SULFUR SOURCES, CHEMISTRY, EXTENT OF DEFICIENCIES, AND APPLICATION CONSIDERATIONS IN THE NORTH CENTRAL REGION OF THE USA

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ABSTRACT

Sulfur (S) has not been considered in the North Central USA region as more than a special-case fertilizer until recently. Originally recommended for canola in the northern plains of North America and throughout the region in sandy, eroded soils, then commonly required in many soils in the western-most states in the region. Reasons for a more widespread need include depleted atmospheric sources, use of low S fertilizers, higher crop yields, and greater annual rainfall in some years. The S soil test is unreliable and non-diagnostic in most areas of the region in most crops. Use of active-optical sensors might be used in the early season of corn growth to identify fields with S deficiency for rescue fertilization. Sulfur is not a fall-applied fertilizer due to its susceptibility to leaching. Elemental S has not been an acceptable source of S in the region due to its slow oxidation by soil microorganisms, particularly in northern areas.

INTRODUCTION

Sulfur (S) is one of fourteen essential mineral nutrients for crops. Figure 1 illustrates the S cycle on a large spatial scale. The source of S for crops is both anthropogenic and natural. Anthropogenic sources can be substantial, and S emissions include sulfur dioxide (SO_2), hydrogen sulfide (H_2S), and a lesser amount of carbonyl sulfide (COS). Natural sources of atmospheric S include volcanic emissions including magma vents, which emit H_2S, oceans and other surface waters, which emit H_2S and COS, atmospheric chemical reactions that transform H_2S and COS into sulfuric acid (H_2SO_4), and emissions from manure. Soil sources of S include degradation of S-bearing minerals, mineralization of plant residues and animal decay, formation and dissolution of sulfate salts, and movement of sulfate-containing groundwater to the soil surface through irrigation of water table fluctuation. Crop production in a S deficient environment can be improved with application of S containing fertilizers or manures.

Natural S sources
Volcanic activity
There were about 380 volcanoes recorded as active within the past century, with about 50 volcanoes active in any given year (Textor et al., 2003). Volcanic activity is clustered in active seismic regions around the globe, with North American volcanic activity concentrated in the western mountains. The closest source of volcanic activity in the NC region is Yellowstone, which erupted last about 600,000 years ago and created the Yellowstone caldera. Magma close to the surface in Yellowstone continuously emits large amounts of S gases, which are easily smelled by tourists in the many magma-heated areas of the National Park. The Yellowstone

basin magma is basaltic in nature, and gases from eruptions and magma vents contain large concentrations of S gases. More than 90 per cent of volcanoes erupting annually have basaltic magma. Ninety per cent of these volcanoes originate at the ocean floor in mid-oceanic ridges (Halmer et al., 2002). Felsic magma is highly differentiated and contains a higher concentration of gases, including S gases. This magma is highly viscous and highly explosive. Magma at convergent plate boundaries are classified as andesitic magmas, and are similar to felsic in their viscosity and explosive nature.
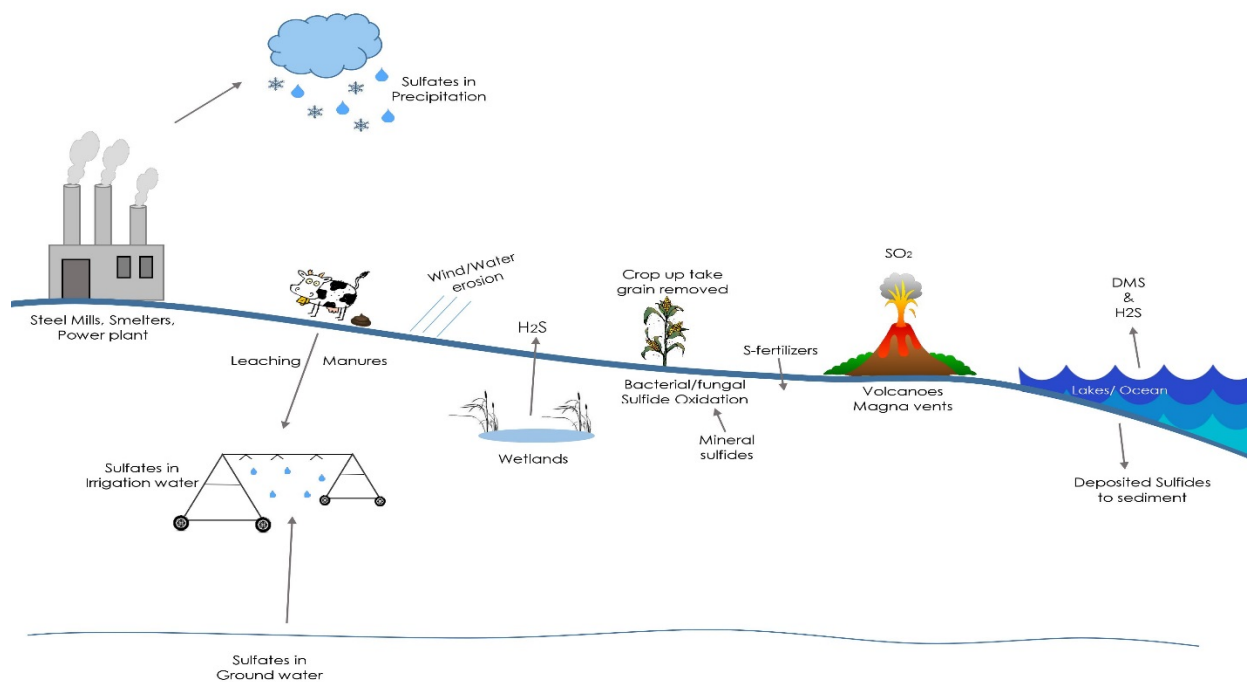

Figure 1. Simplified sulfur cycle. (Drawing by N. Lynnes, NDSU)

They release magma and gas explosively over short time scales and the velocity of emissions often propels gases in the stratosphere, with measurements made exceeding 25 miles in altitude. Volcanoes with these properties also tend to emit gases continuously through vents between eruptions. Estimated annual S gas release by volcanic activity is shown in Table 1.

Table 1. Sulfur gases emitted annually by volcanic activity over the past 100 years. (From Textor et al., 2003).

