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# Environmental Implications of Polymer Coated Urea

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ABSTRACT

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Nitrogen is an essential plant nutrient in the biosphere. Although N is necessary and beneficial for life, it is also a common pollutant in the atmosphere and hydrosphere as it may be lost to the atmosphere as ammonia ($NH_3$) or nitrous oxide ($N_2O$) gases or to groundwater as nitrate ($NO_3^-$) following fertilization. Polymer coated urea (PCU) is one type of N fertilizer which uses temperature-controlled diffusion to control N release to better match plant demand and mitigate environmental losses of N. The objectives of this project were to simultaneously compare the effects of PCU on gaseous (as $N_2O$ and $NH_3$) and aqueous (as $NO_3^-$) N losses to the environment as compared to uncoated urea in grass systems over the entire PCU N-release period and to investigate the viability of photoacoustic infrared spectroscopy as a method to ascertain $N_2O$ and $NH_3$ losses following fertilization. Two field studies were conducted on established turfgrass sites with a mixture of Kentucky bluegrass (KBG; *Poa pratensis* L.) and perennial ryegrass (PRG; *Lolium perenne* L.) in sand (Site 1) and loam (Site 2) soils. Each study compared an untreated control to 200 kg N $ha^{-1}$ applied as either uncoated urea or PCU (Duration 45 CR®). In these studies PCU reduced $NH_3$ emissions by 41-49% and $N_2O$ emissions by 16-54%, while improving growth and verdure. Leachate $NO_3^-$ observations were inconclusive at each site. Glasshouse studies were conducted to compare $N_2O$ and $NH_3$ emissions from PCU and uncoated urea to an untreated control utilizing a non-static, non-flow-through chamber in conjunction with photoacoustic infrared spectroscopy (PAIRS) for gas collection and analysis. Three short-term studies (17-21 d) were done with sand, sandy loam, and loam soils and a full-term (45 d) study with the loam soil. Each study was done in maize (*Zea mays* L.). Volatilization of ammonia was reduced by 72% and 22% in the sandy loam and loam soils, respectively, in 2008-2009 and by 14% in the loam in 2010. Evolution of $N_2O$ was reduced by 42% and 63% in the sandy loam and loam soils in 2008-2009 and by 99% in the loam in 2010. Overall, PCU decreased gaseous losses of N following fertilization while providing a steady supply of N to the plant. The utilization of PAIRS is a viable analysis method which gives higher temporal resolution analysis than is typically reported. These considerable decreases in environmental losses of N are major steps toward conserving natural resources and mitigating the negative environmental impacts associated with N fertilization in grass systems.

Keywords: polymer coated urea, PCU, urea, nitrous oxide, $N_2O$, ammonia, $NH_3$, nitrate, $NO_3^-$, turfgrass, Kentucky blue grass, KBG, maize, volatilization, greenhouse gas

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# Chapter 1

# Polymer Coated Urea in Turfgrass: Mitigating Environmental Impacts and Maintaining Plant Vigor

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## ABSTRACT

Nitrogen is an essential plant nutrient in the biosphere. Although N is necessary and beneficial for life, it is also a common pollutant in the atmosphere and hydrosphere as it may be lost to the atmosphere as ammonia ($NH_3$) or nitrous oxide ($N_2O$) gases or to groundwater as nitrate ($NO_3^-$) following fertilization. Polymer coated urea (PCU) is one type of N fertilizer which uses temperature-controlled diffusion to control N release to better match plant demand and mitigate environmental losses of N. The objectives of this study were to simultaneously compare the effects of PCU on gaseous (as $N_2O$ and $NH_3$) and aqueous (as $NO_3^-$) N losses to the environment as compared to traditional uncoated urea in a cool season turfgrass system over the entire PCU N-release period. Two field studies were conducted on established turfgrass sites with a mixture of Kentucky bluegrass (*Poa pratensis* L.) and perennial ryegrass (*Lolium perenne* L.) in sand (Site 1) and loam (Site 2) soils. Each study compared an untreated control to 200 kg N $ha^{-1}$ applied as either uncoated urea or PCU (Duration 45 CR®). Using uncoated urea as an N fertilizer resulted in 127 – 476% more measured $N_2O$ impact on the environment, whereas PCU was only 25 – 52% higher (not significant) than background emission levels. Compared to urea, PCU reduced $NH_3$ emissions by 41 – 49 % and $N_2O$ emissions by 45 – 73%, while improving growth and verdure over the control. Leachate $NO_3^-$ reductions were inconclusive. These considerable decreases in environmental losses of N are major steps toward conserving natural resources and mitigating the negative environmental impacts associated with N fertilization in turfgrass.


## INTRODUCTION

Nitrogen is an essential plant nutrient in the biosphere. Conversion or fixation of the ubiquitous pool of atmospheric $N_2$ gas to biologically active amine ($RNH_2$) forms occurs through

both abiotic (lightning, combustion, and Haber-Bosch industrial processes) and biotic (microbial and plant) processes. The process of N fixation is essential for life because of biosynthesis into nucleotides used for deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) synthesis and amino acids for protein/enzyme production. Although background levels of natural fixation enable plants to grow in the wild, fertilization with N is required to provide adequate food, fuel, and fiber to sustain the ever-growing human population.

Although N is beneficial and essential for life, it is also a common pollutant in the biosphere. Annual worldwide N fertilizer application is projected to total 139.1 million metric tons in 2011/2012 (FAO 2008). Ideally, applied N is held in the soil until it is absorbed by plants but N may be evolved as ammonia ($NH_3$) or nitrous oxide ($N_2O$) gases or it leaches or runs off as nitrate ($NO_3^-$).

Schlesinger (1992) estimated that 10% of manufactured N fertilizer worldwide is volatilized as $NH_3$ gas. In a growth chamber study using warm-season bentgrass (*Agrostis palustis* Huds.), volatilization of surface-applied N fertilizers was shown to be in excess of 60% over the first 10 days following surface application (Knight et al. 2007). Researchers at Kansas State University found nearly 100% loss of N applied to maize (*Zea mays* L.) from a broadcast liquid urea under worst-case conditions of high temperature (>30 $^oC$), humidity (>95% RH), and wind (>30 km $hr^{-1}$) (Bryan Hopkins, personal communication, 2011). Volatilized $NH_3$ gas from fertilizer is a serious environmental concern because it is more likely to be deposited on land or water bodies than other forms of anthropogenic N. Ammonia deposition in sensitive ecosystems can lead to soil acidification (Sutton et al. 2008) and surface water eutrophication (Boyd 2000). Nitrogen deposition can also lead to plant community loss and reduction of biodiversity (Sutton et al. 2008). Fenn et al. (1998) reported that increased N availability from $NH_3$ deposition in

typically N-limited ecosystems across the globe is leading to unwanted consequences including increased aluminum mobility resulting in forest decline.

In addition to $NH_3$ volatilization, elevated emissions of $N_2O$ are also concerning. On average, 1% of N applied in inorganic forms is lost to the atmosphere as $N_2O$ (GHG Working Group 2010). The actual amount lost is directly related to the type, quantity, and method of application of the applied fertilizer (GHG Working Group 2010). Hirsch et al. (2006) estimated anthropogenic emissions of $N_2O$ have increased by approximately 50% over pre-industrial levels. It is estimated that $N_2O$ emissions directly related to fertilization account for 78% of the total annual anthropogenic $N_2O$ losses, with automobile and industrial pollution making up most of the remainder (USEPA 2007). The environmental concern with $N_2O$ is that it is a long-lived, potent greenhouse gas with a global warming potential 310 times greater than carbon dioxide ($CO_2$) (USEPA 2007). In addition to the ability of $N_2O$ to absorb and retain infrared energy in the atmosphere, it also catalytically destroys ozone ($O_3$) in the troposphere (IPCC 2007), which allows higher levels of ultraviolet (UV) radiation to reach the Earth's surface—resulting in further warming potential and increased UV radiation exposure to living organisms. Emissions of $N_2O$ to the atmosphere via denitrification and nitrification are controlled by many interacting factors. Soil aeration, temperature, texture, ammonium ($NH_4^+$) and $NO_3^-$ concentrations, and microbial community factors all affect the rate of soil $N_2O$ production and loss (Snyder et al. 2007).

Although N losses to the atmosphere are disconcerting and currently dominate public forums, losses to the hydrosphere are also a serious concern. Soil $NO_3^-$ is easily leached below the rooting zone due to similar negative ionic charges associated with soil particles and the $NO_3^-$ molecule. Nitrate (and other forms of N) can also be surface transported through runoff and

erosion, resulting in increased N in surface and ground waters. The amount of N lost is a function of fertilizer source, timing, soil infiltration rate, shoot density, and soil moisture (Easton and Petrovic 2004), as well as percolation rate and macropore flow. In addition to the decreased plant available N that results, excess $NO_3^-$ in watersheds can lead to toxicological problems such as eutrophication (large algal blooms which can lead to anoxic conditions) and drinking water contamination (Mulvaney et al. 2009). Drinking water contaminated with $NO_3^-$ is thought to cause methemoglobinemia (blue baby syndrome) in young animals and human babies (Olson et al. 2009). Excess $NO_3^-$ in watersheds is also toxic to freshwater biota and disrupts nutrient cycling (Fenn et al. 1998).

Along with the need to reduce environmental impacts of excess N losses, it is also important to acknowledge that N fertilizer is manufactured using natural gas and other non-renewable resources. Thus, to conserve non-renewable resources and minimize environmental impacts, minimizing N losses and maximizing plant utilization are critical. Maximizing N uptake by plants is defined as nitrogen use efficiency (NUE, Hopkins et al. 2008).

Optimizing N fertilizer rate, source, timing, and placement are all necessary to reach an ideal balance between grower profitability and NUE. One tactic to increase NUE from a fertilizer source approach is use of controlled-release N (CRN) or slow-release N (SRN). These fertilizers release N into the soil over an extended period of time, ideally match plant needs, and possibly reduce or eliminate labor-intensive and costly in-season N applications (Hopkins et al. 2008). By controlling the release of N from fertilizer into the soil, it is hypothesized that N inefficiencies and losses to the environment will be mitigated, by increasing N retention by the soil and uptake by the plant in relation to the total N applied (Hopkins et al. 2008, Snyder et al. 2007). The concept of CRN and SRN fertilizer materials is not new, but success has varied widely across

plant species and environmental conditions, and expense has prevented wide utilization (Hopkins et al. 2008). More recently, costs of these materials have become more attractive and competitive with traditional N sources.

Polymer-coated urea (PCU) fertilizer is one promising type of CRN that provides improved N-release timing. Soil temperature controls N release rate from PCU—allowing for protection of N during times when the soil is cool and plants are not growing and then enhancing N release as plant growth and N uptake increase (Hopkins et al. 2008). Diffusion of N through the polymer coating is driven by the N concentration gradient—temperature being the primary regulator under irrigated conditions. Some PCU's have been shown to steadily supply the plant with N for longer periods of time following fertilizer application than immediately soluble forms of N, thus enhancing NUE (Wilson et al. 2010, Hutchinson et al. 2003, Hopkins et al. 2008, Patil et al. 2010) and leading to increased crop yield and quality (Blythe et al. 2002, Cahill et al. 2010, Knight et al. 2007, Miltner et al. 2004, Pack and Hutchinson 2003, Worthington et al. 2007). Hyatt et al. (2010) showed that the slower release of PCU can improve economics by eliminating additional in-season N applications.

Research has also demonstrated PCU's ability to mitigate negative environmental impacts associated with N fertilizer (Halvorson et al. 2010a, Pack et al. 2006, Wilson et al. 2010). Polymer-coated urea has been shown to significantly decrease both $NO_3^-$ leaching (Du et al. 2006, Guillard and Kopp 2004, Nelson et al. 2009, Pack et al. 2006, Pack and Hutchinson 2003, Wilson et al. 2010) and $NH_3$ volatilization (Knight et al. 2007, Pereira et al. 2009, Rochette et al. 2009). Nitrous oxide emissions may also be reduced by using PCU (Cao et al. 2006, Halvorson 2008, Halvorson et al. 2010a, Halvorson et al. 2010b, Hyatt et al. 2010, Jassal et al. 2008).

Most of the work done to investigate anthropogenic inputs to the atmosphere from fertilization has been performed in intensive row crop agricultural systems [such as maize, wheat (*Triticum* spp.), and potato (*Solanum tuberosum* L.)]. Much less has been done in grass systems (Bremer 2006, Knight et al. 2007) despite N fertilizers having a huge role for urban turfgrass and agricultural sod, seed, and pasture grass systems. Turfgrass occupies 1.9% of the total surface area of the United States, and is the largest irrigated crop in the country (Milesi et al. 2005). Coupling this wide geographical distribution to known excessive N application by many homeowners and turfgrass managers compared to farmers leads to environmental and economic concerns. The attitude of "if a little is good then more is better" prevails with most people applying N to turf, especially when visual greening is so apparent. Also, homeowners are often uneducated in regard to appropriate rates of fertilizer and methods of correct application.

Permanent sod grass systems require N addition to maximize production efficiency. This is especially true when biomass is removed by mowing, grazing, or harvest. In the case of turfgrass, high rates of N are applied to optimize aesthetics. Agrarian turfgrass landowners apply between 75 and 500 kg N $ha^{-1}$ as fertilizer each year (Milesi et al. 2005). These rates, though comparable to the most intensively cultivated agriculture fields in the world, are often exceeded by urban homeowner applications. This high availability of N can promote plant health and vigor but can just as easily lead to substantial inefficiencies and losses if improperly managed.

The primary objective of this study was to compare N gas evolution, $NO_3^-$ leaching and plant uptake and verdure on cool season turfgrass plots treated with PCU, uncoated urea and untreated control.

