

Chemistry of N Fertilizer Additives

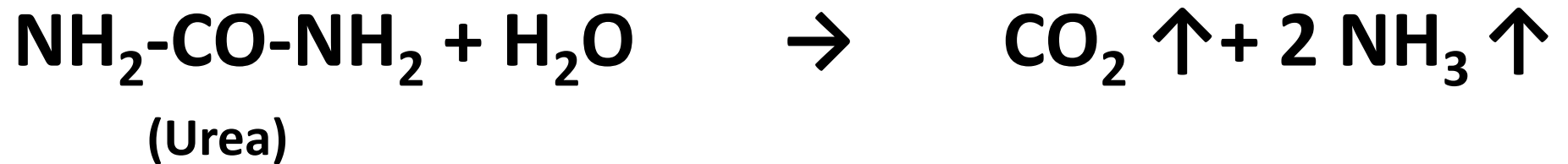
**Dave Franzen, PhD
Professor Soil Science
Extension Soil Specialist
North Dakota State University**

Focus on two processes-

**Ammonia volatilization from urea
caused by the action of urease enzyme**

**Nitrification- bacterial oxidation of
ammonium to nitrate**

Urea is subject to ammonia volatilization if placed on or near the surface.



**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)	117 d*
Urea	158 c
Urea + Agrotain	201 b
SuperU	201 b
UAN	150 c
UAN + Agrotain	179 bc
UAN + Agrotain Plus	175 bc
Ammonium nitrate	239 a

Ammonia volatilization from surface and incorporated urea at various depths-

Rochette et al., 2014, J. Env. Q.

Period-hours	Surface (% loss)	1 inch (% loss)	2 inch (% loss)	3 inch (% loss)
0-166	2.2	18.4	2.6	0.0
167-334	29.5	15.2	3.2	0.1
335-502	15.2	3.8	1.8	0.5
503-598	3.4	1.0	1.0	0.0
Total	50.3	38.4	8.6	0.4

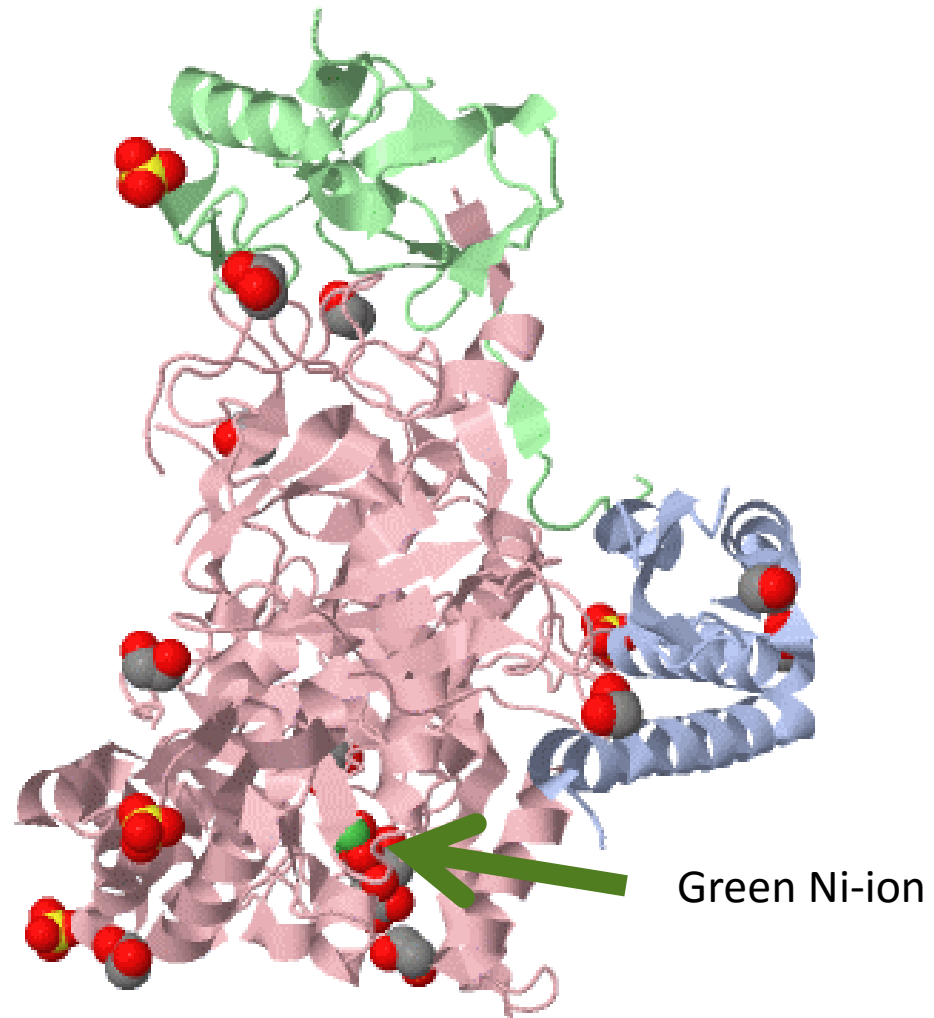
Slightly acid silt loam soil

Urease is produced by plants, bacteria, fungi, invertebrates and is one of the last compounds to degrade after the organism dies.

