Comparative evaluation of Ca chloride and Ca phosphate for extractable sulfur in soils with a wide range in pH

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Abstract

Deficiency of sulfur (S) is becoming widespread in the rainfed systems of India, and there is increasing need for diagnosing the deficiency. Calcium chloride and Ca phosphate are commonly used for extracting available S in soils. Because of cost and the ease of availability locally, we prefer using Ca chloride as an extractant over Ca phosphate, for extracting available S. However, there is paucity of data on the comparative evaluation of the two extractants to extract available S, especially in soils having a wide range in natural pH (from acidic to alkaline range). It is recognized that soil pH plays a dominant role in the adsorption–desorption and extractability of sulfate-S in soils. We compared the extraction of S by Ca chloride and Ca phosphate in 86 Indian soils having a wide range in pH (4.5 to 10.6). Sulfur in the extracts was determined by ICP-AES. Considering all the 86 soil samples tested, there was an excellent agreement between the values of extractable S determined by using the two extractants ($r = 0.96$, $p < 0.001$). However, the correlation coefficient (r) between the values of extractable S by the two reagents, although highly significant, varied among the groups of soil samples according to the range in soil pH. The highest correlation coefficient ($r = 0.99$, $p < 0.0001$, $n = 17$) was found for soils with pH in the alkaline range (8.5–10.6), and the lowest correlation coefficient ($r = 0.71$, $p < 0.0001$, $n = 58$) was obtained with a set of soil samples with pH in the acidic range (4.5–6.5). For soil samples having pH in the near-neutral range (6.7–7.3), an excellent agreement was observed ($r = 0.93$, $p < 0.0001$, $n = 11$) between the extractable-S values obtained by the two extractants. While Ca phosphate extracted higher amount of S compared to Ca chloride in soil samples with pH in the acidic range, the two extractants were equally effective for soil samples with pH in the neutral or alkaline range. Our results suggest that for most of the soils in the semiarid tropical regions, which have pH in the neutral to alkaline range, Ca chloride can replace Ca phosphate as an extractant for removing available S in such soils.

Key words: extractable sulfur / soil pH / correlation coefficient / Ca chloride / Ca phosphate / soil testing

1 Introduction

The deficiency of sulfur (S) as a constraint to crop productivity in intensified, irrigated systems has long been recognized (*Kanwar*, 1972; *Pasricha* and *Fox*, 1993; *Scherer*, 2001). Recent survey of farmers' fields in the semiarid tropical regions of India showed that deficiency of S is also widespread in the rainfed production systems. The results of this research further showed that soil testing was effective in diagnosing S deficiency; and field crops grown on farmers' fields having Ca chloride–extractable S < 8–10 mg kg^{-1} responded positively to the application of S fertilization (*Rego* et al., 2007). The causes of increasing incidence of S deficiency in the rainfed systems of the semiarid regions are that S soil reserve has been exhausted by continuous cropping without the application of S-containing fertilizers; and farmers use fertilizers containing only major nutrients, especially N and P (*El-Swaify* et al., 1985). Moreover, unlike in irrigated systems, the contribution of irrigation water to S supply is also not there under rainfed cropping. The supply of S through the application of manure is generally meager

because these resources are sparingly used and in small quantities (*Rego* et al., 2003).

Several reagents have been proposed to extract available S (extractable S) in soils including water (*Spencer* and *Freney*, 1960; *Fox* et al., 1964), salt solutions such as 0.1 M LiCl (*Tabatabai* and *Bremner*, 1972), 0.15% CaCl$_2$ (*Williams* and *Steinbergs*, 1959), 5 mM MgCl$_2$ (*Roberts* and *Koehler*, 1968), 0.5 N NH$_4$OAc (NH$_4$ acetate) + 0.25 M acetic acid and Bray P-1 (*Hoeft* et al., 1973), and 500 mg P L^{-1} as Ca(H$_2$PO$_4$)$_2$ or KH$_2$PO$_4$ (*Fox* et al., 1964; *Jones* et al., 1972). On the suitability of various extractants, it has been stated that Ca phosphate seems to be one of the best extractants, because phosphate ions displace the adsorbed sulfate, especially in acidic-pH soils and Ca^{2+} ions flocculate the soil colloids (*Fox* et al., 1964; *Harward* and *Reisenauer*, 1966; *Maynard* et al., 1987; *Schmalz* et al., 2001). Among the several factors that influence sulfate sorption–desorption and its extractability by various reagents used for sulfate extraction, soil pH plays a

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J. Plant Nutr. Soil Sci. 2009, *172*, 404–407

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dominant role, and generally the sorption of sulfate is low in soils with pH > 6 (*Ensminger*, 1954; *Curtin* and *Syers*, 1990; *Shahsavani* et al., 2006; *Cui* et al., 2006).