## MATERIALS AND METHODS

Two field studies at two Utah, USA, sites were conducted on established turfgrass, with a mixture of Kentucky bluegrass (KBG; *Poa pratensis* L.) and perennial ryegrass (PRG; *Lolium perenne* L.). Best management practices for growing cool season turfgrass were generally used at both sites. Site 1 in Provo (40°16'1.40"N 111°39'28.59"W) is a sports turfgrass sod farm at Brigham Young University (BYU) with sandy soil (Table 1). Site 2 near Spanish Fork (40°4'1.77"N 111°37'44.99"W) is a turfgrass area at BYU's experimental farm with a Timpanogos Loam soil and located near their weather station (Table 1). At each site, 1 m x 3 m plots were established immediately next to each other in a randomized complete block design with three treatments and six replications. Treatments included application of 0, an untreated control, and 200 kg N $ha^{-1}$ applied as either uncoated urea or polymer coated urea (PCU; Duration 45 CR®, Agrium Advanced Technologies, Loveland, CO). Treatments were uniformly surface applied.

All plots were irrigated with approximately 2 cm water within 12 and 1 h after fertilizer treatment application for sites 1 and 2, respectively. Soil volumetric water content was monitored using Watermark Soil Moisture Sensors (Spectrum Technologies, Plainfield, Illinois, USA) and logged using an AM400 soil moisture data logger (MK Hansen, Wenatchee, Washington, USA). Soil temperature was monitored with a thermistor and logged using the same data logger.

Simplified modified passive flux collection devices were installed near the center of each plot to collect volatilized $NH_3$. Passive flux sampling tubes were vertically oriented (to minimize cross plot gas contamination) with the bottom of each tube 10 cm above the plant-soil interface. Each sampling device consisted of a glass tube (0.7 cm inside diameter x 10 cm length), with the interior coated with 3% oxalic acid in acetic acid to readily react with and collect $NH_3$ from the air that flowed through the tube. Flux tubes were replaced daily for the first two days, then every

three to four days for an additional 21d, until volatilization levels returned to ambient conditions, and then weekly thereafter. When collected for analysis, tubes were capped with rubber septa stoppers immediately to eliminate contamination. The $NH_3$ was extracted from the flux tubes by adding 1 ml of deionized water, recapping with septa stoppers and shaken mechanically using a modified vortex mixer (Labnet International, Inc., Woodbridge, NJ, USA) for 10 minutes. Extracts were then diluted with 2 ml of deionized water and analyzed for $NH_4^+$ using the automated cadmium reduction method (Mulvaney, 1996) with a Lachat colorimetric analyzer (Lachat Instruments, Loveland, CO, USA). Results were expressed as total $NH_3$-N (mg).

Vented poly-vinyl chloride (PVC) static (18 cm diameter x 28 cm height) collection chambers were installed near the center of each plot to collect $N_2O$ gas. These PVC collars were fitted with rubber gaskets on the top lip and buried to a depth of 6-8 cm into the soil. During periodic sampling times, the chamber lid was attached to the top of each chamber and sealed with the rubber gaskets. Samples were taken three days a week for the first three to four weeks after fertilizer application, and once or twice a week thereafter. Samples were taken through a septum on top of the chamber with a 10-ml glass syringe fitted with a rubber stopper at intervals of 15, 30, and 45 min after installing the chamber. Samples were immediately taken to the lab and analyzed with a gas chromatograph coupled with an electron capture detector (Venterea et al. 2009; GC, Agilent 6890N, Agilent Technologies, Santa Clara, California, USA). Samples were generally analyzed within 4-6 h following sampling. Flux was determined as described by Mosier et al. (1991) and by implementing principles of the ideal gas law (PV = nRT) at standard temperature and pressure. Flux was calculated by

$$f = \frac{V \times \Delta C}{A \times \Delta t}$$

Where $V$ is the headspace volume, $\Delta C$ is the change in concentration ($C_o$ - $C_t$) of $N_2O$ as measured by the GC, $A$ is the area of the static chamber, and $\Delta t$ is the time elapsed between $C_o$ and $C_t$.

Suction lysimeters (24 in. 1900 Series, Soil Moisture Corp., Goleta, CA, USA) were installed in three blocks at each site at a 30° angle to a depth of 8-10". Leachate was collected and $NO_3^-$ N concentrations were determined using a Lachat automated analyzer for $NO_3^-$ N by the salicylate nitroprusside method (Mulvaney 1996). Approximately 21 and 45 d after application residual soil $NO_3^-$ N samples were taken at 0-30 and 30-60 cm depths and concentrations were analyzed as described above.

Root and shoot samples were also taken approximately 21 and 45 d after fertilization and dried at 65$^o$ C, ground and then analyzed for total N (Leco® TruSpec® CN elemental determinator, St. Joseph, MI, USA). Verdure assessments were done by giving plots visual ratings on a 1 – 5 scale, with 1 being brown and 5 being dark green.

All data was analyzed for statistical significance by ANOVA and Tukey HSD analyses using JMP 10.8 statistical software (SAS Institute, Cary, NC, USA). Prior to analysis, data was checked for normality and those data sets which did not follow the assumption of normal distribution were log transformed and then analyzed for significance. Significance levels were $\alpha < 0.10$.

## RESULTS AND DISCUSSION

### Nitrous Oxide

Site 1 - The $N_2O$ emissions from uncoated urea application were significantly higher than the control on half of the sampling dates (Fig. 1; $P = 0.10$). In contrast, PCU produced significantly greater $N_2O$ flux than the control on only two sampling periods (of 10), with the

magnitude of those differences much smaller. When comparing the fertilizer sources to each other, the $N_2O$ emissions from uncoated urea were significantly higher than PCU on two sampling days. The PCU never produced significantly greater $N_2O$ flux over uncoated urea during any sampling event. Plots treated with uncoated urea reached a $N_2O$ flux peak approximately five days after fertilization (DOY 277), while plots receiving PCU reached peak flux approximately 26 days (DOY 298) after fertilization.

Total measured $N_2O$ emission at Site 1 from uncoated urea fertilization was 44669 µg $m^{-2}$, which was significantly higher than both the PCU ($P = .00001$) and control ($P < .0001$) treatments which were 11745 and 7749 µg $m^{-2,}$ respectively. It is noteworthy that the sub-sampling occurred on 10 days of the study and the sampling times were 45 minutes each and, therefore, these total amounts do not represent a total cumulative loss but, rather, a representative measure of $N_2O$ loss over the course of the trial. The total measured $N_2O$ emission from PCU application was statistically similar to untreated control. The total measured flux from urea fertilization was 3.8 and 5.8 times that of PCU and the control, respectively (Fig.1). Using uncoated urea as an N fertilizer under these environmental conditions resulted in 476% more measured $N_2O$ impact on the environment, whereas PCU was only 52% higher (not significant) than background emission levels.

Site 2 – Daily comparisons of $N_2O$ emissions from treatments found that there were no significant differences between any treatments on 7 of the 9 d sampled (Fig. 1). Emissions from urea were significantly higher on one day than the control (DOY309) and PCU (DOY 307). The PCU never produced significantly greater $N_2O$ flux over uncoated urea on any sampling event.

Total measured $N_2O$ emission at Site 2 from uncoated urea application was 16425 µg $m^{-2}$ $h^{-1}$, which was significantly different than the PCU and the untreated control, which had fluxes

of 9021 and 7245 µg $m^{-2}$, respectively ($P$ = 0.026 and $P$ = 0.001, respectively) (Fig. 2). The PCU application was statistically similar to the untreated control ($P$ = 0.31). The total measured flux from urea treatments was 1.8 times that of PCU and 2.3 times that of the control. Although the magnitude was not as great as Site 1, using uncoated urea as an N fertilizer resulted in 127% more measured $N_2O$ emission to the atmosphere, whereas PCU was only 25% higher (not significant) than background emission levels.

Because of soil moisture's important role in $N_2O$ emissions via nitrification and denitrification (Bouwman and Boumans 2002), the soil moisture differences at each site likely contributed to the different intensities of $N_2O$ flux seen. Site 1 was irrigated daily (as it had a sand texture, albeit with a perched water table at about 10 cm below the soil surface) and maintained at a somewhat high soil moisture level, while the Site 2 was only irrigated approximately weekly and soil moisture fluctuating less and overall maintained at lower levels than Site 1. Although fine-textured soils typically favor $N_2O$ emissions (Bouwman and Boumans 2002), Site 2 was not maintained at an overall anaerobic threshold at which point denitrification would have commenced. Site 1 also avoided saturation for any longer than a few minutes/hours. Under these aerobic, slightly alkaline soil conditions, nitrification is assumed to be the primary source of $N_2O$ emission.

Hyatt et al. (2010) monitored $N_2O$ emissions from PCU and urea in potato with coarse textured soils and saw reduction levels (39%) within the range of reduction observed in the present study. Other studies have investigated $N_2O$ emissions from turfgrass after fertilization with varying sources of N, not including PCU, and consistently found that fertilizer type affects the emission rate (Bouwman and Boumans 2002, Bergstrom et al. 2001, Bremer 2006, Maggiotto et al. 2000). The significant decreases in $N_2O$ emissions observed in our study are

similar to other studies which investigated various crops fertilized with PCU as an alternative N source—finding lower $N_2O$ emissions for PCU compared to uncoated urea (Blaylock et al. 2005, Halvorson et al. 2008). Decreased emissions of $N_2O$ from fertilization with PCU compared to uncoated urea over the course of a growing season have been documented in barley (*Hordeum vulgare* L.), cabbage (*Brassica oleracea* L.), maize (*Zea mays* L.), and potato (Delgado and Mosier 1996, Cheng et al. 2006, Halvorson et al. 2010, Hyatt et al. 2010). However, some studies have reported a small late-season peak in $N_2O$ flux with PCU, which has been attributed to release of N from PCU (Halvorson et al. 2008). In contrast, the data in the present study showed no significant peaks other than that which occurred immediately after fertilization. It is important to acknowledge that this study was conducted during the fall season to an established sod, with relatively low temperatures that steadily decreased with time. Late season fertilization of N is common and applying a majority of the N at this time is physiologically beneficial to cool season turfgrass species (Christians 2007), which is the reason why this timing was implemented in this study. However, additional work is needed to evaluate $N_2O$ loss following PCU application to cool season turfgrass earlier in the growing season is also needed.

**Ammonia**

Site 1 – The $NH_3$ volatilization from uncoated urea application were significantly higher than the control on one of the sampling dates (Fig. 3; $P = 0.10$). In contrast, PCU produced significantly greater $NH_3$ volatilization than the control during none of the sampling periods (of 5). When comparing the fertilizer sources to each other, $NH_3$ volatilization from uncoated urea was significantly higher than PCU on two sampling days (DOY 271 and 280). The PCU never produced significantly greater $NH_3$ volatilization over uncoated urea during any sampling event.

Plots treated with uncoated urea and PCU reached an $NH_3$ volatilization peak immediately after fertilization (DOY 271).

Cumulative $NH_3$ volatilization from uncoated urea application was significantly higher compared to PCU and the control at Site 1 ($P$ = 0.07 and 0.04, respectively, Fig. 3). The cumulative $NH_3$ volatilization of the uncoated urea plots was 2.0 and 2.1 times that of PCU and control, respectively (Fig. 4). Using PCU as N fertilizer decreased total $NH_3$ volatilization by 41%.

Site 2 – The $NH_3$ volatilization from uncoated urea application were significantly higher than the control on three of the sampling dates (Fig. 3; $P$ = 0.10). In contrast, PCU produced significantly greater $NH_3$ volatilization than the control during none of the sampling periods (of 5). When comparing the fertilizer sources to each other, $NH_3$ volatilization from uncoated urea was significantly higher than PCU on two sampling days (DOY 286 and 288). The PCU never produced significantly greater $NH_3$ volatilization over uncoated urea during any sampling event. Plots treated with uncoated urea and PCU reached an $NH_3$ volatilization peak three days after fertilization (DOY 288).

Similar to Site 1, cumulative $NH_3$ volatilization from uncoated urea was significantly higher than the control ($P$ = 0.09) but statistically equivalent to that of PCU ($P$ = 0.22, Fig. 3). Cumulative $NH_3$ emissions from urea treatments were 2.0 times that of the control. Emissions from PCU treatments were never significantly higher than urea or than the untreated control treatments. At Site 2, PCU decreased $NH_3$ volatilization by 49% as compared to the urea treatments.

The relative reductions of $NH_3$ gas loss found in this study attributable to PCU are similar to those reported in another study with turfgrass (Knight et al. 2007) as well as in maize systems

(Pereira et al. 2009). Knight et al. (2007) conducted growth chamber experiments with a warm season turfgrass species, 'G-2' creeping bentgrass (*Agrostis stolonifera* L.), grown in a loamy sand and found that PCU had the lowest levels of $NH_3$ volatilization among six different forms of N fertilizers tested, with no noticeable spike in volatilization in the 10 d length of the study. However, the PCU used in that study would have been expected to release its N over a longer period of time than 10 d. Our study was conducted over the entire time of anticipated N release from the PCU and we found no spike in the $NH_3$ volatilization later in the season. In the present study, an observed peak in volatilization was observed with PCU, although this peak was identical to the control and significantly smaller in magnitude than with the uncoated urea. This may be attributed to increased climatic variability in our field study as compared to controlled growth chamber for others or the fracturing of the micro-thin polymer coatings during handling and/or fertilizer application (Rosen et al. 2010), which in effect negates the control release properties of the small percentage of damaged fertilizer pellets and rendering them essentially identical to uncoated urea as the urea within the polymer is readily soluble and exposed through the cracks or ruptures in the polymer coating. Overall, our data support the findings of Knight et al. (2007), inasmuch as PCU significantly decreases $NH_3$ emissions when compared to a more readily soluble form of N fertilizer (i.e. urea).

