Sulphur status of soils of the Cerrado region of Brazil and the ability of important agricultural soils of Brazil to oxidize elemental S

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Abstract
Expansion and intensification of agriculture in Brazil is putting increasing pressure on land resources and is increasing the need for good fertilizer management. Use of DAP and MAP, which contain little S, is increasing and freight costs for single superphosphate (SSP), which contains more S than P, may limit its use in areas distant from fertilizer plants. Four soils collected from no tillage sites in the Cerrado area of Brazil responded to P in both the absence and presence of S. There was no response to S in the absence of P in any soil and responses to S were recorded in the presence of P in soybeans in three soils, and in all four soils in maize. In the second pot study statistically significant responses to S were recorded in 13 of 21 soils. Responses to gypsum were recorded in 10 soils; responses to the predominately elemental S containing sulphur enhanced di-ammonium phosphate (DAP-SEF) in 9 soils and to powdered elemental S in 10 soils. Responses to the addition of soil inoculum containing S oxidising organisms, with elemental S occurred on only 2 soils indicating the presence of S oxidizing organisms in most soils studied. Yields following addition of gypsum and DAP-SEF were equal in 10 soils and gypsum produced higher yields than DAP-SEF in 3 soils. This study indicates that the addition of elemental S to DAP is a feasible way of providing S to crops in Brazil. The high nutrient density in an NPS fertilizer such as DAP-SEF, relative to SSP, would be expected to confer freight and spreading cost advantages resulting in lower nutrient costs to farmers.

Key Words
Elemental S, sulphate, Brazil, fertilizer.

Introduction
Sulphur is one of the essential elements required for the normal growth of plants and concentrations of S in plants are lower than that of N and similar to P. Sulphur plays an important role as a constituent of three amino acids which, if not present in adequate quantities, will reduce crop yield and sometimes the quality of produce. For many years, little attention was paid to sulphur as a plant nutrient mainly because it has been applied to soil in incidental inputs in rainfall and volcanic emissions, and as a component of N, P and K fertilizers. The awareness of sulphur deficiency is increasing, as is the development of S deficiency in previously S sufficient areas in many parts of the world. Intensification of cropping systems using high yielding varieties, such as is occurring in Brazil, has accelerated S removal from the soil, which is resulting in more soils becoming S deficient. Increased use of high analysis S free fertilizers has aggravated the S deficiency problem in many cropping systems. Plants take up sulphur from the soil solution as sulphate and, like nitrate, sulphate is mobile in most soils and can be easily leached from the rooting zone. Data from trials conducted in Australia showed that the loss of S from the root zone from an application of elemental S was approximately half that compared to that from gypsum over a 52 week period. Non-sulphate S sources, such as elemental S, must be converted to sulphate before the plant can access it. This oxidation process is primarily carried out by autotrophic bacteria in the *Thiomonas* genus, which use reduced S sources as their energy source. The question arises as to whether these organisms, or other S oxidizers, are present in soils that have not been fertilized with elemental S. This is important if elemental S containing fertilizers are to be introduced into nutrient management packages. Elemental S is an almost ideal fertilizer as it contains 100% nutrients. Since microorganisms that carry out the oxidation process are moisture and temperature dependant, as is the crop demand for S the S supply and demand are in synchrony. The rate of oxidation is also dependent on the particle size of S. This means that there is great scope to manage the release rate of sulphate to the plant to maximize plant uptake and minimize losses by surface runoff and leaching. Research carried out by Blair *et al.* (1979) has shown that plants require S and P early in growth and that oxidation rates are enhanced by intimate mixing of P and elemental S (Lefroy *et al.* 1997), which makes S inclusion into P containing fertilizers an attractive proposition. A process was invented in 2001 to include elemental S into DAP and MAP and a patent for this was filed in 2003. This group of fertilizers, collectively known as Sulphur Enhanced Fertilizers (SEF), is being introduced into agriculture in several countries, including Brazil.

Methods

Two separate studies were undertaken. The first was to investigate the responsiveness of some soils from the Cerrado region of Brazil to P and S and the second on the oxidation of elemental S in important agricultural soils in Brazil. In the first study samples from the 0-0.2 m soil layer were collected in the municipalities of Maracaju and Chapadão do Sul in Mato Grosso do Sul state and from two sites in Rondonopolis, Mato Grosso state. The samples were transported to the University of Sao Paulo, Piracicaba, air dried, screened to 0.2 mm and analyzed for pH, O.M., P, S, K, Ca, Mg, Al, H+Al, B, Cu, Fe, Mn, Zn, sand, silt and clay. The results of these analyses showed very low concentration of P for samples A, C and D, medium concentration of P for sample B and low concentration of S for all samples (Table 14). Clay content followed the order A = B >> C > D.

