NITROGEN FERTILIZER MANAGEMENT OF TEMPORARILY WATERLOGGED SOILS TO IMPROVE CORN PRODUCTION AND REDUCE ENVIRONMENTAL NITROGEN LOSS

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By

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The undersigned, appointed by the dean of the Graduate School,

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NITROGEN FERTILIZER MANAGEMENT OF TEMPORARILY WATERLOGGED SOILS TO IMPROVE CORN PRODUCTION AND REDUCE ENVIRONMENTAL NITROGEN LOSS

Presented by BRENDAN A. ZURWELLER

A candidate for the degree of

Masters of Science

And hereby certify that, in their opinion, it is worthy of acceptance.

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This thesis is dedicated to my mother and father.

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CHAPTER 1

LITERATURE REVIEW

Vulnerability of Midwestern Agricultural Soils to Flooding and Implications of Future Rainfall Predictions on Nitrogen Use Efficiency

The Midwest region of the United States is one of the world's largest contributors to row crop production while producing approximately 255 million Mg of corn (*Zea mays* L.) annually (Niyogi and Mishra, 2013). During the early portion of the growing season, corn is often susceptible to the consequences of extended and high intensity precipitation events that may lead to saturation or flooding of soils. Extended soil saturation or flooding events may cause yield reduction and even crop failure due to abiotic stress. Estimates of annual corn production losses due to intense precipitation events in the Midwest is about 3% and this loss could double by the year 2030 and cause losses of up to $3 billion per year (Rosenzweig et al., 2002).

The increased risk for corn production losses due to soil waterlogging is projected as a result of climate change increasing the probability of extreme precipitation events during the months of March to May (Rosenzweig et al., 2002; Patricola et al., 2012). Other studies have shown by analyzing historical data across the United States, trends of the last frost date occurring earlier in the spring which could eventually result in a shift of earlier corn planting dates (Schoof 2009; Kunkel et al., 2004). If corn planting dates begin earlier in the spring due to warmer temperatures accompanied by possible increases in precipitation, plants could be more susceptible to decreased production in response to extended soil saturation at warmer temperatures. Increases in the probability of warmer spring temperatures and extreme precipitation events as a result of climate change could also exacerbate current challenges associated with nitrogen (N) management in cereal row crop production (Robertson et al., 2012).

During the past 50 years, agriculture has doubled the amount of cereal production in an era known as the "green revolution" as advancements in pesticides and water use, breeding programs, farm equipment and technology, and fertilizer applications have been implemented (Tilman et al. 2001). From 1960 to 1995, the global use of N fertilizer increased seven-fold, currently contributing an annual average of about 100 Tg $year^{-1}$ of reactive N (N_r) to the environment (Tilman et al., 2002; Houlton, 2012). As N fertilizer consumption continues to increase in developing countries, N fertilizer application is expected to triple in cereal production by 2050, which will inevitably increase the amount of N_r if there is no improvement to the current global cereal production nitrogen use efficiency (NUE) of 30 to 50% (Cassman et al. 2002; Smil, 1999). The law of diminishing returns also suggests that increasing fertilizer application over the next 50 years will not be as successful in increasing yields as in the previous 50 years (Tilman et al. 2002). To successfully increase cereal yields to keep up with global food demand while reducing environmental impacts of N_r, research of developing N management strategies to increase NUE under possible climate change scenarios needs to be conducted.

Biological N Transformations Contributing to N Loss in Midwestern Row Crop Production

Urea Hydrolysis

Urea hydrolysis is the biochemical process in which an organic molecule of urea undergoes hydrolysis in the presence of urease enzymes, producing ammonia and bicarbonate as shown in equation 1.1 (Sommer et al., 2004):

$$CO(NH_2)_2 + 2H_2O \rightarrow 2NH_3 + H^+ + HCO_3^- \text{ (Equation 1.1)}$$

Urea hydrolysis is influenced by several factors including soil pH and urease enzyme activity. The percent of extra-cellular urease activity that exists in the soil environment is estimated at 46% and urease activity has been reported to be positively correlated with organic matter and clay minerals (Reynolds et al., 1985; Klose and Tabatabi, 1999; Geisseler et al., 2010). After urea hydrolysis, microbes may assimilate inorganic N for metabolic demands (Sommer et al., 2004).

Urease activity is affected by soil conditions, such as soil water content, pH, and temperature (Sommer et al., 2004). In soils that have soil water content below the permanent wilting point, the amount of urea hydrolysis is relatively low, while the rate of urea hydrolysis generally increases with increasing soil water content above the wilting point (Vlek and Carter, 1983; McInnes et al., 1986; Reynolds and Wolf, 1987; Ali-Kanani et al., 1991). The optimal pH range for urease activity has been reported at 8 to 9, while studies on certain soil types have reported no influence of pH on urease activity (Tabatabai and Bremner, 1972; Ouyang et al., 1998). Recous et al. (1988) reported the half-life of urea mixed with soil was 22, 15, and 6 hours when incubated at temperatures of 4, 10, and 20°C, respectively. This indicates that urea hydrolysis increased as soil temperature increased. The concentration of urea and other organic/inorganic substrates present in the soil environment also contributed to rates of urea hydrolysis (Sommer et al., 2004).

Significant gaseous N loss can occur from ammonia volatilization as a result of urea hydrolysis. About 23% of the global NH_3 emissions are a result of inorganic N and manure applications for row crop fertilization (Bouwman et al., 2002). The most significant soil parameter influencing ammonia volatilization from urea application was soil pH because of its effect on the NH_3/NH_4 ratio (Sommer et al., 2004):

$$NH_4 \leftrightarrow NH_3 + H^+ \quad pKa = 9.48 \text{ (Equation 1.2)}$$

Little ammonia volatilization has been shown to occur if soil pH was less than 7 (Sommer et al., 2004). If pH was greater than 7, the amount of ammonia volatilization increased as pH and temperature increased from increased ammonia concentration (Sommer et al., 2004).

The amount of inorganic carbon can influence soil pH and thus influences the quantity of NH_3 emissions (Sommer et al., 2004). A more basic pH favors the deprotonation of NH_4^+ which results in an increase of available H^+ ions and NH_3 in the soil (Equation 1.2). Soils that have naturally high pH also have more HCO_3^- present (pK_a = 10.4 for HCO_3^-/CO_3^{2-}) (Sommer et al., 2004). The combined effect of H^+ contributed by NH_3 formation, and CO_3^{2-} protonation equalizes soil acidity, while the emission of CO_2 will also favor CO_3^{2-} protonation (Sommer et al., 2004). Due to this equalizing effect, NH_3 emission was greatest with urea application in soils that had carbonates present to buffer the pH change from NH_3 emission, thus maintaining greater NH_3 concentrations for volatilization. The amount of NH_3 emissions drastically increased as the ratio of CO_2/NH_3 increases (Sommer et al., 2004).

Nitrification

After N is transformed to ammonical species it can undergo a series of oxidation reactions predominantly governed by the chemolithoautrophic bacteria, *Nitrosomonas* and *Nitrobacter*, to transform ammonia to nitrite and nitrite to nitrate, respectively (Ferguson et al., 2007). In both reactions, the purpose of oxidation is to supply energy through electron transport for cellular growth by driving H^+-electrochemical gradients for ATP synthesis and reduction of NAD^+ by "reverse electron flow" (Ferguson et al., 2007). The rate limiting step of nitrification is ammonia oxidation involving the compound reaction (Kowalchuk et al., 2001):

$$2H^+ + NH_3 + 2e^- + O_2 \rightarrow NH_2OH + H_2O \text{ (Equation 1.3)}$$

$$NH_2OH + H_2O \rightarrow NO_2^- + 5H^+ + 4e^- \text{ (Equation 1.4)}$$

$$0.5O_2 + 4H^+ + 2e^- \rightarrow H_2O + 2H^+ \text{ (Equation 1.5)}$$

Whereas equation 1.3 is catalyzed by the membrane bound enzyme ammonia monooxygenase (AMO), equation 1.4 is catalyzed by the enzyme hydroxlylamine oxidoreductase (HAO) in the periplasm (Kowalchuk et al., 2001).

The formation of nitrate is believed to predominantly occur in the cytoplasm of *Nitrobacter* from the reaction of (Ferguson et al., 2007):

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ \text{ (Equation 1.6)}$$

where nitrite is oxidized at a cytoplasmic site containing molybdenum and the electrons pass through a series of FeS centers (Ferguson et al., 2007). The route of electron transfer across the membrane through a subunit of Nitrite oxidase (Nor) is unknown, although these two electrons are transported to peripheral protein cytochrome C to be transported to cytochrome aa_3 oxidase for the following reaction (Ferguson et al., 2007):

$$0.5O_2 + 4H^+ \rightarrow H_2O \text{ (Equation 1.7)}$$

the water product of this reaction is then used for the conversion of nitrite to nitrate (Equation 1.6) in the cytosol and results in two protons being transported into the periplasm, maintaining a net neutral electrochemical gradient by transferring two electrons from the conversion of nitrite to nitrate (Ferguson et al., 2007).

High soil water content can be a limiting factor for nitrification if it results in soil hypoxia. Schjønning et al. (2003) reported an increase of nitrification rates with increasing water filled pore space (WFPS) to an optimum of 63, 83, and 83% for soil cores incubated with increasing clay contents of 11, 22, and 34%, respectively. This research also indicated that nitrification rates increased with O_2 diffusivity to an optimum for each soil texture. Although differences in the exact values for optimum nitrification rates in relation to water content and O_2 diffusivity vary greatly in different soil textures and conditions, there is a relationship between a decline in nitrification when increases in WFPS limit O_2 diffusion.

There are also general influences when considering the independent effects of temperature and pH on nitrification rates. Incubation studies with livestock manure have reported nitrification increased as temperature increased from 10, 17, and 24°C (Griffin and Honeycutt, 2000). Standford et al. (1974) found that nitrification rates were inhibited around 35°C. A pH of greater than or equal to 6 allowed for rapid nitrification while nitrification rates decreased when pH was less than or equal to 5 (Subbarao et al., 2006; Sahrawat, 2008).

Once nitrate is formed in the soil it is susceptible to multiple loss mechanisms due to its solubility in water, negative valence, and affinity to serve as an electron acceptor in reduced conditions. Nitrate leaching is considered the greatest mechanism of N loss in agroecosystems with row crop production (Ju et al., 2009; Robertson and Vitousek 2009; Zhou et al., 2012). The global contribution of nitrate leaching from agriculture was estimated to be around 19% of total applied N (Lin et al. 2001). A meta-analysis by Zhou and Butterbach-Bahl (2014) estimated 25 and 13% of applied N were lost in global corn and wheat production by NO_3^- leaching, respectively. Once nitrate was leached from its source, it can be problematic to human health, nutrient enrichment, and gaseous N loss by denitrification.

Denitrification

Denitrification is another major loss mechanism of N applied in row crop production and mostly occurs in soil when the concentration of soil oxygen declines and nitrate becomes the most energetically favorable electron acceptor for biochemical processes. Oxygen depletion occurs in soil as moisture content increases and gas diffuses from the soil pores. Microbes use the existing soil oxygen trapped in the soil media, and reintroduction of oxygen into the soil media is very slow since gases diffuse 10,000 times slower in water than air.

Redox potential is used to estimate the electron activity in the soil environment and can be used to form E_H-pH phase stability diagrams to predict thermodynamically stable mineral reactions in the soil environment (Vaughan et al., 2009). Since oxygen has the highest affinity to accept electrons, the soil environment becomes more electronegative as the concentration of oxygen decreases. The general redox values that reflect microbial activity are 300mV for aerobic conditions, 300 to -50mV for facultative anaerobic activity, and below -50mV is considered as strongly reducing conditions in which obligate reducing microbes flourish (Reddy et al., 2000). After oxygen is no longer present, NO_3^- reduction to N_2 occurs because is it the next highest energy yielding process for microbial respiration (Schink, 2006). This reduction process is the biochemically regulated process termed denitrification.

Due to less efficient ATP production during denitrification, denitrifying microbes only express genes for denitrification enzymes during times when oxygen is lacking (van Spanning et al., 2007). Although this process can be different among organisms, *Paracoccus denitrificans* is one of the model species in which the denitrification process has been studied extensively (van Spanning et al., 2007). The first step in denitrification is the reduction of nitrate which makes the presence of this molecule a requirement for denitrification. Nitrate is imported into the cytoplasm of bacteria and reduces to nitrite by electron transfer through Nitrate reductase (Nar). These electrons are supplied from an electron transport chain that originates from NADH and succinate. The NADH and succinate molecules are also the source of free H^+ ions that are delivered to the periplasm (van Spanning et al., 2007). Once nitrate is reduced to nitrite, it is then exported across the membrane by the nitrate/nitrite antiporter, which maintains an electrically neutral charge so H^+ motive force to the periplasm is not disrupted and membrane polarity is maintained (van Spanning et al., 2007).

Following the export of nitrite to the periplasm, it is further reduced to nitric oxide by the enzyme nitrite reductase (NIR). After the formation of nitric oxide occurs, it is reduced to nitrous oxide through nitric oxide reductases (NOR), and nitrous oxide can be reduce to dinitrogen gas through the enzyme, nitrous oxide reductase (NOS) (van Spanning et al., 2007). This series of reduction reactions has the same source of electrons as the reduction of nitrate, which is the oxidation of NADH and succinate in the cytoplasm (van Spanning et al., 2007). Since chemical reductions following nitrate occur in the periplasm, electrons must be transported across the membrane and delivered to the respective enzymes by water soluble proteins (van Spanning et al., 2007).

Other factors besides soil hypoxia and the presence of nitrate substrate contribute to respiratory denitrification rates. One of these is the amount of available carbon. This is because the oxidation of carbon is a source of electrons that ultimately reduces nitrate so ATP can be synthesized (Mahne and Tiedje, 1995). An incubation study showed a linear increase in total denitrification as microbial respiration increased, and there was a linear decrease in the proportion of N_2O/N_2 as denitrification increased (Miller et al., 2009). These results indicate that more N_2 gas was produced in conditions such as increased soil temperatures and organic carbon, which promoted higher rates of anaerobic respiration and denitrification. At greater denitrification rates, more energy was required to maintain metabolic activity which can be satisfied through the highly exergonic reaction of N_2O to N_2 (Zumft and Körner, 2007).

The range of soil pH has been demonstrated to affect denitrification rates. Optimal pH ranges for denitrification to occur have been reported at 7-8 (Simek and Cooper, 2002). Scientific literature has consistently reported a greater N_2O/N_2 ratio at lower pH values, and at pH 8.5 a direct reduction of NO_3^- to N_2 was shown to occur with no intermediates (Betlach and Tiedje, 1981; Simek and Cooper, 2002).

Dinitrogen and N_2O are the predominant gases emitted during row crop production. Dinitrogen emissions can contribute to significant N loss in poorly drained soils which has a greater potential to reduce crop yields as a result of N deficiency. Jember et al. (1997) reported that 46% of gaseous N emissions in corn production was in the dinitrogen form. The main concern for nitrous oxide in row crop production is due to its persistence in the atmosphere and global warming potential, which is estimated to be about ~300 times greater than for CO_2 and is estimated to be responsible for ~11% of the net anthropogenic radiative force (Solomon et al., 2007). Estimates have reported row crop production contributing ~50% of the global N_2O flux, with a range of 0.5% - 3% of applied N being lost as N_2O (Linquist et al., 2012; Robertson 2004; Stehfest and Bouwman, 2006).

Nitrifier Denitrification

Denitrification also occurs under aerobic conditions during nitrification, but is exclusive to autotrophic NH_3-oxidizers (Wrage et al., 2001). Once NH_3 is oxidized to NO_2^- during nitrification, NO_2^- can be reduced to NO, N_2O, and N_2 (Wrage et al. 2001). Enzymes used by NH_3-oxidizers during NO_2^- reduction are believed to be the same that occur during the reduction of NO_3^- during anaerobic denitrification (Wrage et al., 2001). Recent incubation studies have concluded that N_2O emissions from nitrifier denitrification was significant under ammonical fertilizer use when low oxygen concentrations were present, providing evidence that heterotrophic denitrification using NO_3^- as a substrate is not the only significant source of N_2O emissions under anaerobic soil conditions (Zhu et al., 2013).

Nitrogen Acquisition and Utilization by Plants

Nitrogen Transport

Ammonium and nitrate are the predominate N species absorbed by plants and are delivered to a plant root system by mass flow, diffusion, or root interception (Li et al., 2013). Both NH_4^+ and NO_3^- vary in soil concentration and affinity, which results in the different transport mechanisms of each ion to the plant root. Due the solubility and lack of affinity of NO_3^- to soil colloids, it is primarily delivered to the plant root systems by mass flow of soil solution under adequate moisture content. The plant rhizosphere can establish a high to low pressure potential under adequate moisture by absorbing soil solutes throughout the growing season which will drive mass flow (Li et al., 2013). Because ammonium generally undergoes rapid nitrification in aerobic soils, soil NH_4^+ concentration is usually lower than that of NO_3^- in soil, and its positive charge allows for greater soil sorption as a function of soil cation exchange capacity (CEC). The attraction of NH_4^+ to soil colloids mostly causes the transport of NH_4^+ to roots to be by either root interception or diffusion processes (Li et al., 2013). In both natural and root restricted conditions, Li et al. (2009) observed that NH_4^+ concentration in the rhizosphere and bulk soil was similar while NO_3^- concentration was significantly less in the rhizospere than in bulk soils.

Once absorbed by plant roots, solute transport occurs via the apoplastic, symplastic, or trans-membrane pathways. Symplastic flow requires active transport across the plasma membrane with further solute transport occurring cell to cell by diffusion through plasmodesmata (Li et al., 2013). Apoplastic root flow is passive solute transport until it is restricted by the casparian strip where solute flow is forced to move across the plasma membranes of the endodermis cells (Li et al., 2013). After solutes pass through the endodermis it must cross the plasma membrane of stele cells to be transported to the shoot through xylem sap flow (Grignon et al., 2001).

Nitrogen Assimilation and Storage

The uptake of NO_3^- across the plasma membrane of a cell is an energy-requiring process that is facilitated by NO_3^- transporters and co-transport with $2H^+$ (Li *et al.*, 2013). The co-transport of NO_3^- and $2H^+$ forms a positively charged complex for transport across the plasma membrane with the export of H^+ from the hydrolysis of ATP in order to maintain the electrochemical gradient inside the cell (Ullrich and Novacky, 1981; Ullrich, 1992). Once in the cytosol, NO_3^- can be transported to other plant tissues or stored in the vacuole, and reduced to NO_2^- in the cytoplasm for import into the plastid/chloroplast (Li et al., 2013). Once NO_2^- enters the plastids/chloroplast, it is further reduced to NH_4^+ and assimilated through the glutamine/glutamate synthase (GS/GOGAT) cycle (Masclaux-Daubresse et al., 2010). Nitrate reduced in the cytosol is considered a part of the active N pool (Li et al., 2013).

If high amounts of NO_3^- exist in the soil, plants will take up more N than it can assimilate for storage in vacuole (Li et al., 2013). Nitrate entering the vacuole must cross the tonoplast, facilitated by an antiporter that exports H^+ with the uptake of NO_3^- (De Angeli et al., 2006; Wege et al., 2010; Zifarelli and Pusch, 2009). Since the uptake of NO_3^- and NH_4^+ into the cytosol and NO_3^- into the vacuole result in a cytosol H^+ flux, cell transporters can export H^+ out of the cell or into the vacuole to maintain electrochemical gradients (Sorognia et al., 2001; Wang et al., 2009; Zhu et al., 2009 Kumar and Sharma, 2010; Krebs et al., 2010; Schumacher and Krebs, 2010).

Ammonium uptake from soil also occurs and has its own transporters for facilitating its movement across the plasma membrane and can potentially have less energy requirements than NO_3^- because it can be transported with or without H^+ symport (Masclaux-Daubresse et al., 2010). After entering the cytosol it can be directly assimilated by the GS/GOGAT cycle making it a more energy efficient process than nitrate assimilation since NH_4^+ reduction is not limited to the plastid/chloroplast.

Nitrogen and Carbon Metabolism

Nitrogen is a primary constituent for organic acid synthesis to form about 20 standard amino acids that serve as transportable water soluble intermediates between inorganic N and high molecular weight organic N compounds (HMWOC) such as proteins and nucleic acids (Li et al., 2013; Masclaux-Daubresse et al., 2010; Xu et al., 2012). The formation of these HMWOC is essential for plant life and is dependent upon the coupling of nitrogen and carbon metabolisms since amino acid synthesis requires carbon substrates, energy, and reducing power provided by photosynthesis and respiration for nitrogen assimilation and transamination (Xu et al., 2012). The rate of CO_2 assimilation has been reported to be strongly related to leaf N content, which was proportional to chlorophyll content and ribulose-1,5,-bisphosphate carboxylase/oxygenase (RuBisCO) activity (Evan, 1983). Other studies have shown nitrate assimilation is greater with increasing irradiance and CO_2 fixation (Gastal and Saugier, 1989; Pace et al., 1990). It has been estimated that RuBisCO proteins account for 50% and 20% of the total soluble protein content in leaves of C_3 and C_4 plants, respectively (Xu et al., 2012).

During the vegetative growth phase roots and shoots of plants are the primary sinks of N (Hirel et al., 2007). Ammonium absorbed by the roots is predominantly assimilated into amino acids in the root tissue, and root NO_3^- is transported by xylem with its assimilation into amino acids occurring in the shoot when an adequate N concentration was present, however the proportion of N assimilated in the roots or shoot can vary by plant species (Pate, 1973; Findenegg at al., 1989). Studies have reported that under adequate N conditions developing leaves are sinks for both carbon and nitrogen with the greatest amount of Nir activity occurring in developing leaves, and Nir activity declines as leaves age (Bellaloui and Pilbeam, 1990). Once a leaf matures it becomes a source of carbon and amino acids for plant tissue development (Hirel at el., 2007).

Leaf senescence is a significant internal source of N since 60 to 70% of senescing tissue proteins can be degraded and remobilized via phloem for plant use (Matile, 1992; Brouquisse et al., 2001). Nitrogen remobilization is of particular importance during the reproductive growth phase since protein content is about 10% of healthy cereal grains, which function for storage, metabolic, or structural purposes (Bénétrix and Autran, 2001). It has been estimated for corn that about 45 to 65% of the grain N comes from the distribution of leaf N, with the rest of grain N contribution occurring from N uptake occurring after silking (Hirel et al., 2007). After anthesis 60 to 85% of the N located in the plant can be partitioned to the ear (Ta and Wieland, 1992). A corn plant’s ability to remobilize N from the leaves to the grain results in greater N use efficiency and thus increases grain yield (Hirel et al., 2001). Low N is responsible for reduced grain yield as a result of reduced kernel weight and number of grains due to kernel abortion (Gallais and Hirel, 2004; Paponov et al., 2005).

Nitrogen Partitioning in Limiting Conditions

A response under N limiting conditions during a plant's vegetative growth phase is increasing its root-shoot ratio (Pilbeam, 2011). This phenomenon is a direct result of internal N and carbon partitioning directed to the root system to enhance N supply and root biomass (Ågren and Ingestad, 1987; Levin et al., 1989; Ågren and Franklin, 2003). The source of this N can be from the breakdown of N compounds in leaves and transported via the phloem (Simpson et al., 1982; Jeschke at al., 1985; Cooper and Clarkson, 1989; Larsson et al., 1991). Another significant source of internal N is the supply of NH_4^+ during photorespiration (Hirel et al., 2007). Other studies have shown that under low N uptake conditions, plants typically increase root NO_3^- reduction (Li et al., 2003).

During vegetative growth, there are generally two N deficiency responses that affect the relationship between N content and leaf area. These strategies are a plant reduces its leaf area, resulting in less potential to intercept light while maintaining leaf N concentration, or maintaining leaf area and potential to intercept light while decreasing leaf N concentration (Radin, 1983; Vos et al., 2005). Corn and most monocots undergo the latter response during N deficiency (Muchow and Davis, 1988). This response could potentially be because C_4 plants are more photosynthetically efficient than C_3 plants and require less N demand for RuBisCO production. Although certain monocot species are different to the degree in which they maintain their leaf area, corn plants have been reported to be very efficient at limiting the amount of leaf area reduction under N deficiency even when the amount of photosynthesis per unit leaf area has decreased (Leamire et al., 2008).

Observations of corn seedlings have reported that the rate of root N uptake and translocation to the shoot was primarily based on shoot demands (Engels and Marschner, 1995, 1996). In a study by Engels and Kirkby (2001), treatments were initiated that established low and high N demands in the shoots and roots by subjecting these organs to high and low temperatures. When shoots were subjected to a high temperature, while the roots were subjected to either high or low temperatures, the amount of N uptake remained similar. However, when the shoot was subjected to the low temperature while the root was subjected to the high temperature, the amount of N uptake decreased in comparison to when the shoot was kept at a high temperature. The organs with greater N partitioning resulted in greater biomass accumulation; however, the total amount of biomass for the treatment with high shoot temperature and low root temperature was not much greater than the treatment with low shoot temperature and high root temperature. A higher proportion of N return from the shoots to the root via phloem in the treatment with low shoot temperature and high root temperature was thought to serve as signal for limiting N uptake in the treatment with low shoot temperature and high root temperature.

Effects of Soil Hypoxia on Root Function and O_2 Deficiency Avoidance

Root Respiration Under O_2 Deficiency

During soil saturation plant roots can experience O_2 deficiency which limits respiration through the glycolysis pathway. The threshold for respiration to be limited to glycolysis is termed the critical oxygen point (COP) and is generally around 10% O_2 at 25° C, but can vary among specific plant species (Drew, 1997). If conditions escalate beyond the COP, a lack of oxygen limits respiration energy production to substrate-level phosphorylation of ADP to ATP via glycolysis and fermentation (Alonso et al., 2007;

Sairam et al., 2008). Without O_2 as a terminal electron acceptor in the oxidative phosphorylation electron chain (OPEC), nicotinamide adenine dinucleotide (NAD^+) can no longer be regenerated from the oxidation of nicotinamide adenine dinucleotide dehydrogenase (NADH). With limited regeneration of NAD^+, the citric acid cycle becomes limited for substrates to accept electrons. The fermentation pathway becomes activated and uses pyruvate to form either ethanol or lactate. The formation of ethanol or lactate requires enzymes and NADPH, which becomes NAD^+ after electron donation and can serve as an electron acceptor in the conversion of glyceraldehyde-3-phosphate to 1,3-bisphosphate during glycolysis. Plants can induce degradation of sucrose to hexose-6-phosphates via the sucrose synthase pathway with no ATP requirement in contrast to the invertase pathway which requires two ATP molecules per sucrose molecule (Mustroph et al., 2005; Licausi and Perata, 2009). The energy yield from the aerobic respiration of one molecule of hexose is about 39 molecules of ATP, whereas the fermentation of one molecule of hexose yields a maximum of three molecules of ATP (Geigenberger, 2003).