**Nitrate**

Although $NO_3^-$ leaching data trended towards less concentration for PCU compared to urea, these differences were not significant from both sites Site 1 and 2 ($P$ = 0.66 and 0.52, respectively) due to sample losses at both locations resulting in poor statistical sensitivity.

## Nitrogen Uptake and Verdure

Growth and verdure improvements were observed in all plots receiving N fertilization as compared to the untreated control. At both sites there were no observable differences in verdure or growth between PCU and urea. The average visual rating for both PCU and urea at Site 1 was 4.5 and Site 2 was 3.8. Visual ratings for control plots at each site were ~ 2.5. Increased growth was noticed with both the PCU and urea, but neither treatment appeared greater than the other. Total shoot N concentrations from samples removed on DOY 292 at Site 1 varied significantly among treatments (Table 2). Specifically, N concentration in turfgrass from the urea application was significantly higher than both the control and PCU. Turfgrass grown with PCU application also contained significantly higher shoot N than the control. No other root and shoot samples taken at either site were significant (Table 2). The lack of treatment effects at Site 2 may have been related to a large relatively fresh N pool, high organic matter, and/or high CEC (Table 1) – any one of which might contribute to the lack of treatment effect. More rapid release of N to turf from uncoated urea compared to PCU explains higher N content from urea application. Importantly, levels of shoot N from PCU application were also adequate (Table 2). The adequate range for shoot N levels is from 2.51 – 5.10% in KBG and 3.34 – 5.10% in PRG (Mills and Jones 1996). At Site 1, where there were differences among treatments in shoot N content at DOY 292, N content by DOY 340 were similar regardless of treatment, with values near the bottom of the acceptable range for shoot percent N in KBG and PRG. This is likely due to accumulation of N in the shoots of the control plots, with little biomass increase and a dilution of N in those shoots receiving N fertilizer from growth and clipping. As has been found with other crops (Hopkins et al. 2008, Pack et al., 2006, Wilson et al., 2010), PCU provides ample N to the plant while mitigating environmental losses of $NH_3$ and $N_2O$.

## CONCLUSIONS

Our findings indicate that Kentucky bluegrass/perennial ryegrass cool season turfgrass systems' health and appearance can be maintained and environmental losses as $N_2O$ and $NH_3$ can be mitigated by utilizing PCU. Nitrate leaching is also likely reduced, although not totally substantiated in these studies. There were no indications of N deficiency in turfgrass receiving PCU, as has been demonstrated by similar research in other crops. While providing an adequate N supply, PCU application resulted in decreased NH3 volatilization 41 – 49% compared to urea application. Using uncoated urea as an N fertilizer resulted in 127 – 476% more measured $N_2O$ impact on the environment, whereas PCU was only 25 – 52% higher (not significant) than background emission levels. The large decreases in the emissions of the potent greenhouse gas $N_2O$, as well as reactive atmospheric N as $NH_3$ volatilization, while maintaining turfgrass verdure and growth, are major developments in improving N use efficiency in turf without increasing shoot growth and, therefore, mowing. Our research indicates that there is no downside to PCU under these conditions. Initial additional costs for PCU are potentially compensated for by decreased labor for fertilization and possibly mowing, as well as increased nutrient use efficiency (less fertilizer N needed). Reductions of the magnitude reported herein of $N_2O$ [this long-lived (150 year stratospheric life), potent (310 times the GWP of $CO_2$) greenhouse gas] deserve further investigation by longer term studies under various environmental conditions in all fertilized landscapes.

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## Tables

**Table 1.** Selected soil characteristics for two field studies conducted on established mixed stands of Kentucky bluegrass and perennial ryegrass turf sites in Utah, USA. Site 1 is a sports turfgrass sod farm at Brigham Young University, Provo, UT on a disturbed sand soil and site 2 is at the BYU experimental farm on a Timpanogos loam soil.

| | Location | Soil Texture | $NO_3^-N$ | OM | pH | SAR |
|---|---|---|---|---|---|---|
| | | | --- ppm --- | --- % --- | | |
| Site 1 | Provo, UT | Sand | 2.67 | 0.77 | 6.93 | 0.34 |
| Site 2 | Spanish Fork, UT | Loam | 3.68 | 2.80 | 7.17 | 0.33 |

**Table 2. Root And Shoot N Concentrations For Sites 1 And 2; One In-Season Sample Date, One End-Of-Season Sample Date.** Those values not connected by common letters indicate significant differences at the *P* = 0.05 level; NS = no significance.

| Location | N Source | Julian Day | % N | |
|---|---|---|---|---|
| | | | Roots | Shoots |
| Site 1 | Control | 292 | - | 2.71 C |
| Site 1 | PCU | 292 | - | 4.18 B |
| Site 1 | Urea | 292 | - | 5.05 A |
| Site 1 | Control | 340 | 0.39 NS | 3.87 NS |
| Site 1 | PCU | 340 | 0.84 NS | 3.24 NS |
| Site 1 | Urea | 340 | 0.70 NS | 3.14 NS |
| Site 2 | Control | 316 | - | 3.66 NS |
| Site 2 | PCU | 316 | - | 3.14 NS |
| Site 2 | Urea | 316 | - | 3.99 NS |
| Site 2 | Control | 340 | 0.59 NS | 3.30 NS |
| Site 2 | PCU | 340 | 0.54 NS | 2.70 NS |
| Site 2 | Urea | 340 | 0.56 NS | 2.54 NS |

## Figures

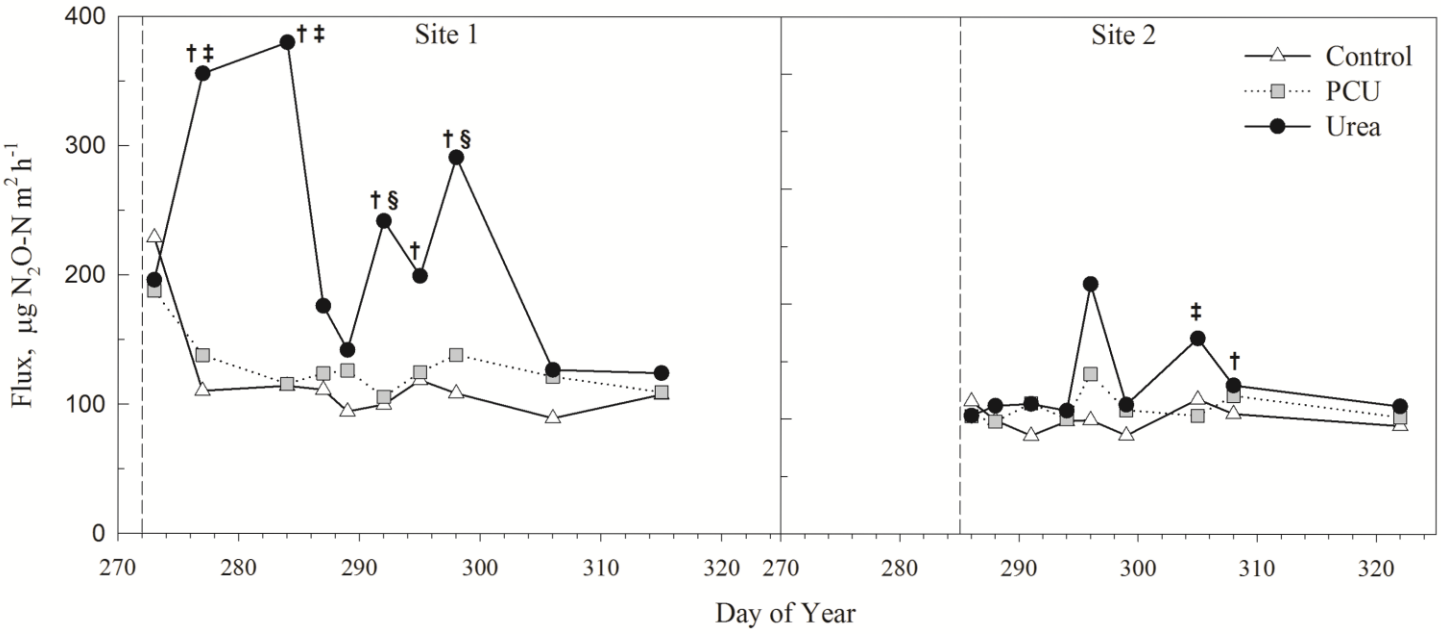


**Figure 1. Daily $N_2O$ Flux for Sites 1 and 2.** Significance indicated by † (urea greater than control), ‡ (urea greater than PCU), and § (PCU greater than control). Vertical dashed lines indicate fertilizer application.

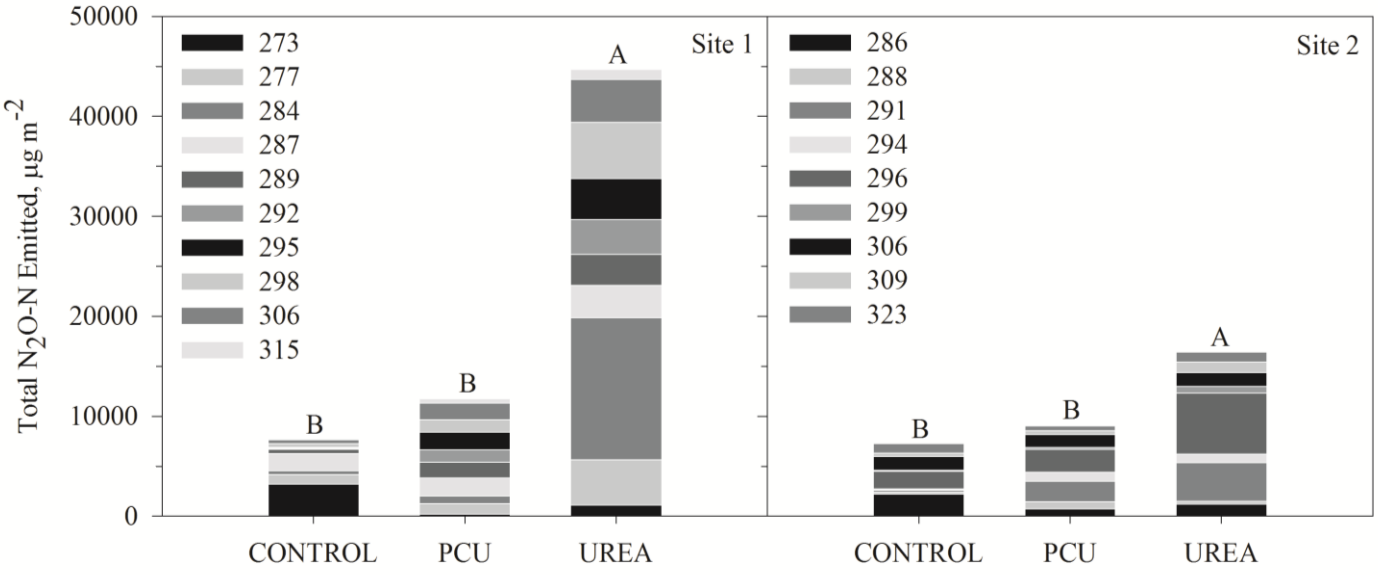


**Figure 2. Cumulative $N_2O$ flux for the field sites from equivalent rates of (200 kg $ha^{-1}$ N) urea and polymer coated urea (PCU) over a period of 45 days after application.** Those treatments not sharing the same letter indicate significant differences ($P$ = 0.05).

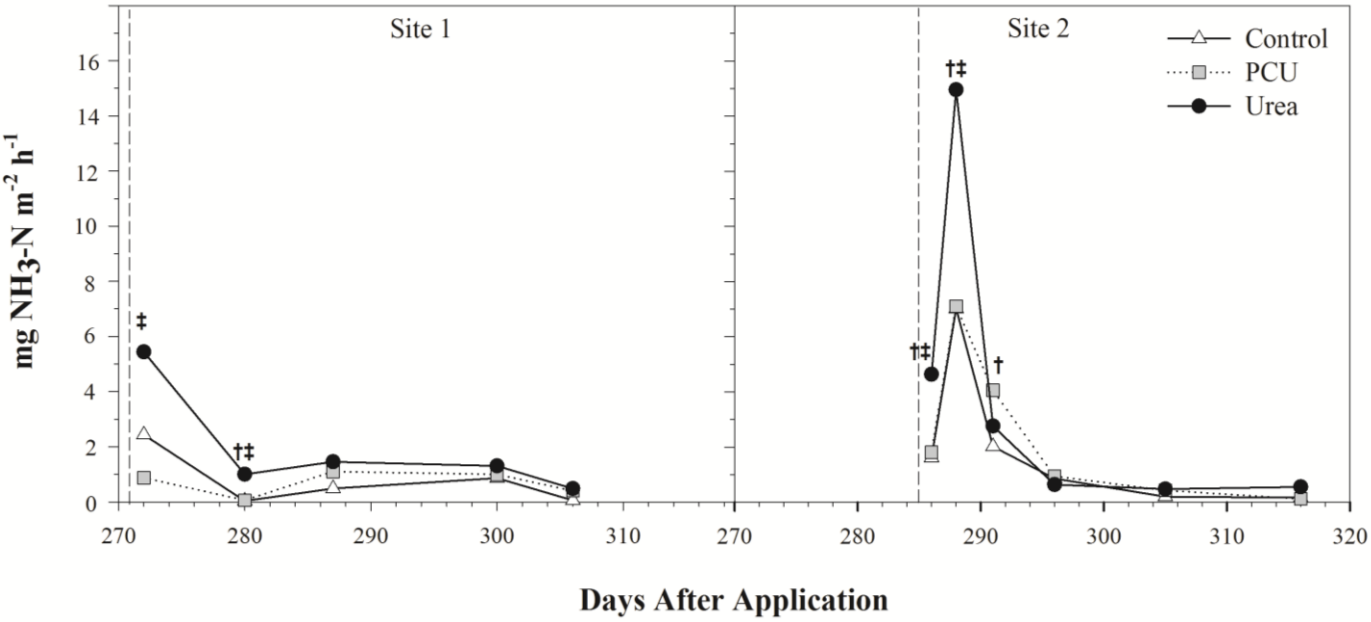


**Figure 3. Passive flux $NH_3$-N values for Sites 1 and 2.** Significance indicated by † (urea greater than control) and ‡ (urea greater than PCU) where $P = 0.05$. Vertical dashed lines indicate fertilizer application.