Results of soil chemical analysis indicated that soil C required liming so $CaCO_3$ and $MgCO_3$ was added to this soil to provide 25 and 8 mmolc/dm^3 of Ca and Mg. Lime was not added to soils A, B and D. The greenhouse test was set up with the four soils (A, B, C and D), with 3 kg of soil per pot, with and without addition of P and S, two crops (soybean and maize) and three replicates. Rates used were 200 and 100 mg/kg of soil of P and S, respectively. Phosphorus was applied as monocalcium phosphate monohydrate and sulphur as potassium sulfate. In the zero sulphur treatments, potassium was added as KCl. Nitrogen was not applied to soybeans (plants were inoculated with *Rhizobium japonicum*) and was applied to maize at 250 mg/kg of N as urea at planting with two additional applications of 100 mg/kg each. To overcome the effects of other nutrients the chloride salts of Cu, Zn, Mn, B, Mo and Fe were applied at rates of 5, 10, 10, 2.5, 1 and 10 mg/kg of soil, respectively. Five seeds of Pioneer 30F33 maize or Conquista soybean were planted per pot and plants were thinned to two per pot seven days after emergence. The pots were watered daily using deionized water to maintain 75% field capacity. The plants were harvested after 50 days, dried at 60^{o}C and weighed. Dry-matter yields were statistically analysed using SAS procedures.

Table 14. Soil analysis of the four samples collected for the greenhouse study.

SS Soil ID	Location	pH($CaCl_2$)	O.M. (g/dm^3)	P (mg/dm^3)	S(mg/dm^3)
A	Maracaju,	4.6	46	6	4
B	Chapadão do Sul	4.7	45	21	4
C	Rondonopolis 1	3.9	25	4	5
D	Rondonopolis 2	5.2	29	2	4

In the second study twenty-one soils from the major agricultural areas of Brazil were selected for the study. Soil samples (0-20 cm) were collected, dried and sent to the University of Sao Paulo, Piricicaba for the study. The soil samples were prepared by drying and sieving to 2 mm. Nutrients to overcome any nutritional effects other than S were applied at the rates of 200, 200 and 200 mg/kg of N, P, and K, respectively, in the form of urea, monocalcium phosphate and potassium chloride. A solution containing micronutrients, but no sulphur, was also applied. An additional amount of 100 mg/kg of P was added in soils with a clay content higher than 30%. Lime was applied at 0.5 g/pot, to overcome Ca and Mg deficiency. The sources of sulphur used were gypsum, DAP-SEF which is a granulated DAP sulphur enhanced fertilizer (16.7-39.4-0-11.7S, 3.8% of sulphur as sulphate S), powder elemental S (S^o) and powdered S^o + soil inoculum. The amount of sulphur applied was 15 mg/kg. A control with no sulphur applied was added. The soil inoculum used was 1g / pot of soil from site 11 mixed with elemental sulphur. Site 11 had shown a response to an elemental S containing MAP indicating that sulphur oxidising microorganisms were present. As DAP-SEF has N and P in addition to S, a solution containing N and P was applied, where applicable, to balance N and P between treatments. The soils were initially cropped with two harvests of millet using all nutrients but no sulphur to reduce bioavailable S. All nutrients, except S, were mixed throughout the soil and the sulphur was localized in a thin layer 2 cm below the soil surface. Brachiaria grass was planted (Nov 01, 2006) with eight plants per pot. During plant growth the soil was maintained at 70% field moisture capacity. After harvesting the plant tissues were dried at 40^{o}C for fifteen days and weighted for dry matter yield.

Results

In the first study responses to P were recorded in all four soils in both the absence and presence of S. There was no response to S in the absence of P in any soil and responses to S were recorded in the presence of P in soybeans in soils A, B and C, and in all four soils in maize (Table 15). Dry-matter yield of soybean was 19.1, 2.3, 26.3 and 9.0 times higher with the application of P in the presence of S on soils A, B, C and D, respectively. For maize the increments were of 15.7, 2.0, 26.9 and 84.0 times, respectively.

