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Available sulphur by different extractants in soils of the state of Ceará, Brazil[1]

Enxofre disponível por diferentes extratores em solos do estado do Ceará, Brasil

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ABSTRACT - Despite the relevance of sulphur (S) to plant development, studies in Brazil on its availability in the soil are restricted to a few crops and regions. The aim of this study was to compare extractants for assessing the availability of S, and establish critical levels for soils in the state of Ceará. In the laboratory, available S was extracted from 23 soils (0 - 0.20 m), using two extractants: a solution of $Ca(H_2PO_4)_2$, 500 mg L^{-1} P in H_2O (MCP) and NH_4OAc in HOAc (AMA). In an experiment set up in a greenhouse, forage sorghum 'EA116' (*Sorghum vulgari* Pers.) was used as an indicator plant in two successive crops. A completely randomised experimental design was employed, in a 23 x 2 factorial scheme with three replications, where the factors corresponded to the soils and to the doses of S (0 and 80 mg per experimental unit). The MCP was more efficient in extracting available S than was the AMA, although the S content obtained by both did show a significant correlation (r = 0.96). The available S using MCP showed a better correlation, with an increase in production and in absorbed S, suggesting MCP to be the most suitable extractant. The critical levels for S were 3.90 and 3.40 mg dm^{-3} for MCP and AMA, respectively.

Key words: Extraction methods. Critical level. Leaf S content.

RESUMO - Apesar da relevância do enxofre (S) para o desenvolvimento das plantas, estudos sobre sua disponibilidade no solo são restritos à algumas culturas e regiões do Brasil. Assim, objetivou-se com este trabalho comparar extratores para avaliar a disponibilidade de S e estabelecer níveis críticos em solos do estado do Ceará. Em laboratório foi extraído o S disponível de 23 solos (0 – 0,20 m), empregando-se dois extratores: soluções de $Ca(H_2PO_4)_2$, 500 mg L^{-1} de P, em H_2O (MCP) e NH_4OAc em HOAc (AMA). Em experimento instalado em casa de vegetação foi usado, como planta indicadora, o sorgo forrageiro (*Sorghum vulgari* Pers.), cultivar EA116, em dois cultivos sucessivos. O delineamento experimental foi inteiramente casualizado, em esquema fatorial (23 x 2), com três repetições. Os termos do fatorial corresponderam aos solos e doses de S (0 e 80 mg por unidade experimental). O MCP apresentou maior eficiência de extração de S disponível que o AMA, embora o teor de S obtido por ambos tenha apresentado correlação significativa (r = 0,96). O S disponível por MCP apresentou melhor correlação com incremento de produção e S absorvido, sugerindo ser o mais indicado. Os níveis críticos de S foram de 3,90 e 3,40 mg dm^{-3} para MCP e AMA, respectivamente.

Key words: Extraction methods. Critical level. Leaf S content.

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INTRODUCTION

Sulphur (S) is considered the fourth most important nutrient for plants, after N, P and K (JAMAL; MOON; ABDIN, 2010), as it is a component of several proteins, enzymes and cofactors (SOLOMON *et al*., 2011). The neglect of this nutrient in fertiliser recommendations, and the drastic reduction in input from the atmosphere (DIVITO *et al*., 2015; VIEIRA-FILHO; LEHMANN; FORNARO, 2015), have been the cause of S deficiency in plants, limiting productivity and reducing product quality (JOHNSON *et al*., 2018; SCHERER, 2009).

The SO_4^{2-} ion is the form absorbed by plants. Adsorption and desorption processes in the soil are mainly controlled by the SO_4^{2-} concentration in the soil solution, the pH, characteristics of the colloidal surfaces, and the concentration of other anions in solution (SCHERER, 2009; ZHAO *et al*., 2017). Due to these processes, SO_4^{2-} is found in the soil at various degrees of availability for plants.

There are various extractants and techniques for assessing available S, but the difficulties in establishing critical levels for soil S by the current methods of analysis are due not only to the loss of efficiency of the method itself (NOVAIS *et al*., 2015), but also to other factors, such as forms of S not accessed by the extraction method, desorption rates compatible with the needs of the plant, absorption at deeper layers, mineralisation rate of the residue and organic matter, and the entry of SO_4^{2-} with rainwater or irrigation, masking the plant's response to S fertilisation (RAMPIM *et al*., 2011; TIECHER *et al*., 2012).

The availability of S in the soil and the requirements of the plant regulate the processes of SO_4^{2-} absorption and assimilation (TAKAHASHI *et al*., 2011), underlining the need to estimate the available soil S so as to correct deficiencies and favour the metabolic processes of the crops.

Standing out among the available extractants for S are 0.5 mol L^{-1} ammonium acetate diluted in 0.25 mol L^{-1} acetic acid (NH_4OAc), and 0.01 mol L^{-1} calcium phosphate ($Ca(H_2PO_4)_2$), considered similar in extraction ability in the 0 – 0.20 m layer in maize and wheat crops (BLUM *et al*., 2014). According to Barrow and Debnath (2015), the adsorption force of phosphate is considered superior to that of SO_4^{2-}, which justifies the use of phosphate solutions to displace the adsorbed SO_4^{2-}. Fernandes, Freire and Oliveira (2007) found that ammonium acetate extractant in acetic acid extracted more S from clayey soils with higher levels of organic matter, while monocalcium phosphate diluted in acetic acid was efficient in extracting sulphur regardless of the physical or chemical characteristics of the soil.