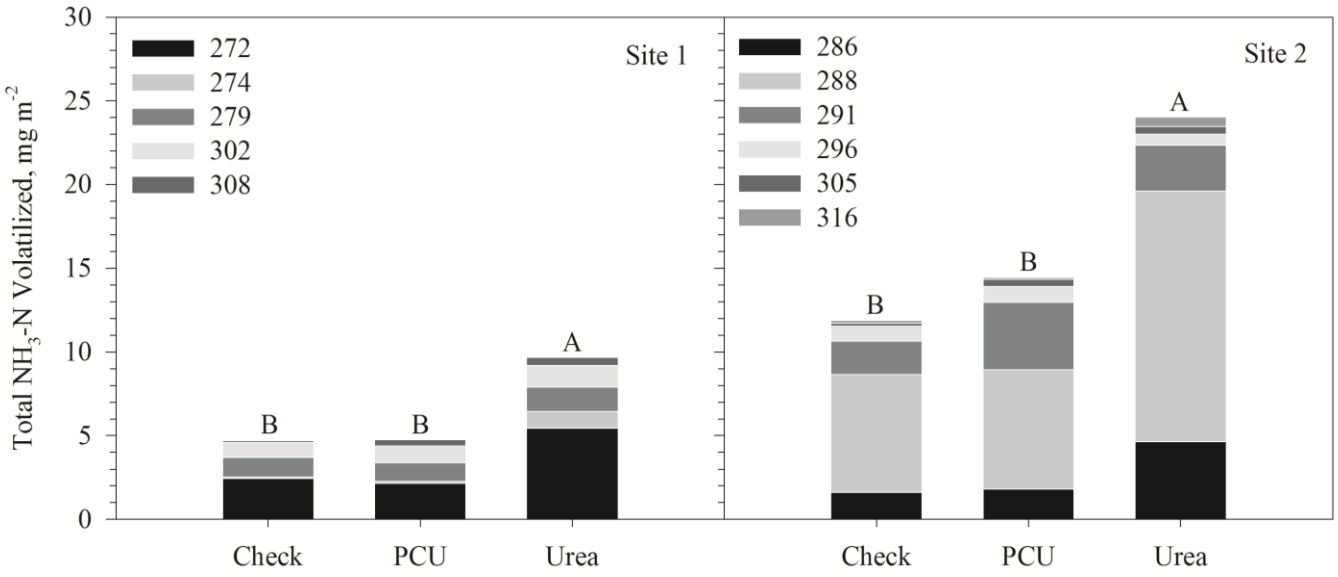


**Figure 4. Cumulative $NH_3$ flux for the field sites from equivalent rates of (200 kg $ha^{-1}$ N) urea and polymer coated urea (PCU) over a period of 45 days after application.** Those treatments not sharing the same letter indicate significant differences ($P$ = 0.05).

# Chapter 2

## Assessing Atmospheric Losses of Nitrogen with Photoacoustic Infrared Spectroscopy: Urea vs. Polymer Coated Urea

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## ABSTRACT

Although N is beneficial and needed for life, it is also a common pollutant in the atmosphere as nitrous oxide ($N_2O$) and ammonia ($NH_3$)—contributed largely from N fertilization. Polymer-coated urea (PCU) fertilizer is one promising type of controlled release fertilizer that provides improved N-release timing. Glasshouse studies were conducted to compare $N_2O$ and $NH_3$ emissions from PCU and uncoated urea to an untreated control utilizing a non-static, non-flow-through chamber in conjunction with photoacoustic infrared spectroscopy (PAIRS) for gas collection and analysis. Three short-term studies (17-21 d) were done with sand, sandy loam, and loam soils and a full-term (45 d) study with the loam soil. Volatilization of ammonia was reduced by 72% and 22% in the sandy loam and loam soils, respectively, in 2008-2009 and by 14% in the loam in 2010. Evolution of $N_2O$ was reduced by 42% and 63% in the sandy loam and loam soils in 2008-2009 and by 99% in the loam in 2010. Overall, PCU decreased gaseous losses of N following fertilization while providing a steady supply of N to the plant. The utilization of PAIRS is a viable analysis method which gives higher temporal resolution analysis than is typically reported.


## INTRODUCTION

Nitrogen is an essential plant nutrient in the biosphere, but the ubiquitous atmospheric form, $N_2$, is not bioavailable. Conversion or fixation of $N_2$ to biologically active amino ($NH_2$) forms occurs through both biotic (microbial) and abiotic (lighting, combustion, and Haber-Bosch industrial processes) processes. These processes are essential for life as N is biosynthesized into the basic building blocks of all living organisms i.e. nucleotides used for deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) synthesis and amino acids used for protein production. Although background levels of natural fixation enable plants to grow in the wild, N fertilization

is needed to provide the food, fuel, and fiber needed to sustain the ever-growing human population.

Despite N being beneficial and critical to life, its anthropogenic use has made it a common pollutant in the atmosphere and hydrosphere. Annual worldwide N fertilizer application is projected to total 139.1 million metric tons in 2011/2012 (FAO 2008). Ideally, applied N is held by the soil until it is taken up by plants. However, some N may be lost as it is evolved as ammonia ($NH_3$) or nitrous oxide ($N_2O$) gases during natural conversion processes or lost as nitrate ($NO_3^-$) from the rooting zone through surface runoff/erosion and leaching to groundwater.

Schlesinger (1992) estimated that 10% of all manufactured N fertilizer worldwide is volatilized as $NH_3$ gas. Volatilization of surface-applied N fertilizers reached an excess of 60% over the first 10 days following fertilization in a growth chamber study using warm-season bentgrass (*Agrostis palustis* Huds (Knight et al. 2007). A near 100% loss of N applied to maize (*Zea mays* L.) was observed in Kansas from a broadcast liquid urea treatment under worst-case conditions of high temperature (>30 $^oC$), humidity (>95% RH), and wind (>30 km $hr^{-1}$) (Ray Lamond and Bryan Hopkins, personal communication 1994). Volatilized $NH_3$ gas from fertilizer application is a serious environmental concern. Ammonia is more likely to deposit on land or water bodies through either wet or dry deposition than other forms of anthropogenic N. Such deposition in sensitive ecosystems can lead to soil acidification (Sutton et al. 2008) and surface water eutrophication (Boyd 2000). Deposition in sensitive ecosystems can also lead to plant community loss and reduction of biodiversity (Sutton et al. 2008). Fenn et al. (1998) reported that increased $NH_3$ deposition in typically N-limited ecosystems across the globe is having unwanted consequences including increased aluminum mobility and resulting forest decline.

Increased levels of atmospheric $NH_3$ also negatively affect air quality by contributing to smog formation (Rochette et al. 2009).

Along with $NH_3$, elevated emissions of $N_2O$ are also concerning. On average, 1% of all N applied as fertilizer in both organic and inorganic forms is lost to the atmosphere as $N_2O$ (GHG Working Group 2010). The actual amount lost is directly related to the type, quantity, and method of application of the applied fertilizer (GHG Working Group 2010). Hirsch et al. (2006) estimated that anthropogenic emissions of $N_2O$ have increased by approximately 50% over pre-industrial levels. It is also estimated that 78% of the total annual anthropogenic $N_2O$ losses are $N_2O$ emissions directly related to fertilization, with automobile and industrial pollution contributing most of the remainder (USEPA 2007). The concerns are that N2O is a long-lived, potent greenhouse gas with a global warming potential 310 times greater than carbon dioxide ($CO_2$) (USEPA 2007) and that it catalytically destroys ozone ($O_3$) in the troposphere (IPCC 2007). Emissions of $N_2O$ to the atmosphere via denitrification and nitrification are controlled by interacting factors such as soil aeration, temperature, texture, ammonium ($NH_4^+$) and $NO_3^-$ concentrations, and microbial community (Snyder et al. 2007).

In addition to the need to reduce environmental impacts of excess N loss, N fertilizer is manufactured using natural gas and other non-renewable resources. Minimizing N losses and maximizing absorption by plants conserve non-renewable resources and minimize environmental impacts. Maximizing N uptake by plants is expressed as N use efficiency (NUE, Hopkins et al. 2008).

Optimizing N fertilizer rate, source, timing, and placement are all essential to reach an ideal balance between economic profitability and NUE. One method of increasing NUE from a fertilizer source approach is to use controlled-release N (CRN) or slow-release N (SRN)

fertilizers which release N into the soil over an extended period of time, ideally matching plant need, possibly reducing or eliminating labor-intensive and costly in-season N applications (Hopkins et al. 2008). It is hypothesized that controlling N release will increase N retention and N uptake and thus mitigate N inefficiencies and losses to the environment (Hopkins et al. 2008, Snyder et al. 2007). The concept of CRN and SRN fertilizer materials is not new, but success has varied widely across plant species and environmental conditions, and expense has prevented wide utilization (Hopkins et al. 2008). More recently, costs of these materials have dropped relative to traditional N sources.

Polymer-coated urea (PCU) fertilizer is one promising CRN that provides improved N-release timing. Rate of N release from PCU is temperature controlled and this protects N during times of cool soil temperatures and slow plant growth and releases N as plant growth and N uptake increase (Hopkins et al. 2008). Diffusion of N through the polymer coating is driven by the N concentration gradient—temperature being the primary regulator under irrigated conditions. Some PCU's steadily supply the plant with N for longer periods of time following fertilizer application than immediately soluble forms of N, thus enhancing NUE (Wilson et al. 2010, Hutchinson et al. 2003, Hopkins et al. 2008, Patil et al. 2010) and leading to increased crop yield and quality (Blythe et al. 2002, Cahill et al. 2010, Knight et al. 2007, Miltner et al. 2004, Pack and Hutchinson 2003, Worthington et al. 2007). Hyatt et al. (2010) showed that the slower release of PCU can improve economics by eliminating additional in-season N applications. Strong evidence supports PCU's ability to mitigate negative environmental impacts associated with N fertilizer (Halvorson et al. 2010a, Pack et al. 2006, Wilson et al. 2010).

Polymer-coated urea has been shown to significantly decrease both $NO_3$-N leaching (Du et al. 2006, Guillard and Kopp 2004, Nelson et al. 2009, Pack et al. 2006, Pack and Hutchinson

2003, Wilson et al. 2010) and $NH_3$ volatilization (Knight et al. 2007, Pereira et al. 2009, Rochette et al. 2009). Nitrous oxide emissions have also been reduced by using PCU (Cao et al. 2006, Halvorson 2008, Halvorson et al. 2010a, Halvorson et al. 2010b, Hyatt et al. 2010, Jassal et al. 2008).

To properly assess $N_2O$ and $NH_3$ emissions from soils under unique N management regimes, appropriate methods of analysis must be used. Due to temporal and spatial variability and the multi-faceted nature of $N_2O$ emissions, reliable estimates are difficult to obtain. The widely used static chamber flux technique takes samples from small areas (< 1 $m^2$) and is relatively inexpensive. However, sampling (typically done as three or more samples per chamber in 15-or 20-minute intervals) and analysis using a gas chromatograph (GC) with an electron capture detector, increase temporal variability and decrease ability to estimate total losses over time. Venterea et al. (2009) stated that nitrous oxide emission estimates range from -60 to 170% of the mean. Increasing the sampling frequency is needed to overcome variability (Mosier et al. 1991). Photoacoustic infrared spectroscopy (PAIRS) is a recently developed method which allows in-field analysis of $N_2O$ concentrations. Advantages of PAIRS include analysis frequency, portability, robustness, and relative ease of use (De Klein et al. 1999).

Another advantage of PAIRS is that it is easily configured to successively analyze $NH_3$. Technological advancements have made capturing and analyzing $NH_3$ more feasible and convenient. In the improved denuder system, air is passed through an acid-coated glass tube under laminar flowand gases are trapped on the tubing wall. The collected ammonia is then extracted and analyzed. This improved method allows for monthly sampling to establish long-term trends. Low-cost passive sampling is another method which allows assessment of spatial variability of $NH_3$ without active air sampling (Sutton et al. 2008). Application of PAIRS in

combination with non-static, non-flowthrough chamber collection techniques provides a system of $NH_3$ analysis which allows low maintenance, high frequency automated sampling and monitoring (Sutton et al. 2008). Increasing the frequency of sampling should decrease temporal variation and provide increased understanding of $NH_3$ emissions following fertilizer-N applications.

Those studies which have implemented PAIRS have commonly done so while utilizing either static chamber or flow-through systems (DeKlein et al. 1999). While incorporating PAIRS analysis into these accepted collection methods has increased the number of sampling events and thereby decreased temporal variability, these collection methods can be expensive to automate and laborious to operate. A non-static, non-flowthrough chamber method which adequately collects evolved gases while remaining open to the atmosphere would minimize some of the associated costs and hassle of sampling.

The objectives of this paper are to test whether: (i) using a simple non-static, non-flow-through chamber system will allow continuous gas measurement and recording using PAIRS analysis in conjunction with a multiplexer, (ii) this method will be effective in semi-quantitatively analyzing gas samples from areas receiving different N sources or N rates in close proximity to one another, and (iii) evolution of $N_2O$ and $NH_3$ following fertilization can be mitigated by using PCU in place of uncoated urea.

