses. Higher rates of NH_3 volatilization also occur with higher pH values (Koelliker and Kissel, 1988). The ammonium ions may enter the soil if a precipitation event occurs soon after fertilization which decreases NH_3 volatilization losses (Kissel et al., 2004). The amount of urea N lost from the system due to NH_3 volatilization is difficult to accurately predict because the loss of fertilizer N is driven by the interaction among many of these factors. Large losses of fertilizer N through NH_3 volatilization have occurred even under low temperatures (Carmona and Byrnes, 1990; Engel et al., 2011). Conversely, Kissel et al. (2004) observed low NH_3 volatilization during August when urea was applied on a day with significant precipitation but high NH_3 volatilization (45–58%) under simulated, minor precipitation events.

To reduce losses from NH_3 volatilization, fertilization in southern forests traditionally occurs during the winter months when there is a higher likelihood of cooler, wetter conditions to move fertilizer N into the soil. Yet weather conditions previously detailed conducive to high NH_3 volatilization still occur during the winter months in the South. Additionally, N application during winter months of plant dormancy may not be optimally synchronous to

plant demand during the growing season (Blazier et al., 2006). To address these issues, enhanced efficiency fertilizers have been developed to provide managers in agroecosystems the ability to apply N more synchronously to plant demand by reducing the risks of N losses (Shaviv, 1996).

Enhanced efficiency fertilizers (EEFs) have been developed to minimize losses through NH_3 volatilization (Hauck, 1985; Goertz, 1993; Azeem et al., 2014). Enhanced efficiency fertilizers that reduce NH_3 volatilization can be divided into two broad categories (Azeem et al., 2014). In the first, a chemical additive, such as N-(n-butyl) thiophosphoric triamide (NBPT) impregnates the urea granule which reduces urease activity near the urea granule (Bremner and Douglas, 1971; Bremner and Chai, 1986; Antisari et al., 1996; Sanz-Cobena et al., 2008). Reducing urease activity allows the urea granule to dissolve and slowly move N into the soil, thus reducing NH_3 volatilization losses (Bremner and Douglas, 1971). A second EEF method is to coat urea granules with a physical barrier, such as with a sulfur (S) or a polymer coating. This approach slows dissolution of the urea granule so that it is released to the environment in a more constant, gradual rate. This may reduce NH_3 volatilization losses and create release rates more synchronous with plant demand during the year (Shaviv, 1996; Blazier et al., 2006).

The primary objective of this research was to determine the effectiveness of three enhanced efficiency fertilizers compared to urea in reducing fertilizer N volatilization losses in mid-rotation loblolly pine plantation systems in the South. We compared NH_3 volatilization losses following fertilization in two different seasons (spring, summer). Two statistical hypotheses were tested in this experiment:

H₀1: There are no differences in NH_3 volatilization between urea and enhanced efficiency fertilizers.

H₀2: There are no differences in NH_3 volatilization for treatments between seasonal applications (spring, summer).

2. Materials and methods

The experiment used a split plot complete block design to test differences in NH_3 volatilization losses. Four fertilizer treatments (main plots) were applied at two different seasons, spring versus summer (split plot) following fertilization in mid-rotation loblolly pine plantations. The fertilizer treatments were the main plots with a single replication of each treatment combination (fertilizer source and season of application) at each individual site. The six sites served as blocks and provided replication. The split plot was the application date (spring, summer). Six sites were selected adjacent to plots in an existing network of forest thinning and fertilization studies in mid-rotation loblolly pine plantations across the South (Fig. 1). Selected climatic and site characteristics are detailed in Table 1 with selected soil chemical and physical data in Table 2.

The four fertilizer treatments were: (1) urea; (2) urea impregnated with N-(n-Butyl) thiophosphoric triamide (NBPT); (3) urea impregnated with N-(n-Butyl) thiophosphoric triamide and coated with monoammonium phosphate and a proprietary binder (CUF); and (4) polymer coated urea (PCU). Urea (46-0-0) was used because it is the most common N fertilizer used in southern forests. The enhanced efficiency fertilizers (EEFs) tested in this study were developed to reduce NH_3 volatilization and release fertilizer N slowly to the environment. In the NBPT treatment (46-0-0), urea granules were impregnated with N-(n-butyl) thiophosphoric triamide at a rate of 26.7% by weight to inhibit urease activity. In the CUF treatment (39-9-0), urea granules were impregnated with NBPT and coated with an aqueous binder containing a boron and copper sulfate solution to slow the release of N to the environment. A coating of monoammonium phosphate was then added to provide P. The PCU treatment (44-0-0) had a polymer coating covering

