Nitrogen Extenders for Nitrogen Fertilizers

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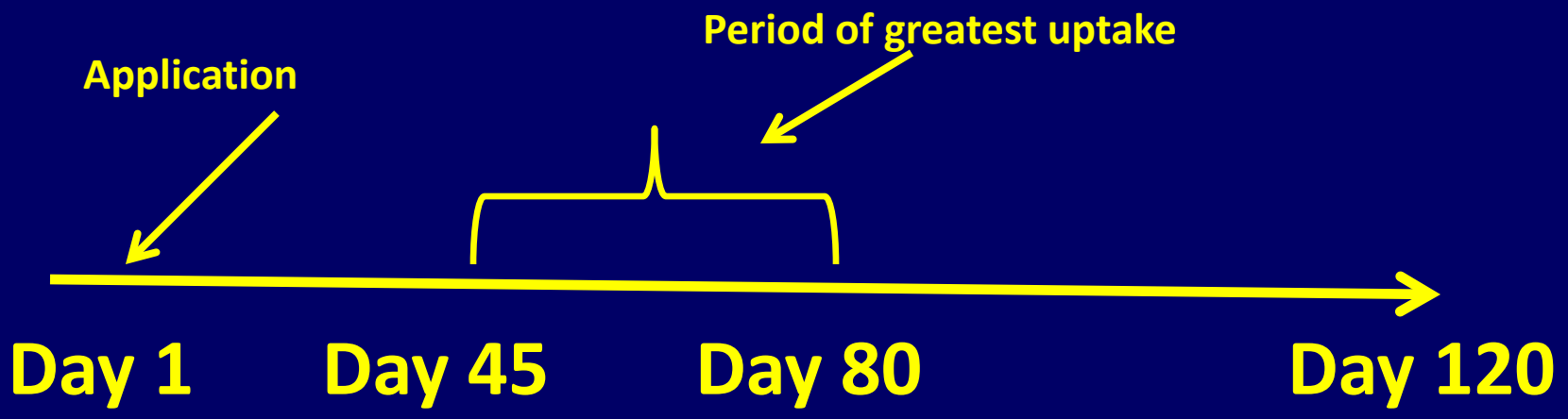
Three main avenues for loss

Ammonia volatilization from urea

Nitrification

Denitrification

Corn N timeline



-Nitrification inhibitors

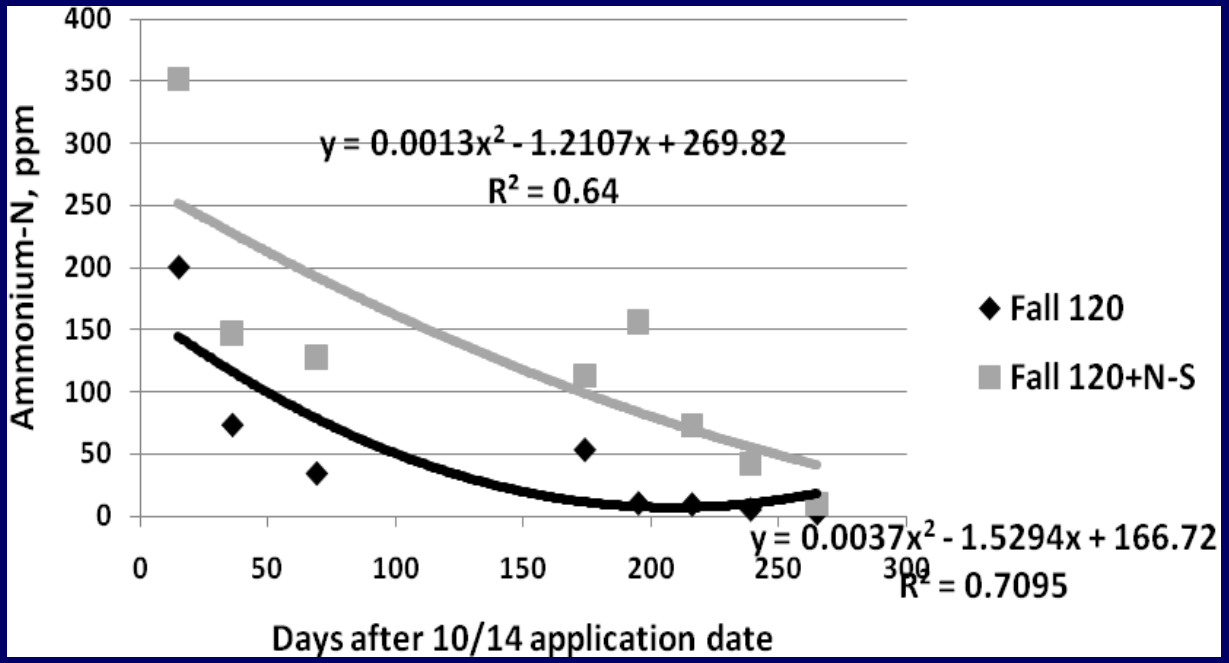
-Urease inhibitor additives

-Nitrification and urease inhibitor

Nitrification inhibitors-

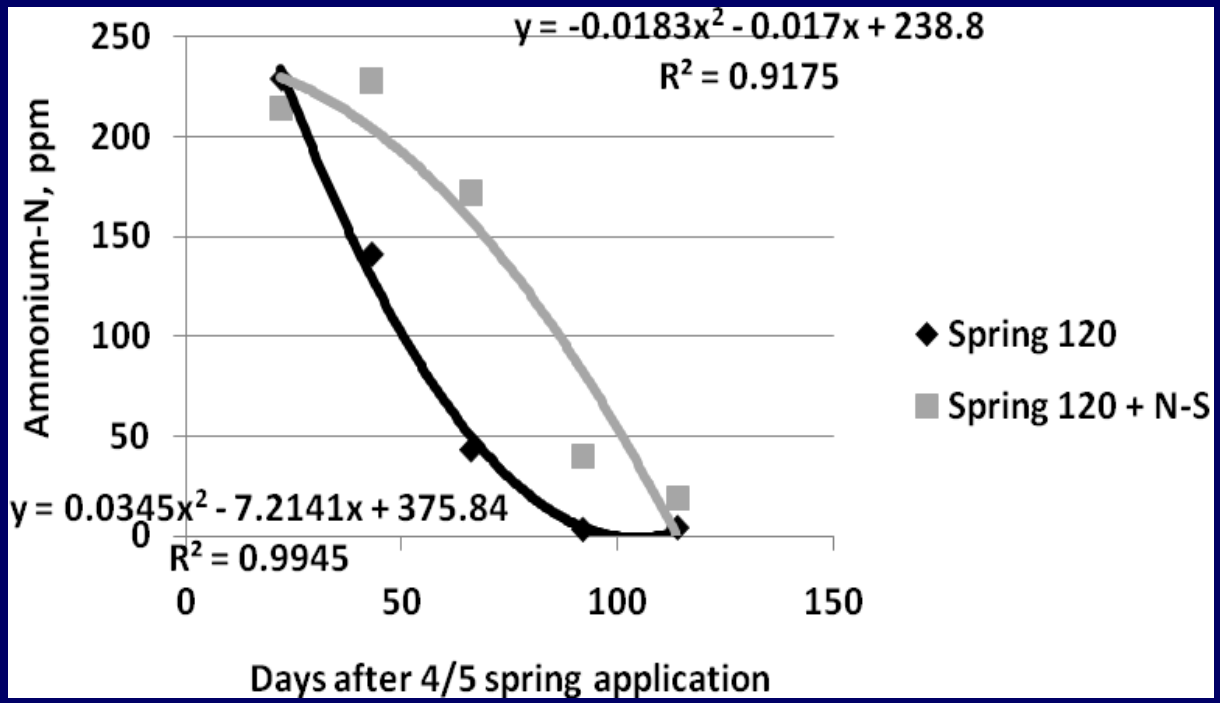
N-Serve® /Instinct®
nitrapyrin (2-chloro-6-[trichloromethyl] pyridine)

DCD, dicyandiamide



Fall N, Touchton et al., 1978

Spring N,Touchton et al., 1978



Some studies showed a yield increase with N-Serve, while others showed no yield increase. Yield increases were more a result of weather between application and N uptake rather than performance of the product.