Despite the importance of S for plants, there is limited information on the critical levels of this element for soils in different regions, especially under semi-arid conditions. It is therefore necessary to carry out studies on the availability of sulphur for plants and its relationship with the characteristics of the soil. Based on the hypothesis that the SO_4^{2-} ion can be extracted with greater or lesser efficiency by different solutions, the aim of this study was to compare the effectiveness of two extractants in assessing the availability of sulphur, and to establish critical levels for representative soils of the semi-arid region of the state of Ceará.

MATERIAL AND METHODS

An experiment was conducted in a greenhouse using soil samples with a wide range of physical and chemical properties belonging to the following classes: Inceptisol, Entisol (Quartzipsament), Entisol (Orthent), Alfisol, Ultisol and Oxisol.

Soil samples were collected from the 0 - 0.20 m surface layer in the districts of Limoeiro do Norte (4 samples), São João do Jaguaribe (1 sample), Itapebuçu (1 sample), Russas (1 sample)), Palhano (2 samples), Palmaceae (1 sample), Aracoiaba (1 sample), Mulungu (2 samples), Baturité (1 sample), Redenção (1 sample), Itaitinga (1 sample), Ipú (1 sample). Tianguá (1 sample), Viçosa do Ceará (1 sample), Ubajara (1 sample), Pentecoste (1 sample) and Pacajus (2 samples). After collection, the samples were air-dried and passed through a 2-mm sieve (ADFS) for physical and chemical analysis (Table 1).

The statistical design was completely randomised, in a 23 x 2 factorial scheme, with three replications, giving a total of 138 experimental units. The factors corresponded to 23 soils and two doses of S (0 and 80 mg dm^{-3}). The experimental unit comprised a black polyethylene plastic bag with a capacity of 2 dm^{-3}, containing 1.6 dm^{-3} of soil and five sorghum plants. The weight of the soil in the experimental units ranged from 1.8 to 2.8 kg, due to the density of the different soil classes used.

In the greenhouse, the soils received a mixture of $CaCO_3$ and $MgCO_3$ at a molar ratio of 3:1 whenever necessary and after homogenisation and wetting were incubated for 30 days. The dose of soil corrective was estimated so as to reach 70% base saturation or 2 $cmol_c$ dm^{-3} of exchangeable Ca + Mg. During incubation, the moisture in the samples was kept close to 80% of field capacity by weighing each week.

At the end of the incubation period, S was applied according to each treatment, using $CaSO_4.2H_2O$ in the form of p.a. reagent. The soils were again homogenised, wetted and incubated for another 10 days, at which time planting was carried out. The treatments with no

S received calcium in the form of $CaCl_2$ in the same proportion as the soils that received the sulphur.

Forage sorghum 'EA116' (*Sorghum vulgari* Pers.) was used as an indicator plant. Sorghum is grown in very dry and/or very hot areas and environmental conditions, where the productivity of other cereals is uneconomical (GALVÃO *et al*., 2015). Another important aspect of forage sorghum is its regrowth capacity, which can reach a production of up to 60% compared to the first cut (VON PINHO *et al*., 2007). The crop is therefore adapted to the semi-arid conditions of Ceará. Furthermore, due to regrowth, there was no need to sow the second crop in the experiment. Ten seeds were sown in each experimental unit. Six days after germination, the plants were thinned, leaving five plants per unit. The experiment was irrigated daily with distilled water.

After thinning, each experimental unit was fertilised based on the nutrient requirements of the crop. The N and K were divided into three equal doses at 6, 15 and 25 days. The reagents and doses, in mg per experimental unit, were NH_4NO_3 (380) and KCl (120-400, based on the K content of the soil). All the P was applied in the form of NaH_2PO_4, (250-750 mg per experimental unit, based on the soil content). Ca and S were applied using $CaSO_4.2H_2O$ and $CaCl_2.2H_2O$ (180 and 100 mg per experimental unit, respectively). Micronutrients were applied (mg per experimental unit) using the following reagents and doses: H_3BO_3 (1.40), $MnCl_2.4H_2O$ (5.50), $ZnCl_2$ (6.00), CuCl (2.00) and $H_2MoO_4.H_2O$ (0.29).

