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Predicting plant sulfur deficiency in soils: results from Ohio

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Abstract We developed a model for plant available sulfur (S) in Ohio soils to predict potential crop plant S deficiency. The model includes inputs of plant available S due to atmospheric deposition and mineralization of soil organic S and output due to leaching. A leaching index was computed using data on annual precipitation; soil pH and clay content that influence sulfate adsorption; and pore water velocity based upon percent sand, silt, and clay. There are five categories of S status ranging from highly deficient to highly sufficient, and the categories are defined based on whether the crop S requirement was 15 or 30 kg S ha⁻¹ vear⁻¹. The final database derived from the model includes 1,473 soil samples representing 443 of the 475 soil series in Ohio. For a crop requiring 15kg S ha⁻¹ year⁻¹, most soils (68.6%) were classified as variably deficient, which implies that the response to S fertilization will be variable but often positive depending on specific crop conditions. For a crop requiring 30kg S ha⁻¹ year⁻¹, 43.2% of soils were classified as variably deficient, but 49.7% were classified as moderately or highly deficient, implying that a response to S fertilization will usually or always occur. The model predicts crop S status for a single state in the USA, but with proper inputs, it should be applicable to other areas.

Keywords Atmospheric sulfur inputs · Organic sulfur mineralization · Plant sulfur deficiency · Soil sulfur deficiency · Soil sulfur model · Sulfur leaching

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Introduction

Sulfur (S) is an element essential for plant growth. It is a macronutrient and, like N, P, K, Ca, and Mg, must be available in relatively large amounts for good crop growth. Sulfur is a constituent of the amino acids cysteine and methionine and hence of protein. When S is deficient, the cysteine and methionine content in plants decreases, and the synthesis of proteins is inhibited (Marschner 1986). Sulfur in plants is also a structural constituent of many coenzymes and secondary plant products or acts as a functional group directly involved in metabolic reactions. Sulfur requirements vary considerably in crops. Alfalfa (Medicago sativa L.), a high S requirement crop, removed almost 40kg S ha⁻¹ from the soil each year when yield was 15Mg ha⁻¹ (Troeh and Thompson 1993). Corn (Zea mays L.), a low S requirement crop, removed 11kg S ha⁻¹ from the soil each year when grain yield was 9.4Mg ha⁻¹ (Hoeft and Fox 1986).

In recent years, deficiencies of S in crops have increased worldwide (Chibber 2007). This is attributed to the decrease of S inputs to the soil system and the increase of S output. Decreased S inputs to soil include use of highly concentrated fertilizers containing little or no S (Scherer 2001) and less S deposition from the atmosphere (National Atmospheric Deposition Program 2007). Increased S output from soil includes intensive cropping systems and increased crop yields that result in more S removal (Ohio Department of Agriculture 2006).

In Wooster, Ohio, annual S deposition (as wet SO_4) gradually decreased from 11.6kg ha⁻¹ in 1979 to 7.3kg ha⁻¹ in 2005 (National Atmospheric Deposition Program 2007) because the SO_2 produced during fuel burning was removed from flue gases via some type of scrubbing technology to meet clean air regulations. This is a 37%

reduction. In Ohio, average yields of hay (mostly alfalfa) increased from 5.5Mg ha⁻¹ in 1977–1979 to 6.5Mg ha⁻¹ in 2003–2005, corn yields increased from 6.8 to 9.6Mg ha⁻¹, soybean [*Glycine max* (L.) Merr] yields from 2.3 to 2.9Mg ha⁻¹, and wheat (*Triticum aestivum* L.) yields from 3.0 to 4.5Mg ha⁻¹ during the same period (Ohio Department of Agriculture 2006). This means that approximately 18% to 50% more S was removed by crops from the soils each year compared to 25years ago. Because of these trends in S inputs and outputs, crop response to S application on agricultural soils will probably occur with greater frequency in the future.

