

SULPHUR FRACTIONS AND THEIR EXTRACTABILITY IN SOME ARID AND SEMI-ARID SOILS OF PAKISTAN

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ABSTRACT

Sulphur as a nutrient has not been included in the regular chemical fertilizer use in crop production in Pakistan. However, some responses to chemical fertilizer containing S coupled with low amount of extractable S in some soils of the country deserves serious consideration. Studies were conducted on 27 soils representative of major agricultural arid and semi-arid areas of Pakistan. Three forms of S (Total, organic and inorganic) were determined for each of those 27 soils. In addition, all these soils were extracted with NaCl, NaHCO₃ and CaCl₂. Organic S contributed 60–98% to the total S in these soils. The inorganic fractions extracted with NaCl, NaHCO₃ or CaCl₂ showed a non-significant positive correlation with the organic matter content of soils.

KEY WORDS : Bioavailability, Inorganic-S, Organic-S, Sulphur fractions

INTRODUCTION

Several factors have contributed to the increasing crop responses to sulphur (S) fertilization during recent years around the world (Morris, 1986). Use of high analysis S-free fertilizers (triple superphosphate and urea in place of single superphosphate and ammonium sulphate respectively) for growing high yielding varieties is probably an important factor for the response. Moreover, the problem of S deficiency has been investigated more extensively for humid and subhumid soils (Coleman, 1966; Tabatabai, 1982). They contained <2 mg SO₄/kg (inorganic) and more than 95% of their total S was in organic forms (Tabatabai, 1982). On the other hand, soils of arid and semi-arid region contain >1000 mg SO₄/kg which can be vulnerable to leaching under heavy downpour (e.g. 70% of 1114 mm annual rainfall in Rawalpindi, Pakistan) during monsoon (PARC, 1985). Majority of the Pakistan soils also had less than 1% organic matter due to low net annual addition under high temperature and alkaline soil reaction

favouring its rapid mineralization. Consideration of S balance sheet showed a deficit of 1 kg/ha which supports recent interest among investigators about S fertilization for crop production in Pakistan (Salcem and David, 1987). Several procedures like CaCl_2 (Williams and Steinbergs, 1959) NaCl , NaHCO_3 (Kilmer and Nearing, 1960) and KH_2PO_4 (Esminger, 1954) are used to extract inorganic (sulphate) form of S (absorbed by plant roots) when testing soil for S deficiency. The present paper reports on S fractions in 27 alkaline-calcareous soils of arid to semi-arid regions of Pakistan. Relationship of S fractions to S extracted by different extractants is also discussed.

MATERIALS AND METHODS

Soils and their characterization

Surface soils samples (0-15 cm) collected from 27 important agricultural soils of Pakistan (Fig. 1) were air-dried and ground to pass through a 2 mm sieve. Their classification and related characteristics determined by standard procedures are reported in Table 1. Soil pH was measured in 1:2 soil to water suspension. Organic carbon was determined by wet-oxidation method of Walkley and Black (1934). Total free- CaCO_3 was estimated by acid neutralization with 6M HCl while CEC was determined by displacing Na with 1M NH_4OAc (pH 7) from oil saturated with 1M NaOAc (pH 8.5) (Richards, 1954). Mechanical analysis was carried out by Bouyoucos (1962) hydrometer method after dispersion with sodium hexa meta phosphate.

Sulphur analyses

Amount of S present in different forms in the 27 surface soil samples was determined in duplicate by the following procedures :

Total sulphur

Total S was determined by igniting 2.5 g of soil sample with 1 g of NaHCO_3 for 3 hours in a porcelain crucible at 500 °C in a muffle furnace. Residue after ignition was extracted with 25 ml of 0.1N $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (Bardsley and Lancaster, 1960). Sulphur in the digest was then determined turbidimetrically (Verma *et al.*, 1977).