Table 1 - Chemical and physical attributes of the soil samples under study

[1/]Soil	[2/]pH	[3/]EC	[4/]Ca+Mg	[5/]Na	[5/]K	[6/]H+Al	[7/]Ex	[8/]V	[9/]N	[10/]OM	[11/]Snd	Slt	Ds	P
		dS m^{-1}	---------- (cmol$_c$ dm^{-3}) ----------					---------- (%) ----------					g cm^{-3}	mg dm^{-3}
1	6.0	0.32	6.7	0.14	0.69	2.3	9.8	76	0.08	1.4	33	42	1.14	1.0
2	6.3	0.35	5.2	0.14	0.39	1.8	7.5	76	0.12	1.5	53	27	1.26	1.0
3	6.5	0.34	11.2	0.22	0.16	1.8	13.4	86	0.05	0.7	46	13	1.40	73.0
4	5.3	0.30	-	0.13	0.16	1.7	2.0	14	0.04	0.8	63	2	1.66	3.0
5	5.7	0.69	7.0	0.43	0.26	3.9	11.6	66	0.17	3.1	43	12	1.13	24.0
6	4.7	0.35	-	0.11	0.05	1.5	1.7	9	0.02	0.4	87	2	1.74	1.0
7	5.3	0.32	3.2	0.21	0.37	1.8	5.8	68	0.04	0.7	72	11	1.49	1.0
8	5.0	0.31	8.5	0.43	0.15	4.0	13.1	69	0.04	0.8	21	28	1.21	2.0
9	5.7	0.37	3.7	0.15	0.30	3.0	7.2	58	0.09	1.7	71	11	1.31	25.0
10	5.0	0.33	3.3	0.18	0.22	3.8	7.5	50	0.07	1.5	68	9	1.41	8.0
11	5.2	0.24	-	0.12	0.15	2.0	2.3	11	0.03	0.7	87	3	1.53	5.0
12	5.4	0.92	4.3	0.30	0.57	3.5	8.7	60	0.14	2.5	58	17	1.23	14.0
13	4.5	0.47	1.0	0.16	0.26	5.8	7.4	21	0.12	2.8	59	17	1.23	7.0
14	5.5	0.74	5.9	0.16	0.40	4.0	9.9	60	0.19	3.5	63	15	1.17	6.0
15	5.5	0.16	-	0.12	0.14	1.3	1.6	16	0.02	0.3	81	6	1.63	2.0
16	4.7	0.19	-	0.10	0.05	1.7	1.9	8	0.01	0.4	93	1	1.47	2.0
17	5.0	0.18	-	0.12	0.04	2.2	2.4	6	0.01	0.5	91	1	1.61	2.0
18	5.6	0.23	-	0.12	0.10	2.3	2.5	8	0.04	0.8	82	2	1.58	5.0
19	3.8	0.20	-	0.04	0.04	4.5	4.6	1	0.06	1.2	76	12	1.32	5.0
20	5.0	0.16	-	0.04	0.11	2.3	2.5	6	0.06	0.8	78	10	1.43	9.0
21	3.8	0.28	-	0.03	0.04	3.8	3.9	2	0.04	5.0	79	7	1.33	10.0
22	5.8	0.20	-	0.10	0.43	2.4	7.0	67	0.12	0.3	79	5	1.37	17.0
23	5.0	0.16	-	0.10	0.06	5.9	7.5	22	0.14	2.4	75	11	1.30	20.0
Amplitude	3.8- 6.5	0.16 - 0.90	- 9.0	0.03 - 0.43	0.04 - 0.69	1.3 - 5.9	1.6 - 13.4	1 - 86	0.01 - 0.19	0.3 - 5.0	21 - 93	1 - 42	1.13 - 1.74	1.0 - 73
Mean	5.2	0.34	5.45	0.16	0.22	2.9	6.2	37	0.07	1.5	68	11	1.39	

[1/] 1 and 2 - CXbe – Inceptisol; 3 and 8 - RRe - Entisol (Psamment); 4, 6, 13, 17 and 18 - PVAd - Ultisol; 5 - RLd - Entisol (Orthent); 7 and 12- SXe – Alfisol; 10, 11 and 14 - PVAe – Ultisol; 15, 16 and 21 - RQo – Entisol (Quartzipsamment); 19, 20 and 23 - LVAd – Oxisol; 9 and 22 - RL – Entisol (Orthent). [2/] pH in H_2O (1:2.5); [3/]EC - Electrical conductivity in dS m^{-1}- determined in the saturation extract and measured with a soilbridge salt bridge; [4/] KCl 1 mol L^{-1} extractant in cmol$_c$ dm^{-3}; [5/] Mehlich-1 extractant, with Na and K determined by flame photometry, and P determined by colorimetry; [6/] 0.5 mol L^{-1} $Ca(OAc)_2$ extractant, pH 7.0; [7/] Ex – Cation exchange capacity; [8/] V – Base saturation (%); [9/] Total nitrogen, Kjedahl method; [10/] OM – Organic matter, Walkley-Black method; [11/]Sand and Clay – pipette method; [12/] Bulk density – Test-tube method

Forty days after sowing, the first cut of the shoots was carried out 5 cm from the ground. A second crop, from the sorghum regrowth, was maintained for 40 days. The second crop also received N, P and K fertiliser and micronutrients using the same doses and reagents. The material collected from each cut was placed in paper bags and taken to the laboratory to be dried in an oven.

