#### Proceedings of the 10<sup>th</sup> Annual Nutrient Management Conference

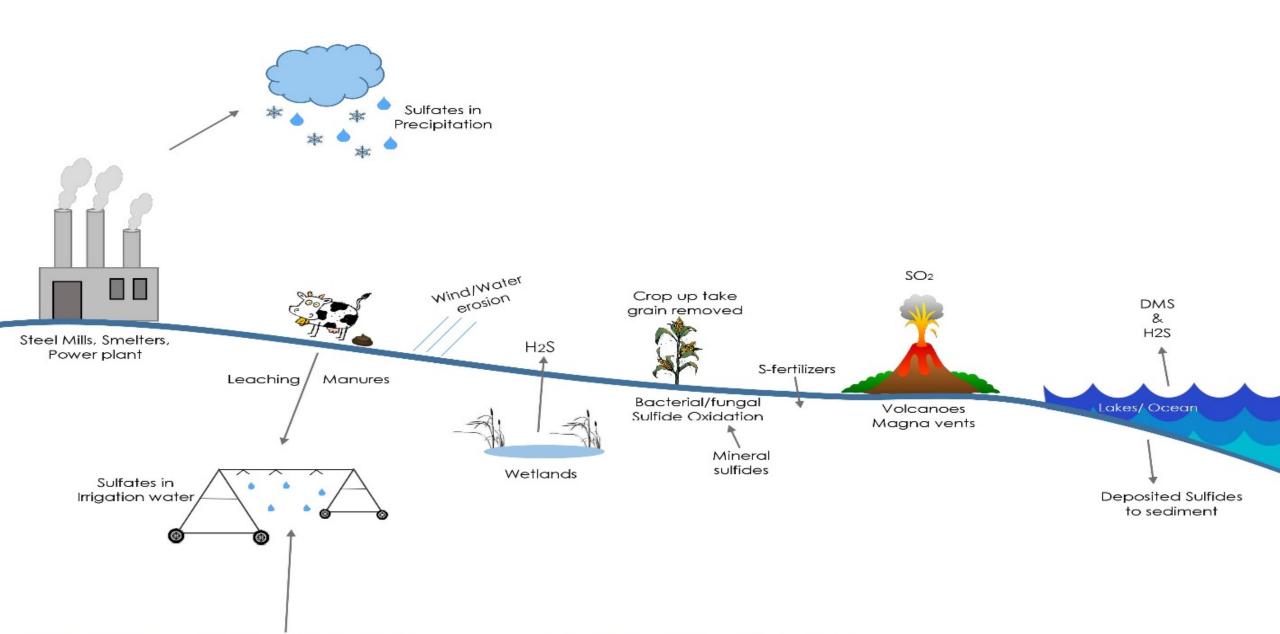




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# Sulfur Sources, Chemistry, Extent of Deficiencies, and Application Considerations for Minnesota

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Sulfates in Ground water

## Sulfur gases emitted annually by volcanic activity over the past 100 years. (From Textor et al., 2003).

Species	SO <sub>2</sub>	H <sub>2</sub> S	COS	CS <sub>2</sub>
Percent by volume	1-25	1-10	10 <sup>-4</sup> - 10 <sup>-2</sup>	10 <sup>-4</sup> – 10 <sup>-2</sup>
1,000 tons per year	1,650 - 55,000	1,100 - 3,100	7 - 110	8 - 105



Mt. St. Helens mushroom cloud as seen 35 miles away in the state of Washington (Rocky Kolberg, image)

Mt. St. Helens, 1980- 1.1 M tons of SO<sub>2</sub>
Mt. Penetubo, 1991, Philippines 18.7 M tons SO<sub>2</sub>
Tambora, Indonesia, 1815, 143 M tons SO<sub>2</sub>

