

## ABSTRACT

Title of Document: NITROGEN MANAGEMENT IN CORN:  
INFLUENCES OF UREA AMMONIUM  
NITRATE (UAN) APPLICATIONS WITH  
AND WITHOUT NITROGEN STABILIZER  
PRODUCTS.

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Corn (*Zea mays*, L.) is a major crop produced in the nutrient sensitive Mid-Atlantic region. Nitrogen use efficiency (NUE) for corn is considered sub-optimal and farmers in the region use a number of best management practices (BMPs) to improve corn NUE. Two sidedress application methods (surface banding and sub-surface injection) and four commercially available nitrogen stabilizer products ('Agrotain', 'Agrotain Plus', 'Instinct', 'Nutrisphere-N') were investigated during 2009-2011 over three N fertilizer rates at nine total locations. Headspace ammonia accumulation (post-sidedress) was indexed to the surface applied UAN treatment and resulted in application method and stabilizer products having a significant effect for headspace ammonia accumulations. Post-harvest inorganic soil nitrogen was not affected by application method or stabilizer products. Yield was not significantly affected by application method or stabilizer products but was affected by N rate. Total plant N concentration was not significantly affected by application method or stabilizer products.

NITROGEN MANAGEMENT IN CORN: INFLUENCES OF UREA AMMONIUM NITRATE  
(UAN) APPLICATIONS WITH AND WITHOUT NITROGEN STABILIZER PRODUCTS.

By

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# Chapter 1: Introduction

## Background and Problem Definition

Nitrogen on average is the most limiting nutrient in corn (*Zea mays* L.) production, second only to available water during the growing season. Demand for corn is increasing as a result of the needs of the livestock feeding industry, the ethanol industry, and to fulfill export markets. Nitrogen demand has increased concurrently. Extensive research has been conducted with different nitrogen fertilizer sources with an emphasis on improving use-efficiency in corn production. Nitrogen availability to the crop is directly related to the amount of loss that occurs via the three major loss pathways; leaching of N as nitrate ( $\text{NO}_3$ ), volatilization of N as ammonia ( $\text{NH}_3$ ), and denitrification of N as dinitrogen oxide ( $\text{N}_2\text{O}$ ) and nitrous ( $\text{N}_2$ ) gases. In the Mid Atlantic region of the United States, urea ammonium nitrate (UAN), a form of nitrogen fertilizer that is subject to loss via these pathways, is the most commonly used nitrogen source.

In the late 1980s and early 1990s, massive algal blooms depleted oxygen levels in the Chesapeake Bay, as well as many of its estuaries, and lead to massive kills of submerged vegetation and fish. Between 3 June, and the early part of August, 2007, Maryland Department of Environment (MDE) investigated 45 reports of fish kills as a result of hypoxic conditions (Chesapeake Bay Foundation, 2007). Eutrophication, an increase in the rate of supply of organic matter (Nixon, 1995), has been identified as the leading cause of hypoxia (oxygen depletion), increased turbidity, and loss of submerged vegetation. The Chesapeake Bay Foundation (CBF) was established in 1967, by a group of private businessmen who had a profound interest in the health of the water they relied on for their living. The early mission of the group was to address

issues that were affecting the Chesapeake Bay. The goal of the CBF became the restoration of the Bay to a level of health that will promote life and growth within its ecosystems ([www.cbf.org](http://www.cbf.org), 2011). Boesch et. al. (2001) summarized the restoration task by stating “the multistate effort to restore the Chesapeake Bay ecosystem by reducing the inputs of nutrients that stimulate organic over-enrichment is one of the world’s most ambitious attempts at large-scale ecosystem restoration.”

Since the initiation of the restoration effort, the Chesapeake Bay has been the focus of extensive research on eutrophication and efforts to reduce nutrient loading. A commitment was made in 1987, to reduce the non-point sources of N and P by 40% by the year 2000, even though the causes and effects of eutrophication were not completely known. Nitrogen and phosphorous were found to be directly related to the algal blooms and non-point sources of nutrient loading were identified; agriculture, turf management as well as runoff and losses associated with field applied manure from confined animal feeding operations (CAFO’s) (Boesch, 2001).

In 1998, the Maryland General Assembly passed the Water Quality Improvement Act which aimed at decreasing nutrient loads by requiring mandatory nutrient management plans on Maryland farms. This act was passed with the intention that the non-point sources of nutrient loading to the Bay that were associated with agriculture would be addressed. A few years after the passage of the Water Quality Improvement Act, Boesch (2001) stated “strong public support and political commitment have allowed the Chesapeake Bay Program to reduce nutrient inputs, particularly from point sources, by 58% for P and 28% for N” but non-point sources have been estimated to only reach 19% and 15% reductions for P and N.

In the last few years there has been increased emphasis, by environmental agencies, to further reduce non-point source nitrogen loading in the Chesapeake Bay Watershed. The

Environmental Protection Agency (EPA) has established and is in the process of implementing Total Maximum Daily Loads (TMDLs) for the tributaries of the Chesapeake Bay. The Chesapeake Bay Foundation (CBF), along with other environmental agencies, continues to lobby in support of more pressure on Maryland's farmers to reduce their use of nitrogen as well as other nutrients. This effort is being undertaken with the hope that it will improve the quality of drinking water, ground water and natural bodies of water associated with the Chesapeake Bay.

In an effort to help alleviate environmental impacts caused by inorganic nitrogen fertilizers, and to improve their use-efficiency, fertilizer companies have incorporated nitrogen stabilizer products into their fertilizer sales and programs. These products are designed to reduce N-loss associated with one or more of the nitrogen loss pathways: volatilization, nitrification and denitrification. Unfortunately, and in an effort to promote and increase product sales, some of these companies have made claims such as increased yield, ability to reduce nitrogen rates, or yearlong nitrogen protection will occur when their product is used (Koch Agronomic Services 2013) (Dow Agrosience, 2013a) (Dow Agrosience, 2013b) (SFP, 2013).

This paper will review the research conducted using the four most common N-fertilizer stabilizer products available in Maryland, as well as two different methods of nitrogen sidedress application (surface banding and sub-surface injection).

## **Justification for Research**

Since the industrial revolution demand for nitrogen by agriculture has continually increased (USDA, 2010). Between 1960 and 2007, nitrogen fertilizer usage increased by over four-fold (Figure 1.1). However, this increase in nitrogen usage has not been efficient. Based on

the corn yield farmers actually attained with studies in Nebraska and Iowa, it was reported that about half of all farmers over applied nitrogen by 20 to 25 percent (Papendick, 1987). It has been estimated that corn nitrogen use efficiency (NUE) is 50% (Hoefl, 2004), suggesting that there is a need to improve the management of nitrogen for corn production.

A factor that has a significant effect on the amount of nitrogen used in corn production is that many of the nitrogen fertilizer sources are susceptible to loss. Three loss pathways are of concern in corn production: denitrification, volatilization, and leaching.

Denitrification is the reduction of nitrate to molecular nitrogen or other gaseous forms of nitrogen. This process occurs with water logged, warm, anaerobic soil conditions and is the result of both heterotrophic and autotrophic bacteria, known as 'denitrifiers'. Hilton et al. (1994) estimated denitrification losses to be 10% to 20%, respectively, for conventional tillage and no-tillage corn production systems.

Volatilization is the loss of nitrogen as free ammonia ( $\text{NH}_3$ ) and is a concern with surface applied fertilizers containing the urea form of N. The conversion of urea to  $\text{NH}_3$ , a highly volatile gas, is catalyzed by the enzyme 'urease'. Urease catalyzes both the removal and subsequent conversion of the functional group  $\text{NH}_2$  from the urea forming  $\text{NH}_3$  which can be released from the soil to the atmosphere (Figure 1.2). The conversion and loss rate in this process is highly dependent on soil type, soil moisture, CEC, pH, temperature, and rainfall; all of which can be variable in soils during the period when corn is sidedressed. Volatilization losses from surface applied urea without incorporation have been estimated as high as 40% (Hargrove et al., 1977; Fowler and Brydon, 1989). Sharpe et al. (1988) estimated volatilization losses up to 21% percent for spring applied N in wheat production systems.

Leaching is the loss of N in the nitrate form ( $\text{NO}_3^-$ ) as a direct result of soil hydrology. Nitrate is a negatively charged molecule which does not bond with the predominant negatively charged soil particles. Due to the high solubility of nitrate and the lack of molecular bonding in the soil, nitrate is susceptible to being 'carried' both laterally and vertically through the soil profile with water. As water carries and relocates the nitrate in the soil profile it sometimes is moved outside the zone that the crop roots reach. Leaching can result in a 10-40 percent loss of applied N depending on time of application, source of fertilizer and the crop being fertilized, which constitutes what is considered by many the largest and most frequent loss pathway (Legg and Meisinger, 1982) (Meisinger et al. 2008).

The two main application times for fertilizer nitrogen in corn used by Maryland farmers are preplant and sidedress. A preplant application is commonly defined as either all or part of the required nitrogen fertilizer supplied prior to or at the time of planting the crop. Use of this application time to supply all the fertilizer nitrogen is problematic. This means that all of the required nitrogen is applied 6-8 weeks prior to the most rapid growth stage of the corn, and thus, it is highly susceptible to loss via the pathways for these 6-8 weeks before crop demand is high. A sidedress application is defined as supply of nitrogen just prior to or during the crop's most rapid growth stages. For corn, a sidedress application is made during growth stages V5-V7 (Aldrich, 1984). This supplies the fertilizer to the corn at a time that coincides with maximum growth and nutrient uptake and eliminates the 6-8 weeks of time that the fertilizer is susceptible to leaching and denitrification losses when supplied pre-plant. However, during the sidedress time of application there are still concerns of loss through leaching during extreme rain events and loss through volatilization due to warm soil surface and air temperatures that can be experienced during June.

In Maryland, common practice for determining how much N to use is to apply one pound of nitrogen per bushel of estimated corn yield per acre when subsurface injecting, i.e. the yield goal approach. However, in a bulletin from University of Maryland Extension (UME) it is noted that when surface banding UAN fertilizer at sidedress time, farmers should increase their application rate by five to ten percent, and if surface applying granular urea, rates should be increased 10-15 percent (Maryland, 2002). In making this recommendation, UME is assuming that one pound of nitrogen will be applied per bushel of expected grain yield, up to two hundred fifty bushels per acre. No additional nitrogen will be applied for expected yields above this level (Maryland, 2002). This is a direct indication by UME that preplant methods, as well as the different sidedress methods, can affect nitrogen use efficiency due to the excess loss that can occur through the loss pathways.

Two methods of applying UAN, the most commonly used fertilizer form of N in Maryland, exist; surface banding and sub-surface injection. Surface banding applies the liquid fertilizer in a concentrated zone roughly 7cm or less in width mid-way between the corn rows. Sub-surface injection is placement of the fertilizer in a concentrated band mid-way between the corn rows but 7.5-10 cm below the soil surface; a location that is closer to the root zone of the crop.

The inefficiencies associated with methods and times of application, losses that can occur before crop utilization, pressures from environmental agencies to reduce N use, and the increasing cost of N fertilizers has created a need for additional methods and/or products that farmers can use to maximize the performance of nitrogen fertilizers.

This study was conducted to evaluate if the use of nitrogen stabilizer products with UAN fertilizer at corn sidedress provides any efficiency benefits. Tested in this study were four

commercially available nitrogen stabilizer products that are registered for use with UAN and being marketed in Maryland. The products are:

1. Agrotain International's 'Agrotain', N-(n-butyl) thiophosphoric triamide ("NBPT"); a volatilization inhibitor
2. Agrotain International's 'Agrotain Plus', N-(n-butyl) thiophosphoric triamide ("NBPT"); volatilization inhibitor and Dicyandiamide ("DCD"); a nitrification inhibitor
3. Dow Agro Sciences' 'Instinct', 2-chloro-6-(trichloromethyl)pyridine ("Nitrapyrin"); a nitrification inhibitor
4. Specialty Fertilizer Products' 'Nutrisphere N', ("Maleic-itaconic copolymer, calcium salt"); a dual purpose product that is a volatilization and nitrification inhibitor.

## **Objectives and Hypotheses**

Objective 1. To measure the influence that the method of UAN application and/or use of selected N-stabilizer products with UAN have on corn grain yield.

Hypotheses:

1. UAN with, and without, select nitrogen stabilizer products and UAN application method will not affect corn grain yield.
2. UAN with a stabilizer product and surface applied will yield equal to UAN sub-surface applied.

Objective 2. Determine if the use of UAN fertilizer with a nitrogen stabilizer product causes an increase in total plant consumption of nitrogen.

Hypothesis: Nitrogen stabilizer products with UAN will not affect post physiological maturity plant tissue total-N concentrations.

Objective 3. To determine if either the method of application of UAN or the addition of a nitrogen stabilizer product to UAN that is surface applied will result in a higher post- harvest soil inorganic-N concentration.

Hypothesis: Neither application method nor use of nitrogen stabilizer products will affect post plant physiological maturity soil inorganic-N concentrations in the top 30cm.

Objective 4. To determine if the method of application of UAN, and/or the use of a nitrogen volatilization inhibitor with UAN, result in different  $\text{NH}_3\text{-N}$  headspace accumulations following post-sidedress application for a period of seven days.

Hypothesis: UAN with a volatilization inhibitor will not differ in headspace ammonia accumulation (HAA) for a defined timeframe following sidedress application compared to either UAN surface banded or UAN sub-surface injected.

## **Research Approach**

During 2009 – 2011 growing seasons, field experiments were conducted at 4 University of Maryland Research and Education Centers (UMRECs). The REC's were representative of Maryland Coastal Plain and Piedmont soils (Table 1.1). Two application methods were evaluated, sub-surface injection and surface banding. Four nitrogen stabilizer products were



tested; Agrotain (NBPT), Agrotain Plus (NBPT + DCD), Instinct (Nitrpyrin), and Nutrisphere N (maleic-itaconic copolymer). The field trials were designed using a randomized complete block design, split plot arrangement of treatments with 4 replications at each location. The six main plots consisted of the four nitrogen stabilizer products mixed in UAN and surface applied and two different application methods of untreated UAN; surface banding and sub-surface injection. The whole plots were split for the three nitrogen rates, 180, 134, and 90 kg ha<sup>-1</sup>. A Control treatment of 0 kg N ha<sup>-1</sup> was included in each replication (Table 1.2). The optimum nitrogen rate (180 kg N ha<sup>-1</sup>) was determined by using the averaged expected yield goals of the three 2009 locations. The sub optimum rates were less 25%, less 50% and less 100% (Control) of the high N rate.

## Tables

Table 1.1. Year, location and soil type description for the 9 sites where this study was conducted.

Location	Year	Latitude	Longitude	Soil Taxonomy	Soil Series	Soil type
Beltsville	2009	39° 0' 42.26" N	76° 49' 41.62" W	Aquic Hapludults	Russett- Christiana complex	Sandy loam
	2010	39° 0' 38.84" N	76° 50' 0.00" W	Aquic Hapludults	Russett- Christiana complex	Sandy loam
	2011	39° 0' 42.26" N	76° 49' 41.62" W	Aquic Hapludults	Russett- Christiana complex	Sandy loam
Clarksville	2009	39° 15' 1.87" N	76° 55' 45.46" W	Typic Fragiudults	Glenelg loam	Silt loam
	2010	39° 14' 57.35" N	76° 55' 44.35" W	Typic Fragiudults	Glenelg loam	Silt loam
	2011	39° 14' 26.35" N	76° 55' 33.31" W	Typic Hapludults	Gladstone loam	Loam
Poplar Hill	2009	38° 21' 25.40" N	5° 46' 3 6.55" W	Typic Hapludults	Mattapex silt loam	Silt loam
	2010	38° 21' 33.23" N	5° 46' 35.74" W	Typic Hapludults	Mattapex silt loam	Silt loam
Wye	2011	8° 54' 57.48" N	76° 8' 35.78" W	Aquic Hapludults- Typic Fragiudults	Mattapex- Butlertown silt loams	Silt Loam

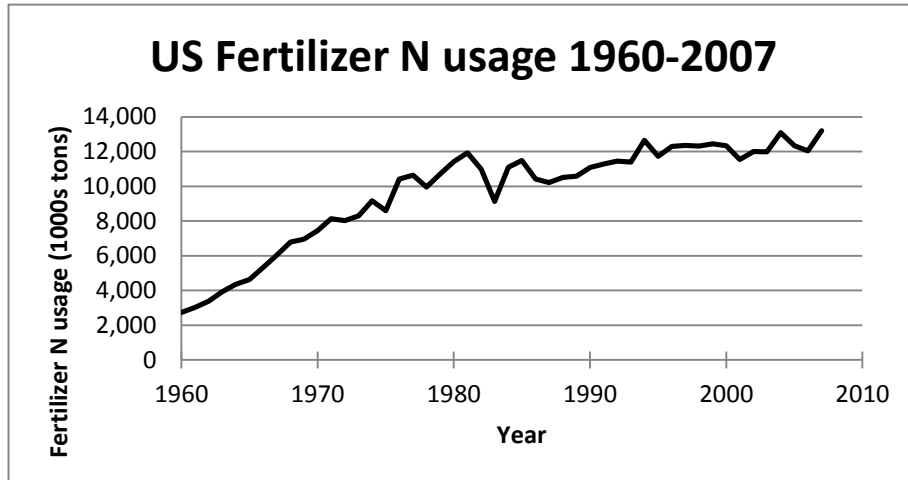
Table 1.2. Main plot and split-plot treatment structures used for the study.

Main Plot	Nitrogen Source and Application Rate ------( kg ha <sup>-1</sup> )-----		
	90	134	180
UAN Injected	30% UAN @ UMD Rate less 50%	30% UAN @ UMD Rate less 25%	30% UAN @ UMD Rate
UAN Surface applied	30% UAN @ UMD Rate less 50%	30% UAN @ UMD Rate less 25%	30% UAN @ UMD Rate
UAN + Agrotain	30% UAN @ UMD Rate less 50%	30% UAN @ UMD Rate less 25%	30% UAN @ UMD Rate
UAN + Agrotain Plus	30% UAN @ UMD Rate less 50%	30% UAN @ UMD Rate less 25%	30% UAN @ UMD Rate
UAN + Instinct	30% UAN @ UMD Rate less 50%	30% UAN @ UMD Rate less 25%	30% UAN @ UMD Rate
UAN + Nutrisphere N	30% UAN @ UMD Rate less 50%	30% UAN @ UMD Rate less 25%	30% UAN @ UMD Rate
Control	x	x	x

\* UMD rate was determined by averaged expected yield goals for all three 2009 farms. Yield goals were based on the farm manager's suggested average yield.

## Figures

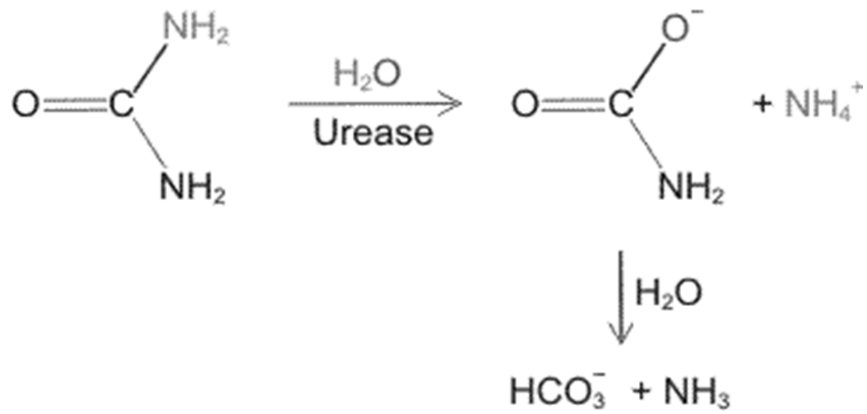
Figure 1.1. United States yearly nitrogen fertilizer usage in agricultural systems, 1960-2007.



USDA, National Agricultural Statistics Service. 2010. <http://www.nass.usda.gov/> Data Retrieved

April, 2010.

Figure 1.2. Chemical structure of urea (left) and the enzymatic process by which it is degraded to ammonium and ammonia, a highly volatile gas.



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## Chapter 2: Literature Review

### Introduction

During the last four years, corn (*Zea mays* L.) accounted for the largest percentage of arable land in Maryland (USDA 2012). Its cultivation can be classified by three tillage systems; no-till (61%), conservation tillage (26.5%), or conventional tillage (12.5%). These three tillage systems accounted for the 198,303 ha of corn planted in Maryland during the 2012 growing season (USDA, 2012).

In the early 1980's, the most common nitrogen fertilizer application practices used in no-till production systems, in the United States, were the surface application of either granular urea or granular ammonium nitrate or surface spraying urea ammonium nitrate (UAN) solution, immediately before or after planting the crop (Mengel, 1982).

During the past couple decades in the Mid-Atlantic region of the United States, there has been increased interest in nitrogen conservation and improvement in nitrogen use efficiency which is being driven by three factors. First and foremost is economics. In 2008, nitrogen prices in the Mid-Atlantic experienced a dramatic increase reaching approximately \$2.20 kg<sup>-1</sup> of nitrogen (approximately \$1.00 lb<sup>-1</sup> N). This price increase affected farmers' profitability and influenced decisions about how much N to use and how to apply it. The second factor is legislation; The Water Quality Improvement Act of 1998 was passed by the Maryland General Assembly. Since this act was passed, considerable attention has been, and continues to be, focused on loss of nutrients from all sources into surface and ground waters. Since agriculture was identified as a major contributor to nutrient loss, the Water Quality Improvement Act placed



new and strict regulations on farmers to control nutrient pollution (Simpson, 1998). The last factor is the environment. The Maryland Department of Environment has imposed on all watersheds in Maryland total maximum daily loads (TMDLs) at the sub-watershed level. These TMDLs led to the establishment of Water Quality Improvement Plans for the various watersheds that are an attempt, through the use of regulations, to curtail excessive nitrogen loss to surface and ground water (Maryland Department of Environment, 2010). The combination of these three factors has farmers searching for more efficient and cost effective ways of supplying nitrogen fertilizer to corn.

The focus of promoting efficient fertilization in the Chesapeake Bay watershed was strengthened in the late 1990's with the Water Quality Improvement Act. Researchers have focused and continue to focus on ways in which the application of nitrogen can be improved for corn production. To take a look at the ways in which improvements have been made we will use the IPNI's 4 R approach to proper nutrient application (IPNI, 2013). The 4-R nutrient stewardship approach is: apply the right source of nutrient, at the right rate, at the right time, and in the right place.

Working backwards with the 4-R's, much research has been conducted identifying the proper zone of application and proper time of application for many crops. One example of application zone and application timing research is a study conducted by Sweeney et al. (2008) who reported on a three year study (2003-2005) in the upland region of the Eastern Great Plains. In this study, the researchers compared the effects of timing of N-P (liquid UAN applications with added phosphorous) applications (spring vs. fall), and application methods (dribbled vs. injected), on corn yields. Over the three year period of the study, corn yield and the number of kernels per ear, significantly increased when nitrogen was applied in the spring compared to the

fall. Sub-surface injection of the UAN fertilizer significantly increased corn grain yields compared to surface dribbling. A significant increase in the number of kernels per ear was also seen when UAN was sub-surface injected compared to surface applied (Sweeney et al., 2008).