Another effect of O_2 deficiency on physiological root function is the drop in cytosol pH, termed cytoplasmic acidification (Felle, 2010). There are still several theories for why this occurs, but it undoubtedly impairs H^+ gradients across membranes that drive the co-transport of molecules in plant cells (Felle, 2010). This has been shown to occur at the tonoplast where ATPase was partially deactivated causing transport across the tonoplast to be limited to passive transport (Felle, 2010).

Cytoplasmic acidosis can also have an effect on root water transport by affecting aquaporins (AQPs), which are membrane proteins that facilitate water transport across membranes. Aquaporin consists of about 15% of the total proteins in a membrane, and has been reported to account for up to 90% of total root water flow (Johanson et al., 1996; Rivers et al., 1997; Martre et al., 2001; Bramley et al., 2006). The histidine residue portion of the protein is located in the cytosol and is sensitive to pH (Tournaire-Roux et al., 2003). Upon cytoplasmic acidification, this residue is protonated which leads to the closing of the aquaporin and therefore a reduction in root water conductivity (Tournaire-Roux et al., 2003).

Plant Adaptations to Avoid O_2 Deficiency

Many crop plants have adaptive mechanisms that can be induced to avoid O_2 deficiency and return tissue back to a state of aerobic respiration. One of these responses is aerenchyma formation, which is the development of specialized tissues that form longitudinal gas-filled void spaces that provide lower resistance pathways for gas diffusion (Armstrong, 1979). By providing low resistance pathways for gas diffusion, a plant can supply oxygen from non-submerged regions of the plant to submerged regions. Aerenchyma can be formed constitutively in crop plants and different formation mechanisms in various plant tissues. Primary aerenchyma forms in the cortex tissue and has been identified in roots of rice (*Oryza sativa* L.), corn (*Zea mays* L.), barley (*Hordeum vulgare* L.), wheat (*Triticum aestivum* L.), and soybean (*Glycine max* L.) (Armstrong, 1979; Jackson and Armstrong, 1999 Evans, 2003; Nishiuchi et al., 2012; Thomas et al. 2005; Yamauchi et al. 2013). Secondary aerenchyma forms outside of the cell cortex and has been found in the stem, hypocotyl, tap root, adventitious roots, and root nodules of soybean (Arikado, 1954; Walker et al., 1983; Saraswati et al.,1992; Mochizuki et al., 2000; Thomas et al. 2005; Yamauchi et al. 2013) .

The mechanism for aerenchyma development in corn under O_2 deficiency is lysogenic aerenchyma formation, where already development cells experience programmed cell death (PCD), leaving void spaces in the cortex (Evans, 2003). Programmed cell death during lysogenic aerenchyma formation is regulated by the gaseous hormone ethylene (Jackson, 1985). The precursor of ethylene is methionine (Met) (Rzewuski and Sauter, 2008). Activation of Met occurs with the dephosphorylating of ATP and S-Adenosyl-methione synthetases (SAMS) converting Met to S-Adenosyl-methione (AdoMet) (Rzewuski and Sauter, 2008). AdoMet serves as the substrate for the biosynthesis of 1-Aminocyclopropane-1-carboxylic acid (ACC) which is catalyzed by the enzyme ACC synthase (Rzewuski and Sauter, 2008). This reaction releases the CH_3—S group of methionine to be recycled through a series of reactions known as the Yang cycle for the generation of the Met in ethylene biosynthesis (Rzewuski and Sauter 2008). The ACC molecule undergoes the conversion to ethylene through the enzyme, ACC oxidase, which has an activation requirement of oxygen (Rzewuski and Sauter, 2008).

Enhanced Efficiency N Products and In Season N as a Management Tool to Mitigate Yield Loss to N Deficiency

Enhanced Efficiency N Products

Enhanced efficiency N (EEN) products are intended to minimize nutrient losses to the environment compared to conventional sources and potentially improve the synchrony of soil N concentrations to plant N demand with an objective to improve nitrogen use efficiency (NUE) and agronomic sustainability. There has been interest in EEN products being applied at pre-planting only compared to split applications that can require additional equipment investments and favorable climatic conditions. One type of

EEN product are considered slow release products that can be applied with traditional fertilizers to retard microbial populations to slow N transformation rates of applied N and reduce high concentrations of mobile N species early in the growing season (Trenkel, 1997; Shaviv et al. 2005; Chien et al. 2009). Other EEN products are controlled released fertilizer formulations that have been coated or encapsulated for delaying N release (Trenkel, 1997; Shaviv et al. 2005; Chien et al. 2009).

Nitrification inhibiters (NI) act on the *Nitrosomonas* bacteria to slow the rate limiting step in the nitrification process of NH_4^+ conversion NO_2^-. The extent of its reliability to increase grain yield, improve NUE, and thus potentially reduce environmental impact has been examined in scientific literature. Burzaco et al. (2013) reported urea treated with 2-chloro-6-(trichloro-methyl) pyridine (nitrapyrin) nitrification inhibitor applied pre-plant in corn production had about 17% greater NUE (grain yield divided by the amount of N fertilizer applied) and 25% greater nitrogen recovery efficiency (NRE), (expressed as N uptake of the above ground biomass in the treated plots minus N uptake of the control, and divided by the amount of N fertilizer applied) than treatments with urea alone, although treatments with NI did not correspond to increased grain yield (GY) and plant N uptake (PNU). These results were contrasted with their meta-analysis of NI's that reported increases in GY and PNU, but not NUE, NRE, and nitrogen internal efficiency (NIE). Other studies have reported increased corn yield from 0.3 to 0.6 Mg ha^{-1} with the use of NI's in comparison to conventional urea in wet years, but no significant increase with NI during a dry year (Gagnon et al., 2012). Reductions in soil N_2O have also had mixed reports depending on management practices and climatic conditions when applying NIs. Omonode and Vyn (2013), reported a 44%

reduction in N_2O emissions compared to sidedress UAN, with 40-50% of the N_2O variability explained by soil moisture, temperature, precipitation, and soil NH_4^+-N concentration. However, Parkin and Hatfield (2010) reported no reduced cumulative annual soil N_2O emissions with an application of nitrapyrin with fall applied anhydrous ammonia.

Urease inhibitors (UI), such as N-(n-butyl) thiophosphoric triamide (NBPT) are chemicals that reduce the activity of soil urease enzymes in order to slow the rate of urea hydrolysis in order to avoid soil ammonia volatilization from increasing pH around the fertilizer granule (Ernst and Massey, 1960; Chien et al., 2009; Soares et al., 2012). Soares et al. (2012) treated conventional urea with NBPT and found a delayed peak in soil NH_3 volatilization loss that ranged from 54 to 72% compared to non-treated conventional urea. Due to a reduction in soil NH_3 volatilization loss, there is potential to provide more N to the plant and increase grain yields. An average of 400 field trials reported increasing grain yields by 0.89 and 0.56 t ha^{-1} by treating urea or UAN with NBPT, respectively (Trenkel, 1997).

A widely-used controlled release fertilizer is polymer coated urea (PCU) which has a slower urea release mechanism by diffusing urea through the polymer membrane into the soil (Chien et al., 2009). During two years of research, Noellsch et al. (2009) reported 1,530 and 1,810 kg ha^{-1} greater corn grain yields with incorporated pre-plant PCU in comparison to conventional urea (CU) at a low-lying landscape position. One year of this study also reported increased N uptake and NRE with PCU in comparison to CU. In contrast to this, Halvorson and Del Grosso (2013) reported no yield increases when comparing PCU to CU. Several recent research studies have compared soil N_2O

emissions with PCU and CU across varying application timings and placement, tillage practices, and under irrigated conditions to find both decreases in N_2O efflux with PCU and no differences between the two fertilizer products (Halvorson and Grosso 2012; Grant et al., 2012; Nash et al., 2012; Asgedom et al., 2013; Halvorson and Del Grosso 2013; Parkin and Hatfield, 2013).

In-Season Rescue N Applications

Saturated soils are prone to N loss due to denitrification and leaching of NO_3^- in poorly or well drained soils, respectively. Significant N losses due to these environmental conditions can result in N deficiency. If N deficiencies occur, in-season applications of N can increase grain yield (Binder et al., 2000; Scharf et al., 2002; Diaz et al., 2008; Nelson et al, 2010). Binder et al. (2000) established an N sufficiency index using the relationship of chlorophyll meter readings between N deficient corn plants that received varying pre-plant N rates, and non-N-deficient corn that received full pre-plant rates to evaluate the severity of N deficiency before in-season N applications. The in-season N application with N deficient corn at V6 resulted in a 12% reduction of grain yield when compared to the non-deficient corn, and increases in grain yield was observed when in-season application were made up to R1. Scharf et al. (2002) delayed N applications in corn to establish N deficiency and made in-season N applications until silking. Results indicated that when compared to control plots that received N applications at planting, little or no grain yield loss occurred up to growth stage V11. Nitrogen fertilizer applications from V12 to V16 corresponded to about a yield loss of 3%. Although yield loss occurred when plants received N applications, relative to non-deficient corn, evidence was presented that plants responded to the applied N. Nelson et al. (2010) evaluated rescue N applications using various N sources with broadcast and between-row banding in corn hybrids at pre-plant, 30 (V3-V4), 60 (V5-V6), 90 (V7-V8), 120 (V9-V10) cm plant length. The study found that both placements were optimal when the plant was 30 cm tall. At heights greater than 30 cm, grain yields started to decline in comparison to the 30 cm height N applications, with broadcast applications having greater yield decreases when compared to between-row banding as corn height increased beyond 30 cm. Grain yield decreases when comparing broadcast application to between-row band at heights greater than 30 cm were attributed to leaf injury from broadcast fertilizer applications. This study concluded that urea treated with NBPT is the best source for broadcast rescue N treatments, while the greatest yield increases were with between-row banding of NH_4NO_3.

RESEARCH OBJECTIVES:

Objective #1: To characterize changes in soil inorganic N, NUE, and corn grain yield response to applications of different EEN fertilizer products subjected to different waterlogging durations.

Hypothesis #1: Enhanced efficiency N fertilizers will maintain higher soil N concentrations throughout the growing season, resulting in greater plant N uptake and higher grain yields than conventional urea. Corn grain yields will also be decreased as soil waterlogging duration increases due to an interactive effect of greater N loss and abiotic stress due to waterlogging.

Objective #2: To evaluate the effect of a rescue application of urea plus urease inhibitor (Agrotain®, Koch Agronomic Services, Wichita, Kansas) after soil waterlogging at growth stage V10 and its effect on NUE and corn grain yield.

Hypothesis #2: A rescue application of urea plus urease inhibitor after soil saturation will provide more available N in the soil with all enhanced efficiency urea treatments, which will result in greater N uptake during reproductive development, promoting higher corn grain yields. A greater rescue N response will be present with increased waterlogging duration due to greater N loss and plant N deficiency.

Objective #3: To measure soil surface N_2O gas efflux resulting from different EEN treatments during different periods of soil saturation.

Hypothesis #3: Waterlogged soils and EEN treatments will emit greater fluxes of N_2O than the same treatments in non-saturated soils due to more favorable conditions for denitrification and higher soil N concentrations present at waterlogging, respectively.

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CHAPTER 2

NITROGEN FERTILIZER MANAGEMENT OF TEMPORARILY WATERLOGGED SOILS TO IMPROVE CORN PRODUCITON

ABSTRACT

Extreme precipitation events during April to June can often cause decreases in corn (*Zea mays* L.) grain yields in the Midwestern United States. Major problems associated with intense precipitation events in corn production include escalated N loss and abiotic crop stress. A two-year study of nitrogen (N) loss of enhanced efficiency N fertilizers during waterlogging durations planted to corn was initiated in 2012 on a poorly-drained claypan soil in Northeast Missouri. The objectives of this study were to determine the effects of waterlogging on preplant and rescue N fertilizer applications on corn production and N availability. Pre-plant fertilizer treatments included a non-treated control (CO), urea (NCU), urea plus nitrapyrin (NCU+NI), and polymer coated urea (PCU) applied at 168 kg N ha^{-1}. Waterlogging durations included a non-waterlogged control, one, and three days when corn was V6. A rescue N application of 83 kg N ha^{-1} of urea plus N-(n-butyl) thiophosphoric triamide (NBPT) (NCU+UI) was applied at V10 to half of all treatments. On the post-waterlogging soil sampling date, PCU had greater inorganic soil N content than NCU by 25.2 and 56.6 kg N ha^{-1} in 2012 and 2013, respectively, to a depth of 30 cm in the plots that received no waterlogging. A significant interactive effect of year, pre-plant N fertilizer, and waterlogging duration was observed on soil NO_3^--N content ($P < 0.10$). In the severe drought year of 2012, there was a 320 kg ha^{-1} yield increase when comparing PCU to NCU in plots where no NCU+UI was applied. When NCU+UI was applied to pre-plant N treatments of NCU and NCU+NI in

2012, there was a 500 and 300 kg ha^{-1} yield increase, respectively. During the 2013 growing season, there was no enhanced efficiency pre-plant fertilizer or rescue N treatment effect on yield; however, although there was a 10% yield reduction after three days of waterlogging.

INTRODUCTION

Cereal Production and Climate Change

The global human population is expected to increase 35% by 2050, requiring an estimated food production increase of 70 to 100% (Bruinsma, 2009; Rosegrant et al., 2009; UNFPA, 2010; van Wart et al., 2013). However, variability in climate from year-to-year and higher incidence of extreme weather has accounted for a high proportion of the reduction in observed yields. For example, Lobell and Field (2007) reported that from the years of 1961 to 2002 at least 29% of the variance in annual global yields of wheat (*Triticum aestivum* L.), rice (*Oryza sativa* L.), corn (*Zea mays* L.), soybeans (*Glycine max* L.), barley (*Hordeum vulgare* L.), and sorghum (*Sorghum bicolor* L.) could be explained by variation in minimum and maximum temperatures and precipitation events. Climate change projections indicate large production regions could see an increase in climate-related grain yield variability from year-to-year and possible increases to the average agronomic loss caused by excessive moisture which has been estimated at $600 million per year in corn production in the Midwestern Corn Belt (Rosenzweig et al., 2002). Villarini et al. (2013) reported increasing trends of heavy rainfall over the north central United States by analyzing daily rainfall records from 447 rain gauge stations. They showed that the area of largest increasing trends was accompanied by the greatest trends of increasing temperature. Future predictions for Midwest temperature is a 1 to 3°

C increase over the next coming decades, along with increase precipitation during the warm season (May to September) resulting from an increased magnitude of intense precipitation events (IPCC, 2007; Schoof et al., 2010; Patricola and Cook, 2012).

Effects of Climate Change on N loss

Lobell (2007) projected that mean temperatures by 2050 in the U.S. Corn Belt during the growing season could increase 3.0° C. Nitrogen mineralization and nitrification rates are temperature dependent processes that could be affected by increased soil temperatures (Melillo et al., 2002). Several studies have shown linear increases of soil mineralization and nitrification with increasing temperatures to an optimum (Campbell et al. 1981; Griffin and Honeycutt, 2000; Standford, 1973; Whalen and Sampedro, 2010). An increase in these soil processes could cause more rapid conversion of organic matter and N fertilizer to the NO_3^- form which is susceptible to N loss through leaching and denitrification. The effects of increased temperature in combination with increased rainfall could exacerbate N loss, possibly resulting in decrease yields and detrimental impacts to human health and the environment.

Physiological Crop Stress in Waterlogged Soils

Abiotic stress associated with soil waterlogging or excessive soil moisture can hinder crop development. Once rhizosphere O_2 is depleted by the plant and microorganisms, its reintroduction by diffusion is slow since gases diffuse about 10,000 times slower in water than air. Soil hypoxia initially limits crop root respiration primarily to the glycolysis and fermentation pathway (Geigenberger, 2003). Another effect of O_2 deficiency on physiological root function is the drop in cytosol pH, termed cytoplasmic acidification which can impair H^+ gradients across membranes that drive transport of molecules in plant cells (Felle, 2010). Cytoplasmic acidosis been shown to cause protonation of the histidine residue of aquaporins which deactivates aquaporins, and therefore reduces root water conductivity and stomatal conductance (Tournaire-Roux et al., 2003). Therefore, crops under waterlogging conditions can suffer internal drought conditions and reduced N uptake.

Improving Corn Grain Production by Improving Nitrogen Use Efficiency and Managing in Season N Deficiency

Enhanced Efficiency N Products

Enhanced efficiency N (EEN) products are intended to minimize the nutrient loss to the environment compared to conventional sources and potentially improve the synchrony of soil N concentrations to plant N demand with an objective to improve nitrogen use efficiency (NUE) and agronomic sustainability. If grain yield benefits can be achieved to offset additional cost, these products could be desirable to farmers in comparison to sidedress applications requiring additional time and equipment investments, favorable climatic conditions, and reduce scheduling conflicts with other planting and pest management operations.

Nitrification inhibitors (NI) are slow-release products that act on *Nitrosomonas* bacteria to slow the rate-limiting step in the nitrification process when NH_4^+ is converted to NO_2^-. The use of NI to increase grain yield, improve NUE, and thus potentially reduce negative environmental impacts has been extensively examined in the scientific literature. For example, Burzaco et al. (2013) reported urea with 2-chloro-6-(trichloro-methyl) pyridine (nitrapyrin) NI applied at pre-plant in corn production had about 17% greater NUENUE (grain yield divided by the amount of N fertilizer applied) and 25% greater nitrogen recovery efficiency (NRE), (expressed as N uptake of the above ground biomass in the treat plots minus N uptake of the control, and divided by the amount of N fertilizer applied) than treatments with urea alone, although treatments with NI did not result in increases in grain yield and plant N uptake (PNU). These results were contrasted with their meta-analysis of NI's that reported increases in grain yield and PNU, but not NUE, NRE, and nitrogen internal efficiency (NIE). Other studies have reported benefits in corn grain yield of 0.3 to 0.6 Mg ha^{-1} with the use of NI's in comparison to conventional urea in wet years but not in a dry year (Gagnon et al., 2012).

Urease inhibitors (UI) are chemicals that reduce the activity of soil urease enzymes in order to slow the rate of urea hydrolysis to avoid soil ammonia volatilization from increasing pH around the fertilizer granule (Ernst and Massey, 1960; Chien et al., 2009; Soares et al., 2012). Soares et al. (2012), treated conventional urea with N-(n-butyl) thiophosphoric triamide (NBPT) UI and found that it delayed the peak soil NH_3 volatilization loss with a 54 and 72% reduction in comparison to that of non-treated conventional urea. Due to a reduction in soil NH_3 volatilization loss there is potential to provide more N to the plant and increase grain yields. An average of 400 field trials reported increasing grain yields by 0.89 and 0.56 t ha^{-1} by treating urea and UAN with NBPT, respectively (Trenkel, 1997).

A widely- used control release fertilizer is polymer coated urea (PCU) which has a slower urea release mechanism of internal swelling of the polymer membrane causing diffusion of urea into the soil (Chien et al., 2009). During two years of research, Noellsch et al. (2009) reported greater corn grain yields of 1,530 and 1,810 kg ha^{-1} with incorporated pre-plant PCU in comparison to conventional urea at a low lying landscape position. One year of this study also reported increases of N uptake and NRE with PCU in comparison to CU. In contrast to this, Halvorson and Del Grosso (2013) reported no yield increases when comparing PCU to conventional urea.

In- Season N Deficiency Treatments

Saturated soils are prone to N loss due to denitrification and leaching of NO_3^- in poorly or well drained soils, respectively. Significant N losses due to these environmental conditions can result in N deficiency. If N deficiencies occur, in-season applications of N or "rescue" N applications can promote an increased grain yield response (Binder et al., 2000; Scharf et al., 2002; Diaz et al., 2008; Nelson et al, 2010). Binder et al. (2000) established an N sufficiency index using the relationship of chlorophyll meter readings between N deficient that received varying pre-plant N rates, and non-N-deficient corn plants that received full pre-plant rates to evaluate the severity of N deficiency before in season N applications. Yield responses were obtained up to growth stage R1 and at V6 yield obtained were 12% of the maximum. Scharf et al. (2002) delayed N applications in corn to establish N deficiency and made in-season N applications until silking. Results indicated that when compared to control plots that received N applications at planting, little or no grain yield loss occurred up to growth stage V11. Nitrogen fertilizer applications from V12 to V16 corresponded to about a yield loss of 3%. Although further yield loss occurred when plants received N applications, evidence was presented that plants responded to the applied N. Nelson et al. (2010) evaluated rescue N applications using various N sources with broadcast and between-row banding in corn hybrids at pre-plant, 30 (V3-V4), 60 (V5-V6), 90 (V7-V8), 120 (V9-V10) cm. The study found that both placements were optimal when the plant was 30 cm tall. At heights greater than 30 cm, grain yields started to decline in comparison to the 30 cm height N applications, with broadcast applications having greater yield decreases when compared to between-row banding as corn height increased past 30 cm. Grain yield decreases at heights greater than 30 cm with broadcast N application were attributed to leaf injury from fertilizer applications. This study concluded that urea treated with NBPT is the preferred source for broadcast rescue N treatments, while the greatest yield increases were with between-row banding of NH_4NO_3.

The objectives of this study was to determine the effects of waterlogging duration, pre-plant N sources and rescue N fertilizer applications on corn production and N availability.

MATERIALS AND METHODS

Site Characterization and Experimental Design

This two-year study was initiated in 2012 and repeated in 2013 on a poorly-drained claypan soil in Northeast Missouri at the University of Missouri's Greenley Memorial Research Center (40° 1' 17" N, 92° 11' 24.9" W). The soil was a Putnam silt loam (fine, smectitic, mesic, Vertic Albaqualfs). Initial soil samples were collected each year prior to the application of treatments to characterize the soil at depth increments of 0-10, 10-20, and 20-30 cm using a stainless steel push probe. All soil samples were air-dried and ground to pass through a sieve with 2 mm openings. The initial soil samples were analyzed by the University of Missouri Soil and Plant Testing Laboratory using standard soil testing procedures (Nathan et al., 2006). Soil bulk density measurements in the field were determined using the core method (Blake et al., 1986). Daily weather conditions for air temperature and precipitation were obtained from a nearby automated weather station located at the Greenley Center. Crop management information is listed in Table 2.1.

Waterlogging duration, and pre-plant EEN, and rescue N fertilizer treatments were arranged in a split-split plot arrangement in a randomized complete block design with three replications. Each plot consisted of six rows (30.5 meters in length with 76.2 cm spacings) planted to DEKALB 62-97VT3 (Monsanto, St. Louis, Missouri) at 79,040 seeds ha^{-1}. Two different field locations were used for the 2012 and 2013 research trials. Waterlogging treatments (0, 1 and 3 days of waterlogging duration) were the main plots and were initiated at the V6 corn growth stage using temporary soil levees to surround each waterlogging block. Vegetative growth stage V6 was determined using the leaf collar method (Abendroth et al., 2011). Ponding of water occurred on the soil surface at a depth of three to five inches. Levees were removed to allow ponded water to escape after the intended waterlogging duration had been achieved.

Nitrogen fertilizer treatments were the sub-plot and included a non-treated control (CO) and pre-plant N fertilizer sources of non-coated urea (NCU), non-coated urea plus nitrapyrin nitrification inhibitor at 2 L ha^{-1} (NCU + NI) (N-Serve®, Dow AgroSciences, Indianapolis, Indiana), and polymer-coated urea (PCU) (ESN®, Agrium, Inc., Calgary, Alberta) were applied at 168 kg N ha^{-1}. All fertilizer N treatments were broadcast applied using a hand spreader and incorporated immediately after application with a Tillol (Landoll Corp., Marysville, KS).

Following the waterlogging treatments, a rescue N fertilizer application of urea at 84 kg ha^{-1} plus NBPT (N-(n-butyl) thiophosphoric triamide) (Agrotain®, Koch Agronomic Services, Wichita, Kansas) urease inhibitor (NCU + UI) at 4.2 L ton^{-1}. This was applied to half of each pre-plant fertilizer treatment at the V10 corn growth stage. The same rescue application rate was used each year, and was determined in 2012 as the economical optimal N rate for yield response at corn growth stage V10 based on SPAD 502 chlorophyll meter readings (Konica Minolta, Hong Kong) and equations provided in Scharf et al. (2006). Chlorophyll meter readings were determined with a ten plant average using the most mature leaf.

Field Measurements

Environmental conditions were characterized during the waterlogging treatment. Measurements of soil surface E_h and pH were recorded with a portable pH and millivolt meter (Oakton 310 pH meter, Vernon Hills, IL) using an Ag/KCl electrode saturated in 4 M KCl solution (Cole Palmer ORP/pH 3' submersible, Vernon Hills, IL). Soil E_h was converted to the standard H_2 reference electrode values (Vepraskas et al., 2002). Soil temperatures (Oakton Temp 10 Thermocouple, Vernon Hills, IL) and a soil samples at a 10 cm depth were collected for determining gravimetric water content.

Soil samples were collected from 0-10, 10-20, and 20-30 cm depths from pre-plant N fertilizer treatments before and after the temporary waterlogging events, and from pre-plant N fertilizer treatments with and without rescue NCU+NI treatments following corn grain harvest by compositing 10 cores per plot using a stainless steel push probe. Each soil sample was analyzed for NH_4^+ and NO_3^- using a 2 M KCl extraction and analysis with a Lachat 8400 series II (Hach Corp., Loveland, CO) automated ion analyzer (QuikChem Method 12-107-06-2-A & 12-107-04-1-B).

At physiological maturity, corn silage was harvested from 3.1 meters of row length and dried at 70° C. Samples were homogenized being ground to pass through a 1 mm sieve and analyzed for total organic total N concentrations with a TruSpec Carbon:Nitrogen analyzer (LECO Corp., Township, Michigan) using the combustion method. Corn grain yields were harvested with a plot combine (Wintersteiger, Salt Lake City, UT) from two center rows in each plot 12.2 meters in length and adjusted to 150 g kg^{-1} moisture. Grain samples were collected from each plot for analysis of extractable starch and protein content (Foss 1241 Infratec, Eden Prairie, MN).

Statistical Analysis

All statistical analysis was performed using the SAS v. 9.3 statistical program (SAS Institute, 2013). Analyses of variance (ANOVA) were determined for all collected data using PROC MIXED. Normality of all data was verified using PROC UNIVARIATE. Data were combined over site years and factors when appropriate as indicated by the ANOVA results. Multiple comparisons significance was determined using Fisher's Protected Least Significant Difference (LSD) at the $P < 0.10$ probability level.

RESULTS AND DISCUSSION

Initial Soil Characteristics

Soil samples were collected before pre-plant N fertilization for 2012 and 2013. Initial soil results indicated an adequate amount of Bray P1-phosphorus and exchangeable potassium, calcium, magnesium based on University of Missouri fertilizer recommendations for corn (Buchholz, 2004) (Table 2.2). The 2012 site had a higher soil pH in the 0-10 cm depth of 0.7 pH units compared to 2013. The concentration of NH_4^+-N plus NO_3^--N prior to pre-plant N treatments was 40.5 and 50.2 mg N kg^{-1} $soil^{-1}$ to a depth of 30 cm for the 2012 and 2013 field locations, respectively. In general, NO_3^--N decreased with sampling depth in 2012, whereas NO_3^--N increased with sampling depth in 2013.