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Inorganic sulphur

Inorganic form of S was extracted by shaking 10 g of soil for 30 min. with 20 ml KH_2PO_4 (500 ppm P) solution at 1:2 soil:extractant ratio. Sulphur in the extract was determined turbidimetrically.

Organic sulphur

It was calculated as the difference between the total S and S that was extracted with KH_2PO_4 assuming that the contents of residual inorganic compounds in well-drained soils are negligible.

Bioavailability of S in soils

Several extractants are used to measure bioavailability of S to plants growing in soil. Three commonly used procedures employed in this study are given below. Sulphur in the different extracts was determined turbidimetrically.

CaCl_2 : 20 g portion of the soil sample was extracted with 40 ml of 0.15% CaCl_2 for 30 min. The suspension was filtered through Whatman No. 42 filter paper.

NaCl : 5 g soil was extracted for 30 min. with 25 ml 1% NaCl solution. Activated charcoal (0.1 g/5g sample) was used to get a clear extract.

NaHCO_3 : 10 g soil was extracted with 40 ml of 0.5 M NaHCO_3 (pH 8.5) for 1 hour in the presence of 0.1 g activated charcoal. The suspension was filtered through Whatman No. 42 filter paper.

RESULTS AND DISCUSSION

All soils were alkaline in reaction with varying degree of calcareousness containing 0.17 to 2.15% organic matter (OM). Most of the soils (81.5%) had <1% OM. Only 5 out of 27 soils had >1% OM (Table 1). Environmental factors and local cultural practices are not conducive for OM build-up in these soils.

Total sulphur in 27 soils was highly variable. It ranged from 16 to 493 mg S/kg soil with an average content of 162 mg S/kg soil (Tables 2 and 3). Most analyses reported on total S are about temperate humid

region soils with relatively high OM content. The soils under study were from arid and semi-arid regions where mean annual temperature ranges from 20 °C in winter to >40 °C in summer. Range of total S found in these soils closely followed that reported for Nigerian soils (44–489 mg S/kg) in Africa by Kang *et al.* (1981), and for Brazilian soils (43–398 mg S/kg) in South America and Iowa soils (55–580 mg S/kg) in USA by Neptune *et al.* (1975). However, average total S content of 162 mg S/kg in these soils was considerably lower than 319 and 273 mg/kg average S content reported in Iowa and Nigerian soils respectively. It was higher than 129 mg/kg average total S content reported for 48 soils of Ghana (Acquaye and Kang, 1987). But average total S content found in Pakistan soils was comparable with 166 mg/kg estimated in Brazilian soils.

Total S was significantly ($P < 0.05$) correlated with organic S, OM and NaHCO_3 extractable S (Table 4). These correlations agree with those reported for Brazilian and Iowa soils (Neptune *et al.*, 1975). Inorganic S in these soils ranged from 2 to 82 mg/kg with an average of 18 mg S/kg (Table 3). Average inorganic S estimated in these soils was more than double the value of 7.8 mg/kg inorganic S found in 48 Ghanaian soils (Acquaye and Kang, 1987). Highly variable contribution of inorganic S towards total S in these soils was 2 to 40% as compared to 6% reported for soils from Ghana (Acquaye and Kang, 1987) and Australia (Frenay, 1967) and 5 and 11% reported for Brazilian and Iowa soils, respectively (Neptune *et al.*, 1975). Higher contribution of inorganic S towards total S in some of these arid and semi-arid soils as compared to humid and sub-humid soils is probably due to their gypsum content. Inorganic S was significantly ($P < 0.01$) correlated with S extracted by CaCl_2 , NaCl , and NaHCO_3 (Table 4). Cation exchange capacity was negatively correlated with inorganic S in these soils.

Organic S in these soils had a wide range of 12 to 484 mg/kg (Table 2). Average organic S of 144 mg/kg (Table 3) found in these soils was close to the average of 121 mg S/kg reported for Ghanaian soils (Acquaye and Kang, 1987). Organic S accounted for 60 to 98% of total S in the soils. Organic S was significantly ($P > 0.05$) correlated with OM (Table 4).