The available S content in the soils under study was determined in the laboratory with the use of two extractants: 1) NH_4OAc 0.5 mol L^{-1} in HOAc 0.25 mol L^{-1} (ammonium acetate in acetic acid - AMA) (BARDSLEY; LANCASTER, 1960). A soil to solution ratio of 1:2.5 (10 g of soil and 25 mL of extractant solution) was used and stirred for 30 minutes, after which 0.25 g of activated charcoal was added and stirred for a further 3 minutes. The suspension was then filtered, and a 10 ml aliquot was transferred to measuring tubes which received 1 ml of 6N HCl with 20 ppm S and 0.5 g of barium chloride. A turbidimetric determination of the S in the samples was carried out within 2 to 8 minutes after the barium chloride had dissolved, using a molecular absorption spectrophotometer at a wavelength of 420 nm. 2) $Ca(H_2PO_4)_2$ in water, with 500 mg P dm^{-3} (monocalcium phosphate in water - MCP) (FOX; OLSON; RHOADS, 1964). For this extractant, a soil to solution ratio of 1:5 was used (20 g of soil and 100 mL of extractant), stirred for 30 min and decanted for 12 to 15 h. From this suspension, 40 ml were removed and concentrated by evaporation at 120 °C until dry. The residue was digested on a hot plate until white smoke was produced, when the temperature was reduced, and digestion continued for another 15 min. After cooling, 10 ml of distilled water and 1 ml of gum acacia solution in acetic acid were added. The S was determined by turbidimetry, using a spectrophotometer at a wavelength of 420 nm.

From the material collected in the greenhouse, the dry matter weight (DMW) was evaluated in the aerial part of the sorghum (g per experimental unit) obtained after drying to constant weight at 60 °C. From the DMW, the relative production (RP) and increase in production (IP) were determined using Equations 1 and 2.

$$RP = \frac{DMW \ \ production \ With \ no \ S}{DMW \ \ production \ With \ no \ S} \times 100 \quad (1)$$

$$IP = 100 - RP \quad (2)$$

With the dry matter ground and passed through a 0.84-mm sieve, the following were determined in perchloric-nitric extract: S by turbidimetry, P by colorimetry and K by flame photometry. N was determined by semi-micro-Kjeldahl distillation in sulphuric extract. The absorption of the nutrients under analysis was determined with the formula: mg of extracted nutrient = % nutrient x dry matter (g per experimental unit) x 10.

The critical levels for S in both the soil and plant were determined by means of the Cate and Nelson graphical method (1965), using the data for available soil S (X) and relative production (Y), and in the treatment with no S, data for the S content of the plant (X) and relative production (Y).

The data from both sorghum crops were submitted to analysis of variance. The relationships between the different attributes evaluated in the soil and in the plant were analysed by simple linear correlation.

RESULTS AND DISCUSSION

Table 2 shows the S content in the soils under natural conditions (without the addition of S), using two extractants. The contents obtained with MCP were greater than those obtained with AMA. The superiority of MCP can be explained by the phosphate ion having greater power to displace the adsorbed sulphate than does the acetate ion, determining higher values of extractable sulphate (AYLMORE; KARIM; QUIRK, 1967; BARROW; DEBNATH, 2015; ZHAO *et al*., 2017). For both extractants, the lower and upper limits of each range of variation in the S content corresponded to the same soils, 16-RQo and 19-LVAd.

Table 3 shows the linear correlation coefficients resulting from the relationships between the available S by the two extractants plus various properties of the soil. The behaviour of both extractants was similar within each property. The correlation coefficients for most soil properties were not significant, possibly due to the varied mineralogical composition of the soils and the narrow range of variation in the values of their properties.

The levels of clay and non-exchangeable H were the only properties that showed a positive correlation ($p \leq 0.01$), revealing clay as a labile and non-labile reservoir of S, possibly forming covalent bonds with the non-exchangeable H. No correlation was found between organic matter and available S, possibly due to the predominance of inorganic forms. The pH also affects the way the plant responds to S fertilisation, so that a higher pH favours leaching of SO_4^{2-} to the subsurface layers (SUTAR *et al*., 2017). This did not occur in the soils under study due to the low pH (≤ 5.8) in 20 of the 23 soils.

Dry matter production (DMW), relative production (RP) and the increase in production (IP) in the two successive cuts are shown in Table 4. Based on these data, the analysis of variance was carried out for the two cuts separately, which by F-test ($p \leq 0.05$) showed significant responses to the S doses, to the soils and to the dose x soil interaction. For this study, only a breakdown of the S doses within each soil was considered.

Table 2 - Available S content by two extractants, monocalcium phosphate (MCP) and ammonium acetate (AMA), in soil samples from the state of Ceará without the addition of S

Extractant	Soil[1/]							
	1CXbe	2CXbe	3RRe	4PVAd	5RLd	6PVAd	7SXe	8RRe
	---------- mg dm^{-3} ----------							
MCP	5.2	2.9	4.3	2.0	4.5	2.3	5.2	5.6
AMA	4.1	2.4	2.7	1.6	4.1	1.8	3.4	4.9
	9RL	10PVAe	11PVAe	12SXe	13PVAd	14PVAe	15RQo	16RQo
	---------- mg dm^{-3} ----------							
MCP	3.2	2.9	1.7	5.9	7.1	6.0	2.3	1.4
AMA	2.5	2.7	1.2	4.1	5.9	5.9	1.9	1.1
	17PVAd	18PVAd	19LVAd	20LVAd	21RQo	22RL	23LVAd	
	---------- mg dm^{-3} ----------							
MCP	2.0	2.1	8.6	4.0	4.8	4.9	5.8	
AMA	1.7	2.2	6.9	2.6	4.2	3.1	4.8	
Amplitude: 7.2 (MCP) and 5.7 (AMA)								
Mean: 4.1 (MCP) and 3.3 (AMA)								