Sulfur-deficient soils are often low in organic matter, coarse-textured, well-drained, and subject to leaching. Crop response to S on any particular soil will vary with crop S requirement, which is high for alfalfa and relatively low for corn and soybean. Alfalfa yield was increased by S application on a silt loam soil in Ohio (Chen et al. 2005). Alfalfa yields were increased by S application on sandy loams but not on silt loams in Minnesota (O'Leary and Rehm 1989; Sloan et al. 1999). Alfalfa yields were not affected by S application in central Maryland in the USA (Vough et al. 1986) and on fine sandy loam soils on Prince Edward Island in Canada (Gupta and MacLeod 1984). In substantial amounts of farmland in western Canada, the yields of corn and soybean were significantly increased by S fertilizer treatments (Beaton and Soper 1986). Soybean and corn also responded to S application on some experimental sites in Ohio (Chen et al. 2005). When experimental sites were located on soils containing a higher concentration of organic matter and receiving greater amounts of S from precipitation and air pollution, soybean yields were not increased (Chen et al. 2005). The research results above clearly demonstrate that crops grown on some soils in Ohio will respond to S fertilizer inputs.

McGrath and Zhao (1995) developed a qualitative model to estimate the risk of S deficiency in cereals in Britain. They used data on atmospheric S deposition, soil organic matter, and factors influencing S leaching (such as soil texture, pH, and annual rainfall) to develop their model. We used a similar S balance approach to develop a model that identifies potential soil series in Ohio where crops having either a low or high S requirement will be responsive to S fertilizer inputs. This was done by combining S inputs from the atmosphere and organic matter, with S outputs via leaching and crop removal. The objective of this research was to provide a statewide model that predicts soils where S is deficient and S fertilizers are needed as a nutrient supplement.

Materials and methods

This work was restricted to soils located in the state of Ohio (north central USA), although the work described is meant

to be applicable to other areas of the USA and the world. The starting point for a material balance on a component, in this case soil S available for crop growth, within a system is Eq. 1 (Felder and Rousseau 2000):

$$Input + Generation = Output + Accumulation$$
(1)

In this model, we are doing a balance on *plant available* S and not on *total S* in the soil. We are assuming that total S in the soil is at steady state. The input term is atmospheric deposition of S, generally as sulfate in acid rain. The generation term represents plant available S produced by mineralization of organic matter. As the soil organic matter is decomposed (or mineralized), S will be released and will become available for plant uptake. For the generation term, we assume that sufficient organic matter containing organic S is returned to the soil each year to maintain S generation at a constant level. The primary outputs or losses from the soil are leaching of sulfate and crop removal of S as harvested grain or forage. The accumulation term represents a change in plant available S in the soil and could be either positive or negative. Substituting these terms into the general equation yields a new equation (Eq. 2) in which the terms on the left of the equal sign contribute available S to soil and the terms on the right are those that remove or store available S in soil.

$$= S(leached) + S(required by crop)$$
$$+ S(accumulated)$$
(2)

S(deposited) + S(mineralized)

Rearranging yields yet another equation (Eq. 3) where the terms on the right represent S availability for plant uptake or storage in soil.

$$S(deposited) + S(mineralized) - S(leached)$$

= S(required by crop) + S(accumulated)(3)

If the amount of S needed for good crop growth is greater than that made available in the soil by atmospheric deposition and organic matter mineralization, the deficit in S could be satisfied, at least in the short term, by a negative S accumulation. This would represent a decrease in plant available S in the soil. We lack information on the accumulation of plant available S in the soil on an annual basis, so we assume that it is at steady state, and the value for S accumulation in soil was, therefore, set to zero. This leads to the following equation (Eq. 4), which was used to evaluate soils in terms of their abilities to supply sufficient S for good crop growth:

$$S(deposited) + S(mineralized) - S(leached)$$

$$= S(required by crop)$$
(4)

If the value of the left side of the equation is less than that required by the growing crop, the crop will suffer some degree of S deficiency. We were not able to compute actual values for the left side because of the difficulty of estimating S (leached). Instead, for each soil, we developed an index of S leaching and subtracted it from a coded value for the sum of S (deposited) + S (mineralized). This coded value for S (deposited) + S (mineralized) was developed with reference to the S requirements of two different crops, corn and alfalfa.

Estimates of S (mineralized) and S (deposited)

Initial input data for development of the S deficiency model was a database of Ohio soils (F. G. Calhoun, personal communication). The database consisted primarily of information collected during the soil survey mapping of each county, plus some additional data collected during research studies. These data, maintained in a FileMaker Pro database, were first imported into an Excel spreadsheet. Only pedons (specific soil sample sites) having soil organic C data were imported because organic C data were necessary for estimating sulfate released by mineralization of organic S. The model was developed only for pedons sampled to a depth of at least 20cm. In any county, a specific soil series might be represented by more than one pedon in the data set. For example, there were cases where nine pedons of a soil series were sampled in a single county. The S status for those soil series with multiple pedons in a county was based on results for all pedons of the series for that county and represents a more robust estimation of S availability. However, most soil series (969) were represented in each county by only one pedon.