Species	SO$_2$	H$_2$S	COS	CS$_2$
Percent by volume	1-25	1-10	$10^{-4} - 10^{-2}$	$10^{-4} - 10^{-2}$
1,000 tons per year	1,650 - 55,000	1,100 - 3,100	7 - 110	8 - 105

Average annual emissions are smoothed values over time. Individual catastrophic eruptions emit huge amounts of S into the upper atmosphere in a short period of time. The Mt. St. Helens eruption in 1980 resulted in emission of about 1.1 million tons of SO$_2$. In contrast, the Pinatubo eruption in the Philippines in 1991 emitted 18.7 million tons. The largest recorded SO$_2$ emission during the past 250 years was from the Tambora eruption in Indonesia in 1815, resulting in an estimated 143 million tons. Sulfur dioxide is transformed to sulfuric acid in the stratosphere over

about 35 days (Bluth et al., 1992). Sulfur from volcanoes was estimated (Graf et al., 1997) to be about 14 per cent of total annual global S gas emissions. Volcanic activity has increased during the past 30 years; however, this trend has been attributed to improved monitoring and detection, not real increases in activity (Halmer et al., 200).

Sulfur dioxide transformation to sulfuric acid in the atmosphere is described by the following formula (Manahan, S.E. 2013):

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

The source of the water for the reaction is ambient water vapor, which is greatly increased by the massive release of water vapor in volcanic eruptions (Joshi and Jones, 2009).

Gas emission from surface waters

Oceans emit large amounts of S gases that contribute to the background S concentrations in the atmosphere. One estimate of S emitted from oceans as gas is about 2 million tons S annually. In addition, particulate S from sea-spray may be emitted at a rate up to 10 million tons per year (Andrea, 1990). Marine algae take up sulfates and produce dimethylsulfonium propionate which is then transformed to dimethyl sulfide (DMS). A portion of DMS diffuses into the atmosphere, where it is oxidized to sulfate (Andreae, 1990). The oxidation of DMS is very complex and it proceeds as a purely physical chemical process. An excellent review of the steps in the oxidation of DMS, associated kinetics and flow chart can be found in Barnes et al. (2006). Coastal wetlands, such as mangrove swamps in Florida, emit about 2.1 million tons S per year globally. Special cases of S gas emissions in oceans are associated with anoxic (no oxygen) zones in the ocean, usually near a continental shelf (Weeks et al., 2004). Once thought to be small intermittent eruptions of H_2S in these waters, remote imagery now reveals that these eruptions occur in vast tracts, sometimes more than 5 million acres (Figure 2).

Although far greater global S gases are emitted by oceans compared to fresh water sources, fresh water lakes and wetlands are associated with the North Central USA region. In fresh water wetlands, typical of many areas of North Dakota, South Dakota, Minnesota, Wisconsin, Michigan and the Prairie Provinces of Canada, rates of S gases, typically consisting of mostly H_2S and DMS amounts to about 2 pounds S per acre of water body per year. Saltmarshes and other ocean associated wetlands such as the mangrove swamps of Florida may emit over 20 pounds S per acre of water body per year (Giblin and Wieder, 1992).

Sulfur bearing minerals

The origin of most S in soils is the original rock. Igneous rock S in the USA contains mostly sulfides in the form of various pyrites, including iron pyrite (FeS_2), pyrrhotite ($Fe_{1-x}S$) and other minor minerals (Parat et al., 2011). Small amounts of sulfates may be present in some magmatic rocks, but sulfides are dominant until weathered. Sedimentary rocks are the product of previous ancient weathering and reconstitution, and therefore contain the products of sulfate chemistry and S reduction (Rickard, 2012). Most of the mineral portions of our soils are a combination of igneous and sedimentary rocks and their weathered products.
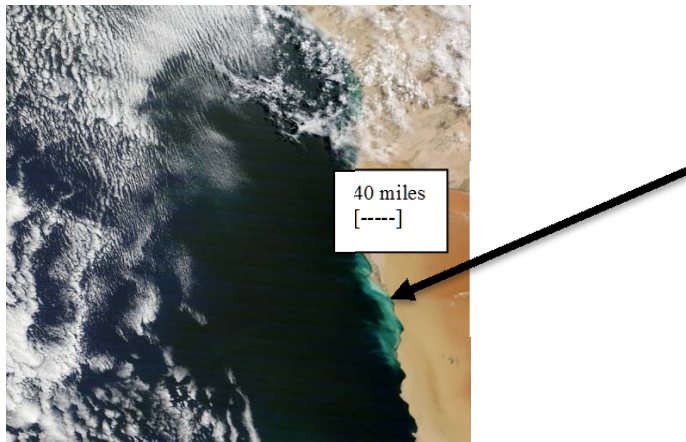
Figure 2. Hydrogen sulfide eruptions from continental shelf sulfate reduction off the coast of Namibia, Africa. NASA image, Earth Observatory satellite, March 13, 2010.

Sulfates are present in the North Central region as sulfate salts of calcium, magnesium and sodium. Although large gypsum ($CaSO_4 \cdot 2\ H_2O$) beds mined in the region were products of ocean shoreline chemistry millions of years ago (Murray, 1964), sulfate salts in North Dakota, northwest Minnesota and South Dakota are the product of recent evaporate chemistry (Skarie et al., 1987). Sulfate salts dominate ground water chemistry in North Dakota except for areas of chloride salts near Grand Forks where artesian water from ancient shale seabed strata contributes to the salt-flat appearance of land directly west of the city. Soluble salts, mostly sulfatic salts, affect most of the crop, pasture and rangeland in North Dakota. Salts are present because summer evaporation exceeds precipitation in most years, and moves groundwater with its salts into surface soils. On the positive side, areas affected by sulfate salts are not affected by S deficiency. However, the negative side is that soluble salts limits yield and can lead to sterilization of land if not managed well (Franzen, 2003). Evaporation of groundwater that is transported to the surface contributes to elevated sulfate, but freezing also can cause precipitation of sulfate salts (Arndt and Richardson, 1989). Sulfate salts also dominate most saline areas of Kansas (Whittemore, 2000), Nebraska (Joeckel and Clement, 2005), and South Dakota (Kennedy, 1994). Salinity, however, is an ephemeral presence (Franzen, 2003). During periods of high rainfall, causing a high water table followed by dry weather, salts are pulled to the surface by capillary action and the concentration of salts and sulfates increase in the crop rooting zone. During periods of high rainfall in soils with either temporal or permanent deep water tables sulfates are leached out of the rooting zone.

