What Agronomists Need to Know About Nitrogen Enhancers and Stabilizers

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Today’s presentation dedicated to two processes:

Ammonia volatilization from urea and the role of urease enzyme
Urease inhibitors (only chemistries known to inhibit urease activity for days, usually about 10)
  - NBPT (Agrotain and others)
  - NPPT (Limus)
  - Ammonium thiosulfate (weak, measureable short-term activity)

Nitrification of ammoniated fertilizers and the role of bacterial oxidation of ammonium to nitrate
Nitrification inhibitors
  - Nitrapyrin (N-Serve and Instinct-eNtrench)
  - Dicyandiamide (Super U, Guardian)
  - Ammonium thiosulfate (weak)
Ammonia Volatilization Can Occur When Urea is Applied on or Near the Soil Surface

\[
\text{NH}_2\text{-CO-NH}_2 + \text{H}_2\text{O} \rightarrow \text{CO}_2 \uparrow + 2 \text{NH}_3 \uparrow
\]  
(Urea)
# Ammonia Volatilization from Surface and Incorporated Urea at Various Depths

<table>
<thead>
<tr>
<th>Period-hours</th>
<th>Surface (% loss)</th>
<th>1 inch (% loss)</th>
<th>2 inch (% loss)</th>
<th>3 inch (% loss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-166 (7d)</td>
<td>2.2</td>
<td>18.4</td>
<td>2.6</td>
<td>0.0</td>
</tr>
<tr>
<td>167-334 (14d)</td>
<td>29.5</td>
<td>15.2</td>
<td>3.2</td>
<td>0.1</td>
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<tr>
<td>335-502 (21d)</td>
<td>15.2</td>
<td>3.8</td>
<td>1.8</td>
<td>0.5</td>
</tr>
<tr>
<td>503-598 (25d)</td>
<td>3.4</td>
<td>1.0</td>
<td>1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Total</td>
<td>50.3</td>
<td>38.4</td>
<td>8.6</td>
<td>0.4</td>
</tr>
</tbody>
</table>

*Source: Rochette et al., 2014, JEQ*

Slightly acid silt loam soil
Factors Affecting Hydrolysis Rate

Soil Urease Concentration

More urease present = greater hydrolysis rate

Urease concentration correlated to soil organic matter content

Crop residue has 20-30 times higher urease concentration than underlying soil
Urease is produced by plants, bacteria, fungi, invertebrates and is one of the last compounds to degrade after the organism dies.
Factors Affecting Hydrolysis Rate

Soil temperature

- Hydrolysis increases with higher temp.

- 35°F → 80°F; hydrolysis rate doubles

- High rate even at 35°F
Factors Affecting Hydrolysis Rate

Soil Water Content

Greatest effect on urea hydrolysis occurs when soils become dry

Little change with soil moisture contents suitable for plant growth (urea dissolves)

At permanent wilting point the hydrolysis rate slows greatly and essentially stops when air dry
Factors Affecting Hydrolysis Rate

Soil pH

UREA HYDROLYSIS

\[(NH\textsubscript{2})\textsubscript{2}CO \rightarrow [(NH\textsubscript{4})\textsubscript{2}CO\textsubscript{3}] \rightarrow 2NH\textsubscript{3} + CO\textsubscript{2} + H\textsubscript{2}O\]

- Hydrolysis by urease enzymes produces ammonium carbonate
- Soil pH under the granule can increase to levels above 9
- Greater volatilization potential at high pH

Urease inhibitor blocks reaction
Urea is acted on in the ‘keyhole’ structure of the urease enzyme
N-(N-Butyl) thiophosphoric triamide

Has same tri-atom configuration as urea

NPPT has same tri-atom structure, but tail has an additional C group

Once the tail is broken down the urease activity is not longer inhibited
ATS does not directly affect the urease enzyme and is only indirectly inhibiting after interacting with soil.