Climatic Conditions

Total cumulative precipitation from planting to grain harvest was 363 and 566 mm for 2012 and 2013, respectively (University of Missouri Extension, 2014) (Figure 2.1). The cumulative 10-year average (2002 to 2011) for precipitation from 1st April to 1st October at Greenley Memorial Research Center was 984 mm and the cumulative rainfall for this respective time period in 2012 and 2013 was 684 and 595 mm, respectively. Severe drought occurred during 2012, and it was the third driest and warmest April to August period in Missouri over the past 120 years (NOAA, 2012). The 2013 growing season had variation throughout the growing season with intense spring rains resulting in the 15th wettest April-June time period during the past 120 years (NAOO, 2013). However, rainfall occurred during the month of August at Greenley Memorial Research Center in 2013. Drier and warmer spring temperatures promoted an earlier planting date in 2012 in comparison to that of 2013 (Figure 2.2). This resulted in an earlier initiation of the waterlogging treatment at growth stage V6 in 2012 than in 2013. Average air temperature during the three day waterlogging treatments was 19.0 and 24.5° C in 2012 and 2013, respectively.

Pre-Waterlogging Soil N

Soil samples collected prior to the implementation of the waterlogging treatments had no yearly or interaction effect on soil NH_4^+-N and NO_3^--N content to a 30 cm depth and were averaged across pre-plant N treatment (Figure 2.3 A&B). These sampling dates occurred 54 days and 34 days after pre-plant fertilizer incorporation in 2012 and 2013, respectively. Plots receiving polymer coated urea had 5.5 kg N ha^{-1} (P=0.1056) greater soil NH_4^+-N content than conventional urea. Plots treated with PCU had 16.9 kg ha^{-1} NO_3^--N (P=0.0733) greater than NCU+NI. Greater soil NH_4^+-N with PCU compared to NCU may be an effect of PCU was still releasing urea from the polymer coated prill resulting in more urea being converted to soil NH_4^+-N. Polymer coated urea had released 67.4 and 80% of its urea by the time the waterlogging treatments were implemented in 2012 and 2013, respectively (Figure 2.4 & 2.5) Nelson et al. (2009) reported reduced subsoil NO_3^--N concentrations 59 days after planting when comparing PCU to NCU, which suggested a slower release of urea with PCU. The lack of difference in soil NO_3^--N between the NCU and NCU+NI treatments suggested that nitrapyrin was no longer affecting nitrification rates at the time of soil sampling when averaged over both years.

Post-Waterlogging Chlorophyll

Chlorophyll content after draining the waterlogged treatments had a site x year interaction (Figure 2.8). In 2012, there was no effect of waterlogging on chlorophyll content. Chlorophyll content in 2013 had a decreasing effect of 4.7 (P=0.0039) (9%) and 17.4 (P<0.0001) (33%) when comparing one and three days of waterlogging to the non-waterlogged control, respectively. When comparing between years with similar days of waterlogging, 2013 had 6.2 (P=0.0007) greater SPAD units in the non-waterlogged control, and 8.5 (P<0.0001) less SPAD units with three days of waterlogging than 2012. Greater chlorophyll content in the non-waterlogged control in 2013 could be a possible result of more N uptake due to 73 mm more precipitation and adequate N prior to the waterlogging treatment than in 2012. The decline in chlorophyll content in 2013 after one and three days of waterlogging suggested greater physiological stress was imposed on the plants during the 2013 waterlogging treatments, which may have been due to 5.5° C greater air temperature during at the time waterlogging treatments were imposed in 2013 compared to 2012. One of the first symptoms of waterlogging is reduced stomatal conductance (Cairns et al., 2012). This stress can limit carbon and nitrogen acquisition and decrease chlorophyll production.

Post-Waterlogging Soil N

Post-waterlogging soil samples were measured for NH_4^+-N and had no yearly or waterlogging effect or interaction when combined to a 30 cm depth. Following the waterlogging treatment, PCU had a 3.4 kg ha^{-1} (P=0.0387) greater soil NH_4^+-N content of 3.4 kg ha^{-1} (P=0.0387) compared to NCU (Figure 2.9). This was similar to the pre-waterlogging soil samples and further suggested that there was longer N release with PCU than NCU. No effect of waterlogging on NH_4^+ was expected since its leaching potential is low and it is not a substrate for microbial anaerobic respiration/denitrification. During the waterlogging treatments, the rate of nitrification can also be reduced due to the lack of oxygen in the soil was waterlogged.

Due to post-waterlogging NO_3^--N interactions among years, data was analyzed separately (Figure 2.10 A&B). In 2012, no difference in soil NO_3^--N content between NCU and NCU+NI, but PCU had a 20.9 (P=0.0444) and 17.8 (P=0.0821) kg NO_3^--N ha^{-1} greater soil content than NCU and NCU+NI in the non-waterlogged control (Figure 2.8 A). After one day of waterlogging, PCU and NCU+NI soil NO_3^--N content was similar, but PCU still maintained 24.6 kg ha^{-1} (P=0.0204) greater soil NO_3^--N content than that of NCU. After three days of waterlogging, there was no significant soil NO_3^--N content differences among plots that received pre-plant N applications. There was a general decrease in soil NO_3^--N content with each pre-plant N fertilizer for each day of waterlogging and a significant decrease occurring in the first day of waterlogging. After one day of waterlogging, there was 28.8 (51%) (P=0.0459), 19.3 (32.4%) (P=0.1675) and 25.1 (67.6%) (P=0.0778) kg soil NO_3^--N ha^{-1} less when compared to the non-waterlogged control for NCU, NCU+NI, and PCU, respectively. Soil NO_3^--N reduction was similar from one to three days of waterlogging for NCU, NCU+NI, and PCU treatments. Sistani et al. (2014) collected soil NO_3^--N samples during spring, mid-season and post-harvest time intervals and observed no greater NO_3^--N concentrations with PCU in comparison to NCU in three growing seasons, except for in one midseason soil sampling time.

The 2013 post-waterlogging soil NO_3^--N content was similar in the non-waterlogged control when comparing NCU+NI and PCU pre-plant fertilizer treatments with both having 52.8 (P=0.0029) and 57.4 kg ha^{-1} NO_3^--N (P=0.0015) greater than NCU, respectively (Figure 2.8B). After one day of waterlogging, there was 51.6 (52.8%) (P=0.0037) and 43.1 (42.1%) (P=0.0122) less kg NO_3^--N ha^{-1} with NCU+NI and PCU when comparing the non-waterlogged control for each pre-plant N fertilizer, respectively. The three day waterlogging treatment was similar to the one day waterlogging treatment in 2012 in that loss was similar.

When comparing similar pre-plant N fertilizers among years, there was 24.9 (P=0.0951) and 38.1 kg NO_3^--N ha^{-1} (P=0.0126) with PCU and NCU+NI in the non-waterlogged treatment during the 2013 growing season, respectively. A possibility for this could be the sampling day occurred more days after fertilizer incorporation in 2012 than 2013 since the rate at which the plants reached growth stage V6 was slower in 2012 with 100 mm more precipitation received in 2013 than 2012 from the time of pre-plant fertilizer incorporation until the post-waterlogging soil sampling dates, which could result in more N loss. Since PCU released urea slower from the prill, it is possible for less soil NO_3^- to be present with this treatment since post-waterlogging soil samples were collected after less time from pre-plant fertilizer incorporation in 2013 versus 2012. This could be a result of 28.1 kg ha^{-1} more NO_3^--N in the soil to a depth of 30 cm prior to pre-plant fertilizer incorporation in 2013 than in 2012 (Table 2.2). This would also give insight to why NCU+NI had greater NO_3^--N in 2013 versus 2012. A possible explanation why NCU did not follow this trend and decreased by 11.7 kg NO_3^--N ha^{-1} (P=0.4267) in 2013 could be a result of more nitrification occurring earlier in the growing season in comparison to NCU+NI and PCU which increased NO_3^--N loss during intense precipitation events two to three weeks after fertilizer incorporation.

Silage N Uptake

Treatment effects for both pre-plant N fertilizer and rescue N application were observed in 2012 for N uptake (Figure 2.11). Non-Coated urea treated with the urease inhibitor generally increased N uptake by 25.7 (P=0.0007), 23.2 (P=0.0018), 8.3 (P=0.2229), and 18.4 (p=0.0106) kg N ha^{-1} for CO, NCU, NCU+NI and PCU, respectively. There was a 12.1 kg N ha^{-1} (P=0.1058) N uptake with PCU compared to NCU+NI in the plots that received the NCU+UI treatment. In one year, Noellsch et al. (2009) reported an increase of 36 kg N ha^{-1} in N uptake with PCU in comparison to NCU on a low lying landscape position on a claypan soil that was prone to greater soil water content than summit and side slope positions. There was a 14.2 (P=0.0324) kg N ha^{-1} decrease in silage harvested when comparing three days of waterlogging to the non-waterlogged control where no rescue N was applied (data not shown).

The 2013 waterlogging treatments had an effect on N uptake in urea treatments with and without NCU+UI (Figure 2.12). In plots not receiving the NCU+UI, there was a 16.8 (P=0.3751) and 36.4 kg N ha^{-1} (P=0.0614) decrease with one and three days of waterlogging when compared to the non-waterlogged control, respectively. Plants receiving NCU+UI had a 21.3 (P=0.2618) and 48.8 kg N ha^{-1} (P=0.0148) decrease with one and three days of waterlogging when compared to the non-waterlogged control, respectively. Since the post-flood soil NO_3^--N data showed no decreases in soil NO_3^--N content from one to three days of waterlogging; it is possible that the additional decrease in silage N uptake with three days of waterlogging was attributed to physiological stress due to waterlogging and not N loss. This is further indicated by a smaller response to NCU+UI of 24.8 (P=0.1118), 20.2 (P=0.1905), and 12.5 (P=0.4152) kg N ha^{-1} uptake for the non-waterlogged, one, and three days of waterlogging.

Grain Yield and Content

There was no effect of waterlogging treatments on grain yield in 2012. The non-rescue, pre-plant N treatments NCU+NI and PCU resulted in a yield increase of 0.30 (P=0.0845) and 0.32 (P=0.0660) Mg ha^{-1} in compared to NCU, which could be a result of an overall greater soil N and N uptake in these treatments when averaged across all waterlogging treatments (Figure 2.13). Gagnon et al. (2011) reported an increase in grain yield in two wet years on a clay soil of 0.80 to 1.60 Mg ha^{-1} and 0.30 to 0.60 Mg ha^{-1} with PCU and NCU+NI when compared to NCU, respectively. Pre-plant N fertilization of NCU and NCU+NI had a 0.50 (P=0.0016) and 0.30 (P=0.0448) Mg ha^{-1} yield increase when treated with a rescue N application of NCU+UI. When combined over waterlogging durations and pre-plant N fertilizers there was a 5 kg m^{-3} greater grain density with the rescue N plus NBPT treatment compared to the no rescue treatments (Table 2.3). Possible reasons why these pre-plant N treatments responded to the NCU+UI and not the PCU pre-plant N treatment was that PCU had adequate N without the NCU+UI treatment for the grain yields produced in the drought year of 2012. There was similar plant populations between the plots with and without rescue N application plus NBPT.

In 2013, there was a decrease in yields with three days of waterlogging in comparison to the non-waterlogged control and one day of waterlogging for both treatments without and with rescue N application (Figure 2.14). For treatments without NCU+UI, but with a three day waterlogging treatment, there was a decrease in yield of 1.00 (P=0.0007) (10%) and 0.87 (P=0.0026) (9%) Mg ha^{-1} when compared to the non-waterlogged control and one day of waterlogging, respectively. This reduction in grain yield with increased days of waterlogging was consistent with the decrease in N uptake with three days of waterlogging. Ren et al. (2014) reported a 20% reduction in grain yield when plants were waterlogged for three days at V6. The waterlogging treatments had similar plant populations, but grain density had a decrease of 11 and 7 kg m^{-3} with non-waterlogging and one day of waterlogging compared to the three days of waterlogging treatment, respectively (Table 2.4).

Grain protein concentration had a general decrease with increasing days of waterlogging for 2012 and 2013 in the presence and absence of the rescue N application (Figure 2.15A). In 2012, the rescue N application increased grain protein of 0.67 (P<.0001), 0.90 (P<.0001), and 0.78% (P<.0001) with no waterlogging, one day of waterlogging, and three days of waterlogging, respectively. This provides further evidence that the additional N uptake with the rescue N treatment was utilized for synthesizing grain proteins, which could be a factor for why there were increases in grain yield with the NCU+UI treatments. In 2013 the rescue application was successful at increasing protein content by 0.23% (P=0.0460) in the three days of waterlogging treatment. Grain protein was less responsive to NCU+UI treatment in 2013 compared to 2012, indicated that additional N uptake with the NCU+UI treatment was not utilized for the grain because there was adequate N available without the NCU+UI treatment.

Grain extractable starch concentration had generally increased with increasing days of waterlogging in both 2012 and 2013 (Figure 2.15B). In 2012, the rescue N application decreased the amount of extractable starch concentration by 0.73 (P=0.0035), 1.1 (P<0.0001), and 1.0 (P<0.0001) in comparison to the plants not receiving the rescue N application for each increased days of waterlogging. In 2013, the rescue N application decreased the amount of extractable starch by 0.48 (P=0.0463) and 0.56 (P=0.0222) in comparison to the plants not receiving the rescue N application for one and three days of waterlogging.

Post-Harvest Soil N

Nitrogen loss due to the waterlogging treatments was still observable in post-harvest soil samples in 2012 (Figure 2.16). When NH_4^+ and NO_3^- content were summed over the sampling depths, there was 29.3 kg N ha^{-1} (P=0.0525) less inorganic N when comparing the one day of waterlogging to the non-waterlogged control in plots that had no rescue N application. In plots that received the rescue N application, there was a decrease of 52.6 kg N ha^{-1} (P=0.0012) when comparing the non-waterlogged control and the three days of waterlogging. There was a significant increase in N soil content with rescue N application for each respective day of waterlogging.

Soil samples collected after harvest in 2013 had a general decrease in inorganic N content with increased days of waterlogging and an increase in inorganic N content with the rescue N application for each respective pre-plant N fertilizer treatment (Figure 2.17). In treatments were rescue N was applied, there was an increase in inorganic N content of 45.1 (P=0.1305) and 61.4 (P=0.0434) kg N ha^{-1} when compared to the non-waterlogged control and 1 day of waterlogging of PCU and NCU pre-plant N fertilizers, respectively. Polymer coated urea had 53.2 kg N ha^{-1} (P=0.0771) greater soil inorganic N content than NCU in treatments of non-waterlogged control where no rescue N was applied. Gagnon et al. (2011) reported an increase in soil NO_3^--N with PCU at harvest in comparison to NCU+NI and urea.

CONCLUSIONS

Treatment effects of pre-plant N fertilizer and waterlogging at V6 had impacts on soil inorganic N content during the two years of this field study. During both site years with contrasting spring precipitation, PCU increased soil inorganic N content later in the vegetative growth period in the absence of waterlogging in compared to NCU. During the 2012 growing season, soil treated with PCU resulted in more N uptake and grain yield when no rescue NCU+UI treatment was applied. Under non-waterlogged conditions further research should be conducted to explore if PCU can be applied at lower rates in comparison to conventional pre-plant N fertilizers, thereby lowering fertilizer cost for the PCU.

For both research years, soil nitrate loss was observed under waterlogged conditions, with the greatest period of NO_3^- loss occurring during the first day of waterlogging. The 2013 season resulted in more NO_3^--N loss than in 2012 which may have been due to increased soil NO_3^--N content and air temperature at the time of waterlogging. With a waterlogging period of three days, there was no advantage of pre-plant enhanced efficiency products maintaining greater soil NO_3^- content. The rescue N application in 2012 indicated that a rescue N application was needed if excessive soil moisture continued for periods of one day or longer, although if applied at later growth stages in growing areas that are susceptible to drought later in the growing season, there is a risk that a rescue N application will be ineffective as observed in the 2013 growing season. Several studies have reported greater yield responses to in-season N applications made at earlier growth stages when compared to later growth stages (Binder et al., 2000; Scharf et al., 2002; Nelson et al., 2010). Yield declines occurred after three days of waterlogging in 2013. The decline in yield with three days of waterlogging in 2013 was probably due to greater physiological stress imposed on the corn plants during the waterlogging than in 2012, as indicated by the post-waterlogging chlorophyll meter readings and reduction in N uptake and grain density and yields. Decreased ear size was noticed in the three days of waterlogging; suggesting the rows and number of kernels established during ear development may have been decreased from three days of waterlogging. If waterlogging occurs during the growing season, this research suggests that air temperature could have a significant impact when assessing management options for mitigating potential decreases in corn grain yield.

During both growing seasons, corn grain yields were most likely impacted by below average rainfall which can decrease carbon assimilation, plant N demand and promote premature senescence. Further research should be implemented to further assess if enhanced efficiency N products and rescue N applications after waterlogged soil conditions can provide economic yield benefits with yearly climate variability. Use of pre-plant enhanced efficiency N products and rescue N applications may provide benefits if waterlogging conditions in earlier vegetative growth are accompanied with adequate soil moisture during the reproductive growth stage, and should be examined under both irrigated and rainfed production systems.

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Table 2.1. Field treatment information and crop management in 2012 and 2013.

Year	Field Treatments and Management	Date	Rate
2012	N application†	3 April	168 kg N ha^{-1}
	nitrapyrin		1.68 kg a.i. ha^{-1}
	Planting date	3 April	79,040 seeds ha^{-1}
	Waterlogging treatments	1 June	
	Rescue N application	20 June	84 kg N ha^{-1}
	NBPT		4.2 L Mg^{-1} $urea^{-1}$
	Weed management		
	PRE	21 April	
	acetochlor‡		2.27 kg a.i ha^{-1}
	atrazine		1.13 kg a.i. ha^{-1}
	POST	14 June	
	mesotrione		0.11 kg a.i. ha^{-1}
	glyphosate		1.50 kg a.i. ha^{-1}
	Harvest date	30 August	
2013	N application	14 May	168 kg N ha^{-1}
	nitrapyrin		1.68 kg a.i. ha^{-1}
	Planting date	14 May	70,040 seeds ha^{-1}
	Waterlogging treatments	18 June	
	Rescue N application	8 July	84 kg N ha^{-1}
	NBPT		4.2 L Mg^{-1} $urea^{-1}$
	Weed management		
	PRE	21 May	
	acetochlor		1.10 kg a.i. ha^{-1}
	clopyralid		0.12 kg a.i. ha^{-1}
	flumetsulam		0.03 kg a.i. ha^{-1}
	glyphosate		1.50 kg a.i. ha^{-1}
	POST	27 June	
	mesotrione		0.10 kg a.i. ha^{-1}
	glyphosate		1.50 kg a.i. ha^{-1}
	Harvest date	23 September	

† Pre-plant N applications were incorporated immediately after surface application.
‡Chemical name for herbicides: acetochlor, 2-chloro-2’-methyl-6’ethyl-N-ethoxymethylacetanilide; atrazine, 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine; flumetsulam, N-(2,6-difluorophenyl)-5-methyl-1,2,4-triazolo-[1,5a]-pyrimidine-2-sulfonamide; glyphosate, N-(phosphonomethyl)glycine; mesotrione, 2-[4-(methylsulfonyl)-2-nitrobenzoyl]-1,3-cyclohexanedione.

Table 2.2. Selected soil properties for soil collected prior to pre-plant N fertilization for the 2012 and 2013. Averaged over three replications by soil depth.

Year†	Depth	OM	pH_s	NA	CEC	Bray 1 P	Exch. Ca	Exch. Mg	Exch. K	B.D.	NO_3^- -N	NH_4^+-N
	- cm -	- g kg^{-1} -		------ $cmol_c$ kg^{-1} -----		---------------------- kg ha^{-1} ----------------------				- g cm^{-3} -	----- mg N kg $soil^{-1}$-----	
2012	0-10	27±3.0	6.1±0.4	1.8±1.4	15.2±1.3	65.0±9	5151±436	395±37	407±61	1.43±0.05	6.7±3.0	11.1±1.9
	10-20	20±3.0	6.3±0.4	1.5±0.9	15.1±0.1	23.2±4	5367±362	380±10	200±14	1.48±0.14	4.1±1.1	7.6±0.7
	20-30	17±2.0	5.5±0.5	4.0±1.3	17.8±2.3	8.60±2	5114±246	570±86	211±20	1.46±0.01	3.0±0.4	8.0±2.1
2013	0-10	28±1.0	5.4±0.1	3.7±0.6	13.9±0.2	83.2±8	3698±148	384±15	438±32	1.11±0.02	11.4±3.0	3.7±0.4
	10-20	20±2.0	5.9±0.3	2.5±0.9	14.0±0.6	26.0±5	4351±204	426±12	221±40	1.30±0.07	11.9±2.4	3.4±0.2
	20-30	18±1.0	5.2±0.5	4.7±2.1	16.5±2.8	14.6±3	4248±179	549±79	235±179	1.26±0.05	16.0±3.8	3.8±0.8

†Abbreviations: B.D, Bulk Density CEC, Cation Exchange Capacity; Exch. Ca, Exchangeable Calcium; Exch. K, Exchangeable Potassium; Exch Mg, Exchangeable Magnesium; NA, Neutralizable Acidity; NH_4^+ -N, Ammonium Nitrogen; NO_3^- -N, Nitrate Nitrogen; OM, Organic Matter; P, Bray-1 Phosphorus; pHs, pH in 0.01 M $CaCl_2$, ±, plus or minus one standard deviation

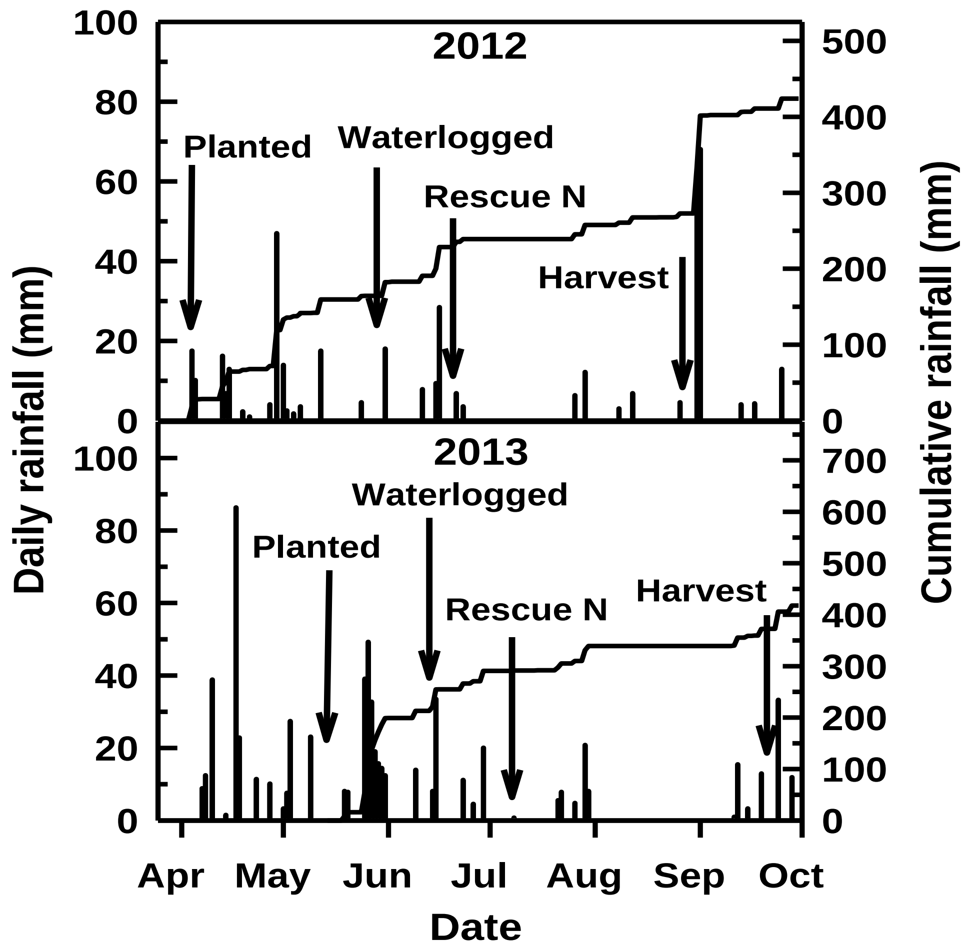

Figure 2.1. Daily and cumulative precipitation from 1 April through 1 October for 2012 and 2013. Cumulative rainfall axis starts at planting for both years.

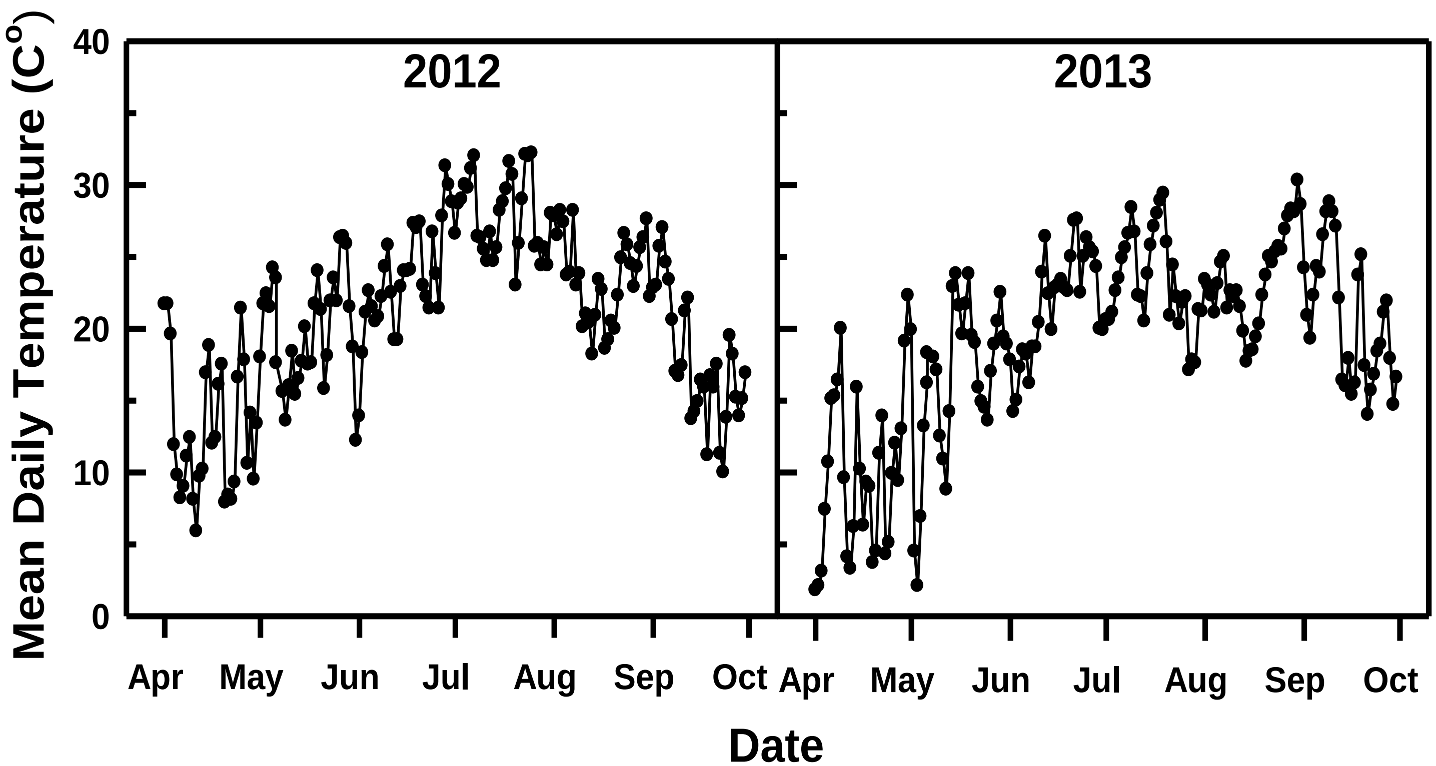

Figure 2.2 Average daily air temperatures from 1 April through 1 October in 2012 and 2013.