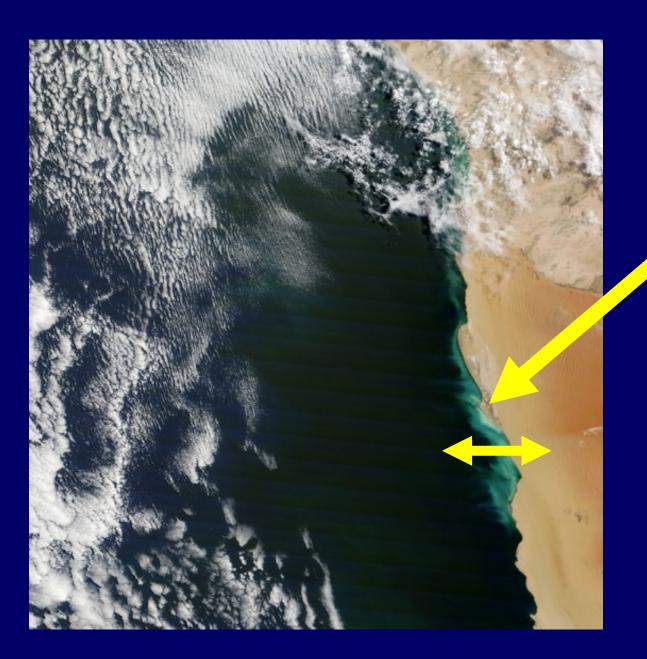
#### Reaction of SO<sub>2</sub> in atmosphere

$$2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4$$

S emissions from oceans and coastal waters amount to about 16 million tons per year.

Rates of S emission from fresh water sources in North Central region of USA average 2 pounds S per acre of water surface.

Mostly as H<sub>2</sub>S and DMS.



## H<sub>2</sub>S eruptions off African coast Namibia

40 miles

Source of S in soils is mostly the origin rock.

Igneous rocks - mostly pyrites (Fe sulfides)

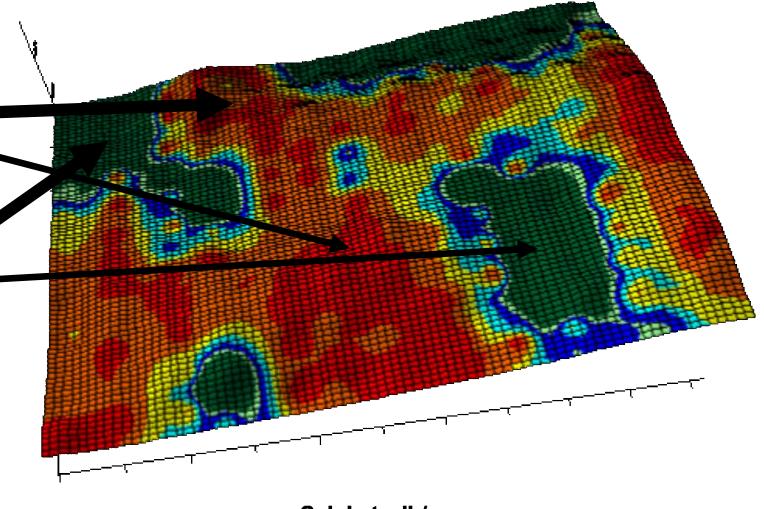
Sedimentary rock contains some igneous rock remnants, as well as products of previous oxidation/reduction reactions

In North Central Region, gypsum deposits are the result of the ancient location of coastal plains.

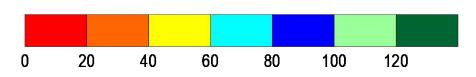
In drier climates of North Dakota/South Dakota and other Great Plains states, groundwater may contain significant gypsum (CaSO<sub>4</sub>), as well as magnesium sulfate and sometimes sodium sulfate.

Surface presence of sulfate is the result of groundwater movement.

Low sulfate at hilltops, ridges, high sulfate in areas with high water tables in local depressions.



Sulphate, lb/acre



#### **S from Human activity- coal**

Coal has been used in industry for over 2,000 years-Greek, Roman, Chinese, probably others.

The contribution of these uses was small until 200 years ago- Industrial Revolution
The exchange of human and animal energy for alternate sources- wood, water.
Locations of industries with respect to wood and water sources resulted in replacement by coal.

EPA was given authority by US Congress to regulate atmospheric emissions. 1990 Clean Air Act.