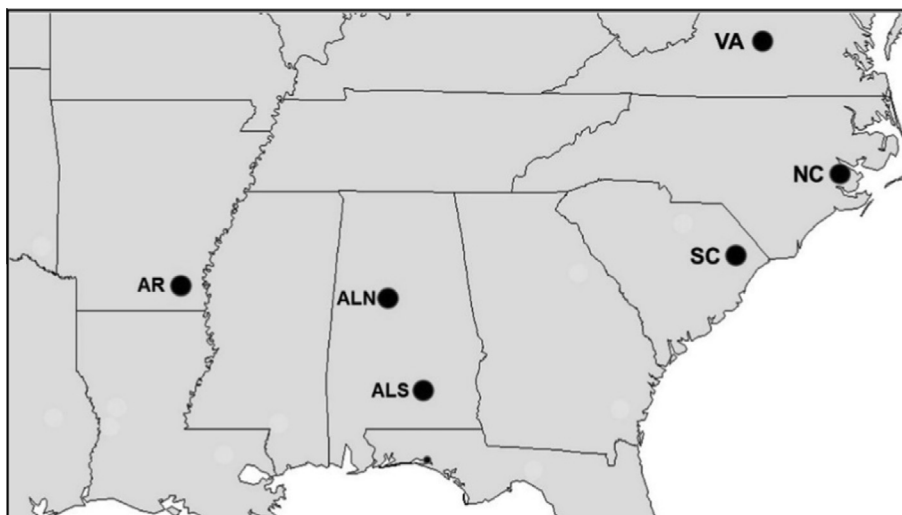


Fig. 1. Location map for sites selected in the southern United States to evaluate ammonia volatilization following fertilization with urea and enhanced efficiency fertilizers enriched with ^{15}N after a spring and summer fertilizer application.

Table 1

Selected climatic and site characteristics for sites in the southern United States selected to evaluate ammonia volatilization following fertilization with urea and enhanced efficiency fertilizers enriched with ^{15}N .

Site	Latitude	Longitude	Altitude (m)	Mean annual precipitation (cm)	Mean annual temperature ($^{\circ}\text{C}$)	Physiographic region	Soil taxonomic class	Soil series	Soil drainage class
VA	37.440087	78.662396	197	109	13	Southern Piedmont	Fine, mixed, subactive, mesic Typic Hapludults	Littlejoe	Well
SC	33.869400	79.289300	2	125	17	Atlantic Coast Flatwoods	Fine, kaolinitic, thermic Umbric Paleaquults	Byars	Very poorly
NC	35.317006	78.514167	0.5	121	16	Atlantic Coast Flatwoods	Fine-silty, mixed, active, thermic Typic Albaquults	Leaf	Poorly
AR	33.422310	91.732651	69	140	16	Western Gulf Coastal Plain	Fine-silty, mixed, active, thermic, Typic Glossaqualfs	Calhoun	Poorly
ALN	33.233371	87.232384	158	125	17	Appalachian Plateau	Loamy-skeletal, mixed, subactive, thermic, shallow, Typic Dystrudepts	Montevallo	Well
ALS	31.659464	86.272045	111	145	26	Southern Coastal Plain	Fine, smectitic, thermic, Typic Hapludults	Arundel	Well

urea granules with pore openings designed to slowly release N ($\sim 80\%$) over a 120 day period. The application rate for all treatments was equivalent to 224 kg N ha^{-1} . Because the CUF treatment contained P in the monoammonium phosphate coating, P was added to the other fertilizer treatment at the equivalent rate of 28 kg P ha^{-1} using triple superphosphate (TSP). The urea granules for all treatments was uniformly labeled with the stable isotope ^{15}N ($\sim 370\text{‰}$, 0.5 AP) (Nadelhoffer and Fry, 1994). All individual fertilizer treatments for both studies were applied by hand to individual microcosms.

Ammonia volatilization losses were determined using an open chamber microcosm methodology detailed by Marshall and Debell (1980) and May and Carlyle (2005). Each microcosm was constructed from a white Schedule 40 polyvinyl chloride pipe (PVC) with an inner diameter of 15.24 cm. Each microcosm was inserted vertically into the soil through the entire organic (O) horizon (Oi + Oe + Oa) into the mineral soil to a depth of 30 cm which severed roots. A 2.5 cm portion of the microcosm remained above the O horizon. The O and mineral soil horizons inside the microcosm were minimally disturbed during insertion.

Immediately prior to each treatment application to individual microcosms, two fertilizer granules were randomly sampled and placed in labeled scintillation vials for ^{15}N analysis that was used in the isotope mass balance calculation for each individual

treatment determination of total ^{15}N recovery. The four fertilizer treatments were applied to the surface of the O horizon in each microcosm. The fertilizer N treatments were applied to randomly selected microcosms on two separate dates. All fertilizer applications in a specific season were made on a single day at individual sites. The spring application dates ranged from March 26 to April 8, 2011, and the summer application dates ranged from June 18 to June 30, 2011. All climatic data was obtained from the nearest weather station to each site. At each site one microcosm for each fertilizer treatment was randomly selected and removed without disturbing the soil inside the microcosm on 1, 15 and 30 days after fertilizer application. An additional mineral soil grab sample (2.5 cm) was taken with a hand trowel immediately below each microcosm at each sampling date to determine if fertilizer ^{15}N had leached below the microcosm. In addition, a control sample was taken with a push adjacent to each microcosm on 1, 15 and 30 days after fertilization to determine the natural abundance ^{15}N . After removal, a plastic cover was secured to the top of the microcosm and plastic wrap to the bottom, and the intact microcosms were placed on ice in a cooler and transported to the laboratory for processing.

