FACTORS AFFECTING AMMONIA VOLATILIZATION FROM LAND-APPLIED BROILER LITTER

by

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(Under the Direction of Miguel Cabrera)

ABSTRACT

Broiler litter is commonly surface-applied to pasture in the southeastern U.S. as a method of waste management and to provide an inexpensive source of nutrients, such as nitrogen (N). Predicting plant-available N derived from litter can be difficult due to losses through ammonia (NH_3) volatilization. Field studies were conducted to determine overall NH_3 loss as affected by environmental variables and litter characteristics. Loss as a percentage of the applied total N (TN) ranged from 0.9 to 10.5% in eleven 28-d studies. Average vapor pressure (VP) and initial ammonium-N plus uric acid-N explained 79% of the variability in cumulative NH_3 loss in nine studies. To better understand the effects of soil water content (WC) and VP on NH_3 loss, two 15-d laboratory studies were performed with two soil WCs (0.03 vs 0.13 g H_2O g^{-1}) at 32 and 92% relative humidity (RH). Results showed that litter can absorb or lose water at a relatively fast rate depending on RH. At 92% RH, NH_3 loss at a soil WC of 0.13 g g^{-1} was much larger than that at 0.03 g g^{-1} (21% vs 11% of TN), whereas at 32% RH, NH_3 loss was only slightly greater at 0.13 than at 0.03 g g^{-1} (5.2 vs 3.2 % of TN). Additionally, litter pH buffering capacity (pHBC) was investigated in 37 samples of broiler litter. Values of pHBC ranged from 187 to 537 mmol H (pH unit kg dry litter)$^{-1}$. Litter pHBC was calibrated to near infrared spectroscopy with R^2=0.90. Combining laboratory and field data, a mechanistic model of litter WC and NH_3 volatilization was developed. Simulated litter WC fluctuations on a diurnal basis ranged from 0.06 to 1.3 g H_2O g litter^{-1}, impacting both mineralization and the pool of ammoniacal-N subject to NH_3 volatilization. The calibrated model simulated NH_3-N loss for 28-d field studies with R^2=0.81. Our data suggest that high initial uric acid-N, ammonium-N, and high VP/RH increase NH_3 volatilization, the latter through rewetting of the litter, which leads to increased N mineralization and NH_3 loss.

INDEX WORDS: Ammonia, volatilization, nitrogen, broiler litter, poultry litter, fertilizer, surface-application, relative humidity, buffering capacity, mineralization.

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INTRODUCTION

Poultry production is a major component of United States agriculture with the value of production of broilers, eggs, turkeys, and chickens totaling $44.1 billion in 2013. Broiler production (*Gallus gallus domesticus*) makes up 70% of that total and is the largest sector of poultry production (USDA, 2014). With the yearly production of approximately 8.6 billion broilers (USDA, 2014), an estimated 12 million Mg of broiler litter is generated annually (Moore, 1998). This by-product of poultry production is most commonly surface-applied to pasture as a way of waste management and to provide an inexpensive/alternative fertilizer for the forage. The land application of broiler litter provides plant nutrients phosphorus, potassium, nitrogen (N) as well as other micro and macro-nutrients (Kingery et al., 1994; Marshall et al., 1998; Mitchell and Tu, 2006).

Compared to other manures, the low water content and relatively high N concentrations of broiler litter favor its use as an alternative fertilizer (Stephenson et al., 1990). However, N in broiler litter can be highly variable and subject to large losses through ammonia ($NH_{3)}$ volatilization, which has been found to range from 4 to 60% of the total N applied in laboratory and field experiments (Brinson et al., 1994; Cabrera and Chiang, 1994; Lau et al., 2008; Lockyer et al., 1989; Marshall, 1998). High and unpredictable losses of N through NH_3 volatilization leads to decreased crop yields and reduced confidence in broiler litter as an alternative N fertilizer (Moore, 1998; Paramasivam et al., 2009).

Ammonia volatilization from poultry litter is a function of the ammonium and organic N content of the litter, mineralization rates of organic N to ammonium, litter pH, and NH_3 transfer from the litter to the atmosphere (Ni, 1999; Rothrock et al., 2010; Sherlock and Goh, 1984; Sommer and Hutchings, 2001). These factors are controlled both by the initial characteristics of the litter and by the environmental conditions in the field after application. Initial ammonium and organic N in litter determine the total pool of N subject to NH_3 loss. Mineralization affects the rate of ammonium release while simultaneously increasing litter pH, favoring increased loss. Both mineralization and the chemical/physical properties controlling volatilization are determined by the temperature and water content of the litter, which in turn are controlled by diurnal and seasonal fluctuations in environmental conditions (Bitzer, 1988; Hadas et al., 1983; Liu et al., 2009; Sherlock and Goh. 1983).

Studies have been conducted to determine the effect of temperature and litter/soil water content on mineralization and volatilization rates of broiler litter (Bitzer, 1988; Cabrera and Chiang, 1994), but information for surface-applied litter is lacking. Further, the application rate of broiler litter to grasslands ranges from 3,000 to 10,000 kg ha^{-1} (Gaskin et al., 2013), which results in a 2 to 4-mm depth, leaving litter primed to interact with atmospheric and surface soil conditions. Broiler litter at typical water contents has a very low water potential (about -30 MPa at 0.25 g H_2O g^{-1} on a dry-weight basis), which under high relative humidity (RH) results in a large water potential gradient between litter and atmosphere. Thus, changes in RH near the soil surface may lead to fluctuating litter water content, N mineralization, and subsequent ammonia volatilization.

Information on the effect of soil water content under contrasting RH on NH_3 volatilization from broiler litter is currently not available. A better understanding of the effect of atmospheric water on litter water content and of the effect of soil water content on NH_3 loss would contribute to the development of a statistical and simulation model for plant-available N from broiler litter. Such a tool driven by environmental variables would be useful to farmers when making decisions regarding the amount of N to apply to obtain optimum grassland productivity with reduced environmental impact. With this in mind, the main objective of this dissertation is to better understand and predict the effect of initial litter characteristics and environmental variables on NH_3 volatilization from surface-applied broiler litter. Specific objectives are to 1) directly measure NH_3 volatilization under field conditions and develop a statistical model to estimate NH_3 volatilization from surface-applied litter; 2) determine the rate of drying or rewetting of broiler litter as a function of RH and to determine the effect soil water contents under high and low RH on NH_3 volatilization from broiler litter under laboratory conditions; 3) determine litter pH buffering capacity and assess the accuracy of near infrared reflectance spectroscopy in determining litter pH buffering capacity; 4) develop a mechanistic model for the surface-application of broiler litter to pasture incorporating existing knowledge about the mechanistic processes of NH_3 volatilization including the effect of atmospheric water on litter WC and the effect of litter WC on organic N mineralization and volatilization.

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CHAPTER 1

LITERATURE REVIEW

BROILER PRODUCTION AND USE AS A FERTILIZER

Poultry production is a major component of United States agriculture with the value of production of broilers, eggs, turkeys, and chickens totaling $44.1 billion in 2013. Broiler production (*Gallus gallus domesticus*) makes up 70% of poultry production (USDA, 2014). Current broiler production is controlled by vertically integrated firms that manage the production process from breeding and hatching to slaughter and marketing, contracting independent farmers to raise the broilers for consumption (NCC, 2012; Pelletier, 2008). Typical broiler production consists of 20,000-bird poultry houses approximately 1800 m^2 in size, with birds reaching market weight after 5-9 weeks, depending on market requirements (AEB, 2013; NCC, 2012; Sims and Luka-Mccafferty, 2002). This intensive, high efficiency production led to approximately 8.5 billion broilers produced in 2013, with much of this production concentrated in the mid-south region of the United States. Currently, Georgia ranks number one in broiler production, producing 1.3 billion birds (15.2 billion kg of broilers) annually (USDA, 2014).

While broiler production has a large economic impact in these regions, the concurrent generation of broiler litter as a waste product has led to serious issues for producers, surrounding communities, and the environment. During poultry production, bedding material (typically wood shavings, peanut hulls, or wheat straw) is added to the floor of the poultry houses where five to six flocks of birds are grown out over a 1-year cycle (Moore et al., 1995). Approximately 1.5 kg of litter is produced for each broiler (and 8 kg of litter yr^{-1} per layer) leading to the annual accumulation of 2 million Mg of broiler litter in Georgia that must be managed and disposed of (AEB, 2013; Moore et al, 1998; USDA, 2014). With the large amount of broiler litter produced, determining optimal methods of utilization and management of this byproduct as a potential pollutant has become increasingly important.

The most common use of broiler litter is surface application to pastures because it is an inexpensive source of nitrogen (N), phosphorus (P), potassium (K), and micronutrients (Marshall et al., 1998). The long term, repeated application of broiler litter to pasture increases organic carbon, total N, total P, and micronutrients in the upper 15 cm of the soil profile (Kingery et al., 1993). Further, repeated application adds a substantial pool of potentially mineralizable organic N (Adeli et al., 2007; Gordillo and Cabrera, 1997; Kingery et al., 1994; Mitchell and Tu, 2006). In the short term, broiler litter can add immediate plant available N in the forms of ammonium (NH_4^+) and nitrate (NO_3^-) as well as add a rapid pool of potentially mineralizable N to the soil surface, supplementing crops throughout the growing season (Kingery et al., 1993, 1994; Mitchell and Tu, 2006).

It is important to note the differences in surface-application as a method of waste disposal in contrast to applying broiler litter as a method of fertilization. It is common for broiler producers to apply broiler litter on nearby land as a method of disposal. Application rates for these purposes are based on maximum allowances of litter to dispose of as much litter as possible. While nutrient management plans are sometimes required for large-scale operations (UDECE, 2012), application rates in these circumstances are often very high. Applications based on disposal are not usually limited by any nutrient, with applications often exceeding crop requirements (Moore, 1998). Conversely, broiler litter is often purchased from broiler facilities as an alternative fertilizer. With fertilizer values increasing with fuel prices, broiler litter at $10-35 per Mg is an inexpensive nutrient source (Dunkley et al. 2011). When the amount of broiler litter applied is limited, the amount and precision of nutrient applications becomes much more important. Due to the inorganic and organic forms of nutrients in litter, making rate recommendations can be difficult, especially with respect to N (Sims and Wolf, 1994). High and unpredictable losses of N through ammonia (NH_3) volatilization lead to decreased crop yields and discourage the use of broiler litter (Moore, 1998; Paramasivam et al., 2009). By understanding and modeling NH_3 losses from surface-applied broiler litter, more accurate predictions of NH_3 loss can be made and in-season recommendations for additional fertilizer N may be made (Sheppard and Bittman, 2013; Sommer and Hutchings, 2001). Through modeling volatilization, the hope is to increase broiler litter use as an alternative fertilizer outside of nutrient-saturated regions. Additionally, encouraging the use of this nutrient-rich byproduct will lessen the use of fossil-fuel-based fertilizers and build healthier soils.

AMMONIA VOLATLIZATION FROM SURFACE-APPLIED BROILER LITTER

Ammonia volatilization is an important pathway of loss of plant-available N from surface-applied broiler litter and a potential environmentally-polluting process (Marshall et al., 1998; Rothrock et al., 2010). Excess NH_3 introduced into the surrounding environment can lead to soil acidification, eutrophication, and reduction of plant biodiversity, as well as, greatly reduce crop yields (Bowman et al., 2008; Salazar et al., 2012). The actual amount of NH_3 loss from surface-applied broiler litter can be highly variable. In laboratory studies, Cabrera and Chiang (1994) showed a range of loss of 3.6 to 13.5% of the total N applied in 13 d, and Brinson et al. (1994) determined a range of loss between 17 to 31% of the total N applied in 21 d. Field studies of NH_3 volatilization have shown different ranges of loss, with relatively minor losses of 3-6% of the total N applied (Marshall et al., 1998) to significant losses of 30 and 45% of the total N applied (Lau et al., 2008; Lockyer et al., 1989). These wide variations increase the difficulty in estimating the nutrient value of litter, but they are not surprising due to the many variables that affect NH_3 volatilization. Ammonia volatilization is a function of manure characteristics, environmental variables, time, rate and method of application (Martinez-Lagos, 2013; Nathan and Malzer, 1994; Sommer and Hutchings, 2001). Whereas time, rate, and method can all be controlled during application, the initial litter characteristics and environmental variables can vary greatly.

The physical, biological, chemical, and environmental factors that affect NH_3 volatilization are interrelated, and it is their combined effect that control NH_3 volatilization. Litter characteristics and environmental variables not only affect the biological aspect of NH_3 volatilization and mineralization, but also the physical and chemical mechanisms of loss (transfer of loss, NH_3/NH_4^+ equilibrium, and NH_3 concentration). The main factors affecting NH_3 volatilization are the initial inorganic and organic N content of broiler litter; the effect of temperature and water on N mineralization; the effect of litter buffering capacity and reactions on litter pH; the effect of pH and temperature on the dissociation constant of NH_3/NH_4^+ equilibrium; and the effect of temperature on the transfer of NH_3 to the atmosphere. (Cabrera et al., 2008; Liu et al., 2009; Ni, 2008; Sommer and Hutchings, 2001; Sherlock and Goh, 1985).

Nitrogen in Broiler Litter

Nitrogen in litter is present in both organic and inorganic forms (Cabrera and Chiang, 1994; Paramasivam et al., 2009). The majority of plant-available N in broiler litter is in the form of organic N-containing compounds that need to be mineralized. Therefore, the mineralization of these compounds in broiler litter is important for plant-available N and NH_3 loss. Microbial communities and enzymes present in poultry litter and in soil are crucial to NH_3 and NH_4^+ production and subsequent NH_3 volatilization. Organic N excreted in poultry litter is comprised primarily of uric acid, urea, and undigested proteins, with urea and uric acid making up about 80% of the organic N (Ritz et al., 2004; Rothrock et al., 2010). The large amount of N in poultry litter is considered to be largely due to the excess proteins and amino acids fed to poultry in commercial operations. For most poultry diets, roughly 33% of N in the feed is incorporated into poultry tissues and eggs and the other 67% is excreted (Ritz et. al, 2004).

Mineralization of uric acid to NH_4^+ undergoes two main enzymatically-mediated equations as shown (Rothrock et al. 2010):

$$\mathrm{C_3H_4N_4O_3(uric\ acid)} + \mathrm{O_2} + 4\mathrm{H_2O} \xrightarrow{\text{uricase}} 2\mathrm{(NH_2)_2CO\ (urea)} + \mathrm{C_2H_3O_3} + \mathrm{H_2O_2} + \mathrm{CO_2} \qquad \text{Eq. [1]}$$

$$2\mathrm{(NH_2)_2CO\ (urea)} + 2\mathrm{H^+} + \mathrm{H_2O} \xrightarrow{\text{urease}} 2\mathrm{NH_4^+} + \mathrm{CO_2} \qquad \text{Eq. [2]}$$

Uric acid degradation is catalyzed by the uricase enzyme and urea hydrolysis is catalyzed by the urease enzyme. The molar ratio of this mineralization equation is 1 uric acid: 2 urea: 4 NH_4^+ (Rothrock et al., 2010). Urease is an extracellular enzyme that can exist without the presence of microorganisms (Klose and Tabatabai, 1999). These enzymes can bind with clay and humic substances, which may stabilize the enzyme or substrate and protect it from degradation (Ciurli et al. 1999; Sylvia et al., 2008). The ability of this enzyme to remain in conditions unfavorable to microbial growth may be a very important factor in understanding mineralization, specifically in broiler litter, which has a very low water potential.

The degradation of uric acid and urea can be relatively fast, with rapid production of NH_3/NH_4^+ in observed poultry houses (Ritz, 2004). Typically, by the time litter is surface-applied, the litter contains an average of 4% total N, of which 40 to 80% is in the organic form (Nahm, 2005; Rothrock et al., 2010; Stephenson et al., 1990). The NH_3 subject to loss after application will be dependent on the initial pools of both inorganic and organic N. While organic N must first undergo mineralization, initial inorganic NH_4^+ in the litter at the time of application will be immediately available for plant uptake, nitrification, or loss. Nitrification of NH_4^+ leads to an overall reduction in NH_3 loss and a decrease in litter pH (Schmidt, 1982):

$$\mathrm{NH_4^+} + 1\tfrac{1}{2}\mathrm{O_2} \rightarrow \mathrm{NO_2^-} + \mathrm{H_2O} + 2\mathrm{H^+} \qquad \text{Eq. [3]}$$

$$\mathrm{NO_2^-} + \tfrac{1}{2}\mathrm{O_2} \rightarrow \mathrm{NO_3^-} \qquad \text{Eq. [4]}$$

However, nitrifying bacteria are often much more sensitive to water content, temperature, and high NH_4^+ concentrations, leading to a delay in nitrification in litter (Bitzer and Sims, 1988; Hadas et al., 1983; Norton, 2008). With the majority of NH_3 loss occurring in the first 7 days after application, nitrification may not have a large effect on reducing overall NH_3 loss (Meisinger and Jokela, 2000).

Nitrogen mineralization in broiler litter is very rapid within the first day, with rates decreasing over time. This pattern of mineralization is suggestive of at least two pools of mineralizable N in broiler litter (Gordillo and Cabrera, 1997; Hadas et al., 1983; Sims 1986). Gordillo and Cabrera (1997) observed that on average, 50% of mineralization in broiler litter occurred within the first 24 hours under optimum conditions, with only 11% of mineralization occurring between days 1 and 7.

Mineralization in broiler litter is typically described using a two-pool, first-order kinetics model where:

$$\mathrm{Nm} = \mathrm{Nf}\left(1 - \mathrm{e}^{-\mathrm{kft}}\right) + \mathrm{Ns}\left(1 - \mathrm{e}^{-\mathrm{kst}}\right) \qquad \text{Eq. [5]}$$

with *Nm* net N mineralized, *Nf* the fast pool of mineralizable N, *Ns* the slow pool of mineralizable N, and *kf* and *ks* the respective rate constants of mineralization as a function of time (t) (Hadas, 1983; Gordillo and Cabrera, 1997). The rate of mineralization will determine the availability of N from the organic pool. The mineralization process increases the pool of ammoniacal-N in solution while simultaneously increasing litter pH (Eq.2), both contributing to an increase in the potential for NH_3 loss (Sherlock and Goh, 1985; Sommer and Hutchings, 2001). Most mineralization studies have been conducted with litters incorporated in soils at field capacity, leading to optimum rates of mineralization. Nitrogen mineralization in broiler litter is driven by enzyme and microbial activity as well as the availability of the substrate (organic N containing compounds) to these enzymes. Therefore, water and temperature play a dominant role in mineralization in broiler litter (Antonopoulos, 1999; Pratt et al., 2002; Sims, 1986).

Effect of Water Content and Temperature on N mineralization

Current literature describing the effect of litter water content on N mineralization is limited. In many studies, mineralization and ammonia volatilization are combined to determine the effects of water on N mineralization in litters. Cabrera and Chiang (1994) looked directly at the water content effect on denitrification and NH_3 volatilization in broiler litter. The study evaluated four water contents (water potentials ranging from -1.55 to -18.19 MPa) in 13-day studies measuring NH_3 evolved from the samples. They found an increase in ammonia volatilization with increasing water content. In another study, Cabrera et al. (1994) determined the effect of fractionated poultry litter on N mineralization and NH_3 volatilization. This experiment tested broiler litters from various poultry houses. The litters ranged from -1.9 to -3.86 MPa. The study determined that between 44.4 and 55.1% organic N mineralized in 14 days. In a 12-week study, Agehara and Warncke (2005) determined 37 to 45% of the organic N mineralized in partially composted poultry manure mixed with soil at increasing water contents. Increasing the soil water content from 50% to 90% water holding capacity increased mineralization by 21%. Additionally, Sims (1986) estimated between 40 to 60% of the added organic N was mineralized within 90 to 150 days when the soil was maintained at field capacity. However, when the soil water content was allowed to dry, the mineralization of organic N was reduced by 30% of the organic N mineralized at field capacity. These studies indicated that increased microbial activity, substrate in solution, and ammonium in solution from elevated water content led to increased mineralization and volatilization from broiler litter (Cabrera and Chiang, 1994).

Water and temperature are intricately linked in mineralization and other biologically mediated processes. Temperature greatly influences the biological activity, chemical, and physical processes in soil and broiler litter. Within tolerable ranges, biological activity typically doubles for every 10°C increase, frequently expressed as a $Q_{10} = 2$ (Sylvia et al., 2008). The effects of temperature on mineralization in broiler litter have previously been determined on litter incorporated into soil. Sims (1986) determined that an increase in temperature led to increased organic N mineralization up to 40°C for poultry litter incorporated into soil, and attributed this to an increase in microbial numbers and activity. The study observed mineralization even at 0°C, but with lower rates. Mineralization rates were shown to be high at 25 and 40°C, with favorable conditions at 25°C leading to increased nitrification. Accumulation of NH_4^+ at 40°C was indicative of increased organic N mineralization but decreased nitrification at this temperature. This indicated that at high temperatures, rapid mineralization may occur leading to a rapid buildup of NH_4^+ in solution, which would favor NH_3 volatilization. However, when high temperatures were introduced in low water incubations, mineralization remained low.

Contrary to this, Hadas et al. (1983) saw no effect of temperature on ground poultry litter incorporated into the soil with temperature treatments of 14, 25, and 35°C in 90 days. The authors state that this small change in the rate of mineralization as a function of temperature is insignificant compared to differences in the characteristics of the litter. Further, the effect of temperature may have a dominant effect on nitrification and N loss compared to mineralization.

Both temperature and water content are related to mineralization of organic N due to effects on the enzymatic and microbial community and substrate availability. The effect of mineralization on NH_3 loss will be through the increase in the NH_3/NH_4^+ available for loss as well as the effect on pH.

Effect of pH and pH Buffering Capacity on Ammonia Volatilization

Whereas mineralization controls the pool of NH_3/NH_4^+ subject to NH_3 volatilization, pH controls the form of ammoniacal-N present in the litter solution, and therefore, the aqueous NH_3 available for loss. Broiler litter pH is especially important in NH_3 losses with surface application. With incorporation into the soil, the high pH of litter as well as the increase in pH by mineralization processes are counterbalanced by the lower soil pH (Meisinger and Jokela, 2000). Litter pH is affected by mineralization (Eq.[2]), nitrification (Eq. [3] and [4]), the buffering capacity of litter, as well as the loss of NH_3 to the atmosphere (Kissel and Cabrera, 2005; Kissel et al., 2008; Ni, 1999). High pH favors volatilization which can be seen by the equilibrium equation:

$$\mathrm{NH_4^+} \leftrightarrow \mathrm{NH_3} + \mathrm{H^+} \qquad \text{Eq. [6]}$$

This reaction has a pKa of 9.25 at 25˚C, indicating that at a pH of 9.25, concentrations of NH_4^+ and NH_3 are equal. However, this equilibrium is sensitive to both temperature and litter water content (Cabrera et al., 2008; Ni, 1999; Kissel and Cabrera, 2005). Litter typically has a pH of 8

(Ritz, 2004), but as mineralization, nitrification, and loss occur, the litter pH changes and, subsequently, the proportion of NH_3 in solution also changes. The magnitude of change in litter pH is a function of the litter pH buffering capacity.

Little research has been done to investigate the pH buffering capacity of broiler litter, but buffering in soils has been studied extensively. Buffering capacity in soil systems is a function of soil organic matter, carbonate equilibrium, oxide and hydroxides, and the dissolution of clay minerals (Bloom, 2000; Ferguson et al., 1984; Nelson and Su, 2010). Similarly, high organic matter content, volatile fatty acids, calcium carbonate and calcium ions (from the addition in feed), and NH_3/NH_4 equilibrium in broiler litter may be the dominant non-microbial pH buffering processes in litter (Derikx et al., 1994; Pocknee and Sumner, 1997). Derikx et al. (1994) proposed that the shape of the buffering curves for swine, cattle, and poultry manures may indicate substances responsible for buffering. The group states that the flatness observed around pH 9.25 is a function of NH_4/NH_3 equilibrium and carbonate ions may contribute to this effect at higher pH. Further, calcium carbonate and the presence of volatile fatty acids may lead to buffering at lower pH. With both of these mechanisms being likely present in both broiler and layer litter, calcium carbonate may have the dominant effect in layer litter from the addition to feed and presence of eggshells. Additionally, the type and size of carbonaceous material used in the bedding material will likely affect litter pH buffering capacity.

Whereas the pH buffering capacity of the litter will determine the pH in the litter and pH will determine the NH_3 in solution, mechanisms of loss such as the dissociation constant, available ammoniacal-N in solution, and the transfer of NH_3 to the atmosphere will be further defined by environmental conditions. Environmental conditions such as temperature and water content affect the biological mineralization that contributes to volatilization, but they also affect the chemical and physical dynamics of NH_3 volatilization.

Effect of Water Content and Temperature on Ammonia Volatilization

Microbial and enzymatic activity will dominate the supply of ammoniacal-N to the litter solution; subsequent loss by volatilization is a function of the form of ammoniacal-N in solution, the concentration of aqueous NH_3, the equilibrium of gaseous and aqueous NH_3, and the transfer of gaseous NH_3 to the surrounding air. These chemical/physical parameters of loss are governed by the temperature and the water status of the litter (Cabrera et al., 2008; Liang, et al., 2014; Liu et al, 2009; Ni, 1999; Sherlock and Goh; 1985).

Overall NH_3 volatilization flux (FNH$_3$) is typically defined as:

$$\mathrm{FNH_3} = \mathrm{K}_G\,([\mathrm{NH_3}]_{\mathrm{surface}} - [\mathrm{NH_3}]_{\mathrm{atm}}) \qquad \text{Eq. [7]}$$

where K_G is the convective/mass transfer coefficient, $[NH_3]_{surface}$ is the NH_3 gas concentration in the litter/soil, and $[NH_3]_{atm}$ is the concentration of NH_3 in the atmosphere (Cabrera et al., 2008). Under field conditions, the $[NH_3]_{atm}$ is typically very low, and most models consider this concentration to be zero. However, $[NH_3]_{atm}$ will be high in production facilities and can be modeled as a function of housing conditions such as ventilation rate and the area of the house (Liu et al., 2009). The convective transfer coefficient is usually derived from empirical data as a function of air velocity and/or temperature (Cabrera et al., 2008; Ni, 1999). In a laboratory wind tunnel system, Liu et al. (2008) determined a range of the mass transfer coefficient from 2.15 to 32.66 m h^{-1} (average 9.88 m h^{-1}) varying with both temperature and air velocity. In their study, air velocities ranged from 0.05 to 2 m s^{-1} and each velocity treatment was exposed to temperatures ranging from 13 to 30˚C. The K_G coefficient was found to decrease as temperature increased and increase with increasing air velocity. A wide range of K_G values has been used to determine NH_3 loss from both urea and manure applications. With the method of obtaining and predicting K_G values differing among studies, reported values range from 0.005 to 42 m h^{-1} and must be adjusted for manure type and environment (Ni, 1999).

Difficulty in determining overall NH_3 loss is further exaggerated as the gas concentration of NH_3 ($[NH_3]_{surface}$) in litter is also affected by temperature and litter water content. The NH_3 gas concentration has previously defined as:

$$[NH_3]_{surface} = [NH_3]_{aq}/K_H \qquad \text{Eq. [8]}$$

where K_H is Henry's constant ($\log K_H = -1.69 + 1477.7/T$ (in degrees Kelvin)) and $[NH_3]_{aq}$ is the concentration of NH_3 in the litter/soil solution (Cabrera et al., 2008; Sherlock and Goh, 1985). The concentration of NH_3 aqueous is a function of the dissociation constant, K_D, pH and NH_4^+:

$$[NH_3]_{aq} = (K_D\,[NH_4^+]_{aq}/[H^+]) \qquad \text{Eq. [9]}$$

where $\log K_D = -0.09018 - 2729.92/T$ (Kelvin), $[H^+]$ is the concentration of protons in solution (Cabrera et al., 2008; Sherlock and Goh, 1985). Both K_H and K_D are defined by temperature, showing that as temperature increases, both partitioning to the gas phase and the concentration of NH_3 increases. Both of these parameters have been defined in aqueous, pure systems that may fail to take into account concentrations seen in litter and other mechanisms such as NH_4^+ sorption (Liang et al., 2013; Liu et al., 2008; Ni, 1999).

Alternative K_H values have been proposed by many authors (Liang, 2013; Ni, 1999). However, Liu (2009) determined that K_H values measured in litter slurry and values predicted through Henry's Law only varied by 4%. Further, the group concluded that even at very low water contents, Henry's constant would still be applicable to determine the gaseous partitioning in broiler litter. The group cited that even at a water content of 5%, average liquid film thickness in the litter matrix would be thick enough (>5 molecules of water) for Henry's Law to apply.

Additionally, Ni (1999) concluded that the non-dimensional form of Henry's constant as a function of temperature was most applicable to modeling and performed well when concentrations were less than 1000 mg L^{-1}.

Similar to K_H, different values of K_D have been determined for manures, but all still as a function of temperature (Ni, 1999). Hashimoto and Ludington (1971) determined that in concentrated chicken manure, the dissociation constant was about one-sixth of the calculated K_D. Liu et al. (2008) determined that when models fail to incorporate adsorption of NH_4^+ K_Ds calculated will greatly over estimate NH_3 in solution. To calculate NH_3 in litter solution, Liu et al. (2008) used the Freundlich isotherm to describe NH_4^+ partitioning between soil and liquid phase as a function of litter water content. Using the total ammoniacal-N in the litter on a dry weight basis (TAN), the Freundlich partition coefficient (K_f), litter water content (WC) and the density of water (ρH_2O), Liu et al. (2008) calculated NH_3 in solution as a function of both water content and temperature:

$$[NH_3]_{aq} = TAN / \{ K_f * 10^{-pH} / K_D / 1000 + WC * (1 + 10^{-pH} / K_D) / \rho H2O \} \qquad \text{Eq. [10]}$$

Combining the equations above into Eq. [10], the effect of temperature and water content on NH_3 volatilization can be seen. Temperature controls the concentration of NH_3 in solution through its effect on NH_4^+/NH_3 equilibrium. Further, increased temperature leads to increased partitioning from aqueous NH_3 to gaseous NH_3, increasing the concentration of gaseous NH_3 and loss. Water content determines the concentration of NH_4^+ in solution at the litter surface affecting Eq. [8] and [9]. With increased water content, there is decreased ammoniacal-N concentration in solution and vice versa with decreased water content (Cabrera et al., 2010). The water content will then control ammonium concentration, compounded with temperature to determine overall flux.

Effect of Other Environmental Variables on Ammonia Volatilization

Rain and Soil Water Content

Rain has been shown to both reduce and stimulate NH_3 volatilization for surface-applied urea fertilizers and broiler litter. Cabrera and Vervoort (1998) determined that simulated rainfall of 40 mm applied directly after litter application led to a decrease in NH_3 volatilization of 49% compared to rainfall applied prior to litter application. The addition of 40 mm of rain to the soil prior to litter application led to large overall losses, 42% of the applied total N. Small additions of rain, 20 mm, led to increased rates of NH_3 directly after application probably due to increased mineralization in the litter layers. Black et al. (1987) observed an increase in volatilization with 16 mm of simulated rain on surface-applied urea to dry soil. Repeated additions of 2 mm of rain over the 27-day study led to significantly greater loss than the single application of 16 mm. When 16 mm additions were made to soil at field capacity, losses were greatly reduced to 2% of the applied total N.

The effect of rain and soil water content can be confounding for NH_3 volatilization, either increasing overall losses through increased mineralization or decreasing losses through increased diffusion or leaching of NH_4 into the soil matrix. For urea fertilizers, high soil water content has been shown to increase NH_3 loss (Cabrera et al., 2010; Kissel et al, 2009; Vlek and Carter, 1983) through increased urea hydrolysis, but an increase in diffusion with increasing water contents has also been shown to occur (Mundy et al.,1995). Kissel et al. (2004) showed that simulated rain on day 7 after urea application to loblolly pine floor led to an increase in NH_3 loss by increasing soil water content without moving the urea and products deeper into the soil. Holcomb et al. (2011) showed that an irrigation rate of 11.4 mm, 1 to 2 h after urea application to soil with winter wheat at a water content of 0.2 m^3 m^{-3} significantly decreased NH_3 losses. The effect of both rain and soil water content will depend on the quantity of water supplied and the duration of the wetting event. When soil water content is high and combined with a small rain event, diffusion processes will be favored decreasing overall loss. However, either small rain events or high initial soil water content will lead to increased mineralization and increased losses.

Wind

Wind speed is also an important factor of NH_3 loss because it determines the gradient of NH_3 in the litter to NH_3 in the atmosphere. Wind speed/air velocity not only controls the mass transfer coefficient, but also impacts evaporative forces in surface-applied broiler litter (Meisinger and Jokel, 2000; Groot Koerkamp et al., 1999). With cattle slurry, Sommer et al. (1991) observed a linear trend between NH_3 loss and wind speed up to speeds of 2.5 m s^{-1}, with no consistent increase at speeds greater than 2.5 m s^{-1}. However, this trend has not been widely observed across all studies (Bussink et al., 1994). It is likely that wind speeds observed under most field conditions are high enough to not limit transport, and other environmental factors are more dominant in overall loss (Sommer and Hutchings, 2001). Wind also might have an important role in diurnal cycles of wetting and drying that affect losses that may not be easily seen in long-term studies (Meisinger and Jokela, 2000).

Relative Humidity

Few studies have been done to evaluate the effect of relative humidity in the air on NH_3 volatilization from animal manures, even less for poultry litter. However, noticeable N losses have been seen in field applications without reasonable explanations from other environmental factors. An extensive literature search yielded only two studies dealing with relative humidity and NH_3 loss from poultry manure, and they had opposing conclusions.

Nathan and Malzer (1993) compared losses in turkey manure and inorganic N fertilizer under surface-applied and incorporated conditions to determine environmental and soil factors that influenced NH_3 loss. The study was done under field conditions on an Estherville sandy loam and accounted for environmental factors such as wind speed, soil and air temperature, relative humidity, and soil water potential. They found consistent diurnal fluctuations in NH_3 volatilization that in general increased with soil temperature and wind speed but was suppressed by relative humidity. Nathan and Malzer (2003) determined that there was a consistent negative correlation between NH_3 volatilization and relative humidity. During their study, correlations were not significant the day of application or Day 6, but the reasons were not explained.

Nimmermark and Gustafsson (2005) did a similar study on laying hen manure in a floor housing system but achieved different results than the previous study (Nathan and Malzer, 1994). The purpose of their experiment was to determine how different ventilation and climate control strategies (temperature and humidity) influenced odor and NH_3 release in laying hen houses. They measured environmental conditions with sensors and an infrared spectrophotometer for the NH_3 measurements. They found that increased relative humidity led to a significant increase in odor and NH_3 emissions. However, they determined that water vapor pressure had a stronger correlation to NH_3 concentrations than relative humidity. They assumed that the effect of relative humidity may directly affect volatilization or indirectly affect soil microorganism activity through the change in the water content of the litter. Like the Nathan and Malzer (1994) study, they found positive correlation between temperature and NH_3 emissions.

The two studies ultimately vary in their conclusions on the effect of relative humidity on NH_3 volatilization from poultry manures. While it can be assumed that there are some variances in turkey manure versus layer hen manure and even broiler litter, all three have high amounts of uric acid and can be assumed to behave in similar manners. In a study of the effect on relative humidity on urea in forest floors, Cabrera et al. (2010) saw that relative humidity can play a significant role in NH_3 volatilization. Results indicated that relative humidity favored NH_3 volatilization by increasing urea dissolution and by altering the water content of the soil and materials on the forest floor. The critical relative humidity (CRH), the relative humidity at which urea dissolves, proved to be a promising indicator of NH_3 volatilization. This has implications for increased NH_3 volatilization in broiler litter due to its high urea content. Cabrera et al. (2010) also commented on the results found by Nathan and Malzer (1994). The negative correlation can be attributed to high wind speed and air temperature; it can also be attributed to the urea and litter being added to a soil at field capacity. The soil at field capacity most likely led to quick dissolution of the urea with water derived from the soil, not the air. The high wind speed and air temperatures caused faster water evaporation which increased the ammonium (NH_4-N) concentration in the aqueous phase at the soil surface leading to increased volatilization at low relative humidity.

The effect of relative humidity on NH_3 volatilization may be dependent on multiple factors. The initial soil or litter water content may greatly affect hydrolysis, lessening the importance of relative humidity. However, relative humidity may change soil and litter moisture content and, therefore, NH_3 volatilization.

MODELING N TRANSFORMATIONS IN BROILER LITTER

In an effort to better predict N applications from both manures and urea fertilizers, many different models of NH_3 loss have been proposed (Genermont and Cellier, 1997; Misselbrook et al., 2004; Sheppard and Bittman, 2013; Sherlock and Goh, 1985). Models can be divided into two main subcategories: statistical/empirical models and mechanistic/process-based models. Statistical models typically consist of one or two main factors, such as pH or total ammoniacal-N, that either predict plant-available N supplied from manure applications or estimate NH_3 volatilization (Sheppard and Bittman, 2013; Sommers and Hutchings, 2001). While these models are simple in structure and easily implemented, they cannot be extrapolated to different manures or regions nor contribute to understanding the mechanisms of NH_3 loss (Misselbrook et al., 2004; Ni, 1999). Mechanistic models, which rely on environmental inputs such as temperature and water content, should have wider applicability as they can be adjusted based on local climate and initial manure characteristics. Additionally, mechanistic models allow for prediction as a function of time, allowing for time-sensitive recommendations for the addition of N fertilizer as a function of loss (Meisinger and Jokela, 2000; Ni, 1999; Sommers and Hutchings, 2001). While many mechanistic models have been developed for the application of slurries or incorporated manures (Chambers, 1999; Genermont and Cellier, 1997; van de Molen et al., 1999) models are lacking for NH_3 loss from surface-applied broiler litter.