Title IV set goal of reduction of S emissions to 10 M tons S less than 1980 USA levels.

Additional regulation included not only large coal using industries, but smaller ones and those using oil and gas.

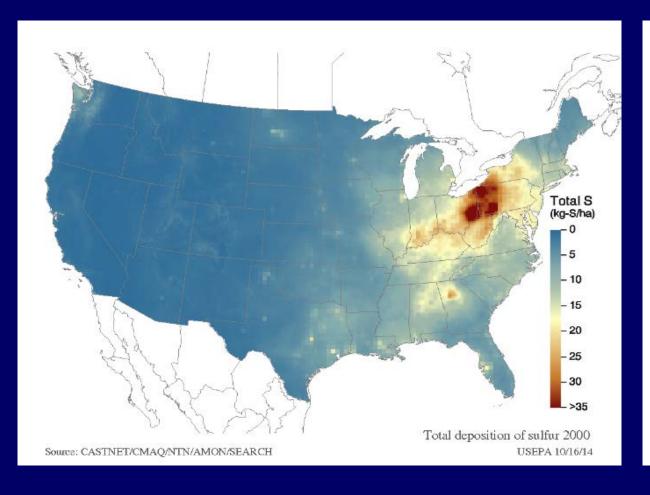
Number of coal-burning industry units by state in the North Central Region as of August, 2015.

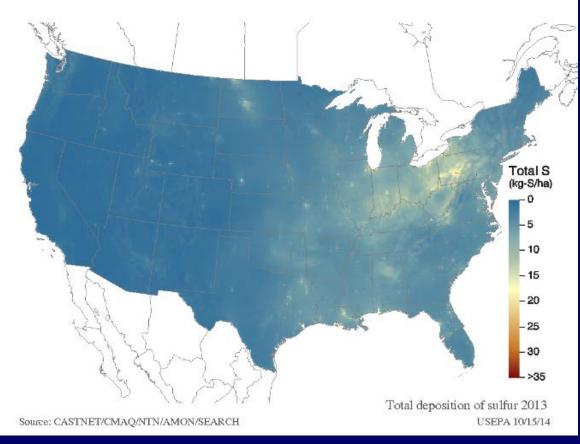
	Number of	
State	coal-burning	
	industries	
Illinois	83	
Indiana	90	
Iowa	28	
Kansas	8	
Michigan	33	
Minnesota	21	
Missouri	24	
Nebraska	8	
North Dakota	10	
Ohio	119	
South Dakota	2	
Wisconsin	27	