All microcosms were stored in a walk-in freezer with a constant temperature of -20.0°C until processed. Upon removal from the freezer, microcosms were thawed and the soil was divided into

Table 2
Selected physical and chemical soil characteristics of loblolly pine stands in the southern United States selected to evaluate ammonia volatilization following fertilization with urea and enhanced efficiency nitrogen fertilizers enriched with ^{15}N .

Site	Depth	BD	CEC	pH	P	K	Ca	Mg	Zn	Mn	Cu	Fe	B	N	C
	cm	g cm^{-3}	cmol kg^{-1}	Water	Mehlich I extractable									Total	
					mg kg^{-1}									g kg^{-1}	
VA	Organic horizon													15.3	315.9
	0–10	1.24	6.40	4.2	3.0	39.3	68.3	14.7	0.5	7.1	0.4	62.7	0.1	1.7	24.9
	10–20	1.32	5.33	4.3	2.3	29.7	44.0	11.7	0.3	4.0	0.6	16.9	0.1	0.5	7.1
	20–30	1.45	5.80	4.4	2.0	39.0	46.0	12.7	0.5	2.4	0.3	29.8	0.1	0.4	8.4
SC	Organic horizon													7.1	252.6
	0–10	1.32	7.10	4.4	4.0	17.0	147.0	24.0	0.4	3.6	0.6	34.9	0.1	3.4	28.6
	10–20	1.35	7.80	4.5	6.0	18.0	217.0	30.0	0.7	2.2	0.5	34.7	0.1	1.2	27.6
	20–30	1.38	7.50	4.6	4.0	16.0	153.0	31.0	0.7	1.1	0.4	75.4	0.1	3.8	13.9
NC	Organic horizon													8.6	309.7
	0–10	1.28	9.5	3.8	8.0	22.0	113.0	22.0	0.6	1.5	0.3	100.3	0.1	1.0	43.5
	10–20	1.31	5.3	4.4	4.0	17.0	59.0	14.0	0.5	0.8	0.4	81.6	0.1	0.6	26.8
	20–30	1.48	4.2	4.4	2.0	16.0	36.0	10.0	0.3	0.3	0.2	74.2	0.1	0.5	15.5
AR	Organic horizon													11.0	279.1
	0–10	1.37	4.90	5.0	4.0	29.0	339.0	85.0	0.6	209.8	0.5	42.1	0.2	1.3	11.2
	10–20	1.41	4.60	5.0	3.0	25.0	265.5	73.0	0.5	192.8	0.5	35.2	0.2	0.7	6.7
	20–30	1.39	4.30	4.9	2.0	21.0	192.0	61.0	0.4	175.7	0.5	28.2	0.1	0.4	5.0
ALN	Organic horizon													9.9	224.7
	0–10	1.27	5.80	5.4	3.0	45.0	449.0	57.0	1.2	126.6	0.5	17.8	0.2	1.9	21.1
	10–20	1.31	4.6	5.4	2.0	44.0	421.0	71.0	0.8	81.7	0.6	13.6	0.2	0.6	6.9
	20–30	1.35	4.6	5.4	2.0	44.0	408.0	65.0	0.9	117.0	0.3	14.6	0.2	0.6	4.4
ALS	Organic horizon													8.7	279.3
	0–10	1.32	15.60	4.2	4.0	76.0	653.0	224.0	0.5	6.3	0.4	53.4	0.2	0.5	21.5
	10–20	1.25	15.35	4.3	3.0	74.0	580.0	207.0	0.5	3.5	0.5	40.7	0.2	0.6	14.4
	20–30	1.36	15.10	4.3	2.0	72.0	507.0	190.0	0.4	0.7	0.5	28.0	0.1	0.4	10.9

four depth increments: O horizon (Oi + Oe + Oa) and the mineral soil increments of 0–10 cm, 10–20 cm, and 20–30 cm. Each depth increment from each microcosm was wet sieved, placed in a labeled double paper bag, dried in a forced air walk-in oven with a constant temperature of 60 °C for 1 week, and weighed. After the depth increments were weighed, O horizon samples were sieved through a 6-mm sieve whereas mineral soil samples were sieved through a 2-mm sieve. All sieved O horizon and mineral sieved soil samples were ground to a very fine powder in a ball mill (Retsch® Mixer Mill MM 200, Haan, Germany) for 2 min at 25 rps to ensure proper homogenization. Between 40 and 45 mg of the ball milled subsamples were weighed in a tin capsule on a Mettler-Toledo® MX5 microbalance (Mettler-Toledo, Inc., Columbus, OH, USA). All instruments prior to isotopic-elemental analysis were cleaned with an ethanol solution and allowed to dry after each sample was processed to reduce potential contamination. The $^{15}\text{N}/^{14}\text{N}$ isotopic ratio and total N of individual samples were analyzed on a coupled elemental analysis-isotope ratio mass spectrometer (IsoPrime 100 EA-IRMS, Isoprime® Ltd., Manchester, UK). The quantity of fertilizer N recovered in each depth increment was determined using an isotope mass balance from measured $\delta^{15}\text{N}$ values and total N content using the method discussed by Nadelhoffer and Fry (1994). Fertilizer N recovered in each depth increment in the microcosm was summed to determine the total recovery in the microcosm. The fertilizer N not recovered was attributed to NH_3 volatilization loss, and expressed as a percentage of the applied fertilizer N.