Yield increases over the seven years in Minnesota were 15 bushels per acre more for fall anhydrous ammonia + N-Serve over fall anhydrous ammonia alone, and 27 bushels per acre more for spring anhydrous ammonia compared to fall anhydrous ammonia (Randall et al., 2008).

Instinct® is a new formulation of Nitrapyrin that can be mixed with ammonium fertilizers and can stay on the soil surface without incorporation.

Research so far at Minnesota, Illinois, Iowa and Nebraska have shown little yield benefit to the use of Instinct over N fertilizer alone, although the product inhibits nitrification.

(Kentucky, Schwab, unpublished data)

Wisconsin-

Corn yield increase with Instinct in 2008, but not 2009.

DCD- a nitrification inhibitor

Found in

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

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

From Malzer et al., 1989

Yield increases in potato with DCD were more consistently achieved with potato in the Malzer survey.

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)

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

Indiana- Purdue, unpublished work by Phillips, Mengel and Walker, 1989.

	Corn Yield bu/acre
Urea surface applied	130
Urea surface applied +Agrotain	143

Illinois, average of four southern Illinois locations, Varsa et al., 1999.

	Corn Yield bu/acre
Urea surface applied	106
Urea surface applied +Agrotain	125

Nitrification and urease inhibitors

Ammonium thiosulfate

Nutrisphere®

ATS has nitrification and urease inhibiting properties.

It is not as effective generally as nitrapyrin, DCD, or NBPT.

ATS is most effective as a nitrification inhibitor at concentrations of 25 ppm S. (0.1% ATS)

Under warm conditions (>60^{o} F), mineralization is complete in a week.

Under cooler temperatures, mineralization is slower; about 3 weeks.

In a fall application of aqua ammonia with ATS compared with nitrapyrin, similar ammonia concentration was found in the spring with the two products (Goos and Johnson, 1999.)

ATS affects the both steps of nitrification- ammonium to nitrate and nitrite to nitrate.

Higher than recommended concentrations of ATS can result in an accumulation of nitrite. Studies that used the recommended concentration of ATS did not see an accumulation of nitrite.

Nutrisphere,
SFP Specialty Products, LLC, Leawood, KS

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

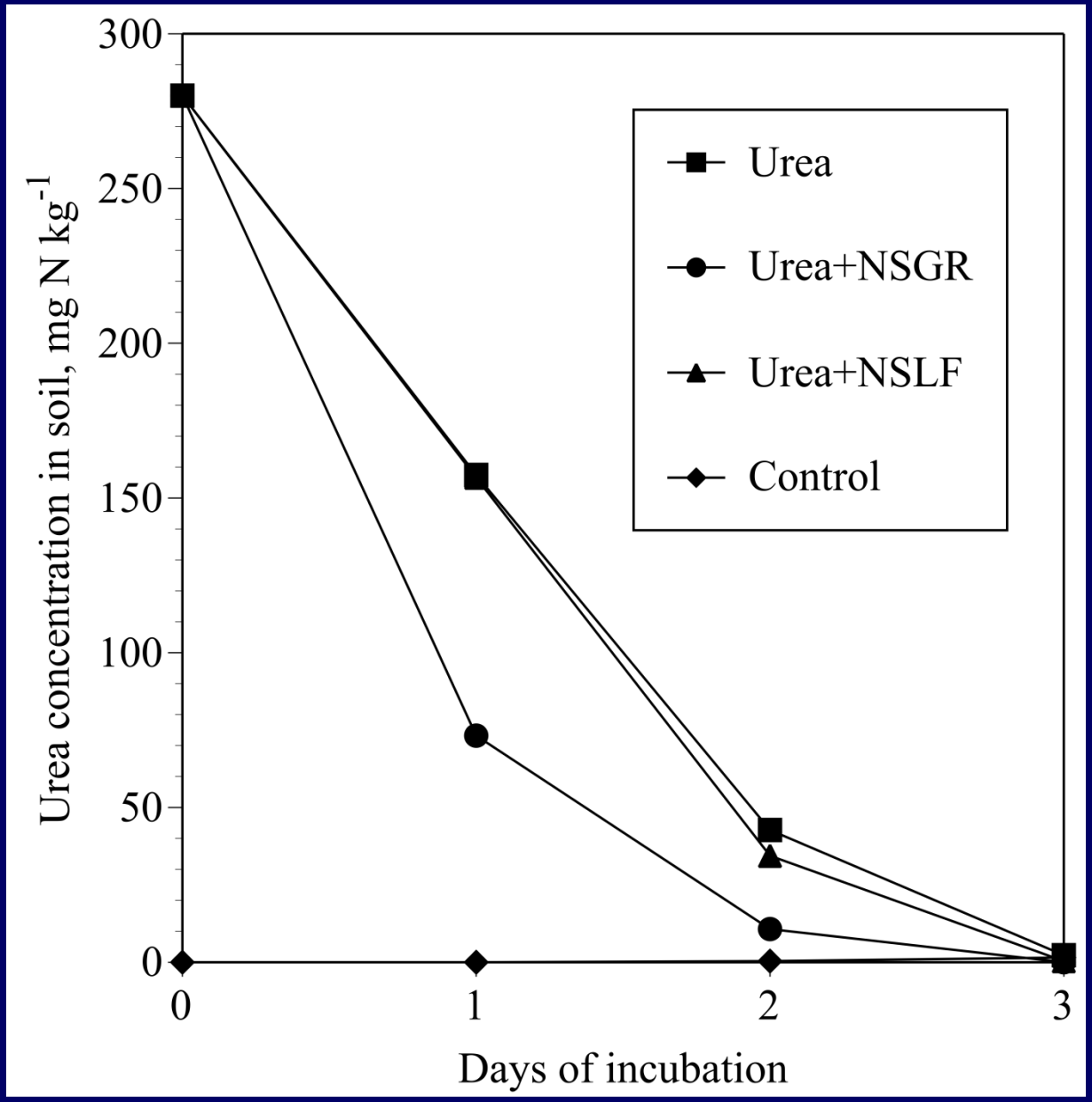
Formulation for liquid fertilizer-
40% maleic-itoconic copolymer, pH 1-2

Product literature states that nitrification inhibition is based on product ability to tie-up copper- a critical metal used by nitrification bacteria.

