



## AN ABSTRACT OF THE THESIS OF

Sarah Kathryn Del Moro for the degree of Master of Science in Soil Science presented on June 4, 2015

Title: Ammonia Volatilization from Nitrogen Fertilizers and Wastewater Reuse in the Columbia Basin

Abstract approved:

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Dan M. Sullivan

Ammonia ( $\text{NH}_3$ ) volatilization and loss from nitrogen (N) fertilizer in agriculture negatively impacts crops, farm profitability, human health and surrounding ecosystems where it is deposited. A significant source of  $\text{NH}_3$  volatilization occurs from surface application of urea on sandy soils with low pH buffering capacity such as those in the semi-arid Columbia Basin region of Oregon and Washington. Ammonia volatilization can be mitigated by using alternative N fertilizers to urea. Effluent from food processing and energy production industries is also used on cropland as an efficient method to conserve water and nutrients. However,  $\text{NH}_3$  emissions from effluent application have not been quantified. The objectives of this study were to: (i) quantify  $\text{NH}_3$ -N loss from urea vs. alternative N fertilizer products in a micrometeorological field study and laboratory incubation experiment, and (ii) quantify  $\text{NH}_3$  emissions from effluent applied to crops using an inverse-dispersion micrometeorological method.

The fertilizers evaluated in field and laboratory trials included urea, polymer-coated urea, sulfur-coated urea, urea treated with urease inhibitor [N-(n-butyl) thiophosphoric triamide (NBPT)] and ammonium sulfate (AS). Mixed and fused N salts were also evaluated, including a blend of urea and AS and a blend of AS:ammonium nitrate (AN). A modified passive flux method was used to estimate  $\text{NH}_3$ -N loss from fertilizers in the field experiment for 33 d after application. In the lab incubation trial,  $\text{NH}_3$  was collected in acid for 43 d after application. In the field trial, cumulative  $\text{NH}_3$ -N loss from urea was 47% of N applied. The alternative N fertilizers reduced  $\text{NH}_3$ -N loss in both the field and laboratory, with the exception of the fused urea:AS

blend. The reduction of  $\text{NH}_3\text{-N}$  loss ranged from 19 to 68% vs. urea in the field, and 16 to 98% vs. urea in the laboratory.

In the second study, a backward Lagrangian stochastic (bLS) model was used to calculate  $\text{NH}_3$  emissions from alfalfa fields receiving effluent water (average  $111 \text{ mg L}^{-1}$  total Kjeldahl N content) generated from a potato processor, a dehydrated onion processor, and a cogeneration plant. An ultraviolet-differential optical absorption spectrometer (UV-DOAS) and three-dimensional sonic anemometer were used to monitor  $\text{NH}_3$  concentrations, wind speed, and temperature for 43 days downwind of the field. The average  $\text{NH}_3\text{-N}$  emission rate was  $1.4 \text{ kg ha}^{-1} \text{ d}^{-1}$  when effluent was applied vs.  $0.5 \text{ kg ha}^{-1} \text{ d}^{-1}$  during irrigation without effluent. The greatest average  $\text{NH}_3\text{-N}$  emission rate of  $6.1 \text{ kg ha}^{-1} \text{ d}^{-1}$  resulted from alfalfa harvest.

These studies provided insight of relative  $\text{NH}_3$  loss among a variety of alternative N fertilizers to urea. Additional N mass balance research will be required to validate the accuracy of these  $\text{NH}_3$  loss quantifications. Compared to urea, all of the alternative fertilizers significantly reduced  $\text{NH}_3\text{-N}$  loss, with greatest benefit resulting from  $\text{NO}_3^-$  and  $\text{NH}_4^+$  fertilizer forms ( $> 60\%$  reduction vs. urea). The average  $\text{NH}_3\text{-N}$  emission rate of  $1.4 \text{ kg ha}^{-1} \text{ d}^{-1}$  observed during effluent application was nearly three times the rate observed from irrigation without effluent. This study confirmed the potential of alternative N fertilizers to reduce  $\text{NH}_3$  emission in agriculture in conditions favoring  $\text{NH}_3$  volatilization. This study also confirmed the need to consider  $\text{NH}_3$  loss when reusing effluent as a nutrient source for crops.

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Ammonia Volatilization from Nitrogen Fertilizers and Wastewater Reuse in the Columbia Basin

by  
Sarah K. Del Moro

A THESIS

submitted to

Oregon State University

in partial fulfillment of  
the requirements for the  
degree of

Master of Science

Presented June 4, 2015  
Commencement June 2016

Master of Science thesis of Sarah Kathryn Del Moro presented on June 4, 2015

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I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

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Sarah K. Del Moro, Author

## ACKNOWLEDGEMENTS

My late advisor and mentor, Dr. Don Horneck, receives my eternal gratitude for his time, knowledge, patience, humor, and continued guidance in all aspects of my graduate experience and additionally, life. Equal gratitude is expressed to my current advisor, Dr. Dan Sullivan for keeping me on track with invaluable metaphors about sandwiches, sports, religion and politics that I will never forget. I cannot fully convey my appreciation to Dr. Horneck and Dr. Sullivan for encouraging me to study soil science and challenging what I was capable of. Words also cannot express my thanks to the other members of my committee, Dr. Christoph Thomas and Dr. April Leytem; not only for sharing an appreciation of horses (Dr. Leytem) or “hops” (Dr. Thomas), but for sharing instruments that were essential for this research, helping to interpret data, and introducing me to the fascinating field of micrometeorology, which I hope to continue studying and applying.

To my parents and family for the lifelong support to pursue my passion for science, in particular my husband and best friend, David, without whose love, support and reluctant acceptance of less-than-extravagant dinners while writing, I would not have finished this thesis.

I would also like to thank the growers in the Columbia Basin, especially Kent and Jake Madison at Madison Farms and Vern Frederickson at Frederickson Farms, for lending their time, fields, information and other resources for this research. Thanks also to Nelson Irrigation, IRZ and Irrigation Specialists for donating and lending equipment and helping to troubleshoot the “mini-pivots”. Innovative growers and agriculture companies, such as these in the Columbia Basin, are the reason for valuable, hands-on research opportunities at university extensions.

Sincere thanks to everyone at the Hermiston Agricultural Research and Extension Center for help and resources relating to this research, support with presentations, including the defense seminar of this thesis, and all the great times and the free coffee. Thanks also to Oregon State University and pretty much everyone on the 3<sup>rd</sup> floor of the ALS building, for foundational knowledge, more great times, and the cheap coffee.

In conclusion, I recognize that my research would not have been possible without funding from Agrium Inc., J.R. Simplot, Koch Agronomic Services, Loveland Products, Inc., Two Rivers Terminal, LLC., Yara North America, and the William Kent Wiley Jr. Graduate Fellowship awarded by the Oregon and American Seed Trade Associations, and I express my gratitude to these companies and organizations.

## CONTRIBTION OF AUTHORS

Dr. Don Horneck and Dr. Dan Sullivan proposed the subject of this research. Dr. Horneck was involved with data collection and interpretation for all chapters. Dr. Sullivan was involved in data interpretation and review for all chapters. Dr. April Leytem and Dr. Christoph Thomas provided instruments and assisted with related data interpretation and review for Chapter 3.



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## DEDICATION

To my husband, David  
And in memory of Don Horneck

**AMMONIA VOLATILIZATION FROM NITROGEN FERTILIZERS AND WASTEWATER REUSE IN THE  
COLUMBIA BASIN**

**GENERAL INTRODUCTION**

Sarah K. Del Moro

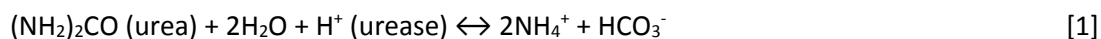


Nitrogen (N) plays a key role for plants, especially in agriculture. Agricultural plants often require abiotically fixed N in their photosynthetic cycle. Nitrogen added to meet crop demand is subject to fixation in soil, loss through nitrate ( $\text{NO}_3$ ) leaching, ammonia ( $\text{NH}_3$ ) volatilization, and nitrous oxide ( $\text{N}_2\text{O}$ ) emissions, so that the average N uptake efficiency of a crop ranges from 40 to 75% of N applied (Allison, 1955; Elkashif et al., 1983). As a result, N is often over-applied to compensate for loss and allow greater crop yields, resulting in poor overall N use efficiency. Nitrogen lost from agricultural land is often deposited in various forms in nearby water systems and ecosystems and can cause serious human and environmental health problems as well as speciation and community changes. These issues present a need to continually investigate ways to increase the efficiency of N use in agriculture.

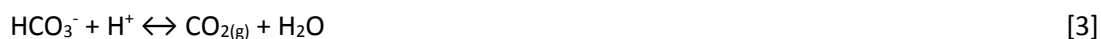
The Columbia River Basin is a semi-arid region of the Pacific Northwest where many irrigated crops are grown. It is often characterized by high winds and well-drained, sandy loam soils with low cation exchange capacity. Some locations within the Columbia Basin also contain calcareous soil. All such conditions are less conducive to  $\text{N}_2\text{O}$  emissions, although they can enhance  $\text{NO}_3$  leaching and  $\text{NH}_3$  volatilization from N fertilizers. Environmental properties that influence  $\text{NH}_3$  volatilization include soil pH buffering capacity, moisture, residue, temperature, and air exchange at the soil surface (Hargrove, 1988; Proctor et al., 2010). The potential for volatilization from most fertilizers can be reduced by incorporating fertilizer into soil mechanically (Rochette et al., 2013), with irrigation (Holcomb et al., 2011), or by choosing a more suitable fertilizer type for a given soil or climate.

Ammonia volatilization is an important form of N loss from ammonium ( $\text{NH}_4$ ) and urea fertilizers, that when lost from fertilized agricultural lands, negatively impacts crop growth, farm profitability, human health and surrounding ecosystems where it is deposited. Ammonia readily reacts with  $\text{NO}_x$  and  $\text{SO}_x$  gases in the atmosphere to produce fine ( $<2.5 \mu\text{m}$ ) light-scattering aerosol particles that are responsible for haze and adverse effects on cardiopulmonary health (Asman et al., 1998; Ferm, 1998; Finlayson-Pitts and Pitts, 1999; Pope and Dockery, 2006). Atmospheric  $\text{NH}_x$ , including secondary aerosols, can also be deposited in N-sensitive ecosystems and alter their speciation (Fenn et al., 2003; Krupa, 2003; Geiser and Neitlich, 2007). For example, N-eutrophied forests in the Columbia River Gorge of OR and WA were found to have a strong association with increased nitrophilous and non-native lichen communities (Fenn et al., 2007).

Many forms of N fertilizer are produced, but the most common is urea. Urea accounts for 56% of global fertilizer consumption (International Fertilizer Industry Association, 2012) due to its relatively high N content (46%), ease and safety of handling, and low cost (Sommer et al.; 2004; Roy and Hammond, 2004). One disadvantage of urea is a greater potential for  $\text{NH}_3$  volatilization. Ammonia loss is enhanced with alkaline soil microsites produced by hydrolysis of urea in the presence of water and the enzyme urease, according to the following reactions (Kissel et al., 1988; Eq. 1-3):



which further reacts as:



The temporary increase of soil pH as hydrolysis consumes  $\text{H}^+$  drives the production of  $\text{NH}_{3(g)}$  from  $\text{NH}_4^+$  at a pKa of 9.25 at 25°C (Kissel et al., 2008). Field and laboratory investigations of  $\text{NH}_3$  volatilization from surface-applied urea to sandy loam soil have reported emissions of up to 80% of applied N (Grant et al., 1996; Vitti et al., 2008; Holcomb, 2011).

In the Columbia Basin, fertilizers such as urea are typically surface-applied in spring and fall when irrigation is unavailable. Without irrigation, growers rely on precipitation to incorporate fertilizers. Aside from incorporating fertilizer, using alternative N fertilizers instead of urea can limit N loss to the environment and increase nutrient availability to crops. Dry, unamended urea has largely been replaced in industrialized countries by more efficient, alternative fertilizers due to its high potential for volatile  $\text{NH}_3$  loss. Some N fertilizers that are expected to emit less  $\text{NH}_3$  on the basis of known chemistry include ammonium sulfate  $[(\text{NH}_4)_2\text{SO}_4 \text{ or AS}]$  and blends that contain ammonium nitrate  $[\text{NH}_4\text{NO}_3 \text{ or AN}]$  (Harrison and Webb, 2001). However, studies of AS and AN products report variable cumulative  $\text{NH}_3$  volatilization, ranging from 0.2 to 45% of applied N (Prasad, 1976; Hayashi et al., 2011; San Francisco et al., 2011), with the greatest emissions resulting from calcareous soil (Hargrove et al., 1977). Urea can also be used more efficiently by coating prills with urease inhibitors, or sulfur and polymer membranes. These technologies reduce the diffusion rate of  $\text{NH}_4$  and allow soil to buffer pH changes from hydrolysis (Jarrell and Boersma, 1980; Clay et al., 1990; Shaviv et al., 2003;). Investigations of  $\text{NH}_3$  volatilization from sulfur-coated urea (SCU) and polymer-coated urea (PCU) have been limited and variable, reporting losses between 1 and 35% of applied N depending on environment and longevity of coatings (Knight et al., 2007; Rochette et

al., 2009; Frame et al., 2012; Jantalia et al., 2012;). One product that has consistently been reported to reduce  $\text{NH}_3$  volatilization by up to 90% when added to urea is the urease inhibitor, N-(n-butyl) thiophosphoric triamide (NBPT) (Grant et al., 1996; Rochette et al., 2009; Engel et al., 2011; Holcomb, 2011). There has also been an emerging practice of partially substituting urea with AS to mitigate  $\text{NH}_3$  volatilization based on the theory that acidity produced by nitrification of  $\text{NH}_4$  can buffer alkaline microsites produced by urea hydrolysis, while additionally diluting urea N to reduce the rate of  $\text{NH}_{3(g)}$  formation (Chien et al., 2011).

In the Columbia Basin, an emerging efficient practice is the reuse of effluent water from food and energy production industries as a biofertilizer in crops. Food processing and energy production industries generate significant volumes of wastewater that historically have been treated and discharged back to an original source, usually nearby rivers. Wastewater treatment processes are costly and can include oxygenation, microbial digestion or disinfection to remove chemicals and compounds. The chemical composition of food processing effluent varies drastically, such that literature does not designate a common value for it, but it typically contains low concentrations of metals and salts, and N, P and K levels that are comparable to the composition of fertilizers (Fuller and Warrick, 1985).

Water resources in general have also become the focus of immense legal, ethical, social and economic debate in agriculture due to increasing drought situations and shifting of agro-ecological zones with climate change (Knowles et al., 2006; IPCC, 2014). Supplemental water applications to crops, or irrigation, allows crops to be grown in arid locations of the world that were previously unsuitable. In the U.S. in 2010, irrigation accounted for approximately 38% of total freshwater withdrawals, with most use occurring in the more arid climates of the Western States (Maupin et al., 2014). In arid locations, water rather than nutrients is the most limiting factor for crop production. Water is not only a limiting resource for agriculture, but also related food processing and energy industries, which accounted for a combined 42% of total U.S. freshwater withdrawals in 2010 (Maupin et al., 2014). Of these major freshwater withdrawals, agriculture accounts for 80- to 90% of true consumption, or loss from the source, due to evapotranspiration, whereas most of the water used by food processing and energy industries is returned to its source (Schaible and Aillery, 2012). These ratios suggest that more than enough effluent water is produced to supply the irrigation requirements of agriculture if the sources are located within a practical delivery distance. Reusing effluent could offset a substantial volume of

freshwater withdrawals that are attributed to agriculture, while also saving the costly treatment processes required to discharge effluent back into freshwater sources.

The Port of Morrow, near Boardman, OR, is a convenient location for the reuse of effluent water on cropland, where approximately 5,000 ha of crops are grown in close proximity to food processors and energy production industries. Because the Columbia Basin has soils characteristically at risk to leach  $\text{NO}_3$  and volatilize  $\text{NH}_3$ , the application of effluent to crops is closely monitored and regulated. Maximum rates and volumes of effluent that can be applied to crops are determined using an N balance, starting with the total Kjeldahl N content of the effluent, less an estimation of crop N uptake and an assumed N loss of 30% attributed to  $\text{NO}_3$  leaching and  $\text{NH}_3$  volatilization. The N budget regulating effluent application to crops considers crop uptake and  $\text{NO}_3$ -N loss based on the irrigation system, soil type, crop type, grower management practices, and even direct measurements of  $\text{NO}_3$  concentrations in the soil profile; however, it is assumed that  $\text{NH}_3$ -N loss from effluent is minimal because effluent is typically acidic, with a pH of less than 5.0. Ammonia volatilization can occur from soluble  $\text{NH}_3$  or when the organic, protein-based N forms in effluent mineralize into ammonium ( $\text{NH}_4$ ) products in soil (Myrold and Bottomley, 2008), which can then release  $\text{NH}_3$ . Based on these reactions, substantial  $\text{NH}_3$ -N loss could be occurring from the application of effluent to crops and alkaline soils in the Columbia Basin and the Port of Morrow.

There have been many investigations of  $\text{NH}_3$  volatilization from manure effluent applied to crops, which has been identified as the most significant source of  $\text{NH}_3$  emissions from agriculture and can produce average  $\text{NH}_3$ -N loss rates of up to 85% of N applied (Lauer et al., 1976; Schilke-Gartley and Sims, 1993; Robinson and Polglase, 2000; Sharpe and Harper, 2002); however, there have not been any investigations to quantify  $\text{NH}_3$  emissions from the reuse of food processing effluent water on crops. In general, emissions can vary depending on amount of irrigation used, temperature, and wind speed, which causes difficulty in determining ideal effluent application rates based solely on effluent-N concentrations (Sims and Stehouwer, 2008). It is important to quantify  $\text{NH}_3$  volatilization from the reuse of effluent water in cropland to mitigate  $\text{NH}_3$  emissions if they are determined significant and more accurately account for  $\text{NH}_3$ -N loss in N budgets. There are several micrometeorological methods available that can measure and estimate  $\text{NH}_3$  emissions from large cropped areas.

One micrometeorological method ideal for estimating  $\text{NH}_3$  flux from a large area is the backward Lagrangian stochastic (bLS) technique. The bLS model determines gas emissions from

a source area ( $Q \text{ kg d}^{-1}$ ) by calculating  $N$  upwind “particle” trajectories from downwind mixing-ratio concentrations ( $C \text{ ppm}_v$ ) measured in excess of background (Flesch et al., 2004). Particle trajectories depend on the wind environment at the study site, which is described by Monin-Obukhov similarity theory (MOST) key parameters of  $u^*$ ,  $L$ ,  $z_0$ , and  $\theta$ , where  $u^*$  is the friction velocity ( $\text{m s}^{-1}$ ),  $L$  is the Obukhov stability length (m),  $z_0$  is the surface roughness length (m), and  $\theta$  is the wind direction ( $^\circ$ ) (Garratt, 1992). These parameters can be calculated from three-dimensional ultrasonic anemometers, along with any measurement of gas concentration. A simpler, passive method, ideal for estimating  $\text{NH}_3$  flux from small treatment plots, is the modified passive flux method (Wood et al., 2000; Holcomb et al., 2011). This method uses time-averaged horizontal flux densities of  $\text{NH}_3$  gas, integrated at multiple sampling heights within an affected air layer above a small, circular, treated plot (Wilson et al., 1982; Denmead et al., 1983). Wind measurements are not necessary, as the gas samplers used in the method are linearly proportional to the mass of  $\text{NH}_3$  collected.

The challenges related to determining  $\text{NH}_3$  volatilization from the complex N fertilizer forms and delivery methods are the subject of this research. Knowledge of loss rates and treatment differences are increasingly important as new methods emerge, become more common, and management of agriculture N loads on the environment becomes more precise. The objectives of this study were to: (i) quantify  $\text{NH}_3$ -N loss differences from urea and alternative N fertilizer products in a micrometeorological field study and laboratory incubation experiment, (ii) quantify  $\text{NH}_3$  emissions from the reuse of effluent water on alfalfa crops using the bLS method, and (iii) develop small-scaled CPIs to allow practical research involving irrigation and solution fertilizer treatments.