A mass balance calculation was used to evaluate fertilizer $\delta^{15}\text{N}$ compared to natural abundance $\delta^{15}\text{N}$ that was adapted from Powlson and Barraclough (1993), Nadelhoffer and Fry (1994) and Nadelhoffer et al., (1995) where:

$$M_{\text{labeled}} = M_{\text{final}}(\delta^{15}\text{N}_{\text{final}} - \delta^{15}\text{N}_{\text{initial}})/(\delta^{15}\text{N}_{\text{labeled}} - \delta^{15}\text{N}_{\text{initial}}) \quad (1)$$

% fertilizer N in soil depth increment

$$= ((\delta^{15}\text{N}_{\text{final}} - \delta^{15}\text{N}_{\text{initial}})/(\delta^{15}\text{N}_{\text{labeled}} - \delta^{15}\text{N}_{\text{initial}})) * 100 \quad (2)$$

where M_{labeled} is the mass of the ^{15}N added to the microcosm; M_{final} is the final mass of soil depth increment N pool; $\delta^{15}\text{N}_{\text{initial}}$ is the natural ^{15}N abundance of the soil depth increment N pool; $\delta^{15}\text{N}_{\text{labeled}}$ is the ^{15}N abundance of the added fertilizer; $\delta^{15}\text{N}_{\text{final}}$ is the final ^{15}N abundance of the soil depth increment N pool. Eq. (2) is the percent of N in the soil depth increment from the fertilizer, Eqs. (3)–(6) was used to calculate the percent fertilizer recovery.

% ^{15}N from label in soil depth increment

$$= ((\delta^{15}\text{N}_{\text{soil depth increment}} - \delta^{15}\text{N}_{\text{initial}})/(\delta^{15}\text{N}_{\text{fertilizer}} - \delta^{15}\text{N}_{\text{initial}})) \quad (3)$$

Total N (g) = (Soil depth increment dry weight * %N)/100 (4)

N derived from fertilizer (g) in soil depth increment

$$= (\text{Total N} * \%^{15}\text{N derived from fertilizer})/100 \quad (5)$$

%N derived from fertilizer in soil depth increment

$$= (\text{N from fertilizer (g) in soil depth increment}/^{15}\text{N fertilizer (g)}) * 100 \quad (6)$$

Ammonia N volatilization loss (%), expressed as a percentage of added fertilizer N not recovered from an individual microcosm, was analyzed using a repeated measure analysis of variance (ANOVA) using PROC MIXED in SAS® 9.4 (SAS Institute, Cary, NC). Several alternative spatial covariate structures were tested, and the optimal structure was the unstructured covariate structure based on Akaike's Information Criteria (AIC). Percent data were arcsin transformed prior to analysis (Gomez and Gomez, 1984). Ammonia N volatilization loss (%) was the response variable for the model, day (1, 15, 30) was the repeated measure, fertilizer treatment (CUF, NBPT, PCU, Urea) and season (spring, summer)

were fixed effects, and site (VA, ALN, AR, ALS, SC, NC) was a random effect. (Littell et al., 2006). Levels of significance were set at $\alpha = 0.05$. The post hoc analysis used was Tukey's HSD.

Pearson's correlations were conducted between treatments and weather variables to assess relationships with NH_3 volatilization loss. Maximum daily relative humidity and mean daily relative humidity were calculated from dewpoint and temperature data (Alduchov and Eskridge, 1996), and mean daily critical relative humidity (CRH) for urea dissolution was calculated from an equation adapted from Elliot and Fox (2014, personal communication) that used temperature and relative humidity. The number of days when mean daily relative humidity was greater than the CRH for each sampling interval (1, 15, 30 days after fertilization) were determined. Pearson's correlation coefficients were calculated for mean NH_3 volatilization from urea and the selected weather data 1 day and 15 consecutive days after fertilization for spring, summer and spring + summer application seasons combined to assess relationships between NH_3 volatilization from urea and weather variables. Strong correlations were defined as $0.5 < |r|$, moderate correlations as $0.3 < |r| < 0.5$, and weak correlations as $0.1 < |r| < 0.3$.

3. Results

Mean NH_3 volatilization losses following urea application in the spring were greater than losses from the EEFs 1, 15 and 30 days after fertilizer application (Figs. 2 and 3, Table 3). There were no

significant differences among the individual EEFs 1 and 15 days after fertilization, but mean NH_3 volatilization losses following CUF application were less than mean NH_3 volatilization losses from NBPT and PCU after 30 days. Mean NH_3 volatilization losses, expressed as a percent of the fertilizer N added, after 1 day were 3.9% for CUF, 9.6% for NBPT, 8.2% for PCU and 25.9% for urea. Fifteen days after fertilization, the mean NH_3 volatilization was 13.7% for CUF, 20.0% for NBPT, 15.3% for PCU, and 35.2% for urea. Thirty days after fertilization, the mean NH_3 volatilization was 15.2% for CUF, 23.5% for NBPT, 21.5% for PCU and 40.0% for urea.