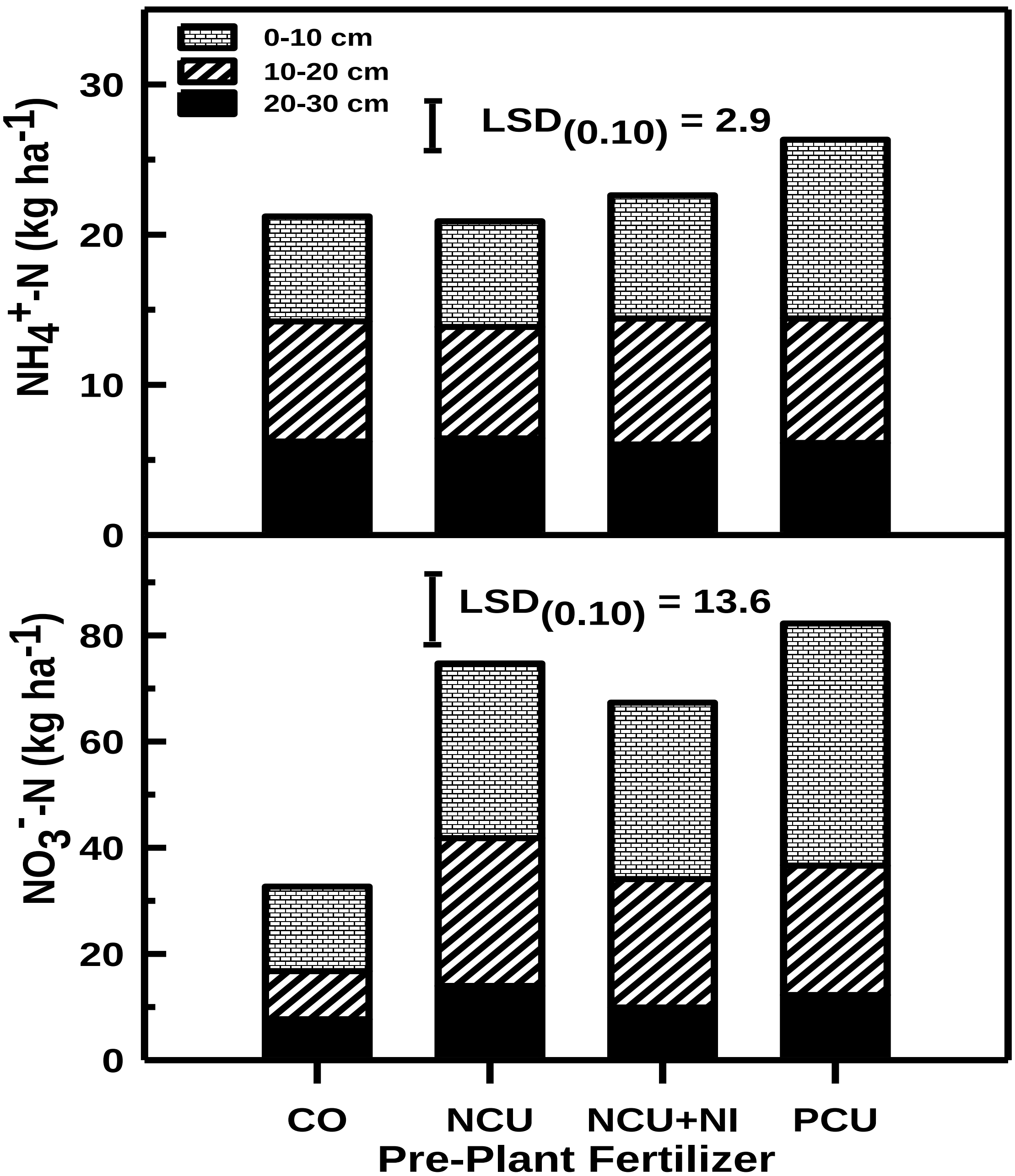

Figure 2.3 A&B. Soil (A) NH_4^+-N and (B) NO_3^--N to a depth of 30 centimeters with different pre-plant N fertilizer applications. Sampling occurred prior to waterlogging treatment (Abbreviations: CO, Control; NCU, Urea; NCU + NI, Urea + nitrapyrin; PCU, polymer coated urea; LSD, least significant difference at $P < 0.10$ comparing pre-plant N treatments to 30 centimeters).

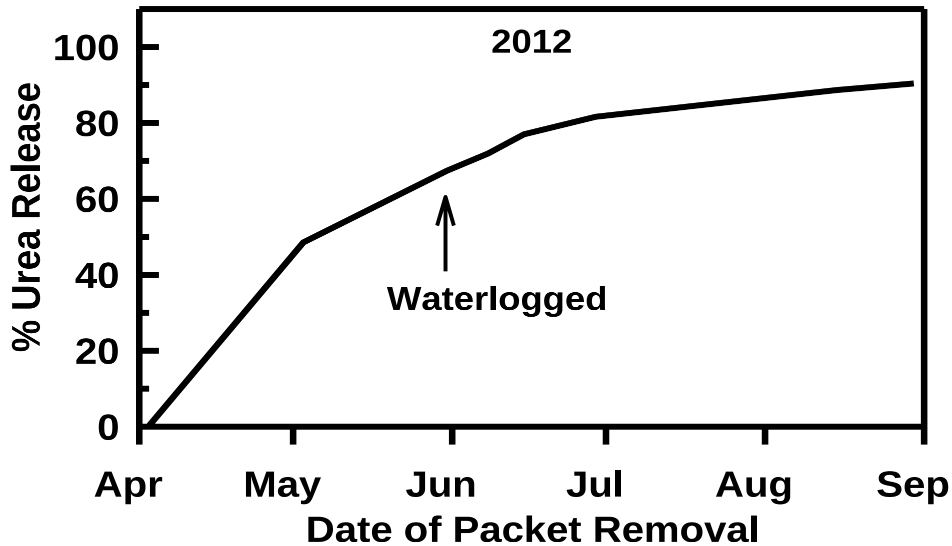

Figure 2.4. Release of polymer coated urea over the growing season in 2012. Data was combined over waterlogging treatments.

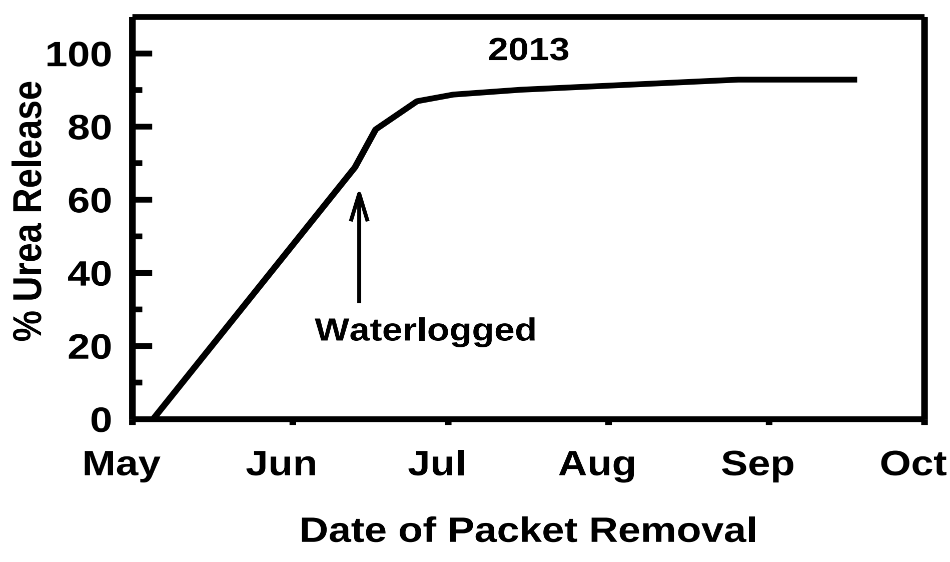

Figure 2.5. Release of polymer coated urea over the growing season in 2013. Data was combined over waterlogging treatments.

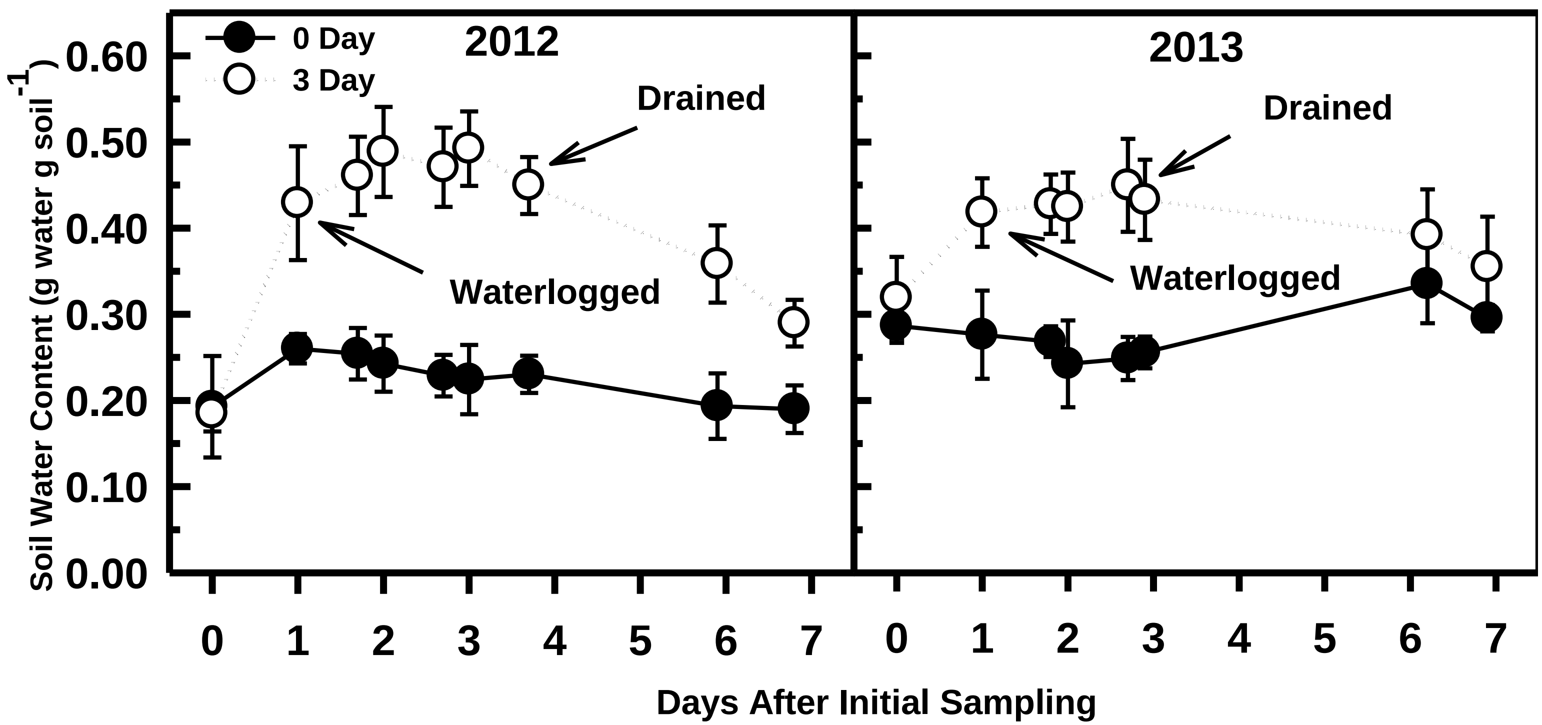

Figure 2.6. Average daily gravimetric soil water content for the no waterlogging and 3 day waterlogging treatments in 2012 and 2013. The first sampling period occurred the day before waterlogging treatments were initiated for both 2012 and 2012. Error bars represent ± one standard deviation across subsamples which were replicated three times.

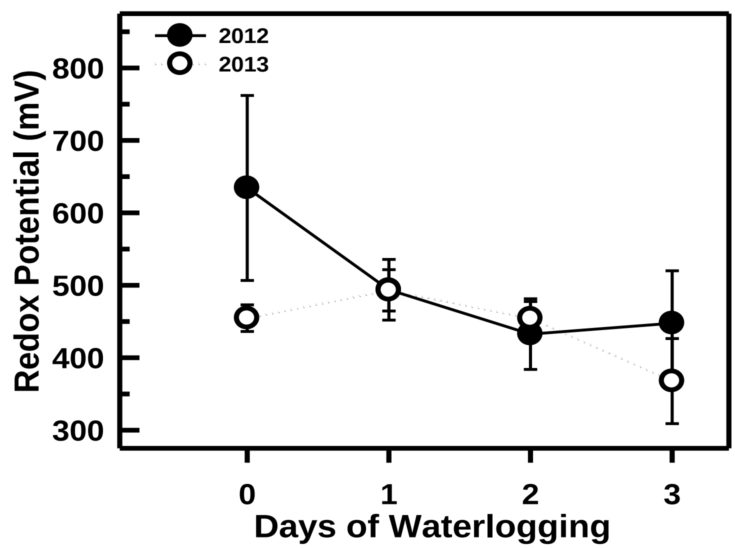

Figure 2.7. Average daily soil surface redox potential during the three day waterlogging duration in 2012 and 2013. The first sampling period occurred right after water was ponded on the soil surface. Error bars represent ± one standard deviation across subsamples and replicated three times.

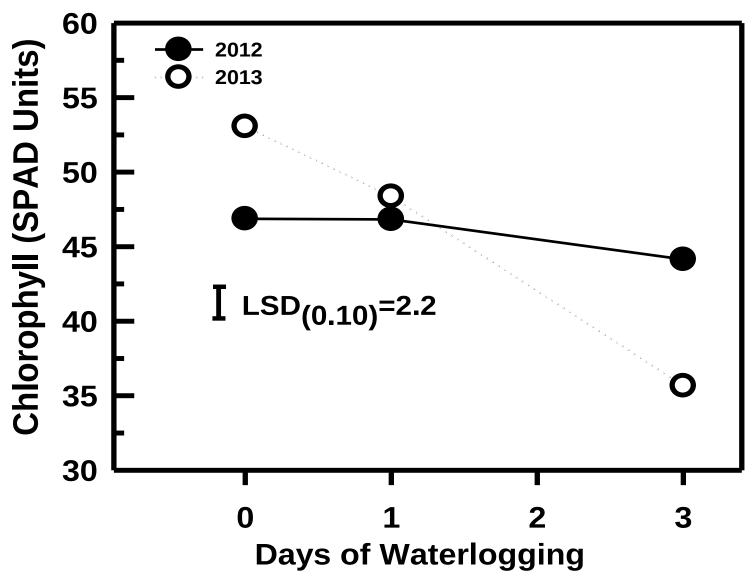

Figure 2.8. Average chlorophyll content of pre-plant N treatments after waterlogging treatments were drained in 2012 and 2013. Measurements were recorded prior to the rescue N application of urea plus NBPT (Abbreviations: LSD, least significant difference at $P < 0.10$

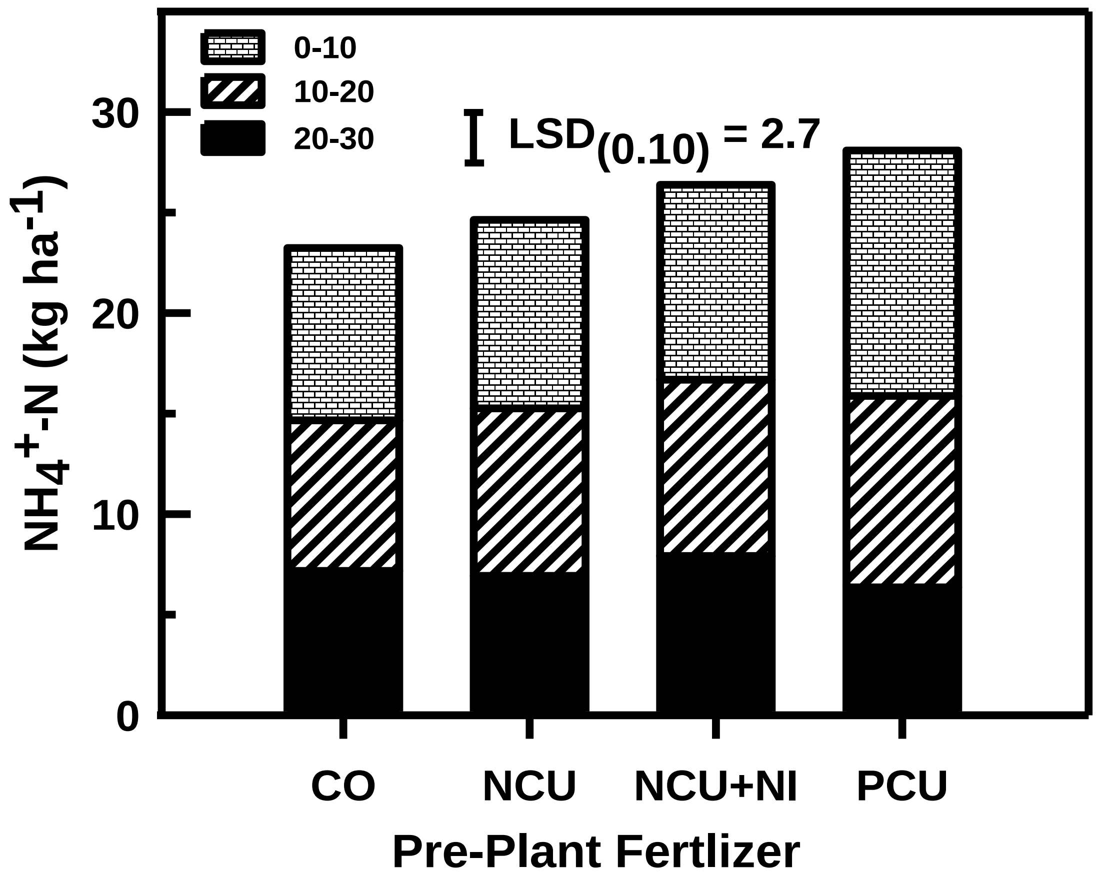

Figure 2.9. Soil NH_4^+-N to a depth of 30 centimeters with different pre-plant fertilizer applications. Data was averaged over waterlogging treatmetns for 2012 and 2013. Sampling occurred three days after the waterlogging treatments were drained (Abbreviations: CO, Control; NCU, Urea; NCU + NI, Urea + nitrification inhibitor; PCU, polymer coated urea; LSD, least significant difference at $P < 0.10$ comparing pre-plant N treatments to 30 centimeters).

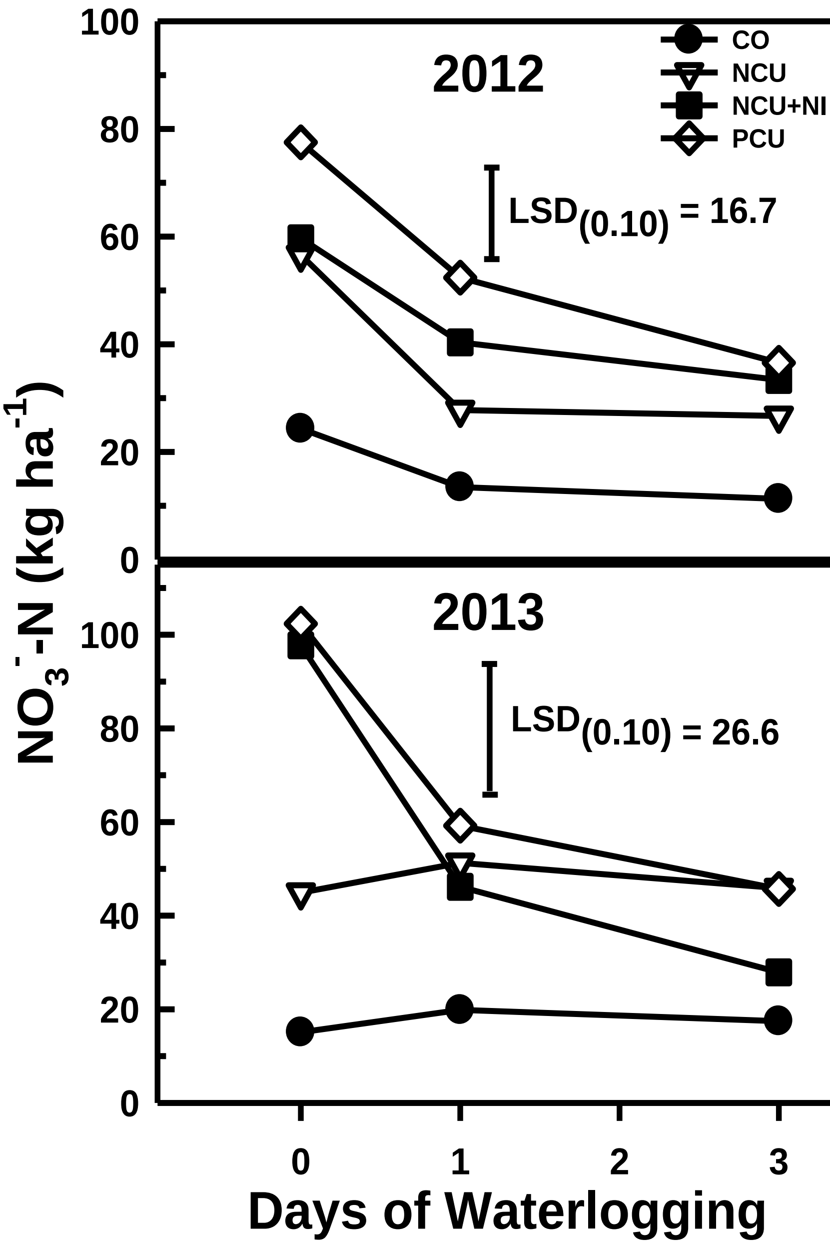

Figure 2.10 A&B Soil NO_3^- -N to a depth of 30 centimeters with different pre-plant fertilizer applications and waterlogging durations in 2012 and 2013. Sampling occurred three days after the waterlogging treatments were drained (Abbreviations: CO, Control; NCU, Urea; NCU + NI, Urea + nitrification inhibitor; PCU, polymer coated urea; LSD, least significant difference at $P< 0.10$ comparing each pre-plant fertilizer treatment for each respective flooding duration).

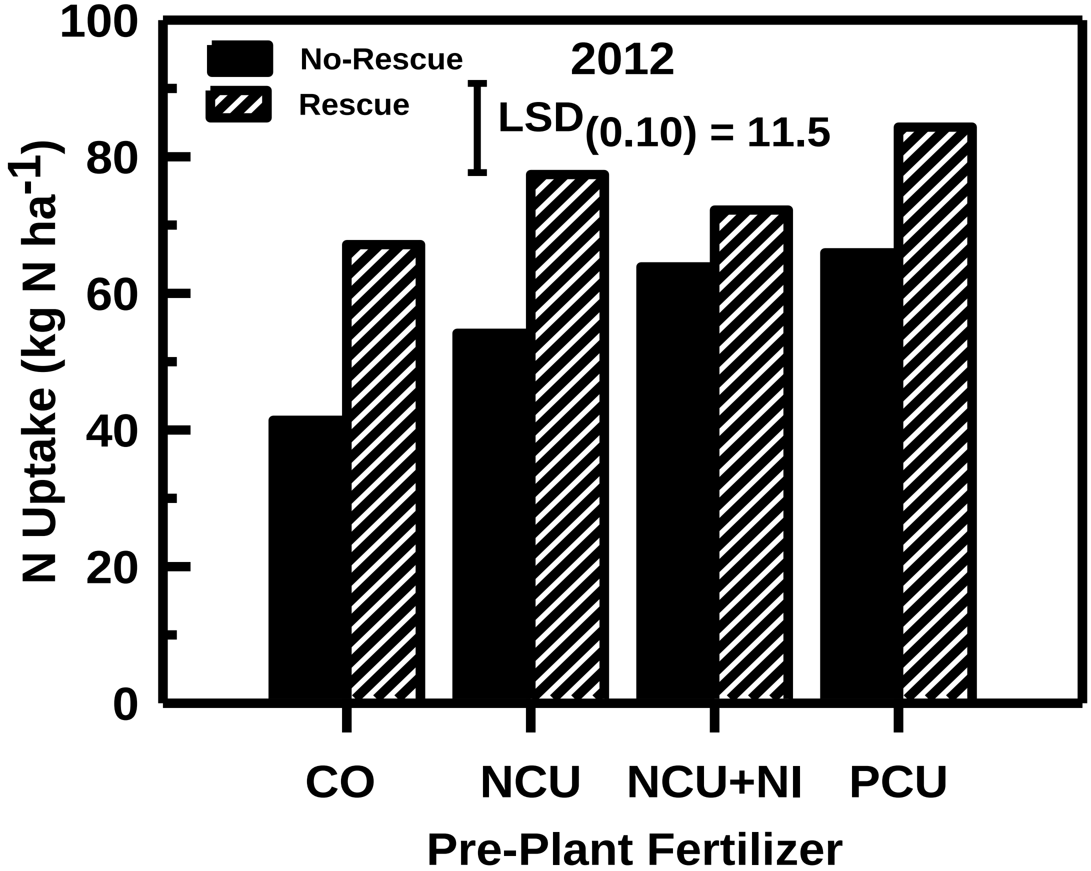

Figure 2.11. Plant N uptake at physiological maturity in 2012 for each pre-plant N fertilizer treatment, with and without rescue N application plus NBPT. Rescue N application was applied at growth stage V10. Data was combined over waterlogging treatments (Abbreviations: CO, Control; NCU, Urea; NCU + NI, Urea + nitrification inhibitor; PCU, polymer coated urea; LSD, least significant difference at $P < 0.10$ comparing no rescue and rescue treatments of similar pre-plant N treatments).