Ammonia volatilization from manure application as a function of time is commonly characterized by Michaelis-Menten curve fitting where:

$$\mathrm{Nt} = \mathrm{Nmax}\left(\frac{\mathrm{t}}{\mathrm{t+Km}}\right) \qquad \text{Eq. [11]}$$

With *Nt* being cumulative loss at time, *t, Nmax* the maximum N loss as *t* approaches infinity, and *Km* is equal to half *Nmax* (Chambers et al., 1999; Misselbrook et al., 2005; Sommer and Ersboll, 1994). Misselbrook et al. (2005) used this equation to predict overall loss from a variety of manures, including poultry litter, as a function of environmental variables and manure characteristics. For poultry litter applied to arable land, the group determined a positive relationship of the *Km* parameter with soil type, temperature, manure dry matter content, manure pH, total ammoniacal-N applied, total ammoniacal and uric acid N applied, and total N applied. The correlation statistic for the determination of *Km* was 0.81. *Nmax* was determined as a function of soil type, wind, rainfall, total ammoniacal-N applied, and total ammoniacal plus uric acid N applied. Overall, the group observed a good fit, R^2=0.92, between the modeled and observed NH_3 emission rates for the experimental data set used to derive the models using these parameters. However, without independent data to validate this model, it is unclear how the model will ultimately perform. The regression equations include variables that are likely strongly correlated, resulting in an inflated correlation coefficient; for example the total ammoniacal-N applied and total ammoniacal plus uric acid N applied. Additionally, the rain coefficient was positive for the *Nmax* determination which conflicts with the effect of rain seen in other studies (Cabrera and Vervoort, 1998). The large number of variables plus potential for colinearity suggests that *Km* and *Nmax* may have been over parameterized in these studies. While loss was adequately described for litter on arable land using these equations, the mechanisms behind volatilization are unclear.

The Volt’Air model was developed by Genermont and Cellier (1997) as a mechanistic model for NH_3 loss for slurry applied to bare soil. This model takes into account both environmental variables as well as easily measured manure and soil characteristics, and consists of six sub-models that model the transfer of NH_3 to the atmosphere, the translocation of N into the soil, the role of soil pH, as wells as other soil parameters. The model was validated successfully in modeling loss as a function of environmental characteristics and agricultural techniques. In an independent study using Volt’Air to model loss from swine slurry application, (Smith et al., 2009) the model successfully estimated overall loss for days 5-19, but severely under predicted loss during the first days after application. Both Genermont and Cellier (1997) and Smith et al. (2009) noted that the model was particularly sensitive to pH. Modeling changes in pH in the manure and in the soil has proven to be difficult (Sommers et al., 2003), leading to under predictions when pH is dramatically changed by mineralization, nitrification, or NH_3 loss.

Similar to Volt'Air, MANNER (Chambers et al., 1999) was designed to model N availability and loss from land-applied manures. Combining both mechanistic and empirical techniques, the model predicts NH_3 volatilization, nitrate leaching, crop uptake, and mineralization from litter characteristics and environmental data. The model adequately predicted the fertilizer N equivalent of poultry litter when the litter was incorporated into the soil surface. When the litter was applied as a top-dress treatment, prediction capability decreased. The authors cited an underestimation of the N volatilization as a cause for under prediction, with increased losses occurring with surface-application of poultry manure.

Many models have been proposed for modeling NH_3 loss from manures surface applied to land. Models like MANNER and Volt'Air have successfully modeled loss from surface applied manures. However, the majority of models are for the use of manure slurries, incorporated manure, or application to bare soil/tilled crops. The surface-application of broiler litter is unique, in that litter is dry and it is surface-applied to existing pasture. With broiler litter applied to the surface of pasture, the interaction of litter and soil are minimized. The effect of soil vegetative cover has shown to lead to 50% higher volatilization in grassland versus bare soil for manure slurry (Thompson et al. 1990). With broiler litter typically being applied "as is" from broiler houses, typically 30% water content, the effect of soil cover may be further magnified. High water content in manure slurry leads to some infiltration, decreasing the effect of pH and losses. Broiler litter will mineralize and volatilize mostly on the grass surface until rainfall or irrigation moves organic N into the soil.

Mechanistic modeling of mineralization and volatilization rates of broiler litter can lead to more precise rate recommendations, plant available N estimations, and decreased environmental degradation from surface-applied litter (Cabrera et al., 2008). Modeling mineralization and volatilization in litter can be simplified into 5 main components: organic N and ammonium present, enzymatic activity, water, temperature, and pH (Cabrera et al., 2008; Nahm, 2005), with minimal losses through denitrification. Many of these factors have yet to be implicitly stated for mineralization in broiler litter, so further research is needed.

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CHAPTER 2

FACTORS AFFECTING AMMONIA LOSS FROM PASTURES FERTILIZED WITH BROILER LITTER[1]

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ABSTRACT

Broiler litter is commonly surface-applied to pasture in the southeastern United States as a method of waste management and to provide an inexpensive source of plant nutrients, such as nitrogen (N). However, predicting plant available N derived from litter can be difficult due to losses through ammonia (NH_3) volatilization. We conducted eleven field studies to determine overall NH_3 loss as affected by environmental variables and litter characteristics. Ammonia loss as a percentage of the applied total N (TN) ranged from 0.9 to 10.5% in eleven 28-d studies conducted from April to November in 2011 and 2012. In two studies, a series of small rain events (2 to 5 mm) combined with elevated soil water content (WC) (greater than 0.2 g H_2O g soil^{-1}) decreased overall NH_3 losses, potentially due to N movement into the soil. In the remaining nine studies, average vapor pressure (VP) and initial ammonium-N (NH_4-N) plus uric acid-N (ANUA) explained 79% of the variability in cumulative NH_3 loss over 28 d. Our data suggest that elevated concentrations of initial uric acid-N and NH_4-N, as well as, elevated VP increase NH_3 losses. The effect of elevated VP on NH_3 losses was attributed to the rewetting of the litter which likely leads to increased N mineralization and NH_4-N in solution. The statistical model developed may help estimate NH_3 losses from surface-applied litter and increase the accuracy of estimating available N under field conditions.

Abbreviations: ANUA, sum of ammoniacal-N and uric acid N; ANUAU, sum of ammonical-N, uric acid, and urea; CRH, critical relative humidity; MN, mineralizable nitrogen; N, nitrogen; NH_3, ammonia; NH_4-N, ammonium-N; NO_3-N, nitrate-N; PI, prediction interval; RH, relative humidity; T, temperature; TN, total nitrogen, VP, vapor pressure; WC, water content.

INTRODUCTION

High demand for inexpensive, lean meat has led to the rapid expansion of broiler (*Gallus gallus domesticus*) production worldwide. In the United States, over 8.5 billion broilers are produced annually, with much of this production heavily concentrated in relatively small regions (USDA, 2013). Approximately 1.5 kg of broiler litter is produced for each bird, leading to broiler litter as a major byproduct of the industry (Moore, 1998). In the state of Georgia alone, approximately 2 million Mg of broiler litter is produced annually with forecasts for increased broiler production in the coming years (USDA, 2010; USDA, 2013). With the large amounts of broiler litter produced, determining optimal methods of management of this byproduct has become increasingly important.

Currently, the most common use of broiler litter is surface application to pastures because it is an inexpensive source of nitrogen (N), phosphorus, potassium, and micronutrients (Marshall et al., 1998). The long term, repeated application of broiler litter to pasture increases organic carbon, total N (TN), total phosphorus, and micronutrients in the upper 15 cm of the soil profile (Kingery et al., 1993). Further, repeated applications add a substantial pool of mineralizable organic N (Gordillo and Cabrera, 1997; Kingery et al., 1994; Mitchell and Tu, 2006). In the short term, broiler litter can add immediate plant available N in the forms of ammonium-N (NH_4-N) and nitrate-N (NO_3-N) as well as a labile pool of mineralizable N (MN) (Kingery et al., 1993, 1994; Mitchell and Tu, 2006). While broiler litter is an effective N fertilizer, the high variability in initial litter N and high potential for N loss through ammonia (NH_3) volatilization make it difficult to obtain accurate N fertilizer value recommendations.

Ammonia volatilization is an important pathway of loss of plant available N from surface-applied broiler litter. Much of the loss occurs within the first few days after application, with decreasing rates of loss over time (Marshall et al., 1998; Meisinger and Jokela, 2000). The actual amount of NH_3 loss can be highly variable. In laboratory studies, Cabrera and Chiang (1994) showed a range of loss of 3.6 to 13.5% of the TN applied in 13 d, and Brinson et al. (1994) determined a range of loss between 17 to 31% of the TN applied in 21 d. Field studies on NH_3 volatilization have shown different ranges of loss, from relatively minor losses of 3-6% of the TN applied (Marshall et al., 1998) to significant losses of 30 and 45% of the TN applied (Lau et al., 2008; Lockyer et al., 1989). Whereas this wide variation increases the difficulty in estimating the nutrient value of litter, this variation is not surprising due to the many variables that affect NH_3 volatilization. Ammonia volatilization is a function of manure characteristics, environmental variables, time, rate and method of application (Martinez-Lagos, 2013; Nathan and Malzer, 1994; Sommer and Hutchings, 2001). Whereas time, rate, and method can all be controlled during application, the initial litter characteristics and environmental variables can vary greatly.

The N present in broiler litter consists of uric acid, urea, inorganic N and other N-containing compounds, but the actual proportions of these components is a function of the feed of the broilers, housing conditions, number of birds, and storage conditions of the litter (Nahm, 2005; Ritz et al., 2004). Organic N excreted in poultry litter is comprised primarily of uric acid, urea, and undigested proteins, with urea and uric acid potentially making up to 80% of the organic N (Rothrock et al., 2010). The amounts of plant available N and NH_4-N subject to NH_3 volatilization are ultimately a function of mineralization of uric acid and urea (Rothrock et al., 2010).

Further compounding the problem of estimating loss, broiler litter application is suggested anytime from early spring to late fall in the southeastern United States (Gaskin et al., 2013). This potentially leads to a wide range of temperature, relative humidity (RH), precipitation, and wind, both seasonally and diurnally, that impact mineralization as well as the physics of volatilization (Sherlock and Goh, 1985; Sommer and Hutchings, 2001).

Many statistical models have been proposed for modeling NH_3 loss from manures surface-applied to land (Huijsmans et al., 2001; Menzi et al., 1998; Misselbrook et al., 2005). Menzi et al. (1998) determined NH_3 loss from liquid cattle manure applied to grassland could be accurately described with an empirical model based on the total ammoniacal-N in the manure and the mean saturation deficit of the air. For poultry manure applied to stubble and growing cereal crops, Misselbrook et al. (2005) accurately modeled NH_3 loss using a Michaelis-Menten approach, initial litter characteristics, and environmental variables. However, these models are for the use of swine and cattle manure slurries, incorporated manure, or manure applied to bare soil or tilled crops. No models currently focus on the application of broiler litter to grass or pasture, which is unique in that litter is in a dry form and surface-applied to existing pasture. With broiler litter applied to the surface of pasture, the interaction of litter and soil are minimized. The effect of soil vegetative cover has shown to lead to 50% greater volatilization in grassland versus bare soil for swine manure slurry (Meisinger and Jokela, 2000; Thompson et al., 1990). With broiler litter being applied "as is" from broiler houses, typically 30% water content (WC), the effect of soil cover may be more pronounced. High WC in manure slurry leads to some infiltration, but broiler litter will mineralize and volatilize mostly on the grass surface until rainfall or irrigation moves N into the surface soil.

With volatilization from broiler litter being a function of both N mineralization and transfer of NH_3 to the atmosphere, litter characteristics and environmental conditions are likely to dominate overall loss. Whereas several studies on NH_3 volatilization from surface-applied broiler litter have been conducted, information looking at a wide range of both environmental variables and litter characteristics under field conditions is lacking. The objectives of this study were to 1) measure NH_3 volatilization under different environmental conditions and 2) develop a statistical model to estimate NH_3 volatilization from surface-applied broiler litter.

MATERIALS AND METHODS

Litter Characteristics

Broiler litter was obtained from a nearby broiler house in a large batch at the beginning of both the 2011 and 2012 studies, leading to different litters for each year. Between studies, the litter was piled and covered using a large tarp to minimize N transformations and NH_3 losses. For each study, litter was removed from the pile into the manure spreader. Extra litter was not returned to the pile after application. At the start of each study, the litter was sampled directly from the spreader (approximately 10 kg) and analyzed for NO_3-N, NH_4-N (Mulvaney, 1996), uric acid (Mowrer et al., 2013), urea, total N and carbon (Nelson and Sommers, 1982), pH (1:5 litter/water), gravimetric WC, and MN. Urea was determined by extracting 1 g litter with 100 mL deionized water containing 1000 mg L^{-1} Ag_2SO_4 for 5 min, filtering through a 0.45-µm filter, and measuring urea colorimetrically (DeManche et al.,1973). Gravimetric WC was determined by drying the litter at 65°C for 48 h, and MN was measured using a modified incubation method from the works of both Gordillo and Cabrera (1997) and Qafoku et al. (2001) for 28 d. Briefly, 1 g of litter was mixed with 200 g soil at 0.16 g H_2O g^{-1} in 500-mL glass jars. Jars were placed in an incubator at 30°C and aerated every 48 h. After 28 d, the control soil and soil-litter mixtures were extracted with 1 mol L^{-1} KCl at 1:5 ratio (Mulvaney, 1996), followed by colorimetric determination for inorganic N (Crooke and Simpson, 1971).

NH_3 Volatilization Studies

These studies were conducted on a tall fescue (*Festuca arundinacea* Schreb) and bermudagrass (*Cynodon dactylon* (L) Pers.) pasture at the Central Research and Education Center of the University of Georgia, which is located near Eatonton, GA (33°24’, 83°29’W). Average annual rainfall for the area is 119.2 cm and average temperature is 18.7°C (AEMN, 2013). The soil at the site was classified as a Pacolet sandy loam (fine, Kaolinitic, thermic Typic Kanhapludults; Perkins et al., 1987), had an average pH (0-5 cm) of 5.65 (1:1 soil/ 0.01 mol L^{-1} $CaCl_2$), a cation exchange capacity of 6.4 $cmol_c$ kg^{-1} and contained 669 g sand kg^{-1}, 143 g clay kg^{-1}, and 188 g silt kg^{-1} (Vaio et al., 2008).

From April to November of both 2011 and 2012, a total of eleven 28-d studies were conducted. For each study, a three-point hitch drop applicator was used to apply 3230 kg litter ha^{-1} (133 kg TN ha^{-1} average) to the surface of four circular plots, each 20 m in diameter. Grass height was maintained between 5 and 7 cm with mowing occurring before each application. The plots were separated by at least 100 m to avoid cross contamination, and a check plot was located upwind to measure background levels of atmospheric NH_3. Repeated applications were made to the same plots for individual studies. Ammonia volatilization was measured using the integrated horizontal flux method with a center-placed, rotating mast holding duplicate passive flux samplers at heights of 0.30, 0.75, 1.50, 2.25, and 3 m (Cabrera et al., 2011). The mast, on ball bearings, rotated with the predominant wind so that passive flux samplers were always facing the wind. Flux samplers were made from glass tubes (10 cm long, 1 cm o.d., 0.7-cm id) coated with 3% oxalic acid and acetone solution. Each sampler consisted of two coated tubes joined together by silicon tubing with a nozzle connected with silicone tubing to the front tube facing the wind. The nozzle consisted of a 1-cm glass tube glued to a steel cap with a 1-mm hole to regulate air flow through the tubes and optimize NH_3 capture. For each study, new samplers were placed immediately after litter application, changed at 14 d, and removed at 28 d. After collection, tubes were tightly capped with plastic caps and taken to the laboratory, where they were extracted for 3 min with 3 mL deionized water, and the extract was analyzed colorimetrically for NH_4-N (Crooke and Simpson, 1971).

Horizontal NH_3 flux (F_{hz}, µg N m^{-2} s^{-1}) was calculated for each replicated sampler using the concentrations of NH_4-N from the two tubes connected in series, C_1 and C_2, (µg N mL^{-1}), the volume of the extractant (V, 3 mL deionized water), the radius of the hole in the steel cap (*r, 0.0005 m*), a correction factor K (0.77), and the time (t, in seconds) during which the tube was exposed:

$$F_{hz} = \frac{(C_1+C_2)V}{2\pi \mathrm{r}^2 \mathrm{Kt}} \qquad \text{Eq.[1]}$$

The two replicates were averaged over each height to determine the horizontal flux. From the horizontal flux (F_{hz}), the vertical flux (F_v, µg N m^{-2} s^{-1}) and total flux were calculated. Vertical flux was calculated by taking the difference in F_{hz} between the treatments (T) and background (b) at each height (h), integrating it over the height increment corresponding to each sampler (Δh) , and dividing the result by the radius of the plot circle, R, as shown below:

$$F_v = \frac{1}{R} \sum_{h=1}^{h=5} \left[\left(F_{hz,T} - F_{hz,b} \right) \Delta h \right] \qquad \text{Eq.[2]}$$

The total flux (g N m^{-2}) from the plots was then calculated by multiplying F_v by the exposure period of the samplers and converting from micrograms N to grams N (Cabrera et al., 2011; Vaio et al., 2008).

During each study, soil samples (0-5 cm) were taken on days 0 (immediately after application), 14, and 28. A total of 15 soil samples were collected from each plot using a soil probe sampler (2 cm o.d.). Soil gravimetric WC was determined on 5 samples by drying at

105°C for 48 h. The remaining soil samples were air-dried, ground, sieved (2 mm), and analyzed for pH (1:1 soil/ 0.01 mol L^{-1} $CaCl_2$; Miller and Kissel, 2010) and inorganic N using 1 mol L^{-1} KCl extraction (Mulvaney, 1996), followed by colorimetric determination (Crooke and Simpson, 1971).

Environmental Measurements

To measure the effect of environmental factors on NH_3 volatilization, a large number of environmental variables were measured at 5-min intervals. During the 2011 studies, a weather station located in the center of the pasture had a Decagon Em50 data logger (Decagon Devices Inc., Pullman, WA) connected to three leaf wetness sensors and a 5TM Water and Temperature Sensor placed at a depth of 5 cm. The station also had CR10X and CR200 data loggers (Campbell Scientific Inc., Logan, UT) connected to air temperature and RH sensors (HMP45C probe, Vaisala, Vantaa, Finland) at 0.4 and 2 m of height, rain gauge (TE525MM, Texas Electronics, Dallas, TX), wind speed and wind direction at 2 m (034B Met One Windset, Met One Instruments, Grants Pass, OR), two soil temperature probes (107-L, Campbell Scientific, Inc.) at 5 cm depth, two soil WC reflectometers (CS625, Campbell Scientific Inc.) at 0-5 cm, two infrared radiometers for surface temperature (SI-111, Apogee Instruments, Logan, UT), and 3 constructed, dew microlysimeters similar to that described by Heusinkveld et al. (2006). In 2012, additional equipment was deployed next to each treatment plot. The equipment consisted of a Em50 Data Logger (Decagon Devices, Inc., Pullman, WA) connected to two dielectric leaf wetness sensors, a 5TM Water and Temperature Sensor (at 5 cm depth), a VP-3 RH and temperature sensor located 0.3 m from the soil surface, and a rain gauge (ECRN-100), all sensors were from Decagon Devices, Inc. In addition, each plot had a CR1000 data logger (Campbell Scientific, Inc.) connected to a constructed dew microlysimeter. These additional stations were used in conjunction with the previously established weather station. Volumetric soil WC measurements taken by the 5TM Water and Temperature Sensors (m^3 m^{-3}) were transformed to gravimetric soil WC (g g^{-1}) by regressing field measurements taken throughout the study to obtain continuous gravimetric WC data. The regression obtained was of the form:

$$\text{Soil Gravimetric WC } (\text{g g}^{-1}) = 0.82 * \text{ Volumetric WC } (\text{m}^3\ \text{m}^{-3}) + 0.013;\ R^2=0.70 \quad \text{Eq. [3]}$$

Due to the importance of hydrolysis of urea in litter to overall NH_3 volatilization (Rothrock et al., 2010; Sherlock and Goh, 1985), the critical relative humidity (CRH) of urea fertilizer was calculated using the equation:

$$\text{CRH (fraction)} = (84.669 - 0.1454 * \text{T} - 0.0055 * \text{T}^2)/100 \qquad \text{Eq. [4]}$$

where *T* is temperature (°C) at the 0.4 m-height and *CRH* is the relative humidity at which urea starts absorbing water from the air and dissolving (Vaio et al., 2008). The proportion of time that RH>CRH was calculated by adding up the 5-min increments where RH>CRH and then dividing that by the total time of the study (Cabrera et al., 2010).

Data Processing and Statistical Analysis

Contamination of flux samplers with wild bird excreta required removal of some of the data. For that purpose, we calculated a 95% prediction interval (PI) for expected variation in N concentration for the tubes based on blank sampling tubes. These PI values ranged from 0 to 0.25 mg N L^{-1} and from 0 to 0.36 mg N L^{-1} for 2011 and 2012, respectively. Variation in replicates that was greater than the PI range was assumed to be from contamination; therefore, the data were replaced with the uncontaminated replication (the smaller value). This was done for each individual tube concentration. Overall, any error using this correction method would lead to an underestimation of total loss.

Weather factors, litter characteristics, and NH_3 loss data were analyzed with SAS version 9.3 using PROC REG (SAS Institute, 2013) to determine the effect of variables on overall loss and to determine relationships among variables. Environmental variables that were highly correlated were regressed individually to avoid multicolinearity. Environmental data were averaged for 1 d, 2 d, 7 d, 14 d, and 28 d in all the studies and regressed against the first 14 d loss, 14-28 d loss, or cumulative 28-d loss. Effects were considered significant at $p<0.05$.

RESULTS AND DISCUSSION

Litter Characteristics

The 2011 and 2012 litters had similar TN and total carbon values, but the distribution of N between organic and inorganic fractions varied between litters (Table 2.1). On average, 12.4% of TN was in the form of NH_4-N in 2011 and 21.8% of TN was present as NH_4-N in 2012. Interestingly, in 2011 the litter contained greater concentrations of uric acid and lower concentrations of urea than in 2012. This may be due to the greater WC of the 2012 litter (0.53 to 0.44 g g^{-1} in 2012 versus 0.20 to 0.28 g g^{-1} in 2011) which may have favored uric acid degradation and overall mineralization (Agehara and Warncke, 2005; Sims, 1986). This potential difference in N mineralization is supported by the measured MN (expressed as percentage of organic N), which was 49.6% for 2011 and 23.3% for 2012. The MN was representative of the maximum mineralization under optimum water and temperature conditions with minimal N loss for a 28-d time period. The 2011 litter also contained greater concentrations of NO_3-N and lower pH indicating that increased nitrification occurred before the litter was collected. The pH of both the 2011 and 2012 litters decreased during the 8-month storage, with a decrease of 0.9 units in 2011 and 0.44 units in 2012. Litter pH and concentrations of uric acid,

NO_3-N, and NH_4-N were within typical ranges reported for broiler litter (Bitzer and Sims, 1988; Gordillo and Cabrera, 1997; Mowrer et al., 2013). However, urea concentrations were lower than those reported by Rothrock et al. (2010). This may have been due to differences in extraction technique. Our unpublished results have shown that urea production and degradation are much more rapid than previously thought, especially when the litter is in solution during extraction. The extraction method we used had a high concentration of microbial/enzymatic inhibitor and a short extraction time (5 min) to decrease uric acid degradation during extraction, while the method of Rothrock et al. (2010) used a 60-min extraction. A longer extraction may have resulted in degradation of uric acid with the production of urea.

Inorganic N in Soil

The application of litter led to an increase in the amount of NH_4-N in the top 5 cm of soil for some of the studies with increased NO_3-N concentrations occurring at the end of the season for both 2011 and 2012 (Fig. 2.1). Due to low NH_4-N concentrations at the end of each study, it is unlikely that repeated applications led to increased NH_3 loss for the following studies. Nitrate accumulation was especially apparent in the 2012 studies where high initial NH_4-N levels in the litter (Table 2.1) most likely rapidly nitrified and remained in the top 5 cm. Ammonium concentrations in the soil were similar to concentrations found by Sistani et al. (2004) for broiler litter applied to bermudagrass, but NO_3-N concentrations in our data were lower than reported by Sistani et al. (2004), likely due to lower application rates in our study. High standard deviations in the data can be explained by variations in litter homogeneity in the field plots. As a result of litter applications, the soil pH increased 0.24 units in 2011 and 0.68 units in 2012 when compared to the background plot. Similarly, Kingery et al. (1994) found that repeated application of broiler litter over 6 years led to an overall increase of 0.5 pH units compared to background plots, and to an overall increase of NO_3-N in the soil profile.

Environmental Conditions

Total rainfall during the study period (April through November) was 246 mm for 2011 and 286 mm for 2012 (Fig. 2.2), amounts that were well below historical average (655 mm) (AEMN, 2013). While rain has been shown to be an important variable on NH_3 volatilization (Cabrera and Vervoort, 1998; Sharpe et al., 2004; Sommer and Hutchings, 2001), the effect of drought allowed us to focus on other environmental variables for the majority of the 11 studies. Average temperatures for the studies ranged from 13.6 to 27.0°C and average wind speed was 1.7 m s^{-1}. Initial gravimetric soil WC varied from 0.08 to 0.23 g g^{-1} (Table 2.2).

Dew microlysimeters used starting in August of 2011 and during all of 2012 recorded an average of 0.2 mm of dew daily. Relative humidity (as a fraction) had a minimum value of 0.25 and a maximum value of 0.99, and the magnitude of diurnal range varied seasonally. Values of CRH ranged between 0.74 and 0.85 as a function of temperature. The proportion of time during which RH>CRH ranged from 42 to 67% throughout the eleven studies, with an average of 52% (Table 2.2).

Ammonia Volatilization

Ammonia volatilization losses ranged from 0.9 to 10.5% of the applied TN in 2011 and 2012 (Fig. 2.2; Table 2.2). Losses fell within the ranges previously reported by Marshall et al. (1998; 1.7 to 6.4% of TN), Sharpe et al. (2004; 3.3 to 24% of TN), and Nathan and Malzer (1994; 7% of TN). When expressed as a percentage of ammoniacal-N applied, the magnitude of NH_3 loss ranged from 5.3 to 78.4%. Studies 3 and 4 in 2011 (3/11 and 4/11; study number/year) showed a steep NH_3 loss slope at 28 d, which suggests that a longer study period may have shown greater losses. The average horizontal flux concentrations for the first 14-d measuring period following the application of litter of all studies for both 2011 and 2012 decreased with increasing height (Fig. 2.3). The pattern of horizontal flux concentrations was similar to Sommer et al. (1996) when measuring NH_3 loss from cattle slurry using passive mast flux samplers. Sommer et al. (1996) observed horizontal NH_3 net flux declined exponentially with mast height. Low NH_3 concentrations measured at the maximum height of the mast indicates the majority of NH_3 lost was measured. Additionally, low NH_3 bypass in the rear tubes, indicated the 14-d measurement period was sufficient for adequate trapping of NH_3 in each study (Cabrera et al., 2011).

The range of NH_3 volatilization across the eleven studies was reflected in the range of litter characteristics and environmental variables observed. Peak ranges of loss occurred during the warmest months of the studies in both years (days 170-252; Fig. 2.2). The lowest loss occurred during Study 2/12 and a lower-than-expected loss occurred in Study 5/12. These two studies were identified as outliers for the purpose of regression. While no study received the amount of rainfall thought to suppress NH_3 volatilization (40 mm; Cabrera and Vervoort, 1998), the combination of repeated small rainfall events (Fig. 2.2) and elevated initial soil WC (Table 2.2) for these two studies is most likely the cause of the observed low losses. The use of air-dried soil by Cabrera and Vervoort (1998) may have led to litter drying, and consequently increased the amount of simulated rain needed to decrease NH_3 loss. Sharpe et al. (2004) suggested a lower threshold of 17 mm rain to decrease losses; out of eleven studies, only Study 3/11 had a rainfall event of this magnitude, but NH_3 loss for this study remained high.

The effect of rain and soil WC can be confounding for NH_3 volatilization, either by increasing overall losses through increased N mineralization, or decreasing losses through increased diffusion or leaching of NH_4-N into the soil matrix. For urea fertilizers, high soil WC has been shown to increase NH_3 loss through increased urea hydrolysis (Cabrera et al., 2010; Kissel et al, 2009; Vlek and Carter, 1983). Conversely, an increase in N diffusion from urea fertilizers with increasing WC, reducing overall loss, has also been shown to occur (Mundy et al., 1995). Kissel et al. (2004) showed that simulated rain on d 7 after urea application to loblolly pine floor led to an increase in NH_3 loss by increasing soil WC without moving the urea and products deeper into the soil. Holcomb et al. (2011) showed that an irrigation rate of 11.4 mm, 1 to 2 h after urea application to soil at a volumetric WC of 0.2 m^3 m^{-3}, significantly decreased NH_3 losses.

In contrasting studies 5/12 and 6/12, the combined effect of soil WC and small rain events can be seen (Fig. 2.4). Both studies had an initial soil WC greater than 0.2 g g^{-1}, and while Study 5/12 maintained higher temperatures and RH, which typically increase volatilization, NH_3 losses were lower than in Study 6/12. The high initial soil WC in Study 6/12 most likely increased N mineralization which led to increased NH_3 losses at the beginning of the study. The subsequent decrease in soil WC combined with the lack of rain, maintained a steeper slope of NH_3 loss in the first 14 d. Further, the decrease in soil WC to less than 0.1 g g^{-1} by d 28 led to some losses during the second half of the study, where no loss was seen after d 14 in Study 5/12. While neither soil WC nor rain alone were sufficient to increase leaching or diffusion, the combination of the two may have led to the movement of NH_4-N deeper into the soil profile, favoring nitrification and decreasing overall losses. For the eleven studies conducted, the threshold of 0.20 g g^{-1} soil WC combined with any amount of rain decreased NH_3 losses, which was attributed to increased movement of NH_4-N into the soil and decrease NH_3 losses.

Modeling Ammonia Loss

While rain, soil WC, and temperature all showed promising trends for predicting NH_3 volatilization, none of these environmental factors proved to be statistically significant. Temperature controls mineralization rates, equilibrium concentrations of NH_4-N and NH_3, and the flux from NH_3 in the litter to NH_3 in the atmosphere (Sims, 1986; Cabrera et al., 2008; Sherlock and Goh, 1985). Under our field conditions, temperature range may have been large enough to see this effect (Table 2.2), but we found no relationship with NH_3 for either 14-d or 28-d loss. Martinez-Lagos et al. (2013) also saw no correlation with temperature when looking at NH_3 loss from dairy slurry applied to permanent grasslands.

Wind speed is also an important factor of NH_3 loss because it determines the gradient of NH_3 in the litter to NH_3 in the atmosphere. However, the high wind speeds measured during our studies likely did not limit transport (Sommer and Hutchings, 2001).

Because many of the environmental variables were correlated with one another (r=0.77 or greater), not all variables were included simultaneously during regression. When variables were highly correlated, such as temperature and vapor pressure (VP), the variable that could explain the most about environmental conditions was included. For example, VP not only describes the amount of water in the air, it is also indicative of temperature.

No individual litter characteristic alone could explain the variability in NH_3 loss seen for the eleven studies. Misselbrook et al. (2005) determined that loss from poultry manure to arable land could be explained by total ammoniacal-N and total ammoniacal-N plus uric acid-N when loss was modeled using a Michaelis-Menten type curve. With uric acid and urea concentrations being important to mineralization and overall loss (Misselbrook et al., 2005; Ritz et al., 2004; Rothrock, 2010), the sum of NH_4-N and uric acid-N (ANUA) and the sum of NH_4-N, uric acid-

N, and urea-N (ANUAU) were included in the regression analysis for 14-d and 28-d NH_3 losses. Regression of the NH_3 losses in nine studies (removing Studies 2/12 and 5/12) indicated significant relationships between initial NH_4-N, ANUA, and ANUAU with both cumulative 14-d and 28-d loss. Stepwise regression using both significant litter characteristics and weather variables showed that 14-d volatilization was best explained by 14-d average VP (kPa) taken at a 2-m height and initial litter NH_4-N concentrations (mg N kg^{-1}) as shown below and in Fig. 2.5.

NH_3 Loss in 14 d (% of applied TN) = -7.55 + 3.13*VP + 0.0011*NH_4-N; $R^2=0.73$ Eq. [5]

The interaction of VP and NH_4-N was not significant ($p=0.22$). The majority of loss from surface-applied broiler litter occurs within the first few days after application (Marshall et al., 1998; Meisinger and Jokela. 2000). While NH_3 loss during the first few days was not measured in this study, a regression equation with the average VP during the first 7 days, as well as initial NH_4-N, was significant and explained 68% of the variability. However, losses were best explained (73%) when VP was averaged over the whole period of measurement (14 d). While no strong relationship was determined for NH_3 loss from 14 to 28 d, regression of initial uric acid-N ($p=0.05$) and VP ($p=0.11$) explained 68% of the variability in NH_3 loss. In agreement with regression results from each time period (i.e., 0-14 d and 14-28 d), cumulative loss over 28 d was modeled as a function of ANUA (mg N kg^{-1}) and 28-d average VP, as:

NH_3 Loss in 28 d (% of applied TN) = -12.02 + 2.92*VP + 0.0015*ANUA; $R^2=0.79$ Eq. [6]

The intercept and all regression coefficients were statistically significant ($p<0.05$), but the interaction of ANUA and VP was not significant ($p=0.20$) for the full model. This statistical model takes into account the effect of initial litter characteristics as well as the effect of increased N mineralization and increased solubility of NH_4-N and mineralization products through rehumidification of the litter by higher VP. Differences in the models representing loss in the first 14 d and cumulative loss over 28 d also indicate the complexity of NH_3 loss under field conditions. The 14-d model likely represents high losses as a function of the initial NH_4-N, where high VP leads to increased NH_4-N in solution and some N mineralization. Mineralization of organic N in this period may not reflect large increase in NH_3, but instead an increase in litter pH that favors NH_3 volatilization (Rothrock et al., 2010). The inclusion of the uric acid-N pool in the 28-d model likely indicates that wetting of litter, through high VP, will lead to increased N mineralization over time which is reflected in overall N loss.

Comparing Studies 2/11 and 4/12, the negative effect of VP on NH_3 loss can be seen (Fig. 2.6). Study 2/11 had a loss of 4.1%, whereas Study 4/12 had a loss of 10.5% even though temperature and wind were similar. In general, VP and RH are synonymous variables, both describing the atmospheric water conditions. Vapor pressure may better describe long-term weather conditions because large fluctuations in RH tend to lead to similar average values over long intervals (Table 2.2). For Study 4/12, RH fluctuations never decreased below 0.4 (fraction) during the 28-d study. Losses were high during the first 14 days, and soil WC remained elevated (14-d average 0.15 g g^{-1}) due to small rain events and increased VP. Vapor pressure for the study was also elevated for the first 14 d when loss was most dramatic and averaged 2.59 kPa over the entire study. For Study 2/11, soil WC averaged 0.10 g g^{-1} for the first 14 d, and RH repeatedly decreased below 0.4; the overall VP average was 2.23 kPa. The negative effect of low VP on NH_3 loss can be observed in Study 2/11 in which increases in soil WC due to rain were followed by rapid decreases due to low VP, likely reducing litter WC as well. As a result, NH_3 losses were low. Though differences in the VP were small between the two studies, increased atmospheric water content was also indicated in the range of RH fluctuations and the proportion RH>CRH. The proportion RH>CRH was 44.6% for Study 2/11 and 66.6% for Study

4/12. VP and other atmospheric water indicators are hypothesized to increase litter WC, increase mineralization and NH_4^+ dissolution, and increase overall NH_3 loss.

Previous studies found similar relationships between atmospheric water and NH_3 volatilization from urea fertilizers. Cabrera et al. (2010) found that NH_3 loss from urea applied to a loblolly pine floor was related to the proportion RH>CRH and to the forest floor WC. Vaio et al. (2008) also saw an increase in NH_3 loss from urea applied to a pasture when there were extensive periods of RH>CRH, elevated temperatures, and low soil WC. In that study, high RH led to increased urea in solution with increased hydrolysis and NH_3 losses. Rothrock et al. (2010) determined urea mineralization was the rate-limiting factor to NH_3 volatilization from poultry litter. Unlike urea fertilizers which are reliant on soil biota and enzymes for hydrolysis, broiler litter is primed with bacteria and uricase/urease enzymes so the effect of water on mineralization has the potential to be much more rapid than in soil. For poultry manure, Nimmermark and Gustafsson (2005) found that increased RH led to a significant increase in odor and NH_3 emissions; further, the group determined that VP had a stronger correlation to NH_3 concentrations than RH. They too assumed that the effect of RH and VP may directly affect volatilization or indirectly affect soil microorganism activity through the change in the WC of the litter.

It must be noted that some studies found a negative relationship between atmospheric water and NH_3 losses. Marshall et al. (1998) cites high RH and heavy dews for low NH_3 losses seen under field conditions, and Nathan and Malzer (1994) found a negative correlation between the rate of NH_3 loss and RH. Both of these studies were conducted on soils with high soil WC, which for Marshall et al. (1998) may have led to ammoniacal-N diffusing into the soil as suggested in some of our studies. Cabrera et al. (2010) also commented on the results from

Nathan and Malzer (1994). They attributed the negative correlation found between NH_3 loss and RH to high wind speed and air temperature, which would have caused faster water evaporation thereby moving ammoniacal-N to the soil surface and increasing NH_3 loss at low RH.