#### S emissions, M tons per year 1975 2000 2010

USA 38 13 8.6

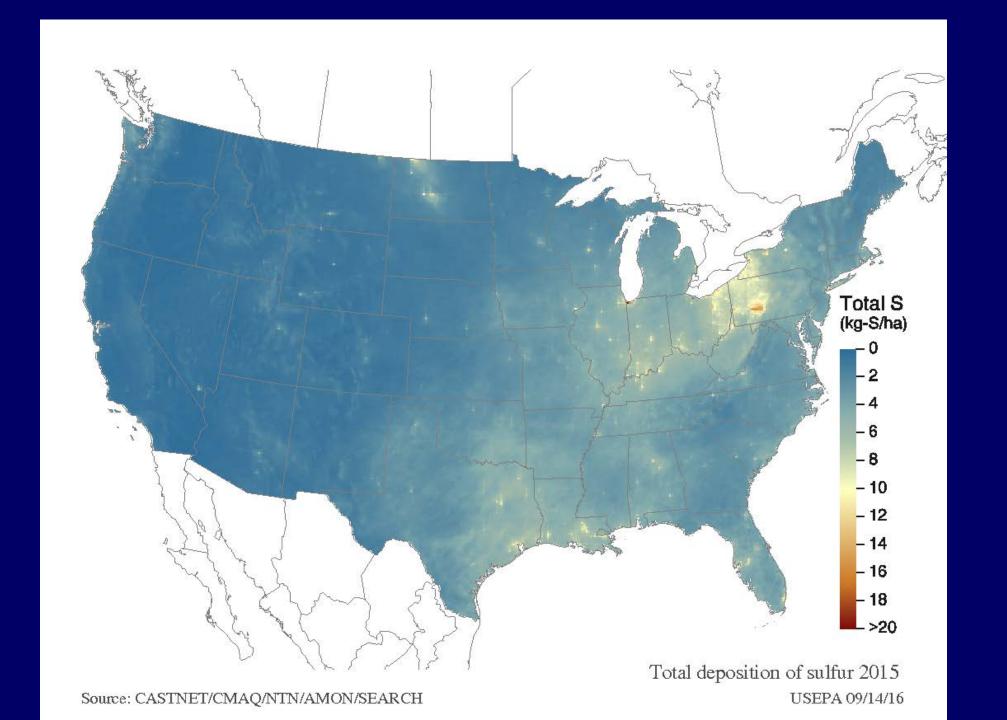
China 13 35 36





2000 S deposition

2013 S deposition



#### **Biological S oxidation-**

Chemolithotrophs- oxidize S when oxidizable S is present

Heterotrophs- oxidize S similarly as chemolithotrophs, but only when other oxidizable materials are not present. They do not have to oxidize S for metabolism and reproduction.

In a Saskatchawan soil survey of S oxidizing organisms, heterotrophs by far dominated the numbers of organisms. (Lawrence and Germida, 1991, Canadian Journal Soil Science).

This may explain the poor oxidation of S in that province and in North Dakota, directly to the SE of the study.

What we perceive as 'natural' sulfur nutrition is really crop uptake from a combination of sulfate received by the soil from the atmosphere from human and natural sources and sulfate available from groundwater capillary action, sulfate-bearing minerals, and S oxidation of sulfides from S oxidizing organisms

Until about 30 years ago, S deficiency in the NC Region was confined to low organic matter (eroded) soils with deep sandy textures.

That changed with the introduction of canola. Canola has always had a special requirement for S far above any crop grown in the region.

#### Yield of canola as affected by sulfur rate, source, and landscape position, Rock Lake, ND, no-till system.

From Deibert et al., 1996.

S rate,		Yield from different soil series/landscape position			
lb/acre	S source	<b>Buse/hilltop</b>	Barnes/slope	Svea/footslope	
		lbs/acre			
0		30	240	1460	
20	Ammonium sulfate	1650	1670	1720	
40	Ammonium sulfate	1800	1860	2170	
40	Elemental S	620	1060	1630	

## S from gypsum and ammonium sulfate compared to MAP and N only preplant on canola yield, 2008 on a Barnes soil (DeSutter and Lukach)

Source	S Rate, Ib/acre S	Canola yield, lb/acre
Flue gas gypsum	20	<b>2110</b> a
Ammonium sulfate	20	<b>2150</b> a
MAP only	0-1	1518 b
N only	0	1550 b

#### Changes in cropping in the region in the past 40 years-

Dramatic increases in yield due to genetic and crop management advances.

Continued topsoil erosion in some areas.

Reduction in anthropogenic-source S deposition.

Increased rainfall/leaching in some years.

In North Dakota, since 2010 S deficiency has been seen on corn on all soil textures. Below is on sandy loam near Oakes, dryland. Green is from farmer 2X2 S application. Greenest plots in N study are check plots.



S deficiency in corn, near Valley City, 2014



### Carrington, 2014 (Teboh and Zilahi-Sebess) Wheat response to S

Sulfur rate, Ib/acre	Yield, bu/acre	Protein, %
0	64	15.2
10	71	15.6

S deficiency in spring wheat near Valley City, 2010



### Response of corn at six locations in Minnesota to sulfur (Rehm, 2005).

\* Response is significant at P > 0.05

Site/texture	S applied, lb/acre		
	0	6	
	Yield, bu/acre		
loamy fine sand	166	174*	
silty clay loam	184	184	
loamy fine sand	99	108*	
Loam	<b>150</b>	161*	
sandy loam	140	154*	
silt loam	149	160*	

Kim, Kaiser, and Lamb, AJ 2013

Applied broadcast S and starter S treatments in corn experiments by landscape position on loam and silt loam soils

When OM < 2%, S increased yield at 2 of 3 sites OM 2-4%, S increased yield at 1 of 3 sites

No yield increase from S when OM >4%.