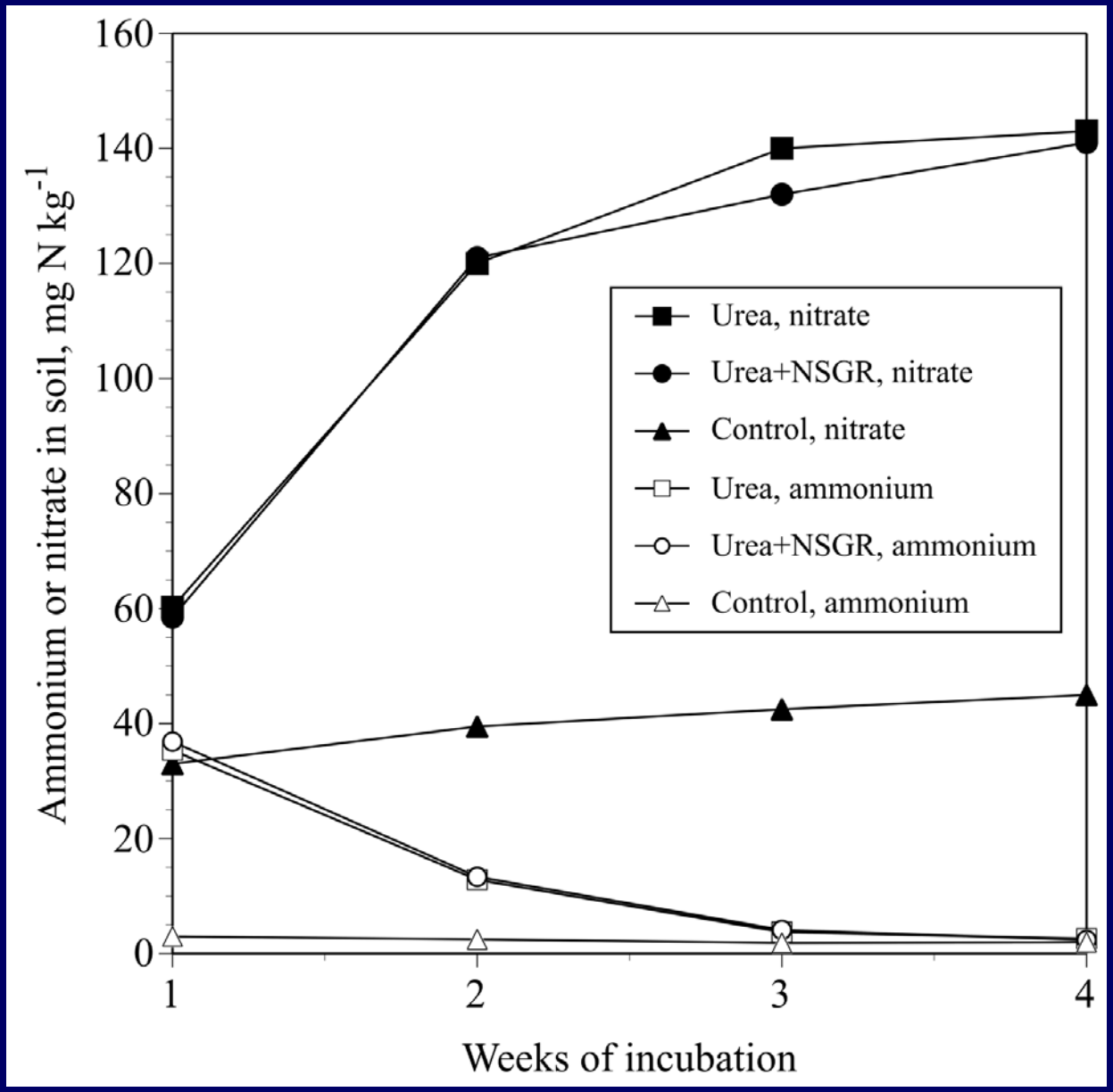
Inhibition of urease activity is due theoretically to a tie-up of soil nickel- a critical metal constituent of urease enzyme.

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.

Treatment	Yield, bu/acre	Earleaf N, %	Grain N, %
Check	152	1.72	1.13
Urea/UAN	168	2.57	1.26
ESN	185	2.96	1.33
Nutrisphere-N	183	2.96	1.35
Agrotain	183	2.98	1.36
LSD 5%	6	0.09	0.04



(Research by R.J. Goos, in Franzen et al., J. Plant Nut 2011)



(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)

N sources	Days after N source application			
	3	7	11	15
	Cumulative NH_3 loss, % of N applied			
Urea	14.5	35.9	51.8	56.9
Ammonium sulfate	0.1	0.2	0.5	0.6
Urea + NBPT†	0.006	2.7	12.9	18.3
Urea + 0.25% NSN	17.6	42.2	57.8	62.7
LSD(0.05)‡	12.2			
LSD(0.05)§	9.6			

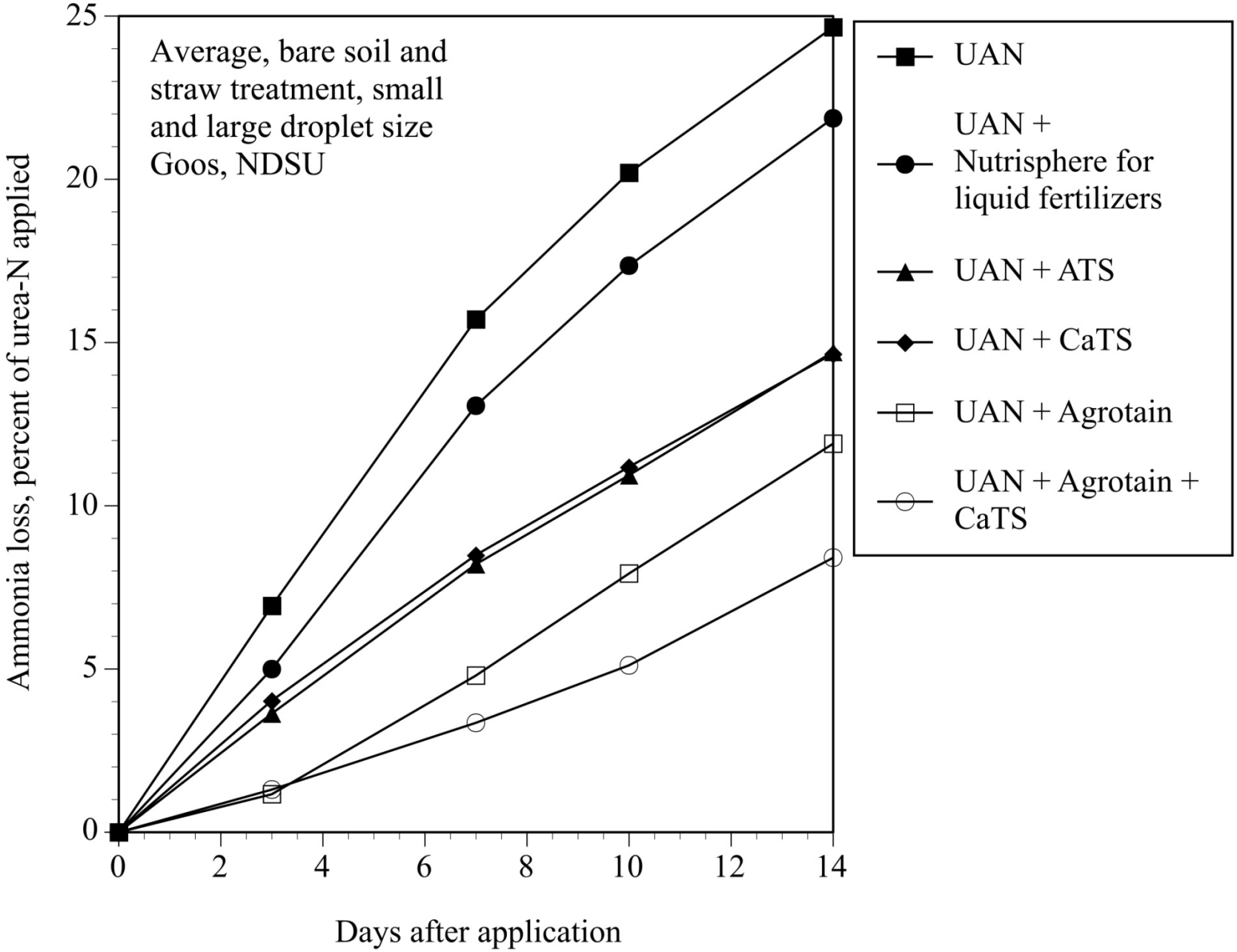
More recent laboratory studies by Dr. Goos