The next step was to sort the data by the number of soil horizons occurring in the upper 20cm of depth to facilitate the calculation of a weighted percent organic C for each pedon (soil). There were 1,152 pedons with one horizon in the upper 20cm, 1,167 with two horizons, 356 with three horizons, 28 with four horizons, and two with five horizons. For each pedon, a weighted average value for percent organic C in the entire 20-cm depth was calculated using the relative thickness and percent organic C for each horizon in the pedon.

The amount of S released by mineralization of organic matter each year was calculated by assuming a soil bulk density of 1.325 g cm^{-3} (i.e. $1,325 \text{ kg m}^{-3}$), a mass ratio of 1kg S for each 60kg C in organic matter (Morra 1986), and that 2% of organic S is mineralized each year. A soil that contains 1% organic C (i.e., 1kg org C/100kg soil) in the upper 20cm of the profile would,

therefore, release 8.83kg S ha⁻¹ each year based upon these assumptions (Eq. 5) where X is equal to 1.

$$\frac{X \ kg \ org \ C}{100 \ kg \ soil} \cdot \frac{10^4 \ m^2}{ha} \cdot 0.2 \ m \ depth$$
$$\cdot \frac{1,325 \ kg \ soil}{1 \ m^3 \ soil} \cdot \frac{1 \ kg \ org \ S}{60 \ kg \ org \ C} \cdot \frac{2 \ kg \ S \ min}{100 \ kg \ org \ S}$$
$$= \frac{8.83 \ kg}{ha} \ S \ min \tag{5}$$

For each pedon, the annual amount of S released by mineralization was calculated as the product of weighted value of percent organic C times the factor value 8.83.

Atmospheric deposition of sulfate was estimated from maps in the National Atmospheric Deposition Program website (National Atmospheric Deposition Program 2007). The maps for sulfate deposition by rainfall in 2002 and 2003 were compared with a state map of Ohio to estimate atmospheric deposition of sulfate for each county in Ohio for each year. Atmospheric deposition of sulfate on each pedon was taken as the 2-year average of the sulfate deposition values for the county in which the pedon occurred. Annual sulfate deposition (kg ha⁻¹) varied from 17.5–19 for 11 counties in northwest and north central Ohio to 26 (for seven counties) and 32 (for Noble County only) in southeast Ohio.

Atmospheric sulfate was converted to elemental S and then added to S released by mineralization to determine the total potential amount of S available for crop growth each year, assuming no leaching. Because crop requirements for S differ, we created a code that related the total potential amount of S available in soil to the crop requirement (Table 1). A crop requirement of 15kg S ha⁻¹ year⁻¹ was designated low, and a requirement of 30kg S ha⁻¹ year⁻¹ was designated high. Soils were, therefore, constrained to categories based on whether the crops growing on them had requirements closer to the 15kg S ha⁻¹ year⁻¹ or the 30kg S ha⁻¹ year⁻¹.

Availability indices were then assigned after subtracting the low (i.e., 15kg S ha⁻¹ year⁻¹) or the high (30kg S ha⁻¹ year⁻¹) amount of S that would be removed by a low- or high-sulfur-requiring crop from the amount of potential S available (Table 1). Table 1 was created to ensure that for soils having the same availability index but differing crop requirements, the same magnitude of leaching will result in a similar final availability of S for the crop after leaching. For example, a soil with total potential S of 35kg ha⁻¹ year⁻¹ and a low crop requirement of 15kg S ha⁻¹ year⁻¹ and a soil with total potential S of 50kg ha⁻¹ year⁻¹ and high crop requirement of 30kg S ha⁻¹ year⁻¹ would both have an availability index of 4. Table 1Coded S availabilityindex for growth of crops

The potential total S available (column 2) is a sum of the available S in soil due to organic matter mineralization (Eq. 5) and the amount of S that is annually introduced to soil by precipitation.

