

**ENHANCED EFFICIENCY NITROGEN FERTILIZER AS TOOL TO CONTROL
NITROGEN LOSS IN ROW CROP PRODUCTION**

A Thesis Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

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May 2024

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ACKNOWLEDGEMENTS

It was a dream come true when I enrolled at the Department of Biosystems Engineering and Soil Science (BESS), University of Tennessee, Knoxville as a graduate student. First and foremost, I am grateful to God for making it possible for me to embark on this new challenge and also ending it well. My sincere thanks and gratitude to my advisor, Dr. Nutifafa Adotey for his overall guidance and support throughout my master's track program. Dr. Adotey took his time to make me understand and appreciate the scope of my research as early as possible, and this gave me the needed leverage and head start. Dr. Adotey made a bold move regarding his choice of me as his first graduate student, and I am grateful for the support of a graduate assistantship offered me for my graduate studies. Dr. Adotey's firm resolve and his disposition to help, interspersed with his constructive criticisms were largely instrumental in my successful completion of this M.S. program. Fafa, I am grateful for the confidence in me, and for every contribution you have made in my life right from the onset of this training until my graduation. My sincere thanks to my thesis committee members, Dr. Daniel Yoder, Dr. Lori Duncan, Dr. Debasish Saha, and Dr. Frank Yin for their individual and collective role in my training program. I am grateful that you made time for me, provided me with timely and valuable feedback, and supported me throughout my studies and research. I am grateful for the encouragement and warmth extended to me by Dr. Scott Stewart, Director of WTREC, during my stay at the station for my research. Dr. Scott always ensured I had a place to stay each time I visited the station for my research work. I am also thankful to all PI's, staff, and graduate students of WTREC for the warmth and friendly atmosphere that always ensued at the station. You made my

research proceed well. I want to thank Wesley Wright, Scot Tucker and David Smith for the design and set up of my experiment, and for helping me out each time I encountered a problem with the system. I also want to thank the Tennessee Department of Agriculture (TDA) for funding my research, and KOCH for providing agronomic input for my research. I would also like to thank Roberts Florence of the University of Tennessee Soil, Plant and Pest Center, Nashville, Tennessee; and Greg of Brookside Laboratories, Inc., New Bremen, Ohio, for analyzing my soils and samples. I am grateful for the support of Dr. Adotey's soil fertility and nutrient management lab members including Research Associates, Dr. Regina Adotey and Nate Montgomery; and Student Interns, Lake Lovorn, and Samuel Carranza, for their role and assistance with soil collection, experimentation, and data collection. I would also like to thank Sydney Logwood, my colleague graduate student with Dr. Adotey for her support and encouragement. I am grateful to Pastor Mills, Lady Tina Mills, and the entire congregation of Amazing Church International, Knoxville for providing the faith background to my graduate studies. I would like to thank my parents, siblings, family, and friends for supporting me in diverse ways. Last, but specially, I would like to express my profound gratitude to my wife, Celestina, and my two daughters, Michelle and Meghan, for standing by me on this journey.

ABSTRACT

The efficiency of urea-based fertilizers is substantially reduced through nitrogen (N) losses via ammonia volatilization. Soil pH, clay content, soil organic matter (SOM), and field capacity can affect ammonia loss. Incubation experiments were conducted on eight soils using a controlled environment system to study the effects of soil properties on ammonia volatilization from urea and urea ammonium nitrate (UAN) applied at 134.5 kg N/ha. Each experiment was set up as a randomized complete block design with four replicates. Ammonia loss was measured on 1, 2, 3, 4, 5, 6, 7, 9, 11, 13, and 16 DAF (days after N application). Cumulative losses of ammonia from UAN and urea ranged from 1.4 - 18.1 % and 10.5 - 26.5 % of total N applied, respectively. Cumulative ammonia losses from urea were higher than UAN in six soils, but the losses were similar for both urea and UAN in the remaining soils. Stepwise regression analysis predicted soil pH and clay content as the most parsimonious model for ammonia loss from both urea and UAN applications. The same experimental setup was used to evaluate the efficacy of different enhanced efficiency N fertilizer (EENF) products in mitigating ammonia volatilization losses in two soils highly susceptible to ammonia volatilization losses. The EENF sources included Urea+ANVOLTM, UAN+ANVOLTM, ESN[®], SUPERU[®], and urea+Excelis[®] which were surface-applied at 134.5 kg N/ha. Cumulative ammonia loss from the EENF products ranged from 3.3 – 10.6 % in soil 1 and 2.2 – 16.1 in soil 2 (% of applied N). Treated urea products were effective in reducing ammonia volatilization loss (% of applied N) by 60.63 – 87.62 and 32.26 – 90.96 % for soils 1 and 2, respectively, when compared to untreated urea. Similarly, the treated UAN reduced ammonia volatilization loss by 26.90 and 69.51

in soils 1 and 2, respectively when compared to untreated UAN. The effectiveness of the EENF treatments in both soils was: ESN[®] > UAN+ANVOL[™] > urea+ANVOL[™] > urea+Excelis[®] > SUPERU[®]. Reliable EENF products are a viable tool to reduce N losses as ammonia, regardless of soil properties.

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CHAPTER ONE: INTRODUCTION AND LITERATURE REVIEW

Introduction

Nitrogen (N) as a macronutrient plays a vital role in supporting the growth and productivity of plants including the synthesis and translocation of phytohormones, and being a constituent of the chlorophyll molecule, amino acids and amino enzymes, nucleic acids, nucleotides, purine, bases, and alkaloids (Ali et al., 2022; Arduini et al., 2018). It is considered the most growth-limiting plant nutrient in cropping systems all over the world because N is very susceptible to several loss pathways such as ammonia volatilization, denitrification, surface leaching, and runoff (Fageria, 2014). In most cases, N fertilization is required to maintain the production of food, fiber, and feed. The exceptions may be with legumes, which fix N, and with virgin soils with relatively high N content (Dinnes et al., 2002). Most growers use both organic and inorganic N fertilizer sources to obtain optimal growth, development and yield of crops. However, the utmost benefits of using these fertilizers can be achieved when best management practices such as the 4 R Nutrient Stewardship practices (right fertilizer source, right rate, right placement and right time) are implemented by growers (Snyder, 2017). Urea-based N fertilizers, the most used N source, are susceptible to significant losses of N through ammonia volatilization, especially in no-till (NT) or minimum tillage production systems where fertilizers are not incorporated into the soil (Jones et al., 2007; Triplett Jr and Dick, 2008).

Literature review

Nitrogen use in row crop production systems

Nitrogen (N) is an important but expensive investment in corn production. Globally, an estimated 120 Tg of chemical N fertilizer is applied annually, an increase of nearly eight times in

annual N consumption in cropping systems since 1961 (FAO, 2017). In the U. S. for instance, expenses related to fertilizer input for corn from 2010 to 2016 accounted for about 37 – 45 % of overall operating cost per year (Zhou et al., 2018). In Tennessee, N fertilizer application accounts for 13 % of total expenses in no-till rainfed corn production (Department of Agriculture and Resource Economics, UT, 2023). Generally, the recommended N rate is more than plants N requirements in order to compensate for losses (Omara et al., 2019). However, this practice has negative effects on N use efficiency (NUE), which measures the quantity of grain produced per unit of fertilizer applied (Watts et al., 2015). It is estimated that the NUE for most cereals worldwide is less than 33 % (Fageria, 2014; Omara et al., 2019). This means that about 67 % of total N applications are lost and could contribute to environmental issues such as diminished air and water quality. Consequently, imbalances between N supply and crop demand have become a considerable environmental and financial risk mainly because of N losses, and this has limited NUE and farm profitability (Fageria, 2014).

Nitrogen sources

There are many different sources of N fertilizer, which can be categorized as organic or inorganic. The organic sources include plant materials, legume green manure, dried blood, cottonseed meal, animal manure, or mulch (Adeli et al., 2016). However, the N concentration of these organic sources of fertilizer is relatively low as compared to the inorganic sources; and only about 50 to 60 % of the immobilized N could be available for plant uptake (Bolan et al., 2010). This means that larger quantities are needed to attain recommended rates of N compared to inorganic N application (Tewolde et al., 2013). An estimated 56 % of all fertilizers consumed across the world were N fertilizer in 2021 (FAO, 2023). The most common inorganic N fertilizers include urea-based (such as urea-ammonium-nitrate, urea-ammonium-phosphate, urea

formaldehyde); ammonium-based (such as anhydrous ammonia, ammonium nitrate, ammonium sulfate); and nitrate-based (such as calcium nitrate, potassium nitrate, magnesium nitrate).

Ammonium nitrate was utilized in many no-till producer fields as a leading source of N in the Southern U. S. However, following governmental restrictions on its use, unit prices have increased and significantly reduced its availability on the market (Yin, 2015). There is evidence to suggest that large retail companies have avoided its use in many States within the Southeast (Zhou et al., 2018).

Anhydrous ammonia contains no water and has nearly 83 % N. It was in the past the preferred source of N in many Corn Belt regions because it was relatively cheap and had higher N content (Kyveryga et al., 2004). Although it is a cheap and readily available source of N, it requires specialized facilities and equipment for storage under pressure, transport to farm, and application (injection) into the soil. The injection also requires trained fertilizer labor with meticulous adherence to procedures. It also poses significant health risk to applicators and anyone who comes near it (Kyveryga et al., 2004).

Urea is a common fertilizer source of N worldwide utilized in crop production mainly because of its relatively low prices and high N content (46 %) compared to other N sources (Engel et al., 2011; Frame, 2017). It is also the preferred choice for farmers because it is readily accessible; and for manufacturers and retailers because of its easy handling and storage characteristics (Li et al., 2015). USDA-ERS (2019) estimated that agricultural urea consumption increased from 142,198 metric tons in 1960 to 7,038,055 tons by 2015. Urea prices have generally tended to increase since the 1970s, being affected by natural gas prices, demand and supply forces and commodity prices. Urea fertilizer exists in dry granular urea (46-0-0) or liquid urea forms and is used in the manufacturing of urea ammonium nitrate solution (UAN) (28-0-0 or 32-0-0). UAN is

a common combination of N sources, with approximately 33% urea, 43% ammonium nitrate, and 25 % water and other materials (Nieuwenhuyse, 2000).

Principal N loss pathways in cropping systems

Plants take up N in the ammonium (NH_4^+) and nitrate (NO_3^-) forms, and often respond better to ammonium and nitrate applications at early and later stages of growth, respectively (Adotey et al., 2020). The most common and relevant losses of N in the soil-plant system occur through ammonia volatilization, leaching of nitrate, and denitrification (Fageria, 2014).

Ammonia volatilization

Loss of N through ammonia volatilization is particularly important in calcareous soils (Mandal et al., 2018). Ammonia volatilization is the conversion of urea-based N fertilizer into ammonia gas that escapes into the atmosphere when the soil pH is above 7. Ammonia volatilization starts with the hydrolysis of urea by the urease enzyme to form ammonium bicarbonate (Kissel et al., 1988). The resulting alkaline microclimate facilitates the production of ammonia gas from ammonium. The potential of ammonia loss is influenced mainly by soil properties such as soil pH, soil organic matter (SOM), and clay content (Sunderlage and Cook, 2018). However, the extent to which ammonia volatilization occurs is dictated by nutrient management practices (especially the 4Rs of fertilizer management) and environmental factors including wind, temperature, and precipitation (Jones et al., 2020).

Ammonia volatilization limits NUE and creates challenges with N management at the farm level through dry or wet deposition (Woodward et al., 2011). All surface applied, unincorporated, ammonium- and ammonia-based fertilizers are subject to volatilization, especially within the first two to three weeks after application (Jones et al., 2007). Losses are higher for the first 3–7 days

after surface broadcast urea (Adotey et al., 2017; Frame, 2017), but can linger to about 9–15 days when little precipitation follows N application (Woodley et al., 2020).

Nitrification and denitrification

Nitrification refers to the biological oxidation of ammonium (NH_4^+) to nitrite (NO_2^-) and then to nitrate (NO_3^-). This process is mediated by *Nitrosomonas* sp. and *Nitrobacter* sp., groups of bacteria common in the soil (Di and Cameron, 2002). Under favorable temperature and soil moisture conditions, rapid transformation of ammonium to nitrate may occur in most fields after N fertilizer application, depending on soil temperature during fertilizer application (Di and Cameron, 2002). Since nitrate is loosely adsorbed onto soil particles and organic matter, and is more mobile in solution than ammonium, it is usually lost through leaching (Ruark et al., 2018). Denitrification, on the other hand, is the microbial-mediated process in which nitrate is used as an electron acceptor in the absence of oxygen (O_2), so reactive N is converted back to inert atmospheric dinitrogen (N_2) (Firestone, 1989). During this process, nitrous oxide (N_2O), a potent greenhouse gas, is produced as an intermediate product of denitrification reaction or a direct product of nitrification (Firestone, 1989). The reduction reaction steps occur as follows:

NO_3^- (nitrate) $\Rightarrow$ NO_2^- (nitrite) $\Rightarrow$ NO (nitric oxide) $\Rightarrow$ N_2O (nitrous oxide) $\Rightarrow$ N_2 (dinitrogen gas).

The production of nitrous oxide through nitrification is favored under aerobic soil conditions, whereas its production by denitrification is facilitated under anaerobic conditions (Dell et al., 2014). Denitrification reduces the effectiveness of N fertilizer applications (Watts et al., 2015). Nitrous oxide is an active GHG with a warming potential nearly 310 times more than that of carbon dioxide (Smith et al., 2007). Despite only an estimated 2 % of applied manure and 2.5 % of N fertilizers being emitted as nitrous oxide into the atmosphere, agricultural soil management contributes nearly 75 % of nitrous oxide into the atmosphere in the U.S. (Smith et al., 2007). In

addition, volatilized ammonia gas in the atmosphere is easily converted to nitrous oxide and contributes to the formation of particulate matter PM_{2.5} which can cause considerable damage to human health and change the energy balance of the climate system (Li et al., 2015).

Nitrate leaching

Nitrate is a form of N that readily dissolves in water and moves freely throughout the soil profile, especially in sandy soils (Omara et al., 2019). This negatively charged ligand is loosely adsorbed by soil particles making it susceptible to leaching losses in cropping systems (Hussain et al., 2019). Nitrate is the principal form of N found in soil solution, and regardless of the source – whether organic or inorganic – excess application or ill-timed application of N becomes surplus to plant requirements (Hussain et al., 2019). The rate of nitrate loss is hugely impacted by the type of soil, and the type and timing of tillage practices being adopted at the farm level (Omara et al., 2019). Nitrate leaching may be facilitated by tillage operations as compared to conservation practices (Hansen and Djurhuus, 1997). For instance, sandy loam may be more impacted by tillage, but coarse sand may not, and delayed tillage may reduce nitrate leaching compared to early tillage (Stenberg et al., 1999).

Studies have shown that the extensive use of inorganic N fertilizers in row crops production is a principal source of nitrate contamination (Padilla Ruiz et al., 2018; Wang et al., 2019). For instance, the recommended rates for corn N applications ranges from 100 to 250 kg N ha⁻¹ yr⁻¹ in the Midwest corn belt of the U.S.; and between 15 to 65 % of this application rate is likely to be lost out of the rooting zone through nitrate leaching (Basso et al., 2016; Randall and Mulla, 2001).

Concentration of nitrate in domestic water above the 10 mg L⁻¹ threshold may be harmful to human life as well as livestock (Dinnes et al., 2002). High nitrate concentration in domestic

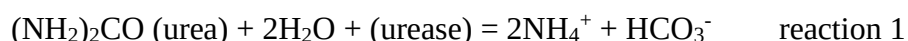
water supply has been correlated with health problems including methemoglobinemia (blue-baby syndrome) and cancer (Brady and Weil, 2002).