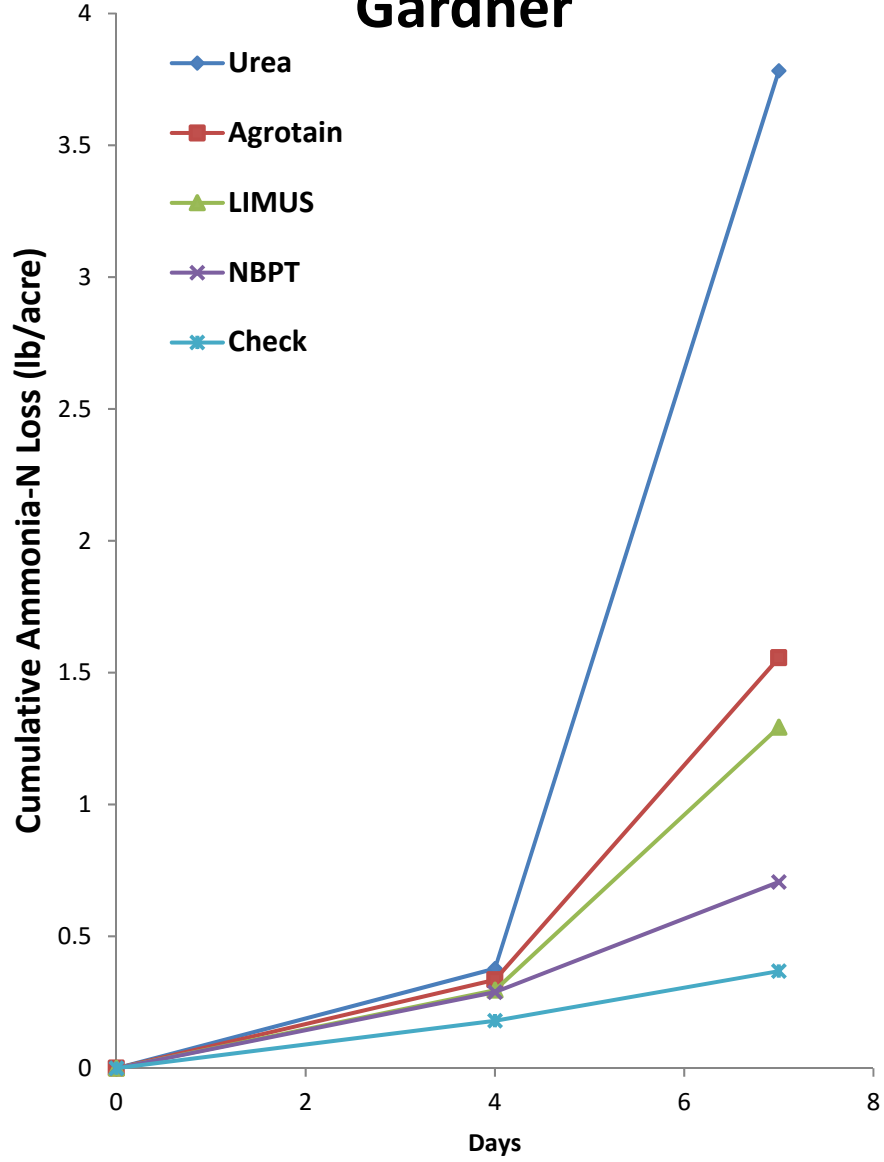
'The Zombie Enzyme'

Urease enzyme

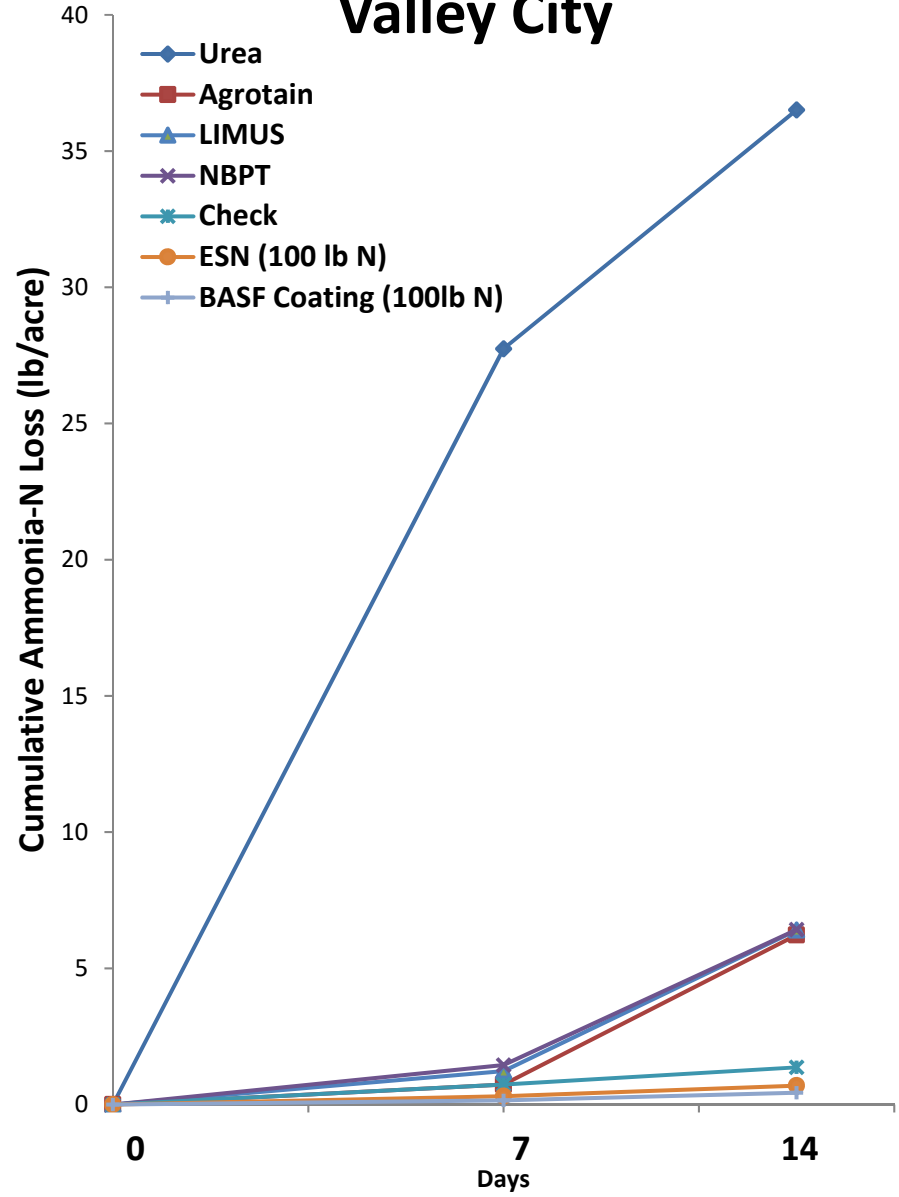
<http://www.proteopedia.org/wiki/index.php/Urease>