Anthropogenic sources of S gas emission

The main sources of anthropogenic S are emissions from oil, gas and coal-fired power plants, steel mills and smelters, grassland burning, crop residue burning, land clearing in forests by burning and irrigation with sulfate containing water. Coal has been used in industry for over 2,000 years. Theophrastus (300 BC) writes about coal as being mined in Greece and used by Greek metal workers. In China, coal was called black stone, with the first recorded use about 2,000 years ago during the Han dynasty and described by Marco Polo during his historic journey to China about 1300 AD (Yinke, 2011). It is unlikely that the burning of coal by these ancient societies contributed greatly to global sulfur levels. It was not until about 200 years ago, soon after the onset of the Industrial Revolution that first coal, then oil, then gas, was used at a great scale (Fernihough and O'Rourke, 2014; Mokyr, 1998).

The Industrial Revolution was first characterized by the replacement of human and animal power with water and chemical power from timber/charcoal, but the limitations of the sources of water power and trees in respect to the burgeoning industry need for local power quickly resulted in the adoption of coal in Europe and then oil products. From early in the Industrial Revolution until today, burning of fossil fuels became the greatest single contributor globally to atmospheric S concentration. For example, S in rainwater in Chicago in 1921-1923, an area with multiple steel mills, smelters, other coal-burning industries and coal powered power plants and coal-heated households was 209 pounds S per acre. Rain water in Ames, IA, however, with limited industry, but probably coal-heated homes, measured 15 pounds S per acre in 1921 (Eriksson, 1952).

The US Clean Air Act of 1990 gave the authority to the US-EPA to reduce toxic gas emissions into the atmosphere through regulation of gas emitting industries (US EPA, 2015). Title IV of the Clean Air Act set a goal of reducing SO_2 emissions to 10 million tons less than 1980 levels at coal-burning electric utilities (Phase 1, 1995), and then mandated reductions at additional industries fired by coal, oil and gas (Phase II, 2000). The number of coal-fired industries in the North Central US states, including power plants and other industries, such as the American Crystal Sugar sugar beet processing plants in North Dakota, are shown in Table 2. The site density of coal-fired industry units increases from west to east within the region. Steel mill numbers have declined since WWII with increase in global competition, and in part with environmental and work place regulations in the US compared with those in China, which are just now starting to develop (Bailey et al., 2009). The location of steel mills in the US is concentrated in the eastern US. Steel mill emissions are subject to similar S emission restrictions as power plants (Figure 3).

Table 2. Number of coal-burning industry units by state in the North Central Region as of August, 2015.

State	Number of 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

US SO_2 emissions in 1975 were about 38 million tons, compared to about 13 million tons for China. In 2000, the US had reduced emissions to about 13 million tons, while China increased emissions to 35 million tons.

The reduction in US S emissions helps explain the trend in sulfate deposition in the USA. In Figure 4, all areas of the North Central Region experienced a reduction in sulfate deposition from 2000 to 2013. In 2010, background deposition of sulfate was low enough in North Dakota that the plumes of the largest coal-fired power plants just to the north of northwest North Dakota (Crosby) in Saskatchewan, and north of Bismarck are easily seen. Generally, all land in the North Central Region of the US receives about half the S from rainfall that it received in 2000, and even less in 2000 than the amount received in 1980.

Sulfur soil chemistry and availability

There are two main S sources in the soil; sulfate and sulfide. Through oxidation and reduction reactions, sulfide can become sulfate, mediated by microorganisms, and sulfate can become sulfide within plants and microorganisms through metabolism, and in anaerobic environments by physical chemistry Eh reactions. There are a large number of bacteria that oxidize sulfides and elemental S to thiosulfate and sulfate (Vidyalakshmi et al., 2009). These are categorized into chemolithotrophs, reproducing and metabolizing only when oxidizable S compounds are available, and heterotrophs, which can use the chemolithotroph method of S oxidation, but do not have to for metabolism and reproduction. The most common chemolithotrophs are *Thiobacillus* sp, *Thiomicrospira* sp, and *Thiosphaera* sp, Heterotrophs include *Paracoccus* sp, *Xanthobacter* sp, *Alcaligens* sp, and *Pseudomonas* sp.
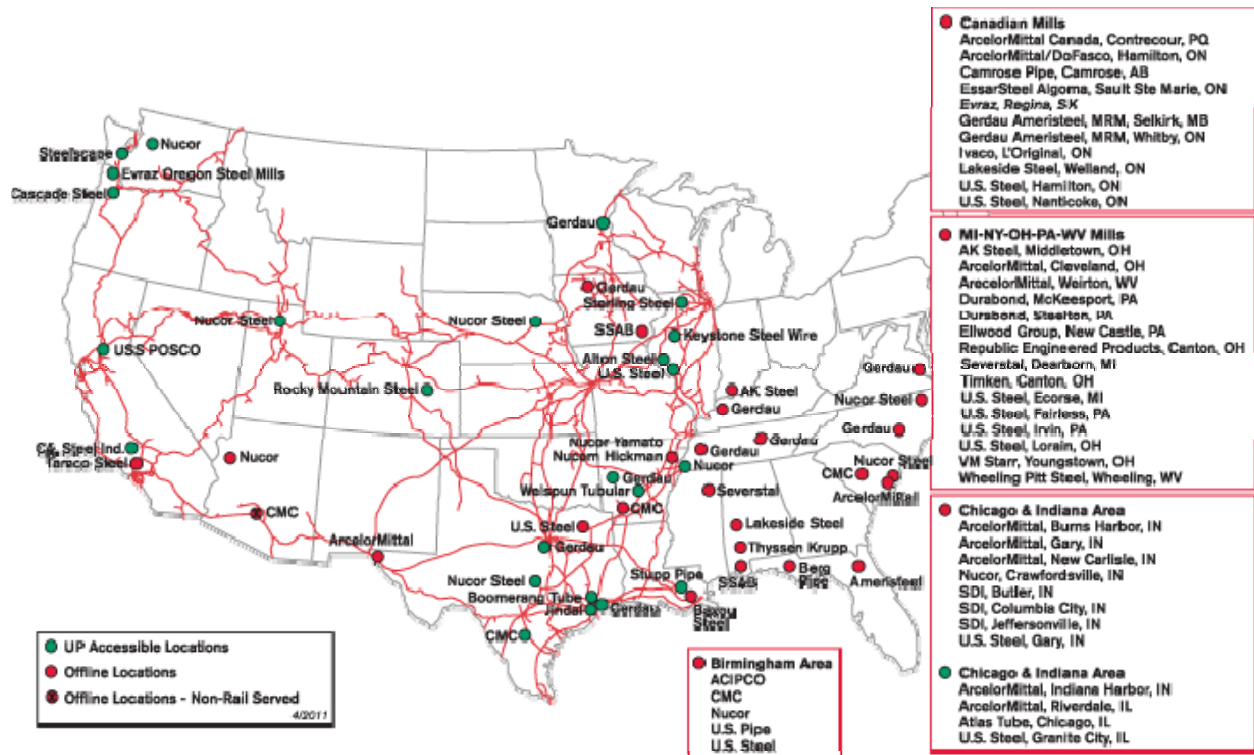

