Protecting the Nitrogen Investment: N Loss Inhibitors Past and Present

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Outline

- Setting the Stage
  - What are the N losses we seek to prevent?
  - Why do these N losses happen?
  - When do these N losses happen?
  - Where do these N losses happen?
- Inhibiting N Losses
  - What is the management objective?
  - What's in the toolbox and how does each tool work?
  - Successes and failures – measured and/or observed.
  - Additional observations/Final thoughts/Summary

What are the N losses we seek to prevent?

- Nitrate-N (NO_3-N) Losses
  - Leaching of nitrate-N
  - Denitrification of nitrate-N
- Ammonia-N (NH_3-N) Losses
  - Ammonia loss due to high soil pH/calcareous soils
  - Ammonia loss due to presence of urease enzyme
    - In eastern US, urease driven ammonia volatilization is more important

Why does Nitrate-N loss happen?

- Soil Properties
  - Nitrate leaching related to soil texture, structure, water holding capacity and subsoil surface chem; well drained profile
  - Nitrate denitrification related to soil temperature, moisture, organic matter level; percolation rate, poorly drained profile
- Weather Conditions
  - Nitrate leaching driven by rainfall
  - Nitrate denitrification driven by warming temps, rainfall

Nitrate Losses

- Leaching and denitrification
- Leaching is a physical/chemical process
- Denitrification is an anaerobic (low oxygen) biological process
- Denitrification is the larger problem, area-wise

$$4(CH_2O) + 4NO_3^- + 4H^+ \rightarrow 4CO_2 + 2N_2O + 6H_2O$$

$$5(CH_2O) + 4NO_3^- + 4H^+ \rightarrow 5CO_2 + 2N_2 + 7H_2O$$

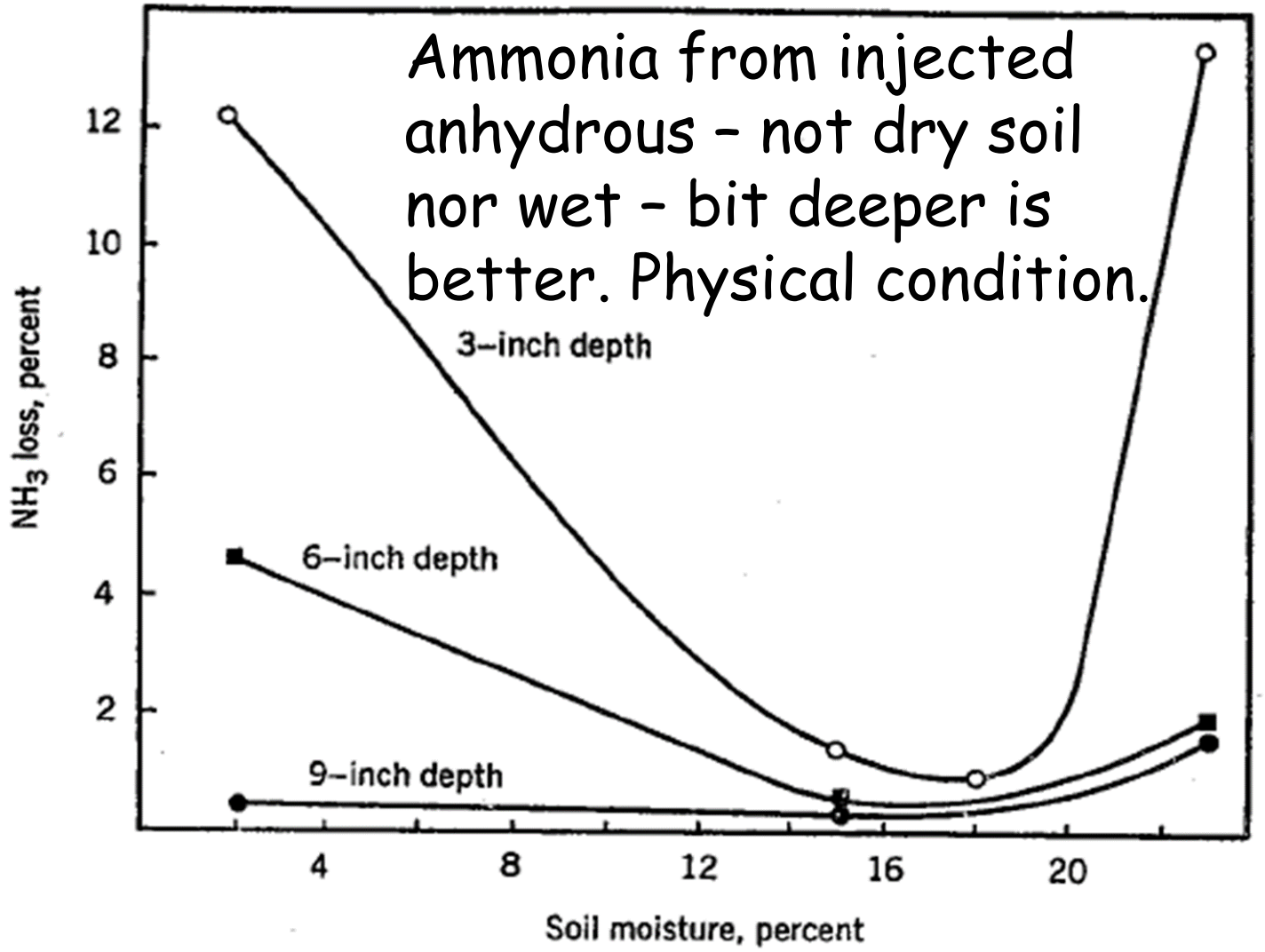
Nitrous oxide (N_2O) loss is about 1% of denitrification loss, but N_2O is a serious greenhouse gas (≈300 x CO_2)

Why does Ammonia-N loss happen?

- Soil Properties
  - Ammonia volatilization, from urea containing materials, is positively related to soil pH, the presence of living/dead residue with urease enzyme, warm soil temperatures, and adequate soil moisture
- Weather Conditions
  - Ammonia volatilization favored by warm, lower humidity air moving (breezily) over moist soil
  - Ammonia volatilization not favored by cold and/or rainy weather

Ammonia Losses

- Volatilization occurs as ammonia gas
- Volatilization can be influenced by physical conditions



Ammonia Losses

- Volatilization occurs as ammonia gas
- Volatilization can be influenced by chemical conditions
- Ammonia volatilization from urea and salts like ammonium sulfate can be driven by calcareous, high pH (7.5 to 8.5) soil

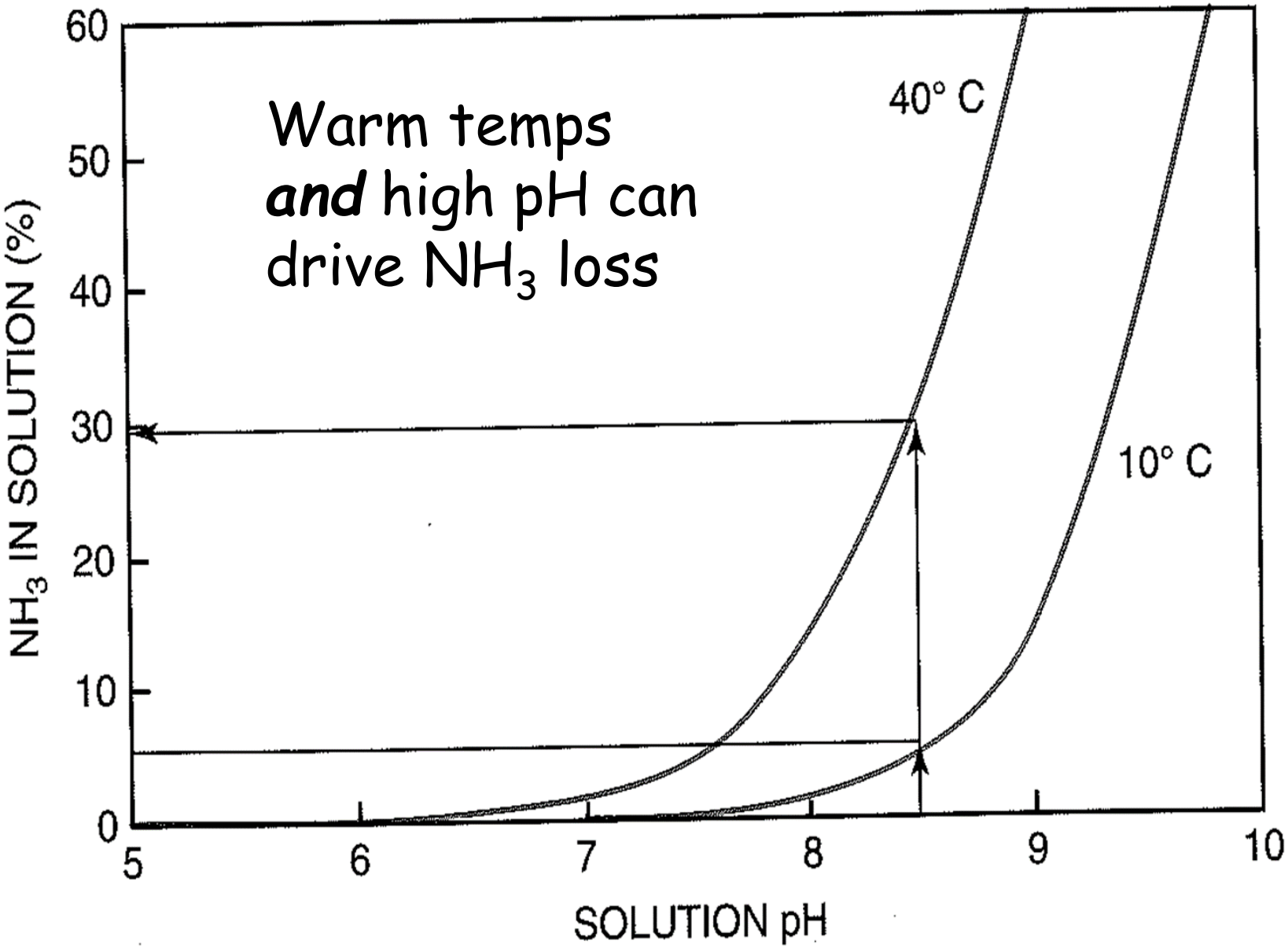
$$(NH_4)_2SO_4 + CaCO_3 + 2H_2O \rightarrow 2NH_4^+ + 2HCO_3^- + 2OH^- + CaSO_4$$

