Nitrogen Fertilizer Management Effects on Soil Processes Affecting N$_2$O Production

Rodney Ventere
Ryosuke Fujinuma
Carl Rosen
Bijesh Maharjan

Funding:
- USDA-NIFA Air Quality Program
- ARS GRACEnet Project

Anhydrous ammonia application equipment:
- John Deere & Company

ASA-CSSA-SSSA Annual Meeting
18 October 2011, San Antonio
Use findings from our recent studies to:

1. Examine how N Fertilizer Mgmt Practices influence underlying processes that control N$_2$O emissions

2. Discuss implications of findings with respect to improved N$_2$O emissions models and challenges for mitigation strategies.
# Fertilizer management comparisons

<table>
<thead>
<tr>
<th>Category</th>
<th>Number of peer-reviewed studies</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Comparison of conventional fertilizer sources</strong></td>
<td></td>
</tr>
<tr>
<td>Anhydrous ammonia (AA) vs. other sources</td>
<td>3</td>
</tr>
<tr>
<td>Other conventional source comparisons</td>
<td>4</td>
</tr>
<tr>
<td><strong>Timing of Application</strong></td>
<td></td>
</tr>
<tr>
<td>Single application vs. multiple split applications</td>
<td>2</td>
</tr>
<tr>
<td>Fall- vs. spring-applied fertilizer</td>
<td>2</td>
</tr>
<tr>
<td>Early spring vs. later application(s)</td>
<td>3</td>
</tr>
<tr>
<td><strong>Physical Placement</strong></td>
<td></td>
</tr>
<tr>
<td>Anhydrous ammonia, placement depth</td>
<td>1</td>
</tr>
<tr>
<td>Other N source, placement depth</td>
<td>2</td>
</tr>
<tr>
<td>Broadcast vs. banding</td>
<td>2</td>
</tr>
</tbody>
</table>

1. To determine if specific management practices (other than reducing the N application rate) can be used to mitigate N$_2$O emissions.

2. To determine if the effectiveness of these practices depends on climate, soil, cropping system or other site-specific factors.

3. To develop quantitative relationships (e.g. emissions factors) that can be used to predict how a change in practice will affect N$_2$O emissions.
Fertilizer management comparisons

- To better understand how mgmt practices & environmental factors interact to regulate fundamental soil processes
- To incorporate this understanding into improved models
### Fertilizer management comparisons

<table>
<thead>
<tr>
<th>Category</th>
<th>Number of peer-reviewed studies</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Comparison of conventional fertilizer sources</strong></td>
<td></td>
</tr>
<tr>
<td>Anhydrous ammonia (AA) vs. other sources</td>
<td>3</td>
</tr>
<tr>
<td>Other conventional source comparisons</td>
<td>3</td>
</tr>
<tr>
<td><strong>Timing of Application</strong></td>
<td></td>
</tr>
<tr>
<td>Single application vs. multiple split applications</td>
<td>1</td>
</tr>
<tr>
<td>Fall- vs. spring-applied fertilizer</td>
<td>2</td>
</tr>
<tr>
<td>Early spring vs. later application(s)</td>
<td>3</td>
</tr>
<tr>
<td><strong>Physical Placement</strong></td>
<td></td>
</tr>
<tr>
<td>Anhydrous ammonia, placement depth</td>
<td>1</td>
</tr>
<tr>
<td>Other N source, placement depth</td>
<td>2</td>
</tr>
<tr>
<td>Broadcast vs. banding</td>
<td>2</td>
</tr>
</tbody>
</table>

1. Compare AA and broadcast urea in a coarse textured soil used for irrigated corn production.

2. Examine effects of AA application depth.

3. Separate experiment in silt loam soil compare broadcast vs. band-applied urea.
Anhydrous Ammonia (AA) and Urea

N Fertilizer Use Statistics

<table>
<thead>
<tr>
<th>% of Total N Fertilizers Used</th>
<th>Anhydrous ammonia</th>
<th>Urea</th>
</tr>
</thead>
<tbody>
<tr>
<td>USA Total</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ERS, 2011 (2008 data)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MN corn</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Survey data (2009 data)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bierman et al. (In review)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

AA + Urea = 58%

AA + Urea = 91%
Anhydrous Ammonia (AA) and Urea

Previous studies in Minnesota:

Reduced $\text{N}_2\text{O}$ emissions with broadcast urea compared to AA:

