

# N<sub>2</sub>O Emissions – Is there anything we can do to cap the well?

Rodney Venterea

US Dept. of Agriculture - ARS

Dept. of Soil, Water, Climate / University of Minnesota

Ryo Fujinuma

John Baker

Kurt Spokas

Michael Dolan

Jason Leonard



Carl Rosen

Charles Hyatt

Bijesh Maharjan



UNIVERSITY OF MINNESOTA

Driven to Discover<sup>SM</sup>

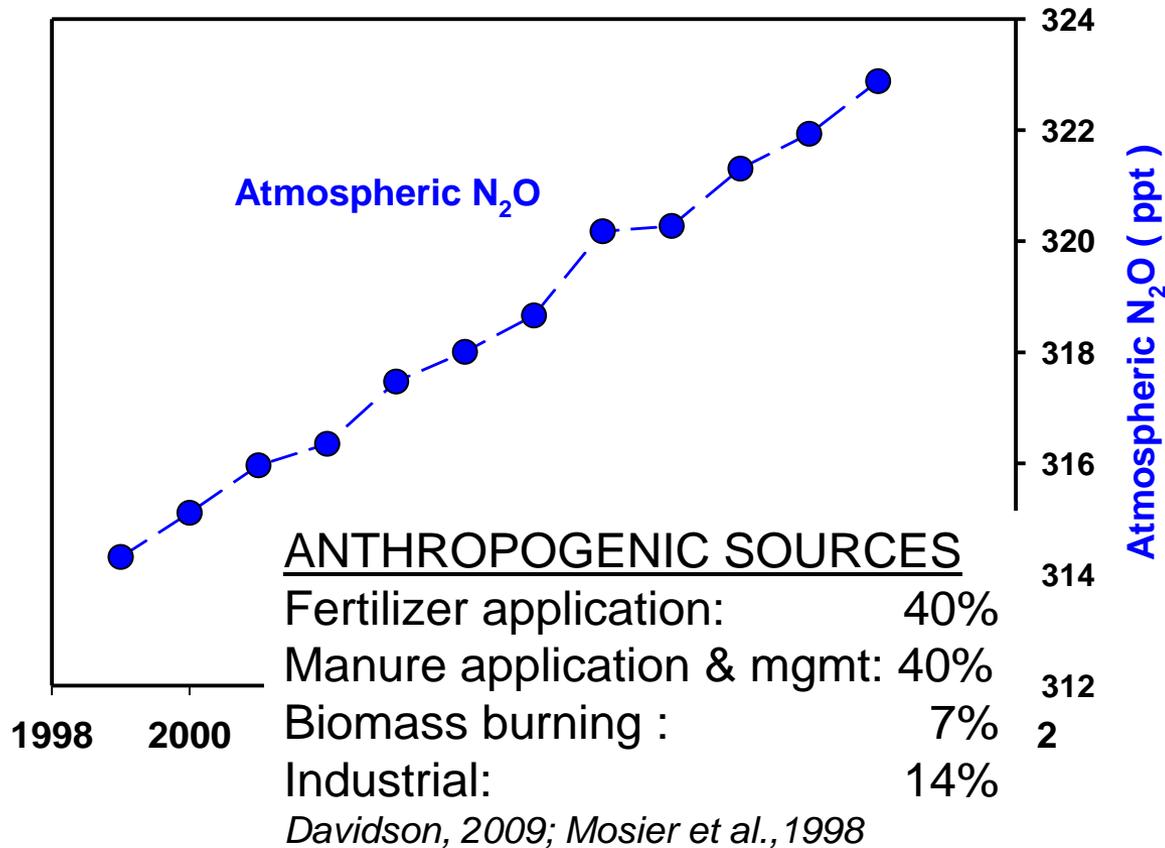
- *NRI-USDA CSREES/NIFA Air Quality Program*
- *USDA-ARS GRACEnet Project*
- *USDA-ARS Post-doctoral Fellowship*
- *International Plant Nutrition Institute's Foundation for Agronomic Research with support from Agrotain Intl. and Agrium Inc.*
- *Minnesota Corn Growers Association*
- *John Deere & Company*
- *Kingenta Corporation*

Is there anything we can do to cap the well?

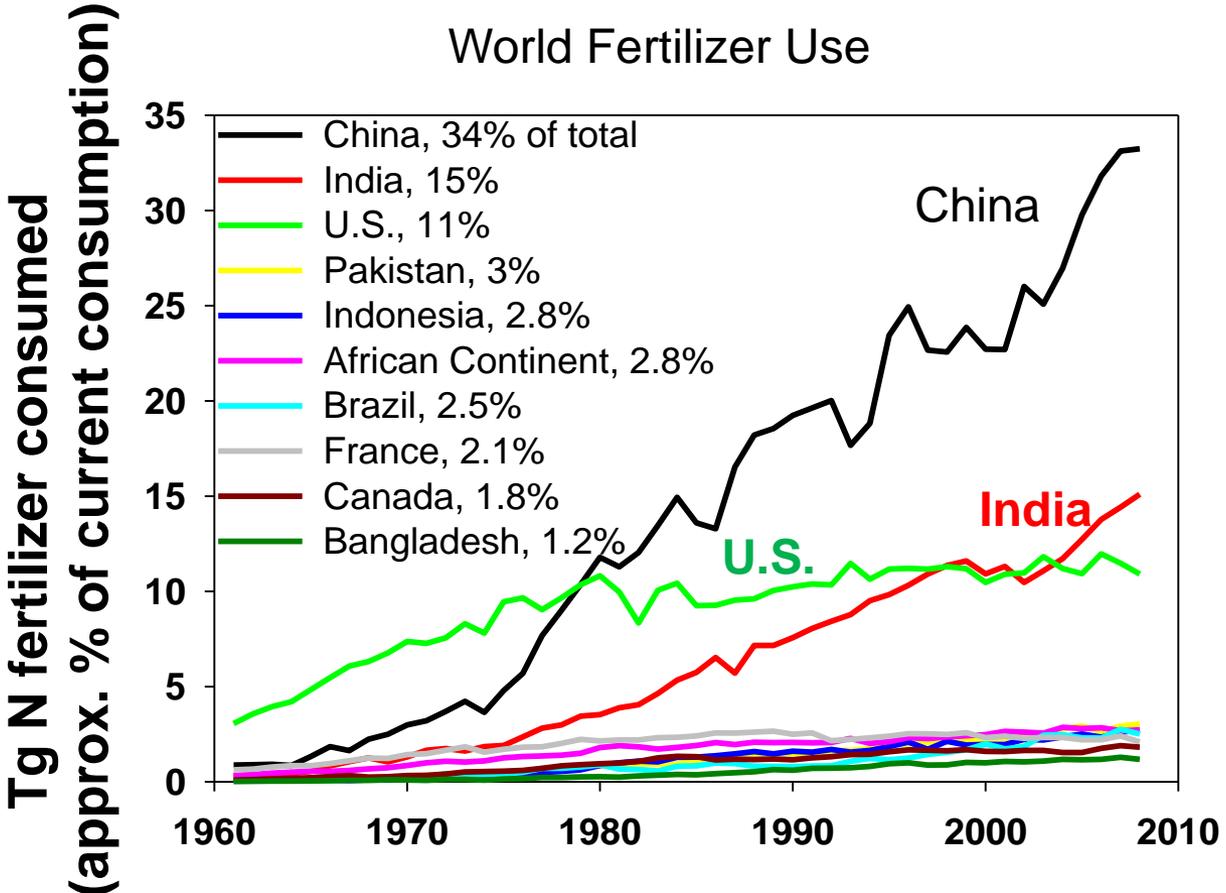


**Atmospheric N<sub>2</sub>O: + 0.25% per year**

**20% above pre-industrial levels**



# World Fertilizer Use



87% of total increase since 1980 occurred in China and India

<http://www.fertilizer.org/>

# GWP = 300 times CO<sub>2</sub>

• 1 kg N<sub>2</sub>O-N ha<sup>-1</sup> ≈ 0.5 Mg CO<sub>2</sub> ha<sup>-1</sup>

• Potential C Sequestration (CCX):

Conversion of cropland to reduced tillage = 1 to 1.5 Mg CO<sub>2</sub> ha<sup>-1</sup>

1 kg N<sub>2</sub>O-N = CO<sub>2</sub> from  
50 gallons of gasoline

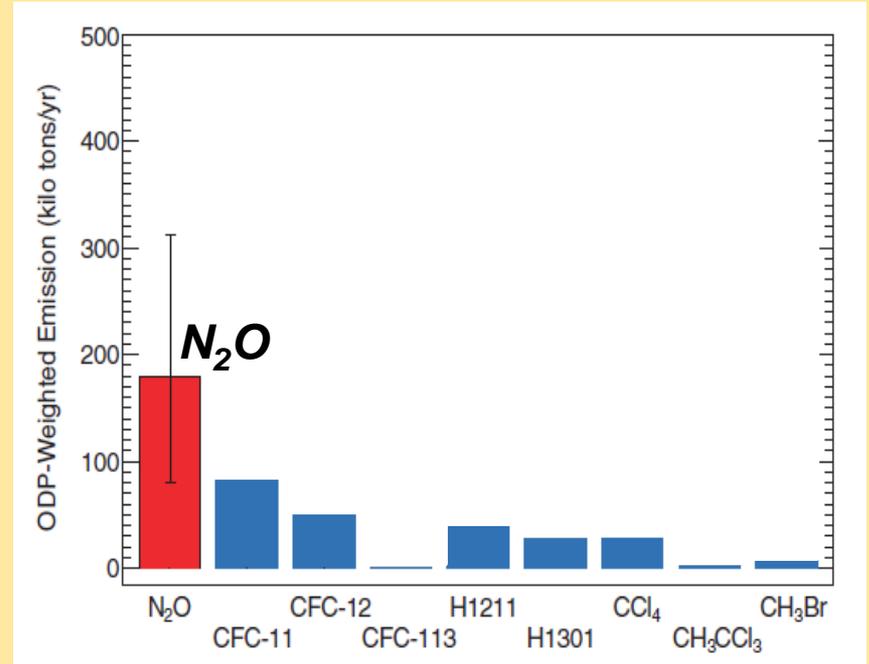
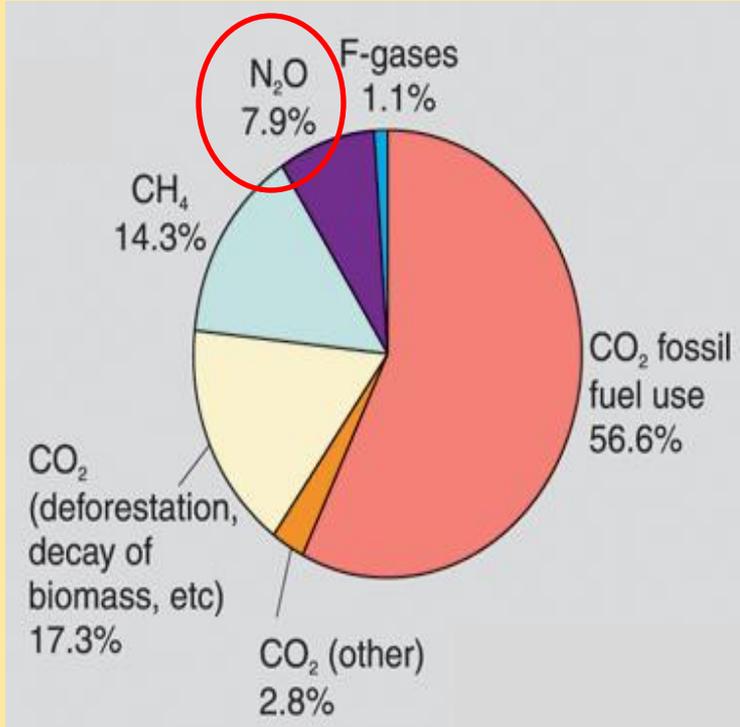


GWP= Global Warming Potential

ODP = Ozone Depleting Potential

IPCC, 2007

Ravishankara et al. *Science*. 2009



% of total anthropogenic GHG emissions

***“By 2050, N<sub>2</sub>O emissions could represent > 30% of peak CFC emissions of 1987.”***

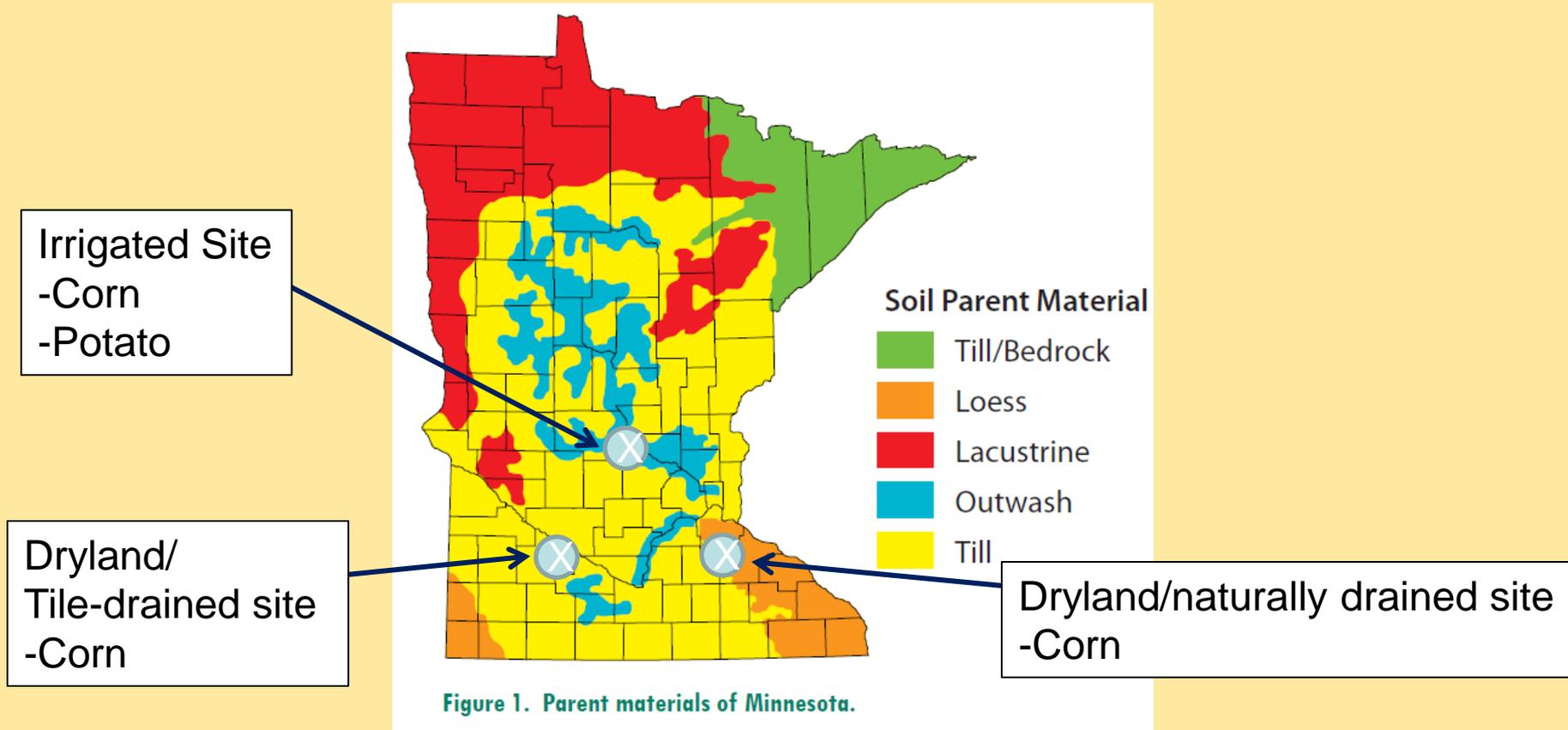
## 30+ Years of Soil N<sub>2</sub>O Emissions Research

1. Developed measurement systems
2. Put constraints on emissions estimates
3. Identified major emissions controls, regulators, and key process
4. Developed emissions models

- Recent emphasis: Develop practical field methods to reduce emissions
- Few empirically-based guidelines for reducing N<sub>2</sub>O while maintaining crop yields

## Objective

- Review our recent research as it relates to N<sub>2</sub>O mitigation efforts
  - Management of synthetic Nitrogen fertilizer
  - Challenges & recommendations for future study



# Gas Flux Chambers



## Pro:

- Plot-scale studies & treatment comparisons
- Inexpensive

## Con:

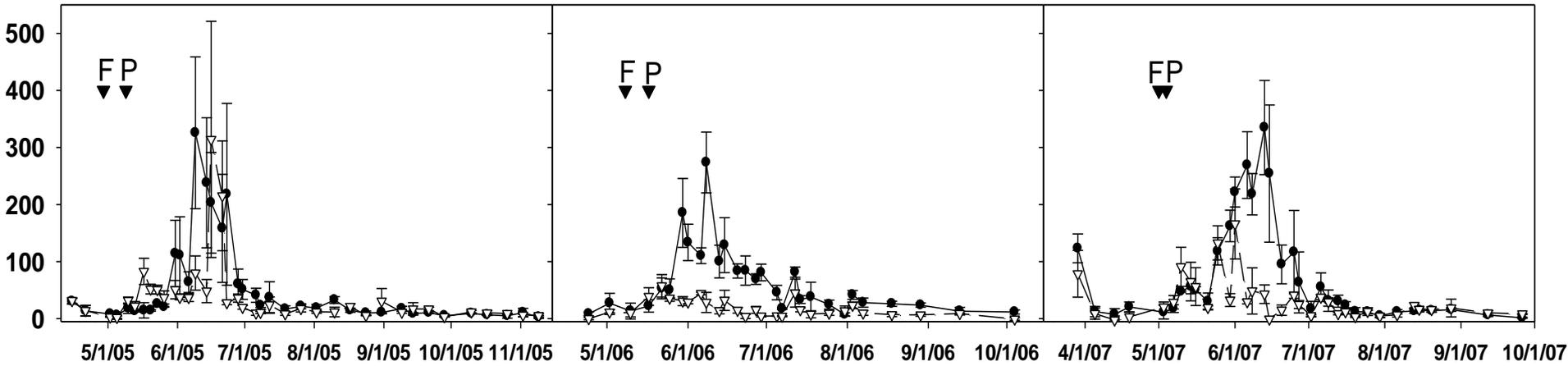
- Limited spatial and temporal coverage
- Physical disturbance



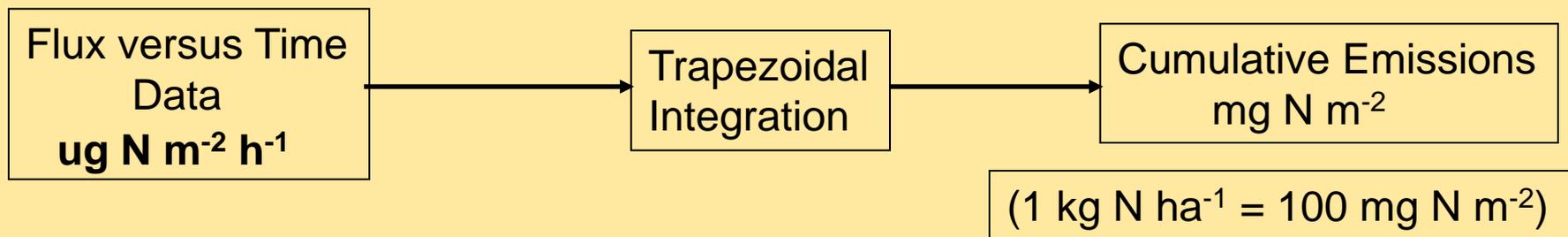
# Automated Chambers



# N<sub>2</sub>O flux ( $\mu\text{g N m}^{-2} \text{h}^{-1}$ ) 2005, 2006, 2007 Growing Seasons

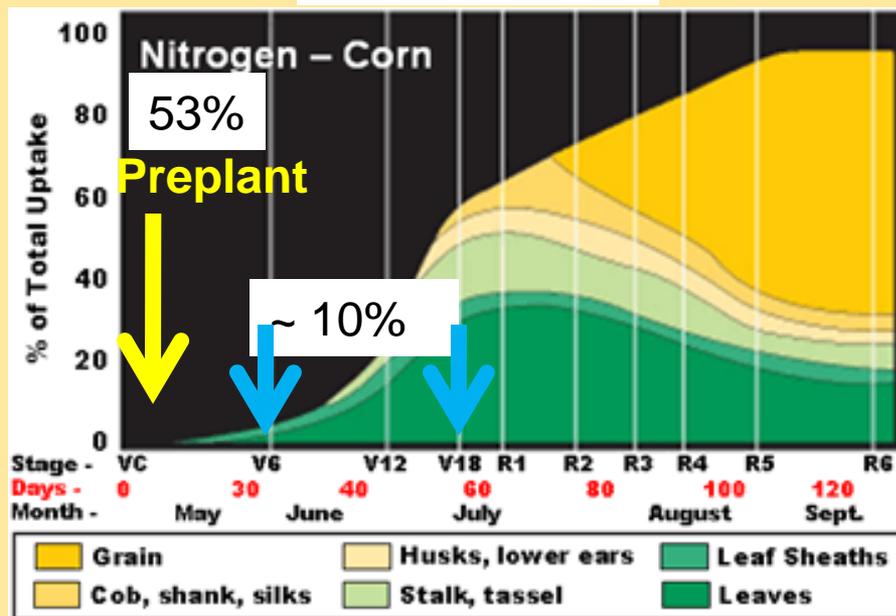


**F = Fertilizer application date**  
**P = Planting date**



# Asynchrony between N fertilizer application and crop N demand

## Corn N Uptake



Iowa State University Extension

High potential for generating N losses:  
Provide substrate for soil microbial population

# Controlled Release Fertilizers (CRFs) for Reducing N<sub>2</sub>O Emissions

GOAL: Achieve more gradual N release over growing season:

1. Polymer-coated urea (PCU): Diffusion through porous coating
2. Nitrification (NI) inhibitors: Blended or co-applied with fertilizer

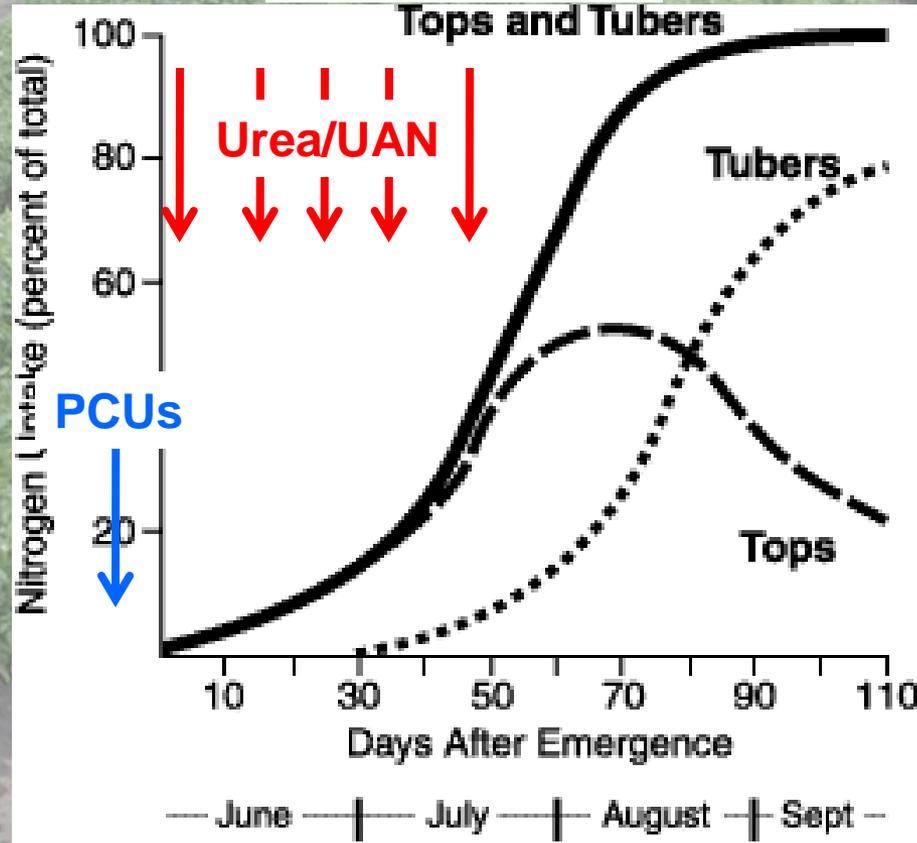
## Meta-analysis of 35 studies (Akiyama et al., 2009)

- On average 35% to 38 % reduction in N<sub>2</sub>O emissions
- Wide variation in effectiveness.
- Yield benefits req'd to justify cost have been inconsistent.