Crop requirement	Potential total S available (kg S ha ⁻¹ year ⁻¹)	Potential S minus crop S requirement (kg S ha^{-1} year ⁻¹)	A (availability index)
Low	0–10	-15 to -5	0
	>10–20	-5 to 5	2
	>20-30	5 to 15	3
	>30-45	15 to 30	4
	>45	>30	5
High	0–25	-30 to -5	0
	>25-35	-5 to 5	2
	>35-45	5 to 15	3
	>45-60	15 to 30	4
	>60	>30	5

Estimates of S leached from soil

Quantitative values of the amounts of S leached from various soils are difficult to obtain. Thus, we decided to develop a risk index of S leaching. Sulfur leaching, generally as the sulfate ion, is affected by the amount of precipitation, soil texture, clay content and mineralogy, and soil pH (Tisdale et. al. 1986). Soil texture influences velocity of water movement through the soil. Clay content and mineralogy and soil pH all influence sulfate adsorption, which reduces S leaching. For each pedon, these factors (except clay mineralogy) were combined to produce an index of S leaching. The index was designed so that the risk of leaching increased as the value of the index increased.

The leaching index (L) for precipitation varied as shown in Table 2. Each county was assigned a leaching index for precipitation that was applied to all soils occurring in the county. Because no Ohio counties receive less than 700-mm annual precipitation, the leaching index for precipitation varied from 2 to 4 for Ohio counties.

Sulfate adsorption increases as clay content increases and as soil pH decreases. Neller (1959) reported extractable sulfate for Florida soils in relation to clay content and soil pH. His data indicated that sulfate adsorption was least for soils with less than 14% clay, intermediate for soils with 14 to 28% clay, and greatest for soils with greater than 28% clay. The leaching index for adsorption as affected by clay content (C) in the soil is provided in Table 2.

Neller's (1959) values for extractable sulfate were variable for soils in the pH range 4.6 to 5.55 but decreased for soils with pH greater than 5.9. Kamprath et al (1956) found that sulfate adsorption decreased as soil pH increased from 4.0 to 6.0. Thus, to account for pH on S leaching potential of Ohio soils, we also created a leaching index for adsorption based upon soil pH (P) as shown in Table 2.

If a pedon had more than one horizon in the upper 20cm, a weighted percent clay and weighted pH were calculated before assigning the leaching index values for clay content and pH.

Soil texture influences solute leaching through its effect on pore water velocity as well as the effect of clay content on solute adsorption. Pore water velocity for saturated flow equals saturated hydraulic conductivity divided by saturated volumetric water content. Saturated hydraulic conductivity and volumetric water content were calculated for each horizon in each pedon by the Rosetta program using percent sand, silt, and clay as inputs (http://ars.usda.gov/ Services/docs.htm?docid=8953). The resulting 4,675 pore water velocities included 4,369 velocities less than 100cm day⁻¹, 286 velocities between 100 and 1,000cm day⁻¹, and 20 velocities greater than 1,000cm day⁻¹. For pedons with more than one horizon, the horizon with lowest pore water

R (rainfall)		C (clay content)		<i>P</i> (pH)		V (pore water velocity)	
Index value	Precipitation	Index value	Clay (%)	Index value	pН	Index value	Velocity (cm day ⁻¹)
1	<700	1	>28	1	<4	1	<100
2	700-850	2	14-28	2	4-6	2	100-1,000
3	850-1,000	3	<14	3	>6	3	>1,000
4	>1.000						

Table 2 Index values assigned to precipitation, soil clay content, soil pH, and soil pore water velocity used to estimate sulfur leaching potential

velocity was used for assigning the leaching index for pore water velocity. The leaching index for pore water velocity (V) as determined by soil texture was assigned to soils as shown in Table 2.

It might be argued that calculating pore water velocity (V) with the Rosetta program and then coding the resulting velocities represents a waste of effort and that soil textural class could be used as an index for leaching. Results for the silt loam textural class show that the calculation was not a waste of effort. There were 2,602 horizons classified as silt loam, and calculated pore water velocities varied from 16.8 to 170.4cm day⁻¹. Fifty-two horizons had V greater than 100cm day⁻¹, but most (1,994 horizons) had V less than or equal to 50cm day⁻¹. The procedure for determining the leaching index for pore water velocity differentiated the leaching susceptibilities for a large group of horizons all classified as silt loam textural class.

The values of R, C, P, and V could be combined and considered as a single entity or leaching value (L) that is related to S leaching for each individual pedon as shown in Eq. 6.