Additionally, the accumulation of nitrate-N in major water resources including the Mississippi River and its tributaries may cause freshwater and marine ecosystem degradation. Eutrophication in the Gulf of Mexico in recent years has been attributed to the changes in aquatic biodiversity population dynamics brought about by the increased incidences of hypoxia (low oxygen conditions) and anoxia (water devoid of oxygen) conditions from nitrate loadings (Turner and Rabalais, 1991). Hypoxic areas in marine or freshwater ecosystems become dead zones that fish and shrimp avoid.

Urea hydrolysis mechanism

Urea is a diamide carbonic acid, usually crystalline, white, odorless and dissolves in water (Junejo et al., 2011). Urea hydrolysis involves the reaction of urea with water, leading to the decomposition of the chemical bonds in both urea and water (Kissel et al., 1988). This reaction is accomplished with the enzyme urease to produce ammonium and bicarbonate ions (HCO_3^-).

The chemical reactions are:



The reaction products of both reactions (HCO_3^- and CO_2) increase the soil pH and accelerate the conversion of NH_4^+ to NH_3 through the following reactions:



Soil urease is a stable enzyme that thrives in soil environments for long periods (Kiss and Simihăian, 2002). Urease in soil is synthesized by bacteria, fungi, archaea, and plants. As an

extracellular enzyme, urease often binds to and stabilizes clay particles (Krajewska, 2009). The functionality of urease in the soil is dictated by prevailing temperature, humidity, cation exchange capacity (CEC), soil pH, and the availability of crop residues on the soil surface (Silva et al., 2017). The rate of conversion of N to ammonia and loss of N through volatilization is enhanced when the urea fertilizer is left on the soil surface (Adotey et al., 2017; Frame et al., 2012). Therefore, urea fertilizer applications followed by mechanical incorporation or water movement into the soil to a depth of about 5 cm are effective in reducing ammonia volatilization losses (Holcomb III et al., 2011).

Factors that influence ammonia volatilization from urea-based fertilizers in row crops

Weather conditions

Environmental drivers including rainfall, temperature, humidity and air exchange at the soil surface directly influence ammonia volatilization loss from a soil (Francis et al., 2008). Ammonia volatilization after urea application is often reduced when followed by a rainfall or irrigation event. Studies have reported that about ½ inch of rain was enough to incorporate urea applied on soil surface and thereby minimize losses due to ammonia volatilization (Jones et al., 2020). It was estimated that nearly 12.5 % reduction in ammonia volatilization loss per centimeter of soil incorporation depth with rainfall is possible (Rochette et al., 2013).

Higher temperature increases urea solubility in water as well as the diffusion of urea and its hydrolysis products (Junejo et al., 2011). High temperature increases the concentration of ammonia in soil solution, and since warm soil solution can barely hold high levels of ammonia, losses to the atmosphere tend to be faster (Jones et al., 2020). In addition, high temperature speeds up the hydrolytic action of the urease enzyme on urea on the soil surface and facilitates the rapid transformation of ammonium to ammonia gas. The extent of ammonia loss through volatilization

is doubled by a temperature rise from 5 to 25 °C, and nearly three times when temperature increased from 25 to 45 °C (Francis et al., 2008).

Cold temperatures may also increase ammonia losses from a soil surface, but through different processes than warm temperatures. Cold temperatures slow down the formation of ammonium from urea, the conversion of ammonium to ammonia gas, the process of nitrification, adsorption of ammonium and nitrate to clays and soil organic matter, immobilization of N by microorganisms, and uptake of N by plant roots. This makes the soil remain moist longer, allowing higher ammonia content in soil solution. This ammonia slowly volatilizes to the atmosphere from the soil. An estimated 40 % of N losses in Montana were recorded for urea applications at soil temperature < 5 °F (Jones et al., 2020); and nearly 12 % of applied N was volatilized at 30 °F on snow covered soils within 5 weeks (Engel et al., 2011).

Urea fertilizer is a hygroscopic material, with the capacity to absorb moisture through contact with liquid water and/or water vapor. Under high humidity conditions, urea pellets absorb moisture from the air and dissolve faster, increasing ammonia volatilization (Dari et al., 2019). Wind typically has a drying effect on soil surfaces and can speed up losses of ammonia due to volatilization (Dari et al., 2019). But wind can also impede volatilization by drying soil surfaces quickly enough to limit urea dissolution underneath (Nathan and Malzer, 1994).

Soil properties

Soil pH

Urea-based fertilizers undergo hydrolysis upon application to a soil surface, raising the soil pH near the urea dissolution. This localized increase in pH favors the conversion of ammonium to ammonia gas, which is rapidly lost to the atmosphere through ammonia volatilization (Kissel et al., 1988). Generally, soils with initial high pH (pH >7.0) are more prone to ammonia losses

compared to neutral to acidic soils (pH 5.0 – 7.0). Since the concentration of ammonia dissolved in water tends to increase under high soil pH and high temperatures, the rate of ammonia volatilization also increases under such conditions (Dari et al., 2019).

Clay content

The removal of hydrogen ions (H^+) from the soil solution through urea hydrolysis raises pH within the vicinity of the fertilizer granule. Because of this, soil properties that resist changes in soil pH may reduce ammonia volatilization in soil. N losses through volatilization are therefore influenced by soil clay content and other indicators of its buffering capacity (Jones et al., 2020). Often, soils with high buffering capacity tend to withstand pH fluctuations and could bind ammonium to clay particles thereby reducing ammonia losses through volatilization.

Soil organic matter (SOM)

SOM refers to the decomposed stable component of organic matter occurring in the soil. It is an integral component of soil buffering capacity, and thus plays a key role in buffering soil pH and reducing the extent of ammonia volatilization. Often, soils with low SOM receiving urea applications are predisposed to higher cumulative ammonia losses (Sunderlage and Cook, 2018). The negatively charged surfaces of SOM adsorb ammonium and reduce its concentration in the soil solution. SOM content can thus influence ammonia loss because of its contribution to pH-dependent negative charges of the soil's cation exchange capacity (CEC), which may temporarily retain ammonia in soils and inhibit ammonia volatilization (Stevens et al., 1989).

Soil moisture (field capacity)

Field capacity is the soil water content after the soil has been saturated and allowed to drain freely for 24 to 48 hours. In wet soils, ammonia volatilization losses are higher when soils are at or near field capacity at the time of urea fertilizer application. Wet soils facilitate urea hydrolysis

but slow the downward movement of hydrolysis products into the soil because the pore spaces are saturated with water. Under dry soil conditions, however, the dry fertilizer is sparingly soluble, which limits biological and chemical reactions needed for ammonia volatilization to occur (Dari et al., 2019). Dry surface fertilizer applications followed by incorporation either by tillage or rainfall/irrigation significantly reduce ammonia volatilization losses.

N management practices

N source

The choice of N fertilization can influence the magnitude of losses that occur at a given field. Although urea is ubiquitous and has a lower per unit price of N, it is highly susceptible to N losses via ammonia volatilization (Engel et al., 2011; Frame, 2017; Jones et al., 2007). Losses due to nitrate leaching from urea applications have also been reported (Shapiro et al., 2016). Studies have shown that cumulative N losses from urea (46-0-0) and UAN (28-0-0 or 32-0-0) are variable, and often higher for urea than UAN (Adotey et al., 2017; Vaio et al., 2008). Surface application of ammonium nitrate (34-0-0) is less susceptible to ammonia volatilization compared to urea (Jones et al., 2020). Ultimately, considerations such as availability, cost, equipment requirement, and convenience of application tend to guide the preference of one N source over another.

N placement

The application of N fertilizer can be broadcast or banded below the soil surface (Jones et al., 2007). N losses through ammonia volatilization can be as high as 64 – 68 % of N with broadcast urea application when left on soil surfaces (Rochette et al., 2009). The losses are often greatest for the first 3-7 days of urea application, but peak losses may be delayed to between 9-15 days with limited rain events following urea application (Drury et al., 2017). Banding of urea beneath the

soil surface appears to reduce the potential for ammonia volatilization compared with surface broadcast applications (Jones et al., 2007; Rochette et al., 2013).

Timing of N application

For crops such as wheat, cotton, grass, and rice, N applications are often synchronized with the time of optimum crop uptake (Scharf, 2020). In contrast, corn sometimes receives the recommended N application in the fall before the planting season in the next spring in some U.S. States. This one-time early preplant N applications often resulted in substantial N loss through several loss pathways including nitrate leaching and ammonia volatilization (Scharf, 2020). In-season applications of N is typical in Tennessee for row crops, where a third of the recommended rate is applied at planting and the two-thirds applied as sidedress (Adotey et al., 2020). Some studies reported that N losses increase with the time interval between N application and timing of planting (Drury et al., 2017).

N application rate

N losses through ammonia volatilization increases linearly with N rate. Adotey et al. (2020) reported that increasing N rate from 0, 67.3, 134.5, and 201.8 kg N/ha resulted in < 0.01, 3.99, 8.87, and 16.86 % loss of N respectively through ammonia volatilization from untreated urea. This resulted in an estimated yield penalty of about 25 % when compared to treated urea. Crops often make use of excess N application as “luxury consumption”, and the residual soil N is often lost through denitrification losses and nitrous oxide emissions (Scharf, 2020).

Fertilizer modifications

Long-term commitment to N management research and technology has facilitated the development of new fertilizer products that perform better than urea fertilizer (Jantalia et al., 2012; Snyder, 2008). These fertilizers are referred to as enhanced efficiency N fertilizers (EENF),

because smaller amounts of these fertilizers can match or even produce higher yield harvest compared to traditional fertilizer products (ME Trenkel, 2010). The common and most applied strategies include polymer coating of urea fertilizers, treating urea or UAN with chemical inhibitors, the use of acidifying agents, and addition of soluble salts of Ca, Mg and/or K with urea (Francis et al., 2008).

Previous studies have shown that these fertilizer products can reduce N losses, especially via ammonia volatilization, denitrification and nitrate leaching losses (Peng et al., 2015; Soares et al., 2012; Watson et al., 2008). For instance, Soares et al. (2012) found that urea treated with NBPT delayed peak ammonia volatilization and reduced ammonia volatilization losses by 54–78 % when compared to untreated urea. But there is paucity of information on the efficacy of several EENF products in different soil and climatic conditions. Although some studies found yield increases (Linguist et al., 2013; Silva et al., 2017), the variability in the effectiveness of these formulations on NUE and crop yield in different soil and environmental conditions has not been adequately tested. In addition, EENF products are often more expensive than uncoated products, and this economic impediment may be a disincentive to their wider diffusion and adoption by farmers (Junejo et al., 2011; Ruark et al., 2018).

N losses, yield, and net returns

The proportion of applied N not utilized by the crop or transformed into soil organic N storage either in microbial biomass or soil organic matter, is subject to loss pathways including volatilization, denitrification, and leaching (Ruark et al., 2018). One meta-analysis study conducted by Gardner and Drinkwater (2009) with ^{15}N recovery found that for each growing season, nearly 42.6 kg N/ha/yr (about 38 % of the total ^{15}N applied) out of the 123 kg N/ha/yr could be lost to the cropping system. But higher N uptake by plants increases the overall NUE of

a cropping system (Weber and McCann, 2015). In reference to N loss via ammonia loss, an average decrease of about 5.3 % in crop yield was reported by Silva et al. (2017) for untreated urea compared to NBPT treatment on fine-textured soils. A study by Zhou et al. (2018) in Milan, Springfield, and Jackson experimental stations with no-till corn showed that treated urea (NBPT and polymer coated) at 123 and 168 kg N/ha produced higher corn yield than untreated urea. The yield differences between treated urea and conventional urea were over 2.0 Mg/ha on average (Table 1-1). Using the Gross Domestic Product Implicit Price Deflator Index in 2015, the studies found a net return that was \$283 ha⁻¹ higher with treated urea than untreated urea (Table 1-1). Prices of N fertilizer continue to rise, therefore the gains with treated N fertilizer products are expected to be higher.

Research goals

Loss of N through ammonia volatilization of urea-based N fertilizers is particularly significant in calcareous soils worldwide, including in Tennessee. The wide use and acceptance of urea and UAN portend that producers are likely to continue with these N fertilizer sources in cropping systems. There is a need to understand how soil properties in the Southeast influence ammonia volatilization under field conditions, and the possibility of deploying key sets of soil indicators as predictors of ammonia volatilization to guide management decisions.

Soil properties including soil pH, SOM, clay content, and moisture content can enhance ammonia losses from urea-based fertilizers applied onto soil surface (Pelster et al., 2019; Sunderlage and Cook, 2018). Soil pH has a strong influence on ammonium (NH₄⁺)/ammonia (NH₃) equilibrium in soil solution (Pelster et al., 2019). High soil pH favors ammonium conversion to ammonia, so soils with initial pH above 7 are more prone to ammonia losses than soils with pH below 7. Generally, ammonia volatilization from urea increases with soil pH; but according to Ferguson et al. (1984),

Table 1-1. Ammonia volatilization losses and corn grain yield at different application rates of untreated urea and treated urea.

N treatment	Active ingredient	Cost per kg of N \$	Yield Mg/ha		Net return \$/ha
N source			123 kg N/ha	168 kg N/ha	
Urea	46 % N	1.05	7.8	8.7	959
Agrotain	20 % NBPT, 46 % N	1.19	9.5	9.3	1243
Environmentally Smart Nitrogen	Polymer coated, 44 % N	1.54	10	10.9	1251

factors that inhibit urea hydrolysis such as buffering capacity have a greater effect on ammonia volatilization than the initial soil pH. Soil properties such as clay content and SOM buffer soil pH, which increases adsorption of ammonium ions to soil colloids and consequently reduces ammonia losses (Sunderlage and Cook, 2018). Soil water content can also affect ammonia volatilization (Al-Kanani et al., 1991; Pelster et al., 2019). Al-Kanani et al. (1991) observed a linear positive relationship between ammonia volatilization and initial water content between 0.2 to 25 %. Considering the differences in the composition and breakdown of urea and UAN fertilizers in the soil, further research is required to test the relationships between soil properties and ammonia loss from urea and UAN applications.

For this first study, soil samples were collected from producer fields, treated and analyzed for soil physical and chemical properties likely to influence ammonia volatilization losses under field conditions. A laboratory study was conducted on eight soils collected from different locations in the Southeast in a controlled incubation environment to determine the extent of ammonia volatilization from urea and UAN. The objectives of the study were to (i) evaluate ammonia volatilization potential of urea and UAN applied onto the eight soils and (ii) correlate ammonia volatilization loss to selected soil properties.

EENF products are recognized as a promising N management tool that can reduce N loss, improve crop productivity, and reduce environmental pollution across various cropping systems. Several EENF products on the U.S. market have not been adequately tested to ascertain their efficacy to reduce ammonia volatilization across different soil types. In addition, ammonia volatilization field trials on EENF products rarely evaluate both forms of N stabilizers and slow-release fertilizer in the same trial. This is partly because the conduct of ammonia volatilization field trials in multiple locations tends to be difficult and expensive due to logistical and time

constraints. Laboratory studies, however, offer a more practical and controlled approach to examine ammonia volatilization potential across different soil types.

In the second study, the incubation study appraised five EENF products on two soils that exhibited high ammonia volatilization loss following untreated urea application. This study's objective was to evaluate the efficacy of different EENF products in mitigating ammonia volatilization losses in highly susceptible soils collected at two different locations in the Southeast.