# Polymer-coated Urea (PCU) for Irrigated Potato Production

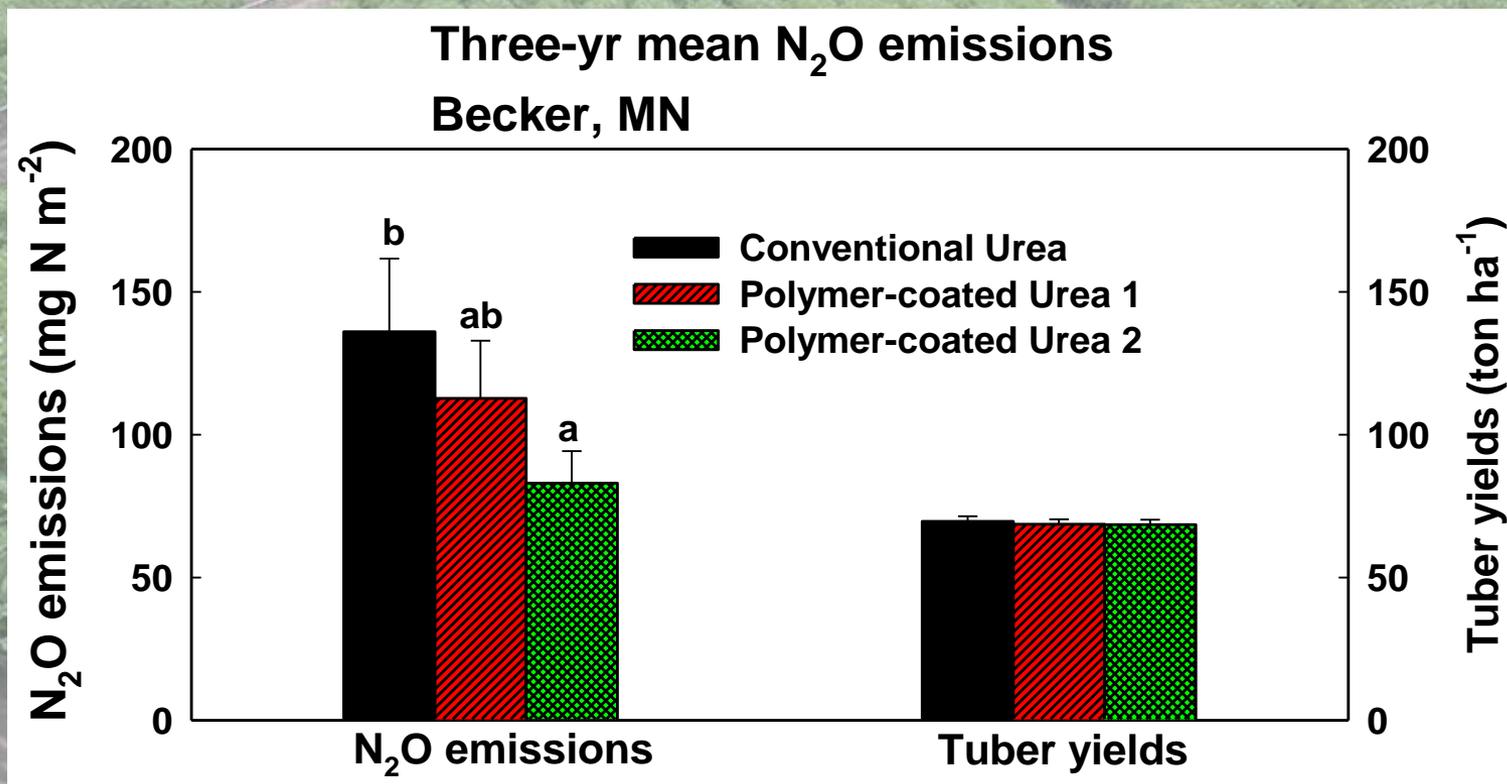
Source	Timing	Rate (kg N ha <sup>-1</sup> )
1. Conventional urea (47%N)	4 split applications	270
2. PCU-1 (44%N)	Before planting	270
3. PCU-2 (42%N)	Before planting	270

Potato N Uptake



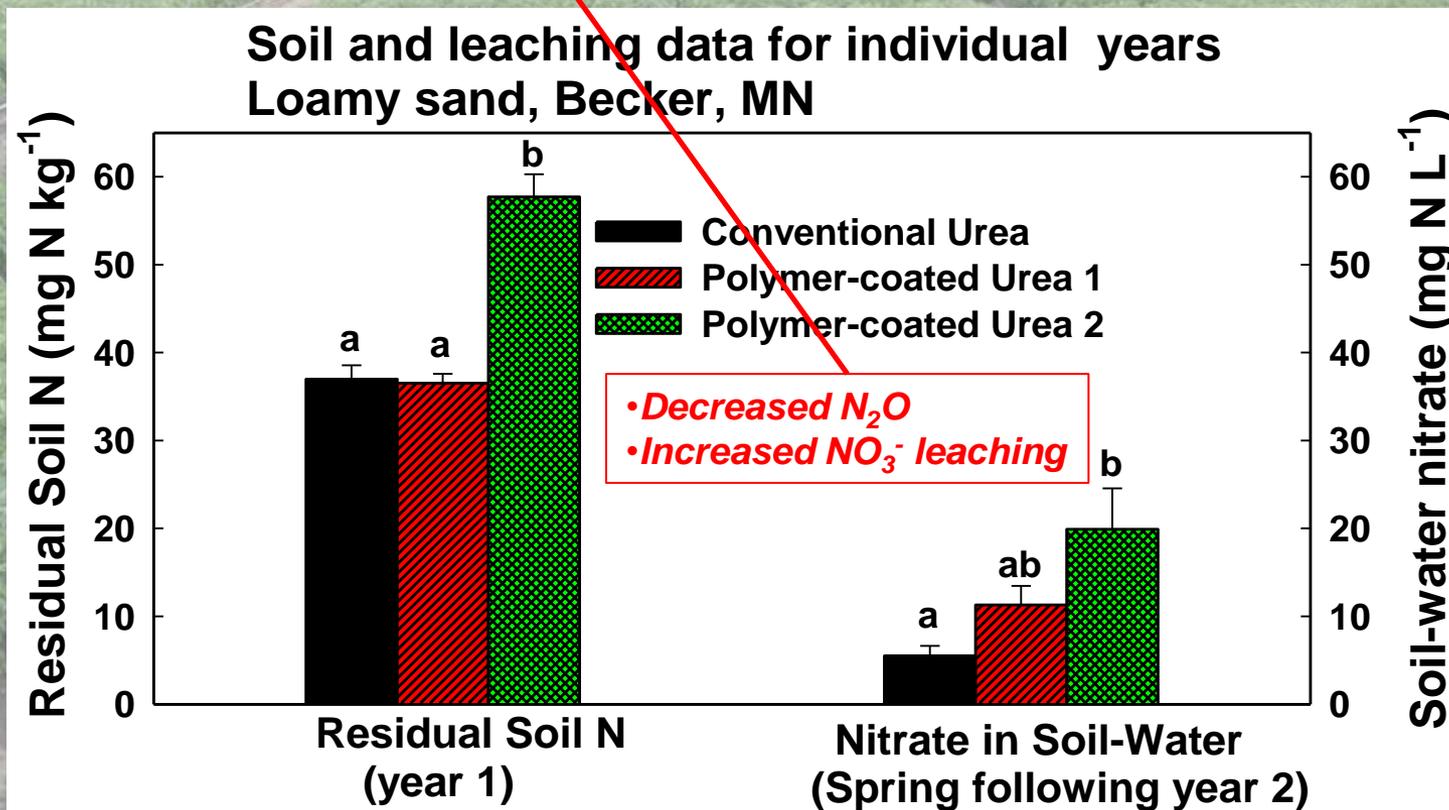
# Controlled Release Fertilizers for Irrigated Potato Production

Source	Timing	Rate (kg N ha <sup>-1</sup> )
1. Conventional urea (47%N)	4 split applications	270
2. PCU-1 (44%N)	Before planting	270
3. PCU-2 (42%N)	Before planting	270

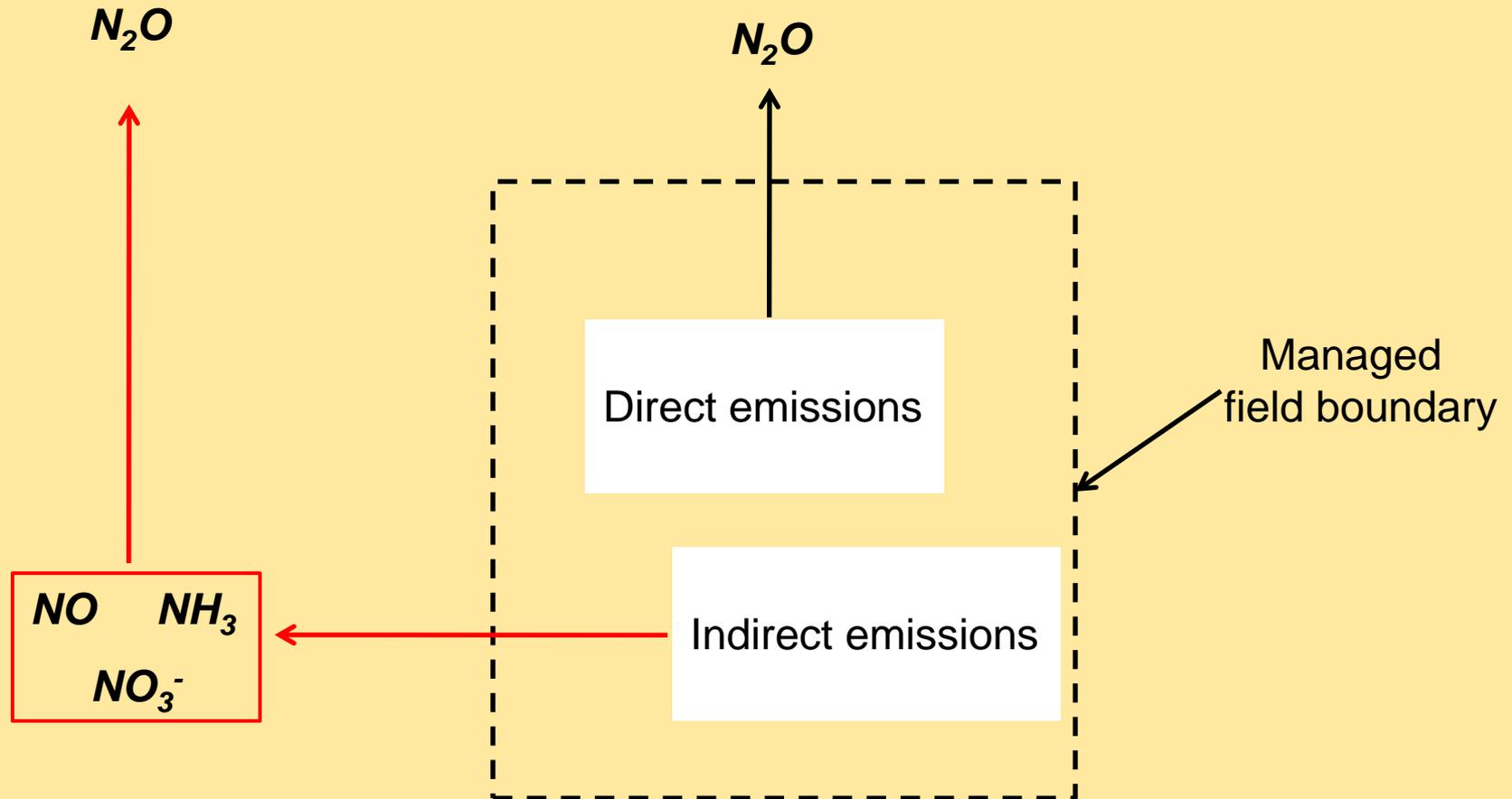


# Controlled Release Fertilizers for Irrigated Potato Production

Source	Timing	Rate (kg N ha <sup>-1</sup> )
1. Conventional urea (47%N)	4 split applications	270
2. PCU-1 (44%N)	Before planting	270
3. PCU-2 (42%N)	Before planting	270



# Direct and Indirect $N_2O$ Emissions



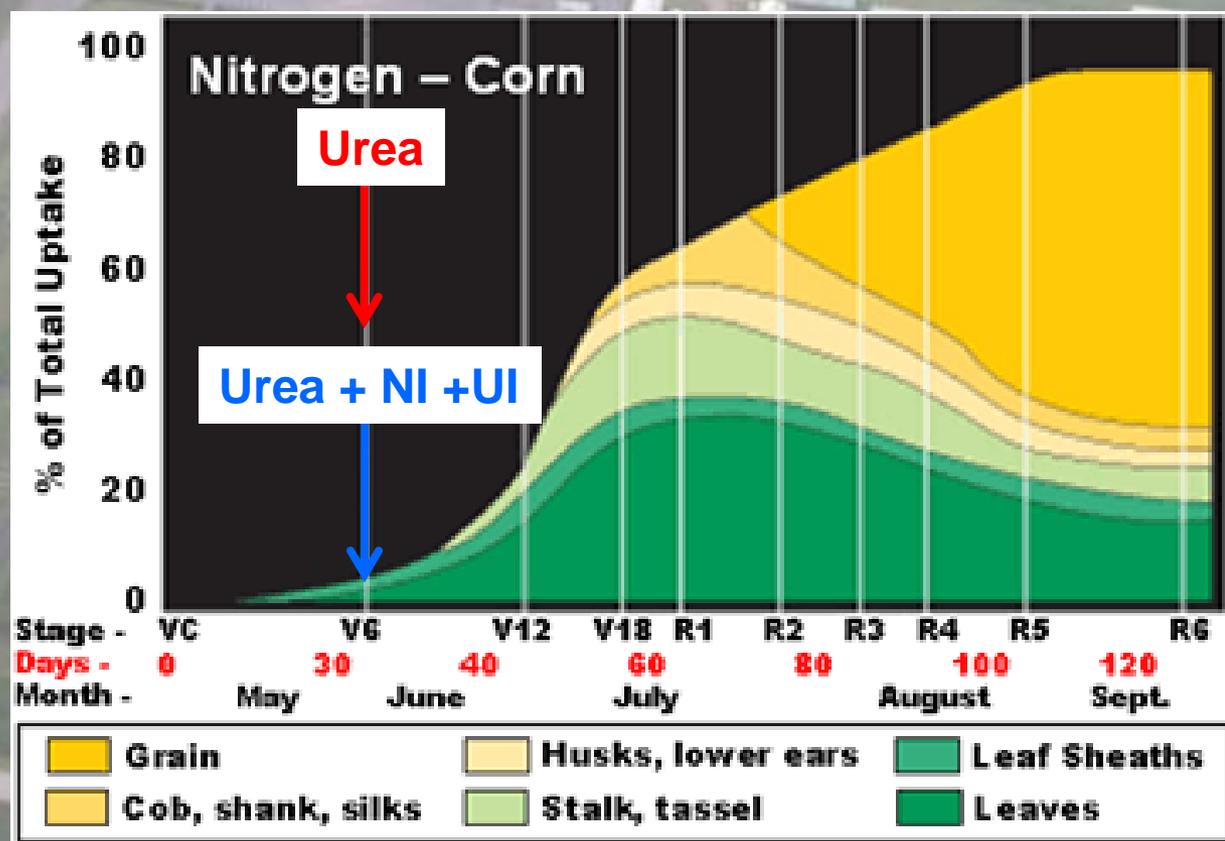
## Challenges:

1. Logistical - measuring all forms of N loss in a single experiment
2. GHG budgeting - estimating fraction of indirect losses converted to  $N_2O$

# Controlled Release Fertilizers for Dryland Corn Production

Source	Timing	Rate (kg N ha <sup>-1</sup> )
1. Conventional urea (47%N)	Sidedress (V4-V6)	146
2. Urea + DCD + NBPT (47%N)	Sidedress (V4-V6)	146

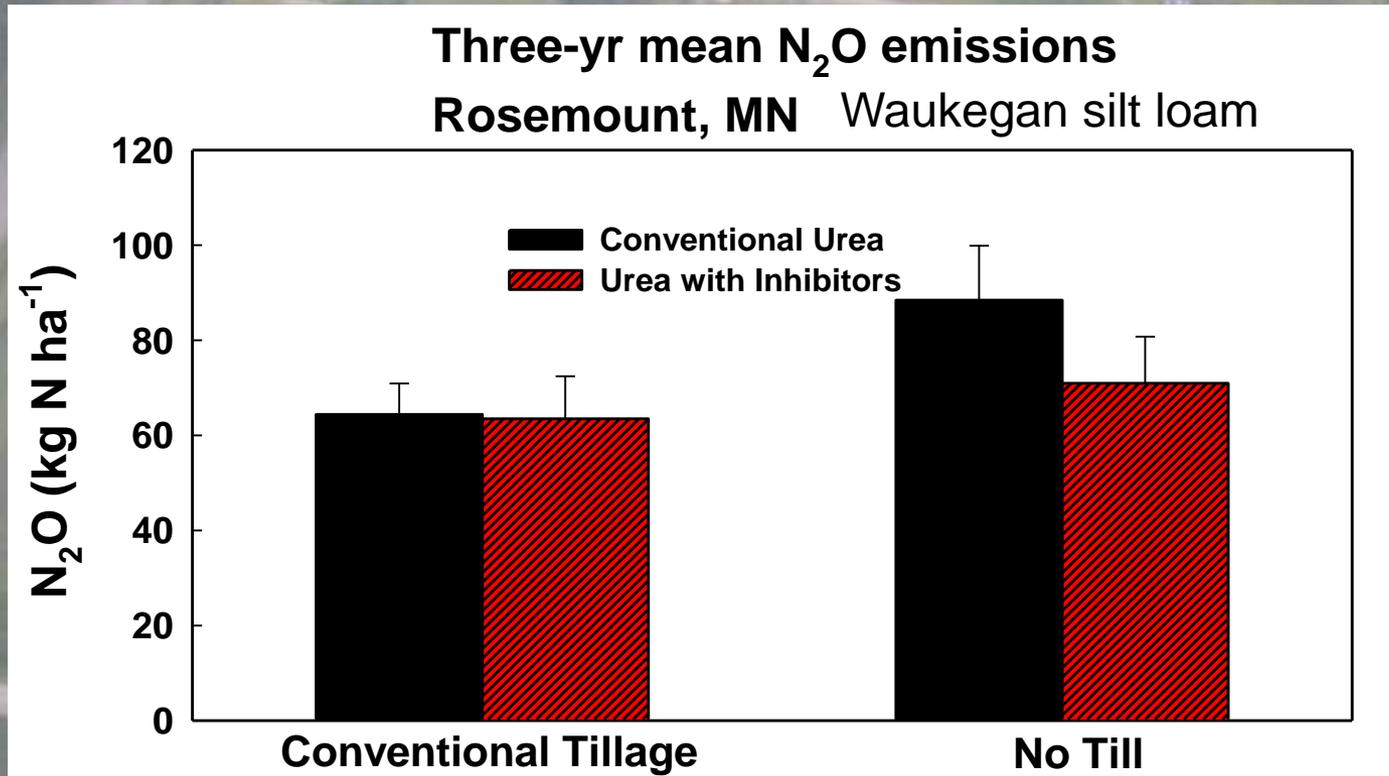
Treatments applied to both CT and NT treatments (in place for > 15 yr)



# Controlled Release Fertilizers for Dryland Corn Production

Source	Timing	Rate (kg N ha <sup>-1</sup> )
1. Conventional urea (47%N)	Sidedress (V4-V6)	146
2. Urea + DCD + NBPT (47%N)	Sidedress (V4-V6)	146

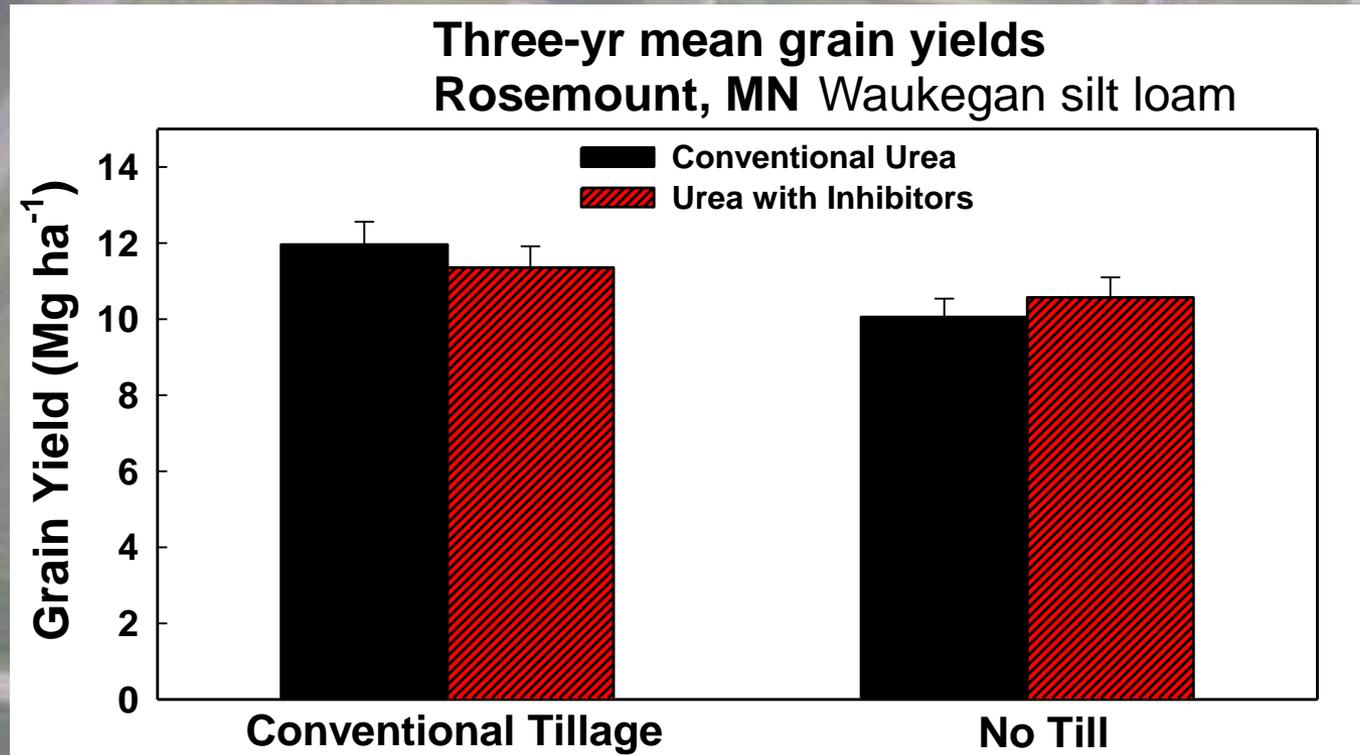
Treatments applied to both CT and NT treatments (in place for > 15 yr)



# Controlled Release Fertilizers for Dryland Corn Production

Source	Timing	Rate (kg N ha <sup>-1</sup> )
1. Conventional urea (47%N)	Sidedress (V4-V6)	146
2. Urea + DCD + NBPT (47%N)	Sidedress (V4-V6)	146

Treatments applied to both CT and NT treatments (in place for > 15 yr)



# Controlled Release Fertilizers

1. No guidelines for knowing when/where specific products will be effective.
2. Many different formulations available, but little systematic comparison.
3. Appears to have potential, but needs to be optimized to site conditions (soil, climate, crop phenology).
  - PCUs: Select correct release rate
  - NIs: Can have short duration of effectiveness (half life decreases with temp)
  - Alternatives may have longer duration are being (e.g. biochar)

# Survey of MN corn producers (MDA/ UMN/ NASS, 2010)

### Use of additives and specialty formulations

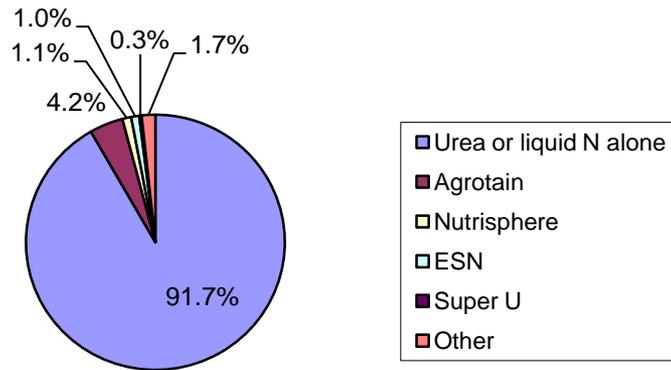
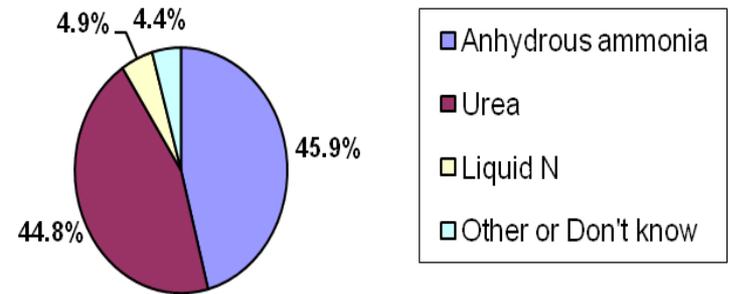