Mean NH_3 volatilization losses following urea fertilization in the summer were significantly greater after 1, 15 and 30 days than mean NH_3 volatilization losses from the EEFs (CUF, NBPT, PCU) except after 1 day, where there was no difference between CUF and urea (Figs. 2 and 3, Table 3). There were no significant differences in mean NH_3 volatilization among the individual EEFs after 1 and 15 days, but after 30 days losses from PCU were less than CUF. Mean NH_3 volatilization losses, expressed as a percent of fertilizer N added, were 18.8% for CUF, 6.7% for NBPT, 11.0% for PCU and 28.5% for urea after 1 day. After 15 days, the mean NH_3 volatilization was 16.6% for CUF, 14.2% for NBPT, 11.4% for PCU, and 45.4% for urea. After 30 days, the mean NH_3 volatilization was 23.3% for CUF, 21.4% for NBPT, 11.8% for PCU and 48.7% for urea.

When the data were combined for the spring and summer application (spring + summer), mean NH_3 volatilization losses were significantly greater following fertilization with urea than

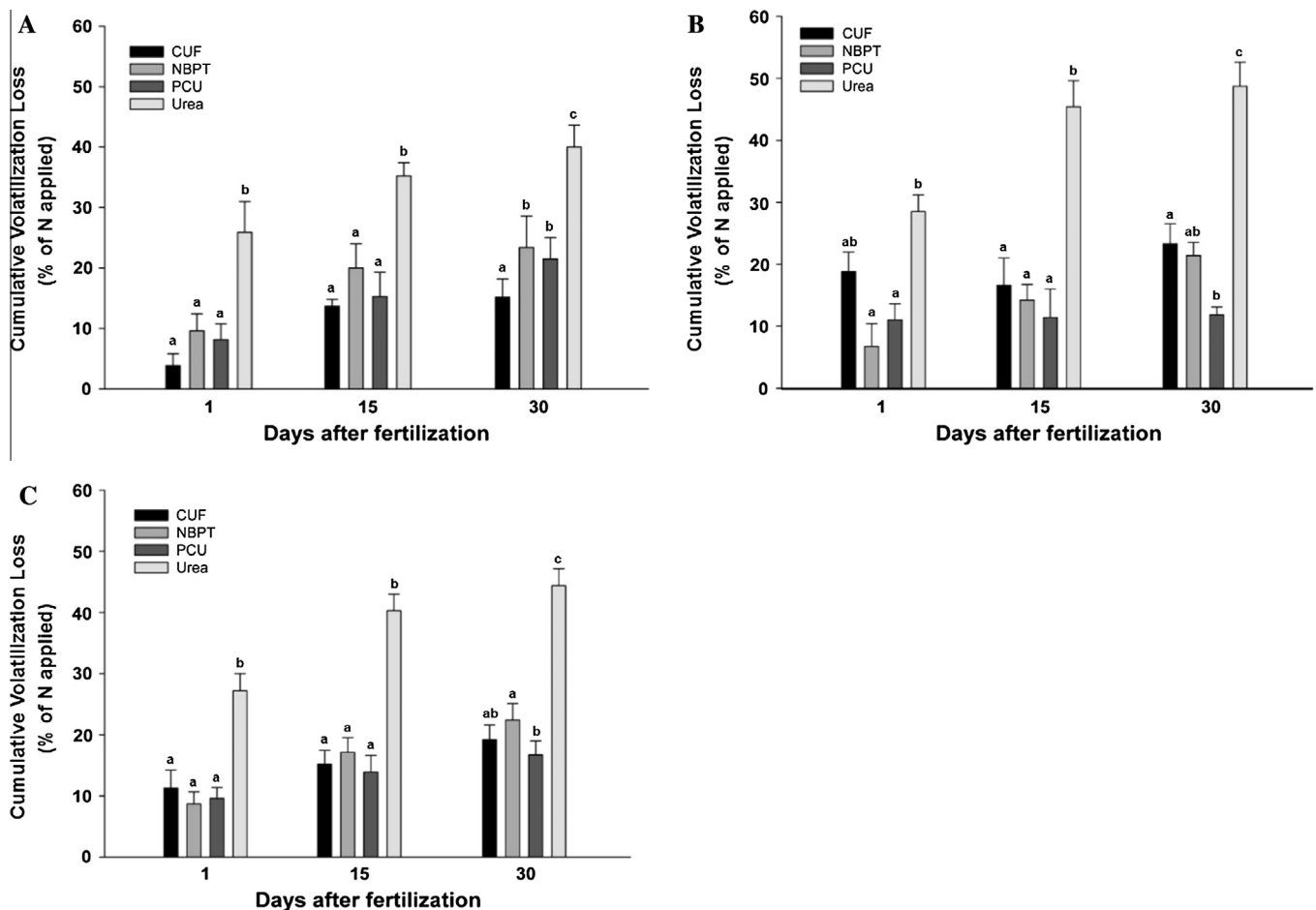


Fig. 2. Cumulative mean volatilization loss from microcosms, expressed as a percent loss of applied N fertilizer, for 6 mid-rotation loblolly pine plantations across the southern United States after a spring (A), summer (B), and spring + summer (C) application of ^{15}N enriched treatments (CUF, NBPT, PCU, urea). Different letters are significant differences at $\alpha = 0.05$, and error bars are the standard error of the mean. The N application rate was 224 kg N ha^{-1} .