Currently in Maryland, the expected yield goal approach is used in determining N rates and addresses the issue of the right rate. Many studies have researched the concept of proper rates, but identifying the proper rate for any given year is only an estimate due to the inability to predict growing season weather conditions following the application. On average, research has done a good job at identifying rates based upon average yields, but current research is being conducted on in-season crop based measurements for fine-tuning proper nutrient application rates.

The concept of the right source has always been tricky to manage. Farmers can choose between manures, granular, and liquid fertilizers. Many fertilizer companies promote special mixtures that are supposed to increase nutrient efficiency. With the current environmental emphasis in Maryland, identification of products that increase nutrient efficiency or decrease nutrient losses have gained much support. The purpose of this study was to identify commercially available products that show potential for addressing increased nutrient efficiency and/or decreased nutrient losses.

## **Nitrogen Stabilizer Product Introduction**

Many nitrogen stabilizer products that can be used with urea and UAN fertilizers have been introduced into the agricultural market as a means to increase nitrogen use efficiency and decrease nutrient losses. These products can be classified into three groups; volatilization

inhibitors, nitrification/denitrification inhibitors, and dual purpose inhibitors. Volatilization inhibitors are designed to decrease urease activity thus reducing the hydrolysis of urea into ammonium and ammonia. Nitrification/denitrification inhibitors target the nitrifying bacteria that convert ammonium into nitrite, and then further to the highly soluble nitrate. They also target the bacteria which during anaerobic conditions use N molecules during respiration. Dual purpose inhibitors claim to prevent loss from the three possible pathways, volatilization, nitrification, and denitrification. A review of commercially available products that were not the focus of this study will be presented first followed by the four products tested in this study.

## **Products Not Included in the Study**

In today's rapidly advancing agricultural industries, stabilized nitrogen sources are continually being developed and marketed. As a result, the review of products not tested in this study, may not include all products which are currently available. Many of these new products are being promoted as enhanced efficiency fertilizers and can be classified into two major groups, polymer coated urea (PCU's) and 'pH modifiers'.

Two new PCU's are urea formaldehyde polymer (UFP) and environmentally safe nitrogen (ESN). The first, UFP, is a new technology that aids in soil retention of the nitrogen. UFP's protect urea from the urease enzyme by incorporating the urea into a polymer chain. This technology was just recently added to the market and is still undergoing third party testing. ESN (environmentally safe nitrogen) is another example of a PCU and is marketed by Agrium. They claim that their polymer coating controls the infiltration of water into the pearl and also controls

the release of the dissolved urea based upon soil temperature and soil moisture (Agrium, 2013). The study described below is just one example of the mixed reviews of UFP.

Cahill et al. (2007) reported on a study in which they evaluated the effect on corn production of UAN and a UFP across multiple N rates. The UFP was applied only at planting while UAN was split applied (part at planting and the rest at sidedress). The authors observed that weather influenced the results observed for this study. The 2004 growing season had average rainfall while 2005 had below average rainfall. At the Tidewater location in 2004 (dryland site), there were significantly better yields for the UFP compared to UAN. In contrast, the Sandhills location in 2004 (irrigated site), had no yield differences between treatments. However, in 2005, the dryland site had no significant yield differences between treatments but at the Sandhill location UAN had better yields compared to UFP. With the reduced rainfall in 2005, the UFP was able to protect the urea pearl without being dissolved. The irrigation increased the degradation rate of the UFP reducing its effectiveness.

There are two fertilizers currently being marketed that are described as pH modifiers; 1) ammonium thiosulfate and 2) urea calcium ammonium nitrate (UCAN) which is marketed as YaraLiva<sup>TM</sup>CN-9®. Ammonium thiosulfate incorporates a sulfur compound into the product that acidifies the soil below the optimum pH for ammonia volatilization, a process that also aids in slowing bacterial enzymatic activity. This soil reaction reduces the loss potential of the ammonium component of the fertilizer. The second fertilizer, UCAN, is UAN with calcium and the micronutrient boron incorporated. The theory behind UCAN is that the calcium will increase soil pH in the zone of application which is supposed to increase nitrogen bonding in the soil. Yara also claims that the added calcium in the mixture stimulates good rooting, stress-free growth, strong cell walls, firmer tissue, improved fruit quality, and better storage (Yara, 2013).

The PCUs and pH modifiers are all pre-made mixtures or urea pearls that are manufactured and must be purchased as such. The four products tested in this study focused on additives that can be tank mixed with UAN (28, 30, or 32% N mixtures) just prior to application.

## **Products of Interest**

### **Instinct**

The oldest of the commercially available nitrogen stabilizer additives is nitrapyrin, commercially known as N-Serve, and has been in use as a nitrification inhibitor since the late 1960's. The chemical comprising N-Serve is nitrapyrin (2-chloro-6-[trichloromethyl] pyridine) which is labeled by the Environmental Protection Agency (EPA) as a bacteriostat. Bacteriostat is a general classification given to any substance, or product, which inhibits growth or multiplication of bacteria. Nitrapyrin works by reducing the activity of one of the two nitrifying bacteria, *Nitrosomonas*, which is responsible for the conversion of ammonium to nitrite, the first step of nitrification. One of the major weaknesses of the N-Serve form of nitrapyrin is its volatility when surface applied which resulted in the product being labeled for incorporation use only. This prevented the use of N-Serve (nitrapyrin) with surface applied UAN. Yield performance with the use of N-Serve is mixed, however multiple studies show that it does reduce nitrification.

In 2009, Dow Agrosiences released a reformulated version of nitrapyrin for use with surface applications. This product is marketed using the trade name Instinct. The difference with Instinct compared to N-Serve is the addition of naphthalene which reduces the volatility of

nitrapyrin when surface applied. Instinct is promoted to have many benefits including a 7% yield increase compared to untreated N sources (Dow Agrosiences, 2010). Under a 24(c) Special Local Needs Registration in Iowa in 2008, on-farm field trials showed that fields treated with Instinct out yielded non-treated fields by an average of 0.31 tonne ha<sup>-1</sup> (Dow Agrosiences, 2012).

### **Agrotain and Agrotain Plus**

Two products marketed by Agrotain International, a company purchased by Koch Agronomic Services LLC, in October 2011, are Agrotain and Agrotain Plus. Both these products contain N-(n-butyl) thiophosphoric triamide (“NBPT”); a urease inhibitor that slows ammonia volatilization rates. It achieves this reduction by inhibiting the urease enzyme that catalyzes the hydrolysis of the urea molecule. Agrotain Plus has the added chemical Dicyandiamide (DCD), a chemical that inhibits the first stage of nitrification [change of ammonium (NH<sub>4</sub><sup>+</sup>) to nitrite (NO<sub>2</sub><sup>-</sup>)], by rendering the bacteria's enzymes ineffective. Agrotain International promotes both their products as protectants for surface applied nitrogen fertilizers by providing more nitrogen to the crop and increasing yields (Agrotain International LLC, 2010).

### **Nutrisphere N**

The fourth product tested in this study is Nutrisphere-N. This product was released in 2007 by Specialty Fertilizer Products and is promoted to be a dual purpose product (volatilization/nitrification inhibitor). Specialty Fertilizer Products describes Nutrisphere-N as a maleic-itaconic copolymer calcium salt. Company literature claims Nutrisphere-N provides year-long volatilization and nitrification protection (Specialty Fertilizer Products, 2009). The

mode of action is proprietary and thus unpublished as of the last inquiry I made, April 2010. In 2011 Nutrisphere-N was being promoted as "...the most advanced dual-action urease and nitrification inhibitor on the market...." (Specialty Fertilizer Products, 2011).

## **Product Performance**

Studies dating back as far as 1962, have investigated the effect of nitrapyrin on ammonium and urea based fertilizers. Swezey and Turner (1962) determined that nitrapyrin increased yield of cotton (*Gossypium hirsutum* L.) through increasing the efficiency of ammonium sulfate, anhydrous and aqueous ammonia and urea fertilizers. They also observed increased yields in sweet corn when nitrapyrin was included with ammonium sulfate and anhydrous ammonia and increased yields for sugar beets (*Beta vulgaris* L.P) with ammonium sulfate (Swezey, 1962). In Illinois experiments conducted by Touchton et al. (1978a, 1978b, 1979a), nitrapyrin was found to be an effective nitrification inhibitor when applied with anhydrous ammonia or urea in corn production. However, Touchton et al. (1979b) showed no increase in corn N uptake or grain yield. In Minnesota Randall et al. (2003) and Randall and Vetsch (2005) reported higher corn grain yields when nitrapyrin was included with fall applied N. Bundy and Bremner (1973) investigated 24 compounds, including nitrapyrin, that were claimed as nitrification inhibitors in a lab study using 3 different Iowa soils. They concluded that nitrapyrin was the most effective nitrification inhibitor across all three soil types, and that temperature was a factor in the overall effectiveness of all the inhibitors tested (Bundy and Bremner, 1973).

Two other products, 'NBPT' and 'DCD', have been around for many years. Through the lab evaluations conducted by Bundy and Bremner (1973), DCD was found to be an effective nitrification inhibitor in soils when field conditions were conducive to nitrification. In 1986, field studies conducted by Buresh et al. (1988) with lowland rice (*Oryza sativa* L.), NBPT along with other inhibitors tested, were found to be effective tools for reducing ammonia loss in flooded rice paddies, and given the proper conditions could translate into yield increases, although the increases may be small.

Frye et al. (1990) conducted a Kentucky study to evaluate the urease inhibitor Agrotain with surface applications of urea and urea ammonium nitrate (UAN) in the production of fescue (*Festuca arundinacea* L.). When Agrotain was used with urea and UAN, fescue yields were increased 13% over urea with no Agrotain, but only 3% over UAN with no Agrotain. Frye et al. (1990) also investigated Agrotain with surface applications of urea and UAN at corn yield limiting rates. Average corn yields were increased by 0.94 tonne ha<sup>-1</sup> when Agrotain was used with urea compared to urea without Agrotain and 0.40 tonne ha<sup>-1</sup> over UAN without Agrotain.

In 2004, a study was conducted in Kentucky to assess performance of no-till corn with surface applications of ammonium nitrate, SuperU, and UAN and urea with, and without, Agrotain. Agrotain with urea increased corn grain yield over untreated urea by 2.88 tonne ha<sup>-1</sup> and UAN treated with Agrotain increased corn yield over untreated UAN by 1.94 tonne ha<sup>-1</sup>. The authors concluded that at suboptimum rates of N, both UAN and urea mixed with Agrotain resulted in increased yields over unprotected UAN and urea. However, they noted that yield was substantially lower for the urea and UAN treatments when compared to an ammonium nitrate application (Schwab and Murdock, 2011).



Scharf et al. (2005) reported on a Missouri study comparing 14 fertilizer treatments for the reduction of ammonia volatilization in no-till corn and wheat (*Triticum aestivum* L.). The study included four injected treatments: anhydrous ammonia (AA), ammonium nitrate (AN), urea ammonium nitrate (UAN), and a urea solution; ten broadcast treatments: AA, AN, urea, SuperU, urea+Agrotain, urea+tillage, gel-coated urea, polymer-coated urea, UAN, UAN+Agrotain, and UAN+Agrotain Plus. The scope of this study is limited to only one year of data, but due to the size of the study the results will be reviewed. First, UAN and UAN+Agrotain Plus broadcast treatments yielded significantly less than the broadcast urea treatment. This was attributed to the field being in no-till production which caused the UAN that was surface applied to be bound to the soybean residues on the soil surface. In contrast to the outcome for UAN surface applied, the UAN injection treatment yielded significantly more than the surface applied UAN treatments. There were no yield differences among the seven urea treatments. Scharf et al. (2005) noted that in 2004, Missouri had optimum growing conditions in which record corn yields were obtained, which in their opinion, explained the lack of differences among the urea treatments.

A 2007 study was conducted at Princeton, Kentucky by Schwab and Murdock (2011) which included ammonium nitrate (AN), Super U (urea coated with Agrotain Plus), ESN, urea, urea with Agrotain, and urea with Nutrisphere N. The authors concluded that urea with Nutrisphere N was less effective than urea with Agrotain under high volatilization loss conditions. Under sub optimum N rates, AN performed better than all the urea treatments due to the zero volatilization potential associated with AN. AN, urea with Agrotain, Super U, and ESN yielded the same. Urea with Nutrisphere N produced the same as unprotected urea. Schwab concluded by stating, "Similar comparisons, made in other years and locations across Kentucky,

also show Nutrisphere-N is not as effective as other currently available products for reducing nitrogen losses” (Schwab and Murdock, 2011).

In 2008, lab evaluations were conducted to investigate the N release profiles of UAN, UAN+Nutrisphere-N, UCAN and ESN using five soil types representative of North Carolina agriculture (Cahill et al., 2010). Soil nitrate and ammonium concentrations of each of the treatments were measured and tracked during an 84 day period. They concluded that the release time of UAN, UAN+Nutrisphere N, and UCAN were similar, but ESN had a release time that ranged 7-42 days and was slower than the other treatments. The authors further concluded that the use of alternative N fertilizers to UAN in North Carolina corn and wheat production systems provides little agronomic benefit.

Research on nitrogen additives was conducted for Bermudagrass (*Cynodon dactylon* L.) production on two different sites in Georgia during the 2008 and 2009 growing seasons (Connell et al., 2011). Treatments included ammonium nitrate, urea, four Enhanced Efficiency Urea (EEU) formulations, NBPT-treated urea (Agrotain), NBPT/DCD-treated urea (Agrotain Plus), a polymer coated urea, and a maleic–itaconic copolymer –treated urea (Nutrisphere-N). Also included was UAN, UAN with Agrotain and UAN with Agrotain Plus. It was concluded that the use of UAN treatments produced results that were generally intermediate in effect relative to urea and ammonium nitrate for the response variables monitored during the study. Ammonium nitrate usually performed the best followed by UAN treatments and then urea. Urea treated with Agrotain reduced volatilization loss and under some conditions increased yield compared to untreated urea. Urea treated with Nutrisphere N did not differ from the untreated urea in any of the response variables. UAN treated with either Agrotain or Agrotain Plus did not affect its

performance. The authors also concluded that AN generally performed superior agronomically relative to urea-based N sources. They also reported that the use of enhanced efficiency N products neither increases nor decreases the risk of  $\text{NO}_3\text{-N}$  accumulation in forage Bermudagrass (Connell et al., 2011).

Cahill et al. (2010) conducted field studies with corn at Coastal Plain, Piedmont, and Mountain sites in North Carolina during 2008 and 2009 growing seasons. They compared surface banded treatments of UAN, UAN + Nutrisphere N, ESN and UCAN. In 2008, fields were conventionally tilled, and in 2009 the Coastal Plain and Mountain sites were no-till planted, while the Piedmont site was conventional tillage. At the Coastal Plain site there were no significant effects of fertilizer source on corn grain yield over the two years and no stover yield effect in 2008. In 2009, ESN produced higher stover yields than UAN while Nutrisphere N and UCAN were similar to UAN. At the Mountain site all fertilizer sources produced similar grain yields across both years, but Nutrisphere N and ESN produced higher stover yields compared to UAN during 2008 and 2009. The Piedmont site showed no nitrogen source effect on grain yields in 2008, the result of droughty conditions, but in 2009, UAN had lower grain yields than Nutrisphere N, ESN and UCAN. Nutrisphere N produced higher stover yields than UAN, UCAN and ESN in 2008, but there were no differences in 2009. Over all, nitrogen source had no effect on corn grain yield for five of the six site years. The authors did suggest that Nutrisphere N provided an agronomic advantage compared to UAN for stover production in the Mountain site.

Nine different lab studies were conducted in North Dakota evaluating Nutrisphere N, Agrotain (NBPT), DCD, Instinct (low volatility nitrpyrin), Ammonium Thiosulfate and Calcium Thiosulfate with urea (granular and in solution) and UAN. Other products that were

evaluated in this study were NStay, StayN, NZone, and OAC (Goos, 2011). Incubations using soil were completed comparing different combinations of products at their labeled rates with urea and UAN to identify products that reduced urea hydrolysis, ammonia volatilization, and nitrification rates. Studies one and two compared urea solution with and without Nutrisphere N and it was concluded that Nutrisphere N had no effect on urea hydrolysis as well as no effect on nitrification rates. Studies three and four compared urea granules with, and without, Nutrisphere N and found that Nutrisphere N had only a slight reducing effect for ammonia volatilization and no effect on the nitrification rate. Study five compared ammonia volatilization from UAN and UAN mixed with one of the following ATS, CaTS, Agrotain, Agrotain + CaTS, and Nutrisphere N. The effectiveness of the additives, from most to least effective, was:

Agrotain + CaTS > Agrotain > ATS = CaTS > Nutrisphere N > UAN.

Goos concluded that when Nutrisphere N was mixed with liquid UAN, it created an acidic compound that suppressed the pH of the UAN to 3.5, which he believes to be the likely explanation for the slight reduction in ammonia volatilization. Study six compared untreated urea granules, with urea granules mixed with each of the following: Nutrisphere N, NZone, StayN, NStay, OAC, and Agrotain. Out of all the products tested in study six, urea treated with Agrotain was the only additive that resulted in significant reductions in ammonia volatilization. Studies seven and eight evaluated untreated granular urea and granular urea with OAC, Agrotain, Nutrisphere N, NZone, StayN, and NStay, for urea hydrolysis rate reductions (study seven) and urea granules with Instinct, SuperU, OAC, Nutrisphere N, NStay, StayN, and NZone for nitrification rate reductions (study eight). Agrotain and OAC were the only products that

effectively slowed urea hydrolysis while Instinct (nitrapyrin) and SuperU (DCD) were the only two that inhibited nitrification rates.

Study nine evaluated Agrotain, Nutrisphere N, NZone, StayN, and NStay at different rates of product application to the soil for their ability to inhibit urease activity. Goos concluded that Agrotain (NBPT) significantly inhibited urease concentrations at use rates as low as 2 mg kg<sup>-1</sup> additive concentration in the soil, and that the other products had no effect on urease at use rates of 200 mg kg<sup>-1</sup>. Across the nine studies, Nutrisphere N had no effect on urea hydrolysis or nitrification rates when used with urea solution, no effect on nitrification when used with urea granules, and little effect on ammonia volatilization when used in combination with urea granules. It was also concluded that Nutrisphere N was less effective than Agrotain, ammonium thiosulfate, or calcium thiosulfate in reduction of ammonia volatilization. Both SuperU (DCD) and Instinct (nitrapyrin) slowed nitrification rates and Agrotain was found to significantly inhibit soil urease activity (Goos, 2011).

## **Conclusion**

This literature review has made one thing very evident; there is a lot of variable data regarding the performance of stabilized nitrogen as well as variability in the performance of the different nitrogen stabilizer products. Ammonium nitrate appears to be an effective and stable form of nitrogen fertilizer, but due to government regulations and restrictions it is no longer easily obtained. The research does seem to agree that products that contain NBPT show effective volatilization inhibition and that DCD is an effective nitrification inhibitor if the appropriate

conditions for volatilization and nitrification are present. Nitrapyrin has mixed reviews, but it has the potential to impede nitrification, and reduce nitrate leaching, if appropriate conditions are present. There appears to be consensus that no added benefit occurs when these products are used with optimum N rates. This is not surprising because nitrogen use efficiency has been estimated to be 50% (Hoeft, 2004). However, multiple researchers seem to agree that there is the potential for yield increase at sub-optimum rates if NBPT, DCD, or Nitrapyrin are used in conjunction with nitrogen fertilizer sources that can be subject to volatilization, or nitrification losses under the appropriate conditions. Products that contain DCD, NBPT, and Nitrapyrin appear to function as protective tools when appropriate N loss conditions are present. On average, they are not yield enhancers.

From the lab-oriented research reviewed for this paper, there is consensus that Nutrisphere N neither inhibits ammonia volatilization nor nitrification rates. Field studies reported in this review also fail to show any yield increase from the use of Nutrisphere N when compared to unprotected urea, or UAN, either at optimum or below optimum N rates.

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# **Chapter 3: Evaluation of Ammonia Accumulation in the Headspace of Static Collection Chambers and Soil Urea Concentrations Following UAN Sidedress Applications to Corn**

## **Introduction**

Urea ammonium nitrate (UAN) is susceptible to ammonia volatilization. UAN is comprised of urea,  $\text{CO}(\text{NH}_2)_2$  (Figure 1.2), ammonium  $\text{NH}_4^+$ , and nitrate  $\text{NO}_3^-$ . The urea component accounts for 50% of the total N in UAN, and is susceptible to loss via ammonia volatilization when it is hydrolyzed. Hydrolysis is achieved through an enzyme catalyzed reaction. The enzyme, urease, is produced by soil bacteria. The reaction is a two-step process; first the enzyme replaces one of the  $\text{NH}_2$  functional groups on the urea [ $\text{CO}(\text{NH}_2)_2$ ] with an oxygen molecule causing the release of an ammonium molecule,  $\text{NH}_4^+$ . Second, if conditions are hot, and relatively dry, the released ammonium molecule can be changed further forming bicarbonate ( $\text{HCO}_3^-$ ) and ammonia ( $\text{NH}_3$ ), a highly volatile gas which dissipates into the atmosphere.

Another N loss pathway for UAN is through the reduction of the ammonium component of the fertilizer which also accounts for 30% of the N in solution. Since soils are predominantly negatively charged the ammonium component of UAN is readily bound to the soil particles if adequate soil contact is achieved with the fertilizer. However, if either soil contact is not achieved during UAN application, or if there are not enough negatively charged bonding sites in the soil to tie up the ammonium molecules, ammonium can readily convert to ammonia which is released to the atmosphere.

As mentioned in Chapter 1, ammonia volatilization can account for 5-20% of N loss if suitable conditions for loss are present and/or proper nitrogen management is not practiced. Optimum conditions for ammonia volatilization are warm weather and relatively dry soils. Maryland corn farmers are typically sidedressing their corn during June through as late as early July. It is not uncommon for droughty conditions to prevail during that period which creates conditions conducive to ammonia loss for sidedressed UAN fertilizer.

Since a loss of up to 20% can have a significant impact on available N during the growing season, sidedress application methods are designed to maximize nitrogen use efficiency and minimize loss. The accepted standard for limiting ammonia volatilization is sub-surface injection of UAN solution. This maximizes soil contact with the fertilizer which enhances the bonding of ammonium ( $\text{NH}_4^+$ ) to the predominant negative charges in the soil. However, for various reasons sub-surface injection is not always practiced. Farmer reasons for not injecting are: 1) the added cost of fuel required to pull the injection bar; 2) either high clay content soils or rocky soils which inhibit the injector from achieving the proper depth; 3) and the increase in application time due to the slower speed for injection compared to surface applications.

Another option to help curtail the loss of N is for farmers to surface apply the UAN in a concentrated band (i.e. surface banding). The concentrated band of UAN, which has a pH of about 7, however as ammonia is lost from the solution the UAN becomes extremely acidic and can decrease the soil pH in the zone of application resulting in temporarily slowed bacterial activity. The ability of this method to protect N may be minor during hot, dry conditions and thus provides no guarantee of loss protection. A second application method that is currently available is the inclusion of a volatilization inhibitor with the UAN.