$$NH_4^+ + HCO_3^- \rightarrow NH_3 + CO_2 + H_2O$$

$$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$$

Ammonia volatilization driven by soil chemical conditions

- Volatilization occurs as ammonia gas
- Volatilization driven by interaction of chemical and physical conditions



Ammonia Losses

- Volatilization occurs as ammonia gas
- Volatilization can be influenced by biological conditions
- Ammonia volatilization from urea-UAN materials is often driven by urease enzyme-induced chemical hydrolysis: Step 1
- Step 2 is simple acid-base neutralization chemistry

$$CO(NH_2)_2 + H^+ + 2H_2O \leftrightarrows 2NH_4^+ + HCO_3^- \quad \text{Step 1}$$

$$\downarrow$$

$$NH_4^+ + HCO_3^- \rightarrow NH_3 + CO_2 + H_2O \quad \text{Step 2}$$

Urease is exogenous – found on surfaces of soil, living/dead plant tissues

When do these losses happen?

- Nitrate-N Losses
  - Leaching losses happen anytime rainfall infiltration exceeds soil water holding capacity – largely late fall, winter, spring and early summer
  - Denitrification losses happen as above, but need soil temps warm enough to support biological activity – late winter, spring and early summer
- Ammonia-N Losses
  - Ammonia volatilization via urease favored by warm, lower humidity air, wind and moist soil (conditions that favor enzyme activity and ammonia mobility) – late spring and summer

Where do these losses happen?

- Nitrate-N Losses
  - Leaching losses usually occur in generally upland fields containing largely sandy textured and/or well drained soils
  - Denitrification losses usually occur in lowland fields containing medium to fine textured and more poorly drained soils
- Ammonia-N Losses
  - Ammonia volatilization losses can occur in about any field, given the right conditions

Inhibiting N Losses

- Management Objective(s)
  - Insurance – guarding against N loss, regardless the fertilizer N rate
  - Reducing the N rate – replacing usually lost fertilizer N with inhibitor investment – expecting equal/better N nutrition and yield
  - Optimized N management for carbon credit market (offset), to provide GHG 'inset' credit for various downstream (value/supply chain) grain buyers/users, or for USDA/NRCS program (e.g., Conservation Stewardship Program), need to stay with conservation tillage soil management

What's in the toolbox and how does each tool work?

- Non-Chemical Options
  - Avoiding nitrate-N leaching and denitrification loss
    - N rate and timing strongly linked. The earlier you apply, the more you need. Our springs are getting warmer and often, wetter. Want to plant corn early. When the N?
    - On moderately well drained to poorly drained soils, rates of nitrogen can be decreased by 30 to 50 lb N/acre if as much as two-thirds of the total fert N is applied 4 to 6 weeks after planting.
    - Plan to split/delay N on as many acres as can, starting with acres having the wettest natured soils.

Guarding Against N Loss

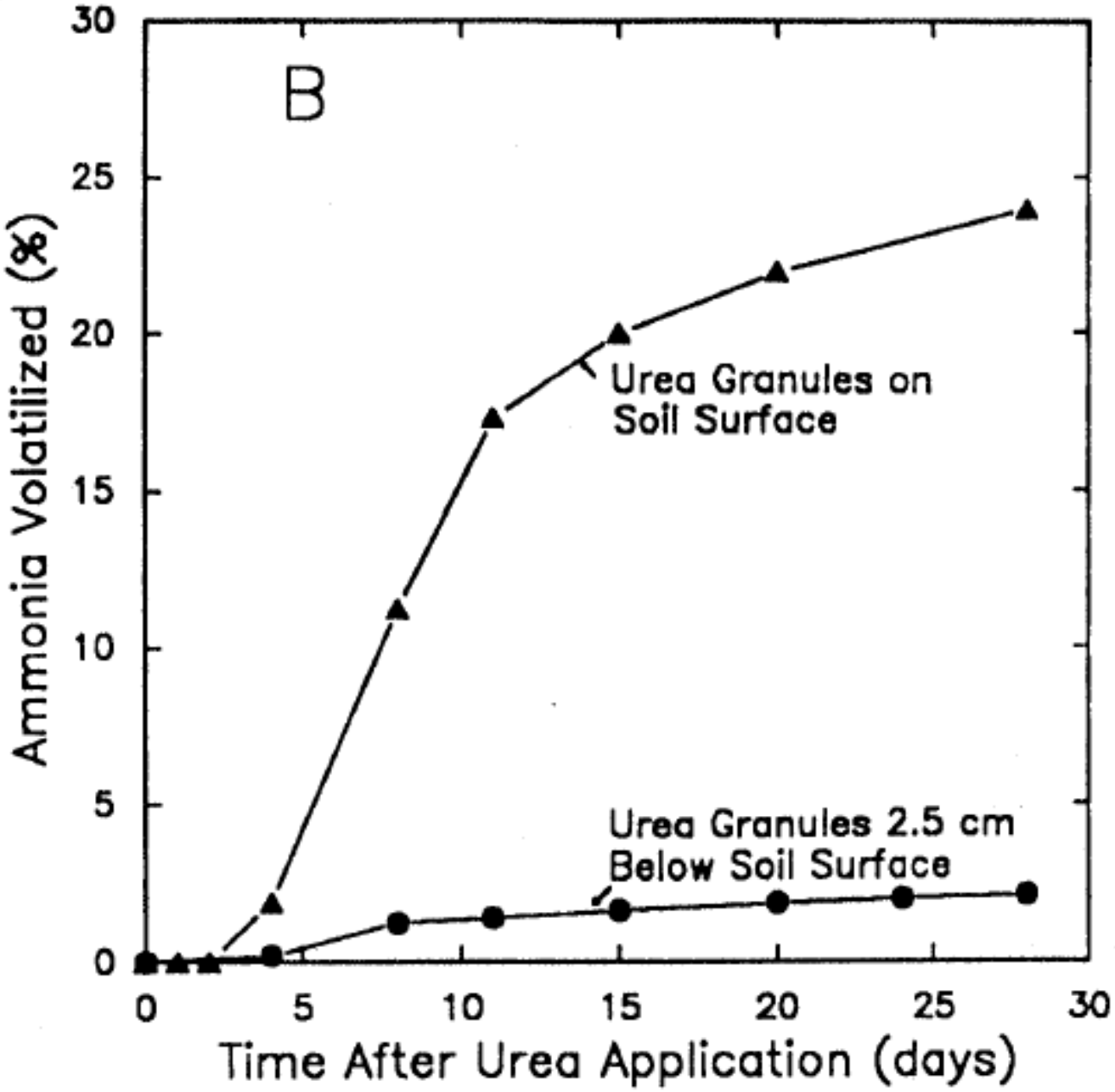
Delayed/Split N Timing – reduce the probability of denitrification and leaching of nitrate-N

What's in the toolbox and how does each tool work?

- Non-Chemical Options
  - Avoiding ammonia-N volatilization loss
    - Avoid urea or UAN, favoring ammonium nitrate or ammonium sulfate
    - Apply urea or UAN prior to 1 May (wheat and cool season grass forage crops)
    - Place/incorporate urea or UAN below the soil surface
    - Don't broadcast UAN across the entire soil surface when that surface covered with residues – dribble band
    - Consider the near-term weather – apply urea/UAN up to 72 hours ahead of forecast rain event of 0.5 inch+

Guarding Against N Loss

Injecting UAN Below Residues/Soil Surface – reduce the probability of volatilization (and immobilization) losses of available N


B
Ammonia Volatilized (%)
30
25
20
15
10
5
0
Urea Granules on
Soil Surface
Urea Granules 2.5 cm
Below Soil Surface
0
5
10
15
20
25
30
Time After Urea Application (days)

Black, 1997

Rained Yesterday – Sunny/Breezy Today. Does This Situation Call For A Urease Inhibitor?