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**AMMONIA VOLATILIZATION FROM UREA AND ALTERNATIVE NITROGEN FERTILIZERS IN SEMI-  
ARID COLUMBIA BASIN**

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Styled according to Soil Science Society of America Journal  
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## ABSTRACT

Ammonia ( $\text{NH}_3$ ) volatilization from urea fertilizer negatively impacts crops, farm profitability, human health and surrounding ecosystems where it is deposited. Substantial  $\text{NH}_3$  loss can occur when urea is surface-applied without incorporation. Dry, unamended urea can be replaced with alternative N fertilizers that may be less susceptible to  $\text{NH}_3$  volatilization. The purpose of this study was to quantify  $\text{NH}_3$ -N loss from urea vs. alternative N fertilizer products in a micrometeorological field study and a laboratory incubation experiment. The fertilizers evaluated in field and laboratory trials included urea, polymer-coated urea, sulfur-coated urea, urea treated with urease inhibitor [N-(n-butyl) thiophosphoric triamide (NBPT)] and ammonium sulfate (AS). Mixed and fused N salts were also evaluated, including a blend of urea and AS and a blend of AS and ammonium nitrate (AN). A modified passive flux method was used to estimate  $\text{NH}_3$ -N loss from fertilizers in the field experiment for 33 d after application. In the laboratory, an acid trap was used to collect volatilized  $\text{NH}_3$  from fertilizers in incubation chambers for 43 d after application. Cumulative  $\text{NH}_3$ -N loss from urea was 47% of N applied in the field experiment. The alternative N fertilizers reduced  $\text{NH}_3$  loss by 19 to 68% vs. urea in the field, and by 16 to 99% vs. urea in the laboratory. The most effective alternatives were AS and ASN (>60% reduced  $\text{NH}_3$  loss vs. urea), which supply N in the  $\text{NH}_4^+$  or  $\text{NO}_3^-$  forms. Co-application of urea and AS provided the least benefit in reducing  $\text{NH}_3$  loss.

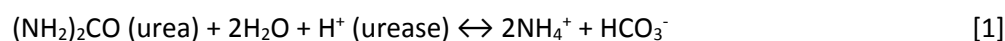
## INTRODUCTION

Ammonia ( $\text{NH}_3$ ) volatilization is an important pathway for nitrogen (N) loss from ammonium ( $\text{NH}_4$ ) and urea fertilizers in agriculture. According to the global  $\text{NH}_3$  budget compiled by Bouwman et al. (2002), fertilizer use in developing and industrialized countries accounts for 18 and 7% of global  $\text{NH}_3$  emissions, respectively. Ammonia loss from fertilized agricultural systems negatively impacts crop growth, farm profitability, human health and surrounding ecosystems where it is deposited (Asman, et al., 1998). Ammonia readily reacts with  $\text{NO}_x$  and  $\text{SO}_x$  gases in the atmosphere to produce fine (< 2.5  $\mu\text{m}$ ), light-scattering aerosol particles that are responsible for haze and adverse effects on cardiopulmonary health (Asman et al., 1998; Ferm, 1998; Finlayson-Pitts and Pitts, 1999; Pope and Dockery, 2006). Atmospheric  $\text{NH}_x$ , including secondary aerosols, can also be deposited in N-sensitive ecosystems and alter

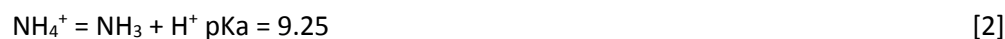
their speciation (Fenn et al., 2003; Krupa, 2003; Geiser and Neitlich, 2007). For example, N-eutrophied forests in the Columbia River Gorge of OR and WA responded to increased N inputs with increased prevalence of nitrophilous and non-native lichen communities (Fenn et al., 2007).

The Columbia River Basin is an irrigated, semi-arid region of the Pacific Northwest. It is characterized by frequent high-speed winds and well-drained, sandy soils with low CEC ( $\leq 20$  cmol<sub>c</sub> kg<sup>-1</sup>). Some locations in the Columbia Basin contain calcareous soil. Soils with low CEC and free lime can enhance NH<sub>3</sub> volatilization from surface-applied N fertilizers. Other environmental properties that influence NH<sub>3</sub> volatilization include initial soil moisture content, crop residue, temperature, and air exchange at the soil surface (Hargrove, 1988; Proctor et al., 2010). The potential for volatilization from most fertilizers can be reduced by incorporating fertilizer into soil with tillage (Rochette, et al., 2013), with irrigation (Holcomb et al., 2011), or by choosing a more suitable fertilizer type for a given soil or climate.

The most common N fertilizer is urea, which accounts for approximately 56% of global N fertilizer consumption (International Fertilizer Industry Association, 2012) due to its relatively high N content (46%), ease and safety of handling, and low cost (Sommer et al., 2004; Roy and Hammond, 2004). One disadvantage of urea is a greater potential for NH<sub>3</sub> volatilization. Ammonia loss is enhanced with alkaline soil microsites produced by hydrolysis of urea in the presence of water and the enzyme urease, according to the following reactions (Kissel et al., 1988; Eq. 1-3):



which further reacts as:



The temporary increase in soil pH as hydrolysis consumes H<sup>+</sup> drives the production of NH<sub>3(g)</sub> from NH<sub>4</sub><sup>+</sup> at a pKa of 9.25 at 25°C (Kissel et al., 2008). Field and laboratory investigations of NH<sub>3</sub> volatilization from surface-applied urea to sandy soils have reported emissions of up to 80% of N applied (Table 2.1).

Dry, unamended urea is often replaced in industrialized countries by more efficient, alternative fertilizers because of its high potential for NH<sub>3</sub> volatilization. It accounts for 21% of N fertilizer consumption in the United States (International Fertilizer Industry Association, 2012). Alternative N fertilizers that are expected to emit less NH<sub>3</sub> on the basis of known chemistry include ammonium sulfate [(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> or AS] and blends that contain ammonium nitrate

[ $\text{NH}_4\text{NO}_3$  or AN] (Harrison and Webb, 2001). However, studies of AS and AN products reported variable cumulative  $\text{NH}_3$  volatilization, ranging from 0.2 to 45% of applied N (Table 2.1), with greatest emissions resulting from calcareous soil (Hargrove et al., 1977). Urea can also be used more efficiently by coating prills with urease inhibitors, or sulfur and polymer membranes. These technologies are meant to slowly release urea and promote diffusion into soil, thereby allowing soil to buffer increasing pH from hydrolysis (Jarrell and Boersma; 1979, Shaviv, et al., 2003; Clay et al., 1990). Investigations of  $\text{NH}_3$  volatilization from sulfur-coated urea (SCU) and polymer-coated urea (PCU) have been limited and variable, reporting losses from 1 to 35% of applied N depending on environment and longevity of coatings (Table 2.1). One product that has consistently been reported to reduce  $\text{NH}_3$  volatilization when added to urea is the urease inhibitor, N-(n-butyl) thiophosphoric triamide (NBPT) (Table 2.1). Adding NBPT to urea reduced  $\text{NH}_3$ -N loss in 10 out of 11 past studies, with median reduction in  $\text{NH}_3$ -N loss of approximately 60% vs. unamended urea. Ammonia volatilization from urea can also be reduced by partially substituting it with AS, based on the theory that acidity produced by nitrification of  $\text{NH}_4$  in AS can buffer alkaline microsites produced by urea hydrolysis (Chien et al., 2011). A related pilot fertilizer product of chemically reacted urea and AS in a single granule [fused urea(AS)] was recently developed to achieve more uniform application of  $\text{NH}_4$  and urea so that nitrification and hydrolysis reactions happen within the same soil microsite. Few published studies of  $\text{NH}_3$  volatilization from products of mixed urea(AS) exist, and none of them have been micrometeorological field investigations. Lara-Cabezas et al. (1997) and Vitti et al. (2002) reported significant reduction of  $\text{NH}_3$  volatilization by partially substituting urea with AS.

Evaluations of  $\text{NH}_3$  loss from alternative N fertilizers are required to establish competitiveness with urea in terms of price per unit of retained N for crops, especially for growing regions that use urea as a primary N fertilizer source. Ammonia volatilization is also an important loss pathway that is necessary to quantify for accurate N budgets. The objectives of this study were to (i) quantify  $\text{NH}_3$ -N loss from alternative fertilizers in a field setting using a micrometeorological method, and (ii) evaluate  $\text{NH}_3$ -N loss from fertilizers in a controlled environment using a laboratory incubation study.

## MATERIALS AND METHODS

The N fertilizer treatments compared in this study, their chemical composition, grade and other selected properties are presented in Table 2.2. In the field experiment,  $\text{NH}_3$  volatilization was compared among the following N fertilizers: 1) urea, 2) urea coated with NBPT (urea + NBPT), 3) a urea and AS blend [urea(AS)], 4) a fused granule of urea(AS), 5) AS, 6) a fused composite of AS and AN (ASN), and 7) SCU. Polymer coated urea (PCU) was added to the laboratory incubation experiment, but was not tested in the field. Fertilizer treatments that required preparation before they could be applied included urea + NBPT and urea(AS). To prepare urea + NBPT, urea prills were evenly coated with liquid NBPT solution (26.7% a.i.), sold under the trade name Agrotain Ultra (Koch Fertilizer, LLC), at the label-recommended rate of 3.1 L  $\text{Mg}^{-1}$  urea. Urea(AS) treatments were prepared as a bulk-blended composition of 79% urea and 21% AS, the same composition as the fused urea(AS). Fertilizer treatments were applied at a rate of 168 kg N  $\text{ha}^{-1}$  in both field and laboratory experiments.

#### Field Site and Experimental Design

The field experiment was conducted in Morrow County, OR between Aug. 20<sup>th</sup> and Sept. 25<sup>th</sup>, 2013 on a 50 ha commercial field mapped as an Irrigon fine sandy loam (a mesic Xeric Haplocambid), 0 to 12% slopes. The field contained wheat (*Triticum aestivum*) straw plowed to a depth of 10 cm with disc cultivators, and surface soil (3 cm depth) pH ranged from 7.3 to 7.9 (1:2 w/v soil/deionized water suspension; Gavlak et al., 2005). Before the experiment began,  $\text{NO}_3\text{-N}$  content of the field was approximately 15 kg  $\text{ha}^{-1}$  and  $\text{NH}_4\text{-N}$  content was approximately 5 kg  $\text{ha}^{-1}$  to a depth of 30 cm. Irrigation (50 mm) was applied 1 d before the experiment through a center-pivot sprinkler system. The purpose of pre-irrigating was to create uniform surface soil moisture and deliberately increase the rate of urea hydrolysis. Irrigation was not applied at any other time during the study. Fertilizer treatments were broadcast by hand at an N application rate of 168 kg  $\text{ha}^{-1}$  inside circular plots (30 m diameter) separated by at least 100 m to avoid wind drift  $\text{NH}_3$  contamination (Vaio et al., 2008).

The treatment plots were randomly arranged in four blocks of equally sized, 90° wedges (Fig. 2.1). Each wedge corresponded to the different surroundings of the field: 30 m from the north edge of the field was a hybrid poplar tree (*Populus spp.*) plantation that was continually harvested during the study; 100 m from the east edge was a 50 ha alfalfa (*Medicago sativa*) field that was cut and harvested between Aug. 28<sup>th</sup> and 31<sup>st</sup>, 2013; dune land spanned to the south of

the field, and a fallow, 55 ha field was positioned 30 m from the west edge of the experiment site (Fig. 2.1). These surroundings constituted possible differences in ambient  $\text{NH}_3$  concentration inside the field depending on wind direction, especially from harvested alfalfa and poplar trees (Freney et al., 1983), that were accounted for by measuring background  $\text{NH}_3$  outside of each of the four quadrants of the field and at least 100 m away from any treatment plot. An Adcon Telemetry (Klosterneuberg, Austria) weather station was also placed at the experiment site to record 15-min average wind speed and direction, precipitation, humidity, soil temperature (20 cm depth) and air temperature; however, wind speed and direction data failed to record from the mobile weather station and was sourced instead from an AgriMet weather station located approximately 6 km from the field site (Bureau of Reclamation; Boise, ID).

### Modified Passive Flux Method and Data Analysis

We used a modified passive flux method to estimate  $\text{NH}_3$  gas flux from fertilized plots (Wood et al., 2000; Holcomb et al., 2011). Emission estimates were calculated from time-averaged horizontal flux densities of  $\text{NH}_3$  gas, integrated at multiple sampling heights within an affected air layer above a small, circular treated plot (Wilson et al., 1982; Denmead et al., 1983). This approach used to require separate, instantaneous measurements of horizontal wind velocity and  $\text{NH}_3$  gas concentrations which often overestimated true flux density after accounting for background  $\text{NH}_3$  and time averaging (Raupach and Legg, 1984). To simplify and reduce the error of the horizontal flux determination, Leuning et al. (1984) designed a new gas sampler that established a linear, proportional relationship between the mass of  $\text{NH}_3$  collected and horizontal wind speed, determined and calibrated through wind tunnel tests.

The current modified passive flux method evolved from further simplifications of the Leuning samplers. Glass tubes (0.7 cm i.d. and 20 cm long) are coated with oxalic acid (deposited with 3% w/v oxalic acid in acetone solution, evaporated) on the inside to react with and trap  $\text{NH}_3$  from air as  $\text{NH}_4$  (Schjørring et al., 1992; Wood et al., 2000; Vaio et al., 2008; Cabrera et al., 2011; Holcomb et al., 2011). Samplers are fastened with an entrance nozzle that consists of silicon tubing attached to a stainless steel disc (Mikrolab Aarhus A/S, Axel Kiers Vej 34, DK-8270 Højebjerg, Denmark) containing a 1 mm i.d. hole in the center to decrease wind speed and friction resistance through the sampler. This apparatus generates greater  $\text{NH}_3$  collection efficiency for a more accurate flux density determination (Schjørring et al., 1992).

Flux samplers were arranged at five heights of 0.45, 0.75, 1.50, 2.25, and 3.00 m on a 3 m pole attached to a wind vane to rotate samplers, entrance nozzle first, into the wind. Poles were placed on a level, metal base (30 cm<sup>2</sup>) in the center of treated plots and in untreated background locations. A tripod was also attached to poles approximately 1 m from the base to anchor the systems against strong wind gusts (Wood et al., 2000 and Holcomb et al., 2011). At the end of each sampling interval, flux samplers were removed and replaced with new, unexposed, acid-coated samplers. The removed samplers were immediately sealed at both ends with 10 mm plastic caps and stored under refrigeration in closed Ziploc bags until laboratory analysis. Exposed samplers were exchanged at 1- to 3-day intervals for 33 d after application (DAA). Samplers were exchanged more frequently in the beginning of the study when urea hydrolysis and NH<sub>3</sub> volatilization were expected to be more active. Longer exposure periods were used near the end of the study after lab analyses indicated that NH<sub>3</sub> flux was diminishing. Following laboratory analysis, flux samplers were cleaned in a 560 °C furnace for 1 h (Cabrera et al., 2011).

Sorbed NH<sub>4</sub>-N was eluted from flux samplers in the laboratory by adding 2 mL of deionized water, capping tube ends and shaking them for 10 minutes. The elution was colorimetrically analyzed for NH<sub>4</sub>-N concentration using the modified indophenol blue method described by Sims et al. (1995). This method reacts NH<sub>4</sub> with citrate, salicylate nitroprusside and hypochlorite to produce the indophenol blue complex. The blue color from reacted ammonium was spectrophotometrically determined at 650 nm using a microtiter plate reader. Horizontal NH<sub>3</sub>-N flux ( $F_x$ ,  $\mu\text{g m}^{-2} \text{s}^{-1}$ ) from each sampler was then calculated using equation 4:

$$F_x = \frac{CV}{\pi r^2 K \Delta t} \quad [4]$$

Where:

C is the concentration of NH<sub>4</sub>-N ( $\mu\text{g mL}^{-1}$ ) eluted from sampling tubes,

V is the volume of deionized water (2 mL) used to elute NH<sub>4</sub>,

r is the radius of the hole in the disc of the nozzle (0.0005 m),

K is the correction factor (0.77) for reduced air speed in the sampler accounting for increased NH<sub>3</sub> collection efficiency, determined by Schjørring et al. (1992),

and  $\Delta t$  is the time interval (s) for which samplers were exposed.

Net horizontal flux from each treated plot ( $F_{x \text{ trt}}$ ) was determined by subtracting background NH<sub>3</sub> emissions ( $F_{x, \text{ bkg}}$ ). Background samplers measured free convective NH<sub>3</sub> and could not be used to



account for contamination between treatment plots within the field. Additionally, wind did not come from a consistent direction for more than 50% of any sampling period, which prevented inference of the source of background  $\text{NH}_3$  from field surroundings. Therefore, average ambient  $\text{NH}_3$  was estimated by averaging all four background measurements together. Total flux density ( $F$ ,  $\mu\text{g N m}^{-2} \text{s}^{-1}$ ) was then estimated by integrating horizontal fluxes with vertical intervals measured by each sampler using equation 5:

$$F = \frac{1}{R} \sum (F_{x_{trt}} - F_{x_{bkg}}) \Delta h \quad [5]$$

Where

$R$  is the mean fetch length, or radius, of the treatment plot (15 m),

and  $\Delta h$  represents the height intervals measured by each sampler.

Net flux was multiplied by the time interval of exposure to calculate  $\text{NH}_3\text{-N}$  loss. Cumulative  $\text{NH}_3\text{-N}$  loss from each treatment and replicated block in the field experiment was analyzed using mixed model analysis of variance (ANOVA) procedures, in which fertilizer treatments were assigned as the fixed-effect variable and blocks were assigned as the random-effect. Means were separated with a LSD test at the 0.05 probability level using Statistix 9 (Analytical Software, 2008).

### Laboratory Experiment

The laboratory experiment was conducted under controlled conditions in volatilization chambers maintained at  $15.6 \pm 1^\circ\text{C}$ , close to the average temperature during normal fall and spring fertilization times at the field site. Incubation chambers consisted of 1 L, glass, open-top jars covered with thin plastic sandwich bags, loosely sealed with a rubber band to minimize air escape without creating anaerobic conditions. The chambers were filled with  $250 \pm 1$  g of non-farmed, Adkins fine sandy loam soil (a coarse-loamy, mixed, Haplocalcid) that had been bulked, mixed, air-dried, and passed through a 2 mm sieve. Approximately 0.3 L of the jar contained soil and 0.7 L of the jar contained air. The soil was brought to uniform field capacity ( $-75$  kPa or 16% moisture w/w) by adding 40 mL of deionized water. The moist soil was equilibrated to  $15.6^\circ\text{C}$  before applying fertilizer treatments. The purpose of the moisture was to maximize  $\text{NH}_3$  volatilization as evaporation drives water upward, which occurs as initial soil water potential approaches  $-100$  kPa (Al-Kanani, et al., 1991). Fertilizer treatments and formulations tested were

1) urea, 2) urea + NBPT, 3) urea(AS), 4) fused urea(AS), 5) AS, 6) ASN, 7) SCU and 8) PCU, with five replications in a completely randomized design. Control treatments of unfertilized soil were included to account for any diffusive  $\text{NH}_3$  contamination between chambers.

Fertilizers were weighed on an analytical balance and applied to surface soil at an N rate of  $114 \pm 2 \text{ mg chamber}^{-1}$  (equivalent to  $168 \text{ kg ha}^{-1}$  on a surface-area basis). None of the fertilizer prills were crushed or otherwise physically altered outside of the described preparation. Volatilized  $\text{NH}_3$  from each treatment was captured in an acid trap (2 mL of a 3% w/v oxalic acid in deionized water solution, contained in a 2 mL microcentrifuge tube), centrally suspended 5 cm above the soil surface. The  $\text{NH}_3$  trapping capacity of each tube was 14.2% of N applied. Tubes were removed, capped, refrigerated and replaced with new tubes and solution at 1- to 3 day intervals for 43 DAA. The acid trap solutions were analyzed colorimetrically for  $\text{NH}_4\text{-N}$  concentration using the indophenol blue method described by Sims et al. (1995). Because the chambers were devoid of wind, results were not transformed into a flux estimate; instead, the mass of collected  $\text{NH}_4\text{-N}$  (concentration of  $\text{NH}_4\text{-N}$  ( $\mu\text{g mL}^{-1}$ ) multiplied by the volume of solution used to collect it (2 mL)) was expressed as a percentage of N applied. Cumulative  $\text{NH}_3\text{-N}$  loss from each treatment was subjected to an ANOVA, and pairwise differences of means were compared with an LSD test at the 0.05 probability level using Statistix 9 (Analytical Software, 2008).