Many soils in central/south Minnesota have OM 4-8%.

Before 2005, S deficiency in Iowa was virtually unknown. A series of experiments in 2005-2006 showed a consistent response to S in some soils.

In 2007 17 of 20 sites showed a significant response to S In 2008, 11 of 25 sites showed a significant response to S Average response to S was 13 bu/acre

When grouped by texture within responsive sites, heavier soil increase was 15 bu/acre

Sandier soil increase was 28 bu/acre (Sawyer, 2009)

lowa S rescue on corn. 40 lb S/acre as gypsum broadcast side-dress early season after on-set of deficiency symptoms. Sawyer, 2009.

Site/Texture	Yield w/o S	Yield w/S
1 / loamy fine sand	123	151
2 / loamy fine sand	154	198
3 / loamy fine sand	88	108
4 / loam	196	204 (NS)
5 / silt loam	118	171
6 / silt loam	129	167
Across all sites	129	167

In Wisconsin, frequency and likely location of S deficiency has little changed from historic tendencies- sandier, low OM soils, with alfalfa most likely crop to show deficiencies.



Kansas- response of crops varies with water and years. Dry years, little response; wetter years more response. Greater response on sandier lows, low OM.



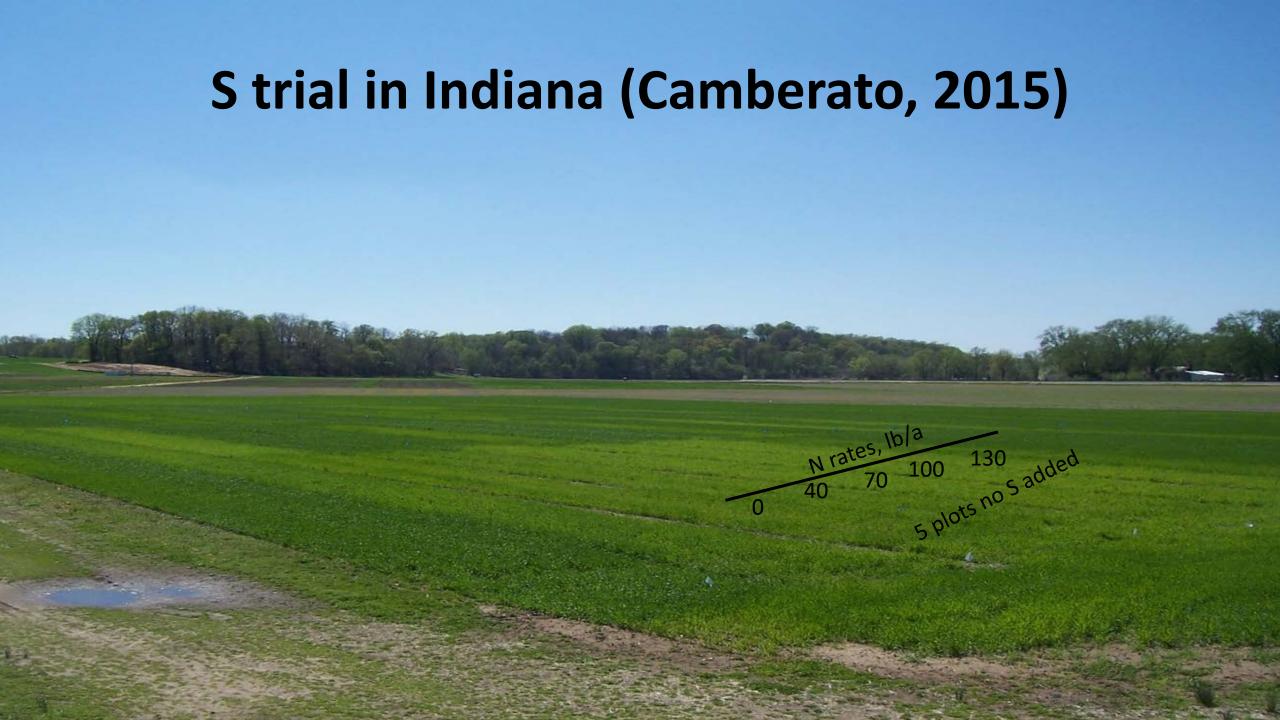
Early spring S deficiency in winter wheat,
Mengel. S treatments increased yield 15 bu/a

#### Kansas field image S deficiency in winter wheat. (Mengel)



In Michigan, Indiana, Missouri and Ohio, historic S deficiencies have been on low organic matter deep sandy soils. S deficiency has moved beyond these historic areas.