Gardner



Valley City

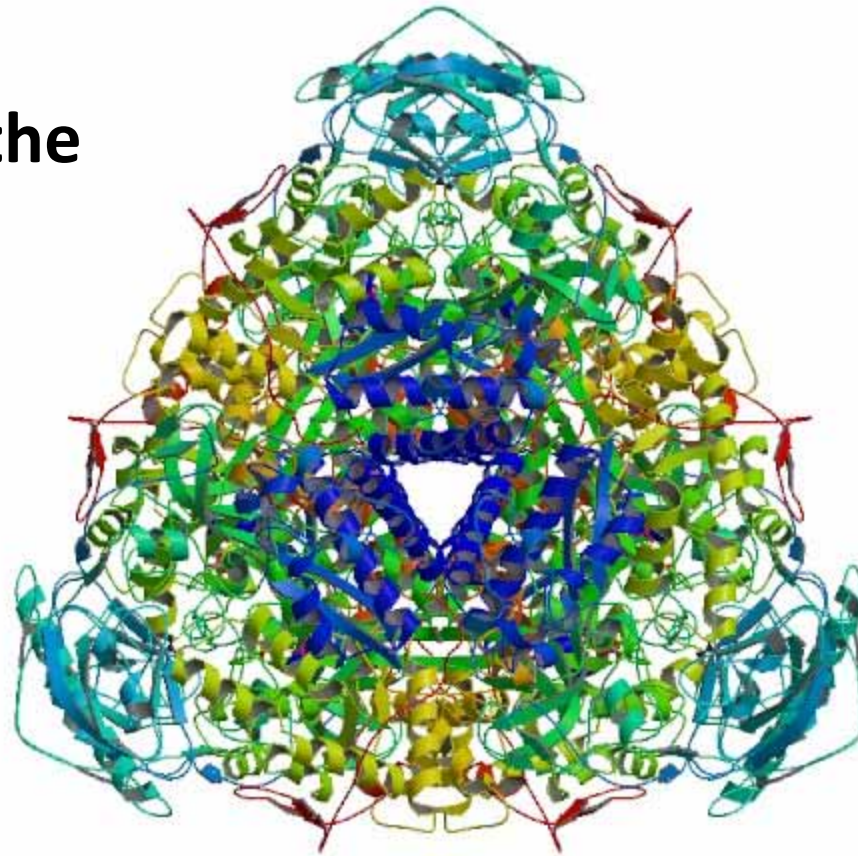


Ammonia volatility from surface/near surface application increases with

Residue

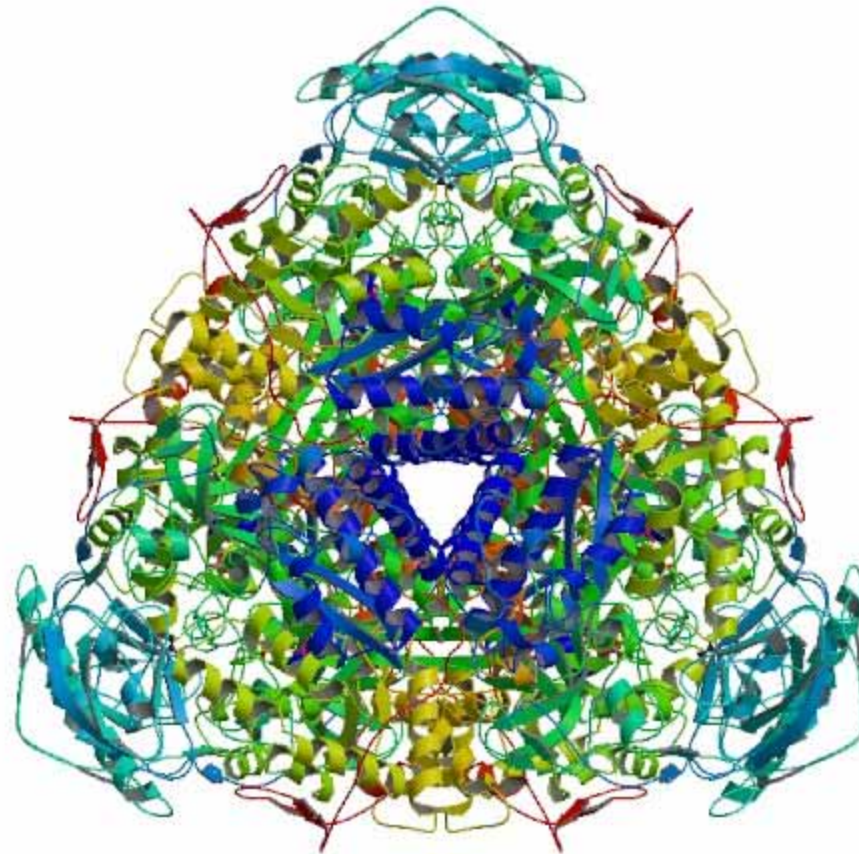
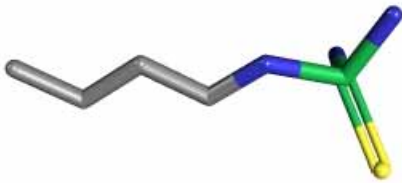
Soil pH