## RESULTS

### Field Study

Daily weather conditions at the field site were ideal to enhance  $\text{NH}_3$  volatilization and increase measurement efficiency, with the exception of two storms that occurred at 17 and 27 DAA. Some of the masts were knocked down by wind gusts on 27 DAA, causing greater variability in the results from that sampling period. Cumulative precipitation at the experiment site totaled 35.1 mm from individual rainfall events of 0.2 mm at 1 DAA, 3.3 mm at 6 DAA, 3.8 mm at 14 DAA, 15.8 mm at 17 DAA, 11.8 mm at 27 DAA and 0.2 mm at 32 DAA (Fig. 2.3a). Wind speed (15-min average recordings) fluctuated between  $0.0$  and  $1.5 \text{ m s}^{-1}$  and averaged  $0.3 \text{ m s}^{-1}$  from the southwest (Fig. 2.3b and Fig. 2.4). Relative humidity varied between 15.2 and 96.5% and averaged 55.8%. Air temperature fluctuated between  $5.0$  and  $35.2^\circ\text{C}$ , with an average of

21.0°C (Fig. 2.3a). Soil temperature at a depth of 20 cm ranged between 13.8 to 40.0°C and averaged 25.2°C (Fig. 2.3a). Air and soil temperatures were warmer during the first 15 DAA of the field study. Temperatures dropped immediately after each storm on 17 and 27 DAA and progressively became cooler near the conclusion of the field study.

Ammonia concentrations were not consistent among the four background measurements outside the field (Fig. 2.6). The average  $\text{NH}_3\text{-N}$  concentration of all four background measurements (used generally to account for ambient  $\text{NH}_3$ ) ranged between 0.65 and 3.65  $\text{kg ha}^{-1} \text{d}^{-1}$ . The progression of  $\text{NH}_3$  loss from all of the urea-based fertilizers followed a similar pattern with fluxes peaking at 15 DAA, then leveling off through the remainder of the study. The least cumulative  $\text{NH}_3\text{-N}$  loss was observed from non-urea fertilizers: 18.0% of N applied was lost from AS and 14.8% of N applied was lost from ASN. The progression of  $\text{NH}_3$  loss from AS and ASN followed a different pattern than the urea-based fertilizers. Ammonia fluxes of AS and ASN did not peak at 15 DAA, but rather continued at an almost constant but low rate through the entire study. The greatest cumulative  $\text{NH}_3$  loss among the N fertilizer treatments resulted from urea, which averaged 46.7% of N applied. All other treatments significantly ( $p < 0.05$ ) reduced  $\text{NH}_3$  loss vs. urea (Fig. 2.2a). The fused urea(AS) product was not different from, and even resulted in greater  $\text{NH}_3$  loss than, the bulk blended urea(AS). Cumulative  $\text{NH}_3\text{-N}$  loss totaled 38.0% of N applied from fused urea(AS) and 33.8% of N applied from bulked urea(AS). Cumulative  $\text{NH}_3\text{-N}$  loss was not different between coated products of urea + NBPT and SCU. Total  $\text{NH}_3\text{-N}$  loss amounted to 28.5% of N applied from urea + NBPT and 22.5% of N applied from SCU.

### Incubation Study

Under the controlled 15.6°C conditions in the incubation experiment,  $\text{NH}_3$  concentrations were close to nil from unfertilized treatments; only trace concentrations were collected between 1 and 14 DAA that were representative of slight diffusive contamination of the incubator from volatilizing N fertilizers. Minimal cumulative  $\text{NH}_3$  concentrations, equal to or less than 0.1% of N applied, were collected from AS, ASN, and PCU treatments by the end of the 43 d incubation, all of which were not significantly different ( $p < 0.05$ ) from the unfertilized control (Fig. 2.5a). Cumulative  $\text{NH}_3\text{-N}$  loss from SCU was 0.8% of N applied and not significantly different from PCU. The greatest significant  $\text{NH}_3\text{-N}$  losses were 3.0% of N applied from fused

urea(AS) and 2.8% of N applied from urea. Average  $\text{NH}_3$ -N loss and relative reductions vs. urea are presented in Table 2.3.

Ammonia loss from AS and ASN in the laboratory did not follow the steady, linear, cumulative emission pattern observed in the field experiment. Most urea-based fertilizers followed a linear to exponential  $\text{NH}_3$  loss progression until approximately 14 DAA, after which minimal  $\text{NH}_3$  loss rates were observed. A slightly different  $\text{NH}_3$  loss pattern was observed from urea + NBPT treatments, which followed a less inclined, more prolonged increase in rate of  $\text{NH}_3$  loss until approximately 24 DAA. This progression of  $\text{NH}_3$  loss from urea + NBPT in the laboratory contrasts from the field study, in which urea + NBPT followed a more similar pattern of  $\text{NH}_3$  loss to the other urea-based fertilizers.

The relative differences in  $\text{NH}_3$  loss among the alternative fertilizers vs. urea were consistent in the field and laboratory study, with the exception of fused urea(AS) (Table 2.3.). Fused urea(AS) averaged 5.7% greater  $\text{NH}_3$  loss vs. urea in the laboratory study. Aside from fused urea(AS), all of the alternative fertilizers significantly reduced  $\text{NH}_3$  loss vs. urea. Alternative fertilizers that reduced  $\text{NH}_3$  loss by >95% vs. urea included AS, ASN and PCU.

## DISCUSSION

### Urease Inhibitor

The cumulative  $\text{NH}_3$ -N loss observed from urea in the field study (46.7% of N applied) was of similar magnitude to  $\text{NH}_3$ -N loss observed in previous studies in the Columbia Basin (30 to 60% of N applied), where urea was surface-applied in favorable environmental conditions for  $\text{NH}_3$  loss (Holcomb, 2011 and Horneck et al., 2011). However, cumulative  $\text{NH}_3$ -N loss observed from urea + NBPT in this study (28.5% of N applied) was of greater magnitude than most other micrometeorological field studies reported in literature (Table 2.1). Only one study reported  $\text{NH}_3$ -N loss from urea + NBPT that was similar in magnitude, averaging 36% of N applied, as measured from field chambers on a sandy soil in Canada (Rawluk et al., 2001). Studies in the Columbia Basin reported cumulative  $\text{NH}_3$ -N loss from urea + NBPT that ranged from 0 to 10% of N applied (Holcomb, 2011; Horneck et al., 2011).

The urease inhibitor, NBPT, acts by allowing urea to diffuse into a larger volume of soil so that increasing pH from urea hydrolysis is buffered (Clay et al., 1990; Christianson et al., 1993;

Sanz-Cobena et al., 2008). The efficacy of NBPT depends on its longevity, which is reduced in high temperatures (Hendrickson and Douglass, 1993; Watson et al., 2008). Holcomb (2011) monitored urea hydrolysis from urea + NBPT in a laboratory incubation study in moist soil at 26°C and observed 50% urea hydrolysis at 10 DAA, and 90% urea hydrolysis at 17 DAA. In our field and laboratory studies,  $\text{NH}_3$  volatilization from urea + NBPT was suppressed until approximately 15 DAA. After 20 DAA, the daily  $\text{NH}_3\text{-N}$  loss rate from urea + NBPT surpassed the  $\text{NH}_3\text{-N}$  loss rate of other fertilizers, which suggests that NBPT degraded after 15 DAA (Fig. 2.2b and 2.5b). The average temperature at the field site was 21°C, high enough to promote degradation of NBPT after 14 DAA.

#### Urea and Ammonium Sulfate

Urease inhibitors are meant to promote diffusion of urea and allow increased pH from hydrolysis to be buffered by a greater volume of soil. Conversely, movement of  $\text{NH}_4^+$  in AS is limited by CEC and will eventually undergo nitrification near the microsite of application (Norton, 2008). The efficacy of reducing  $\text{NH}_3$  loss from urea by partially substituting it with AS depends on the ability of nitrification of  $\text{NH}_4^+$  in AS to neutralize high soil pH resulting from urea hydrolysis. One would expect no interaction between urea and AS to yield  $\text{NH}_3\text{-N}$  loss equal to the weighted average of  $\text{NH}_3\text{-N}$  loss produced by urea and AS separately. This theoretical, cumulative, weighted average  $\text{NH}_3\text{-N}$  loss from urea and AS 41% of N applied in the field study and 2.83% of N applied in the incubation study. The cumulative and daily  $\text{NH}_3\text{-N}$  loss observed from the fused urea(AS) product in our field trial (38% of N applied) and incubation trial (2.96% of N applied) confirmed limited or negative interaction between urea and AS.

Nitrification can occur within a few days following the application of  $\text{NH}_4^+$  to soil, but can also be inhibited by high initial salt or  $\text{NH}_3$  concentrations (Mendum et al., 1999; Norton, 2008). If urea hydrolysis occurred more rapidly than nitrification, the subsequent production of  $\text{NH}_3$  could inhibit nitrification, and additionally, the  $\text{NH}_4^+$  provided by AS would also be at risk to volatilize in the high pH environment resulting from urea hydrolysis. These effects could be maximized when both urea and AS are confined to the same soil microsite, such as the case with fused urea(AS).

#### Other Alternative Fertilizers

The fertilizers SCU, PCU, AS, and ASN substantially reduced  $\text{NH}_3\text{-N}$  loss compared to urea in both the field and incubation study. However, the magnitude of  $\text{NH}_3\text{-N}$  loss observed from SCU, AS and ASN was greater than expected in the field trial. Past studies have reported cumulative  $\text{NH}_3\text{-N}$  loss from AS of up to 45% of N applied on calcareous soils (Hargrove et al., 1977; Gezgin, et al., 1995). Calcareous soils are expected to precipitate  $\text{CaSO}_4$  from AS, lead to increased soil pH, and subsequently more  $\text{NH}_3$  volatilization (Hargrove et al., 1977). Otherwise, minimal  $\text{NH}_3$  volatilization is expected from AS and ASN since N is supplied in forms other than urea that do not undergo hydrolysis. We did not identify the percent free lime in the soil at our field site. The magnitude of  $\text{NH}_3\text{-N}$  loss from SCU was greater than expected early in the study, when coatings are expected to remain intact. A sharp release of  $\text{NH}_3$  from SCU occurred between 20 and 25 DAA, indicating the degradation of coatings following significant precipitation events. The  $\text{NH}_3\text{-N}$  loss rate from SCU was greater in the first 10 DAA than the rest of the study, and could have been a result of invisible cracks in the coatings that were releasing urea (Fig. 2.2b and 2.5b).

#### Background Measurements and Overall Magnitude of Results

Ammonia loss results of this study were relatively large in magnitude compared to results from literature, especially for AS and ASN treatments. Elevated magnitudes of  $\text{NH}_3$  loss could be explained by (i) favorable environmental conditions for maximum  $\text{NH}_3$  volatilization, (ii) uncertainty related to analysis methods, or (iii) contamination of treatment plot or background measurements.

The characteristics of the field and the experimental design favored  $\text{NH}_3$  loss in this study. In addition to favorable weather conditions for  $\text{NH}_3$  volatilization, the sandy, low-CEC field also contained plowed wheat straw. The majority of straw was tilled beneath the soil surface and did not prevent contact of fertilizers with soil or evaporation processes. Wheat and other plant residues are known to absorb moisture and promote microbial and urease activity in soil, which can result in elevated  $\text{NH}_3\text{-N}$  loss from urea fertilizers (Kissel et al., 2008). Initial soil water conditions also have an important impact on  $\text{NH}_3$  loss potential. Jones et al. (2011) observed greatest  $\text{NH}_3\text{-N}$  loss of up to 44% of N applied from urea to wet soil surfaces followed by slow drying with little or no precipitation. Water movement toward the soil surface during

evaporation promotes the release of volatilized  $\text{NH}_3$  from soil. We applied approximately 50 mm of irrigation prior to fertilizer application, and average daily evaporation rates during the study were approximately  $40 \text{ mm d}^{-1}$ , as measured from a pan evaporation monitor at an Agrimet weather station located within the same county as the field site (Agrimet, Bureau of Reclamation; Boise, ID). The average air temperature at our field site of  $21.0^\circ\text{C}$ , tilled wheat residue, and sandy soil with low CEC that was moist before fertilizer application are all factors that may have contributed to elevated magnitude of  $\text{NH}_3$  loss in our field study (Holcomb, 2011; Sommer et al., 2004).

Another possible explanation of large  $\text{NH}_3$ -N loss magnitudes in the field could be the uncertainty related to the modified passive flux method. This would be sourced from inherent  $\text{NH}_3$  emissions from soil on the field regardless of fertilization. It would have been ideal to account for the inherent  $\text{NH}_3$  emissions of the cultivated field by placing at least one more background mast within the field itself; however, space was too limited after installing treatment plots to provide the separation distance necessary for an in-field background. Inherent  $\text{NH}_3$  volatilization from an unfertilized field could cause erroneous observations of slow, steady  $\text{NH}_3$  loss rates, for example: the linear trend of  $\text{NH}_3$ -N loss over time observed from AS and ASN in the field study.

The most plausible explanation for the elevated  $\text{NH}_3$  emissions observed in the field could be the contamination of air above the treatment plots or backgrounds. Four background masts were installed nearly equidistant from each other outside of the northwest, southwest, southeast and northeast quadrants of the field (Fig. 2.1). Treatment plots were placed at least 100 m apart, and background masts were placed at least 100 m away from any treatment plot. Among each of the four blocks of the field,  $\text{NH}_3$ -N loss from all fertilizers was greatest from Blocks 3 and 4, located on the western half of the field and least from Blocks 1 and 2, located on the eastern half of the field. The lowest cumulative  $\text{NH}_3$ -N losses of 9.9% of N applied from AS and 8.6% of N applied from ASN were observed in Block 1, after accounting for background  $\text{NH}_3$ . In all other blocks,  $\text{NH}_3$ -N loss from AS and ASN was not only greater, but followed a slightly similar  $\text{NH}_3$  loss pattern of progression to that of urea, even though this should not be observed due to the absence of urea hydrolysis. Because the  $\text{NH}_3$  loss pattern of AS and ASN deviated from urea in Block 1,  $\text{NH}_3$  measurements from Block 1 were likely less contaminated than the rest of the field. Contamination of treatment plots could not be accounted for or measured by the background masts outside of the field that were only capable of monitoring free convective

NH<sub>3</sub>. Evaluations of possible contamination based on wind direction were also not trustworthy due to the use of off-site wind measurements and wind direction consistency of no more than 50% of any one sampling period. Therefore, NH<sub>3</sub> loss estimates from Block 1 are likely more accurate than those from Blocks 2, 3 and 4.

While the magnitude of NH<sub>3</sub>-N loss differed between the field and laboratory studies, the laboratory results supported the relative differences among alternative fertilizers observed in the field. The laboratory study was more reflective of the efficacy of alternative fertilizers to reduce NH<sub>3</sub> volatilization vs. urea than the field study due to less variation related to the within-field soil characteristics, potential background NH<sub>3</sub> contamination, variable wind speed and direction and storms. The low magnitude of NH<sub>3</sub>-N loss observed in the laboratory resulted from the lack of environmental drivers of NH<sub>3</sub> volatilization that were present in the field study, with the exception of evaporation from pre-moistened soil. The absence of wind also prevented a flux estimation to be calculated. Soil used in the incubation study had not previously been farmed, and was devoid of debris, rocks and crop residue, contrasting to the soil of the field study that contained plowed wheat straw. The laboratory study showed that alternative fertilizers AS, ASN, PCU and SCU reduced NH<sub>3</sub> loss to nearly zero and these fertilizers could potentially be worth more per unit of N than urea. Fused urea(AS) was not effective in reducing NH<sub>3</sub> loss vs. urea alone. Minimal or no NH<sub>3</sub> loss occurred from any of the fertilizers after 25 DAA.

The alternative N fertilizers evaluated in this study could provide significant environmental and economic benefit by retaining N for crop use that would otherwise be lost to the atmosphere from the use of unamended urea. Typical NH<sub>3</sub>-N loss from urea ranges from 30 to 60% of N applied to surface of similar soil with similar management scenarios to the Columbia Basin region (Holcomb, 2011 and Horneck et al., 2011). Urea + NBPT reduced NH<sub>3</sub>-N loss vs urea by at least 30% in this study, which equates to N retention of at least an additional 10% for plants (30% reduction x 30% NH<sub>3</sub>-N loss). For alternative fertilizers that reduced NH<sub>3</sub>-N loss by more than 60% vs. urea, an additional 18% of N could be saved for plants (60% reduction x 30% NH<sub>3</sub>-N loss).

## CONCLUSIONS

This study provided quantification of NH<sub>3</sub>-N loss from a variety of alternative N fertilizers to urea in the semi-arid climate of the Columbia Basin. Published quantifications of NH<sub>3</sub>



volatilization from many of the alternative N fertilizers evaluated in this study have been limited and variable. We found that NBPT is capable of reducing  $\text{NH}_3$  loss vs. urea by more than 30%, and other alternative fertilizers, AS, ASN, SCU and PCU are capable of reducing  $\text{NH}_3$  loss vs. urea by more than 50%. According to the results of both the field and laboratory studies, the benefit of partially substituting urea with AS is less predictable.

The certainty that alternative N fertilizers can reduce  $\text{NH}_3$  loss compared to urea depends on the interaction of their specific chemistries with the environments they are used in, and therefore, further evaluations of these fertilizers will be required in different environments to gain understanding of average expected  $\text{NH}_3$ -N loss. Growers will typically surface-apply N fertilizer in fall or spring when irrigation water is not available to incorporate it. Incorporation instead occurs when fertilizer application has been timed with a forecasted rainfall. We evaluated  $\text{NH}_3$  loss from urea and alternative fertilizers in Aug. and Sept., which are unrealistic fertilization times, because our focus was to measure relative  $\text{NH}_3$  loss with limited and late rainfall. Within 15 DAA,  $\text{NH}_3$ -N loss from urea averaged 33.6% of N applied in the field study. In this same time frame, NBPT and alternative fertilizers AS, ASN, SCU and PCU reduced  $\text{NH}_3$  loss vs. urea by more than 50% in both the laboratory and the field. Because the risk of  $\text{NH}_3$  loss is greater within the first 15 DAA of applying urea fertilizers, it is best to apply fertilizer in accordance with rain. In situations where rain remains elusive, this study offers certainty from both field and laboratory tests that adding NBPT to urea or using alternative N fertilizers of AS, ASN, SCU or PCU will limit  $\text{NH}_3$  volatilization from similar soils and climates, resulting in less error in N fertilization rate for crops in the absence of free lime and less N loading to the environment. More complete evaluations of total N availability for crops should consider other soil types (i.e. calcareous), other pathways of N loss (i.e. leaching of  $\text{NO}_3^-$ ), and current price or availability of the alternative fertilizer.

#### ACKNOWLEDGEMENTS

Funding for this research was provided by J.R. Simplot Company, Koch Agronomic Services, LLC, Two Rivers Terminal, LLC, and Yara North America, Incorporated. Madison Farms of Echo, Oregon provided their field for this experiment.