Figure 3. Steel mill locations in the USA, August, 2015.
http://www.up.com/customers/ind-prod/metals/steel-mill/index.htm Accessed August, 2015.

Within the genus of chemolithotrophs are species with varying abilities for S oxidation and the rate of oxidation. Some species of *Thiobacillus*, including *T. novellus*, *T. acidophilus*, *T. aquaesulis* are classified as heterotrophs, as well as *Thiosphaera pantotroph* and *Thiomicrospira*

thyasirae. The implication of heterotroph populations which dominate a soil is that oxidizable S may not be readily oxidized if there is another substrate for the microorganism to metabolize more easily to achieve the same metabolic result. In Saskatchewan (Lawrence and Germida, 1991), 35 soils within the Province were assessed for presence of S oxidizing bacteria and characterized for species. No evidence of the obligate chemolithotrophs *Thiobacillus thiooxidans* or *T. ferooxidans* was found. The dominant populations of S oxidizing bacteria were heterotrophic and exhibited a passive trend to oxidizing elemental S.
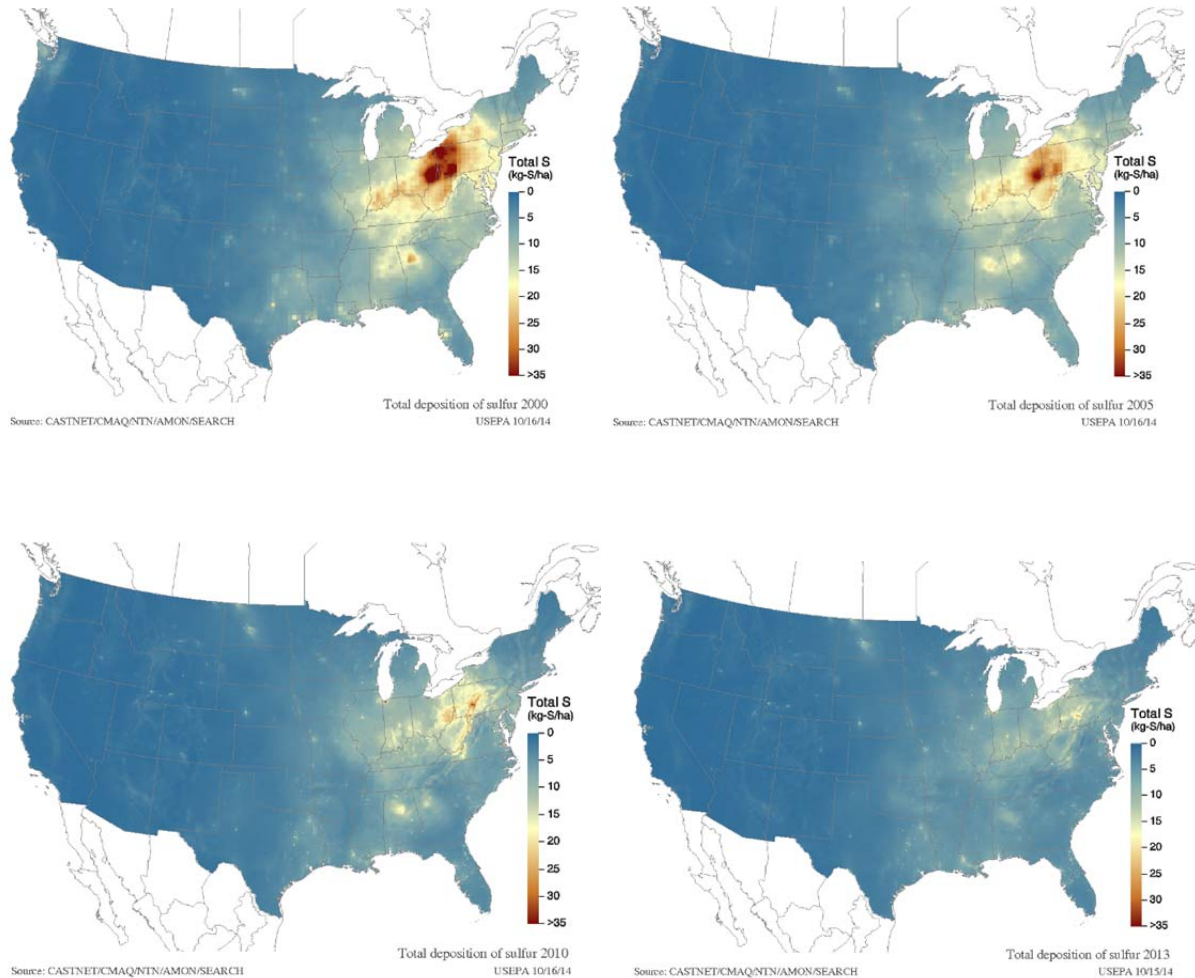

Figure 4. Annual total deposition of S on the contiguous 48 US states, 2000 (upper left), 2005 (upper right), 2010 (lower left) and 2013 (lower right). http://nadp.isws.illinois.edu/ Accessed August, 2015. Values in kg/ha. To convert, multiply scale value times 0.89 .