Three of the products included in this study are promoted for their ability to slow and/or control ammonia volatilization. These products are Agrotain, Agrotain Plus, and Nutrisphere-N. One objective of this research was to compare surface banded UAN at sidedress with these products, to surface banded UAN and sub-surface injected UAN for ammonia volatilization and urea concentration changes. The experimental hypothesis was: UAN with a volatilization inhibitor will not differ in long term headspace ammonia accumulation (HAA) following sidedress application compared to either UAN surface banded or UAN sub-surface injected. Headspace ammonia accumulation was monitored for a seven day period following sidedress application in the highest corn N rate treatment,  $180 \text{ kg ha}^{-1}$ , at all site years. In 2010, to quantify changes in soil urea concentration, soil samples were collected from the same plots that HAAs were measured during the seven day period following sidedress applications. A control treatment was also monitored to measure ambient ammonia release from the soil, which was not expected to be present, as well as measure base levels and changes in soil urea concentrations.

## **Materials and Methods**

Between 2009 and 2011, nine field experiments were established at University of Maryland Research and Education Centers (Table 3.1) with soils representative of the Coastal Plain and Piedmont regions of Maryland (Table 1.1). The experimental design was a randomized complete block with a split plot arrangement of treatments and four replications. The main plot factor was the nitrogen stabilizer products and/or the application methods and the split plot factor was nitrogen rates; 90, 134, and  $180 \text{ kg N ha}^{-1}$  (Table 1.2). A control plot, no nitrogen added, was included as a reference. The fertilizer N source was liquid UAN (30% N as urea-ammonium

nitrate solution) (Table 1.2). Due to field size constraints at Clarksville, the Agrotain main plot factor was omitted from the treatment structure all three years, and in 2011, the study at Clarksville was only replicated 3 times. Corn hybrids used were Pioneer brand ‘33B54’ (2009) and Pioneer brand ‘35K09AM1’ (2010 and 2011). Pioneer brand ‘33B54’ is a 113 day corn relative maturity (CRM) hybrid while ‘35K09AM1’ is a 106 day CRM hybrid. Hybrids were switched, in 2010, due to the discontinuation of Pioneer brand ‘33B54’. All sites were planted at 73,000 seeds ha<sup>-1</sup>, in 76 cm spaced rows, between late April and mid-May (Table 3.1) utilizing the no-till planters at each location. In all years, 34 kg N ha<sup>-1</sup> starter fertilizer was applied with the planter and the balance of each N rate treatment was supplied as a sidedress application between corn growth stages V5 and V7, (Aldrich, 1984). Sidedress treatments were applied using a Spray Mate II Automatic Rate Controller (Microt-Trak Systems Inc. Eagle Lake, MN) on a custom 6 row applicator capable of surface banding applications as well as sub-surface injection. Products were mixed with the UAN at time of application and products were used at the manufacturer’s suggested rates; Agrotain 2.11 L tonne<sup>-1</sup> UAN (64 oz ton<sup>-1</sup> UAN), Agrotain Plus 30 kg tonne<sup>-1</sup> UAN (15 lb ton<sup>-1</sup> UAN), Instinct 2.55 L ha<sup>-1</sup> UAN (35 oz acre<sup>-1</sup>), Nutrisphere N 0.5% by volume (0.5 gallons/99.5 gallons UAN). Surface applied treatments were streamed onto the soil surface with drop-tubes which were located approximately 15 cm above the soil and placed the fertilizer approximately mid-way between the corn rows. The sub-surface injected treatments were applied using the Yetter Coulter Injection system (Yetter Manufacturing Inc., Colchester, IL) that placed the treatments approximately 7.5 to 10 cm below the soil surface and mid-way between the rows.

As the treatments were being applied, wooden stakes were placed into the streamed zone throughout each plot that received the 180 kg ha<sup>-1</sup> rate. These stakes marked the exact placement

of the UAN solution and aided in easy site identification for placement of the gas detection chambers (Chamber Material/Construction See Pg. 39). A gas detection chamber was placed into each designated plot directly over the zone of application and hammered the requisite 5 cm into the soil. Chambers were then plugged and left undisturbed until the next sampling time. At the time of sampling, a Drager ammonia gas detection tube of adequate range was selected and headspace ammonia accumulations within the chamber were measured utilizing a Drager Accuro Gas Detection Pump. The sampling procedure involved 1) removal of the neoprene plug from the PVC cap, 2) placement of the sampling tube through the hole and approximately half the length of the sampling tube into the chamber, and 3) drawing an air sample with the pump (amount of air drawn was per Drager instructions and based upon size of Drager tube used) through the detection tube. After sampling, chambers were removed from their placement site, allowed to have any ammonia trapped within to dissipate, and placed in a new location within the plot that was approximately 15.0 cm from the previous sampling spot and directly over the zone of application. The neoprene plug was placed back in the chamber, the chamber was left undisturbed, and allowed to collect ammonia until the next sampling date. On each sampling date, daily high temperature and total precipitation since the previous sampling date were recorded. An effort was made to measure HAA at the same time each day. HAA data was indexed to the surface banded UAN treatment and analyzed for each day of measurement and each location as a randomized complete block design using the mixed method in SAS with an F-protected Tukey's mean separation when a significant alpha value of 0.05 occurred.

### **Ammonia Collection Chamber and Drager Measurement Device**

Headspace ammonia accumulation was measured using a static gas collection chamber. Each chamber consisted of 10.16 cm diameter schedule 40 poly vinyl chloride (PVC) pipe cut to

a length of 17.41 cm. A PVC cap with a 1.27 cm hole drilled in its center was glued, using PVC glue, onto one end of the pipe providing an air tight seal. Each chamber was marked on the outside at a distance of 5.08 cm from the open end of the chamber and 12.33 cm from the capped end of the chamber. When driven into the soil, a total of 1.0 L head space would remain above the soil surface. Chambers were driven into the soil with a rubber mallet to the 5.08 cm depth mark and a neoprene 1.27 cm tapered plug was placed in the hole in the top of the chamber. Initial chamber placement was done randomly near the center of the plot which allowed for adequate area in either direction of the plot for future placement of the chamber during sampling, seven days following sidedress application.

HAA was measured utilizing Drager Ammonia Gas Detection tubes and a Drager Accuro Gas Detector Pump (Drager part number: BVS 04 ATEX H 068; Drager Safety AG & Co. KGaA, Luebeck, Germany). In 2009 and 2010, two different ranged tubes were utilized to measure the ammonia concentration within the head space of each chamber; 0.25 – 3.0 ppm ammonia concentration range (Drager part number: 8101711) or 5.0 - 100.0 ppm ammonia concentration range (Drager part number: 8101941). In 2011, three different range tubes were available, the two previously mentioned and a 5.0 - 600.0 ppm ammonia concentration range tube (Drager part number: CH20501).

### **Soil Urea Concentrations**

To measure changes in urea concentration, soil samples were collected on each date that an ammonia measurement was made. Four soil cores to a depth of 30 cm were taken at random locations throughout the plot, but directly from the zone of application as defined by the wooden stakes. Each core was broken into two depths, 0-15cm and 15-30 cm, placed inside a zip lock

bag which was placed into a cooler that contained dry ice. Following completion of sampling, samples were kept frozen in a -20 °C freezer. To avoid warming of the samples which would have supported microbial activity that would have allowed conversion of some urea to ammonium, all soil sample preparations for analysis were conducted in the -20 °C freezer to maintain their frozen state. Using a hammer mill, samples were ground to pass through a 2.0 mm sieve. Three grams of soil from each sample were weighed into an extraction bottle. When the extractions were conducted, samples were removed from the freezer and 30 ml of 2.0M KCl was added to each extraction bottle. Bottles were shaken for 30 minutes using an Eberbach reciprocating shaker (Ann Arbor, Michigan), allowed to settle for 30 minutes after shaking, and then the contents of each bottle were filtered through a piece of Whatman No. 42 filter paper (Buckinghamshire, United Kingdom). The exudate was collected, bottled and frozen at -20 °C until analysis. Soil urea exudate was analyzed using a modified Diacetyl Monoxime colorimetric method as described by Sullivan and Havlin (1991). Analysis was completed using a Lachat Instruments, Quick Chem Continuous Flow Ion Analyzer (Hach Company, Loveland, CO). A randomized complete block with a split plot arrangement of treatments was the model used for statistical analysis of the soil urea concentrations. The analyses were conducted using the mixed method in SAS with a Tukey's F-protected mean separation approach for analyses that had a significant alpha value of 0.05.

## **Results and Discussion**

In 2009 at Beltsville, the sidedress treatments were applied on 6 June. Daily high temperatures which were recorded for each day, following the sidedress applications, ranged



from 23°C to 32°C. Total precipitation for the two weeks following application was 6.1 cm (Table 3.2) with 1.9 cm occurring within the first 24 hours after application and an additional 1.7 cm occurring during the second 24 hour period following application (Figure 3.1). The location of the study in 2009 was on a sandy loam soil with low cation exchange capacity (CEC) (Table 1.1). CEC and OM for the 2009 Beltsville site location were 2.9 and 1.8%, respectively. During the months of April, May, and June above average rainfall occurred providing adequate soil moisture (Table 5.2) at sidedress time. Significant differences among treatment HAA for each measurement day were observed (Figure 3.1). HAA index on day one following application resulted in significantly more HAA for the surface banded UAN than all other treatments. On the third day following application surface applied UAN and Nutrisphere N had similar HAA, and both had higher accumulation than the control, injected UAN and Agrotain Plus. On day seven, Agrotain Plus had accumulation comparable to surface applied UAN and Nutrisphere N treatments. Injected UAN was significantly less than surface banded UAN, Agrotain Plus and Nutrisphere N but had significantly greater HAA than the control (Figure 3.1). The rain events that occurred during the first, second and seventh days did not slow HAA for surface UAN during this period indicating that on soils with higher sand content, and during high temperatures, precipitation events may not inhibit volatilization of ammonia. Agrotain Plus was comparable to the injected UAN treatment for the first two sampling days while Nutrisphere N showed similar losses to the surface banded UAN for the third and seventh days following application. The injected UAN treatment performed the best out of all of the treatments, but Agrotain Plus did provide protection against HAA for days one and three.

Soil type complex for the study at Beltsville in 2010, was the same as 2009 (Russett – Christiana complex), but the study site was at a slightly lower elevation along a wooded lot

(Table 1.1) and had a CEC of 4.2 and OM of 1.9%. During the 2010 growing season, Beltsville experienced below average rainfall, rainfall totaling 1.25cm or greater below the monthly average, during the months of April and June, average rainfall during the months of May and July, and above average rainfall during July and September (Table 5.2). Although July experienced near average rainfall, the fourteen days following the sidedress applications (8 June) only accumulated 2.1 cm of rain and had daily high temperatures ranging from 26 - 36° C (Table 3.2). This hot dry period following sidedress applications increased the chances for nitrogen loss via ammonia volatilization. In 2010 (Figure 3.2), surface banded UAN had higher HAA during the first and second days following application compared to the other treatments. However, by the third and fourth days following application Nutrisphere N and surface applied UAN were not different and both had higher HAA than the Control, Injected UAN, Agrotain, and Agrotain Plus. On the seventh day Agrotain had the highest HAA accumulations followed by Nutrisphere N, Agrotain Plus, surface banded UAN, injected UAN, and then the control. HAA for Injected UAN was not statistically different than the Control on all sampling days in 2010. Agrotain Plus and Agrotain had comparable HAA to the Injected UAN treatment for the first four days following application while Nutrisphere N, though it slowed HAA during the first two days following application, performed similarly to surface applied UAN during days three, four, and seven. The most striking difference between 2009 and 2010 HAA data was the failure in 2009 for the precipitation received to reduce HAA during the subsequent sampling days. Although temperatures were slightly warmer in 2010 compared to 2009, the Injected UAN treatment incurred little to no ammonia loss in both years. This demonstrates the effectiveness of sub-surface injection as the optimum way to reduce ammonia volatilization when sidedress applying UAN to corn.

In 2010, soil urea concentrations were measured to observe if the volatilization inhibitors slowed the hydrolysis of the urea component of the UAN fertilizer (Figure 3.3). The patterns that were seen in the 2010, HAA measurements also showed up in the soil urea concentrations. The high amount of variability inherent in this data, particularly for the first three days of sampling, was the result of the difficulty with inserting the soil probe solely within the application zone which caused variable amounts of fertilizer and product to be collected. However, the data does support logical response trends. The nitrogen stabilizer products/application method main plot factor did have a significant effect on soil urea concentrations. Agrotain and Agrotain Plus, two stabilizer products that contain a urease inhibitor, slowed the rate of urea hydrolysis during the 7 day period following application. This is evident by higher urea concentration for these two treatments on days three, four, and seven (Fig. 3.3). By day three, surface applied UAN, Nutrisphere N, and Injected UAN were not significantly different compared to the control. This response in urea parallels the HAA patterns observed for surface applied UAN and Nutrisphere-N (Fig. 3.2). Both those treatments had high HAA during days three and four, which coincides with the low amounts of urea observed for those two days. This indicates that the urea in these two treatments was hydrolyzed and the resultant ammonia was dissipated into the atmosphere. The urea concentration for Injected UAN also declined to low levels by days three and four. However, in this case, the ammonia that was the result of the hydrolysis of urea was not lost as shown by the amount of HAA for the Injected UAN treatment in Figure 3.2. Instead, because the hydrolysis of urea occurred in the soil, the ammonia for the Injected UAN was bound to the soil particles. By day seven, all treatments had very low levels of urea. This day seven outcome shows that Agrotain and Agrotain Plus provide approximately seven days of protection against urease activity.

The 2011 growing season at Beltsville experienced similar patterns to 2010. Soil CEC and OM were 4.1 and 2.5%, respectively. Sidedress treatments were applied on 1 June (Table 3.1). April was the only month which experienced average rainfall. Below average rainfall occurred during the months of May and June. Total accumulation of rain during the 21 days following sidedress applications was 2.7 cm and daily high temperatures ranged from 27 to 37° C (Table 3.2). The droughty conditions following sidedress application created suitable conditions in which N loss via volatilization could occur (Fig. 3.4). On sampling day one, Nutrisphere N had the highest accumulation and was found to be significantly greater than both Injected UAN and the Control which incurred the lowest accumulations. On the third day following application, no treatments were found to be statistically different but Nutrisphere N accumulations were almost eight times greater than the surface banded UAN. All treatments had accumulations that were statistically similar and lower on day four compared to day three. This is attributed to the cooler temperature for that day (26.9° C was the high) and is an example of how a small drop in temperature can influence headspace ammonia accumulations. The temperature returned to greater than 30° C by the seventh day when all treatments were found to have significantly less HAA compared to surface applied UAN. Throughout the measurement period, the Injected UAN proved that it provided the best protection for sidedress UAN by consistently having the least amount of HAA.

The Clarksville site in 2009 had a finer textured soil in comparison to the other site locations, and it had a CEC of 9.1 and OM of 1.8%. At Clarksville in 2009, there was above average rainfall during the months of April and May, and below average precipitation during the month of June (Table 3.2). Sidedress applications were made on 16 June, and daily high temperatures following application ranged from 18-32°C. Total rainfall during the 14 days

following sidedress was 3.4 cm (Table 3.2). Due to the lower temperatures experienced, ammonia volatilization potential was greatly reduced. The timely rainfall during May in association with the finer textured soil allowed for ample soil moisture at the time of the sidedress application. Accompanying this adequate soil moisture was 2.5 cm rainfall during days one and two, and a 0.9 cm rainfall event on the seventh day following sidedress application which aided in N infiltration into the soil profile (Table 3.2). HAA at Clarksville in 2009 was much lower than occurred at Beltsville in 2009. As for stabilizer product performance, Nutrisphere N had the highest ammonia loss on days one, two, three and seven (Fig. 3.5). On day two, 2.0 cm of rain fell (Table 3.2) reducing ammonia volatilization potential (Figure 3.5). On day three, Nutrisphere N was found to have significantly increased HAA compared to the Agrotain Plus, Injected UAN, and the Control treatments. On day seven, Nutrisphere N was significantly greater than the Injected UAN and Control treatments but similar to surface banded UAN and Agrotain Plus treatments. The combination of adequate soil moisture at sidedress time, finer textured soil with higher CEC, and rainfall soon after sidedress application provided optimum conditions that reduced ammonia volatilization potential particularly for the surface applied sidedress treatments.

In 2010, Clarksville received below average rainfall in April, May, and June, average rainfall in July and August, and above average rainfall in September (Table 5.2). During the 21 day period following sidedress applications, daily high temperatures ranged from 31° C to 37° C while total precipitation of 0.6 cm was received. Soil CEC was 9.9 and OM was 2.6%. There was no significant treatment effect on HAA for any of the sampling days (Figure 3.6). However, Nutrisphere N had the highest HAAs for the first three days while Agrotain Plus had similar accumulations to the Injected UAN treatment. By day four all treatments were showing similar

accumulations (Figure 3.6). Although treatments did not show any significant HAA differences for days two, three, four and seven following sidedress application, on the fourteenth day all treatments had significantly higher losses than Injected UAN (Figure 3.6). The response at Clarksville in 2010 shows the importance of soil type and soil properties in minimizing ammonia volatilization. The low soil moisture at sidedress application coupled with the hot, dry weather after application should have provided conditions suitable for ammonia volatilization.

Soil urea concentrations among the treatments at Clarksville in 2010 differed (Fig. 3.7). On the first day following application, Agrotain Plus, Injected UAN, Nutrisphere N and surface applied UAN were not different. However, Agrotain Plus and Nutrisphere N were found to be significantly greater than the Control. On day two, both Nutrisphere N and Agrotain Plus, showed indications of inhibiting urea hydrolysis however neither was different from surface applied UAN. Nutrisphere N had significantly higher urea than Injected UAN on day two. However, by day three all treatments had equal urea concentrations and by day seven no treatments had any significant amounts of urea left.

At Clarksville in 2011, April experienced above average rainfall while the months of May and June experienced below average rainfall (Table 5.2). These conditions created dry soil conditions at the date of sidedress, 2 June (Table 3.2). The soil at Clarksville for this site year was a finer textured soil which had a soil CEC of 8.4 and an OM of 1.6. Daily high temperatures during the 21 days following sidedress applications ranged from 24 - 37°C. With daily high temperatures of 35°C and 37°C, respectively, and zero rainfall during the first four days following sidedress applications, conditions during this time frame were favorable for ammonia volatilization (Table 3.2). As experienced during the three years at Beltsville, Nutrisphere N and surface applied UAN had the highest HAAs on the first and third days following sidedress

applications, however, none of the treatments were found to be significantly different at  $\alpha=0.05$  (Figure 3.8). On day three of sampling, Injected UAN experienced a jump in HAA which was unexpected. This was attributed to the fact that with the finer soil type and with greater gravel content at this location the injection tool was not always able to obtain a depth of 10 cm. On day four, surface applied UAN had the highest loss which was significantly greater than all other treatments. By day seven, Agrotain Plus, Nutrisphere N, and surface banded UAN had similar accumulation and were significantly greater than the injected UAN and Control. Agrotain Plus provided a three to four day window of protection which occurred during two of the three years (2010 and 2011) at Clarksville. Nutrisphere N had a more variable performance at Clarksville compared to Beltsville. In 2010, it provided similar protection as Agrotain Plus for soil urea throughout the week of sampling. However, statistically it was not greater than any other surface applied treatment.

During the 2009 growing season at Poplar Hill, normal rainfall was experienced during all the growing season months except for August when it received almost double the average monthly rainfall (Table 5.2). There was ample soil moisture at the time of sidedress application, 22 June (Table 3.2). Daily high temperatures ranged from 27 to 32°C, and no rainfall was received during the first 14 days following the sidedress applications. This two-week post-applications weather pattern created conditions that were conducive to ammonia volatilization (Figure 3.9). Soil texture at the Poplar Hill site in 2009 was a silt loam (Table 1.1) which is representative of much of Maryland's Lower Eastern Shore farm land. As previously observed at Clarksville and Beltsville, surface applied UAN and Nutrisphere N had significantly higher HAA occur during the first and third days following application compared to the Control, Injected UAN and Agrotain Plus. On day seven, Agrotain Plus started to show accumulation that was

comparable to that measured for the surface banded UAN and Nutrisphere N and all three treatments were significantly greater than the Control and Injected UAN treatments.

At the Poplar Hill site in 2010, the soil texture was silt loam with a CEC of 4.1 and an OM of 1.4%. The 2010 growing season experienced below average rainfall for the months of April (-64%), May (-54%), and June (-16%) (Table 5.2) resulting in extremely dry soil conditions at the time of sidedress application, 22 June (Table 3.2). Although total rainfall for the months of June and July were below average, the rain received during the 14 days following the sidedress applications was timely (Table 3.2). The total rain accumulation during those 14 days was 4.7 cm and temperatures ranged from 33 to 38°C (Table 3.2). These extremely high temperatures increased the chance for ammonia volatilization to occur (Fig. 3.10). On the first day following application 1.35 cm of precipitation was accumulated and very low HAA resulted (Figure 3.10). Injected UAN and the Control were significantly less than the surface banded UAN. All other treatments were not different. On the second day following application, an additional 1.75 cm of rain fell. Even with these two significant rain events, measurements on the third day following application found Nutrisphere N to have the highest HAA. Injected UAN limited HAA the most and had accumulations similar to the control treatment. On day seven, an additional 1.15 cm of precipitation was accumulated and again Injected UAN and the Control had significantly less HAA than the surface banded UAN. All other treatments performed similarly. Surface applied UAN had the highest HAA on day 1, while the injected UAN treatment stood out as the best method for minimizing HAA throughout the sampling period (Figure 3.10).

Soil urea concentrations at Poplar Hill in 2010 show the impact of a rain event following sidedress application (Figure 3.11). On the first day following sidedress applications, all



treatments had similar soil urea concentrations. With a total of 3.1 cm of precipitation occurring on the first two days following application, by the third day when soil samples were collected, soil urea concentrations were negligible. As occurred at Beltsville, and Clarksville, the performance of Agrotain Plus at Poplar Hill indicated that this product provides about a seven day window of protection against ammonia volatilization. Agrotain, at Poplar Hill in 2010, showed slightly less effectiveness than at the other locations, but still provided, at minimum, a three day period of protection. In addition, the performance of all treatments at Poplar Hill during 2010, demonstrated that when a rain event occurs following the sidedress application of UAN, it can reduce the amount of ammonia volatilization that occurs.