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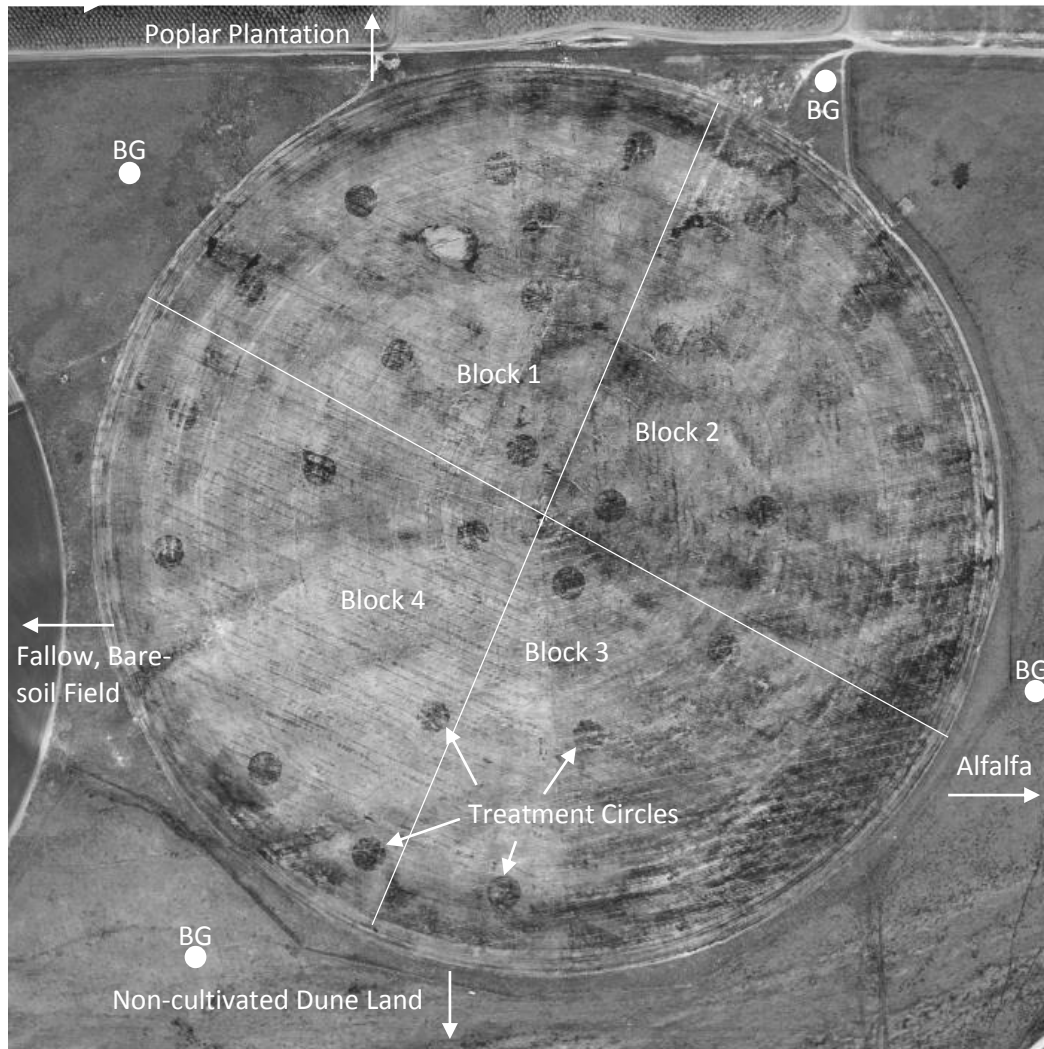
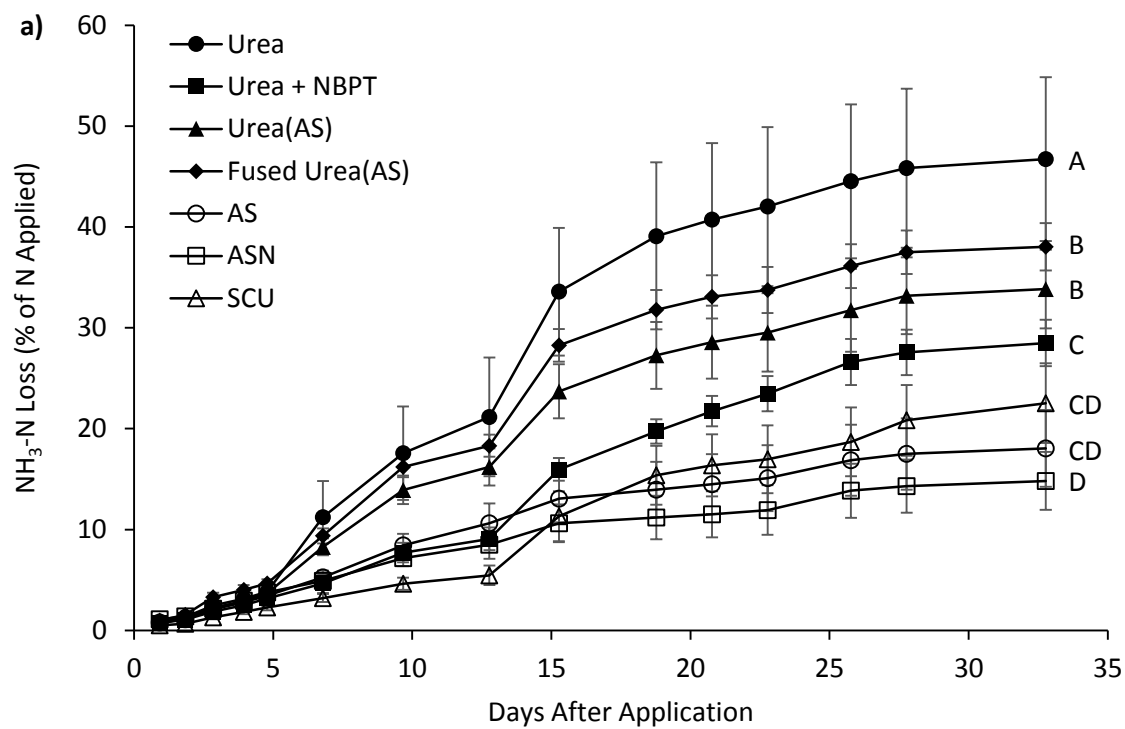


Figure 2.1. Aerial image of the 50 ha field site taken one week following conclusion of experiment. Lines delineate the division of blocks, and small circles of increased vegetation indicate the location of circular treatment plots. Surroundings consisted of a hybrid poplar tree (*Populus spp.*) plantation 30 m from the north edge of the field; an alfalfa (*Medicago sativa*) field 100 m from the east edge, dune land to the south of the field, and a fallow, 55 ha field positioned 30 m from the west edge of the experiment site. Background measurement locations are indicated with white dots next to "BG".





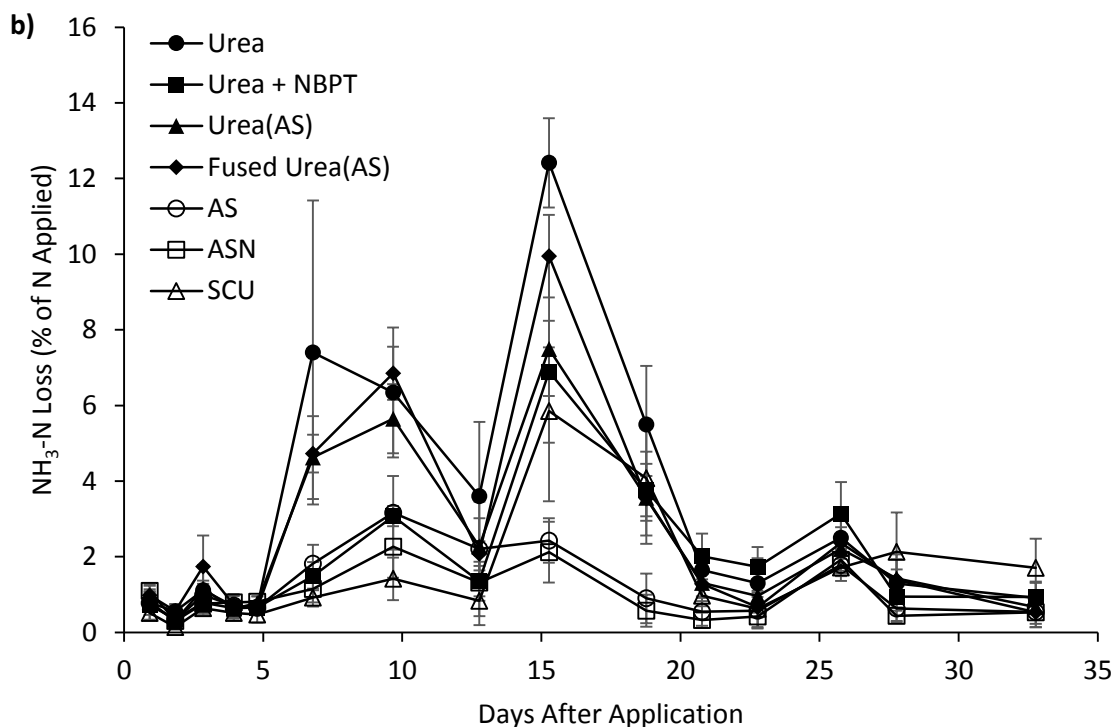


Figure 2.2. Average (a) cumulative and (b) daily  $\text{NH}_3$  loss between the period of Aug. 20 and Sept. 25, 2013, following application of 7 different N fertilizer treatments applied at a rate of  $168 \text{ kg N ha}^{-1}$  to Irrigon fine sandy loam soil containing plowed wheat straw to a 10 cm depth. Treatments applied were 1) urea, 2) N-(n-butyl) thiophosphoric triamide (NBPT)-coated urea (urea +NBPT), 3) urea partially substituted with 21% ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ) (AS), bulked (urea(AS)), 4) a chemically reacted, homogenous granule of urea(AS), 5) AS, 6) chemically reacted AS and ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) (AN) in a fused granule (ASN), and 7) sulfur-coated urea (SCU). Letters following the lines indicate significant differences in cumulative  $\text{NH}_3$  loss between treatments according to LSD at  $P = 0.05$ .

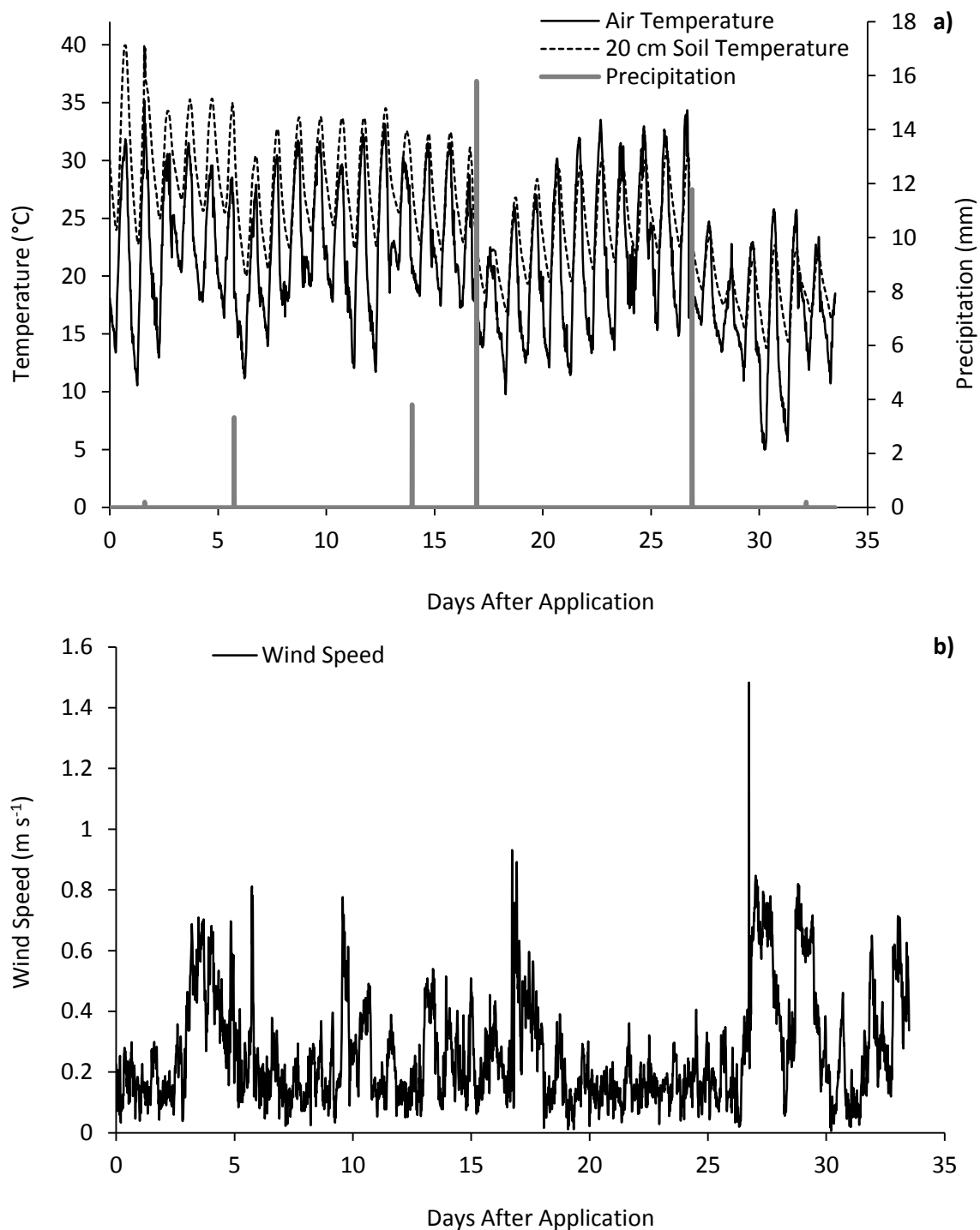


Figure 2.3. (a) Average 15-min air temperature, soil temperature (at 20 cm depth), and daily precipitation, and (b) average 15-min wind speed during the study period of Aug. 20 to Sept. 25, 2013. Wind speed measurements taken 6 km from field site location.

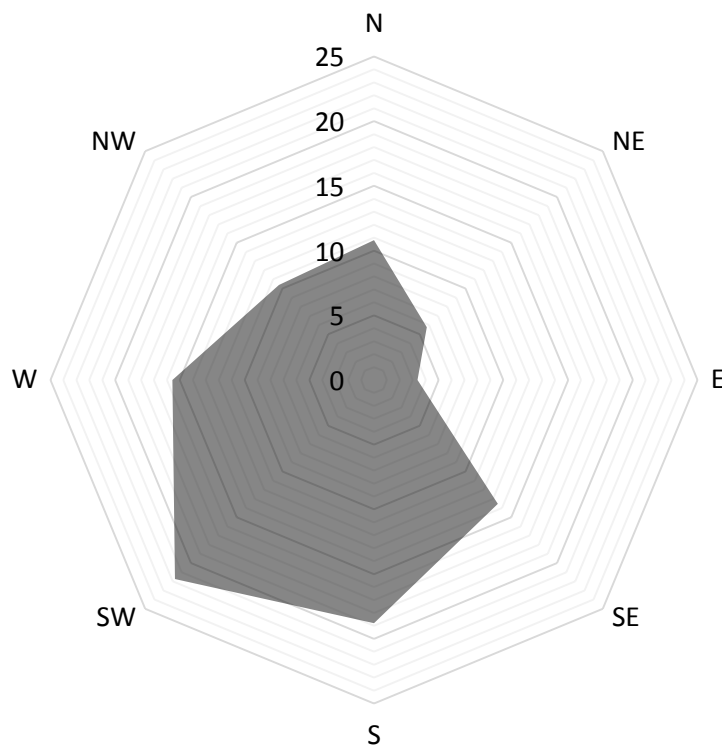
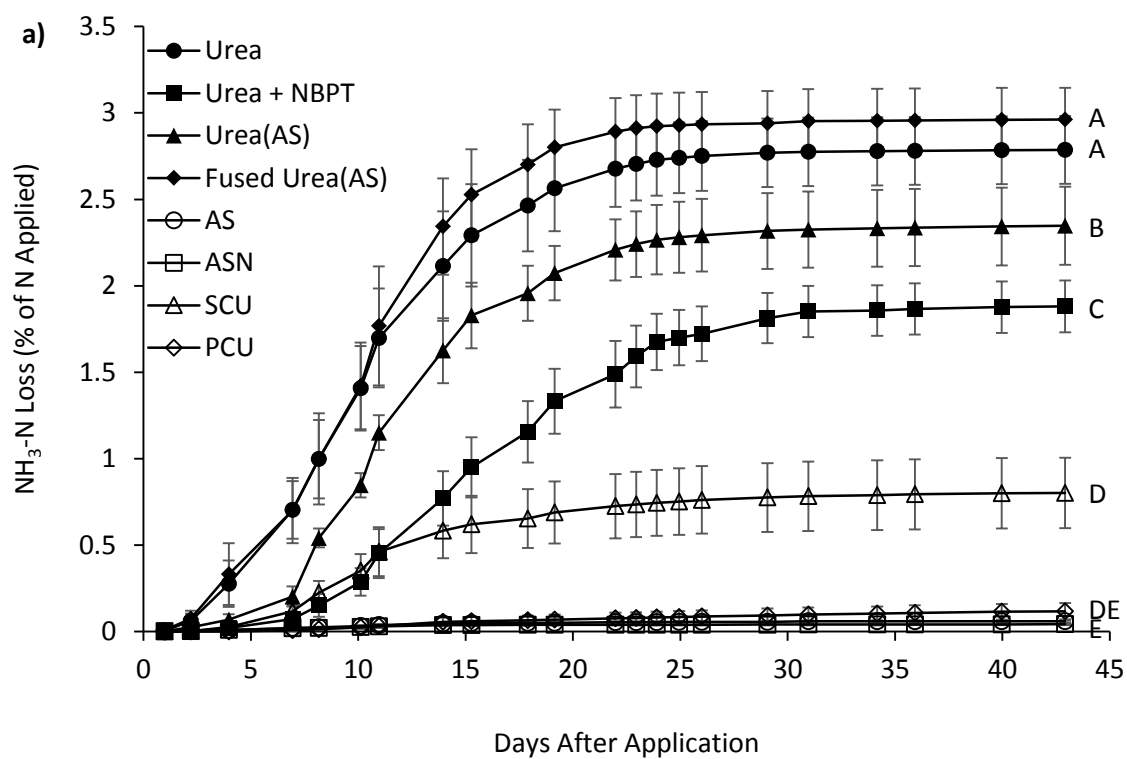


Figure 2.4. Percentage of 15-min wind direction measurements among north (N), northeast (NE), east (E), southeast (SE), south (S), southwest (SW), west (W), and northwest (NW) directions during the study period of Aug. 20 and Sept. 25, 2013.



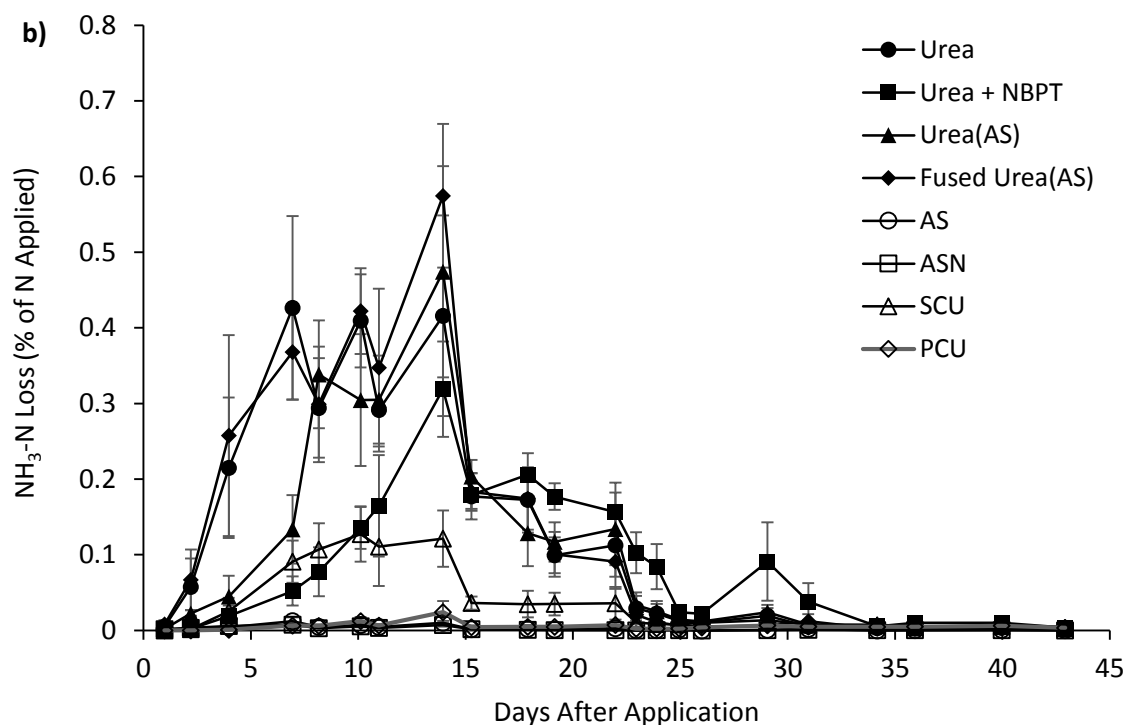


Figure 2.5. Average (a) cumulative and (b) daily  $\text{NH}_3$  loss from laboratory investigation of eight N fertilizer treatments applied at a rate of  $168 \text{ kg N ha}^{-1}$  to Adkins fine sandy loam soil and an unfertilized control of bare soil in chambers incubated at  $15.6^\circ\text{C}$ . Treatments applied were 1) urea, 2) N-(n-butyl) thiophosphoric triamide (NBPT)-coated urea (urea + NBPT), 3) urea partially substituted with 21% ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ) (AS), bulked (urea(AS)), 4) a chemically reacted, homogenous granule of urea(AS), 5) AS, 6) chemically reacted AS and ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) (AN) in a fused granule (ASN), 7) sulfur-coated urea (SCU), and 8) polymer-coated urea (PCU). Letters following the lines indicate significant differences in cumulative  $\text{NH}_3$  loss between treatments according to LSD at  $P = 0.05$ .