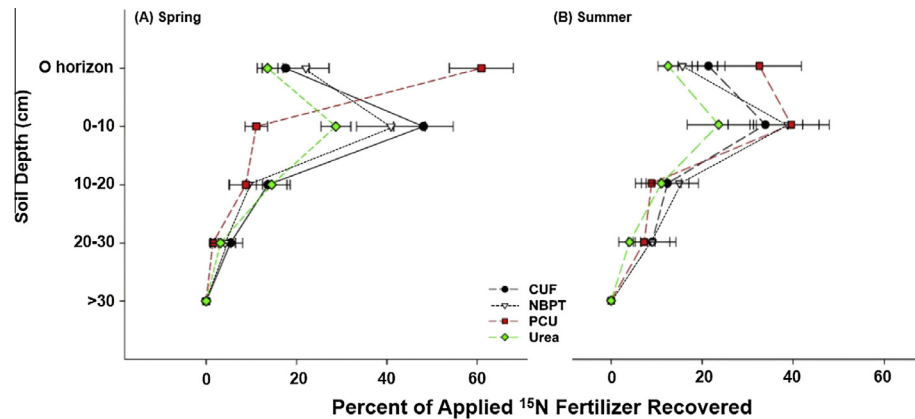


Fig. 3. The mean percent recovery of applied ^{15}N enriched fertilizers in microcosms, by soil depth increment, for spring and summer application after 30 days. The >30 cm increment is immediately below the microcosm. Error bars are the standard error of the mean.

Table 3

$P > |t|$ values for treatment (CUF, NBPT, PCU, urea) contrasts for mean ammonia volatilization loss for days (1, 15, 30) after application of ^{15}N enriched nitrogen fertilizers during two seasons (spring, summer) and combined seasons (spring + summer) at 6 mid-rotation loblolly pine plantations in the southern United States. The nitrogen application rate was 224 kg N ha^{-1} .

Treatment contrast	Number of days following fertilizer application						Overall (spring + summer)		
	Spring			Summer			Overall (spring + summer)		
	1	15	30	1	15	30	1	15	30
Urea vs. CUF	<0.0001	<0.0001	<0.0001	0.1119	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Urea vs. NBPT	0.0006	0.0036	0.0033	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Urea vs. PCU	0.0002	0.0250	0.0002	0.0003	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
CUF vs. NBPT	0.2025	0.2062	0.0287	0.3358	0.9182	0.6285	0.4007	0.5760	0.1962
CUF vs. PCU	0.3380	0.7575	0.0002	0.0866	0.8454	0.4061	0.5809	0.7105	0.4314
NBPT vs. PCU	0.7461	0.3359	0.1811	0.4635	0.9979	0.7267	0.7711	0.3540	0.0412

the EEFs after 1, 15 and 30 days (Fig. 2, Table 3). There were no significant differences among the individual EEFs 1 and 15 days after fertilization, but mean NH_3 volatilization losses were greater following fertilization with NBPT than PCU after 30 days. Mean NH_3 volatilization losses, expressed as a percent of fertilizer N added, were 11.3% for CUF, 8.7% for NBPT, 9.6% for PCU and 27.3% for urea after 1 day. The mean NH_3 volatilization was 15.2% for CUF, 17.1% for NBPT, 13.9% for PCU, and 40.3% for urea after 15 days. After 30 days, the mean NH_3 volatilization was 19.2% for CUF, 22.4% for NBPT, 16.7% for PCU and 44.4% for urea.

Ammonia volatilization losses from urea during the first 15 days following the spring application were strongly correlated with maximum daily temperature (0.579), mean daily temperature (0.808) and cumulative days when daily mean relative humidity exceeded critical relative humidity (0.697). Moderate negative correlations occurred with maximum daily relative humidity (−0.406), and a positive correlation with mean daily relative humidity (0.470). Following summer application, NH_3 volatilization was positively correlated with maximum daily relative humidity (0.403) and mean daily relative humidity (0.322). When data for mean NH_3 volatilization losses after 15 days following spring and summer applications were combined, a strong positive correlation existed with the cumulative days when mean daily relative humidity was greater than the critical relative humidity (0.573), and moderate positive correlations existed with maximum daily temperature (0.406) and cumulative precipitation (0.386). Correlations between weather data and cumulative mean NH_3 volatilization loss over 30 days, expressed as a percentage of N applied, following fertilization with urea for spring, summer and spring + summer data were generally poor.

4. Discussion

Our study focused on assessing NH_3 volatilization following N fertilization with urea and enhanced efficiency N containing fertilizers in loblolly pine plantations in the southern United States. By installing a study across the entire region where loblolly pine plantations are operationally grown, we hoped to improve the understanding of the magnitude of fertilizer N loss across the region compared to a detailed study in a single location or smaller area as done by others (Volk, 1970; Nõmmik, 1973; Kissel et al., 2004; Elliot and Fox, 2014). This study tested two primary hypotheses: (1) whether differences existed in NH_3 volatilization between urea and enhanced efficiency fertilizers; and (2) whether differences existed in NH_3 volatilization among treatments between application seasons.