At the Wye in 2011, the soil type was silt loam (Table 1.1) with a CEC of 6 and OM of 1.4%. Above average rainfall was received during the month of April while below average rainfall was received during the months of May (-36%), June (-38%) and July (-34%) (Table 5.2). When sidedress applications were applied on 6 June, soil moisture was low and total rainfall accumulation during the 21 days following application was only 0.9 cm (Table 3.2). Daily high temperatures ranged from 24 to 35°C, with the temperature on each of the first three days following application greater than 30°C (Table 3.2). The lack of rainfall, particularly during June after the treatments were sidedressed, and the high temperatures experienced, created conditions that were conducive to ammonia volatilization. The treatments had a significant effect on HAA during days one and four following sidedress application (Figure 3.12). Regardless of the highly favorable loss conditions present during the first four days following sidedress applications, Agrotain, Agrotain Plus, Injected UAN, and the Control had little HAA and were not significantly different (Figure 3.12). Surface applied UAN had HAA that was different from all other treatments on day one except Nutrisphere N. Nutrisphere N had the second highest

HAA and was significantly greater than the HAA for the Control and Injected UAN treatments. On days three and four, surface applied UAN and Nutrisphere N, still had the highest HAA values and both were greater than the Control, Agrotain, Agrotain Plus and Injected UAN treatments. Agrotain and Agrotain Plus consistently had HAA amounts that were no different than Injected UAN during the first four days of measurements. On day seven, surface applied UAN had the highest HAA and Nutrisphere N incurred the second highest amount. Agrotain Plus and Injected UAN had similar amounts of HAA on day seven, and both had a lesser amount compared to Agrotain, indicating that perhaps Agrotain Plus provides a slightly longer window of protection than Agrotain. A similar pattern of loss was seen at this location as occurred at the other locations for Nutrisphere N; it incurred similar HAA as surface applied UAN. Agrotain, and Agrotain Plus provided a four day window of protection before increased HAA started to occur (Figure 3.12). As was observed at all other locations, Injected UAN proved to be the best sidedress application method to minimize ammonia loss and was comparable to the control treatment.

Other field research has been conducted to investigate the performance of these volatilization/urease inhibitors. Field studies conducted by Buresh et al. (1988) with lowland rice (*Oryza sativa* L.) found that NBPT along with other inhibitors tested were effective tools for reducing ammonia loss in flooded rice paddies. In 2008, lab evaluations were conducted to investigate the N release profiles of UAN, UAN+Nutrisphere-N, UCAN and ESN using five soil types representative of North Carolina agriculture (Cahill et al., 2010). The authors concluded that the release time of UAN, UAN+Nutrisphere N, and UCAN were similar, but ESN had a release time that ranged 7-42 days and was slower than the other treatments.

Nine different lab studies conducted by Goos (2011) evaluated Nutrisphere N, Agrotain (NBPT), DCD, Instinct (low volatility nitrpyrin), Ammonium Thiosulfate and Calcium Thiosulfate with urea (granular and in solution) and UAN. Incubations using soil were completed comparing different combinations of products, at their labeled rates, both with urea, and UAN, to identify products that reduced urea hydrolysis, ammonia volatilization, and nitrification rates. Nutrisphere N was found to have no effect on urea hydrolysis and nitrification rates, and had only a slight effect on ammonia volatilization. Agrotain was found to be the most effective ammonia volatilization inhibitor and proved to be the only effective inhibitor when mixed with urea granules. Agrotain was also found to effectively reduce nitrification rates (Goos, 2011).

## **Conclusions**

The best method for protecting sidedress UAN against headspace ammonia accumulation was sub-surface injection. Although sub-surface injection did not aid in soil urea retention it maximizes UAN soil contact which maximizes ammonium bonding in the soil.

Agrotain and Agrotain Plus repeatedly provided protection against HAA during the first second and third days following the sidedress applications. This response was seen when weather and soil moisture conditions were conducive for ammonia volatilization. This performance was confirmed with the changes in soil urea concentration measured during 2010, in which Agrotain, and Agrotain Plus, slowed the hydrolysis of urea for three to four days following sidedress application (Figures 3.3 and 3.7). When significant precipitation occurred, the protective performance of Agrotain, and Agrotain Plus was reduced. The same occurred for all other

products and methods and was the result of the infiltration and bonding of UAN in the soil (Figure 3.11).

Nutrisphere N consistently produced headspace ammonia accumulations for sampling days two, three, four, and seven that were similar to surface applied UAN. This indicates that Nutrisphere-N is not an effective volatilization inhibitor, at least during the initial week following application of UAN. However, Nutrisphere N did show urease inhibitor activity at what proved to be one site only, Clarksville in 2010 (Fig. 3.7).

Using headspace ammonia accumulation, this study revealed that soil type has a major role in retaining ammonium. The Clarksville sites were representative of a finer textured soil type with higher CEC and OM. In addition, during droughty conditions, the soil type at this location retains soil moisture longer compared to the other locations where the test was conducted. These factors resulted in HAA at Clarksville being considerably less compared to the other sites during the three years the products were tested. Another important finding with this research was the amount of headspace ammonia accumulation that occurred on the sandier textured soils after what seemed to be substantial rain event/s. This occurred at Beltsville (2009) and Poplar Hill (2010) and was opposite of what was expected. The rain events on a finer textured soil (Clarksville) seemed to function as expected for reducing HAA. However, in the situations where precipitation was not enough to curtail HAA, Injected UAN performed the best. Agrotain, and Agrotain Plus provided an additional three to four day protective window for surface applied UAN against HAA, allowing additional time for adequate rainfall for incorporation of UAN to occur.



## Tables

Table 3.1. Dates for planting, sidedressing, harvesting, and soil sampling at the nine site years where the study was conducted.

Location	Year	Planted	Sidedressed	Harvested	Soil Sampling
Beltsville					
	2009	11-May	8-Jun	29-Sep	28-Sep
	2010	14-May	8-Jun	24-Sep	28-Sep
	2011	3-May	1-Jun	30-Sep	31-Sep
Clarksville					
	2009	15-May	16-Jun	12-Oct	9-Nov
	2010	10-May	11-Jun	11-Oct	15-Oct
	2011	5-May	2-Jun	6-Oct	7-Oct
Poplar Hill					
	2009	16-May	22-Jun	5-Oct	21-Oct
	2010	30-Apr	23-Jun	18-Oct	20-Oct
Wye					
	2011	3-May	6-Jun	16-Sep	1-Oct

Table 3.2. Total rainfall accumulations and daily high temperature experienced since the previous sampling date for each site year location. “Day 0” represents the day of application.

Location	Date of Sidedress		Days Following Application								
			0	1	2	3	4	7	14	21	
Beltsville											
	6/6/2009	Temp °C	32	23	28	28		30	30		
		Rain (cm)		1.9	1.7	0		2.5	0		
	6/7/2010	Temp °C	26	30	23	35	36	33	33		
		Rain (cm)		0	0.3	0	0	0	1.8		
	5/31/2011	Temp °C	36	37		29	27	32	27	31	
		Rain (cm)		0		0	0	0.1	0.4	2.2	
Clarksville											
	6/16/2009	Temp °C	23	18	27	27		28	32		
		Rain (cm)		0.5	2	0		0.9	0		
	6/10/2010	Temp °C	31	32	34	37	32	34	37		
		Rain (cm)		0	0	0	0.3	0.3	0		
	6/2/2011	Temp °C	35	37		29	26	24	27	35	
		Rain (cm)		0		0.1	0	0.7	1.6	0	
Poplar Hill											
	6/22/2009	Temp °C	29	27	29	31		32	32		
		Rain (cm)		0	0	0		0	0		
	6/22/2010	Temp °C	36	38	36	38	33	33	36		
		Rain (cm)		1.4	1.8	0	0	1.2	0.3		
Wye											
	6/6/2011	Temp °C	31	31		35	28	24	27	30	
		Rain (cm)		0		0	0	0.7	0.1	0.1	

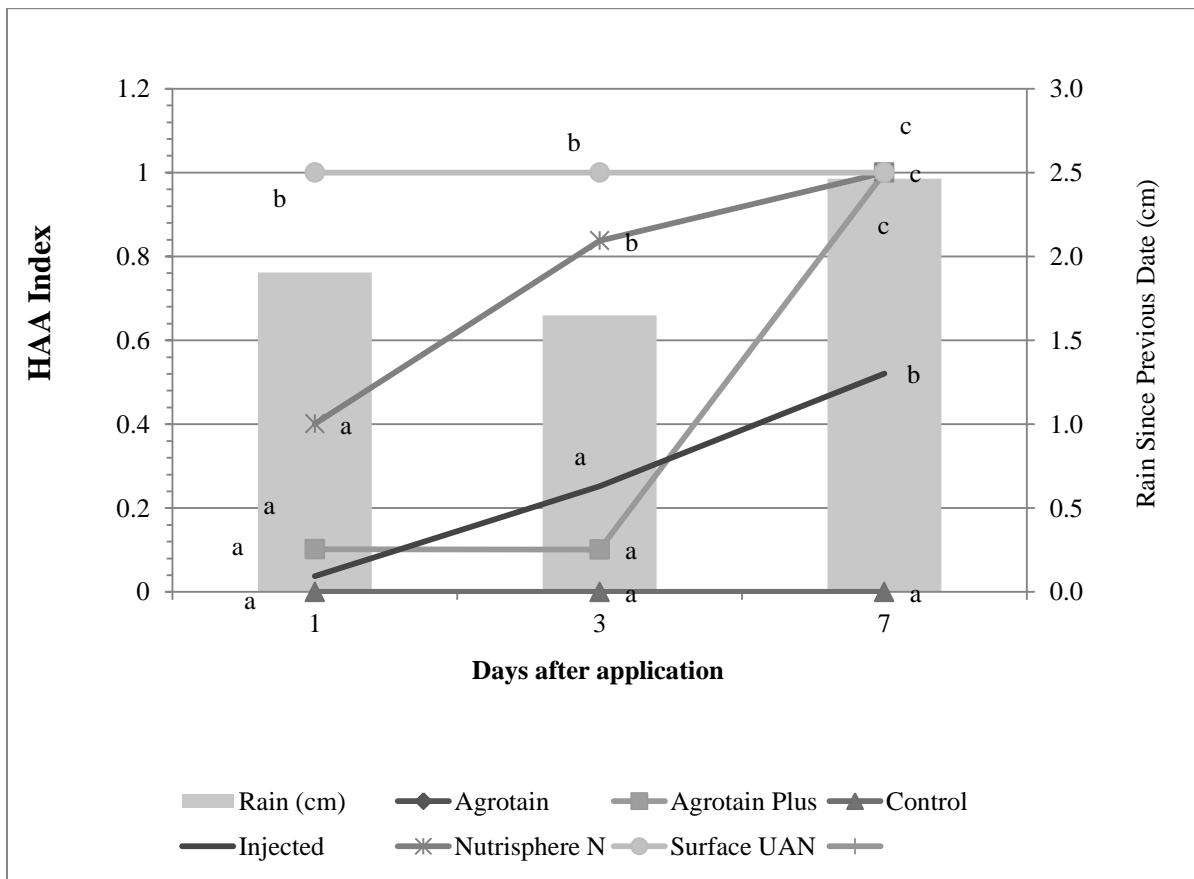
\* Rain (cm) is the total rainfall that accumulated from the previous measurement date.

\*\* Temp °C is the daily high temperature experienced during the day the sample was taken.

\*\*\* Days following application with missing values indicate days in which samples were not collected.

## Figures

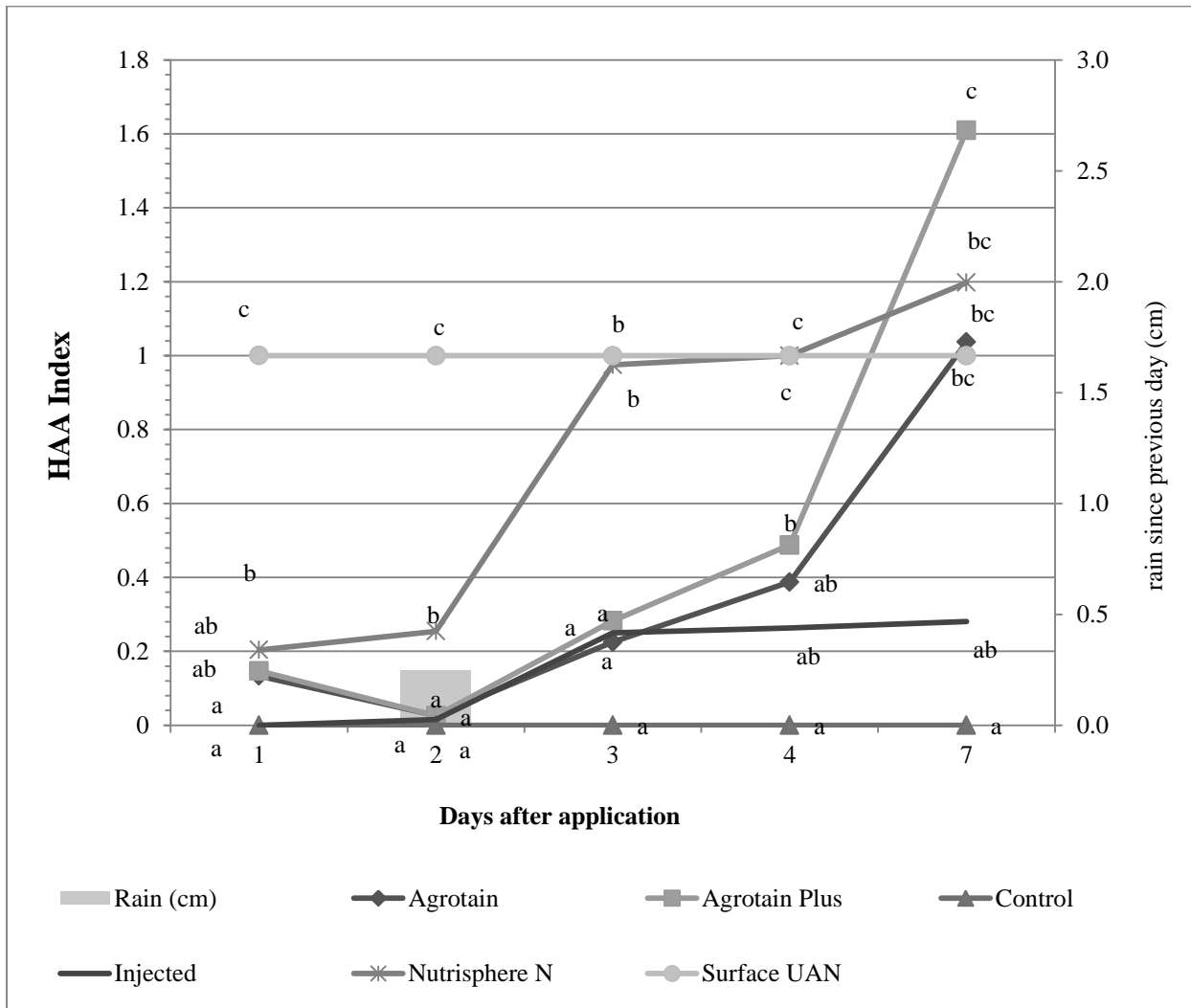
Figure 3.1. Indexed headspace ammonia accumulation (HAA) periodically measured in the static gas chambers for the four treatments and the control for the seven day period after application at Beltsville in 2009. HAA for each treatment is indexed to the surface applied UAN treatment. Accumulated precipitation since the previous sampling day is reported.



†Means within each day with a different lowercase letter are significantly different at  $p \leq 0.05$ .

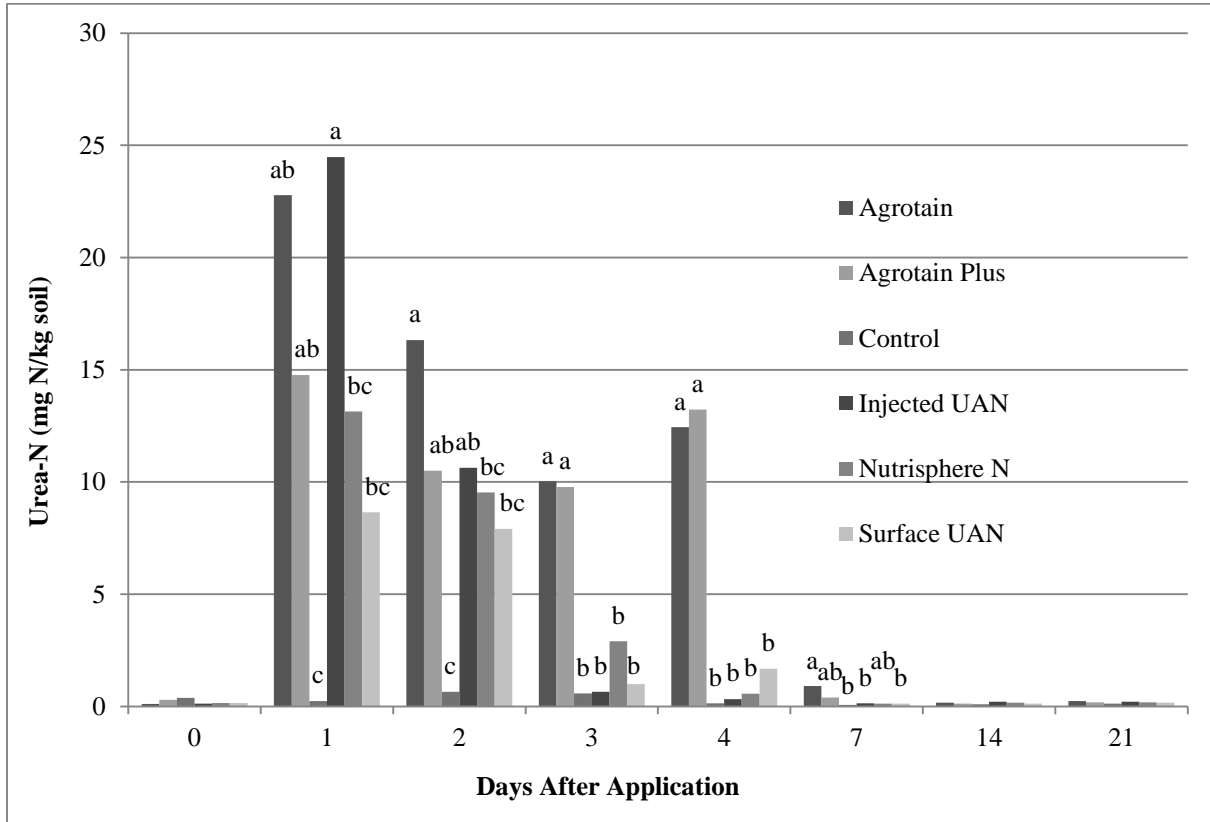


Figure 3.2. Indexed headspace ammonia accumulation (HAA) periodically measured in the static gas chambers for the four treatments and the control for the seven day period after application at Beltsville in 2010. HAA for each treatment is indexed to the surface applied UAN treatment. Accumulated precipitation since the previous sampling day is reported.



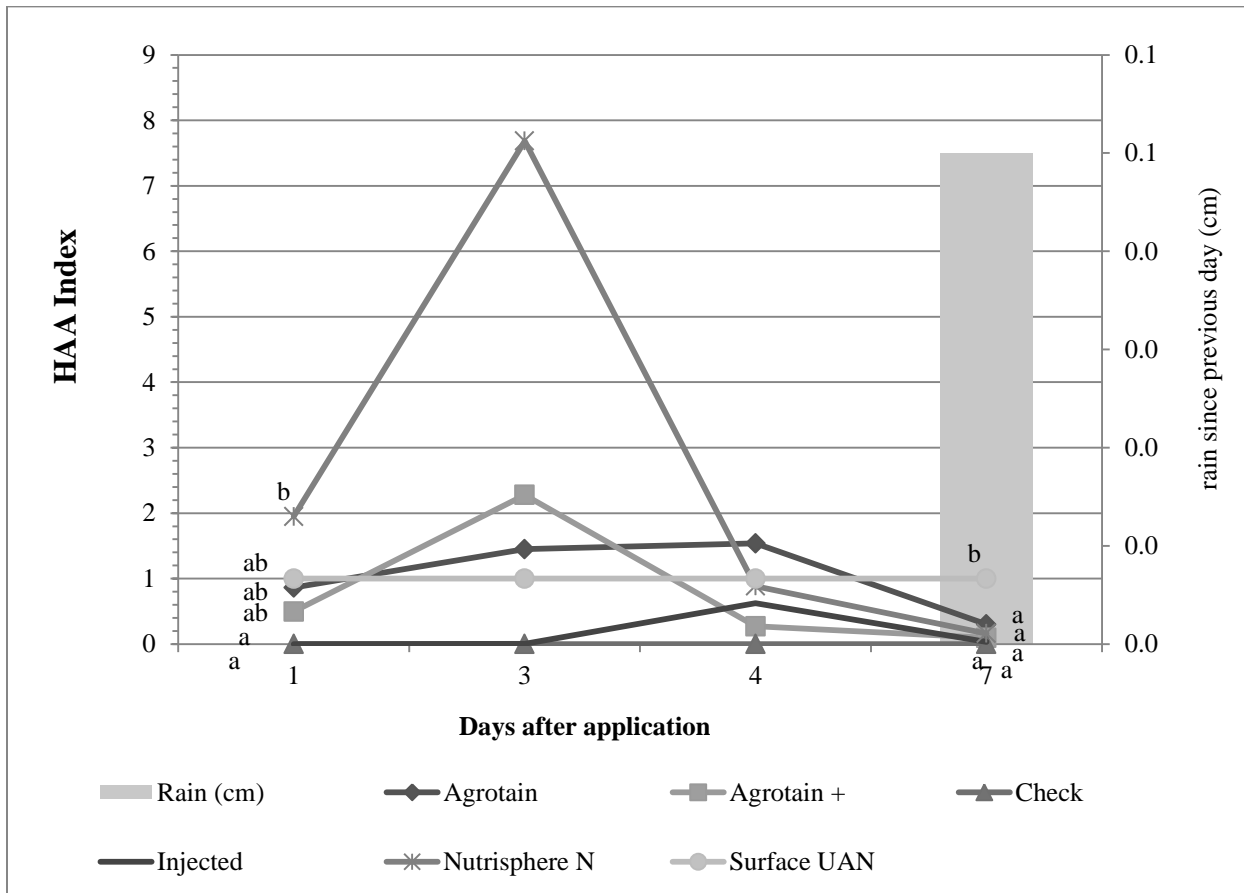
†Means within each day with different lettering are significantly different at  $p \leq 0.05$ .

Figure 3.3. Soil urea concentrations in the top 15 cm of soil taken directly from the treatment application zone, at Beltsville, in 2010. Samples were collected on the same days which ammonia volatilization measurements were collected following sidedress application.