Thiosulfate reacts rapidly and abiotically with soil, forming tetrathionate and liberating Fe$^{2+}$ and Mn$^{2+}$.

\[
2 \text{Fe(OH)}_3 + 2 \text{S}_2\text{O}_3^{-2} + 6 \text{H}^+ \rightarrow 2\text{Fe}^{2+} + \text{S}_4\text{O}_6^{-2} + 6 \text{H}_2\text{O}
\]

\[
\text{MnO}_2 + 2 \text{S}_2\text{O}_3^{-2} + 4\text{H}^+ \rightarrow \text{Mn}^{2+} + \text{S}_4\text{O}_6^{-2} + 2 \text{H}_2\text{O}
\]

Adapted from Goos, 1987, NC Ext. Ind. Soil Fertility Conf.
## Yield for Side-Dressed No-Till Corn in Hardin Co. KY

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

Source: Schwab and Murdock, 2009
N Sources for No-till Corn
Eight Site-years, 1995-98

Yield benefit compared to check treatment (70 bu/ac)

Put your money in the right place

Ebelhar et al., 2010
Nutrient Management

**Gardner**

- Urea
- Agrotain
- LIMUS
- NBPT
- Check

**Valley City**

- Urea
- Agrotain
- LIMUS
- NBPT
- Check
- ESN (100 lb N)
- BASF Coating (100 lb N)

Source: D. Franzen
Factors Affecting Volatilization Potential of Surface Applied Urea or Materials Containing Free Ammonia

- Unincorporated surface applications (specially with N rate > 100 lb N/A)
- Crop residues on soil surface
- Warm, moist, drying soil conditions
- Neutral to high soil pH
- Sandy soils, low buffering capacity
Nitrification

\[ \text{NH}_4^+ \xrightarrow{\text{‘Slow’}} \text{NO}_2^- \xrightarrow{\text{‘Fast’}} \text{NO}_3^- \]

Factors influencing rate of transformation

- Moisture (moist, not saturated)
- Temperature- max ~ 80F, min 32F
- pH- favored by pH > 7 slowed by pH < 6
Nitrification Inhibitors

\[ \text{NH}_4^+ \xrightarrow{\text{Nitrosomonas}} \text{NO}_2^- \xrightarrow{\text{Nitrobacter}} \text{NO}_3^- \]

Ammonium | Nitrite | Nitrate

Nitrapyrin
Dicyandiamide
Ammonium thiosulfate (weak)
Nitrification Inhibitor

**Generic Name:** 2-chloro-6-(trichloromethyl)pyridine

**Common Name:** nitrapyrin

**Trade Name:** N-Serve, Instinct (eNtrench)
Inherent Issues with N-Serve for Ammonia

Corrosive-
• Replace aluminum float-gauges with stainless steel
• Replace normal acme gaskets with BunaN gaskets/Teflon
• First time use, be prepared to clean out screens frequently on first tank fill of each tank

Direct injection system (not an endorsement)
Nitrapyrin in the Soil

- Volatile (needs to be incorporated) 2-3 times more than the most volatile incorporated herbicides
- Water insoluble
- In soil nitrapyrin has a half-life of <3 to 35 days, depending on soil type (degree of absorption by soil)
- Bacteriostatic and bactericidal (regulated pesticide)
- Active at concentrations as low as 1 ppm
- **Degradation is rapid soon after application**
- Nitrapyrin movement and degradation
  - It is not affected substantially by pH or clay
    - Acid pH (pH <5.5) = slower degrade
    - Increasing clay content = slower degradation
  - Nitrapyrin absorbed by OM
    - Higher degradation in coarse texture and low OM soils
Nitrapyrin Degradation

• Low temperature increases persistence and bioactivity of nitrapyrin
• Decomposes readily in water and with sunlight
• At 77 °F
  – in water in the dark - ½ life is 7.7 days *(only 2 days at 95 °F)*
  – in water in sunlight - ½ life is 0.5 days

![Chemical Structure]

6-chloropicolinic acid
Why 50 ºF?

- Cooler temperatures reduce
- 1) bacterial activity
- 2) nitrapyrin breakdown
Temperature Affects Ability of N-Serve to Preserve Ammonium

Average of 80 and 160 lb N acre⁻¹ and 1.77 and 3.54 ppm N-Serve
Temperature and Soil Affects Nitrapyrin Persistence

Cooler Temperatures Reduce 1) Bacterial Activity and 2) Nitrapyrin Breakdown

Nitrapyrin applied at 1.77 and 3.54 ppm to Drummer and 1 and 2 ppm to Cisne. Touchton et al., 1979 Agron. J. 71:865-869
Temperature and Soil Affects Ability of N-Serve to Preserve Ammonium

Average of 80 and 160 lb N acre\(^{-1}\) and 1-2 ppm N-Serve
How Far Does Nitrapyrin Move?