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

Goos, 2012


Goos, 2012



- Goos, 2012 (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).

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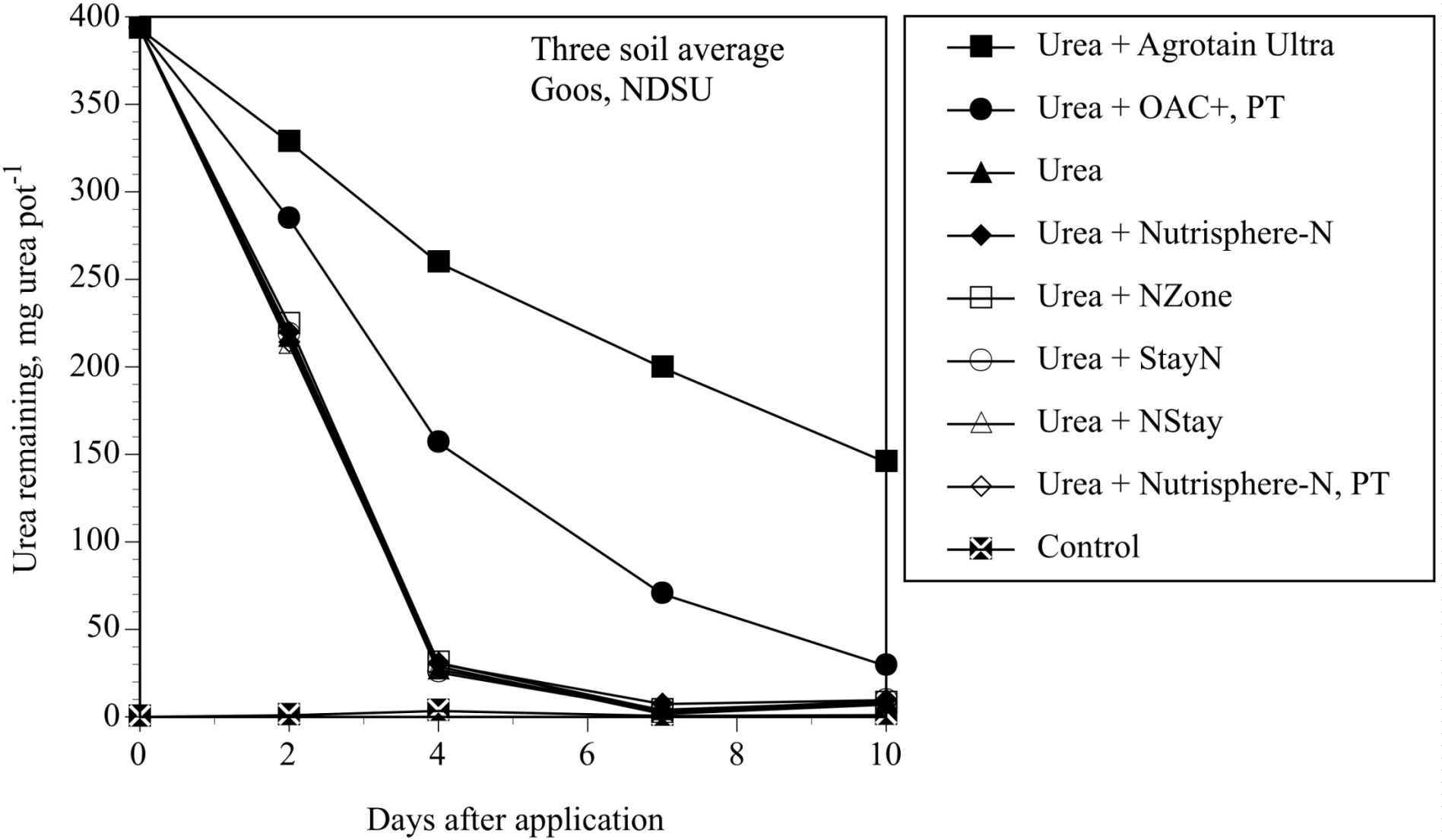
Goos, 2012