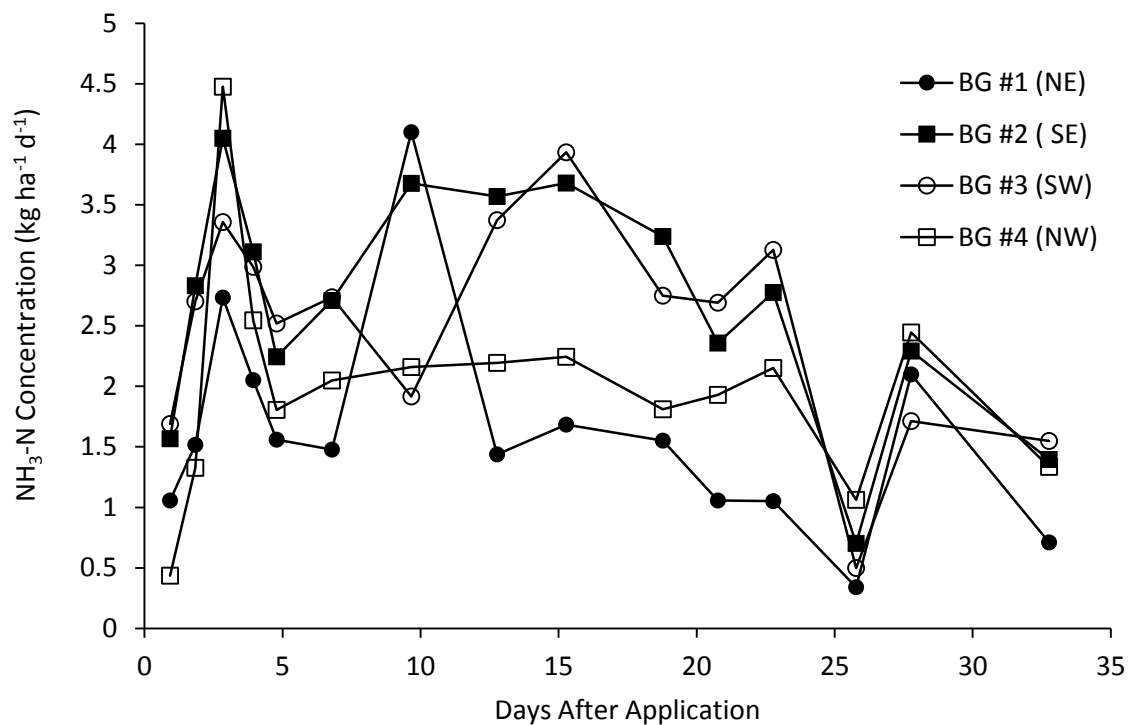


Figure 2.6. Ammonia concentrations measured by each background mast in the northeast (NE), southeast (SE), southwest (SW), and northwest (NW) locations outside of the field site.

Table 2.1. Averages or ranges of NH<sub>3</sub>-N loss from N fertilizer sources

Authors	Environment	NH <sub>3</sub> -N loss <sup>†</sup>						
		Urea	Urea + NBPT	Urea (AS)	AS	AN	SCU	PCU
-----% of N applied-----								
Dawar et al., 2011	Grazed pasture; silt loam soil	17-19	5-6					
Engel et al., 2011	Semi-arid field; cold, sandy loam soil	3-44	6.9					
Frame, et al., 2012	Laboratory incubation; silt loam soil	34-37	18-24				19-35	
Grant et al., 1996	Wheat field; sandy loam soil	38-83	3-13					
Gezgin, et al., 1995	Wheat field; calcareous soil	4-12	1-6		14-20	4-6		
Hargrove et al., 1977	Bermudagrass field; calcareous clay soil				36-45	3-10		
Harrison and Webb, 2001	Review of field investigations	6-47			2-18	<4		
Hayashi et al., 2011	Wheat field; clay loam soil				<1			
He et al., 1999	Laboratory Incubation; fine sandy soil	21			22	18		
Holcomb, 2011	Irrigated wheat and grass fields; fine sandy loam soil	3-60	4		6			
Jantalia, et al., 2012	Open and semi-open field chambers; clay loam soil	2-3						2-4
Kissel, et al., 2012	Loblolly pine forest chambers; sandy loam soil	4-41						
Knight et al., 2007	Putting green; loamy sand soil	36-40				1-2	13-27	<1-1
Lara-Cabezas et al., 1997	Corn field; clay loam soil	41		23				
Oenema, et al., 1993	Laboratory flux experiment; loamy sand soil	6		5				
Prasad, 1976	Laboratory incubation; various soil textures	8-21			7-17			
Rawluk et al., 2001	Feld chambers; clay loam and fine sandy loam soil	20-50	4-36					
Rochette et al., 2009	Field wind tunnels; silt clay loam soil	10-27	5					4
San Francisco et al., 2011	Laboratory incubation; various soil textures	2-59	4-34			<1-24		
Sanz-Cobena, et al., 2008	Sunflower field; silt loam soil	10	6					
Soares, et al., 2012	Laboratory incubation; cultivated, loam soil	28-37	6-17					
Turner et al., 2010	Wheat field; clay loam soil	10						
Vaio et al., 2008	Tall fescue field; sandy loam soil	12-46						
Vitti, et al., 2002	Laboratory incubation; sandy loam soil	81		46-77				

<sup>†</sup> NBPT, N-(n-butyl) thiophosphoric triamide; AS, ammonium sulfate; Urea(AS), urea partially substituted with AS; AN, ammonium nitrate; SCU/PCU, sulfur/polymer-coated urea.

Table 2.2. Fertilizer treatment details, including N content, form, mode of action to reduce NH<sub>3</sub> volatilization, brand, manufacturer and other information.

Treatment <sup>†</sup>	N Content	Form	Theorized Mode of Action	Brand	Manufacturer	Other Information
Urea	46	Prills	N/A	N/A	N/A	
Urea + NBPT	46	Liquid coat	Urease inhibitor	Agrotain Ultra	Koch Fertilizer, LLC (Wichita, KS, USA)	
Urea(AS)	40	Bulked prills and granules	Nitrification reduces pH	N/A	N/A	79 % urea : 21% AS, contains 5% S
Fused Urea(AS)	40	Fused prills	Nitrification reduces pH	N/A	N/A	79 % urea : 21% AS, contains 5% S
AS	21	Granules	Non-urea product	N/A	N/A	Contains 24% S
ASN	26	Fused prills	Non-urea product	Fūsn	J. R. Simplot (Boise, ID, USA) and Honeywell (Morris Township, NJ, USA)	NH <sub>4</sub> SO <sub>4</sub> ·2(NH <sub>4</sub> NO <sub>3</sub> ) double salt, contains 13% S
SCU	39	Prills	Sulfur coating	N/A	Registered Distributor: Two Rivers Terminal, LLC (Moses Lake, WA, USA)	Contains 12% S
PCU	44	Prills	Polymer coating	ESN	Agrium (Calgary, AB, Canada)	

<sup>†</sup> NBPT, N-(n-butyl) thiophosphoric triamide; AS, ammonium sulfate; Urea(AS), urea partially substituted with AS; Fused urea(AS), chemically reacted, homogenous granule of urea(AS); ASN, chemically reacted AS and ammonium nitrate (AN) in a fused granule; SCU/PCU, sulfur/polymer-coated urea.

Table 2.3. Total  $\text{NH}_3\text{-N}$  loss resulting from field and laboratory experiments of fertilizer treatments and their relative percent reduction compared to urea.

Treatment <sup>†</sup>	Field	Reduction vs. Urea	Laboratory	Reduction vs. Urea
	% of N applied	----%----	% of N applied	----%----
No Fertilizer	-	-	0.02 E	-
Urea	46.7 A*	0	2.80 A	0
Urea + NBPT	28.5 C	39	1.88 C	33
Urea(AS)	33.8 B	28	2.35 B	16
Fused Urea(AS)	38.0 B	19	2.96 A	-6
AS	18.0 CD	62	0.06 E	98
ASN	14.8 D	69	0.04 E	99
SCU	22.5 CD	52	0.80 D	71
PCU	-	-	0.12 DE	96

† NBPT, N-(n-butyl) thiophosphoric triamide; AS, ammonium sulfate; Urea(AS), urea partially substituted with AS; Fused urea(AS), chemically reacted, homogenous granule of urea(AS); ASN, chemically reacted AS and ammonium nitrate (AN) in a fused granule; SCU/PCU, sulfur/polymer-coated urea.

\*Values followed by the same letter are not significantly different according to LSD at  $P = 0.05$ .



**AMMONIA EMISSIONS FROM THE REUSE OF FOOD PROCESSING EFFLUENT ON IRRIGATED  
ALFALFA**

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## ABSTRACT

Effluent from food processing and energy production industries is applied to cropland as an efficient method to conserve water and nutrients. However, ammonia ( $\text{NH}_3$ ) emission resulting from effluent application has not been quantified. The nitrogen (N) use efficiency of crops receiving effluent is estimated to be 70% for regulatory purposes. Our objective was to quantify  $\text{NH}_3$  emission from effluent reuse on center-pivot irrigated alfalfa in the semi-arid Columbia Basin. A backward Lagrangian stochastic (bLS) model was used to calculate  $\text{NH}_3$  emissions from alfalfa fields receiving effluent water (average  $111 \text{ mg L}^{-1}$  total Kjeldahl N content). Effluent from a potato processor, a dehydrated onion processor, and a cogeneration plant were held in a mixing pond, then diluted with river or groundwater prior to application. An ultraviolet-differential optical absorption spectrometer (UV-DOAS) monitored  $\text{NH}_3$  and a three-dimensional sonic anemometer monitored wind speed, direction and temperature downwind of the field site for 43 days, from Jul. 3, 2013 to Aug. 27, 2013. The average  $\text{NH}_3\text{-N}$  emission rate was  $1.4 \text{ kg ha}^{-1} \text{ d}^{-1}$  when effluent was applied vs.  $0.5 \text{ kg ha}^{-1} \text{ d}^{-1}$  from irrigation with river or groundwater irrigation only. The greatest  $\text{NH}_3\text{-N}$  emission rate was observed during harvest of the alfalfa, which averaged  $6.1 \text{ kg ha}^{-1} \text{ d}^{-1}$ . The outcome of this study suggests that  $\text{NH}_3$  emission is significantly greater from effluent irrigation vs. river or groundwater irrigation. Future studies will be required in different crops, environments and effluent compositions to establish more accurate regulatory N budgets for wastewater reuse.

## INTRODUCTION

Water resources have become the focus of legal, ethical, social and economic debate in agriculture due to increasing drought and shifting of agro-ecological zones with climate change (Knowles et al., 2006; IPCC, 2014). Supplemental water applications to crops, or irrigation, allows crops to be grown in arid locations of the world that were previously unsuitable. In the U.S. in 2010, irrigation accounted for approximately 38% of total freshwater withdrawals, with a significant portion used in arid climates of the western U.S. where water, rather than nutrients, is the most limiting resource for crop production (Maupin et al., 2014). Water is not only a limiting resource for agriculture, but also related food processing and energy industries, which accounted for a combined 42% of total U.S. freshwater withdrawals in 2010 (Maupin et al.,

2014). Of all freshwater withdrawals, agriculture accounts for 80 to 90% of true consumption via evapotranspiration, whereas most of the water used by food processing and energy industries is returned to its source (Schaible and Aillery, 2012). Effluent generated by industries cannot be returned to freshwater sources before extensive and costly treatment measures that consist of oxygenation, microbial digestion, or disinfection. Microorganisms in soil are also capable of decomposing the organic material in effluent with minimal pollution hazards (Smith, 1976). The chemical composition of food processing effluent varies, but typically consists of low concentrations of metals and salts, and nitrogen (N), phosphorous (P) and potassium (K) levels capable of meeting crop nutrition needs (Fuller and Warrick, 1985). Therefore, value in the conservation of water and nutrients has been realized by reusing effluent as a fertilizer on nearby cropland.

The reuse of industrial effluent as a fertilizer is common in the Columbia River Basin region of OR and WA, especially at the Port of Morrow, near Boardman, OR, where approximately 5,000 ha of crops are grown in close proximity to food processors and energy production industries. The application of effluent to crops is regulated by the Oregon state Department of Environmental Quality (DEQ) to prevent overloading and subsequent pollution of groundwater, public areas and other ecosystems. The DEQ permits a maximum application rate and total application volume of effluent assuming that the short-term N uptake efficiency is approximately 70% of N applied. This assumption equates wastewater effluent application to an efficient N fertilizer application. Crop N uptake efficiencies greater than 60% in season of application are considered highly efficient for many crops. Processes contributing to less than 100% N uptake efficiency include nitrate ( $\text{NO}_3^-$ ) leaching, ammonia ( $\text{NH}_3$ ) volatilization, and immobilization of N in soil organic matter.

In the Columbia Basin, most soils are neutral to alkaline in pH and sandy-textured, favoring  $\text{NH}_3$  volatilization. The Port of Morrow has been designated as a Groundwater Management Area (GWMA) by the OR DEQ because of confirmed groundwater  $\text{NO}_3^-$  contamination. As a result, soil  $\text{NO}_3^-$ -N concentrations are monitored in cropping systems under DEQ permit, including those receiving effluent. Ammonia loss resulting from effluent irrigation has not previously been determined, and is assumed to be minimal. Ammonia loss can occur from volatilization of soluble  $\text{NH}_3$  in effluent or when the organic, protein-based N forms in effluent mineralize into ammonium ( $\text{NH}_4^+$ ) products in soil (Myrold and Bottomley, 2008). The assumption of minimal  $\text{NH}_3$ -N loss from effluent stems from knowledge that  $\text{NH}_4^+$  from acidic

(pH < 5) effluent is not likely to convert to  $\text{NH}_{3(g)}$ , and N from effluent moves into soil when applied with more than 1.25 cm of (Harper et al., 1983; Kissel et al., 2008). The formation of  $\text{NH}_{3(g)}$  occurs when  $\text{NH}_4^+$  dissociates a proton ( $\text{H}^+$ ), a reaction that increases at pH values above 7, with a pKa of 9.25 at 25°C (Kissel et al., 2008). Based on this reaction, substantial  $\text{NH}_3\text{-N}$  loss could occur from the application of effluent to the characteristically alkaline pH soils of the Columbia Basin. Volatilized  $\text{NH}_3$  from fertilizers, including effluent, can react with  $\text{NO}_x$  and  $\text{SO}_x$  gases to produce fine (<2.5  $\mu\text{m}$ ), light-scattering aerosol particles that are responsible for haze, adverse effects on cardiopulmonary health, and alteration of N-sensitive ecosystems where it is deposited (Asman et al., 1998; Ferm, 1998; Finlayson-Pitts and Pitts, 1999; Fenn et al., 2003; Krupa, 2003; Pope and Dockery, 2006; Geiser and Neitlich, 2007). For example, N-eutrophied forests in the Columbia River Gorge, west of the Port of Morrow, responded to increased N inputs with increased prevalence of nitrophilous and non-native lichen communities (Fenn et al., 2007).

Several investigations of  $\text{NH}_3$  volatilization from manure effluent applied to crops have reported average  $\text{NH}_3\text{-N}$  loss rates of up to 85% of total  $\text{NH}_4\text{-N}$  applied (Lauer et al., 1976; Schilke-Gartley and Sims, 1993; Robinson and Polglase, 2000; Sharpe and Harper, 2002). Post-application transformations and processes of municipal and food processing effluent-N have also been investigated (Adamczyk, 1977; Smith et al., 1977; King, 1984; Keith and Lehman, 1986; Crites et al., 2000; USEPA, 2006). Information is not available, however, on  $\text{NH}_3$  volatilization resulting from food processing effluent applied to crops. Of all the crops permitted for effluent application, alfalfa (*Medicago sativa*) is one of the most common and most efficient at removing N (USEPA, 2006). The overall objective of this study was to quantify  $\text{NH}_3\text{-N}$  loss from the reuse of food processing effluent on alfalfa fields near the Port of Morrow, OR.

## MATERIALS AND METHODS

### Field Sites

This study took place on two fields, consecutively, between Jul. 3 and Aug. 27, 2013 at a commercial farm at the Port of Morrow, in Morrow County, OR. Both fields were mapped as Quincy loamy fine sand (mixed, mesic Xeric Torripsamments), 2 to 12% slopes, and delivered irrigation and effluent water through center-pivot sprinkler systems that rotated about each

field on a 24-hr schedule. Irrigation water was sourced from either the Columbia River (river) or groundwater wells (well). Groundwater at the farm contains 35 to 50 mg L<sup>-1</sup> NO<sub>3</sub><sup>-</sup>-N concentrations. An analysis of the effluent was provided between the months of Apr. and Jun., which reported an average of 111 mg L<sup>-1</sup> total Kjeldahl N, with 34% in the form of NH<sub>4</sub><sup>+</sup> and an average pH of 4.6. The effluent was supplied by a potato processor, a dehydrated onion processor, a creamery, and a cogeneration plant. The effluent was not analyzed for any other nutrients. Pure effluent was never directly applied; rather it was mixed with varying volumes of river or well irrigation water to dilute the acidity of the effluent and to achieve an overall N application rate of approximately 8 kg ha<sup>-1</sup> d<sup>-1</sup>. The timeline of effluent applications and different events for each field are presented in Table 3.1 and described in the following.

The initial investigation took place for 12 days, from Jul. 3 to Jul. 14, 2013 on a 33 ha field (Field 1) split between 13 ha of alfalfa on the north, and 20 ha of corn (*Zea mays*) on the south. Effluent was applied only to the 13 ha of alfalfa. The field was centrally located on the farm and surrounded by several larger, irrigated and cultivated fields. Measurements began on Field 1 during an application of effluent and river water irrigation. A total effluent-N application of approximately 60 kg ha<sup>-1</sup> was applied by Jul. 9, when irrigation transitioned to river water only. River water irrigation continued through the conclusion of the study on Jul. 14. The alfalfa grew from approximately 17.5 to 23.0 cm during the Field 1 study.

After the initial investigation on Field 1, monitoring equipment was moved to a larger, more remote field (Field 2) to reduce the risk of background NH<sub>3</sub> contamination. Field 2 also provided a more homogenous source area, with a 51 ha crop of only alfalfa. Ammonia emissions from Field 2 were monitored for 31 days between Jul. 27 and Aug. 27, 2013. Measurements began during river water irrigation on Jul. 27. On Aug. 1, irrigation was turned off, and neither irrigation nor effluent was applied again until Aug. 10. Between Aug. 1 and 10, the alfalfa was harvested by first being cut (Aug. 1), laid in rows to dry (Aug. 2), rows turned to continue drying (Aug 5), rows baled (Aug. 7), and finally bales removed from field (Aug. 9). Tractors were used in the field for all harvest processes. Irrigation began again on Aug. 10, from groundwater wells. Effluent and well-water irrigation was applied on Aug. 13 through the conclusion of the Field 2 study on Aug. 27, totaling to 56 kg ha<sup>-1</sup> effluent-N applied. The alfalfa grew to approximately 87 cm by harvest on Aug. 1, when it was cut to approximately 5 cm above ground. At the conclusion of the study on Aug. 27, the alfalfa had regrown to approximately 73 cm.

## Instrumentation and Measurements

We used a backward Lagrangian stochastic (bLS) micrometeorological technique to calculate  $\text{NH}_3$  flux from the alfalfa fields receiving effluent (Flesch et al., 2004). The bLS model determines gas emissions from a source area ( $Q \text{ kg d}^{-1}$ ) by calculating  $N$  upwind “particle” trajectories from downwind mixing-ratio concentrations ( $C \text{ ppm}_v$ ) measured in excess of background. Particle trajectories depend on the wind environment at the study site, which is described by Monin-Obukhov similarity theory (MOST) key parameters of  $u^*$ ,  $L$ ,  $z_0$ , and  $\theta$ , where  $u^*$  is the friction velocity ( $\text{m s}^{-1}$ ),  $L$  is the Obukhov stability length (m),  $z_0$  is the surface roughness length (m), and  $\theta$  is the wind direction ( $^\circ$ ) (Garratt, 1992). The MOST parameters were calculated from three-dimensional wind speeds and sonic temperature measured by ultrasonic anemometers (Model 81000V on Field 1, Model 81000VRE on Field 2; R.M. Young Company; Traverse City, MI). Downwind  $\text{NH}_{3(g)}$  concentrations were measured using an open-path, ultraviolet-differential optical absorption spectrometer (UV-DOAS) in a line-average between the UV emitter and detector (UV Sentry; Cerex Monitoring Solutions, LLC, Atlanta, GA). All instruments were installed in the northeast (downwind) region outside of each field, with the UV-DOAS path aligned perpendicular to mean wind; however, separation distances and acquisition frequencies differed between Field 1 and Field 2 (Table 3.2). Background  $\text{NH}_3$  was accounted for with one UV-DOAS measurement on each field from a wind direction that was not from the source area and taken during time periods when effluent was not being applied.