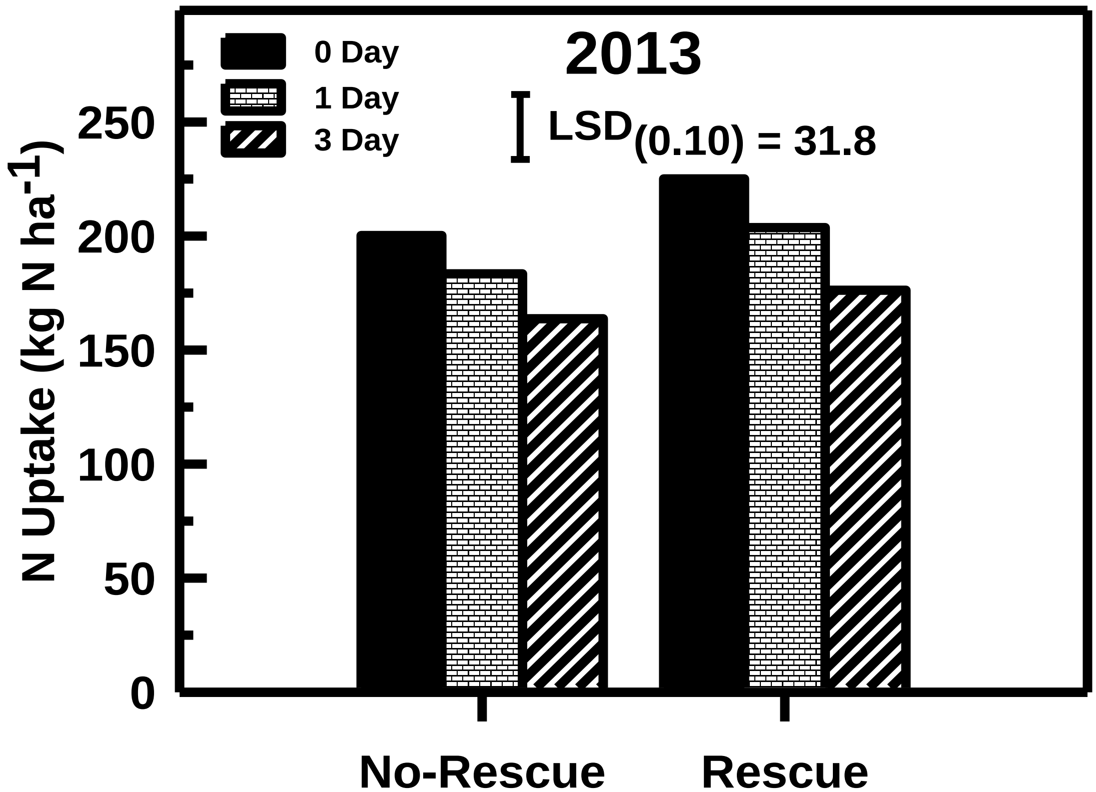

Figure 2.12. Plant N uptake at physiological maturity in 2013 comparing plants that experienced different waterlogging durations, with and without rescue N application plus NBPT. Rescue N application plus NBPT was applied at growth stage V10 in 2012. Data was combined over pre-plant N fertilizers (LSD, least significant difference at $P < 0.10$ comparing days of waterlogging without and with rescue N treatment).

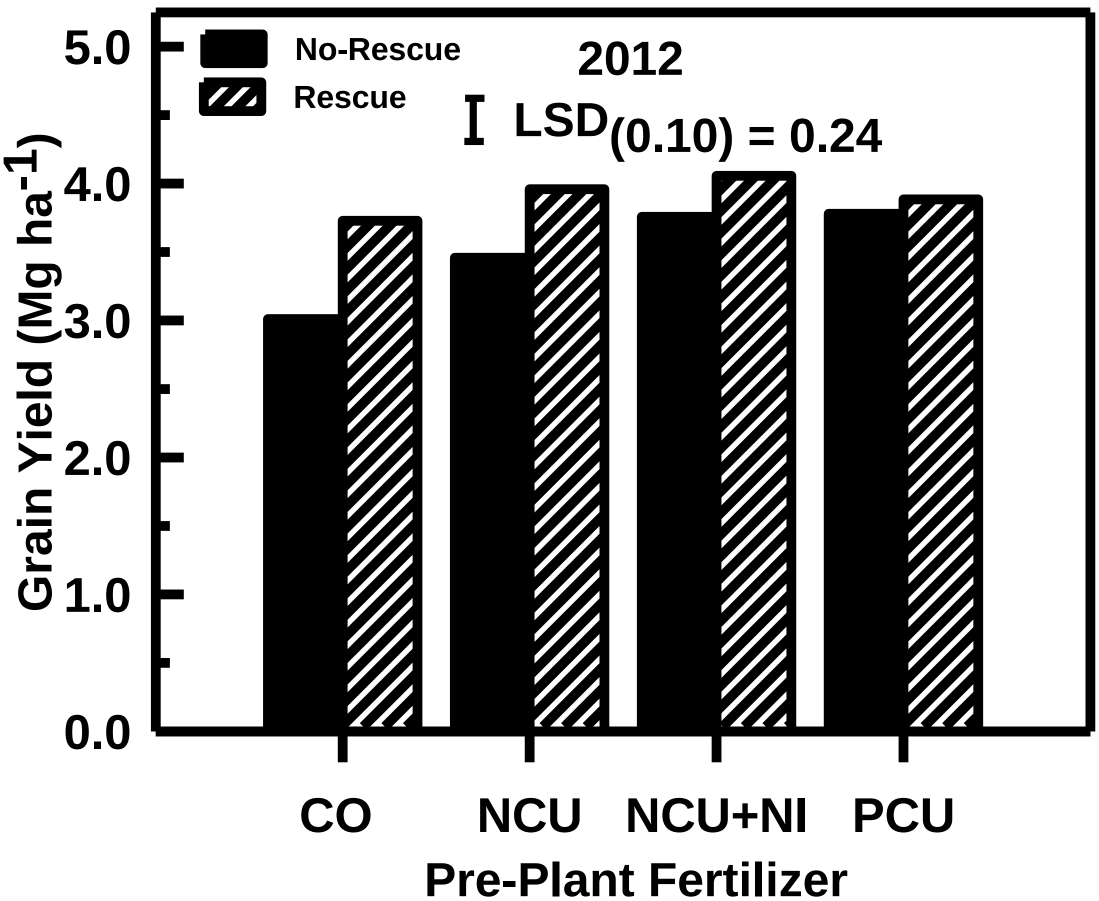

Figure 2.13. Average corn grain yield of pre-plant N fertilizers in 2012 with and without rescue N treatment plus NBPT. Data was combined over waterlogging treatments (Abbreviations: CO, Control; NCU, Urea; NCU + NI, Urea + nitrification inhibitor; PCU, polymer coated urea; LSD, least significant difference at $P< 0.10$ between corn grain yields without and with rescue N treatments of similar pre-plant N treatment).

Table 2.3. Plant population and grain density in 2012. Data is combined over pre-plant N treatments and waterlogging treatments.

Year	Rescue N treatments	Plant population	Grain density
2012		--- plants ha^{-1} ---	---- kg m^{-3} ----
	No-Rescue N	41,486	1,257
	Rescue N plus NBPT	40,768	1,262
	LSD (*P*<0.10)	NS	4.7

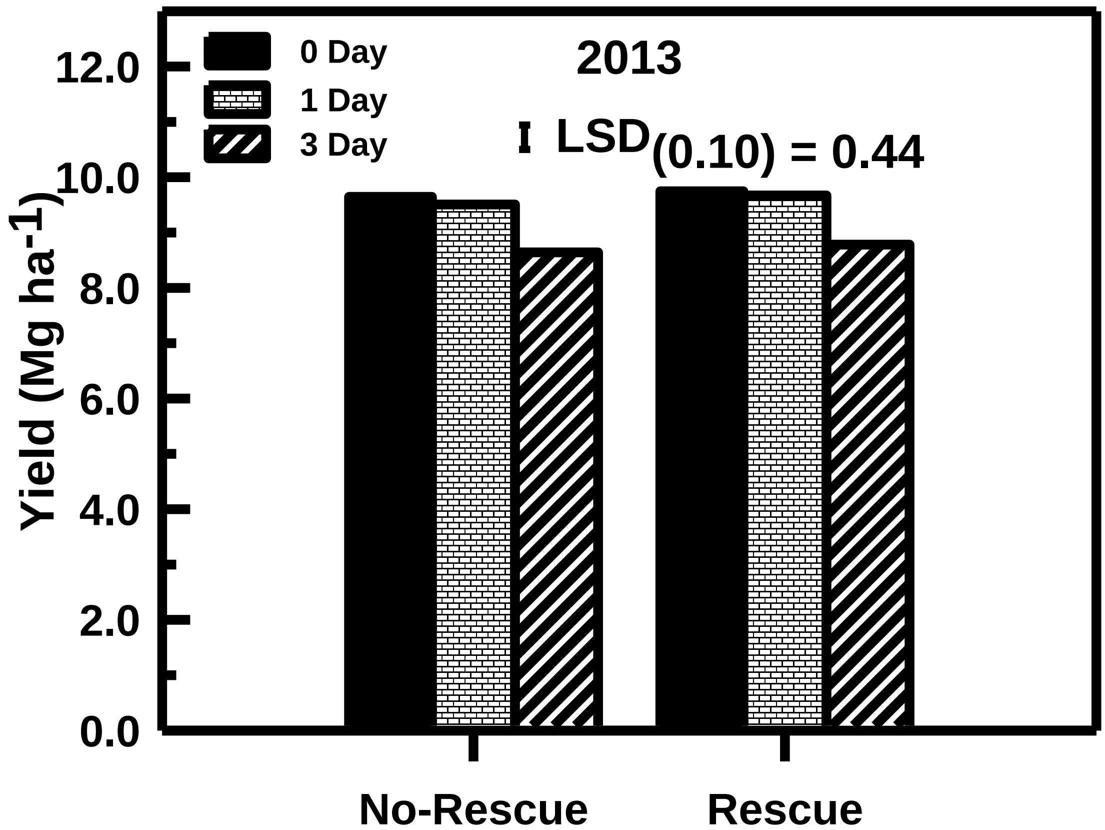

Figure 2.14. Average corn grain yield for each day of waterlogging in 2013, with and without rescue N treatment plus NBPT. Data was combined over pre-plant N fertilizers (LSD, least significant difference at *P*< 0.10 between corn grain yields per day of waterlogging without and with rescue N treatment).

Table 2.4. Plant population and grain density in 2013. Data is combined over pre-plant N treatments and rescue N application plus NBPT.

Year	Waterlogging treatments	Plant population	Grain density
2013	days	--- plants ha^{-1} ---	--- kg m^{-3} ----
	0	69,761	1,279
	1	66,891	1,275
	3	69,402	1,268
	LSD (*P*<0.10)	NS	6.0

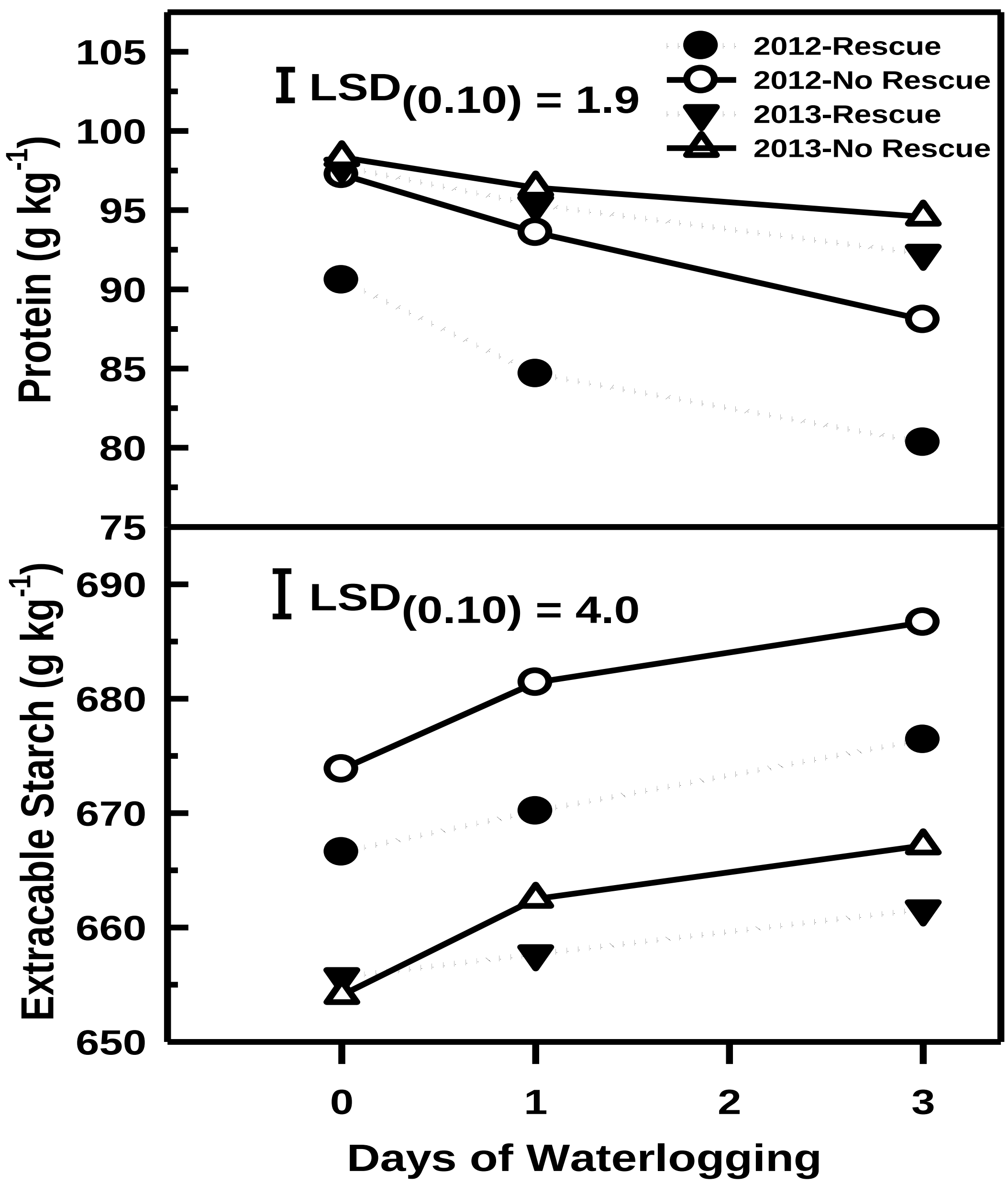

Figure 2.15 A&B. Corn grain (A) protein and (B) extractable starch concentration in 2012 and 2013 with and with rescue N application plus NBPT for each day of waterlogging. Data was combined over pre-plant N fertilizers (Abbreviations: LSD, least significant difference at *P*< 0.10 between grain yield means of different flooding durations).

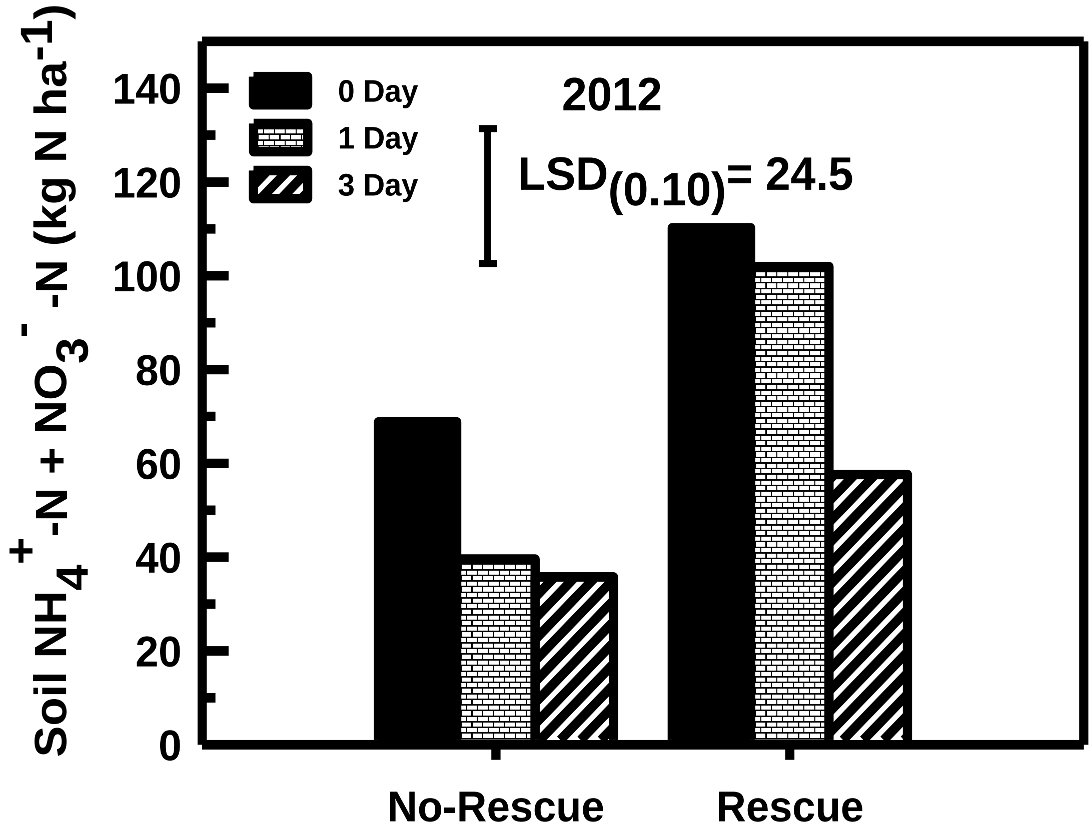

Figure 2.16. Soil NH_4^+-N plus NO_3^--N to a depth of 30 cm as affected by days of waterlogging with and without rescue N application plus NBPT following the 2012 grain harvest. Data was combined over pre-plant N fertilizers. (Abbreviations: LSD, least significant difference at *P*< 0.10 comparing waterlogging durations for no rescue and rescue treatments).

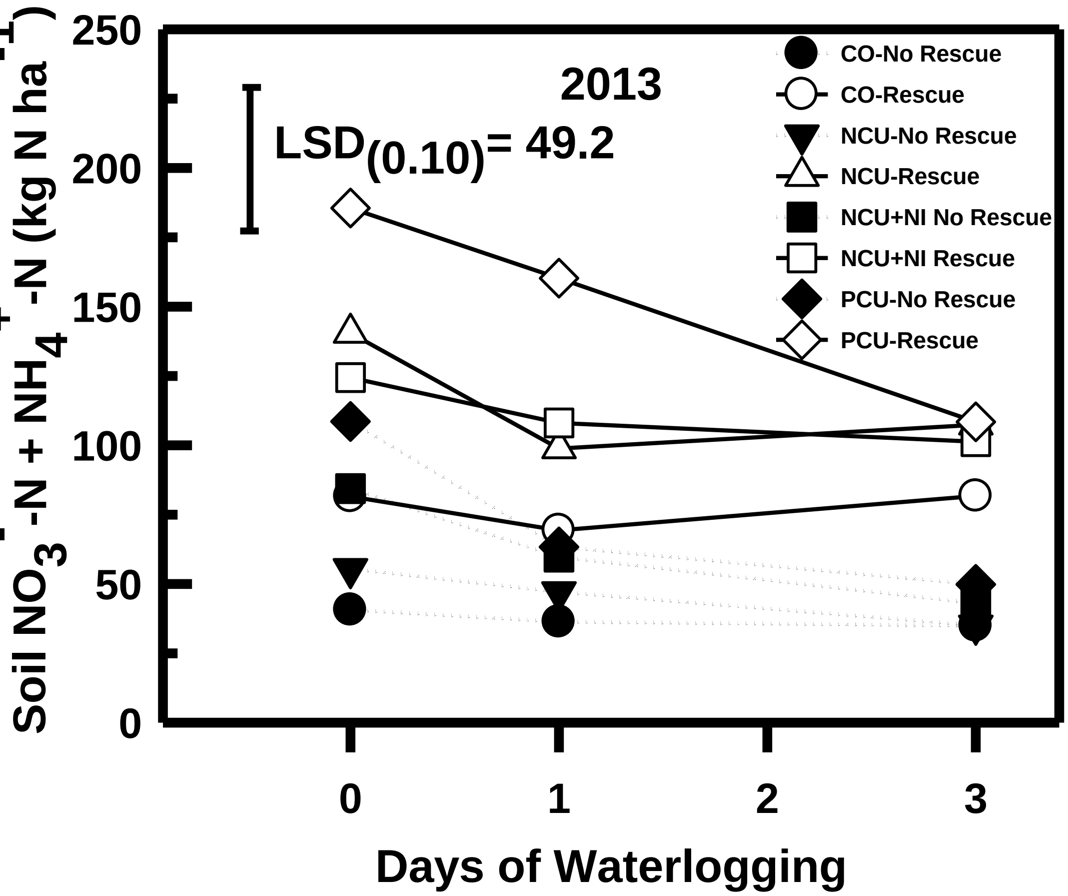

Figure 2.17. Soil NH_4^+-N plus NO_3^--N to a depth of 30 cm designated by each day of waterlogging with and without rescue N application for each pre-plant N fertilizer treatment following the 2013 grain harvest (Abbreviations: CO, Control; NCU, Urea; NCU + NI, Urea + nitrification inhibitor; PCU, polymer coated urea; LSD, least significant difference at $P < 0.10$ pre-plant N fertilizers for each respective waterlogging duration and with rescue and without rescue N application).

CHAPTER 3

SOIL NITROUS OXIDE EMISSIONS AS AFFECTED BY ENHANCED EFFICIENCY NITROGEN FERTILIZERS AND TEMPORARILY WATERLOGGED CONDITONS

ABSTRACT

Poorly-drained claypan soils in the Midwestern United States are susceptible to soil saturation periods shortly after pre-plant N fertilization, which potentially resulting in large amounts of soil surface N_2O emissions. The effect of enhanced efficiency nitrogen (EEN) fertilizer management on soil N_2O emissions has been extensively researched for corn (*Zea mays* L.) production. However, little research has evaluated soil N_2O emissions with EEN and conventional N fertilizers under waterlogged conditions in poorly drained claypan soils. A two-year study of soil N_2O emissions with application of EEN fertilizer products during three days of waterlogging planted to corn was initiated in 2012 on a poorly-drained claypan soil in Northeast Missouri. The objective of this study was to determine soil N_2O emissions during and initially following three days of soil waterlogging with the use of EEN and conventional N fertilizers. Treatments consisted of a non-treated control (CO), urea (NCU), urea plus nitrapyrin (NCU+NI), and polymer coated urea (PCU) (N-Serve®, Dow AgroSciences) (ESN® Agrium, Inc.) broadcast applied at 168 kg N ha^{-1}. In 2012, greater cumulative soil N_2O-N emissions of (2.8 kg N_2O-N ha^{-1}) were observed with PCU in comparison to NCU over the entire sampling period. A significant portion of cumulative soil N_2O emissions were associated with the soil drying phase in 2012, in which PCU and NCU+NI had greater emissions (1.9 and 1.2 kg N_2O-N ha^{-1}) compared to NCU. During the 2013 growing, season pre-plant N

treatments had no significant differences in cumulative N_2O-N over the entire sampling period (soil waterlogging and drying). Although NCU had 0.89 kg N_2O ha^{-1} greater emissions than PCU during the waterlogging period, NCU+NI had less cumulative emissions during the soil drying phase in 2013 (0.83 and 0.89 kg N_2O-N ha^{-1} in comparison to NCU and PCU, respectively). The proportion of N fertilizer lost as N_2O-N averaged over all pre-plant N treatments during the 2012 and 2013 sampling periods in the non-waterlogged soils was 0.04% and 0.03%, and 1.1% and 2.6% in the waterlogged soils, respectively.

INTRODUCTION

Nitrous Oxide Emissions in Agriculture

Nitrous oxide (N_2O) is a persistent greenhouse gas in the environment with an estimated half-life of 166 ± 16 years in the atmosphere (Prinn et al., 1990). With a global warming potential 298 times that of CO_2, it is responsible for 11% of the net anthropogenic radiating force, and for the destruction of stratosphere ozone (Soloman et al., 2007; Wuebbles 2009; Millar et al., 2010). A significant source of N_2O are emissions from agricultural soils that have been subjected to a seven-fold increase of global nitrogen (N) fertilizer use from 1960 to 1995, and another three-fold increase in N fertilizer use is possible to occur by the year 2050 (Tilman et al., 2002). Global N demand and application in agricultural systems will undoubtedly contribute more reactive N (N_r) to the environment, this will increase soil N_2O emissions through the nitrification and denitrification processes in soils (Millar et al., 2010).

Denitrification in Claypan Soils

The United States is currently the third largest consumer of N fertilizer and U.S. agricultural cropping systems account for approximately 71% of U.S. N_2O emissions (FAO, 2009; USEPA, 2013). An agricultural area of the United States that is susceptible to N_2O loss is the Central Claypan Region that comprises 4 million hectares in parts of Missouri, Illinois, and Kansas (Anderson et al., 1990; Nash et al., 2013). Claypan soils are characterized by low permeability which is susceptible to soil saturation following a precipitation event which can create favorable conditions for soil denitrification and soil N_2O efflux. In general, the optimal water-filled pore space (WFPS) for denitrification N_2O emissions is from 60 to 80%, whereas WFPS over 80% starts to favor generation of dinitrogen (N_2) gaseous species (Zhu and Sikora, 1995). In a meta-analysis from 846 N_2O emission measurements in agricultural fields, Bouwman et al. (2002) found that soil N_2O emissions were 35% greater in poorly drained soils compared to well drained soils. Other factors that affect soil N_2O emissions include soil available carbon, NO_3^- concentration, temperature, and pH (Bakken and Dörsch, 2007).

Enhanced Efficiency N Fertilizers

According to the Association of American Plant Food Control Officials (AAPFCO), enhanced efficiency N (EEN) fertilizer products are intended to increase plant N uptake and reduce the nutrient loss to the environment compared to conventional fertilizer source. Several studies have examined the effectiveness of both polymer coated urea (PCU) and non-coated urea treated with nitrapyrin nitrification inhibitor (NCU+NI) EEN products in reducing soil N_2O emissions under corn production. Halvorson et al.

(2014) reported a 42% reduction in soil N_2O emissions with PCU in comparison to urea under irrigated corn production on a clay loam soil when no-till and strip-till were practiced, but no significant reduction in emissions with conventional tillage. Bronson et al. (1992) reported a three-fold reduction in soil N_2O emissions with NCU+NI in comparison to urea when measured in the first 40 days after N fertilization. A meta-analysis by Akiyama et al. (2010) combined results of 35 studies to get an overall effectiveness of EEN products on N_2O emissions across varying environmental factors and field management. They concluded that nitrification inhibitors and PCU reduced N_2O emissions on average by 38 and 35% compared to non-treated and conventional fertilizers, respectively.

Many studies have examined the effectiveness of PCU and NCU+NI in reducing N_2O emissions in corn, but little research has observed these products under temporary waterlogging conditions in poorly drained upland soils planted to corn. Poorly drained claypan soils in Northeast Missouri are vulnerable to extended soil saturation periods during the spring months possibly affected by high intensity rainfall events that occur during this period. Villarini et al. (2013) reported increasing trends of heavy rainfall over the north central United States by analyzing daily rainfall records from 447 rain gauge stations. Future predictions for the mid-21st Century are generally wetter conditions during the months of April to May for the U.S. Midwest region which may have an effect on N fertilizer management in the region (Patricola and Cook, 2012). The spring time period is exceptionally susceptible to large pulses of N_2O emissions because pre-plant N fertilizer is applied at this time and increased soil N_2O emissions are often a function of increased soil moisture and soil NO_3^- concentration (Bakken and Dörsch, 2007).