Chart does not include nitrapyrin use

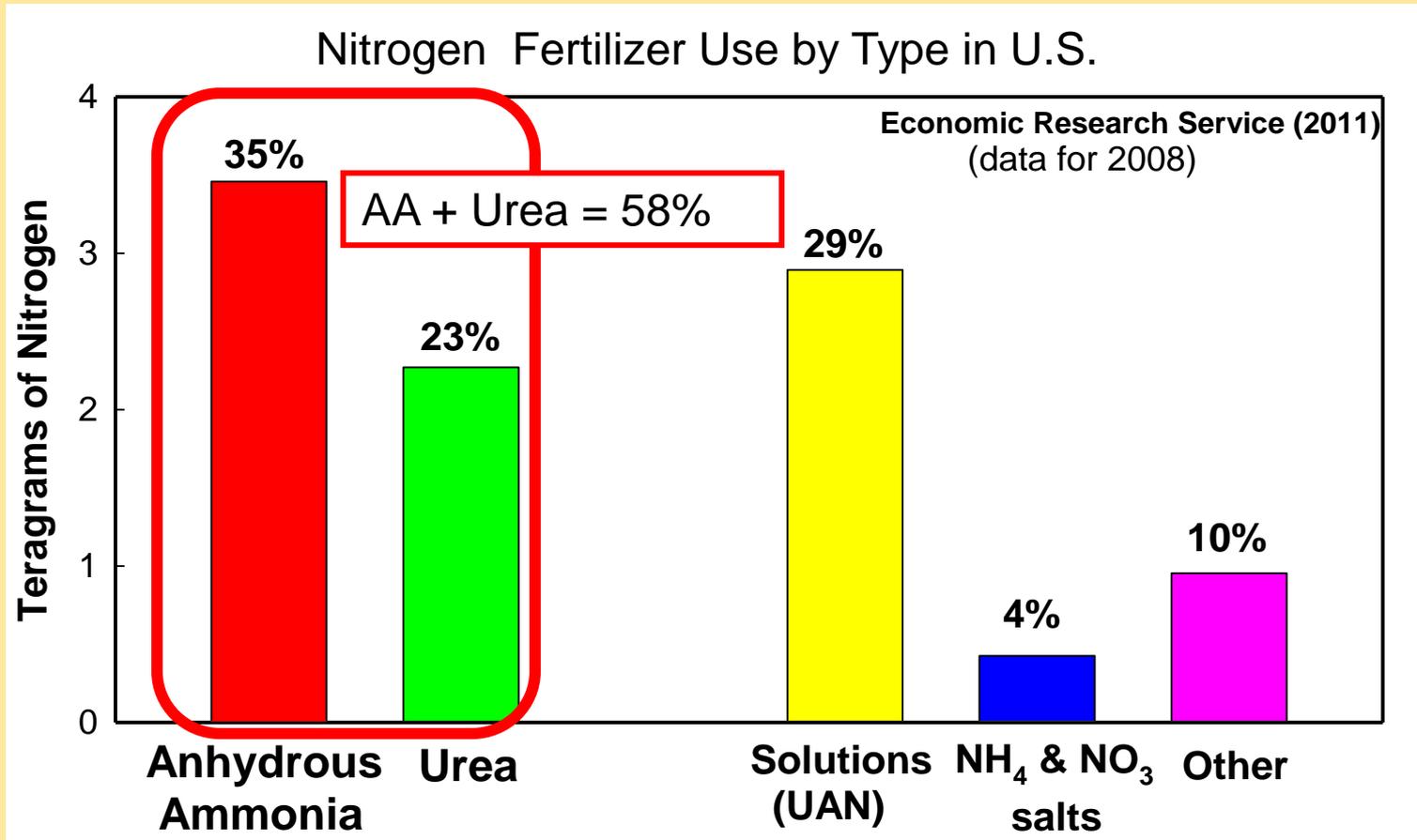
### Form of the majority of N fertilizer applied (State-wide)



**AA + Urea = 91%**

- 8.3% : CRFs other than nitrapyrin
- 9.5% : nitrapyrin (fall AA application)

# Fertilizer Source Effects: Conventional Sources

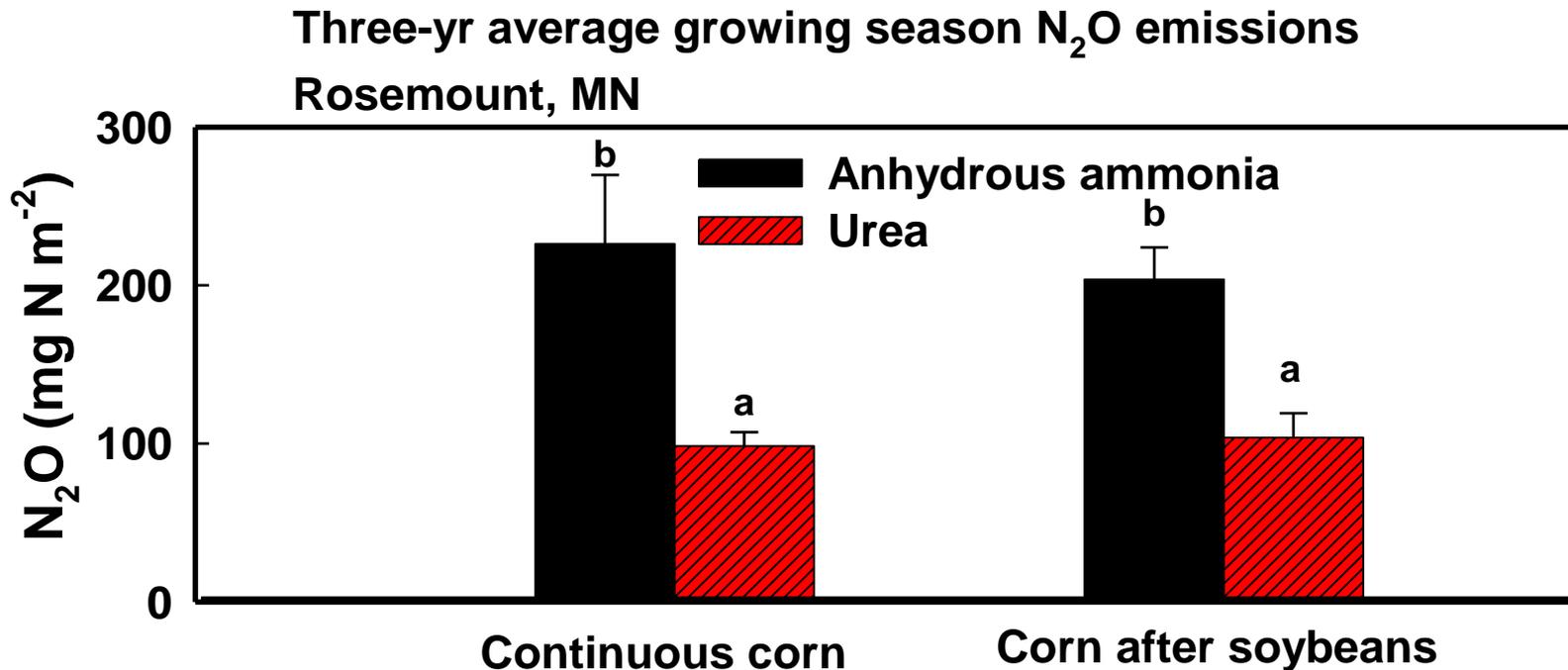


Only 1 site-year of data comparing N<sub>2</sub>O emissions with AA and Urea prior to 2005 (Thornton et al., 1996)

# Anhydrous Ammonia versus Urea: Dryland Corn

Source	Timing	Placement	Rate (kg N ha <sup>-1</sup> )
1. Urea (47%N)	Pre-plant	Broadcast and incorporated	146
2. AA (82%N)	Pre-plant	Injected into subsurface band	146

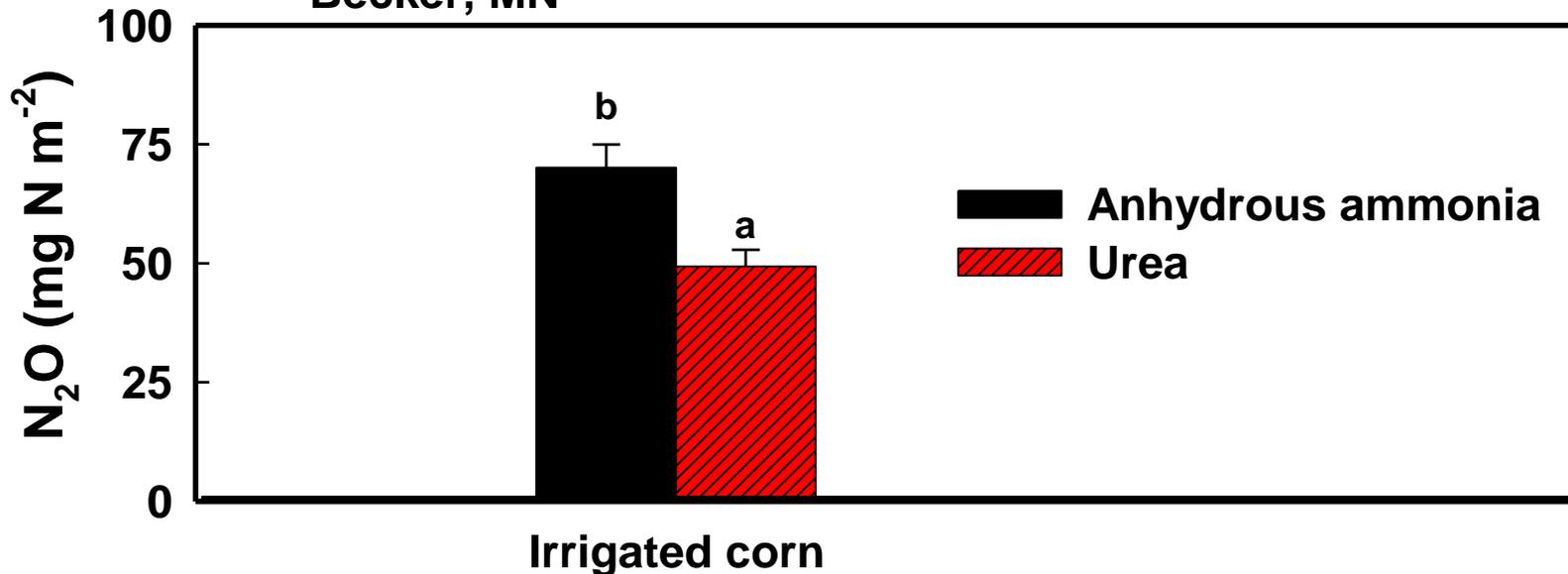
Treatments applied to both Corn following Corn and Corn following Soybean



# Anhydrous Ammonia versus Urea: Irrigated Corn

Source	Timing	Placement	Rate (kg N ha <sup>-1</sup> )
1. Urea (47%N)	Pre-plant/Sidedress	Broadcast and incorporated	90 / 90
2. AA (82%N)	Pre-plant/Sidedress	Injected and banded	90 / 90

Two-yr average growing season N<sub>2</sub>O emissions  
Becker, MN



# Anhydrous Ammonia versus Urea

GHG Impact of Change in Practice  
(some wild extrapolations)

<b>Emissions Factor (EF) Assessment</b>	
<b>Study</b>	<b>EF<sub>AA</sub> : EF<sub>urea</sub></b>
<b>Thornton et al. (1996)</b>	<b>1.94</b>
<b>Venterea et al. (2010)</b>	<b>2.60</b>
<b>Fujinuma et al. (2011)</b>	<b>1.53</b>
<b>Average</b>	<b>2.0</b>

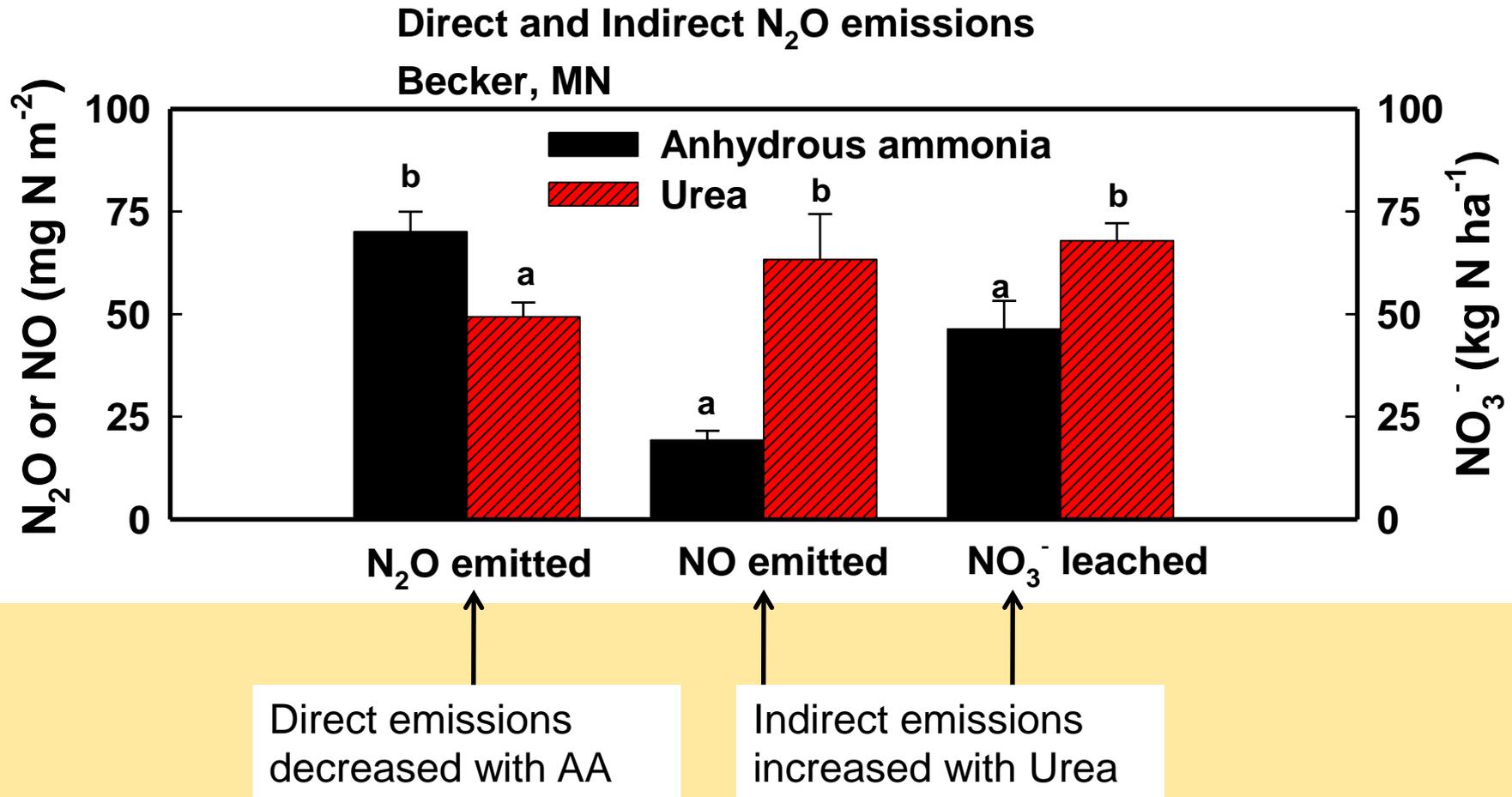
- Assume EF ratio applies to all non-AA sources
- Complete shift away from AA → 25% reduction in fertilizer-derived N<sub>2</sub>O emissions across the U.S.
- But it's probably not that simple, more studies needed.

## Worldwide AA Use

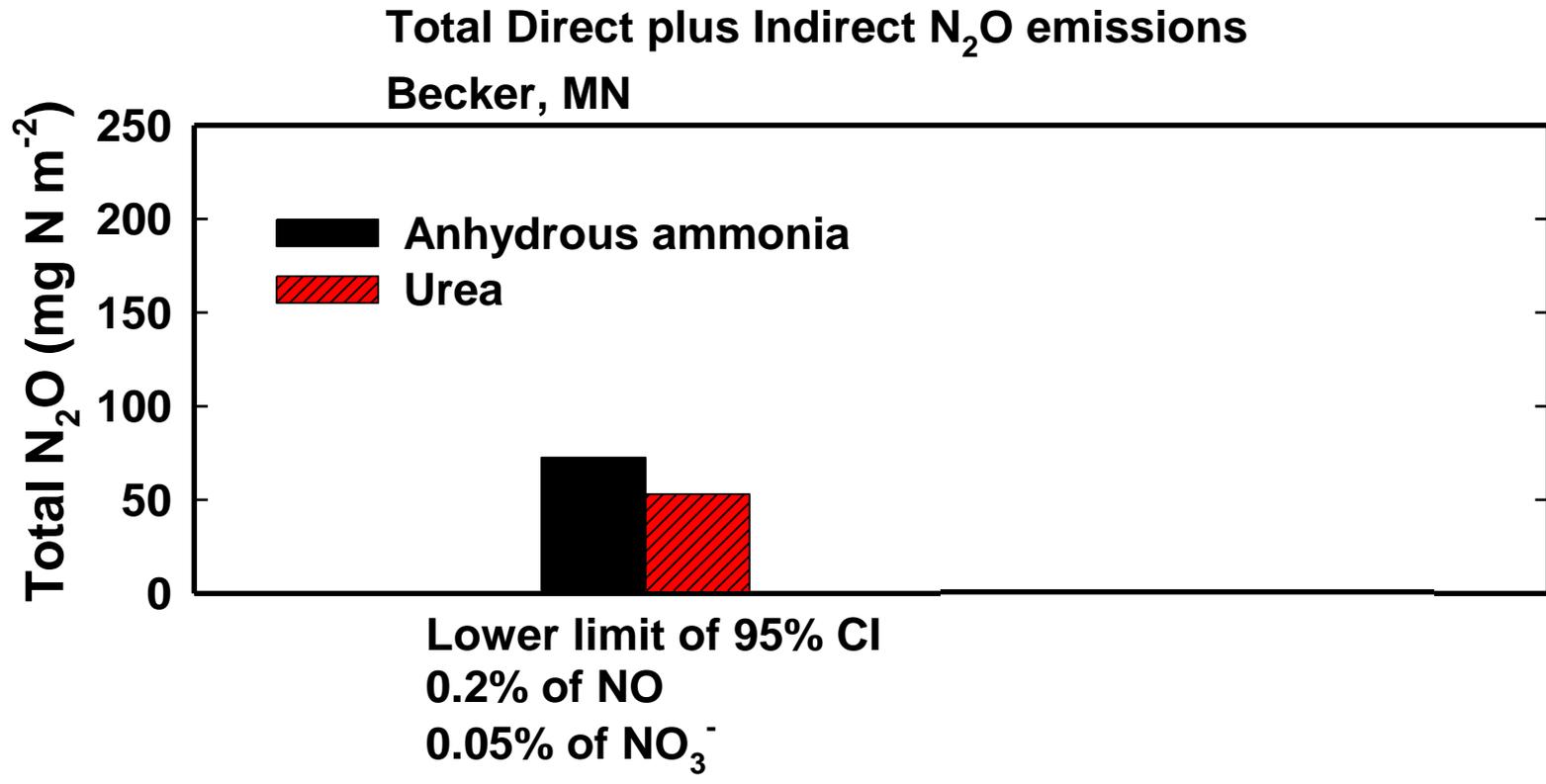
<b>U.S.</b>	<b>85%</b>
<b>Canada</b>	<b>13%</b>
<b>Mexico</b>	<b>1%</b>
<b>Rest of world</b>	<b>1%</b>

*(IFA Statistics)*

# Anhydrous Ammonia versus Urea: Indirect N<sub>2</sub>O Emissions

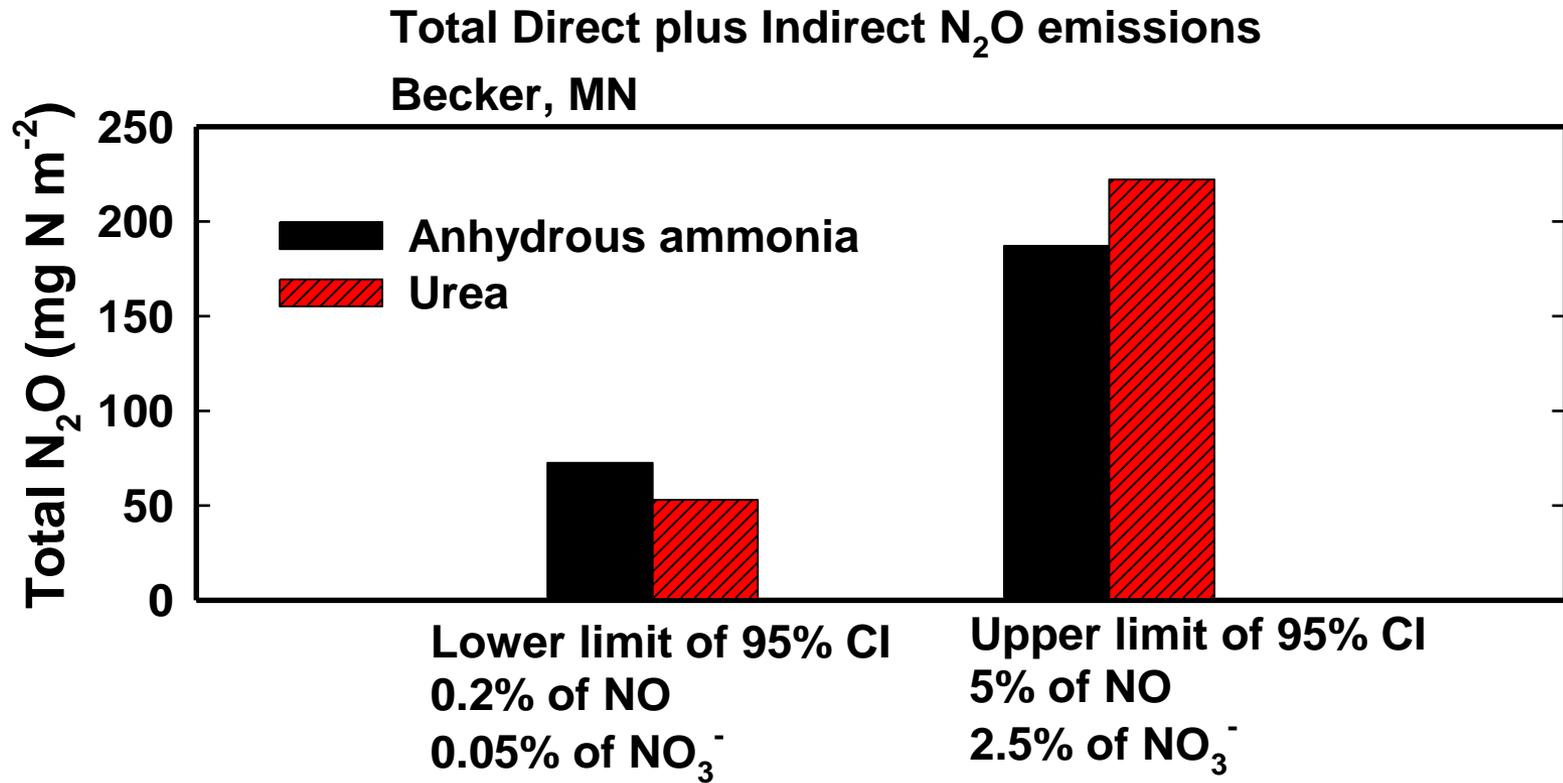


# Anhydrous Ammonia versus Urea: Indirect N<sub>2</sub>O Emissions



2006 IPCC Guidelines for National Greenhouse Gas Inventories. De Klein et al.

# Anhydrous Ammonia versus Urea: Indirect N<sub>2</sub>O Emissions



2006 IPCC Guidelines for National Greenhouse Gas Inventories. De Klein et al.

# Fertilizer Placement Effects

(very few studies)