- Silt loam soil under varying tillage

- Silt loam soil with varying crop rotation

Venterea et al. (2005; 2010)
**Anhydrous Ammonia versus Urea: Two-year study in Irrigated Corn**

<table>
<thead>
<tr>
<th>Location</th>
<th>Parent material</th>
<th>Texture</th>
<th>Soil C</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Becker, MN</td>
<td>Outwash</td>
<td>Loamy sand</td>
<td>1.0%</td>
<td>5.0</td>
</tr>
</tbody>
</table>

**Source** | **Placement**
--- | ---
1. Urea     | Broadcast and incorporated
2. AA       | Injected at approx. 20 cm depth
3. AA       | Injected at approx. 10 cm depth

All sources applied in two split applications of 90 kg N ha$^{-1}$ each:
- 50% prior to planting
- 50% as side dress 4-6 weeks after planting
Anhydrous Ammonia versus Urea: Two-year study in Irrigated Corn

Growing Season N$_2$O Emissions

- Shallow AA
- Deep AA
- Broadcast Urea

Fujinuma et al. JEQ (2011)
Anhydrous Ammonia (AA) and Urea

Reduced growing season $N_2O$ emissions with broadcast urea:

<table>
<thead>
<tr>
<th>Soil Type &amp; Conditions</th>
<th>Percent Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silt loam soil under varying tillage (1 yr)</td>
<td></td>
</tr>
<tr>
<td>- No till</td>
<td>50</td>
</tr>
<tr>
<td>- Biennial tillage</td>
<td>81</td>
</tr>
<tr>
<td>- Conventional tillage</td>
<td>79</td>
</tr>
<tr>
<td>Silt loam soil with varying crop rotation (3 yr)</td>
<td></td>
</tr>
<tr>
<td>- Continuous corn</td>
<td>57</td>
</tr>
<tr>
<td>- Corn/soybean</td>
<td>50</td>
</tr>
<tr>
<td>Loamy sand with varying AA application depth (2 yr)</td>
<td></td>
</tr>
<tr>
<td>- Shallow AA injection</td>
<td>29</td>
</tr>
<tr>
<td>- Deep AA injection</td>
<td>67</td>
</tr>
</tbody>
</table>
Why are $\text{N}_2\text{O}$ emissions greater with Anhydrous Ammonia?

Peak $\text{N}_2\text{O}$ fluxes occurred under aerobic conditions

$\text{N}_2\text{O}$ flux

WFPS

Loamy sand, Becker, MN

Fujinuma et al. JEQ (2011)

Soil gas $\text{O}_2$ concentration (%)

Soil gas $\text{N}_2\text{O}$ concentration (ppm)

23 June 2006, WFPS = 42%

Silt-loam soil, Rosemount, MN

Unpublished data
Why are N$_2$O emissions greater with Anhydrous Ammonia?

NO$_2^-$ accumulates in soil when AA is applied.

Fujinuma, Maharjan & Venterea (Unpublished)
Why are $N_2O$ emissions greater with Anhydrous Ammonia?

Decoupling of the two steps of nitrification

- Fertilizer addition: $NH_4^+$
- Nitrification step I: $NO_2^-$
- Nitrification step II: $NO_3^-$

Usually present at low levels: $AOB$, $NOB$
Why are $\text{N}_2\text{O}$ emissions greater with Anhydrous Ammonia?

Decoupling of the two steps of nitrification

- Concentrated Band
  - $\text{NH}_3/\text{NH}_4^+$

- Nitrification step I
  - $\text{AOB}$

- Nitrification step II
  - $\text{NOB}$

- Accumulation

- $\text{N}_2\text{O}$

- Elevated pH

- Free ammonia toxicity
  - Aleem and Alexander (1960)
  - Anthonisen et al. (1976)
Why are N$_2$O emissions greater with Anhydrous Ammonia?

Release of dissolved organic carbon from SOM

**Soil Dissolved Organic Carbon**
Corn after Soybean, 2006

Soil DOC (g C g$^{-1}$)

10-20 cm

Venterea et al. SSSAJ (2010)
Why are $\text{N}_2\text{O}$ emissions greater with Anhydrous Ammonia?