In Nebraska, sulfate in irrigation water has been sufficient to supply S to most fields. Dry-land sandy soils are susceptible in wet year.



# Sulfur deficiency in wheat (IN)

 General yellowing of all leaves (less so in old leaves than with N deficiency)



## Sulfate loss occurs in the winter (IN)

Time period	Rainfall, inches	SO <sub>4</sub> -S lost from 36" soil profile
Wheat harvest → Soybean harvest	20	7
Soybean harvest → Spring	10	19
Spring → Wheat harvest	21	6
Wheat harvest → Soybean harvest	28	1

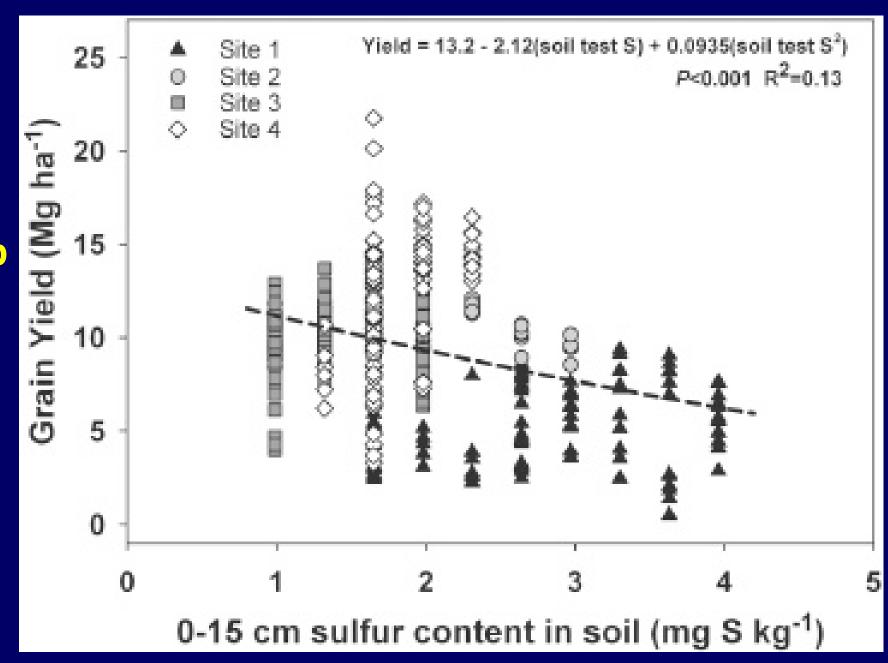
The current S soil testing procedure in the North Central Region is the Monocalcium Phosphate Extraction Procedure.

The acetic acid form of this procedure was identified by Hoeft et al. (1973) as the method that most predicted S deficiency and response in alfalfa.