Table 15. Dry-matter yield (g/pot) of soybean and maize as affected by P and S.

Soil ID	S applied (mg/kg)	Soybean DM yield (g/pot) P applied (mg/kg)		Maize DM yield (g/pot) P applied (mg/kg)	
		0	200	0	200
A	0	1.7	28.9	4.3	36.5
	100	1.9	36.4	4.6	72.3
		lsd = 4.1		9.0	
B	0	11.2	22.3	15.0	46.4
	100	12.2	27.9	35.6	69.9
		lsd = 5.5		6.6	
C	0	0.2	11.8	1.7	45.6
	100	0.7	18.4	2.6	70.0
		lsd = 6.1		8.6	
D	0	0.2	0.9	0.6	42.7
	100	0.3	2.7	0.7	58.8
		Ns		7.0	

Dry-matter yield of soybean was 1.3, 1.3, 1.6 and 3 times higher with the application of S in the presence of P in soils A, B, C and D, respectively. For maize the increments were of 2.0, 1.5, 1.5 and 1.4 times, respectively. As expected, response to S was lower than the response to P, but dry-matter yields with the application of S in the presence of P were statistically higher than without the application of S in the presence of P. Low dry-matter yield of soybean in soil C, and especially in soil D, was due to B toxicity in these sandy soils. In the second study statistically significant responses to S were recorded in 13 of the 21 soils (Table 3). Responses to gypsum were recorded on 10 soils, responses to the predominately elemental S containing DAP-SEF on 9 soils and to powdered elemental S on 10 soils. Addition of soil inoculum resulted in an increase in yield above the S^0 treatment on only 2 soils (4 and 7). Yields following addition of gypsum and DAP-SEF were equal in 10 soils and gypsum produced higher yields than DAP-SEF in 3 soils.

Table 16. Sulphur responses in dry matter yield (g/pot) of Bracharia grown in 21 soils from throughout Brazil. Numbers in bold parentheses are significantly different from the control in that soil.

Soil #	Control	Gypsum	DAP-SEF	So	So + inoculation	S response	Inoculation response	DAP-SEF v Gypsum
	(--------------------------------	g/pot	------------------------------)					
1	20.5	24.2	22.8	23.4	*28.2* [A]	yes	yes	equal
2	21.4	*28.0*	*26.2*	25.5	*28.4*	yes	no	equal
3	26.2	27.7	29.5	28.3	26.7	no	no	-
4	19.8	*28.8*	*28.6*	*24.5*	*31.4*	yes	yes	equal
5	28.3	25.8	29.2	26.0	29.0	no	no	-
6	21.8	24.3	25.7	26.2	25.0	no	no	-
7	26.5	29.7	27.9	27.1	*32.1*	yes	yes	equal
8	16.8	21.5	19.2	*23.2*	17.6	yes	no	Equal
9	13.0	11.3	14.2	12.4	11.7	no	no	-
10	20.9	*26.6*	*28.6*	*31.5*	*30.1*	yes	no	Equal
11	24.5	*31.3*	*30.1*	*33.5*	*34.2*	yes	no	Equal
12	21.3	*34.5*	*29.0*	*32.4*	*35.1*	yes	no	inferior
13	12.5	*22.6*	*21.8*	*21.4*	*23.5*	yes	no	Equal
14	18.8	*24.6*	*24.1*	*26.1*	*28.2*	yes	no	Equal
15	17.6	*26.1*	*23.8*	*27.2*	*26.7*	yes	no	Equal
16	11.3	*16.6*	14.6	*17.9*	*18.3*	yes	no	inferior
17	25.3	26.3	28.4	28.0	24.7	no	no	-
18	9.2	*21.5*	*16.4*	*15.4*	*17.9*	yes	no	inferior
19	7.0	4.3	5.7	3.6	4.8	no	no	-
20	7.6	9.7	9.5	11.2	9.3	no	no	-
21	18.9	19.8	18.6	22.6	21.8	no	no	-
S response		10	9	11	12	13	3	

[A] Numbers in bold italics are significantly different from the control

Conclusion

The four soils from the Cerrado region of Brazil studied here were very responsive to P and three of the four were responsive to S in the presence of P. In a wider survey of 21 soils, 13 were found to be responsive to S and there was little difference in the yield produced from sulphate and elemental S. Introduction of S oxidising organisms had little effect on crop yield which indicates that elemental S containing fertilizers could be satisfactorily introduced into Brazilian agriculture.

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