[1/]1,2 - CXbe – Inceptisol; 3, 8 - RRe - Entisol (Psamment); 4,6,13,17,18 - PVAd - Ultisol; 5 - RLd - Entisol (Orthent); 7,12- SXe – Alfisol; 10,11,14 - PVAe – Ultisol; 15,16,21 - RQo – Entisol (Quartzipsamment); 19,20,23 - LVAd – Oxisol; 9,22 - RL – Entisol (Orthent)

Table 3 - Correlation coefficient and linear regression equations for available sulphur (Y) by two extractants, monocalcium phosphate (MCP) and ammonium acetate (AMA), with various soil attributes

Property	Equation	R
% clay	$\hat{Y}$ = 2.17 + 0.09 X (MCP)	0.51**
	$\hat{Y}$ = 1.36 + 0.11 X (AMA)	0.54**
% organic matter	$\hat{Y}$ = 3.26 +0.07 X (MCP)	0.24^{ns}
	$\hat{Y}$ = 2.30 + 0.16 X (AMA)	0.38^{ns}
pH	$\hat{Y}$ = 8.95 – 0.99 X (MCP)	-0.27^{ns}
	$\hat{Y}$ = 7.89 – 0.85 X (AMA)	-0.31^{ns}
Sum of bases	$\hat{Y}$ = 3.55 + 0.07 X (MCP)	0.25^{ns}
	$\hat{Y}$ = 3.01 + 0.17 X (AMA)	0.34^{ns}
Non-exchangeable H	$\hat{Y}$ = 0.12 + 0.57 X (MCP)	0.85**
	$\hat{Y}$ = 0.17 + 1.39 X (AMA)	0.89**
Al^{3+}	$\hat{Y}$ = 0.39 + 0.04 X (MCP)	0.30^{ns}
	$\hat{Y}$ = 2.57 + 1.45 X (AMA)	0.30^{ns}
V%	$\hat{Y}$ = 31.86 + 1.02 X (MCP)	0.10^{ns}
	$\hat{Y}$ = 3.28 + 0.004 X (AMA)	0.07^{ns}

ns – not significant; ** - significant at level of 1%

Table 4 - Dry matter production (DMW), relative production (RP) and increase in production (IP) by plants of forage sorghum in treatments with S (So) and with no S (S_1)

Soil	DMW				RP		IP	
	1st cut		2nd cut		1st cut	2nd cut	1st cut	2nd cut
	S0	S1	S0	S1				
	---------- g per experimental unit ----------				---------- (%) ----------			

Continuation Table 4

1 CXbe	10.73 a	11.27 a	8.50 b	17.17 a	95	50	5	51
2 CXbe	9.70 a	10.80 a	9.73 b	18.57 a	90	52	10	48
3 RRe	10.43 a	11.87 a	6.40 b	14.50 a	88	44	12	56
4 PVAd	3.38 b	9.22 a	5.63 b	11.57 a	37	49	63	51
5 RLd	11.76 a	9.25 b	16.56 a	18.04 a	127	92	--	8
6 PVAd	6.64 b	8.11 a	5.20 b	16.24 a	82	32	18	68
7 SXe	10.48 b	11.19 a	7.75 b	15.65 a	94	50	6	51
8 RRe	9.28 a	10.16 a	13.60 b	19.52 a	91	70	9	30
9 RL	10.61 a	11.55 a	12.10 b	21.11 a	92	57	8	43
10 PVAe	12.04 a	12.14 a	12.98 b	20.92 a	99	62	1	38
11 PVAe	8.53 b	12.00a	6.36b	22.05 a	71	29	29	71
12 SXe	12.19 a	10.09 b	16.81 b	23.98 a	121	70	-	30
13 PVAd	13.64 a	13.67 a	16.70 b	22.72 a	100	74	-	27
14 PVAe	13.56 a	13.91 a	12.38 b	23.04 a	97	54	3	46
15 RQo	7.09 b	9.94 a	4.41 b	17.53 a	71	25	29	75
16 RQo	7.57 b	10.07 a	4.18 b	16.11 a	75	26	25	74
17 PVAd	9.74 a	10.28 a	5.03 b	17.81 a	95	28	5	72
18 PVAd	7.56 b	11.19 a	7.11 b	20.92 a	68	34	32	66
19 LVAd	7.50 a	7.02 a	15.96 a	18.68 a	107	85	-	15
20 LVAd	10.61 a	8.73 b	15.14 b	21.92 a	122	69	-	31
21 RQo	9.27 a	10.03 a	11.91 b	22.26 a	92	54	8	47
22 RL	13.27 a	12.62 a	14.54 b	21.13 a	105	69	-	32
23 LVAd	9.97 a	9.78 a	12.08 b	27.62 a	102	44	-	56
Mean	9.80	10.64	10.48	19.50	-	-	-	-

Mean values followed by the same letter in a row for each variable and cut did not differ by F-test ($p \leq 0.05$). [1/] 1,2 - CXbe – Inceptisol; 3, 8 - RRe - Entisol (Psamment); 4,6,13,17,18 - PVAd - Ultisol; 5 - RLd - Entisol (Orthent); 7,12- SXe – Alfisol; 10,11,14 - PVAe – Ultisol; 15,16,21 - RQo – Entisol (Quartzipsamment); 19,20,23 - LVAd – Oxisol; 9 - RL - Entisol (Orthent)

