Volatilization Losses from Urea

Dave Franzen
North Dakota State University
• Urea, urea hydrolysis, and urease inhibitors
  – Urea is made by reacting ammonia and carbon dioxide
    • \(2 \text{NH}_3 + \text{CO}_2 \rightarrow \text{urea} + \text{H}_2\text{O}\)
  – Upon application to soil, the opposite occurs
    • \(\text{Urea} + \text{H}_2\text{O} \rightarrow 2 \text{NH}_3 + \text{CO}_2\)
• The second reaction is catalyzed by an enzyme called urease

From Goos 2009
• Urease
  – One of the most widespread enzymes in Nature
  – Microbes, plants, blood, crop residues, humus...all exhibit urease activity

• The reaction is very fast
  – Reaction kinetics measured in terms of DAYS (not weeks)

(from Goos, 2009)
Urea applied to stubble-rich surface, ND (Goos data)
NBPT (N-(n-butyl) thiophosphoric acid triamide)

Agrotain

Competes for active sites on the urease enzyme and ties up activity for about 10 days, depending on weather conditions.
Yield for side-dressed no-till corn in Hardin County, KY. (From Schwab and Murdock, 2009)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Yield, bushels per acre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Check (50 lb N/acre preplant N only)</td>
<td>117d*</td>
</tr>
<tr>
<td>Urea</td>
<td>158c</td>
</tr>
<tr>
<td>Urea + Agrotain</td>
<td>201b</td>
</tr>
<tr>
<td>SuperU</td>
<td>201b</td>
</tr>
<tr>
<td>UAN</td>
<td>150c</td>
</tr>
<tr>
<td>UAN + Agrotain</td>
<td>179bc</td>
</tr>
<tr>
<td>UAN + Agrotain Plus</td>
<td>175bc</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
<td>239a</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Flat Rate N Treatment</th>
<th>Corn Yield (bu/acre)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea surface applied</td>
<td>130</td>
</tr>
<tr>
<td>Urea surface applied + Agrotain</td>
<td>143</td>
</tr>
</tbody>
</table>
Illinois, average of four southern Illinois locations, Varsa et al., 1999.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Corn Yield bu/acre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea surface applied</td>
<td>106</td>
</tr>
<tr>
<td>Urea surface applied +Agrotain</td>
<td>125</td>
</tr>
</tbody>
</table>
Additional possible urease inhibitors

Ammonium thiosulfate

Nutrisphere®
Nutrisphere,
SFP Specialty Products, LLC, Leawood, KS

Formulation for dry fertilizer-
30-60% maleic-itoconic copolymer,
pH 2.5-5

Formulation for liquid fertilizer-
40% maleic-itoconic copolymer, pH 1-2
Inhibition of urease activity is due theoretically to a tie-up of soil nickel-a critical metal constituent of urease enzyme.
Effects of N additive, averaged over source (UAN and urea) and N rate on corn grain yield, earleaf-N and grain-N, Scandia, KS (2-year average). From Gordon, 2008.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Yield, bu/acre</th>
<th>Earleaf N, %</th>
<th>Grain N, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Check</td>
<td>152</td>
<td>1.72</td>
<td>1.13</td>
</tr>
<tr>
<td>Urea/UAN</td>
<td>168</td>
<td>2.57</td>
<td>1.26</td>
</tr>
<tr>
<td>ESN</td>
<td>185</td>
<td>2.96</td>
<td>1.33</td>
</tr>
<tr>
<td>Nutrisphere-N</td>
<td>183</td>
<td>2.96</td>
<td>1.35</td>
</tr>
<tr>
<td>Agrotain</td>
<td>183</td>
<td>2.98</td>
<td>1.36</td>
</tr>
<tr>
<td>LSD 5%</td>
<td>6</td>
<td>0.09</td>
<td>0.04</td>
</tr>
</tbody>
</table>
(Research by R.J. Goos, in Franzen et al., J. Plant Nut 2011)
Cumulative ammonia volatilization losses for urea, ammonium sulfate, urea + NBPT, and urea + 0.25% Nutrisphere (NSN) from a Dewitt silt loam soil during a 15-day laboratory incubation at 25°C. (Norman data, University Arkansas, Fayetteville, from Franzen et al., 2011)

<table>
<thead>
<tr>
<th>N sources</th>
<th>Days after N source application</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3</td>
</tr>
<tr>
<td><strong>Cumulative NH₃ loss, % of N applied</strong></td>
<td></td>
</tr>
<tr>
<td>Urea</td>
<td>14.5</td>
</tr>
<tr>
<td>Ammonium sulfate</td>
<td>0.1</td>
</tr>
<tr>
<td>Urea + NBPT†</td>
<td>0.006</td>
</tr>
<tr>
<td>Urea + 0.25% NSN</td>
<td>17.6</td>
</tr>
<tr>
<td><strong>LSD(0.05)</strong>‡</td>
<td>12.2</td>
</tr>
<tr>
<td><strong>LSD(0.05)</strong>§</td>
<td>9.6</td>
</tr>
</tbody>
</table>
More recent laboratory studies by Dr. Goos