N Placement Matters, Especially in NT Corn After Corn

	UAN			
N Rate lb N/A	broad-cast	surface band	injected	N Rate average
	NT corn after corn yield (bu/A)			
80	89	118	125	111
160	108	133	141	127
240	114	138	154	136
Placement average	104	130	135	

What's in the toolbox and how does each tool work?

- Chemical Options
  - Avoiding nitrate-N leaching and denitrification loss
    - Nitrification inhibitors. Inhibit formation of nitrate-N.
    - Polymer coated solid materials. Slow fert N release to 'match' crop N uptake needs.
  - Avoiding ammonia-N volatilization loss
    - Urease inhibitors. Inhibit enzyme activity, urea hydrolysis and ammonia-N formation.
    - Polymer coated solid materials. Slow release to 'match' crop N uptake needs.

Nitrification Inhibitors

UKAg
Department of Plant and Soil Sciences

Nitrification Inhibitors

- *Examples:*
  - *Nitrapyrin: N-Serve (anhydrous), Instinct (urea & UAN)*
  - *Pronitridine: Centuro (anhydrous & UAN)*
  - *new chemistry*
  - *Dicyandiamide (DCD): Agrotain Plus and Super U (these also contain NBPT, a urease inhibitor)*

Nitrification Inhibitors: New(er) Formulations

- Nitrapyrin – new formulations for new uses: N-Serve (anhydrous) » Instinct (urea, UAN): 0.5 to 1 lb ai/A

N-Serve®
Optinyte™ technology
NITROGEN STABILIZER

Instinct NXTGEN®
Optinyte™ technology
NITROGEN STABILIZER

- DCD, dicyandiamide – new formulations for urea and UAN, with urease inhibitor: rate depends upon N rate (10 to 12 lb/ton)

SUPER U

AGROTAIN PLUS

Nitrapyrin and Pronitridine as Pesticides: FIFRA Registered

Federal Insecticide, Fungicide and Rodenticide Act
EPA Registration Number: 62719-657
This chemical is a pesticide product registered by the Environmental Protection Agency and is subject to certain labeling requirements under federal pesticide law. These requirements differ from the classification criteria and hazard information required for safety data sheets, and for workplace labels of non-pesticide chemicals. Following is the hazard information as required on the pesticide label:

CAUTION

Causes moderate eye irritation
Prolonged or frequently repeated skin contact may cause allergic reactions in some individuals.

Shouldn't all nitrification inhibitors be required to register?

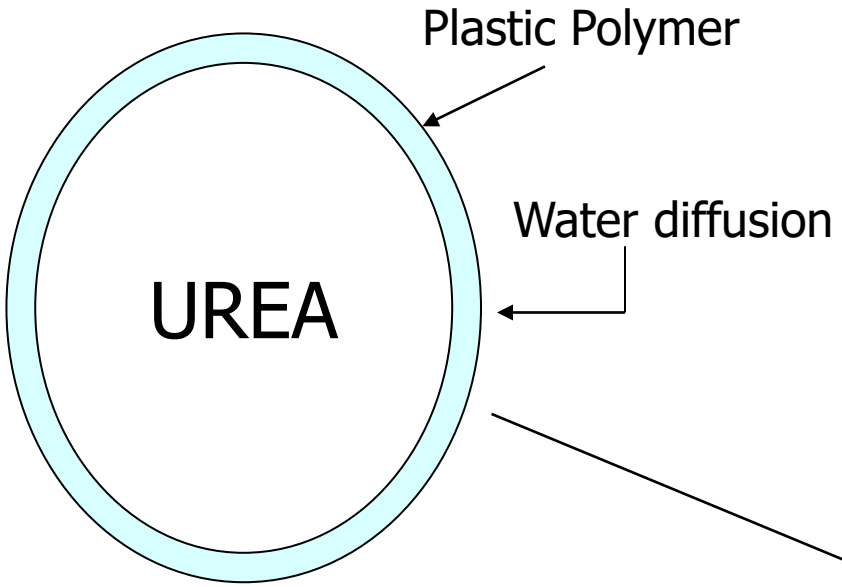
Purported Nitrification Inhibitors

- Maleic-itaconic copolymer calcium salt
- Calcium aminoethylpiperazine and heteropolysaccharides

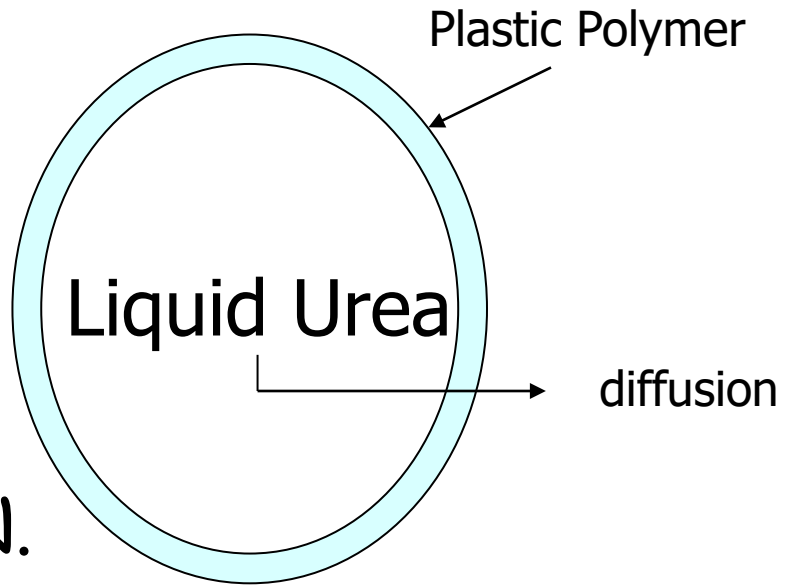
Polymer Coated Urea

ESN first hydrates, the entrained urea then dissolves and diffuses outward.

Hydration



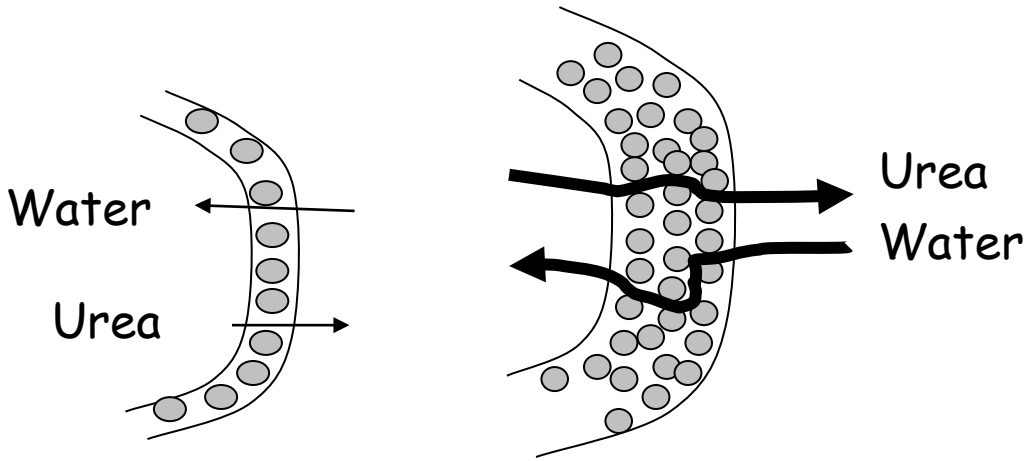
Release



There are other polymers.
None as commercially available as ESN.