Our first hypothesis that no differences in NH_3 volatilization existed between urea and enhanced efficiency fertilizers was rejected. Ammonia volatilization losses in 30 days were significantly lower for enhanced efficiency fertilizers (CUF, NBPT, PCU) compared to urea following both spring and summer applications. Significantly less NH_3 volatilization occurred with all enhanced efficiency fertilizers, and when differences were present among individual enhanced efficiency fertilizers they were small. With urea, NH_3 volatilization losses were large following fertilization in both spring and summer, ranging from 25% to 30% of fertilizer N lost after a single day. Losses following fertilization with EEFs were much less compared to urea. Ammonia volatilization losses continued to increase through time for all fertilizers. The incremental additional loss through 15 days and 30 days after fertilization were greater for urea than the EEFs. The result for these

fertilizer treatments agree with those of other studies which have generally found the largest losses for NH_3 volatilization for urea occurring between 1 day and 7 days after application (Craig and Wollum, 1982; Clay et al., 1990; Kissel et al., 2009; Elliot and Fox, 2014).

The major loss pathway of the fertilizer N for this study was through NH_3 volatilization. Urea hydrolysis, facilitated by urease, produces ammonium carbonate which dissociates into ammonium (NH_4^+) and bicarbonate (HCO_3^-). The bicarbonate consumes hydrogen (H^+) ions near the dissolving urea granule which raises the surrounding pH (Hauck and Stephenson, 1965). Once pH is raised above 7, the ammonium ions (NH_4^+) can be converted to ammonia (NH_3) which can be lost to the atmosphere. Higher rates of precipitation immediately following fertilization with urea, in excess of 1.27 cm, can dissolve the urea and move it into the soil, reducing NH_3 volatilization (Kissel et al., 2004). The sites for this study all had only minor (less than 12 mm) or no precipitation events within the first few days following fertilization. Minor precipitation events coinciding with warm temperatures following urea fertilization can exacerbate losses through the NH_3 volatilization pathway (Kissel et al., 2004) which occurred in our study and likely caused large losses for urea. Conversely, studies have shown large precipitation events after fertilization with urea can move fertilizer N into the soil profile rapidly (Kissel et al., 2004). Once the fertilizer N moved into the acidic soil at our study sites, it became more difficult for NH_4^+ to convert to NH_3 due to the soil pH buffering capacity (Ferguson et al., 1984). Two of the enhanced efficiency fertilizers we used in this study, CUF and NBPT, used NBPT to reduce urease activity for a short period, allowing time for precipitation to move the urea into the soil and thereby reducing losses from NH_3 volatilization.

We rejected our second hypothesis that there were no differences in NH_3 volatilization between application seasons (spring versus summer). There was a significant interaction between treatment and season indicating larger NH_3 volatilization losses following the summer application (Table 2). Losses from urea were greater in the summer compared to spring. Sites generally experienced higher temperatures, more days when relative humidity exceeded critical relative humidity, and few large precipitation events following the summer fertilizer application. As previously discussed, this type of weather increases the chances for NH_3 volatilization from urea (Koelliker and Kissel, 1988; Moyo et al., 1989; Kissel et al., 2004). When there is insufficient precipitation to move dissolved urea into the soil, NH_3 losses may be large (Kissel et al., 2004).

Differences in NH_3 volatilization among the EEF treatments were small and somewhat variable. After one day in the summer, losses from the CUF treatment were greater compared to spring, but similar after 15 and 30 days. For the NBPT and PCU treatments, losses were less each day for the summer compared to the spring. When reviewing the data from individual sites, there were more frequent, smaller precipitation events during the summer compared to the spring at most sites. Several small precipitation events during this period may initiate fertilizer N from the EEFs into the soil, whereas larger losses could occur with urea as found by Kissel et al. (2004). The NBPT added to the CUF and NBPT treatments generally decrease urease activity for approximately two weeks (Shaviv, 1996). The polymer coating in the PCU treatment is designed to allow moisture to diffuse through the polymer coating which then expands and diffuses the dissolved urea through the polymer coating, gradually releasing fertilizer N to the environment. For the summer application period, more frequent, smaller precipitation events may have increased in the release and movement of N into the soil for PCU.

An additional question this research could address was the effect of weather on NH_3 volatilization following urea fertilization.

Similar to others (Cabrera et al., 2005, 2010; Elliot and Fox, 2014) we found a strong correlation between NH_3 volatilization from urea and the number of days which relative humidity exceeded the calculated critical relative humidity immediately following fertilization (Elliot and Fox, 2014). When relative humidity exceeds the threshold of critical relative humidity, urea hydrolysis occurs and can lead to NH_3 volatilization (Cabrera et al., 2005).

Results from this study indicated NH_3 volatilization was not always strongly correlated with rainfall or temperature measured at local weather stations. In spite of this, the results from our regional study demonstrate that the amount of urea N lost due to NH_3 volatilization is difficult to accurately predict because the loss of fertilizer N is affected by many factors. High surficial wind speed (Watkins et al., 1972; Kissel et al., 2004), low precipitation (Craig and Wollum, 1982; Kissel et al., 2004) and high air temperature (Gould et al., 1973; Craig and Wollum, 1982; Koelliker and Kissel, 1988) increase NH_3 volatilization. The interaction between temperature and rainfall were illustrated by Kissel et al. (2004) who observed low NH_3 volatilization during August when urea was applied on the same day as a significant precipitation event, but high volatilization (45–58%) following minor precipitation events.