## MATERIALS AND METHODS

21-Day Studies - Three glasshouse studies were conducted at Brigham Young University (Provo, Utah, N 40° 14’41.3536 W 111° 38’ 57.4216). Other than soil texture (Table 1) and time of year, each study was nearly identical. The first study (Loam) was conducted from 14 Nov through 4 Dec 2008 (21 d) on a Timpanogos loam soil collected from the BYU research station

(40°4’1.77”N 111°37’44.99”W). The second study (Sand) was conducted from 16 Dec 2008 through 9 January 2009 on a manufactured sand soil (obtained from inert crushed quartz from a quarry in Emit, ID, USA). The third study (Sandy Loam) was conducted from 24 Jan through 13 Feb 2009 with a composited soil comprised of a 50/50 mixture of the manufactured sand and the Timpanogos loam. The loam soil was air-dried , rocks removed, and soil clods larger than 4 cm diameter were broken up, then mixed thoroughly—avoiding pulverizing the soil’s structure (sand soil did not require drying or removal of rock).

Treatments included: 1) an untreated control, 2) 336 kg N $ha^{-1}$ urea (46% N), 3) 224 kg N $ha^{-1}$ urea and 4) 224 kg N $ha^{-1}$ PCU (44-0-0; Environmentally Smart N, ESN®, Agrium Advanced Technologies, Loveland, CO, USA). Three replications of these four treatments were applied to soil in chambers arranged in a randomized complete block design (RCBD). The high rate of urea chosen was based on an approximated full agronomic rate for maize. The reduced rates of urea and PCU were chosen based on preliminary field data (Hopkins et al., 2008) suggesting that PCU has nutrient use efficiency (NUE) approximately 1/3 better than uncoated urea. Analytical instrument limitations (see below) dictated a maximum of 12 experimental units for these studies and, therefore, PCU was not evaluated at the 336 kg N $ha^{-1}$ rate.

Twelve vented non-static, non-flow-through chambers were constructed out of standard 19 L polyvinyl chloride (PVC) buckets (30 cm diameter x 37 cm height). The bottom of each chamber was vented to allow water to move freely out and air to move freely in or out of the soil while simultaneously retaining the soil using a landscape fabric liner (Weed-barrier® 1 oz., DeWitt Company, Sikeston, MO, USA). Chamber lids were constructed from fitted standard 19 L PVC bucket lids, sealed onto each chamber. A hole was cut in the center of each lid to accommodate a 13 cm diameter by 12 cm length PVC pipe sealed to the lid with acrylic latex

silicone caulk. The PVC pipe reached to within 1-3 cm of the soil surface and to 2-3 cm above the lid. This was designed to minimize gas contamination from one chamber to another, to maximize accumulation of soil evolved gases in the head space in the chamber yet to allow gas exchange with the atmosphere.

Each chamber contained approximately 13.5 kg of soil filled to within 8-12 cm of the top. Maize (Pioneer 35F38) was hydroponically germinated and 4 individual plants with shoots 8-12-cm high were transplanted into soil in the chambers with the plants extending up through the PVC pipe. On day one of each trial, fertilizer treatments were applied , mixed into the top 5 cm of soil, and soils were immediately planted to maize, irrigated with municipal water (EC <280) to saturation, and gas sampling was initiated. Targeted day and nocturnal air temperatures were 25$^{o}$C and 15$^{o}$C, respectively, although limitations in heating/cooling capacity resulted in ranges of 20-29$^{o}$C daytime and 11-16$^{o}$C nighttime. Natural light was supplemented with artificial light (Hubbell high pressure sodium lamps) to maintain a 14/10-hour light/dark cycle.

Gas samples, from emission of $N_2O$ and volatilization of $NH_3$, were collected using an Innova 1309 12-port sampling unit (multiplexer) and analyzed with an Innova 1412 Photoacoustic Field Gas Analyzer (Lumasense Technologies, Santa Clara, CA, USA), via photoacoustic infrared spectroscopy (PAIRS; DeKlein, 1999). Gas samples were transported from the head space above the soil using a pump on the PAIRS unit to pull the sample through 6 m of 4 mm I.D. HDPE tubing to the detector. The PAIRS unit was connected to a computer which controlled gas sampling ($N_2O$ and $NH_3$) time intervals, and analysis. A complete sample set (12) was automatically sampled every 30 minutes; cycling continuously throughout the 21 days of experiments.

45 Day Study – The 21-Day Studies were conducted for only 21 d to refine methodology for the PAIRS analysis and determine "early season" N losses when losses from urea are more likely and plants are less likely to utilize soil N. A follow up study on the Timpanogos loam soil was conducted to evaluate gaseous losses over the full term of anticipated N release from PCU. The PCU used in the 20 Day Studies, ESN®, is an agronomic product designed with an S-shaped release curve to match crop demand for N over 60-90 d. Duration CR45® (44-0-0, Agrium Advanced Technologies, Loveland, CO, USA), is the PCU used in this 45-Day Study, and is also provided by Agrium Advanced Technologies but allows a nearly linear release of N for 45 days at 20° C in saturated conditions. The conditions of this study (20-29 °C and near saturation) were such that N release would occur more quickly than the anticipated release timing. Intended us of Duration CR45® is with perennial landscape plants. The shorter release period of Duration CR45® made it an ideal candidate for a glasshouse study.

This study was conducted in the BYU glasshouse from 13Dec 2010 to 27 Jan 2011. Treatments included: 1) an untreated control, 2) 200 kg N $ha^{-1}$ urea, and 3) 200 kg N $ha^{-1}$ PCU. Four replications of these three treatments were applied to soil in a RCBD. On day one of each trial, fertilizer treatments were applied to the surface, and soils were immediately planted to maize, irrigated with municipal water (EC <280) to saturation, and gas sampling was initiated. Treatments were all surface-applied. Temperatures and light cycles were the same as for the above mentioned studies.

Twelve chambers were constructed in similar fashion to those described previously, with the following modification. The PVC tube was pushed 5 cm into the soil. The PVC tube had four equally spaced holes, 5 mm in diameter, drilled through the tube wall 5-8 cm from the soil

interface to maximize accumulation of soil evolved gases in the head space in the chamber, yet also allow gas exchange with the atmosphere.

Soil volumetric water content was monitored using Watermark Soil Moisture Sensors (Spectrum Technologies, Plainfield, IL, USA) and logged using an AM400 soil moisture data logger (MK Hansen, Wenatchee, WA, USA), and soil temperature was monitored and logged using a common thermistor and the AM400 data logger.

Collection and analysis of $N_2O$ and $NH_3$ emissions were completed in a nearly identical fashion as the earlier mentioned studies utilizing PAIRS analysis, although the sampling interval was shortened to 11 minutes for higher temporal resolution. Concentrations, as determined by the PAIRS analyzer, were obtained (Fig. 1 and Fig. 2), compiled, and used to determine daily flux for each chamber. Daily flux was determined by using the maximum daily concentration and the minimum daily concentration which occurred prior in that day to the maximum concentration. Flux was then calculated by

$$f = \frac{V \times \Delta C}{A \times \Delta t}$$

Where $V$ is the headspace volume, $\Delta C$ is the change in concentration ($C_{max} - C_{min}$) of $N_2O$ and $NH_3$ as measured by PAIRS, $A$ is the area of the chamber not including the 13 cm diameter center used for plant growth, and $\Delta t$ is the time elapsed between $C_{min}$ and $C_{max}$. The daily gas concentrations were used to determine the change in time and change in concentration for input to the above equation. Concentrations were corrected using the ideal gas law, assuming standard temperature and pressure. Because this flux value was taken over an extended period of time (in some cases over six hours) it was assumed to be representative for that given day. To determine mass of N lost, daily flux values were assumed to be constant for a 24-h period.

Daily gas concentrations were analyzed using ANOVA. Loss of N as $NH_3$ and $N_2O$ were then analyzed for statistical significance by ANOVA and Tukey HSD analyses using JMP 10.8 statistical software (SAS Institute, Cary, NC, USA) with $\alpha = 0.05$.

## RESULTS AND DISCUSSION

### Ammonia

21-D Studies - The fertilizer source by time interaction generally was significant and therefore daily measurements of $NH_3$ concentrations are presented for each treatment for the three soils (Fig. 1). There were no significant differences in overall accumulated $NH_3$ flux among the three treatments in the sand soil ($P = 0.3304$; Fig. 1). The individual day differences from the different N sources were small, variable and not of practical significance (Fig. 1). The extremely low concentrations and fluxes observed are likely due to the sand soil being biologically inert and associated low levels of the urease enzyme. A small microbial enumeration analysis using soil extract agar and Jensen's agar and colony counts were unusually low (70,000 and 0 microorganisms $g^{-1}$, respectively) and confirm the hypothesis that the sand soil was relatively biologically inert.

There were significantly higher $NH_3$ concentrations evolved from both full and reduced rates of urea than from PCU and control treatments on all but days 1 and 2 for the sandy loam soil (Fig. 1 and Table 2). During these two days, concentration levels remained near background levels for all treatments (Fig. 1). The $NH_3$ concentration differences among the two rates of urea also differed significantly from each other often—generally the full rate of urea was significantly higher than the low rate (days 9-19).

Total cumulative N loss from $NH_3$ volatilization (daily summed from the first to the last day of the study) was also significantly higher for the reduced rate of urea treatment than both

the PCU and control ($P < 0.0001$, Fig. 2). There was no difference between the urea treatments ($P = 0.9998$) or between the PCU and the control ($P = 0.9816$). Fertilization with PCU rather than urea resulted in an average reduction of $NH_3$ volatilization of 72% when compared the two rates of urea (Fig. 2).

Similar to another study done with corn in a sandy loam (Clay et al. 1990), elevated $NH_3$ volatilization did not appear until 2 d after fertilization for both rates of urea (Fig. 1) in the Sandy Loam Study. This is likely due to a relatively slow increase in soil pH in areas immediately adjacent to the fertilizer granules, and following this increase in soil pH, $NH_3$ volatilization conditions were optimized and flux levels were elevated. Volatilization reached its peak after 6 d and then remained elevated compared to the PCU and control for the duration of the study. However, volatilization from urea after d 6 gradually subsided toward background levels.

Significantly higher $NH_3$ concentrations from volatilization were observed in the Loam Study from both full and reduced urea treatments than the PCU and control. The only exceptions were days 1 – 4 on which samples were contaminated from a leak repair in some of chambers. Ammonia concentrations from PCU were significantly higher than the control on all included days except but days 9-13.

Cumulative $NH_3$-N volatilization loss was also significantly lower for the control than for both urea rates and PCU ($P = <.0001$, Fig. 2). There was no difference between the two urea treatments ($P = 0.9033$) nor between PCU and either the full or reduced rates of urea ($P = 0.2490$ and 0.0562, respectively). Fertilization with PCU rather than urea resulted in no significant reduction in N lost via $NH_3$ volatilization in this loam soil (Fig. 2). Despite the lack of significance in flux, PCU produced significantly lower $NH_3$ concentration levels than both urea treatments on individual days (Fig. 2; Table 2).

Appreciable volatilization occurred a day earlier in the loam soil than in the sandy loam. This may be because of relatively more urease enzyme and/or soil moisture in the loam compared to the sandy loam soil. Volatilization peaked after 6 d for the reduced urea treatment and after 7 d for the full urea treatment (Fig. 1) and thereafter levels waned and trended toward background levels until the termination of the study at 18 d. Blaise and Prasad (1994) performed laboratory studies in which urea and PCU were surface applied to a bare sandy loam soil and found significant reductions (up to 53%) in $NH_3$ loss by using PCU in both aerobic and anaerobic conditions. Our findings in the Sandy Loam Study were in line with their findings. However, in a loam soil there were no significant reductions in total N loss from $NH_3$ volatilization with PCU.

45-D Study –There was significantly higher $NH_3$ concentration in the head space from volatilization of urea than PCU and control treatments on 22 of the first 26 days (d 1, 5 – 18, and 20 – 26; Fig. 3 and Table 2). Ammonia concentrations from urea were also significantly higher than PCU on days 4 and 27 – 30 but similar to the control on those same days. All $NH_3$-N concentrations returned to background levels beginning on day 31and there were no significant differences among N sources thereafter. In this long-term study, $NH_3$ volatilization from PCU was never statistically higher than from urea (Fig. 3, Table 2).

Cumulative N loss from $NH_3$ volatilization was also significantly higher for urea than either PCU or control treatments ($P$ = <0.0001, Fig. 4), but equal for PCU and the control (0.9999). Fertilization with PCU resulted in reduction of N loss from $NH_3$ volatilization of 52% compared to urea (Fig. 3).

**Nitrous Oxide**

21-D Studies – Unlike $NH_3$ volatilization and all other studies, there was no day by source interaction for $N_2O$ emissions in the Sand Study. The generally low concentrations and

fluxes are likely due to relatively low soil microbe populations. Microbial enumeration analysis using soil extract agar and Jensen's agar confirmed unusually low colony counts in this soil (70,000 and 0 microorganismsg$^{-1}$, respectively) and supported the idea that this sand soil was nearly biologically inert. Likely due to the low microbial impact, N2O evolution was near background levels for all treatments (Fig. 3) and any significant differences observed over the course of the study were of no practical significance (less than 0.10 mg $L^{-1}$ difference; Fig. 2) and will not be discussed further. There were significantly higher $N_2O$ concentrations in the head space above both rates of urea compared to the PCU and control treatments from day 3 through 18 (Table 2, Fig. 1). Concentrations of $N_2O$ were at significantly higher levels for the full rate of urea than the reduced rate of urea rate twice (d 5 and 21) and for PCU treatments than the control twice also (d 1 and 5). Thus, $N_2O$ evolution was higher from urea than PCU 73% of the days and similar on the other 27% of the days (Table 2).