In the first cut, for seven of the soils under study, the plants responded positively to the application of S, with 4PVAd standing out due to an increase in production of 63% (Table 4). In general, the soils provided enough S to meet the demands of the plant, which, as a Poacea, has a low S requirement. Singh *et al*. (2015) also found that the agronomic efficiency of rice grains per kg of applied S was reduced as the availability of the S increased. In addition to the low S demand of sorghum, the low response during the first cut can be explained by the increase in P availability (fertilisation) which, due to competition for the phosphate ion by the exchange sites, displaced SO_4^{2-} to the soil solution (BARROW; DEBNATH, 2015; POZZA *et al*., 2007).

With the second cut, except for two soils (5-RLd and 19-LVAd), plants not fertilised with S had a lower DMW (Table 4). This shows the vulnerability of the soil after being used with no S fertilisation, which leads to increased S deficiency in the crops, and limits productivity and product quality (JOHNSON *et al*., 2018; SCHERER, 2009; VERMEIREN *et al*., 2018). In the fertilised soils, the response was due to the greater availability of S in the labile phase, and the plant regrowth already having a developed root system, thereby reducing the input of photoassimilates and nutrients for root development.

Sulphur availability maximises the activity of the nitrogenase enzyme in N-deficient soils (DEVI *et al*., 2012), contributes to a proper N to S ratio in the plant and, consequently, increases protein synthesis, production and product quality (IBAÑEZ *et al*., 2020; JAMAL; MOON; ABDIN, 2010; STEINFURTH *et al*., 2012).

The increase in production (IP) in the first cut varied from almost zero to 63%, but in most soils the IP was less than 20% (Table 4), underlining the low response

to the added S. There was a greater response in the second cut, with the IP ranging from 8% to 75%, and 15 soils showing more than a 40% increase in production.

In the first cut, the critical level for soil S was 2.40 mg dm^{-3} for both MCP and AMA (Figures 1A and 1C). Below these values, the probability of nutrient deficiency is great, with a consequent response to fertilisation (CATE JUNIOR; NELSON, 1965). For this cut, it was found that 16 soils had an available S content greater than the critical level established for both extractants, explaining the low response of the plants in the first cut.

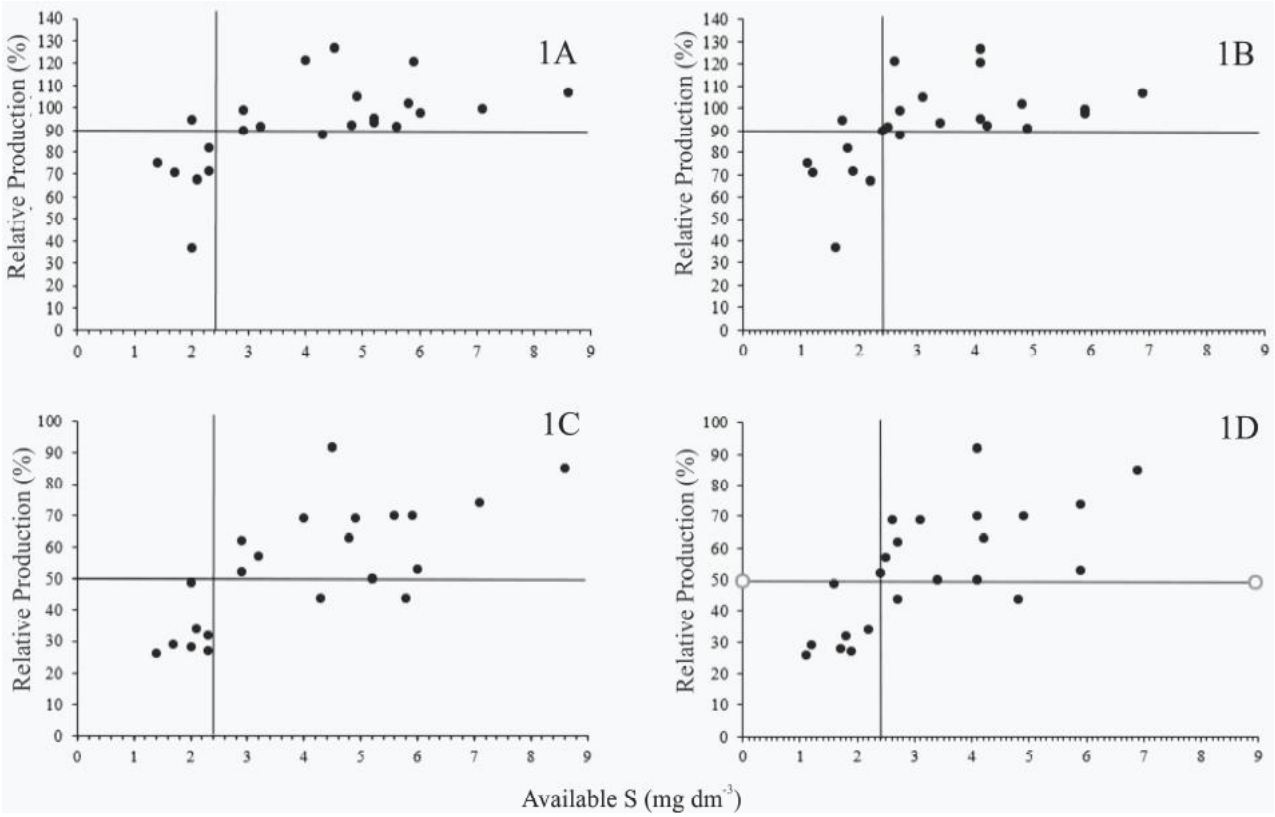
In the second cut (Figures 1B and 1D), keeping the same critical level of 2.40 mg dm^{-3}, the number of soils that showed an available S content greater than the critical level was reduced to 13 and 14, using MCP and AMA respectively. However, using both extractants, the RP went up to 50%, with only one soil having an RP greater than 90%.