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**CHAPTER TWO: THE EXTENT OF AMMONIA VOLATILIZATION FROM
SURFACE-APPLIED UREA AND UREA AMMONIUM NITRATE AS INFLUENCED
BY SOIL PROPERTIES**

Abstract

Soil properties including soil pH, clay content, soil organic matter (SOM), and field capacity can affect ammonia loss from urea-based fertilizers, but there is limited information on how these soil properties affect ammonia volatilization loss from surface-applied urea and urea ammonium nitrate (UAN) on the same soil. To develop that information, a series of incubation experiments were conducted on eight soils using a customized controlled environment incubation system to study the effects of selected soil properties on ammonia volatilization from UAN and urea applied at 134.5 kg N/ha. The experiment was set up as a randomized complete block design with four replicates. Ammonia loss was measured 1, 2, 3, 4, 5, 6, 7, 9, 11, 13, and 16 DAF (days after N application). Soil pH, SOM, clay content, and field capacity were determined for each soil and used as predictors of ammonia loss. Cumulative losses of ammonia from UAN and urea ranged from 1.4 - 18.1 % and 10.5 - 26.5 % of total N applied, respectively. Cumulative ammonia loss was higher for urea in six soils than UAN, but the losses were similar for both urea and UAN in the remaining soils. There was a significant and strong relationship between cumulative ammonia loss from UAN and selected soil properties contrary to the non-significant and weak relationship observed for urea. Stepwise regression analysis showed soil pH and clay content as the soil properties that best predicted cumulative ammonia loss from both urea and UAN application.

Introduction

Urea and urea ammonium nitrate (UAN) are common urea-based fertilizers utilized by farmers in the U.S. Urea is synthesized in dry granular or liquid forms (Jones et al., 2007), with granular urea accounting for more than 25 % of overall nitrogen (N) fertilizer usage in the U.S. (USDA-ERS, 2019). Urea is one of the most utilized N fertilizers because it is relatively inexpensive and has convenient handling, storage characteristics, and accessibility compared to

other N sources (Engel et al., 2011; Frame, 2017; Li et al., 2015). On the other hand, UAN solution (32-0-0) is synthesized from ammonium nitrate and urea, with its composition made of approximately 33 % urea, 43 % ammonium nitrate, and 25 % water and other materials (Nieuwenhuyse, 2000). The exact estimates of UAN usage in the U.S. are unavailable, but at nearly 43 % of N solution used in the U.S., UAN has the largest share of the N solution market.

Surface application without incorporation into the soil makes the urea and UAN susceptible to N losses through ammonia volatilization (Adotey et al., 2017; Frame, 2017; Sunderlage and Cook, 2018). No-till or minimum tillage is widely adopted in the U.S. to reduce soil erosion and runoff as well as improve soil health. It was estimated that more than 26 % of total arable land in the U.S. are under no-till, an increase of nearly 8 % between 2012 and 2017 (USDA-NASS, 2019). Reduced tillage practices also increased by 27.5 % within the same period, and together with no-till accounted for about 50 % of total cropland acres (USDA-NASS, 2019). In Tennessee, an estimated 80 % of total field corn is under no-till production system (McClure, 2020). The practice is suitable for diverse croplands including sloping areas that are often prone to erosion. The availability of equipment such as planters and spreaders designed for no-tillage operations allows minimum seedbed disturbance and a firmer surface for seeding through crop residue (McClure, 2020).

In no-till systems, most growers surface-broadcast their N fertilizers onto the soil without incorporation (Triplett Jr and Dick, 2008). As a result, ammonia loss under no-till systems tends to be higher than tilled systems, especially for urea-based fertilizers (Jones et al., 2007). Ammonia volatilization occurs when the ammonium produced during urea hydrolysis or under high soil pH is converted to ammonia (Eagle et al., 2017; Kissel et al., 1988). Most of these losses occur within 3 to 5 DAF (days after fertilizer application), with peak losses occurring within 3 DAF (Adotey et al.,

2017; Keller and Mengel, 1986; Soares et al., 2012; Stevens et al., 1989). Peak ammonia loss may be delayed up to 15 DAF with rainfall events. Nitrogen losses through ammonia volatilization can be as high as 46 and 21 % of total N with surface-broadcast urea and UAN applications, respectively (Cabrera et al., 2023; Vaio et al., 2008). Ammonia volatilization limits nitrogen use efficiency (NUE), reduces productivity, lowers profits, and increases potential environmental pollution concerns (Woodward et al., 2011).

Soil properties including soil pH, soil organic matter (SOM), clay content, and moisture content can dictate the magnitude of ammonia loss from urea-based fertilizers applied onto soil surface (Pelster et al., 2019; Sunderlage and Cook, 2018). Soil pH has a strong influence on ammonium (NH_4^+)/ammonia (NH_3) equilibrium in soil solution (Pelster et al., 2019). High soil pH favors ammonium conversion to ammonia, therefore soils with initial pH above 7 are more prone to ammonia losses than soils with pH below 7. Generally, ammonia volatilization from urea increases with soil pH; but according to Ferguson et al. (1984), factors that inhibit urea hydrolysis such as buffering capacity have a greater effect on ammonia volatilization than the initial soil pH. Soil properties such as clay content and SOM buffer soil pH, which increases adsorption of ammonium ions to soil colloids and consequently reduces ammonia losses (Sunderlage and Cook, 2018). Many studies have documented an inverse relationship between clay and SOM content and urea ammonia loss, which indicates that high clay content and SOM may reduce ammonia volatilization (Al-Kanani et al., 1991; San Francisco et al., 2011; Sunderlage and Cook, 2018; Whitehead and Raistrick, 1990). Soil water content can also affect ammonia volatilization (Al-Kanani et al., 1991; Pelster et al., 2019). Al-Kanani et al. (1991) observed a linear positive relationship between ammonia volatilization and initial water content between 0.2 to 25 %.

Urea hydrolysis does not occur with UAN, so no ammonia is formed from the urea portion of UAN, in contrast to pure urea that undergoes complete hydrolysis. Generally, ammonia volatilization losses from surface application of UAN tend to be lower than surface application of urea. Some studies, however, found higher ammonia losses from UAN than urea (Cabrera et al., 2023 and Jantalia et al., 2012). This may be an indication that the relationship between soil properties and ammonia volatilization losses for urea and UAN may be different. Most of the studies that examined the relationship between soil properties and ammonia volatilization focused on surface-applied granular urea (Corstanje et al., 2008; Pelster et al., 2019; Stevens et al., 1989; Sunderlage and Cook, 2018). There is paucity of research on the influence of soil properties on ammonia volatilization losses from urea and UAN applied onto the same soil. Ammonia volatilization studies that evaluated both urea and UAN focused on ammonia loss potential and mitigation strategies (Cabrera et al., 2023; Keller and Mengel, 1986; Lasisi et al., 2020; Vaio et al., 2008; Woodley et al., 2020) or evaluated only one soil property (Al-Kanani et al., 1991). Considering the differences in the composition and breakdown of urea and UAN fertilizers in the soil, further research is required to test the relationships between soil properties and ammonia losses from UAN.

In addition, conducting field trials in multiple locations to measure ammonia volatilization is difficult and expensive because of the logistical and time constraints. Laboratory studies, however, offer a more practical and controlled approach to examine ammonia volatilization potential across different soil types. Hopefully, the results from such laboratory studies can be used to generate models to predict potential ammonia loss across a wider variety of field situations. This study hypothesized that (i) ammonia loss will be higher for urea than UAN applied onto eight soils and (ii) ammonia loss will correlate with soil pH, SOM, clay content, and field capacity which can be used to predict ammonia volatilization losses. The objectives of the study were to (i) evaluate ammonia volatilization

potential of urea and UAN applied onto the eight soils and (ii) correlate ammonia volatilization loss to selected soil properties.

Materials and methods

Experimental design and treatments

A completely randomized design was used to evaluate ammonia volatilization from urea and UAN applied onto eight soils. In addition, an unfertilized treatment was included in the experiment as a control. The experiment was replicated four times for a total of 96 ($n = 3$ N treatments $\times$ 8 soils $\times$ 4 replications) experimental units. The N fertilizer sources used for this experiment included untreated urea and UAN applied at an equivalent rate of 134.5 kg N/ha. The soils used were from soil samples collected at 0-15 cm from eight geographically distant production fields in West Tennessee which have been under no-till cropland management for decades. The soil samples were air-dried, ground, and sieved through a 2-mm sieve. A composite soil sample for each location was analyzed for soil organic matter content by loss of ignition method (Sikora and Hardy, 2014), soil pH by 1:1 soil/water ratio method (Sikora and Kissel, 2014), Mehlich III extractable soil test nutrients (Zhang et al., 2014), soil nitrate-N and ammonium-N by 2 M KCl extraction method (Miller and Sonon, 2014), and soil texture by hydrometer method (Huluka and Miller, 2014). The information on each soil is presented in Table 2-1.

Ammonia volatilization was measured using a controlled environment incubation system, which can handle only 24 experimental units in a single run. Two soils were evaluated during each run ($n = 3$ N treatments $\times$ 2 soils $\times$ 4 replications). The experiment was conducted four times under

Table 2-1. The soil series and selected properties of the eight soils.

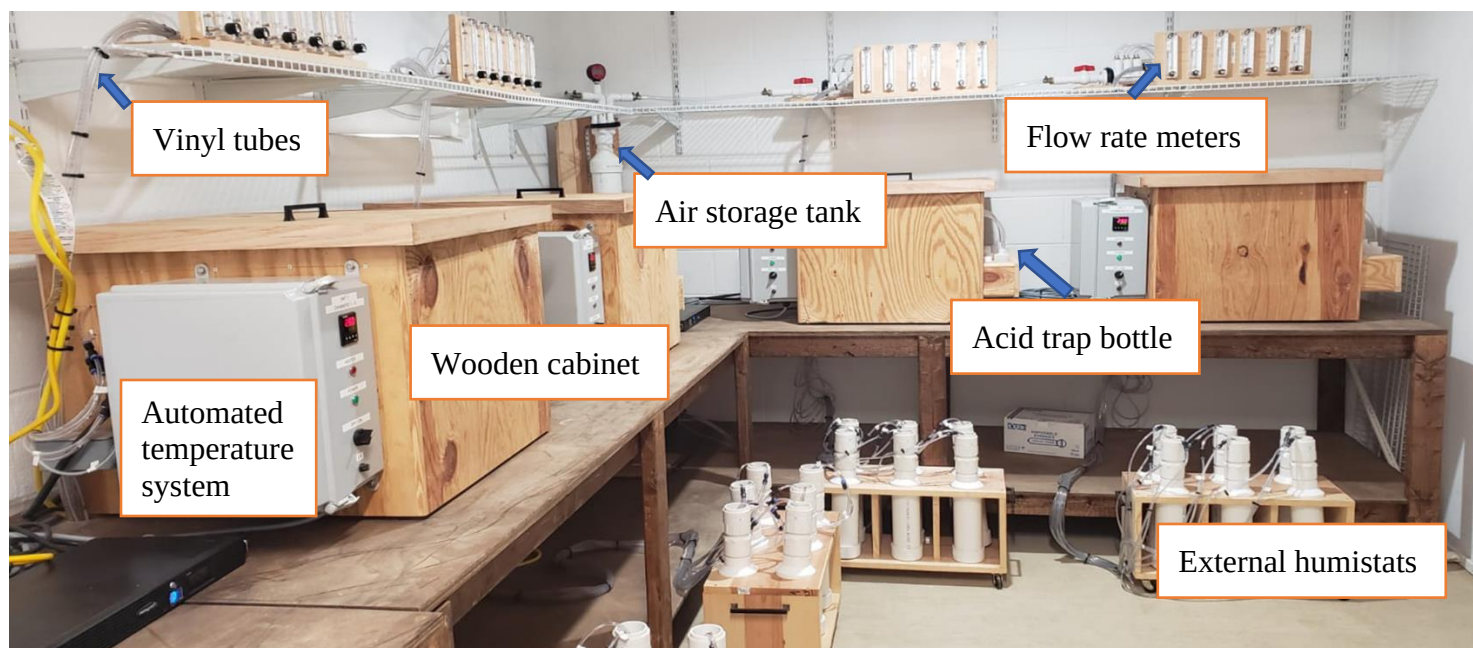
Soil #	Soil series name	Soil pH	Clay content	Sand content	SOM [†]	Field capacity
		1:1	-----	g/kg	-----	
1	Loring silt loam, 2-5 % slopes	5.8	140	360	34	300
2	Loring silt loam, 8-12 % slopes	5.2	160	400	34	340
3	Memphis silt loam, 8 to 12 % slopes	6.1	180	280	31	350
4	Memphis silt loam, 5 to 8 % slopes	7.9	140	340	21	240
5	Calloway silt loam, 0 to 2 % slopes	7.4	140	400	28	280
6	Robinsonville loam	7.2	140	360	26	320
7	Memphis silt loam, 5 to 8 % slopes	6.0	180	320	42	370
8	Loring silt loam, 8 to 12 % slopes, severely eroded	5.8	160	560	34	300

[†]SOM, Soil organic matter

similar environmental conditions to evaluate all the soil collected from the eight locations.

Ammonia volatilization study

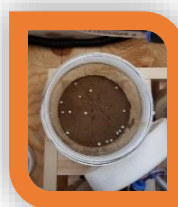
The controlled environment incubation system was operated at uniform conditions throughout the experiment. This was to ensure that any differences of ammonia volatilization losses measured were due to the N treatments applied. The room temperature was maintained at 28 °C, air flow rate through the system was set at 1 L m⁻¹, and the air was near 100 % saturation before being connected to the soil surfaces within the wooden cabinets. The controlled environment incubation system used in this study was similar to systems described by Woodward et al. (2011) in their study (Figure 2-1). The rapid and precise in-lab controlled environment system consists of a pump, 2 distribution manifolds, 24 flow meters, 2 outer humistats, and 4 insulated cabinet boxes made up of several components. Air supply to the system was supplied by the air pump (DDL80-101, Gast Manufacturing Inc., Benton Harbor, MI) that filled the distribution manifolds. Each distribution manifold supplied air to six flow meters (0.4-5.0 L min⁻¹ flow meters 22461-50, Cole-Parmer Instrument Co., Vernon Hills, IL) via 4.3 mm ID vinyl tubing. This vinyl tubing was used to supply air throughout the system. Air from the flow meters was saturated by passing it through a set of closed PVC pipe cylinders (external humistats) containing water. Saturated air exiting the external humistats was then passed through a second set of smaller cylinders (internal humistats) containing water within the cabinet. The cabinets (61 x 61 x 49 cm³) and their lids are constructed using a 0.95 cm thick plywood and were fitted with 1.3 cm thick polystyrene sheath insulation. The heat was generated using an angular aluminum strip attached to a silicone rubber heat strip (2.5 x 20 cm², 80 W total, SRFG-108/10-P, Omega Engineering Inc., Stamford CN) and mounted on a rectangular block inside the cabinet. Heat circulation was aided by an electric fan (2000 rpm, 15 V, 60 Hz, 0.10 A, CGAC1225L-BC, CoolerGuys.com, Kirkland,



500 g soil
wetted to 2/3
field capacity



Incubation of
soils for 48
hours in cabinet



Treated soil
with urea



Treated soil
with UAN



Oil less pump



Soil beakers
covered and
connected

Figure 2-1: Controlled environment incubation system and associated components.

WA) and a wooden baffle with end at an angle ($1.9 \times 30.8 \times 28 \text{ cm}^3$). A wooden crate inside the cabinet ensures uniform heat distribution around the glass chambers. The chambers consisted of threaded glass beakers and a 3-hole cap (21650 B, Kimble Chase Life Science and Research Products LLC, Vineland, NJ). The holes served as entry and exit ports for air and as ports allowing thermocouple temperature measurement within each chamber (TT36-18U-6-SB, Omega Engineering Inc., Stamford, CN). Air exiting the chamber was passed through acid trap bottles containing 100 mL of 0.02 M orthophosphoric acid acids to capture N in the exhaust gas.