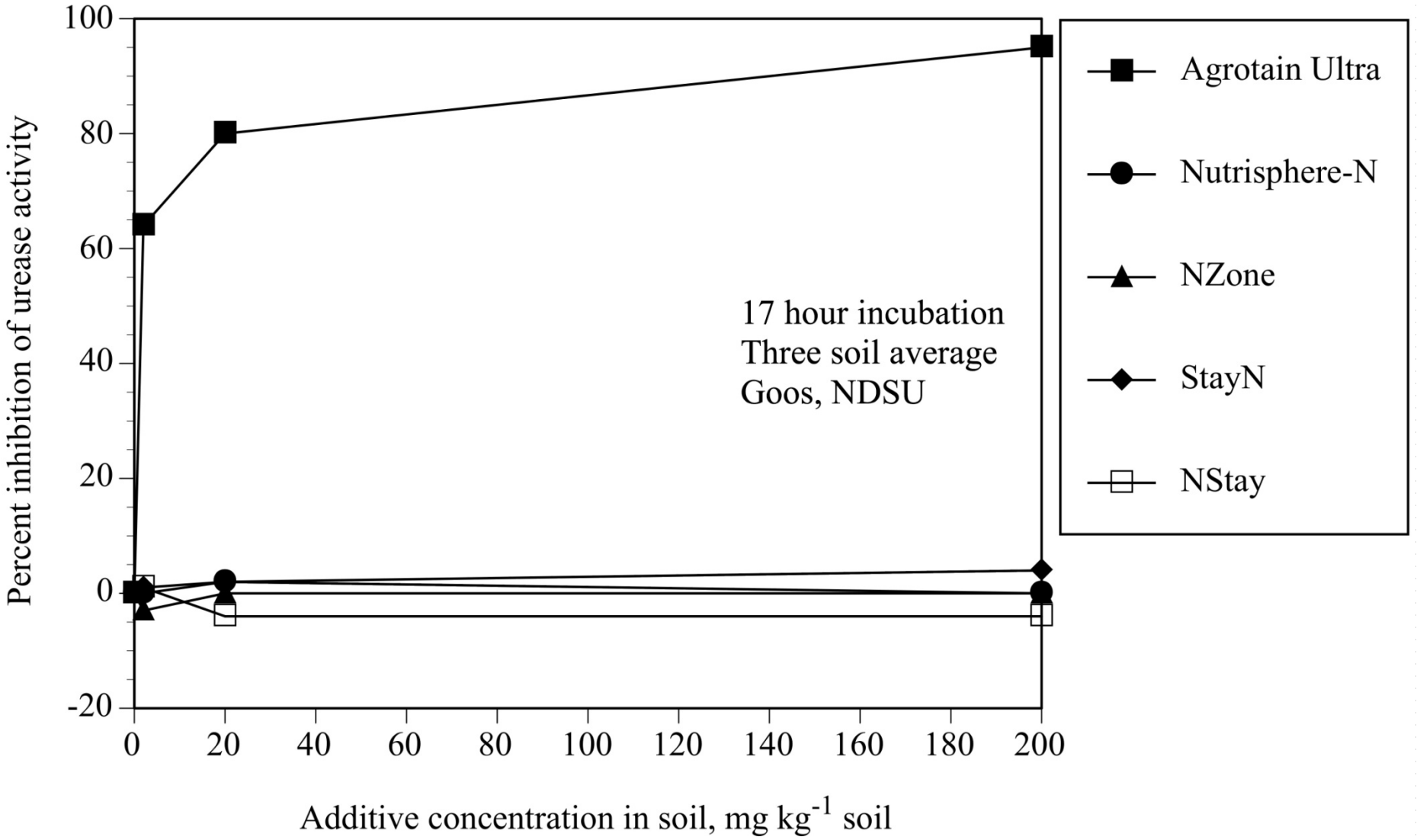


- Goos, 2012, unpublished

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

Goos, 2012

Goos, 2012



- Goos, 2012 unpublished

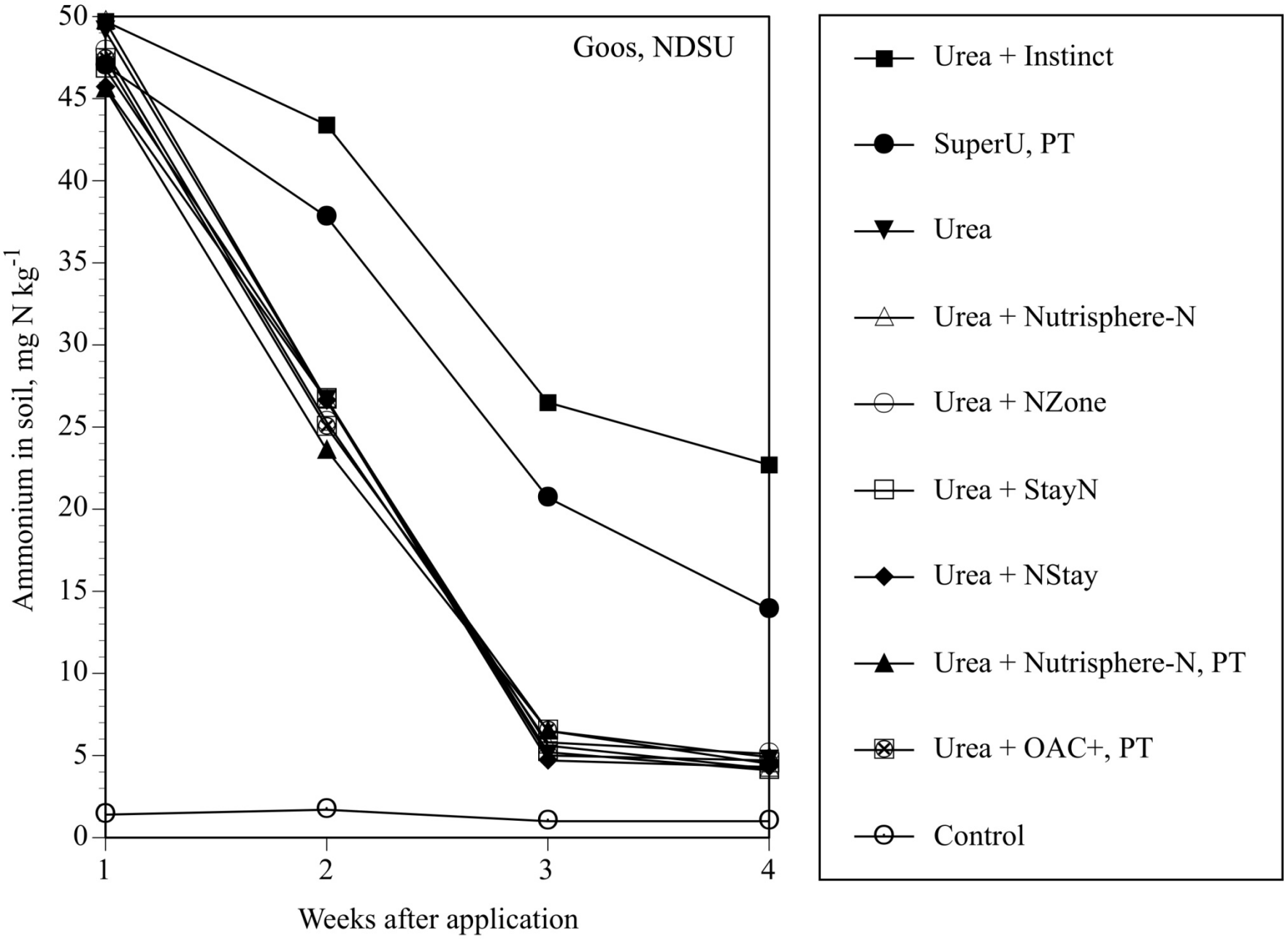
Nitrification studies

- Urea granules incubated with soil with minimal water movement
- Residual ammonium determined after 1, 2, 3, and 4 weeks