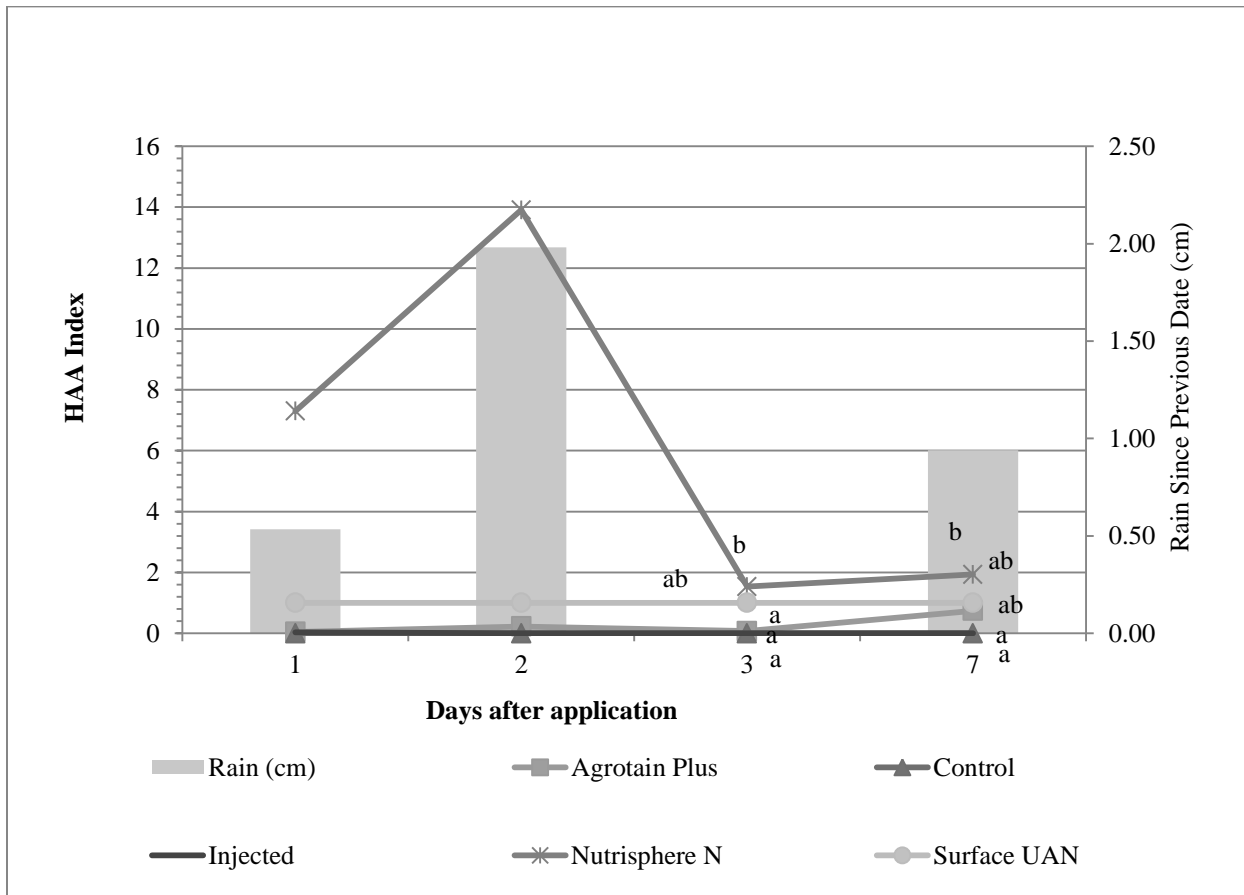
†Means within each day with different lettering are significantly different at  $p \leq 0.05$ .

Figure 3.4. Indexed headspace ammonia accumulation (HAA) periodically measured in the static gas chambers for the four treatments and the control for the seven day period after application at Beltsville in 2011. HAA for each treatment is indexed to the surface applied UAN treatment. Accumulated precipitation since the previous sampling day is reported.



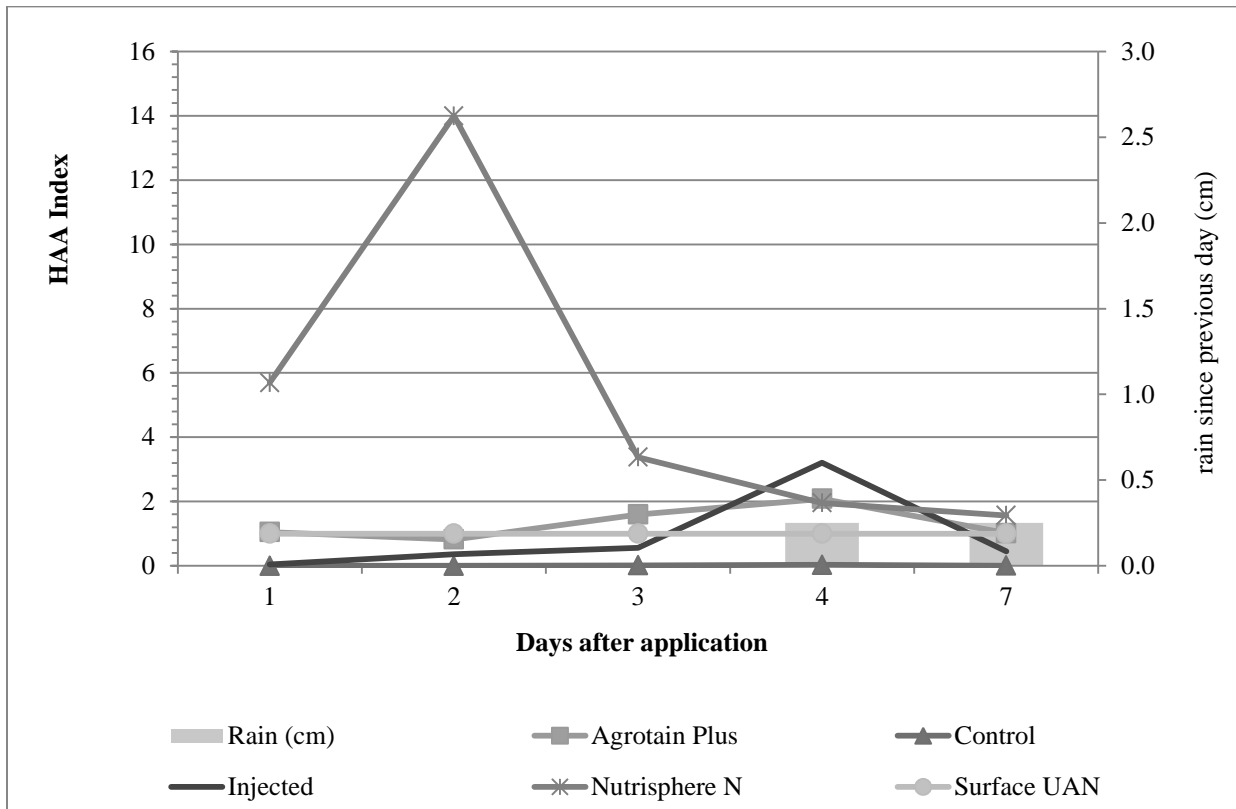
†Means within each day with different lettering are significantly different at  $p \leq 0.05$ .

Figure 3.5. Indexed headspace ammonia accumulation (HAA) periodically measured in the static gas chambers for the four treatments and the control for the seven day period after application at Clarksville in 2009. HAA for each treatment is indexed to the surface applied UAN treatment. Accumulated precipitation since the previous sampling day is reported.



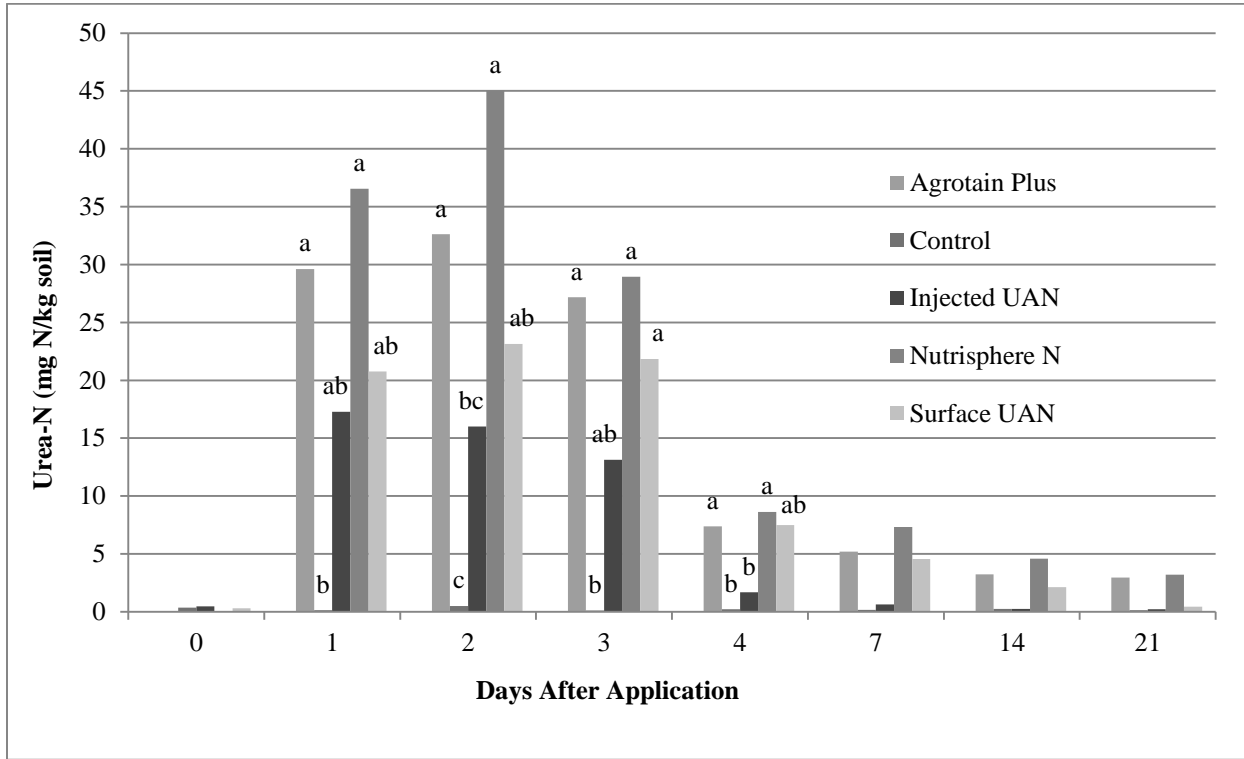
†Means within each day with different lettering are significantly different at  $p \leq 0.05$ .

Figure 3.6. Indexed headspace ammonia accumulation (HAA) periodically measured in the static gas chambers for the four treatments and the control for the seven day period after application at Clarksville in 2010. HAA for each treatment is indexed to the surface applied UAN treatment. Accumulated precipitation since the previous sampling day is reported.



†Means within each day with different lettering are significantly different at  $p \leq 0.05$ .

Figure 3.7. Soil Urea concentrations in the top 15 cm of soil taken directly from the treatment application zone, at Clarksville, in 2010. Samples were collected on the same days which ammonia volatilization measurements were collected following sidedress application.

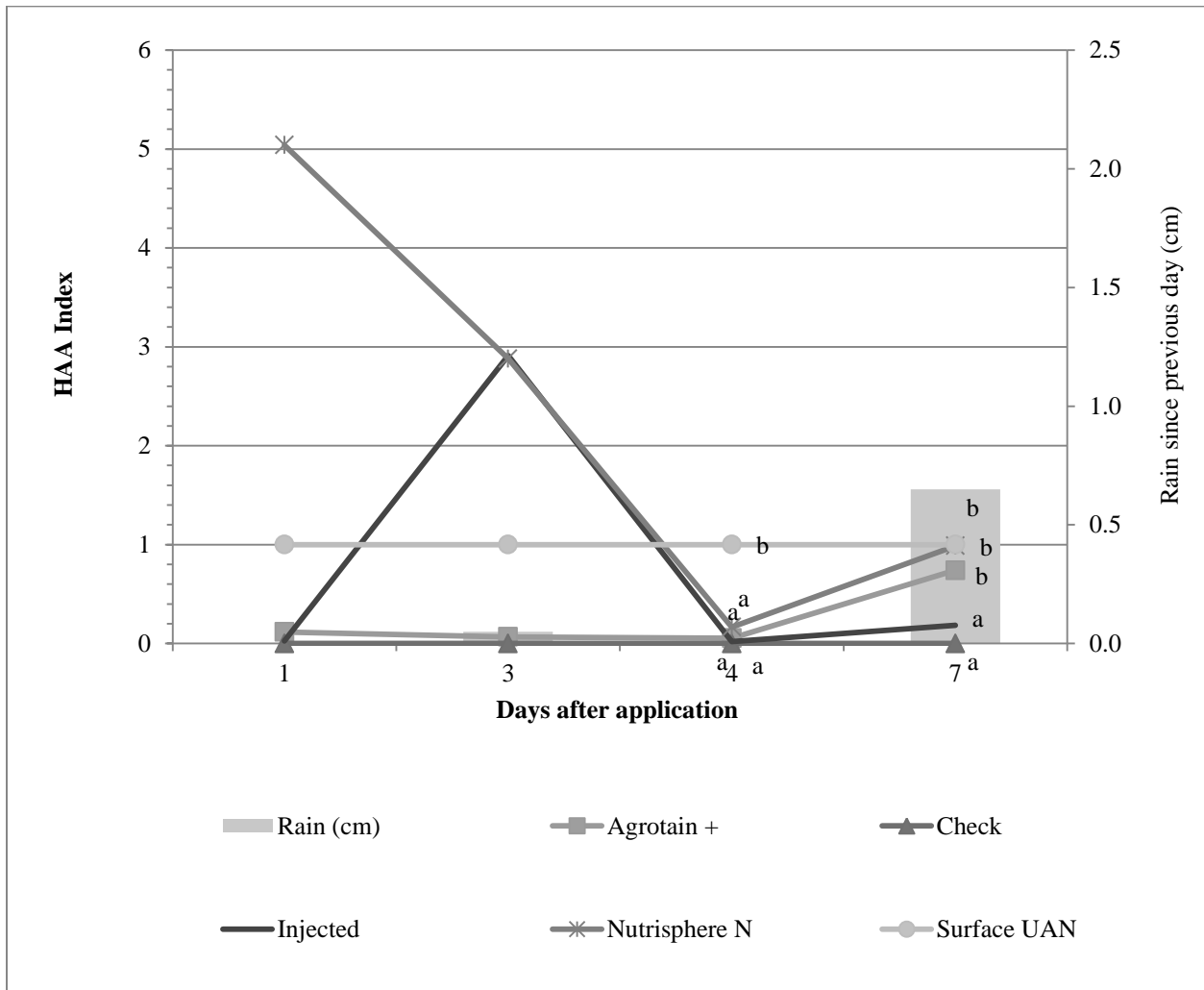


† Means within each day with different lettering are significantly different at  $p \leq 0.05$ .

\* “UAN” in the graphs legend indicates the Surface Applied UAN treatment.

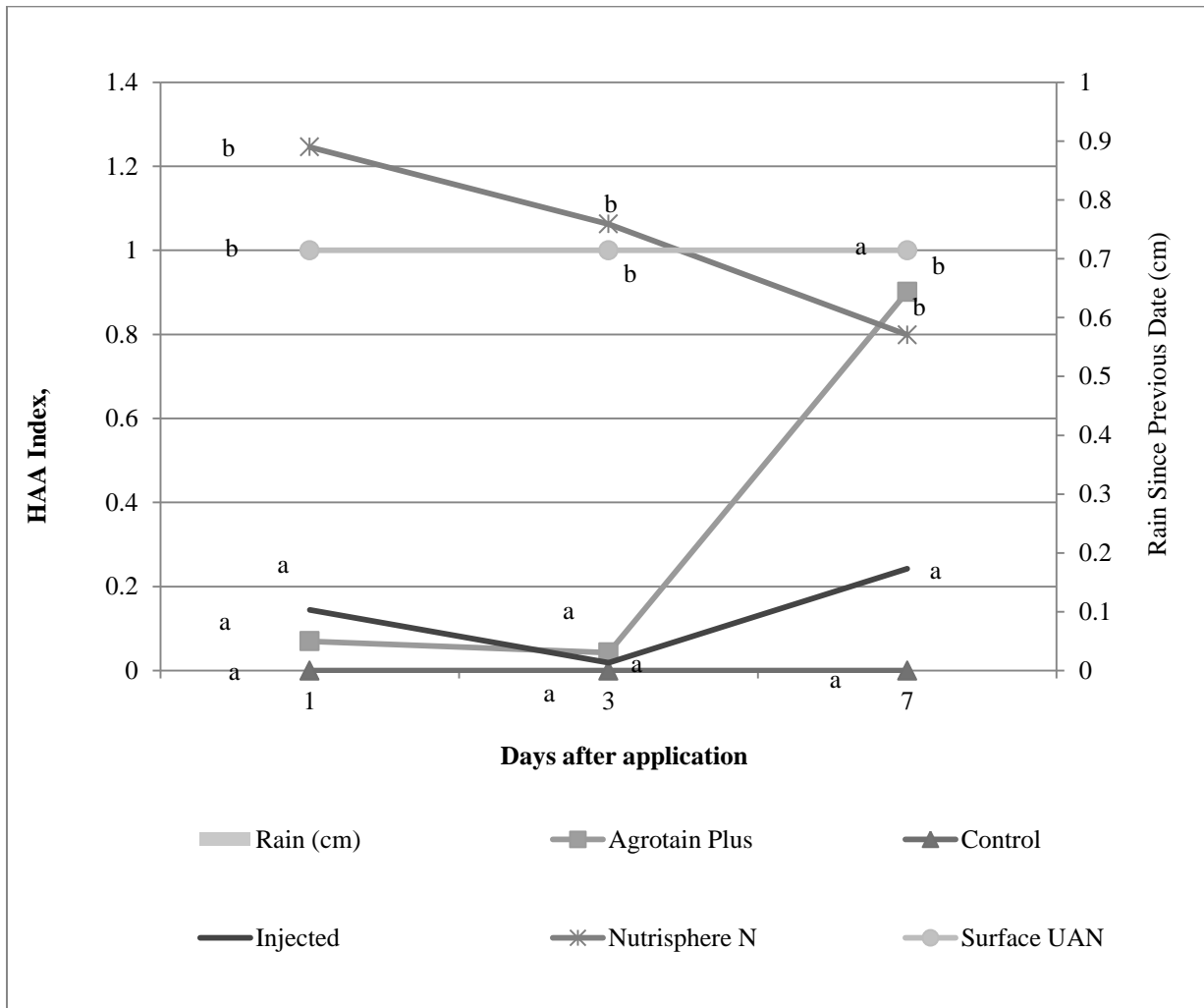
\*\* “Injected” in the graphs legend indicates the Injected UAN treatment.

Figure 3.8. Indexed headspace ammonia accumulation (HAA) periodically measured in the static gas chambers for the four treatments and the control for the seven day period after application at Clarksville in 2011. HAA for each treatment is indexed to the surface applied UAN treatment. Accumulated precipitation since the previous sampling day is reported.



†Means within each day with different lettering are significantly different at  $p \leq 0.05$ .

Figure 3.9. Indexed headspace ammonia accumulation (HAA) periodically measured in the static gas chambers for the four treatments and the control for the seven day period after application at Poplar Hill in 2009. HAA for each treatment is indexed to the surface applied UAN treatment. Accumulated precipitation since the previous sampling day is reported.



† Means within each day with different lettering are significantly different at  $p \leq 0.05$ .



Figure 3.10. Indexed headspace ammonia accumulation (HAA) periodically measured in the static gas chambers for the four treatments and the control for the seven day period after application at Poplar Hill in 2010. HAA for each treatment is indexed to the surface applied UAN treatment. Accumulated precipitation since the previous sampling day is reported.

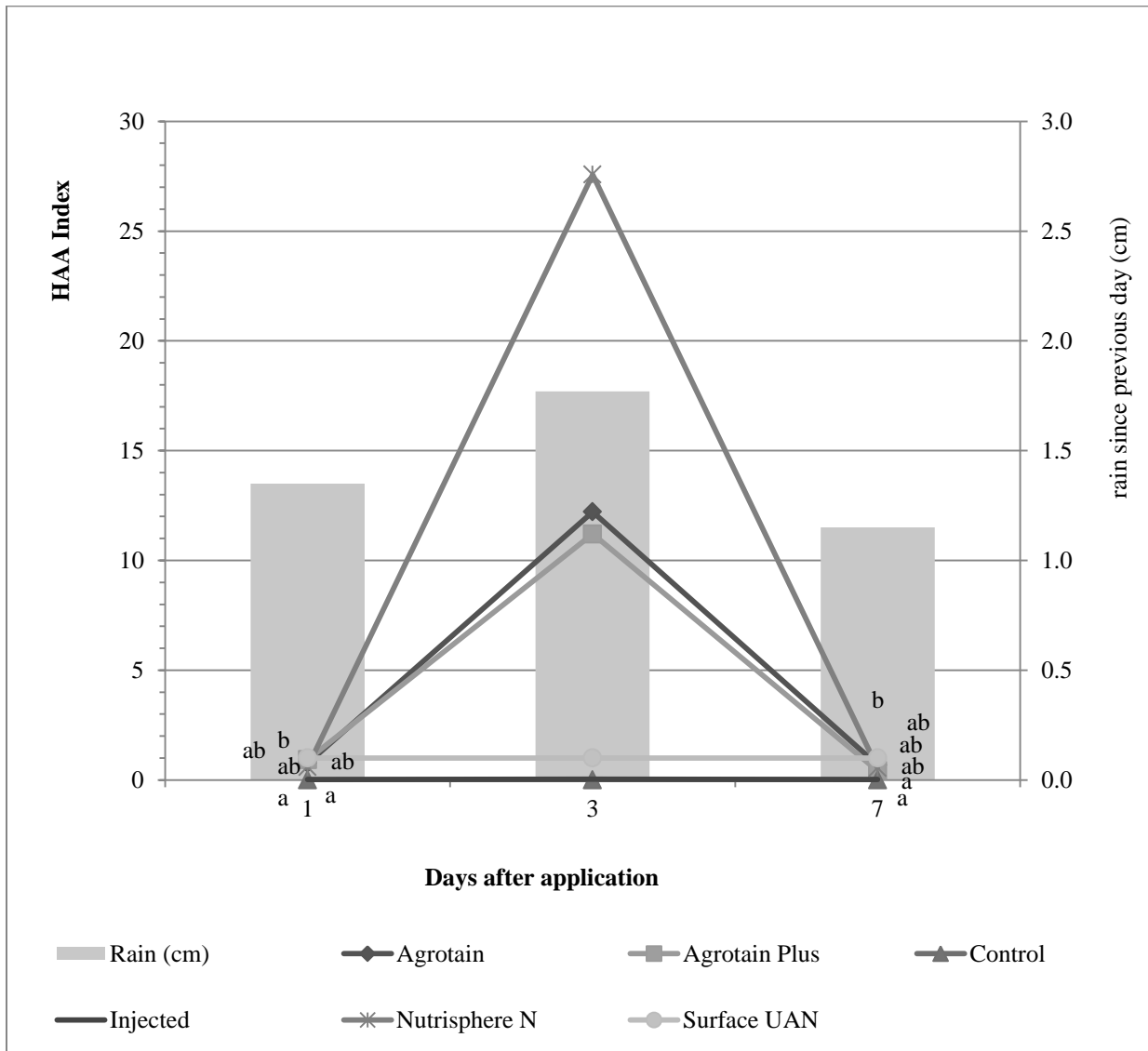
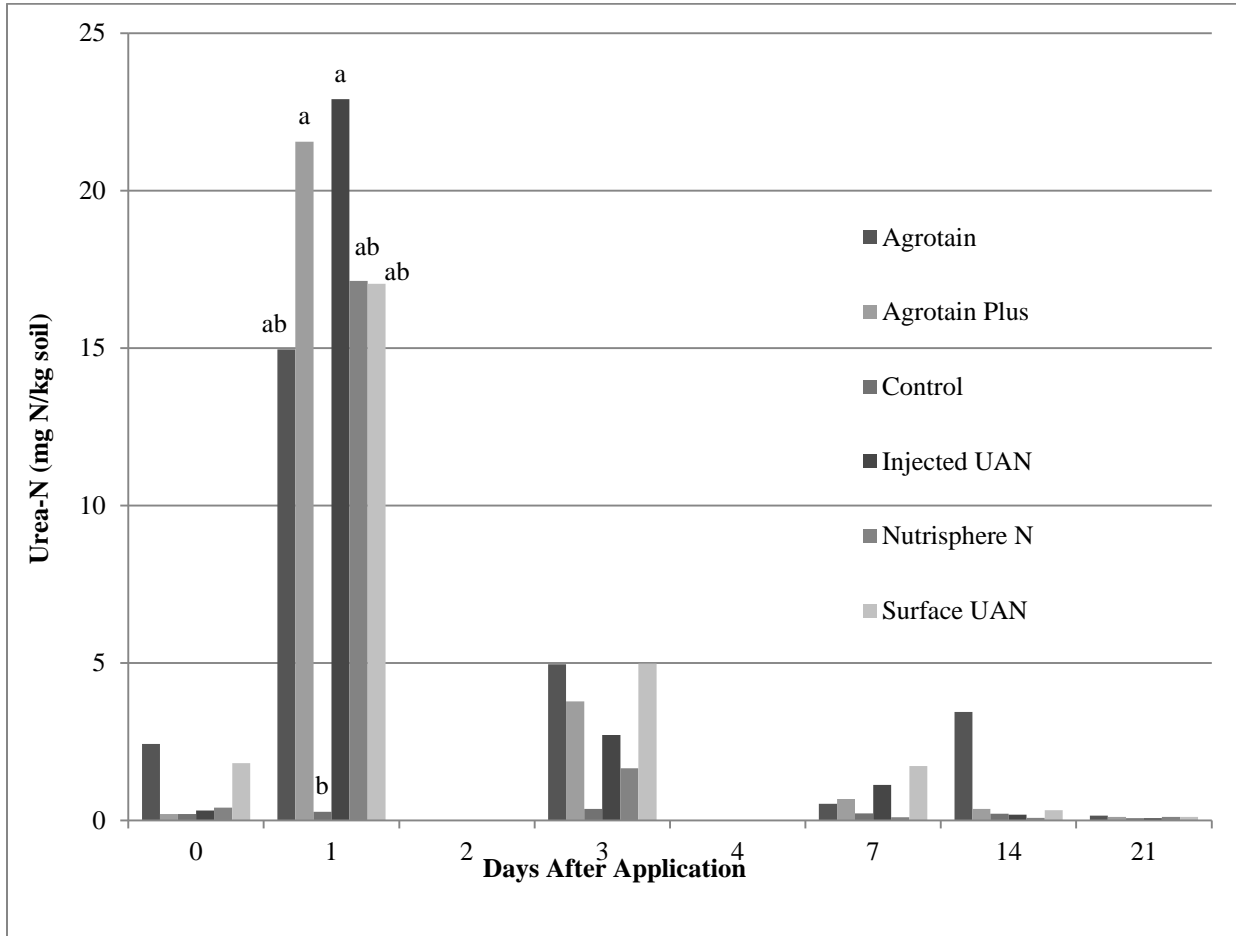


Figure 3.11. Soil urea concentrations in the top 15 cm of soil taken directly from the treatment application zone, at Poplar Hill, in 2010. Samples were collected on the same days which ammonia volatilization measurements were collected following sidedress application.