Objective of these studies

- To compare several new fertilizer additives to older products
- New additives: Nutrisphere-N, StayN, N-Zone, NStay, OAC+
- Older products: Nitrapyrin, DCD, ATS, CaTS, NBPT

- Paper by Goos, 2012 Great Plains Soil Fertility Proceedings
Average, bare soil and straw treatment, small and large droplet size
Goos, NDSU

- Goos (paper in review)
• Urea hydrolysis studies

• Urea pellets placed on top of 2” of moist soil
• Urea hydrolysis followed for 10 days
• Three soils (2-ND, 1-IA)

Goos, 2012
Goos, 2012

Three soil average
Goos, NDSU

- Urea + Agrotain Ultra
- Urea + OAC+, PT
- Urea
- Urea + Nutrisphere-N
- Urea + NZone
- Urea + StayN
- Urea + NStay
- Urea + Nutrisphere-N, PT
- Control

Urea remaining, mg urea pot⁻¹

Days after application

Goos, 2012
• Urease inhibition studies
• Additives incubated with soil at 2, 20, 200 ppm
• Urease activity determined, 17 hour incubation

Goos, 2012
17 hour incubation
Three soil average
Goos, NDSU

Percent inhibition of urease activity

Additive concentration in soil, mg kg$^{-1}$ soil

Goos, 2012
Conclusions...

• None of the new products worked as well as the “old” products
• These reactions are hard to control, so if you need an inhibitor, use the most effective ones available
Objectives

- To evaluate NSN as a soil urease inhibitor
- To evaluate the proposed mode of action of NSN
- To evaluate NSN as an inhibitor of jackbean (Canavalia ensiformis) urease at pH 7

- Presented at American Society Agronomy meetings, Cincinnati, OH, October, 2012, R.J. Goos
Experiment 1

- 0.1 mL of a 15% urea solution, w and w/o 0.5% NSN for LF
- 25 g of soil
- Extraction after 1, 2, 3 days
- Residual urea measured

Slide from Goos, 2012
Experiment 1

2 soil average
Goos, NDSU

Urea remaining, mg N kg\(^{-1}\)

Days after application

Slide from Goos, 2012

- Urea solution
- Urea solution +
- Nutrisphere for liquid fertilizers
- Control
Experiment 2

- 100 kg/ha of N: granular urea,
  urea + NSN,
  urea + NSN, pretreated (PT),
  urea + Agrotain Ultra (AU)
- 500 g of soil
- Residual urea measured after 2, 4, 7, and 10 days

Slide from Goos, 2012
• Experiment 2

3-soil average
Goos, NDSU

Urea remaining, mg/pot

Days after application

Goos, 2012
• Experiment 3
• 10 g soil, field capacity
• 5 mg urea (500 mg/kg), alone or with:
• 1 to 500 mg MIP/kg, as NSN for granular urea (NSN) or NSN Quick Dry for granular urea (NSN-QD)
• 1 or 5 mg NBPT/kg, as Agrotain Ultra (AU)
• 12 hour incubation, 25 C
• Residual urea determined

Goos, 2012
Experiment 3 (% Inhibition)

3-soil average, 12 hour incubation
Goos, NDSU

Urea remaining, mg/assay

Active ingredient, mg/kg in soil

Goos, 2012
• Proposed mode of action for NSN
• "This high-charge density dicarboxylic copolymer.....is theorized to provide suppressive effects on the urease enzyme through sequestration of the nickel ions in urease.”\(^1\)
• “...pulls the nickel out of the urease molecule, destabilizing the molecule rendering it ineffective...”\(^2\)

\(^1\) Blaylock and Murphy, Fluid Journal, Fall 2006
\(^2\) Sanders. Presentation before the Fertilizer Outlook and Technology Conference, 8 November 2007.
• "In the soil the high negative charge density of Nutrisphere-N sequesters nickel essential for bacterial production of the metalloenzyme urease."³

• Experiment 4
• Thirteen carboxylic acids with differing stability constants for Ni$^{2+}$ added to soil at 50 mg/kg
• NSN and NSN-QD added at 50 mg MIP/kg
• AU added at 1 and 5 mg NBPT/kg
• 3 soils, 12 hour incubation, 25 C