The general S cycling in soil is outlined in Schoenau and Germida (1992). Sulfur is required by plants and microorganisms, so any S in the system either enters these biological pools, or may be lost from the system through leaching or as H_2S or DMS gases in flooded systems. As mineral S is added into the system from rainfall, it may be taken up by microorganisms and then slowly released to plants directly as sulfate or indirectly after oxidation by microorganisms. Plant

residues may release sulfate if taken up in excess, or more commonly after microorganism oxidation of sulfides. The organic matter component of soils has an inherent C/N ratio, but also has an inherent N/S ration, usually about 10/1. As N is mineralized, S is also released into the soil solution as an inorganic nutrient.

Background or 'natural' S nutrition is therefore a combination of S received from the atmosphere originating from natural and anthropogenic sources, release of inorganic S from microorganism activity on soil organic matter and residue decomposition, presence of soluble sulfate salts, and the slow release from soil mineral sources. If the requirements of crop growth exceed that which these background sources supply, or the supply of these sources is lost due to excessive rainfall and subsequent leaching beyond the depth of the roots for uptake, supplemental S is required.

Status of S deficiency in the North Central Region

Serious cultivation of canola began in North Dakota about 1994. Canola is a rape seed bred in Canada for low erucic acid which is unpalatable to humans (Gupta and Pratap, 2007). Since its early cultivation in Canada, canola has been known for its particular sensitivity to low soil S levels and has a greater requirement for S compared to most other crops, including other mustard family crops (Grant, 1991; Franzen and Grant, 2008). The most severe S deficiencies were observed on eroded hilltops and slopes, leading to investigation of S availability on the landscape (Roberts and Bettany, 1985). Greater levels of total S in lower landscapes were the result of a higher water table and greater organic matter containing greater amounts of organic S compared to upper landscape positions. A landscape based experiment was conducted in North Dakota using different S rates and sources (Deibert and Halley, 1996). The results indicated that S deficiency in canola can be catastrophic, there were large differences in S response possible between hilltop, slope and footslope positions, and elemental S application performed better than the check, but was not nearly as effective as an equivalent S rate as ammonium sulfate (21-0-0-24S).

Table 3. 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	Buse/hilltop	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

† Elemental S used was a premium fertilizer with very small particles bound with bentonite clay for quick particle breakdown and dispersion in the soil.

Apart from canola, the frequency of S deficiency has increased across most of the central and western region. One reason for the dramatic increase is increased yield. Low to modest yields of all crops require proportionally less S compared to the high yields of today. Twenty years ago, 100 bu/acre spring wheat yields were almost unknown in North Dakota and the Canadian Prairies, whereas today they are more and more commonplace. In Illinois, 250 bu/acre corn yields were the stuff of yield contests in the 1970's whereas today they are commonplace.

Yields of all crops have increased when environment permits, and therefore so does the nutrient requirements. In all of the North Central states, S deficiency has been recognized and S fertilization has been recommended on coarse-textured soils with low organic matter for corn production (Franzen and Grant, 1998; Rehm and Clapp, 2008) for more than 30 years. Spring S application as a sulfate or thiosulfate source has been most effective in overcoming deficiency. Banded and broadcast application of S has been equally effective, as long as adequate amounts of S are applied. In a band, this usually implies that application some distance away from the seed, such as the 2 inch to the side and 2 inch below the seed configuration, is necessary to avoid salt injury.

During the past 10 years, increasing reports of S deficiency on soils once thought immune to deficiency have been made. Five sites in North Dakota as part of an N-rate study conducted from 2010 to 2014 were affected by S deficiency. Rescue S applications were made at V5 and the studies were salvaged. Three of these S deficient sites were silty clay loam texture with over 5 per cent organic matter. The author's standard procedure for establishing N rate trials now requires preplant application of 20 pounds per acre S as gypsum prior to planting. In 2015, several sites were green islands in a sea of yellow corn, and S deficiency symptoms affected roughly half the corn fields in eastern North Dakota (Franzen, 2015). Teboh and Zilahi-Sebess recorded a 7 bu/acre spring wheat yield increase and a half point increase in grain protein with the application of 20 lb/acre S as ammonium sulfate.

Frequency of S responses have increased recently in Illinois. In the mid to late 1970's, Hoeft et al. (1985) conducted a series of S trials across Illinois and found that yield was increased due to S application at only 5 of 82 sites. Sulfur responses were confined to soils with low organic matter and deep sandy profiles. Fernandez et al. (2012) reported small plot and field strip trial responses to S on sandy soils, but also some silt loam sites with medium organic matter levels. Mean yield increase at responsive sites was 13 bu/acre. Frequency of responses in Illinois from 2009 to 2011 was greater than those experienced by Hoeft et al. (2012) twenty-five years before.

In Indiana, corn responses to S have been confined to coarse-textured, low organic matter soils until recently. Sulfur response trials on wheat in 2010 found more widespread S deficiency even on some moderate organic matter silt loams (Camberato and Casteel, 2010). Researchers in Ohio have recorded responses in corn to S application on low organic matter, sandy soils, and University recommendations include application of S on similar soils. Responses have not been observed on medium or higher clay textured soils (Lentz, personal communication, August, 2015). Sulfur studies are on-going in Ohio.

Sulfur deficiency has not been a historic problem in Michigan, probably because of large amounts of atmospheric S deposition from Great Lakes coal/oil/gas fired industries until lately (Vitosh et al., 1994). Some documented S deficiencies on low organic matter, sandy soils in kidney bean and corn were noted.

In Wisconsin, S deficiency in alfalfa on sandy, low organic soils has been reported and researched for over thirty years (Hoeft et al., 1973). Sulfur deficiency continues to be a problem in alfalfa in southwest Wisconsin (Lakoski personal communication, August, 2015). Sulfur deficiency can also be observed in corn on sandy and loamy soils in central and western Wisconsin and also on silt loam soils shallow to bedrock (< 30 inches of soil over bedrock).