CONCLUSIONS

Ammonia volatilization from surface-applied broiler litter is a complex function of both litter characteristics and environmental variables. Due to this complexity, finding variables that can statistically model NH_3 volatilization may greatly aid in fertilizer equivalency recommendations for surface-applied litter. Ammonia volatilization losses in eleven field studies ranged from 0.9 to 10.5% of the applied TN from April to November of both 2011 and 2012. In two studies, small rain events in combination with high initial soil WC decreased NH_3 losses, probably due to increased movement of ammoniacal-N into the soil. In the remaining nine studies, initial NH_4-N plus uric acid-N concentrations in broiler litter and average VP were correlated with overall loss, explaining 79% of variability. Although the particular mechanism of the relationship of VP was not identified in this study, it was hypothesized that high VP leads to litter rewetting, increased NH_4-N dissolution, increased mineralization, and increased NH_3 volatilization. Overall, this model could lead to better estimations of NH_3 loss for surface-applied broiler litter to pastures in the southeastern United States.

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TABLES AND FIGURES

Table 2.1. Litter characteristics determined at the time of application for each study.

Study	NH_4-N	NO_3-N	Uric Acid	Urea	Initial WC	Carbon	Total N	pH
Study No./Year	----------------------------mg kg^{-1} dry litter----------------------------				g g^{-1} dwb	g kg^{-1} dwb	g kg^{-1} dwb	
1/11	4127 ± 303	1587 ± 45	7053 ± 1187	256 ± 3	0.28	300	40.0 ± 1.4	7.86
2/11	4333 ± 237	1066 ± 104	8081 ± 1781	255 ± 16	0.26	300	39.5 ± 2.1	7.86
3/11	4228 ± 100	981 ± 102	11274 ± 2963	330 ± 16	0.20	320	41.6 ± 0.2	7.48
4/11	5223 ± 596	689 ± 191	10960 ±1057	156 ± 9	0.23	320	41.8 ± 0.1	7.43
5/11	4853 ± 642	850 ± 215	8328 ± 1685	361 ± 28	0.24	370	43.5 ± 3.8	6.96
1/12	6724 ± 21	777 ± 6	4095 ± 967	349 ± 15	0.55	330	39.5 ± 0.4	8.78
2/12	7216 ± 53	736 ± 24	4250 ± 314	542 ± 12	0.46	310	40.0 ± 0.4	8.43
3/12	7430 ± 189	325 ± 4	5143 ± 295	528 ± 14.	0.50	320	40.6 ± 0.4	8.48
4/12	7216 ± 102	419 ± 9	3763 ± 850	817 ± 110	0.45	300	40.9 ± 0.4	8.13
5/12	7228 ± 102	893 ± 168	4803 ± 215	1151 ± 106	0.43	320	42.1 ± 0.4	8.10
6/12	8009 ± 160	299 ± 5	4749 ± 1289	1021 ± 32	0.43	310	43.0 ± 0.4	8.34

Table 2.2. Total NH_3-N loss % of applied TN) over 28 d for eleven studies in which pasture plots received surface-applied broiler litter at a rate of 133 kg TN ha^{-1}, average air temperature, wind, RH, RH>CRH and VP at 2m; cumulative rain and initial soil water content for each study.

Study	Date	N applied	Loss	Avg. Soil Temp	Avg. Wind	Avg. Air Temp	Avg. RH	Avg. VP	Cumulative Rain	Initial Soil WC	RH> CRH
Study No./Year		kg N ha^{-1}	% applied TN	°C	m s^{-1}	°C	frac	kPa	mm	g g^{-1}	%
1/11	4/25/2011	129	2.5 ± 0.7	25.9	2.5	20.1	0.71	1.63	19.9	0.17	42.0
2/11	6/1/2011	128	4.1 ± 0.9	32.5	1.8	26.2	0.70	2.23	33.5	0.09	44.6
3/11	7/5/2011	134	7.2 ± 1.3	33.8	1.6	26.7	0.79	2.69	119.2	0.19	58.0
4/11	8/12/2011	135	9.8 ± 0.2	33.6	1.8	25.2	0.70	2.15	27.3	0.11	46.7
5/11	10/7/2011	141	3.8 ± 1.4	25.1	1.7	13.6	0.76	1.18	46.0	0.10	60.2
1/12	4/6/2012	127	5.3 ± 2.8	26.6	2.0	18.6	0.71	1.38	12.4	0.10	42.7
2/12	5/10/2012	129	0.9 ± 1.5	30.4	1.6	21.8	0.73	1.82	41.4	0.22	51.1
3/12	6/19/2012	131	9.1 ± 2	34.4	1.6	26.4	0.71	2.29	72.3	0.10	46.6
4/12	7/25/2012	132	10.5 ± 0	34.7	1.5	25.3	0.82	2.59	89.7	0.11	66.6
5/12	8/24/2012	136	2.9 ± 1.9	33.7	1.4	24.2	0.86	2.56	66.4	0.21	64.0
6/12	10/4/2012	139	4.7 ± 1	27.8	1.8	15.5	0.76	1.33	4.0	0.23	53.2

Figure 2.1. Soil inorganic N (NO_3-N and NH_4-N) dynamics following surface application of broiler litter at 133 kg TN ha^{-1} in 2011 and 2012. (X indicates the time of each application of broiler litter). Bars represent standard deviation.

Figure 2.2. Ammonia volatilization (% of TN) from surface application of broiler litter at 133 kg TN ha^{-1} in eleven studies conducted in 2011 and 2012, temperature at 5-min intervals taken at 2 m height, and rainfall (mm). Bars represent standard deviation.

Figure 2.3. Average horizontal flux of NH_3-N (µg N m^{-2} s^{-1}) at different flux sampler heights for the first 14 days of eleven 28-d studies in which pasture plots received surface-applied broiler litter at 133 kg TN ha^{-1} (Background flux subtracted; Bars represent standard deviation).

Figure 2.4. Cumulative NH_3-N loss from pasture that received surface-applied broiler litter at 133 kg TN ha^{-1} in two 28-d studies (Studies 5 and 6 of 2012; 5/12 and 6/12), with RH and critical RH (at 5-min intervals taken at 2 m), soil water content (g g^{-1}), and VP (kPa at 5-min intervals taken at 2 m) as a function of day of the year. Bars represent standard deviation.

Figure 2.5. The effect of initial NH_4-N of the litter and average 14-d VP taken at 2 m on cumulative 14-d NH_3 volatilized (% of TN applied) from surface-applied broiler litter to pasture plots at 133 kg N ha^{-1} in nine studies conducted in 2011 and 2012.

Figure 2.6. Cumulative NH_3-N loss from pasture that received surface-applied broiler litter at 133 kg TN ha^{-1} in two 28-d studies (Study 2 of 2011 and Study 4 of 2012; 2/11 and 4/12), with RH and critical RH (at 5-min intervals taken at 2 m), soil water content (g g^{-1}), and VP (kPa at 5-min intervals taken at 2 m) as a function of day of the year. Bars represent standard deviation.

Figure 2.1.

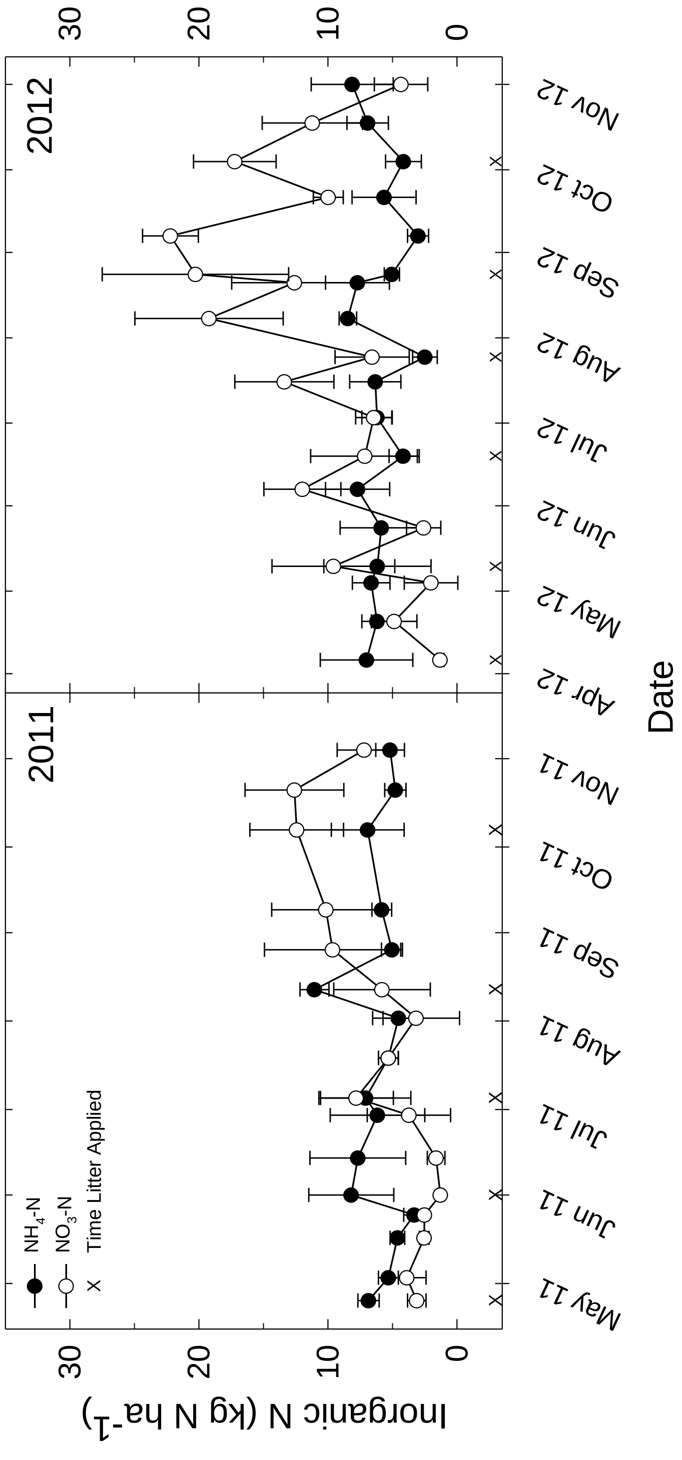

2011
2012
NH$_4$-N
NO$_3$-N
X Time Litter Applied
Inorganic N (kg N ha^{-1})
0
10
20
30
May 11
Jun 11
Jul 11
Aug 11
Sep 11
Oct 11
Nov 11
Apr 12
May 12
Jun 12
Jul 12
Aug 12
Sep 12
Oct 12
Nov 12
Date

Figure 2.2.

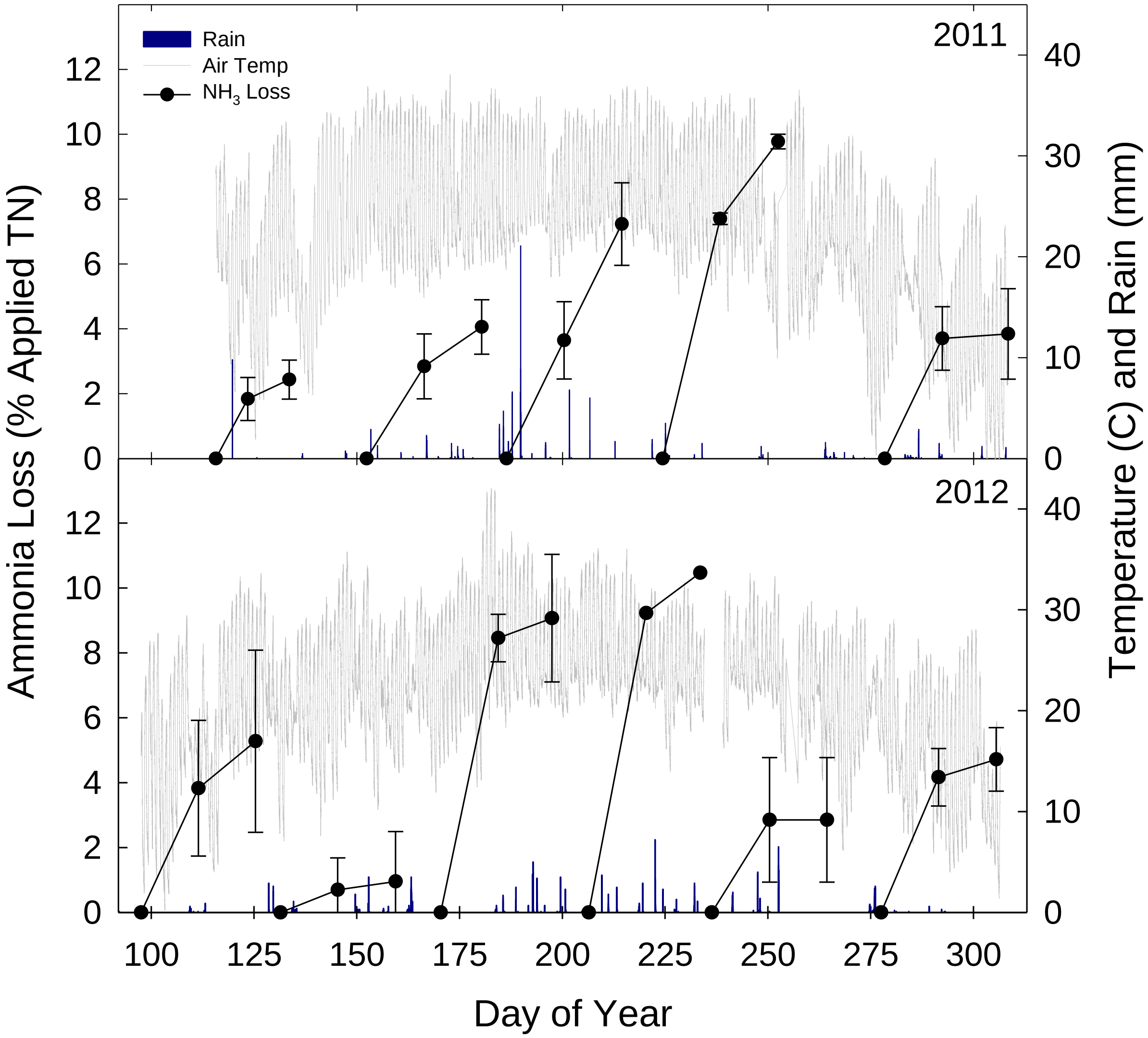
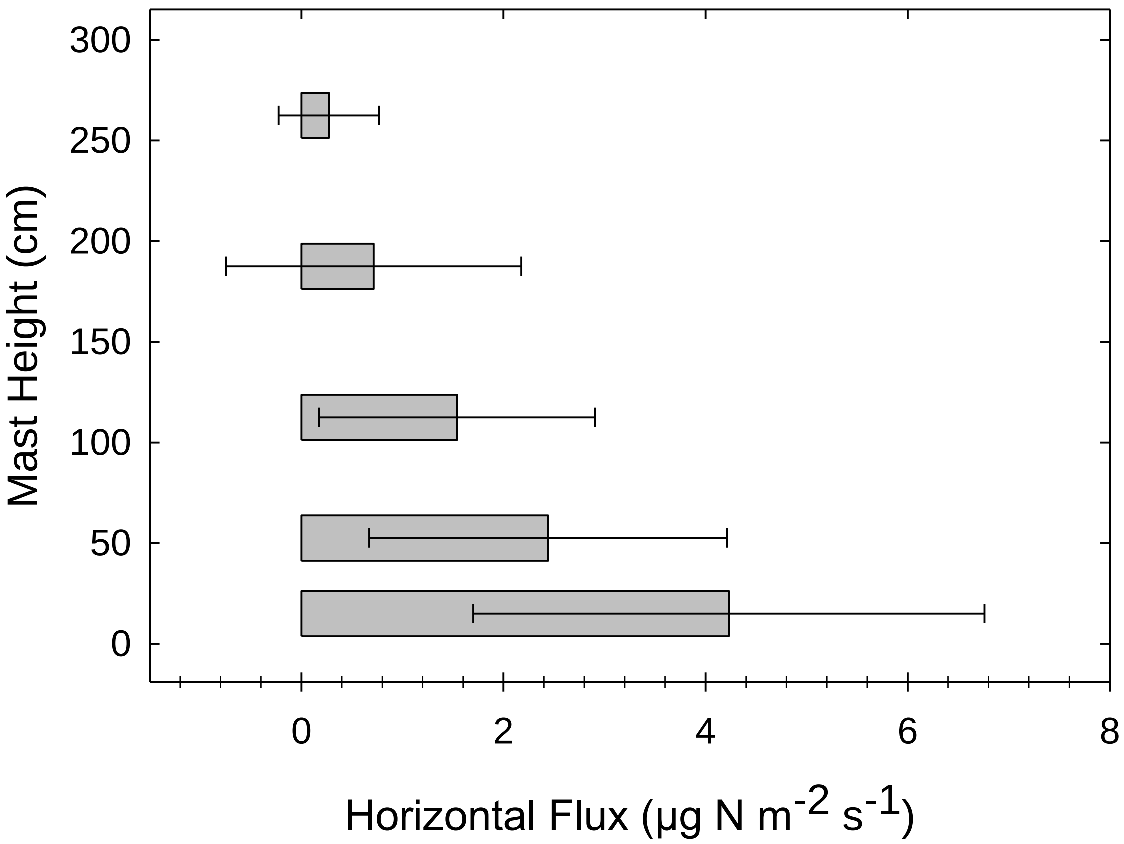
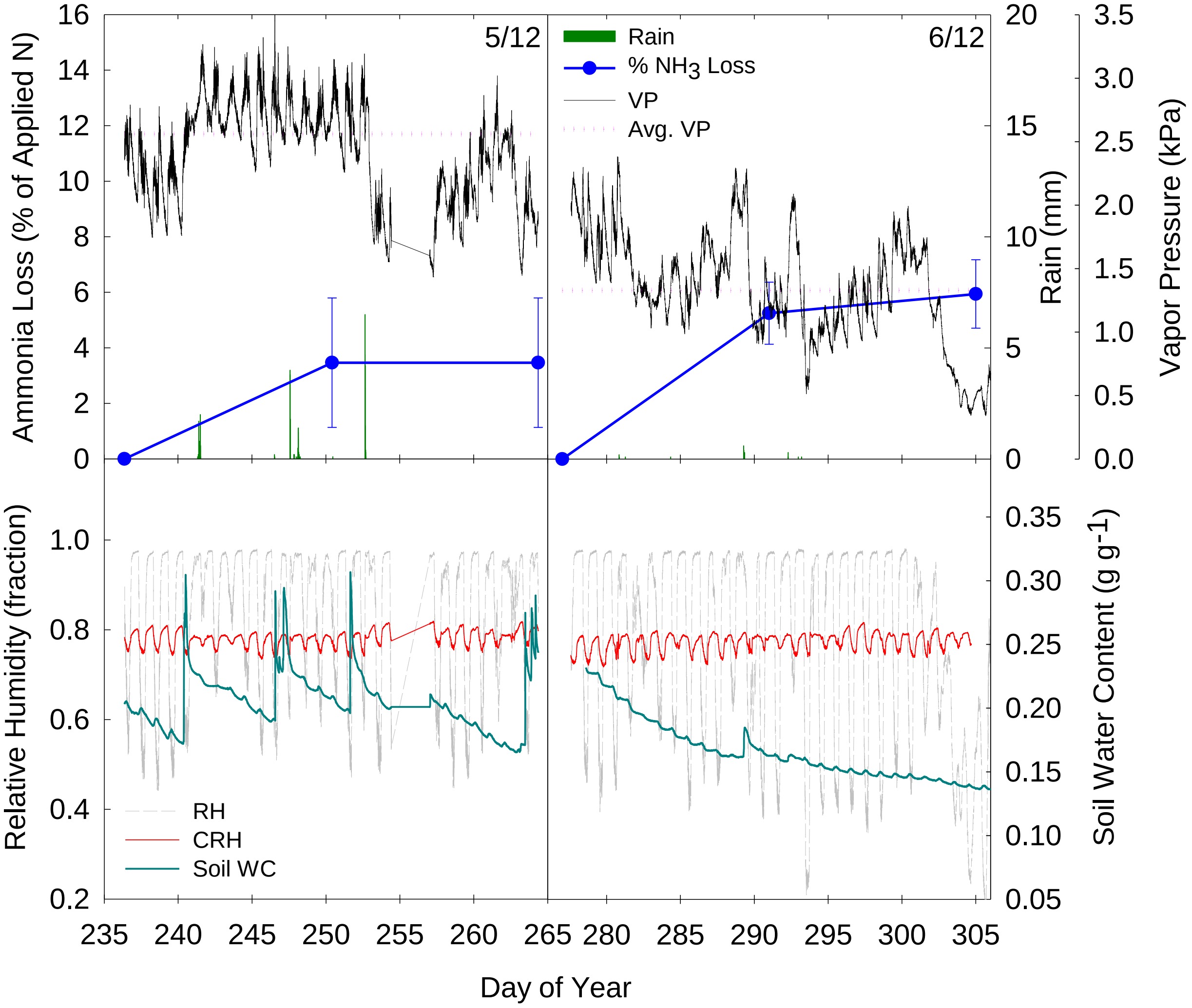

Rain
Air Temp
NH3 Loss
2011
2012
Ammonia Loss (% Applied TN)
0
2
4
6
8
10
12
Temperature (C) and Rain (mm)
0
10
20
30
40
100
125
150
175
200
225
250
275
300
Day of Year

Figure 2.3.



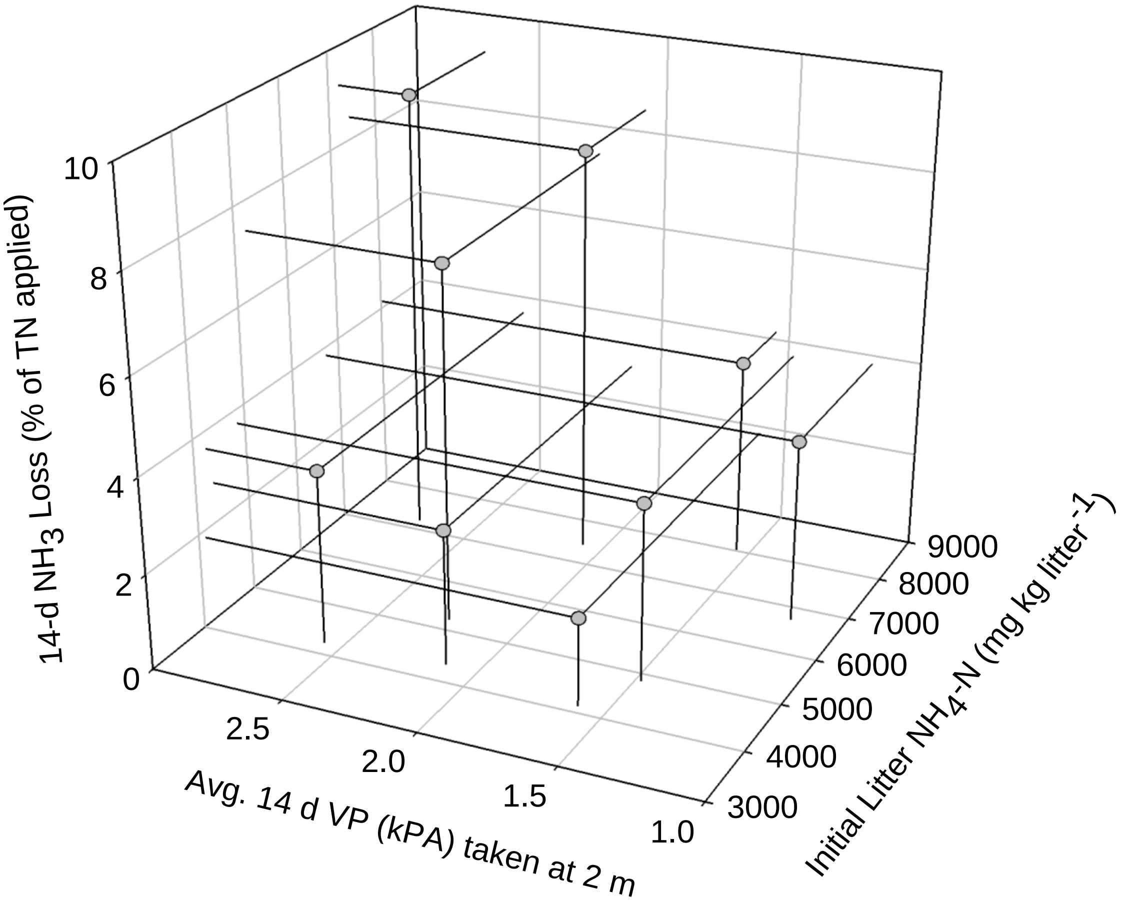
Mast Height (cm)
300
250
200
150
100
50
0
0
2
4
6
8
Horizontal Flux (μg N m^{-2} s^{-1})

Figure 2.4.



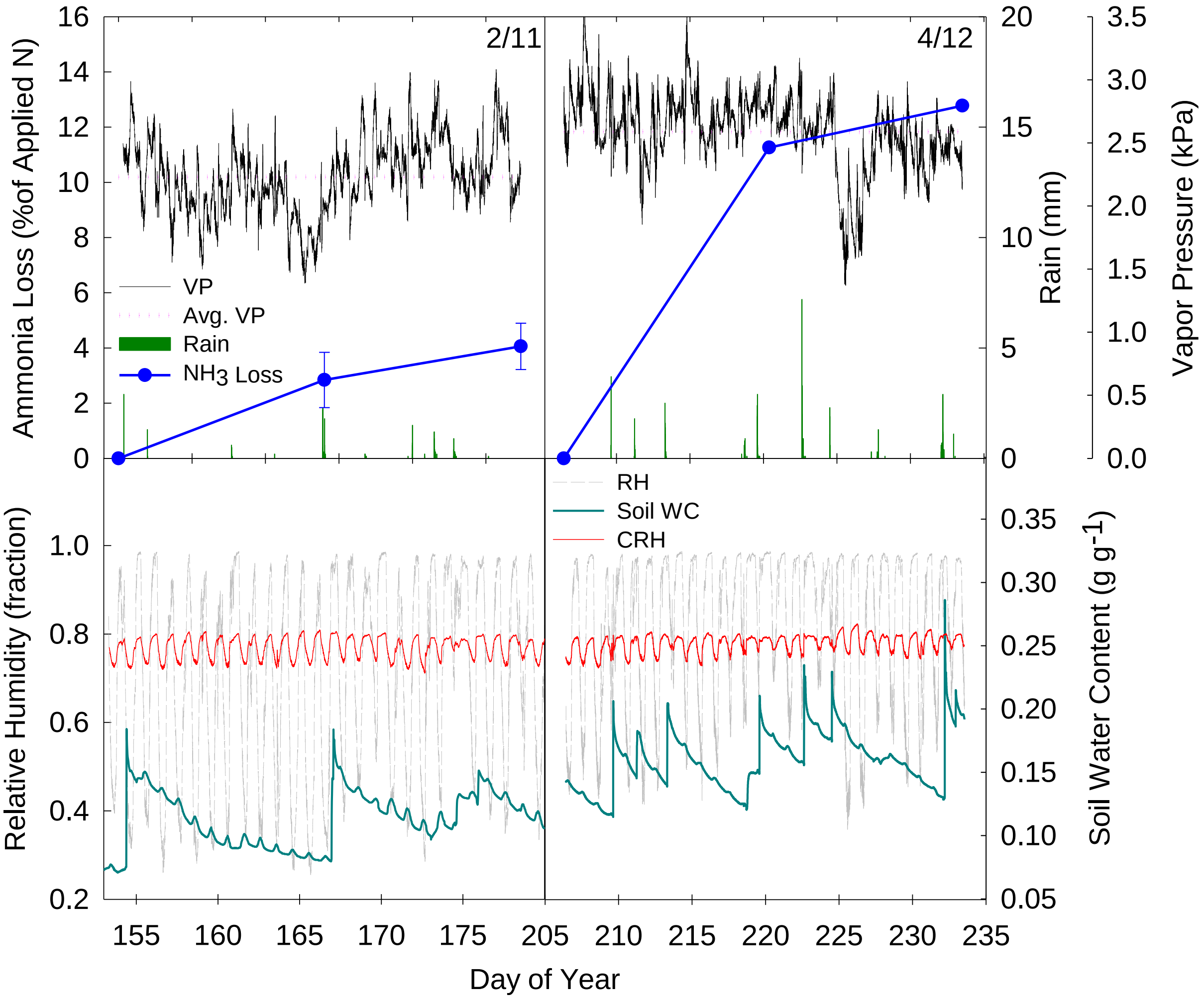
5/12
6/12
Rain
% NH3 Loss
VP
Avg. VP
Ammonia Loss (% of Applied N)
16
14
12
10
8
6
4
2
0
Rain (mm)
20
15
10
5
0
Vapor Pressure (kPa)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Relative Humidity (fraction)
1.0
0.8
0.6
0.4
0.2
RH
CRH
Soil WC
Soil Water Content (g g-1)
0.35
0.30
0.25
0.20
0.15
0.10
0.05
235
240
245
250
255
260
265
280
285
290
295
300
305
Day of Year

Figure 2.5.



14-d NH_3 Loss (% of TN applied)
10
8
6
4
2
0
2.5
2.0
1.5
1.0
Avg. 14 d VP (kPA) taken at 2 m
9000
8000
7000
6000
5000
4000
3000
Initial Litter NH_4-N (mg kg litter^{-1})

Figure 2.6.


2/11
4/12
Ammonia Loss (%of Applied N)
0
2
4
6
8
10
12
14
16
Rain (mm)
0
5
10
15
20
Vapor Pressure (kPa)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
VP
Avg. VP
Rain
NH3 Loss
RH
Soil WC
CRH
Relative Humidity (fraction)
0.2
0.4
0.6
0.8
1.0
Soil Water Content (g g-1)
0.05
0.10
0.15
0.20
0.25
0.30
0.35
155
160
165
170
175
205
210
215
220
225
230
235
Day of Year

CHAPTER 3

AMMONIA VOLATLIZATION FROM SURFACE-APPLIED BROILER LITTER: EFFCT OF SOIL WATER CONTENT AT CONTRASTING HUMIDITIES[1]

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[1] Cassity-Duffey, K., M.L Cabrera, and J.A. Rema. Submitted to Soil Sci. Soc. Am. J. Doi:10.2136/sssaj2014.07.0294. Reprinted here with permission of publisher.

ABSTRACT

Broiler litter is commonly applied to grasslands as fertilizer, where it undergoes nitrogen (N) losses through ammonia (NH_3) volatilization. Ammonia losses represent not only a loss of plant-available N, but also a source of environmental contamination. Previous research has shown that NH_3 volatilization from broiler litter is affected by environmental conditions, but the effects of atmospheric water and soil water content (WC) are not well understood. We conducted a study at constant 94% relative humidity (RH) to evaluate rewetting of broiler litter, and one study at 32% RH to evaluate drying of broiler litter. We also conducted two laboratory studies to evaluate the effect of soil WC (0.03 vs 0.13 g H_2O g^{-1}) at either 32 or 92% RH on NH_3 volatilization from surface-applied broiler litter. Results of the drying and rewetting studies showed that broiler litter can absorb or lose water at a relatively fast rate depending on RH. Ammonia volatilization was greater from wet soil (0.13 g g^{-1} soil WC) than from drier soil (0.03 g g^{-1} soil WC) under the high relative humidity (92%), with losses of 21% and 11% of total N, respectively. In contrast, NH_3 loss was only slightly greater from wet (0.13 g g^{-1} soil WC) versus dry (0.03 g g^{-1} soil WC) soil at 32% RH, with losses of 5.2 and 3.2 % of total N, respectively. These findings indicate that both soil WC and RH may play an important role in NH_3 volatilization. Further research should evaluate the effect of diurnal RH changes on NH_3 loss from surface-applied broiler litter.

Abbreviations: AirMPa, atmospheric air water potential; LitterMPa, litter water potential; N, nitrogen; NH_3, ammonia; NH_4-N, ammonium-N; NO_3-N, nitrate-N; RH, relative humidity; WC, water content.

INTRODUCTION

Broiler litter, a major byproduct of the broiler industry, is a heterogeneous mixture of excreta, bedding material, feathers, and wasted feed. In the state of Georgia alone, approximately 2 million Mg of broiler litter was produced in 2012 (USDA, 2013) leaving a large source of nutrient-rich litter that must be disposed (Moore, 1998). Broiler litter is commonly surface-applied to pasture or no-till cropland, by farmers lacking subsurface application equipment as a method of both waste management and to provide an inexpensive or alternative fertilizer. The land application of broiler litter provides the plant nutrients phosphorus, potassium, nitrogen (N), as well as other micro and macro-nutrients (Kingery et al., 1994; Marshall et al., 1998; Mitchell and Tu, 2006). The low water content (WC) and relatively high N concentrations of broiler litter, relative to other manures, favors its use as an alternative fertilizer (Stephenson et al., 1990). However, N in broiler litter can be highly variable and subject to large losses through NH_3 volatilization, which has been found to range from 4 to 60% of the total N applied in laboratory and field experiments (Brinson et al., 1994; Cabrera and Chiang, 1994; Lau et al., 2008; Lockyer et al., 1989; Marshall, 1998). This wide range of NH_3 loss increases the difficulty in making application rate recommendations and predicting NH_3 loss for surface-applied litter (Nathan and Malzer, 1994; Sommer and Hutchings, 2001).

Although management strategies such as timing and application method can reduce NH_3 volatilization, soil conditions and local climatic variables also influence volatilization (Martinez-Lagos, 2013; Sommer and Hutchings, 2001). With N in broiler litter being present both in inorganic and organic forms, environmental variables not only affect the chemical and physical properties controlling volatilization but also N mineralization. On average, broiler litter contains 4% total N, and the organic pool (primarily uric acid and urea) typically constitutes 40 to 80% of total N (Nahm, 2005; Rothrock et al., 2010; Stephenson et al., 1990). The mineralization process increases the pool of ammoniacal-N in solution while simultaneously increasing litter pH, both contributing to an increase in the potential for NH_3 loss (Sherlock and Goh, 1985; Sommer and Hutchings, 2001). Nitrogen mineralization is microbially and enzymatically mediated and therefore a function of WC and temperature (Antonopoulos, 1999; Pratt et al., 2002; Sims, 1986). In addition to affecting N mineralization, the WC of the litter also controls the concentration of ammoniacal-N in solution, the dissolution of urea, and the diffusion of N into the soil, which further affects NH_3 volatilization (Cabrera et al., 2008; Vlek and Carter, 1983).

Under field conditions, the WC of the litter may be affected by rain events, relative humidity (RH), and the soil water content. Rain events of 17 and 40 mm have shown to decrease NH_3 losses from litter through increasing N diffusion or movement into the soil (Cabrera and Vervoort, 1998; Sharpe et al., 2004). In contrast, increases in RH and soil WC may increase litter WC, increase N mineralization, and increase volatilization without favoring diffusion into the soil. Typical broiler litter application rates to grasslands range from 3,000 to 10,000 kg ha^{-1} (Gaskin et al., 2013), resulting in a 2 to 4-mm litter depth, leaving litter primed to interact with atmospheric and surface soil conditions.

Broiler litter at a typical WC has a very low water potential (about -30 MPa at 0.25 g H_2O g^{-1} on a dry-weight basis), which under high RH results in a large water potential gradient between litter and atmosphere (unpublished data, 2013). Thus, changes in RH near the soil surface may lead to fluctuating litter WC, N mineralization, changes in ammoniacal-N concentrations, and subsequent NH_3 volatilization.. Diurnal fluctuations in NH_3 volatilization from surface-applied litter have been observed by Pote and Meisinger (2014), with increased rates of NH_3 volatilization during daytime hours with high temperature and high vapor pressure deficit. These diurnal fluctuations may be representative of the effect of RH on litter WC. During daytime hours, high temperature and low RH may lead to litter drying and increased ammoniacal-N in the litter solution and increased loss. High RH during evening or night hours likely lead to increased litter WC and mineralization, feeding the pool of ammoniacal-N subject to loss the following day.

Cassity-Duffey et al. (2014) recommended that further work on the effect of RH and soil WC would improve our understanding of NH_3 loss from broiler litter. Reynolds and Wolf (1987) determined that both high RH and elevated soil WC led to urea dissolution and NH_3 volatilization from prilled urea applied to the soil surface, and that low RH led to low NH_3 losses regardless of soil WC. Similarly, in a study conducted by Cabrera et al. (2010), both high RH and elevated initial soil WC increased urea dissolution and the amount of hydrolized urea applied to the forest floor. Although RH and WC have been shown to influence NH_3 loss for urea, previous studies for poultry litter have been contradictory. Both negative and positive correlations have been found between RH and NH_3 loss from poultry litter, but the confounding factor for these studies may have been the effect of soil WC (Nathan and Malzer, 1994; Nimmermark and Gustafsson, 2005).

Information on the effect of soil WC under contrasting RH on NH_3 volatilization from broiler litter is currently not available. A better understanding of the effect of atmospheric water on litter WC and of the effect of soil WC on NH_3 loss would contribute to the development of a simulation model for plant-available N from broiler litter. Such a tool driven by environmental variables would be useful to farmers when making decisions regarding the amount of N to apply to obtain optimum grassland productivity with reduced environmental impact. With this in mind, the objectives of this study were to 1) evaluate the effect of RH on the rate of litter drying or rewetting at two contrasting RH (32 and 94% RH), and 2) determine the effect of two soil WCs (0.03 and 0.13 g H_2O g^{-1}) at contrasting high (92%) and low (32%) RH on NH_3 volatilization from broiler litter under laboratory conditions.