In Field 1, the UV-DOAS was installed at a height of 1.5 m, 24.0 m from the edge of the field, and 7.6 m from the edge of the pivot irrigation spray zone. The line-average separation distance between the UV emitter and detector was 24.4 m, and average  $\text{NH}_3$  concentrations were recorded every minute. The sonic anemometer used on Field 1 was installed near the UV-DOAS, at a height of 3.0 m and 32 m from the edge of the field. Wind speed, sonic temperature and statistics were recorded in 15-min intervals. At the conclusion of the Field 1 study, the UV-DOAS was moved to the same general northeast position outside of Field 2, at a height of 1.5 m, 21.3 m from the edge of the field and 14.0 m from the edge of the pivot irrigation spray zone. The emitter and detector were separated by 23.2 m. The sonic anemometer was installed 7.6 m directly upwind of the UV-DOAS path. Measurement acquisition frequencies were increased in the Field 2 study for both the sonic anemometer and the UV-DOAS in order to better examine data quality. Average  $\text{NH}_3$  concentrations were recorded by the UV-DOAS every 10 s, and the

sonic anemometer measured three-dimensional wind speeds, temperature and statistics at 20 Hz. Additional 15-min measurements of precipitation were sourced from an Agrimet weather station (Bureau of Reclamation; Boise, ID) located approximately 9 km east of the field sites.

## Data Processing

We used interactive software, WindTrax (Thunder Beach Scientific, Nanaimo, Canada), to calculate the  $\text{NH}_3$  emission rates in this study. WindTrax combines the bLS technique with a mapping interface for sensors and source areas. Satellite imagery was used to map each field and place sensors in their correct locations with the interface. Each 15-min average collection of downwind  $\text{NH}_3$  concentration and MOST parameters were used in a bLS model that calculated the upwind trajectory of 50,000 particles through the UV-DOAS path. Details of the calculations of the MOST input parameters from the original wind data are described in Flesch et al. (2004). Daily surface roughness length,  $z_0$ , was estimated based on a linear logarithmic relationship to crop height, described in a review by Plate (1971). A linear daily growth rate was assumed between the crop heights measured immediately before and after harvest. Values for ambient atmospheric pressure and temperature were required to convert  $\text{NH}_3$  mixing-ratio concentrations ( $\text{ppm}_v$ ) to absolute concentrations ( $\text{mg kg}^{-1}$ ). We used the sonic temperature of each 15-min observation period, and one average ambient atmospheric pressure of 105 kPa for all observations on both Field 1 and Field 2, estimated from an elevation of approximately 105 m above sea level.

The MOST parameters were also used to filter error-prone observations under free convective and very stable conditions, including Obukhov stability length,  $|L| \leq 10$  m and frictional wind speed,  $u^* \leq 0.15 \text{ m s}^{-1}$ . The observation periods were also filtered by wind direction to include only those from the direction of the source alfalfa fields, between 110- and 360°. Resulting filtered  $\text{NH}_3\text{-N}$  loss calculated by the bLS model was plotted in a time-series, and  $\text{NH}_3\text{-N}$  emissions corresponding to each field event were averaged. We assumed that averaging the emission results strictly between the monitoring dates of each field event transition (effluent to irrigation to harvest, and so on) would incur significant interference from the previous event, i.e., the complete application of irrigation following effluent or harvest required a 24-hr period for the pivot irrigation system to rotate around the field. To reduce this overlap,

only observations within more discrete monitoring windows, separated by at least 24 hours, were used to investigate  $\text{NH}_3$  emissions corresponding to each field event.

## RESULTS AND DISCUSSION

### Environmental Conditions

Environmental conditions at the field site were ideal to enhance N mineralization and subsequent  $\text{NH}_3$  volatilization, and were similar during the monitoring periods of Field 1 and Field 2 (Table 3.3). During the Field 1 investigation, wind speed (15-min average results) fluctuated between 0.2 and 7.2  $\text{m s}^{-1}$  with an average of 2.7  $\text{m s}^{-1}$  (Fig. 3.1a). Air temperature ranged between 9.5 and 36.0°C, with an average of 24.1°C (Fig. 3.1b). There were no precipitation events during the Field 1 study. Total precipitation during the Field 2 study amounted to only 2 mm, accumulated from Aug 21 to Aug. 22. Wind speed fluctuated between 0.0 and 9.0  $\text{m s}^{-1}$ , with an average of 2.0  $\text{m s}^{-1}$  (Fig. 3.2a). Average air temperature was 24.0°C, and ranged from 12.0 to 36.0°C (Fig. 3.2b). Unfortunately, wind measurements were not recorded between the dates of Jul. 23 and Jul. 28; therefore, emissions could not be calculated during this time period. Approximately 15% (167 out of 1114) of 15-min observations on Field 1 and 35% (1000 out of 2877) of 15-min observations on Field 2 were valid according to MOST criteria.

The MOST criteria used to filter observations in this study eliminated a substantial portion of overall 15-min observations. On Field 1, 24% of 15-min observations were not from the wind direction of the source area. Of the remaining measurements, 62% were removed with  $|L| \leq 10 \text{ m}$  and/or  $u^* \leq 0.15 \text{ m s}^{-1}$ . On Field 2, 22% of 15-min observations were removed based on wind direction, while 45% of remaining observations were removed based on  $|L|$  and  $u^*$ . Low values for  $|L|$  and  $u^*$  occurred more often in the transition times from day to night.

### Emissions from Effluent and Irrigation

The  $\text{NH}_3$  emission results from Field 1 events were sufficiently separated after filtering based on MOST criteria; however, results from Field 2 events were calculated from more discrete monitoring dates separated by 24 hours (Table 3.3, Fig. 3.3 and Fig. 3.4). The combined



NH<sub>3</sub>-N emissions from Field 1 and Field 2 averaged 1.4 kg ha<sup>-1</sup> d<sup>-1</sup> from effluent applications and 0.5 kg ha<sup>-1</sup> d<sup>-1</sup> from irrigation. The distributions of 15-min observations during effluent application and irrigation are presented in Fig. 3.5a and 3.5b. Median combined NH<sub>3</sub>-N emissions from effluent observations were approximately 1.3 kg ha<sup>-1</sup> d<sup>-1</sup> from effluent and 0.3 kg ha<sup>-1</sup> d<sup>-1</sup> from irrigation, indicating a skewedness in observations toward greater emission rates. There was a slight, yet opposite, diurnal trend in NH<sub>3</sub> emissions from both effluent and irrigation applications (Fig. 3.7a and 3.7b). Combined average NH<sub>3</sub>-N emissions from effluent were approximately 0.65 kg ha<sup>-1</sup> d<sup>-1</sup> greater at midday than at night, while from irrigation, emissions were approximately 1.0 kg ha<sup>-1</sup> d<sup>-1</sup> less at midday than at night.

Diurnal trends in NH<sub>3</sub> emissions similar to our observations from effluent have been documented by several studies involving manure or other forms of N application to agricultural land. Chantigny et al. (2004) noted a strong diurnal trend in NH<sub>3</sub> volatilization following the application of pig slurry to bare soil, with 60 to 80% greater emissions occurring midday. Hargrove (1988) reviewed several studies of NH<sub>3</sub> emissions from N fertilizers, noting the diurnal trend of maximum NH<sub>3</sub> loss rates occurring between 1000 and 1200 h. Ammonia emissions in general tend to peak near midday in similar latitudes to the field site in this study, coinciding with increasing soil temperatures, atmospheric turbulence, and evapotranspiration (Asman, 1998).

The contradictory diurnal trend of NH<sub>3</sub> emissions observed during irrigation is more difficult to relate to a direct cause than that of effluent observations, as diurnal NH<sub>3</sub> cycling from unfertilized cropping systems is an effect of soil and plant absorption and desorption processes. Bidirectional absorption-desorption of NH<sub>3</sub> depends on the compensation point of plant leaves (between approximately 0.1 to 20 nmol NH<sub>3</sub> mol<sup>-1</sup> air), above which, ambient NH<sub>3</sub> is absorbed by leaves and below which, leaves release NH<sub>3</sub> to the atmosphere (Farquhar et al., 1980; Asman, et al., 1998). This plant-atmosphere flux of NH<sub>3</sub> is quantifiable in the absence of N fertilization, when desorption is not effected by a constant, high ambient NH<sub>3</sub> concentration. Studies investigating NH<sub>3</sub>-N emissions from live plants have reported a highly variable range between 1 and 75 kg ha<sup>-1</sup> d<sup>-1</sup> (Francis et al., 2008). The drastic range in reported NH<sub>3</sub> emissions from live plants has been found to be dependent on crop type (specifically C<sub>3</sub> vs. C<sub>4</sub> photosynthesizing types), N content, pH, growth stage, temperature, C sources and location. Dabney and Bouldin (1990) estimated that alfalfa has a compensation point of 2 nmol NH<sub>3</sub> mol<sup>-1</sup> air based on measured fluxes of NH<sub>3</sub> and NH<sub>4</sub> at 1 m above an unfertilized alfalfa crop. Hanstein et al. (1999)

found that  $\text{NH}_3$  uptake by three different grass species was strongly supported by photorespiration. The magnitude of diurnal  $\text{NH}_3$  exchange is expected to be larger for  $\text{C}_3$  plants than for  $\text{C}_4$  plants (Francis et al., 2008). The unusual diurnal trend in  $\text{NH}_3$  emissions observed during irrigation in our study may be more dependent on factors of N presence in irrigation, and the sudden change in C supplies as effluent transitions to irrigation. Schjoerring et al. (2000) found that sugarbeet (*Beta vulgaris*) plants supplied with  $\text{NO}_3^-$ , rather than  $\text{NH}_4^+$ , had lower apoplastic  $\text{NH}_4^+$  concentrations and were temporarily C-limited in the light as a result of repressed respiration. Because the re-assimilation of  $\text{NH}_3$  in plants depends on the availability of C substrates, it is possible that the swift transition from C-rich effluent to C-poor irrigation water could have caused differences in photorespiration and  $\text{NH}_3$  exchange that are not typical. Effluent is also acidic, compared to the more neutral pH of pure irrigation water. Ammonia exchange is also affected by plant and aqueous phase pH. We did not directly measure the pH of effluent + water vs. water-only irrigation, but the confirmed acidity of the effluent would be expected to contrast with a higher pH in irrigation water.

The bLS micrometeorological technique determined combined  $\text{NH}_3$  emissions from effluent, the alfalfa crop and soil and was not able to strictly measure  $\text{NH}_3$  emissions from any one source. Assigning the measured  $\text{NH}_3$  emissions to a source is confounded by the responses of living plant processes to effluent and irrigation. Additionally, the diurnal pattern observed in both effluent and irrigation could be confounded with the 24-hr rotation of the pivot irrigation system around the fields. The  $\text{NH}_3$  emissions observed from effluent application and irrigation in this study spanned an appropriate number of days and alfalfa growth stages to assume minimal error in their relative differences outside of the possible complex plant interactions that could have occurred, as described above.

#### Emissions from Alfalfa Harvest

The greatest  $\text{NH}_3\text{-N}$  emissions observed in this study were from the period of alfalfa harvest on Field 2, which averaged  $6.1 \text{ kg ha}^{-1} \text{ d}^{-1}$ . The distribution of 15-min observations during the alfalfa harvest are presented in Fig. 3.6. Median  $\text{NH}_3\text{-N}$  emissions from harvest observations were approximately  $5.8 \text{ kg ha}^{-1} \text{ d}^{-1}$ , indicating a skewedness toward greater emission rates. No diurnal trend was apparent during alfalfa harvest.

We observed the release of significantly more  $\text{NH}_3$  during alfalfa harvest than any other period of time in the study, which is most likely a result of senescing plant tissue or contamination from tractors used during harvest. Some studies that have investigated the release of  $\text{NH}_3$  from harvested crops reported high  $\text{NH}_3$  emissions from senescing plants. The greatest  $\text{NH}_3$  emissions occur from high N status crops that become decomposed in moist or humid environments (Francis et al., 2008). Janzen and McGinn (1991) found as much as 14% of alfalfa-N can volatilize into  $\text{NH}_3$  when cut and used as a green manure. Less than 1% of herbage-N actually volatilizes into  $\text{NH}_3$  when plant material is dried rather than decomposed, however, such as the situation with alfalfa harvested for forage hay production (Whitehead et al., 1988). Dabney and Bouldin (1985) determined that harvest of alfalfa emitted an additional  $2.3 \text{ kg } \text{NH}_3\text{-N ha}^{-1}$  above typical emissions from live alfalfa. Mattsson and Schjoerring (2003) predicted the  $\text{NH}_3$  compensation point of dead or senescing plant tissue by investigating apoplastic  $\text{NH}_4^+$  concentrations from cut and senescing leaves. They predicted that leaves with a relatively high N status (C:N = 10:1) could release 6 to  $8 \text{ nmol } \text{NH}_3 \text{ mol}^{-1} \text{ air}$ . The alfalfa in our study had a C:N ratio of 13:1, estimated from 20% crude protein content in bale samples. It is also possible that tractor exhaust or dust produced by harvest activities could have caused interference or similar absorption spectrums with the UV-DOA  $\text{NH}_3$  measurements. Generally, research indicates that cut alfalfa in the environmental conditions prevailing at our field site can be expected to release considerable levels of  $\text{NH}_3$ .

## CONCLUSIONS

Ammonia emissions from the reuse of food processing effluent on crops have received limited investigation in the Columbia Basin, and this study provided an initial idea of expected emission rates. We observed an average  $\text{NH}_3\text{-N}$  emission rate from effluent applied to alfalfa of  $1.4 \text{ kg } \text{ha}^{-1} \text{ d}^{-1}$ , which was  $0.9 \text{ kg } \text{ha}^{-1} \text{ d}^{-1}$  greater than emissions during irrigation without effluent. This study also confirmed that alfalfa harvest releases significant amounts of  $\text{NH}_3$ . We observed an average  $\text{NH}_3\text{-N}$  emission rate of  $6.1 \text{ kg } \text{ha}^{-1} \text{ d}^{-1}$  over an 8-d harvest process of cutting, drying and baling alfalfa for hay production. Several interactions involving movement of  $\text{NH}_3$  among the soil-plant-atmosphere system could have caused difficulty in direct comparisons of measured  $\text{NH}_3$  between irrigation vs. effluent. These interactions could be better understood in future studies by directly measuring the pH, C and N content of all irrigation and effluent

treatments as they are being applied to the crop through the irrigation system. Past studies have established a range of expected values for the soil-plant-atmosphere  $\text{NH}_3$  exchange, but this information is particularly limited for alfalfa. It may also be possible to capture  $\text{NH}_3$  emissions from soil and plants individually by incorporating other non-micrometeorological measurement techniques, such as field chambers. The objective of this study was to quantify  $\text{NH}_3$ -N emission from effluent applied to crops in a field setting with the contribution of typical environmental conditions; a situation suitable for the bLS micrometeorological technique.

While the process of applying effluent to crops is overall more efficient than treating and discharging effluent water back to a freshwater source, the prolonged use of effluent could cause environmental loading of  $\text{NH}_3$  that will require continued monitoring and mitigation in the future if emissions are determined significant. Industrial effluent application to crops will continue to become more common, for example: The effluent reuse system at the Port of Morrow is expected to increase in capacity by 100% in the near future. We did not quantify the  $\text{NO}_3$  leached, greenhouse gas,  $\text{N}_2\text{O}$ , and other  $\text{NO}_x$  species that might be produced by the reuse of effluent. Despite accounting for background emissions, we were unable to separate  $\text{NH}_3$  contributions from differences in soil-plant-atmosphere processes between effluent vs. irrigation. Future research of  $\text{NH}_3$  emissions from effluent reuse in agriculture will require investigations of different crops, environments and effluent compositions for accurate regulatory N budgets.

## ACKNOWLEDGEMENTS

The authors wish to thank Frederickson Farms, located in Morrow County, OR for providing the fields for this study.

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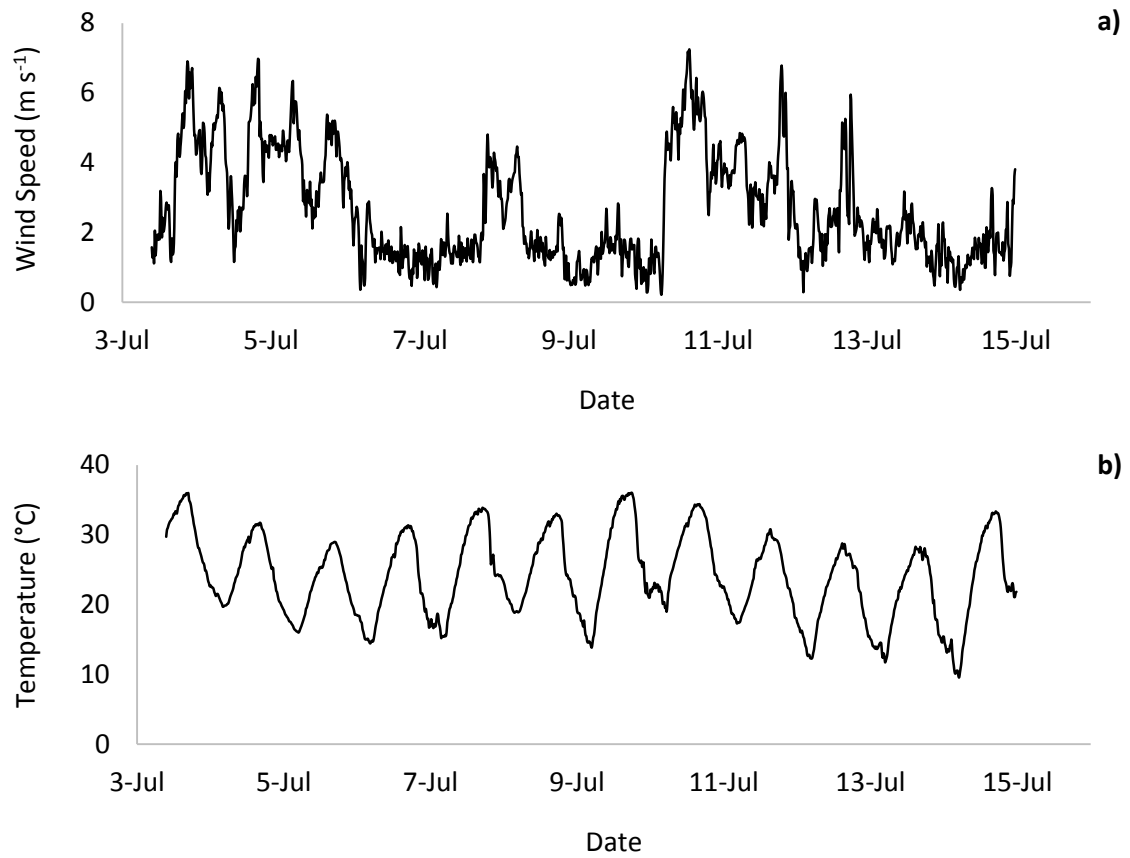


Figure 3.1. Average 15-min (a) wind speed and (b) air temperature during the Field 1 study period of Jul. 3 to Jul. 14, 2013.