Iowa began to record S deficiencies for the first time in 2005 with dramatic alfalfa yield increases with S fertilization (Sawyer et al., 2009). This was followed in 2006 on sites suspected of having S deficiency study in corn, with the S source (40 lb/acre S as calcium sulfate) applied during early corn growth. Yield increases in 2006 were recorded at five of the six chosen sites,

with a mean yield increase of 38 bu/acre (Sawyer, 2009). Studies were expanded in 2007 and 2008, with sites chosen to represent major soils of the north-central Iowa region. Corn yield was increased at 17 of 20 sites in 2007 and 11 of 25 sites in 2008. Yield increase averaged about 15 bu/acre in fine-textured sites and 28 bu/acre in coarse-textured sites. Between 2006 and 2013, 47 percent of 110 Iowa S rate trials had yield increases.

Missouri has only observed S deficiency in low organic matter, sandy soils (P. Scharf, August, 2015 personal communication). No increase or expansion of S deficiency in corn has been noted. Kansas has had a long history of S deficiency on low organic matter, sandy soils (D. Mengel, personal communication, August, 2015). Yield increases in S were also recorded in wheat, grain sorghum, alfalfa, bromegrass and tall fescue. Most of these studies were conducted on low organic matter soils, but some bromegrass responses to S were observed on soils with organic matter greater than 3 percent (Lamond, 1997). Until recently, yield increase of crops to S application was confined to these traditionally S-lacking soils. Yield increase to S application was recorded at three sites in Kansas in 2012 (Widmar and Ruiz Diaz, 2012).

In Minnesota, S has been recommended for use in sandy, low organic matter soils for many years (Rehm and Clapp, 2008). With a series of studies begun in 1999, corn yield increases with S were recorded in loam and silt loam soils, but not in a silty clay loam textured soil (Rehm, 2005). Kim et al. (2013) expanded on previous work and found corn yield response to a S deficiency in a higher organic matter loam soil in Minnesota. Although it is unusual to experience a soybean yield increase to S, Kaiser and Kim (2013) increased soybean yield in a low organic matter (<2%) silt loam soil. Two additional soybean sites with soils having higher organic matter were not responsive to S.

In Nebraska, irrigation water has enough sulfate S to cover most crop needs, but S application through the irrigation pivot is still common in the sand hills, the irrigated sands of north central Nebraska, and sandy soils in river valleys in central and south Nebraska fields (Ferguson, Wortman and Shapiro, personal communications, August, 2015). As much as 50 lb/acre of S as ammonium thiosulfate through the irrigation pivot or ammonium sulfate or sulpha-mag is applied annually to some fields.

Diagnostic value of S soil tests

Tabatabai (1996) reviewed a large number of methods for S determination in soils. Due to relationships found by Probert (1976) between $Ca(H_2PO_4)_2$ extracted sulfate and plant uptake, researchers generally accept the monocalcium phosphate extraction procedure as the one that would be most related to crop production. This test is the analysis most often used by laboratories in the North Central USA region as a guide to growers on soil S status. Research by others in the 1960's and early 1970's supported the monocalcium phosphate extractant to some degree (Fox et al., 1964; Hoeft et al., 1973). Hoeft et al. (1973) found that of the extractants examined, the monocalcium phosphate with 2N acetic acid performed the best and the monocalcium phosphate without 2N acetic acid was not as good at predicting alfalfa yield as a sulfate-S extractant. Soon after this report was published, practitioners found that the acetic acid version of the extractant was more unwieldy to use compared to the water-based monocalcium phosphate extractant and so with rare exception the acetic acid based extractant is not used. Despite the overwhelming adoption by laboratories of the monocalcium phosphate extractant, the extractant is not very diagnostic with regards to most crops. All other extractants tested to date have similarly been non-diagnostic in the soils in which they have been used.

In the 2005 to present Iowa work on S application to corn, extractable sulfate-S was not related to yield response in the check plots. Sulfate concentrations higher than 10 ppm would be regarded as non-responsive, but some of these sites responded to S. The non-relationship of the current sulfate-S soil test with corn yield is shown in Figure 5.

Extractable sulfate-S was also non-diagnostic in a summary of 10 years of sulfur fertilization trials at both Brookings and Beresford, SD (Gelderman, unpublished data). No response was observed at Brookings over 10 years, despite low S soil test numbers, while at Beresford, about a 4 bu/acre average response was documented. The relationship of corn response to sulfate-S soil test levels in SD over 17 years is shown in Figure 6. The relationship of extractant to canola yield response to S in North Dakota is low (Lukach, personal communication, 2012). In 2014 in North Dakota, a yield increase in spring wheat with S application was recorded with a 'high' beginning soil sulfate test (Teboh and Zilhi-Sebess, 2014).

A KCl extractant-based available S as sulfate soil test was published by Blair et al. (1991) in which there seemed to be an excellent relationship between extracted sulfate-S and yield. On closer examination of the data the formula for prediction is based on two sets of soils, those that have variable yields and nearly always have a low S soil test and soils that are high yielding over a wide range of extractable S values. Putting the two data sets together results can be statistically forced to form a steep quadratic curve, with a nearly vertical component from one soil group, and an unresponsive horizontal component from the other soil group. Kim and Kaiser (2013) used this extractant in their Minnesota study and found no relationship between test results and yield.

One reason why a better sulfur soil test has not been developed in the US is that before 2005, general S deficiency was not widespread, localized, and considered of minor importance. The large number of S deficiencies across this large region provides a stage for the testing and development of new ideas for soil testing and prediction of S deficiency not available in the region previously.