Due to the cost and the ease of availability locally as reasons, we prefer to employ Ca chloride solution for the extraction of available S in the tropical soils of India. The objective of the present study therefore was to compare the efficacy of Ca chloride with that of Ca phosphate for the extraction of available S in Indian soils having a wide range in pH.

2 Materials and methods

For this study, a total of 86 soil samples was selected from a large number of samples received in the ICRISAT (International Crops Research Institute for the Semi-Arid Tropics) Central Analytical Services Laboratory from diverse agro-climatic on-farm sites in India. The objective was to select soil samples that covered the widest possible range in soil pH, which impacts sulfate sorption–desorption and extractability. The soil samples selected captured a wide range in pH, which varied from 4.5 to 10.6. A large proportion of the samples belonged to Alfisols, but also included some Vertisols and Ultisols; and the soil samples varied in texture and were low in organic matter (OM).

Soil samples (5 g) were extracted with 50 mL of 0.15% Ca chloride ($CaCl_2$) or with 50 mL of Ca phosphate [$Ca(H_2PO_4)_2 \cdot H_2O$] (500 mg P L^{-1}) by shaking the contents in Nalgene bottles for 30 min. The filtered extracts were analyzed for extractable S [sulfate (SO_4^{2-})-S plus organic S in solution]

using ICP-AES (inductively coupled plasma–atomic emission spectroscopy) (*Tabatabai*, 1996). All soil analyses for extractable S were performed in triplicate, and the values presented are the means of three replications.

The results were statistically analyzed. The test of significance on S extracted by the two extractants was done using unpaired t-test. Regression analysis was performed to determine the relationships between the values of available S extracted by Ca chloride and Ca phosphate reagents for all soil samples and separately for the sets of soil samples with pH in the acidic, neutral, and alkaline range.

3 Results and discussion

The comparative results of extractable S in soil samples extracted by Ca phosphate (Ca phosphate–S) and Ca chloride ($CaCl_2$–S) reagents are shown in Tabs. 1–3. The values presented are the means of three replications. The results showed that the difference between values of extracted S was not significant ($p < 0.005$) for soil samples with pH in the neutral (6.7–7.3) (Tab. 1) or alkaline range (8.5–10.6) (Tab. 2). However, the difference between the values of removed S by

Table 1: Extractable S removed by Ca phosphate (Ca phosphate–S) and Ca chloride ($CaCl_2$–S) reagents in 11 soil samples with pH in the neutral range (6.9–7.3). The difference between the values of SO_4^{2-}-S extracted by the two extractants was not significant; SD is standard deviation of mean, and SE is standard error of mean.

Sample No.	Extracted S (mg kg^{-1})	
	Ca phosphate–S	CaCl$_2$–S
1	5.1 ± 0.22	4.3 ± 0.06
2	3.4 ± 0.09	2.7 ± 0.03
3	4.4 ± 0.12	3.7 ± 0.15
4	5.4 ± 0.19	4.7 ± 0.07
5	3.9 ± 0.41	3.5 ± 0.06
6	10.8 ± 0.15	6.2 ± 0.49
7	10.4 ± 0.27	6.7 ± 0.62
8	10.4 ± 0.30	6.8 ± 0.38
9	7.3 ± 0.30	7.1 ± 0.35
10	20.0 ± 0.58	24.7 ± 0.33
11	9.0 ± 0.58	8.7 ± 0.33
Range	3.4–20.0	2.7–24.7
Mean	8.18	7.19
SD	4.8	6.1
SE	1.45	1.83

Table 2: Extractable S removed by Ca phosphate (Ca phosphate–S) and Ca chloride ($CaCl_2$–S) reagents in 17 soil samples with pH in the alkaline range (8.5–10.6). The difference between the values of SO_4^{2-}-S extracted by the two extractants was not significant; SD is standard deviation of mean, and SE is standard error of mean.