To start the experiment, the glass jars were filled with 500 g of air-dried soil and moistened to two-thirds of the soil field capacity (Table 2-1). The moistened soil was incubated at a constant temperature of 28 °C for 48 h prior to N treatment applications. At the end of incubation, an equivalent rate of 134.5 kg N/ha — based on the exposed soil surface area in the glass jar — of urea or UAN was applied onto the soil. The UAN treatments were administered onto the soil surface with a pipette. The air pump supplied dry air to the system through the distribution manifold. The flow rate meters ensured that the air flow was set to 1 L m^{-1} . The dried air from the pump was moistened by the external and internal humistats containing deionized water. Vinyl tubes conducted air flow throughout the system. The nearly 100 % humidified air exiting the internal humistats forced out any ammonia gas at the soil surface. The ammonia gas from N fertilizer and soil was captured in 100 mL of 0.02 M orthophosphoric acid in the traps, which were changed and analyzed 1, 2, 3, 4, 5, 6, 7, 9, 11, 13, and 16 DAF. The ammonium content of the acid traps was determined with the aid of an automated TL-2800 Single Channel ammonium and nitrate analyzer equipped with autosamplers (Timberline Instruments, Boulder CO) at the University of Tennessee Soil, Plant and Pest Center, Nashville, Tennessee.

Statistical analysis

A SAS Proc Glimix model was used to examine the effects of N source, soil types, and their interactions on cumulative ammonia loss at 1, 3, 7, and 16 DAF (SAS Institute, 2023). Mean separation was determined using Tukey's HSD at $\alpha = 0.05$. Multiple, linear, and stepwise regression analyses were used to test the relationships between cumulative ammonia volatilization loss at the end of the experiment (16 DAF) and pH, SOM, clay content, and field capacity. The stepwise regression models were compared using the Akaike information criteria (AIC) and adjusted R^2 values. The model with the highest AIC and adjusted R^2 values was deemed to have predicted ammonia volatilization best for each soil. Data visualization and construction of plots was done with SigmaPlot 15 (Grafiti, 2020). Furthermore, the Pearson correlation analysis was performed in SAS to determine relationships among the soil indicator predictors studied.

Results and discussion

Ammonia volatilization losses

The dynamics of ammonia losses from UAN and urea application at each sampling day of the experiment are shown in Figure 2-2a & b. All differences reported below are significant at $\alpha = 0.05$. Loss of ammonia was detected within 1 DAF regardless of the N source for all soils, and the peak losses occurred either 2 or 3 DAF and were generally higher for urea than UAN.

This is consistent with other published incubation experiments (Adotey et al., 2017; Keller and Mengel, 1986; Soares et al., 2012; Vaio et al., 2008), which recorded peak losses on either 2 or 3 DAF. In a laboratory experiment, Keller and Mengel (1986) reported that the maximum loss from both urea and UAN occurred by 1 DAF. In contrast, Adotey (2023) found that peak ammonia loss occurred at different sampling times for urea and UAN applications, with maximum loss occurring

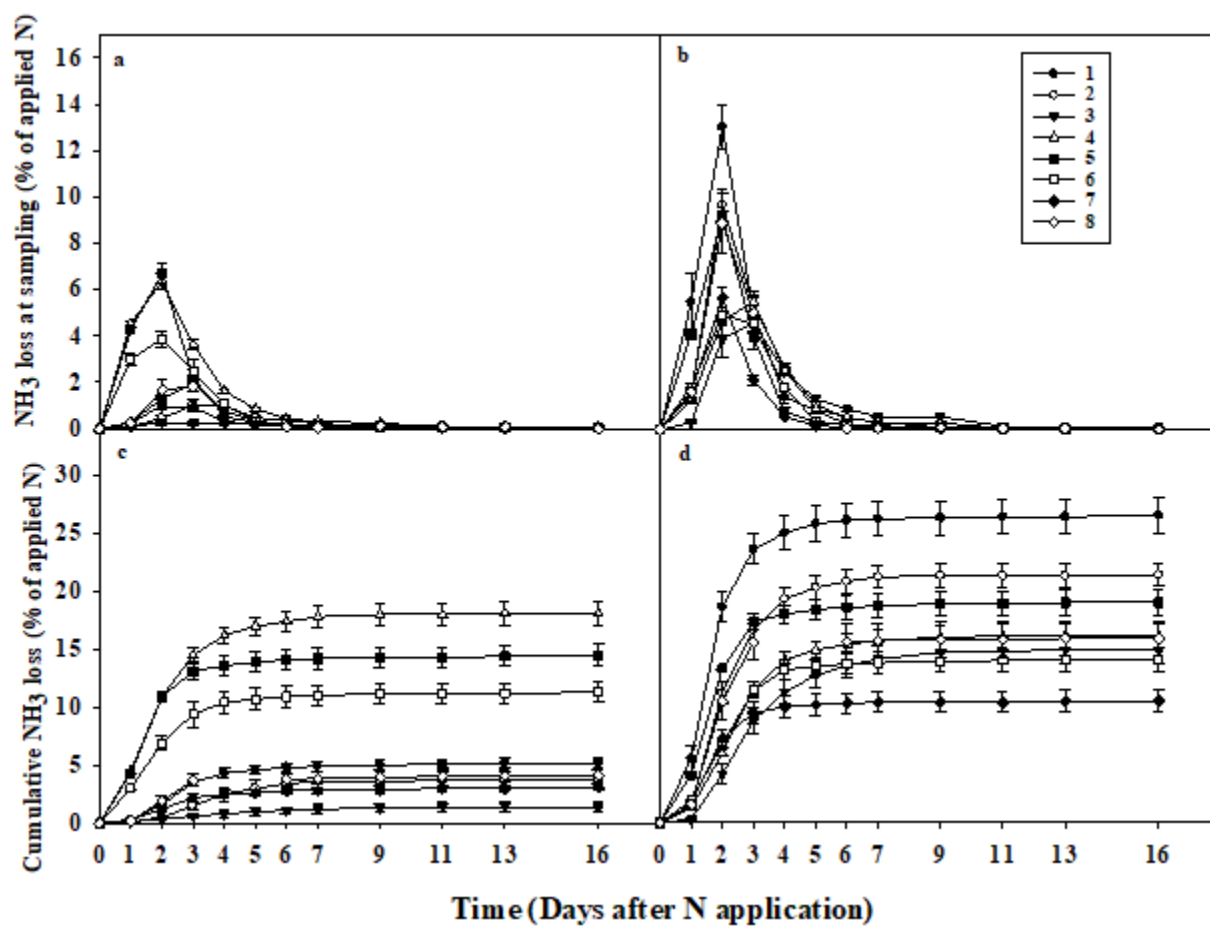


Figure 2-2. Ammonia loss at sampling from surface-applied (a) urea ammonium nitrate and (b) urea. Cumulative ammonia loss 16 days after fertilizer application from surface applied (c) urea ammonium nitrate and (b) Urea onto 8 soils.

on 2 and 4 DAF for urea and UAN, respectively.

Previous studies reported higher losses of ammonia from urea than UAN during period of maximum ammonia loss (Adotey, 2023) as was observed in soils 1, 2, 3, 7, and 8. This observation is because urea hydrolysis does not occur in UAN; therefore, very little to no ammonia is formed from the urea portion of UAN compared to urea which completely undergoes urea hydrolysis. Norman et al. (2009) explained that the rapid hydrolysis often measured within the first few days after N application is most likely because of a spike in soil pH induced by urea hydrolysis. Jantalia et al. (2012) found higher ammonia loss from UAN compared to urea application during the peak ammonia loss as was depicted in soils 4, 5, and 6 in this experiment. The soil used in their experiment was a clay loam with soil pH of 7.8.

Soil pH and the composition of N fertilizers may partly explain the higher ammonia loss from UAN than urea in soils 4, and 6 on the first sampling day in this experiment. These soils were alkaline, with soil pH ranging from 7.2 to 7.9. UAN is made up of urea, ammonium, and nitrate, in contrast to urea-N fertilizer which is composed of 100 % urea (Nieuwenhuyse, 2000). This makes the initial concentration of ammonium in UAN significantly higher than in urea. In alkaline soils, the high soil pH favors the rapid conversion of ammonium to ammonia, hence the higher initial loss from UAN. The losses for both UAN and urea applications declined rapidly and consequently leveled off at 7 DAF (Figure 2-1a & b). The plateauing of losses on day 7 suggests completion of urea hydrolysis or decrease in hydrolysable N fertilizers (Al-Kanani et al., 1991).

The cumulative ammonia loss with time was curvilinear regardless of N source and soil (Figure 2-2c & d). A substantial amount of ammonia loss occurred within the first 3 DAF and then plateaued almost between 7 and 16 DAF (Table 2-2). Cumulative losses of ammonia from UAN and urea ranged from 1.4 - 18.1 and 10.5 - 26.5 % of total N applied, respectively. This is similar

Table 2-2. Interactive effect between N source and cumulative ammonia volatilization on 1, 3, 7 and 16 DAF for each soil.

Soil	UAN				Urea			
	1DAF	3DAF	7DAF	16DAF	1DAF	3DAF	7DAF	16DAF
	-----% of applied N-----							
1	0.3 c	3.5 b	4.9 b	5.2 b	5.5 b	23.6 a	26.2 a	26.5 a
2	0.1 e	1.5 de	3.6 cd	3.8 c	1.5 de	16.6 b	21.2 a	21.4 a
3	0.1 c	0.6 c	1.2 c	1.4 c	0.3 c	8.8 b	14.1 a	14.9 a
4	4.5 e	14.5 c	17.8 ab	18.1 a	1.3 f	11.5 d	15.7 bc	16.1 a-c
5	4.3 c	13.1 b	14.2 b	14.5 b	4.1 c	17.3 a	18.7 a	19.0 a
6	3.0 c	9.4 b	11.0 b	11.3 b	1.9 c	11.4 b	13.8 a	14.0 a
7	0.3 c	2.2 b	2.8 b	3.1 b	1.6 bc	9.5 a	10.4 a	10.5 a
8	0.2 c	3.7 b	3.8 b	4.1 b	1.6 bc	15.6 a	15.1 a	15.5 a

DAF, Days after fertilizer application

Means followed by the same letter within a row are not significantly different at $\alpha = 0.05$

to the ammonia losses reported by Vaio et al. (2008) after 31 days of incubation with losses at 21.6 and 11 % of applied N for urea and UAN, respectively.

There was interaction effect of N source and soil on cumulative ammonia loss on 1, 3, 7, 16 DAF for this study (Table 2-2). Cumulative ammonia loss from urea was higher than UAN in corresponding soils on the 16 DAF except for soils 4 and 6 (Figure 2-3). Other studies have reported that UAN lost a similar or higher amount of ammonia than urea (Cambrera et al., 2023; Jantalia et al., 2012). Studies by Cabrera et al. (2023) and Vaio et al. (2008) attributed higher losses from UAN applications to the influence of critical relative humidity (CRH). According to these studies, the low CRH (18 - 20 %) of UAN than urea (72 - 80 %) meant that UAN absorbed moisture from its surrounding more rapidly than urea, which would only absorb moisture when the relative humidity reached 80 %.

The highest cumulative ammonia loss (18.1 % of applied N) from UAN occurred in soil 4 and was higher than the other soils (Table 2-3, Figure 2-3). The soil properties of soil 4 may partly explain this pattern of losses. Soil 4 had the highest soil pH and relatively lower SOM and field capacity among the 8 soils. These results showed there were no differences in ammonia volatilization losses in soils 1, 2, 7, and 8 (3.1 - 5.2 % of total N applied), which were lower than the remaining soil except for soil 3 (1.4 % of total N applied). The losses observed in soil 3 were lower than the other soils. With urea application, the least (10.5 % of applied N) and highest loss (26.5 % of total N applied) occurred in soils 7 and 1, respectively (Table 2-3). The total ammonia loss from urea was similar among soils 3, 4, 6, and 8, which were lower than the other soils except soil 7.

Some published studies reported that high initial pH can increase ammonia loss with surface-applied urea (San Francisco et al., 2011), but this was not observed in this experiment. The

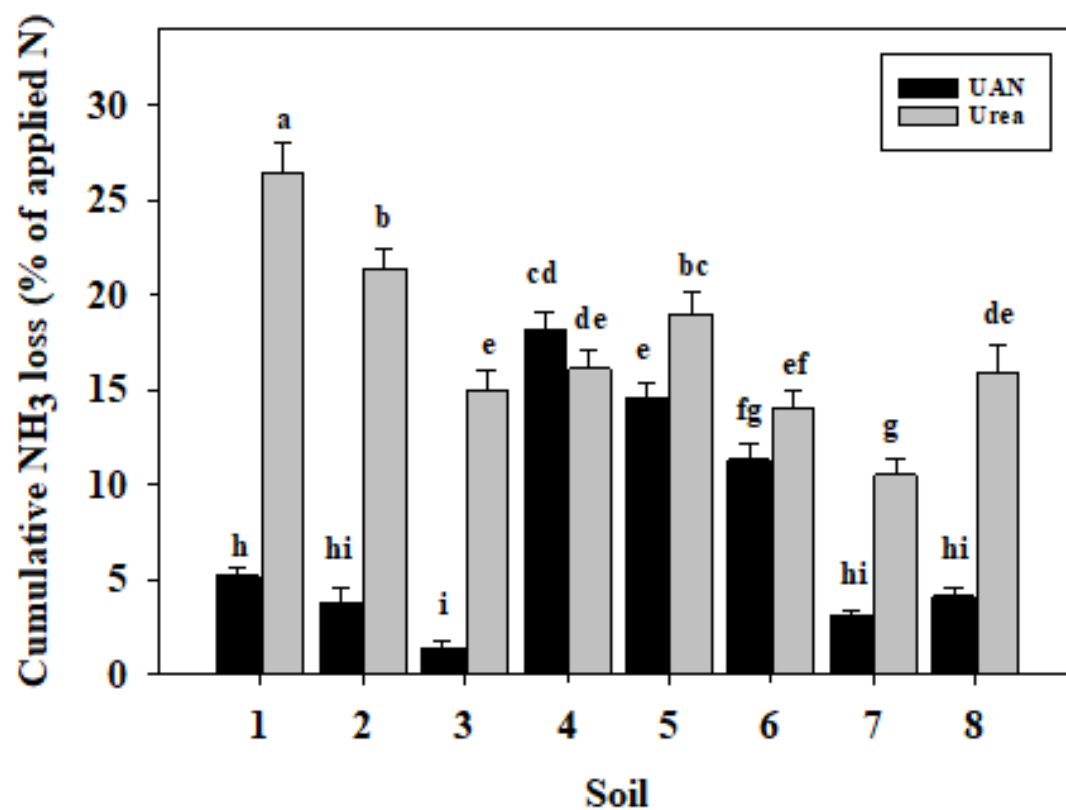


Figure 2-3. Cumulative ammonia loss 16 DAF from surface applied UAN and urea onto eight soils.

Table 2-3. Interactive effect between N source and soil on cumulative ammonia volatilization on 1, 3, 7 and 16 DAF.

N Source	Soil	1DAF	3DAF	7DAF	16DAF
-----% of applied N-----					
UAN	1	0.3 ef	3.5 h	4.9 h	5.2 h
	2	0.1 f	1.5 hi	3.6 hi	3.8 hi
	3	0.1 f	0.6 i	1.2 i	1.4 i
	4	4.5 ab	14.5 cd	17.8 cd	18.1 cd
	5	4.3 b	13.1 de	14.2 e	14.5 e
	6	3.0 c	9.4 fg	11.0 fg	11.3 fg
	7	0.3 ef	2.2 hi	2.8 hi	3.1 hi
	8	0.2 ef	3.7 h	3.8 hi	4.1 hi
Urea	1	5.5 a	23.6 a	26.2 a	26.5 a
	2	1.5 d	16.6 bc	21.2 b	21.4 b
	3	0.3 ef	8.8 g	14.1 e	14.9 e
	4	1.3 de	11.5 ef	15.7 de	16.1 de
	5	4.1 bc	17.3 b	18.7 bc	19.0 bc
	6	1.9 d	11.4 ef	13.8 ef	14.0 ef
	7	1.6 d	9.5 fg	10.4 g	10.5 g
	8	1.6 d	15.6 b-d	15.7 de	15.5 de

DAF, Days after fertilizer application

Means followed by the same letter within a column are not significantly different at $\alpha = 0.05$

highest ammonia loss was not observed in the soil with the highest soil pH, which supports findings by Ferguson et al. (1984) and Stevens et al. (1989) that the amount of ammonia loss is dependent not only on the initial soil pH, but also on the buffering capacity of the soil. In poorly buffered soils, initial soil pH may substantially influence ammonia volatilization. Consistent with this observation, Adotey et al. (2017) found lower ammonia loss from urea applied onto soil with pH of 7.4 than soil with pH of 6.6.