One strategy for the use of active-optical sensors in determining the need for side-dress N in corn and its rate is to establish an N non-limiting area within the field of interest. Nitrogen rate studies in North Dakota indicate that the use of such an N non-limiting area would also serve to reveal S deficiency (Figure 7). If N in a crop is deficient, there are signals within the crop that result in deconstruction of N containing compounds, such as proteins, and relocate these compounds to newer growth. If N and S are both deficient, S is also relocated along with the N in these compounds, since S is present in several amino acids and other N containing compounds. If N is not deficient, and S is deficient, there is no signal in crops to deconstruct these compounds and relocate them. The result is that when N is adequately supplied, S deficiency symptoms are intensified. In an N non-limiting area within a S deficient field, the N non-limiting area will be the most yellow area of the field. If this is detected either visually or with an active-optical sensor, S should be applied immediately to remedy the condition (Sharma et al., 2015).
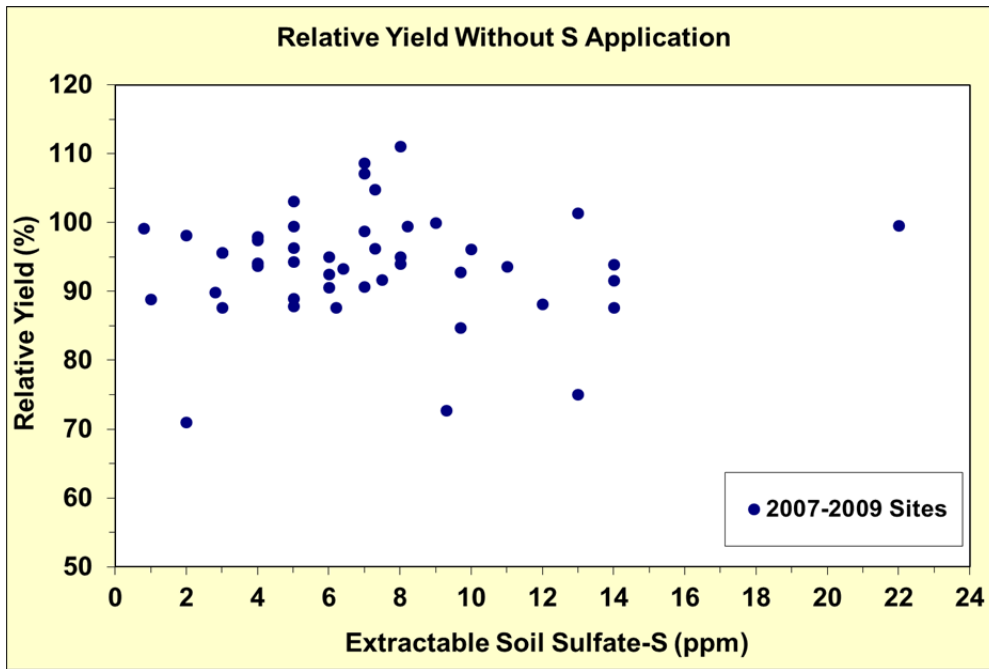
Figure 5. Relative corn yield in relation to sulfate-S soil test, Iowa (Sawyer).
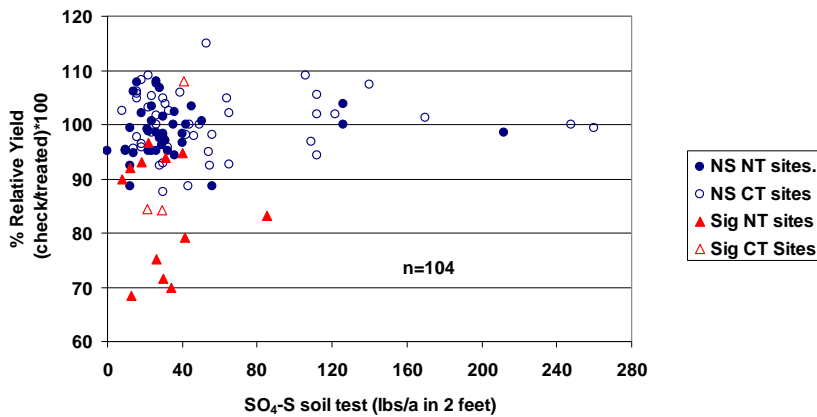

Figure 6. Relative corn yield in relation to sulfate-S soil test, South Dakota, 1990-2007.

Figure 7. Sulfur-deficient N rate study near Oakes, ND, spring 2014. Yellowest plots are high N rates. Greenest plots are low N rates. Following S application, the high N rate plots became the greenest and check plots were least green. Grower had applied 10 pound per acre S in a 2X2 band as ammonium thiosulfate to corn surrounding our plot area (foreground).

If a suitable S soil test is found, variability of S within a field is a concern. In North Dakota, extractable sulfate-S was one of the most variable nutrients analyzed in site-specific nutrient management experiments, with values in soil cores to 2 feet in depth varying from under 10 lb S/acre to nearly 1000 pounds S per acre within a 40 acre field (Figure 8). Therefore, regardless of what method is used to try to predict the S status of soils, sampling with consideration of the mobility of sulfur would be advisable.
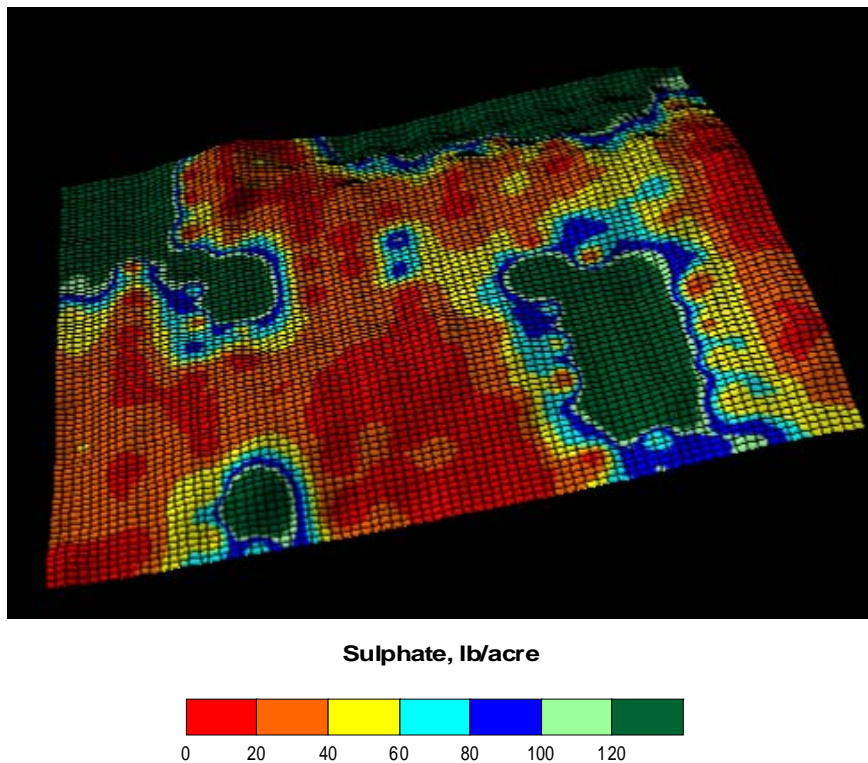
Sulphate, lb/acre

Figure 8. Variability of sulfate-S analyzed from a 110-foot grid over a 40-acre field near Valley City, ND. High sulfate areas tend to be local depressions and lowest sulfate are in low organic matter upland soils, usually, but not always associated with coarser textured soils.