Cumulative $N_2O$-N losses from the full rate of urea were significantly greater than the reduced urea treatments in the Sandy Loam Study at the P = 0.0728 level (Fig. 3). Both rates of urea were significantly greater than both the PCU and control treatments ($P < 0.0001$). Cumulative $N_2O$ losses for control and PCU treatments were equivalent ($P = 0.7592$). Fertilization with PCU instead of urea resulted in reduction of $N_2O$ emissions of 16% compared to the reduced rate of urea (Fig. 2).

As with $NH_3$ volatilization data, data for days 2 – 5 of the Loam Study are omitted from statistical analyses due to known analytical errors encountered. However, there were significantly higher $N_2O$ concentrations in the head space above the two rates of urea than the PCU and control treatments on all other days of the study (except d 1; Fig. 1, Table 2). The $N_2O$ concentrations of the full rate of urea were also significantly higher than the reduced rate on all

days of the study. The PCU and control were statistically equivalent until day 18, after which$N_2O$ evolution with PCU was significantly higher than the control until the termination of the study on day 21 (Fig. 1, Table 2).

Cumulative $N_2O$-N losses from the two urea treatments in the Loam Study were statistically equivalent (Fig. 2; $P = 0.3913$). The full rate of urea evolved significantly more $N_2O$-N than both the PCU and control treatments ($P = 0.0005$ and $< 0.0001$, respectively). The PCU treatments also lost less $N_2O$-N than the reduced rate of urea ($P = 0.0278$) and were equivalent to the control. The reduced rate of urea had near significant losses of $N_20$-N compared to the control at the $P = 0.0843$ level. Fertilization with PCU rather than urea resulted in a 59% reduction of $N_2O$ emissions when compared to the reduced rate of urea (Fig. 2).

No visual plant growth or health differences were detectable in the short-term studies with sand, sandy loam or loam soils among PCU and either full or reduced applications of urea. Thus, fertilization with PCU rather than urea maintained plant health and resulted in reductions of $N_20$ and $NH_3$ emissions (Fig. 1 and 2; Table 2).

45-D Study – There were significantly higher $N_2O$ concentrations in the head space from the urea treatment than the PCU and control treatments on all days during the study (except for day 1 when concentrations were equivalent to that of the control; Fig. 3, Table 2). From d 12 through 45 (termination of the study), $N_2O$ concentrations for PCU were also significantly higher than the control, but also significantly lower than the equivalent rate of urea application (Fig. 3).

Cumulative $N_2O$-N losses from the urea treatments were significantly larger than both the PCU and control treatments (Fig. 4; $P < 0.0001$) and the PCU and control treatments were statistically equivalent ($P = 0.6261$). Fertilization with 136 kg N $ha^{-1}$ from PCU resulted in an 87% reduction of $N_2O$ emissions compared to 136 kg N $ha^{-1}$ from urea.

Emissions of $N_2O$ from PCU in the 21-d loam study increased slightly in the last three days of the trial and these measurements raised questions that were addressed with the 45-day study. Other researchers have reported increased $N_2O$ emissions from PCU at later times than from urea (Halverson and Del Grosso 2010a). The 45-d study was conducted using a similar PCU as used in short-term experiments (Duration CR45®) except designed with a shorter release time (45 d) to ascertain whether increased $N_2O$ flux from PCU would occur after 21 days. There were slightly but significantly elevated $N_2O$ emissions from PCU compared to the control from d 3 through 11 but not during the 12 to 45 d period. Nitrous oxide flux from urea increased beginning on d 4, reached a peak after 15-16 d and decreased slightly each day thereafter, never reaching background levels even after 45 days (Fig. 3). From our four studies it is clear that $N_2O$ evolution from PCU is minimal compared to urea even over the full 45 day period for which PCU was designed for release (Fig. 1 and 3).

Halverson and Del Grosso (2010a) performed a study in which they compared readily soluble dry granular urea to "enhanced efficiency" N fertilizers, including PCU (ESN®). This was a multi-year study in an irrigated no-till corn cropping system with clay loam soils. For gas sampling and collection they used the static-chamber method and then used gas chromatography (GC) to analyze the samples. Similar to our findings, they saw significant decreases in $N_2O$ emissions from PCU compared to urea. Unlike their study, any observed differences between control and PCU occurred in the first 3-20 days and there was no noticeable peak in flux from PCU which would suggest a flush of N to the soil solution. Rather, levels of $N_2O$ were slightly higher than the control for the duration of the study and usually not significantly different from the control.

Our results also support the findings of those who have documented decreased emissions of $N_2O$ from fertilization with PCU compared to uncoated urea in barley, cabbage, corn, potato, and turfgrass (Delgado and Mosier, 1996, Cheng et al., 2006, Halvorson et al., 2010, Hyatt et al., 2010, Maggiotto et al. 2000). Ours is the first to observe these $N_2O$ fluxes using PAIRS analysis and to provide more than a snapshot of $N_2O$ flux following fertilization. In other studies $N_2O$ flux was measured at most daily and more typically 2-3 times $week^{-1}$ and flux estimated via linear interpolation. Mosier et al. (1991) suggested that sampling frequency be increased to account for the innately large temporal variability associated with the biologically mediated flux of $N_2O$. Venterea et al. (2009) observed a large variability in the accepted static chamber/GC method and suggested ways to minimize the inevitable variance. This study demonstrates that by using PAIRS analysis, temporally high resolution measures can be made and utilized to observe the gaseous losses of N following fertilization.

There were no noticeable differences in plant health throughout the duration of these studies, which further supports the findings of others (Halverson and Del Grosso 2010a, Hopkins et al. 2008, Pack et al., 2006, Wilson et al., 2010) that use of PCU maintains and often enhances crop yield and quality.

## CONCLUSION

While providing an adequate N supply and maintaining plant health (Wilson et al. 2010, Hutchinson et al. 2003, Hopkins et al. 2008, Patil et al. 2010), PCU treatments were also able to decrease $N_2O$ and $NH_3$ evolution significantly compared to urea. The large decreases in the emissions of the potent greenhouse gas $N_2O$ and the atmospheric reactive $NH_3$, while adequately supplying N to the plant, are major improvements to N-use efficiency. Our data suggest that PCU is a viable option to decrease loss of N following fertilizer application.

Utilizing PAIRS analysis with non-static, non-flow through chambers provided a temporally high-resolution simultaneous and continuous viewpoint of both $N_2O$ and $NH_3$ emissions. This research indicates that this method is useful, effective and likely more accurate than methods employing far fewer sampling times. Additional research should be done to determine the variability associated with this method, as well as a design for a chamber which would allow for relatively easy continuous field sampling to be accomplished. Nitrogen losses from urea as $NH_3$ were reduced by 45% on average and losses as $N_2O$ were reduced by 40% on average.

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## TABLES

**Table 1. Select Soil Characteristics for the 21 D and 45 D Studies.** The sand was obtained from a quartz mine in Idaho, the loam used in both the 21 and 45 d studies was a native Timpanogos loam, and the sandy loam was a 50/50 mixture of the two.

| Study | Soil | Sand | Clay | $NO_3^-$ N | OM | pH |
|---|---|---|---|---|---|---|
| | | --- % --- | --- % --- | --- ppm --- | --- % --- | |
| 21 Day | Sand | 86.72 | 4.2 | 2.0 | 0.5 | 7.2 |
| 21 Day | Sandy Loam | 58.1 | 17.2 | 4.9 | 2.3 | 7.1 |
| 21 Day, 45 Day | Loam | 29.4 | 30.2 | 7.8 | 4.0 | 7.1 |

**Table 2. Statistical Patterns of $N_2O$ and $NH_3$ Concentration (ml $L^{-1}$) Levels.** Those columns in the same study which do not share a common letter were significantly different at the $P = 0.05$ level.

| Study | Soil | Patterns Most Often Significant ($P < .05$) | | | | Days | Proportion |
|---|---|---|---|---|---|---|---|
| | | Control | PCU91 | Urea91 | Urea136 | Observed | of Days, % |
| | | ---------- $NH_3$ ---------- | | | | | |
| Short-term textural | Sand | No pattern occurred more than once | | | | | |
| Short-term textural | Sandy loam | C | C | B | A | 9-16 | 37 |
| | | B | B | A | A | 3-4, 7-8 | 21 |
| | | D | C | B | A | 17-19 | 16 |
| Short-term textural | Clay Loam | D | C | B | A | 5-8, 14-20 | 69 |
| | | C | C | B | A | 9-13 | 31 |
| Long Term | Sandy Clay Loam | B | n/a | B | A | 5-18, 20-26 | 47 |
| | | A | n/a | A | A | 31-45 | 11 |
| | | AB | n/a | B | A | 4, 27-30 | 33 |
| | | ---------- $N_2O$ ---------- | | | | | |
| Short-term textural | Sand | Insignificant day by source interaction | | | | | |
| Short-term textural | Sandy loam | B | B | A | A | 3-4, 7-18 | 64 |
| | | C | B | A | A | 1, 6 | 9 |
| Short-term textural | Clay Loam | C | C | B | A | 6-18 | 65 |
| | | D | C | B | A | 19-21 | 15 |
| Long Term | Sandy Clay Loam | C | n/a | B | A | 3-11 | 76 |
| | | B | n/a | B | A | 12-45 | 20 |

## FIGURES

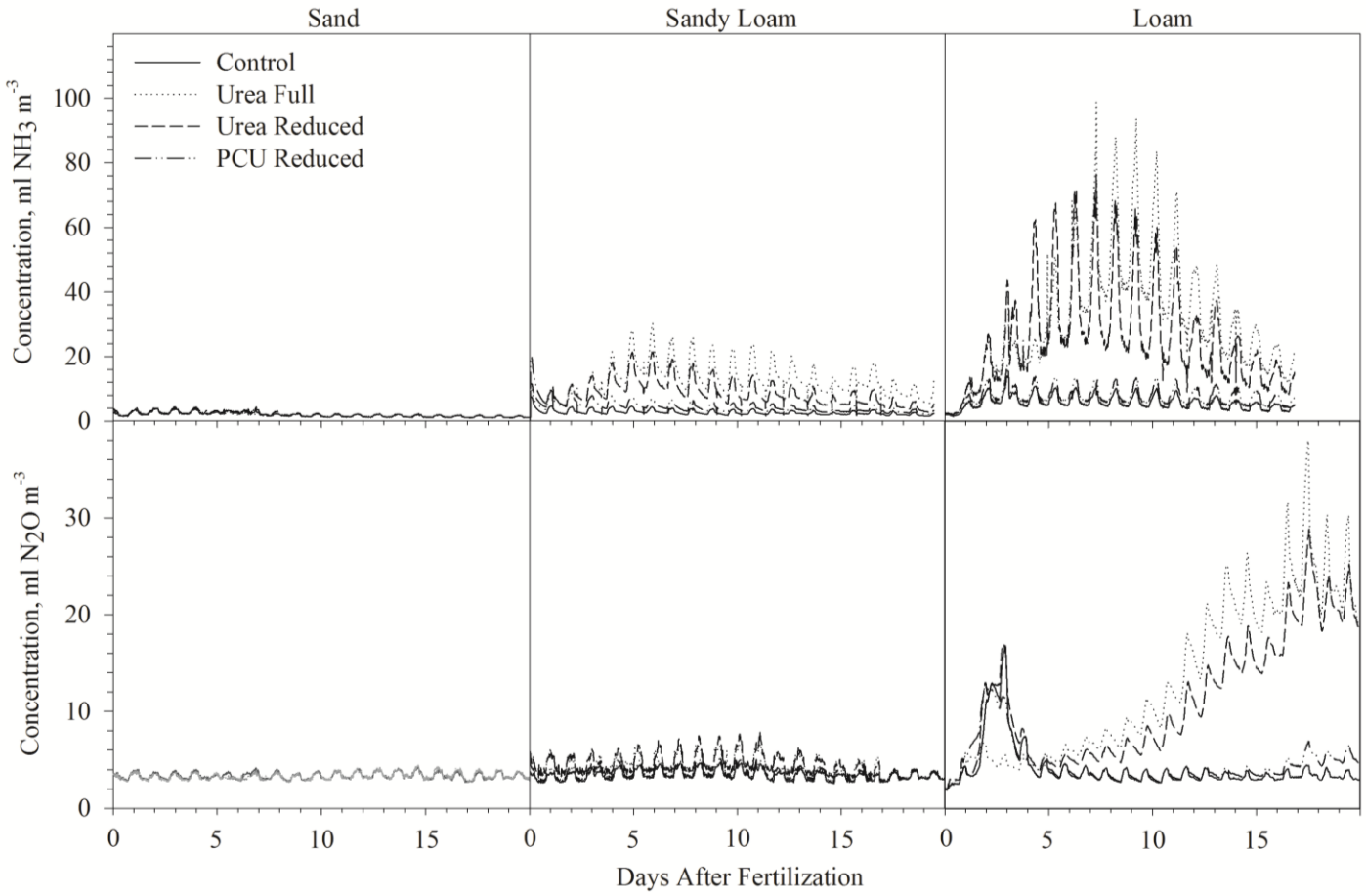


**Figure 1. Concentration of $N_2O$ and $NH_3$ in chamber headspace for 21 D Studies.** Samples were collected and analyzed every 30 min. to give this high-resolution view of the changes in concentration over time. These values were used to find the daily maximum concentration and the daily minimum which occurred prior to the maximum to estimate flux. Each day was analyzed individually and the statistics are reported in Table 2.