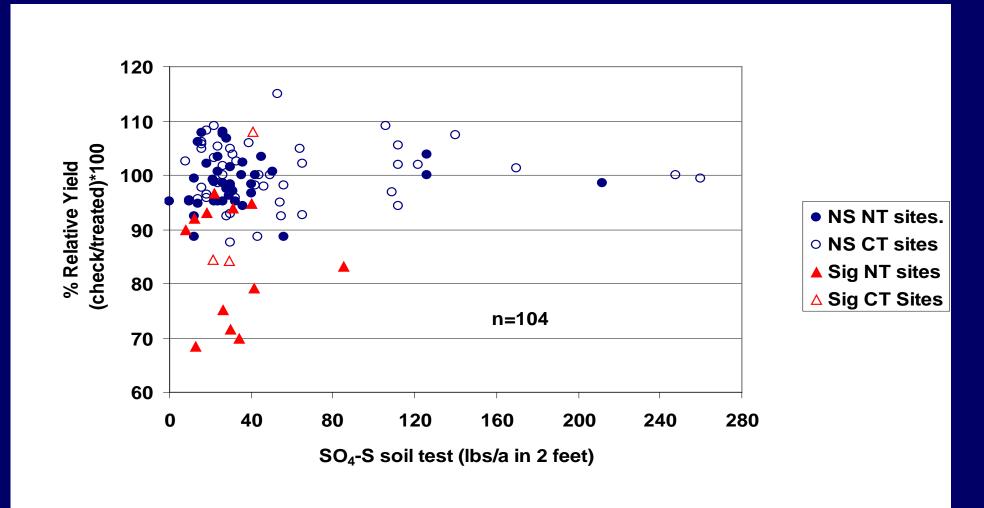
The acetic acid MP method is tedious, so an alternate method of MP was soon adopted. This alternate method was tested by Hoeft et al. and found not nearly as predictive as the acetic acid method.

Early in his Illinois career, Hoeft tried to use the acetic acid MP method to predict S response in corn, and found it unpredictive.