Sample No.	Extracted S (mg kg^{-1})	
	Ca phosphate–S	CaCl$_2$–S
1	17.5 ± 0.19	20.0 ± 0.58
2	5.7 ± 0.17	8.1 ± 0.58
3	11.1 ± 0.20	13.9 ± 0.26
4	12.1 ± 0.15	14.8 ± 0.45
5	4.9 ± 0.13	8.2 ± 0.72
6	4.0 ± 0.03	5.3 ± 0.22
7	10.4 ± 0.62	7.0 ± 0.81
8	9.0 ± 0.03	8.2 ± 0.0
9	39.3 ± 0.88	45.0 ± 2.0
10	80.0 ± 3.06	68.3 ± 0.88
11	29.0 ± 0.0	28.3 ± 0.33
12	89.0 ± 1.0	65.7 ± 1.86
13	64.7 ± 0.33	51.8 ± 0.79
14	168.7 ± 9.70	156.7 ± 3.38
15	15.7 ± 1.20	24.0 ± 1.0
16	51.7 ± 2.03	48.0 ± 1.15
17	9.0 ± 0.58	9.3 ± 0.88
Range	4.0–168.7	5.3–156.7
Mean	36.57	34.27
SD	43.62	38.01
SE	10.58	9.22

Table 3: Extractable S extracted by Ca phosphate (Ca phosphate–S) and Ca chloride ($CaCl_2$–S) reagents in 58 soil samples with pH in the acidic range (4.5–6.5). The difference between the values of SO_4^{2-}-S removed by the two extractants was highly significant ($p < 0.0001$); SD is standard deviation of mean, and SE is standard error of mean.

Sample No.	Extracted S (mg kg⁻¹)		Sample No.	Extracted S (mg kg⁻¹)	
	Ca phosphate–S	$CaCl_2$–S		Ca phosphate–S	$CaCl_2$–S
1	11.5 ± 0.32	3.1 ± 0.19	32	12.1 ± 0.59	3.7 ± 0.4
2	10.1 ± 0.06	3.0 ± 0.09	33	8.8 ± 0.65	2.8 ± 0.22
3	3.0 ± 0.03	1.3 ± 0.12	34	22.2 ± 0.44	5.5 ± 0.41
4	6.6 ± 0.06	1.2 ± 0.17	35	7.8 ± 0.07	7.4 ± 0.13
5	16.5 ± 0.18	4.4 ± 0.26	36	6.3 ± 0.27	7.0 ± 0.33
6	3.0 ± 0.09	0.8 ± 0.12	37	8.1 ± 0.18	6.0 ± 0.41
7	2.8 ± 0.00	1.2 ± 0.15	38	5.5 ± 0.35	4.6 ± 0.48
8	3.8 ± 0.09	1.1 ± 0.18	39	1.6 ± 0.20	3.2 ± 0.27
9	4.7 ± 0.12	1.8 ± 0.17	40	5.0 ± 0.19	6.2 ± 0.29
10	11.0 ± 0.35	6.8 ± 0.15	41	6.6 ± 0.30	6.3 ± 0.46
11	6.2 ± 0.26	2.8 ± 0.35	42	9.8 ± 0.21	5.9 ± 0.29
12	2.6 ± 0.12	1.7 ± 0.43	43	4.9 ± 0.67	6.5 ± 0.2
13	2.5 ± 0.30	1.1 ± 0.07	44	4.2 ± 0.70	5.4 ± 0.78
14	4.5 ± 0.23	2.8 ± 0.35	45	6.1 ± 0.40	7.4 ± 1.13
15	5.8 ± 0.55	1.2 ± 0.06	46	7.7 ± 0.27	5.7 ± 0.38
16	8.1 ± 0.44	4.5 ± 0.12	47	6.3 ± 0.88	4.3 ± 0.88
17	7.1 ± 0.26	4.4 ± 0.03	48	8 ± 0.58	2.3 ± 0.33
18	12.2 ± 0.26	5.6 ± 0.0	49	24.3 ± 0.33	3.0 ± 0.58
19	10.0 ± 0.12	4.8 ± 0.19	50	17.0 ± 1.00	2.0 ± 0.0
20	7.5 ± 0.93	5.6 ± 0.38	51	44.3 ± 0.33	17.0 ± 1.15
21	7.1 ± 0.38	3.4 ± 0.07	52	9.0 ± 0.00	7.7 ± 0.33
22	5.1 ± 0.20	3.3 ± 0.12	53	7.3 ± 0.33	4.7 ± 0.67
23	5.1 ± 0.46	3.2 ± 0.06	54	28.0 ± 1.15	6.7 ± 0.33
24	8.3 ± 0.12	5.6 ± 0.03	55	37.3 ± 0.88	20.7 ± 0.67
25	7.5 ± 0.32	5.4 ± 0.17	56	114.0 ± 4.51	68.0 ± 7.37
26	21.4 ± 0.41	9.0 ± 0.66	57	9.0 ± 0.00	9.0 ± 1
27	13.2 ± 0.10	4.2 ± 0.54	58	9.3 ± 0.88	7.0 ± 0.00
28	5.8 ± 0.20	3.7 ± 0.76	Range	1.6–44.3	0.8–20.7
29	6.8 ± 0.15	3.6 ± 0.27	Mean	9.9	4.9
30	13.7 ± 0.18	5.2 ± 0.58	SD	8.1	3.4
31	11.8 ± 0.89	6.1 ± 0.18	SE	1.07	0.45