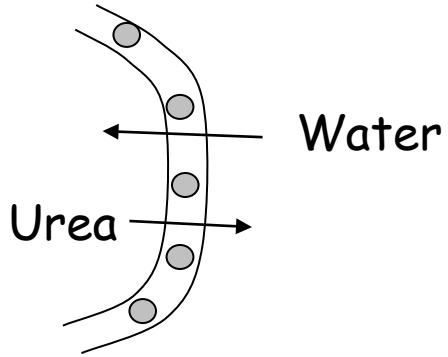
Factors Controlling Release Rate

Wall Thickness



Very Slow Release

Temperature ↑



Polymer Porosity Expands
Very Fast Release


Urease Inhibitors

Urease Inhibitors

- *Examples:*
  - *NBPT: Agrotain, off-patent products*
  - *Thiosulfate salts (K, Ca, NH_4)*
  - *NPPT: Limus (BASF)*

  - *Modified NBPT (duromide): Anvol*
  - *new chemistry*

  - *Agrotain Plus and Super U: contain NBPT and DCD (urease and nitrification inhibitors)*

NBPT

- NBPT molecule is/has been "off patent"
  - NBPT private label products now on the market
  - Agrotain = NBPT + solvent: "under patent"
  - Koch is licensing the older NBPT-solvent combo: (Helena, etc.)
  - Koch International has a new solvent for NBPT that is going "under patent"

Purported Urease Inhibitors

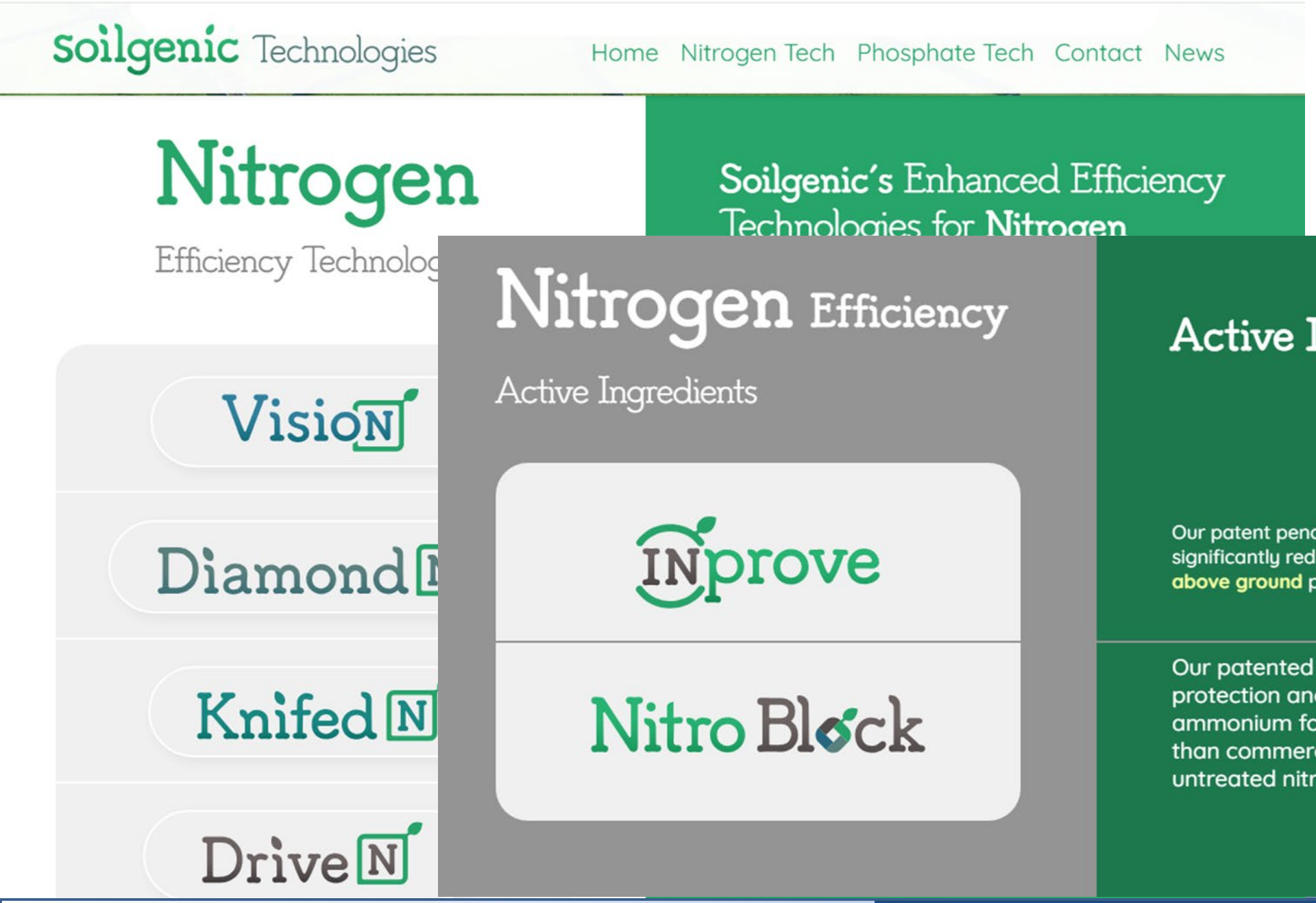
- Maleic-itaconic copolymer calcium salt
- Calcium aminoethylpiperazine and heteropolysaccharides

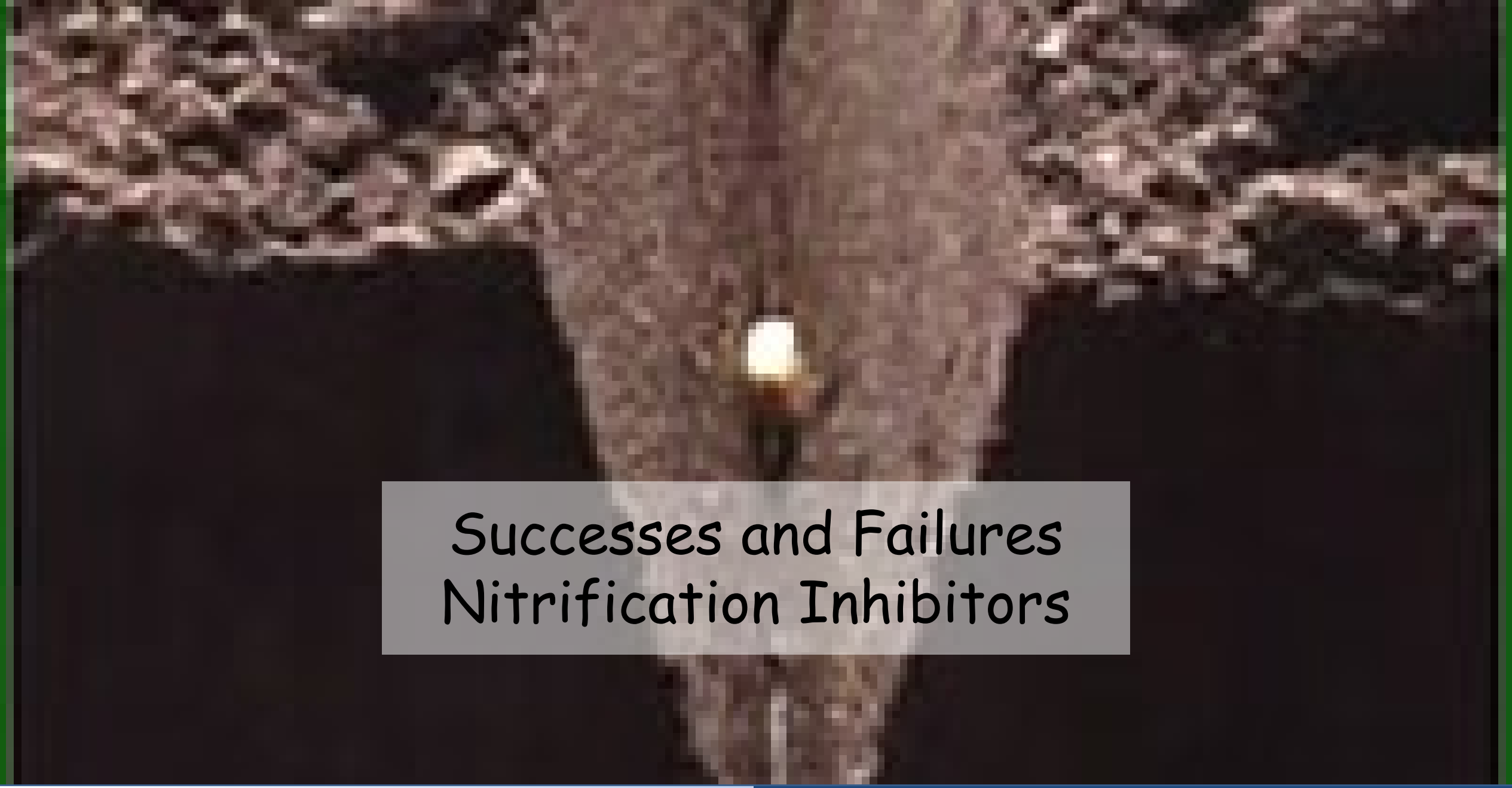
NutriSphere-N

WL Willowood USA NSTAY

STAY-N®

New Players New Products?





Successes and Failures Nitrification Inhibitors

UKAg Department of Plant and Soil Sciences

Comparison Number	fertilizer N rate	Grain Yield: Without Nitrapyrin	Grain Yield: With Nitrapyrin	Grain Yield Difference	Grain Yield Ratio
	lb N/acre	bu/acre			
1	200	176	189	13	1.07
2	178	139	174	34	1.24
3	165	134	142	8	1.06
4	175	182	189	7	1.04
5	164	160	191	31	1.19
6	200	213	213	1	1.00
7	160	137	138	1	1.01
8	160	119	111	-8	0.93
9	212	167	163	-4	0.97
10	160	168	185	17	1.10
11	190	204	214	10	1.05
12	130	99	129	30	1.30
13	130	113	133	20	1.17
average	171	155	167	12*	1.09

* Statistically significant difference at the 95% level of confidence.

Preplant N on wet soils?