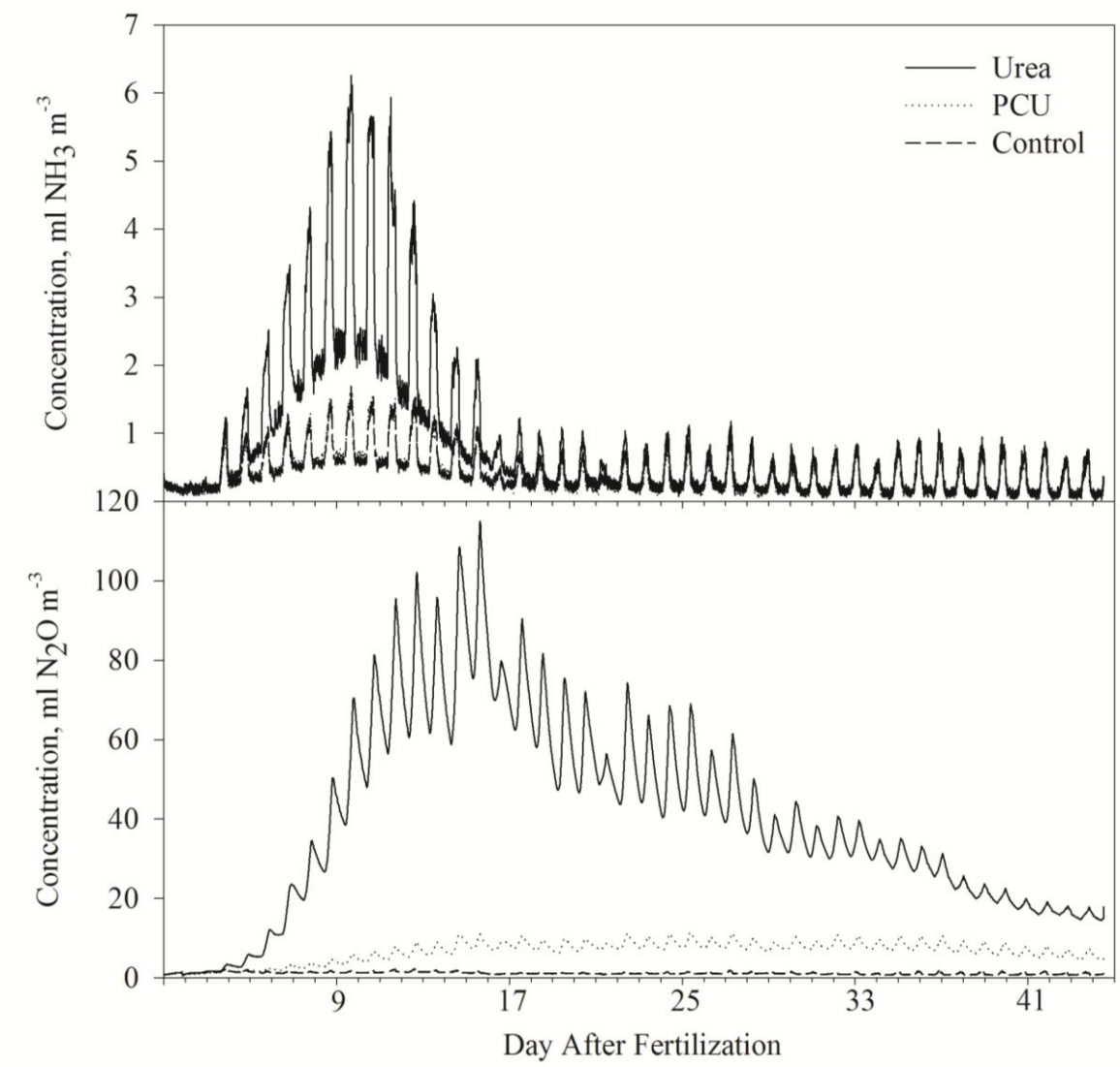


**Figure 2. Concentration of $N_2O$ and $NH_3$ in chamber headspace for 45 D Study.** Samples were collected and analyzed every 11 min. to give this high-resolution view of the changes in concentration over time. These values were used to find the daily maximum concentration and the daily minimum which occurred prior to the maximum to estimate flux. Each day was analyzed individually and the statistics are reported in Table 2.

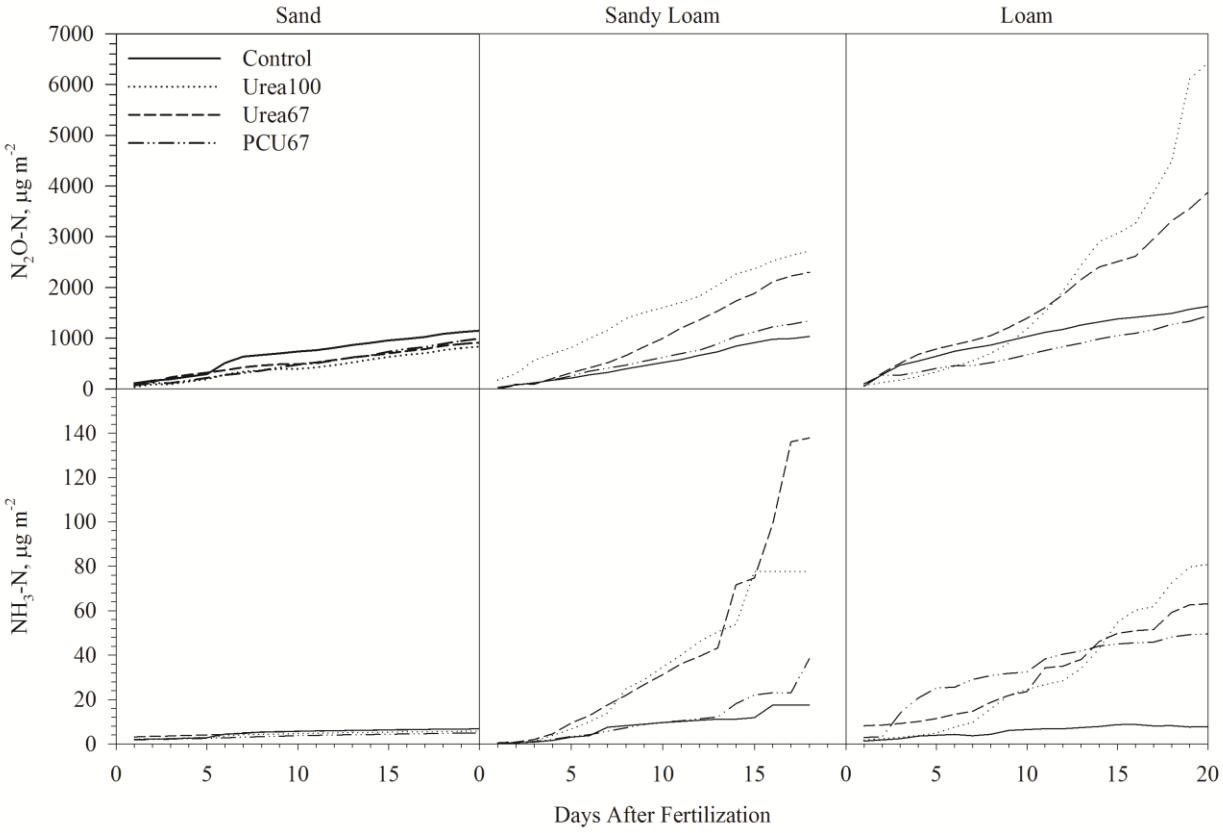


**Figure 3. Total N Loss from $N_2O$ Emission and $NH_3$ Volatilization in 21 D Studies.** The total N loss from urea treatments was consistently significantly higher than the PCU treatments.

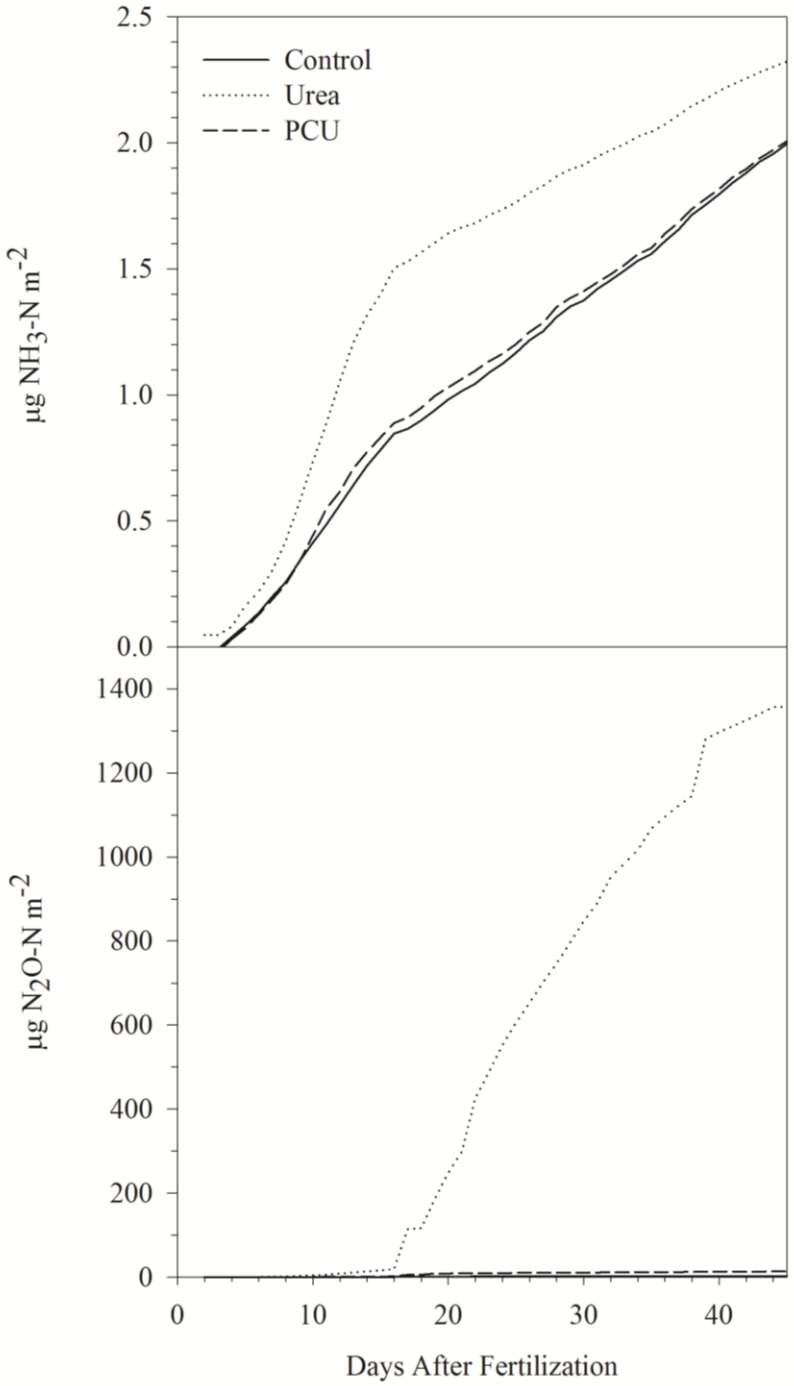


**Figure 4. Total N Loss from $N_2O$ Emission and $NH_3$ Volatilization in 45 Day Study.** The total N loss from urea treatments was consistently significantly higher than the PCU treatments.

# APPENDIX A

# LITERATURE REVIEW

## Nitrogen Cycle

Nitrogen is found in a wide variety of forms and oxidation states in the environment. The cycling of nitrogen affects how N is found in the environment. Certain forms of N cause concerns when in high concentrations, including $NO_3^-$ in the ground and surface water, and gaseous N compounds which contribute to large-scale environmental problems including acid rain, catalytic ozone depletion, excess N deposition, and climate change. The major forms that N is found in include dinitrogen gas ($N_2$), organic N (biomass and soil organic matter), and ammonium and nitrate ions. Dinitrogen gas is present in the highest concentrations in ecosystems. Soil organic N is the next most prevalent, followed by plant organic N. Soil inorganic N pools are typically found in much lower concentrations compared to the previously mentioned pools, due to their high turnover and reactivity rates.

This transformation of N is defined as the N cycle. A common source of N in fertilized systems is urea. Urea is usually surface-applied as small pellets. Once these pellets come in contact with the soil surface, the extracellular enzyme urease can hydrolyze urea into carbon dioxide and ammonia. This hydrolysis converts urea into the bioavailable ammonia form of N.

The assimilation of ammonium by microbes and plants occurs via two pathways: glutamate dehydrogenase and glutamine synthetase-glutamate synthase (GOGAT). Where relatively high levels (> 0.5 mg N $kg^{-1}$ soil) of $NH_4^+$ are found, the glutamine dehydrogenase pathway is used to assimilate $NH_4^+$. However, in most soils $NH_4^+$ is found in low concentrations. Under these conditions, the complex GOGAT pathway is used. The amino acid glutamate is the product of these assimilation pathways. The $NH_4^+$ found in glutamate is readily transferred into other amino acids. The net production of $NH_4^+$ in soils is a result of biotic and environmental factors and the carbon:nitrogen ratio. At high pH (> 7) $NH_4^+$ may be volatilized. Although this

may be a significant loss in some situations, most $NH_4^+$ in the soil solution is utilized by plant uptake, microbial uptake, or converted to nitrate by nitrifying bacteria.

The nitrification process commonly converts $NH_3$ to $NO_3^-$ via oxidation pathways. Ammonia-oxidizing bacteria first convert $NH_3$ to nitrite ($NO_2^-$) by chemoautotrophic *Nitroso*-genera bacteria (*i.e. Nitrosomonas*), followed by further oxidation of $NO_2^-$ to $NO_3^-$ by chemoautotrophic *Nitro*-genera bacteria (*i.e. Nitrobacter*). The reactions of these conversions are:

*Ammonia Oxidation.*

$$NH_3 + 1.5O_2 \rightarrow NO_2^- + H^+ + H_2O$$

*Nitrite Oxidation.*

$$NO_2^- + 0.5O_2 \rightarrow NO_3^-$$

Ammonia oxidation can result in $N_2O$ emissions and soil acidification. For every mole of $NH_4^+$ that is oxidized, one mole of $H^+$ is released, thus acidifying the soil. Nitrous oxide emissions stem from nitrite reductase (contained within ammonia oxidizers), which reduces $NO_2^-$ to $N_2O$. This occurs in small amounts under well-aerated conditions, but as oxygen becomes more limited $N_2O$ emissions from ammonia oxidation increase because $NO_2^-$ is used as an electron acceptor. Nitrification may be a large source of $N_2O$ emissions in some environments.