Relationship
S test to
grain yield
Kim/Kaiser/Lamb

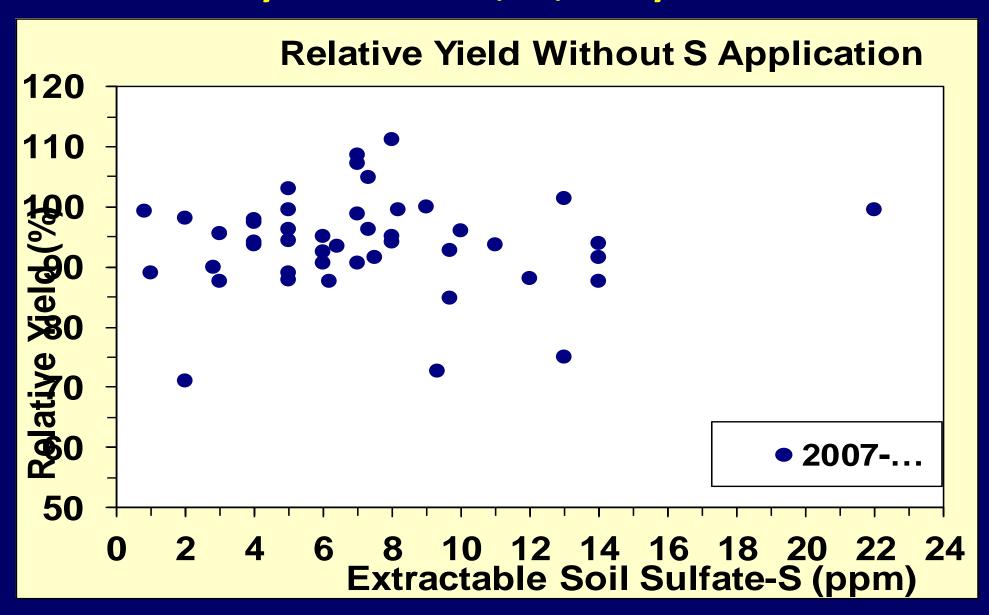


#### Relative corn grain yield to S soil test, Gelderman, SD.



No relationship of relative yield with S soil test

#### Relative corn yield to S test, IA, Sawyer.

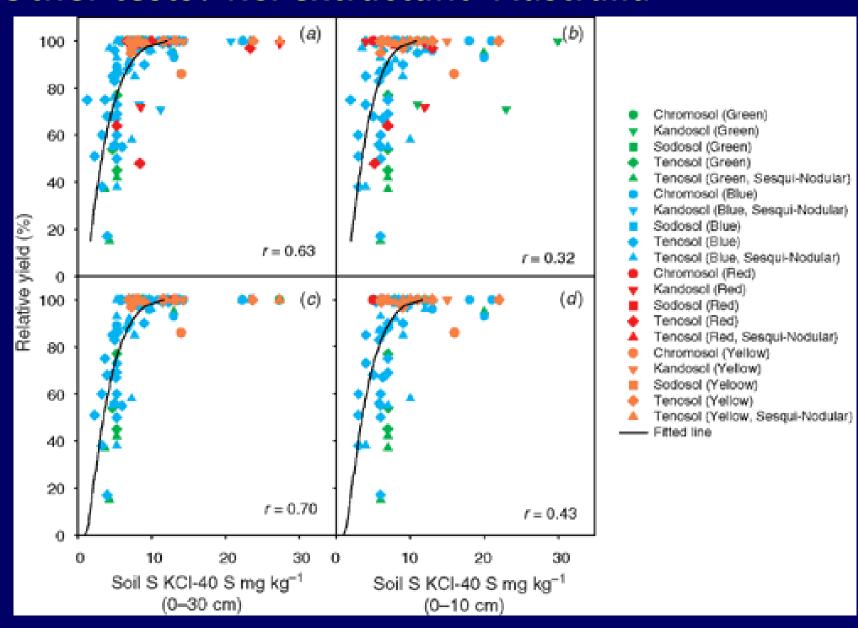


The sulfate-S soil test is non-diagnostic and should not be used as the sole diagnostic strategy to determine whether crops might need S or not.

In ND, canola always receives 20 pounds sulfate-S regardless of any conditions.

Other crops, fall rainfall, snowmelt, early spring rains, soil texture, length of spring rain and persistence of wetness in forecast, landscape position all play a role. Soybean and sunflower particularly not very S responsive. Grain crops and corn are responsive.

#### Other tests? KCl extractant- Australia



The construction of this graph makes it look like there is a relationship. However, the response of one type of soil is a vertical line and response of the other is horizontal. Including both on the same graph seems to make a relationship. **But the responses** are negative and soil specific.

The increased area of S deficiency may provide an opportunity to test different extraction methods.

A snapshot sulfate extraction does not look like a good predictor.

Maybe a method that explores sulfate release over time?????

S sourcesManures- varies with analysis
Dry manure 1-3 lb S / ton
Liquid manure 4-9 lb S / ton

Previous crop residues-Kaiser found that soybean response to S lower when S was applied to corn the year before. Some of the S released to soybean probably comes from residue decomposition.

#### S sources-

Ammonium sulfate (20 to 21 - 0-0-24S)

Gypsum (0-0-0-14to20S)

Potassium sulfate (0-0-50-18S)

Potassium magnesium sulfate (0-0-22-22S)

Ammonium thiosulfate 12-0-0-26S Potassium thiosulfate 0-0-25-17S

#### **Elemental S?**

Consistently less effective across the NC Region rate S/rate S with sulfate/thiosulfate sources.

Type of S used in trials is almost always a very fine grind, bound with bentonite to improve dispersion. Oxidation is the problem, not fineness of material.

# Yield of canola as affected by sulfur rate, source, and landscape position, Rock Lake, ND, no-till system.

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## Timing of S application-

Just as nitrate is not a fall fertilizer, neither is sulfate.

Elemental S applied in the fall will partially oxidize to sulfate, which will leach in the spring- leaving elemental S which oxidizes slowly. Not a great plan.

Sulfur is a spring fertilizer.

## **Summary of discussion-**

Increased crop yield, soil erosion, higher rainfall years and continued decline in atmospheric S deposition is resulting in greater acreage expansion of S deficient soils.

S deficiency is moving east. Practitioners need to stay alert and pay attention to LOCAL research.

## **Summary of discussion-**

In North Dakota, my recommendations are:

For canola- always 20 lb/a sulfate/thiosulfate S
For corn- always 15-20 lb/a sulfate/thiosulfate S
For small grains- always 10-20 lb/a sulfate/thiosulfate S
For potato- S as recommended in circulars

Other crops not as responsive (soybean for example) very sandy, low organic matter soils. Others, be vigilant.

## **Summary of discussion-**

An N-rich strip may serve as a sentinel to possible early-season S deficiency.