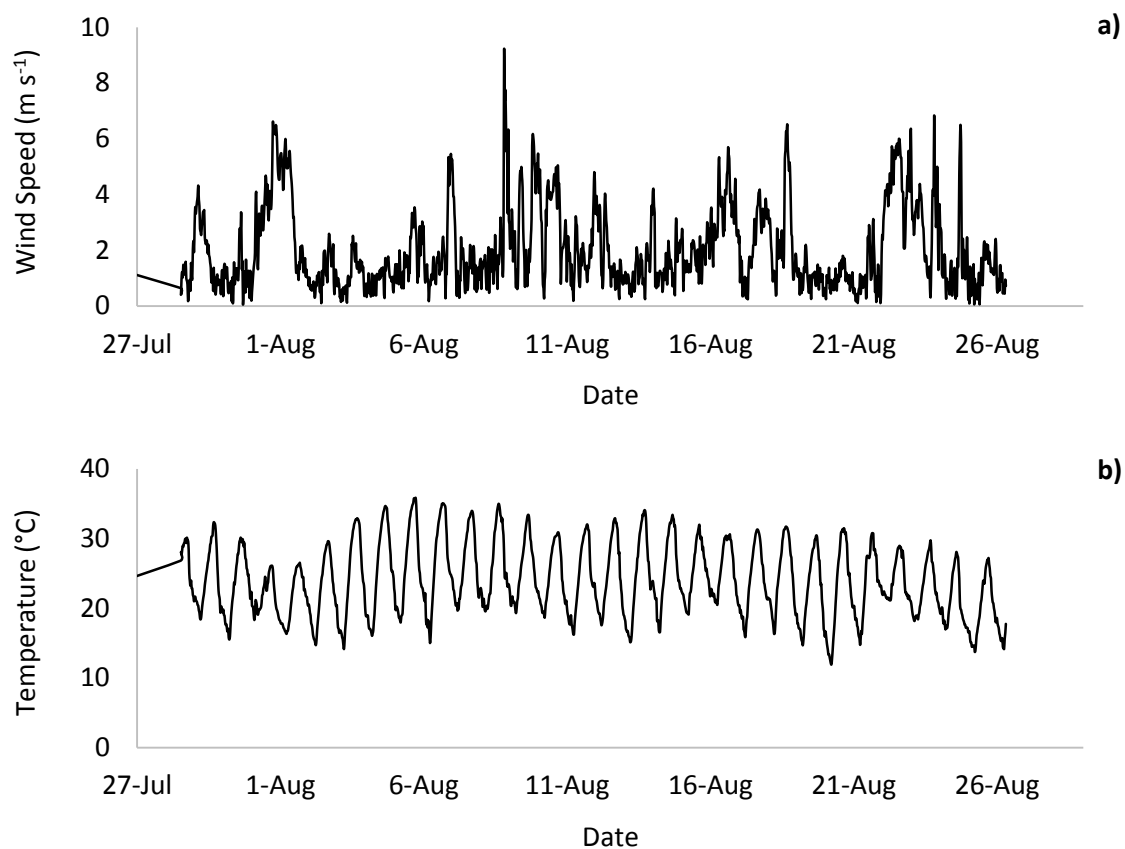


Figure 3.2. Average 15-min (a) wind speed and (b) temperature during the Field 2 study period of Jul. 23 to Aug. 27, 2013.

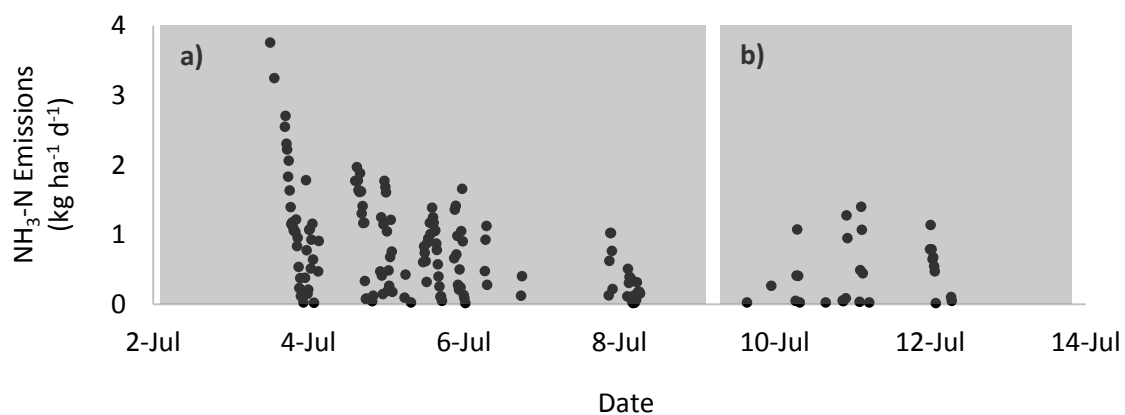


Fig. 3.3 Time-series of 15-min average  $\text{NH}_3\text{-N}$  loss from Field 1 during (a) effluent application and (b) river-sourced irrigation.

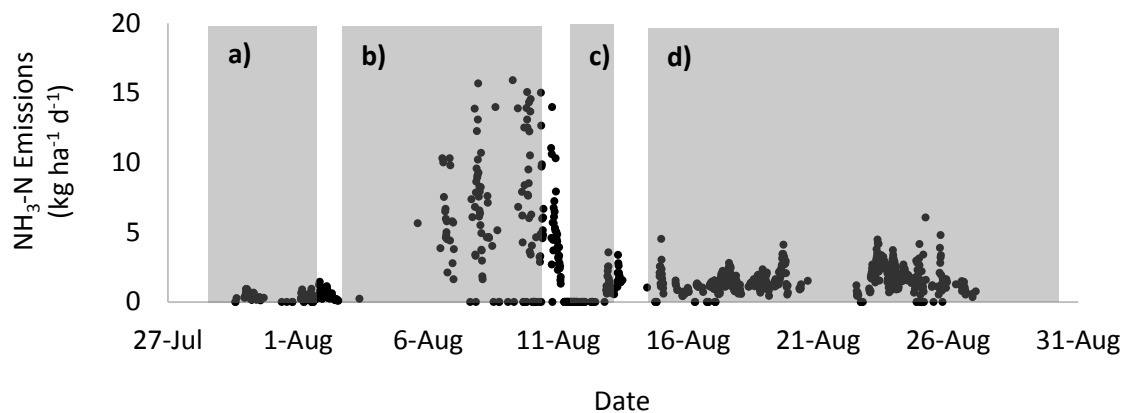


Figure 3.4. Average 15-min NH<sub>3</sub>-N loss of Field 2, through applications of (a) river irrigation, (b) harvest with no irrigation, (c) well irrigation, and (d) effluent mixed with well irrigation. Observations between the grey-shaded areas were within the 24-hr transition between field events, and were not included in further analyses.

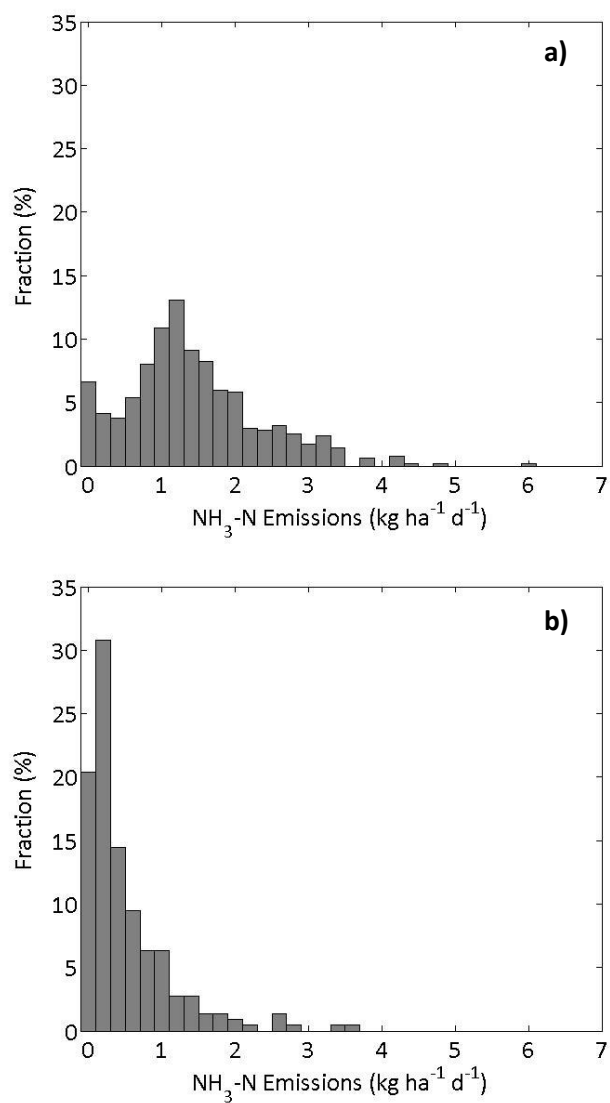


Figure 3.5. Distribution of combined 15-min average  $\text{NH}_3\text{-N}$  emissions from (a) effluent, and (b) irrigation on Field 1 and Field 2 as a fraction of total measurements.

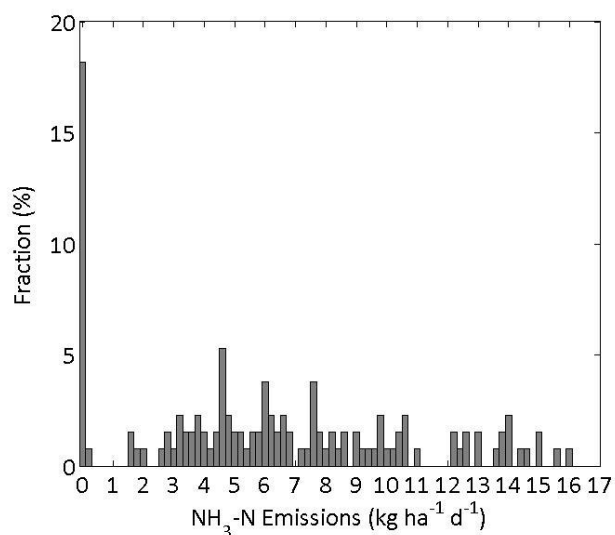


Figure 3.6. Distribution of 15-min average  $\text{NH}_3\text{-N}$  emissions during alfalfa harvest on Field 2 as a fraction of total measurements.

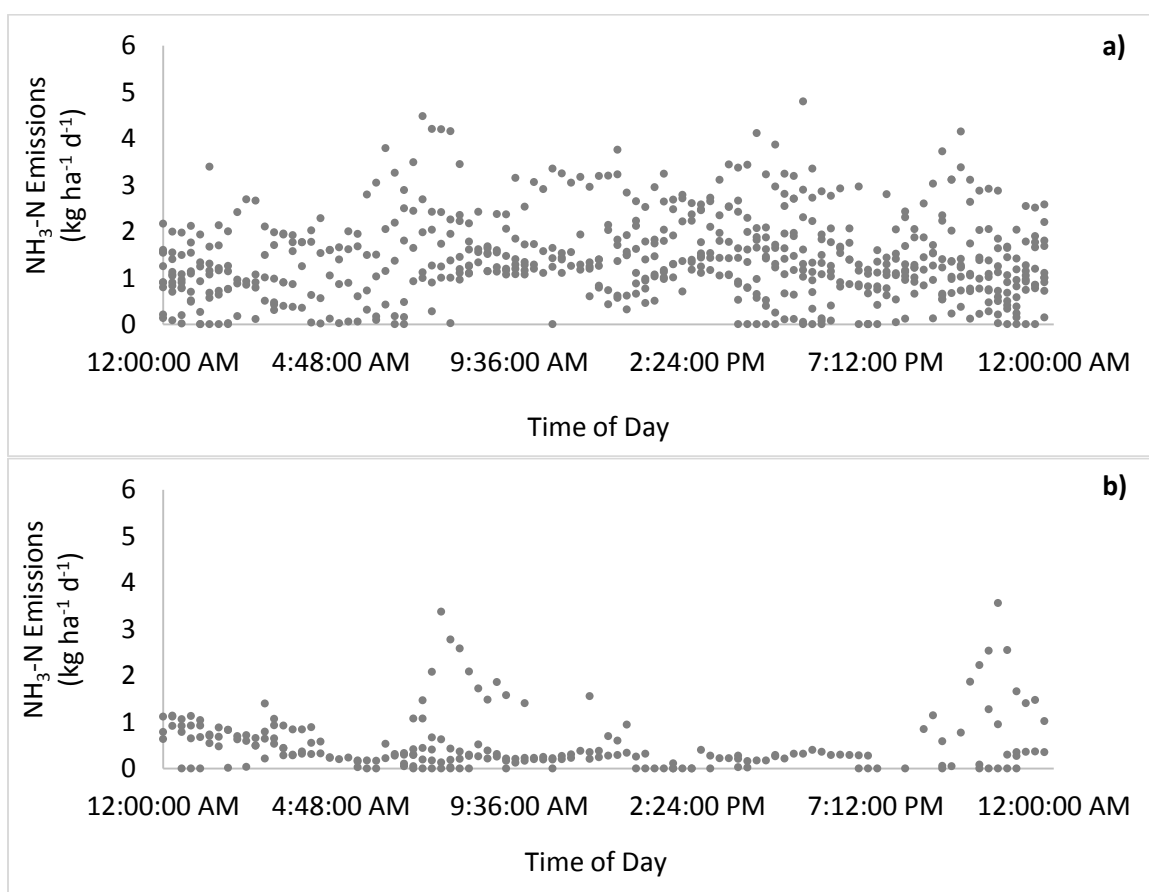


Figure 3.7. Diurnal pattern of  $\text{NH}_3\text{-N}$  emissions during combined observations of (a) effluent application and (b) irrigation on both Field 1 and Field 2.

Table 3.1. Timeline including irrigation sources, effluent-N application rates, crop height, and description of field events.

Monitoring dates	Irrigation sources	Crop height	Field events
		---cm---	
<b>Field 1</b>			
3 Jul. (1330 h)	Effluent + River	17.8	Monitoring begins
9 Jul. (0815 h)	River	20.3	Effluent stops, river water irrigation only
14 Jul. (2200 h)	River	22.9	Monitoring ends
<b>Field 2</b>			
27 Jul. (1900 h)	River	73.3	Monitoring begins
01 Aug. (1900 h)	Off	87.0	Irrigation turned off
02 Aug. (0900 h)	Off	5.00	Harvest begins: Alfalfa cut, laid in rows to dry
05 Aug. (0900 h)	Off	13.2	Harvest: Drying rows turned
07 Aug. (0900 h)	Off	18.7	Harvest: Drying rows baled
09 Aug. (0900 h)	Off	24.1	Harvest ends: Bales removed from field
10 Aug. (1915 h)	Well	26.9	Well water irrigation begins
13 Aug. (1900 h)	Effluent + Well	37.8	Effluent added to well water irrigation
27 Aug. (0900 h)	Effluent + Well	73.3	Monitoring ends

Table 3.2. Instrument placement, separation distances and measurement acquisition frequencies on Field 1 and Field 2.

Measurement	Field 1	Field 2
<b>UV-DOAS<sup>†</sup></b>		
Height above ground level (m)	1.5	1.5
Emitter and detector averaging-path length (m)	24.4	23.2
Distance from field (m)	24.0	21.3
Distance from spray zone edge (m)	7.6	14.0
Measurement frequency (s)	60	10
<b>Ultrasonic Anemometers</b>		
Height above ground level (m)	3	3
Distance from field (m)	32	13.7
Perpendicular distance from UV-DOAS path (m)	8.0	7.6
Measurement frequency (Hz)	1	20

<sup>†</sup> UV-DOAS, Ultraviolet-differential optical absorption spectrometer

Table 3.3. Average and median NH<sub>3</sub>-N emission rates, wind speed, temperature (°C), and monitoring dates for field events on Field 1 and Field 2.

Monitoring dates	Average NH <sub>3</sub> -N emissions	Median NH <sub>3</sub> -N emissions	Weather conditions			Field event descriptions
			Wind speed	Wind direction	Temp	
	kg ha <sup>-1</sup> d <sup>-1</sup>	kg ha <sup>-1</sup> d <sup>-1</sup>	m s <sup>-1</sup>	degrees	°C	
<b>Field 1</b>						
3 Jul .(1330 h) to 9 Jul. (0830 h)	0.82 (0.69)†	0.72	2.79 (1.63)	200 (79)	24.2 (5.65)	Effluent + River
9 Jul (0900 h) to 14 Jul (2200 h)	0.46 (0.43)	0.41	2.52 (1.51)	201 (66)	23.7 (6.48)	River Irrigation
<b>Field 2</b>						
28 Jul (1915 h) to 1 Aug (1900 h)	0.31 (0.22)	0.27	1.59 (1.03)	173 (76)	23.8 (4.41)	River Irrigation
2 Aug (1915) to 10 Aug (1900)	6.10 (4.44)	5.78	1.65 (1.27)	149 (92)	25.3 (5.77)	Harvest
11 Aug (1915 h) to 13 Aug (1900 h)	1.00 (0.90)	0.86	1.95 (1.00)	196 (50)	24.4 (5.05)	Well Irrigation
14 Aug (1915 h) to 27 Aug (0900 h)	1.59 (0.89)	1.43	2.07 (1.46)	188 (68)	23.2 (4.89)	Effluent + Well

† Values in parentheses are SD.

## **GENERAL CONCLUSIONS**

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This research identified several alternative N fertilizers to urea that can reduce  $\text{NH}_3$  loss and improve N use efficiency for crops. Ammonia volatilization from the alternative N fertilizers evaluated in the field trial ranged from 14.8 to 38.0% of N applied vs. 46.7% of N applied from urea. Of the alternative fertilizers, the greatest reduction of  $\text{NH}_3$  loss resulted from  $\text{NO}_3^-$  and  $\text{NH}_4^+$  fertilizer forms (> 60% reduction vs. urea), followed by SCU and PCU (>50% reduction vs. urea), and urea + NBPT (>30% reduction vs. urea). According to the results of both the field and laboratory studies, the benefit of partially substituting urea with AS is less reliable. This research also provided an initial idea of expected emission rates from effluent application to alfalfa. We observed an average  $\text{NH}_3\text{-N}$  emission rate from effluent applied to alfalfa of  $1.4 \text{ kg ha}^{-1} \text{ d}^{-1}$ , which was  $0.9 \text{ kg ha}^{-1} \text{ d}^{-1}$  greater than emissions during irrigation without effluent. This research also provided an unexpected opportunity to observe  $\text{NH}_3\text{-N}$  emissions from alfalfa harvest, which averaged  $6.1 \text{ kg ha}^{-1} \text{ d}^{-1}$  over an 8-d process of cutting, drying and baling alfalfa for hay production.

The certainty that alternative N fertilizers can reduce  $\text{NH}_3$  loss compared to urea depends on the interaction of their specific chemistries and the environments they are used in. With the continual development of alternative N fertilizers vs. urea, and expected increase of effluent reuse by approximately 100% in some locations in the near future, more studies are needed to investigate the interactions of each N source with different environmental conditions and the subsequent emissions that are produced. With urea fertilizers, the risk of  $\text{NH}_3$  loss is greatest within the first 15 DAA of application, and the best mitigation is still incorporation via tillage or rain. In situations where incorporation of fertilizer is not likely, this study offers certainty from both field and laboratory tests that adding NBPT to urea or using alternative N fertilizers of AS, ASN, SCU or PCU will limit  $\text{NH}_3$  volatilization, resulting in less error in N fertilization rate for crops from similar soils and less N loading to the environment. More complete evaluations of total N availability for crops should consider other soil types (i.e. calcareous), other pathways of N loss (i.e. leaching of  $\text{NO}_3^-$ ), and current price or availability of the alternative fertilizer.