Alternative S prediction strategies

Of the states that have a history of substantial regions that have experienced repeated seasons of S deficiency in some soils, extractable S is usually a factor within the recommendation equation. Kansas has such an equation (Lamond, 1997), as does Nebraska although Nebraska's recommendations are in the form of a chart with soil test sulfate and organic matter as factors (Shapiro et al., 2008). In North Dakota, growers are urged to track fall and spring rainfall, and winter snowmelt. If any precipitation at these times is greater than normal, S deficiency on small grains and corn should be anticipated and spring applications made to prevent it, regardless of any soil test value. In-season, paired plant tissue analysis for S from an area where S is deficient compared to plant tissue S from an area where plants are healthy can be a helpful diagnosis. An unpaired sample from a field is discouraged because of spatial variability of individual plant S status, wide variation in S concentration from critical level nutrient charts and varietal variation (Mallarino, 2013).

Sulfur amendment sources and application

Manure is available as a S amendment to some producers. The amount of S per ton of dry manure varies from 1 to 3 lb S/ton, while the S in liquid manure varies from 4 to 9 pounds S per 1,000 gallons. Manure is an organic source (not necessarily organic by what is meant at the grocery store, but organic in terms of carbon chemistry). As such, some S may be an immediately usable form, while the majority may need decomposition for the S to be released to a form available to plants. Usable S in dry manure varies from <1 to 2 pounds S per ton and S in

liquid manure varies from 2 to 5 lb S/1,000 gallons (Lamond, 1997). A manure analysis is required for the best estimate of total S content of the manure, and referring to a recent state manure nutrient availability publication within the state where the farm is located would be highly recommended.

Sulfur content of the most common S fertilizers available in the region are listed in Table 4. All of the materials in Table 4 have been found by many North Central researchers to be highly effective in increasing yield of crops under S deficient conditions in the region both preplant and in-season. Elemental S is not independently listed because researchers who have included it in their studies conclude that although yield is increased with its use, other products are more effective in increasing yields. A full discussion of the problems of oxidation of elemental S to sulfate is provided in Franzen and Grant (2008). The property of all effective S fertilizers are that they are best used in the spring. In the region, highest soil moisture and the greatest opportunity for leaching loss is in the early spring before planting. Therefore, a fall application is the worst time to apply sulfate or thiosulfate fertilizers. Although it puts enormous pressure on the logistics of fertilizer suppliers, S fertilizers are spring fertilizers. Ammonium sulfate, potassium magnesium sulfate, the Mosaic MES products, gypsum and potassium sulfate are dry granular products. Ammonium sulfate application twenty years ago suffered from segregation problems when smaller crystal/granule sizes were used. Ammonium sulfate granules are now provided by most manufacturers to minimize segregation during blending and to allow for more even application. Gypsum formulations are currently in the growing-pains process, but there are some manufacturers that formulate a granule compatible with other fertilizer blending products. Ammonium thiosulfate and potassium thiosulfate are liquid fertilizers, with ammonium thiosulfate currently the product most widely sold. Much ammonium thiosulfate is applied through an irrigation pivot, however, sizable tonnage is applied as a 2X2 band at planting and mixed with UAN solutions for a dribbled or coulter applied side-dress application. Ammonium thiosulfate has reduced stand in some studies when applied directly with the seed at low rates, but especially at higher rates (Rehm, 2005).

Table 4. Major effective fertilizer S sources used in the North Central USA region, 2015.

Fertilizer	N	P_2O_5	K_2O	S
		percent		
Ammonium sulfate	20-21	0	0	24
Ammonium thiosulfate	12	0	0	26
Calcium sulfate/hydrated (Gypsum)	0	0	0	18.6
Potassium sulfate	0	0	50	17.6
Potassium thiosulfate	0	0	20	17
Potassium magnesium sulfate	0	0	22	22
MES 15 (50% ammonium sulfate, 50 % elemental S)	13	33	0	15

Unless fall, winter and early spring rainfall is low, S application should be spring applied. In a recent Illinois study, only 6% of labeled S from fall applied sulfate was present in the surface 36 inches of soil compared with 40% from spring application (Degryse et al., 2015).

SUMMARY

In North Dakota, most of Minnesota, Wisconsin, Iowa, South Dakota, Nebraska, Kansas, and parts of Illinois and Indiana, anthropogenic contributions have become so small that most S from rainfall comes from natural sources, with background levels no greater than 10 pounds S per acre, with much of the area less than 5 pounds S per acre. Sulfur deficiency is much more common in several states than in the past. Corn, wheat, alfalfa and bromegrass appear to be particularly susceptible, along with canola. Occasional deficiencies are also observed in soybean, but responses to S have been small and few. The most effective S fertilizers are those that contain sulfate or thiosulfate. Elemental S has some value, but is not nearly as effective at similar rates compared to sulfate and thiosulfate alternatives. Diagnostic soil tests are currently very poor. The widespread high frequency of S deficiency in some states is an opportunity to work towards an improved diagnostic method.

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APPENDIX - Sulfur Deficiency Symptoms of Selected North Central Region Crops

Early season canola S deficiency symptoms- interveinal chlorosis, auxin-type symptoms. Franzen image, NDSU.

Mid-season canola S deficiency symptoms, bronze appearance of plants from a distance, purpling and upright growth at close inspection. Flowers may be white or non-existent. Franzen image NDSU.

Wheat. Yellowing of upper, newer leaves, green leaves below. Franzen image, NDSU.

Corn. Yellowing upper leaves, striped appearance.
Franzen image, NDSU.

Alfalfa S deficiency, small, yellow leaves compared with normal, Darlington, WI.
Image courtesy of R. Schmidt and C. Laboski.

Alfalfa deficiency across a Wisconsin landscape, yellowing plants particularly on hilltops and eroded slopes.
Courtesy of T. Bay and C. Laboski.

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