Goos, 2012

Goos, 2012

Goos, 2012



- Goos, 2012 unpublished

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

Goos, 2012

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

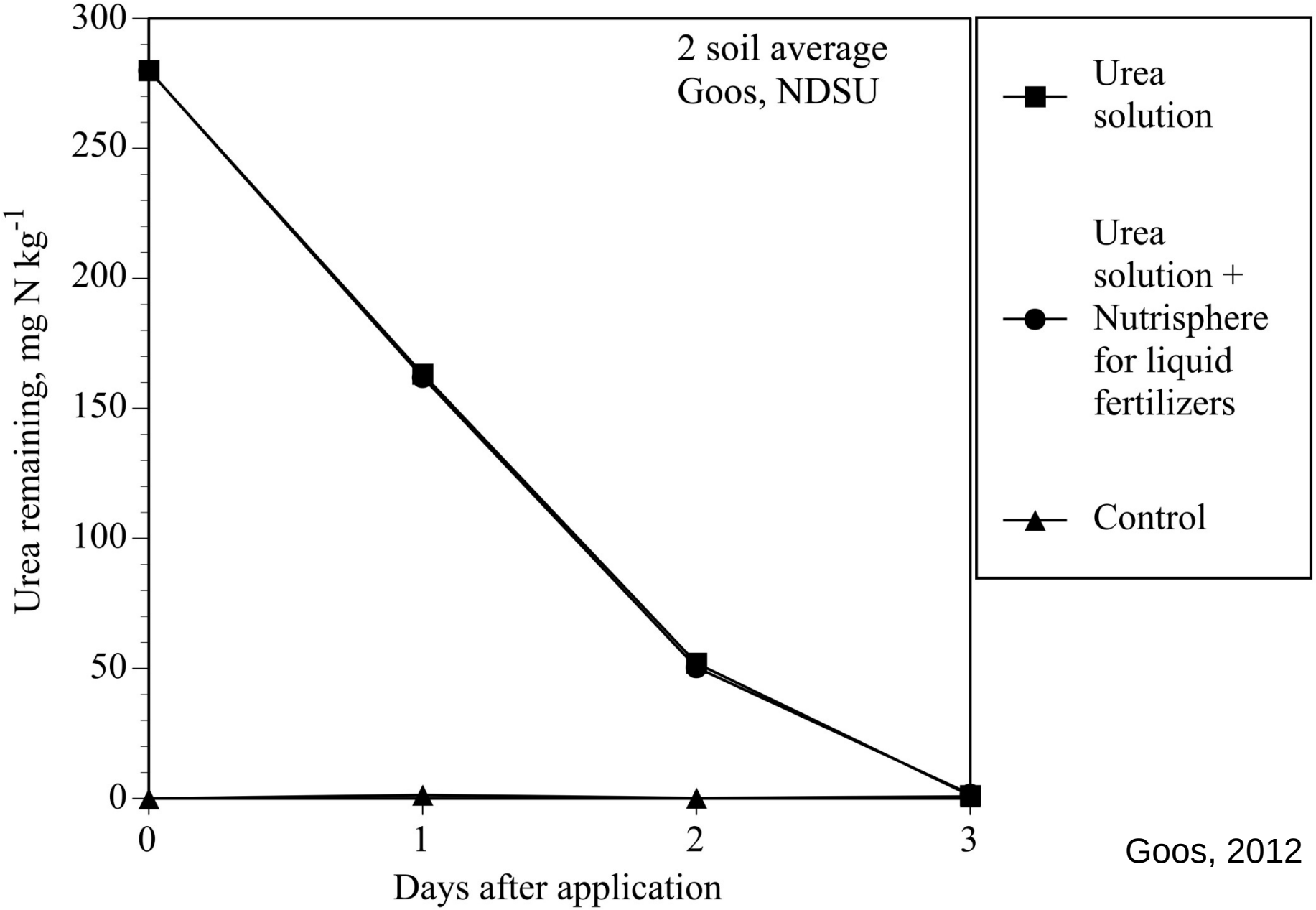
- Presented at American Society Agronomy meetings, Cincinnati, OH, October, 2012, R.J. Goos

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

Goos, 2012

Experiment 1



Goos, 2012

Experiment 2

- 100 kg/ha of N:

  granular urea,

  urea + NSN,

  urea + NSN, pretreated (PT),

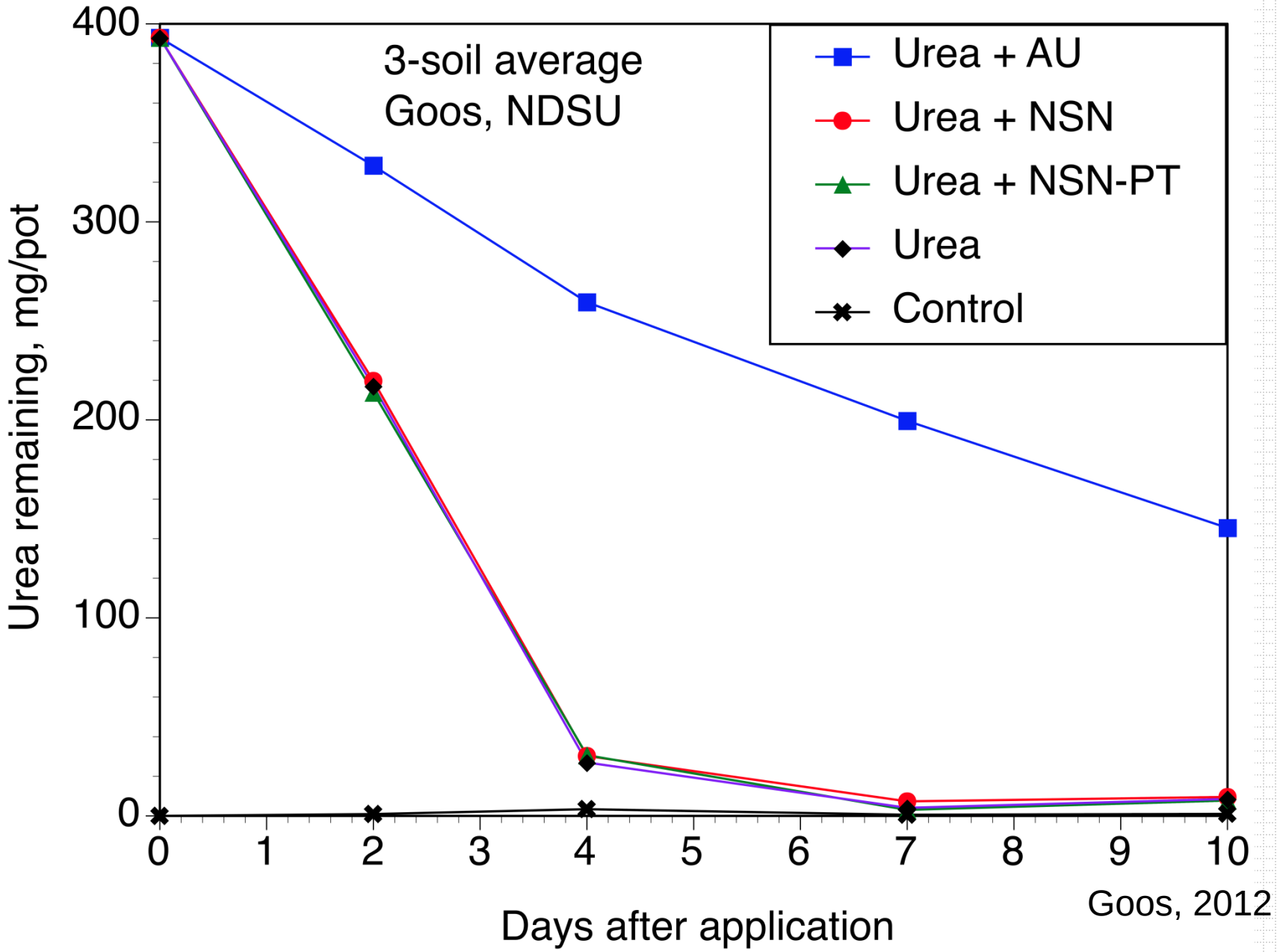
  urea + Agrotain Ultra (AU)
- 500 g of soil
- Residual urea