The probability of nitrification taking place in the soil is dependent upon the nitrifying microbial population, aeration (aerobic conditions preferred), N and other nutrient availability, temperature, pH (nitrifiers are predominantly neutrophilic), water potential, salinity, and presence or absence of inhibitors. Nitrate is the primary product of nitrification. Similar to $NH_4^+$, $NO_3^-$ can have various fates in the environment.

Nitrate is not limited to its negative effects; it can also be assimilated by plants. Nitrate immobilization (plant assimilation) is generally relatively small compared to $NH_4^+$ immobilization because it is energetically expensive for the plant. In order to be assimilated, the $NO_3^-$ molecule is first reduced to $NH_4^+$ and then can be utilized by amino acids. Under some conditions, $NO_3^-$ can be reduced but not assimilated; non-respiratory denitrification is one such reduction pathway. This reduction can lead to N losses to the atmosphere as $N_2O$.

Non-respiratory denitrification plays a small role as compared to respiratory denitrification (commonly denitrification). This dissimilatory nitrate reduction process converts $NO_3^-$ to the nitrogenous gases $N_2$ and $N_2O$. The reaction is as follows:

$$2NO_3^- + 5H_2 + 2H^+ \rightarrow N_2 + 6\ H_2O$$

In C limiting soils, this is the most important reductive process due to its energetic yield. Denitrification is performed under anaerobic conditions by denitrifying prokaryotic bacteria (e.g. *Pseudomonas*, *Bacillus*). Denitrification is a four-step process: 1) reduction of $NO_3^-$ to $NO_2^-$ by the nitrate reductase enzyme, 2) reduction of $NO_2^-$ to nitric oxide (NO) by the nitrite reductase enzyme, 3) conversion of NO to $N_2O$ by nitric oxide reductase, and 4) reduction of $N_2O$ to $N_2$ by the nitrous oxide reductase enzyme.

Similar to nitrification, denitrification rates are affected by various environmental factors. Denitrification predominantly occurs under anaerobic conditions as denitrifying enzyme activity is inhibited when oxygen levels reach approximately one tenth that of atmospheric levels. Rates of denitrification reach their maximum generally at 80% water filled pore space (WFPS). When conditions are aerobic, denitrification can be limited by nitrate and/or carbon concentrations.

Other environmental factors which affect denitrification are temperature (mesophilic), pH (neutral preferred, though not much research has been done on high pH soils), and soil type.

## Nitrogen in Plants

The state of N on the earth is paradoxical. Although N is generally found in higher concentrations than all other mineral nutrients in plants (up to 6%, Taiz 2006) and the fact that there is approximately $1.67 \times 10^{23}$ g of N, 98% of which is found in the lithosphere (rocks, soils, sediments, etc.), it is also the most commonly deficient mineral nutrient in plants. Most N is not plant-available because it is found in an organic form which cannot be assimilated. As discussed above, plants can only assimilate $NO_3^-$ and $NH_4^+$.

Nitrogen is a key nutrient for plant growth and function, and is found in the chlorophyll molecule, amino acids, proteins, enzymes, nucleic acids, and many other compounds (RNA and DNA) (Fry 2004). Nitrogen deficiencies inhibit synthesis of these compounds and, as a result, restrict the growth of all plant parts, which leads to early senescence. Plants with N deficiency generally appear chlorotic and have stunted growth. The pattern of N chlorosis appearance can be diagnostic in that it appears uniformly across the leaf blade and is first visible in older leaves.

Nitrogen's essentiality leads to efficient use following assimilation. Nitrogen is only lost from plants by rain or mist-induced foliage leaching or defoliation (Barker, 2007). Repeated removal of plant biomass by harvesting or mowing can result in depleted soil N reserves. Nitrogen does not sufficiently regenerate for high yield and crop use following removal—it must be replenished through addition of fertilizer, soil amendments, and, to a lesser degree, through atmospheric deposition, irrigation, and fixation of atmospheric N by legumes and some soil microbes. Atmospheric deposition and N fixation commonly do not provide adequate amounts of N. To meet demands for crop production and most urban landscapes, N fertilization is required.

Permanent sod cropping systems, such as turfgrass and pasture, demand high amounts of N. This is especially true when biomass is removed by grazing or harvest for forage materials or, in the case of turfgrass, simply for aesthetics. Land owners apply up to 500 kg N $ha^{-1}$ as fertilizer each year. These rates are comparable to the most intensively cultivated agriculture fields in the world (Hall, 2008), yet are often exceeded by homeowner applications.

Ideally, the rate at which the N is supplied to the plant would match the plant need precisely. This ideal is not possible due to inherent inefficiencies or "leaks" in the system. However, best management practices (BMPs) can result in substantial increases in NUE. The key to good fertilizer stewardship depends on using the right source, at the right rate, at the right time, and with the right placement (Snyder2007).

## Nitrogen Fertilizers and the Associated Environmental Concerns

The most commonly used dry N fertilizer worldwide is urea ($CO(NH_2)_2$; 46% N). Urea, like most other commercially produced N fertilizer, is an ammonical (derived from natural gas) source of N. Once it hydrolyzes, such as when applied to the soil surface, it converts to $NH_3$ which can be held in the soil, assimilated by the plant, volatilized and lost to the atmosphere, or converted to nitrate via nitrification. Increased applications of N fertilizer have been linked with increases in atmospheric $NH_3$ (Sutton 2008).

### I. Ammonia

Atmospheric ammonia is an environmental concern because it is more likely to deposit on land (through wet or dry deposition) than other forms of anthropogenic N. Deposition of this atmospheric ammonia to sensitive ecosystems can lead to soil acidification and surface water eutrophication. Additions of N in certain ecosystems can also lead to plant community loss (Sutton 2008). Fenn (1998) related that increased N availability due to $NH_3$ deposition in

typically N-limited terrestrial, freshwater, and marine ecosystems across the globe is having unwanted and adverse consequences including increased aluminum mobility, and forest decline. Classifying major sources of anthropogenic $NH_3$ is an important step to make reductions, but this has been difficult to do until fairly recently.

Understanding $NH_3$ emissions is difficult due to the nature of the gas. It has been difficult historically to separate $NH_3$ from aerosol $NH_4^+$, and for years it was only reported as the sum $NH_3$+$NH_4^+$ (total inorganic ammonia). To understand long-term trends, however, this separation was necessary. Technological advancements have made analyzing $NH_3$ much more feasible and convenient. A denuder (device used to separate a gas from an aerosol) system, where air is passed through an acid-coated glass tube under laminar flow, traps gases on the tubing wall. The collected ammonia is then extracted and analyzed. This method has been improved over the years to allow for monthly sampling of long-term trends. Low-cost passive sampling is another method which allows for the assessing of spatial variability of $NH_3$ without active air sampling (Sutton, 2008). Photoacoustic infrared spectroscopy (PAIRS) is a recently developed method of $NH_3$ analysis which provides low maintenance, high frequency automated sampling and monitoring (Sutton, 2008). Increasing the frequency of sampling may decrease temporal variation and provide increased understanding of $NH_3$ emissions following fertilizer-N applications.

## II. Nitrate

Following conversion to ammonia, N is then converted to $NO_3^-$ via nitrification. Due to its negative ionic charge it can be easily leached and enter surface and ground waters. In addition to the decrease in plant available N that results, excess $NO_3^-$ in watersheds can lead to toxicological problems (Mulvaney, 2009) such as eutrophication (large algal blooms which can

lead to anoxic conditions), and drinking water contamination. Drinking water contaminated with $NO_3^-$ can cause methemoglobinemia (blue baby syndrome) in young animals and human babies (Olson, 2009), and may react with free amines to form carcinogenic nitrosamines. Nitrate in watersheds can lead to nitrate-induced toxic effects on freshwater biota, disruption of nutrient cycling, and eutrophication of water bodies (Fenn, 1998).

## III. Nitrous Oxide

Following conversion to nitrate, the N cycle is completed via denitrification and the evolution of $N_2$, the gas which makes up 78% of the atmosphere. Denitrification and nitrification have been classified as "leaky pathways", as each commonly does not go to completion and resultantly emits $N_2O$. On average, 1% of all nitrogen applied as fertilizer in inorganic forms is emitted as $N_2O$, and the actual amount lost is directly related to the type, quantity, and method of application of that fertilizer (GHG Working Group 2010). Hirsch et al. (2006) related that emissions of $N_2O$ have increased by approximately 50% over pre-industrial levels due to anthropogenic causes. Although agriculture generates less than 10% of the total anthropogenic greenhouse gas emissions in the United States, it is estimated that agricultural nitrous oxide emissions account for 78% of the total annual anthropogenic $N_2O$ losses (USEPA, 2007). Nitrous oxide is a potent greenhouse gas, with a global warming potential 296 times that of $CO_2$ per unit. Long-lived in the atmosphere (up to 150 years), $N_2O$ catalystically destroys ozone in the troposphere. Emissions via denitrification and nitrification are controlled by many interacting factors, which complicate understanding the issue. Soil aeration, temperature, texture, ammonium concentration, nitrate concentration, as well as microbial community factors, all affect the rate of soil $N_2O$ production (Snyder 2007).

Due to temporal and spatial variability and the multi-faceted nature of $N_2O$ emissions, reliable estimates are difficult to obtain. Static chamber flux techniques are widely used. This method takes samples from small areas, < 1 $m^2$, and is relatively inexpensive. However, sampling (typically done as three or more samples per chamber in 15-or 20-minute intervals) and analysis using a gas chromatograph (GC) with an electron capture detector, increase temporal variability. Venterea (2009) stated that nitrous oxide emission estimates range from -60 to 170% of the mean. Increasing the sampling frequency is needed to overcome variability (Mosier, 1990). Photoacoustic infrared spectroscopy (PAIRS) is a recently developed method which allows in-field analysis of $N_2O$ concentrations. PAIRS analyzers are advantageous due to their analysis frequency, portability, robustness, and relative ease of use (De Klein, 1999). The Innova 1412 Photoacoustic Field Gas Analyzer is a promising PAIRS device which can analyze individual samples in less than 60 seconds and be daisy-chained to two 24-point multiplexers, allowing for fully automated sampling and analysis. DeKlein (1996, 1999) indicated that using a PAIRS analyzer was accurate and effective in laboratory experiments, but found evidence for some leakage from the instrument (which one did they use?) when compared to GC analysis. Further work must be done to validate whether or not a PAIRS analyzer can reliably and accurately detect $N_2O$ emissions from the soil and provide increased understanding of $N_2O$ emissions from soils following fertilizer-N application.

**Improving NUE**

By controlling the release of N from fertilizer into the soil, it is hypothesized that N inefficiencies and losses to the environment will be mitigated. Controlled-release N (CRN) and slow-release N (SRN) sources are fertilizers that release N into the soil over an extended period of time, ideally matching plant need, possibly reducing or eliminating labor-intensive and costly

in-season N applications and increasing NUE and environmental quality (Hopkins 2008). CRN fertilizers are coated or encapsulated and SRN fertilizers are low-solubility compounds, primarily sulfur-coated urea, urea-formaldehydes, methylene ureas, and triazine compounds. The concept of CRN and SRN fertilizer materials is not new, but success varied widely across plant species and environmental conditions, and expense prevented wide utilization (Hopkins 2008).

Polymer-coated urea (PCU) fertilizers are one promising type of CRN that can potentially provide improved N-release timing. Soil temperature controls N release rate and simultaneously influences plant growth and nutrient demand (Hopkins 2008). The release process consists of diffusion of water through the coating, dissolution of urea inside the particle, and diffusion of urea solution through the coating into soil solution. Diffusion is driven by the concentration gradient—temperature being the primary regulator under irrigated conditions. PCU has been shown to steadily supply the plant with N for longer periods of time following fertilizer application, leading to increased crop yield and quality (Blythe 2002, Cahill 2010, Knight 2007, Miltner 2004, Pack 2003, Worthington 2007), due to enhanced NUE (Wilson 2010, Hutchinson 2003, Hopkins 2008, Patil 2010). Hyatt (2010) showed that the slower release of PCU can improve economics by eliminating additional in-season N applications. In addition to financial and direct plant benefits of the controlled release of N from PCU, research has also demonstrated PCU's ability to mitigate negative environmental impacts associated with N fertilizer (Halverson 2010, Pack 2006, Wilson 2010). Nitrate leaching has been shown to be significantly decreased by using PCU under some environmental conditions (Du 2006, Guillard 2004, Nelson 2009, Pack 2006, Pack 2003, Wilson 2010). Ammonia volatilization can also be reduced using PCU (Knight 2007, Pereira 2009, Rochette 2009). With the impending introduction of new air quality regulations, $N_2O$ emissions have received a large amount of attention. PCU has been shown to

reduce $N_2O$ emissions under some conditions (Cao 2006, Halverson 2008, Halverson 2010a, Halverson 2010b, Hyatt 2010), yet some have reported no difference or even substantial increases when compared to soluble forms of N (Jassal 2008, Jiang 2010) .

Most of the work done to investigate the differences in N environmental losses has been performed in intensive agricultural systems (maize, wheat, and rice), but little has been done to investigate the impacts of PCU on NUE in grass systems (Bremer 2006, Knight 2007) despite these fertilizers having a large role in the turfgrass and permanent sod markets. Grass systems, especially turfgrass, typically receive high amounts of N fertilizer and irrigation water. These conditions can promote plant health and vigor if managed appropriately, but improper management results in substantial losses to the environment as discussed previously.

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