**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.

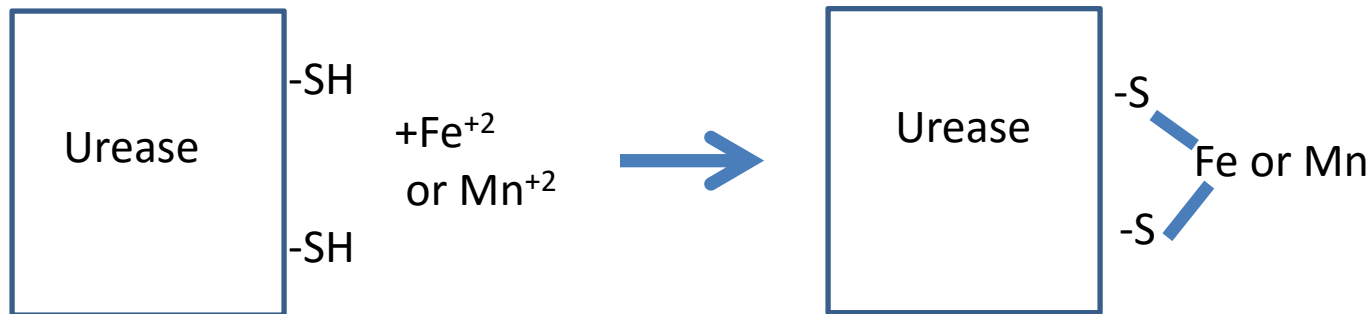
**NBPT (Agrotain and siblings)
and
NPPT (Limus)**

**are the only chemistries known to inhibit
urease activity for days (usually about 10)**

**Ammonium thiosulfate has measureable
short-term activity, but NBPT is much better.**

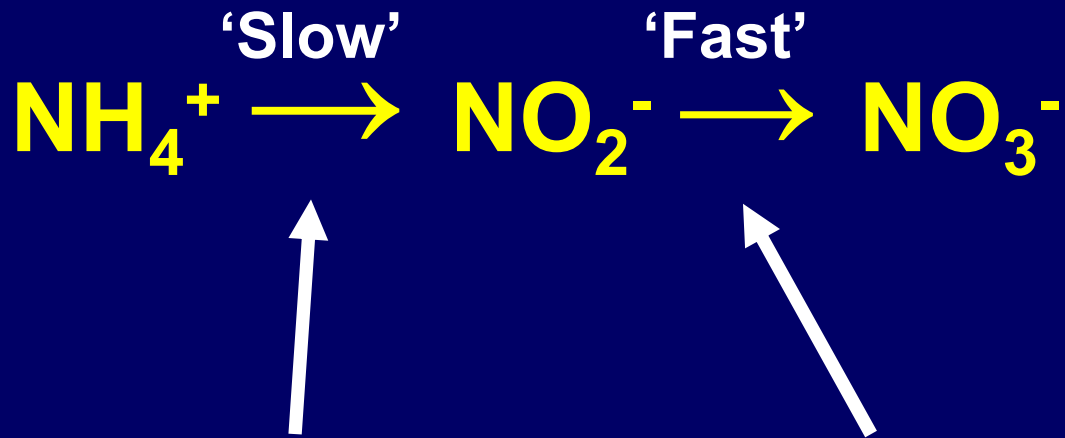
ATS does not directly affect the urease enzyme and is only indirectly inhibiting after interacting with soil-

Thiosulfate reacts rapidly and abiotically with soil, forming tetrathionate and liberating Fe²⁺ and Mn²⁺



Adapted from Goos, 1987, NC Ext. Ind. Soil Fertility Conf.