MATERIALS AND METHODS

Broiler Litter and Soil Characteristics

Broiler litter was collected from a broiler house with wood shavings as the bedding material, passed through a 2-mm sieve, and stored covered at 4°C before use. The litter was analyzed for nitrate (NO_3-N), ammonium (NH_4-N) (Mulvaney, 1996), uric acid (Morwer et al., 2013), urea, total N and C (Nelson and Sommers, 1982), pH (1:5 litter/water), WC, and mineralizable N (described below). Urea was determined using an extraction method developed by our lab group: 1 g of litter was extracted for 5 min with 100 mL deionized water containing 1000 mg L^{-1} Ag_2SO_4, filtered through a 0.45-µm filter, and urea was measured colorimetrically using the method proposed by DeManche et al. (1973). Water content was determined by drying the litter at 65°C for 48 h and N mineralized in 28 d was measured using a modified incubation method from the works of both Gordillo and Cabrera (1997) and Qafoku et al. (2001). Briefly, 1 g of litter was mixed with 200 g soil at 0.16 g g^{-1} in 500-mL glass jars, which were placed in an incubator at 30°C and aerated every 48 h. After 28 d, control soil and soil-litter mixtures were extracted with 1 mol L^{-1} KCl at 1:5 ratio (Mulvaney, 1996), and the extract was analyzed colorimetrically for inorganic N (Crooke and Simpson, 1971; Keeny and Nelson, 1982). Litter characteristics results are presented in Table 3.1.

A water release curve was developed for the litter to relate gravimetric WC and litter water potential. The water potential of broiler litter at various WCs from saturation to “as is” was determined in triplicate with a Dewpoint Potentiometer (Decagon Devices Inc., Logan, UT). Nonlinear regression was performed on the data using SAS PROC NLIN (SAS Institute, Inc., Cary, NC) yielding the following equation,

$$\mathrm{WP} = -4.94 * \mathrm{WC}^{-1.22} \qquad \text{Eq. [1]}$$

where WC is g H_2O g litter^{-1} and WP is litter water potential (MPa).

Soil was obtained from the upper 15 cm of an area mapped as a Cecil loamy sand (fine, Kaolinitic, thermic Typic Kanhapludult) (NRCS, 2013) at the University of Georgia Plant Sciences Farm (Athens, GA). The soil was air-dried, passed through 2-mm sieve, and soil WC was determined by drying at 105°C for 48 h. Particle size distribution was determined using the pipette method (Miller and Miller, 1982). The soil had an average pH of 5.5 (1:1 soil/ 0.01 mol L^{-1} $CaCl_2$; Miller and Kissel, 2010), 703 g sand kg^{-1}, 161 g silt kg^{-1}, and 135 g clay kg^{-1}.

Gravimetric soil WC at field capacity (-0.03 MPa), was determined with a pressure plate apparatus (0.19 g H_2O g^{-1}). Soil water potential was estimated from a soil water release curve developed using the Dewpoint Potentiometer at low water potentials and the pressure plate value for field capacity. Initial inorganic N of the soil was measured using 1 mol L^{-1} KCl extraction (Mulvaney, 1996), followed by colorimetric determination (Crooke and Simpson, 1971; Keeny and Nelson, 1982). Initial NH_4-N in the soil was 5.4 mg kg dry soil^{-1} and initial NO_3-N was 170 mg kg dry soil^{-1}.

Dynamic Flow-Through System

The laboratory apparatus used to measure both the change in litter water potential as a function of RH and the effect of soil WC at contrasting RH values on NH_3 loss was a flow-through system with humidity control described by Cabrera et al. (2005). Briefly, the chambers were constructed from acrylic tubes (4.4-cm diameter) cut into 10-cm sections. The cylinders were closed at both ends with No. 10 rubber stoppers, with the top rubber stopper having inlet and outlet ports for the movement of sweep air. The air in the system could be humidified to approximately 93% (94% in the litter wetting study and 92% in the NH_3 volatilization study) or 32% RH by bubbling it through deionized water or saturated $CaCl_2$ solution, respectively. The actual RH obtained in the system varied throughout each experiment, likely due to variations in the RH of the air in the lab due to temperature and outside RH conditions; this was especially apparent when trying to achieve high RH. The sweep air that passed over each chamber was regulated to 0.2 L min^{-1} and bubbled through 50 mL of 0.05 M H_2SO_4 to trap volatilized NH_3 during the volatilization experiment. The system was set up inside a Precision Model 815 incubator (Precision Scientific, Winchester, VA) at 25 ± 2° C. Relative humidity and temperature were monitored and recorded at 5-min intervals with a Vaisala HMP45AC probe (Vaisala Inc., Woburn, MA) connected to a CR10 datalogger (Campbell Scientific, Logan, UT).

Evaluation of litter drying/rewetting

Using the flow-through system described above, two separate studies were conducted to determine both the effect of high and low RH on litter water potential. For the high atmospheric water treatment (94% RH), 2 g of broiler litter (2 mm depth) with an initial WC of 0.25 g H_2O g^{-1} (-27 MPa) was placed in round sampling cups (4 cm o.d.) for the Decagon Dewpoint Potentiometer. The cups were placed inside the flow-through chambers, and at set intervals ranging from 0.08 to 30 h, three cups were removed and the litter WP was measured as described above. To determine the effect of low atmospheric water (32% RH) on drying of broiler litter, a similar study was conducted with litter at an initial WC of 1.35 g H_2O g^{-1} (-3.4 MPa) and with the system using saturated $CaCl_2$ to create a low RH environment.

Relative humidity values were converted to air water potential values (MPa) with the following equation:

$$\text{Air Water Potential (MPa)} = \frac{\text{R x T}}{\text{V}} * \ln(\text{RH}) * 1\ \text{MPa}/1{,}000{,}000\ \text{Pa} \qquad \text{Eq. [2]}$$

where R = gas constant (8.314 J K^{o-1} mol^{-1}); T = absolute temperature (K^o),

V = partial molar volume of water (1.8 x 10^{-5} m^3 mol^{-1}); RH = relative humidity as ratio (0-1).

Using Stella® Modeling Software v. 9.0.3 and the water release curve, the change in litter WC with time ((dWC/dt, g H_2O mm (g litter h)$^{-1}$) in the drying and rewetting studies) was modeled as a function of the gradient between atmospheric water potential (*AirMPa*) and litter water potential (*LitterMPa*), as indicated below.

$$\frac{dWC}{dt} = -\text{k} * (\text{AirMPa(t)} - \text{LitterMPa(t)}) \qquad \text{Eq. [3]}$$

where k (g H_2O (g litter h MPa)$^{-1}$) is a function of litter water potential and time.

Evaluation of soil water content effect on ammonia volatilization

Two separate studies were conducted to determine the effect of soil WC on NH_3 volatilization using a dynamic flow-through system: one at 92% RH, and one at 32% RH. In each RH study, two treatments of gravimetric soil WCs were used, 0.03 g H_2O g^{-1} (dry) and 0.13 g H_2O g^{-1}(wet). Prior to soil packing, soil was rewetted by adding deionized water in small increments over vacuum to maintain soil structure and avoid soil puddling. Each experimental unit consisted of soil (90 g dry-weight-equivalent) packed into an acrylic tube (described above) to a bulk density of 1.25 g cm^{-3}, thereby leaving 4 cm of headspace in the chamber for sweep air flow. In each study, five experimental units at each soil WC treatment received litter (1.09 g litter at 0.30 g H_2O g^{-1} WC) on the soil surface. This was equivalent to a rate of 5,520 kg dry litter ha^{-1}. Two experimental units were left unamended as controls for each soil WC treatment. Treatments were arranged in a completely randomized design.

Each study was conducted for 15 d, with NH_3 traps changed on Days 1, 2, 3, 5, 7, 9, and 15. The NH_3 traps were analyzed for NH_4-N colorimetrically (Keeny and Nelson, 1982). After Day 15, broiler litter was scraped from the surface and the soil was removed in 5-mm layers to measure soil WC (two replicates) and to measure inorganic N (three replicates), as described above. Because of difficulty in avoiding some contamination of litter with soil, which would affect litter WC determination by drying, the WC of the litter was determined by calculating the water in the entire profile from weight measurements, subtracting the contribution of water from the soil, and assuming the rest of the water in the profile was associated with the litter layer. Control treatments were subtracted from litter treatments to determine the contribution of litter to the soil inorganic N with depth and to NH_3 loss. Data of soil WC, inorganic N, and cumulative NH_3 loss were subjected to analysis of variance using PROC GLM (SAS Institute, Inc., Cary, NC) and treatment means were separated using Fisher's Protected LSD at $p=0.05$.

RESULTS AND DISCUSSION

Evaluation of litter drying/rewetting

In the litter rewetting and drying studies, litter water potential reached equilibrium with the atmosphere after 31 h, but most changes occurred within the first 15 h (Fig. 3.1). At 94% RH, litter water potential increased from – 27.0 MPa (0.25 g H_2O g^{-1}) to -6.4 MPa (0.76 g H_2O g^{-1}). At 32% RH, litter lost water rapidly and had an overall change in water potential from -3.4 MPa (1.35 g H_2O g^{-1}) to -154.6 MPa (0.06 g H_2O g^{-1}). In broiler production houses, Weaver and Meijerhof (1991) observed significant effects of RH on the litter WC beginning at day 7 and continuing to day 42. Although the effects of the RH on litter WC were similar to those determined in our study, rates in litter wetting and drying observed by Weaver and Meijerhof were lower than results determined in this study. These reduced rates are most likely due to increased litter depth and the continuous deposition of excreta from the existing flock under production conditions.

The changes observed in litter WC in both 31-h studies (rewetting and drying) could be adequately modeled with Eq. [3], which indicates that the change in WC with time (dWC/dt) is proportional to the gradient in water potential between the litter and the atmosphere (AirMPa – LitterMPa), with the proportionality coefficient (k in (g H_2O (g hr MPa)$^{-1}$)) being a function of litter water potential, as shown below:

k = -0.0009 + -1.10 x 10^{-5} * LitterMPa +-3.52 * 10^{-8} LitterMPa^2 (for drying litter);

k =-1.50*-LitterMPa$^{-2.27}$ (for rewetting litter).

The calibrated model was used to estimate WC of the broiler litter layer in the low soil WC treatments of the NH_3 volatilization studies (0.03 g H_2O g-1), in which the contribution of soil water to the broiler litter WC was nil or minimal, as described below.

Evaluation of soil water content effect on NH_3 volatilization

Study 1: 0.03 vs 0.13 g H_2O g^{-1} *at 92% RH*

Ammonia losses on day 1 were similar between the two soil treatments (Fig. 3.2), but by Day 3, the rate of loss in the dry soil treatment was smaller and that trend continued for the remainder of the study. In the dry soil treatment, the soil WC did not change during the study. The WC of the litter layer had an initial value of 0.30 and a final value of 0.31 g H_2O g^{-1} by Day 15 (Table 3.2). This lack of change in litter WC does not match the expected value based on the study on litter rewetting, in which litter exposed to 94% RH reached a water content of 0.76 g g^{-1} after 31 h. To investigate the cause for the low final WC in the litter, the calibrated model of Eq. [3] was used to simulate litter WC with the RH data recorded during the 15-d study. Results of this modeling exercise showed that the litter WC of 0.31 g H_2O g^{-1} on Day 15 was caused by an unintentional reduction in RH below 85% during the last 2.5 d of the study, additionally a reduction near 85% occurred in the first 2 day of the study but litter WC content recovered (Fig. 3.2). Furthermore, model results indicated that the WC of the litter layer was about 0.63 g H_2O g^{-1} just before the RH decreased below 85% (Fig. 3.2). This may have led to decreased mineralization during this time period, potentially reducing losses.

To confirm these model results, these data were compared to data determined in a preliminary study at a similarly low soil WC (0.07 g H_2O g^{-1}, -1.1 MPa) under the same intended conditions of the previous study (consistent, constant 92% RH). In the preliminary study we found no change in WC during 15 d (as observed before), the same cumulative loss of NH_3 (11.3%), and a final WC of the litter of 0.65 g H_2O g^{-1} (Fig. 3.3). Furthermore, for this preliminary study, the model of Eq. [3] estimated a WC of 0.63 g H_2O g^{-1} on Day 15, which is very close to the measured value of 0.65. These results suggest that the values modeled for the dry soil treatment were good approximations (Fig. 3.2) for the changes in litter water content during the 15-d study. Thus, according to the modeled results, in the dry soil treatment, broiler litter gained water from the atmosphere (92% RH), which led to increased N mineralization (as described below) and to a cumulative NH_3 loss of 11.3% of the applied N (Table 3.3). Similarly, Reynolds and Wolfe (1987) found that urea surface applied to soil at -1.5 MPa and exposed to 85% RH, lost 36% of the applied urea-N through NH_3 volatilization. Their study indicated that the high RH promoted urea hydrolysis even though the WC of the soil was low.

In the wet soil treatment, the soil lost 0.01 g H_2O g^{-1} by Day 15, and the broiler litter increased in WC from 0.30 to 0.65 g H_2O g^{-1} (Table 3.2). It is likely that the broiler litter gained water not only from the atmosphere but also from the soil, which led to increased N mineralization and to a cumulative NH_3 loss of 21% (Table 3.3). In addition to increasing N mineralization (Sims, 1986), increased litter WC may have led to dissolution of initial NH_4-N, thereby increasing the ammoniacal-N in solution available for loss as NH_3 (Cabrera and Chiang, 1994).

Nitrogen mineralization from broiler litter was 13.5% of the applied N in the dry soil treatment (% Inorganic N recovered at 15 d – % Initial Inorganic N= 30.0-16.5 = 13.5), and 26.3% of the applied N in the wet soil treatment (42.8-16.5 = 26.3). These differences in overall N mineralization were likely due to the effect of WC on microbial and enzymatic communities. In soils, Klose and Tabatabai (1999) determined the existence of extracellular urease, as well as, urease associated with the microbial biomass. It is likely that broiler litter also contains extracellular enzymes (such as uricase and urease) as well as enzymes associated with the microbial biomass. However, at the high salt concentrations and typical low water potentials of broiler litter, much of the litter uricase and urease enzymes are likely to be present without their microbial counterparts. As WC increases, microbial growth would increase, which would favor degradation of other N-containing compounds in the litter through enzymes produced by the microorganisms (Groot Koerkamp, 1994; Sylvia et al., 1998).

In the dry soil treatment, water limitation in the litter may have limited microbial growth and led to mineralization of uric acid and urea through extracellular enzymes. This hypothesis is in part supported by the similar values of the sum of initial urea+uric acid in the litter (13.1% of applied N) and the estimated N mineralization in the dry soil treatment (13.5% of the applied N). In contrast, the estimated N mineralized in the wet soil treatment (26.3%) suggests the increase in litter WC may have led to increased microbial growth with the consequent degradation of additional N-containing compounds. The amount of soil inorganic N derived from the litter was significantly different between treatments (Table 3.3). Soil inorganic N was 12.1% of the total N applied in the dry treatment and 16.3% in the wet treatment. Both soil water treatments showed similar NH_4-N diffusion down to 30 mm into the soil profile (Fig. 3.4; top left), but the wet treatment had greater NO_3-N in the soil than the dry treatment. This difference was likely due to the higher soil WC of the wet treatment, which led to more nitrification (Fig. 3.5) (Sims, 1986; Havlin et al, 2005; Norton, 2008).

Study 2: 0.03 vs 0.13 g g-1 at 32% RH

Differences in daily NH_3 loss were observed at the beginning of the study, when the wet soil treatment had greater rates of loss in days 2 and 3 before losses leveled off (Fig. 3.2, bottom). At the low RH used in this study (32%), the high atmospheric demand led to a significant soil WC decrease in the wet soil treatment and to significant litter WC decreases in both treatments. The soil WC decreased from 0.13 to 0.02 g H_2O g^{-1} in the wet soil treatment, and from 0.03 to 0.01 g H_2O g^{-1} in the dry soil treatment. Similarly, the litter WC changed from 0.31 to 0.05 g H_2O g^{-1} (Table 3.2) in the wet soil treatment and from 0.31 to 0.06 g H_2O g^{-1} in the dry soil treatment (Table 3.2). Modeled values for litter WC showed a quick decrease in litter WC within the first day (Fig. 3.22). Although final WC results for soil and broiler litter were similar in both treatments, the high initial soil WC of the wet treatment may have led to an initial increase in litter WC, which probably caused a slight increase in N mineralization. As a result, the wet soil treatment had a larger NH_3 loss than the dry soil treatment (5.2 % vs 3.2%; Table 3). This hypothesis is supported by the larger amount of NO_3-N in the litter from the wet treatment, which indicates conditions favorable for nitrification and consequently favorable for N mineralization (Fig. 3.5).

Reynolds and Wolf (1987) found that when urea was surface applied to soil at field capacity and treated with 25% air RH, NH_3 losses were significantly reduced (11% of the applied N) compared to losses observed at 85% air RH, and the soil profile was dried to wilting point within 51 h. However, prior to soil drying, pH dramatically increased in the surface layers, indicating urea hydrolysis. While WC became low in both the litter and soil layer in the wet soil treatment, it is likely that there was a period in which the high soil WC favored some mineralization and nitrification. Even with this effect, losses in the wet soil treatment remained low through a rapid drying and a decrease in N mineralization.

CONCLUSIONS

Our results showed that broiler litter can absorb or lose significant amounts of water to the atmosphere depending on the gradient in water potential between litter and atmosphere. Results also showed soil WC can affect the WC of surface-applied broiler litter as well as NH_3 loss, but those effects may vary with RH. Losses were greatest at high RH and high soil WC. A soil at low WC (0.03 $g\ g^{-1}$, -7.3 MPa) exposed to 92% RH had a relatively high loss of NH_3 (11.2% of applied N) caused by an increase in litter WC, which in turn stimulated N mineralization. In contrast, the same soil at high WC (0.13 $g\ g^{-1}$, -0.9 MPa) and exposed to 32% RH had a small loss of NH_3 (5.2% of applied N), which was caused by a fast decrease in the WC of broiler litter, with a consequent low N mineralization. Additional laboratory and field research is needed to develop a better understanding of the effect RH and soil WC on NH_3 volatilization under diurnal RH and temperatures changes, with the goal of developing a simulation model for NH_3 loss under field conditions for surface-applied broiler litter.

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TABLES AND FIGURES

Table 3.1. Characteristics determined for the broiler litter used in the ammonia volatilization experiments conducted at 32 and 92% relative humidity.

Litter Characteristics	Value ± st. dev.
pH (1:5)	8.5 ± 0.01
Total N (g kg^{-1})	28 ± 0.1
Total C (g kg^{-1})	280 ± 1
Water Content (g kg^{-1})	303 ± 6
NH_4-N (mg kg^{-1})	4308 ± 185
NO_3-N (mg kg^{-1})	304 ± 16
Urea-N (mg kg^{-1})	114 ± 3
Uric acid-N (mg kg^{-1})	3624 ± 186
MN (g N kg Org N^{-1})†	515 ± 88

† Mineralized N in 28 d at 30°C.

Table 3.2. Initial and final water contents and water potentials for both the soil and litter layer in the ammonia volatilization experiments at 32 and 92% relative humidity for 15-d.

Study	RH	Soil WC		Litter WC	
		Initial	Final	Initial	Final
	% (MPa)	---- g H_2O g soil^{-1} (MPa)----		---- g H_2O g litter^{-1} (MPa) ----	
1	92 (-11.4)	0.03 (-7.3)a†	0.03 (-7.3)a	0.30 (-21.5)a	0.31 (-20.6)a
		0.13 (-0.09)a	0.12 (-0.1)a	0.30 (-21.5)a	0.65 (-8.35)b
2	32 (-156.9)	0.03 (-7.3)a	0.01 (-46.6)a	0.31 (-20.6)a	0.06 (-152.9)b
		0.13 (-0.09)a	0.02 (-24.5)b	0.31 (-20.6)a	0.05 (-191.0)b

† Within a study and row, means with different letters are significantly different according to Fisher's LSD at $p<0.05$.

Table 3.3. Distribution of inorganic N as % of applied total N for each ammonia volatilization study.

	Study 1: 92% RH		Study 2: 32% RH	
	-g H_2O g $soil^{-1}$--		--g H_2O g $soil^{-1}$--	
	0.03	0.13	0.03	0.13
Volatilized	11.3b[†] (74)[*]	21.0a (139)	3.2b (21)	5.2a (34)
Litter	6.6a	5.5a	4.9a	5.4a
Soil	12.1b	16.3a	4.1a	4.8a
Total	30.0b	42.8a	12.9b	15.7a

† Within a study and row, means with different letters are significantly different according to Fisher's LSD at $p<0.05$.

*Value in parentheses represents ammonia volatilization as a percent of the ammonium-N applied.

Figure 3.1. Measured and modeled broiler litter water potential for the litter wetting/drying experiment as a function of time at constant 32% or 94% relative humidity (dashed line denotes air water potential; bars indicate standard deviations).

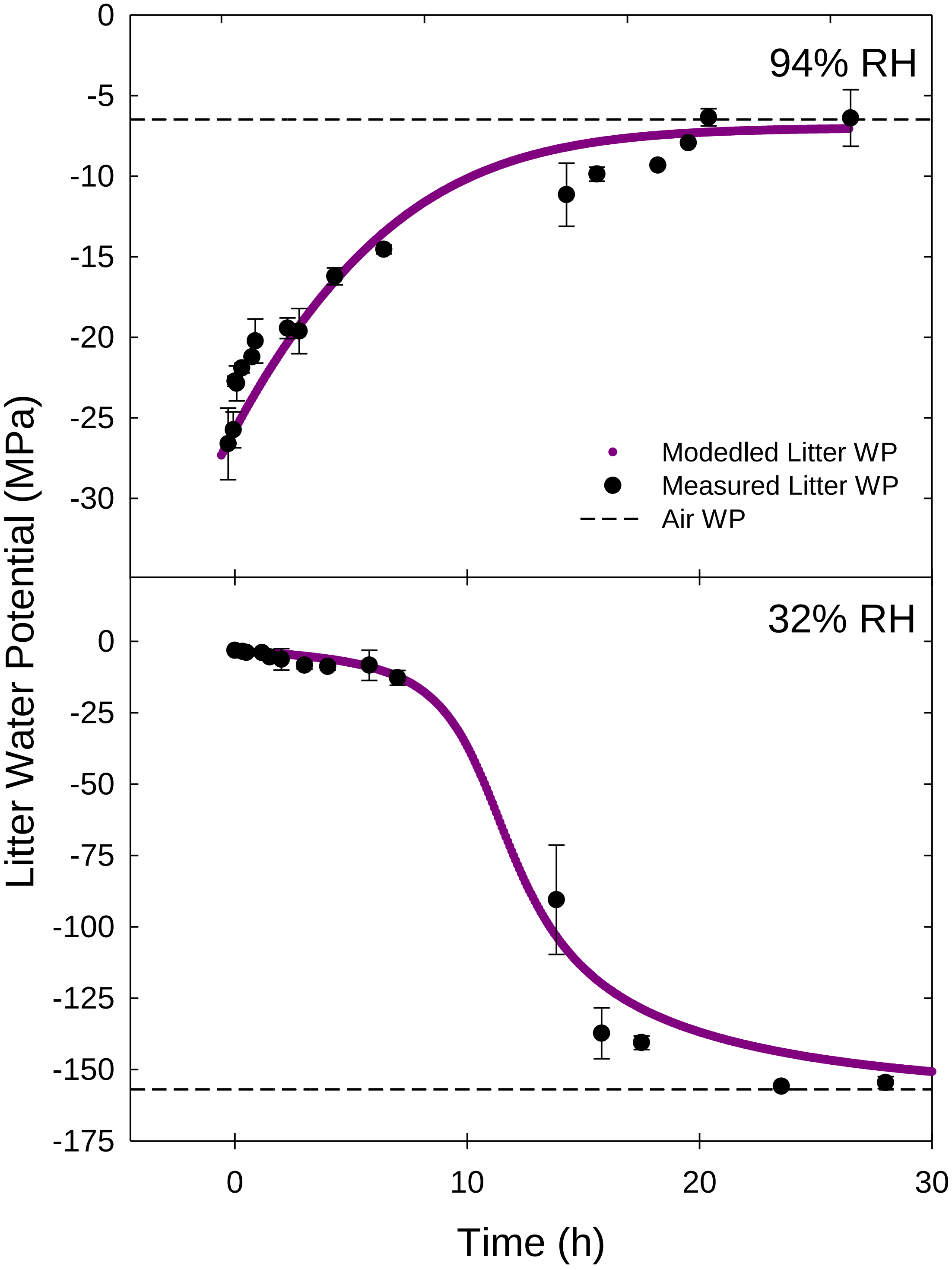
Figure 3.2. Cumulative ammonia volatilization from surface-applied broiler litter in soil at 0.03 or 0.13 g H_2O g^{-1} during 15 d at 32% or 92% relative humidity (dotted line represents litter water content modeled for each study as a function of relative humidity; bars indicate standard deviations).

Figure 3.3. Cumulative ammonia volatilization and modeled litter water content for the preliminary volatilization study conducted at 92% at 0.07 g H_2O g^{-1}(dotted line represents litter water content modeled for each study as a function of relative humidity; bars indicate standard deviations).

Figure 3.4. Final ammonium-N and nitrate-N with depth for the ammonia volatilization experiment with surface-applied broiler litter to soil at 0.03 or 0.13 g H_2O g^{-1} and kept at 32% or 92% relative humidity for 15 d (bars indicate standard deviations).

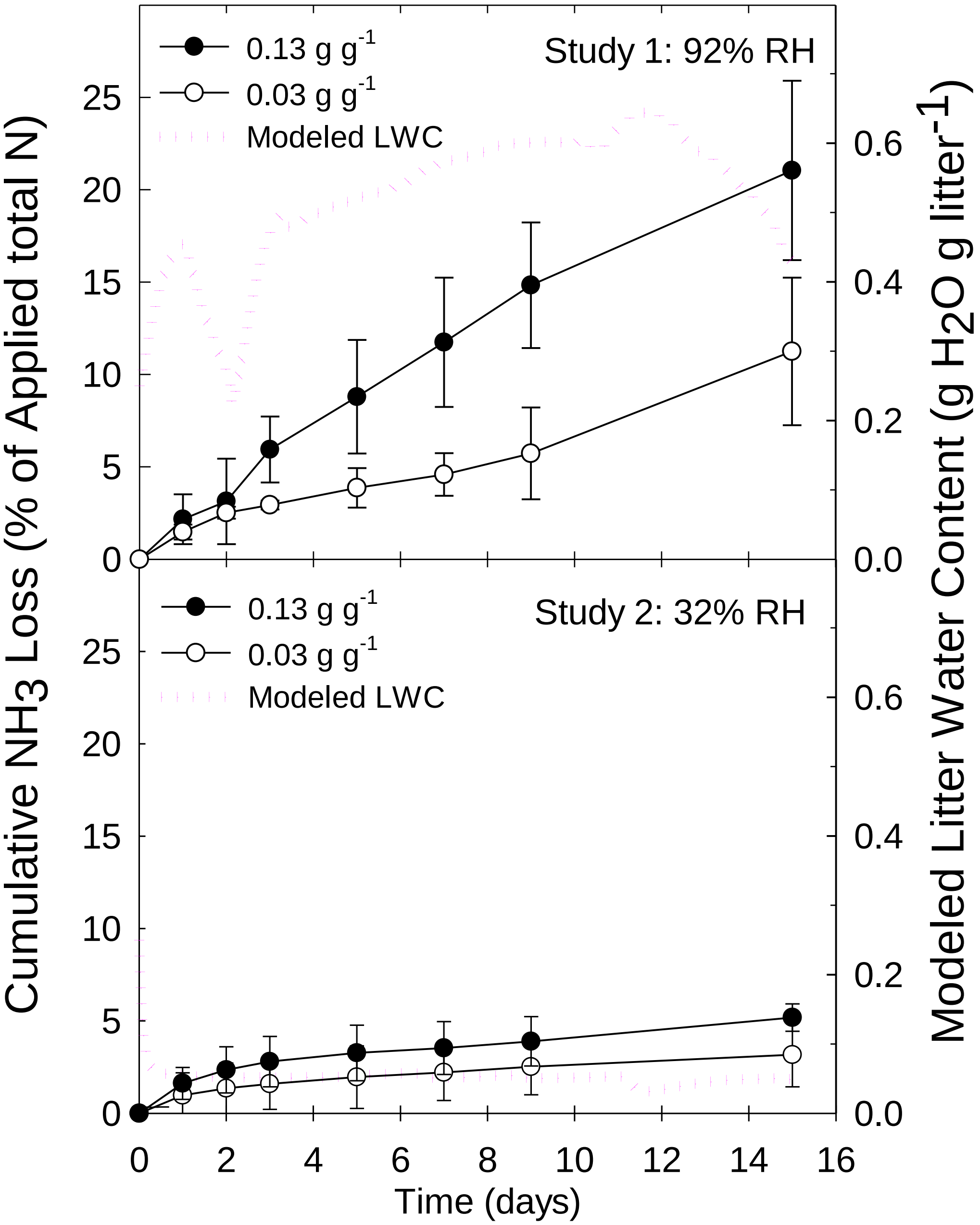
Figure 3.5. Final inorganic N in the soil and litter layers at 15 d in studies with surface-applied broiler litter to soil at 0.03 or 0.13 g H_2O g^{-1} and kept at 32% or 92% relative humidity. Within each study and variable, means with different letters are significantly different according to Fisher's LSD at $p<0.05$).

Figure 3.1.



94% RH
32% RH
Modedled Litter WP
Measured Litter WP
Air WP
Litter Water Potential (MPa)
Time (h)
0
-5
-10
-15
-20
-25
-30
0
-25
-50
-75
-100
-125
-150
-175
0
10
20
30

Figure 3.2.



0.13 g g-1
0.03 g g-1
Modeled LWC
Study 1: 92% RH
Study 2: 32% RH
Cumulative NH3 Loss (% of Applied total N)
Modeled Litter Water Content (g H2O g litter-1)
Time (days)
0
5
10
15
20
25
0.0
0.2
0.4
0.6
0
2
4
6
8
10
12
14
16

Figure 3.3.

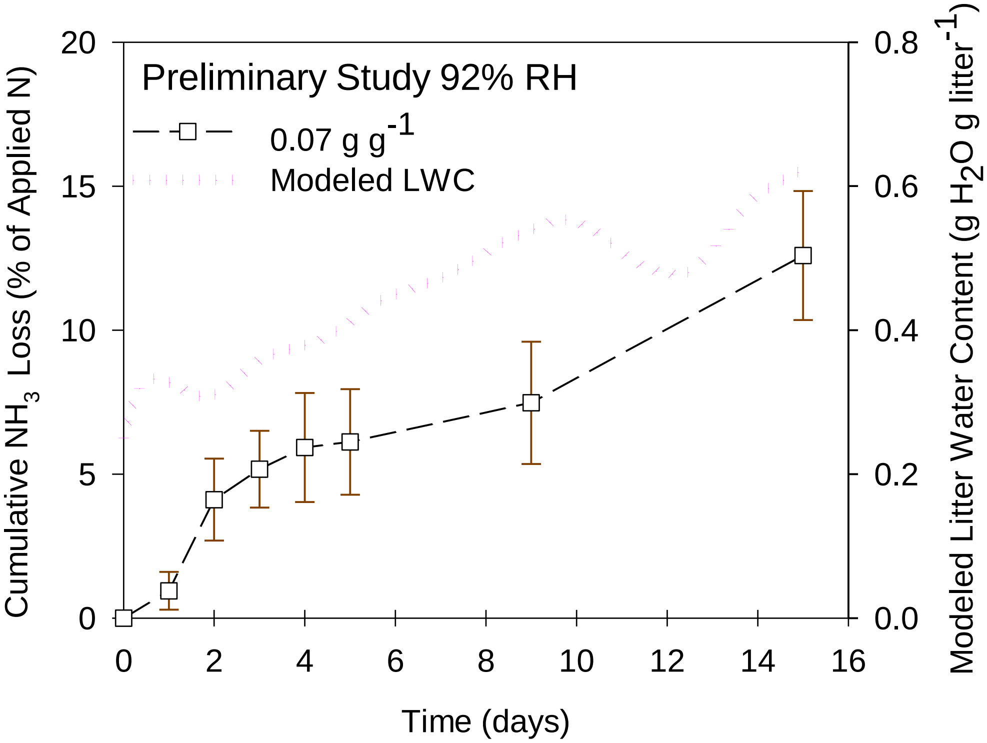
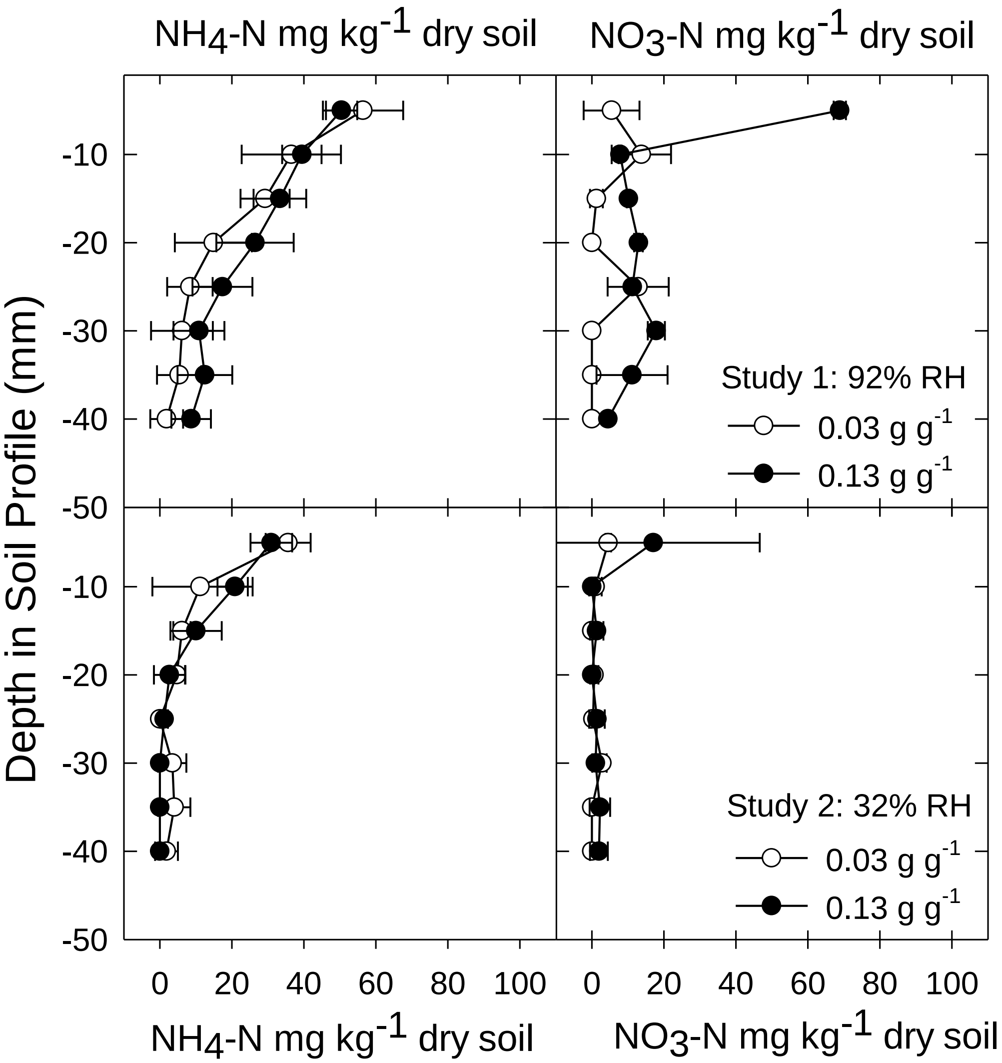
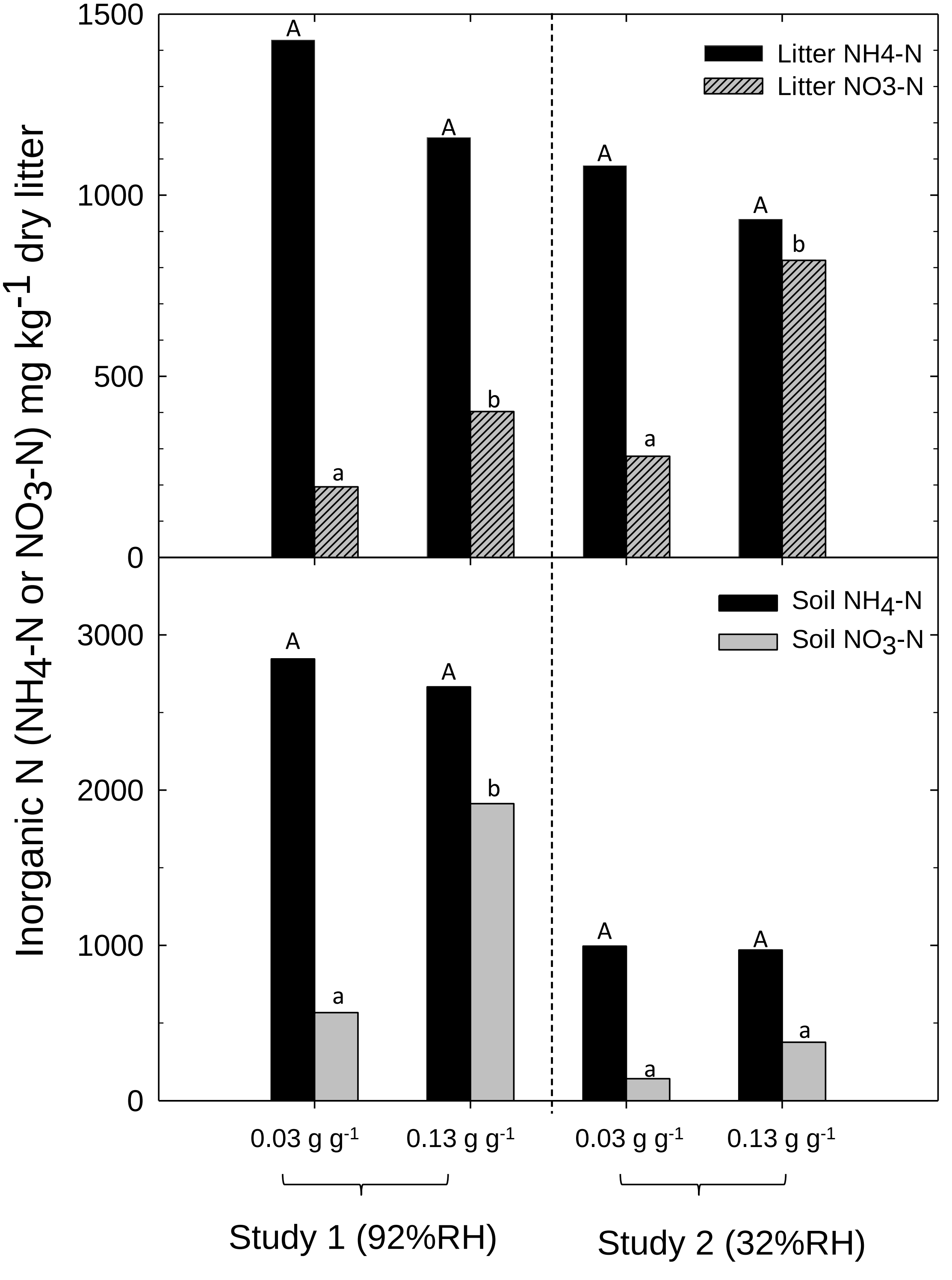

Preliminary Study 92% RH
0.07 g g^{-1}
Modeled LWC
Cumulative NH_3 Loss (% of Applied N)
Modeled Litter Water Content (g H_2O g litter^{-1})
Time (days)
0
5
10
15
20
0.0
0.2
0.4
0.6
0.8
0
2
4
6
8
10
12
14
16

Figure 3.4.