Conventional “Deep” Applicator



New “Shallow” Applicator



## Conventional AA Injection

- Slow tractor speed with high fuel use
- 15-18 cm deep band

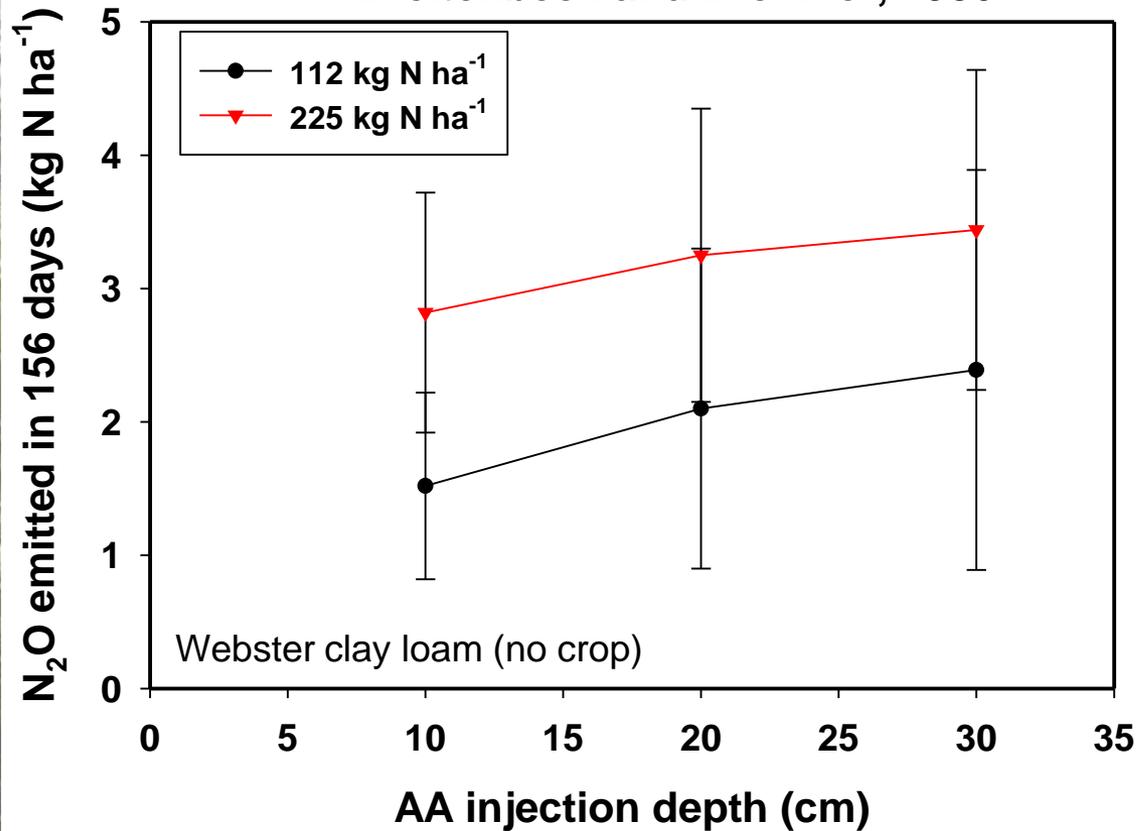
## Shallow AA injection

- Faster speed
- 10-12 cm deep band
- Improved soil closure
- Less fuel use

# Fertilizer Placement Effects

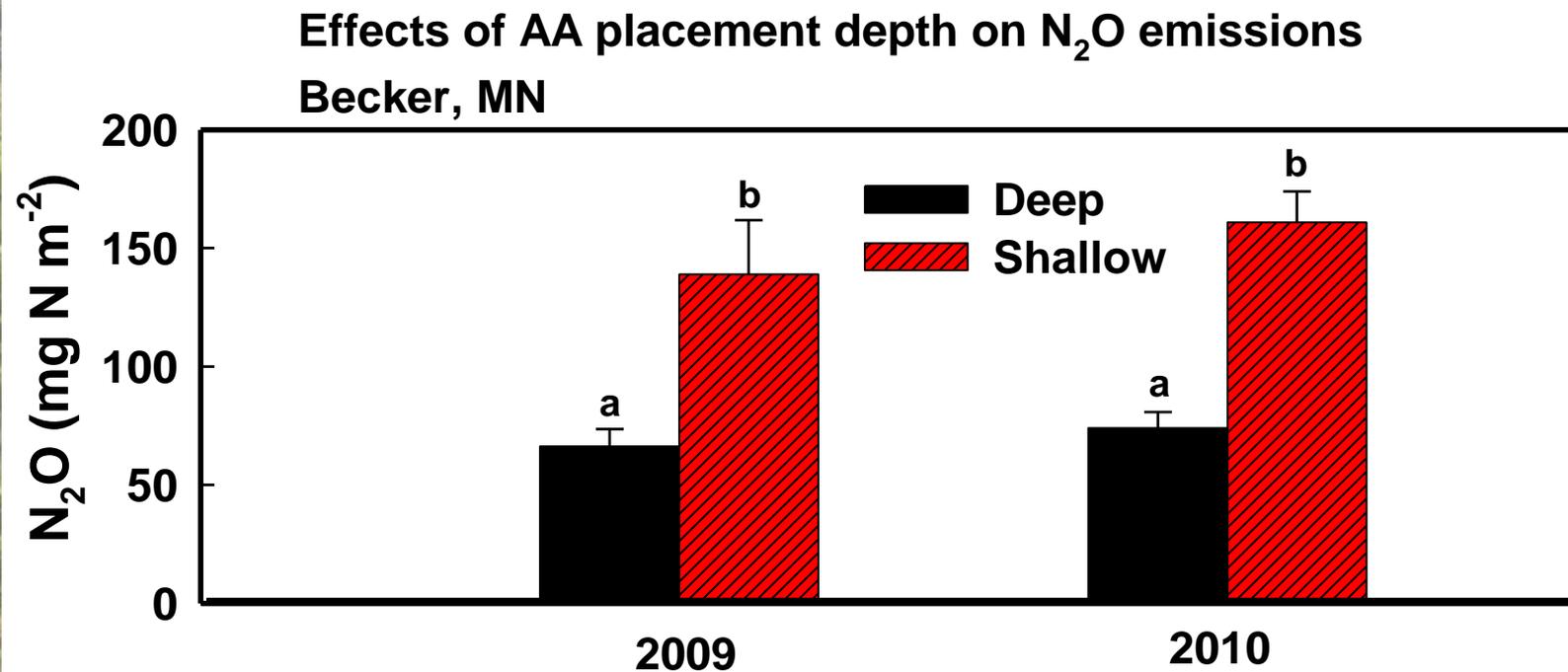
## Effect of AA Injection Depth on N<sub>2</sub>O Emissions

Breitenbeck and Bremner, 1986



# Anhydrous Ammonia Placement Effects: Irrigated Corn

Source	Timing	Placement	Rate (kg N ha <sup>-1</sup> )
1. AA	Pre-plant/Sidedress	18 cm	90 / 90
2. AA	Pre-plant/Sidedress	12 cm	90 / 90

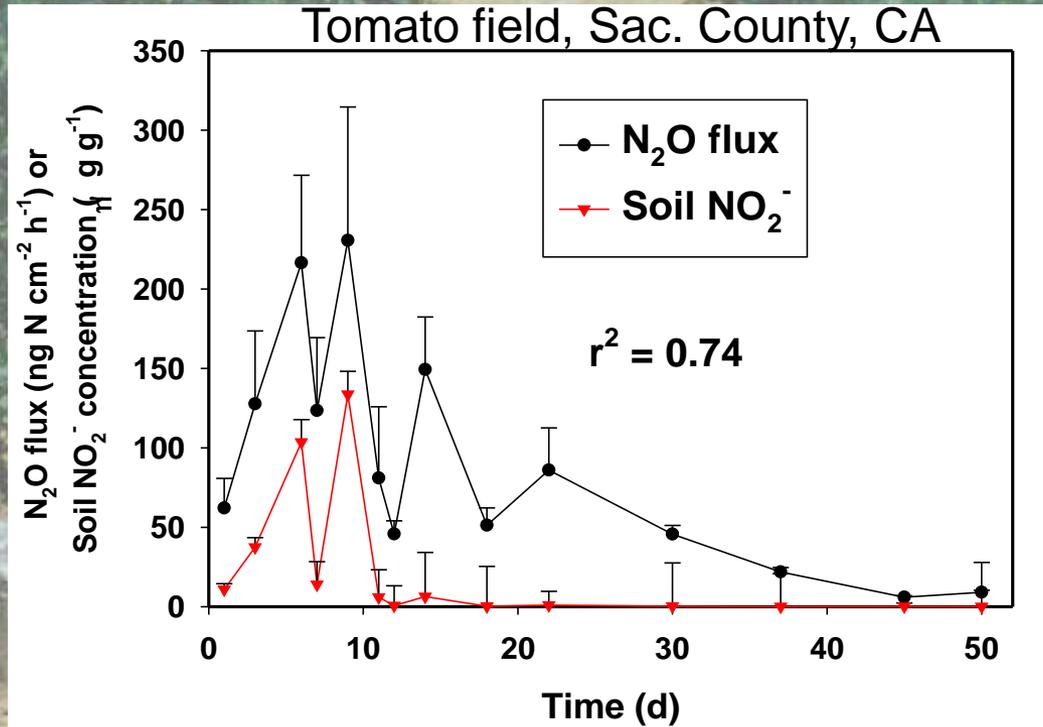


WHY ?

Repeating experiment in finer texture soil

# Greater N<sub>2</sub>O Emissions with Anhydrous Ammonia

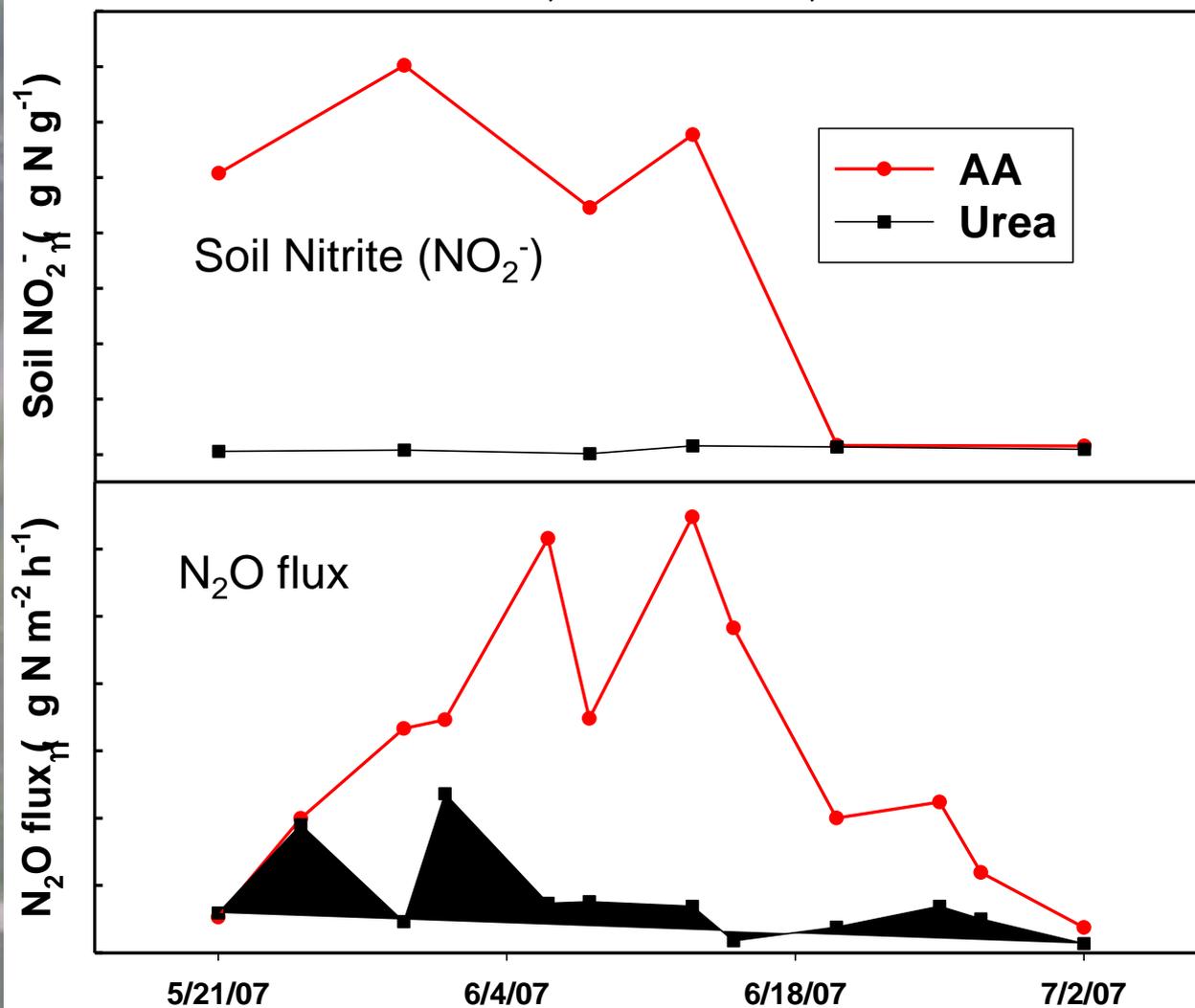
Elevated Soil Nitrite (NO<sub>2</sub><sup>-</sup>)



# Greater N<sub>2</sub>O Emissions with Anhydrous Ammonia

Elevated Soil Nitrite (NO<sub>2</sub><sup>-</sup>)

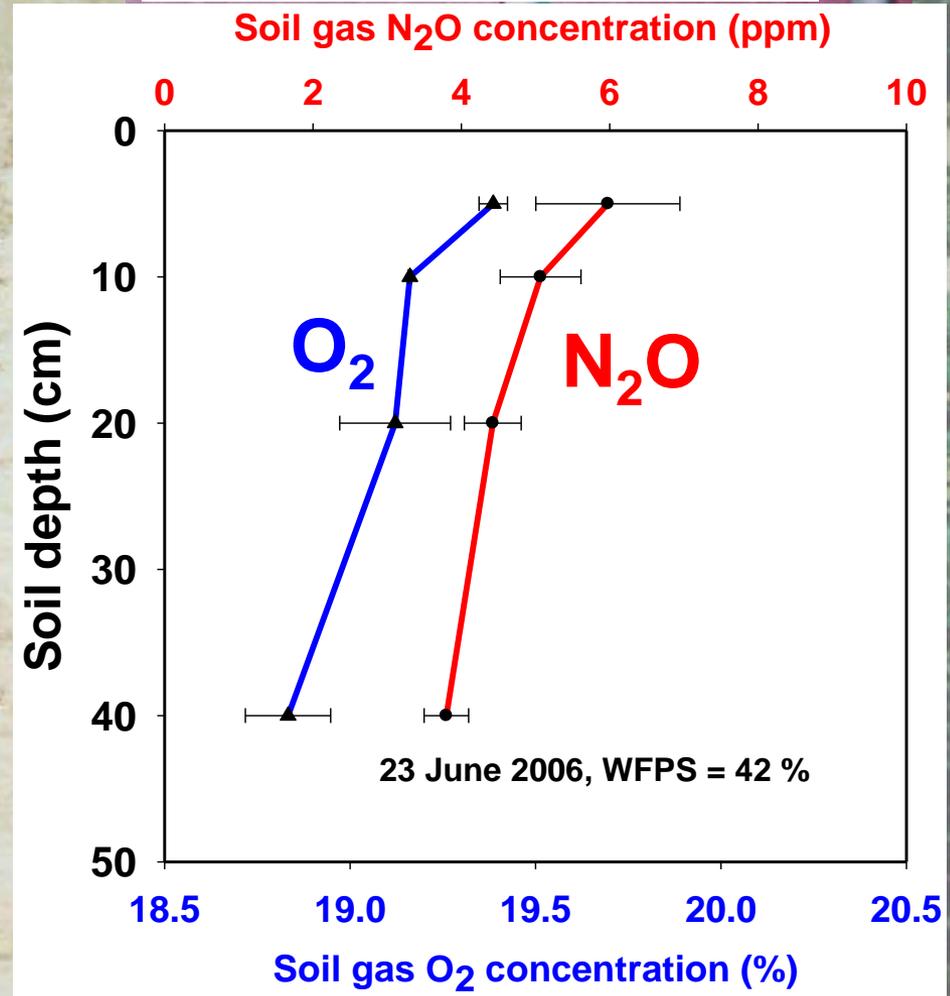
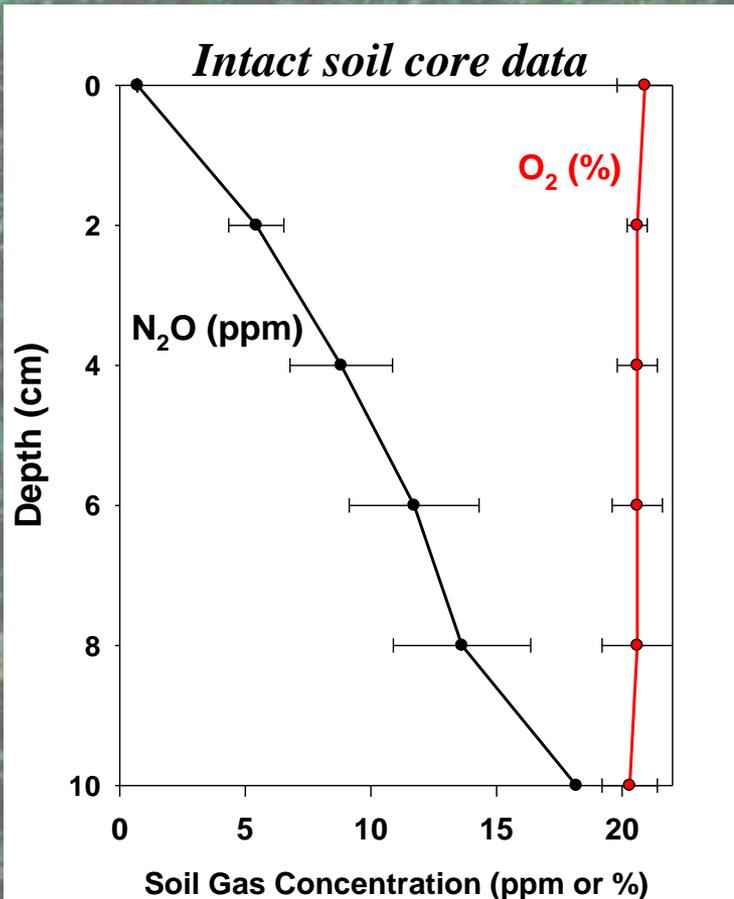
Corn field, Rosemount, MN



# Greater N<sub>2</sub>O Emissions with Anhydrous Ammonia

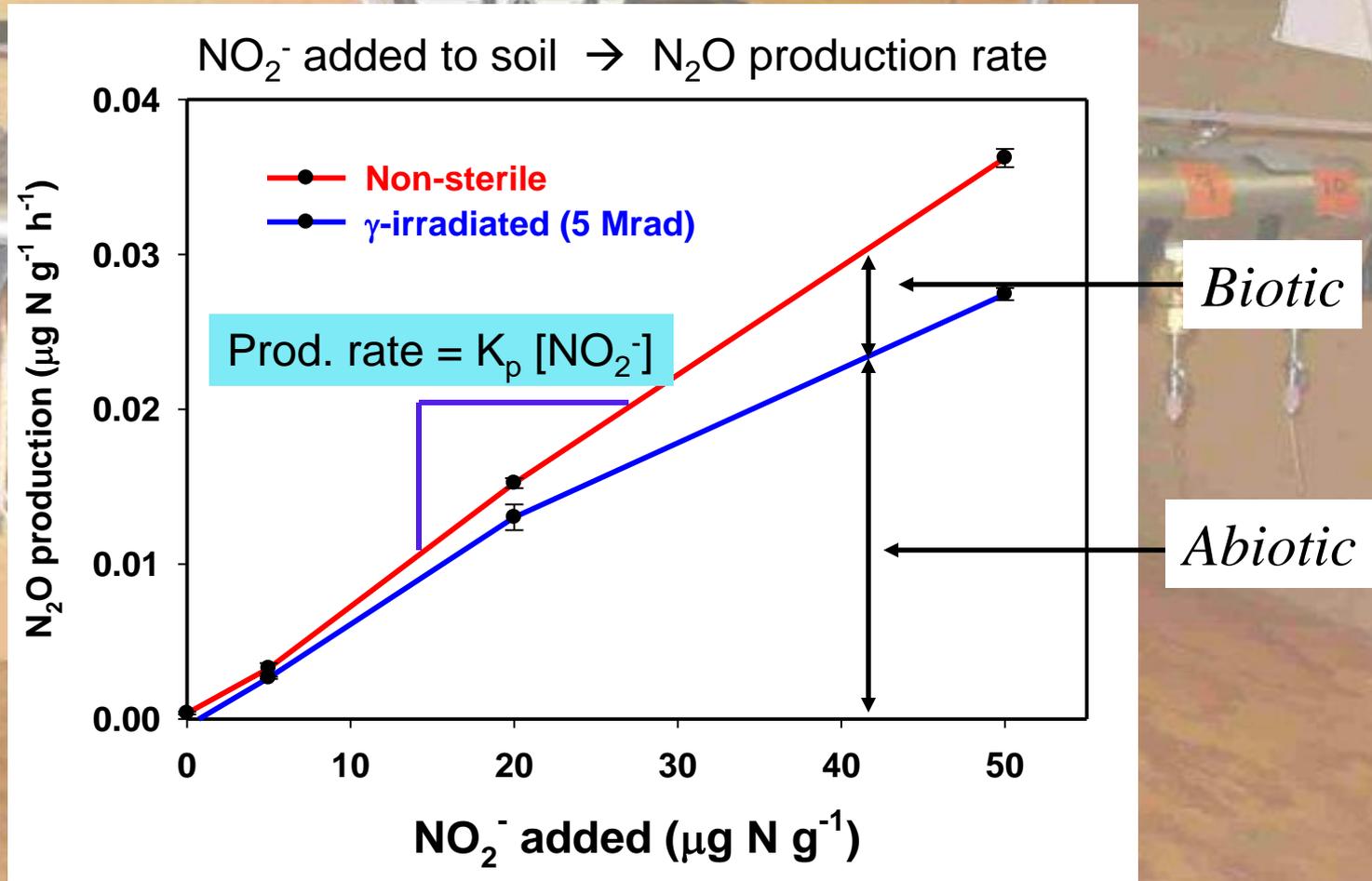
Aerobic conditions

Corn field, Rosemount, MN

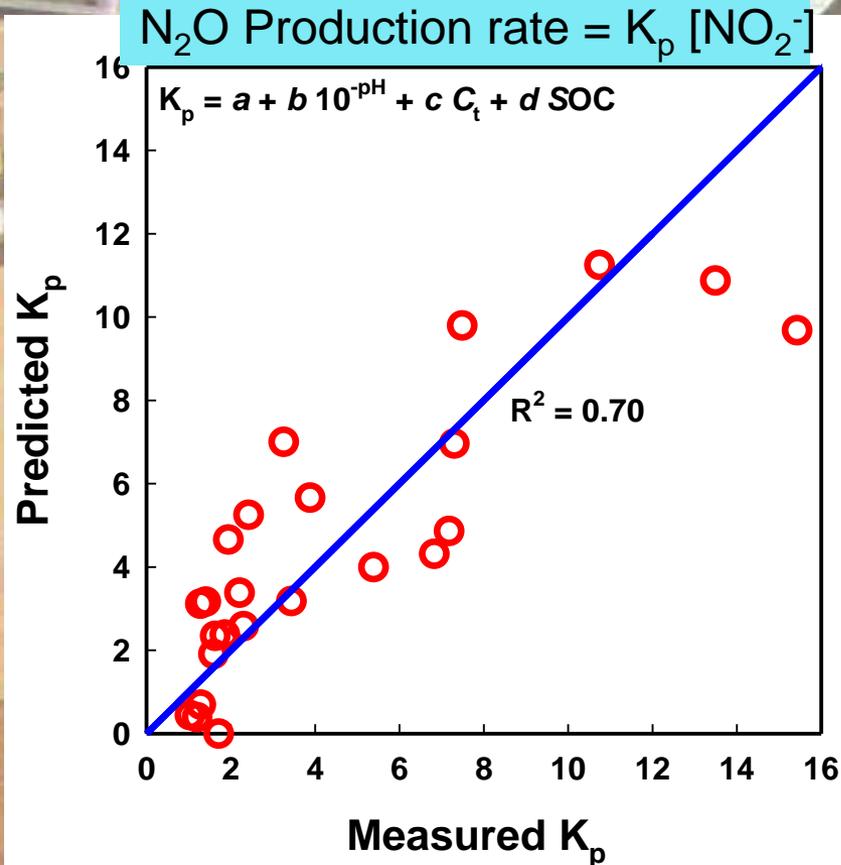


Venterea and Rolston, 2002.  
*Soil Sci.* 167.