Nitrification-



Nitrosomonas spp *Nitrobacter spp*

Factors influencing rate of transformation-

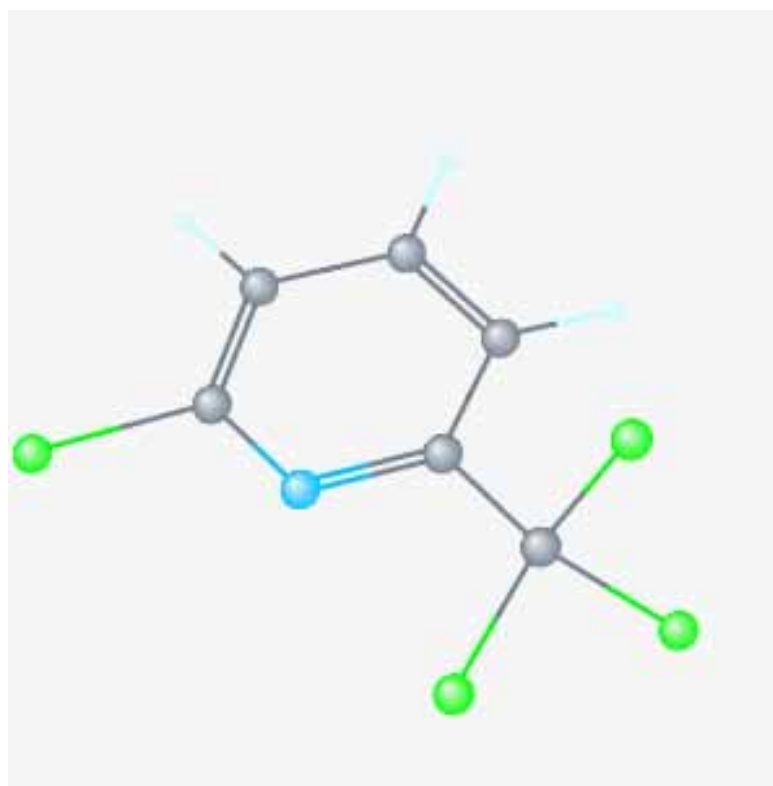
Moisture (moist, not saturated)

Temperature- max ~ 80F, min 32F

pH- favored by pH > 7 slowed by pH < 6

Nitrapyrin-

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

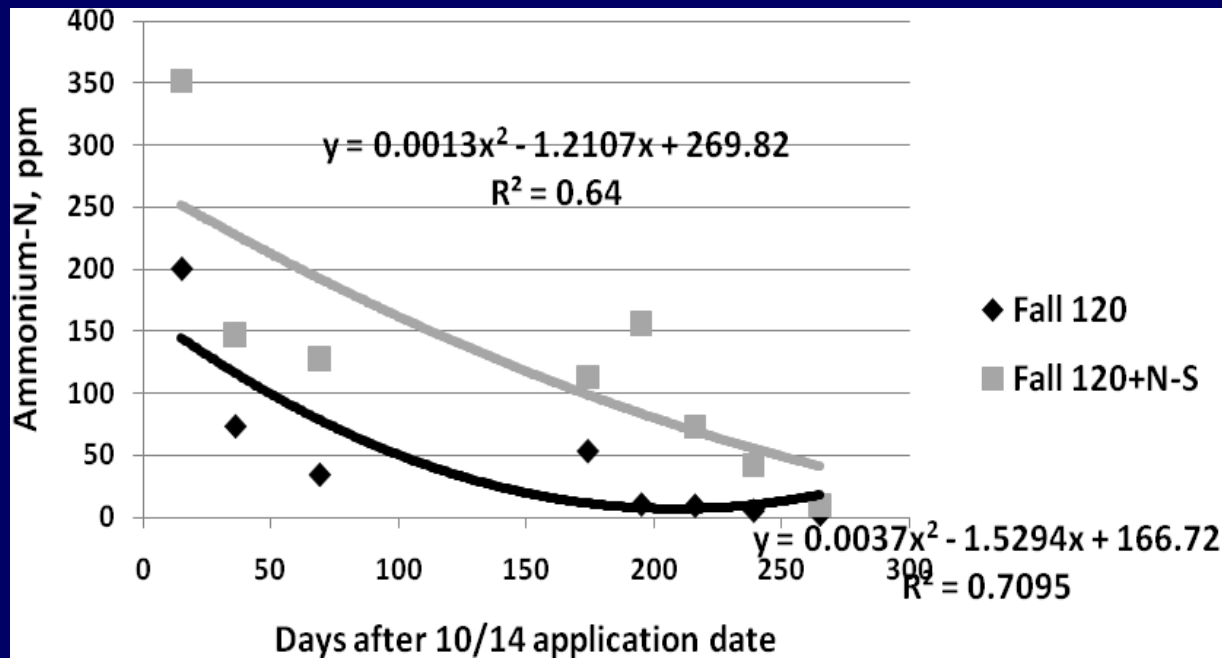


From PubChem

<https://pubchem.ncbi.nlm.nih.gov/compound/nitrapyrin#section=3D-Conformer>

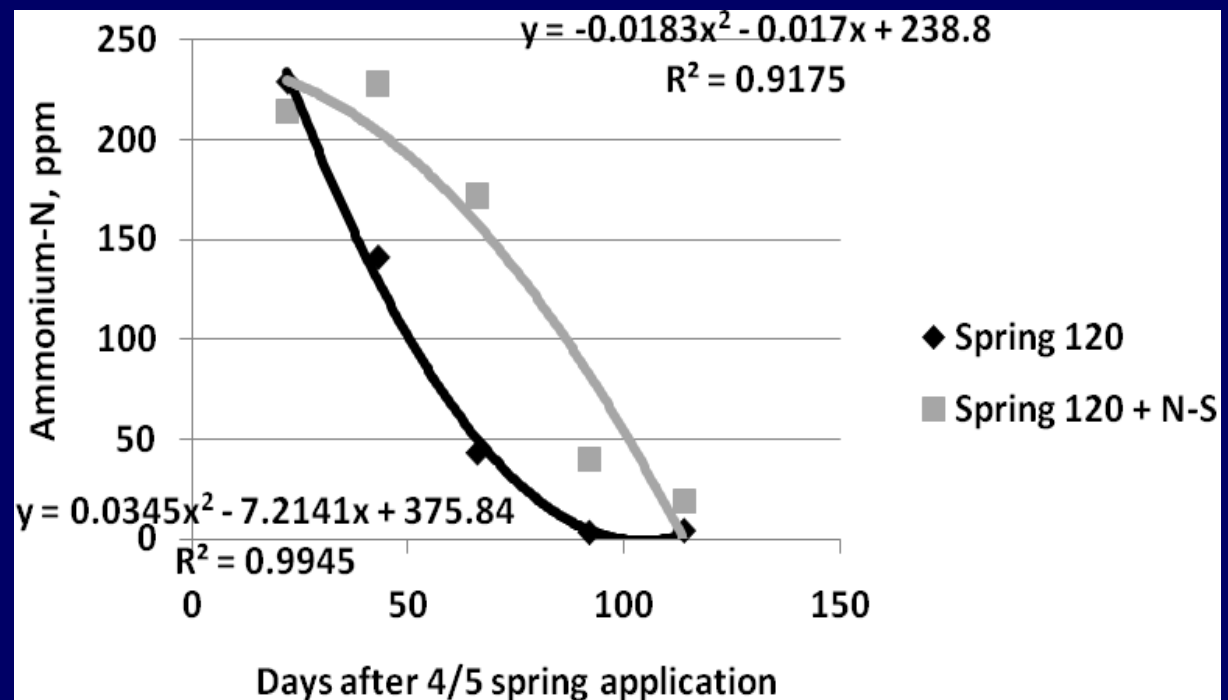
Nitrapyrin mode of action is a bacteriocide