Relationship between ammonia volatilization and soil properties

The relationships between ammonia loss and soil properties were different for UAN and urea applications, therefore the results of the relationships were reported separately for each N source. Of all the soil properties examined, soil pH was the single property most correlated with ammonia loss from UAN application. Stepwise regression analysis predicted soil pH and clay content as the soil properties that best correlated with cumulative ammonia loss from UAN application (combined $R^2 = 0.90$). There was a significant relationship between cumulative ammonia loss from UAN and the selected soil properties using a linear/curvilinear regression model (Table 2-4). A negative curvilinear relationship was observed between cumulative ammonia loss and clay content ($R^2 = 0.86$) for UAN, suggesting that as clay content decreased from 180 to 140 g/kg, the capacity of the soil to volatilize ammonia increases. However, the effect of clay content on ammonia volatilization was marginal at 140 g/kg (Figure 2-4).

Al Kanani et al. (1991) observed that an increase in clay content reduced volatilization loss from UAN, but those authors evaluated only 2 soils. Most published literature focused on the relationship between clay content and ammonia loss from urea. Literature suggests that the negative charges on clay increase the cation exchange capacity (CEC) of soil, so soils with higher clay content adsorb greater amounts of ammonium, which minimizes the amount of ammonium

Table 2-4. Simple linear/curvilinear regression equation and coefficient of determination (R^2) for clay content, soil pH, soil organic matter, and field capacity.

N source	Clay	Soil pH	SOM[†]	FC[§]
Urea				
Equation	$-1.43x + 39.45$	$-1.39x + 26.21$	$-1.51x + 21.89$	$-0.38x + 29.22$
R^2	0.26	0.07	0.03	0.10
UAN				
Equation	$0.08x^2 - 1.48x + 20.48$	$5.93x - 30.42$	$-8.56x + 33.88$	$-1.22x + 45.75$
R^2	0.90**	0.84**	0.65*	0.69*

[†]SOM, Soil organic matter; [§]FC, Field capacity; *, Statistically significant at 0.05; ***, Statistical significance at $\alpha = 0.001$

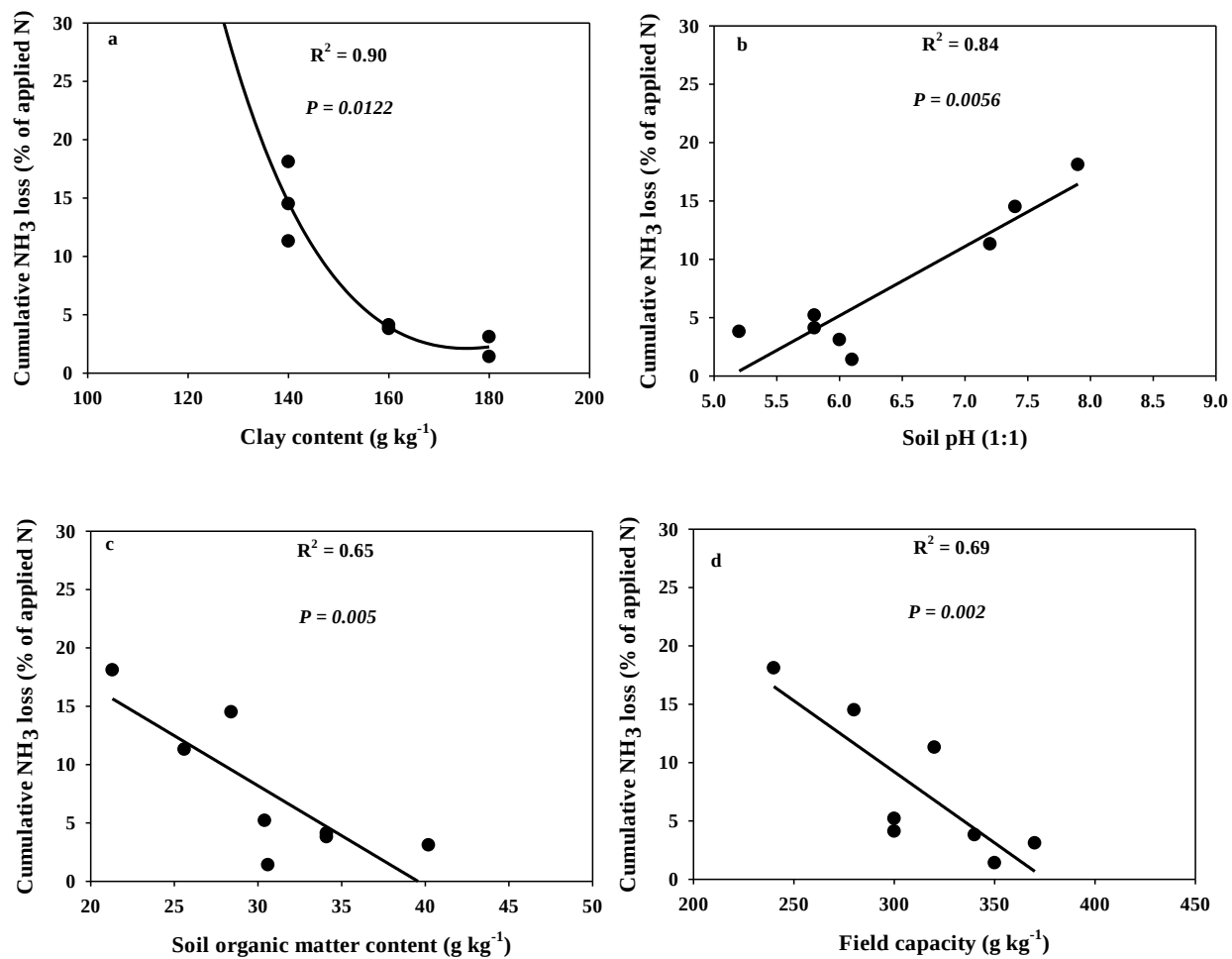


Figure 2-4. Relationship between cumulative ammonia loss 16 DAF from surface applied UAN and (a) clay content (b) soil pH (1:1), (c) Soil organic matter content, and (d) Field capacity of eight soils.

available in the soil to be volatilized as ammonia (Gameh et al., 1990).

The cumulative ammonia loss had an inverse linear correlation with field capacity ($R^2 = 0.69$) and SOM ($R^2 = 0.65$); but positive linearly with soil pH ($R^2 = 0.84$) (Figure 2-4). A strong relationship between soil pH was expected since ammonia loss from UAN is not dependent on urea hydrolysis, which can be affected by the buffering capacity of the soil. Studies by Stevens et al. (1989) found that SOM content influenced ammonia loss because of its contribution to pH-dependent negative charges to the CEC of a soil, which may temporarily retain ammonia in soils and inhibit ammonia volatilization.

There was no significant relationship between cumulative ammonia loss from urea and selected soil properties using the linear regression model (Table 2-4). Stepwise regression predicted that ammonia loss from urea was best predicted by soil pH and clay content (combined $R^2 = 0.62$). Cumulative ammonia losses with urea treatment were poorly and negatively correlated with field capacity ($R^2 = 0.10$), soil pH ($R^2 = 0.07$), clay content ($R^2 = 0.26$), and SOM ($R^2 = 0.03$) (Figure 2-5), which is contrary to information published in literature (San Francisco et al., 2011; Sunderlage and Cook, 2018). San Francisco et al. (2011) reported a significant ($R^2 = 0.74$) relationship between clay content and ammonia loss from urea applied onto 12 soils whose clay contents ranged from 7 to 27 %. In contrast, the narrow range of clay content (140 to 180 g/kg) may partly explain the poor correlation observed in this study.

The effect of soil pH on ammonia volatilization from urea has been well researched, and previous studies have linked soil pH to higher ammonia volatilization. Ferguson et al. (1984) reported that other properties such as buffering capacity can have greater effect than soil pH.

The strong negative correlation between ammonia loss and field capacity for the UAN application and the weak negative correlation with urea conflicts with the linear positive

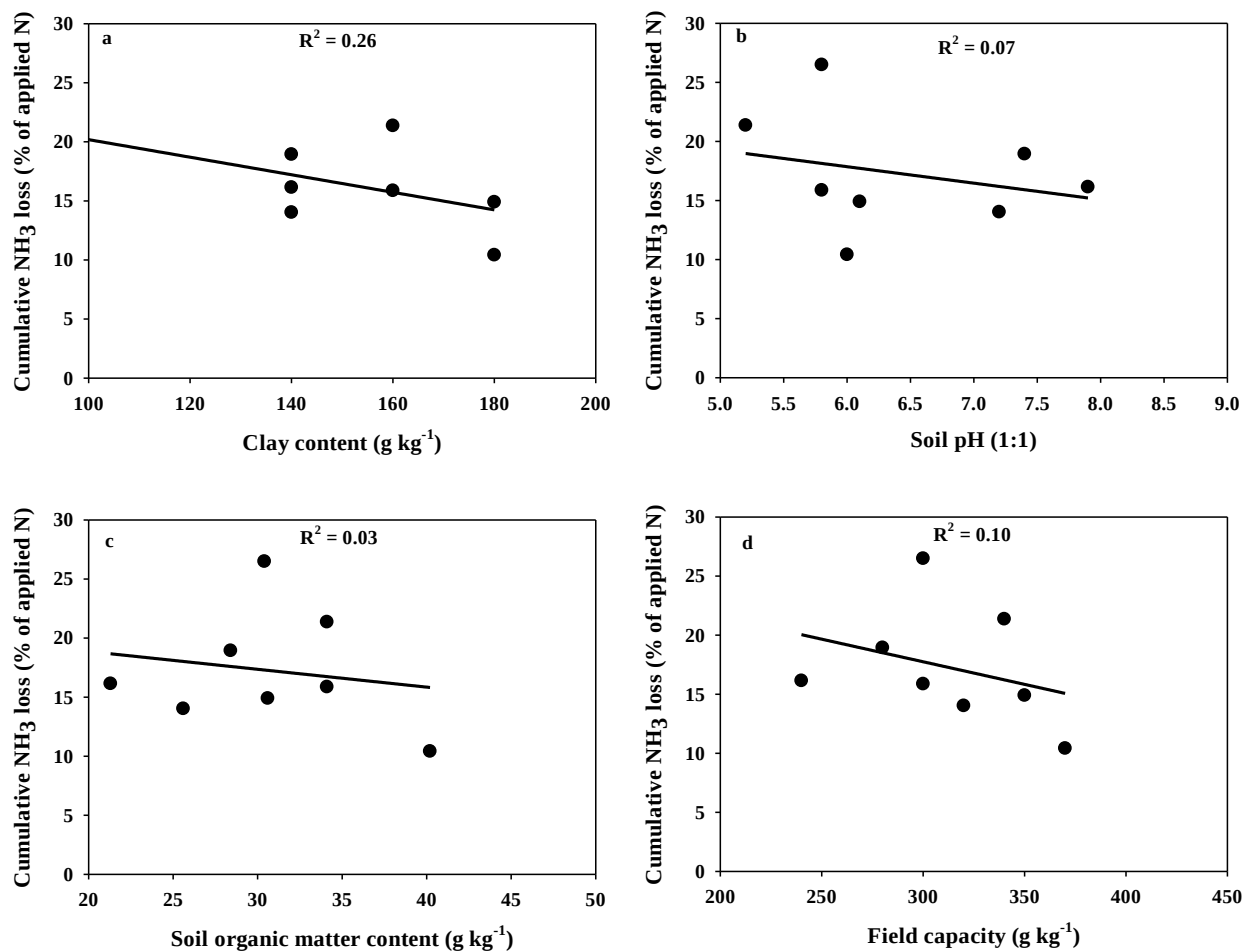


Figure 2-5. Relationship between cumulative ammonia loss 16 DAF from surface applied urea and (a) clay content (b) soil pH (1:1), (c) Soil organic matter content, and (d) Field capacity of eight soils.

relationship observed by Al-Kanani et al. (1991). The main difference is that for this study the initial water content was fixed at 75 % of the soil's field capacity in contrast to the 0.2 – 25 % used in the study by Al-Kanani et al. (1991). The authors alluded to a water content threshold for which the linear correlation was valid; suggesting that the observed relationship may be variable across different soil types. Urea hydrolysis thrives on adequate moisture in the soil and sufficient airflow above the soil is required to facilitate ammonia volatilization (Pelster et al., 2019). The inverse relationship in this study was likely because the urea hydrolysis was curtailed by the two-thirds field capacity.

The Pearson correlation coefficient among soil properties is shown in Table 2-5, where the correlations of clay content with SOM and FC, soil pH and SOM, and SOM with FC were significant ($P < 0.05$). Clay content correlated negatively with soil pH ($r = -0.57$), but positively with SOM ($r = 0.73$) and FC ($r = 0.79$). A strong correlation between clay content and SOM was expected due to their overall contribution to the buffering capacity of soil. An increased buffering capacity indicates the soil's ability to withstand changes in soil pH which is key to minimizing ammonia volatilization. This possibly explains why soil pH correlated negatively with clay content and SOM ($r = 0.79$). Because field capacity contributed to reduced ammonia volatilization, the negative correlation of soil pH to field capacity ($r = 0.68$) was expected. The positive correlation between field capacity and SOM ($r = 0.78$) as well as with clay content was consistent.

Conclusion

Regardless of N source, most of the ammonia loss occurs within the first 5 DAF, with a higher and earlier peak of ammonia loss from urea than UAN. Overall, cumulative ammonia volatilization loss from urea was higher than UAN in six out of the 8 soils used in this experiment.

Table 2-5. Pearson correlation coefficients among soil properties.

	Clay content	pH	SOM [†]	FC [§]
Clay	1			
pH	-0.56933	1		
SOM	0.733933*	-0.78766*	1	
FC	0.79302*	-0.67798	0.781656*	1

[†]SOM, Soil organic matter; [§]FC, Field capacity * , Statistically significant at $\alpha = 0.05$

The cumulative ammonia losses with UAN and urea were similar in the remaining soils which also had pH above 7. This result demonstrates that growers with preference for surface application of UAN on soils with pH greater than 7 are likely to lose more N than usual through ammonia volatilization. Soil properties differentially influenced ammonia losses from surface-applied urea and UAN fertilizer sources. Whereas there was a significant and strong relationship between cumulative ammonia loss and soil properties for UAN, a non-significant and weak relationship was found between cumulative ammonia loss and soil properties for urea. Stepwise regression analysis predicted soil pH and clay content as the soil properties that best predicted cumulative ammonia loss from both UAN and urea applications.

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**CHAPTER THREE: ENHANCED EFFICIENCY NITROGEN FERTILIZER AS TOOL
TO CONTROL NITROGEN LOSS IN ROW CROP PRODUCTION**

Abstract

Chemical coating of urea and urea ammonium nitrate (UAN) with additives such as N-(butyl) thiophosphoric triamide (NBPT), dicyandiamide (DCD), or physical coating urea with a polymer can significantly minimize ammonia volatilization losses from unincorporated, surface applications of urea and UAN. The effectiveness of some of these modified forms of urea and UAN, also referred to as enhanced efficiency N fertilizer (EENF) products, has not been consistent. Incubation experiments were conducted with two soils that exhibited high ammonia volatilization losses following untreated urea application to evaluate the inhibition potential of ammonia volatilization losses by five EENF products using a customized controlled environment system. The experiments were set up as randomized complete block design with four replicates. The EENF treatments included urea+ANVOLTM, UAN+ANVOLTM, ESN[®], SUPERU[®], and urea+Excelis[®] which were surface-applied at 134.5 kg N/ha. Untreated urea and UAN were included in the trial as controls. Ammonia loss was measured 1, 2, 3, 4, 5, 6, 7, 9, 11, 13, and 16 DAF (days after N treatment application). Cumulative ammonia loss from the EENF products ranged from 3.3 – 10.6 and 2.2 – 16.1 % of applied N in soil 1 and soil 2, respectively. All the urea treated products were effective in reducing ammonia volatilization loss (% of applied N) by 60.63 – 87.62 and 32.26 – 90.96 % for soils 1 and 2, respectively, when compared to untreated urea. Similarly, the treated UAN reduced ammonia volatilization loss by 26.90 and 69.51 in soils 1 and 2 compared to untreated UAN. The effectiveness of the EENF treatments in both soils was: ESN[®] > UAN+ANVOLTM > urea+ANVOLTM > urea+Excelis[®] > SUPERU[®]. Reliable EENF products are a viable tool to reduce N losses as ammonia, regardless of the soil properties.