Leaching values
$$(L) = R + (C+P)/2 + V$$
 (6)

The value of [R + (C + P)/2 + V] could vary from 4 to 10. The leaching index for precipitation (*R*) could vary from 1 to 4, while the other indexes (*C*, *P*, and *V*) could only vary from 1 to 3. This implies that greater importance was placed on precipitation as a cause for S leaching. This is reasonable because if there is no precipitation, there is no leaching, regardless of other soil characteristics. In addition, the clay content and pH index values were combined into a single average value, and this effectively reduces their influence on the final S score. This was also felt to be appropriate based on their presumed relative effect on S leaching as compared to precipitation amounts and pore water velocities.

Assigning S availability scores

The coded availability index values (A) in Table 1 were combined with leaching values (L) developed for leaching losses (Eq. 6). A final S score was then calculated and assigned to each pedon based upon the following equation:

Final S score (SC) =
$$A - L$$
 (7)

where A is the availability index value (Table 1) and L is the leaching value determined by calculation according to Eq. 6. An average for SC was calculated for each soil series in a county from the scores for the individual pedons if there was more than one pedon of that series in a county. The average SC value for each soil was then used to rate each soil in the database as to whether a crop response would be expected if fertilizer S was applied for crops with either a low or high S requirement for good growth. SC values for individual pedons varied from -10 to +1 (Table 3). Based on these scores, soil S status categories were created which represented soils that were highly deficient, moderately deficient, variably deficient, sufficient, and highly sufficient in plant available S. The results of the final S database in Excel were then exported back to FileMaker Pro and to Microsoft Access.

Results

The final S status database contains 1,473 individual soil samples that represented 443 of the 475 soil series distributed in Ohio's 88 counties. The number of counties in which a soil series occurred varied from 1 to 23. For example, the Ava soil series, which only occurred in Adams County, was one of 182 series that only occurred in a single county. The Blount soil series occurred in 23 counties. There were 27 soil series in the database that occurred in ten or more counties.

The distribution of soils among the five S status categories is listed in Table 4. For a crop requiring 15kg S ha⁻¹ year⁻¹, which is the approximate amount required by corn (Hoeft and Fox 1986), most of the soils (68.6%) are classified as variably deficient with respect to S status. Only 1.2% are classified as moderately deficient and 0.14% as highly deficient. For a crop requiring 30kg S ha⁻¹ year⁻¹, for example alfalfa (Hoeft and Fox 1986), 43.2% of the soils are rated as variably deficient, 44.5% are considered to be moderately deficient, and 5.2% are highly deficient.

Table 3 Description of S status categories

Final S acors (SC) – S status satasam: — Explanation of satasam:	
Explanation of category	
-10 to -7.5 Highly deficient Response to S fertilization will almost always occur	
-7.5 to -6 Moderately deficient Response to S fertilization will usually occur	
-6 to -3 Variably deficient Response to S fertilization will often occur depending on specific crop conditions (rainf	ill, etc.)
-3 to -1 Sufficient Response to S fertilization unlikely but might occur under certain conditions	
-1 to +1 Highly sufficient Response to S fertilization unlikely under any circumstances	

Crop S requirement (kg S ha ⁻¹ year ⁻¹)	Soils	Soils identified in each S status category					
		Highly deficient	Moderately deficient	Variably deficient	Adequate	Highly sufficient	
15	No.	2	17	1,010	416	28	
	Pct.	0.14	1.2	68.6	28.2	1.9	
30	No.	77	655	636	96	9	
	Pct.	5.2	44.5	43.2	6.5	0.6	

Table 4 Number and percentage of Ohio soils classified in each soil S availability category for crops requiring either 15 or 30kg S ha⁻¹ year⁻¹

No. number, Pct. percentage of soils in each soil sulfur availability classification

A closer look at the soils that fell into the highly deficient category when a high-S-requiring crop (e.g., alfalfa) is grown was conducted. A total of 77 soils (5.2%) in Ohio were classified as highly deficient (Table 4). These 77 soils often included the same soil series more than once because they were included in more than one county of Ohio. Thus, the 77 highly deficient soils mentioned above were actually distributed among 57 soil series (Table 5). This number was obtained by summing the 44 soil series found in only one county, plus the nine soil series found in two different counties (i.e., 18 soils), plus the three soil series found in three different counties (i.e., nine soils), plus the one soil series that was found in six different counties (i.e., six soils) for a total of 77 soils (44+18+9+6). A similar breakdown of the 655 soils that were moderately deficient for a crop requiring 30kg S ha⁻¹ year⁻¹ is also provided in Table 5. This revealed that the individual 655 soils were represented by a total of 270 different soil series or 57% of the total 475 soil series in Ohio.