Active at concentrations as low as 1 ppm



Fall N, Touchton et al., 1978
N-Serve 24, Illinois

Spring N, Touchton et al., 1978
N-Serve 24, Illinois



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).

Inherent issues with N-Serve for ammonia

Corrosive-

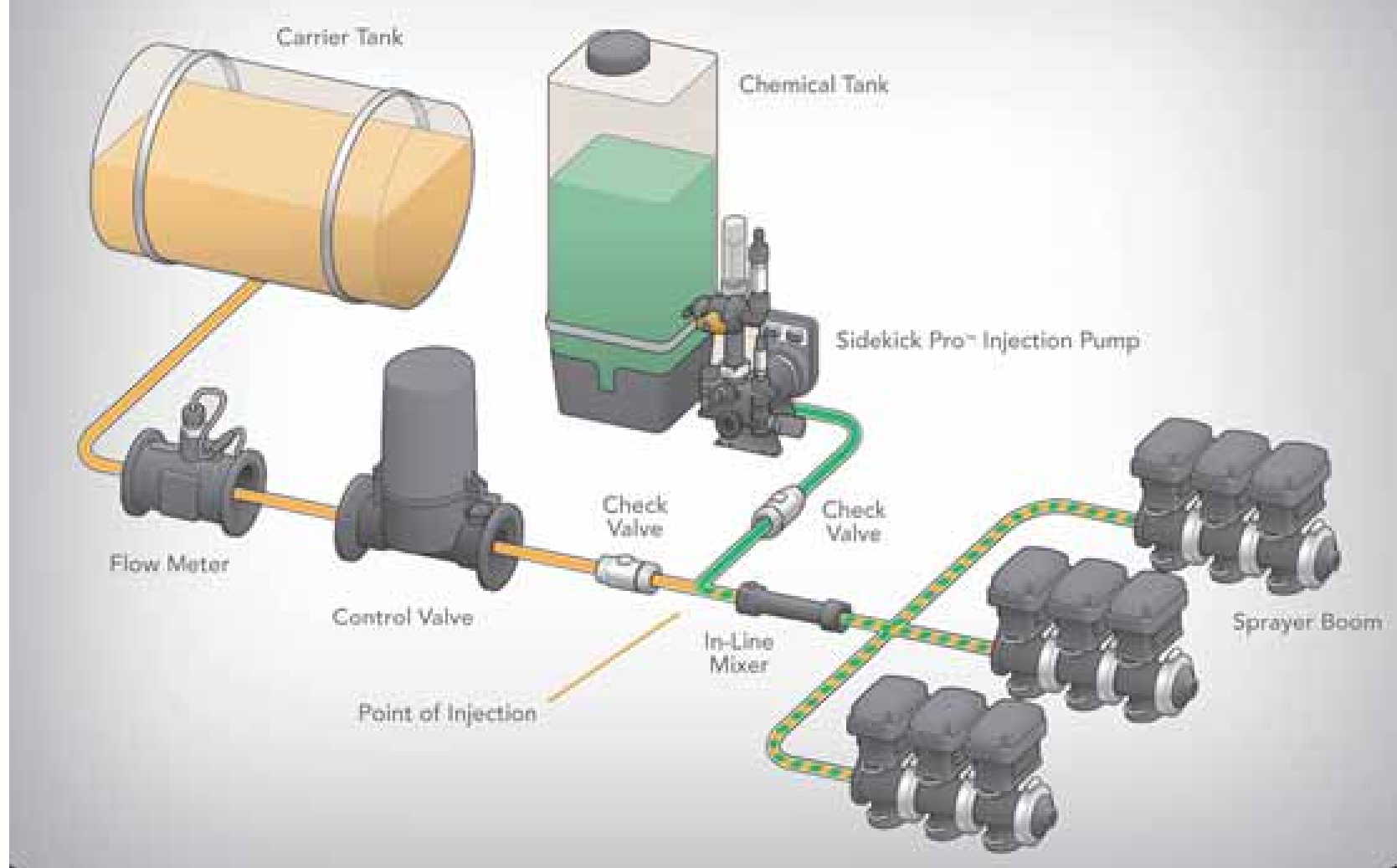
Replace aluminum float-gauges with stainless steel

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

Volatility- 2-3 times more than the most volatile incorporated herbicides

RAVEN DIRECT INJECTION SYSTEM



Direct injection system (not an endorsement)