Release of dissolved organic carbon from SOM

- Anhydrous ammonia
- Organic acid deprotonation
- Dispersion of organic colloids

$\text{N}_2\text{O}$

Nitrification
$\text{NO}_2^-$ reactions
(Venterea, 2007)

Increased DOC

Denitrification
$\text{N}_2\text{O}$

Tomasiewicz and Henry (1985)
Myers and Thien (1988)
Norman et al. (1988)
Clay et al. (1995)
Why are N$_2$O emissions greater with **Shallow** Anhydrous Ammonia?

Release of dissolved organic carbon from SOM

<table>
<thead>
<tr>
<th>SOM content (%)</th>
<th>Depth (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0</td>
</tr>
<tr>
<td>1.5</td>
<td>5</td>
</tr>
<tr>
<td>2.0</td>
<td>10</td>
</tr>
<tr>
<td>2.5</td>
<td>15</td>
</tr>
<tr>
<td>3.0</td>
<td>20</td>
</tr>
</tbody>
</table>

**HYPOTHESIS:**
More DOC released with shallow injection due to higher SOM at shallower depth?

**HYPOTHESIS:**
More microbial activity and nitrification at shallower depth

*Fujinuma et al. JEQ (2011)*
Banded Versus Broadcast Urea: Ongoing study in Rainfed Corn

<table>
<thead>
<tr>
<th>Location</th>
<th>Parent material</th>
<th>Texture</th>
<th>Soil C</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>St. Paul, MN</td>
<td>Till</td>
<td>Silt loam</td>
<td>2.0%</td>
<td>6.0</td>
</tr>
</tbody>
</table>

Goal: Isolate effects of physical placement from chemical formulation

<table>
<thead>
<tr>
<th>Source</th>
<th>Placement</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Urea</td>
<td>Broadcast and incorporated</td>
</tr>
<tr>
<td>2. Urea</td>
<td>Subsurface band (5 cm deep, 5 cm wide)</td>
</tr>
</tbody>
</table>

Both treatments applied post-emergence in single application of 150 kg N ha$^{-1}$
Daily $\text{N}_2\text{O}$ flux

- Broadcast urea
- Banded urea

Fertilizer added

Growing season total emissions
Banded 4.2 kg N ha\(^{-1}\)
Broadcast 1.7 kg N ha\(^{-1}\) (60 % reduction)

Maharjan et al. (Unpublished)
Why are N$_2$O emissions greater with Banded Urea?

NO$_2^-$ accumulates in soil with banded urea

Maharjan et al. (Unpublished)

Similar trends found by Engel et al. JEQ (2010)
Why are $N_2O$ emissions greater with AA and Banded Urea?

Can these processes be accurately modeled and predicted?

1. Predicting the accumulation of soil $NO_2^-$

2. Predicting $N_2O$ emissions when the $NO_2^-$ concentration is known

- Elevated pH
- Free ammonia toxicity

Concentrated Band

$NH_3/NH_4^+$

Nitrification step I

$N_2O$

Nitrification step II

$NO_3^-$

High $O_2$: Little potential for $N_2O$ reduction to $N_2$

$N_2$
Predicting $\text{N}_2\text{O}$ emissions when the $\text{NO}_2^-$ concentration is known

$\text{N}_2\text{O}$

$\text{NO}_2^-$

Laboratory $\text{NO}_2^-$ addition experiments: Aerobic conditions

Rate coefficient = $K_p$

"Chemo-denitrification"

"Nitrifier-denitrification"

"Biotic"

"Abiotic"

Venterea (2007)
Predicting $\text{N}_2\text{O}$ emissions when the $\text{NO}_2^-$ concentration is known

First-order model
$\text{N}_2\text{O}$ Production Rate $= K_p [\text{NO}_2^-]$

Temperature Sensitivity of $K_p$

$K_p = A \exp (-E_a/RT)$

$E_a$ (kJ mol$^{-1}$)

- 5 %
- 21 %

CT soil 66 56
NT soil 71 60
Forest soil 85 78

$K_p$ pos. correlated: SOM, DOC, acidity

$K_p = a + b 10^{-pH} + c C_t + d \text{DOC}$

$R^2 = 0.70$

Measured $K_p$

Predicted $K_p$

Venterea (2007)
Predicting $N_2O$ emissions when the $NO_2^-$ concentration is known

Complications for modeling:

1. Vertical and lateral non-uniformity of the soil $NO_2^-$ distribution due to banding
2. Two-dimensional gas diffusion
Predicting $N_2O$ emissions when the $NO_2^-$ concentration is known

Complications for modeling:

1. Vertical and lateral non-uniformity of the soil $NO_2^-$ distribution due to banding
2. Two-dimensional gas diffusion

1. Assumed a 2-D Gaussian distribution of $NO_2^-$ concentration that varied with time using spatial and temporal interpolation of measured $NO_2^-$ data (spoonfed):

   ![Graph showing soil nitrite concentration](image)

   Used as model input: Example of input data for a given point in time.