Consider a nitrification inhibitor

1 qt nitrapyrin/A

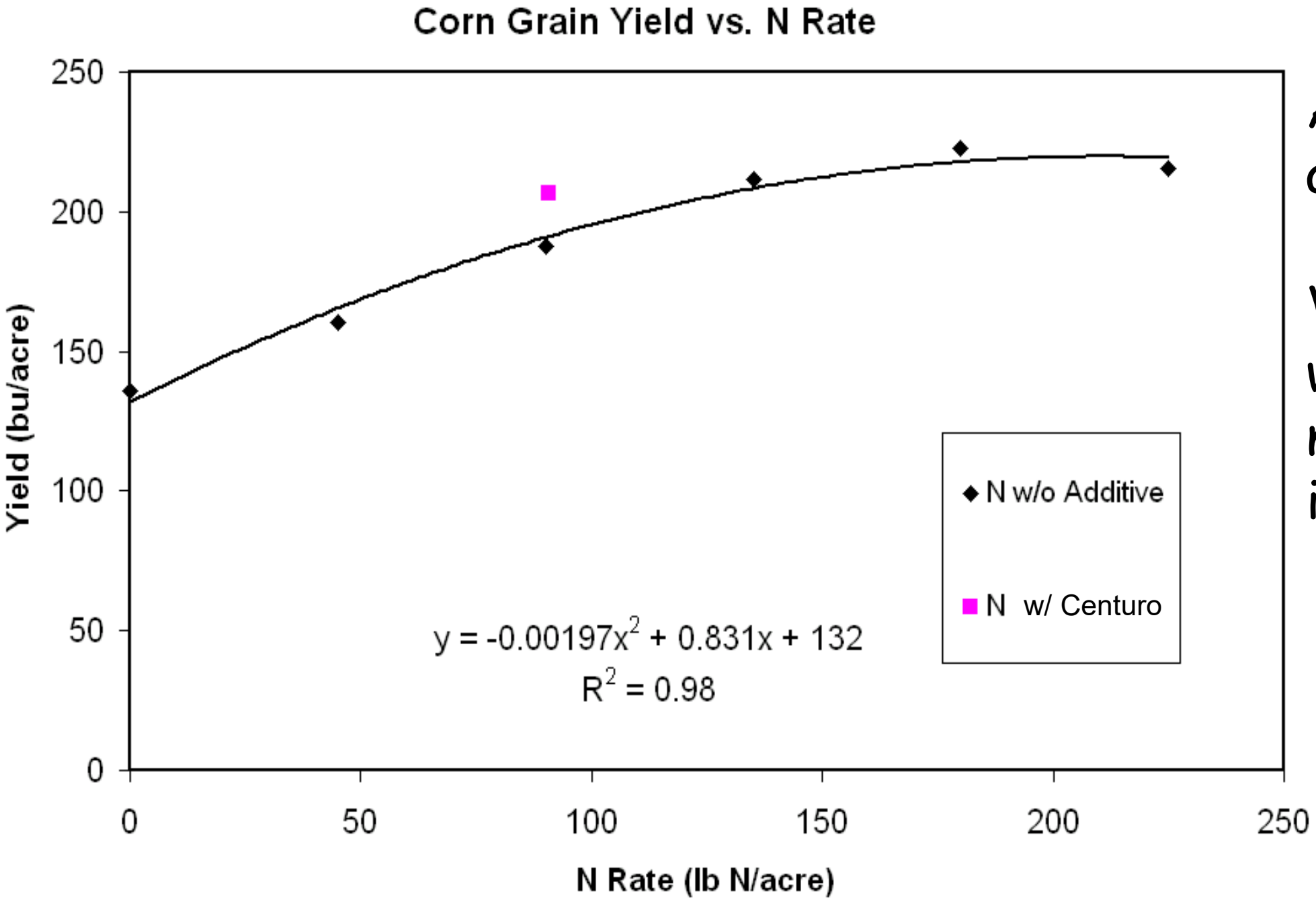
Starters Might Include An Inhibitor

N	P_2O_5	N-Serve	Corn yield response
-----lb/acre-----			bu/acre
0	0	0	---
16	0	0	- 1
16	0	0.4	+ 20
0	54	0	- 6
16	54	0	-1
16	54	0.4	+ 18

Conditions Need To Favor Both N and N-Serve

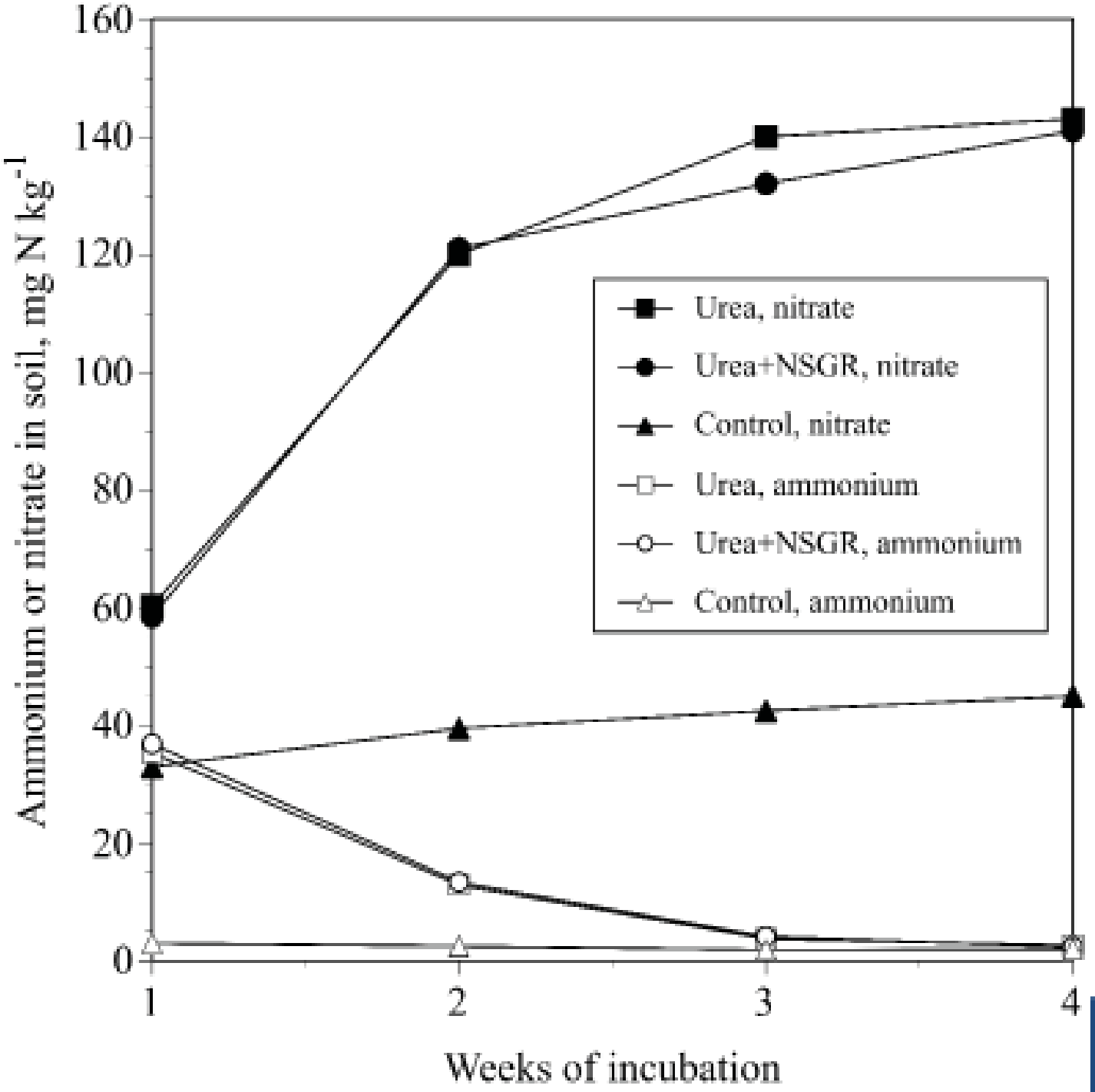
Corn Grain Yield- Lexington - 2009

N Source	N Rate lb N/acre	Grain Yield bu/acre
control	0	116d
UAN	80	189c
UAN + Instinct	80	204bc
UAN	120	218b
UAN + Instinct	120	241a



At-plant N on a wet soil.

With and without a nitrification inhibitor.



Nitrification with and without NSGR, Nutrisphere for granules

Goos, North Dakota State Univ.