# Laboratory kinetics experiments: N<sub>2</sub>O production under aerobic conditions



# Laboratory kinetics experiments: N<sub>2</sub>O production under aerobic conditions

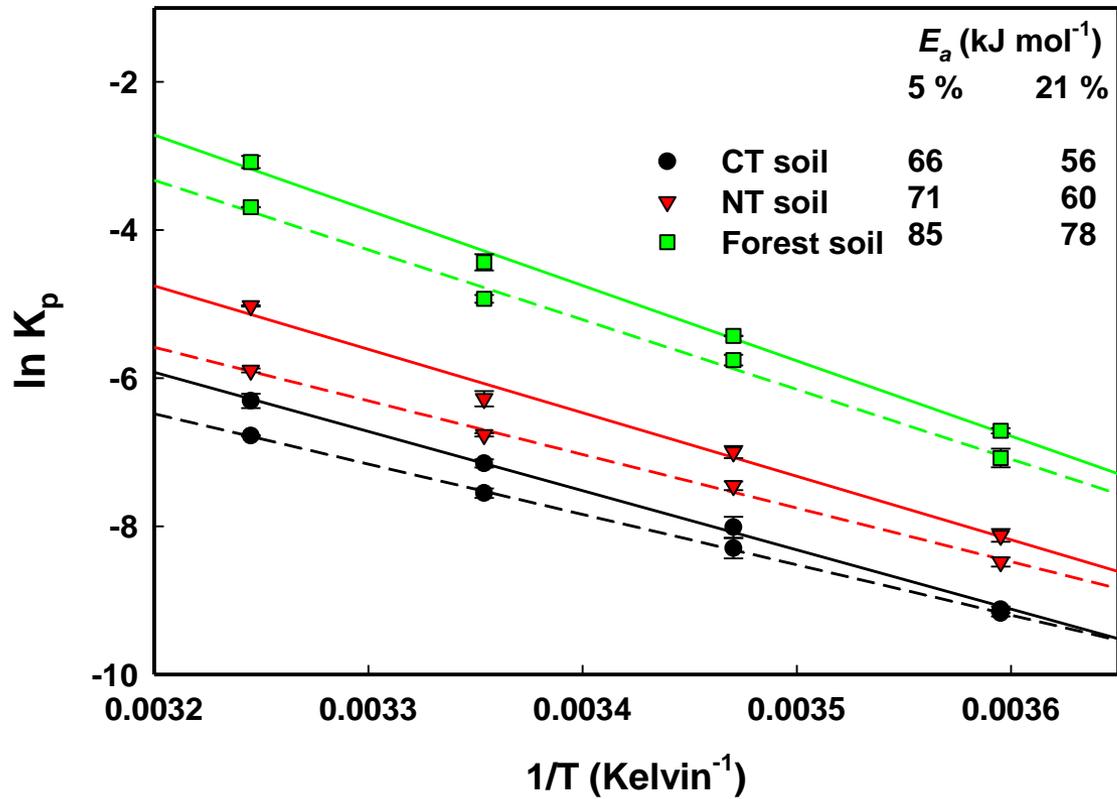


Rate coefficient correlated with:

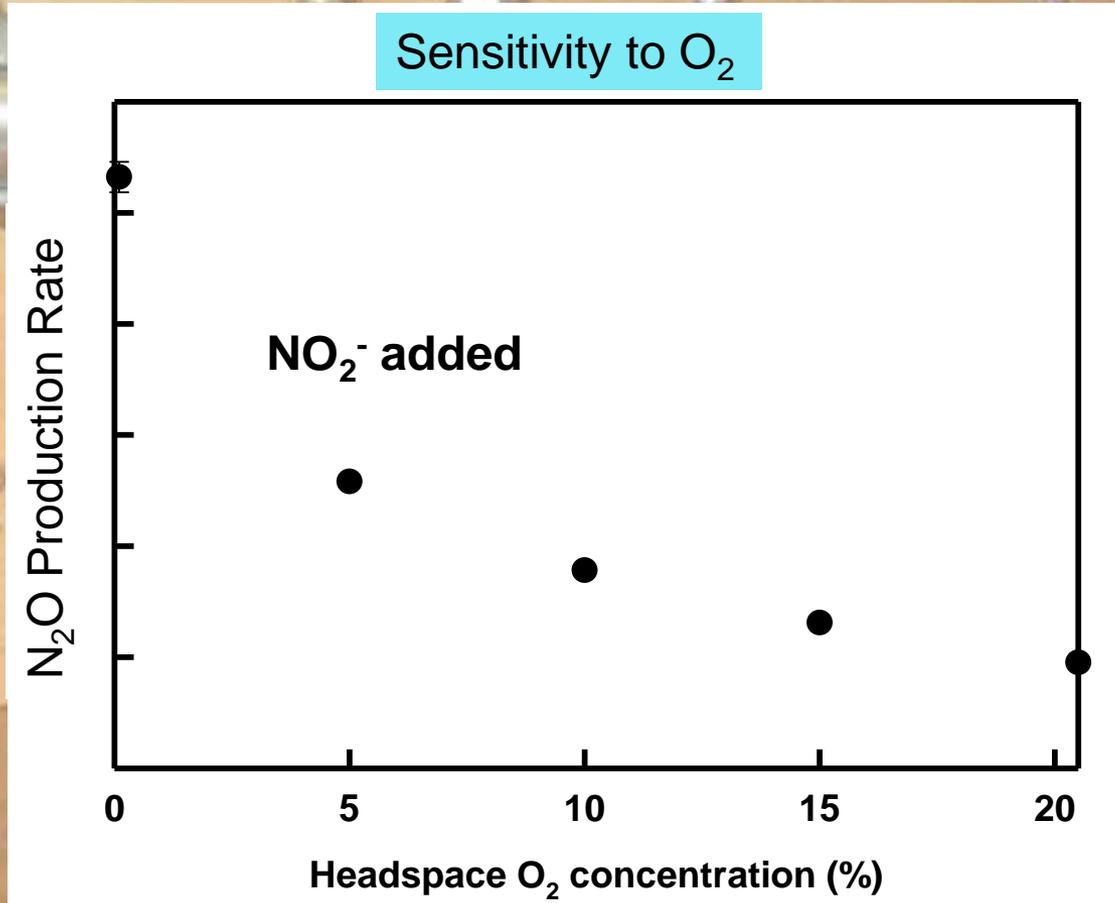
- Acidity ( $10^{-\text{pH}}$ )
- Total organic carbon ( $C_t$ )
- Soluble organic carbon (SOC)

# Laboratory kinetics experiments: N<sub>2</sub>O production under aerobic conditions

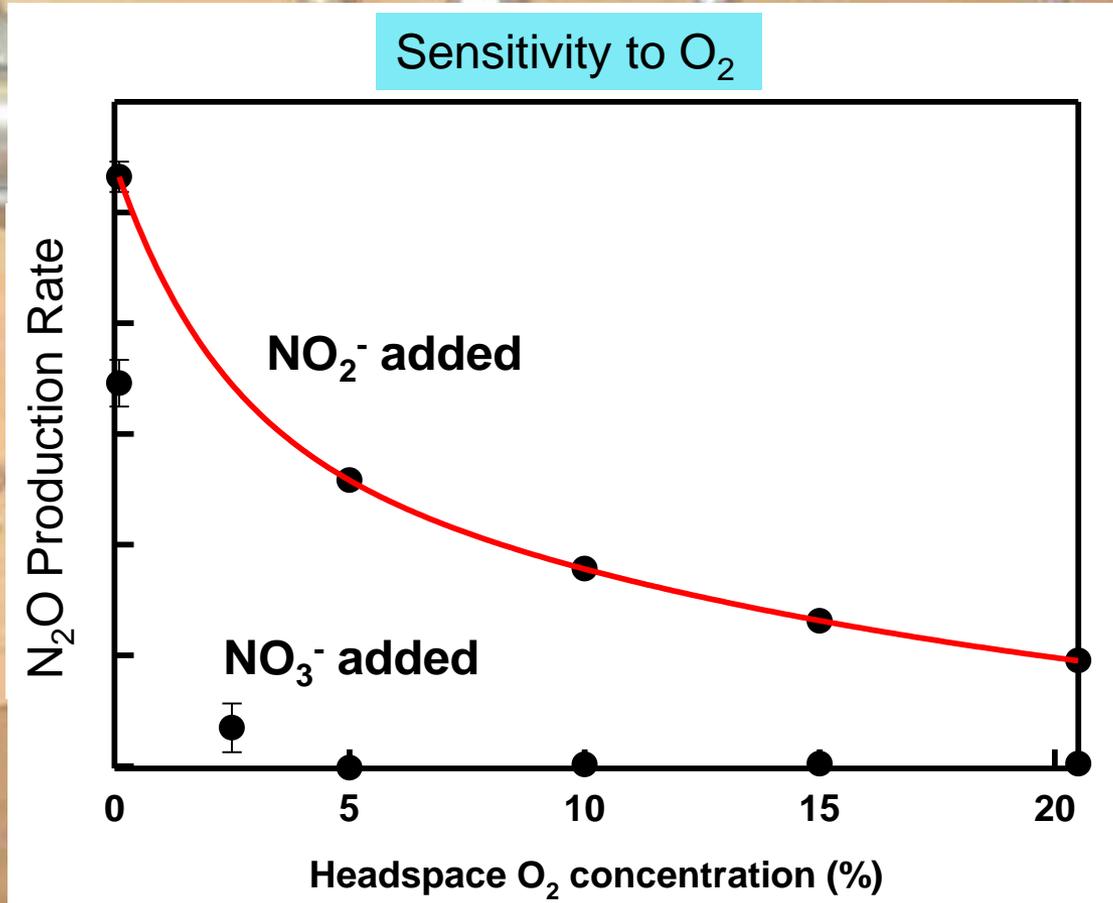
## Temperature Sensitivity



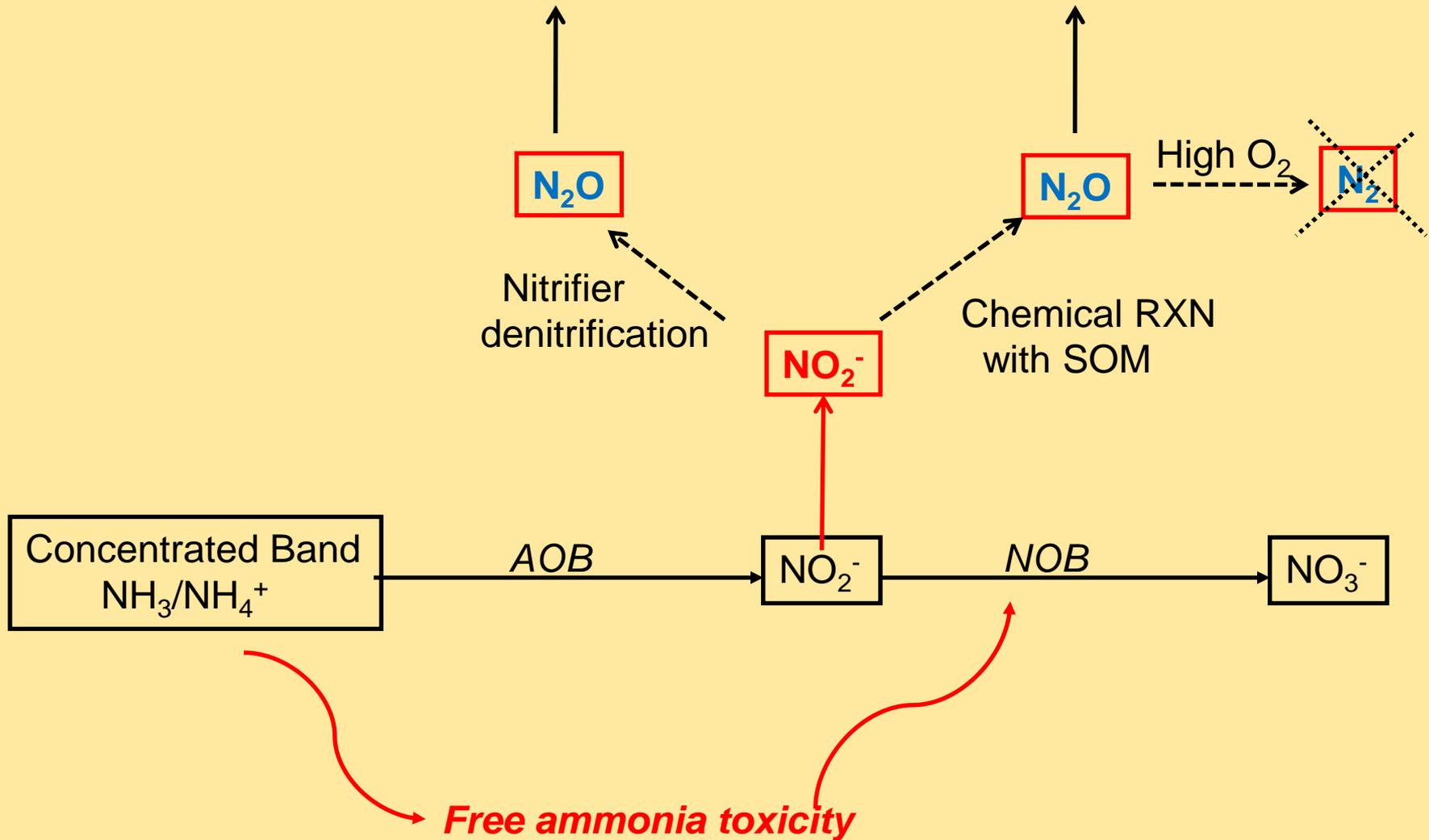
# Laboratory kinetics experiments: N<sub>2</sub>O production under aerobic conditions



# Laboratory kinetics experiments: N<sub>2</sub>O production under aerobic conditions

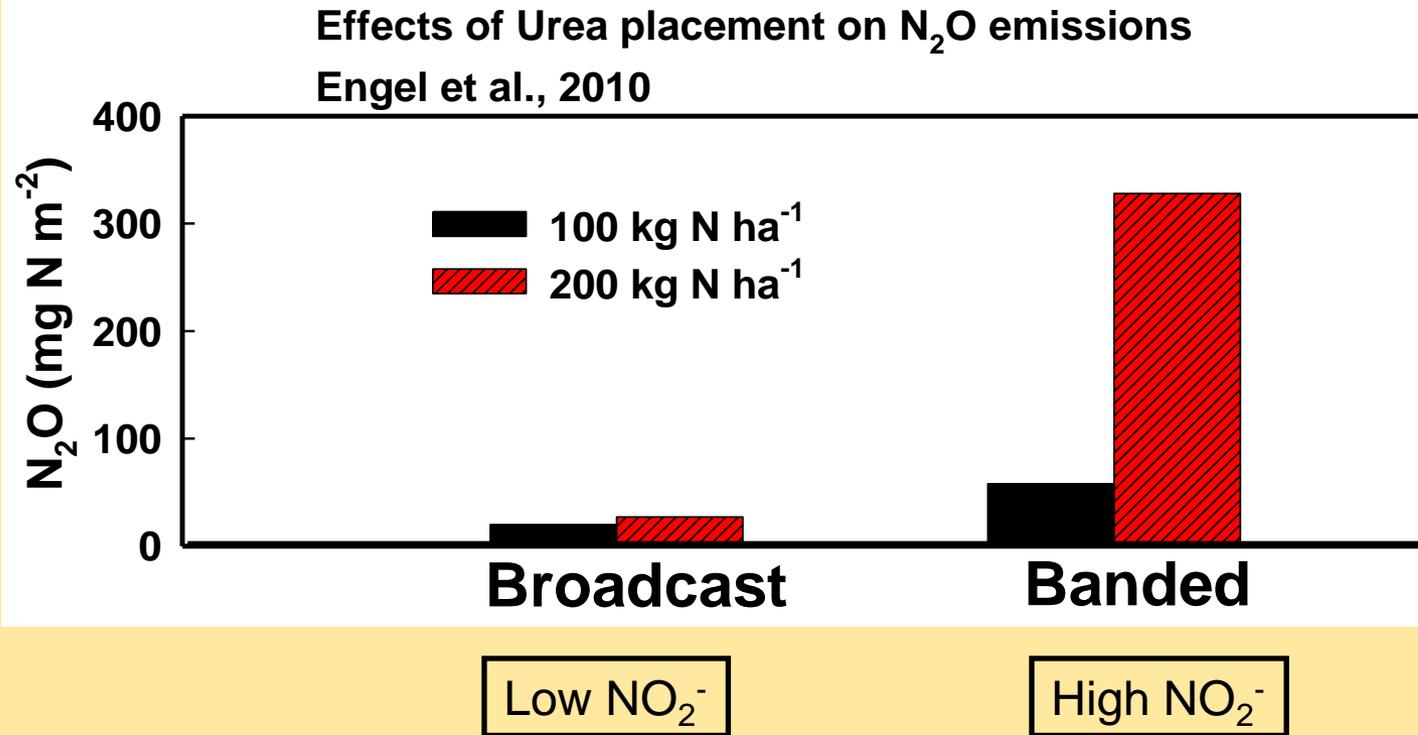


# Nitrite-driven N<sub>2</sub>O production



# Nitrite-driven N<sub>2</sub>O production

## Banding of Urea



# Nitrite-driven N<sub>2</sub>O production

## Banding as a beneficial fertilizer management practice

### Conserves Nitrogen/ Increases NUE

- Slows nitrification and nitrate leaching
- Limits contact with soil microbes
- Increases root access to N
- Decreases distance from plant to N source

*Malhi et al., 1985. 1991; Yadvinder-Singh et al., 1994*  
*Robertson and Vitousek, 2009*

- With banding, it may be possible to have:
  - Greater overall NUE
  - And greater N<sub>2</sub>O emissions
- N<sub>2</sub>O emissions usually are < 5% of applied N.
- More study needed.

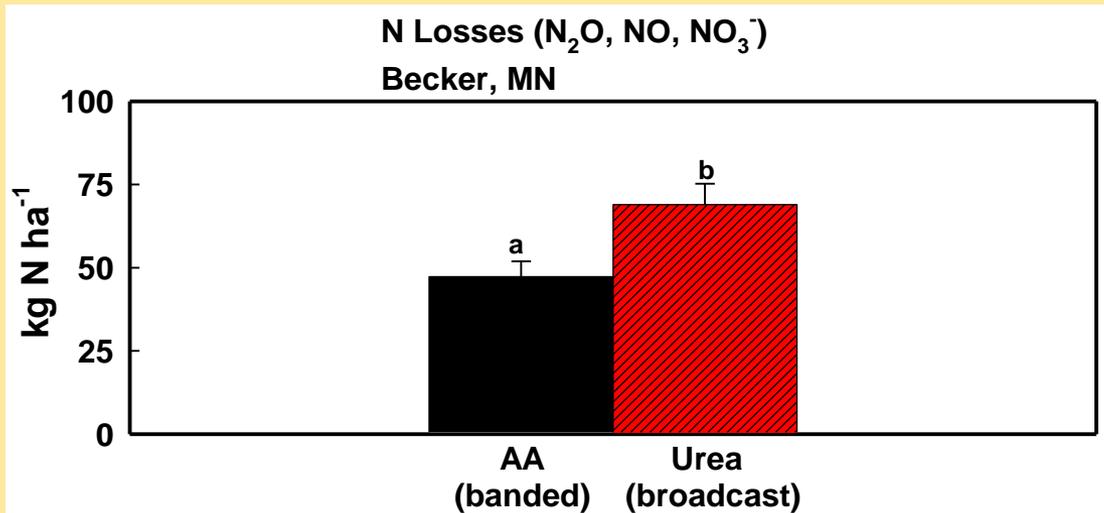
# Nitrite-driven N<sub>2</sub>O production

Banding as a beneficial fertilizer management practice

## Conserves Nitrogen/ Increases NUE

- Slows nitrification and nitrate leaching
- Limits contact with soil microbes
- Increases root access to N
- Decreases distance from plant to N source

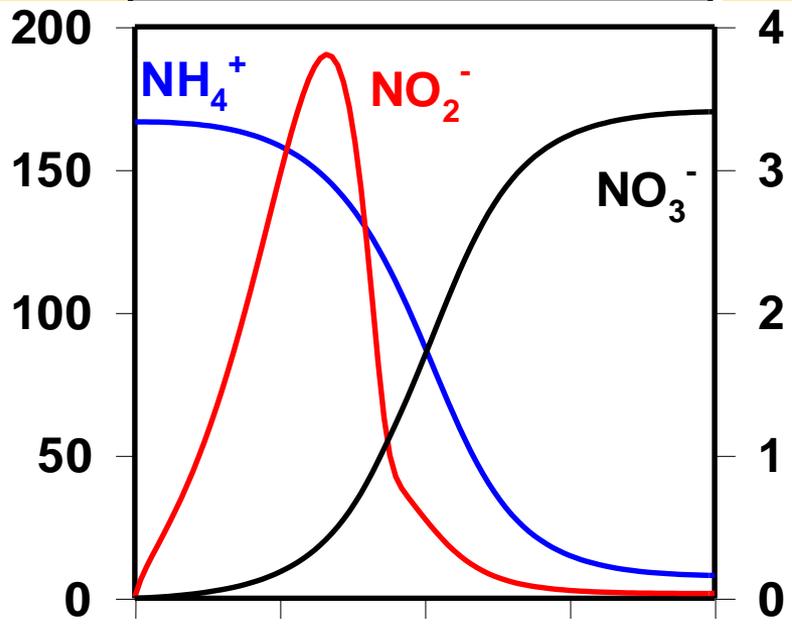
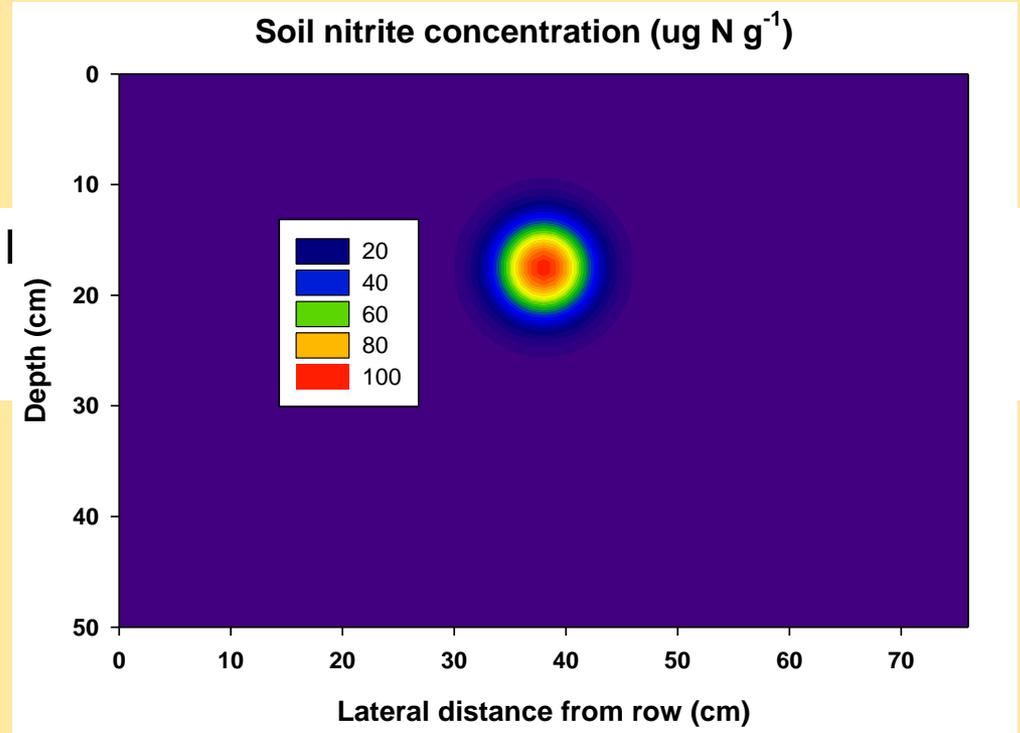
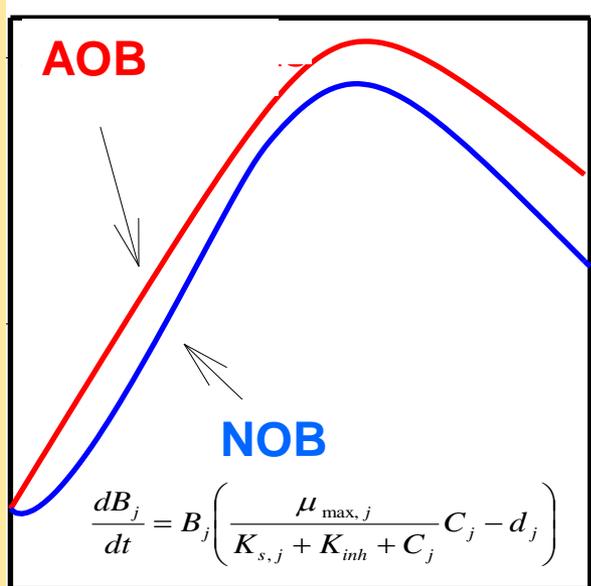
*Malhi et al., 1985. 1991; Yadvinder-Singh et al., 1994*  
*Robertson and Vitousek, 2009*



Is there an optimum banding intensity or thickness that maximizes NUE and minimizes N<sub>2</sub>O emissions ?