Significant N_2O emissions are also possible under anaerobic conditions as a result of nitrifying denitrification, which occur under waterlogged conditions or as a soil dries from a saturated state. Zhu et al. (2012) observed increased N_2O production through the NH_3 oxidative pathway when O_2 concentrations decreased from 21 to 0.5% oxygen and N_2O production was greater through the NH_3 oxidative pathway in comparison to the heterotrophic denitrification pathway at 3% O_2. Field studies in rice production have reported 74% of cumulative N_2O emissions occurred during the soil drying phases of controlled irrigation in comparison to 20% during drainage at mid-season and maturity with traditional irrigation (Peng et al., 2011). In a four-year field study by Ji et al. (2012), controlled released fertilizers reduced N_2O emissions 13% compared to urea.

The objective of this study was to determine the effects of soil waterlogging duration and applications of conventional and EEN fertilizer products on soil N_2O emissions under a corn production system in a poorly-drained claypan soil.

MATERIALS AND METHODS

Site Characterization and Experimental Design

This two-year study was initiated in 2012 on a poorly-drained claypan soil in Northeast Missouri at the University of Missouri's Greenley Memorial Research Center (40° 1' 17" N, 92° 11' 24.9" W). The soil was classified as a Putnam silt loam (fine, smectitic, mesic, Vertic Albaqualfs). Initial soil samples were collected each year prior to the application of treatments to characterize the soil at depth increments of 0-10, 10-

20, and 20-30 cm using a stainless steel push probe. Composite samples of 10 subsamples were collected in each of the untreated replicates. All soil samples were air-dried and ground to pass through a sieve with 2 mm openings. The initial soil samples were analyzed by the University of Missouri Soil and Plant Testing Laboratory using standard soil testing procedures (Nathan et al., 2006). Soil bulk density measurements in the field were determined using the core method at depth increments of 0-10, 10-20, and 20-30 cm and one core for each depth were taken per replicate (Blake et al., 1986). Daily weather conditions for air temperature and precipitation were obtained from an automated weather station located within 500 m of the experiment.

The waterlogging duration and pre-plant N fertilizer treatments were arranged in a split-split plot arrangement in a randomized complete block design with three replications. Each plot consisted of six rows (30.5 meters in length with 76.2 cm between rows) planted to ‘DEKALB 62-97VT3’ (Monsanto, St. Louis, Missouri) at 79,040 seeds ha^{-1}. Two different field locations were used for the 2012 and 2013 research trials.

Waterlogging treatments (0 and 3 days of waterlogging duration) of three to five inched of ponded water were the main plots and were initiated at V6 using temporary soil levees to surround each flooding block. Vegetative growth stage V6 was determined using the leaf collar method (Abendroth et al., 2011). Levees were removed to allow ponded water to escape after a three day waterlogging duration had been achieved.

Nitrogen fertilizer treatments of a non-treated control (CO) and pre-plant N fertilizer sources of non-coated urea (NCU), non-coated urea plus nitrapyrin (2-chloro-6-(trichloro-methyl) pyridine) nitrification inhibitor at 2 L ha^{-1} (NCU + NI) (N-Serve®, Dow AgroSciences, Indianapolis, Indiana), and polymer-coated urea (PCU) (ESN®, Agrium, Inc., Calgary, Alberta) were applied at 168 kg N ha^{-1}. All fertilizer N treatments were broadcast using a hand spreader and incorporated immediately after application using a Tilloll (Landoll Corp., Marysville, KS).

Field Measurements

Measurements for soil N_2O efflux estimations were in accordance with the USDA-ARS GRACEnet protocol for trace gas sampling and analysis (Parkin et al., 2010). Soil N_2O gas efflux measurements were sampled the day prior to initiating waterlogging treatments, two times daily during the three day waterlogging period, and two times following the draining of the waterlogging treatment. In 2012, the N_2O gas efflux measurements were sampled two and four days after the three day waterlogging treatment had been drained, but were measured two and three days following the three day waterlogging duration in 2013. Soil N_2O-N emissions for the soil waterlogging and drying periods were determined by interpolating between gas efflux measurements after 3 days of waterlogging.

Two PVC static ring chambers 23 cm long by 20 cm in diameter were placed 7.5 cm into the soil surface of the corn row for each pre-plant N treatment replication in the non-waterlogged control and three days of waterlogging treatment. Each static chamber was vented using a 10 cm long by 0.64 cm diameter copper tubing installed into a rubber cap equipped with a sampling port (Swaglog, bulkhead connector with Shimadzu septa plug). The volume of chamber headspace sampled for soil N_2O efflux estimations was 25 ml and was injected into a evacuated 12 ml glass vial immediately after sampling (Labco Exetainer, Labco, United Kingdom) at time intervals of 0, 30, and 60 minutes.

Analysis of N_2O was determined on an automated gas chromatograph (GC) (Shimadzu, Kyoto, Japan). Gas effluxes were assessed for curvi-linearity using the empirical data curvi-linearity index equation with a GC precision of 2% (Parkin et al., 2010). For curvi-linear data the Hutchingson and Mosier algorithm was used in determining gas efflux and linear regression was used to determine soil N_2O efflux for non-curvilinear data (Parkin et al., 2010).

Environmental conditions were characterized during gas sampling times. Measurements of soil surface E_h and pH were recorded in the plots where flooding occurred with a portable pH and millivolt meter using an Ag/AgCl electrode saturated in 4 M KCl solution (Oakton 310 pH meter, Vernon Hills, IL; Cole Palmer ORP/pH 3' submersible, Vernon Hills, IL). Soil E_h was converted to the standard H_2 reference electrode values (Vepraskas et al., 2002). At each gas sampling chamber, soil temperatures and a soil sample at a 10 cm depth were collected (Oakton Temp 10 Thermocouple, Vernon Hills, IL). These soil samples were analyzed for soil gravimetric water content and soil NO_3^- concentration using a 2 M KCl extraction and analysis with a Lachat 8400 series II automated ion analyzer (Hach Corp., Loveland, CO) (QuikChem Method 12-107-04-1-B).

Statistical Analysis

All statistical analysis was performed using SAS v. 9.3 (SAS Institute, 2013). Analyses of variance (ANOVA) were determined for all collected data using PROC

MIXED. Normality of all data was verified using PROC UNIVARIATE. Multiple comparisons significance was determined using Fisher's Protected Least Significant Difference (LSD) at the $P \leq 0.10$ probability level.

RESULTS AND DISCUSSION

Initial Soil Characteristics

Initial soil results indicated an adequate amount of Bray I-P and exchangeable potassium, calcium, magnesium based on University of Missouri fertilizer recommendations for corn (Buchholz, 2004) (Table 3.1). The 2012 site had a higher soil pH_s in the 0-10 cm depth (0.7) in comparison to 2013. The concentration of NH_4^+-N plus NO_3^- -N prior to pre-plant N treatments was 40.5 and 50.2 mg N kg^{-1} soil when summed to a depth of 30 cm for 2012 and 2013, respectively. In general, 2012 had a decrease in soil NO_3^--N with increasing sampling depth, whereas NO_3^--N increased with sampling depth in 2013.

Climatic Conditions

Total cumulative precipitation from seed planting to grain harvest was 363 and 566 mm for 2012 and 2013, respectively (University of Missouri Extension, 2014) (Figure 3.1). Severe drought occurred during 2012 and it was recorded as the third driest and warmest April-August time period in Missouri over the past 120 years (NOAA, 2012). There was variation throughout the 2013 growing season with intense spring rains resulting in the 15th wettest April-June time period during the past 120 years (NOAA, 2013). Drier and warmer spring temperatures promoted an earlier planting date in 2012 in comparison to that of 2013 (Figure 3.1). This resulted in an earlier initiation of the waterlogging treatment at growth stage V6 in 2012 than in 2013. Average air temperature during the three day waterlogging treatments was 19.0 and 24.5°C for 2012 and 2013, respectively. There was 18 mm of precipitation received the day prior to implementing the waterlogging treatments in 2012 and in 2013 a precipitation event of 33.5 mm had occurred three days prior to waterlogging.

Waterlogging Conditions

Greater air temperatures in 2013 resulted in warmer soil temperatures (4.2° C) during N_2O sampling times compared to 2012 (Figure 3.3). In both research seasons, no significant temperature differences were observed between non-waterlogged and waterlogged soils. The average gravimetric soil water content during gas sampling in 2012 was 0.22 and 0.40 g water g^{-1} $soil^{-1}$ for the non-waterlogged and waterlogged treatments, respectively (Figure 3.4). In 2013, the non-waterlogged treatment had an average gravimetric water content of 0.31 g water g^{-1} $soil^{-1}$ and the waterlogged treatment had an average gravimetric water content of 0.36 g water g^{-1} $soil^{-1}$. Soil surface E_h after three days of waterlogging averaged 448 and 368 mV in 2012 and 2013, respectively. This is considered the threshold between a weakly reduced suboxic to oxic soil environment (Figure 3.5) (Berner et al., 1981; Zhi-Guang, 1985; Sposito et al., 1989; Reddy et al., 2000). In an soil incubation study, Hernandez-Ramirez et al. (2008) attributed increased soil N_2O emissions under moderate reducing conditions at a E_h in the range of 420 to 575 mV in both soils that had a history of either UAN or manure application.

Soil Nitrate Concentration

In 2012, greater soil NO_3^--N concentrations of 45.4 (P=0.0053) and 49.5 (P=0.0024) mg kg^{-1} soil were observed with pre-plant N fertilizer treatments of NCU+NI and PCU in comparison to NCU in the waterlogging plots prior to waterlogging. At the first sampling period after waterlogging there was 26.4 (P=0.0888) and 34.3 (P=0.0338) greater mg NO_3^--N kg^{-1} $soil^{-1}$ with NCU+NI and PCU compared to NCU, respectively (Figure 3.6). After three days of waterlogging, no differences were observed in soil surface NO_3^--N concentrations among pre-plant N fertilizers that were waterlogged, but PCU in the non-waterlogged treatment was 46.6 (P=0.0074) and 35.5 (P=0.0012) mg NO_3^--N kg^{-1} soil greater than NCU and NCU+NI, respectively. Two days after draining the waterlogging treatment, the soil surface NO_3^--N concentration was 71.0 mg kg^{-1} soil (86%) (P<0.0001) greater in the non-waterlogged control compared to the waterlogged treatment when averaged across pre-plant N fertilizer treatments.

In 2013, there was significantly less soil surface NO_3^--N concentrations on every sampling period after one day of waterlogging when averaged across pre-plant N treatments (Figure 3.7). At the end of the waterlogging duration, there was 32.3 mg NO_3-N kg^{-1} (61%) (P=0.0040) greater concentration in the soil of the non-waterlogged control compared to the waterlogged treatment when averaged across pre-plant N fertilizer treatments. After two and three days of soil drainage, there were greater NO_3^--N concentrations of 41.4 (P=0.0003) (79%) and 26.7 (P=0.0165) (64%) mg kg^{-1} in the soil when comparing the non-waterlogged control to the waterlogged treatment averaged across all pre-plant N treatments.

Soil N_2O Emissions

In 2012, cumulative N_2O-N losses in the waterlogged treatment were 0.53, 0.97, 2.60, and 3.74 kg ha^{-1} for pre-plant N treatments of CO, NCU, NCU+NI, and PCU, respectively (Figure 3.8). Polymer coated urea had 2.8 kg ha^{-1} (P=0.0288) greater cumulative soil N_2O-N emissions compared to that of NCU over the entire sampling period of the three day waterlogging treatment. This may have been due to increased soil NO_3^--N concentration of 25.1 mg kg^{-1} soil (p=0.0422) with PCU in comparison to that of NCU when averaged across all sampling times. Under rainfed conditions, Nash et al. (2012) observed similar emissions with NCU than PCU on a claypan soil. Under irrigated corn in a clay loam soil, Halvorson et al. (2014) reported no significant reduction of cumulative N_2O emission with PCU under conventional tillage. These results indicated that yearly climate and timing of soil saturation may be significant factors in the amounts of soil N_2O emissions relative to N fertilization and planting date.

Soil NO_3^--N concentrations in 2012 were not significantly different (P=0.4639) between PCU and NCU+NI, but both were significantly greater than NCU over the gas sampling period in the plots that received three days of water logging. There was a greater concentration of soil NH_4^+-N (10.0 mg kg^{-1}) (P=0.0020) with PCU compared to NCU+NI (Figure 3.9) after three days of waterlogging plots, but no significance difference in soil NH_4^+-N concentration between NCU+NI and NCU (P=0.6202). This indicates that additional cumulative soil N_2O-N emission with PCU versus NCU+NI, although insignificant, may have been a result of greater soil NH_4^+-N concentrations contributing N_2O through the NH_3 oxidizing pathway. The lack of difference in NH_4^+-N concentration between NCU and NCU+NI during the entire gas sampling period suggest nitrapyrin activity was no longer effective at significantly reducing nitrification rates 59 days after N fertilization under the environmental conditions of this research. However, greater concentrations of soil NO_3^--N with NCU+NI than NCU before and at soil waterlogging suggest nitrapyrin was possibly effective at delaying nitrification and NO_3^--N loss early after N fertilization. Omonode and Vyn, (2013) reported an increased half-life of UAN when band-applied with UAN with nitrapyrin from 15 to 25 days in comparison to band applied UAN without nitrapyrin.

Separating cumulative N_2O-N emissions by only the period with three days of waterlogging had no observed differences between pre-plant N treatments, although increased emissions of 1.2 (p=0.0830) and 1.9 (P=0.0064) kg N_2O-N ha^{-1} resulted from NCU+NI and PCU in comparison to NCU during the soil drying phase of sampling, respectively (Figure 3.10A). This may indicate that the cumulative N_2O emission for PCU and NCU+NI that occurred over the entire gas sampling time was more significantly impacted during the drying down period than the waterlogging period. However, NCU had less cumulative emission during the drying down period than the flooding period.

Increased soil N_2O emissions during the soil drying period may have been attributed to O_2 re-introduction into the soil pores as gravimetric water content decreased by 20.5%. Several studies have observed peak soil N_2O emissions when WFPS is at a range of 75 to 80% (Hansen et al., 1993; Khalil and Baggs, 2005; Sey et al., 2008). Peng et al. (2011) observed 79% of the cumulative soil N_2O emission occurred during the drying phase in rice production.

Over the total measurement period insignificant cumulative N_2O emissions of 0.0432, 0.0942, 0.1458, and 0.0889 kg N_2O-N ha^{-1} was observed in the non-waterlogged control of CO, NCU, NCU+NI, and PCU, respectively (Figure 3.11). Subtracting cumulative soil N_2O of the non-fertilized control from the pre-plant N treatments showed an average of 0.04% and 1.1% of total fertilizer N applied lost as N_2O-N in the non-waterlogged control and waterlogged treatments, respectively.

Cumulative N_2O emissions in 2013 for the entire gas sampling period was insignificant with 0.21, 5.58, 3.58, and 4.80 kg N_2O-N ha^{-1} being emitted in the CO, NCU, NCU+NI, and PCU with three days of waterlogging (Figure 3.12). When pre-plant N treatments were analyzed during only the period of soil waterlogging, NCU-fertilized soil had 0.89 kg N_2O-N (P=0.0731) greater emissions than PCU. Halvorson and Del Grosso (2012) reported 0.4% less cumulative emissions of N_2O-N with PCU in comparison to NCU in an irrigated clay loam soil under no-till. When separated by a period of soil drying, NCU+NI had 0.83 (p=0.0946) and 0.87 (P=0.0806) kg N_2O ha^{-1} less cumulative soil N_2O emissions than NCU and PCU, respectively (Figure 3.9B). Burzaco et al. (2013) reported a decrease of 0.60 kg ha^{-1} of cumulative soil N_2O-N averaged across two research years with the use of UAN treated plus nitrapyrin.

Soil NO_3^--N concentrations at either sampling times during the drying period were not significantly different between NCU+NI, NCU or PCU. Polymer coated urea had greater NH_4^+-N than NCU and NCU+NI at sampling times during the drying period, although there was no significant differences between NCU and NCU+NI (Figure 3.13). This result may indicate that greater cumulative soil N_2O-N emission during the drying period could be associated with the nitrification process. Kool et al. (2011) reported that nitrifier denitrification can be more significant in N_2O-N production than NO_3^--N denitrification at both 50 and 70% WFPS.

In the non-waterlogged control, there were no significant differences in cumulative N_2O emissions of CO, NCU, NCU+NI, and PCU pre-plant N treatments when estimated over the entire sampling period. These treatments emitted 0.05, 0.52, 0.76, and 0.61 kg N_2O-N ha^{-1}, respectively (Figure 3.14). Subtracting cumulative soil N_2O of the non-fertilized control from the pre-plant N treatments showed an average of 0.03% and 2.6% of total N applied loss as N_2O-N in the non-waterlogged control and waterlogged treatments over the entire sampling period, respectively. Nash et al. (2012) reported a range of 2.8 to 3.0% of N fertilizer loss as N_2O-N with NCU and PCU in claypan soils, respectively. The pulses of N_2O in this research associated with soil waterlogging and drying are in accordance with a report by Venterea et al. (2010) stating that pulses of soil N_2O emissions commonly accounted for a large proportion of annual emissions (>65%).

CONCLUSIONS

The 2012 growing season had warmer and drier climatic conditions in early spring in comparison to relatively cooler and wetter conditions observed in 2013. This difference in climatic conditions significantly impacted soil properties leading up to V6 corn growth stage when the three days of waterlogging was initiated. In 2012, the waterlogging treatment occurred 59 days after planting which promoted higher soil N concentration differences between the controlled released PCU and NCU fertilizer treatments. These differences in soil N caused a greater observed cumulative N_2O-N emission during the three day waterlogging duration and soil drying with PCU in comparison to NCU. In 2013, the three day waterlogging duration occurred 34 days after fertilization and NO_3^--N concentrations were similar among NCU and PCU, with PCU having slightly greater NO_3^--N concentrations than NCU+NI, which resulted in no significant differences in N_2O-N emissions over the entire gas sampling period. The emissions associated with only the period of waterlogging showed NCU emitted more N_2O-N than PCU. The NCU+NI had lower cumulative emission during the soil drying phase which provides an indication that NH_3 nitrifying denitrification may have been contributing significantly to soil N_2O-N production during the drying phase and the activity of nitrapyrin reducing nitrification resulted in less N_2O-N emission.

During both years significant increases of N_2O-N emissions were observed when comparing non-waterlogging and waterlogging conditions in which cumulative fertilizer induced N_2O-N soil emissions were 0.04%, 1.1% and 0.03% and 2.6% for 2012 and 2013, respectively. Warmer temperatures of 5.5°C in 2013 and timing of waterlogging treatment relative to N application may have impacted the amount of cumulative N_2O between years. This study shows that significant pulses of N_2O attributed to waterlogging can present a significant proportion of the cumulative N_2O-N emissions for an entire growing season in poorly drained soils.

Given the significant amount of N_2O-N production that can be associated with a waterlogging event during corn production and its environmental impacts, future research may further evaluate the effectiveness of EEN products or other management practices (e.g., drainage) that may reduce the duration of waterlogging and dry-down events to lower soil N_2O emissions and to further quantify soil N_2O-N emission variability that can be a result of yearly climatic variation and management practices in poorly drained or alluvial soils. The prediction of the increased occurrence of extreme weather events in the Midwest region, including more frequent intense rainfall events during the spring, highlights the urgency of conducting this type of research.

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Table 3.1. Selected initial soil characteristics for 2012 and 2013. Data was averaged over three replications by soil depth.

Year[†]	Depth	OM	pH_s	NA	CEC	Bray 1 P	Exch. Ca	Exch. Mg	Exch. K	B.D.	NO_3^- -N	NH_4^+-N
	- cm -	- g kg^{-1} -		----- $cmol_c$ kg^{-1} -----		----------- kg ha^{-1} -----------				- g cm^{-3} -	----- mg N kg $soil^{-1}$------	
2012	0-10	27±3.0	6.1±0.4	1.8±1.4	15.2±1.3	65.0±9	5151±436	395±37	407±61	1.43±0.05	6.7±3.0	11.1±1.9
	10-20	20±3.0	6.3±0.4	1.5±0.9	15.1±0.1	23.2±4	5367±362	380±10	200±14	1.48±0.14	4.1±1.1	7.6±0.7
	20-30	17±2.0	5.5±0.5	4.0±1.3	17.8±2.3	8.60±2	5114±246	570±86	211±20	1.46±0.01	3.0±0.4	8.0±2.1
2013	0-10	28±1.0	5.4±0.1	3.7±0.6	13.9±0.2	83.2±8	3698±148	384±15	438±32	1.11±0.02	11.4±3.0	3.7±0.4
	10-20	20±2.0	5.9±0.3	2.5±0.9	14.0±0.6	26.0±5	4351±204	426±12	221±40	1.30±0.07	11.9±2.4	3.4±0.2
	20-30	18±1.0	5.2±0.5	4.7±2.1	16.5±2.8	14.6±3	4248±179	549±79	235±179	1.26±0.05	16.0±3.8	3.8±0.8

†Abbreviations: pH_s in 0.01 M $CaCl_2$; NA, Neutralizable Acidity; OM, Organic Matter; P, Bray-1 Phosphorus; Exch. Ca, Exchangeable Calcium; Exch Mg, Exchangeable Magnesium; Exch. K, Exchangeable Potassium; CEC, Cation Exchange Capacity; B.D, Bulk Density; NO_3^- -N, Nitrate Nitrogen; NH_4^+ -N, Ammonium Nitrogen; ±, plus or minus one standard deviation.

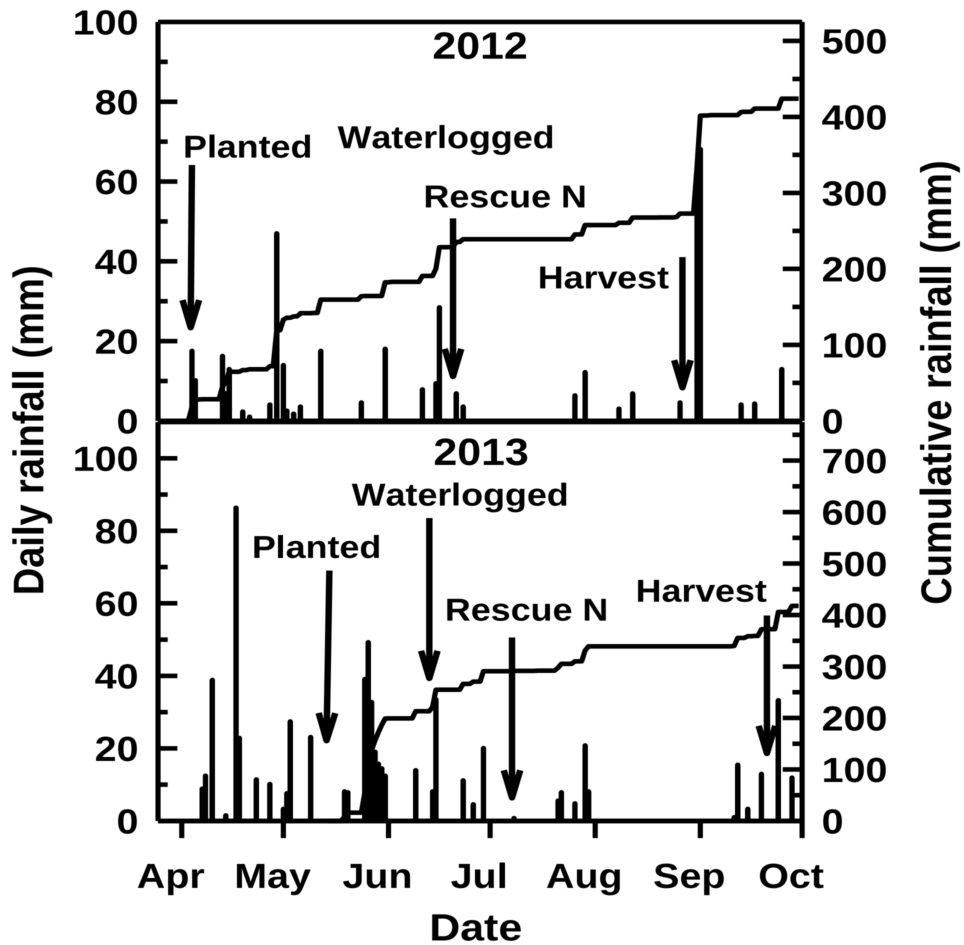

Figure 3.1. Daily and cumulative precipitation from 1 April through 1 October for 2012 and 2013. Cumulative rainfall axis starts at planting for both years.

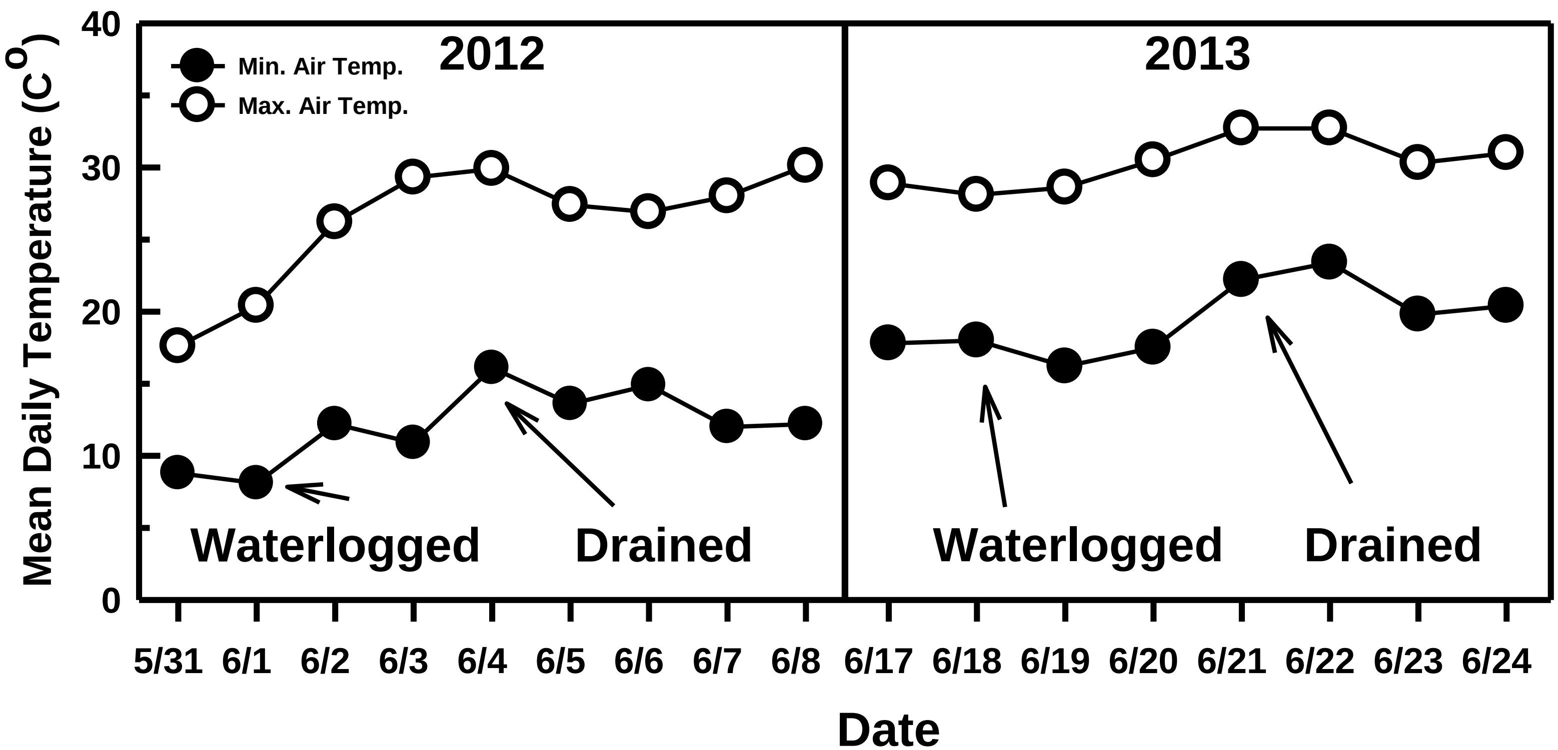

Figure 3.2. Average maximum and minimum daily air temperatures during the gas sampling period in 2012 and 2013.