The values obtained for critical level (CL) are below the range of variation in available S, of between 5 and 14 mg dm^{-3} for species with a low and high S demand, respectively (CARMONA *et al*., 2009; NASCIMENTO; MORELLI, 1980; PIAS *et al*., 2019). However, Fontes *et al*. (1982) found a CL of 1.2 mg dm^{-3}, close to that found in this study, using sorghum and MCP in water.

The low CL found in this study is attributed to the low S requirement of the crop, since more demanding species require levels greater than 7.5 mg dm^{-3}, especially in soils with low levels of clay and organic matter (PIAS *et al*., 2019). Some studies of soils with an S content greater than 4 mg dm^{-3} found no plant response to S, except for *Brassica napus* L. var. *napus* (canola) (RHEINHEIMER *et al*., 2007; TIECHER *et al*., 2012), which is included in the group with a high S requirement.

The critical level (CL) was obtained for the two successive cuts by relating the relative production with the S content of the plants with no fertilisation (Figures 2A and 2B). In the first cut, the CL for S in the leaf tissue was 0.6 g S kg^{-1} for a relative production greater than 90%. In the second cut, except for one soil, all the plants had an RP of less than 90%, with levels below the CL in most soils. Due to data dispersion, it was not possible to establish the CL for S in plants fertilised with the nutrient.

Figure 1 - Relationship between the relative production of dry matter weight in sorghum plants and the available S, for MCP in the first cut (A) and second cut (C), and for AMA in the first cut (B) and second cut (D)



The S concentration in plant tissue varies between 1 and 5 g kg^{-1}, with the concentration decreasing in the following order: Cruciferae, Leguminosae and Gramineae (LUCHETA; LAMBAIS, 2012). The low levels of S found in this study can therefore be explained by sorghum being a species with a low S requirement. Studies reviewed by Pias *et al*. (2019) showed that maize and wheat, from the same family as sorghum, had a critical level for leaf S in the range of 0.8 to 2.5 mg dm^{-3}, with a relative grain production greater than 65%. S deficiency affects the growth, development, resistance to disease, and performance of the plants, and has a great impact on the nutritional quality of the crops (KORPIVA; MALAGOLI; TAKAHASHI, 2019).

The successive cultivation of sorghum without the addition of S caused a reduction of S in the leaf tissue to below the CL in the plants of 17 soils (Figures 2A and 2B). The S content of plant tissue is an uncertain variable due to its low correlation with production (DIVITO *et al*., 2015; FRANDOLOSO *et al*., 2010; MODA *et al*., 2013). However, analysis of the leaf tissue can be an effective tool for monitoring the need for S fertilisation in soils with low SO_4^{-2} availability (PIAS *et al*., 2019), as in the soils under study.

The values for relative production as a function of the N/S and P/S ratios were plotted in Figures 3A and 3B, respectively. For N/S, the critical level (CL) was 22.5, values above that level indicate a S deficiency, limiting dry matter production in the sorghum. It was found that in the first cut, the plants in 10 soils had an N/S ratio lower than the CL and an RP greater than 90%; in six soils the plants had an N/S ratio greater than the CL and an RP equal to or greater than 90%. In the second cut, except for one soil, the RP of the plants was less than 90%, caused by the S expended by the first crop.

Although the N/S ratio did not remain st table throughout the growth cycle of the plant, it can be used as a tool for diagnosing S during cultivation. As a result,

Figure 2 - Relative production as a function of plant S content and the critical level for S in sorghum plants, in the first cut (A) and the second cut (B)