# Modeling nitrite-driven N<sub>2</sub>O emissions

Biomass



# Tillage Management Effects on N<sub>2</sub>O Emissions

Potential for N<sub>2</sub>O emissions to enhance (or offset) GHG benefits of reduced tillage

## Properties affected by long-term tillage mgmt

Bulk density

Water content

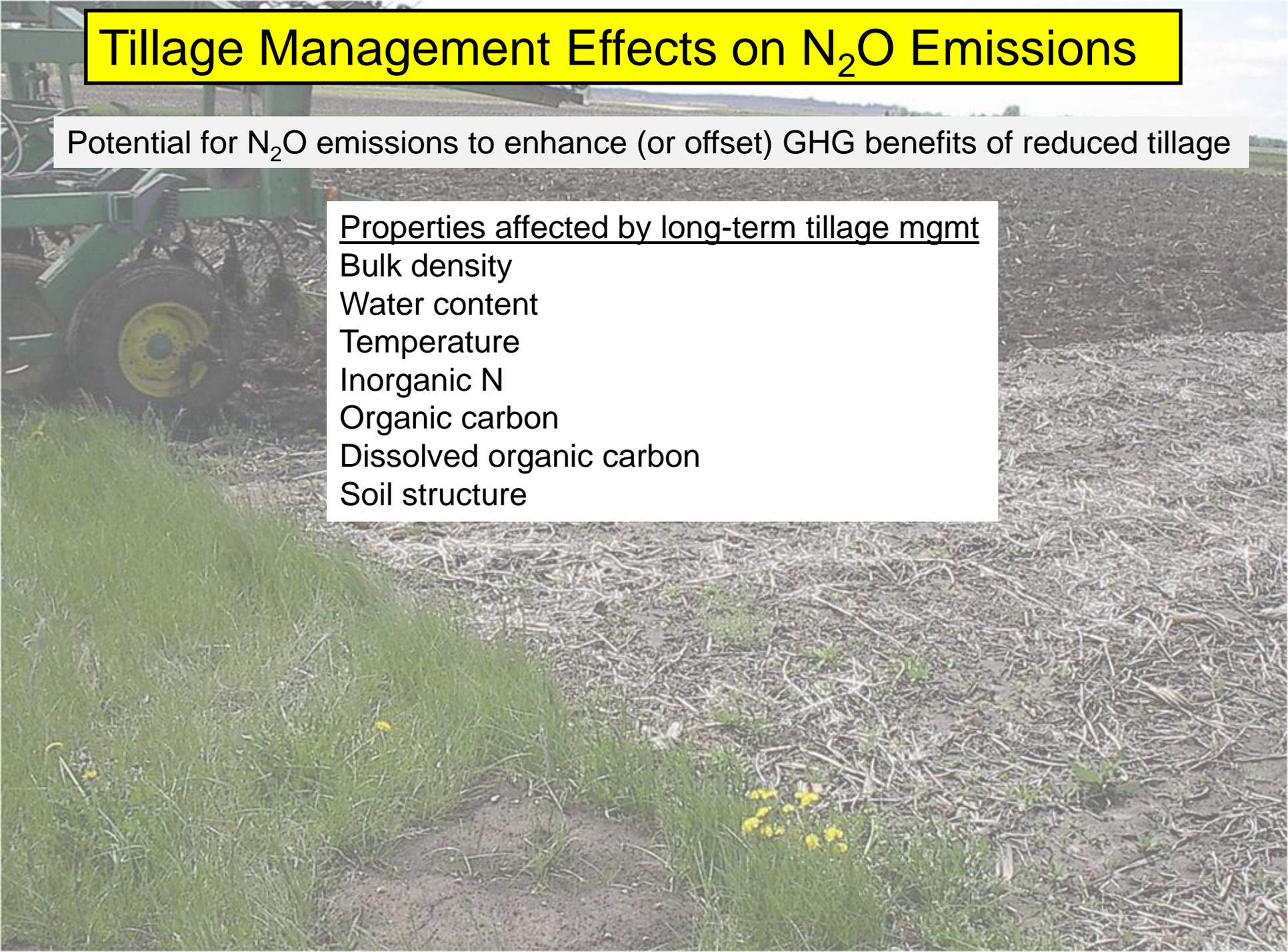
Temperature

Inorganic N

Organic carbon

Dissolved organic carbon

Soil structure



# Tillage Management Effects on N<sub>2</sub>O Emissions

Potential for N<sub>2</sub>O emissions to enhance (or offset) GHG benefits of reduced tillage

## Properties affected by long-term tillage mgmt

Bulk density  
Water content  
Temperature  
Inorganic N  
Organic carbon  
Dissolved organic carbon  
Soil structure

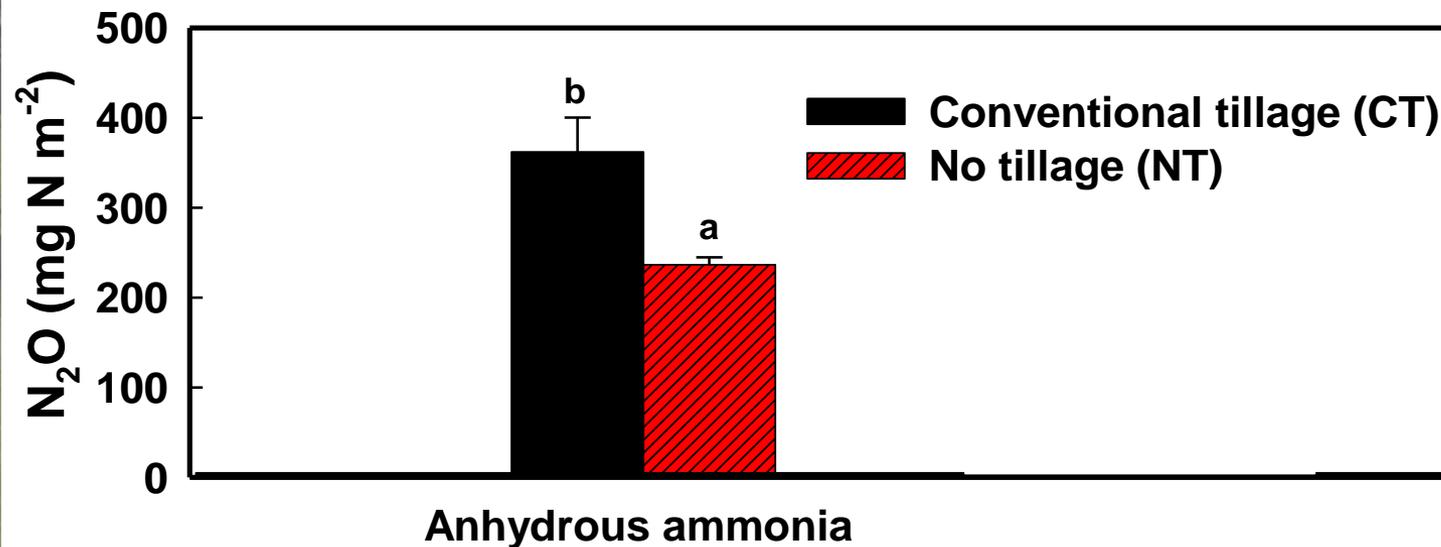
NT Greater

Not different

CT Greater

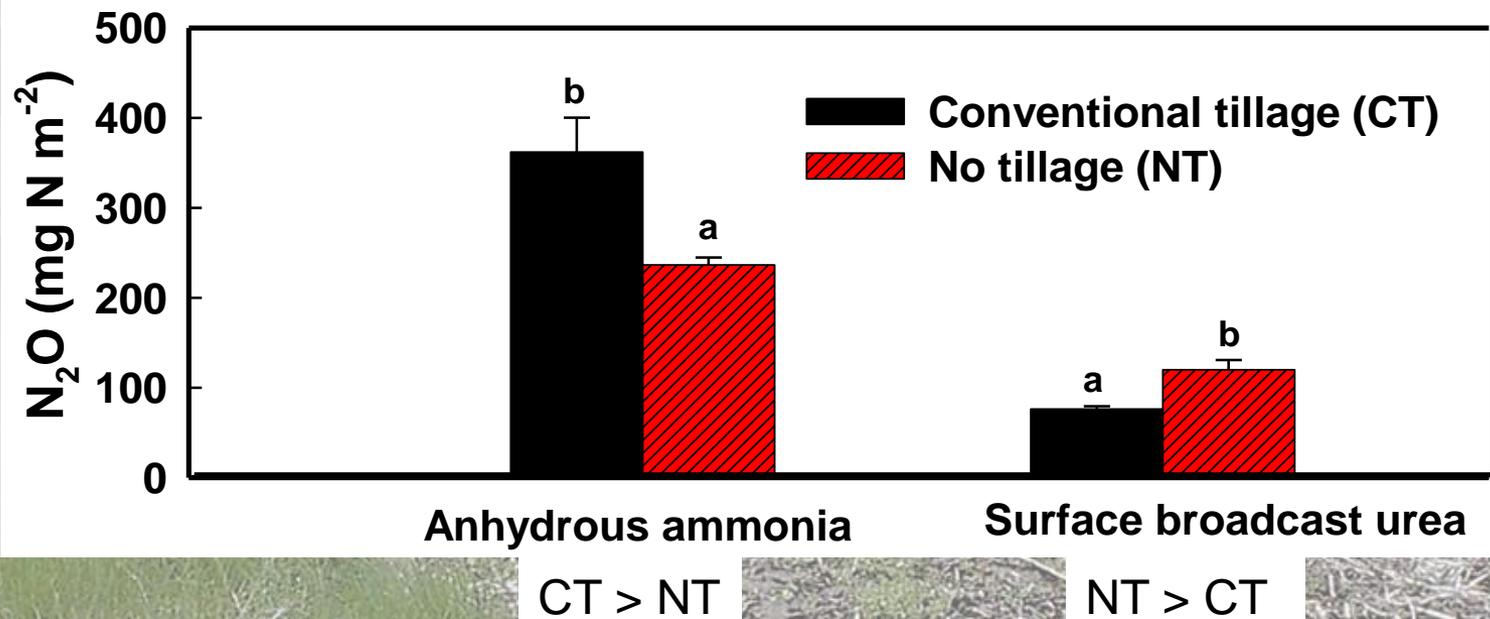
NT > CT	NT = CT	CT > NT
Aulakh et al. 1984	Lemke et al. 1999	Jacinthe and Dick, 1997
MacKenzie et al. 1998	Robertson et al. 2000	Kessavalou et al. 1998
Ball et al., 1999	Choudhary et al. 2002	Lemke et al. 1999
Yamulki and Jarvis 2002	Kaharabata et al. 2003	Kaharabata et al. 2003
Baggs et al., 2003	Liu et al., 2005	Liu et al., 2005
Koga et al. 2004	Rochette et al., 2008	Venterea et al., 2005
Venterea et al., 2005		Ussiri et al., 2009
Rochette et al., 2008		Halvorson et al., 2010
Grageda-Cabrera et al., 2011		Omonode et al., 2011

# Tillage Management Effects on N<sub>2</sub>O Emissions

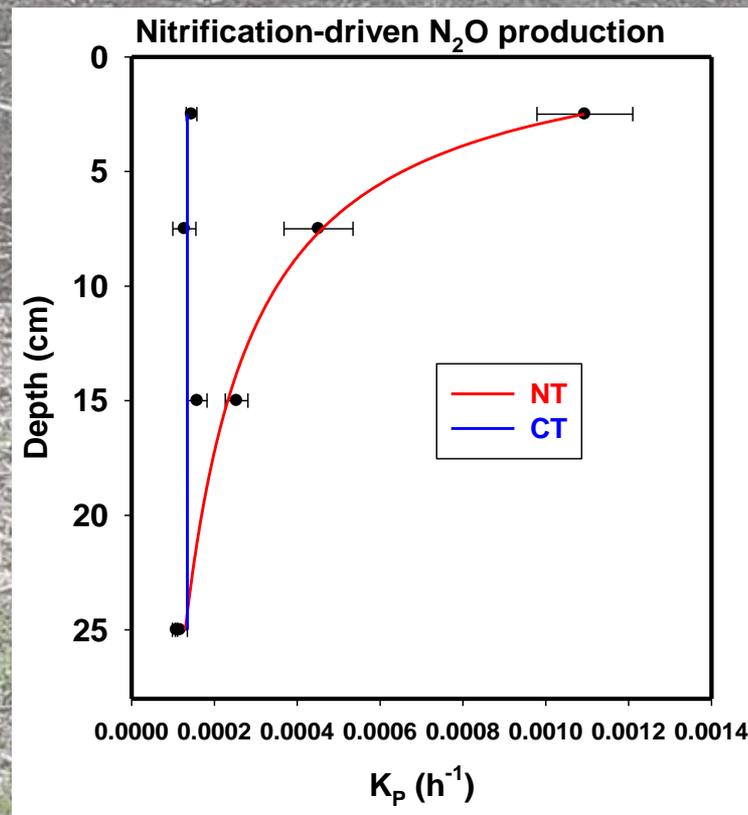
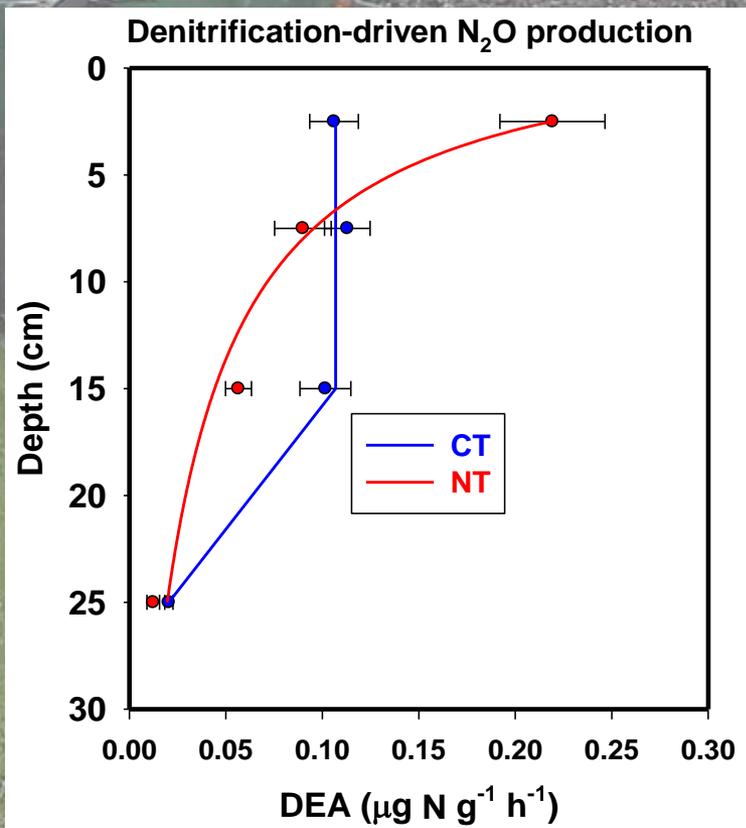


CT > NT

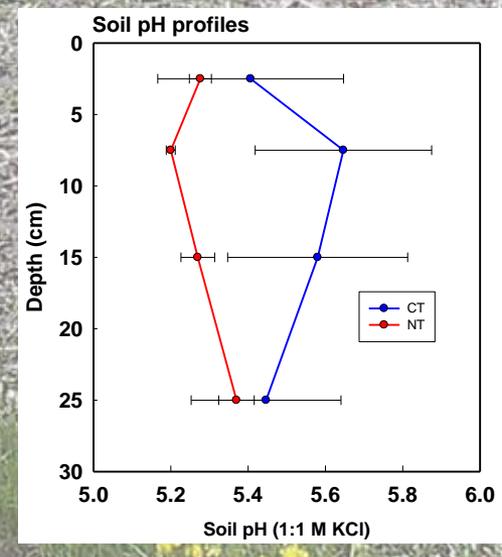
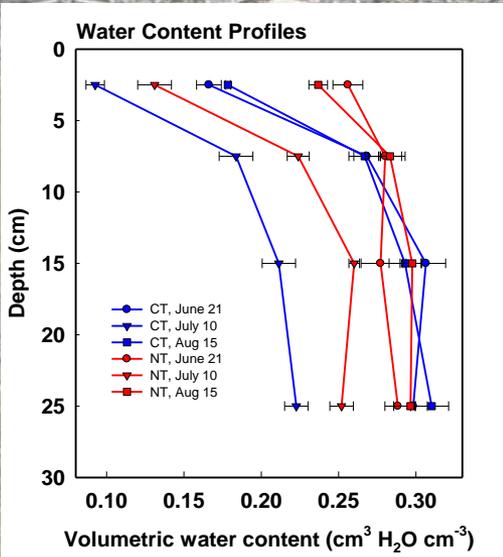
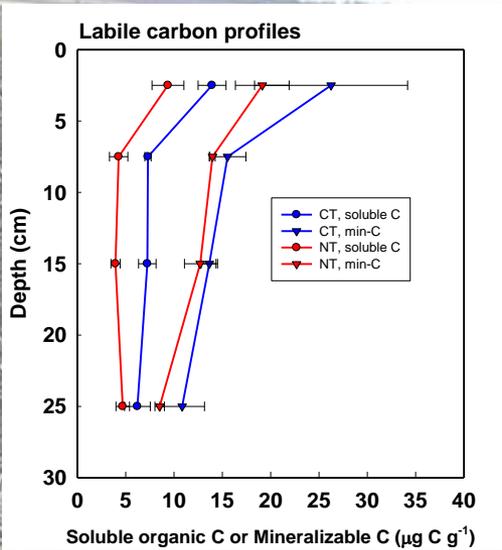
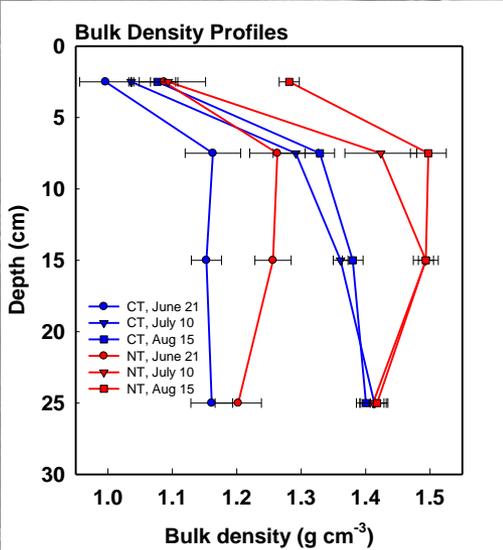
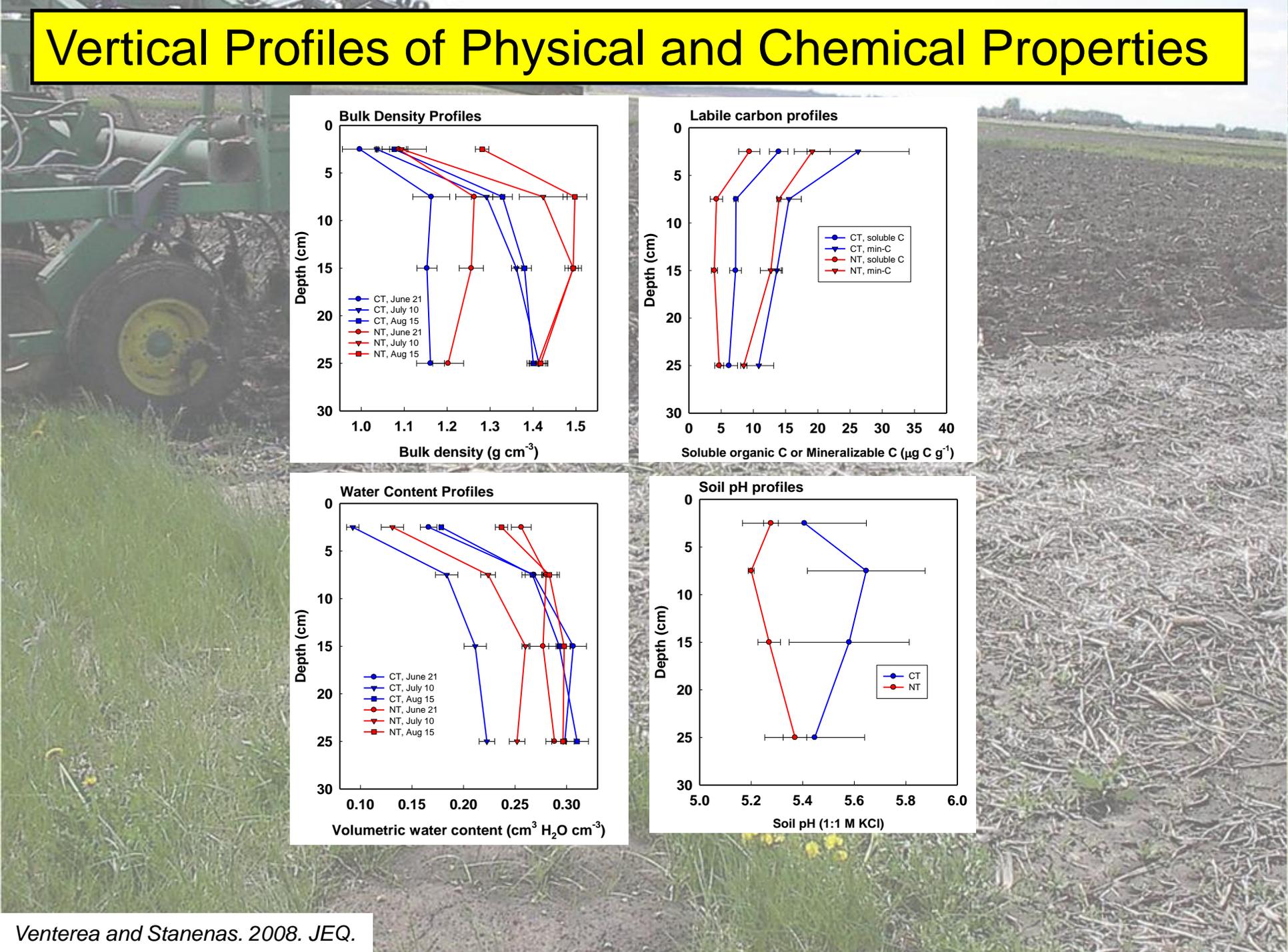
# Tillage Management Effects on N<sub>2</sub>O Emissions



# Vertical Profiles of Potential N<sub>2</sub>O Production

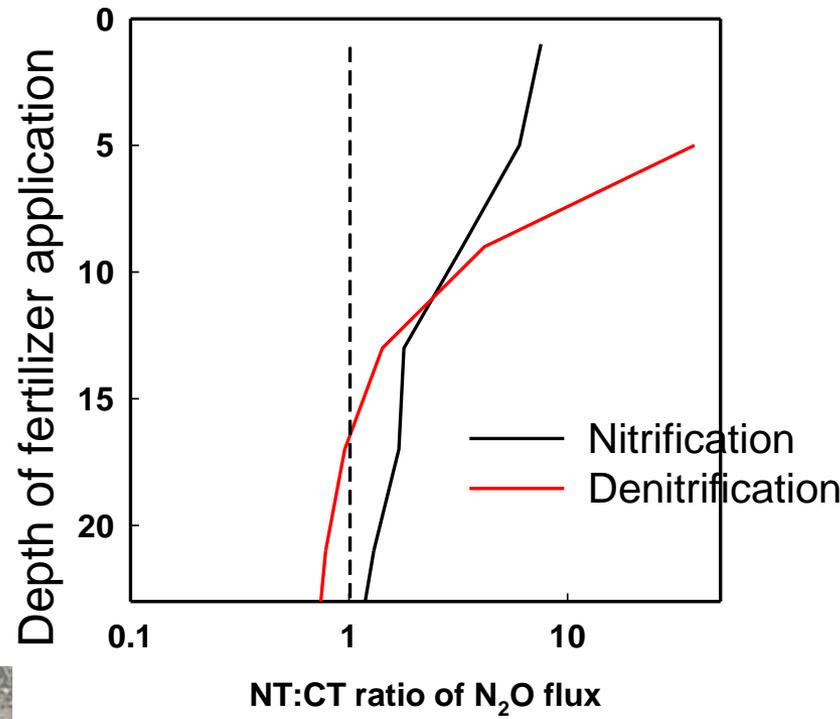


# Vertical Profiles of Physical and Chemical Properties



# Modeling Tillage-Fertilizer Interaction Effects

Diffusion model	$-\frac{d}{dz} \left( D_p \frac{d[N_2O]}{dz} \right) = \rho[P - S]$	
	Source Term	Sink Term
Denitrification	$P = \phi \left( \frac{V_{\max}^{NO_3^-} [NO_3^-]}{K_m^{NO_3^-} + [NO_3^-]} \right) \left( \frac{[C]}{K_m^C + [C]} \right)$	$S = \phi \left( \frac{V_{\max}^{N_2O} H[N_2O]}{K_m^{N_2O} + H[N_2O]} \right) \left( \frac{[C]}{K_m^C + [C]} \right)$
Nitrification	$P = K_p [NO_2^-]$	$S = 0$