Introduction

Ammonia volatilization is recognized as one of the most common and relevant losses of nitrogen (N) in cropping systems (Awale and Chatterjee, 2017; Chuong et al., 2020; Fageria, 2014); and it is particularly significant in calcareous soils (Mandal et al., 2018). Ammonia volatilization has a negative impact on N use efficiency (NUE), which measures the quantity of grain produced per unit of fertilizer applied, and which is estimated at 0.68 in the U.S. and Canada (Zhang et al., 2015). Grain yield losses have often correlated positively with ammonia volatilization, with yield losses as high as 25 % reported for field corn (Adotey, 2023).

Studies have long shown higher ammonia volatilization losses from unincorporated, surface-applied urea-based N fertilizers in no-till production systems than tillage-based systems (Francis et al., 2008; Palma et al., 1998). The ubiquitous urease enzyme in the soil facilitates the hydrolysis of urea, leading to the decomposition of the chemical bonds in both urea and water to produce ammonium (NH_4^+) and bicarbonate (HCO_3^-) (Kissel et al., 1988). This reaction increases the soil pH around the urea granule and accelerates conversion of ammonium to ammonia gas, which is lost to the atmosphere (Junejo et al., 2011; Lasisi et al., 2020). Soil properties (e.g., soil pH, clay content, soil organic matter (SOM), moisture content) determine the potential of ammonia loss with surface-applied urea, but the extent of ammonia loss is driven by environmental conditions (e.g., temperature, precipitation, relative humidity, and wind), and fertilizer management practices (fertilizer source, rate, placement, and time) (Al-Kanani et al., 1991; San Francisco et al., 2011; Sunderlage and Cook, 2018). Studies have shown that ammonia volatilization may exceed 20 % of applied N over a 14-day incubation (Adotey et al., 2017; Frame et al., 2012; Lasisi et al., 2020).

In addition to ammonia volatilization, N losses occur via nitrification. Ammonium from urea hydrolysis can be oxidized to nitrite (NO_2^-) and then to nitrate (NO_3^-). Under favorable temperature and soil moisture conditions, rapid transformation of ammonium to nitrate occur in most soils immediately after N fertilizer application (Ruark et al., 2018). In saturated soils, however, without oxygen, nitrate is used as an electron acceptor to convert reactive N back to inert atmospheric dinitrogen. This microbial-mediated process is referred to as denitrification (Ruark et al., 2018).

Several strategies have been studied to minimize ammonia loss from urea, including the use of enhanced efficiency N fertilizer (EENF), tested using field trials and/or laboratory experiments (Adams et al., 2018; Awale and Chatterjee, 2017; Dillon et al., 2012; Frame, 2017). According to the Association of American Plant Food Control Officials (2013), the broader category of enhanced efficiency fertilizers (EEF) are “fertilizer products with characteristics that allow increased plant uptake and reduce the potential of nutrient losses to the environment (e.g., gaseous losses, leaching, or runoff) when compared to an appropriate reference product”. For EENF (the nitrogen-directed forms of EEF), there are two forms of stabilized N fertilizers – urease inhibitors and nitrification inhibitors – and these contain one or more compounds that extend the stability of a certain form of N. Urease inhibitors temporarily inhibit the function and activity of the urease enzyme, lowering ammonia volatilization (ME Trenkel, 2010). The commonly used urease inhibitors include N-(butyl) thiophosphoric triamide (NBPT), hydroquinone (HQ), and phenylphosphorodiamidate (PPD or PPDA) (ME Trenkel, 2010). The NBPT has been extensively studied and widely used to reduce ammonia volatilization from surface application of urea-based fertilizers (Frame et al., 2012; Silva et al., 2017; Soares et al., 2012; Watson et al., 2008). Urea treated with NBPT delayed peak ammonia volatilization and reduced ammonia volatilization

losses by 54 –78 % when compared to untreated urea application (Soares et al., 2012). A review of several articles reported at least 3.5 days delay in peak volatilization and a 52 % reduction in total ammonia volatilization from NBPT-treated urea compared to untreated urea (Silva et al., 2017).

The nitrification inhibitors minimize nitrification by altering the activities of ammonium oxidizing bacteria, *Nitrosomonas sp* (Ruark et al., 2018). Common compounds used as nitrification inhibitors include nitrapyrin [2-chloro-6-(trichloromethyl-pyridine)], dicyandiamide (DCD), and 3,4-dimethylpyrazole phosphate (DMPP) (ME Trenkel, 2010). Nitrification inhibitors may reduce nitrate leaching, but their effectiveness in reducing ammonia volatilization losses is variable (Frame, 2017). The DCD compound is widely used to chemically coat urea and ammonium sulfate (Di and Cameron, 2016). The DCD inhibits functionality but does not decimate *Nitrosomonas* bacteria entirely, and the biological activities of other soil microorganisms are not suppressed with long term use of DCD (Ruark et al., 2018). One meta-analysis study showed that the ammonium-N content in soil with N fertilizers treated with DCD and DMPP were greater than untreated N forms (Yang et al., 2016).

Some EENF products are formulated with a combination of urease and nitrification inhibitors, the most common being NBPT and DCD mixtures. Research results show higher efficiency of NBPT by itself in reducing ammonia losses than when applied together with DCD (Jantalia et al., 2012). But Soares et al. (2012) found that the combination of DCD- and NBPT-treated urea resulted in higher ammonia volatilization compared to untreated urea.

Slow-release N fertilizers are generally physically coated with compounds that slow the N release over time compared to the untreated forms. Slow-release N fertilizers can lower ammonia volatilization and nitrate losses, especially in coarse texture soils (Peng et al., 2015), but their

effectiveness on NUE and crop yield vary greatly depending on soil and environmental conditions. The use of slow-release fertilizer products by farmers is limited because they tend to be more expensive than uncoated products, so are usually utilized in turf and other high-value applications (Junejo et al., 2011).

Several EENF products with varying formulation and NBPT concentration are being marketed in the U.S., but there is limited information on their efficacy in reducing ammonia volatilization losses. Volatilization field trials on EENF products rarely evaluate both forms of N stabilizers and slow-release fertilizer in the same trial. This is partly because the conduct of ammonia volatilization field trials in multiple locations tends to be difficult and expensive due to logistical and time constraints. Laboratory studies, however, offer a more practical and controlled approach to examine ammonia volatilization potential across different soil types. The results from such comparative studies may contribute to the fine-tuning of best N management practices involving the EENF products in wide use across the Southeast U.S. This study hypothesized that ammonia loss will differ between the different EENF products across the two soil types. This incubation study's objective was to evaluate the efficacy of different EENF products in mitigating ammonia volatilization losses in highly susceptible soils collected at two different locations in the Southeast U.S.

Materials and methods

Experimental design and treatments

The experiment was set up as a completely randomized design of seven N treatments, two soils, and four replications for a total of 56 ($n = 7 \times 2 \times 4$) experimental units. The study examined the performance of EENF products on ammonia volatilization losses from untreated urea (46–0–

0) and UAN (32–0–0) applied to two soils. Four EENF products were evaluated for urea, whilst only one EENF product was evaluated for UAN. The EENF products for urea included (1) a slow-release fertilizer, Environmentally Smart Nitrogen (ESN[®]) (44–0–0); (2) an NBPT-treated urea, urea+ANVOL[™]; (3) an NBPT- and DCD-formulated urea, SUPERU[®] (46–0–0); and (4) an NBPT- and DCD-treated urea, urea+Excelis[®] (46–0–0). The EENF product for UAN was an NBPT-treated UAN, UAN+ANVOL[™]. Information on these EENF products is provided in Table 3-1. Thus, seven N fertilizer treatments were evaluated in this trial: untreated urea, urea+ANVOL[™], urea+Excelis[®], ESN[®], SUPERU[®], untreated UAN, and UAN+ANVOL[™]. The N treatments used for this experiment were applied at an equivalent rate of 134.5 kg N/ha.

The soils used were from soil samples collected at 0 – 15 cm from two geographically distant production fields in West Tennessee which have been under no-till cropland management for decades. The soils used in this experiment were Loring silt loam and Grenada silt loam which showed high ammonia volatilization loss potential following untreated urea application. The soil samples were air-dried, ground, and sieved through a 2-mm sieve. A composite soil sample for each location was analyzed for soil organic matter content by loss on ignition method (Sikora and Hardy, 2014), soil pH by 1:1 soil/water ratio method (Sikora and Kissel, 2014), and soil texture by hydrometer method (Huluka and Miller, 2014). The soil series and selected soil properties for each location are presented in Table 3-2.

Ammonia volatilization study

The controlled environment incubation system was operated at uniform conditions throughout the experiment. This was to ensure that any differences of ammonia volatilization losses measured were due to the N treatments applied. The room temperature was maintained at 28 °C, air flow rate through the system was set at 1 L m⁻¹, and the air was near 100 % saturation

Table 3-1. Enhance efficiency N fertilizer (EENF) used, manufacturers, fertilizer additives and recommended application rates.

EENF	Type of EENF	Company	Name & conc. (%) of active ingredients	CAS Registration numbers	Application rate (l/kg)
ANVOL TM	Nitrogen stabilizer	Koch Industries	NBPT (10-20 %)	94317-64-3	0.0014 (Urea) and 0.0007 (UAN)
			Duromide (20-30 %)	2093385-47-6	
			N-methyl-2-pyrrolidone (<10 %)	872-50-4	
Urea+Excelis [®]	Nitrogen stabilizer	Timac Agro, USA	NBPT (12 %)	94317-64-3	0.0019 (Urea) and 0.0021 (UAN)
			DCD (2 %)	461-58-5	
			Other extracts (0.8 %)	8000-78-0	
ESN [®]	Slow-release	Agrium U.S. Inc	Urea (>95 %)	57-13-6	N/A
			Castor oil (4 %)	67700-69-0	
			Imidodicarbonic diamide (<1 %)	108-19-0	
SUPERU [®]	Nitrogen stabilizer	Koch Industries	Urea (60-100 %)	57-13-6	N/A
			DCD (0.85 %)	461-58-5	
			NBPT (0.06 %)	94317-64-3	
			N-Methyl-2-pyrrolidone (<0.1 %)	872-50-4	

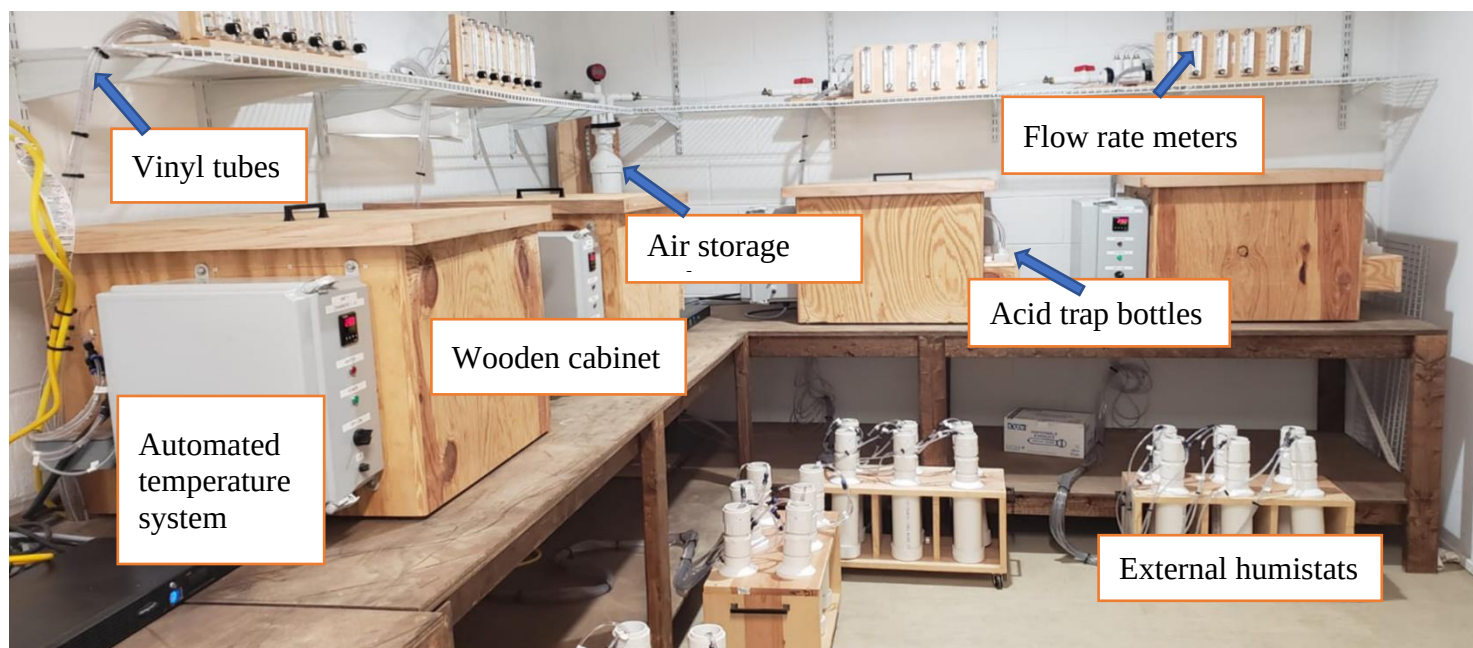
Table 3-2. The soil series and selected properties of the two soils.

Soil #	Soil series name	Soil pH	Clay content	Sand content	SOM[†]	Field capacity
		1:1	-----	g/kg	-----	
1	Loring silt loam, 2-5 % slopes	5.8	140	360	34.0	300
2	Grenada silt loam, 2-5% slope	7.0	180	330	40.2	320

[†]SOM, Soil organic matter

before being connected to the soil surfaces within the wooden cabinets. The system used study was similar to systems described by Woodward et al. (2011). The rapid and precise in-lab controlled environment system consists of a pump, two distribution manifolds, twenty four flow meters, two outer humistats, and four insulated cabinet boxes made up of several components (Figure 3-1). The air to the system was supplied by an air pump (DDL80-101, Gast Manufacturing Inc., Benton Harbor, MI) that filled the distribution manifolds. Each distribution manifold supplied air to six flow meters ($0.4\text{--}5.0\text{ L min}^{-1}$ flow meters 22461-50, Cole-Parmer Instrument Co., Vernon Hills, IL) via 4.3 mm ID vinyl tubing. This vinyl tubing was used to supply air throughout the system. Air from the flow meters was saturated by passing it through a set of closed PVC pipe cylinders (external humistats) containing water. Saturated air exiting the external humistats was then passed through a second set of smaller cylinders (internal humistats) containing water within the cabinet. The cabinets ($61 \times 61 \times 49\text{ cm}^3$) and their lids were constructed using a 0.95 cm thick plywood and were fitted with 1.3 cm thick polystyrene sheet insulation. Each cabinet was heated using an angular aluminum strip attached to a silicone rubber heat strip ($2.5 \times 20\text{ cm}^2$, 80 W total, SRFG-108/10-P, Omega Engineering Inc., Stamford CN) and mounted on a rectangular block inside the cabinet. Heat circulation was aided by an electric fan (2000 rpm, 15 V, 60 Hz, 0.10 A) (CGAC1225L-BC, CoolerGuys.com, Kirkland, WA) and a wooden baffle with end at an angle ($1.9 \times 30.8 \times 28\text{ cm}^3$). A wooden crate inside the cabinet ensured uniform heat distribution around the glass chambers.