Successes and Failures Urease Inhibitors

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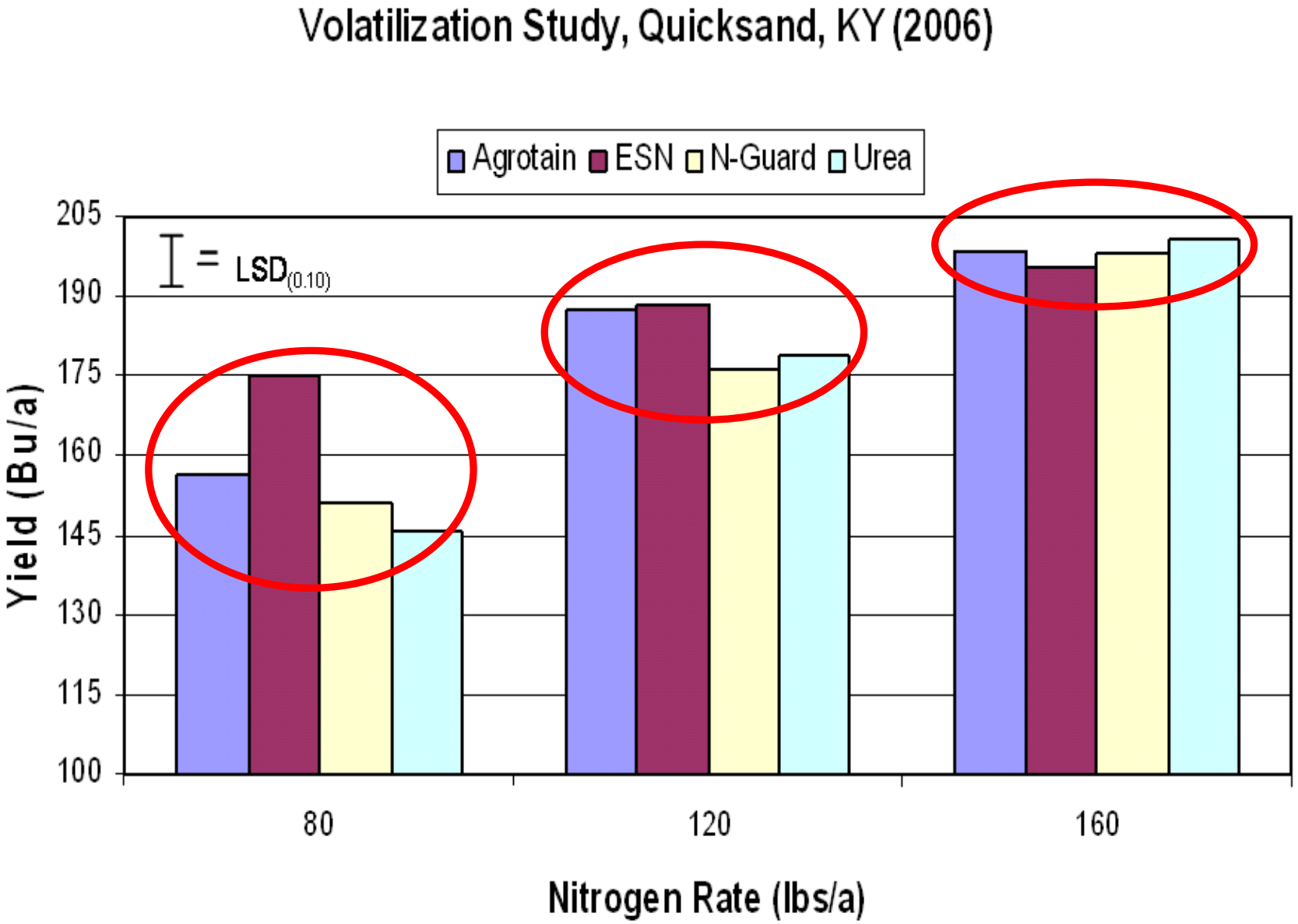
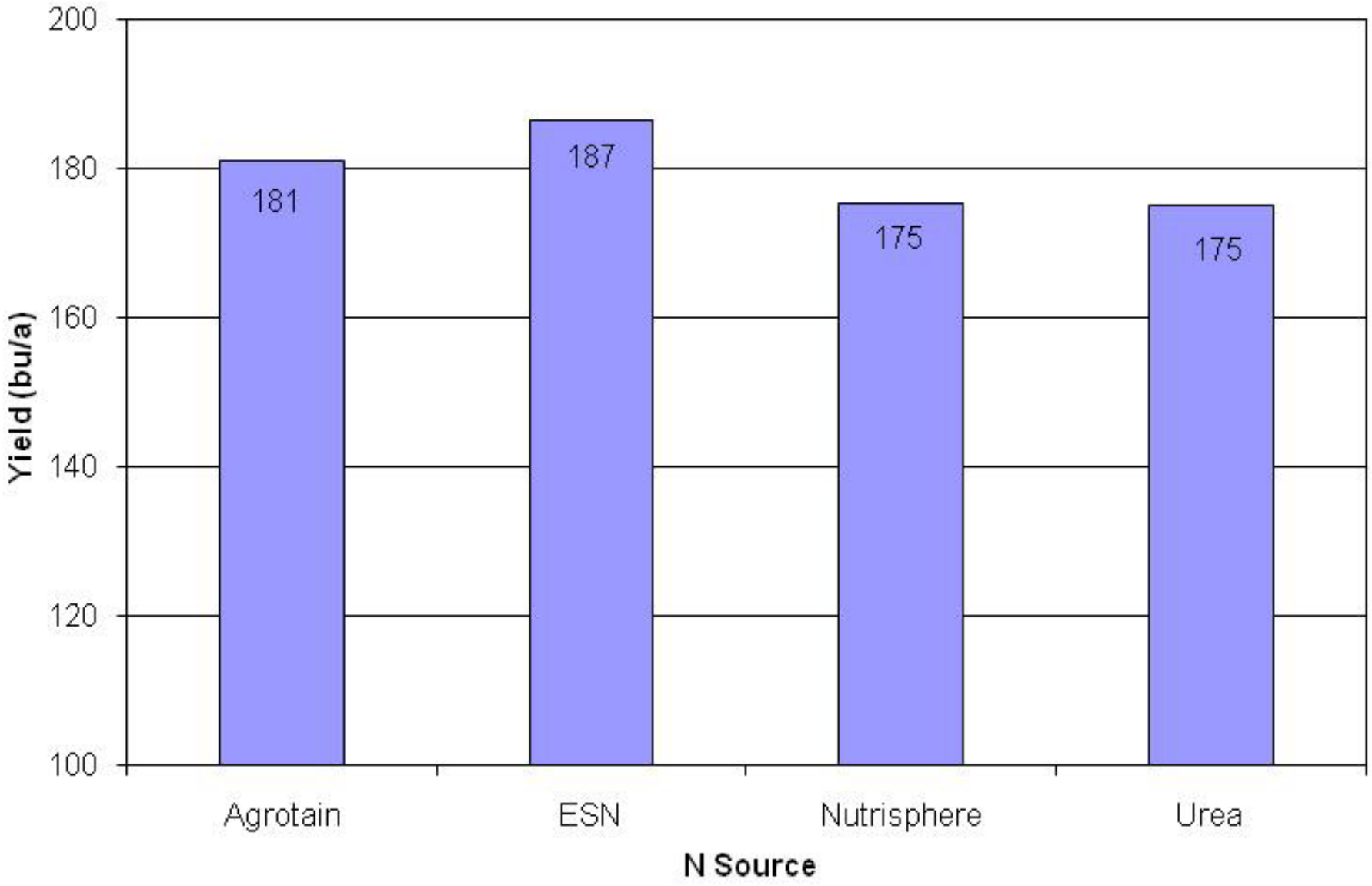
Department of Plant and Soil Sciences

Sometimes, just adding more urea is the best choice.