NH4-N mg kg-1 dry soil
NO3-N mg kg-1 dry soil
Depth in Soil Profile (mm)
-10
-20
-30
-40
-50
Study 1: 92% RH
0.03 g g-1
0.13 g g-1
Study 2: 32% RH
0.03 g g-1
0.13 g g-1
0
20
40
60
80
100

Figure 3.5.



Inorganic N (NH4-N or NO3-N) mg kg-1 dry litter
1500
1000
500
0
3000
2000
1000
0
Litter NH4-N
Litter NO3-N
Soil NH4-N
Soil NO3-N
A
a
A
b
A
a
A
b
A
a
A
b
A
a
A
a
0.03 g g-1
0.13 g g-1
0.03 g g-1
0.13 g g-1
Study 1 (92%RH)
Study 2 (32%RH)

CHAPTER 4

POULTRY LITTER PH BUFFERING CAPACITY[1]

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[1] Cassity-Duffey, K., M.L Cabrera, J. Mowrer, and D.E. Kissel. To be submitted to the Journal of Environmental Quality.

ABSTRACT

Litter pH is affected by nitrification, mineralization, and from the addition of acidifying chemicals such as aluminum sulfate (alum), all acting on the litter pH buffering capacity (pHBC). Thus, the pHBC of poultry litter is needed to estimate pH changes. Our objectives were to 1) determine pHBC of a wide range of litters 2) assess the accuracy of near infrared reflectance spectroscopy (NIR) to determining litter pHBC and 3) demonstrate the use of litter pHBC to increase the accuracy of alum additions. Litter pHBC was determined by titration and calculated from both linear and sigmoidal curves. For the 37 litters measured, linear pHBC ranged from 187 to 537 mmol H (pH unit kg dry litter)$^{-1}$. Both linear and sigmoidal functions provided accurate predictions of pHBC, with most $R^2 > 0.90$. The linear pHBC determined and scanned on as “as is” water content had a NIR calibration of $R^2=0.90$ for the 37 litters measured. Using the litter pHBC, an empirical model was derived to determine the amount of alum needed to create a target final pH. The model performed well in the pH range of 6.5 to 7.5 (RMSE=0.07), but under predicted the amount of alum needed to reach pH below 6. The lack of model performance was attributed to potential phosphorus, nitrogen, and zinc reactions with alum. Increased understanding of litter pHBC will aid both in modeling NH_3 volatilization from surface-applied poultry litter as well as in estimating rates of alum applications.

Abbreviations: N, nitrogen; NIR, near infrared reflectance spectroscopy; P, phosphorus; pHBC; pH buffering capacity; pHf, final pH; pHi, initial pH.

Abbreviations: NIR, near infrared reflectance spectroscopy; pHBC, pH buffering capacity; pHf, final pH; pHi, initial pH.

INTRODUCTION

In 2013, the U.S. poultry production of broilers and eggs had a farm gate value of $33 billion dollars (USDA, 2014). Although poultry production has a very important role in U.S. agriculture, increased poultry production results in large quantities of poultry litter as a waste by-product. Approximately 1.5 kg of litter is generated for each broiler produced, leading to the annual accumulation of 12 million Mg of broiler litter nationwide that must be managed and disposed (AEB, 2013; ASAE, 1998; Moore, 1998; USDA, 2013). During poultry production, bedding material (typically wood shavings, peanut hulls, or wheat straw) is added to the floor of the poultry houses where five to six flocks of birds are grown out over a 1-year cycle (Moore et al., 1995). This leads to a heterogeneous mixture of excreta, bedding, feathers and wasted feed that is removed from the houses and directly land applied or stacked for later disposal. The litter characteristics are a function of the number of flocks grown, housing conditions, feed, and storage conditions which vary greatly between operations and even within individual houses (Nahm, 2005; Nimmermark and Gustafsson, 2005).

Poultry litter is typically applied to crops as an inexpensive alternative to inorganic fertilizers and is commonly surface-applied to pasture (Marshall et al., 1998). Poultry litter contains higher phosphorus (P) and nitrogen (N) concentrations than other manures and also provides other micro and macronutrients like calcium, magnesium, and potassium (Mitchell and Tu, 2006; Stephenson et al., 1990). Conversely, it is this high nutrient content combined with large variations in litter composition that make management strategies difficult to prescribe during poultry production and at the time of land application; this is especially true in terms of N. Both in house and following land application, ammonia (NH_3) volatilization from the degradation of uric acid and urea lead to potential health and environmental concerns, as well as, decreasing the efficacy of litter as an alternative N fertilizer (Marshall et al., 1998; Rothrock et al., 2010; Sims and Luka-Mcafferty, 2002). High NH_3 concentrations in poultry houses can lead to decreased growth rates and egg production, increased bird mortality, and cause dangerous working conditions (Moore et al., 2000; Ritz et al., 2004; Sims and Luka-Mcafferty, 2002). Volatilization from surface-applied poultry litter can significantly reduce plant-available N and reduce overall crop yield. Further, excess NH_3 introduced into the surrounding environment from either source can lead to soil acidification and reduce plant biodiversity (Bowman et al., 2008; Cabrera and Chiang, 1994; Lau et al., 2008; Kim and Choi, 2008).

Ammonia volatilization from poultry litter is a function of the ammonium (NH_4^+) and organic N contents of the litter, mineralization rates of organic N to NH_4^+, litter pH, and the transfer of NH_3 from the litter to the atmosphere (Ni, 1999; Ritz et al., 2004; Sherlock and Goh, 1984; Sommer and Hutchings, 2001). The litter pH is a dominant factor in NH_3 volatilization because it determines the proportion of ammoniaical-N in solution that is present as NH_3. Processes that affect poultry litter pH are dynamic, litter pH is affected by mineralization, nitrification, the loss of NH_3, and/or and the addition of acidifying agents (Cabrera et al., 2008; Kim and Choi; 2009; Sims, 1986). Mineralization of organic N in litter is a function of microbial and enzymatic activity as shown in Eq. 1 and Eq. 2 (Rothrock et al., 2010):

$$\mathrm{C_3H_4N_4O_3\ (uric\ acid) + O_2 + 4H_2O} \xrightarrow{uricase}$$
$$\mathrm{2(NH_2)_2CO\ (urea) + C_2H_2O_3 + H_2O_2 + CO_2} \qquad \text{Eq. [1]}$$

$$\mathrm{(NH_2)_2CO\ (urea) + 2H^+ + H_2O} \xrightarrow{urease} \mathrm{2NH_4^+ + CO_2} \qquad \text{Eq. [2]}$$

The hydrolysis of one mole of urea leads to the consumption of two protons (H^+) and the release of two moles NH_4^+. Overall, this mineralization process increases litter pH, which in turn, increases the deprotanation of NH_4^+ to NH_3 (Kissel and Cabrera, 2005) where:

$$\mathrm{NH_4^+} \longrightarrow \mathrm{NH_3} + \mathrm{H^+} \ \text{pka} = 9.25 \text{ at } 25°\mathrm{C} \qquad \text{Eq. [3]}$$

Thus, an increase in litter pH and temperature causes an increase in NH_3 in the litter solution, which subsequently favors NH_3 volatilization. At pH below 7 NH_3 losses are significantly reduced (Kissel and Cabrera, 2005; Ni,1999).

Alternatively, NH_4^+ and NH_3 can undergo nitrification which could lead to potential decreases in litter pH and NH_3 losses where (Schmidt, 1982):

$$NH_4^+ + 1\frac{1}{2}O_2 \rightarrow NO_2^- + H_2O + 2H^+ \qquad \text{Eq. [4]}$$

$$NO_2^- + \frac{1}{2}O_2 \rightarrow NO_3^- \qquad \text{Eq. [5]}$$

Additionally, many management strategies include the use of acidifying agents to decrease litter pH and NH_3 loss. Aluminum sulfate (alum) is commonly applied in house to reduce NH_3 emissions during production. Through a hydrolysis reaction, alum potentially released six moles of protons for each mole of alum dissociated (Moore et al., 2000):

$$\mathrm{Al_2(SO_4)_3 \cdot 14H_2O + 6H_2O \rightarrow 2Al(OH)_3 + 3SO_4^{2-} + 6H^+ + 14\,H_2O} \qquad \text{Eq. [6]}$$

The extent to which these processes affect pH are a function of the pH buffering capacity (pHBC) of the litter. The ability of litter to buffer its pH against proton (H) addition or removal is important to understanding the mechanisms and dynamics of NH_3 volatilization from poultry litter, both during production and after land application. Knowing the pH and the pHBC of litters would allow improved accuracy in the amount of acidifying agents, such as alum, and could lead to increased precision for modeling NH_3 loss for surface-applied poultry litter.

Currently, determination of pHBC of poultry litter is not a part of the routine analysis. Titrations to determine pHBC curves are time consuming and laborious. The use of near infrared reflectance spectroscopy (NIR) has increased in soil and manure testing laboratories (Quafoku et al., 2001; Stenberg, et al., 2010). NIR has been shown to be a useful tool in estimating litter inorganic N, uric acid, total carbon and total N (Mowrer et al., 2014) in poultry litter and may be a useful tool to quickly estimate pHBC. Accurately and rapidly predicting litter pHBC will increase the accuracy in modeling NH_3 volatilization both in the field and in poultry production settings, increasing the ability to predict plant-available N and increase the precision of alum use. The objectives of this study were to 1) determine the pHBC of poultry litter samples 2) assess the potential of of NIR spectroscopy to estimate litter pHBC and 3) demonstrate the use of litter pHBC to increase the accuracy of alum additions for a desired litter pH.

MATERIALS AND METHODS

Litter Characteristics

A total of 37 poultry litters were collected from the samples sent for analysis to the University of Georgia Soil, Plant, and Water Laboratory (Athens, GA). Litters underwent routine analysis for total calcium, potassium, magnesium, manganese, iron, aluminum, boron, copper, zinc, sodium, sulfur, and P (ICP AES EPA method 6010b, digestion EPA method 3052; USEPA, 2013). NIR was used to determine total carbon and total N (Mowrer et al., 2014). The gravimetric water content of the litter was determined by drying it at 65°C for 48 h and initial litter pH was determined at 1:5 litter/water mixture using an Accumet AB15 pH Meter (Cole-Parmer, Vernon Hills, IL). Samples were stored in sealed containers at 4°C while not in use. The range of litter characteristics determined in this study are presented in Table 4.1.

Litter Buffering Capacity

To determine the pHBC curves of the litters, titrations were performed using standardized HCl and NaOH (0.5 M) additions from 0 to 1000 mmol kg litter^{-1} (dry weight basis). For each acid/base treatment, two replicates were used: 1 g (at native water content) of litter was placed in 50-mL centrifuge tubes, acid/base was added and total volume was brought up to 20 mL using deionized water. Samples were shaken for 5 min, 12 h, and 24 h and pH was measured using an Accumet AB15 pH Meter (Cole-Parmer, Vernon Hills, IL). The analysis of the first litter indicated possible mineralization and nitrification during the shaking time. To eliminate the effect of microbial reactions on litter pH, 500 mg L^{-1} Ag_2SO_4 was added as an enzymatic and microbial inhibitor. The pHBC of each litter was analyzed by regression analysis for both acid and base additions at "as is" water content and on a dry weight basis. Linear regression analysis was performed using SAS v. 9.3 PROC REG (SAS Institute, 2013). Data were fit using the equation:

$$A\ (mmol\ H\ kg\ litter^{-1}) = m * pH + C \qquad \text{Eq. [7]}$$

where A is the amount of acid or base added (positive for base additions and negative for acid additions), m is the pHBC (mmol H (kg litter pH)$^{-1.}$

Data obtained through titration were also fit to a sigmoidal curve defined by Nelson and Su (2010). The use of the sigmoidal function allowed for the calculation of the pHBC as a function of litter pH. Using SigmaPlot® Dynamic Fit Wizard, the curve was fit using the Marquardt-Levenberg algorithm which determined the values of the parameters by minimizing the sum of squares of differences between the actual and fitted values through iteration. The four-parameter sigmoidal function can be described by the equation (Nelson and Su, 2010):

$$pH = pHmin + \frac{a}{1+e^{\frac{-(A-Amid)}{b}}} \qquad \text{Eq.[8]}$$

where *pHmin* is the minimum pH reached through acid addition, *a* is the difference between the maximum pH reached and *pHmin*, *A* is the amount of acid or based used (positive for base additions and negative for acid additions), *Amid* is the value of *A* at the inflection point, and *b* defines the shape of the curve. The *pHmid* which is the *pHmin+a/2* was also determined for midpoint calculations of buffering capacity (Nelson and Su, 2010). The pHBC was calculated by solving for *A* in Eq. [8] and taking the first derivative of the derived equation:

$$\frac{dA}{dpH\ kg\ litter} = \left(\frac{ab}{(a+pHmin-pH)(pH-pHmin)}\right) = \frac{mmol\ H}{pH\ unit\ kg\ litter} \qquad \text{Eq.[9]}$$

Litter characteristics and both calculated linear and sigmoidal pHBCs were analyzed using SAS v. 9.3 PROC REG to determine possible correlations. To determine if the fitted lines for individual litters were uniquely different and could not be represented by a single overall model (“full model”),, residual sum of squares analysis was used (Milliken and DeBruin, 1978). Significant difference between the full model and the cumulative individual models would indicate differences in pHBC among the litters.

Near Infrared Reflectance Spectroscopy Measurements

NIR measurements were made on a Foss NIR systems 6500 and using WINISI WINSCAN v. 1.50 software (FOSS North America, Eden Prairie, MN). Each litter was packed into a ring sampling cup (IH-0386) at “as is” water content (approximately 5 g), and was scanned from 400-2500 nm at 2-nm intervals. Software reported reflectance as log (1/R), where R is reflectance. Spectral analysis consisted of the second derivative treatment of log (1/R) using 4-nm gap spacing which was then regressed against the three different determinations of buffering capacity: 1) the linear pHBC calculated on a dry weight basis, 2) the linear pHBC calculated at the “as is” water content, and 3) the pHBC calculated at *pHmid* determined by the sigmoidal fit. Statistical analysis was performed by the software package including calibration and a cross-validation procedure of the data for all three fits of pHBC. Cross validation consisted of the removal of every fifth sample for its use for validation during calibration. This validation procedure was repeated so that every sample was used for both calibration and validation.

Litter pH and Alum

To determine if the pHBC of the litter could increase the accuracy of alum additions, an empirical model was derived to estimate alum additions for a target pH change. The amount of alum hydrate ($Al_2(SO_4)_3 \bullet 18H_2O$) needed to reduce litter pH was calculated using the initial pH (pHi), a target final pH (pHf), the litter pHBC, and the acid equivalent of aluminum (Al^{3+}) where:

$$\frac{mmol\ H}{kg\ dry\ litter} = \int_{pHi}^{pHf} pHBC\ dpH \qquad \text{Eq. [10]}$$

and

$$\frac{g\ alum}{kg\ dry\ litter} = \frac{mmol\ H}{kg\ dry\ litter}\ x\ \frac{mmol\ Al^{3+}}{mmol\ H}\ x\ \frac{mmol\ Al^{3+}}{mmol\ alum} x\ \frac{666.42\ g\ alum}{mmol\ alum} \qquad \text{Eq. [11]}$$

Although alum can potentially form six moles of protons for each mole of alum hydrolyzed (Eq.[6]), the actual acid equivalent of alum (mmol H to mmol Al^{3+}) is a function of pH and the potential for formation of $Al_x(OH)_x$ products (Fournier et al., 2008). To determine the acid equivalent of alum as a function of pH, titrations of $AlCl_3$ (0.02, 0.04, and 0.08 mol Al^{3+} L^{-1} in 1 N NaCl) with 0.5 N NaOH were performed. Fitting the titration data for all Al^{3+} concentrations with the sigmoidal curve described above led to the following equation:

$$\frac{mmol\ H}{mmol\ Al^{3+} ph\ unit} = 2.7 - 0.15\ x \ln\left(\frac{6.97+3.64\ - pH}{pH-3.64}\right) \qquad \text{Eq. [12]}$$

where the acid equivalent could be calculated at pHf in Eq. [12].

Using ten litters from the 37 litters mentioned above, alum rates were calculated from the empirical model above to achieve a decrease in pH from pHi to a range of target pHfs from 5 to

7.5 in 0.5 increments. With two reps for each alum addition, the calculated alum rate (g kg litter^{-1}) was added to 5 g litter (dry weight basis) with 100 mL solution (500 mg L^{-1} Ag_2SO_4), shaken for 24 h, and the pH was measured.

RESULTS AND DISCUSSION

Litter Buffering Capacity

A preliminary study conducted on measuring litter pHBC on Litter 1 indicated that mineralization and nitrification processes may have affected litter pH during the 12 h and 24 h shake times (Fig. 4.1, top). The large decrease in litter pH at the 24 h shake time was most likely due to nitrification occurring in the litter (Eq.4 and 5). While the litter was in solution, it was likely that air in the head space combined with constant shaking led to overall aerobic conditions which enabled rapid nitrification in the samples (Norton, 2008). Additionally, Litter 1 contained an initial 4300 mg kg^{-1} NH_4-N, which provided a large amount of substrate for nitrification. The addition of 500 mg L^{-1} Ag_2SO_4 adequately inhibited microbial/enzymatic activity, leading to similar curves for the 12 h and 24 h shaking times (Fig. 4.1). To allow for ample equilibrium time and to inhibit microbial activity, the 24 h shaking time and addition of Ag_2SO_4 was adopted to determine the remaining litter pHBCs. Currently, no standard procedures exist to measure pHBC in litter, and calcium carbonate equivalent procedures rely on both the addition of strong acids and boiling of the litter/acid solution (Horwitz, 1980). Our proposed method allows for the ability to measure the effect of the litter on pH in equilibrium without undermining the structure of the litter.

Linear pHBC ranged from 187 to 537 mmol H (pH unit kg dry litter)$^{-1}$ with the full model for all litters measured being 287 mmol H (pH unit kg dry litter)$^{-1}$ (Table 4.2). Linear models were statistically different from the "full" linear model (p value <0.001 and had good overall fit with only three litters being below an adjusted R^2 of 0.90. The pHBC calculated from sigmoidal fits at *pHmid* predicted lower pHBCs for all litters except the "full" model, with a range of 161 to 456 mmol H (pH unit kg dry litter) $^{-1}$. Again, the individual models were statistically different from the "full" sigmoidal model (p value <0.001). For all litters, the sigmoidal fit had a higher adjusted R^2 value than the linear fit. However, four of the litters could not be fit to the sigmoidal curve using the parameters defined (Table 4.2). The Linear pHBC and Sigmoidal pHBC at *phmid* were linearly related with a R^2 of 0.68.

The increased goodness of fit with the sigmoidal curve is more clearly demonstrated by Fig. 4.2. Whereas the linear fit adequately describes the mid-range of both acid and base additions, increasing additions led to the distinct shape of the pH plateauing. Interestingly, the midpoint and the degree in which the lines curved varied among the litters. Litter 13 has similar fits between linear and sigmoidal curves, with 0.98 adjusted R^2 for both and a more linear sigmoidal curve. Litters 14 and 24 have increased goodness of fit with the sigmoidal curves, but the linear curve also had high adjusted R^2 values of 0.99 and 0.98 respectively. In contrast, Litter 11 has a distinct shape that is much better characterized by the sigmoidal equation (Fig. 4.2). Sigmoidal shapes for cattle and poultry manure buffering curves have been determined by Derikx et al. (1994) with additions up to 5000 mmol H kg dry weight^{-1}. The goodness of fit for the linear curves may have been reflective of the overall range of acid/base added and the corresponding range of pH. The minimum pH achieved through acid additions was 4.98 whereas the maximum pH obtained through the addition of base was 10.6. Increased additions of acid/base leading to a larger pH range would likely decrease the ability of the linear model to fit pHBC data, with the sigmoidal shape likely becoming more dominant. However, it is unlikely that mineralization, nitrification, or even alum additions could lead to pH shifts of this magnitude. Nitrification is typically reduced or inhibited at pH below 6.5 due to the decrease in NH_3 as a substrate (Burton and Prosser, 2001; Norton, 2008). At pH greater than 9.25 (at 25˚C), NH_3 loss is favored; this loss counters increased pH from mineralization (Eq. [3]; Kissel and Cabrera, 2005). With alum additions of 1816 kg alum house^{-1}, Moore et al. (2000) observed an initial drop in litter pH from 8 to 5.7. With these observations for the pH range of broiler litter in mind, acid/base additions used in this experiment were representative of potential changes in litter pH.

Whereas differences in the two fits are small, the benefit of the sigmoidal curves for determining pHBC allows for the modeling of the pHBC as a function of pH as opposed to a single value across all pH ranges (Nelson and Su, 2010). The increased accuracy in estimating pHBC may be particularly important when pHBC is used in computer simulation model calibration and model validation for NH_3 loss (Cabrera et al., 2008; Kissel et al., 2012). As pH increases/decreases away from the defined *pHmid*, pHBC also increases (Fig. 4.3). The extent to which pHBC increases is a function of the curvature of the sigmoidal function, parameter *b* (Table 4.3; Fig 4.3). As the *b* parameter increases, the extent to which the pHBC changes as a function of pH decreases, further demonstrated with Eq. [9]. Litter 13, with a *b* =485.27, remains relatively linear across the pH range of 6.5 to 9.5; whereas Litters 2, 11, and 14 have pHBCs with distinct parabolic shapes across the same pH range. However, calculating pHBC with a sigmoidal function does have limitations. Litter pHBC calculated with the sigmoidal equation is strictly limited by the range of pH measured and the *pHmin* parameter defined by the fit. As the pH approaches *pHmin* or *pHmi*d + *a* (the maximum pH measured), the calculated pHBC will rise rapidly until becoming negative as defined by Eq. [9]. When calculating pH outside of the experimentally determined pHBC, the calculated pHBC may be overestimated or invalid. When choosing the sigmoidal versus linear models, factors such as pH range, time, and needed accuracy must be taken into account.

Litter pHBCs were regressed against water content and individual litter characteristics (range in Table 4.1). No litter characteristic showed a relationship with the linear pHBC calculated on a dry or "as is" weight basis, or the sigmoidal pHBC at pHmid. Buffering capacity in soil systems is a function of soil organic matter, carbonate equilibrium, oxide and hydroxides, and the dissolution of clay minerals (Bloom, 2000; Ferguson et al., 1984; Nelson and Su, 2010). Similarly, high organic matter content, volatile fatty acids, calcium carbonate and calcium ions (from the addition in feed), and NH_3/NH_4 equilibrium in broiler litter may be the dominant non-microbial buffering processes in litter (Derikx et al., 1994; Pocknee and Sumner, 1997).

Derikx et al. (1994) proposed that the shape of the buffering curves for swine, cattle, and poultry manures may indicate substances responsible for buffering. The group states that the flatness observed around pH 9.25 is a function of NH_4/NH_3 equilibrium and carbonate ions may contribute to this effect at higher pH. Further, calcium carbonate and the presence of volatile fatty acids may have led to buffering at low pH. With both of these mechanisms credible in broiler and layer litter, calcium carbonate may have the dominant effect in layer litter from the addition of excess calcium to feed and presence of eggshells. Additionally, the potential formation of polymers Al-phosphates/variscite ($Al(PO_4)\bullet 2H_2O$) and struvite ($MgNH_4PO_4.6H_2O$) has been proposed in broiler litter and animal slurry (Moore et al., 2000; Peak et al., 2002; Sommer and Husted, 1995). High P and high Al may lead to variscite formation at lower pH favoring H buffering in litters. Eight litters contained Al values upward of 10 g kg^{-1} total Al and alum additions may favor this reaction. High P and NH_4^+ are common in litters which could potentially lead to struvite formation, aiding in buffering at high pH ranges when the litter is in solution. With a wide range of both inorganic and organic components in poultry litter, there are likely many mechanisms participating in buffering. Dominant mechanisms will likely be a function of housing, storage, removal, and feed. For example, excess calcium carbonate from feed, the bedding material used, or the amount of soil removed from the housing floor could lead to very different sources of buffering in poultry litter.

Near Infrared Reflectance Spectroscopy Measurements

NIR calibration for the 37 litters with the linear pHBC calculated at the "as is" water content and NIR predictions resulted in a calibration R^2 of 0.902 and a corrected standard error of prediction of 19.15. Calibration fits decreased with linear pHBC expressed on a dry weight basis with an overall R^2 of 0.66 (Fig. 4.4). Data fit using the sigmoidal *pHmid* pHBC had a R^2 of 0.50 and corrected standard error of 46.55. The high correlation with pHBC on an "as is basis" versus pHBC on a dry weight basis could not be explained by the water contents of the litters. Regression between litter pHBC and litter water content showed no relationship with the correlation of linear pHBC "as is" or linear pHBC on dry weight basis with litter water content and both having an R^2 of 0.05. With NIR performed on "as is" litters, the stronger relationship may be a function of concentration of buffering constituents in the litter solution. Strong calibrations on NIR have been determined for litter water content (Mowrer et al., 2014). Using this factor, litter pHBC could be transformed on a dry weight basis as needed. Although calibration statistics were strong for the linear "as is" pHBC, validation statistics were less than optimal. The 1-validation ratio (VR) was 0.29 and the standard error of cross-validation (SECV) was 51.9. This low validation of the NIR model may be a function of the sample size. Although 37 litters with a wide range of characteristics were measured for pHBC, increasing the sample size and independent validation may lead to this being a useful tool in soil and manure testing laboratories.

Whereas relationships with soil pH and NIR have been previously determined, with R^2 from 0.5 to 0.71 (Chang et al., 2001; Islam et al., 2003; Viscarra Rossel et al., 2006), there is no NIR spectral response directly associated with pH or liming requirement (Stenberg et al., 2010). Viscarra Rossel et al. (2006) observed in mid infrared reflectance spectroscopy positive contributions from organic acids and smectite for pH in calcium chloride determinations. Similar to pH, it is unlikely that a particular or singular spectral response led to the high correlation for pHBC, instead pHBC is likely predicted from many constituents. Litter pHBC will be a function of both the acid and alkaline components of the litter which could be present in a large range of the spectra.

Litter pH and Alum

Alum additions calculated from Eq. 11, led to a range of alum additions from 38 to 200 g alum kg litter^{-1} to achieve the target pHfs ranging from 5 to 7.5 for the ten litters. The model performed well for predicting the amount of alum needed to achieve the target pHfs in the higher pH range (6.5 to 7.5) but model accuracy decreased with decreasing pH (Fig. 4.5). The root mean square error (RMSE) of the model over the entire pH range was 0.63, but was reduced to 0.07 when calculated from the range of pH from 6.5 to7.5. Interestingly even with individual litter pHBCs incorporated in the model, the performance of the model varied with each litter. The model under predicted the amount of alum needed to drop litter pHf in the range of 5 to 6 for the majority of the litters, however, Litters 22 and 24 responded to alum additions as a function of pHBC as expected.

With the alum experiment being conducted under the exact same conditions as the determination of the litter pHBC (1:20 litter/ solution ratio; 500 mg L^{-1} Ag_2SO_4; and 24 h shake time), issues with the empirical model were likely derived from the calculations of the alum acid equivalency (Eq.13). The alum acid equivalency was determined in a pure solution, which in contrast to the complex solution chemistry of poultry litter, may have failed to determine the effect of other constituents on Al hydrolysis reactions. To further understand differences in the prediction capability of the empirical model, the RMSE was calculated for each litter and regressed against individual litter characteristics. Regression analysis indicated that the RMSE was positively correlated (p-value<0.1) to total P, N, and zinc with R^2 values of 0.34, 0.39, and 0.32 respectively. These relationships indicate that these constituents likely reduce the acid equivalency of Al at low pH, potentially through precipitation reactions, interactions with other cations, or binding with the litter organic matter.

With the ability of alum to greatly reduce P solubility in litter extracts and in runoff after land-application (Moore et al., 2000; Moore and Miller, 1994; Warren et al., 2008), increasing concentrations of P in the poultry litter may have reduced the Al acid equivalency in this study. Theoretically, alum additions to poultry litter will reduce soluble phosphorus either through the formation of $Al(OH)_3$ floc (pH 6 to 8), which reduces both inorganic P and organic P in solution through the flocculation of organic matter, or under at low pH (<6) through the formation of $AlPO_4$ (Cook et al., 1993; Moore and Miller, 1994). No direct evidence for the precipitation of $AlPO_4$ has yet been determined. However, Peak et al. (2002) determined through X-ray adsorption near-edge structure spectroscopy that phosphate reacts with amorphous $Al(OH)_3$ via adsorption in alum-treated litter. Additionally, Hunger et al. (2004) determined that 40% of the total P in alum-amended litter was associated with Al. Either $AlPO_4$ formation or amorphous

$Al(OH)_3$ adsorption to P in the litter may have reduced the Al ions in solution, affecting the hydrolysis series of Al and reducing the overall effect on litter pH.

While the mechanisms of alum and P in broiler litter have been well studied, the effect of total N on the prediction capability of Eq. 12 is unclear. The relationship between increased total N in the litters and decreased prediction capability may be representative of the adsorption of Al to organic N compounds, removing Al from solution. Tan et al. (1971) proposed the formation of Al-organic matter complexes in the extract of poultry litter through covalent bonds with amino or hydroxyl groups in the litter organic matter. Litter contains an average of 3% total N, of which 40 to 80% is organic (Nahm, 2005; Rothrock et al., 2010; Stephenson et al., 1990). Increasing organic N compounds may reduce the acid equivalency of the alum, but those data for organic N are not available for the litters used in this study.

Similar to total N, the effect of zinc on the prediction capability of the alum model is ambiguous. However, Moore et al., (1998) determined an average reduction of 56% of zinc concentrations in runoff from land-applied poultry litter with the addition of alum. While the group did not elaborate on the mechanism of zinc reduction, they did hypothesize the reduced affinity of copper to soluble organic carbon in alum treated litter and the potential for $Al(OH)_3$ sorption of copper. Additionally, Jackson et al. (2003) determined that the major species of zinc in poultry litter was present as a neutral complex. As pH drops with the addition of alum, these zinc complexes may dissociate, act as an acidity sink and reduce the acid equivalency.

The proposed model for alum additions shows the importance of litter pHBC to determining the effect of alum on litter pH. The model accurately predicted pHf in the range of 6.5 to 7.5. This work represents the first step to making more precise alum recommendations: understanding litter pHBC and the potential reactions of alum added to poultry litter. Alum has been shown to significantly reduce NH_3 loss and increase bird weights when additions lead to a drop in litter pH to or below 7 (Kim and Choi, 2008; Moore et al, 2000). This drop in pH also leads to N retention in house and during composting and reduced P in runoff from the application of litter, favoring its use as an alternative fertilizer (Delaune et al.; 2004; Moore et al., 1999; Sims and Luka-McCafferty, 2002). However, due to varying litter pHBC and alum reactions, the target pH of the litter is not always reached, discouraging the use of this product. With the potential ability to quickly predict litter pHBC from NIR and the incorporation of pHBC into alum recommendations, further research on these tools may reduce alum additions, encouraging the use of this product in house, during composting, and for fertilizer use.

CONCLUSIONS

Litter pHBC was accurately determined using the addition of microbial inhibitors and a shaking time of 24 hr, leading to near equilibrium reactions. The pHBC was adequately fit to both linear and sigmoidal curves, with sigmoidal curves defining buffering capacity as a function of litter pH. Sigmoidal curves may lead to more accurate estimations of pHBC for uses in a defined pH range, but linear pHBC was fit well to NIR estimations and alum additions. Poultry litter pHBC ranged from 187 to 537 mmol H (pH unit kg dry litter) $^{-1}$ with average being 287 mmol H (pH unit kg dry litter) $^{-1}$. No litter characteristic measured could explain significant differences among pHBC, but literature suggests that measuring $CaCO_3$, organic matter, and volatile fatty acids may increase the understanding of the mechanism behind buffering in litter. Additionally, NIR shows promise in accurately and quickly estimating litter pHBC (calibration R^2 0.90), but further studies need to be conducted for model validation. The pHBC derived empirical model accurately predicted the amount of alum needed to drop litter pH for the range of pH 6.5 to 7.5, but under estimated alum additions to drop litter pH below 6. The reduced prediction capability was attributed to interactions of Al with P, N, and zinc, reducing the acid equivalency of alum. With further research, the precision use of alum can be increased, favoring the proper use of this chemical. Increasing alum use will increase bird and human health during production and increase N and phosphorus retention in litter. Additionally, accurately measuring litter pHBC will also lead to improved capabilities for modeling NH_3 volatilization from surface-applied broiler litter for crop production, encouraging the use and disposal of this byproduct.

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TABLES AND FIGURES

Table 4.1. Range of initial poultry litter characteristics used for the determination of litter pH buffering capacity.

Element (g kg dry litter^{-1})	Min	Max.	Avg. ± st.dev.
P	7.7	107.5	31.6 ± 19.7
K	15.9	86.3	42.8 ± 17
Ca	16	232.7	55.5 ± 48.1
Mg	4.4	22.3	9 ± 3.8
S	4	21.8	10.6 ± 4.6
Mn	0.3	1.5	0.7 ± 0.3
Fe	0.3	23.9	3.7 ± 4.4
Al	0.2	48.7	6.2 ± 8.9
B	0	0.2	0.1 ± 0.03
Cu	0	1.2	0.4 ± 0.3
Zn	0.2	1.3	0.6 ± 0.2
Na	2.2	24.3	5 ± 2.2
C	278.4	791.9	439.3 ± 119.9
N	14	73.4	42.8 ± 12.2
pH†	6.52	8.84	8.04 ± 0.61

†pH measured at 1:10 g litter to mL H_2O

Table 4.2. Poultry litter water content, linear pH buffering capacity, and sigmoidal pH buffering capacity calculated at the sigmoidal pHmin with their respective fits for all litters (full model) and 37 litters measured.

Litter	WC g kg dry litter^{-1}	Linear pHBC mmol OH (pH unit kg dry litter^{-1})	R^2	Sigmoidal pHBC† mmol OH (pH unit kg dry litter^{-1}	R^2
Full	-	286.7	0.76	295.6	0.777
1	300	330.9	0.966	230.0	0.993
2	318	356.0	0.981	290.3	0.995
3	371	345.2	0.984	285.2	0.997
4	522	368.3	0.956	291.5	0.997
5	275	544.7	0.963	438.8	0.986
6	741	517.4	0.987	456.3	0.992
7	229	525.9	0.927	291.6	0.997
8	346	330.7	0.982	250.1	0.995
9	467	406.1	0.977	336.4	0.994
10	548	382.6	0.972	328.3	0.977
11	257	265.4	0.960	173.5	0.989
12	497	392.4	0.986	309.4	0.996
13	244	300.9	0.979	262.7	0.986
14	427	399.7	0.989	319.7	0.997
15	580	537.4	0.940	•	•
16	380	358.2	0.963	272.7	0.987
17	280	344.3	0.740	294.8	0.916
18	280	349.3	0.830	•	•
19	470	440.1	0.942	310.8	0.985
20	363	373.7	0.961	301.0	0.944
21	335	389.0	0.978	287.1	0.994
22	528	318.8	0.970	•	•
23	637	459.5	0.975	363.4	0.993
24	271	357.6	0.982	290.4	0.989
25	404	332.0	0.984	241.4	0.995
26	366	343.4	0.974	237.0	0.997
27	292	320.8	0.963	218.8	0.989
28	356	354.6	0.962	•	•
29	411	394.6	0.990	338.5	0.994
30	1053	421.0	0.887	305.0	0.964
31	420	334.9	0.986	277.9	0.994
32	407	403.9	0.983	359.3	0.985
33	429	239.6	0.976	171.2	0.994
34	438	257.3	0.989	206.9	0.998
35	172	217.9	0.987	170.6	0.996
36	554	189.7	0.983	161.1	0.996
37	359	219.1	0.982	174.3	0.997

† calculated at pH mid;
• data would not fit to sigmoidal curve

Table 4.3. The fit parameters determined by the sigmoidal curve of the poultry litter pH buffering capacity for four litters.