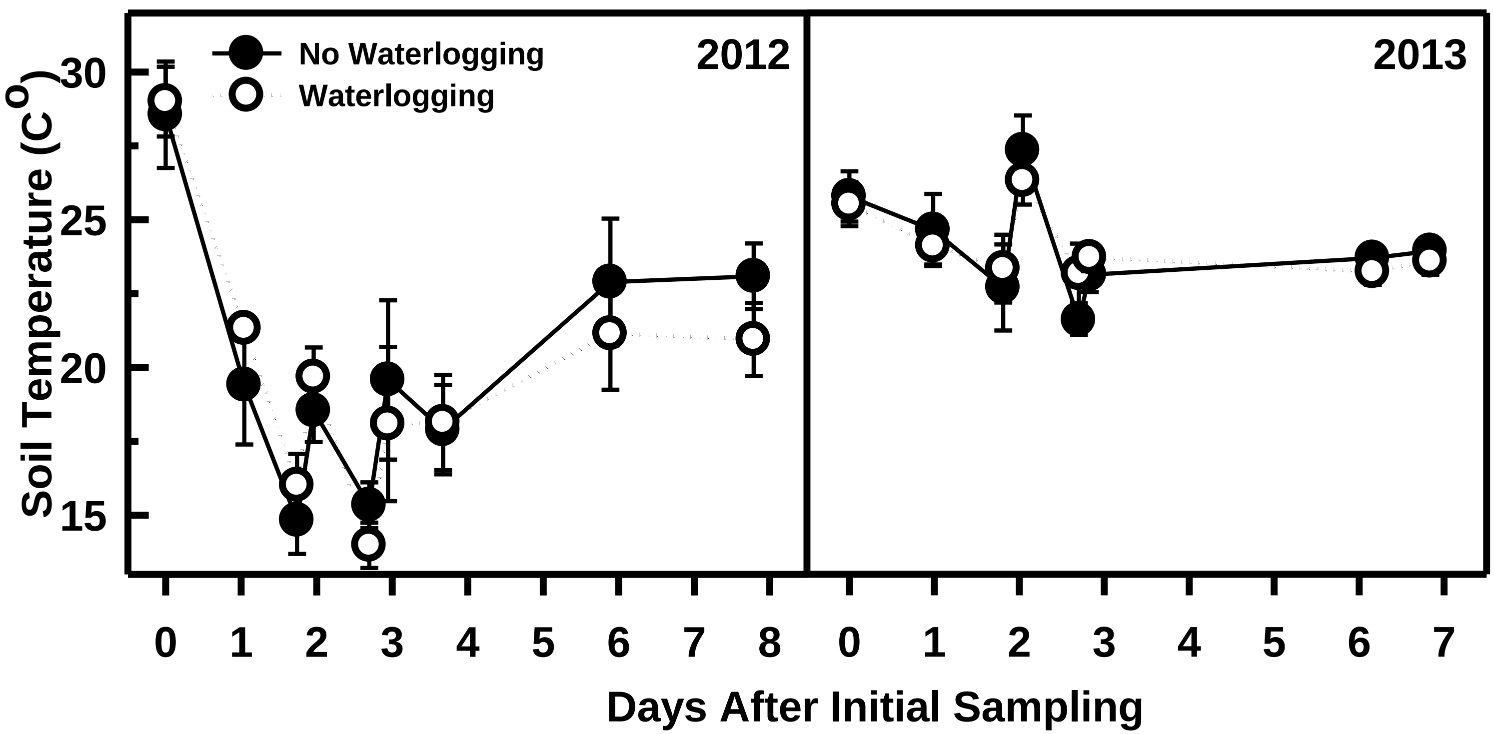

Figure 3.3. Average soil temperatures at a depth of 10 cm recorded at the time of gas sampling in the non-waterlogged and waterlogged treatments for 2012 and 2013 at the Greenley Memorial Research Center.

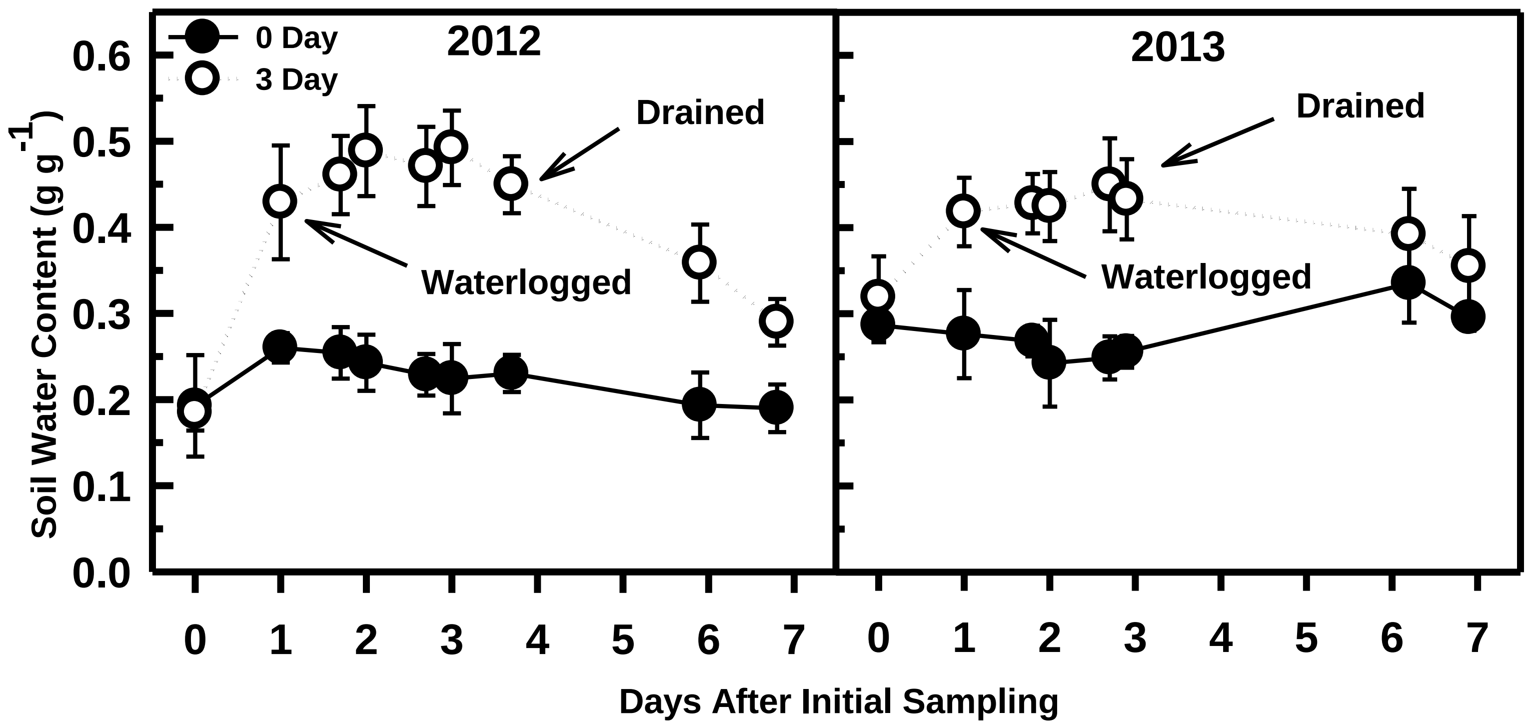

Figure 3.4. Average daily gravimetric moisture content for the no waterlogging and three day waterlogging treatments in 2012 and 2013. The first sampling period occurred the day before waterlogging treatments were initiated for both 2012 and 2012. Error bars represent ± one standard deviation across subsamples that were replicated three times.

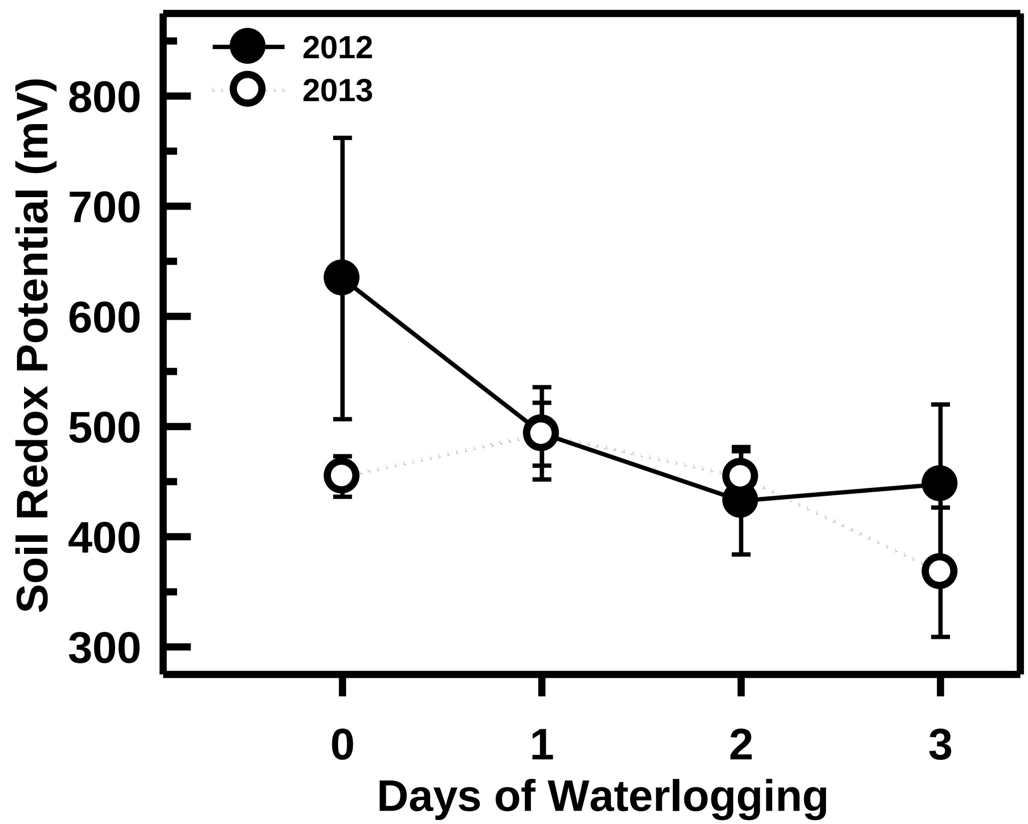

Figure 3.5. Average daily soil redox potential during the three day waterlogging duration in 2012 and 2013. The first sampling period occurred right after water was ponded on the soil surface. Error bars represent ± one standard deviation across subsamples that were replicated three times.

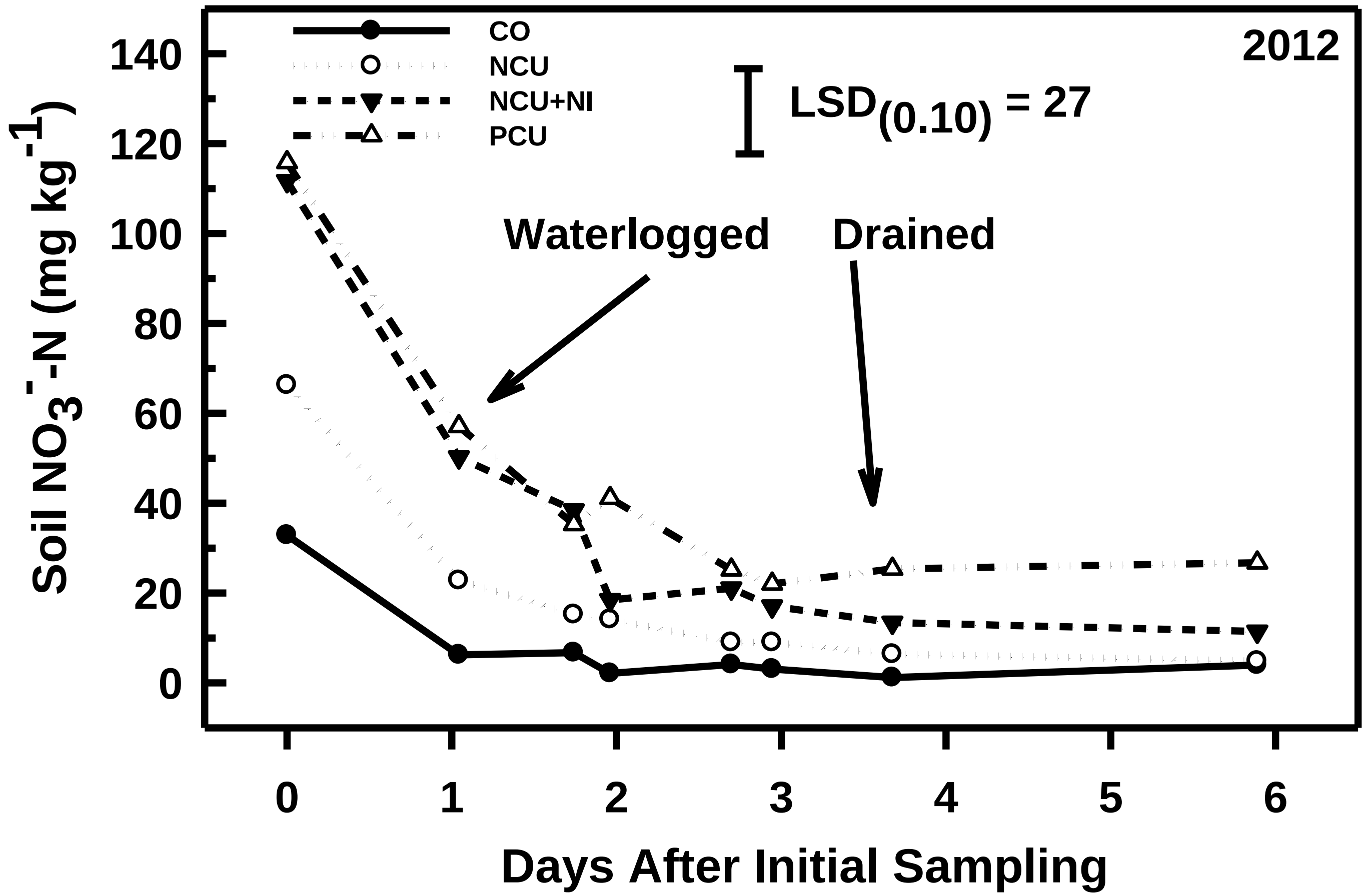

Figure 3.6. Soil NO_3^--N measured at the time of gas sampling to a depth of 10 cm for each pre-plant N fertilizer treatment in the waterlogged treatments in 2012 (Abbreviations: CO, Control; NCU, Urea; NCU + NI, Urea + nitrification inhibitor; PCU, polymer coated urea; LSD, least significant difference at $P < 0.10$ comparing pre-plant N treatments at similar times in the waterlogged treatments).

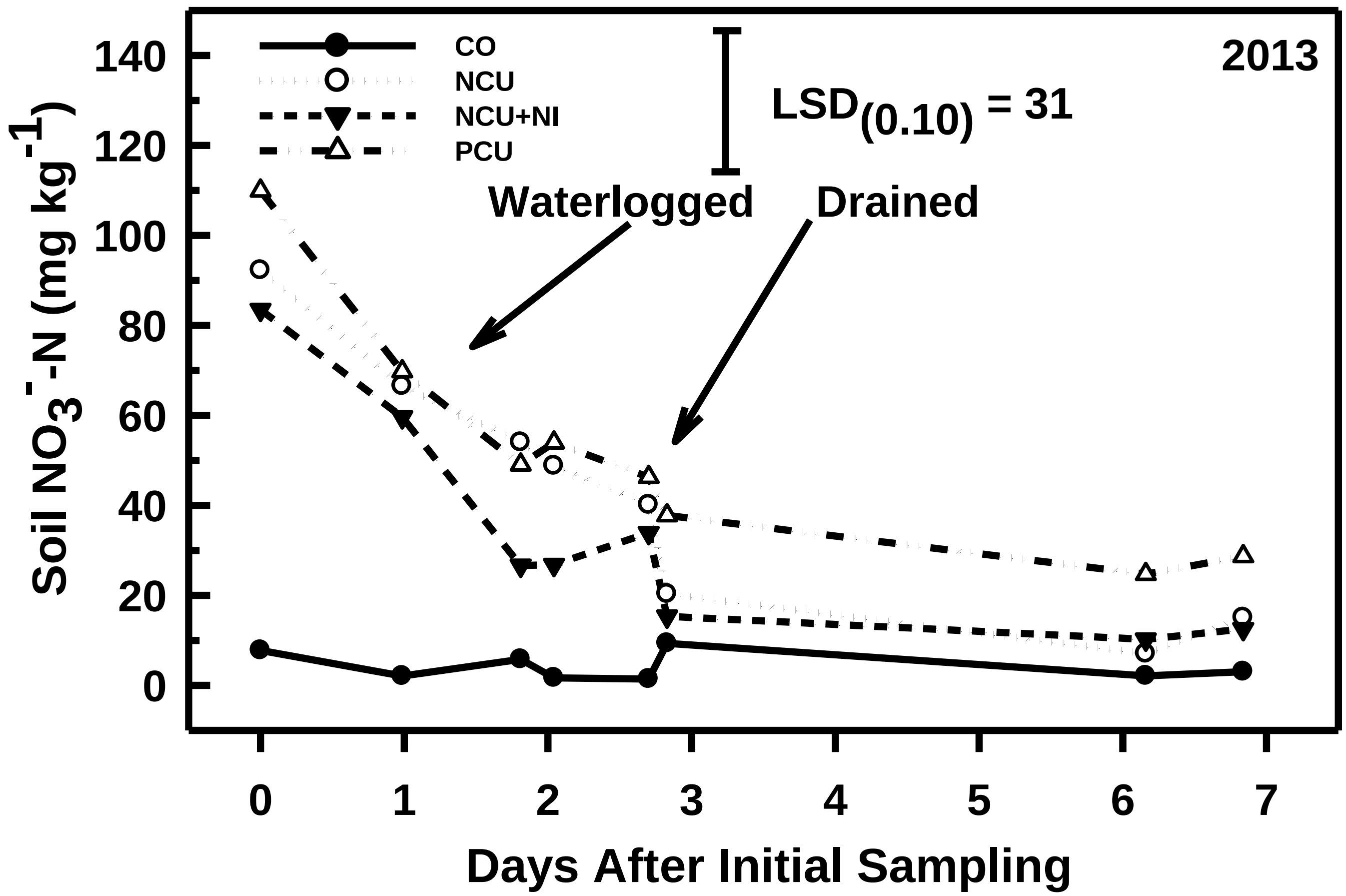

Figure 3.7. Soil NO_3^--N measured at the time of gas sampling to a depth of 10 cm for each pre-plant N fertilizer treatment in the waterlogged treatments in 2013 (Abbreviations: CO, Control; NCU, Urea; NCU + NI, Urea + nitrification inhibitor; PCU, polymer coated urea; LSD, least significant difference at $P < 0.10$ comparing pre-plant N treatments at similar times in the n waterlogged treatments).

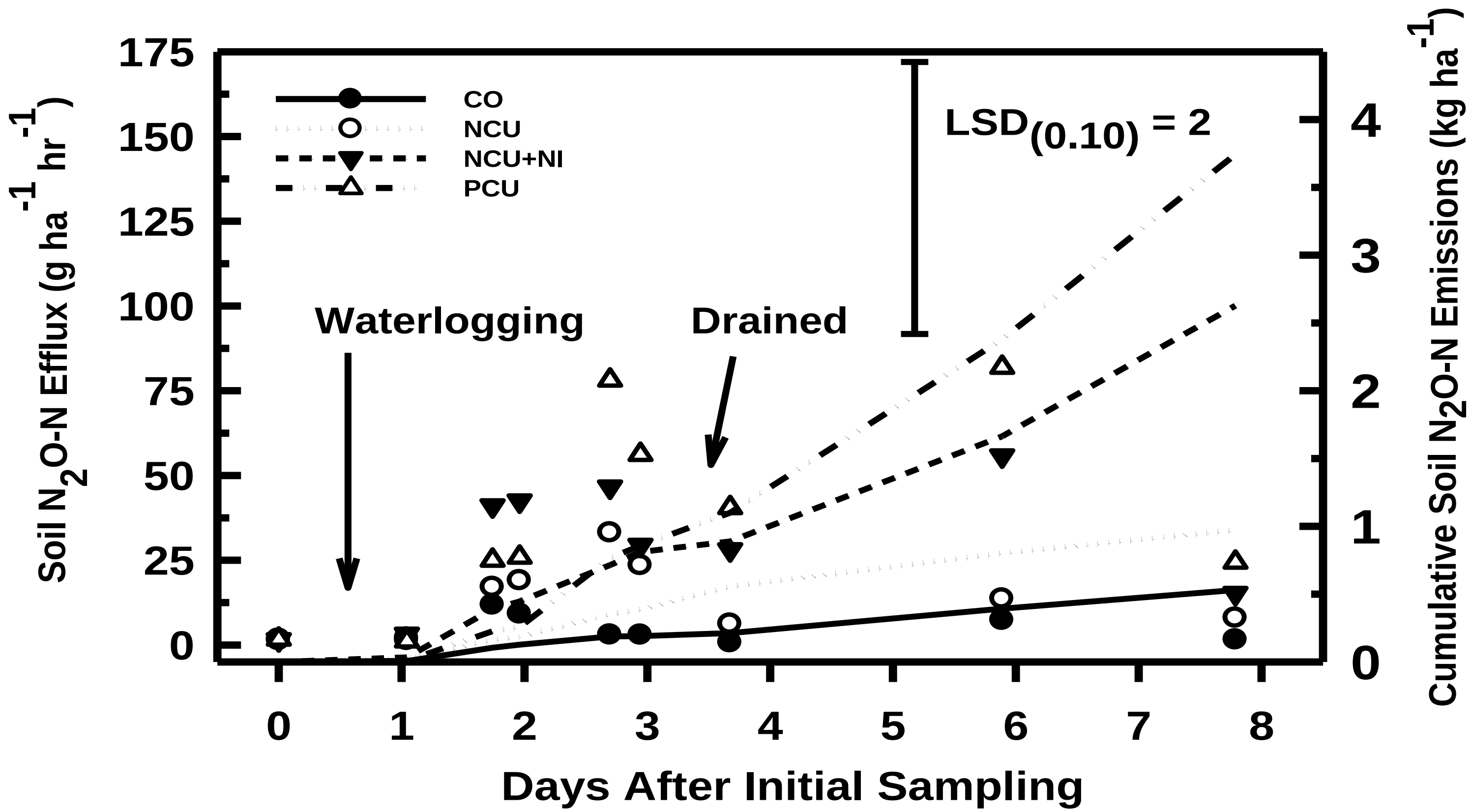

Figure 3.8. Soil N_2O gas efflux and cumulative N_2O emissions for each pre-plant N treatment in the waterlogged treatment in 2012 (Abbreviations: CO, Control; NCU, Urea; NCU + NI, Urea + nitrification inhibitor; PCU, polymer coated urea; LSD, least significant difference at $P < 0.10$ comparing cumulative gas emissions among pre-plant N treatments).

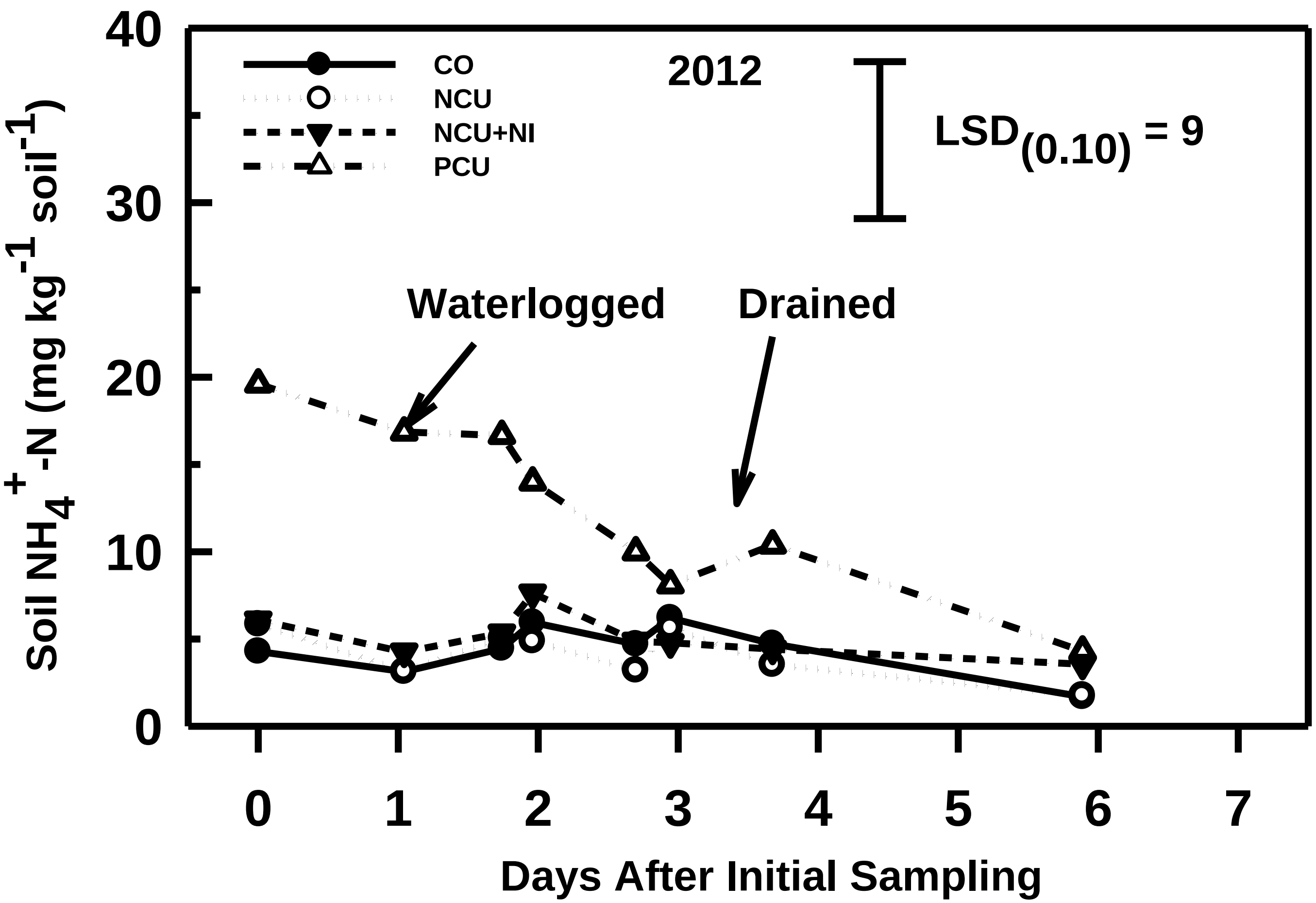

Figure 3.9. Soil NH_4^+-N measured at the time of gas sampling to a depth of 10 cm for each pre-plant N fertilizer treatment in the waterlogged treatments in 2012 (Abbreviations: CO, Control; NCU, Urea; NCU + NI, Urea + nitrification inhibitor; PCU, polymer coated urea; LSD, least significant difference at $P < 0.10$ comparing pre-plant N treatments at similar times).