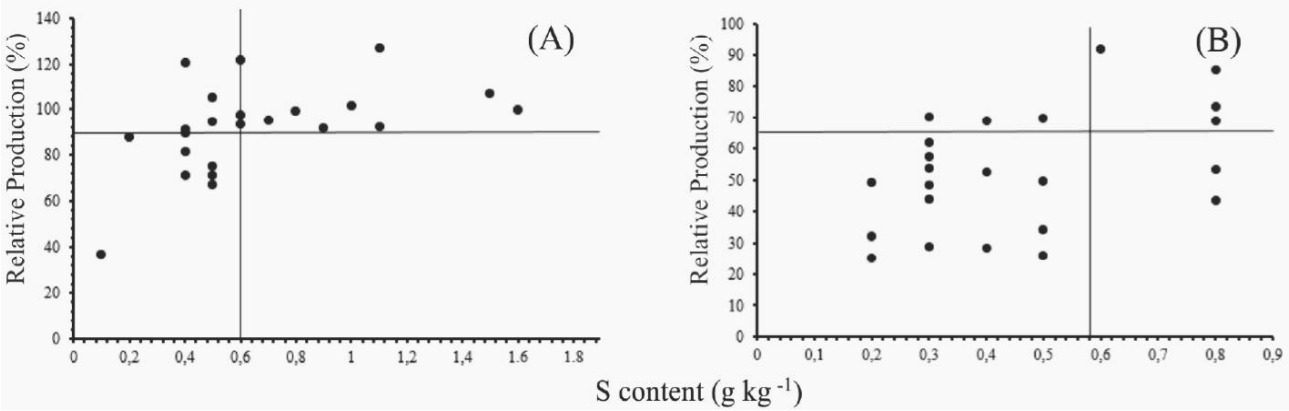
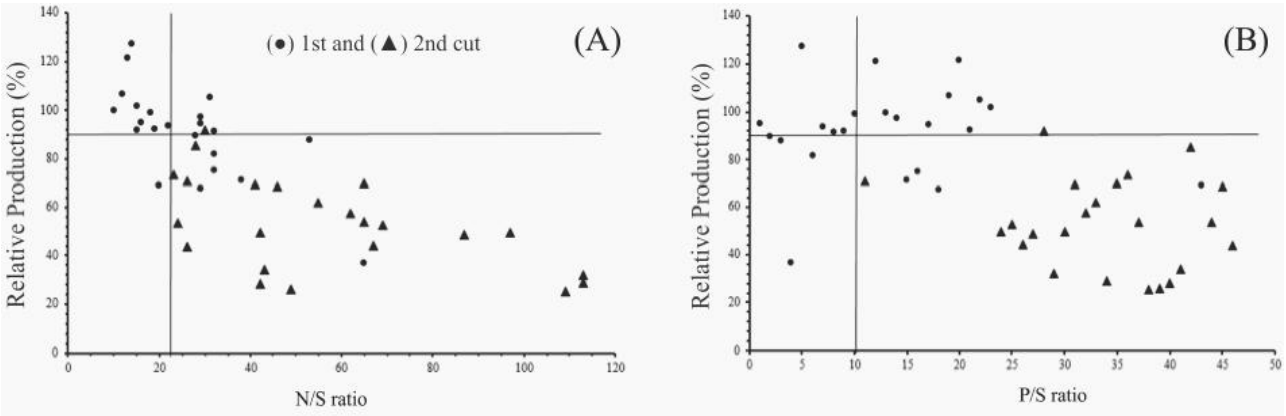


Figure 3 - Critical level for the N/S (A) and P/S (B) ratios in two cuts of sorghum from the treatment with no sulphur (S_0)



for diagnosing S deficiency in wheat, Reussi Calvo *et al*. (2012) suggested determining the S concentration in the tissue and the N/S ratio. Ercoli *et al.* (2011) point out that this ratio should be used for soils with good S availability, as plants tend to absorb far more S than they require (luxury consumption).

Relative production as a function of the P/S ratio was plotted in Figure 3B, where the critical level (CL) obtained was 10. This relationship proved to be unreliable due to the high RP in plants with a CL greater than 10.

Comparing available S by the two extractants, a statistically significant, positive linear correlation was found at a level of 1% ($r^2 = 0.92$). In principle, this close correlation suggests that both extractants can be used to assess the available S.

When the available S was correlated with the absorbed S (S-Abs) and the increase dry matter production of the aerial part of the sorghum (IP) (Table 5), it was found that in both cuts the extractants showed a positive linear correlation with the S-Abs and a negative correlation with the IP. However, the MCP extractant proved to be superior, showing a greater correlation with both variables.

Thus, despite the correlation showing the possibility of using both extractants for assessing the available S, as also seen by Blum *et al*. (2014) in maize and wheat, MCP should be preferred, as it shows a higher correlation with the increase in production and with the S absorbed by the plants. The availability of S in the soil and the requirements of the plant regulate the processes of SO_4^{2-} absorption and assimilation (TAKAHASHI *et al*., 2011). By properly estimating the available soil S, deficiencies can be corrected, favouring the metabolic processes of the crops and increasing productivity.

Table 5 - Correlation coefficients between the soil S extracted with monocalcium phosphate (MCP) and ammonium acetate (AMA), and the S absorbed (S-abs) by the plants and the increase in production (IP), in both cuts

Variable	Correlation coefficient	
	1st cut	2nd cut
S-abs x S – MCP	0.89**	0.74**
S-abs x S – AMA	0.63**	0.69**
IP x S - MCP	-0.64**	-0.71**
IP x S - AMA	-0.60**	-0.54**

*Significant at a level of 5%; **Significant at a level of 1%

CONCLUSIONS

1. The critical levels of S in forage sorghum for the soils under study were 3.90 and 3.40 mg dm^{-3} for the MCP and AMA extractants, respectively;
2. The available S by monocalcium phosphate (MCP) showed a better correlation with the increase in production and the S absorbed by the plants for the soils under study;
3. MCP is the recommended extractant for assessing available S in the soils of Ceará.

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