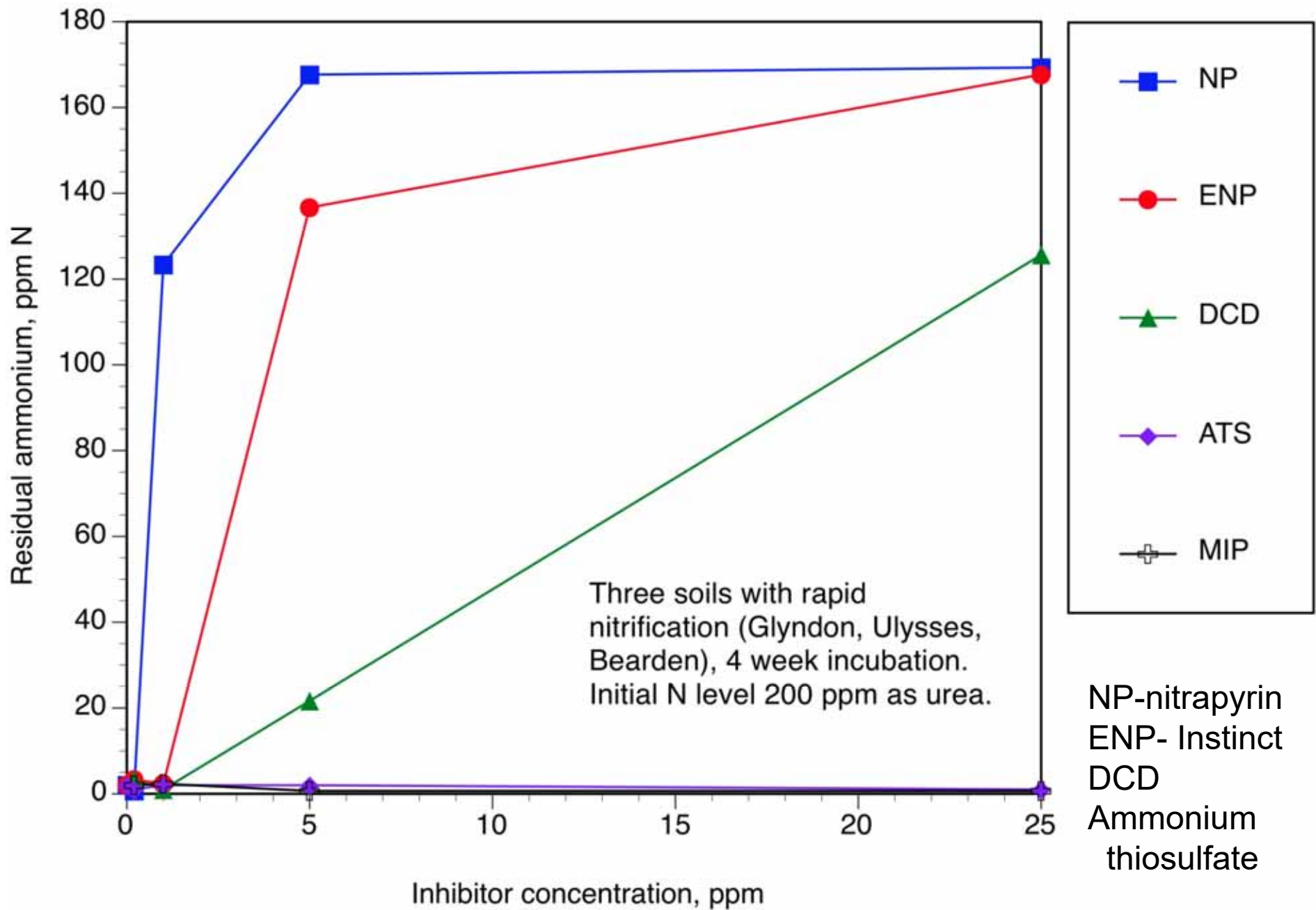
Instinct[®] is a new formulation of Nitrpyrin that can be mixed with ammonium fertilizers and can stay on the soil surface without incorporation.

The formulation is microencapsulated nitrpyrin.

That means that nitrpyrin release is slow compared to nitrpyrin for ammonia.

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.



Instinct performance in other studies-

Purdue, 2012 (Ferrel, MS Thesis with Camberado)

Instinct had no effect on nitrification, either ammonia left in the system or nitrate produced by the N application w/o inhibitor. DCD effectively inhibited nitrification in the same study.

**Field study, Purdue
(Omonode and Vyn, 2013, AJ)**

**Instinct treated UAN had higher ammonium
and lower nitrate than untreated UAN.**

**Nitrification was significantly reduced.
Nitrous oxide emissions were reduced 44%.**

Wisconsin 2008-2012

Laboski and Andraski, 2013 Wis Fert and Lime

Soil ammonium levels were higher and soil nitrate levels lower with Instinct than without.

Yield increases documented, as well as sites with no yield differences.