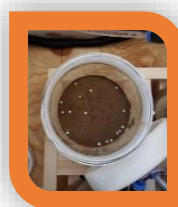
The chambers consisted of threaded glass beakers and a 3-hole cap (21650 B, Kimble Chase Life Science and Research Products LLC, Vineland, NJ). The holes served as entry and exit ports for air and as ports allowing thermocouple temperature measurement within each chamber (TT36-18U-6-SB, Omega Engineering Inc., Stamford, CN). Air exiting the chamber.



500 g soil
wetted to 2/3
field capacity



Incubation of
soils for 48
hours in cabinet



Treated soil
with urea



Treated soil
with UAN



Oil less pump



Soil beakers
covered and
connected

Figure 3-1: Controlled environment incubation system and associated components.

To start the experiment, the glass jars were filled with 500 g of air-dried soil and moistened to two-thirds of the soil field capacity (Table 3-1). The moistened soil was incubated at a constant temperature of 28 °C for 48 h prior to N treatment applications. At the end of incubation, an equivalent rate of urea or UAN was applied onto the soil at a rate of 134.5 kg N/ha, based on the exposed soil surface area in the glass jar. The UAN treatments were administered onto the soil surface with a pipette.

The air pump supplied dry air to the system through the distribution manifold, and the flow rate meters were set to ensure an air flow to each chamber of 1 L m⁻¹. The dried air from the pump was moistened by the external and internal humistats containing deionized water. Vinyl tubes conducted air flow throughout the system. The nearly 100 % humidified air exiting the internal humistats forced out any ammonia gas at the soil surface. The ammonia gas leaving the chamber with the airflow soil was captured in 100 mL of 0.02 M orthophosphoric acid in bubble traps, which were changed and analyzed on 1, 2, 3, 4, 5, 6, 7, 9, 11, 13, and 16 DAF. The ammonium content of the acid traps was determined with the aid of an automated TL-2800 Single Channel ammonium and nitrate analyzer equipped with autosamplers (Timberline Instruments, Boulder CO) at the University of Tennessee Soil, Plant and Pest Center, Nashville, Tennessee.

Statistical analysis

A SAS Proc Glimix model was used to examine the effects of N source, soil properties, and their interactions on cumulative ammonia loss at 1, 3, 7, and 16 DAF (SAS Institute, 2023). Mean separation was determined using Tukey's HSD at $\alpha = 0.05$. The ammonia loss inhibition potential of the EENF products was computed with reference to untreated urea and UAN. Data visualization and construction of plots was done with SigmaPlot 15 (Grafiti, 2020).

Results and discussion

Ammonia volatilization following EENF application

The pattern of ammonia loss from all seven N treatments (ESN[®], SUPERU[®], urea+Excelis[®], urea+ANVOL[™], UAN+ANVOL[™], untreated UAN, and untreated urea) for each sampling day for both soils are shown in Figure 3-2 a & b. All differences reported below are significant at $\alpha = 0.05$. The highest ammonia loss at sampling for untreated urea and untreated UAN were 13.1 and 2 % of applied N, and occurred on 2 and 3 DAF, respectively in soil 1. In soil 2, peak losses of 11.7 and 7.1 % of applied N from untreated urea and untreated UAN, respectively, occurred on 2 DAF. In both soils, ammonia loss at sampling thereafter declined rapidly for the rest of the incubation period (Figure 3-2 a & c). Ammonia losses were detected from all the N treatments on 1 DAF irrespective of the soil. Ammonia loss at sampling for untreated urea applied onto soil 1 was higher than the other N treatments on 1 DAF onto the same soil. But untreated urea and UAN volatilized similar amounts of ammonia in soil 2, which were both higher than the remaining N treatments (Table 3-3).

These results with untreated urea agree with other published incubation studies (Adotey, 2023; Damodar Reddy and Sharma, 2000; Frame, 2017; Frame et al., 2012; Soares et al., 2012), where peak losses occurred by 2 or 3 DAF. In a similar laboratory experiment with three different soils, Frame (2017) reported that the highest ammonia volatilization occurred on 2, 1, and 2 DAF for Raub, Wheeling, and Pella soils, respectively. The maximum ammonia loss from untreated urea in a separate incubation trial by Frame et al. (2012) occurred on 2 DAF. Similarly, Adotey (2023) found that the highest ammonia loss from uncoated urea occurred on 2 DAF. Damodar Reddy and Sharma (2000) showed that the ammonia loss at sampling was highest on 3 DAF in their 10-day incubation studies. The results are also similar to Soares et al. (2012) who reported

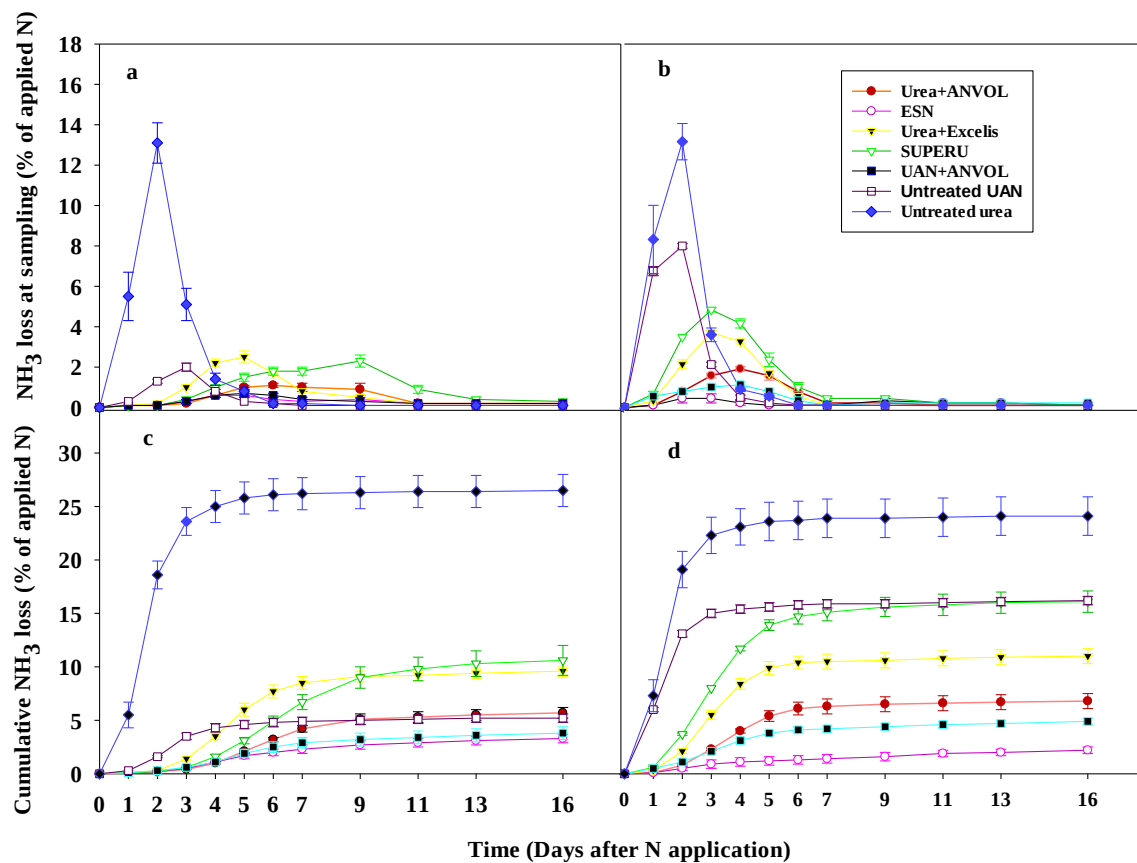


Figure 3-2. Ammonia loss at sampling from surface application of urea+ANVOLTM, ESN[®], urea+Excelis[®], SUPERU[®], UAN+ANVOLTM, untreated UAN, and untreated urea onto (a) soil 1 (b) soil 2. Cumulative ammonia loss 16 days after surface application of urea+ANVOLTM, ESN[®], urea+Excelis[®], SUPERU[®], UAN+ANVOLTM, untreated UAN, and untreated urea onto (c) soil 1 and (d) soil 2.

Table 3-3. Interactive effect between N source and cumulative ammonia volatilization (% of applied N) on 1, 3, 7 and 16 DAF in the two soils.

Soil	N source	1 DAF†	3 DAF	7 DAF	16 DAF
		----- % of applied N -----			
1	Untreated urea	5.49 b	23.61 a	26.22 a	26.49 a
	Untreated UAN	0.26 c	3.52 e	4.85 fg	5.24 de
	SuperU®	0.11 c	0.59 f	6.62 ef	10.43 c
	Urea+Excelis®	0.10 c	1.35 f	8.53 de	9.58 c
	Urea+ANVOL™	0.10 c	0.40 f	4.18 fgh	5.65 de
	UAN+ANVOL™	0.10 c	0.58 f	2.88 ghi	3.83 ef
	ESN®	0.10 c	0.53 f	2.28 hi	3.28 ef
2	Untreated urea	7.35 a	22.32 a	23.87 b	24.12 a
	Untreated UAN	6.00 a	15.00 b	15.85 c	16.17 b
	SUPERU®	0.59 c	8.11 c	15.36 c	16.34 b
	Urea+Excelis®	0.25 c	5.45 d	10.50 d	11.03 c
	Urea+ANVOL™	0.13 c	2.21 ef	6.20 ef	6.67 d
	UAN+ANVOL™	0.48 c	2.07 ef	4.23 fgh	4.93 de
	ESN®	0.11 c	0.88 f	1.38 i	2.18 f

†DAF, Days after fertilizer application

Means followed by the same letter within a column are not significantly different $\alpha = 0.05$

that maximum losses from uncoated urea occurred on 3 DAF. Other studies, however, observed that maximum ammonia fluxes lingered more than the 2 or 3 DAF. For instance, Awale and Chatterjee (2017) found that uncoated urea volatilized at the highest on 4 DAF in the two soils used for incubation studies. For untreated UAN, while Adotey (2023) reported that the highest ammonia losses occurred on 4 DAF, Keller and Mengel (1986) found maximum volatilization on 1 DAF.

Previous studies have attributed the earlier and higher fluxes of untreated urea compared to UAN and the other N sources to urea hydrolysis, which is often rapid within the first 2-3 DAF (Zaman and Blennerhassett, 2010). Griggs et al. (2007) showed that soil surface pH increased from 6.6 to 8.4 and remained high following urea application, and this alkaline soil pH may promote ammonia volatilization. The rapid breakdown of urea increases the ammoniacal-N in solution following urea application, which may be easily converted to ammonia and lost via ammonia volatilization (Al-Kanani et al., 1991). Because urea hydrolysis does not occur in UAN, it was expected to see lower ammonia fluxes from the urea portion of UAN compared to urea which hydrolyzed completely. The plateauing and declining of losses after 2 and 3 DAF suggest the completion of urea hydrolysis for urea or decrease in hydrolysable N fertilizers for both untreated urea and untreated UAN (Al-Kanani et al., 1991).

Ammonia loss at sampling was low for EENF treatments compared to untreated urea and UAN and ranged between 0.1 – 2.5 % and 0.1 – 4.3 % of applied N for the first 7 DAF for soils 1 and 2, respectively (Figure 3-2 a & b; Table 3-4 & 3-5). The high spikes in ammonia loss pattern observed for untreated urea and UAN was not observed with the amended products because the losses were more uniform across the sampling interval (Figure 3-2 a & b). The detection of ammonia fluxes with the treated urea and UAN suggests that urea hydrolysis still occurred, albeit

Table 3-4. Ammonia loss at sampling from urea+ANVOL™, ESN®, urea+Excelis®, SUPERU®, UAN+ANVOL™, untreated urea and UAN on soil 1.

Treatment	Sampling time (days after treatment application)										
	1	2	3	4	5	6	7	9	11	13	16
	----- ammonia loss (% of applied N) -----										
	-										
Urea+ANVOL™	0.1	0.1	0.2	0.6	1.0	1.1	1.0	0.9	0.2	0.2	0.2
UAN+ANVOL™	0.1	0.1	0.3	0.6	0.7	0.6	0.4	0.3	0.2	0.2	0.2
ESN®	0.1	0.1	0.3	0.6	0.6	0.4	0.3	0.4	0.2	0.2	0.2
Urea+Excelis®	0.1	0.2	1.0	2.2	2.5	1.7	0.8	0.5	0.2	0.2	0.2
SUPERU®	0.1	0.1	0.4	1.0	1.5	1.8	1.8	2.3	0.9	0.4	0.3
Untreated UAN	0.3	1.3	2.0	0.8	0.3	0.2	0.1	0.1	0.1	0.1	0.1
Untreated urea	5.5	13.1	5.1	1.4	0.8	0.2	0.2	0.1	0.1	0.1	0.1

Table 3-5. Ammonia loss at sampling from urea+ANVOL™, ESN®, urea+Excelis®, SUPERU®, UAN+ANVOL™, untreated urea and UAN on soil 2

Treatment	Sampling time (days after treatment application)										
	1	2	3	4	5	6	7	9	11	13	16
	----- ammonia loss (% of applied N) -----										
Urea+ANVOL™	0.1	0.7	1.4	1.7	1.4	0.7	0.2	0.2	0.1	0.1	0.1
UAN+ANVOL™	0.5	0.7	0.9	1.0	0.7	0.3	0.1	0.2	0.2	0.2	0.2
ESN®	0.1	0.4	0.4	0.2	0.1	0.1	0.1	0.3	0.2	0.2	0.1
Urea+Excelis®	0.3	1.9	3.3	2.9	1.5	0.5	0.1	0.1	0.1	0.1	0.1
SUPERU®	0.6	3.1	4.3	3.7	2.1	0.9	0.4	0.4	0.2	0.2	0.1
Untreated UAN	6.0	7.1	1.9	0.4	0.2	0.1	0.1	0.1	0.1	0.1	0.1
Untreated urea	7.4	11.7	3.2	0.8	0.5	0.1	0.1	0.1	0.1	0.1	0.1

at a reduced rate.

The results of this study are consistent with previously published studies which reported that amended urea was effective in reducing ammonia volatilization, especially during the first few DAF. When urea was amended with 0.3 g/Kg of NBPT, Adotey et al. (2017) reported that the losses were lower and ranged from 0.26 – 1.18 %, 0.07 – 2.42 %, 0.06 – 1.57 % and 0.04 – 1.62 % within the first 7 DAF for Crowley H, Crowley L, Kinder, and Mowata soils, respectively. When the NBPT concentration was increased to 0.6 and 0.9 g/Kg, the inhibition of ammonia losses increased, and the losses were further delayed. Although Al-Kanani et al. (1991) found that ammonia loss for coated urea was first detected on 7 DAF, the lack of ammonia flux during the first 6 DAF was likely because of inadequate soil moisture content to initiate urea hydrolysis until on 7 DAF when the urea had absorbed enough moisture from the environment.

The maximum volatilization in soil 1 (for urea+ANVOLTM, ESN[®], urea+Excelis[®], SUPERU[®], UAN+ANVOLTM) occurred on 6, 4, 5, 9, and 5 DAF, respectively (Table 3-4). In soil 2, peak ammonia losses for urea+ANVOLTM, ESN[®], urea+Excelis[®], SUPERU[®], UAN+ANVOLTM occurred on 4, 2, 3, 3, 3 DAF, respectively (Table 3-5). Compared to untreated urea and UAN, the EENF treatments delayed peak ammonia losses by at least 1 – 6 days and 0 – 2 days in soils 1 and 2, respectively.