It must be noted that it is possible for the same soil to have a different S status in different counties because of

Table 5 Numbers of soil series rated moderately deficient or highly deficient versus the number of counties in which those soil series received those ratings for a crop requiring 30kg S ha⁻¹ year⁻¹

Number of soil series				
Moderately deficient	Highly deficient	Number of counties		
128	44	1		
57	9	2		
34	3	3		
18		4		
9		5		
8	1	6		
1		7		
4		8		
5		9		
5		10		
1		11		
Total=270	Total=57			

variations in atmospheric S deposition via rainfall, soil organic C, or factors that affect S leaching. Overall, 296 of 475 soil series in Ohio are classified as at least moderately deficient in one or more counties when growing a crop such as alfalfa.

Discussion

The database for Ohio resulting from this S model is easy to use because it is searchable by soil series name. The user does not need any detailed knowledge of the soils of interest but only the correct series names. There is variation among counties in the percentage of soil series represented in the data set. A soil series known to be present in a county but not included in the database may often be found in an adjacent county. However, its predicted S status in the adjacent county may differ slightly from what would be predicted in the county of interest because of differences in atmospheric S deposition via rainfall, soil organic C, or factors that affect S leaching.

It is possible to estimate the S status of any new soil not in the data set simply by applying the algorithm used in the model. This requires data on soil organic C, pH, and percentages of sand, silt, and clay.

Several factors influence the accuracy of this model for predicting crop sulfur deficiency. Our estimate of atmospheric S deposition is less than the true value because we did not include dry S deposition in our estimate. Dry S deposition accounted for approximately 40-50% of total S deposition for three sites in Ohio from 2003 to 2005 (US EPA Clean Air Status and Trends Network 2007). The omission of dry S deposition would act to increase the number of soils classified as S-deficient.

The release of S by mineralization of organic matter is an important source of S particularly for soils that have at least 1% soil organic C. A soil with 1% organic C would mineralize as much S (8.8kg S ha⁻¹ year⁻¹) as obtained from the highest rates of atmospheric wet deposition (8.8 to 10.7kg S ha⁻¹ year⁻¹). To estimate S mineralization, we made assumptions about soil bulk density, mass ratio of S to C in soil organic matter, and percentage of organic S that is mineralized each year. Errors in these assumptions would influence the estimate of S mineralized and probably the resultant S nutrition status of some soils. The absolute effect of such errors on estimated S mineralization increases as soil organic C concentration increases. This model predicts that a soil with 1% soil organic C will release $8.8 \text{kg S ha}^{-1} \text{ year}^{-1}$ by mineralization. If the true value is 50% larger, the absolute error in S mineralization would vary from 4.4 kg S ha⁻¹ year⁻¹ for a soil with 1% soil organic C to 17.6 kg S ha⁻¹ year⁻¹ for a soil with 4% soil organic C.

To estimate S mineralization, we assumed a uniform bulk density of 1.325g cm⁻³ for all soils. This is an idealized bulk density for a soil having the same particle density as quartz (2.65g cm⁻³) and 50% total porosity. Soil organic C is a strong determinant (predictor) of soil bulk density, so there is some error in assuming a uniform bulk density for a range of soils differing in organic C concentrations. The database of 1,473 soils had 143 soils with less than 1% soil organic C, 831 soils with 1% to 2% soil organic C, 426 soils with 2% to 3.9% soil organic C, and 73 soils with greater than 3.9% soil organic C. Heuscher et al. (2005) provided two equations predicting bulk density using either soil organic C or square root of soil organic C as the independent variables. For a soil to have a bulk density of 1.325g cm^{-3} , the equations require a soil organic C of 3.90% if soil organic C is the predictor and 2.55% if the square root of soil organic C is the predictor. It is likely that for soils with less than 2% soil organic C, assuming a bulk density of 1.325g cm⁻³ underestimates the true bulk density and resultant S mineralization and increases the number of those soils classified as S-deficient. For a soil with 1% or 2% soil organic C and using these values to predict a bulk density yields results of 1.539 or 1.465g cm⁻³, respectively. If the square root of soil organic C is used as the predictor, the bulk density values are 1.487 and 1.374g cm⁻³, respectively. Thus, to gain a sense of error involved in our model, these values can be compared to the assumed bulk density value of 1.325g cm⁻³. In summary, the assumed bulk density of 1.325g cm⁻³ probably underestimates S mineralization by approximately 16% for the 831 soils that contain soil organic at concentrations of 1% to 2% while also underestimating S mineralization by approximately 11% for the 426 soils that have 2.0% to 3.9% soil organic C concentrations. For the 73 soils with greater than 3.9% soil organic C concentrations, the assumed bulk density of 1.325g cm⁻³ probably overestimates bulk density and the mass of S mineralization. The effect for these few soils is to improve (elevate) their presumed S status.