Fujinuma & Venterea (Unpublished)
Predicting $N_2O$ emissions when the $NO_2^-$ concentration is known

Complications for modeling:

1. Vertical and lateral non-uniformity of the soil $NO_2^-$ distribution due to banding
2. Two-dimensional gas diffusion

2. Used 2-D diffusion model to describe $N_2O$ transport:

$$R \frac{\partial C}{\partial t} = \frac{\partial}{\partial z} \left( D \frac{\partial C}{\partial z} \right) + \frac{\partial}{\partial y} \left( D \frac{\partial C}{\partial y} \right) + K_p(T) [NO_2^-]$$

Solved numerically using finite difference methods to predict surface emissions:

Measured temperature & water content used as inputs for parameter estimation.
Predicting $N_2O$ emissions when the $NO_2^-$ concentration is known

Model – data comparison

- Black dots = data (measured 4 times/day)
- Blue line = model

Assumed: No $N_2O$ produced from denitrification
No $N_2O$ consumption by denitrification

Not predicting $NO_2^-$

Fujinuma & Venterea (Unpublished)
1. To make a useful model, we need better understanding of factors that promote nitrite accumulation; under what conditions it occurs and to what extent.

2. We have working two-step nitrification model, but we’re guessing at the parameters and kinetics - trying to fill those in with some experiments.

3. Detailed model useful primarily as research tool. Practical predictive model might need to be simplified.

1. Transient nitrite accumulation can be an important process; more work needed to determine under what conditions.

2. Majority of data show that a banding application of N fertilizer (AA or urea) will increase N$_2$O emissions.

3. Banding can increase Nitrogen Use Efficiency by:
   - Improving root access to N
   - Decreasing fertilizer-soil contact, N immobilization & volatilization
   - Slowing overall nitrification rate and decrease nitrate leaching
     (e.g., Malhi et al. 2001; Yadvinder-Singh et al. 1994)

Trade-off between N$_2$O emissions and NUE?
3. Trade-off between N$_2$O emissions and NUE?

**Graph:**
- **Title:** N fertilizer Recovery Efficiency (%)
- **X-axis:** 2009
- **Y-axis:** % of Fertilizer N Recovered
- **Bars:**
  - Black: Shallow AA
  - Red: Deep AA
  - Green: Urea

**Implications:**
- Greatest N$_2$O emissions and Greatest NUE

**Possible explanations:**
- Possible because N$_2$O represents a small % of N applied.
- Greater root density at shallow depths in sandy irrigated soil.

*Fujinuma et al. JEQ (2011)*
3. Trade-off between $N_2O$ emissions and NUE?

- Even though N applied weeks after planting, large $N_2O$ response observed.
- May have been less nitrate produced/leached, and more N uptake.
- But the 1st step of nitrification still can proceed rapidly to generate nitrite and $N_2O$.

_Fujinuma et al. JEQ (2011)_
Implications and Complications

3. Trade-off between \( \text{N}_2\text{O} \) emissions and NUE?

- Comparison of 3 banded fertilizer sources (UAN, CAN, AqA)
- Nitrate losses may have been reduced, but both \( \text{N}_2\text{O} \) emissions and NUE were greater.

Positive correlation between \( \text{N}_2\text{O} \) Emissions and NUE

\[ r^2 = 0.93 \]
\[ r^2 = 0.99 \]

4. Improving NUE is absolutely important; in all cases will help to reduce indirect N\textsubscript{2}O emissions and other environmental impacts. And in some cases reduce decreased direct N\textsubscript{2}O emissions.

5. But to develop improved mitigation strategies and models of direct N\textsubscript{2}O emissions, we need better understanding of short-term microbial and chemical responses to N fertilizer additions.

Models (of whatever type) need to account for:

- Factors affecting nitrite accumulation.
- Chemical N\textsubscript{2}O production (chemo-denitrification); can be responsible for more than 50% of the N\textsubscript{2}O production.
- Vertical stratification of microbial & chemical processes.