Model predictions

# Tillage Management Effects on N<sub>2</sub>O Emissions

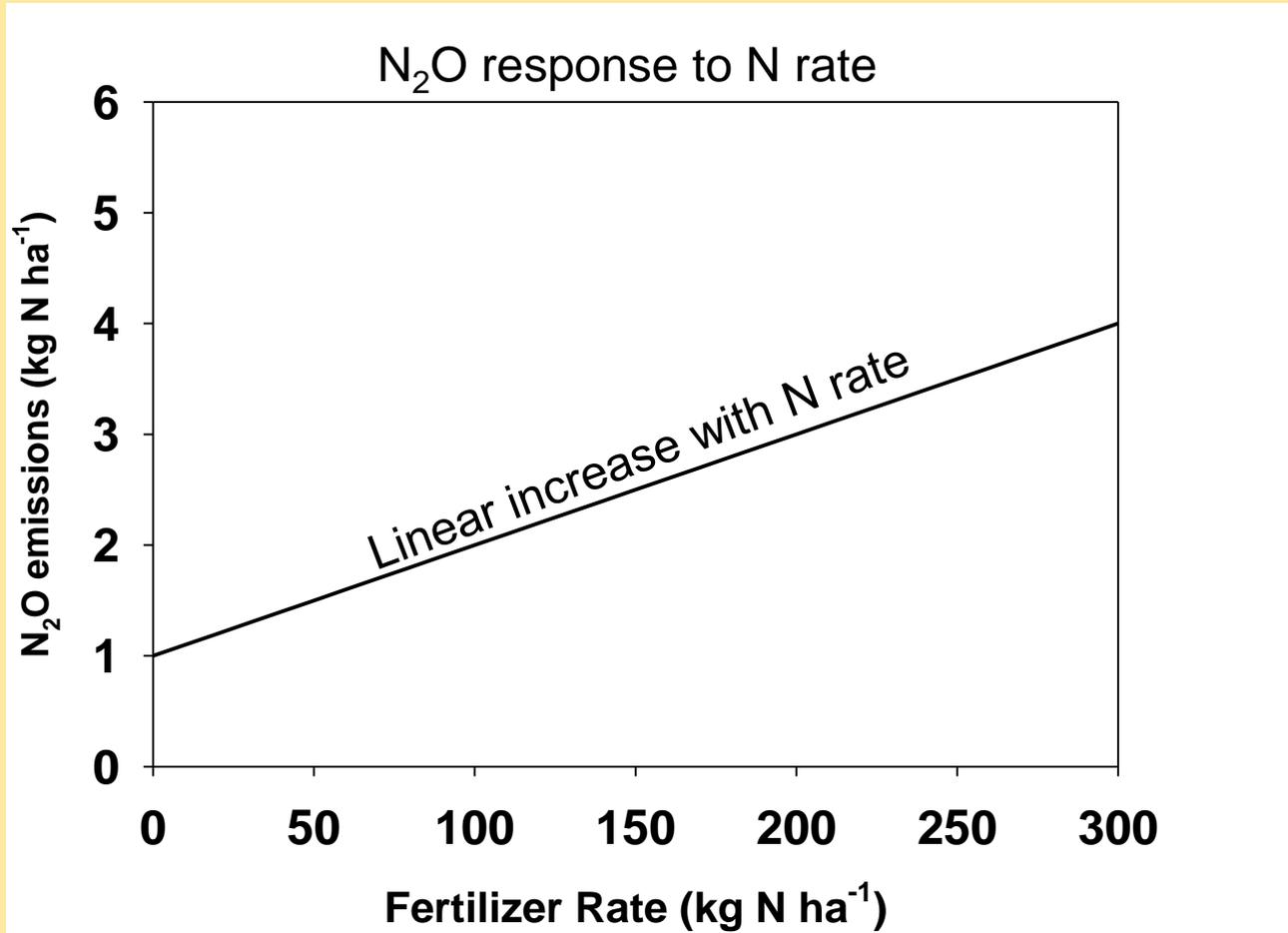
NT > CT	NT = CT	CT > NT
MacKenzie et al. 1998 Ball et al., 1999 Yamulki and Jarvis 2002 Baggs et al., 2003 Venterea et al., 2005 Grageda-Cabrera et al., 2011	Lemke et al. 1999 Robertson et al. 2000 Choudhary et al. 2002 Kaharabata et al. 2003 Liu et al., 2005 Rochette et al., 2008	Jacinthe and Dick, 1997 Lemke et al. 1999 Liu et al., 2005 Venterea et al., 2005 Ussiri et al., 2009 Omonode et al., 2011
Koga et al. 2004 Rochette et al., 2008 Aulakh et al. 1984		Kaharabata et al. 2003 Kessavalou et al. 1998 Halvorson et al., 2010

Agrees with tillage-by-placement pattern  
(12/18)

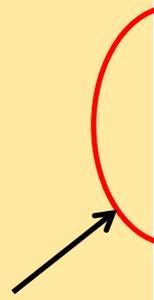
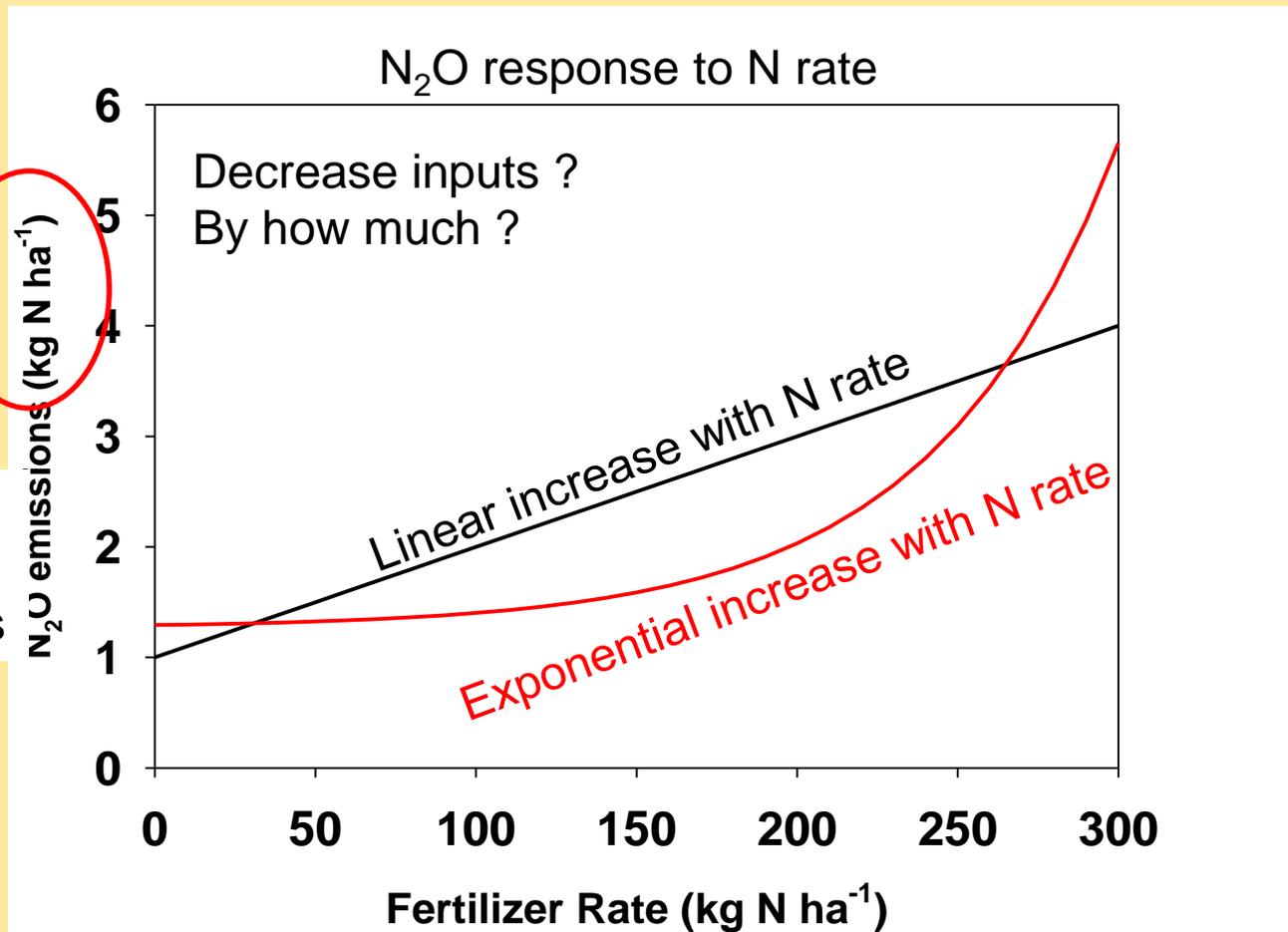
Mixed application or no information (5/18)

Disagrees with tillage-by-placement pattern  
(1/18)

# Fertilizer Rate Effects on N<sub>2</sub>O emissions



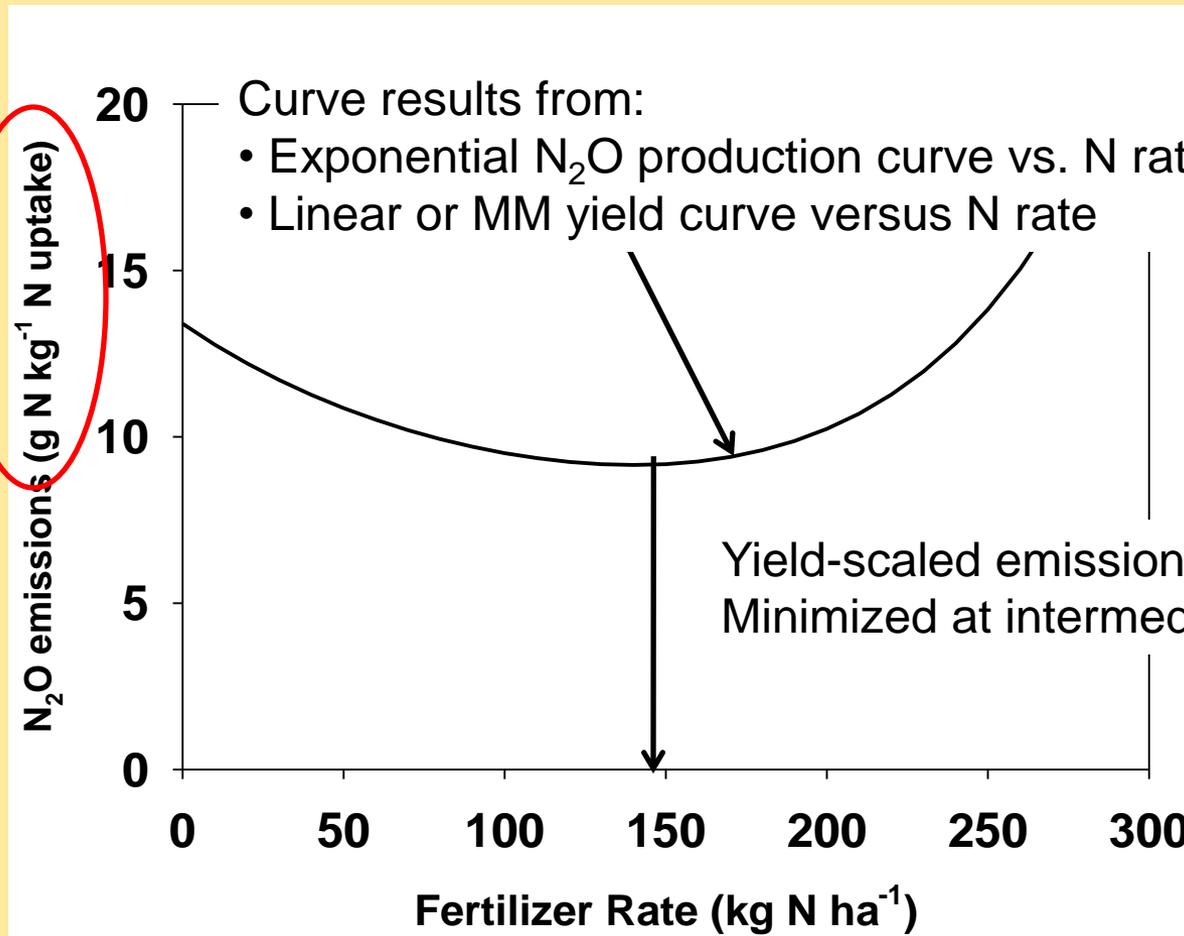
# Fertilizer Rate Effects on N<sub>2</sub>O emissions



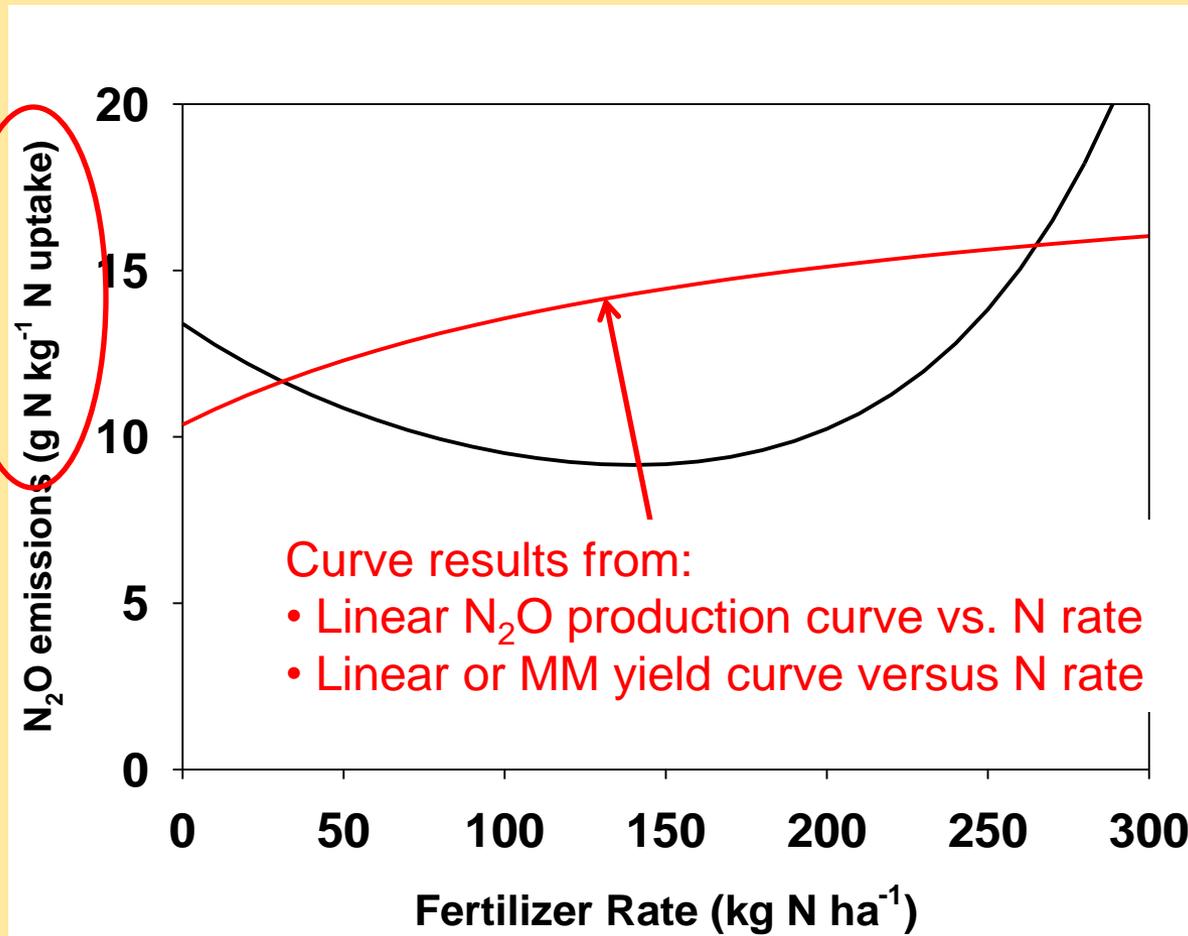
Emissions  
Expressed  
on area-basis

# Fertilizer Rate Effects on N<sub>2</sub>O emissions

Emissions expressed on a yield-scaled basis



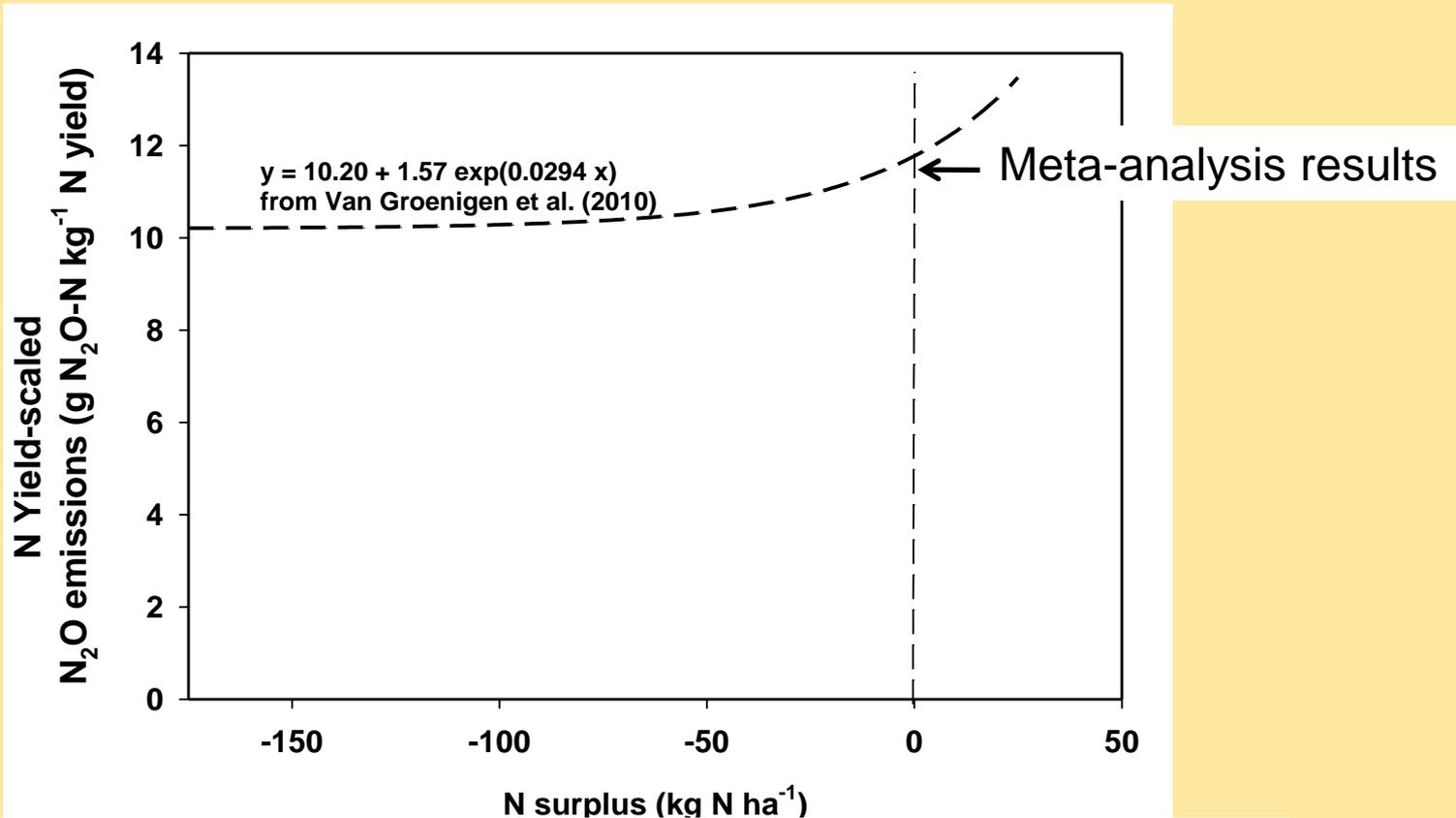
# Fertilizer Rate Effects on N<sub>2</sub>O emissions



Emissions expressed on a yield-scaled basis

# Nitrogen Use Efficiency and N<sub>2</sub>O emissions

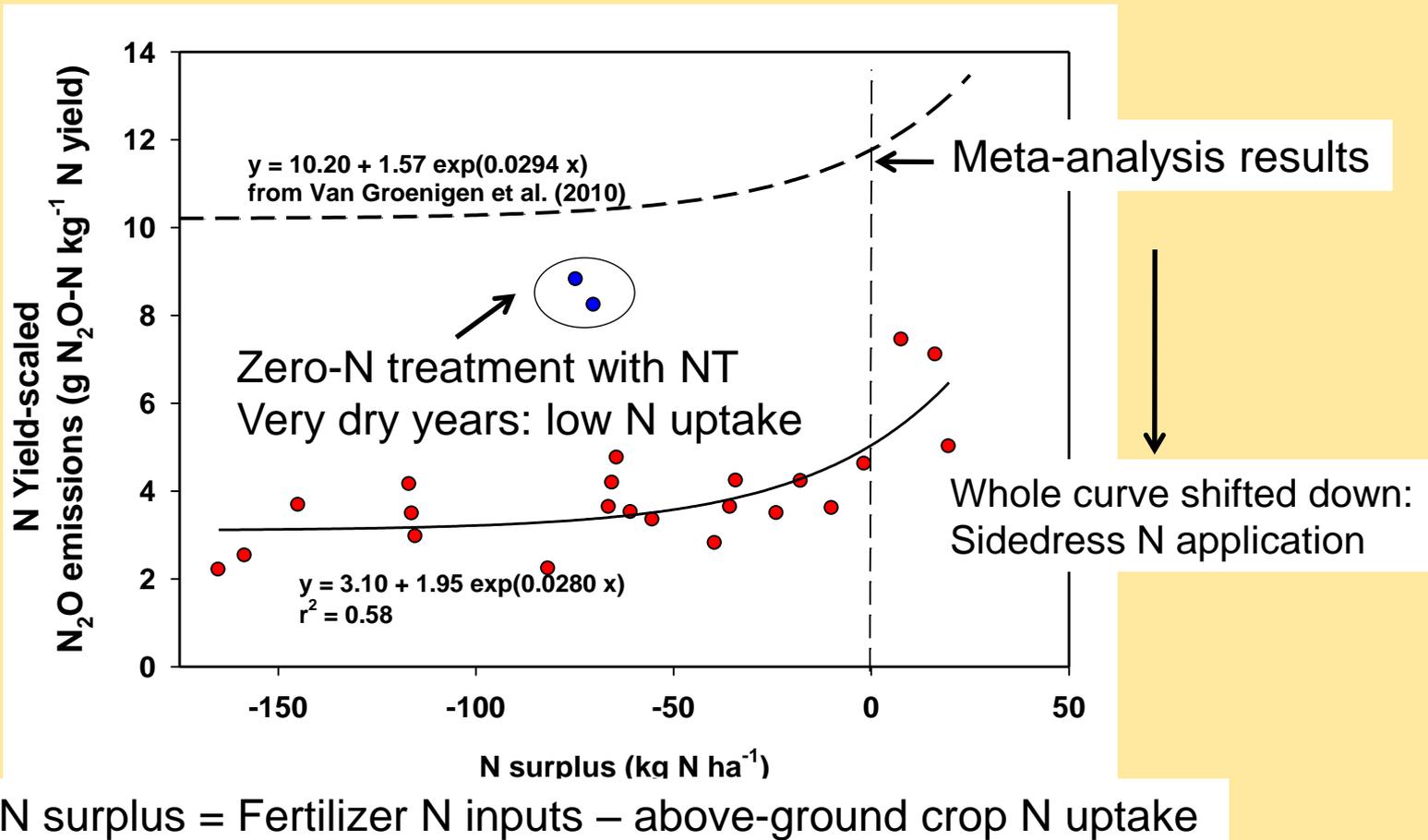
Another elegant idea: N<sub>2</sub>O emissions will be minimized when NUE is maximized



N surplus = Fertilizer N inputs – above-ground crop N uptake

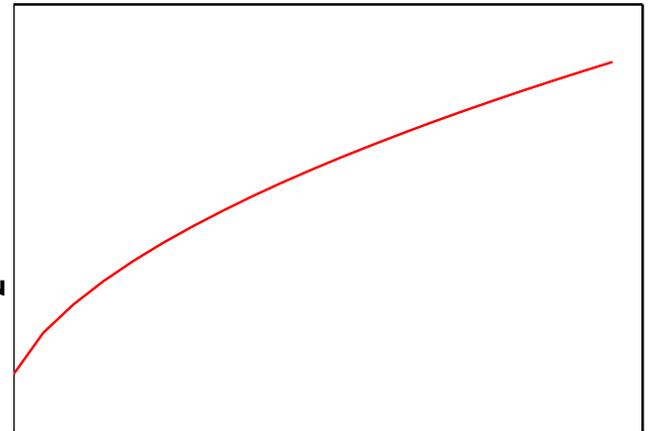
# Nitrogen Use Efficiency and N<sub>2</sub>O emissions

Another elegant idea: N<sub>2</sub>O emissions will be minimized when NUE is maximized