Slide from Goos, 2012
<table>
<thead>
<tr>
<th>Test inhibitor</th>
<th>Ni(^{2+}) stab. const.</th>
<th>Urea remaining</th>
<th>Percent Inhibition</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>--</td>
<td>1.07</td>
<td>--</td>
</tr>
<tr>
<td>Itaconic acid</td>
<td>1.8</td>
<td>1.17</td>
<td>2</td>
</tr>
<tr>
<td>Maleic acid</td>
<td>2.0</td>
<td>1.23</td>
<td>4</td>
</tr>
<tr>
<td>Malic acid</td>
<td>3.2</td>
<td>1.10</td>
<td>1</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>5.3</td>
<td>1.13</td>
<td>2</td>
</tr>
<tr>
<td>Citric acid</td>
<td>5.4</td>
<td>1.12</td>
<td>1</td>
</tr>
<tr>
<td>Salicylic acid</td>
<td>7.0</td>
<td>1.12</td>
<td>2</td>
</tr>
<tr>
<td>Imidodiacetic acid</td>
<td>8.1</td>
<td>1.14</td>
<td>2</td>
</tr>
<tr>
<td>NTA</td>
<td>11.5</td>
<td>1.11</td>
<td>1</td>
</tr>
<tr>
<td>EGTA</td>
<td>13.5</td>
<td>1.08</td>
<td>0</td>
</tr>
<tr>
<td>HEDTA</td>
<td>17.1</td>
<td>1.02</td>
<td>-1</td>
</tr>
<tr>
<td>EDTA</td>
<td>18.5</td>
<td>1.04</td>
<td>-1</td>
</tr>
<tr>
<td>DTPA</td>
<td>20.2</td>
<td>1.07</td>
<td>0</td>
</tr>
<tr>
<td>CDTA</td>
<td>20.2</td>
<td>1.04</td>
<td>-1</td>
</tr>
<tr>
<td>NSN</td>
<td>--</td>
<td>1.06</td>
<td>0</td>
</tr>
<tr>
<td>NSN-QD</td>
<td>--</td>
<td>1.04</td>
<td>-1</td>
</tr>
<tr>
<td>NBPT, 1 mg/kg</td>
<td>--</td>
<td>3.52</td>
<td>62</td>
</tr>
<tr>
<td>NBPT, 5 mg/kg</td>
<td>--</td>
<td>3.88</td>
<td>72</td>
</tr>
</tbody>
</table>

Except as noted, all materials added at 50 mg/kg

*Slide from Goos, 2012*
• Experiment 5
• 5 mL THAM (0.2 M, pH 7)
• 5 mL jackbean urease solution
• 5 mL test inhibitor
  – 4 mg/L NBPT as AU
  – 40 mg/L MIP as NSN or NSN-QD
• Shake 1 hour, 25 C
• Add 5 mL urea substrate (200 mg/L)
• Take samples after 5, 30, 60, 90, 120 min of shaking, residual urea determined

Slide from Goos, 2012
• Experiment 5

![Graph showing the effect of different inhibitors on the urea in reaction mixture over time. The x-axis represents the time of reaction in minutes, ranging from 0 to 120. The y-axis represents the urea in reaction mixture in mg/L, ranging from 0 to 50. The graph includes lines for AU, 1 mg NBPT/L, No inhibitor, NSN, 10 mg MIP/L, and NSN-QD, 10 mg MIP/L, each with distinct markers and colors. The data source is Goos, 2012.]
• Experiment 6
• 5 mL THAM (0.2 M, pH 7)
• 5 mL jackbean urease solution
• 5 mL test inhibitor
  – 0.04 to 4 mg/L NBPT as AU
  – 0.04 to 400 mg/L MIP as NSN or NSN-QD
• Shake 1 hour
• Add 5 mL urea substrate (200 mg/L)
• Residual urea determined after 120 min of shaking

Goos, 2012
Experiment 6

Goos, 2012
• Experiment 1--NSN did not inhibit hydrolysis of droplets of urea applied to soil
• Experiment 2--NSN did not inhibit hydrolysis of urea granules applied to soil
• Experiment 3--NSN provided little or no inhibition of soil urease, at rates up to 500 mg/kg of active ingredient
• Experiment 4--Nickel sequestration by carboxylic acids is an unlikely mode of action for soil urease inhibition
• Experiments 5, 6--NSN did not inhibit purified jackbean urease at pH 7
Laboratory studies clearly show that Nutrisphere has no nitrification or urease inhibiting properties. What is most curious is why some studies show some response.

<table>
<thead>
<tr>
<th></th>
<th>No Response</th>
<th>Positive</th>
</tr>
</thead>
<tbody>
<tr>
<td>North Dakota</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>Kansas</td>
<td>7</td>
<td>5 (4 at Scandia)</td>
</tr>
<tr>
<td>Minnesota</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>Illinois</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Arkansas/Mississippi</td>
<td>3</td>
<td>0</td>
</tr>
</tbody>
</table>

Idaho work on barley showed a yield increase, but no increase in N uptake. No yield increase in wheat
One possible reason for the yield increase is the pH of the product, particularly with the liquid formulation. Acid pH lowers the rate of nitrification. Perhaps it is not the Nutrisphere that is active. Perhaps it is its acidity?
SUMMARY-

Agrotain is a proven urease inhibitor. Its use is becoming increasingly more common in no-till systems that still rely on surface application of urea.
SUMMARY-

Ammonium thiosulfate is a limited use urease inhibitor due to the rate of mineralization of the fertilizer. It may be of some value if used at the correct rate, but other products appear to be more consistent in their activity.
SUMMARY-

Nutrisphere has no urease inhibition properties and should not be used for these purposes. The claimed mode of action for the urease activity of maleic itoconic acid was investigated and the research found that the mode of action claimed is unjustified.
SUMMARY-

N-Zone has no nitrification properties and is not labeled as a urease inhibitor. N-Stay and Stay-N were both tested as urease inhibitors and as nitrification inhibitors. The results of careful laboratory experiments did not support their use for these purposes.