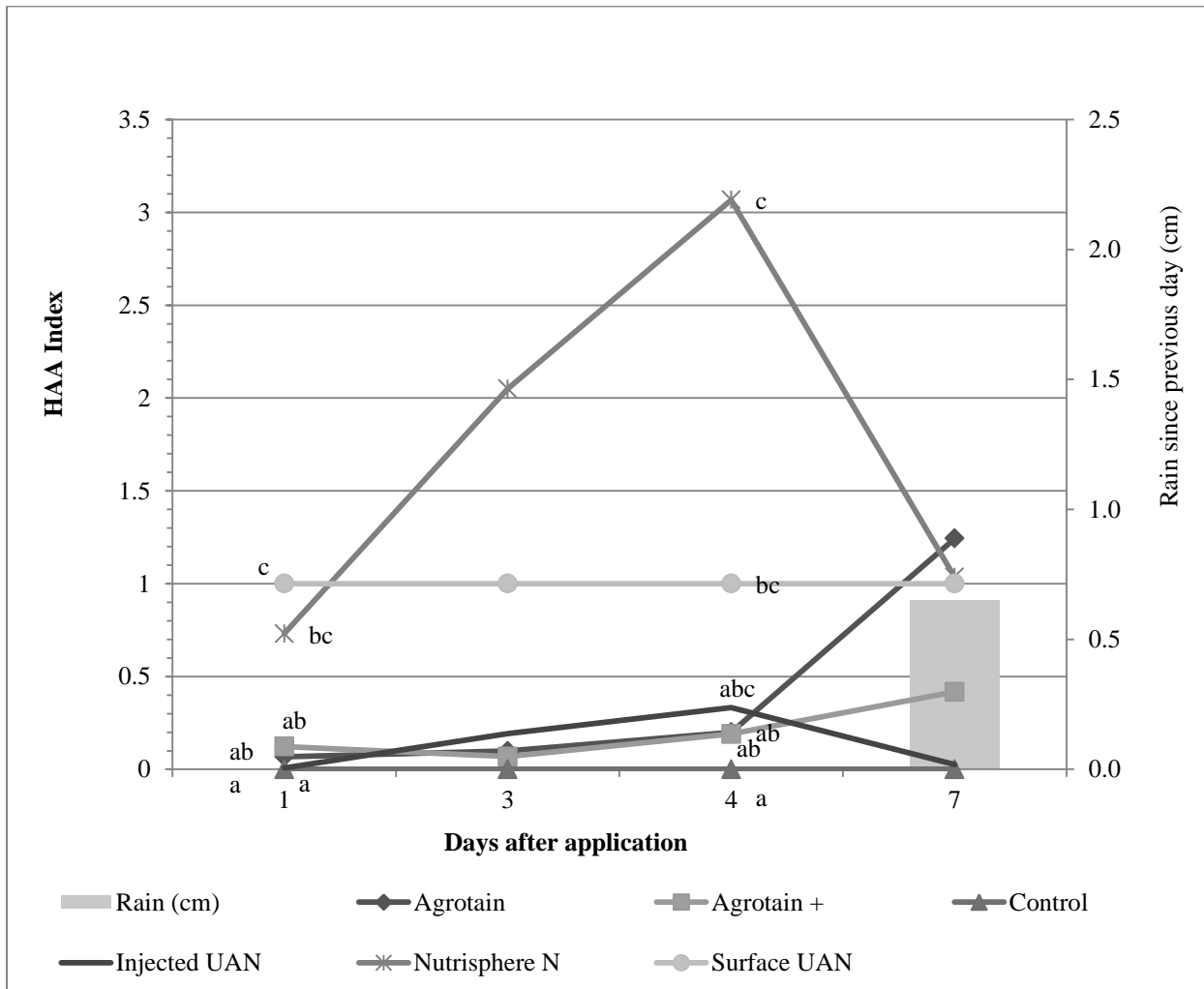


† Means within each day with different lettering are significantly different at  $p \leq 0.05$ .

\* “UAN” in the graphs legend indicates the Surface Applied UAN treatment.

\*\* “Injected” in the graphs legend indicates the Injected UAN treatment.

Figure 3.12. Indexed headspace ammonia accumulation (HAA) periodically measured in the static gas chambers for the four treatments and the control for the seven day period after application at the Wye in 2011. HAA for each treatment is indexed to the surface applied UAN treatment. Accumulated precipitation since the previous sampling day is reported.



†Means within each day with different lettering are significantly different at  $p \leq 0.05$ .

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## **Chapter 4: Influence of Nitrogen Stabilizer Products and Sidedress Application Methods with UAN on Post-Harvest Soil Inorganic-N Concentrations**

### **Introduction**

Dryland corn production in Maryland frequently suffers from localized and regional drought. Drought is considered the leading cause of excess residual nitrogen accumulation in agricultural fields. Over the last ten years Maryland has suffered from summer drought during four out of the ten years. This unfavorable weather significantly impacts corn production. The concern about excess residual nitrogen is that it subsequently moves from the fields. This loss of N has negative impacts on water quality, but it also represents an economic loss to corn producers. Since the implementation of the Clean Water Act in 1972, much focus has been directed to controlling the non-point sources of water pollution; one of which is nitrate leaching from agricultural fields. Many Best Management Practices (BMP's) are currently being utilized by farmers to help control and reduce non-point source nutrient loss. However, with the implementation of the EPA's Total Maximum Daily Loads (TMDLs) program non-point source nutrient pollution of water is receiving renewed scrutiny.

Urea Ammonium Nitrate (UAN) is the most widely used form of N fertilizer by Maryland corn producers. This form, as are all forms of nitrogen fertilizer, is highly susceptible to nitrate leaching. UAN liquid fertilizer is comprised of 25% each of nitrate-N and ammonium-N, and 50% urea-N. The nitrate component is highly susceptible to leaching, but through the process of urea hydrolysis and nitrification, which converts the urea and ammonium into nitrate, the remaining 75% of the N is also subject to nitrate leaching.

In order to help reduce end of season nitrate leaching farmers aim to balance N uptake by the crop with N inputs calculated to meet the anticipated yield of the crop. However, these inputs are last supplied to the crop three months, or more, before it is harvested, and with no knowledge of what the weather will be during those three months. The variability of weather (primarily precipitation) that can occur is the major reason why corn nitrogen use efficiency is relatively poor. Hoefl (2004) estimated corn nitrogen use efficiency to be 50%. Thus, the excess residual nitrogen following a corn crop has considerable risk of leaching.

The use of cover crops which can sequester some of the fall residual soil nitrogen before it can leach during the soil moisture recharge season provides one way in which nitrate leaching may be limited. The use of IPNI's 4 R N management approach is another way in which losses can be curtailed. However, with the release of Specialty Fertilizer Products' (SFP), 'Nutrisphere N', a new method of protecting residual nitrate from leaching was claimed. The company claim is: Nutrisphere N will provide season long protection of nitrogen, from the time of application to the intended crop to the subsequent crop's utilization, when the liquid form of Nutrisphere N is added in 28, 30, or 32% UAN solutions (Specialty Fertilizer Products, 2013). No other nitrogen stabilizer product evaluated in this research made such a claim. Post-harvest soil inorganic-N concentrations were measured to determine if higher soil inorganic-N concentrations were present when Nutrisphere N was used. The objective was to identify if any of the nitrogen stabilizer products (including Nutrisphere N) or application methods provided season long nitrogen protection thus affecting post-harvest soil inorganic nitrogen concentrations. The hypothesis was: UAN injected and surface applied UAN with and without nitrogen stabilizer products would have equal post-harvest soil inorganic nitrogen concentrations.

## Materials and Methods

Between 2009 and 2011, nine field experiments were established, at University of Maryland Research and Education Centers (Table 3.1) with soils representative of the Coastal Plain and Piedmont regions of Maryland (Table 1.1). The experimental design was a randomized complete block with a split plot arrangement of treatments and four replications. The main plot factor was the nitrogen stabilizer products and/or the application methods and the split plot factor was nitrogen rates; 90, 134, and 180 kg N ha<sup>-1</sup> (Table 1.2). A Control treatment, no nitrogen added, was included as a reference. The fertilizer N source was liquid UAN (30% N as urea-ammonium nitrate solution) (Table 1.2). Due to field size constraints at Clarksville, the Agrotain main plot factor was omitted from the treatment structure all three years and, in 2011, the study at Clarksville was only replicated 3 times. Corn hybrids used were Pioneer brand '33B54' (2009), and Pioneer brand '35K09AM1' (2010 and 2011). Pioneer brand '33B54' is a 113 day corn relative maturity (CRM) hybrid while '35K09AM1' is a 106 day CRM hybrid. Hybrids were switched in 2010 due to the discontinuation of Pioneer brand '33B54'. All sites were planted at 73,000 seeds ha<sup>-1</sup> in 76 cm spaced rows between late April and mid-May (Table 3.1) utilizing the no-till planters at each location. In all years 34 kg N ha<sup>-1</sup> starter fertilizer was applied with the planter, and the balance of each N rate treatment was supplied as a sidedress application between corn growth stages V5 and V7 (Aldrich, 1984). Sidedress treatments were applied using a Spray Mate II Automatic Rate Controller (Microt-Trak Systems Inc. Eagle Lake, MN) on a custom 6 row applicator capable of surface banding applications as well as sub-surface injection. Products were mixed into the UAN at time of application and products were used at the manufacturer's suggested rates; Agrotain 2.11 L tonne<sup>-1</sup> UAN (64 oz ton<sup>-1</sup> UAN), Agrotain

Plus 30 kg tonne<sup>-1</sup> UAN (15 lb ton<sup>-1</sup> UAN), Instinct 2.55 L ha<sup>-1</sup> UAN (35 oz acre<sup>-1</sup>), Nutrisphere N 0.5% by volume (0.5 gallons/99.5 gallons UAN). Surface applied treatments were streamed onto the soil surface with drop-tubes which were located approximately 15 cm above the soil and placed the fertilizer approximately mid-way between the corn rows. The sub-surface injected treatments were applied using the Yetter Coulter Injection system (Yetter Manufacturing Inc., Colchester, IL) that placed the treatments approximately 7.5 to 10 cm below the soil surface and mid-way between the rows.

Soil samples were taken post-harvest to a depth of 60 cm. Eight cores per plot were collected with four samples from mid-way between rows three and four of the six-row plots, and two samples each taken from within rows three and four. Samples were divided into 0 – 30 cm and 30 – 60 cm segments and air dried at 21° C for a minimum of one week. Samples were ground using a hammer mill to pass through a 2.0 mm sieve and 3.0 grams of soil were weighed into extraction bottles. Thirty ml of 2.0M KCl was added to the extraction bottle and the bottles were shaken for 30 minutes using an Eberbach reciprocating shaker (Ann Arbor, Michigan). After shaking, samples were allowed to settle for 30 minutes and then filtered through a Whatman No. 42 filter paper (Buckinghamshire, United Kingdom). Extractant was collected, bottled, and frozen at -20° C until analysis. Soil extractant was analyzed for ammonium and nitrate concentrations per the analysis method as described by Lachat (1987). Analysis was completed using a Lachat Instruments, Quick Chem Continuous Flow Ion Analyzer (Hach Company, Loveland, CO). Nitrogen in the forms of nitrate (NO<sub>3</sub>-N) and ammonium (NH<sub>4</sub>-N) concentrations were combined for total inorganic nitrogen (inorganic-N) in the soil. Soil inorganic N concentrations were analyzed as a RCB-split plot using a repeated measures method



in SAS with a Tukey F-protected mean separation approach when a significant alpha value of 0.05 was observed.

## **Results and Discussion**

During the 2010 growing season, Beltsville experienced below average rainfall (1.25cm or more below average) during the months of April, June, and July, average rainfall during May and above average rainfall during the months of August and September (Table 5.2). Although July experienced what would be considered average rainfall, the fourteen days following the sidedress applications (8 June) only received 2.1 cm of rain and daily high temperatures ranged from 26-36°C (Table 3.2). This hot, dry period following sidedress applications can affect corn growth and development which could result in decreased nitrogen uptake. The corn was harvested on 24 September and the soil samples were collected on September 28. Yields at Beltsville in 2010 were very good ranging from 7.4 tonne ha<sup>-1</sup> (control) to 8.7 tonne ha<sup>-1</sup> average for the 134 kg ha<sup>-1</sup> N rate (Table 5.1). The analysis of the data indicated there were no two- or three-way interactions among nitrogen stabilizer products/application methods, nitrogen rates, and soil sample depths. Also there was no response to the main plot factor or sub plot factor (Table 4.2 and 4.3). There was a significant depth effect for soil inorganic-N concentrations with the top 30 cm having 0.66 mg N kg<sup>-1</sup> soil and the bottom 30 cm having 0.47 mg N kg<sup>-1</sup> soil (p<0.01) (Table 4.1). The lack of differences was expected due to the 20+ cm of rain that was received in August and early September (Table 5.3). The above average grain yields in 2010 (Table 5.1) most likely would have resulted in relatively low residual soil N at this site, but when

grain yield was combined with the extreme precipitation that occurred in August and September, low residual soil N concentrations were guaranteed.

The 2011 growing season at Beltsville experienced average precipitation in April, with below average rainfall occurring during the months of May (41% of average), June (66% of average), and July (91% of average), and above average precipitation in August, and September. For the months of August and September, over 56 cm of rain was deposited first by a hurricane which was followed by a tropical storm (Table 5.2). These rain events occurred prior to harvest and soil sampling. Total accumulation of rain during the 21 days following sidedress applications (31 May) was 2.7 cm and daily high temperatures ranged from 27°C to 37°C (Table 3.2). The droughty conditions and hotter temperatures during late June and early July created crop stress which can result in reduced yield and lead to reduced N uptake by the crop. In 2011, grain was harvested (yield was more than 50% below the average for the location) (Table 5.1) on 30 September, and soil samples were collected the next day. The data was analyzed and it was determined that there were no significant interactions among rate, depth or nitrogen stabilizer products/application methods (Figure 4.1). Neither stabilizer product/application method nor rate had any significant effects (Tables 4.2 and 4.3). There was a significant depth effect with more inorganic-N found in the 0 – 30 cm depth than the 30 – 60 cm depth,  $p < 0.01$  (Table 4.1). There was a much higher concentration of soil N in 2011 compared to 2010 (Table 4.1). The dramatic difference between the 2010 and 2011 soil inorganic-N concentrations at Beltsville is attributed to poor crop uptake during 2011, which can be seen in the yield data for the two years; poor yields in 2011 and excellent yields in 2010 (Table 5.1).

Clarksville in 2010 received below average rainfall in April (78% of average), May (52% of average) and June (44% of average), near average rainfall in July and August, and above

average rainfall in September (130% of average) (Table 5.2). During the 21 day period following sidedress applications (10 June) daily high temperatures ranged from 31° C to 37° C with a total precipitation of 0.6 cm over the 3 weeks. Although Clarksville experienced a long dry period early in the season, the finer textured soil type at the site provided adequate soil moisture to carry the crop and tie up the nitrogen supplied at sidedress. Clarksville corn was harvested on 11 October and soil samples were collected on 15 October. There was no rate by depth interaction and all rates had concentrations equal to or lower than 2.0 mg N kg<sup>-1</sup> soil (Table 4.3). The Control had almost double the concentration of inorganic-N in the top 30 cm compared with the bottom 30 cm (Figure 4.3). Two significant interactions were observed; treatment by depth (p=0.02) and rate by depth (p=0.0496). For the treatment by depth interaction, Agrotain Plus had a higher concentration of N in the top 30 cm compared to the N concentration in the 30 – 60 cm depth (Figure 4.2). Nutrisphere N had significantly higher inorganic-N concentrations in the 30-60 cm depth than the 0-30 cm depth. The soil N concentrations for the Control treatment in the top 30 cm was 1.41 mg N kg soil and 0.85 mg N kg soil in the bottom 30 – 60 cm depth, which was not statistically different than any other treatment. All treatments had concentrations lower than or equal to 2 mg N kg soil which is low.

Clarksville, in 2011, experienced above average precipitation in the month of April (143% above average) while the months of May (63% of average) and June (42% of average), were well below average. July, August and September all received well above average (over 150%) rainfall with 33.6 cm of rain occurring in the latter half of August and early September (Table 5.2). Daily high temperatures during the 21 days following sidedress applications ranged from 24 - 37°C and a total precipitation of 2.4 cm fell. Soil samples were collected on the day following harvest, 7 October. Analysis of the soil inorganic-N concentrations found no

significant interactions and no differences among rates, treatments, and sample depths (Tables 4.1, 4.2, and 4.3). Even though soil samples were collected after the tropical storms had deposited 15.0 cm of rain in the second half of August, soil inorganic N concentrations were considered relatively high. Grain yields in 2011 were much lower than in 2010 (approximately 80-95% of average), even though better overall precipitation throughout the growing season occurred in 2011. This helps to explain why there was roughly a fourfold difference in soil inorganic-N concentrations between 2010 and 2011. An interesting aspect of Clarksville was that the Control treatment inorganic-N concentrations were not different compared to any other treatment in 2010, and in 2011 (Table 4.2). Also, in 2011, the Control treatment yielded 1.1 tonne ha<sup>-1</sup> less than the 90 kg N ha<sup>-1</sup> rate, and in 2010, the Control yielded 0.6 tonne ha<sup>-1</sup> less than the 90 kg N ha<sup>-1</sup> rate (Table 5.1). These two factors indicate that adequate N mineralization occurred throughout the growing season to meet crop requirements at low N rates, but yield was not maximized at these lower rates in 2011. With the finer soil texture at Clarksville, little in terms of crop requirements needs to be done to provide season long protection for soil inorganic-N.

At Poplar Hill during the 2010 growing season, below average rainfall was received for the months of April (-64%), May (-54%), June (-16%) and July (-25%) (Table 3.2). The analysis of the data determined that no interactions among stabilizer products/application methods, N fertilizer rate, and sampling depth were present for soil inorganic-N concentrations. There was a significant depth effect with more N found in the 0 – 30 cm depth than found in the 30 – 60 cm depth,  $p < 0.01$  (Table 4.1). Also, rate significantly affected inorganic-N soil concentrations,  $p < 0.01$ , with 0, 90 and 134 kg N ha<sup>-1</sup> rates having less inorganic N than the 180 kg N ha<sup>-1</sup> rate (Table 4.3). The difference between the three lower rates and the high N rate was not surprising

since corn yields increased as nitrogen rates increased and were maximized at the 134 kg N ha<sup>-1</sup> rate (Table 5.1). Soil inorganic-N concentrations were found to be significantly different at rates 0 and 134 kg N ha<sup>-1</sup>, compared to the 180 kg N ha<sup>-1</sup> and 90 kg N ha<sup>-1</sup>, compared to the 180 kg ha<sup>-1</sup>, however are considered to be low.

At the Wye in 2011 above average rainfall was received during the months of April, August, and September, with tropical storm systems depositing 62.5 cm of rain during the latter half of August and early September. Below average rainfall occurred during the months of May (-36%), June (-38%) and July (-34%) (Table 3.2). The lack of rainfall during May, June, and July plus high temperatures created stress conditions that occurred just prior and during pollination. Similar patterns for end of season soil N concentration to what was observed at the other locations were seen at the Wye. There were no two-way or three-way interactions that influenced soil inorganic-N concentrations. The stabilizer products/application method treatments had no effect on soil inorganic-N concentrations (Table 4.2). There was a significant soil depth response,  $p < 0.01$ , (Table 4.1) and a significant effect caused by nitrogen rate,  $p < 0.01$  (Table 4.3). The same patterns seen at Poplar Hill in 2010 were seen at the Wye in 2011 with the 0 – 30 cm depth having significantly more soil inorganic-N than the 30 – 60 cm depth (Table 4.1) and the three lower N rates (0, 90, 134 kg N ha<sup>-1</sup>) having significantly less inorganic-N than the high N rate (180 kg N ha<sup>-1</sup>). This was an expected outcome since corn yields were maximized at the 134 kg N ha<sup>-1</sup> rate. Also, the below average corn yields (Table 5.1) and low plant N uptake (Table 6.2) in 2011, were contributing factors to higher residual soil inorganic-N (Table 4.1).