  measured after

  2, 4, 7, and 10 days

Goos, 2012

- Experiment 2

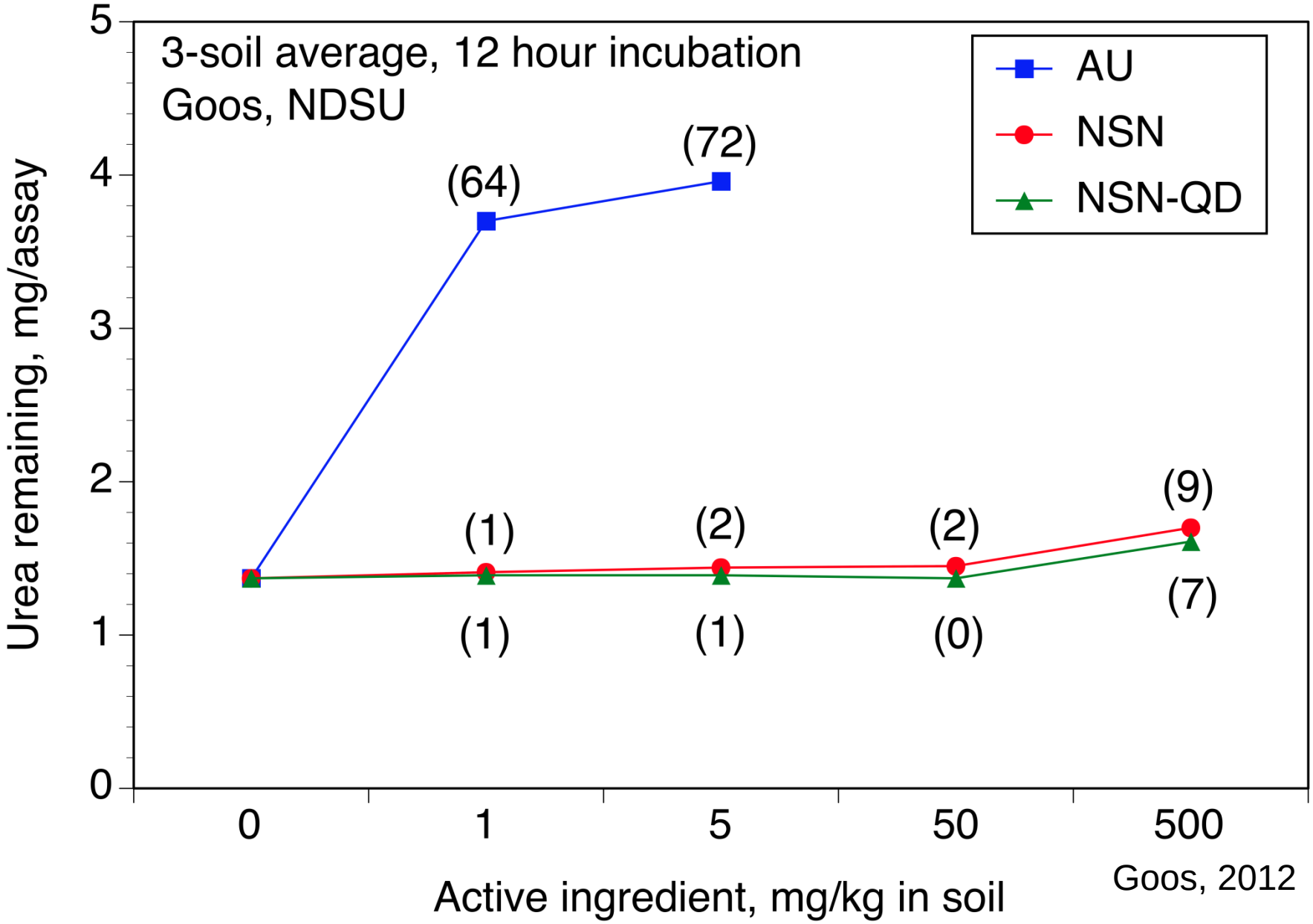


- Experiment 3
- 10 g soil, field capacity
- 5 mg urea (500 mg/kg), alone or with:
- 1 to 500 mg MIP/kg, as NSN for granular urea (NSN) or NSN Quick Dry for granular urea (NSN-QD)
- 1 or 5 mg NBPT/kg, as Agrotain Ultra (AU)
- 12 hour incubation, 25 C
- Residual urea determined

Goos, 2012


Goos, 2012

Experiment 3 (% Inhibition)



- 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.

Goos, 2012

- "In the soil the high negative charge density of Nutrisphere-N sequesters nickel essential for bacterial production of the metalloenzyme urease."[3]

- [3]Tindall and Mooso. Proceedings of the Western Nutrient Management Conference, 2011.