DCD- Dicyandiamide

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

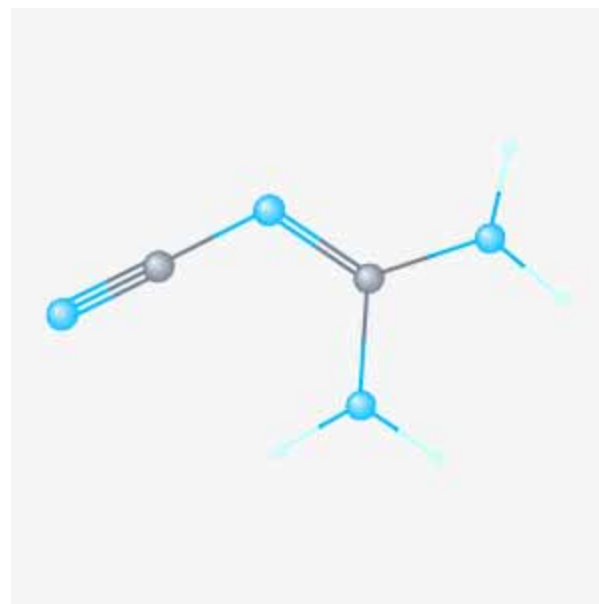
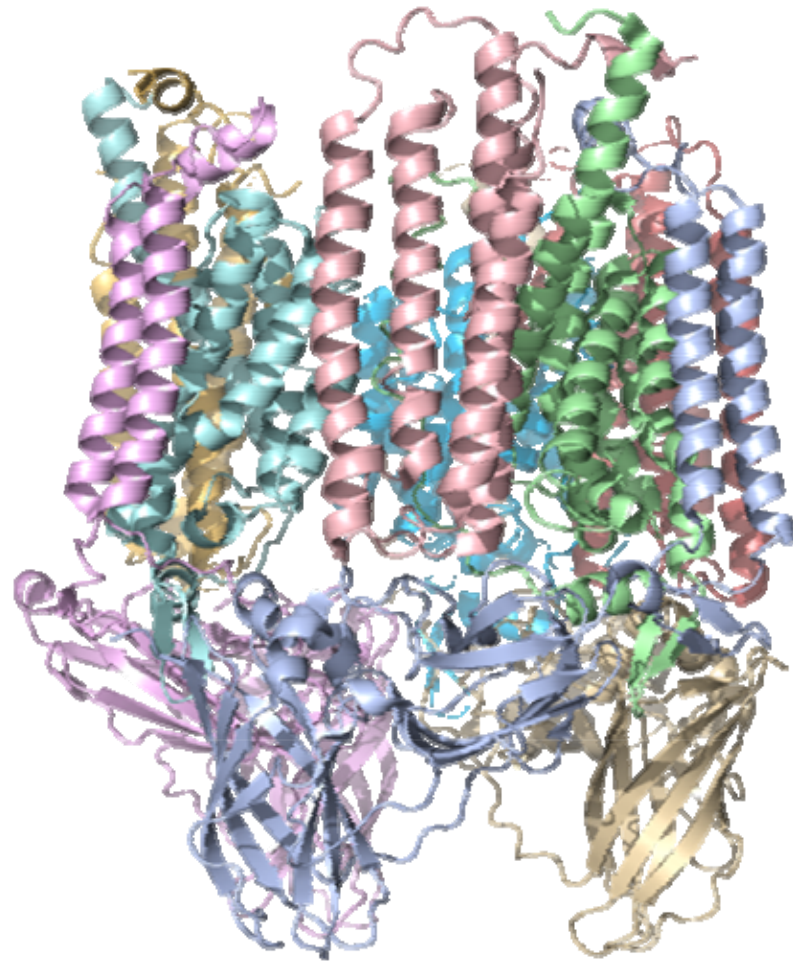


Image from PubChem

<https://pubchem.ncbi.nlm.nih.gov/compound/Dicyandiamide#section=Top>

**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

http://www.genome.jp/dbget-bin/www_bget?mca:MCA1797+mca:MCA2854

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.

Best commercial product is about 1.2%

DCD is about 67% N

**Rates used in successful
nitrification inhibition range
from 1 to 5 % of N in mix as
DCD.**

**It is hard to find DCD content on
labels.**

DCD

From Malzer et al., 1989

No. of comparisons

Timing	No. of comparisons		Average response %
	Total	With significant advantage	
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

Illinois-

4 locations over 12 years, ESN was similar in corn yield to urea + Agrotain, and 3 bu/a higher in yield than urea alone.

In 4 years of no-till, ESN was 21 bu/a better than urea surface-applied.

(Ebelhar et al., 2010)

Minnesota-

**3 different ESN application methods-
deep band (4 inches), broadcast incorporated
fall and spring resulted in similar corn yield
to urea using the same methods over a
4-year period.**

(Randall and Vetsch, 2009)

Kansas-

**At drier locations, ESN not beneficial
to corn or grain sorghum.**

**At wetter locations, some studies showed
a benefit to its use.**

(Weber et al., 2009a and 2009b)

**In Michigan in winter wheat,
fall ESN at the 60 lb N/acre rate
produced higher yield than urea.
Not at the 90 lb N/acre rate.**

(Warncke, MSU)

50/50 blends of urea/ENS?

**KS studies (Weber and Mengel, 2009)
compared to straight ESN or Urea.**

**Results showed that in some years, the
blend was superior, and in some years
it was not.**

Best fit for ESN-

Spring wheat/Durum- in soil

**Corn as a blend in preplant to keep
plant healthy until side-dress**

Maybe a 4 part urea/1 part ESN blend

**Enough ESN to carry N into late
grain fill season for higher protein.**

Start with odd products-

'Biologicals'

Expensive starter fertilizers

Humic substances

Foliar enhancers

There is little scientific evidence that any of these are either more effective than their conventional counterparts (starters) or that they have any positive effect on yield under field conditions.

<http://extension.agron.iastate.edu/compendium/index.aspx>

You can find this link at the bottom of my home page

<Dave Franzen NDSU>

**Type in product name or product category to view
research papers on these products**