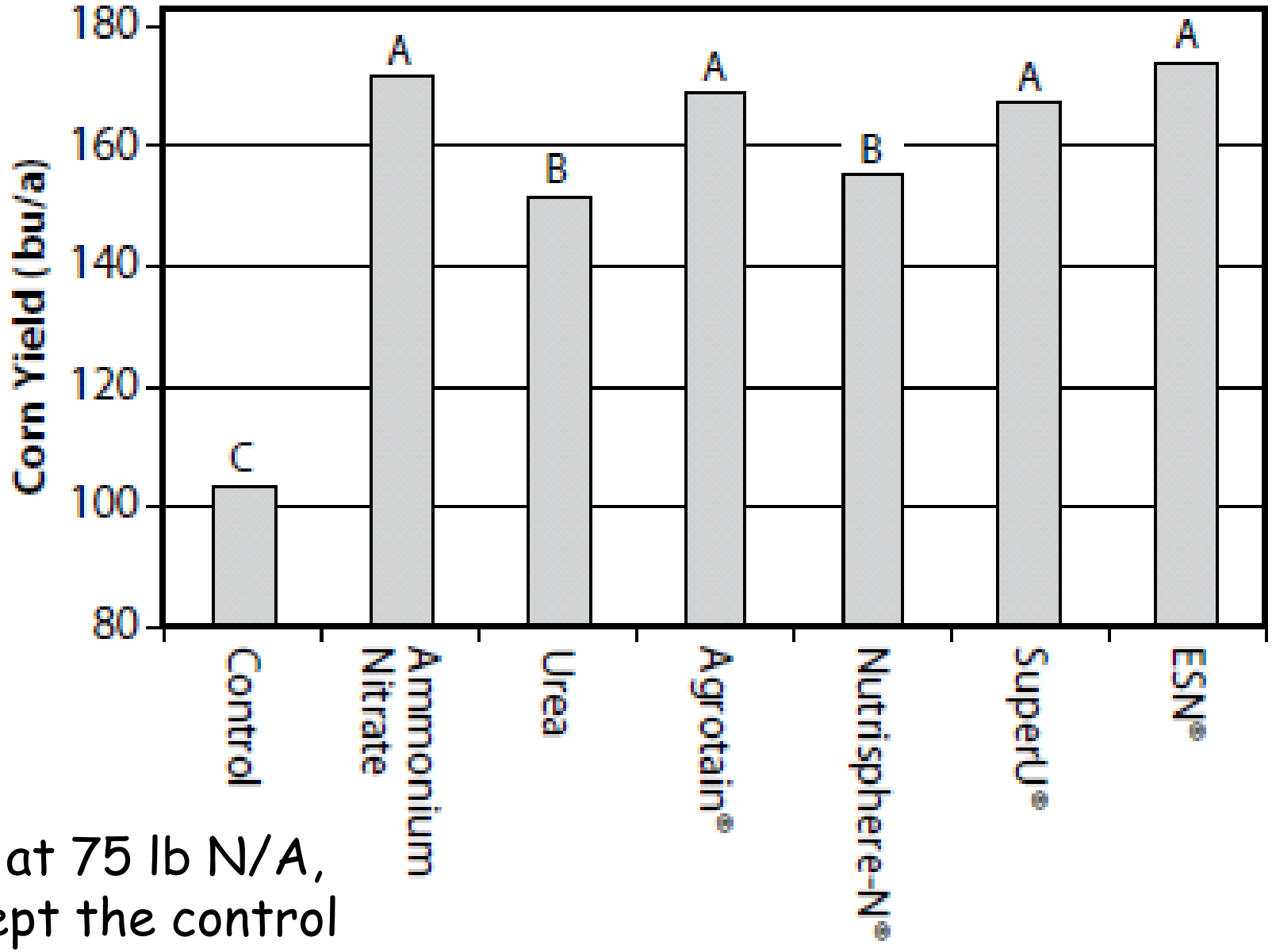


Schwab

Quicksand, 2008 - Sometimes Rainfall "Incorporates" Urea



Sometimes, You Need An Inhibitor That Works



All at 75 lb N/A, except the control

Schwab & Murdock, 2010

Nitrogen Timing Study - 2021

Table 1. Site information.

Site Number	County – Soil Series	Corn Hybrid	Planting Date
1	Christian – Pembroke	Stewart 14DD339	15 April
2	Breckinridge – Sadler	Pioneer 1197AM	16 April
3	Warren – Pembroke	Stewart 14DD339	17 April
4	Fayette – Lanton	Pioneer 1197AM	20 April
5	Larue – Elk	Stewart 14DD339	27 April
6	Caldwell – Crider	Pioneer 1197AM	12 May

N Source/Placement: SuperU Surface Broadcast

Nitrogen Timing Study - 2021

Table 2. Grain Yield Response – By Trial Site.

Treatment Description	bu/acre, by Site						
	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Ave.
0 early 160 V8	242a†	192a	221a	166a	232b	262a	219
40 AP†† 120 V8	252a	184a	236a	169a	256a	259a	226
40 V2 120 V8	239a	193a	231a	161a	232b	263a	220
40 V4 120 V8	255a	199a	227a	166a	236b	265a	225
40 V6 120 V8	247a	195a	230a	177a	228b	263a	223
0 early 120 V8	253a	196a	215a	162a	242ab	249b	220
Site Ave. (reps)	248 (4)	192 (5)	227 (4)	167 (5)	238 (4)	260 (5)	222

†For any site, treatment yield values followed by the same letter are not significantly different at the 90 % level of confidence.
††AP = at planting.

120 lb N gives 220 bu/acre = 0.545 lb N/bu corn

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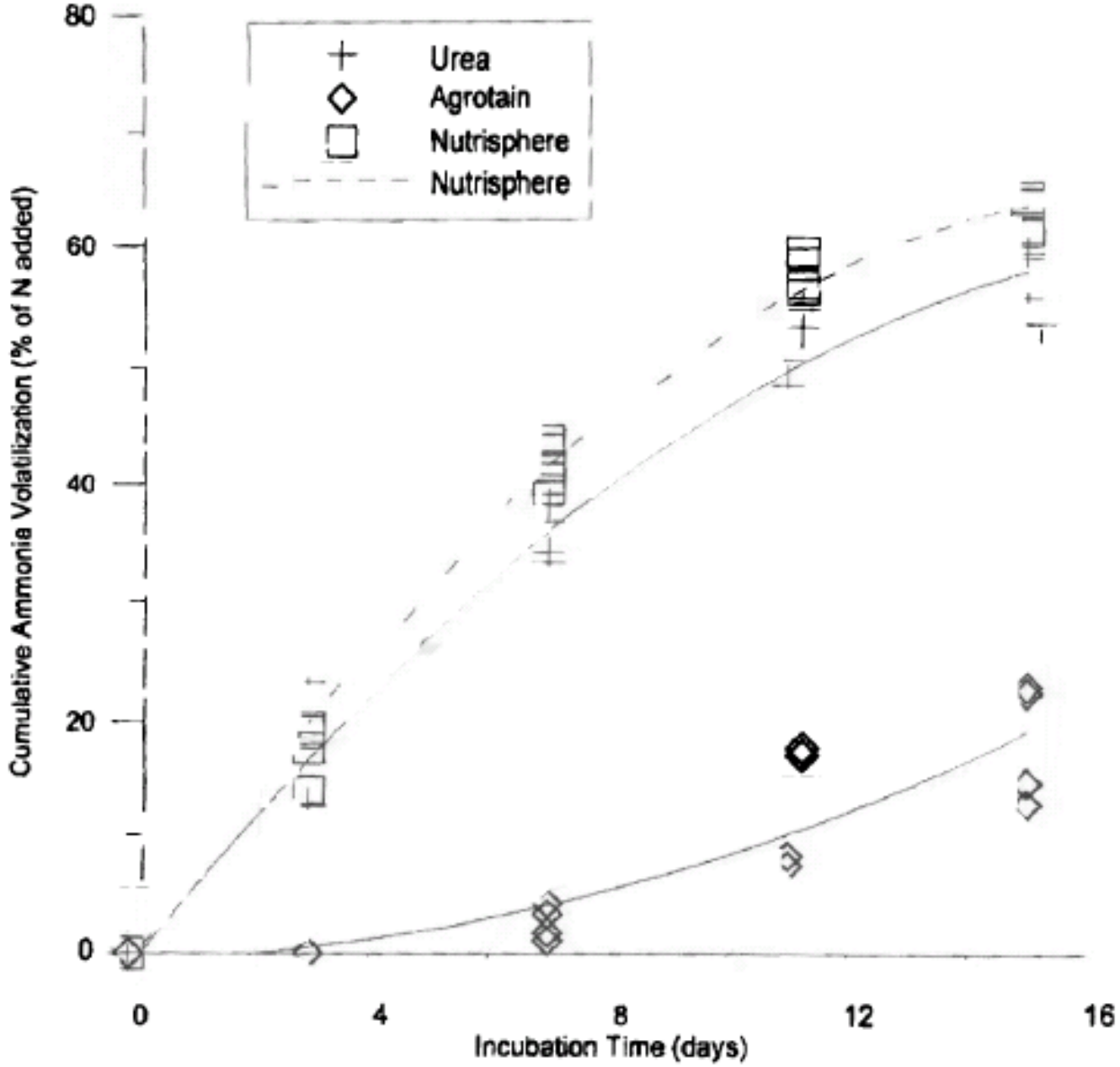
120 lb N/acre same as 160 lb N/acre and gives 220 bu/acre = 0.545 lb N/bu corn