Goos, 2012

- 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

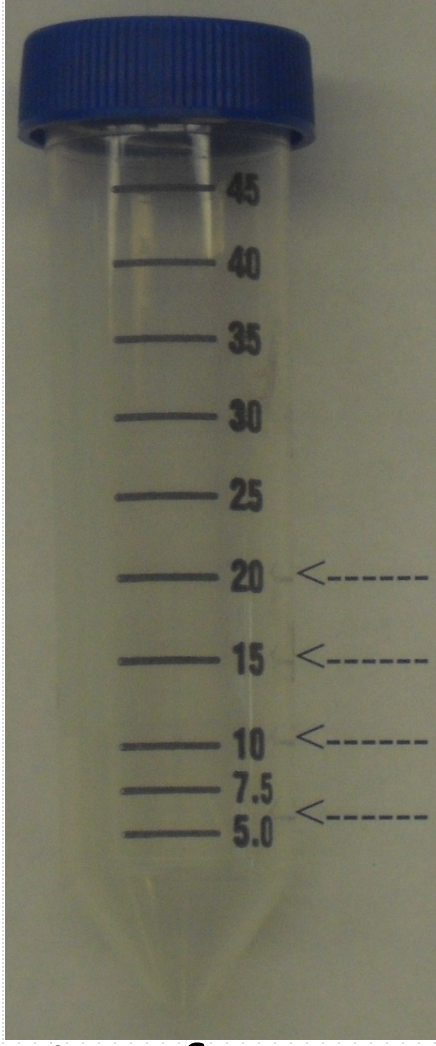
Goos, 2012

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

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

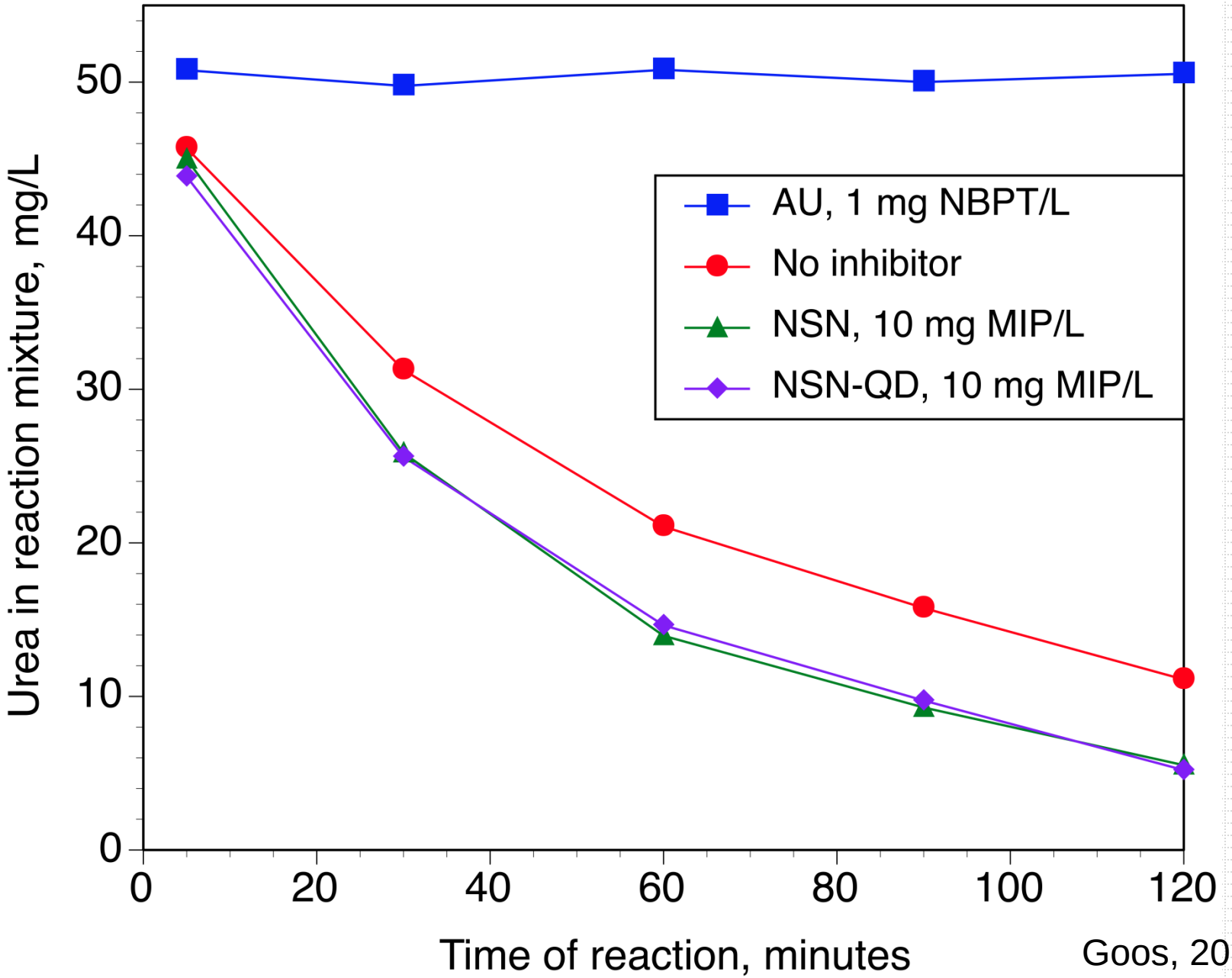
Goos, 2012

- 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



Goos, 2012

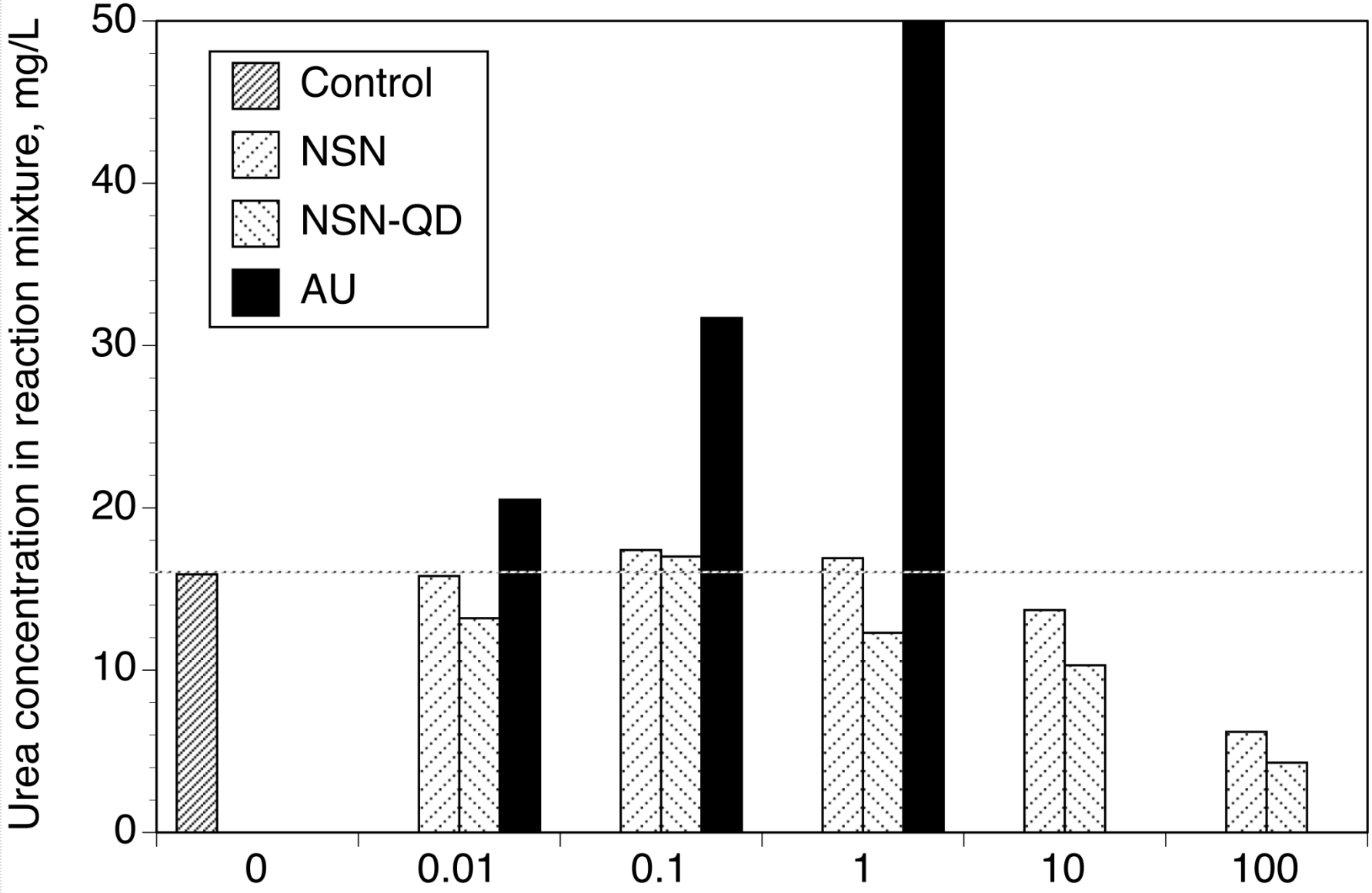
- Experiment 5



- 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

Goos, 2012

Laboratory studies clearly show that Nutrisphere has no nitrification or urease inhibiting properties. What is most curious is why some studies show some response.

	No Response	Positive
North Dakota	10	0
Kansas	7	5 (4 at Scandia)
Minnesota	2	0
Illinois	3	1
Arkansas/Mississippi	3	0

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-

Nitrapyrin and DCD are proven nitrification inhibitors. Their use is limited due to the inability to predict when they would be economically beneficial. Growers tend to use these products to push their timing and spread work loads, rather than use them to improve overall N use efficiency

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 nitrification and 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 nitrification or urease inhibition properties and should not be used for these purposes.

The mode of action 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.