# The "Chamber Effect"

Chamber  $N_2O$  concentration



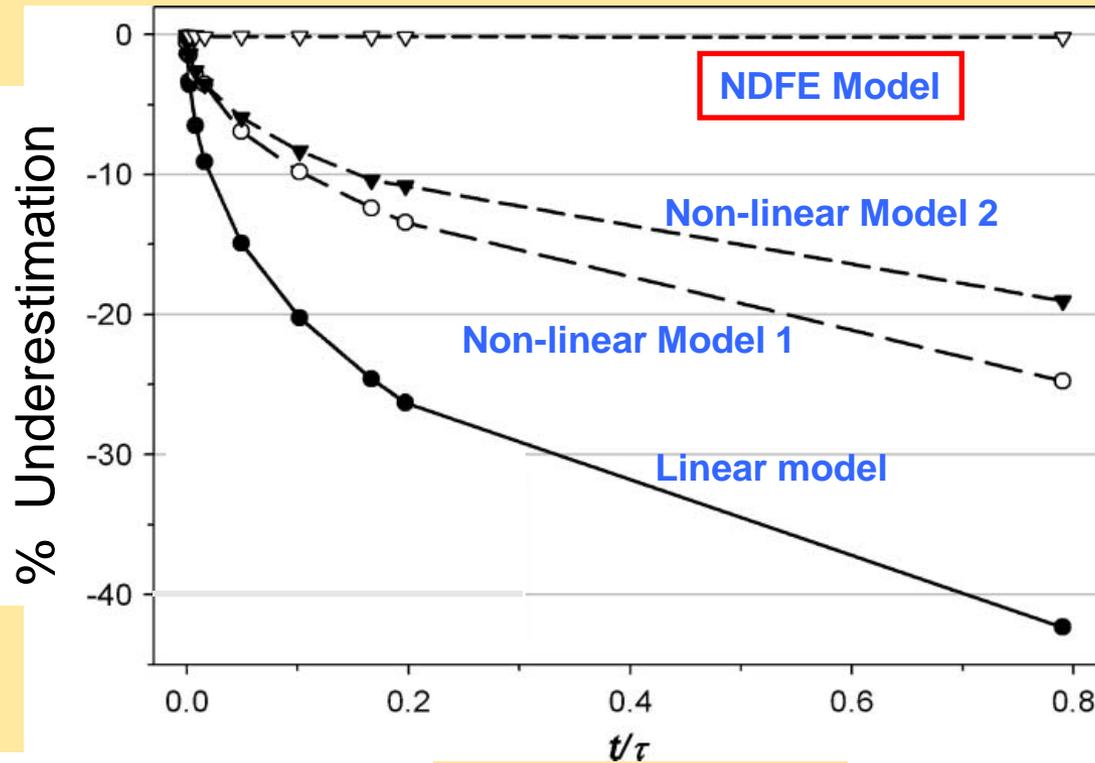
Time after chamber deployed

Suppression of concentration gradient,  
decreasing flux with time



Underestimation of  
pre-deployment flux

# The "Chamber Effect"



Smaller chamber  
Shorter deployment time



Larger chamber  
Longer deployment time

**Less porous soil**

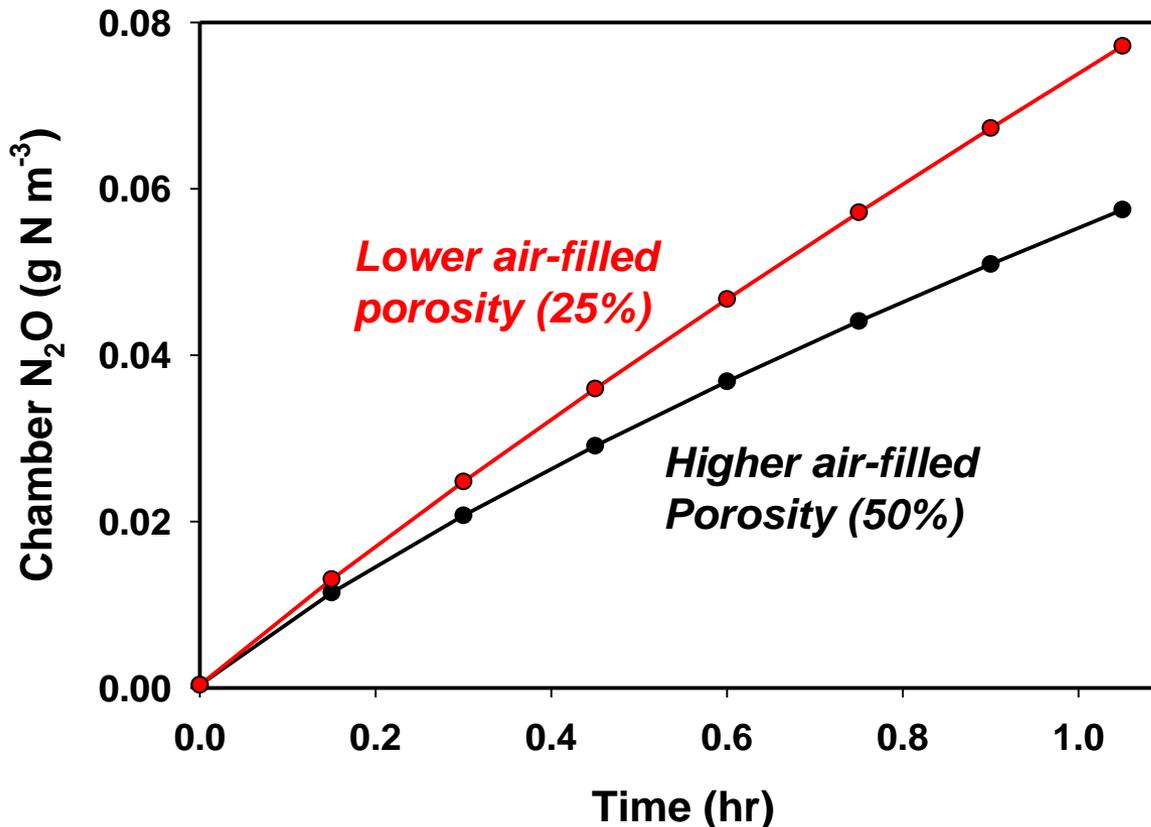


**More porous soil**

## Underestimation of fluxes in more porous soil

Artifacts can confound treatment effects:

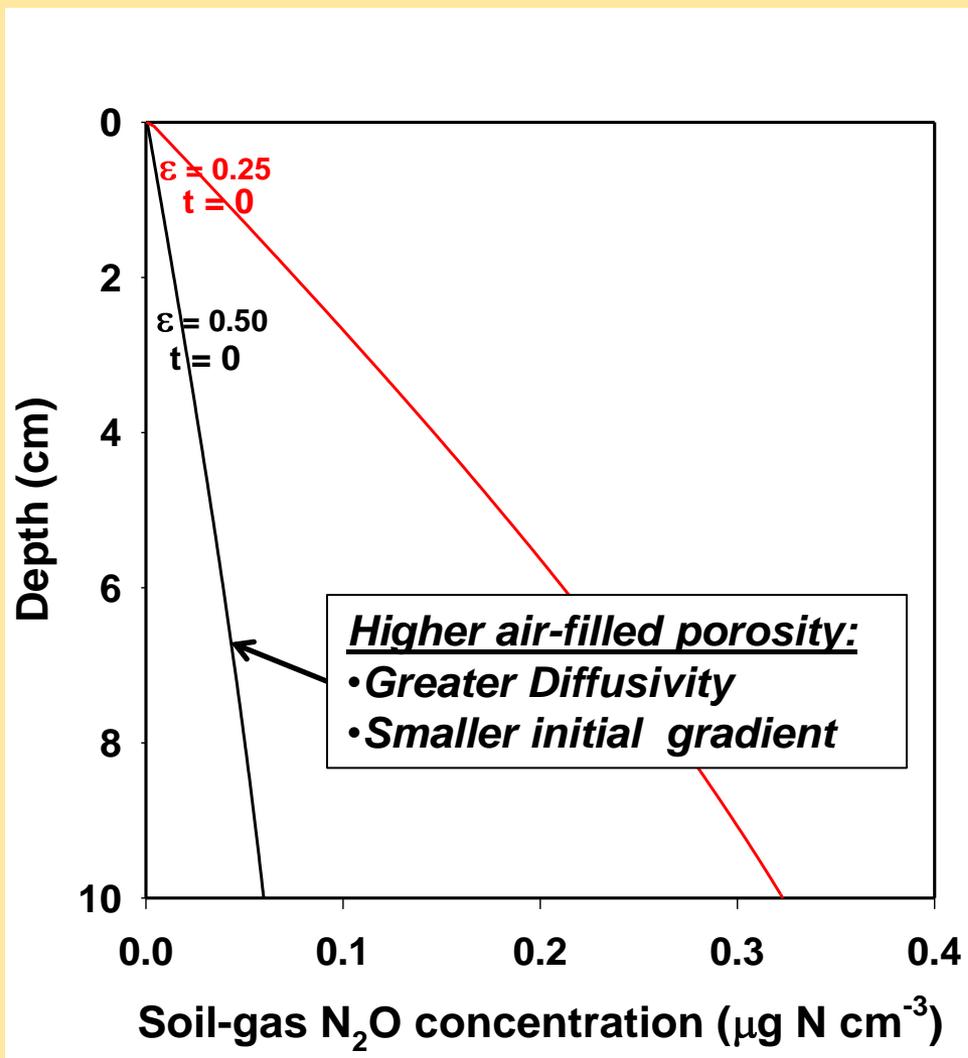
- Tillage, organic amendments → bulk density or water content



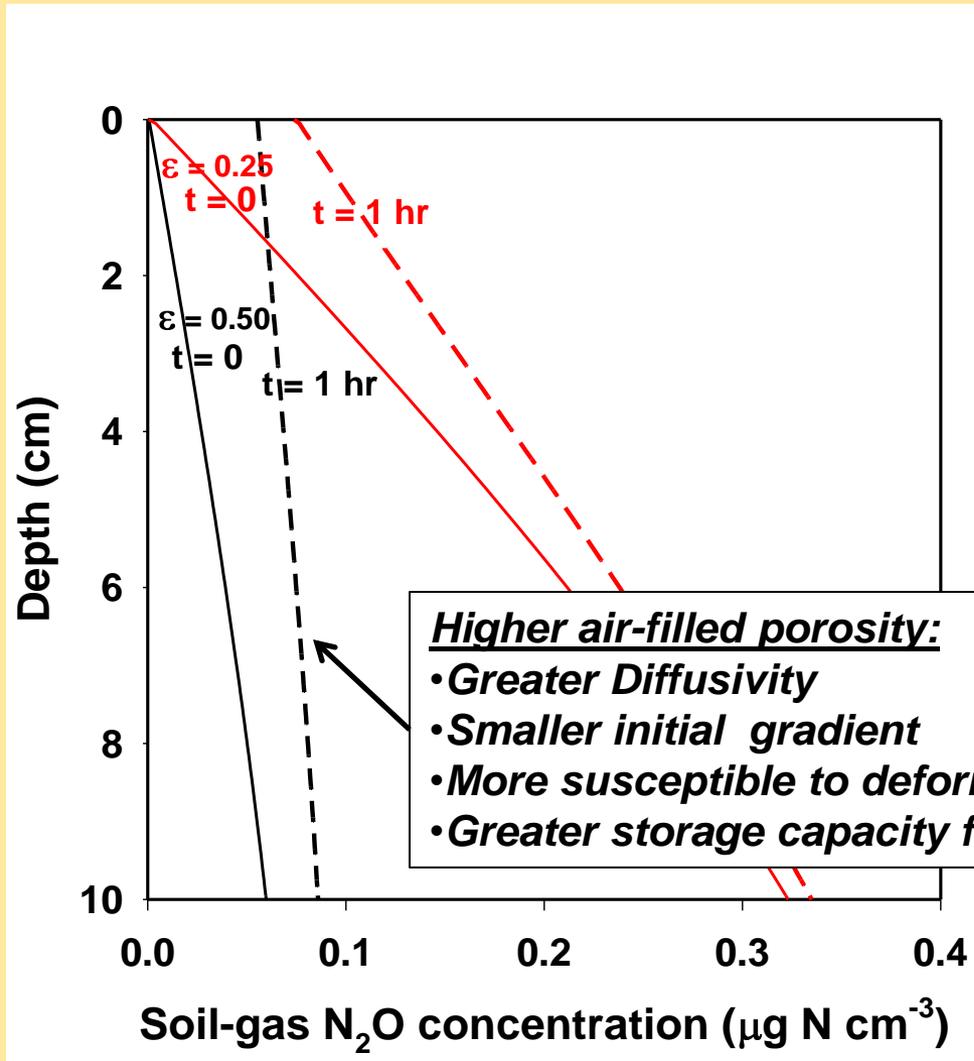
Curves generated by numerical model

- Both soils have same pre-deployment flux

# Underestimation of fluxes in more porous soil



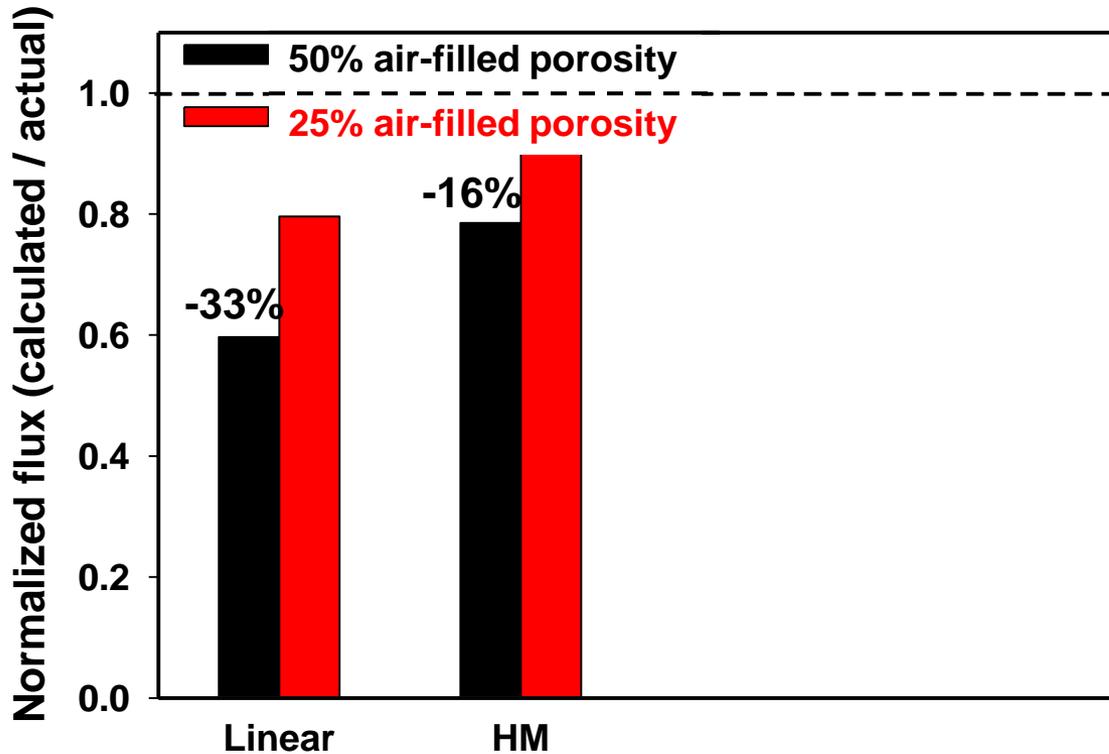
# Underestimation of fluxes in more porous soil



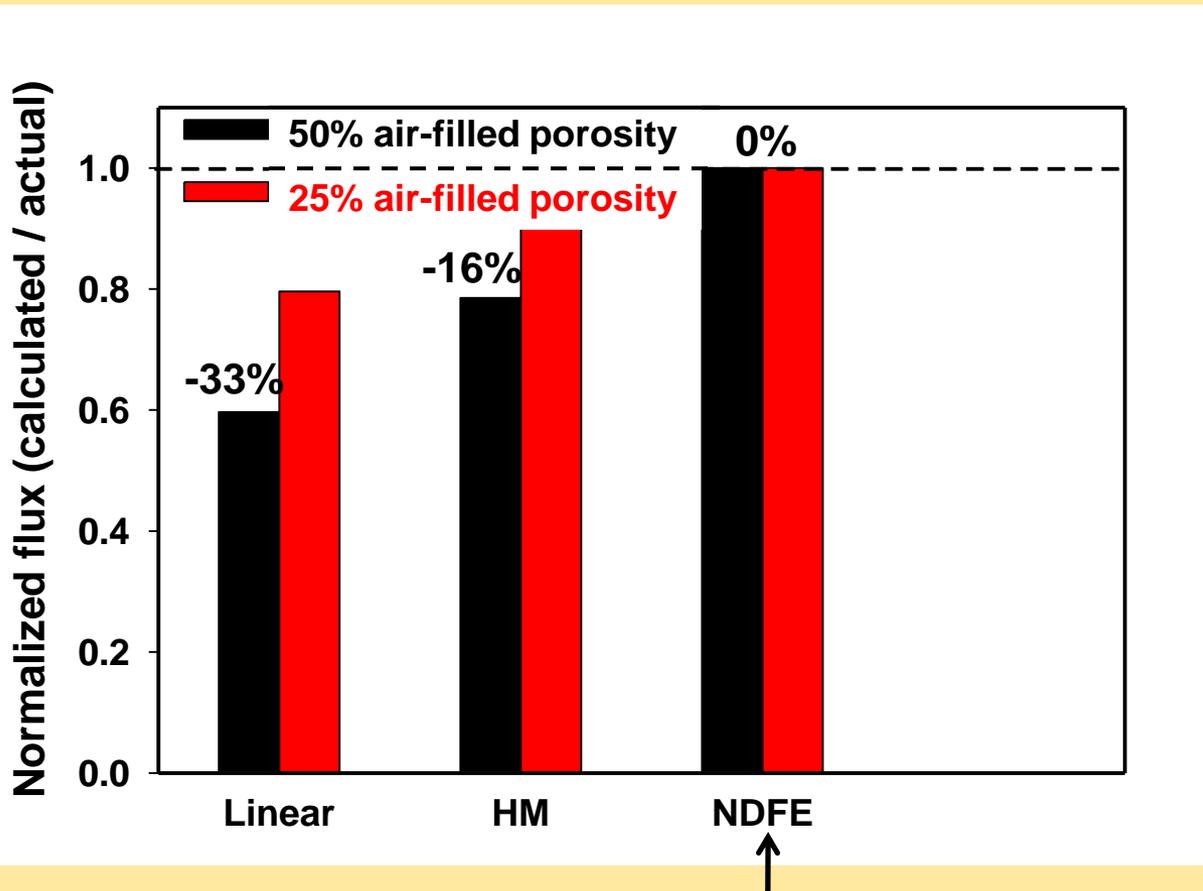
## Underestimation of fluxes in more porous soil

Artifacts can confound treatment effects:

- Tillage, organic amendments → bulk density or water content

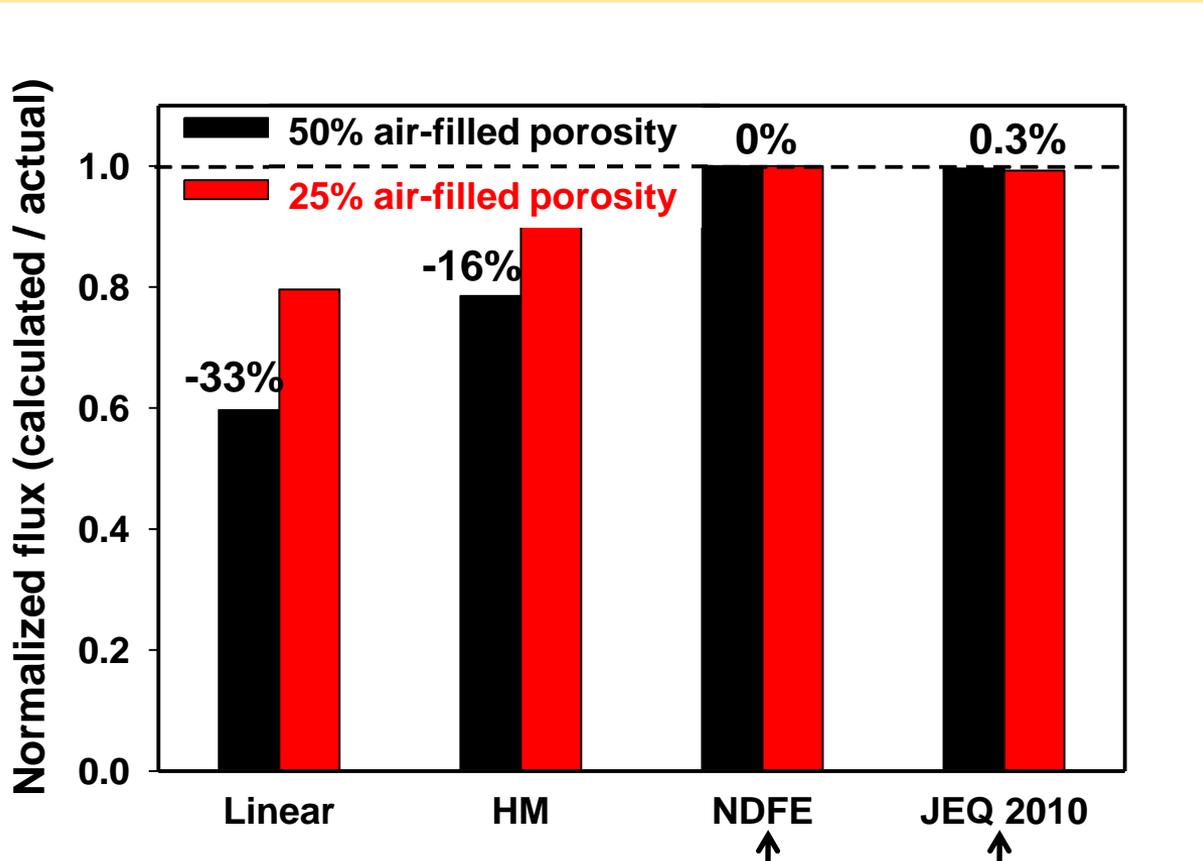


# Underestimation of fluxes in more porous soil



- Gives multiple solutions
- Inefficient
- Not exact for non-uniform soil

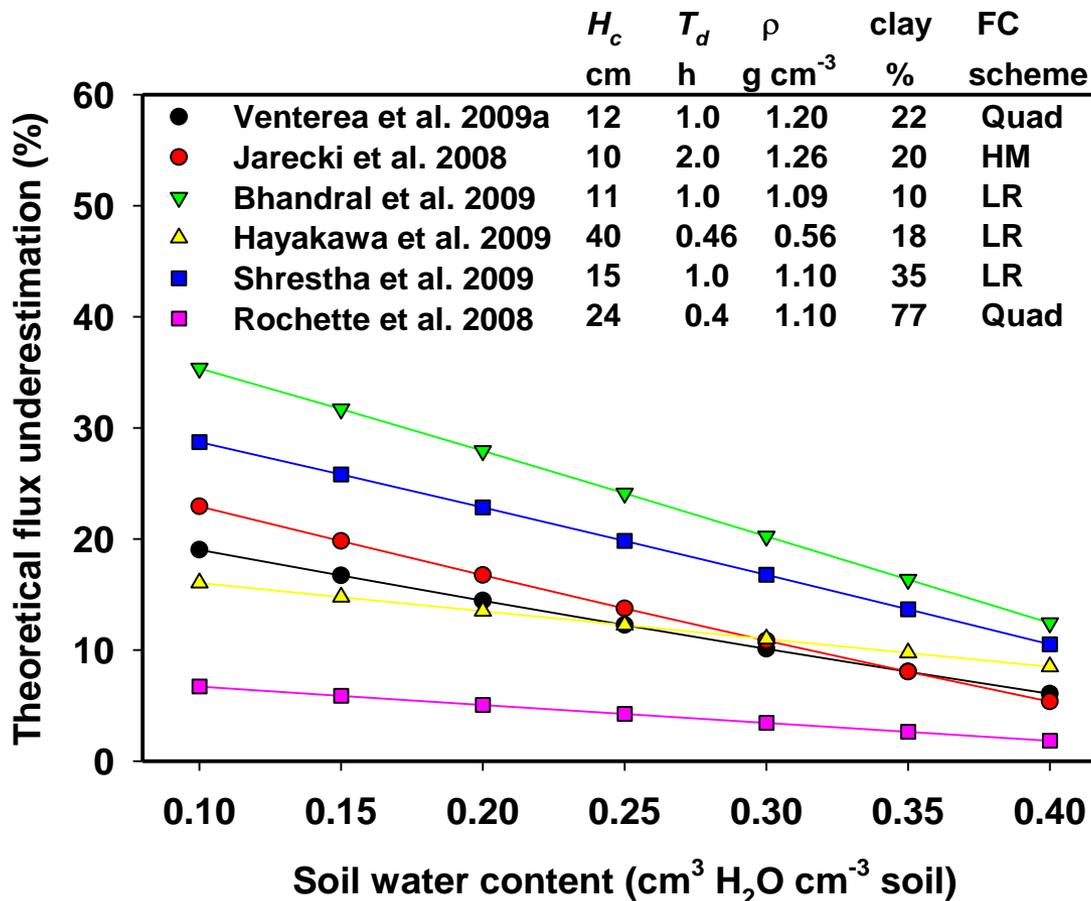
# Underestimation of fluxes in more porous soil



- Gives multiple solutions
- Inefficient
- Not exact for non-uniform soil

- Requires bulk density, water content data (sources of error)

# Non-uniformity of Flux Measurement Methods



1. More consensus in methods needed
2. Refinement necessary to improve absolute accuracy:
  - More use of micro-meteorological methods
  - Faster response/higher precision instruments (shorter deployment times)

## Conclusions

1. More studies needed to better determine optimization fertilizer management practices:
  1. Depth of placement
  2. Banding intensity
  3. Source and timing
2. GPS-guided N application technology to better match rate and placement with crop demand and yield potential
3. Emissions models that better account for differences due to (i) source, (ii) placement, and (iii) interactions among multiple factors

## Conclusions

Optimization of fertilizer management is only part of solution; range of activities is required:

1. Edge of field denitrification barriers / bioreactors or controlled drainage systems to reduce stream nitrate inputs:
  - Do practices designed to stimulate denitrification increase net  $N_2O$  emissions ?
2. Cover cropping / companion cropping / more diverse rotations to reduce N requirements and retain more N during non-growing season
3. Restoration of riparian vegetation
4. Improved animal mgmt to reduce excess N in manures
5. Improved manure mgmt....