To estimate S mineralization, we used a relatively high mass ratio of 1kg S to 60kg C in soil organic matter, which

was based on 2years of data for the Canfield soil in Ohio (Morra 1986). Four other Ohio soils had C/S ratios varying from 68 to 86. Tabatabai (2005) reported an average ratio of 1kg S to 92kg C in soil organic matter for six Iowa soils. If our mass ratio is too high in S, this would overestimate the mass of S released by mineralization and act to decrease the number of soils classified as S-deficient.

Our estimate that 2% of organic S is mineralized each year mimics McGrath and Zhao (1995) and is within a range reported by Scherer (2001). Because 2% is a small value, there is potential for substantial error if the true value has an absolute value that is slightly larger or smaller than 2%. If the true value is 1.5%, our estimate of S mineralization would be 33% too large. If the true value is 2.5%, our estimate would be low by 20% of the true mineralization rate. The assumption of a specific percentage of organic S mineralized each year has the potential to cause the greatest error in any model of plant available S. If the true percentage of organic S mineralized each year is 4% instead of 2%, this would represent a doubling of S mineralized each year, and the effect of the doubling is greater as soil organic C content increases.

The predicted S status for each soil series is probably fairly robust with respect to errors in the estimated S mineralization. This is due to the range of 10 (or 15) kg S $ha^{-1} vear^{-1}$ for each availability index (Table 1). An error of 10 in total potential S available would usually cause a unit change in the availability index, and a unit change in the availability index would cause a change in predicted S status only if the final S score was on the border between two status conditions. Most (974 of 1,473) of the soils had less than 2% soil organic C. A soil with 2% soil organic C is predicted to mineralize 17.6kg S ha⁻¹ year⁻¹, so an error of 10kg S ha⁻¹ year⁻¹ would represent a large 56% error in S mineralization. As soil organic C decreases, the percent error required to cause a 10kg S ha⁻¹ year⁻¹ change in total potential S increases proportionately, so the likelihood that an error in S mineralization has caused an erroneous determination of S status decreases.

The predicted S status for each soil series (in each county) depends not only on the values of the availability index (A) but also on the overall leaching index (L). The availability index (A) is primarily influenced by the rate of S mineralization, and we have already discussed some of the possible errors in the estimate of S mineralization. The overall leaching index (L) is a black box. We are certain of the direction of the effects of the various components of the overall leaching index, but we have no idea of the actual mass of S leached. For simplicity, we have treated the components of the leaching index as additive, but the true relation among them is probably not simply additive.

Confidence in the ability of this model to predict crop S status may come from comparisons with field experiments.

Chen et al (2005) measured alfalfa response to S fertilization for 2years on Canfield and Chili soils in Wayne County, Belmore soil in Hancock County, Negley soil in Pike County, and Rimer soil in Sandusky County. Only the Canfield soil is present in the data set in the county where crop yields were measured. The S status for the other soils may be estimated because they are present in the data set in one or more adjacent counties, but not in the county where the crop yields were measured. The Rimer soil (moderately deficient by the model) and the Belmore soil (variably to moderately deficient) did not show significant alfalfa yield responses to S fertilization. The Canfield soil (variably deficient) and the Chili soil (moderately deficient) each had a significant yield response in 1 of the 2years. The Negley soil (moderately deficient) showed a significant yield response for both crop years. Obviously, we have no knowledge of farm management practices and whether S may have been added to soils as a component of other fertilizer inputs of P and N. However, overall, agreement between the model predictions and field results are fairly reasonable and good and provide a rapid first estimate of soil that may be deficient in S when growing crops such as alfalfa or corn.