- No more than **3 inches** from release point
  - Not affected by nitrapyrin rate
  - Highest concentrations and recovery within 1 inch of point of release with concentration gradient to 3 inches
- Increasing rates of anhydrous ammonia had no effect on nitrapyrin movement or degradation
- Most ammonia within 1-2 inches from release point
- Overall retention zone 3-4 inches from release point but can move further
## Time of Application, MN. (Ag J. 97:472-478)

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<td>161</td>
<td>158</td>
<td>153</td>
<td>186</td>
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<td>109</td>
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<tr>
<td>Fall Y</td>
<td></td>
<td></td>
<td>170</td>
<td>151</td>
<td>154</td>
<td>189</td>
<td>207</td>
<td>154</td>
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<tr>
<td>Spring N</td>
<td></td>
<td></td>
<td>175</td>
<td>144</td>
<td>154</td>
<td>180</td>
<td>195</td>
<td>187</td>
</tr>
<tr>
<td>Spring Y</td>
<td></td>
<td></td>
<td>175</td>
<td>149</td>
<td>168</td>
<td>182</td>
<td>204</td>
<td>178</td>
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### Appl. Time (T)

<table>
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<td>Fall</td>
<td>166**</td>
<td>155</td>
<td>153**</td>
<td>187**</td>
<td>203</td>
<td>131***</td>
<td>166***</td>
<td></td>
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<tr>
<td>Spring</td>
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<td>147</td>
<td>161</td>
<td>181</td>
<td>199</td>
<td>182</td>
<td>174</td>
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### NP

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<tr>
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<td>168</td>
<td>151</td>
<td>153**</td>
<td>183</td>
<td>197</td>
<td>148***</td>
<td>167***</td>
<td></td>
</tr>
<tr>
<td>Yes</td>
<td>172</td>
<td>150</td>
<td>161</td>
<td>185</td>
<td>205</td>
<td>166</td>
<td>173</td>
<td></td>
</tr>
</tbody>
</table>

### T x PN (p<0.1)

<p>| | | | | | | | |</p>
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</tbody>
</table>

6yr average TxNP interaction indicates 10 bu increase for NP in fall but only 4 bu/a in the spring
## Nitrified N Over Time & N Source

<table>
<thead>
<tr>
<th>N Source</th>
<th>Weeks after application</th>
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<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>% of fertilizer as NO₃-N</td>
<td></td>
</tr>
<tr>
<td>Anhydrous Ammonia (AA)</td>
<td>0</td>
</tr>
<tr>
<td>AA + N-Serve</td>
<td>0</td>
</tr>
<tr>
<td>Urea</td>
<td>0</td>
</tr>
<tr>
<td>Urea + N-Serve</td>
<td>0</td>
</tr>
<tr>
<td>UNA solution</td>
<td>25</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
<td>50</td>
</tr>
</tbody>
</table>
Instinct® (eNtrench) is a new formulation of Nitrapyrin that can be mixed with ammonium fertilizers and can stay on the soil surface without incorporation.

The formulation is microencapsulated Nitrapyrin.

That means that Nitrapyrin release is slow compared to Nitrapyrin for ammonia.
Instinct trials, 11 Site-Years

- Corn yield (bu acre⁻¹)
- Nitrogen rate (lb N acre⁻¹)

- UAN
- UAN+
Release rates of Instinct indicated a slow release through the encapsulation, with only 14% released in a 70 day incubation study (Menelas, 2014, PhD thesis, Purdue)

Speculated that use in the field might be better if soil pH/soil biology acted on the microencapsulation
Dicynandiamide (DCD) – Showa Denko
also known as cyanoguanidine

First developed as a fertilizer (66.7-0-0)
Found that DCD was toxic to plants when DCD was used at rates equivalent to use as a fertilizer

- About 67% N, 10% of total N content of mixed fertilizer as NI
  - slow-release N source and NI
- Rates used in successful nitrification inhibition range from 1 to 5 % of N in mix as DCD
- Non-volatile
- Soluble in water
- DCD is bacteriostatic
- It interferes with bacteria metabolism, preventing replication
- Mode of action proposed is inhibition of ammonia monooxygenase, a key enzyme in nitrification

Ammonia monooxygenase

Nutrient Management

DCD- a nitrification inhibitor found in:

AgrotainPlus (Agrotain, Int.)
SuperU (Agrotain, Int.)
Guardian DF (Conklin)
Guardian DL (Conklin)
Others.....