The results support the observation that amending urea not only lowers peak losses, but also extends the time over which losses occur. Frame (2017) observed the maximum ammonia loss for NBPT-treated urea occurred on 5 DAF. In the 2 soils examined by Soares et al. (2012), urea amended with NBPT lowered and delayed peak fluxes of ammonia until 7 and 9 DAF. In a review of several related articles, Silver et al. (2017) showed that urea treated with NBPT resulted in at least 3.5 days delay in peak volatilization after NBPT applications compared to untreated urea.

The cumulative ammonia loss with time was curvilinear regardless of N treatment and soil type (Figure 3-1 c & d). Cumulative ammonia loss on 16 DAF for untreated urea was 26.49 and 24.12 % (of applied N) in soils 1 and 2, respectively; and these were higher than all the other N treatments in corresponding soils. The losses from untreated urea in soil 1 accounted for nearly 4.7, 2.5, 2.8, 4.7, 6.9, and 8.1 times more than untreated UAN, SUPERU[®], urea+Excelis[®], urea+ANVOL[™], UAN+ANVOL[™], and ESN[®], respectively. The loss of ammonia from untreated urea in soil 2 was 1.5, 1.5, 2.2, 3.6, 4.9, and 11.1 times more than untreated UAN, SUPERU[®], urea+Excelis[®], urea+ANVOL[™], UAN+ANVOL[™], and ESN[®], respectively.

The results are within the cumulative loss range of 8.2 – 31 % (of applied N) for the two soils examined at 5 °C and 15 °C, respectively by Watson et al. (2008), and similar to the 28 % of total N reported by Soares et al. (2012). The results were much higher, however, than the 4.2 % for Zaman et al. (2008), and the 4.3 % in sandy loam soil and 0.2 % of applied N in silty clay soil reported by Awale and Chatterjee (2017). Conversely, this study's results were lower than the cumulative ammonia losses of 40.1, 44.5, and 38.2 % of applied N reported by Frame (2017) for the Raub, Wheeling, and Pella soils, respectively, as well as the incubation study results of 36.8 and 33.9 % of applied N by Frame et al. (2012). The observed differences in ammonia volatilization losses across studies may arise because of soil properties, type and conditions of experimentation, and method of detecting ammonia volatilization losses.

The cumulative losses on 16 DAF from untreated UAN were comparable to urea+ANVOL[™], UAN+ANVOL[™], and ESN[®], but lower than SUPERU[®] and urea+Excelis[®] for soil 1 (Table 3-3). Cumulative ammonia losses on 3 and 7 DAF were higher for untreated UAN than the other N treatments; but comparable with SUPERU[®], urea+ANVOL[™] and UAN+ANVOL[™] for soil 1. However, the cumulative ammonia losses for untreated UAN and

SUPERU[®] were similar on 7 and 16 DAF and were higher than the other N treatments (Table 3-3). SUPERU[®], urea+Excelis[®], urea+ANVOL[™], UAN+ANVOL[™], and ESN[®] volatilized similar amounts of ammonia on 3 DAF. The losses from urea+Excelis[®] and SUPERU[®] were similar, but higher than urea+ANVOL[™], UAN+ANVOL[™], and ESN[®] on 7 DAF in soil 1. In soil 2, the losses were higher for untreated UAN than the other N treatments on 3 DAF, but similar to SUPERU[®] on 7 and 16 DAF except for untreated urea (Table 3-3). The cumulative losses with urea+Excelis[®] were higher on 3, 7, and 16 DAF than urea+ANVOL[™], UAN+ANVOL[™], and ESN[®]. Cumulative ammonia volatilization for urea+ANVOL[™] and UAN+ANVOL[™] were similar on 3, 7 and 16 DAF but higher than ESN[®].

Cumulative ammonia loss on 16 DAF was in the increasing order of ESN[®] < UAN+ANVOL[™] < urea+ANVOL[™] < urea+Excelis[®] < SUPERU[®] in both soils (Figure 3-3). For soil 1 the percent inhibition of ammonia volatilization by the EENF (% of applied N) were 60.63, 63.84, 78.67, 26.90, and 87.62 %, and for soil 2 were 32.26, 31.79, 59.18, 69.51, and 67.32 % for SUPERU[®], urea+Excelis[®], urea+ANVOL[™], UAN+ANVOL[™], ESN[®] fertilizers, respectively, compared to their untreated forms (Table 3-6). The percentage inhibition when NBPT alone was applied to urea was 78.67 % in soil 1 and 59.18 % in soil 2 (Table 3-6).

The results are consistent with the range of previously published studies that reported that the addition of NBPT to urea significantly reduced ammonia volatilization compared to unamended urea. When urea was amended with varying NBPT concentrations of 100, 250, 500, 750 or 1000 mg/kg, Watson et al. (2008) found 61.2, 69.9, 74.2, 79.2, and 79.8 % reduction in ammonia volatilization, respectively, compared to unamended urea. Soares et al. (2012) reported of a 79 % inhibition when urea was treated with NBPT (6 % of applied N) compared to untreated urea (28 %). Zaman et al. (2008) found a 55 % reduction when urea was treated with NBPT

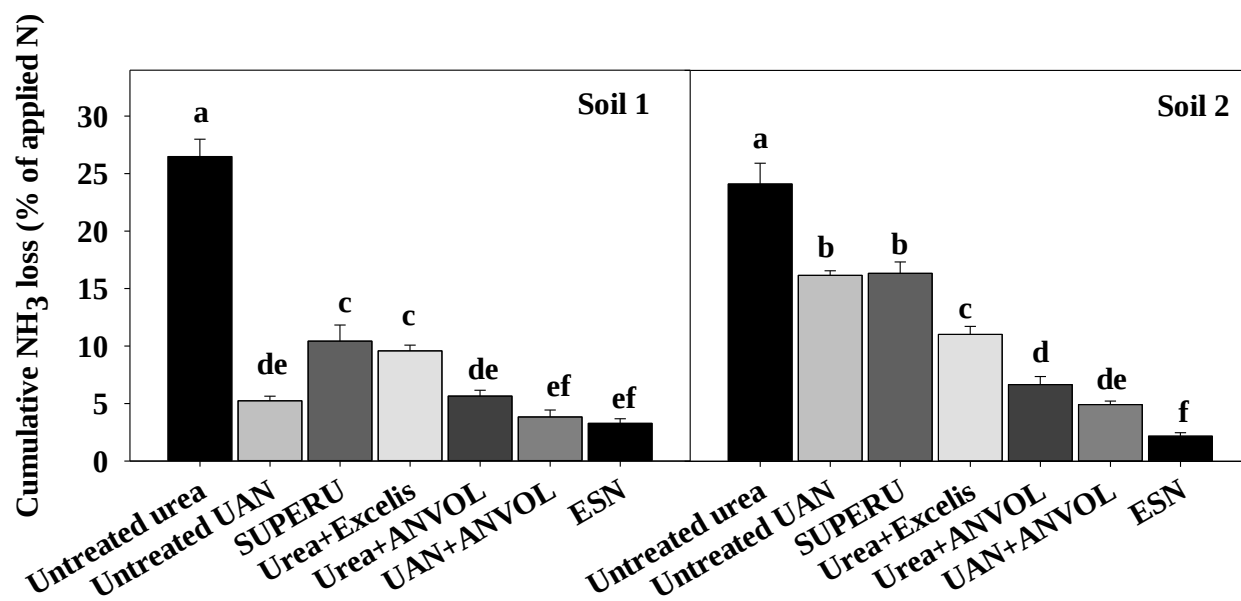


Figure 3-3. Cumulative ammonia loss 16 days after surface application of urea+ANVOLTM, ESN[®], urea+Excelis[®], SUPERU[®], UAN+ANVOLTM, untreated UAN, and untreated urea onto two soils. Bars with the same letter are not significantly different across the two soils

Table 3-6. Comparison of the effect of EENF on ammonia loss (% of applied N) and its inhibition with urea.

N treatment	Soil 1		Soil 2	
	NH ₃ loss (% of applied N)	% inhibition [†]	NH ₃ loss (% of applied N)	% inhibition [†]
Untreated Urea	26.49	-	24.12	-
Untreated UAN	5.24	-	16.17	-
SUPERU [®]	10.43	60.63	16.34	32.26
Urea+Excelis [®]	9.58	63.84	11.03	54.27
Urea+ANVOL [™]	5.65	78.67	6.67	72.35
UAN+ANVOL [™]	3.83	26.90*	4.93	69.51*
ESN [®]	3.28	87.62	2.18	90.96

[†] % inhibition = (urea – EENF)/untreated urea*100, where EENF represents SUPERU[®], urea+Excelis[®], urea+ANVOL[™], ESN fertilizers

* % inhibition = (UAN – UAN+ANVOL[™])/untreated UAN*100

(1.9 % of applied N) compared to the untreated urea (4.2 % of applied N). Awale and Chatterjee (2017), showed that amending urea with NBPT reduced ammonia volatilization by 32.3 and 71.4 % in sandy loam and silty clay soils, respectively. Manunza et al. (1999) explained that the two nickel (Ni) atoms of the urease enzyme bonds with one of the amide groups and oxygen atoms of the NBPT to form a cation bridge, which allows the oxygen atom on the bridge to form a strong hydrogen bond with the other amide group of the NBPT. Unlike untreated urea, which is easily degraded by the urease enzyme, this three-point bond of the NBPT molecule with the urease enzyme binding sites temporarily stops functionality of the urease enzyme and lowers ammonia loss (Manunza et al., 1999).

In this study, DCD did not improve the efficiency of NBPT. The relatively higher cumulative losses observed for combinations of NBPT and DCD in SUPERU[®] and urea+Excelis[®] is consistent with previous studies. For the entire 42-day incubation period, Awale and Chatterjee (2017) reported that SUPERU[®] volatilized more in two soils than urea amended with NBPT alone. Soares et al. (2012) showed that urea mixed with NBPT and DCD volatilized 15 – 17 % compared to 6 % by NBPT alone in one trial, and 28 – 33 % compared to 17 % of applied N with urea treated with NBPT alone in another. Surprisingly, Zaman et al. (2008) reported that mixtures of urea and DCD increased ammonia loss (5.7 % of applied N) compared to untreated urea (4.2 % of applied N). These findings by Zaman et al (2008) were similar to those made by Soares et al. (2012) that DCD significantly increased ammonia volatilization by 19 % compared to untreated urea.

The higher cumulative ammonia loss with SUPERU[®] (higher DCD than NBPT concentration) compared to urea+Excelis[®] (higher NBPT than DCD concentration) (Figure 3-3) may suggest that NBPT was more effective in reducing ammonia loss than DCD. The mechanism by which ammonia loss increases with DCD and NBPT combinations has not been fully

elucidated, but Soares et al. (2012) suggest that it may be due to processes other than urea hydrolysis, because both DCD and NBPT belong to the amide group of compounds. According to Gioacchini et al. (2002), through the inhibition of nitrification and urea hydrolysis in the soil, DCD increases the concentration of ammonium and soil pH at the soil surface; and these conditions might be responsible for the reduced NBPT efficacy when combined with DCD. The sampling losses with SUPERU[®] and urea+Excelis[®] in this study continued to be high, similar to what was observed by Soares et al. (2012) during the incubation period. But unlike findings by Soares et al. (2012) and Zaman et al. (2008), where urea amended with DCD volatilized more ammonia than untreated urea, in this study the cumulative losses for untreated urea were higher than SUPERU[®] and urea+Excelis[®] at the end of incubation in both soils (Figure 3 c & d).

The results of this study are consistent with the previously published studies on the effectiveness of ESN[®] to reduce ammonia volatilization (Awale and Chatterjee, 2017; Rochette et al., 2009a). Rochette et al. (2009a) reported that ammonia loss from ESN[®] was 3.9 and 0.9 % (of applied N) for 1 and 10 DAF, respectively, corresponding to about 50 - 60 % reduction in ammonia losses compared to untreated urea. The observed effectiveness of the ESN[®] in reducing ammonia losses from surface application of untreated urea is often attributed to the coating of the ESN[®] granules by hydrophobic materials, which are less affected by soil and climatic conditions (Ruark et al., 2018). The polymer coating also regulates the amount of N released into soil solution, thus reducing the concentration of ammonium available for urea hydrolysis, lowering ammonia volatilization (Rochette et al., 2009a). Some studies suggest that ammonia loss could spike with ESN[®] application at later stages of experimentation (Awale and Chatterjee, 2017; Jantalia et al., 2012), but this was not observed after 16 days of incubation during which the losses declined with time in this study.

Soils and ammonia volatilization

For untreated urea, there was a difference in ammonia loss between soils on 1 and 7 DAF; whereas untreated UAN was different on 1, 3, 7, and 16 DAF (Table 3-3). Ammonia loss differed for SUPERU[®] on 3, 7, and 16 DAF; and urea+Excelis[®] only differed on 3 DAF in the 2 soils. For all days in which differences occurred among N treatments, soil 2 was higher (Table 3-4). The pH of 7 for soil 2 may predispose the untreated urea to a more rapid hydrolysis compared to the pH of 5.8 for soil 1. This may also explain why soil 1 showed delayed ammonia volatilization losses (1-6 DAF), a couple of days more than soil 2 (0-2 DAF) when the EENF products were applied. This agrees with published studies that high initial soil pH can speed up and increase ammonia loss with surface application of urea (San Francisco et al., 2011). According to Fenn and Hossner (1985), low soil pH conditions tend to facilitate ammonia conversion to ammonium, which minimizes N losses through ammonia volatilization. The observed influence of initial soil pH on ammonia volatilization with urea may suggest that both soils were poorly buffered (Ferguson et al., 1984; Stevens et al., 1989). Although UAN does not undergo hydrolysis, the soil pH of 7 favored the conversion of ammonium in solution to ammonia which may be lost through ammonia volatilization. This may explain the higher losses in soil 2 compared to soil 1 for untreated UAN application.

Overall, the greatest returns on EENF applications are more likely to be achieved under soil and environmental conditions that were most suitable for ammonia volatilization losses from urea and UAN, including high soil pH, warm temperatures, and low soil buffering capacity (Hargrove, 1988).

Conclusion

Amending the urea and UAN with NBPT, DCD, or polymer-coating delayed the time and reduced the amount of maximum ammonia loss, ultimately reducing cumulative ammonia loss in this study. The effectiveness of the EENF products was in the decreasing order of ESN[®] > UAN+ANVOL[™] > urea+ANVOL[™] > urea+Excelis[®] > SUPERU[®]. For soil 1, the EENF treatments reduced ammonia volatilization (% of applied N) by 60.63, 63.84, 78.67, and 87.62 % compared to 32.26, 31.79, 59.18, and 67.32 % for soil 2 for SUPERU[®], urea+Excelis[®], urea+ANVOL[™] and ESN[®] products, respectively, in comparison to untreated urea. The UAN+ANVOL[™] reduced ammonia loss by 26.90 and 69.51 % in soil 1 and soil 2, respectively compared to untreated UAN. The slow-release fertilizer, ESN[®] was more effective than NBPT in minimizing ammonia loss, and urea treated with NBPT alone (urea+ANVOL[™]) was more efficient at inhibiting ammonia losses than when urea was amended with both NBPT and DCD (SUPERU[®] and urea+Excelis[®]).

The efficacy of EENF products may best be realized under soils susceptible to ammonia volatilization from urea applications. Therefore, soil properties such as pH and buffering capacity may influence the timing of peak ammonia losses and the magnitude of these losses. Because the additives used to treat urea and UAN degrade with time in the soil, rainfall or irrigation events may become necessary after about 7 DAF to cause the downward diffusion of urea and ammonia to minimize losses, regardless of the soil type. Otherwise, ammonia volatilization losses with treated urea could rise steadily to reach values similar to untreated urea, especially in soils that are prone to ammonia volatilization losses. Growers in Tennessee may benefit from judicious EENF applications.

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