Urea applied under wetter, cooler periods tends to reduce NH_3 volatilization losses (Ferguson and Kissel, 1986; Moyo et al., 1989; Cabrera et al., 2010) due to rapid urea dissolution (Black et al., 1987; Paramasivam and Alva, 1997) which moves N into the soil compared to urea remaining on the soil surface. This is a primary reason why in the past urea has been commonly applied during winter months in loblolly pine plantations in the South. However, large losses of fertilizer N through NH_3 volatilization have occurred even under low temperatures (Carmona and Byrnes, 1990; Engel et al., 2011). In the southeastern United States, even in the winter the high temperatures and high relative humidity can stimulate urease activity increasing NH_3 volatilization (Craig and Wollum, 1982; Ferguson and Kissel, 1986; Moyo et al., 1989).

Although NH_3 volatilization was the primary loss pathway in this study, three additional loss pathways could have occurred in this experiment. First, fertilizer N uptake by trees was eliminated by the severing of roots by the insertion of microcosms into the soil. Second, fertilizer N leaching, determined through ^{15}N analysis, was undetectable based on the sampling directly below (>30 cm) each microcosm on all sampling dates for all treatments for this study (Fig. 3). If this loss pathway was important, samples immediately below the bottom of the microcosm (>30 cm soil increment) should have had elevated ^{15}N signatures which did not occur. Third, denitrification was not significant in this study because there were no differences in N losses between well versus poorly drained soils in this experiment. Recent work on similar sites used in this study specifically examining denitrification after fertilization found denitrification losses were relative low during spring and summer months (Shrestha et al., 2014). Denitrification occurs in anaerobic environments when nitrate functions as the terminal electron acceptor during the oxidation of soil organic matter. Although certain sites for this study were classified as poorly drained, all microcosms installed at these sites were all located on top of beds which were in aerobic soil (Kelting et al., 1998; Shrestha et al., 2014). Although low levels of fertilizer N loss may have occurred through both leaching and denitrification, we concluded that NH_3 volatilization was the primary loss pathway for N in our microcosm systems.

A primary benefit of this study is the results are drawn from an extensive geographic area, encompassing the entire region where loblolly pine plantations are operationally fertilized. Because this study does encompass such an extensive region, and hence large range of climatic and edaphic variables, a synthesis of significant factors helps to support the results specific to NH_3 volatilization

after N fertilization of other studies in forest ecosystems that are an assessment of a single or smaller regional sites. Additionally, the open chamber system design of the microcosm does not have the potential limitations of closed chamber systems that can manipulate pressure, temperature or wind speed, although the results of this study still should be viewed as an index and not absolute values.

This study provides continued evidence that although weather conditions can be important in determining NH_3 volatilization losses from urea, they do not translate to the same losses for enhanced efficiency fertilizers. These results provide evidence to forest managers that enhanced efficiency fertilizers can significantly reduce NH_3 volatilization losses of fertilizer N across the entire range of southern loblolly plantations, regardless of the season of application. Reducing fertilizer N losses with enhanced efficiency fertilizers could reduce N application rates. Use of enhanced efficiency fertilizers may also extend the amount of plant available N further into the rotation. These combined characteristics of enhanced efficiency fertilizers would translate to improved forest productivity and fertilizer N use efficiency in southern loblolly pine plantations in the future, providing improvements to the economic viability and environmental stewardship of fertilizer use in loblolly pine plantations in the southern United States.

5. Conclusions

The primary results for this research were that significantly lower NH_3 volatilization losses occurred from all forms of N containing enhanced efficiency fertilizers (CUF, NBPT, PCU) over extensive ecophysiological regions of the southern United States in mid-rotation loblolly pine stands compared to the conventional current standard of forest fertilization, urea. These results indicate that enhanced efficiency N containing fertilizers can reduce NH_3 volatilization losses over a significant range of weather and edaphic factors compared to urea. These findings may translate to improved fertilizer N use efficiency in southern loblolly pine plantation systems by retaining more fertilizer N in the system, with the possibility of reducing application rates of N in the future. These findings are important to the continued direction of improving productivity in southern loblolly pine plantations. Using enhanced efficiency fertilizers may also provide the ability for forest managers to apply fertilizer N in a more synchronous manner to plant demand under conditions where large NH_3 volatilization losses occur with urea, continuing to improve fertilizer N use efficiency in these systems. Viewed collectively, these results indicate that NH_3 volatilization can be decreased significantly using any of the enhanced efficiency fertilizers in this study (CUF, NBPT, PCU) when compared to urea under a diverse range of climatic and site variables for pine plantations in the southern United States. These results provide forest managers a level of certainty that if NH_3 volatilization is a concern, enhanced efficiency N containing fertilizers may assist in retaining more fertilizer N in the system, translating to a potentially higher fertilizer N use efficiency over the rotation of the stand.

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