Litter	y0	Amid	x0	b	pHmid
2	5.86	4.6	-154.52	333.86	8.16
11	5.97	4.22	15.64	183.06	8.08
13	4.38	7.39	211.46	485.27	8.075
14	6.04	4.27	-65.26	341.25	8.175

Figure 4.1. The determination of the litter pH buffering capacity with Litter 1 without and without the addition of 500 mg L^{-1} Ag2SO4 for shaking times 5 min, 12 h, and 24 h.

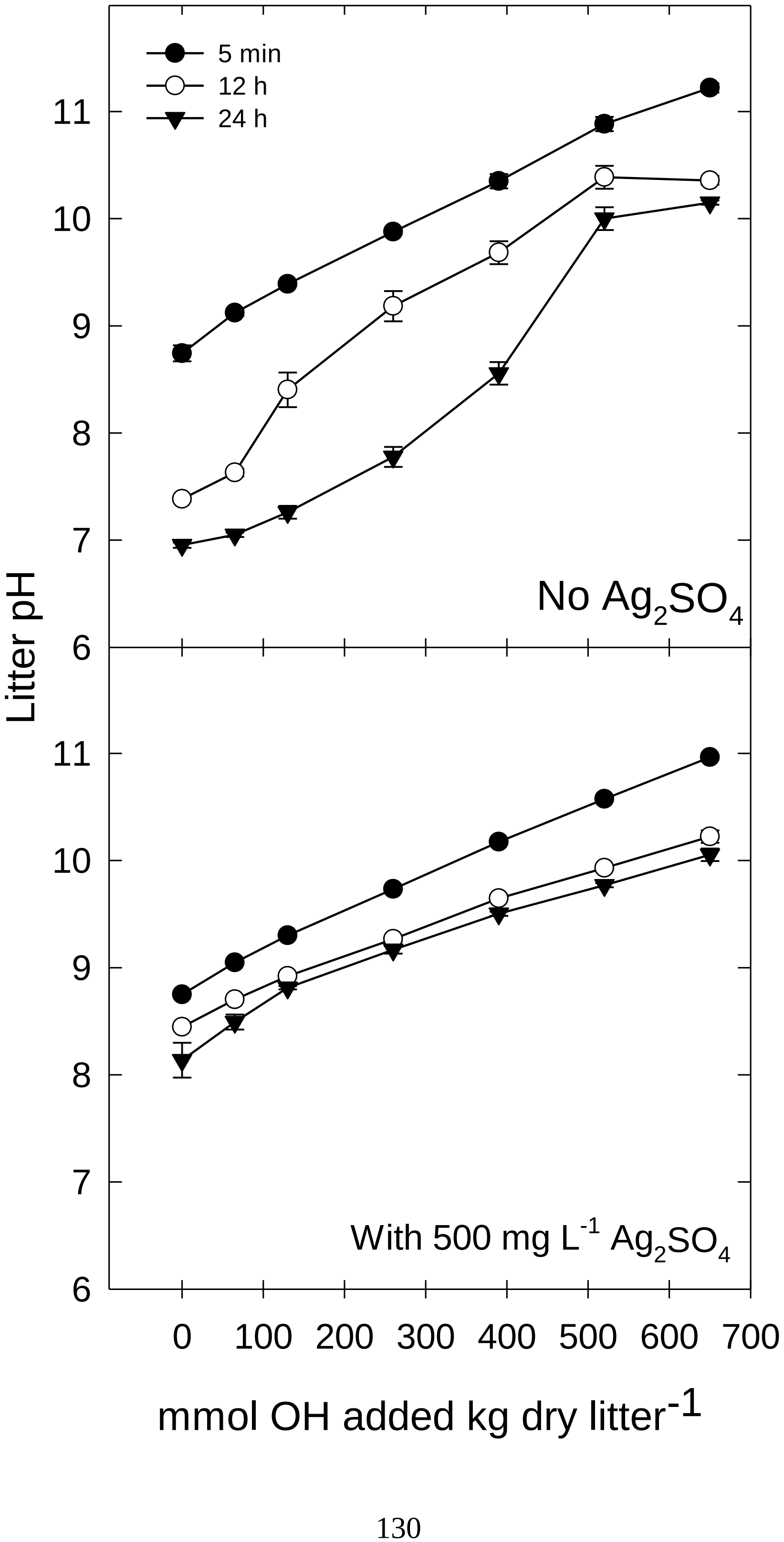
Figure 4.2. Differences in linear and sigmoidal fit of litter pH buffering capacity of Litters 11, 13, 14, and 24.

Figure 4.3. Changes in litter pH buffering capacity as a function of pH in the pH range of 6.5 to 9.5 using derivative of sigmoidal curves.

Figure 4.4 NIR predictions for linear litter pH buffering capacity on an “as is” water content basis and dry weight basis.

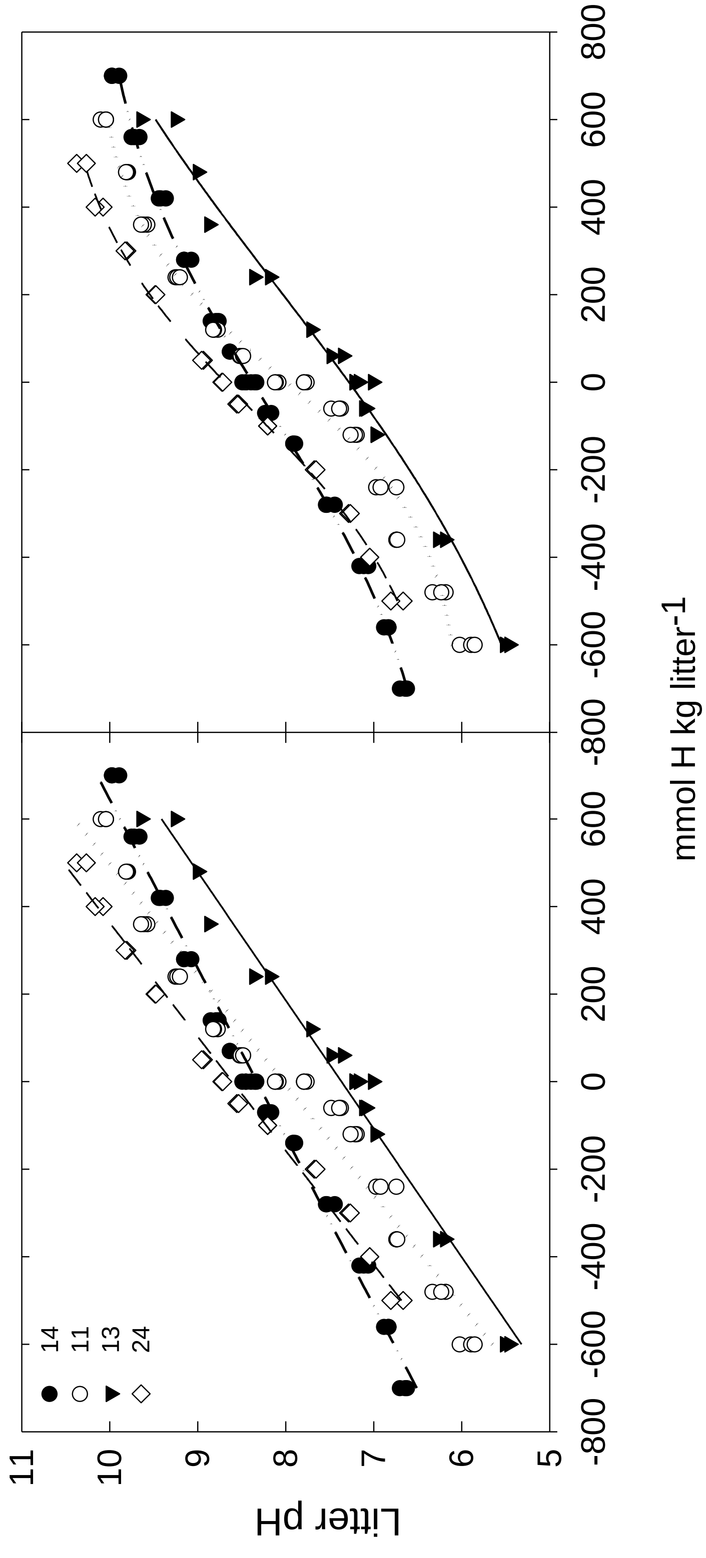
Figure 4.5. Litter pH predicted through alum additions using the empirical model versus litter pH measured after alum additions.

Figure 4.1.



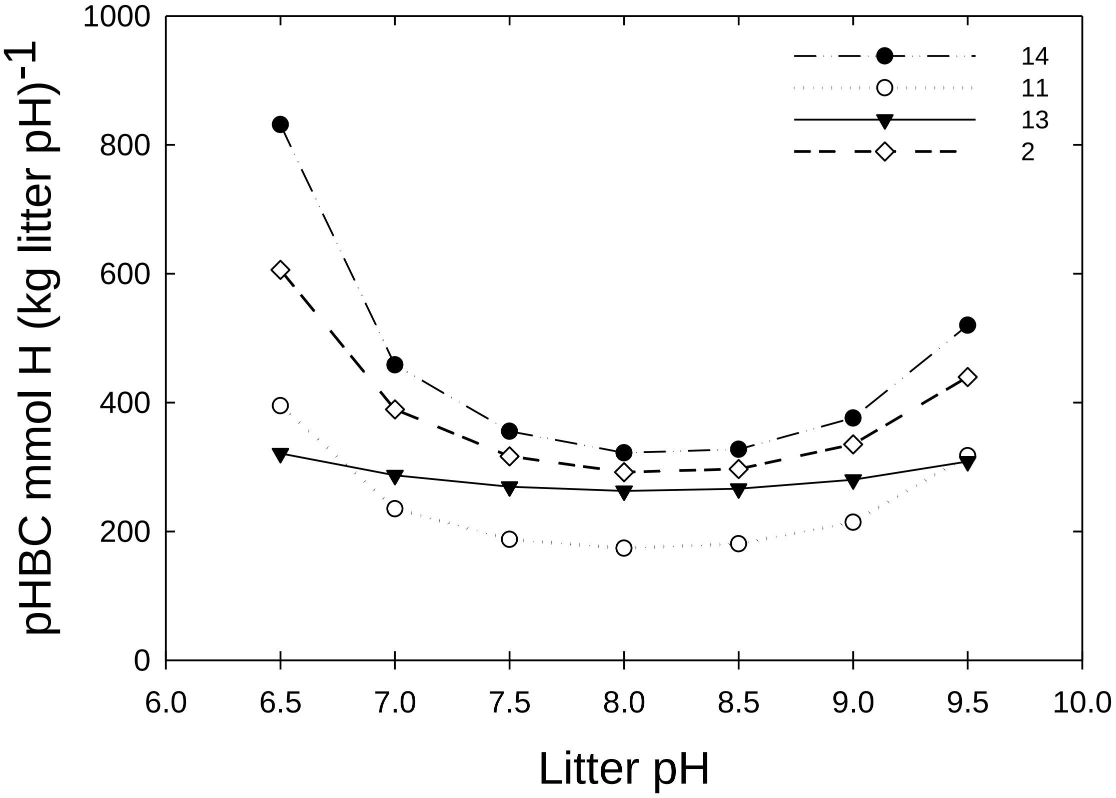
● 5 min
○ 12 h
▼ 24 h
No Ag_2SO_4
With 500 mg L^{-1} Ag_2SO_4
Litter pH
6
7
8
9
10
11
0
100
200
300
400
500
600
700
mmol OH added kg dry litter^{-1}

Figure 4.2.



Litter pH
11
10
9
8
7
6
5
-800
-600
-400
-200
0
200
400
600
800
mmol H kg litter-1
● 14
○ 11
▼ 13
◇ 24

Figure 4.3.



pHBC mmol H (kg litter pH)$^{-1}$
1000
800
600
400
200
0
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
Litter pH
14
11
13
2

Figure 4.4.

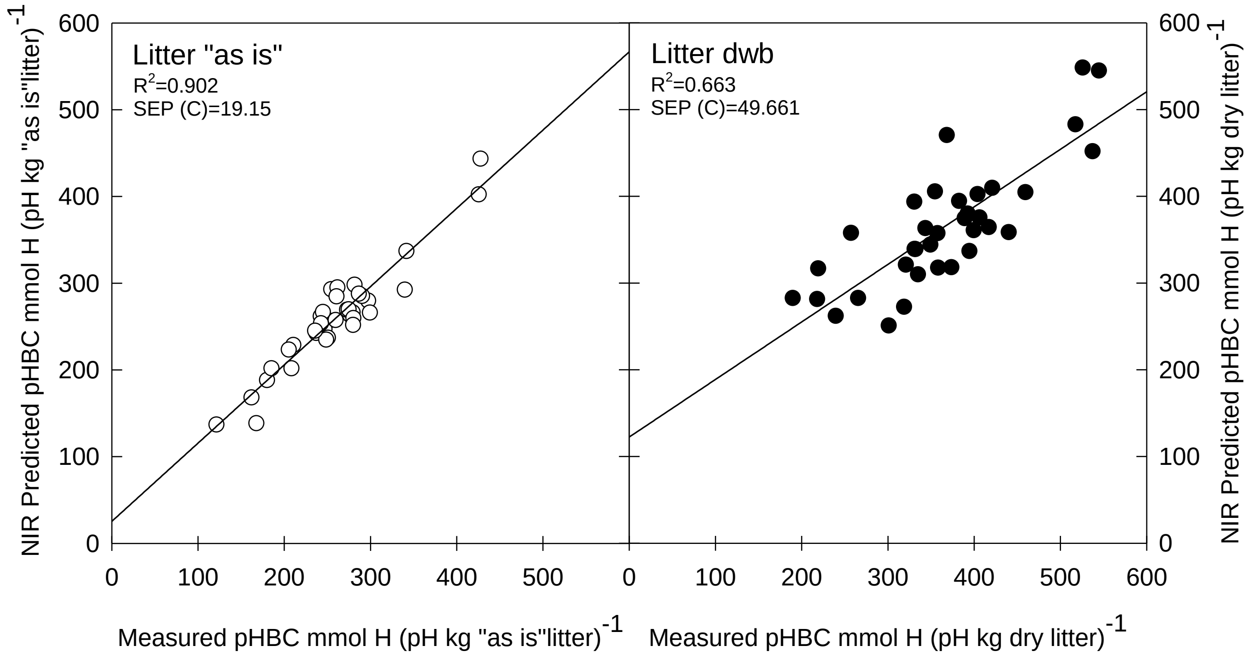
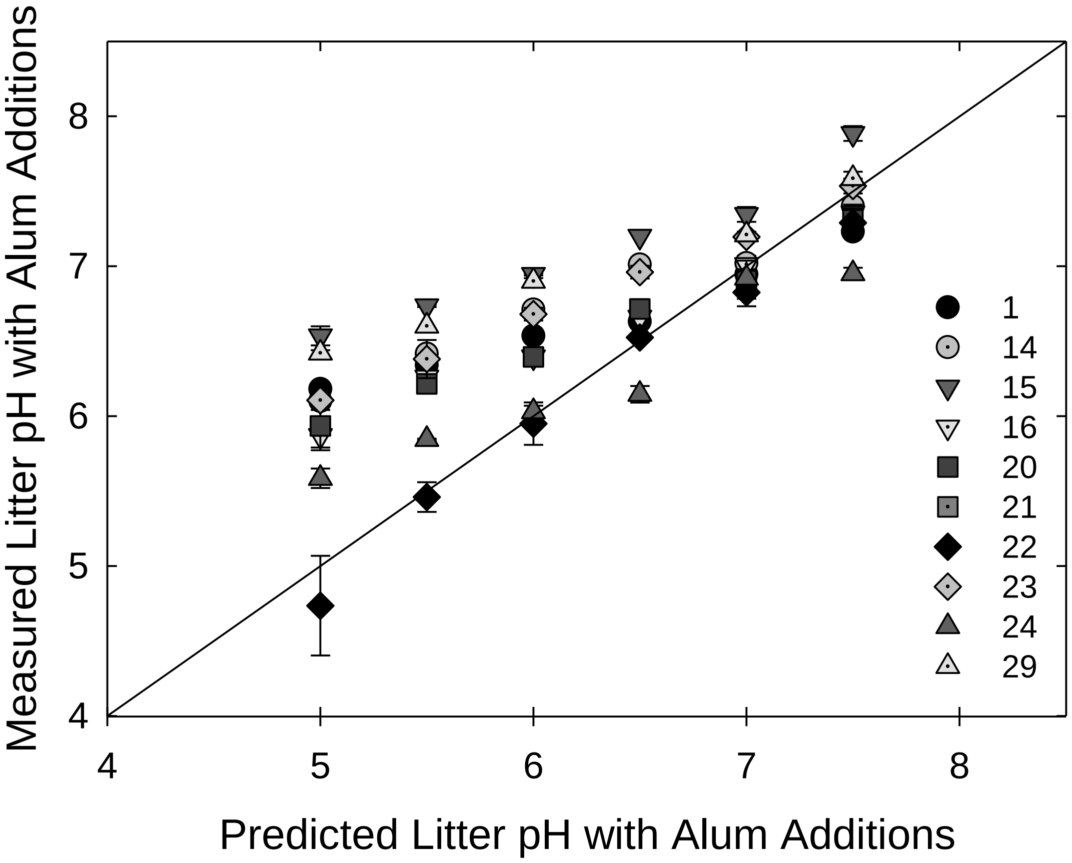

Litter "as is"
R²=0.902
SEP (C)=19.15
Litter dwb
R²=0.663
SEP (C)=49.661
NIR Predicted pHBC mmol H (pH kg "as is"litter)-1
NIR Predicted pHBC mmol H (pH kg dry litter)-1
Measured pHBC mmol H (pH kg "as is"litter)-1
Measured pHBC mmol H (pH kg dry litter)-1
0
100
200
300
400
500
600

Figure 4.5.



Measured Litter pH with Alum Additions
Predicted Litter pH with Alum Additions
4
5
6
7
8
4
5
6
7
8
1
14
15
16
20
21
22
23
24
29

CHAPTER 5

MODELING AMMONIA VOLATLIZATION FROM SURFACE-APPLIED BROILER LITTER[1]

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[1] Cassity-Duffey, K., M.L Cabrera, and J. Rema. To be submitted to Ecological Modeling.

ABSTRACT

Ammonia (NH_3) volatilization from surface-applied broiler litter can lead to large losses of plant available nitrogen (N) to the atmosphere, reducing the efficacy of broiler litter as fertilizer. Ammonia volatilization is a function of both initial litter characteristics and weather conditions after application. A mechanistic model was developed to simulate NH_3 loss from surface-applied litter under varying relative humidity (RH) and temperature conditions in laboratory studies conducted using a dynamic flow through chamber. The model contained sub-models for litter water content (WC), organic N mineralization, ammoniacal-N equilibrium, adsorption, and gas partitioning. In lab and field studies, the WC sub-model accurately (R^2=0.82) simulated the effect of diurnal changes of RH and temperature on litter WC, which fluctuated on a diurnal basis from 0.05 to 1.5 g H_2O g litter^{-1}, impacting both mineralization and the pool of NH_4-N/NH_3-N subject to NH_3 volatilization. Incorporating the litter WC sub-model into a mechanistic NH_3 volatilization model, simulated NH_3-N loss for 28-d field studies with R^2=0.81. Results determined in this study suggest that modeling the effect of RH on litter WC will improve estimations of litter mineralization and volatilization as well as increase the understanding of the mechanisms of NH_3 loss from surface-applied broiler litter.

Abbreviations: See Appendix 5.1.

INTRODUCTION

The surface-application of broiler litter to pasture is a common practice in the southeastern United States to supply plant micro and macro-nutrients and improve soil fertility (Marshall et al., 1998; Mitchell and Tu, 2006). Broiler litter is an inexpensive alternative to traditional fertilizers because it costs $10 to 35 per Mg (Dunkley et al. 2011) and provides a valuable source of plant available nitrogen (N) (Bitzer and Sims, 1988; Gordillo and Cabrera; Nicholson et al., 1996). However, plant-available N in broiler litter can be highly variable and subject to large losses through ammonia (NH_3) volatilization, which has been found to range from 4 to 60% of the total N (TN) applied in laboratory and field experiments (Brinson et al., 1994; Cabrera and Chiang, 1994; Lau et al., 2008; Lockyer et al., 1989; Marshall, 1998).

Nitrogen lost through NH_3 volatilization can lead to a substantial decrease in the N fertilizer value of litter and potentially lead to environmental degradation through the introduction of excess nutrients into the surrounding ecosystem (Pelletier, 2008; Søgarrd et al., 2002). University and state agricultural laboratories typically cite that 50 to 60% of the applied TN in broiler litter will be available to crops (Mowrer et al., 2014), however, these recommendations fail to take into account differences in N mineralization and NH_3 loss as a function of environmental conditions throughout the growing season. Adequate prediction of available N is reliant on accurate measurements of initial litter characteristics, the understanding of mineralization of organic N to inorganic N, and improving prediction capabilities for NH_3 loss. Mechanistic or process-based models represent an important tool that can increase the accuracy of litter application for producers and increase the understanding of mechanisms behind NH_3 volatilization. Mechanistic models allow for differences in litter composition as well as climate and allow for predicting loss over time (Montes et al., 2009; Ni, 1999).

Currently, there are a number of mechanistic models proposed for the prediction of NH_3 loss for land-applied manures (Genermont and Cellier, 1997; Montes et al., 2009; Ni,1999). However, most models have been developed for the application of swine and cattle manure slurries to arable land with few models investigating broiler/poultry litter. The model MANNER (Chambers et al., 1999) has been validated with poultry litter applied to grain stubble and cropland. While MANNER accurately predicted plant-available N with poultry litter incorporated into the soil, when poultry litter was applied as a top dressing on the soil surface, the prediction capability of the model decreased. Additionally, Thompson et al. (1990) determined that vegetative cover led to a 50% increase in NH_3 loss for surface-applied swine slurry. The surface-application of broiler litter not only reduces the interaction of litter and soil, but it also increases interaction of litter with atmospheric conditions, subjecting it to temperature and water fluctuations on a seasonal and diurnal basis.

Previous work by our lab group (Cassity-Duffey et al., 2014a; Cassity-Duffey et al., 2014b.) and work by Nimmermark and Gustafsson (2005) indicate that atmospheric water relative humidity (RH) and vapor pressure (VP) can lead to increased litter water content (WC), increased mineralization, and increased NH_3 volatilization. Pote and Meisinger (2014) determined that the rate of NH_3 volatilization was consistently affected by diurnal fluctuations and, seemingly contradictory to the studies above, was inversely related to VP. The combination of these findings indicate that NH_3 volatilization is a function of the diurnal fluctuations of temperature and litter WC, where high VP favors mineralization during the nighttime hours and low VP favors the rapid loss of NH_3 during midday. Understanding this rewetting/drying cycle in surface-applied broiler litter may lead to more accurate modeling of NH_3 loss from broiler litter.

Ammonia volatilization is a function of initial litter characteristics, weather conditions, mineralization of organic N, litter pH, and the transfer of NH_3 to the atmosphere (Cabrera et al., 2008; Sherlock and Goh, 1985). The objective of this study was to develop a mechanistic model for the surface-application of broiler litter to pasture, incorporating existing knowledge about the mechanistic processes of NH_3 volatilization with new information gathered specific to surface-applied broiler litter including i) the effect of atmospheric water on litter WC and ii) the effect of diurnal changes in litter WC on organic N mineralization and volatilization.

MODEL DESCRIPTION

Structure

The model was created with Stella® v. 9.0.3 Modeling Software (Isee Systems Inc., Lebanon, NH) with a time step of 1/12 h. A simplified representation of the model structure is presented in Fig. 5.1. The model stocks were initialized using initial litter characteristic utilizing the "input" option on the interface page of the Stella® Software. To adequately model NH_3 volatilization from surface-applied broiler litter, it was necessary to model litter WC (dWC/dt), N mineralization (dOrgN/dt), nitrification (dNO_3N/dt), litter pH, NH_4^+ adsorption (dNH_4-Nad/dt), and N diffusion/movement into the soil (dDiff/dt and dMove/dt), in addition to the actual process of NH_3 volatilization (Appendix 5.1). Although denitrification and immobilization represent important N pathways, these processes were not included in the model. Cabrera and Chiang (1994) observed relatively low losses of N through denitrification (0-200 mg N kg litter^{-1}) compared to the relatively high losses through volatilization (1000-3000 mg N kg litter^{-1}) at varying WCs. Their results indicate denitrification plays a minor role in calculating overall N loss from broiler litter. Additionally, the C:N ratio of litter averages 20 (Nahm, 2003) favoring mineralization in broiler litter and indicating minimal or no immobilization was likely over the time period used in this model.

For a mechanistic model to be successful, the model must consist of as few parameters as possible, and these inputs must be easily measured and obtainable (Chambers et al., 1999; Genermont and Cellier, 1997). With this in mind, the majority of litter characteristics needed for model initialization are currently available from routine analysis; nitrate-N (NO_3-N), ammonium-N(NH_4-N), TN, WC, and litter pH. Other input parameters including, uric acid-N (UAN), mineralizable N (MN), and litter pH buffering capacity (pHBC), have shown promise to be accurately and quickly estimated through near infared spectrocospy (Mowrer et al., 2014b; Cassity-Duffey et al., 2014c). For the purpose of this model, all inputs are expressed as µg N g litter^{-1}. In addition to these parameter inputs, the rate of broiler litter application (kg ha^{-1}) must also be known. The different processes included in the model are described below.

Litter Water Content Sub-Model

Litter WC was modeled as a function of RH using the method proposed by Cassity-Duffey et al. (2014b). The effect of air water potential (WP) on litter drying and rewetting as a function of time was calculated using the difference in litter WP and air WP and a constant (*k*). Flux of water in or out of the litter water content stock was modeled using the equation:

$$\frac{dWC}{dt} = -k * (\mathrm{AirMPa}(t) - \mathrm{LitterMPa}(t)) \qquad \text{Eq. [1]}$$

where *dWC/dt* is the rate of wetting/drying and *k* is the rate constant. The value of *k* [g H_2O (g h MPa)$^{-1}$] varied depending on whether the litter was drying or rewetting as indicated below:

k (drying) = $(-0.0009 + -1.10 * 10^{-5} * \mathrm{LitterMPa} + -3.52 * 10^{-8}\ \mathrm{LitterMPa}^{2}) * 0.001$;

k (wetting) $= (-1.50 * -\mathrm{LitterMPa}^{-2.27}) * 0.001$

Litter WC was transformed to litter WP using a water release curve (Fig. 5.2), which was determined with a WP4C Decagon Potentiameter Model (Decagon Devices Inc., Pullman, WA):

$$\mathrm{WP} = -4.94 * \mathrm{WC}^{-1.22} \qquad \text{Eq. [2]}$$

where WC is g H_2O g litter^{-1} and WP is litter water potential (MPa).

Air WP was calculated from RH and temperature using the equation:

$$\text{Water Potential (MPa)} = \frac{\mathrm{R\,x\,T}}{\mathrm{V}} * \ln(\mathrm{RH}) * 1\ \mathrm{MPa}/1{,}000{,}000\ \mathrm{Pa}, \qquad \text{Eq. [3]}$$

where R is the gas constant (8.314 J K^{-1} mol^{-1}), T is absolute temperature (K^{o}), V is the partial molar volume of water (1.8 x 10^{-5} m^{3} mol^{-1}), and RH is represented as a fraction from 0 to 1.

Nitrogen Mineralization

Organic N mineralization to inorganic NH_4-N was modeled using the two-pool model suggested by Gordillo and Cabrera (1997) and Hadas et al. (1983). The two-pool model consists of a fast pool of mineralizable N (*Nf*) and a slow pool of mineralizable N (*Ns*), each with respective mineralization constants, *kf* and *ks*. The sum of the two pools is equivalent to the potentially mineralizable organic N in the litter (PMON). The initial amount of PMON in the litter was calculated using the equation:

$$\mathrm{PMON}\ (\mu\mathrm{g\ mineralizable\ N\ g\ litter} - 1) = \mathrm{MN} * (\mathrm{TN} - (\mathrm{NO3} - \mathrm{N}) - (\mathrm{NH4} - \mathrm{N})) \qquad \text{Eq. [4]}$$

where MN is µg N mineralizable µg organic N^{-1}, and $(TN\text{-}(NO_3\text{-}N)\text{-}(NH_4\text{-}N))$ (µg organic N g litter^{1}) is indicative of the initial organic N in the litter.

Cassity-Duffey et al. (2014b) determined that N mineralized in 14 d was similar to the initial urea and UAN. Using this relationship, the *Nf* stock was initialized (µg N g litter^{-1}) using the sum of the initial urea-N and UAN concentrations where:

$$\mathrm{Nf}\ (\mathrm{g}\ \mu\mathrm{g\ N\ g\ litter}^{-1}) = \mathrm{UAN} + \mathrm{Urea\text{-}N} \qquad \text{Eq. [5]}$$

The *Ns* stock was initialized using the difference in the PMON and the *Nf* stock.

Rate constants of N mineralization were determined by Gordillo and Cabrera (1997) at 25°C. The *ks* values varied little between the 15 measured litters with an average value of 0.036 d^{-1}, which was used in this model. The constant kf (d^{-1}) was found to have the relationship:

$$\mathrm{kf} = 0.39 + 0.08 * \mathrm{TN} - 0.20 * \mathrm{UAN} \qquad \text{Eq. [6]}$$

where the equation described 62% of the variation in *kf*s measured, and where TN and UAN are expressed in g N kg $litter^{-1}$.

Nitrogen mineralization in broiler litter is driven by enzymatic and microbial activity as well as by the availability of the substrate (organic N containing compounds) to these enzymes (Rothrock et al., 2010; Sims, 1986). Therefore, water and temperature play a dominant role in mineralization of broiler litter (Antonopoulos, 1999; Pratt et al., 2002; Sims, 1986). To incorporate the effect of temperature and litter water content on overall mineralization, both a temperature factor (TF) and a water factor (WF) were obtained from the literature. Little information currently exists for the effect of temperature and water on the rate mineralization in broiler litter. Organic N excreted in poultry litter is comprised primarily of uric acid, urea, and undigested proteins, with urea and uric acid making up about 80% of the organic N (Ritz et al., 2004; Rothrock et al., 2010). Taking this into consideration, data for urea and uric acid degradation was used for the TF and WF determination, as described below.

Moyo et al. (1989) determined the effect of temperature on urea degradation in two soils fertilized with urea fertilizer. The group determined that urea degradation was fit well using the Arrhenius equation, with urea activation energy averaging 51.5 kJ $mol^{-1.}$ For both soils, the average activation energy corresponded to a Q_{10} of approximately 2 in the temperature range of 5 to 45°C. Using the Van't Hoff Function (Cabrera et al., 2008), the TF was calculated as:

$TF = Q_{10}^{(T2-T1)/10}$ Eq. [7]

where $T1$ is the temperature used to determine mineralization (25° C), $T2$ is the temperature for which mineralization needs to be calculated in a given time step, and Q_{10} is 2.

Mowrer et al. (2014a) determined the rate of UAN degradation as a function of litter WP through a 38-d incubation experiment for four litters at three different WCs (as-is litter WC, 600 g kg^{-1}, and 750 g kg^{-1}). Using the data (d 0 and 27) from this experiment, the relative rate of UAN degradation as a function of WC was determined. The relative rate, also the WF, was regressed against litter WP (Fig. 5.3) yielding the equation:

$\mathrm{WF} = -0.375 * \ln(-\mathrm{LitterWP}) + 1.4$; $R^2=0.94$ Eq. [8]

where the WF ranges from 0 to 1 and litter WP is expressed in (-MPa).

Mineralization from both pools was modeled using first-order kinetics. Mineralization for the fast pool (*Nf*) was modeled assuming the most limiting factor will control the rate of mineralization (Cabrera et al., 2008):

$\frac{\mathrm{dNf}}{\mathrm{dt}} = \mathrm{kf} * \mathrm{Nf} * \mathrm{Minimum}\ (\mathrm{TF}, \mathrm{WF})$ Eq. [9]

where *kf* was described by Eq. [6] and *Nf* is uric acid-N plus urea-N (µg N g^{-1} litter; Eq.[5]).

With the initial low WC of surface-applied litter, mineralization is likely limited to existing extracellular enzymatic activity. As WC increases, microbial growth would increase, which would favor increased mineralization in the litter through additional enzymes produced by microorganisms (Groot Koerkamp, 1994; Sylvia et al., 1998). To take into account this delay in the growth of the microbial community as a factor of litter WC, the WF for the *Ns* pool was reduced by 80% and modeled as a function of the interaction of the WF and TF (See Appendix 5.1).

Nitrification

The NH_3 subject to loss after application will be dependent on the initial pools of both NH_4-N and organic N. For the purposes of accurately modeling the pool of NH_4-N available for loss and the change in litter pH, nitrification was modeled as a function of temperature, WC, and the delay of nitrifier growth due to high levels of NH_4-N:

$$\frac{dNO_3-N}{dt} = knit * NH_4 - N * IF \qquad \text{Eq. [10]}$$

where *knit* is the rate constant of nitrification as a function of temperature and WC (Cameron and Kowalenkn, 1976) and *IF* is the inhibition factor by NH_4-N for the first step of nitrification, nitration.

The inhibition factor was determined by work in wastewater from Carrera et al. (2003). The group determined that the Aiba equation best described the inhibition of nitration (the first step of nitrification) by NH_4-N. Using their data, the rate of nitration was determined as a function of NH_4-N concentrations predicted in the litter. The *IF* was then calculated as a function of the rate divided by the optimal rate, yielding the *IF* with a range from 0 to 1 (See Appendix 5.1).

Litter pH and Buffering Capacity

Litter pH is affected by mineralization, nitrification, the litter pH buffering capacity (pHBC), as well the equilibrium NH_4-N/NH_3-N (Kissel and Cabrera, 2005; Kissel et al., 2008; Ni, 1999). Litter pH was modeled with increases in pH as a function of mineralization and decreases in pH as a function of both NH_4/NH_3 equilibrium and nitrification. The extent of the change in pH was modeled as function of the litter pHBC. Litter pH was initialized with the initial litter pH and the change in pH was modeled as:

$$\frac{\mathrm{dpH}}{\mathrm{dt}}(\mathrm{increase}) = \frac{\frac{\mathrm{dOrgN}}{\mathrm{dt}}}{(14 * pHBC)} \qquad \text{Eq. [11]}$$

$$\frac{\mathrm{dpH}}{\mathrm{dt}}\ (\mathrm{decrease}) = \frac{\left(\frac{\mathrm{dNH_3-N}}{\mathrm{dt}} + 2 * \frac{\mathrm{dNO_3-N}}{\mathrm{dt}}\right)}{(14 * \mathrm{pHBC})} \qquad \text{Eq. [12]}$$

where $dNH_3\text{-}N_{aq}/dt$ is the rate of change of the equilibrium between aqueous NH_4-N and NH_3-N. Eq. [11] describes the increase in pH caused by the consumption of 1 mmol H^+ for each mmol of N mineralized, while Eq. [12] describes the decrease in pH caused by the production of 2 mmol H^+ per mmol of N nitrified as well as by the production of 1 mmol of H^+ per mmol of NH_4^+ converted to NH_3.

Ammonium Adsorption/Desorption from the Litter Matrix

Liang et al. (2013) modeled NH_4-N equilibrium adsorption in broiler litter and broiler cake in the pH range of 4-7 using the Freundlich isotherm:

$$\mathrm{r} = \mathrm{kF} * \mathrm{C}^{1/\mathrm{n}} \qquad \text{Eq. [13]}$$

where *r* is adsorbed NH_4-N (mg kg^{-1}) at equilibrium, *kF* is the Freundlich partition coefficient (L kg^{-1}), *C* is the NH_4-N concentration (mg L^{-1}), and *n* is the Freundlich coefficient.

The adsorption/desorption kinetics of NH_4-N to the solid phases was modeled as a function of adsorbed NH_4-N (µg N g $litter^{-1}$) at equilibrium (Eq.15) and the actual amount of adsorbed NH_4-N (Wahab et al., 2010):

$$\frac{\mathrm{dNH_4-Nad}}{\mathrm{dt}} = \mathrm{kad} * \mathrm{r} - \mathrm{NH_4} - \mathrm{Nad} \qquad \text{Eq. [14]}$$

where *kad* was determined as 0.394 min^{-1} by Wahab et al. (2014) for ammonium adsorption to sawdust, *r* is amount adsorbed at equilibrium, and $NH_4\text{-}Nad$ is the amount adsorbed at time t. Modeling this flux as a biflow allowed for both adsorption and desorption.