Cumulative ammonia volatilization from urea, urea+Agrotain, and urea+Nutrisphere

R. Norman, Univ. of Arkansas

Additional Observations
Some Final Thoughts

The Right Rate of Generic NBPT

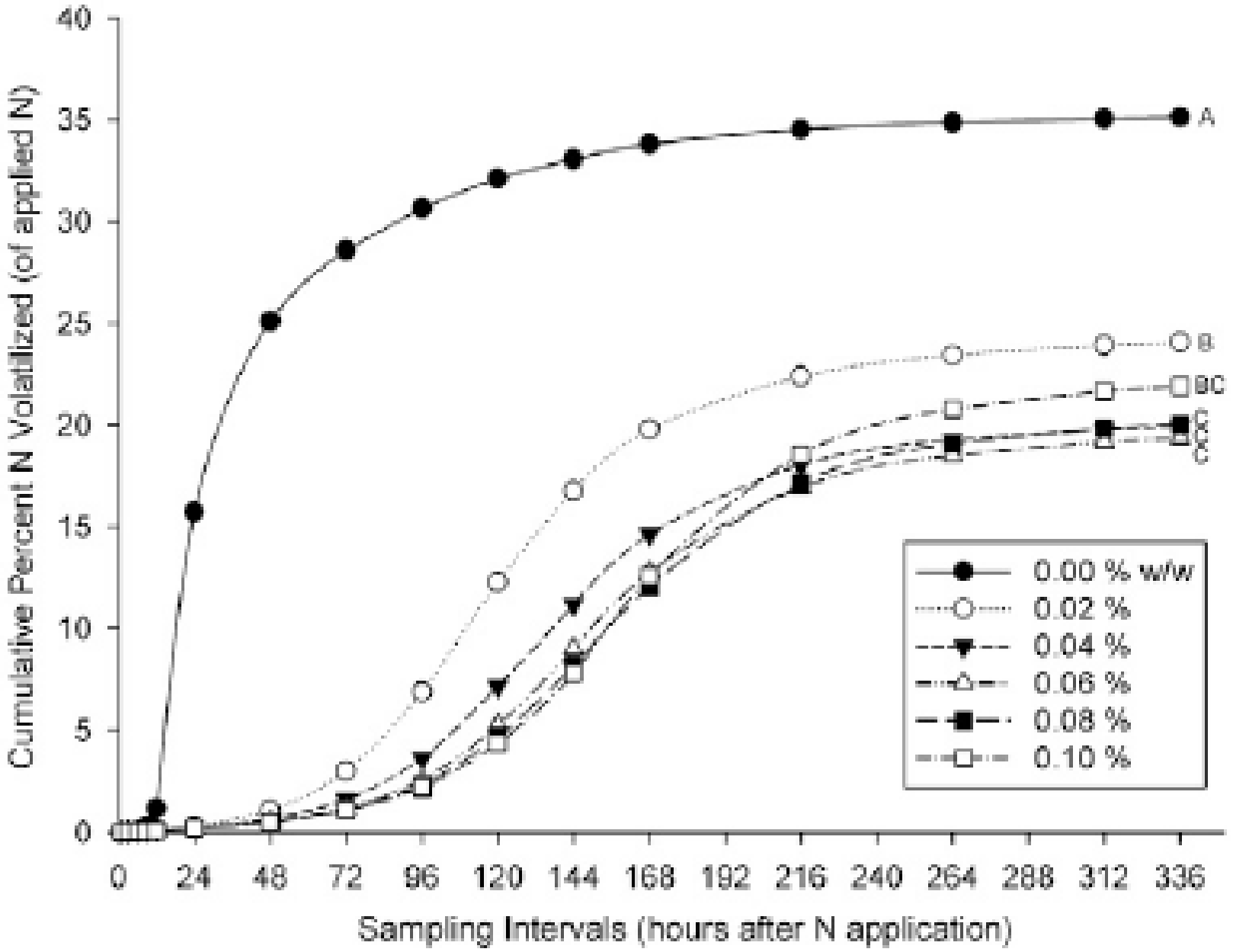
- NBPT rate is "per ton", not "per acre"; best at or somewhat greater than 1.2 lb ai/ton urea, 0.06 % ai, 600 ppm ai.
- Rate as low as 0.02 % ai, 0.4 lb ai/ton, substantially lowers total volatilization.
- That said, 0.04 % ai, 0.8 lb ai/ton, works pretty well in most instances.
- Latest Agrotain product weighs 10 lb/gal, is 30% NBPT = 3 lb ai/gal. Rate per ton of urea is 1.2 lb ai/3.0 lb ai/gal = 0.4 gal or 1.6 qt.

Laboratory NBPT Rate Research:

Rate as low as 0.02% ai greatly lowered total volatilization.

Rate of 0.04% ai worked better.

To get greatest ***delay*** in volatilization, need at least 0.06% ai, 1.2 lb ai/ton urea, (600 ppm ai).



Frame et al., 2012

Inhibitor Label Use Rates

Active Ingredient (ai)	Inhibitor Class	N Source Applied To	Use Rate
NBPT (Agrotain & other generics	urease	Urea, UAN	1.3 – 1.6 lb NBPT*/ton
NPPT (Limus – also contains NBPT	urease	Urea, UAN	0.26 – 0.38 lb NPPT/ton 0.75 – 1.15 lb NBPT*/ton
Duromide (Anvol – also contains NBPT	urease	Urea, UAN	0.94 lb duromide/ton 0.56 lb NBPT*/ton
Nitrapyrin (N-Serve, Instinct NXTGEN	nitrification	Anhydrous (N-Serve); Urea, UAN (Instinct NXTGEN)	0.25 – 1.0 lb ai/acre
Dicyandiamide (DCD)	nitrification	Urea (SuperU), UAN	12 – 17 lb ai/ton
Pronitridine (Centuro)	Nitrification	Anhydrous, UAN	3.725 lb/ton UAN 7.45 lb/ton anhydrous

Some Labels Make Applying Any Rate Difficult

Fertilizer Additive for Nitrogen Stabilization

NOT A PLANT FOOD INGREDIENT OR FERTILIZER

ACTIVE INGREDIENTS:
N-Butyl-thiophosphoric triamide (NBPT), hydroxyphenolic acids, diols, and pyrrolidones 100.00%

PRINCIPLE FUNCTIONING AGENTS:
NBPT, alcohols, paraffins, surfactants, emulsifiers and co-polymers
Total 100.0%

PATENT PENDING

CAUTION
KEEP OUT OF REACH OF CHILDREN

Guaranteed Analysis

17%.....N-(n-butyl)-thiophosphoric triamide (NBPT)
23%.....Dicyandiamide (DCD)
50-60%.....1-1'-sulfinylbis

PRECAUTIONARY STATEMENTS

STORAGE

Keep packaging closed, securely fastened and upright. Store away from food, drink and animal feed. Long-term storage temperatures above 100°F (38°C) and longterm storage of open containers may cause the product to degrade, and release harmful gases. Store between 14°F (-10°C) and 100°F (38°C). Rotate stock, so that oldest product is used first.

Some Labels Make Applying Enough AI Difficult

Other hazards which do not result in classification

Repeated or prolonged contact with skin may cause dermatitis.

SUPPLEMENTAL LABEL INFORMATION: Restricted to professional users. Do not apply directly to soil, always mix with fertilizer for application.

For Chemical Emergency:

FOR EMERGENCIES INVOLVING A SPILL, LEAK, FIRE, EXPOSURE OR ACCIDENT CONTACT: CHEMTREC 800-424-9300 within the United States and Canada, or 703-527-3887 for international collect calls.

FIRST AID

Have the product container with you when calling a poison control center or doctor, or going for treatment.

IF IN EYES: Immediately call a poison center, doctor or physician. Rinse cautiously with water for several minutes. Remove contact lenses if present, after the first 5 minutes, then continue cautiously rinsing eye.

IF ON SKIN OR CLOTHING: Take off contaminated clothing and wash

post-planting applications. The benefit of N-Edge Pro as a urease and nitrification inhibitor is a result of its ability to retard the hydrolysis of urea and control volatility, preventing ammonia loss while the urea is on the soil surface, as well as to prevent ammonium loss in the form of nitrates or nitrous oxide by runoff or denitrification.

Many factors in the environment contribute to volatilization. These factors should be considered when choosing the appropriate rate:

1. High soil moisture
2. Drying conditions (sun, wind, and humidity)
3. High temperatures
4. High soil pH
5. Length of control needed

N-Edge Pro recommended use rate:

UREA	3 qt/ton UREA
UAN	1.5 qt/ton UAN
Liquid Manure	8-32 oz/A

Guaranteed Analysis
17%.....N-(n-butyl)-thiophosphoric triamide (NBPT)
23%.....Dicyandiamide (DCD)
50-60%.....1-1'-sulfinylbis

PRECAUTIONARY STATEMENTS
Combustible Liquid. Causes serious eye damage. Suspected of
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IF ON SKIN OR CLOTHING: Take off contaminated clothing and wash

STORAGE
Keep packaging closed, securely fastened and upright. Store away from food, drink and animal feed. Long-term storage temperatures above 100°F (38°C) and longterm storage of open containers may cause the product to degrade, and release harmful gases. Store between 14°F (-10°C) and 100°F (38°C). Rotate stock, so that oldest product is used first.

Application Rates: N-Edge Pro is a nitrogen stabilizer specific for

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is
n of

17% NBPT x 9.76 lb/gal x 0.75 gal/ton urea
= 1.24 lb NBPT/ton -- an acceptable rate

23% DCD x 9.76 lb/gal x 0.75 gal/ton urea
= 1.68 lb DCD/ton -- an unacceptable rate

Should reduce volatilization. Won't do anything about nitrate-N leaching or denitrification.

Liquid Manure	8-32 oz/A

Summary

- The suite of reliable nitrification and urease inhibitor/N stabilizer products will continue to slowly grow (new chemistry has been found and is being evaluated).
- The suite of unreliable inhibitor/stabilizer products will also likely continue to grow.
- Many are called. Fewer are effective.

Nitrogen

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