Conclusions

Crop response to a fertilizer element is greatest when that element is present in least supply. A model was developed that estimates S availability in soil to crops based on soil organic matter mineralization and inputs from rainfall and that lost from soil via leaching. This model is meant to rapidly identify soils that may be moderately or highly deficient in S and thus aid in decisions related to whether S fertilizer should be applied to soil to improve crop growth and yield.

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References

Beaton JD, Soper RJ (1986) Plant response to sulfur in western Canada. In: Tabatabai MA (ed) Sulfur in agriculture. Agronomy no. 27. American Society of Agronomy, Madison, WI, p 375– 403

- Chen L, Dick WA, Nelson S Jr (2005) Flue gas desulfurization products as sulfur sources for alfalfa and soybean. Agron J 97:265–271
- Chibber N (2007) Sulphur deficiency in Madhya Pradesh soil leads to poor harvest. Down to Earth (August 15, 2007) Available at: http://www.downtoearth.org.in/full6.asp?foldername=20070815 and filename=news
- Felder RM, Rousseau RW (2000) Elementary principles of chemical processes, 3rd edn. Wiley, New York, NY, p 675
- Gupta UC, MacLeod JA (1984) Effect of various sources of sulfur on yield and sulfur concentration of cereals and forages. Can J Soil Sci 64:403–409
- Heuscher SA, Brandt CC, Jardine PM (2005) Using soil physical and chemical properties to estimate bulk density. Soil Sci Soc Am J 69:51–56
- Hoeft RG, Fox RH (1986) Plant response to sulfur in the Midwest and northeastern United States. In: Tabatabai MA (ed) Sulfur in agriculture. Agronomy no. 27. American Society of Agronomy, Madison, WI, p 345–356
- Kamprath EJ, Nelson WL, Fritts JW (1956) The effect of pH, sulfate and phosphate concentrations on the adsorption of sulfate by soils. Soil Sci Soc Am Proc 20:463–466
- Marschner H (1986) Mineral nutrition of higher plants. Academic, London
- McGrath SP, Zhao FJ (1995) A risk assessment of sulphur deficiency in cereals using soil and atmospheric deposition data. Soil Use Manage 11:110–114
- Morra MJ (1986) Gaps in the sulfur cycle: biogenic hydrogen sulfide production and atmospheric deposition. Ph.D Dissertation. Ohio State University, Columbus, OH, p 245
- National Atmospheric Deposition Program (2007) Annual data summary for site OH 71. Available at: http://nadp.sws.uiuc.edu/ sites/ntnmap.asp? Site verified on July 24, 2007
- Neller JR (1959) Extractable sulfate sulfur in soils of Florida in relation to the amount of clay in the profile. Soil Sci Soc Am Proc 23:346–348
- O'Leary MJ, Rehm GW (1989) Effect of sulfur on forage yield and quality of alfalfa. J Fertil Issues 6:6–11
- Ohio Department of Agriculture (2006) Ohio Agricultural Statistics Annual Report 2005. Columbus, OH
- Scherer HW (2001) Sulphur in crop production—invited paper. Eur J Agron 14:81–111
- Sloan JJ, Dowdy RH, Dolan MS, Rehm GW (1999) Plant and soil responses to field-applied flue gas desulfurization residue. Fuel 78:169–174
- Tabatabai MA (2005) Chemistry of sulfur in soils. In: Tabatabai MA, Sparks DL (eds) Chemical processes in soils. SSSA Book Series no. 8. Soil Science Society of America, Madison, WI, p 193–226
- Troeh FR, Thompson LM (1993) Soils and soil fertility, 5th edn. Oxford University Press, New York, NY, p 462
- Tisdale SL, Reneau RB Jr, Patou JS (1986) Atlas of sulfur deficiencies. In: Tabatabai MA (ed) Sulfur in agriculture. Agronomy no. 27. American Society of Agronomy, Madison, WI, p 295–322
- US EPA Clean Air Status and Trends Network (2007) Total deposition. Available at http://www.epa.gov/castnet/maptotal. html. Site verified on August 13, 2007
- Vough LR, Weil RR, Decker AM (1986) Fertilizing alfalfa for higher yields. Proceedings of Forage Grassland Conference, University of Kentucky, Lexington, KY, pp 230–234