Ammonium Diffusion from the Litter Layer to the Soil Layer

The flux of NH_4-N from the litter layer to the soil below was modeled as a function of the diffusion of aqueous NH_4-N in the litter.

$$\frac{\mathrm{dDiff-N}}{\mathrm{dt}} = \mathrm{kred} * \mathrm{D_l} * \mathrm{C} \qquad \text{Eq. [15]}$$

where *kred* is a reduction coefficient, D_l is the diffusion coefficient of NH_4-N in free water (1.176×10^{-4} cm^2 min^{-1}; Wang et al., 1998), and C is the concentration of NH_4-N in solution (ug mL^{-1}). The reduction coefficient was fit during model calibration and the equation was modified by the volume of water in 1 cm^3 of litter to represent decreased diffusion with decreased water flow. The diffusion was reduced by 75% for the field models to simulate reduced contact between the litter layer and soil due to grass/thatch.

Ammoniacal-N Equilibrium

The concentration of aqueous NH_3 is a function of the dissociation constant (*kD*), pH and the NH_4-N concentration:

$$[\mathrm{NH3-N}]\mathrm{aq} = (\mathrm{kD}\,[\mathrm{NH_4-N}]\mathrm{aq}/[\mathrm{H^+}]) \qquad \text{Eq. [16]}$$

where log *kD*=-0.09018-2729.92/T (Kelvin), $[H^+]$ is the concentration of protons in solution, and the concentration of $[NH_3\text{-}N]_{aq}$ and $[NH_4\text{-}N]_{aq}$ in solution (Cabrera et al., 2008; Sherlock and Goh, 1985). Ammoniacal-N equilibrium was modeled as function of the difference in theoretical equilibrium calculated in Eq. [15] and the aqueous NH_3-N stock. This allowed for the flow between stocks to be a function of the instantaneous equilibrium reaction (Ni, 1999):

$$\frac{\mathrm{dNH_3-N}}{\mathrm{dt}} = \text{Theoretical equilbrium} - \mathrm{NH_3} - \mathrm{Naq} \qquad \text{Eq. [17]}$$

where equilibrium was modeled as a function of molar concentration and transformed back to model units using the litter WC.

Ammonia Gas Partitioning and Loss

Ammonia gas partitioning was modeled using Henry's Law:

$$[\mathrm{NH_3-N}]\mathrm{gas} = \frac{[\mathrm{NH_3-N}]\mathrm{aq}}{kH} \qquad \text{Eq. [18]}$$

where *kH* is Henry's constant (log *kH*=-1.69+1477.7/ T (in degrees Kelvin)) and $[NH_3\text{-}N]_{aq}$ is the concentration of NH_3-N in the litter solution (Cabrera et al., 2008; Sherlock and Goh, 1985). Alternative *kH* values have been proposed by many authors (Liang, 2013; Ni, 1999). However, Liu (2009) determined that *kH* values measured in litter slurry and values predicted through Henry's Law only varied by 4%. Further, the group concluded that even at very low WCs, Henry's constant would still be applicable to determine the gaseous partitioning in broiler litter. The group cited that even at a water content of 5%, average liquid film thickness in the litter matrix would be thick enough (>5 molecules of water) for Henry's Law to apply.

Henry's law is based on molar equilibrium between the gas phase and the liquid phase with the final units of gaseous NH_3-N (NH_3-N_{gas}) as µg N cm^{-3}. To maintain model units, µg N g^{-1}, this gas volume was transformed using the bulk density and particle density of broiler litter to calculate porosity and the depth of application (See Appendix 5.1). Average bulk density for the litter was 0.35 g cm^{-3}. Particle density for broiler litter determined by Bernhart (2007) averaged 1.43 g cm^{-3}. The NH_3-N_{gas} was transformed to model units (Appendix 5.1) as a function of the percent air space in one gram of litter (porosity multiplied by litter volume (cm^3) minus the litter WC). To maintain instantaneous equilibrium with NH_3-N_{gas} and NH_3-N_{aq}, flow was modeled as function of the calculated theoretical NH_3-N_{gas} where:

$$\frac{\mathrm{dNH_3-Ngas}}{\mathrm{dt}} = \text{Theoretical Partition} - \mathrm{NH_3} - \mathrm{Ngas} \qquad \text{Eq. [19]}$$

The loss of NH_3-N_{gas} from the surface of the litter to the atmosphere was modeled during calibration. This was modeled as a function of the dimensionless coefficient (*kG*) and the difference in the concentration of NH_3-N_{gas} in the surface and NH_3-N_{gas} in the air. Under field conditions, the concentration of NH_3-N in the air is typically very low and most models consider this concentration to be zero (Cabrera et al, 2008; Ni, 1999). Thus, volatilization (NH_3-$N_{loss)}$ was modeled as the flow:

$$\frac{\mathrm{dNH_3-N\ loss}}{\mathrm{dt}} = \mathrm{kG} * \mathrm{NH_3} - \mathrm{N\ gas} \qquad \text{Eq. [20]}$$

where *kG* was adjusted during model calibration.

Ammonium Movement due to Rain

To simulate the effects of rain on NH_3 volatilization observed during field studies conducted in 2011 and 2012 (Cassity-Duffey et al., 2014a), a "movement" flow was added to increase the movement of NH_4-N_{aq} into the soil layer. Previous studies have determined that the addition of rain for broiler litter and urea fertilizers can significantly decrease NH_3 volatilization by increasing N movement into the soil surface (Cabrera and Vervoort, 1998; Holcomb et al., 2011). The effect of movement due to rain will also be a function of the soil WC. Black et al. (1987) observed an increase in volatilization with 16 mm of simulated rain on surface-applied urea to dry soil. The group determined that repeated additions of 2 mm of rain over a 27-day study led to significantly greater loss than the single application of 16 mm. When simulated rain additions were made to soil at field capacity, losses were greatly reduced to 2% of the applied total N. To take into account this combined effect of soil WC and rain, movement from the NH_4-N_{aq} stock was modeled where:

$$\frac{DMove}{dt} = \mathrm{if\ Soil\ WC} > 0.16\ \mathrm{and\ Rain\ \ then\ (Rain/Litter\ Application\ Rate\ } + \mathrm{Litter\ WC)} * \mathrm{C\ else\ 0} \qquad \text{Eq.[21]}$$

where *dMove/dt* is the downward movement of NH_4-N, *rain* is in (mL cm^{-2}), *Litter Application Rate* is g cm^2, *Litter WC* is gH_2O g $litter^{-1}$, and *C* is the concentration of NH_4-N in the litter solution (mg L^{-1}).

EXPERIMENTAL METHODS: LITTER WATER SUB-MODEL

Laboratory Experiment

Using a dynamic flow-through system (Cassity-Duffey, 2014b), diurnal fluctuations of RH and temperature were simulated. Temperature fluctuations were controlled using a CN9600 Series Autotune Temperature Control connected to CB9-SW-Grafix Software (Omega; Stamford,CT). Temperature ranged from 6 to 27°C and RH ranged from 27 to 89% in 24-h intervals during the experiment. The RH of the air was regulated by bubbling intake air through saturated $CaCl_2$, with RH changes being controlled through temperature fluctuations. Relative humidity and temperature were monitored and recorded at 5-min intervals with a Vaisala HMP45AC probe connected to a CR10 datalogger (Campbell Scientific, Logan, UT). To mimic the depth of typical applications of broiler litter, 2 g of broiler litter (initial WC of 0.28 g H_2O g^{-1}) was placed in sampling cups (4-cm o.d., 1-cm height) for the WP4C Decagon Dewpoint Potentiometer (Decagon Devices Inc., Pullman, WA). The cups were placed inside the flow-through chambers (acrylic tube, 4.4-cm diameter, cut into 10-cm sections), and the sweep air that passed over each chamber was regulated to 0.2 L min^{-1}. Initial litter WP was measured, and samples were allowed to equilibrate for 80 h in the flow-through system. From 80 to 100 h, four sampling times were chosen and three cups were removed for each time. At each sampling time, the litter WP was measured.

Field Experiment

To validate the WC sub-model, a 3-d field study was conducted in May 2014. Similar to the experimental design for the flow-through system, 2 g of broiler litter with an initial WC of 0.27 g H_2O g^{-1} was placed in sampling cups for the Decagon Dewpoint Potentiometer and set outside in a pasture beginning at 0830 h. Samples were placed under a plastic tent approximately 10 cm from the soil surface from midnight to dawn to decrease the effect of dew deposition on litter water content. An Em50 Data Logger (Decagon Devices, Inc., Pullman, WA) connected to one dielectric leaf wetness sensor, a 5TM Water and Temperature Sensor (5 cm), and a VP-3 relative humidity and temperature sensor located 0.3 m from the soil surface (all sensors from Decagon Devices, Inc.) were placed near the sampling cups to record weather data at 5-min intervals. Samples were removed periodically over 53 h in replicates of three and the water potential was measured using the Decagon Dewpoint Potentiameter. Sampling was spaced over the 53-h time period to ensure different temperature and RH conditions.

EXPERIMENTAL METHODS: AMMONIA VOLATILIZATION

Laboratory Experiment

For the calibration of the NH_3 volatilization model, data from two 15-d laboratory experiments were used (Cassity-Duffey, 2014b for details). Briefly, two separate studies were conducted to determine the effect of soil WC on NH_3 volatilization using the dynamic flow-through system: one at 92% RH, and one at 32% RH. The MN of the litter was 515 (g N kg Org N^{-1}) and initial litter characteristics are presented in Table 5.1. In each RH study, two treatments of gravimetric soil WC were used, 0.03 g H_2O g^{-1} (dry) and 0.13 g H_2O g^{-1}(wet) For the purposes of model calibration, only the dry soil treatments were used from each study. The system was set at a constant 25° with a sweep air that passed over each chamber regulated to 0.2 L min^{-1}. Ammonia was trapped using 0.05 N H_2SO_4 and changed at 1, 2, 3, 5, 7, 9, and 15 d. Litter and soil samples were measured for WC and inorganic N on d 15.

Field Experiment

Eleven 28-d studies were conducted in field pastures located in Eatonton, GA from April to October in 2011 and 2012 (Cassity-Duffey et al., 2014a; for full details). These studies used passive flux wind vane systems to determine NH_3 loss from surface-applied broiler litter to pasture. The passive flux wind vane mast was located in the center of 20-m circular plots. Broiler litter was applied at a rate of 3230 kg ha^{-1} (approximately 120 kg total N ha^{-1}) to 4 plots and tested for initial litter characteristics at the time of application (Table 5.1). The MN of the litter was 496 and 233 (g N kg Org N^{-1}) for the 2011 and 2012 litter respectively, and initial litter characteristics are presented in Table 5.1. Cumulative NH_3 volatilized was measured at 14 and 28 d. A local weather station provided local environmental conditions including soil and air temperature, wind speed and direction, rainfall, and RH. Weather data used in modeling were averaged from 5-min to 1-h intervals due to limitations in the Stella software. Temperature and RH were modeled from the data at 0.4 m height and input graphically into the model. The model was run for each of the eleven studies and model accuracy was determined from both NH_3 loss at 14 d and cumulative NH_3 loss at 28 d.

STATISTICAL ANALYSES

Regression analysis was performed on the modeled versus measured data using Sigma Plot® Regression Fit Wizard (San Jose, CA). Root mean square error (RMSE) was determined from model and measured means to determine model performance. Additionally, Lack of Fit

(LOFIT) was performed for NH_3 volatilization simulations for the lab and field data as described by Whitmore (1991). The LOFIT method partitions the sum of squares differences between the modeled and the mean of the measured data as well as the sum of squares differences within the replicates of the measure data. This analysis provided a very robust analysis for data with replicates and is representative of the "pure error" due to experimentation as well as the "lack of fit" to the modeled data (Whitmore, 1991). Sensitivity analysis was performed on parameters ks, the partition coefficient, and kG, the transfer coefficient, by varying the parameters by 20% and using data over the full time period (28 d) for the field Study 411.

RESULTS AND DISCUSSION

Litter Water Sub-Model Calibration with Laboratory Data

The litter water content sub-model was developed using Stella® over 120 h with the initial litter WC and RH and temperature data collected from the diurnal flow-through experiment. Using the model description above (Eq. [1]), the model failed to accurately predict litter WP. A regression of the measured litter WP versus the predicted litter WP led to a low R^2 of 0.53. The model under-predicted both the rate of litter rewetting and litter drying for the laboratory data. Measured data ranged from -34 (MPa) to -153 MPa over the measurement period, but the initial model predicted a range of -90 to -140 MPa. The initial rate constants (k values) were measured at a constant temperature and RH as described by Cassity-Duffey et al. (2014b), and likely failed to incorporate the effect of rapid changes in temperature and RH on litter rewetting and drying.

Modeling the evaporation of water from litter in broiler houses, Groot Koerkamp et al. (1999) determined that evaporation rates were related to temperature, air velocity, and the difference in the water VP of the air and litter. Because air velocity was the same in the experiments that derived the k values and the calibration experiment, we added temperature to the litter water content sub-model. For that purpose, we multiplied temperature (°C) by k for both rewetting and drying conditions as shown below:

$$\frac{\mathrm{dWC}}{\mathrm{dt}} = -\mathrm{k} * \left(\mathrm{AirMPa} - \mathrm{LitterMPa}\right) * \mathrm{T} \qquad \text{Eq. [22]}$$

where k is the wetting/drying constant determined by Cassity-Duffey et al. (2014b) and T is the air temperature in °C.

With this modification to the WC sub-model, regression of the modeled litter WP versus measured litter WP led to an R= 0.99. The regression equation had a slope of 1.3 and an intercept of 10 due to the underestimation of the model at low RH; the model predicted -187 MPa compared to the measured -153 MPa at RH of 0.27. However, when these WP are transformed to WC, differences are negligible at 0.05 and 0.06 g H_2O g^{-1}, respectively.

Litter Water Sub-Model Testing with Field Data

The temperature-corrected WC sub-model accurately predicted measured data from the 53-h field study (Fig. 5.4 and 5.5), in which air temperature fluctuated from 15 to 32°C and RH from 0.39 to 0.95. The minimum measured litter WC occurred midday (from 1300 to 1700 h) at 0.03 g H_2O g^{-1} with corresponding litter water potential of -270 MPa. Maximum measured litter WC occurred early morning near 700 h reaching 0.4 g H_2O g^{-1} (-14 MPa). The model failed to predict the extreme lows in WP seen in late afternoon, which are likely a function of evaporation during time of high heat and sun exposure. However, these lows in WP were not as low in the litter WC sub-model. Additionally, these lows will not affect the mineralization process because according to Fig. 5.3, the WF of mineralization will be 0 below WP of -40 MPa. The RMSE of the litter WC data was 0.07 g H_2O g^{-1}, indicating small deviation from the modeled and measured values. When data were expressed as litter WC, the model fit the data with the equation:

$$\text{Measured Litter WC} = 0.82 * \text{Modeled Litter WC} + 0.018;\ R^2=0.82. \qquad \text{Eq. [23]}$$

The diurnal litter WC sub-model was incorporated into the model for NH_3 loss for the field data to incorporate the large fluctuations seen in litter WC and its effect on N mineralization and NH_3 volatilization.

Ammonia Volatilization: Model Calibration with Laboratory Data

For the purposes of model calibration, the initial litter characteristics (Table 5.1) and RH and temperature data from the 32% and 92% RH studies were used as inputs in the model described above. The litter water sub-model was used as described by Eq. [1-3] to simulate litter rewetting under constant temperature and RH conditions. Experimental data were used to calibrate nitrification, adsorption of NH_4-N, diffusion, as well as the determination of the transfer coefficient (kG).

Ammonium adsorption (Eq. [14-16]) modeled as described by Liang et al. (2013) overestimated the transfer of adsorbed NH_4-N from the aqueous phase, greatly reducing the pool of ammoniacal-N available for loss. By dividing the adsorbed NH_4-N at equilibrium by the amount of time used by Liang et al. (2013; 6 hr), values were obtained that more closely matched the values observed at the end of the laboratory experiments (Table 5.2). Ammonium-N concentrations simulated for each study (ug ml^{-1}) were much higher (10,000+ ug ml^{-1} at low WCs) than values used for the adsorption isotherm by Liang et al. (2013).

The nitrification rate, diffusion reduction coefficient, and the transfer coefficient (*kG*) were determined through calibration (Table 5.2). The rate constant of nitrification described by Cameron and Kowalenko (1976) in soil was reduced by 90% to achieve the amount of nitrification observed in the experiments. A reduction coefficient of 0.3 worked well for modeling diffusion in both studies. Overall, volatilization was not sensitive to variation in the *kG* coefficient, with equilibrium and the partition from the liquid to the gas phase dominating loss. The *kG* coefficient was modeled as function of temperature (K) to ensure movement from the gaseous litter N pool to the atmosphere.

After model calibration, the model simulation worked well for both the 92% and 32% RH experiments (Table 5.2; Fig. 5.5). The model predicted overall NH_3 volatilization for the 92% RH experiment as 10.4% compared to the measured 11.3% of the applied TN and 3.8% compared to 3.2% of the applied TN for the 32% RH experiment. Nitrification and mineralization compared well to experimental data for both studies (Table 5.2). Nitrogen mineralization from broiler litter was 13.5% of the applied N in the in the 92% RH experiment (% Inorganic N recovered at 15 d – % Initial Inorganic N= 30.0-16.5 = 13.5) compared to the 13.9% N mineralized determined through initial model simulation.

For the 32% RH study, NH_4-N in the litter was overestimated and diffusion in to the soil profile was underestimated. Under the dry conditions observed for the 32% RH experiment, it is likely that the model better represents the actual division of NH_4-N than the experimental data. The relatively high amounts of NH_4-N observed in the experimental data was most likely due difficulty in removing all of the litter layer from the soil surface. Additionally, the low WC (0.03 g g^{-1} (Fig.5.6), would favor increased ammoniacal-N in solution and strong adsorption of ammoniacal-N to the litter layer (Liang et al., 2014), reducing diffusion into the soil profile.

Regression analysis provided a good fit of the modeled versus measured data with an R^2=0.88. The model slope was near 1 (0.84) and the intercept of the regression model was low at 0.25. The RSME of the model for both experiments was 1.0 (NH_3-N as % of applied TN).

LOFIT analysis determined a good fit for the modeled and measured data of the 32% RH experiment, but failed for the analysis of the 92% data, likely due an overestimation of the model for losses in the mid-range of the experiment (Fig. 5.6).

Ammonia Volatilization: Model Testing with Field Data

The model calibrated with laboratory data using the diurnal WC sub-model and movement flux (Eq. [21]) was used to simulate field NH_3-N volatilization losses. The initial model tended to underestimate the cumulative loss for both the 2011 and 2012. The RMSE of the model for both years was 3.8 NH_3-N as % of applied TN and the regression of the model versus measured data yielded an R^2 of 0.34 with a slope of 1.08 and an intercept of 2.04. The model predicted losses well for the Studies 111, 211, and 112, predicting within 1% of the measured value. Additionally, the incorporation of the movement due to rain led to good estimated values (within 1.5% of the measured) for studies 212 and 512, where elevated soil WC and rain events were hypothesized to have led to low losses (Cassity-Duffey et al., 2014a). The model underestimated loss for studies conducted mid-summer with the highest average temperature and RH. It was hypothesized that the failure of the model was related to the mineralization rate of organic N in the litter. With the fast pool mineralizing rapidly in all studies, the mineralization of the slow pool was investigated.

The mineralization constant (*ks*) was derived for the slow pool using the average value (0.0015 hr^{-1}) determined by Gordillo and Cabrera (1998). Calibration was performed on the *ks* value with 10 simulation runs for each study for a range of 0.0015 to 0.1 hr^{-1} with the five 2011 studies. The value of *ks* that best modeled the data was recorded and regressed against initial litter characteristics (Table 5.1). The values of *ks* of each study were correlated to the TN of the litter (R^2=0.93):

$$\mathrm{ks} = 0.0003 * \mathrm{TN} - 1.1896 \qquad \text{Eq. [24]}$$

where *ks* (hr^{-1}) is the mineralization constant of the *Ns* pool determined through calibration and TN is the initial total N of the litter (mg kg^{-1}).

For the field studies, broiler litter was obtained from a nearby broiler house in a large batch at the beginning of both the 2011 and 2012 studies, leading to different litters for each year. Between studies, the litter was piled and covered using a large tarp to minimize N transformations and NH_3 losses. The amount of N should remain constant with covered litter, but the TN tended to increase with time for each year. Higher TN concentrations are probably reflective of carbon transformations in the litter, where carbon mineralization results in carbon dioxide losses, resulting in an apparent increase in TN (Moore et al., 1995). With this in mind, the relationship of *ks* and TN is more likely reflective of the microbial/fungal community present at the time of application. The increase in TN and the decrease in litter pH (Table 5.1) may be reflective of increased microbial growth and increased fungal growth in the litter during storage (Rothrock et al., 2010). It is likely that, as the microbial community shifts towards increased bacterial growth and increased fungal growth, the ability of litter fauna to degrade large organic N compounds increases, subsequently favoring the increased rate of mineralization of the Ns pool (Groot Koerkamp, 1994; Sylvia et al., 1998). While this estimation works well for this model, further studies needed to be conducted to determine the actual constituents of the slow pool and the rate of mineralization for surface applied litter.

The incorporation of the determined *ks* greatly improved model accuracy, increasing the R^2 to 0.61. An additional coefficient (1.5) was multiplied against the partition flux to increase the rates of overall loss; however, increasing *kG* had no effect. This partition coefficient might be representative of the effects of evaporation on flux that would occur under field conditions.

The removal of Study 412 as an outlier led to an R^2 0.81 for all studies (Fig. 5.7) with regression analysis yielding a slope of 0.99 and an intercept of 0.26. The reasons for the inability to model Study 412 are unclear. Experimental values for Study 412 were reduced to a single replication due to contamination of three of the four plots by cattle, which may have overestimated the actual loss observed during that study. The calibration of the field model with ks and the partition coefficient reduced the RMSE of the model to 1.2 NH_3-N as % TN applied, however LOFIT failed for the model.

The average modeled litter WC for each study ranged from 0.21 to 0.58 g H_2O g litter^{-1}. Average modeled litter WC values are reflected in the average VP measured for each study (Table 5.3). Diurnally, litter WP fluctuated from approximately -3 to -150 MPa (1.3 to 0.06 g H_2O g litter^{-1}) depending on RH and temperature conditions. The model simulated N mineralization as a function of both temperature and litter WC. For all studies, the *Nf* pool was mineralized during the 28-d simulation, and the *Ns* pool mineralization contributed to major differences in total mineralization and volatilization among the studies. The amount of N available to crops over 28-d was estimated through model simulation (Table 5.3) as described below:

$$\text{N Available to Crops } = \text{Initial Inorg. N Applied } + \text{ Mineralized N} - \text{ NH}_3 - \text{N Loss}; \text{ [Eq.25]}$$

where the units are expressed as a percent of the TN applied and mineralized N and NH_3-N loss were estimated through the model. The model estimated between 15-33% of the applied N will be available to crops over the 28-d, and the available N will be a function of the effect of environmental conditions, mineralization, and loss. Model results indicated the need for estimations of mineralization and loss throughout the growing season compared to current recommendation strategy that 50-60% of applied TN from litter will become crop available.

The diurnal wetting and drying cycle simulated in the model led to increased NH_3-N in solution and loss during peak daylight hours, whereas litter rewetting during times of high RH favored mineralization and decreased NH_3-N in solution (Fig. 5.8). This simulated diurnal pattern was similar to those described by Pote and Meisinger (2014) for surface-applied broiler litter under field conditions. The group determined that the rates of NH_3-N volatilization were consistently affected by diurnal fluctuations, where peak losses occurred during the day from temperatures 28 to 31°C and losses neared zero overnight. The combination of these findings with simulated models results indicate that NH_3-N volatilization is a function of the diurnal fluctuations of temperature and litter WC due to changes in both litter solution and mineralization. It is likely that high atmospheric WC during the evening/nighttime increases litter WC, favoring mineralization and decreasing the ammoniacal-N in solution through dilution. During daytime hours, low atmospheric WC increases NH_3-N in solution through evaporation, favoring increased NH_3-N loss.

Sensitivity Analysis

Sensitivity analysis was performed for the *ks*, *kG*, and partition coefficient for NH_3-N loss for Study 411 (Table 5.4). As noted earlier, the model was not sensitive to the *kG*, with a variation of *kG* of ± 20% there was no change in NH_3 loss. The model did vary with changes to the *ks* and partition coefficient (Table 5.4). With the model calibrated to *ks*, this sensitivity likely does not affect model performance, but indicates the need for further analysis of the mineralization of the slow pool of organic N. Similarly, the sensitivity analysis indicated that the partition coefficient is important to simulating overall loss. While Liu et al. (2009) determined that Henry's constant is applicable at very low WC, current research is lacking for the effect of evaporation and diurnal fluctuations on the partition of NH_3-N from the aqueous to gas phase.

CONCLUSIONS

Ammonia volatilization from surface-applied broiler litter is a complex function of both litter characteristics and environmental variables, which greatly increase the difficulty in accurately predicting loss. Ammonia volatilization will be a function of initial litter characteristics, weather conditions, mineralization of organic N, litter pH, and the transfer of NH_3 to the atmosphere. Weather conditions control volatilization and mineralization both through temperature and the effect of atmospheric water on litter WC. Using the gradient between air WP, and the litter WP, the effect of RH on litter WC was accurately modeled with an $R^2=0.82$ under field conditions. Simulated litter WC fluctuated on a diurnal basis from 0.05 to 1.5 g H_2O g litter^{-1}, impacting both mineralization and the pool of ammoniacal-N subject to NH_3 volatilization. Incorporating the litter WC sub-model into a mechanistic NH_3 volatilization model with a modified mineralization constant for the slow pool of organic N, the NH_3-N loss for 28-d field studies was accurately estimated with a $R^2=0.81$. The model describes the importance of litter WC, initial NH_4-N pools, and mineralization to overall loss. Overall, this model could lead to better estimations and understanding of NH_3 loss and available N for surface-applied broiler litter to pastures.

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TABLES AND FIGURES

Table 5.1. Initial litter characteristics determined for experimental studies used during model simulation.

Study	NH_4-N	NO_3-N	Uric Acid N	Urea N	Initial WC	Total N	pH	BC
Study No./Year	----------------mg kg^{-1} dry litter----------------				-------------g g^{-1} dry litter--------			mmol OH kg^{-1} pH $unit^{-1}$
Lab	4308 ± 185	304 ± 185	3624 ± 187	114 ± 3	0.31	28.0 ± 1.4	8.5	330.88
111	4127 ± 303	1587 ± 45	2349 ± 888	118 ± 1	0.28	40.0 ± 1.4	7.86	265.4
211	4333 ± 237	1066 ± 104	2690 ± 750	117 ± 7	0.26	39.5 ± 2.1	7.86	265.4
311	4228 ± 100	981 ± 102	4386 ± 1447	151 ± 7	0.2	41.6 ± 0.2	7.48	264.0
411	5223 ± 596	689 ± 191	4327 ± 1428	72 ± 4	0.23	41.8 ± 0.1	7.42	300.8
511	4853 ± 642	850 ± 215	2773 ± 915	166 ± 13	0.24	43.5 ± 3.8	7.09	300.9
112	6724 ± 21	777 ± 6	1363 ± 450	160 ± 7	0.55	39.5 ± 0.4	8.78	382.6
212	7216 ± 53	736 ± 24	1415 ± 467	249 ± 5	0.46	40.0 ± 0.4	8.43	372.4
312	7430 ± 189	325 ± 4	1712 ± 565	242 ± 6	0.5	40.6 ± 0.4	8.48	392.4
412	7216 ± 102	419 ± 9	1253 ± 413	375 ± 51	0.45	40.9 ± 0.4	8.3	407.8
512	7228 ± 102	893 ± 168	1599 ± 527	529 ± 49	0.43	42.1 ± 0.4	8.1	364.5
612	8009 ± 160	299 ± 5	1581 ± 522	469 ± 15	0.43	43.0 ± 0.4	8.34	399.6

Table 5.2. Nitrogen (N) recovered during laboratory experiments and mineralized organic N with predicted model recoveries and mineralization, standard deviation from the experimental measurements is presented in parentheses.

	92% RH		32% RH	
	Measured	Modeled	Measured	Modeled
	--------% of Total N Applied--------			
Volatilized	11.3 (4)	10.4	3.2 (1.7)	3.8
Litter NH_4- N	5.7 (1.2)	6.2†	3.9 (0.5)	8.6†
Soil NH_4- N	10.1 (1.5)	9.3	3.5 (0.5)	1.1
Litter + Soil NO_{3-}N	2.9 (0.8)	4.2	3.4 (0.2)	2.9
Min. Org. N	13.5	13.9	0	0

† Sum of adsorbed NH4-N and aqueous NH4-N pools and then end of the model run

Table 5.3. Average vapor pressure and air temperature (at 2 m) observed during the 2011 and 2012 field studies with initial ammonium-N initial, potentially mineralizable N (PMN) , and volatilization as % of applied total N (TN). Modeled organic N mineralization (as % of applied PMN or TN), average litter WC, and volatilization (as % of applied TN).

Measured					Modeled			
Study	Avg. VP	Avg. Temp	Inorganic N Applied	NH_3 Loss	Avg. Litter WC	Mineralized N	NH_3 Loss	Est N Available† to crops (28 days)
Study No./Year	kPa	°C	% of TN Applied		g g^{-1} litter	% of TN Applied		
111.0	1.6	20.1	10.3	2.5 ± 0.7	0.25	7.4	3.0	14.7
211.0	2.2	26.2	11.0	4.1 ± 0.9	0.33	8.9	4.0	15.9
311.0	2.7	26.7	10.2	7.2 ± 1.3	0.55	31.7	9.4	32.5
411.0	2.2	25.2	12.5	9.8 ± 0.2	0.36	23.8	9.7	26.6
511.0	1.2	13.6	11.2	3.8 ± 1.4	0.50	26.8	5.4	32.6
112.0	1.5	18.6	17.0	5.3 ± 2.8	0.33	4.1	5.7	15.4
212.0	1.8	21.8	18.0	0.9 ± 1.5	0.35	5.8	3.4	20.4
312.0	2.3	26.4	18.3	9.1 ± 2	0.35	8.4	8.7	18
412.0	2.6	25.3	17.6	10.5 ± 0	0.49	11.9	5.3	24.2
512.0	2.6	24.2	17.2	2.9 ± 1.9	0.58	14.6	3.7	28.1
612.0	1.3	15.5	18.6	4.7 ± 1	0.50	11.9	3.4	27.1

† Estimated N Available to crops over 28 =Inorganic N Applied + Mineralized N-Loss

Table 5.4. Sensitivity analysis of the mass transfer coefficient (kG), mineralization constant of the slow pool (ks), and the partition coefficient. Parameters were varied ± 20% and simulated for Study 411. Values in parentheses are the percent change in NH_3-N loss from the standard value (0%).

	kG	Ks	Partition Coef.
Parameter Variation	Cumulative NH_3-N Volatilization (% N applied)		
-20%	9.66 (0)	8.39 (-13)	8.53 (-12)
0%	9.66 (0)	9.66 (0)	9.66 (0)
+20%	9.66 (0)	10.29 (+6)	10.59 (+10)

Figure 5.1. A simplified representation of the model stocks and flows used to simulate ammonia volatilization.

Figure 5.2. The water release curve developed to transform litter water content (g H_2O g^{-1} dry litter) to litter water potential (-MPa).

Figure 5.3. The calculated effect of litter water potential on the rate of uric acid- N degradation from Morwer et al. (*In Press*) for the determination of the litter water factor (WF).

Figure 5.4. Temperature and relative humidity (RH) data averaged hourly for the litter water content (WC) field experiment with measured litter WC as a function of time with modeled litter water potential (WP) and litter WC.

Figure 5.5. Plotted values of measured versus modeled litter water content for the litter water content field experiment.

Figure 5.6. Ammonia volatilization over 14 d (360 h) from experimental data with modeled litter water content and volatilization.

Figure 5.7. Modeled ammonia volatilization versus measured ammonia volatilization for 14-d loss and cumulative 28-d loss for 11 field studies conducted in 2011 and 2012. Study 412 was identified as an outlier for regression analysis (circled).

Figure 5.8. Modeled litter water content, relative humidity, temperature, the rate of mineralization, and the concentrations of aqueous ammonia-N in the litter solution for the first 4 days of Study 311.

Figure 5.1.

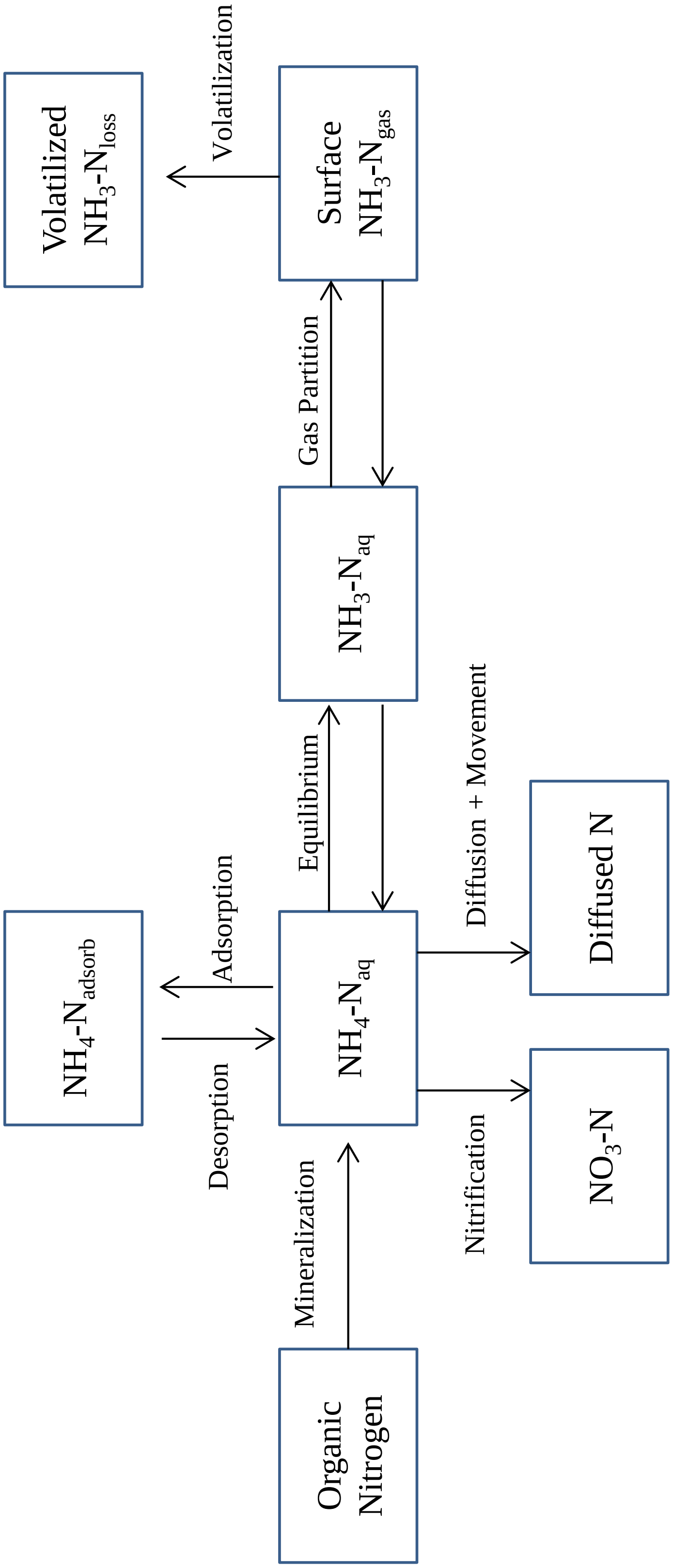

Organic Nitrogen
Mineralization
$NH_4\text{-}N_{aq}$
Desorption
Adsorption
$NH_4\text{-}N_{adsorb}$
Nitrification
$NO_3\text{-}N$
Diffusion + Movement
Diffused N
Equilibrium
$NH_3\text{-}N_{aq}$
Gas Partition
Surface $NH_3\text{-}N_{gas}$
Volatilization
Volatilized $NH_3\text{-}N_{loss}$

Figure 5.2.

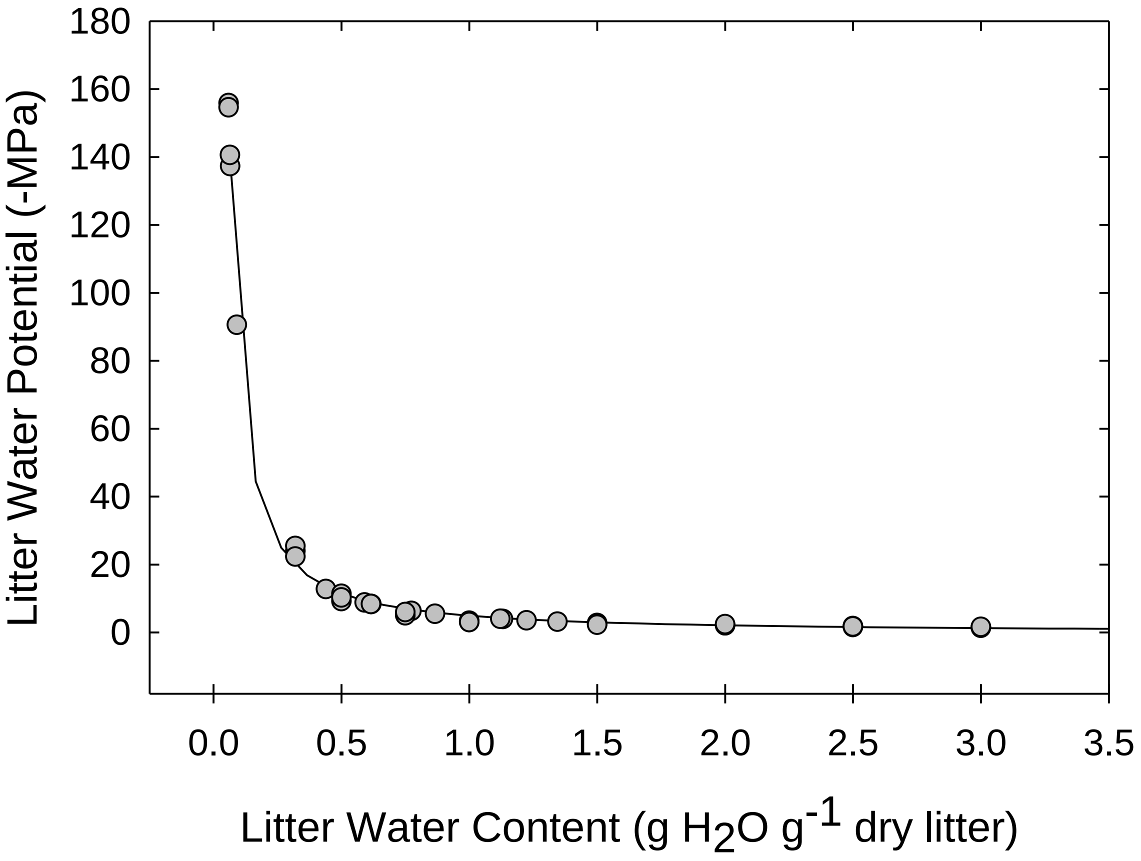

Litter Water Potential (-MPa)
180
160
140
120
100
80
60
40
20
0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
Litter Water Content (g H_2O g^{-1} dry litter)

Figure. 5.3.