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## APPENDICES

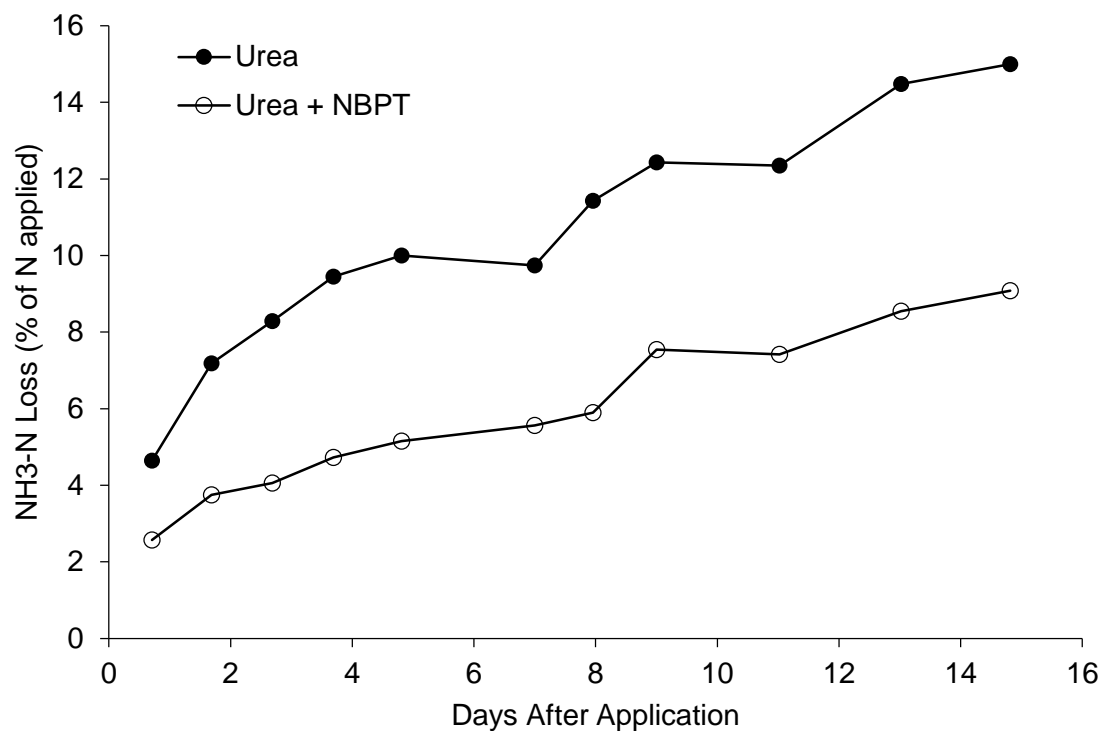


Figure 4.1. Cumulative loss of  $\text{NH}_3$  during the period of Aug 1 to Aug 16 2013 from urea and urea treated with N-(n-butyl) thiophosphoric triamide (NBPT) applied at an N rate of  $168 \text{ kg ha}^{-1}$ .

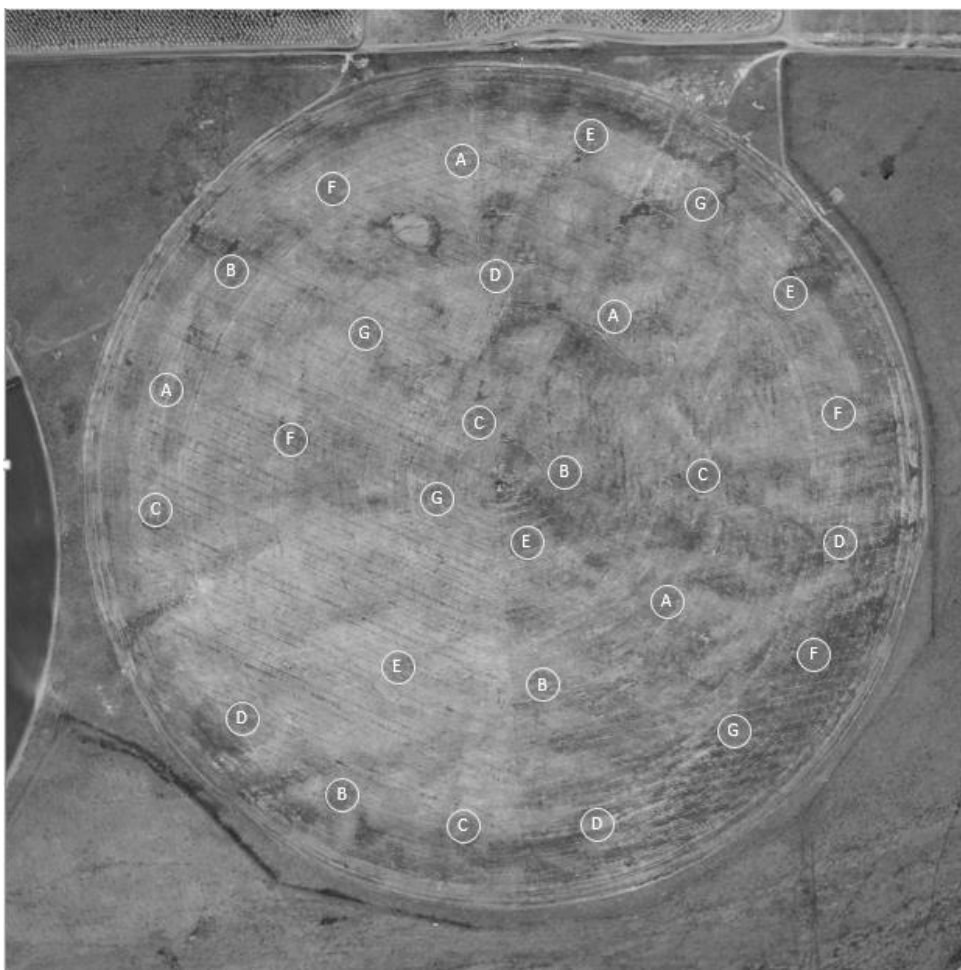


Figure 4.2. Position of alternative fertilizer treatment plots within the field site. Treatments include: A) urea, B) N-(n-butyl) thiophosphoric triamide (NBPT)-coated urea (urea +NBPT), C) ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ) (AS), D) urea partially substituted with 21% AS (urea(AS)), E) a chemically reacted, homogenous granule of urea(AS), F) chemically reacted AS and ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) (AN) in a fused granule (ASN), G) sulfur-coated urea (SCU).

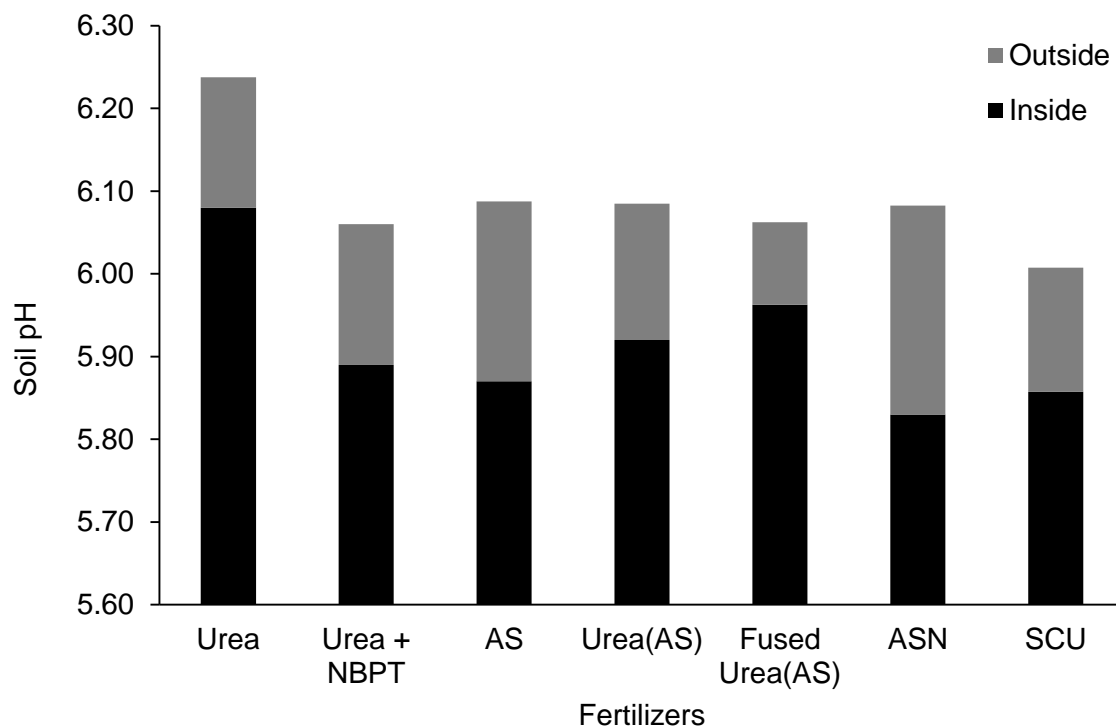


Figure 4.3. Average soil pH differences at the conclusion of the field study from the inside and outside of fertilizer treatment plots. Treatments include: 1) urea, 2) N-(n-butyl) thiophosphoric triamide (NBPT)-coated urea (urea +NBPT), 3) ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ) (AS), 4) urea partially substituted with 21% AS (urea(AS)), 5) a chemically reacted, homogenous granule of urea(AS), 6) chemically reacted AS and ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) (AN) in a fused granule (ASN), 7) sulfur-coated urea (SCU).

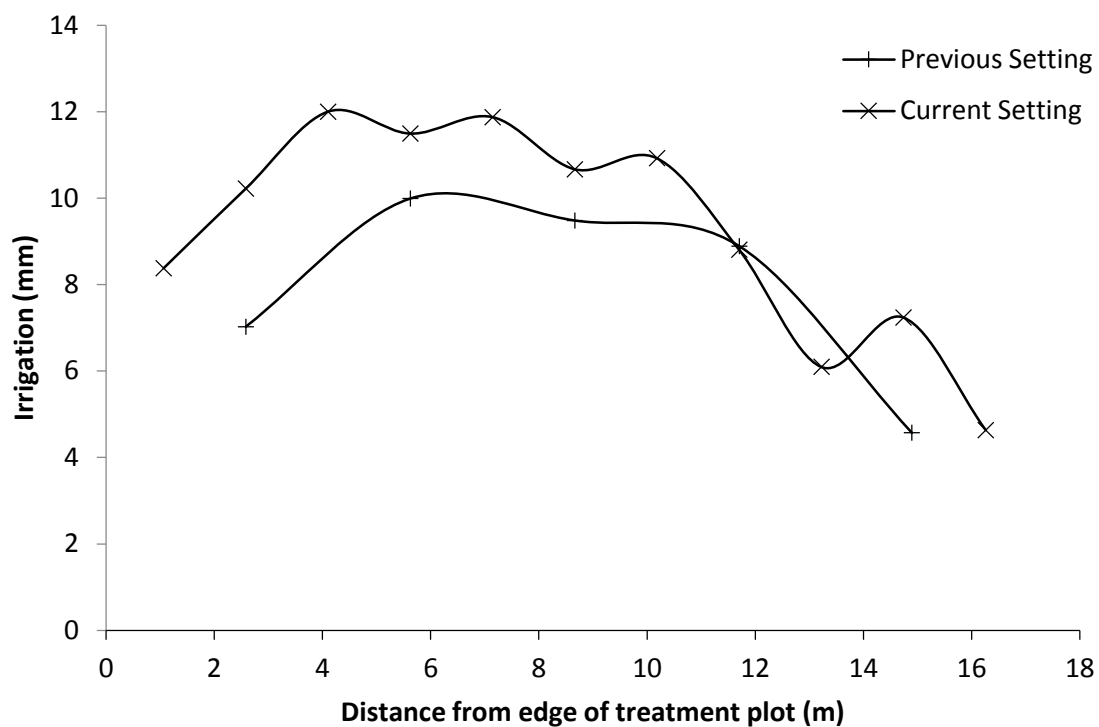


Figure 4.4. Results related to mini-pivot research during the period of Jul. 2013 to Jun. 2014. Distribution of 12.7 mm irrigation from edge to center on a 0.1 ha center-pivot irrigation system before and after sprinkler nozzle adjustment.

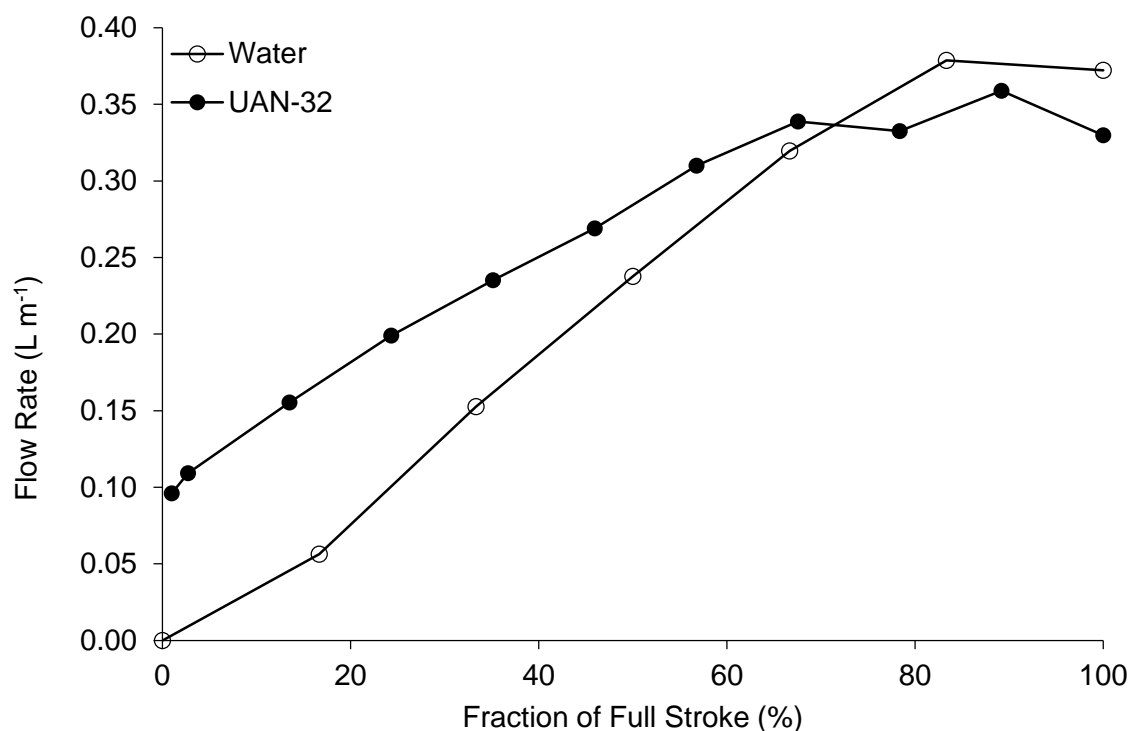


Figure 4.5. Results related to mini-pivot research during the period of Jul. 2013 to Jun. 2014. Flow rates of water and urea ammonium nitrate, 32% N content (UAN-32), through low-volume pump used with 0.1-ha center-pivot irrigation systems (26.5 L hr<sup>-1</sup> maximum, 400 Series, Ozawa R&D Inc., Kerman, CA, USA).

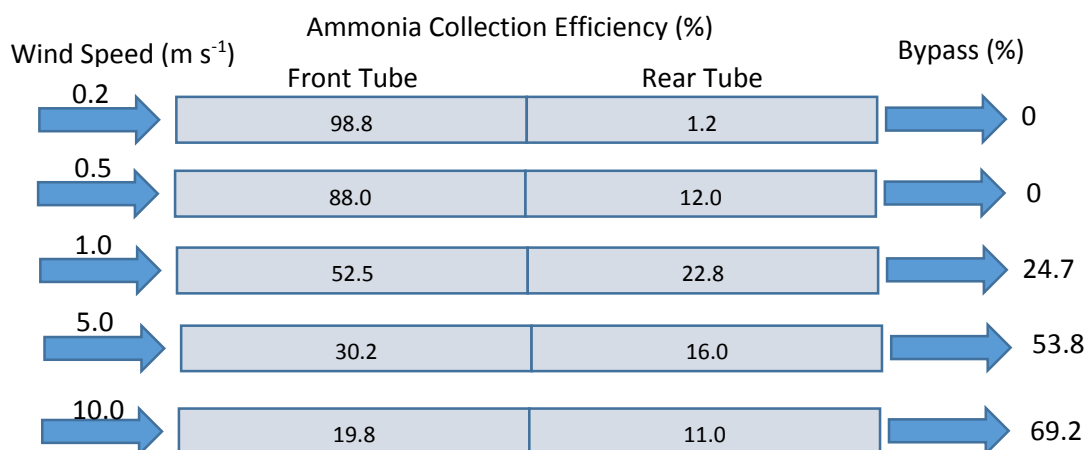


Figure 4.6. Results related to mini-pivot research during the period of Jul. 2013 to Jun. 2014. Bypass of NH<sub>3</sub> through two sampling tubes connected in series without a nozzle at various wind speeds in a wind tunnel test. Courtesy of Cabrera, M.L., 2015.

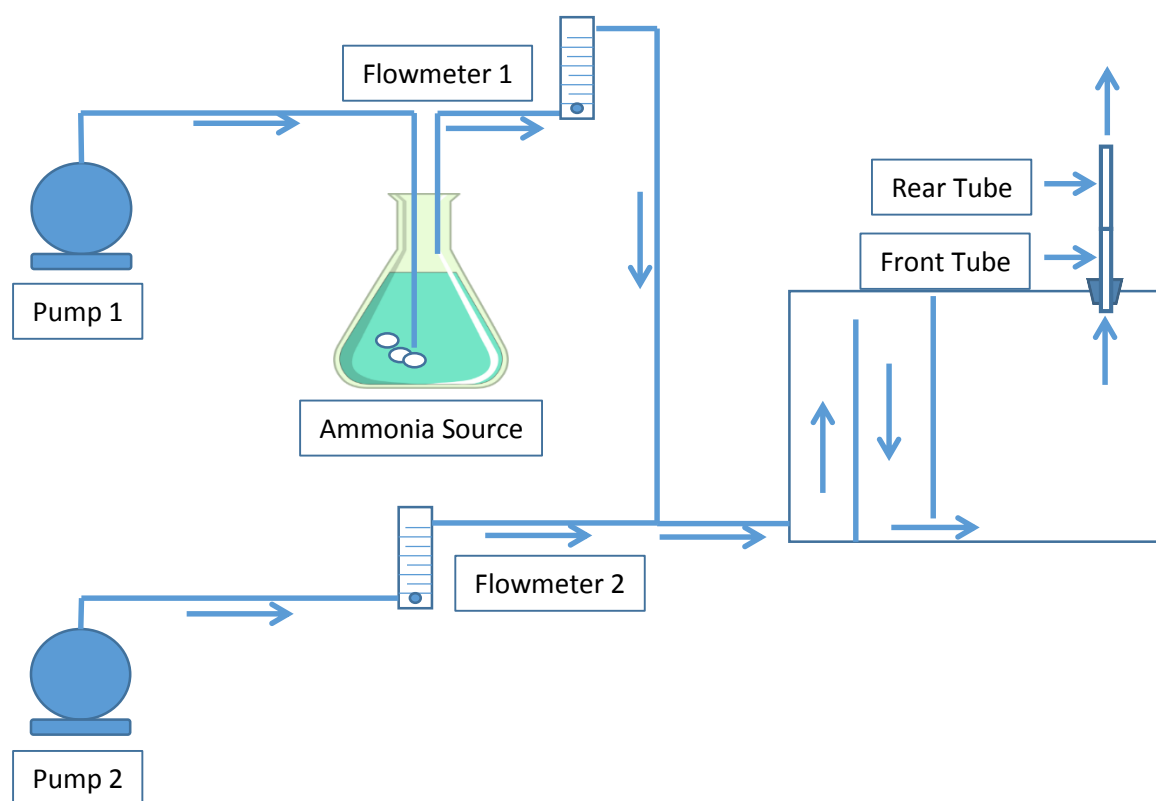


Figure. 4.7. Results related to mini-pivot research during the period of Jul. 2013 to Jun. 2014. Schematic of  $\text{NH}_3$  bypass wind tunnel test. Courtesy of Cabrera, M.L., 2015.



Hours After Application	Replication	Cumulative NH <sub>3</sub> -N Loss		
		Fertilized	Unfertilized	Difference
		-----% of N applied-----		
32	1	2.1	0.4	1.7
55	1	3.2	0.6	2.6
5	2	3.9	2.4	1.5
28	2	4.4	2.5	1.9
77	2	7.3	3.3	4.0
46	3	5.8	0.5	5.3
92	3	7.2	2.0	5.2

Table 4.1. Results related to mini-pivot research during the period of Jul. 2013 to Jun. 2014. Cumulative NH<sub>3</sub>-N loss measurements using periphery-mast modified passive flux method to compare 12.7 mm irrigation with and without injected urea ammonium nitrate, 32% N content (UAN-32), applied at N rate of 67.2 kg ha<sup>-1</sup>.

Hours After Application	Replication	Cumulative NH <sub>3</sub> -N Loss		
		Fertilized	Unfertilized	Difference
		-----% of N applied-----		
32	1	0.9	0.9	0.0
55	1	2.1	1.4	0.7
33	2*	0.4	0.1	0.3
81	2*	0.4	0.5	-0.1
45	3	1.6	0.8	0.8
92	3	2.7	1.7	1.0

Table 4.2. Results related to mini-pivot research during the period of Jul. 2013 to Jun. 2014. Cumulative NH<sub>3</sub>-N loss measurements using center-mast modified passive flux method to compare 12.7 mm irrigation with and without injected urea ammonium nitrate, 32% N content (UAN-32), applied at N rate of 67.2 kg ha<sup>-1</sup>.

\* Measurements taken from samplers without nozzle.