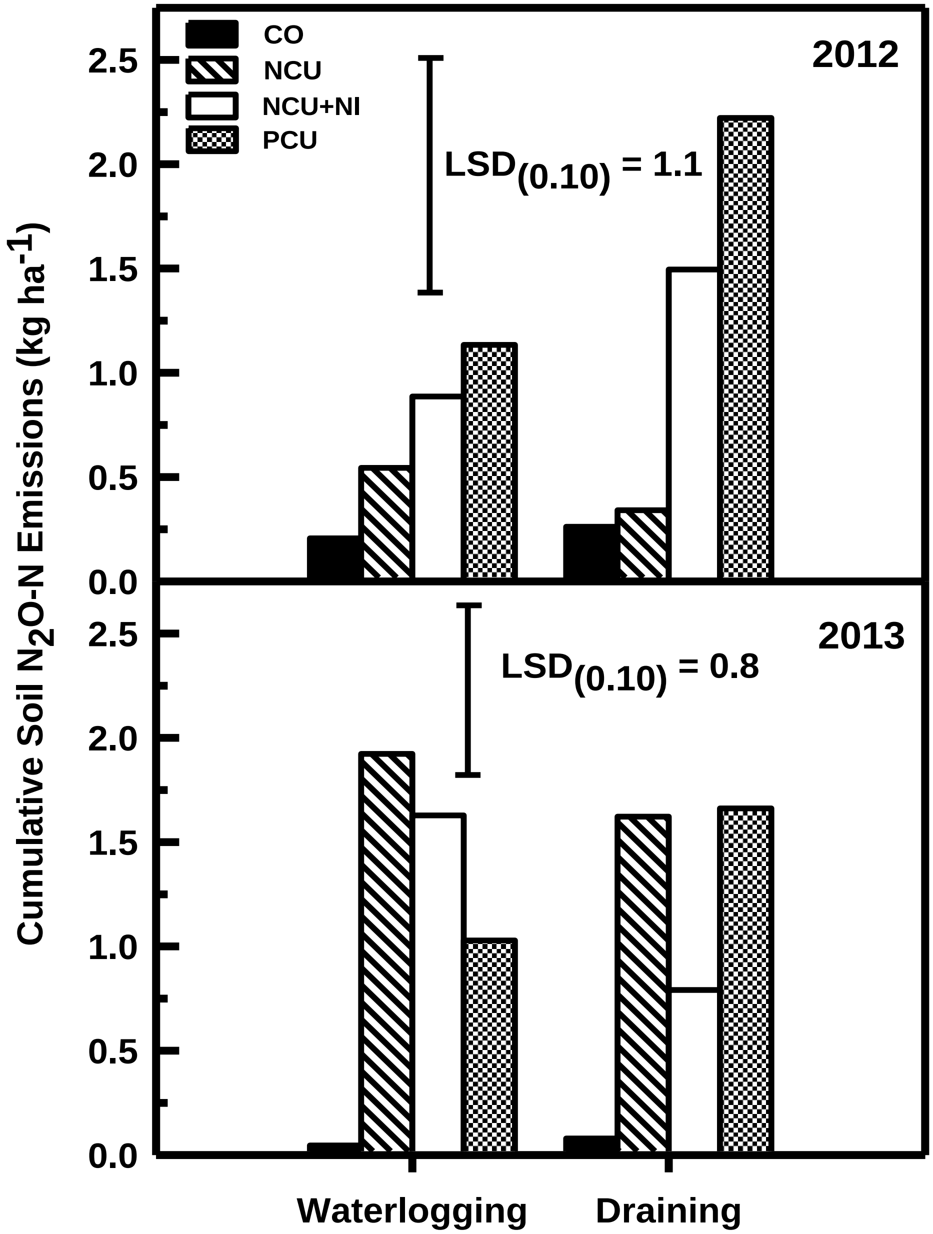

Figure 3.10 Cumulative N_2O emissions for each pre-plant N treatment with three days of waterlogging and period of draining in 2012(A) and 2013(B) (Abbreviations: CO, Control; NCU, Urea; NCU + NI, Urea + nitrification inhibitor; PCU, polymer coated urea; LSD, least significant difference at $P < 0.10$ comparing cumulative gas emissions from 3 days of waterlogging and draining period for each pre-plant N treatment).

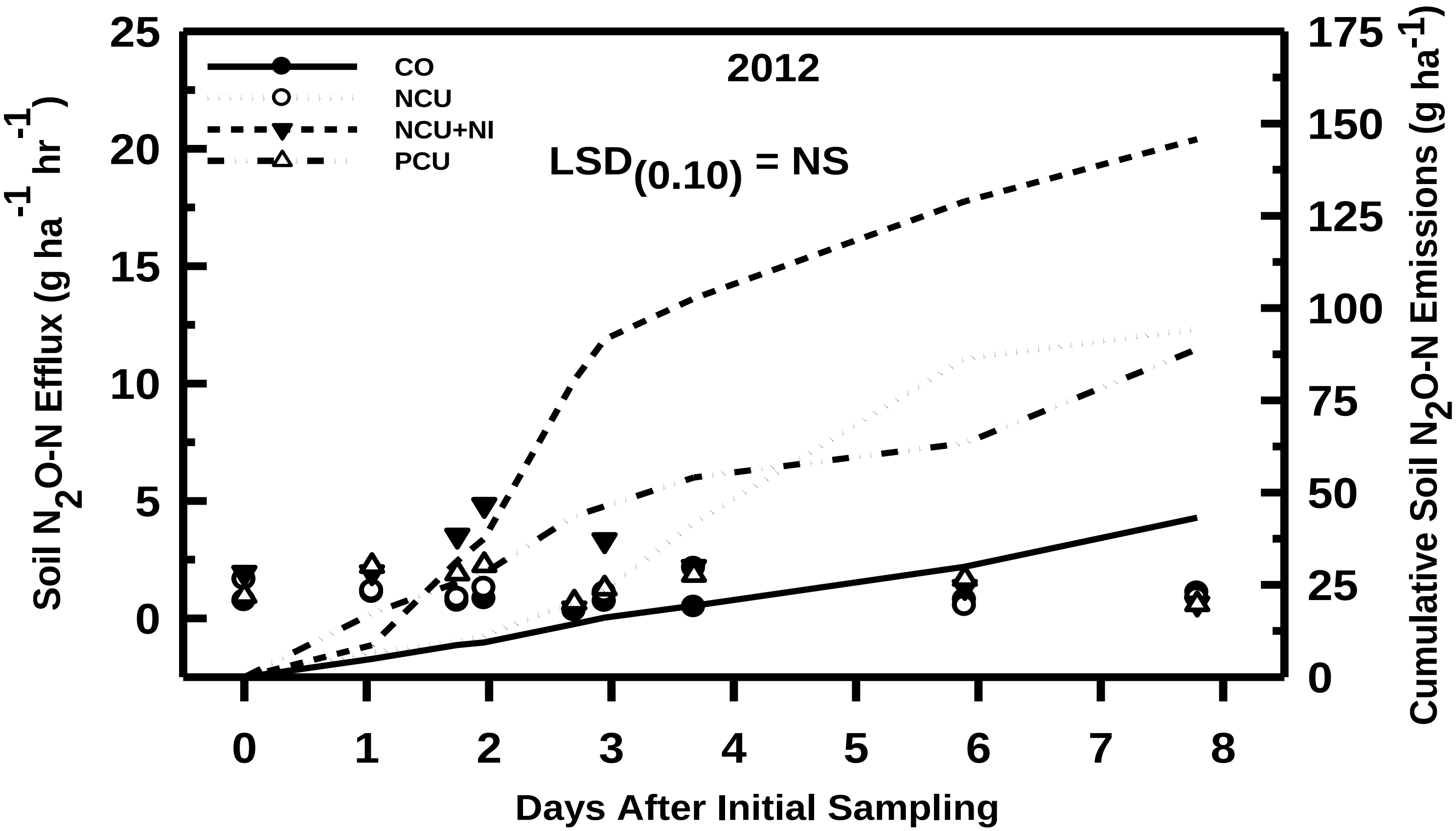

Figure 3.11. Soil N_2O gas efflux and cumulative N_2O emissions for each pre-plant N treatment in the non-waterlogged treatment in 2012 (Abbreviations: CO, Control; NCU, Urea; NCU + NI, Urea + nitrification inhibitor; PCU, polymer coated urea; LSD, least significant difference at $P < 0.10$ comparing cumulative gas emissions among pre-plant N treatments).

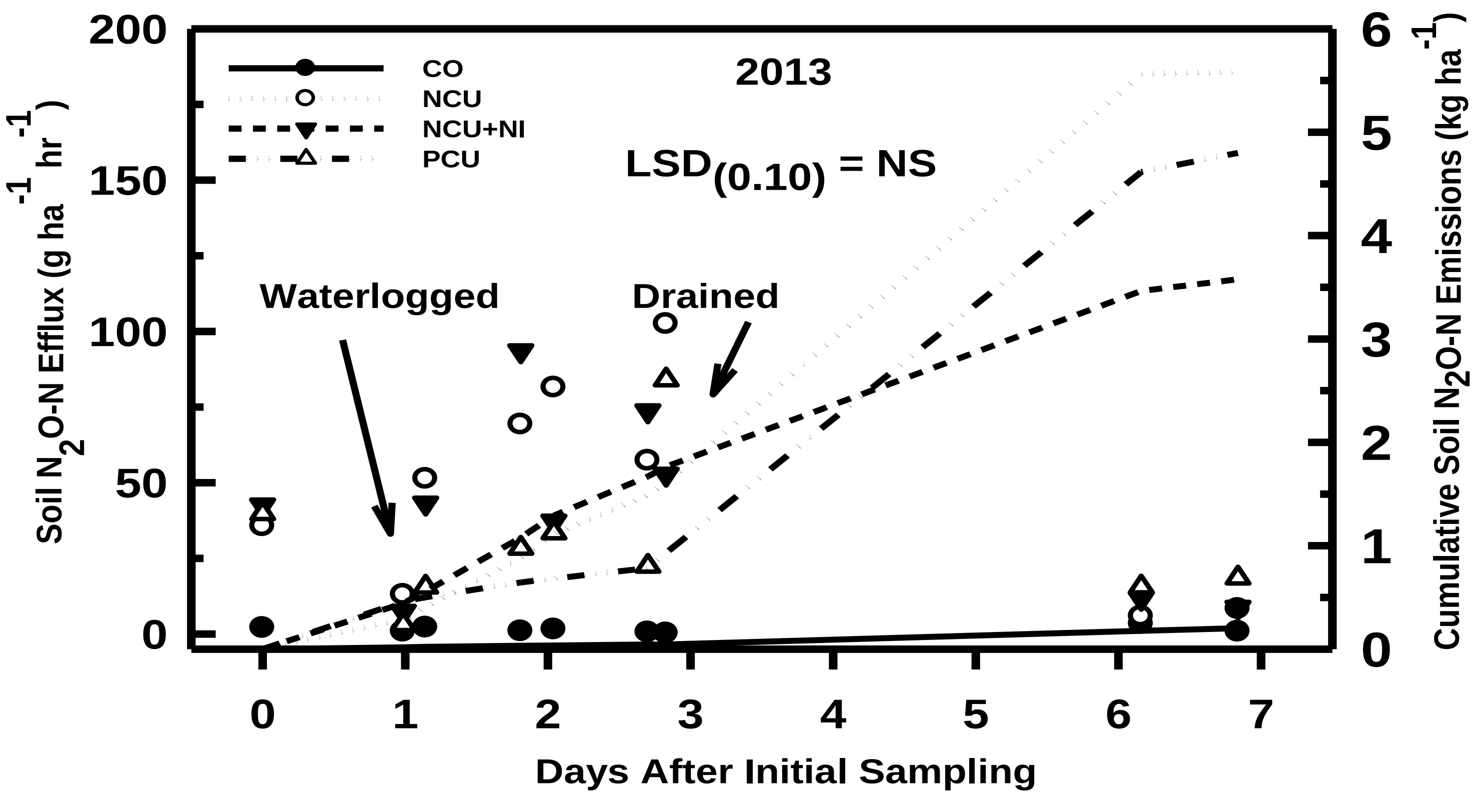

Figure 3.12. Soil N_2O gas efflux and cumulative N_2O emissions in for each pre-plant N treatment in the waterlogged treatment in 2013 (Abbreviations: CO, Control; NCU, Urea; NCU + NI, Urea + nitrification inhibitor; PCU, polymer coated urea; LSD, least significant difference at $P < 0.10$ comparing cumulative gas emissions among pre-plant N treatments).

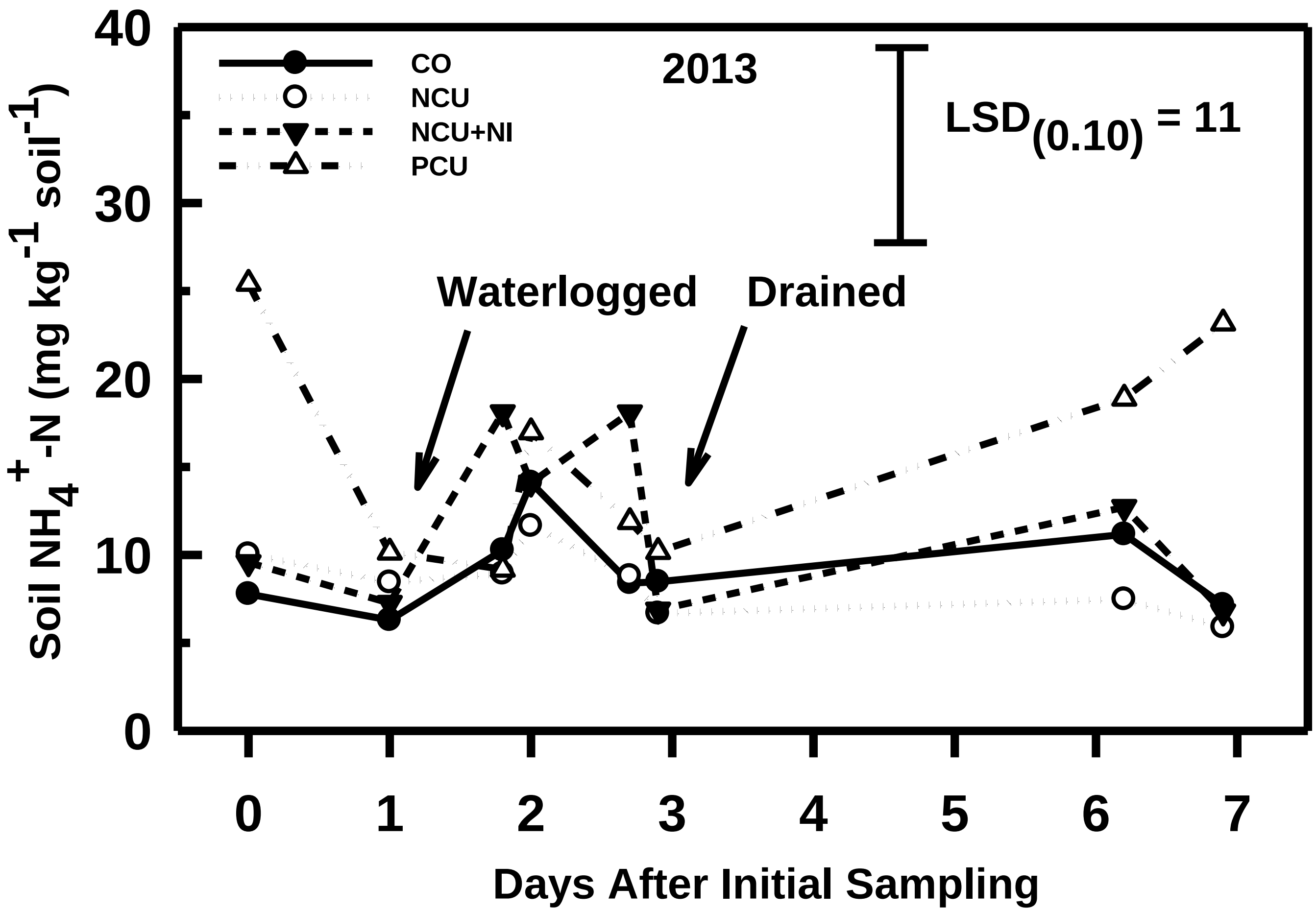

Figure 3.13. Soil NH_4^+ measured at the time of gas sampling to a depth of 10 cm for each pre-plant N fertilizer treatment in the waterlogged treatments in 2013 (Abbreviations: CO, Control; NCU, Urea; NCU + NI, Urea + nitrification inhibitor; PCU, polymer coated urea; LSD, least significant difference at $P < 0.10$ comparing pre-plant N treatments at similar times).

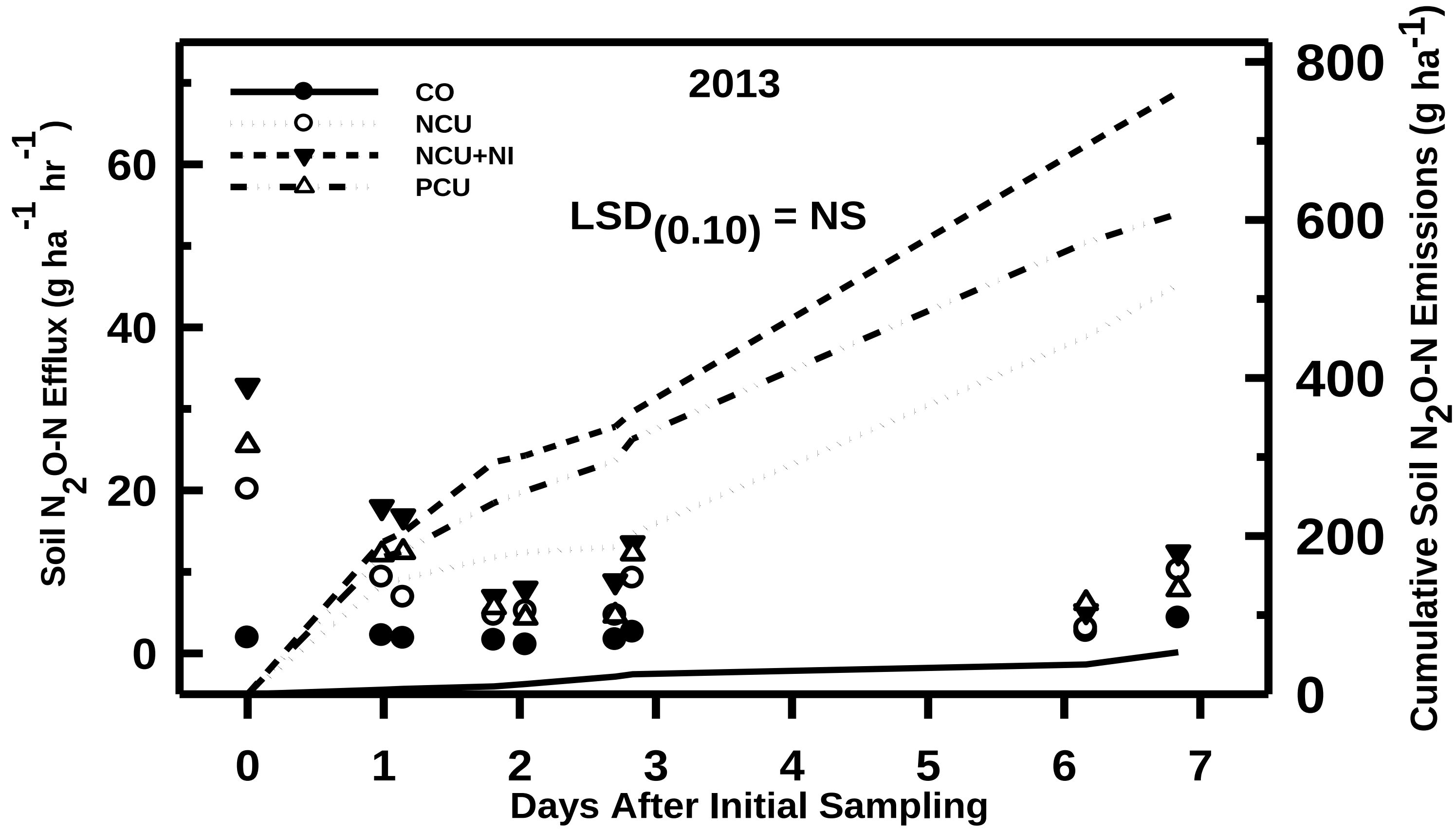

Figure 3.14. Soil N_2O gas efflux and cumulative N_2O emissions in for each pre-plant N treatment in the non-waterlogged treatment in 2013 (Abbreviations: CO, Control; NCU, Urea; NCU + NI, Urea + nitrification inhibitor; PCU, polymer coated urea; LSD, least significant difference at $P < 0.10$ comparing cumulative gas emissions among pre-plant N treatments).

CHAPTER 4

OVERALL CONCLUSIONS

Poorly drained claypan soils in Northeast Missouri are vulnerable to periods of soil saturation that can result in reduced corn grain yields possibly due to abiotic stress with low available oxygen in the soil pores or from N deficiency due to escalated soil N loss. Nitrogen loss in soils with poor drainage is primarily a result of lateral flow, such as surface runoff, and the denitrification process which can cause production of the greenhouse and ozone-depleting gas, N_2O. The N lost due to denitrification also reduces plant N uptake and grain N partitioning and may represent a significant loss in economic value due to a decrease in potential grain production and a loss of the funds invested in the fertilizer input.

Studies related to the changing climate in the Midwest Region indicate that more extreme weather events, such as a higher incidence of intense rainfall events during the spring season, may be occurring. Such trends further highlight the greater risk for N fertilizer management that farmers may have to face in the future since areas with poorly-drained soils may be especially susceptible to increased soil N loss with more extreme weather events.

Research that addresses improvements in both pre-plant and post-flood N fertilizer management may be critical for assisting farmers to manage the effects of waterlogged soils. The pre-plant N fertilization management practices evaluated in this research trial were to evaluate the effectiveness of EEN fertilizer products at minimizing N loss under soil waterlogging durations with an attempt to synchronize soil N concentrations to plant N demand. Post-flood or rescue N fertilizer applications was also evaluated for their assistance in compensating for soil N loss that occurs during the waterlogging event.

In 2012, there was minimal response of grain yield to EEN and rescue N applications, while these yield responses to the different N fertilizer treatments were absent in 2013. The increases in grain yield during 2012 with EEN or rescue N application were probably not significant enough to offset the higher prices associated with EEN products or additional application of NCU+UI rescue N application. However, in both years significant water stress occurred due to drought and it is likely that this was more of a limitation to grain yields than soil N availability. Since PCU was effective at increasing soil N concentrations further research should evaluate its potential under non-drought conditions.

This research also observed that N loss was greatly affected by the amount of soil NO_3^--N at the time of the waterlogging duration. This indicates that the timing and respective amount of N applied at is a viable management strategy to evaluate. Since PCU was effective at controlling its release which maintained greater NH_4^+-N and NO_3^--N later into the growing season, it may have potential as a starter fertilizer in split N application situations. This would minimize the amount of higher priced PCU applied and allow for soil, plant, and general N loss assessments to be made for a second in season application of conventional fertilizer.

In 2013, when a less severe drought occurred and waterlogging was implemented later in the growing season resulting in warmer temperatures, no reduction in grain yields were observed with one day of waterlogging, despite this being the period of most significant NO_3^--N loss. In this same year, significant yield reductions occured after three days of waterlogging, but there was no response to the rescue N application. In years where yield outlook is comparable to 2013, a rescue N fertilizer application following a similar waterlogging event may not be beneficial. Assessment of soil and plant N should be determined if practical, and rescue N application should be applied with caution at growth stage V10 or later in areas where drought conditions may persist after a rescue N application.

Soil N_2O emissions were variable by year, probably due to differences in climatic conditions of air/soil temperatures at the time of waterlogging and the amount of precipitation received prior to waterlogging. The greater cumulative N_2O emissions over the entire sampling period with PCU in 2012 was most likely caused by the higher soil NO_3^--N concentration at the time of waterlogging. Non-coated urea treated with nitrapyrin had lower soil N_2O emissions during the soil drying phase than PCU and NCU in 2013.These results suggest that pulse N_2O emissions during a waterlogging event are dependent on soil temperature, soil NO_3^--N concentration, and possibly the ability of nitrapyrin to reduce N_2O emissions during NH_3 oxidation associated with soil drying. All of these factors affecting soil N_2O emissions are a function of how long the waterlogging event occurs after N fertilization. Split N applications with PCU as a starter fertilizer may also be a viable N management practice in reducing soil NO_3^--N during spring months when high amounts of precipitation are more probable, thus reducing N_2O-N emissions.

Of major significance is the amount of NO_3^--N loss, large cumulative soil N_2O emissions, and decreased corn yields in 2013 that occurred during a relatively short waterlogging event as compared to that of soils that were not waterlogged. Over three days of waterlogging, there was an average 50% reduction of soil NO_3^--N in fertilized plots, with 1.9% of the fertilizer N applied lost through soil N_2O emissions when averaged for 2012 and 2013, and corn grain yields decreased an average 10% in 2013. These results indicate that further research on management practices, such as different EEN fertilizer sources and timing of N applications, as well as improved drainage and other methods to decrease waterlogging, may need continued investigation for both their effects on corn production as well as their impact on environmental N loss.