## Conclusion

Upon review of the 6 site years of data representing three soil types in Maryland, neither nitrogen stabilizer products, when applied with UAN solution at sidedress, nor application method at sidedress, had an effect on the amount of post-harvest residual soil inorganic-N. It is important to note that for four out of the six locations, where soil inorganic-N was measured; there were higher concentration of soil inorganic-N in the top 30 cm of soil compared to the lower 30 cm of soil (Table 4.1). Similar results were reported by Forrestal et al. (2012) in which the top 30 cm of soil were consistently found to have higher concentrations of  $\text{NO}_3\text{-N}$  compared to lower soil profile depths. This was observed even in years when excessive rainfall occurred late in the season. It must also be noted that weather conditions during the growing season, which can effect crop production, play a larger role in residual soil inorganic-N concentrations than end of season precipitation. Similar results were seen by Forrestal et al. (2012) in which they concluded that droughty conditions during the growing season play a larger role in residual soil nitrate than end of season precipitation.

The most interesting observation (Table 4.3) is that the inorganic-N concentration for the 0 N rate was no different than what was observed for the other N rates, with a couple of exceptions. This phenomenon is attributed to the fact that the N rates used in this study were based on realistic yield goals determined by long term field averages. In order to have seen an increase in residual soil inorganic-N concentrations, excessive N rates would be required. Also, for 2011, since the crop did not use much of the supplied N (fall soil N levels comparable to the 0 N rate), there is some suspicion that high amounts were possibly lost via the hurricane and subsequent tropical storm that occurred in late August and early September.

According to the results of this study, there is no evidence to support the claim made by the company producing Nutrisphere N that this product is a season long nitrogen protector. In fact, none of the tested products or application methods affected post-harvest residual soil inorganic-N concentrations (Table 4.2). It is also concluded that crop production and growing conditions during the season play a large role in determining residual soil inorganic-N concentrations.

## Tables

Table 4.1. Post-harvest soil inorganic-N ( $\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$ ) concentrations averaged across the six treatments for depths 0-30cm and 30-60cm. The concentration for the top 60cm is included and is an average of the top 0 – 30cm depth and bottom 30 – 60cm depth.

Location	Year	Depth (cm)		
		0-30	30-60	avg. 0-60
Inorganic N ( $\text{mg N kg}^{-1}$ soil)				
<u>Beltsville</u>				
	2010	0.66 a	0.47 b	0.56
	2011	4.65 a	3.78 b	4.22
<u>Clarksville</u>				
	2010	1.73	1.52	1.62
	2011	7.07	6.92	6.99
<u>Poplar-Hill</u>				
	2010	0.76 a	0.50 b	0.63
<u>Wye</u>				
	2011	8.90 a	6.46 b	7.68

† Means within a row for columns 0-30 and 30-60 for each site year with different lettering are significantly different at  $p \leq 0.05$ .



Table 4.2. Post-harvest soil inorganic-N ( $\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$ ) concentration measured in the top 60cm of soil for the Control and six treatments for the six site years.

Location	Year	Treatment						Surface UAN
		Control	Agrotain	Agrotain Plus	Injected UAN	Instinct	Nutrisphere N	
Inorganic N top 60cm ( $\text{mg N kg}^{-1}$ soil)								
<u>Beltsville</u>	2010	0.5	0.5	0.6	0.6	0.6	0.5	0.6
	2011	4.2	4.3	4.1	4.7	3.8	4.0	4.4
<u>Clarksville</u>	2010	1.1		1.6	1.5	1.8	2.0	1.5
	2011	7.4		6.4	8.3	6.3	7.3	6.4
<u>Poplar Hill</u>	2010	0.6	0.6	0.6	0.7	0.6	0.6	0.7
<u>Wye</u>	2011	7.9	6.9	7.5	8.0	8.0	7.9	7.6

Table 4.3. Post-harvest soil inorganic-N ( $\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$ ) concentrations measured for rates 90, 134 and 180 ( $\text{kg N ha}^{-1}$ ) and the control treatment in the top 60 cm of soil for the six site years.

Location	Year	Fertilizer N $\text{kg N ha}^{-1}$			
		Control	90	134	180
—————Inorganic-N 0 - 60 cm soil ( $\text{mg N kg}^{-1}$ soil)—————					
<u>Beltsville</u>	2010	0.5	0.5	0.6	0.6
	2011	4.2	4.0	4.5	4.2
<u>Clarksville</u>	2010	1.1	1.4	1.7	2.0
	2011	7.4	6.1	8.0	6.7
<u>Poplar Hill</u>	2010	0.6 b	0.5 b	0.6 b	0.8 a
<u>Wye</u>	2011	7.9 b	7.1 b	7.2 b	8.7 a

†Means in each row with different lettering are significantly different at  $p \leq 0.05$ .

## Figures

Figure 4.1. Post-harvest soil inorganic-N ( $\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$ ) concentrations measured in the top 60 cm of soil for the six treatments at N fertilization rates 90, 134, and 180 ( $\text{kg N ha}^{-1}$ ) at Beltsville in 2011. Post-harvest soil inorganic-N concentration for the Control treatment was 4.2 mg N kg soil.

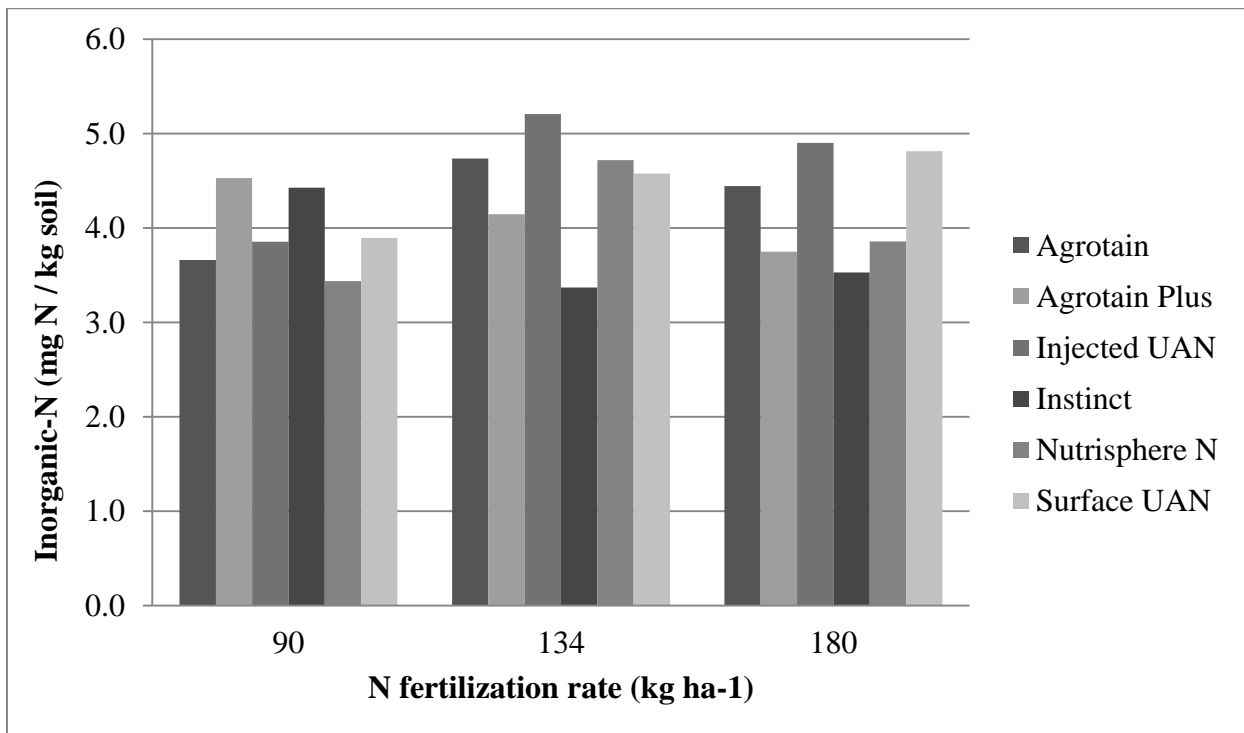
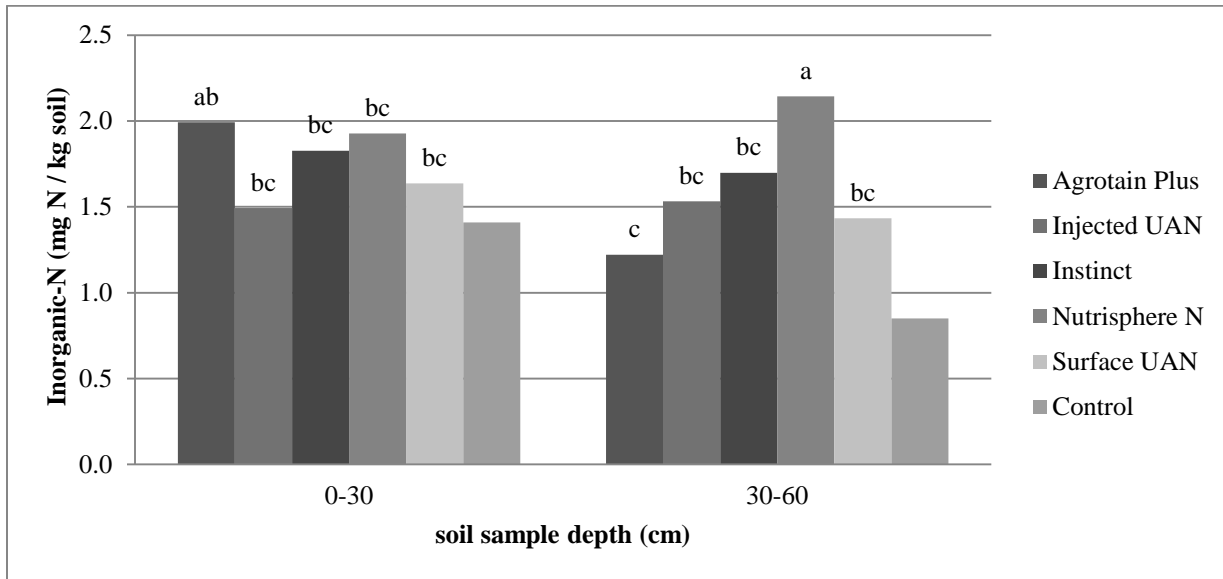


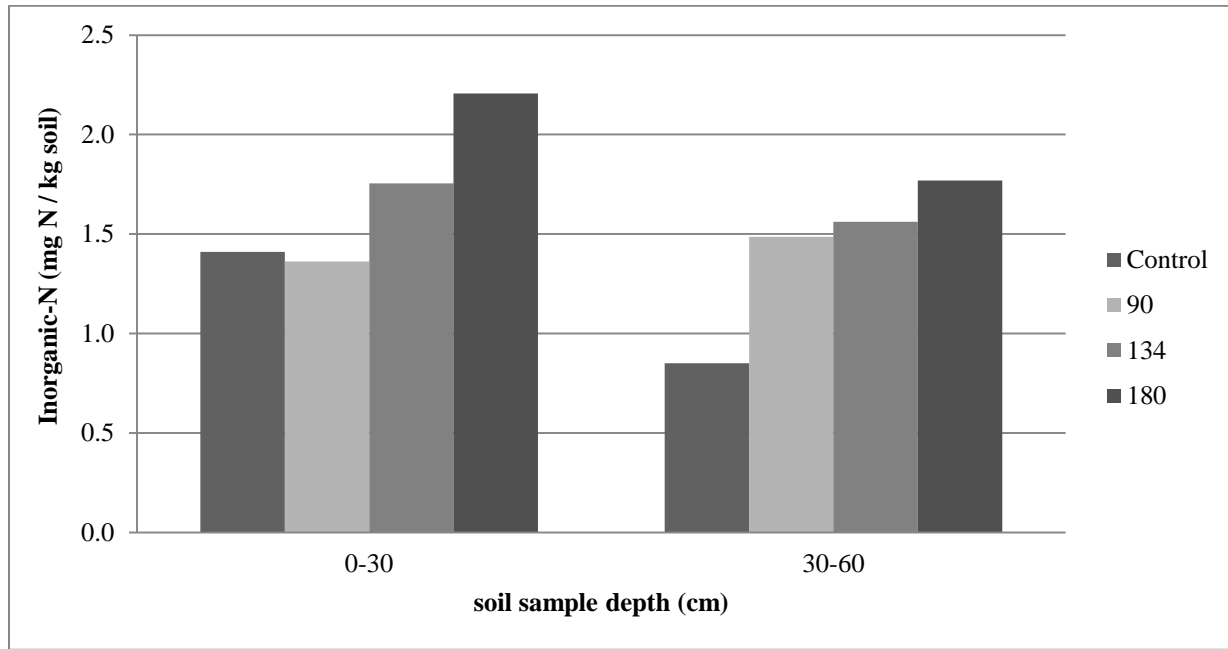
Figure 4.2. Post-harvest soil inorganic-N ( $\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$ ) concentrations measured at soil sampling depths of 0-30 cm and 30-60 cm for the five treatments and the control at Clarksville in 2010.



† Means across both depths with different lettering are significantly different at  $p \leq 0.05$ .

\* The Control treatment was not included in the statistical analysis but is included as a reference point for the field conditions having no fertilizer applied to the crop.

Figure 4.3. Post-harvest soil inorganic-N ( $\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$ ) concentrations measured at soil sampling depths of 0-30 cm and 30-60 cm for N fertilization rates 90, 134, 180 ( $\text{kg N ha}^{-1}$ ) and the Control at Clarksville in 2010.



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Retrieved: March 14, 2013.

## **Chapter 5: Effects of UAN application methods and the use of nitrogen stabilizer products on corn grain yield.**

### **Introduction**

Farmers are continually striving to improve profitability. One way farmers can increase profitability is by increasing yield without increasing inputs. Claims of increased yield are one way in which fertilizer companies have sold fertilizers, sometimes with little regard for farmers' profitability. Some of the company's marketing nitrogen stabilizer products make similar claims of increased yields with the use of their product when fertilizing corn with nitrogen.

Another way farmers can increase profitability is by reducing input costs. One of the most costly inputs in corn production is nitrogen fertilizer which, in 2008, reached \$2.20 kg<sup>-1</sup> N (\$1.00 lb<sup>-1</sup> N) in Maryland. With average nitrogen rates in Maryland pushing 196 kg ha<sup>-1</sup> farmers desire to optimize the corn yield with nitrogen applications that occur prior to when the majority of the nutrient is consumed by the crop, i.e. during its most rapid growth stages. In addition, the timing of N applications occurs with little information about the weather for the rest of the season. Thus, the N that is supplied is subject either to potential loss or to non-utilization, which makes matching N rates to the actual yield of the crop difficult, and results in relatively low use efficiency of the nutrient.

Over the last 11 years, Maryland's average yield has been 7.86 tonne ha<sup>-1</sup>. Using the state average yield and the average N rate (196 kg ha<sup>-1</sup>), each tonne of corn grain produced in Maryland, requires nearly 25 kg N. Improvement in efficiency of N use can be achieved either by attaining greater yields or by reducing the amount of N used per tonne of grain produced. One

objective of this study was to compare the effect that nitrogen stabilizer products and/or nitrogen application methods have on yield at optimum or reduced nitrogen rates.

## **Materials and Methods**

Between 2009 and 2011, nine field experiments were established at University of Maryland Research and Education Centers (Table 3.1) with soils representative of the Coastal Plain and Piedmont regions of Maryland (Table 1.1). The experimental design was a randomized complete block with a split plot arrangement of treatments and four replications. The main plot factor was the nitrogen stabilizer products and/or the application methods and the split plot factor was nitrogen rates; 90, 134, and 180 kg N ha<sup>-1</sup> (Table 1.2). A Control plot, no nitrogen added, was included as a reference, and received no application of N. The fertilizer N source was liquid UAN (30% N as urea-ammonium nitrate solution) (Table 1.2). Due to field size constraints at Clarksville, the Agrotain main plot factor was omitted from the treatment structure all three years and, in 2011, the study at Clarksville was only replicated 3 times. Corn hybrids used were Pioneer brand '33B54' (2009) and Pioneer brand '35K09AM1' (2010 and 2011). Pioneer brand '33B54' is a 113 day corn relative maturity (CRM) hybrid while '35K09AM1' is a 106 day CRM hybrid. Hybrids were switched in 2010 due to the discontinuation of Pioneer brand '33B54'. All sites were planted at 73,000 seeds ha<sup>-1</sup> in 76 cm spaced rows between late April and mid-May (Table 3.1) utilizing the no-till planters at each location. In all years, 34 kg N ha<sup>-1</sup> starter fertilizer was applied with the planter to plots receiving sidedress applications, and the balance of each N rate treatment was supplied as a sidedress application between corn growth stages V5 and V7 (Aldrich, 1984). Sidedress treatments were applied using a Spray Mate II



Automatic Rate Controller (Micro-Trak Systems Inc. Eagle Lake, MN) on a custom 6 row applicator capable of surface banding applications as well as sub-surface injection. Products were mixed into the UAN at time of application and products were used at the manufacturer's suggested rates; Agrotain 2.11 L tonne<sup>-1</sup> UAN (64 oz ton<sup>-1</sup> UAN), Agrotain Plus 30 kg tonne<sup>-1</sup> UAN (15 lb ton<sup>-1</sup> UAN), Instinct 2.55 L ha<sup>-1</sup> UAN (35 oz acre<sup>-1</sup>), Nutrisphere N 0.5% by volume (0.5 gallons/99.5 gallons UAN). Surface applied treatments were streamed onto the soil surface with drop-tubes which were located approximately 15 cm above the soil and placed the fertilizer approximately mid-way between the corn rows. The sub-surface injected treatments were applied using the Yetter Coulter Injection system (Yetter Manufacturing Inc., Colchester, IL) that placed the treatments approximately 7.5 to 10 cm below the soil surface and mid-way between the rows.

Plots were harvested following physiological maturity (Table 3.1) to measure grain yields. Harvest was completed using a Massey Ferguson 8-XP plot combine (Kincaid Equipment Manufacturing; Haven, KS). Grain weight and moisture content were recorded by the onboard Harvest Master data collection system (Juniper Systems; Logan, UT) as each plot was harvested. Plot weights were standardized to 15.5% moisture and converted to kg ha<sup>-1</sup>. Yield was analyzed as a RCB-split plot using the mixed method in SAS with a mean separation Tukey F-protected approach with an alpha value of 0.05.

The objective of this portion of the study was to identify whether nitrogen stabilizer products and/or application method, have an effect on corn grain yield. The two hypotheses were: 1) UAN surface applied with a nitrogen stabilizer product will yield equal to either UAN surface applied or UAN injected without a nitrogen stabilizer product; 2) a reduced N rate (less 25% and 50% N rates) with a stabilizer product will yield equal to the highest N rate (state recommendation) of UAN injected without a nitrogen stabilizer product. In order to test these

hypotheses N responsive site years (8) were identified (Table 5.1). Hypotheses were then tested within a location using only years that were responsive to the N rates.

## **Results and Discussion**

Nitrogen fertilization was generally required at all locations indicated by the positive grain yield response at the majority of sites. Corn grain yields increased in response to N fertilizer applications at all sites in 2009, two of three sites in 2010, and all sites in 2011 (Table 5.1), however, yields were maximized at different rates of N fertilization (Table 5.1). The one location where there was no response to N rates was Clarksville in 2010 (Table 5.1). The 2010 response at Clarksville is believed to be a result of the finer texture soil which has a CEC of 9.9, organic matter of 2.6%, and a pH of 6.3. This site location also has a history of manure application, although no manure had been applied in the previous 3 years. At Beltsville in 2009, there was no yield response to N rates above the 90 kg N ha<sup>-1</sup> rate (Table 5.1). In 2009, Beltsville's lack of response across the three nitrogen rates was identified to be the result of a micronutrient deficiency. The deficiency was identified by soil test and plant analysis information the following spring when aborted wheat spikes were observed.

A combined analysis of variance was conducted for the nitrogen responsive site years, with year designated as a random variable and location as a fixed variable. This analysis determined that there was no interaction between nitrogen stabilizer product or application method and nitrogen rate,  $\alpha=0.05$ . The analysis of variance also determined that nitrogen stabilizer product and/or application method had no effect on yield at any of the locations

( $\alpha=0.05$ ). However, all sites showed a significant effect for N rate ( $p \leq 0.05$ ) and yield significantly increased as nitrogen rate increased (Table 5.1).

During the 2010 growing season, Beltsville experienced rainfall that was 1.25cm or greater below the monthly average during the months of April and June, average rainfall during May and July, and above average rainfall during the months of August and September (Table 5.2). Although July experienced what would be considered average rainfall, the fourteen days following the sidedress applications (8 June) only accumulated 2.1 cm of rain and daily high temperatures ranged from 26-36°C (Table 3.2). This hot, dry period just prior, and following sidedress applications created conditions that were conducive to N loss through ammonia volatilization (Figure 3.2) and can also have an effect on ear size determination. In 2010, Beltsville showed no significant yield differences to N rates above the 0 kg ha<sup>-1</sup> rate which was expected due to the average rainfall during the months of May and June which provided adequate soil moisture to the crop and aided in N mineralization. There was no significant treatment effect seen in 2010, which may be a result of the above average yield obtained as a result of timely growing season precipitation.

The 2011 growing season at Beltsville experienced average rainfall in the month of April, and below average rainfall during the months of May (-59%), June (-67%), and July (-34%). Total accumulation of rain during the 21 days following sidedress applications was 2.7 cm and daily high temperatures ranged from 27 to 37°C (Table 3.2). Hot temperatures and droughty conditions during late June and early July can increase crop stress and have a significant effect on ear size determination and lead to N loss via volatilization. During the latter half of August and early September, tropical storms deposited over 56 cm of rain (Table 5.2), but during the beginning of August drought conditions were still present. The conditions during both 2010 and

2011 at Beltsville were much more conducive to ammonia volatilization contributing to N loss following sidedress than to loss of N from either leaching or denitrification. In 2011, yields for all treatments were below average, and considered poor; the result of the droughty conditions during the growing season. However, significant yield responses were observed between the 0, 90, and 134 kg N ha<sup>-1</sup> rates. There was no significant yield increase from 134 to 180 kg N ha<sup>-1</sup> rates (Table 5.1). Although there was a significant yield increase due to nitrogen rate in 2011, there was not a significant product or application method effect.

In 2009, Clarksville received average rainfall during the month of April and above average during the month of May, creating soil moisture conditions that were good, at the time the crop was sidedressed. The slightly below average rainfall in June combined with adequate soil moisture from previous months provided adequate moisture to the crop and supported good ear size formation. Although below average precipitation fell during the months of July (-60%), and August (-22%) (Table 3.2), the moisture holding capacity of the soil combined with adequate precipitation early in the growing season were able to support the crop throughout the growing season. Sidedress applications were made on 16 June and daily high temperatures ranged from 18 - 32°C with a total rainfall of 3.4 cm during the 14 days following sidedress (Table 3.2). With the lower temperatures experienced, ammonia volatilization potential was greatly reduced, and with the dispersed small rain events, leaching and denitrification were unlikely during 2009. The conditions during the second half of June also reduced crop stress during the period in which ear sized was determined. Yields in 2009 were above average which can be seen with the yield attained in the Control treatment, 10.9 tonne ha<sup>-1</sup> (Table 5.1).