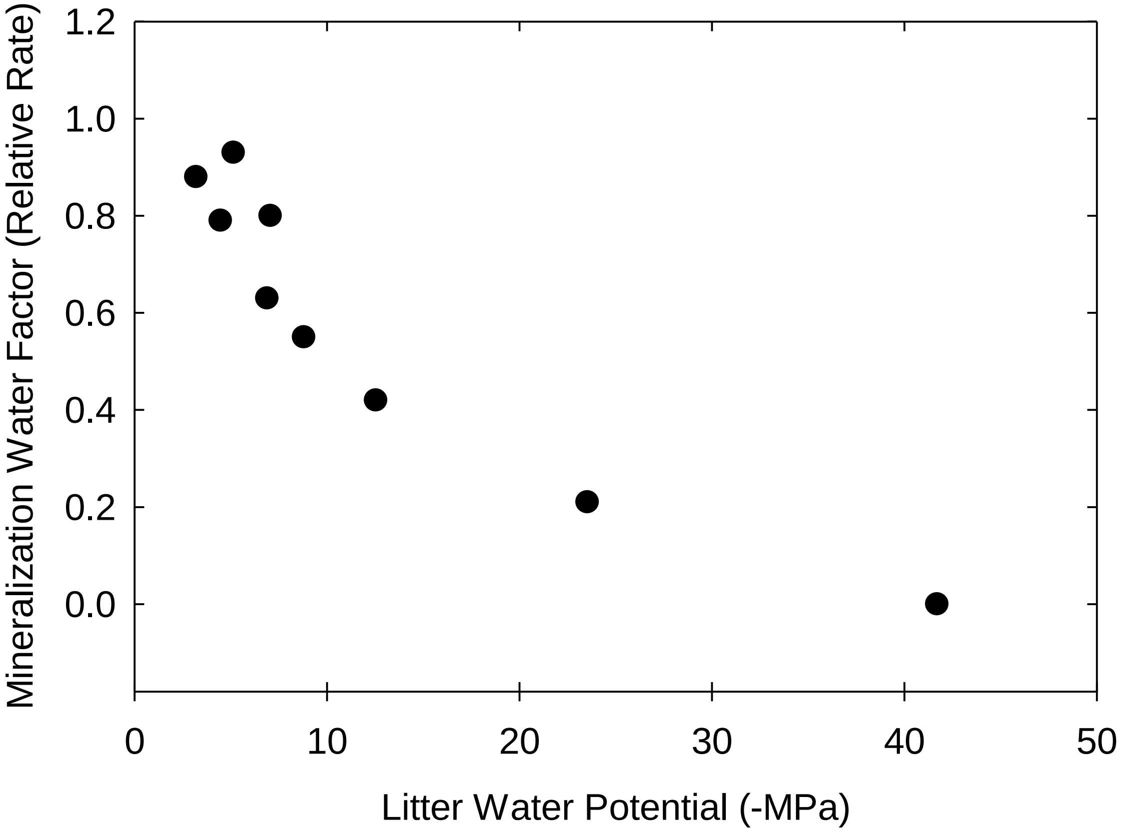

Mineralization Water Factor (Relative Rate)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
40
50
Litter Water Potential (-MPa)

Figure. 5.4.

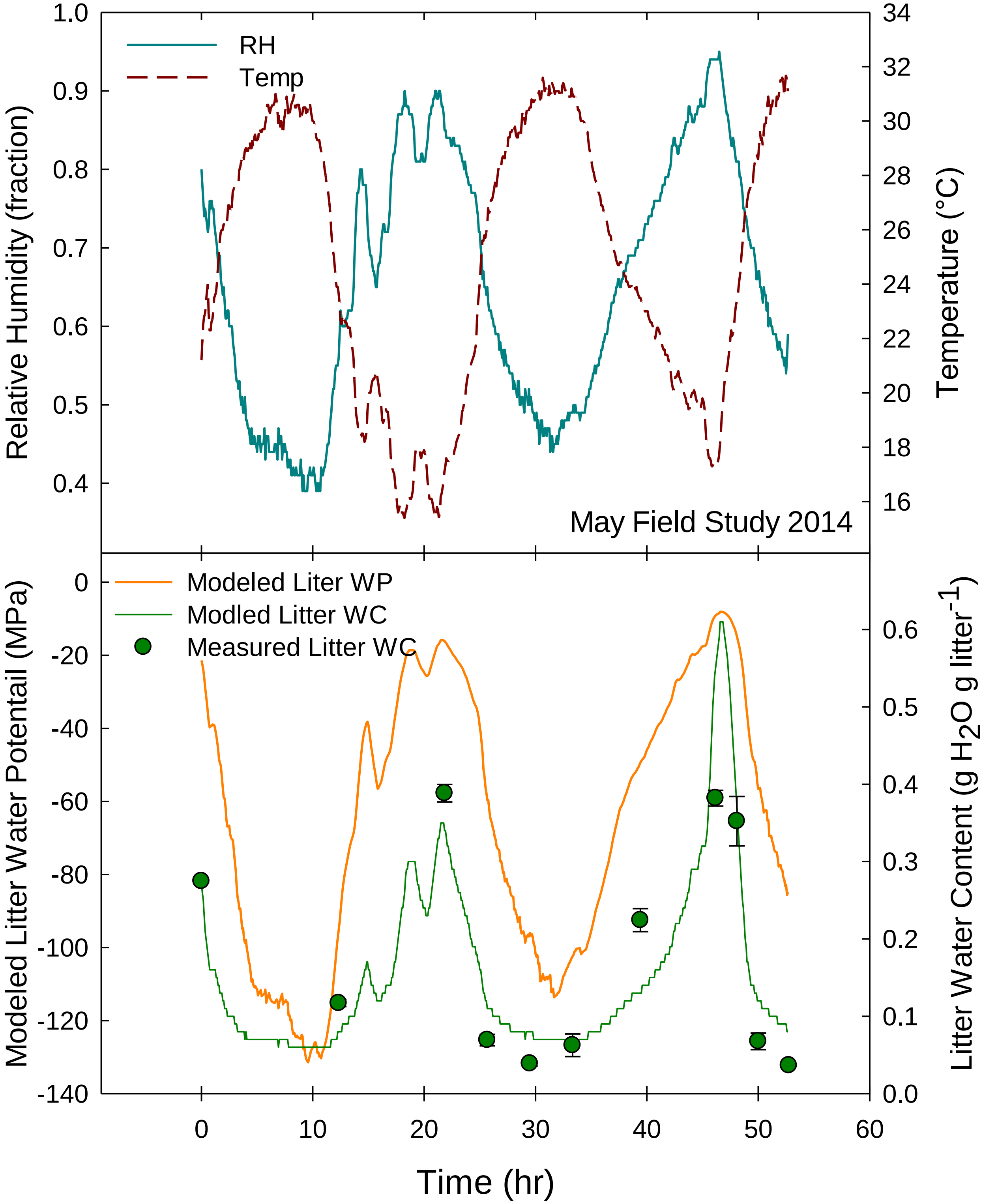
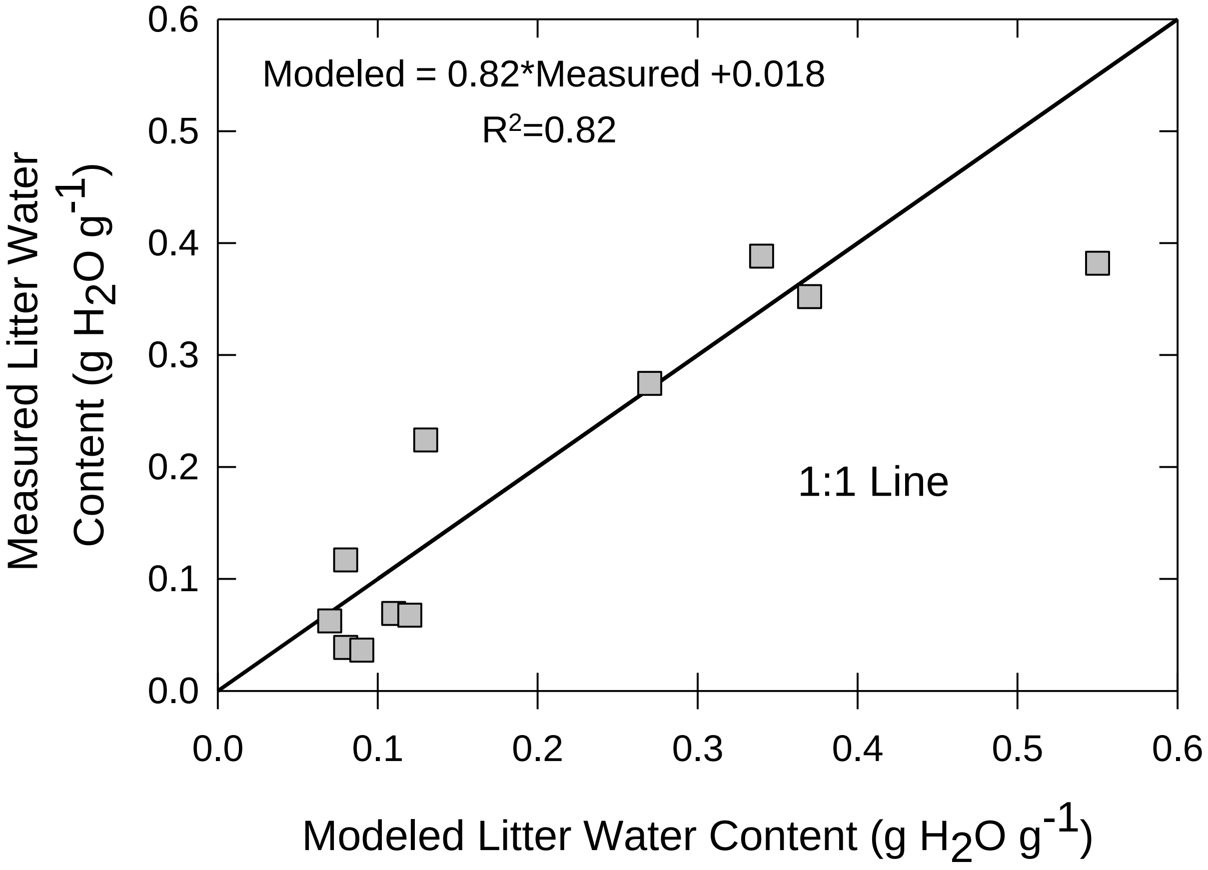

RH
Temp
May Field Study 2014
Relative Humidity (fraction)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
Temperature (°C)
34
32
30
28
26
24
22
20
18
16
Modeled Liter WP
Modled Litter WC
Measured Litter WC
Modeled Litter Water Potentail (MPa)
0
-20
-40
-60
-80
-100
-120
-140
Litter Water Content (g H_2O g litter^{-1})
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
10
20
30
40
50
60
Time (hr)

Figure 5.5.



0.6
0.5
0.4
0.3
0.2
0.1
0.0
Modeled = 0.82*Measured +0.018
R^2=0.82
1:1 Line
Measured Litter Water Content (g H_2O g^{-1})
0.0
0.1
0.2
0.3
0.4
0.5
0.6
Modeled Litter Water Content (g H_2O g^{-1})

Figure. 5.6.

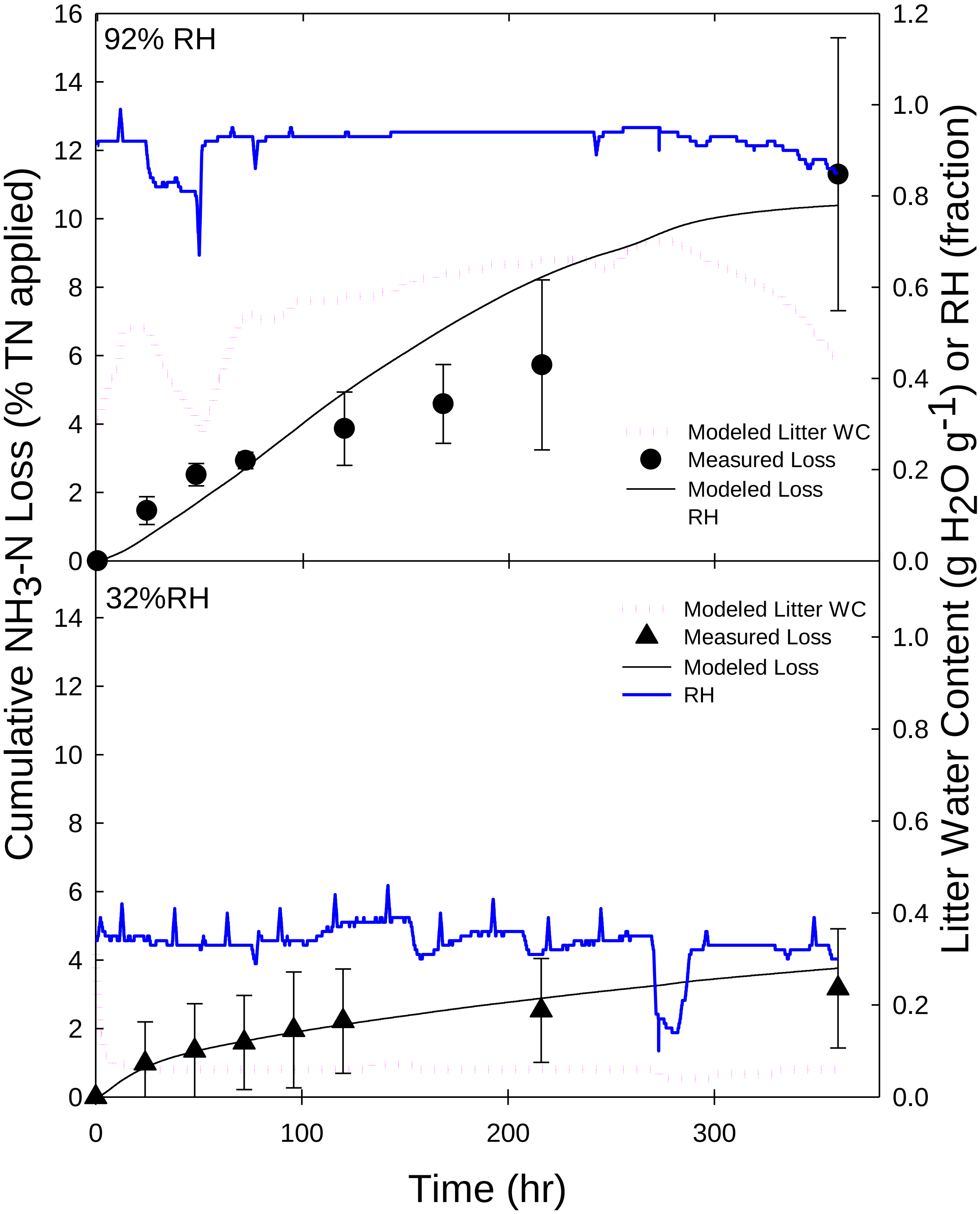

92% RH
32%RH
Modeled Litter WC
Measured Loss
Modeled Loss
RH
Modeled Litter WC
Measured Loss
Modeled Loss
RH
Cumulative NH_3-N Loss (% TN applied)
Litter Water Content (g H_2O g^{-1}) or RH (fraction)
Time (hr)
0
100
200
300
0
2
4
6
8
10
12
14
16
0.0
0.2
0.4
0.6
0.8
1.0
1.2

Figure 5.7.

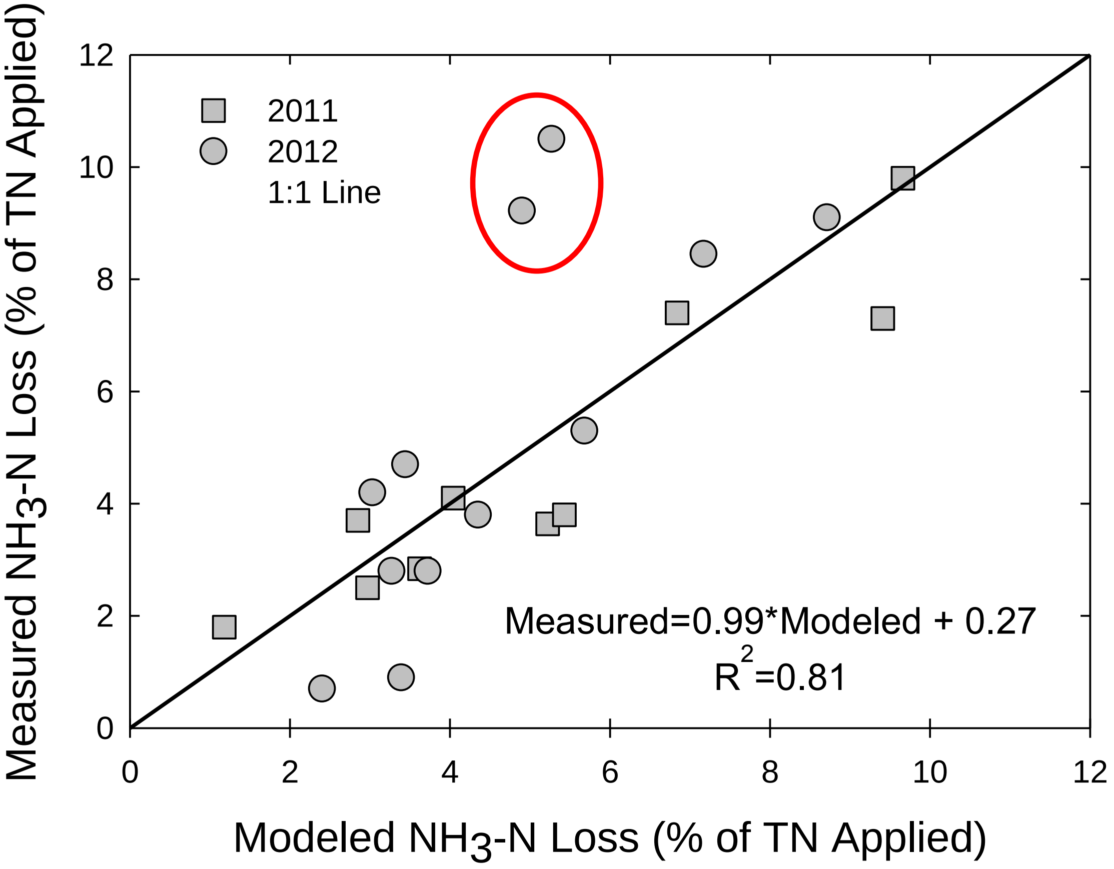
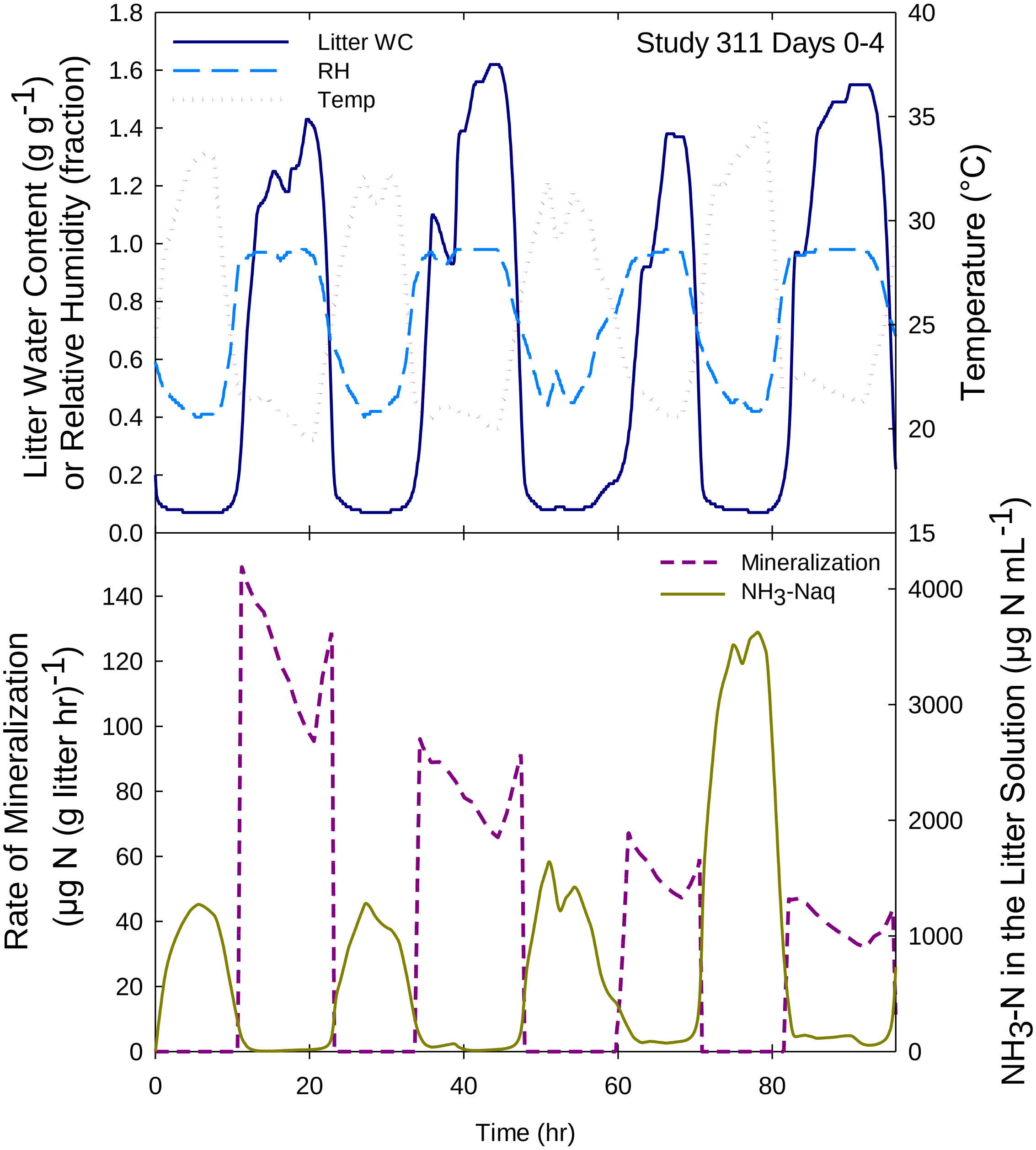

12
10
8
6
4
2
0
Measured NH3-N Loss (% of TN Applied)
0
2
4
6
8
10
12
Modeled NH3-N Loss (% of TN Applied)
2011
2012
1:1 Line
Measured=0.99*Modeled + 0.27
R2=0.81

Figure. 5.8.


Litter WC
RH
Temp
Study 311 Days 0-4
Litter Water Content ($g\ g^{-1}$)
or Relative Humidity (fraction)
Temperature (°C)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
15
20
25
30
35
40
Mineralization
NH_3-Naq
Rate of Mineralization
(µg N (g litter hr)$^{-1}$)
NH_3-N in the Litter Solution (µg N mL^{-1})
0
20
40
60
80
100
120
140
0
1000
2000
3000
4000
0
20
40
60
80
Time (hr)

Appendix 5.1.

1. Litter Water Sub-Model: Flux of water between the atmosphere and the litter on the surface

For static conditions:

$$\frac{\mathrm{dWC}}{\mathrm{dt}} = -\mathrm{k} * (\mathrm{AirMPa} - \mathrm{LitterMPa})$$

For diurnal fluctuations:

$$\frac{\mathrm{dWC}}{\mathrm{dt}} = -\mathrm{k} * (\mathrm{AirMPa} - \mathrm{LitterMPa}) * \mathrm{T}$$

where *dWC/dt* is the rate of wetting/drying, *T* is the air temperature in °C, and *k* is rate constant [g H_2O m $(g\ h\ MPa)^{-1}$] defined as:

k (drying) = (-0.0009 + -1.10*10^{-5} *LitterMPa +- 3.52*10^{-8} LitterMPa^2)*0.001;

k (wetting) =(-1.50*-LitterMPa$^{-2.27}$)*0.001.

2. Mineralization of Organic N Fast Pool

$$\frac{\mathrm{dNf}}{\mathrm{dt}} = \mathrm{kf} * \mathrm{Nf} * \mathrm{Minimum}\ (\mathrm{TF}, \mathrm{WF})$$

where *dNf/dt* is the mineralization of fast pool, *Nf* is fast pool of organic N (µg N g litter^{-1}), *kf* is the rate constant of mineralization (hr^{-1}) (Gordillo and Cabrera, 1994), *TF* is temperature factor of mineralization, and *WF* is the water factor of mineralization.

$\mathrm{kf} = (0.39 + 0.08 * \mathrm{TN} - 0.20 * \mathrm{UAN})/24$; (Gordillo and Cabrea, 1997) TN and UAN is expressed in g N kg litter^{-1};

$$TF = Q_{10}^{\frac{T2-T1}{10}}$$

where *T1* is the optimal temperature for mineralization and *T2* is the temperature during simulation (Cabrera et al., 2008);

$$\mathrm{WF} = -0.375 * \ln(-\mathrm{LitterWP}) + 1.4$$

	where the WF ranges from 0 to 1 and litter WP is expressed in (-MPa) from (Mowrer et al., 2014a).
2b. Mineralization of Organic N Slow Pool	$\frac{\mathrm{dNs}}{\mathrm{dt}} = \mathrm{ks} * \mathrm{Ns} * \ (\mathrm{TF} * (\mathrm{WF} * 0.2))$ where *dNs/dt* is the mineralization of the slow pool, *Ns* is the slow pool of organic N (µg N g litter^{-1}) and *ks* is rate constant of mineralization (hr^{-1}). Initial $\mathrm{Ns} = \ \mathrm{PMON} - \mathrm{Nf}$; where PMON is the potential mineralizable organic N (µg N g litter^{-1}). $\mathrm{ks} \ = \ 0.0003 * \mathrm{TN} \ - \ 1.1896$ where *ks* was fit to the 2011 field data.
3. Nitrification	$\frac{\mathrm{dNO_3{-}N}}{\mathrm{dt}} = \mathrm{knit} * \mathrm{NH_4} - \mathrm{N} * \mathrm{IF}$ where *knit* is the rate constant of nitrification as a function of temperature and WC (Cameron and Kowalenkn. 1976) and *IF* is the inhibition factor by NH4-N. The inhibition factor was determined by work in wastewater from Carrera et al. (2003). $\mathrm{IF} = \mathrm{Rate\ of} \frac{\mathrm{Nitration}}{\mathrm{Max\ rate\ of\ Nitration}}$ $\mathrm{Rate} = \ \mathrm{rmax} * \mathrm{S}/\mathrm{Ks} + \mathrm{S}\exp(-\mathrm{S}/\mathrm{KIA})$ Where *rmax* is the maximum substrate rate, *S* is the substrate concentration (ug NH4-N mL^{-1}), *Ks* is the half saturation coefficient, and *KIA* is the Aiba inhibtion coefficicient. Values for the coefficients were determined by Carrera et al. (2003) and the maximum rate of nitration was determined with concentrations of NH4-N observed through modeling.

4. Litter pH and changes in litter pH as a function of buffering capacity

$$\frac{\mathrm{dpH}}{\mathrm{dt}}(\text{increase}) = \frac{\frac{\mathrm{dOrgN}}{\mathrm{dt}}}{(14 * pHBC)}$$

$$\frac{\mathrm{dpH}}{\mathrm{dt}}\ (\text{decrease}) = \frac{\left(\frac{\mathrm{dNH_3-N}}{\mathrm{dt}} + 2 * \frac{\mathrm{dNO_3-N}}{\mathrm{dt}}\right)}{(14 * \mathrm{pHBC})}$$

where $dNH_3\text{-}N_{aq}/dt$ is the rate of change of the equilibrium between aqueous NH_4-N and NH_3-N.

5. Adsorption of NH_4-Naq to solid phase

$$\frac{\mathrm{dNH_4-Nad}}{\mathrm{dt}} = \mathrm{kad} * \mathrm{r} - \mathrm{NH_4} - \mathrm{Nad}$$

where *kad* was determined as 0.394 min^{-1} by Wahab et al. (2014) for ammonium adsorption to sawdust, *r* is amount adsorbed at equilibrium, and $NH_4\text{-}Nad$ is the amount adsorbed at time t.

$$\mathrm{r} = \mathrm{kF} * \mathrm{C}^{1/n}$$

where *r* is adsorbed NH_4-N (mg kg^{-1}) at equilibrium, *kF* is the Freundlich partition coefficient (L kg^{-1}), *C* is the NH_4-N concentration (mg L^{-1}), and *n* is the Freundlich coefficient (Liang et al., 2013).

6. Ammonium Diffusion to the Soil Layer

$$\frac{\mathrm{dDiff-N}}{\mathrm{dt}} = \mathrm{kred} * \mathrm{D_l} * \mathrm{C}$$

where *kred* is a reduction coefficient, D_l is the diffusion coefficient of NH_4-N in free water (1.176 x 10^{-4} cm^2 min^{-1}; Wang et al., 1998), and C is the concentration of NH_4-N in solution (ug mL^{-1}).

7. Ammoniacal-N Equilibrium

$$\frac{\mathrm{dNH_3-N}}{\mathrm{dt}} = \text{Theoretical equilbrium} - \mathrm{NH_3} - \mathrm{Naq}$$

where the difference between the theoretical equilibrium and actual pool allow for instantaneous calculations from pool of NH_3-Naq;

$$[\mathrm{NH3} - \mathrm{N}]\mathrm{aq} = (\mathrm{kD}\ [\mathrm{NH_4} - \mathrm{N}]\mathrm{aq}/[\mathrm{H^+}])$$

where log *kD*=-0.09018-2729.92/T (Kelvin), $[H^+]$ is the concentration of protons in solution, and the concentration of $[NH_3\text{-}N]_{aq}$ and $[NH_4\text{-}N]_{aq}$ in solution (Cabrera et al., 2008; Sherlock and Goh, 1985).

Theoretical Equilibrium is calculated on molar basis and back transformed into model units (µg N g litter^{-1}) using litter water content (g H_2O g litter^{-1}).

8. Ammonia Gas Partitioning

$$\frac{\mathrm{dNH_3{-}Ngas}}{\mathrm{dt}} = \mathrm{Theoretical\ Partition} - \mathrm{NH_3} - \mathrm{Ngas}$$

where the difference between the theoretical partition and actual pool allow for instantaneous calculations from pool of NH_3-Ngas;

$$[\mathrm{NH_3} - \mathrm{N}]\mathrm{gas} = \frac{[\mathrm{NH_3} - \mathrm{N}]\mathrm{aq}}{kH}$$

where kH is Henry's constant (log kH=-1.69+1477.7/ T (in degrees Kelvin)) and $[NH_3\text{-}N]_{aq}$ is the concentration of NH_3-N in the litter solution (Cabrera et al., 2008; Sherlock and Goh, 1985).

Theoretical Partition is calculated on concentration basis (µg N mL^{-1}) and back transformed into model units (µg N g litter^{-1}) using the volume of gas in the litter volume.

$$Depth\ of\ app. = \frac{Litter\ Application}{BD}$$

where *BD* is bulk density in g cm^{-3}, *Litter Application* is g cm^{-2}, and *Depth of app* is the height of the litter on the surface (cm).

$$Litter\ volume = \frac{Litter\ Application\ dwb}{Depth\ of\ app.}$$

where the *Litter volume* is cm^{3} per 1 g of dry litter and *Litter Application* is converted to dry weight using the litter WC.

$$Litter\ gas = Porosity \times Litter\ Volume - Litter\ Water$$

Where *Litter gas* was expressed as g cm^{3,} *Porosity* was calculated using the litter BD and particle density (%) and *Litter Water* was calculated based on g of litter per cm^{3} volume.

$$NH_3 - Ngas\ litter = \frac{[NH_3 - N]gas}{Litter\ gas}$$

where NH_3-Ngas is calculated on concentration basis (µg N mL^{-1}) and transformed to NH_3-Ngaslitter (µg N g litter^{-1}).

CONCLUSION

Ammonia (NH_3) volatilization from surface-applied broiler litter is a complex function of both litter characteristics and environmental variables. Due to this complexity, finding variables that can statistically and/or mechanistically model NH_3 volatilization may greatly aid in fertilizer equivalency recommendations for surface-applied litter. Our results showed that broiler litter can absorb or lose significant amounts of water to the atmosphere depending on the gradient in water potential between the litter and atmosphere. This change in litter water content can, in turn, affect both the mineralization and volatilization processes.

Ammonia volatilization losses in eleven field studies ranged from 0.9 to 10.5% of the applied TN from April to November of both 2011 and 2012. In two studies, small rain events in combination with high initial soil water content decreased NH_3 losses, probably due to increased movement of ammoniacal-N into the soil. In the remaining nine studies, a statistical model incorporating the initial ammonium-N plus uric acid-N concentrations in broiler litter with average vapor pressure explained 79% of the variability observed in NH_3 loss. The effect of elevated vapor pressure on NH_3 losses was attributed to the rewetting of the litter which likely leads to increased nitrogen mineralization and ammoniacal-N in solution. The statistical model developed may help estimate NH_3 losses from surface-applied litter and increase the accuracy of estimating available nitrogen under field conditions.

Results from laboratory experiments at contrasting relative humidities also showed that soil water content can affect the water content of surface-applied broiler litter and NH_3 loss, but those effects varied with relative humidity. Ammonia losses were greatest at high relative humidity and high soil water content. A soil at very low water content (0.03 g g^{-1}, -7.3 MPa) exposed to 92% relative humidity had a relatively high loss of NH_3 (11.2% of applied N) caused by an increase in litter water content. In contrast, the same soil at high water content (0.13 g g^{-1}, -0.9 MPa) and exposed to 32% relative humidity had a small loss of NH_3 (5.2% of applied N), which was caused by a fast decrease in the WC of broiler litter, with a consequent low nitrogen mineralization.

Litter pH is affected by nitrification, mineralization, and from the addition of acidifying chemicals such as aluminum sulfate (alum), all acting on the litter pH buffering capacity (pHBC). Thus, the pHBC of poultry litter is needed to estimate pH changes accurately both for the addition of alum and leads to increased precision for modeling NH_3 loss for surface-applied poultry litter. A new procedure was developed for measuring litter pHBC through titration and was calibrated with near infrared reflectance spectroscopy (NIR). Poultry litter pHBC ranged from 187 to 537 mmol H (pH unit kg dry litter)$^{-1}$ with the average being 287 mmol H (pH unit kg dry litter)$^{-1}$. The pHBC was adequately fit to both linear and sigmoidal curves, with sigmoidal curves defining buffering capacity as a function of litter pH. Sigmoidal curves may lead to more accurate estimations of pHBC for uses in a defined pH range, but linear pHBC was fit well to NIR estimations and alum additions. NIR shows promise in accurately and quickly estimating litter pHBC (calibration R^2 0.90), but further studies need to be conducted for model validation.

Combing results determined in Chapters 2 through 4, a simulation model for estimating NH_3 volatilization was developed using Stella® v. 9.0.3 Modeling Software. Using the gradient between air water potential, as a function of relative humidity, and the litter water potential, the effect of relative humidity on litter water content was accurately modeled with an R^2=0.82 under field conditions. Simulated litter water content fluctuated on a diurnal basis from 0.05 to 1.5 g H_2O g litter^{-1}, impacting both mineralization and the pool of ammoniacal-N subject to NH_3 volatilization. Incorporating the litter water content sub-model into a mechanistic NH_3 volatilization with a modified mineralization constant for the slow pool of organic N, modeled NH_3 loss for 28-d field studies with R^2=0.81. The model describes the importance of litter water content, initial ammonium-N pools, and mineralization to overall loss.

The results presented here indicate that NH_3 volatilization is a function of the diurnal fluctuations of temperature and litter water content due to changes in both litter solution and mineralization. High atmospheric water content during the evening/nighttime increases litter water content, likely favoring mineralization and decreasing the ammoniacal-N in solution through dilution. During daytime hours, low atmospheric water content increases NH_3 in solution through evaporation, favoring increased NH_3 loss. Overall, the statistical and mechanistic models presented in this research could lead to better estimations and understanding of NH_3 loss and plant-available nitrogen for surface-applied broiler litter to pastures.