



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.

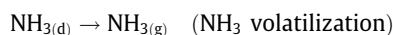
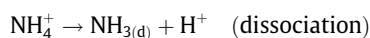
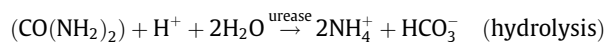
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1. Introduction

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, 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

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