In 2011 at Clarksville, April experienced above average rainfall (+0.43%) while below average rainfall was experienced during the months of May (-37%), and June (-58%). Above

average rainfall was received during the months of July (+63%), August (+71%) and September (+84%). In the latter half of August and the first half of September, over 33.6 cm of rain fell, but was too late in the season to have an effect on yield (Table 5.2). Daily high temperatures during the 21 days following sidedress applications ranged from 24-37°C. With daily high temperatures of 35 and 37°C, respectively, and zero rainfall during the first two days following sidedress applications (Table 3.2), conditions during those two days were favorable for ammonia volatilization (Figure 3.8). Field conditions during early June created crop stress which coincided with the period of development in which ear size was being determined, causing a significant effect on yield. Yields in 2011 were much lower than in 2009, which is partially attributed to the below average precipitation during the months of May and June in 2011. The reduced yields may also be partially attributed to the study site. Although the site in 2009 had not received manure since 2007, the field did have a history of manure application. The site used in 2011 was further from the dairy operation and consequently was a field that had no history of manure application. Due to these conditions neither nitrogen stabilizer products nor application method significantly affected yield ( $\alpha=0.05$ ) (Table 5.1). However, during both these years, nitrogen rate significantly affected yield (Table 5.1). During 2009, yield was optimized at the 134 kg N ha<sup>-1</sup> rate while in 2011 optimum yield was attained at 90 kg N ha<sup>-1</sup>.

During the 2009 growing season, Poplar Hill experienced normal rainfall during the months of April, May, and June, below average precipitation in July (- 25%) and almost double the monthly average for August (+ %75) (Table 5.2). Corn was planted on 16 May (Table 3.1) during which adequate soil moisture was present. Sidedress N applications occurred on the 22 June (Table 3.1) and daily high temperatures following sidedress applications ranged from 27 to 32°C (Table 3.2). No rainfall was received during the first 14 days following sidedress

applications (Table 3.2) which also coincided with ear size determination. This two-week post-application weather pattern created situations that were conducive to ammonia volatilization, discussed in Chapter 3 (Table 3.9). Adequate rainfall early in the growing season resulted in ample soil moisture to carry the crop through the dry month of July. Thus, the dry period in July created little stress on the crop during pollination and as a result did not reduce yields. Grain yields in 2009 at Poplar Hill were considered to be average. Neither application method nor nitrogen stabilizers effected corn grain yield during 2009. Yield significantly increased as N rates increased and was maximized at the 180 kg N ha<sup>-1</sup> rate (Table 5.1).

During the 2010 growing season, Poplar Hill experienced below average rainfall for the months of April, May, June and July. Although total rainfall for the months of June and July, were below average (Table 5.2), the rain received during those two months was timely during the 14 days following the sidedress applications (Table 3.2), and during the period in July when pollination occurred. The total rain accumulation during these 14 days totaled 4.7 cm. Temperatures ranged from 33 to 38°C during the 14 days following sidedress (Table 3.2). These extreme high temperatures increased the chance for ammonia volatilization to occur and although rainfall did occur the amounts were not significant enough to increase the chance of nitrate leaching. This period also coincided with the development stage in which ear size is determined. Although conditions following sidedress were conducive to ammonia volatilization, and treatment had a significant effect on ammonia volatilization (Figure 3.10), there was not a significant yield increase caused by any of the stabilizer products and/or application methods,  $\alpha=0.05$ . This indicates that although significant ammonia volatilization reductions were seen with some products and application methods, not enough nitrogen conservation occurred to

result in a treatment effect for yield. Corn yield increased significantly up to the 134 kg N ha<sup>-1</sup> with no significant increase between 134 kg N ha<sup>-1</sup> and 180 kg N ha<sup>-1</sup> (Table 5.1).

At the Wye in 2011, above average rainfall was received during the months of April, August, and September. During the months of May, June, and July below average rainfall was deposited (averaged about 70% of normal over the three months) (Table 5.2). At the time of planting, 3 May (Table 3.1), soil moisture was adequate, but with below average rainfall during the 3 subsequent months crop stress was inevitable (Table 3.2). Sidedress applications were applied on 6 June and total rainfall accumulation during the 21 days following application was 0.9 cm (Table 3.2).. Daily high temperatures ranged from 24 to 35°C, with the first three days following application greater than 30°C (Table 3.2). The lack of rainfall and high temperatures following sidedress applications created conditions that were conducive to excessive ammonia volatilization (see Chapter 3) and created crop stress early in the season. The stress created in early June also coincided with the crop development stage in which ear size is determined. The below average rainfall during the months of June and July decreased the chances of leaching or denitrification following the sidedress applications however this drought period in which pollination occurred reduced yield potential at this location. Upon analysis, it was found that nitrogen stabilizers and/or application method did not have a significant effect on yield ( $\alpha=0.05$ ). However, yield did respond to nitrogen rates ( $p\leq 0.05$ ) (Table 5.2). This significant increase was optimized at 134 kg N ha<sup>-1</sup>.

Similar results have been seen by other researchers. Cahill et al. (2010) found that Nutrisphere N did not increase corn or wheat yields when compared to UAN. Sistani et al. (2011) found no yield increase in no-till corn production when using UAN +Agrotain Plus compared to UAN or any of the other enhanced efficiency fertilizers that were tested. Halvorson

et al. (2010) found that UAN with Agrotain Plus can be a useful tool for reducing nitrous oxide emissions, when compared to urea in no-till corn production, but grain yields were not significantly affected when these products, along with others, were compared. Similar results again were seen in 2011 by Halvorson when a similar study including UAN and UAN+Agrotain Plus was conducted in a strip-till system in corn (Halvorson, 2011).

## **Conclusions**

Although there was, on average, a positive response from increased nitrogen rates, proper nitrogen management and maximized nitrogen efficiency will fall upon farmers knowing and managing proper and realistic yield goals based on historic field yields. The results of this study show that nitrogen stabilizers and/or application methods did not significantly affect corn yields. In conclusion, no significant yield differences were observed among sidedress treatments with any of the nitrogen stabilizer products tested (Agrotain, Agrotain Plus, Nutrisphere N, Instinct), nor were there yield differences that can be attributed to either sidedress UAN surface applied or sidedress injected UAN. Over the three years of this study corn yields were observed to be highly variable, even within locations. With corn yields across all locations ranging from 1.4 tonne ha<sup>-1</sup> to 10.9 tonne ha<sup>-1</sup> for the 0 kg N ha<sup>-1</sup> rate and yields ranging from 3.6 tonne ha<sup>-1</sup> to 13.7 tonne ha<sup>-1</sup> for the 180 kg N ha<sup>-1</sup> rate (Table 5.1), one thing became evident; achieving economic optimum yields is dependent on more than proper nitrogen management. Soil type, timely rainfall, weather during ear size determination and pollination, field history, and proper nutrient management all play a major role in nitrogen use efficiency. Even though the stabilizer products/application methods used may have been effective in reducing N losses through the



three loss pathways, under the given field conditions, the fact that they work to protect N in no way guarantees there will be a yield benefit.

## Tables

Table 5.1. Corn grain yield averaged across main plot factor for each nitrogen rate at each site year.

Location	Year	Fertilizer N kg ha <sup>-1</sup>			
		Control	90	134	180
—————tonne ha <sup>-1</sup> —————					
Beltsville	2009	1.9b	4.4a	5.2a	5.0a
	2010	7.4b	8.5a	8.7a	8.6a
	2011	1.4c	2.5b	3.3a	3.6a
Clarksville	2009	10.9c	12.6b	13.1ab	13.7a
	2010	9.9	10.5	10.3	10.2
	2011	6.1c	7.2b	7.9b	8.7a
Poplar Hill	2009	4.8d	7.8c	9.7b	10.5a
	2010	7.9c	9.3b	10.0a	10.4a
Wye	2011	4.5c	6.7b	7.0ab	8.0a

†Means in each row with different lettering are significantly different at  $p \leq 0.05$ .

Table 5.2. Site location monthly rainfall accumulations experienced during the 2009, 2010, and 2011 growing seasons and each location's 30 year average monthly rainfall.

Location	Year	Precipitation cm					
		April	May	June	July	August	September
Beltsville	2009	12.5	20.9	19.2	3.5	13.9	7.7
	2010	4.9	10.8	6.2	9.1	20.7	16.4
	2011	8.4	4.5	3.1	6.6	25.1	30.9
	Avg. 1981-2010	8.5	11.0	9.4	10.0	8.3	10.4
Clarksville	2009	9.1	16.3	8.2	3.7	6.9	4.5
	2010	6.9	5.6	4.5	8.6	8.4	13.1
	2011	12.6	6.7	4.3	15.2	15.0	18.6
	Avg. 1981-2010	8.8	10.7	10.2	9.3	8.8	10.1
Poplar Hill	2009	10.2	9.9	9.7	8.6	21.1	9.4
	2010	3.3	4.1	8.4	8.6	10.7	15.2
	Avg. 1981-2010	9.2	8.9	10.0	11.5	12.1	10.3
Wye	2011	10.9	6.8	6.1	7.3	39.9	22.5
	Avg. 1981-2010	9.8	10.6	9.8	11.1	10.8	10.2

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## **Chapter 6: Plant nitrogen concentration to assess corn nitrogen management with nitrogen stabilizer products and application methods.**

### **Introduction**

There are many investigations concerning the causes of the currently high N supplementation in corn production. Raun and Shepers (2008) concluded that historically in developed countries the main cause for over-fertilization is the relatively cheap cost of nitrogen fertilizers. There are plant growth and development issues that have been associated with excess N supplementation that must be considered. One of these is lodging. In 1958, Nelson summarized that excessive N supplementation in field corn that was not affected by European corn borer damage or root rot, resulted in increased lodging caused by late season storms. Another issue that can result with excessive N supplementation is too high N concentrations in corn silage, which can also occur with normal N supplementation when drought conditions occur in the summer. Excessive N concentration in the silage poses a health risk issue when it is fed to animals. Another problem associated with supplementation beyond what the crop will use is excessive residual soil N. During the past three decades, in Maryland, drought frequency has been about 4 out of every 10 years resulting in excessive residual N in the soil of fields where corn was produced. In order to help immobilize some of this residual N, Maryland created its Cover Crop Program. With both environmental concerns and physiological concerns associated with excess N supplementation in corn proper N fertilization is extremely important.

One way excess N accumulation in the corn plant can be evaluated is by testing whole plant tissue following physiological maturity. Tissue tests have proven to be an excellent tool for assessing nutrient status of corn and grain sorghum (Jones et al., 1990). Research conducted by

Krantz et al. in 1948 suggested that determination of plant nutrient status and growing season uptake can be accomplished through plant tissue analysis. They concluded that there were four main objectives that could be satisfied using plant tissue analysis; (i) to aid in determining the nutrient supplying power of the soil; (ii) to aid in determining the effect of treatment on nutrient supply in the plant; (iii) to study the relationship between the nutrient status of the plant and crop performance as an aid in predicting fertilizer requirements; and (iv) to help lay the foundation for approaching new problems or surveying unknown regions to determining where critical plant and nutritional experimentation should be conducted (Krantz et al., 1948). These objectives were verified by Jones in 1986.

The second objective described by Krantz et al. (1948) is to aid in determining the effect of treatment on nutrient supply in the plant. It was this objective that served as the basis for utilizing whole plant tissue samples in this study. The objective was to determine if the use of UAN fertilizer with a nitrogen stabilizer product and/or the application method affected total plant nitrogen concentrations following physiological maturity.

Hypothesis: UAN applied with a stabilizer product and/or specific application method will affect total plant N concentrations.

## **Materials and Methods**

Between 2009 and 2011, nine field experiments were established at University of Maryland Research and Education Centers (Table 3.1) with soils representative of the Coastal Plain and Piedmont regions of Maryland (Table 1.1). The experimental design was a randomized complete block with a split plot arrangement of treatments and four replications. The main plot

factor was the nitrogen stabilizer products and/or the application methods and the split plot factor were nitrogen rates; 90, 134, and 180 kg N ha<sup>-1</sup> (Table 1.2). A Control treatment, no nitrogen added, was included as a reference. The fertilizer N source was liquid UAN (30% N as urea-ammonium nitrate solution) (Table 1.2). Due to field size constraints at Clarksville, the Agrotain main plot factor was omitted from the treatment structure all three years and, in 2011, the study at Clarksville was only replicated 3 times. Corn hybrids used were Pioneer brand ‘33B54’ (2009) and Pioneer brand ‘35K09AM1’ (2010 and 2011). Pioneer brand ‘33B54’ is a 113 day corn relative maturity (CRM) hybrid while ‘35K09AM1’ is a 106 day CRM hybrid. Hybrids were switched in 2010, due to the discontinuation of Pioneer brand ‘33B54’. All sites were planted at 73,000 seeds ha<sup>-1</sup> in 76 cm spaced rows between late April and mid-May (Table 3.1) utilizing the no-till planters at each location. In all years, 34 kg N ha<sup>-1</sup> starter fertilizer was applied with the planter and the balance of each N rate treatment was supplied as a sidedress application between corn growth stages V5 and V7, (Aldrich, 1984). Sidedress treatments were applied using a Spray Mate II Automatic Rate Controller (Micro-Trak Systems Inc. Eagle Lake, MN) on a custom 6 row applicator capable of surface banding applications as well as sub-surface injection. Products were mixed into the UAN at time of application and products were used at the manufacturer’s suggested rates; Agrotain 2.11 L tonne<sup>-1</sup> UAN (64 oz ton<sup>-1</sup> UAN), Agrotain Plus 30 kg tonne<sup>-1</sup> UAN (15 lb ton<sup>-1</sup> UAN), Instinct 2.55 L ha<sup>-1</sup> UAN (35 oz acre<sup>-1</sup>), Nutrisphere N 0.5% by volume (0.5 gallons/99.5 gallons UAN). Surface applied treatments were streamed onto the soil surface with drop-tubes which were located approximately 15 cm above the soil and placed the fertilizer approximately mid-way between the corn rows. The sub-surface injected treatments were applied using the Yetter Coulter Injection system (Yetter Manufacturing Inc., Colchester, IL) that placed the treatments approximately 7.5 to 10 cm below the soil surface and mid-way between the rows.

Whole plant corn samples were collected following physiological maturity and analyzed for total N concentration from all locations in 2010 and 2011. Four plants were randomly selected from each of rows two and five of each plot and cut between 2.5 and 7.5 cm above the soil surface. The plants were then course ground in the field utilizing a chipper shredder to aid in drying time and further sample processing. Samples were oven dried at 60° C until all moisture was removed. Samples were then processed following the procedures for Determination of %C, %H, and %N in Plant, Manure and Soil described by Campbell (1992) and followed by the University of Maryland's, Department of Environmental Sciences laboratory. Dried samples were ground in a Wiley mill to pass a 0.5 mm sieve. A 0.2 gram ground sample was packed into tin capsules, LECO part # 502-040, and analyzed for total plant N via the combustion method utilizing a LECO CHN-2000 Analyzer (LECO Corporation, St. Joseph, Mich.). Plant total nitrogen concentration was analyzed as a RCBD-split plot using the mixed method in SAS with a Tukey adjusted alpha value of 0.05. Data is reported as grams of N per kilogram of plant material.

## **Results and Discussion**

Analysis of the data determined that within a location, the year did not have a significant effect on plant total N. Therefore the data has been averaged over 2010 and 2011 for Beltsville and Clarksville. Application of a nitrogen stabilizer product and/or method of application had no significant effect on plant total N at any of the locations (Table 6.1). However, there was an increase in plant total N as nitrogen rate increased at all locations (Table 6.2).



At Beltsville, there was no significant response to N rate between the 0 and 90 kg N ha<sup>-1</sup> rates, but there were significant increases from 90 to 134 kg N ha<sup>-1</sup> and from 134 to 180 kg N ha<sup>-1</sup> rates ( $p \leq 0.05$ ) (Table 6.2).

At Clarksville, no significant differences in plant total N were observed for the 0, 90, and 134 kg N ha<sup>-1</sup> rates. There were also no significant differences between the 90, 134, and 180 kg N ha<sup>-1</sup> rates. However, it was found that plant total N significantly increased between the 0 and 180 kg N ha<sup>-1</sup> rates,  $p \leq 0.05$  (Figure 6.2).

At Poplar Hill, in 2010, there was no significant difference in plant total N between the 0 and 90 kg N ha<sup>-1</sup> rates. Plant total N did significantly increase between the 90 to the 134 kg N ha<sup>-1</sup> rates,  $p \leq 0.05$ , and then again between the 134 and 180 kg N ha<sup>-1</sup> rates,  $p \leq 0.05$  (Table 6.2).

At Wye in 2011, there were no significant differences in plant total N between the 0, 90, and 134 kg N ha<sup>-1</sup> rates. The 180 kg N ha<sup>-1</sup> rate was found to have significantly more nitrogen in the plant material compared to the 0 and 90 kg N ha<sup>-1</sup> rates,  $p \leq 0.05$ , however it was not significantly different from the 134 kg N ha<sup>-1</sup> rate (Table 6.2). Concentrations at the Wye were less compared to the other locations in 2011, and considered to be a result of below average rainfall in May, June, and July (Figure 5.2).

## **Conclusions**

In this study, there were no significant differences in plant N concentrations among the nitrogen stabilizer products and/or application methods tested. However, plant N, on average, increased as nitrogen rate increased, but the magnitude of the response was found to be location dependent. The lack of response to either product or application method indicates that neither

influenced end of season nitrogen concentration in corn plants. However, as nitrogen rates increased so did plant N concentrations. One noticeable fact was that the Wye had only about 60% of the total N compared to the other locations (Table 6.2). This may be a result of early season crop stress and overall poor performance which can be seen in the yield data. Another contributing factor may be that there were excessive losses of ammonia in 2011 at the Wye.

Although some products do protect the nitrogen from certain loss pathways, as seen in the head space accumulation of ammonia data and soil urea concentrations, there apparently was not enough nitrogen conservation occurring to provide season long protection and allow late season luxury consumption which would have been measured with the end of season whole plant N concentration. This also indicates that the high N rate was not an excessively high nitrogen rate given the weather conditions experienced during crop production.

One factor that had a major effect on plant N concentration was rainfall during the growing season. Although there were periods of drought experienced during July of 2010 and 2011, there is no indication that luxury consumption of nitrogen occurred late in the season. During periods of drought little to no soil nitrate was lost due to the lack of precipitation. However, when extreme end of season rain events occur, as in 2011, nitrate was susceptible to end of season leaching. In turn, since products and application method did not have a significant effect on nitrogen concentration within the plant, it is believed that nitrogen stabilizers and/or application methods do not affect end of season corn plant-N concentrations. Also, it is believed that although some products (Agrotain and Agrotain Plus) and application method (UAN Injection) do prevent volatilization loss early in the season, these practices do not conserve enough nitrogen to have an effect on end of season plant-N concentrations.

In conclusion, neither nitrogen stabilizer products when used with UAN nor application method of UAN have a significant effect on end of season plant nitrogen concentrations. On average, an increase in the amount of applied nitrogen did result in an increase in nitrogen concentrations within the whole plant. This is important to note since luxury consumption will occur in years when N is over supplied to the crop and growing season conditions allow for luxury consumption.

## Tables

Table 6.1. End of season total plant nitrogen for corn averaged over the years at each location the data was collected for each nitrogen stabilizer product and/or application method tested.

Site/ Years averaged	Product/Method					
	Agrotain	Agrotain Plus	Injected	Instinct	Nutrisphere N	UAN
	g N kg <sup>-1</sup> plant material					
Beltsville '10 '11	9.7	9.2	10.1	9.9	9.7	9.5
Clarksville '10 '11		9.4	10.3	9.9	9.6	9.9
Poplar Hill '10	10.5	11.3	10.5	10.4	11.2	10.5
Wye '11	6.2	6.7	6.0	6.5	6.4	6.4

Table 6.2. End of season plant total nitrogen for each nitrogen rate and the control treatment tested for the six site years that data was collected.

Site / years averaged	Fertilizer N kg ha <sup>-1</sup>			
	0	90	134	180
	g N/ kg plant material			
Beltsville '10 '11	7.8 b	9.0 b	9.9 a	10.2 a
Clarksville '10 '11	8.7 b	9.6 ab	9.6 a	10.2 a
Poplar Hill '10	8.6 c	9.8 c	10.8 b	11.6 a
Wye '11	4.8 b	5.6 b	6.4 ab	7.1 a

†Means in each row with different lowercase letters are significantly different at  $p \leq 0.05$ .

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## **Future Research and Concluding Remarks**

The best method for minimizing headspace ammonia accumulation was subsurface injection of UAN. Two of the urease inhibitor products tested, Agrotain and Agrotain Plus, on average provided a four to seven day window of protection against headspace ammonia accumulation as well as slowing urea hydrolysis. Nutrisphere N, the third urease inhibitor product tested, did not provide any appreciable protection as shown by the similar patterns of headspace ammonia accumulation to the surface applied UAN treatment. Surface applied UAN, on average, had the highest headspace ammonia accumulation.

Based on the three site locations in 2010, Injected UAN provided no protection against urea hydrolysis and, in fact, in some cases appears to have increased the rate of conversion from the urea form. This, however, was a benefit because the UAN was in direct contact with the soil which resulted in the reduction of headspace ammonia accumulation. Agrotain, and Agrotain Plus did show protection against urea hydrolysis for a period of three to seven days following application at the three sites in 2010. The variability in the length of protection time was dependent on field conditions at application and weather conditions post application. Nutrisphere N showed no protective effect on urea hydrolysis inhibition based on the similar urea conversion response it had to surface applied UAN at the Beltsville and Poplar Hill locations, however Nutrisphere N did show a delayed urea hydrolysis at the Clarksville location. Surface applied UAN provided no protection against urea hydrolysis compared to the other methods and products included in this study.

The use of a nitrogen stabilizer product and/or application method did not have a significant effect on end of season total plant N concentration. In some cases, plant N was significantly affected by N rates. However, it was noticed that weather during the growing

season as well as crop stress apparently played a major factor in the determination of end of season N concentration in the total plant.

Post-harvest soil inorganic-N was not significantly affected by nitrogen stabilizer product and/or application method. However, post-harvest soil inorganic-N concentrations were affected by N rates and, on average, there were higher concentrations of N in the top 30 cm than the lower 30 cm of soil. As seen with many other variables, post-harvest soil inorganic-N concentrations were affected by late season precipitation and crop performance throughout the growing season.

Corn grain yield was not significantly affected by nitrogen stabilizer products and/or application method. However, N rate did have an effect on grain yield when N rates were suboptimum and were the yield limiting component. Growing season weather conditions and precipitation played a major role in determining yearly yields. Soil types were also a major factor in determining yields.

In situations when N loss is expected to occur with the application of UAN solution, subsurface injection provides the greatest protection against loss. In cases when injection is not possible the use of the urease inhibitor 'Agrotain', and dual purpose inhibitor 'Agrotain Plus', often provided a four to seven day stabilization of urea, which gives rainfall a better chance to move urea into the soil. However the performance of Agrotain and Agrotain Plus was shown to be weather dependent.



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