the two extractants was highly significant ($p < 0.0001$) in soils with pH in the acidic range (4.5–6.5); and Ca phosphate extracted higher amounts of S than did Ca chloride (Tab. 3).

The regression analysis between the values of S extracted by Ca chloride ($CaCl_2$–S) and Ca phosphate (Ca phosphate–S) reagents for all the 86 soil samples studied showed that they were highly significantly correlated ($r = 0.96$, $p < 0.001$, $n = 86$) (Tab. 4).

Although highly significant, the correlation coefficient (r) between $CaCl_2$–S and Ca phosphate–S varied among the sets of samples grouped according to range in soil pH—acidic, neutral, or alkaline. The highest correlation coefficient ($r = 0.99$, $p < 0.0001$, $n = 17$) between the extractable-S values by the two reagents was obtained with the set of 17 soil samples having pH ranging between 8.5 and 10.6, and the lowest correlation coefficient ($r = 0.71$, $p < 0.0001$, $n = 58$) was observed with the set of 58 soil samples with pH ranging from 4.5 to 6.5 (Tab. 4). The correlation coefficient between the values of extracted S by the two extractants was also highly significant ($r = 0.93$, $p < 0.0001$, $n = 11$) for a set of 11 soil samples with pH in the near-neutral range (6.7 to 7.3) (Tab. 4).

Table 4: Relationships between S removed by Ca phosphate (Ca phosphate–S) and Ca chloride (CaCl$_2$–S) reagents in soil samples grouped according to pH range.

No. of samples	pH range	Regression equation	Correlation coefficient (*r*)
17	8.5–10.6	Ca phosphate–S = –2.3 + 1.14 CaCl$_2$–S	0.99 ($p < 0.0001$)
11	6.7–7.3	Ca phosphate–S = –2.9 + 0.73 CaCl$_2$–S	0.93 ($p < 0.0001$)
58	4.5–6.5	Ca phosphate–S = 1.62 + 1.68 CaCl$_2$–S	0.71 ($p < 0.0001$)
86	4.5–10.6	Ca phosphate–S = 3.92 + 1.07 CaCl$_2$–S	0.96 ($p < 0.0001$)

Clearly, Ca phosphate– and Ca chloride–salt solutions extract similar amounts of S in neutral to alkaline soils. However, Ca phosphate extracts significantly higher amounts of S in acidic soils. It is generally accepted that S is taken up by plants in the form of sulfate. Soil pH greatly affects the extraction of S from soil by Ca chloride and Ca phosphate (*cf.*, section 1.). When soil pH is in the neutral and alkaline range, soil particles predominantly carry negative charges and sulfate ions are present in soil solution, leading to extraction of similar amounts of S by both Ca chloride and Ca phosphate. However, when soil pH is in acidic range, soil particles carry some positive charges and, thus, adsorb sulfate. The capability of phosphate to displace sulfate adsorbed on soil-particle surface is stronger than that of chloride; and thus, Ca phosphate extracts significantly greater amounts of S from soils with pH in the acidic range (*Ensminger*, 1954; *Curtin and Syers*, 1990; *Shahsavani* et al., 2006).

4 Conclusions

Our results with soil samples having a wide range in natural pH demonstrated that Ca chloride and Ca phosphate extract similar amounts of S in soil samples with pH in the neutral or alkaline range. However, our results also showed that Ca phosphate extracted significantly higher amounts of available S in soil samples with pH in the acidic range (4.5–6.5). The results imply that Ca chloride may be used as an extractant for determining available S in the semiarid tropical soils with pH ranging from neutral to alkaline.

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