Needs to be added at >1% of total N content of fertilizer needing protection
Higher %DCD delays nitrification longer
It is hard to find DCD content on labels

<table>
<thead>
<tr>
<th>Timing</th>
<th>No. of comparisons</th>
<th>DCD</th>
<th>With significant advantage</th>
<th>Average response %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fall</td>
<td>4</td>
<td>1</td>
<td>+1.6</td>
<td></td>
</tr>
<tr>
<td>Spring</td>
<td>15</td>
<td>3</td>
<td>+3.4</td>
<td></td>
</tr>
<tr>
<td>Sidedress</td>
<td>3</td>
<td>1</td>
<td>+1.4</td>
<td></td>
</tr>
<tr>
<td>N Source</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonium sulfate</td>
<td>2</td>
<td>0</td>
<td>-1.0</td>
<td></td>
</tr>
<tr>
<td>Anhydrous ammonia</td>
<td>6</td>
<td>1</td>
<td>+3.6</td>
<td></td>
</tr>
<tr>
<td>Urea</td>
<td>4</td>
<td>4</td>
<td>+2.2</td>
<td></td>
</tr>
</tbody>
</table>

From G. Malzer et al., 1989
DCD and urea have similar mobility

Figure 2a. Distribution of 112 kg DCD-N/ha and 112 kg urea-N/ha applied in a 5-mm slug followed by a 10-cm application of water.
DCD and NH$_4^+$ separate with rainfall

- Not a good inhibitor for early spring or fall
- Reduced effectiveness with higher OM or higher temperatures (degradation)
“Thus, this research suggests that ATS cannot be recommended solely as a nitrification inhibitor. However, it should be recognized that if ATS is used as a sulfur fertilizer then some inhibition of nitrification may occur.”

Jay Goos, North Dakota State Univ., professor and patent holder ATS as a nitrification inhibitor.

Nutrient Management

Conditions when NI will not increase grain yield

- Seasons and soil types where N loss is minimal
- Seasons and soil types were N loss conditions occur after the NI has become ineffective
- When soil plus fertilizer N far exceeds crop N requirement
- When NI and NH$_4^+$ become separated in the soil
- When positional availability of NH$_4^+$ is a factor under dry soil conditions
Effectiveness of NI increases.....

• With cool soil temperatures
  – Less NI breakdown
  – Reduced recovery of nitrifiers
• With low initial soil pH
  – Reduced recovery of nitrifiers
• With low, banded N rates
  – Proximity of NI to NH$_4^+$
  – High ionic strength reduces nitrifiers and NI decomposition
ESN- Agrium

How ESN works (Agrium website)
# Nitrogen Timing, Placement and Source Effects on Corn Yield After Soybean, So. MN

<table>
<thead>
<tr>
<th>Timing</th>
<th>Placement</th>
<th>Source</th>
<th>Yield bu/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fall</td>
<td>band (4 in)</td>
<td>Urea (100)</td>
<td>164b</td>
</tr>
<tr>
<td>Fall</td>
<td>band (4 in)</td>
<td>ESN (100)</td>
<td>168b</td>
</tr>
<tr>
<td>Fall</td>
<td>bcast</td>
<td>ESN</td>
<td>149c</td>
</tr>
<tr>
<td>PP</td>
<td>bcast incorp</td>
<td>Urea (100)</td>
<td>179a</td>
</tr>
<tr>
<td>PP</td>
<td>bcast incorp</td>
<td>ESN (100)</td>
<td>176a</td>
</tr>
<tr>
<td>PP</td>
<td>inject</td>
<td>AA (120)</td>
<td>185a</td>
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<tr>
<td>Post plt</td>
<td>surf bcast</td>
<td>ESN</td>
<td>185a</td>
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<tr>
<td>None</td>
<td>----</td>
<td>----</td>
<td>97d</td>
</tr>
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Yield at 160 lb N/acre, 2012

- Nutrient Management

![Bar chart showing corn yield (bu/acre) at different nitrogen treatments (0/160, 40/120, 80/80, 120/40, 160/0). The bars are labeled with letters indicating significant differences: 'a', 'b', 'ab'.]
Yield at 160 lb N/acre, 2012

Comparing different rates of sidedress ESN and sidedress urea, the yields are as follows:

- 0/160: 1.60
- 40/120: 1.60
- 80/80: 1.00
- 120/40: 1.00
- 160/0: 1.00

The yields are marked with letters:
- a: 1.60
- b: 1.00

The highest yield is achieved with 0/160 and 40/120, while the lowest is with 80/80, 120/40, and 160/0.
Non-Traditional Products

How much will I get back from this investment?
Is this an investment?

http://extension.agron.iastate.edu/compendium/

- **Typical claims**
  - Replace fertilizers and cost less
  - Make nutrients in the soil more available
  - Supply micronutrients
  - It’s a natural product

- Use testimonials by farmers and partial data
Thank You