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Different electrolytes namely, CaCl_2 , NaCl and NaHCO_3 used to predict S bioavailability in soils for plant uptake extracted variable quantities of S in the soils (Table 2). Amount of S extracted significantly ($P < 0.01$) correlated with inorganic S which explains 14% ($r = 0.37$) of the variation in total S. Conversely organic S explained 96% ($r = 0.98$) of the variation in total S and these procedures were hardly correlated with this form of S which was 60 to 98% in soils. However, organic S has been reported to contribute towards plant S uptake during a crop growth season. Therefore, it is imperative for a viable prediction by S chemical soil test to incorporate a knowledge of S mineralization from soil organic fractions, because it usually obscures the relation between soil S and plant S uptake.

CONCLUSIONS

It can be concluded that organic S accounted for 60 to 98% of total S in 27 surface samples of arid and semi-arid region soils which generally had $< 1\%$ OM. Inorganic S accounted for 2 to 40% of total S. Total, organic and inorganic S ranged from 16 to 493, 12 to 484 and 2 to 82 mg/kg, respectively. Their average contents were 162 mg/kg total S, 144 mg/kg organic S and 18 mg/kg inorganic S. Organic matter content in the soils was significantly related to total S and organic S. Quantities of S extracted by CaCl_2 , NaCl and NaHCO_3 procedures of measuring S bioavailability in soils to plants were significantly correlated with inorganic S which explains 14% variation in total S. They hardly had any correlation with main reservoir (organic) S in soils. Contribution of organic S towards plant S uptake during a growth season cannot be ruled out. Therefore, studies regarding mineralization-immobilization of S in these soils are warranted.

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Table 1. Physical and chemical characteristics of the experimental soils

Soil	Sub group	Particle size distribution			pH (1:1)	CEC (me/100g)	CaCO ₃ (%)	CM (%)
		Sand (%)	Silt (%)	Clay (%)				
Dhamman	Typic camborthid	65.5	11.0	24.4	8.3	8.1	4.0	0.22
Missa	Typic Ustocrept	12.6	75.8	11.6	8.3	8.7	14.8	0.86
Pacca	Aquic Camborthid	6.2	48.9	44.9	8.3	7.7	7.7	0.26
Rasalpur	Typic Ustochrept	65.4	27.5	7.1	8.3	2.9	7.4	0.60
Soltanpur	Fluventic Camborthid	12.8	67.0	20.2	8.2	6.9	1.7	0.51
Nabipur	Typic Camborthid	18.9	45.0	36.0	8.4	11.8	0.8	0.25
Bhalwal	Ustollic Haplargid	12.0	72.1	15.9	8.3	14.8	3.5	0.52
Hafizabad	Ustalfic Haplargid	37.6	50.1	12.3	7.8	4.8	2.4	0.65
Lyallpur	Ustalfic Haplargid	19.5	66.9	13.6	8.2	12.3	5.1	1.08
Hrripur	Fluventic Camborthid	15.6	14.1	40.3	7.8	13.8	5.5	2.15
Peshawer	Udic Haplustalf	8.3	64.7	27.8	8.3	12.9	17.7	0.81
Shahpur	Fluventic Camborthid	7.1	37.1	55.7	9.1	10.6	4.4	1.07
Tharpal	Fluventic Camborthid	64.8	13.2	21.9	8.4	7.1	6.8	0.65
Warsak	Udic Ustochrept	16.5	66.9	16.6	8.3	6.8	0.5	0.22
Balkasar	Udic Haplustalf	69.7	18.1	12.2	8.0	8.6	0.3	0.17
Guliana	Udic Haplustalf	6.8	73.9	19.3	8.2	12.2	1.6	0.72
Gujranwala	Udic Haplustalf	27.0	54.8	18.2	7.7	10.6	1.2	0.77
Pindorian	Udic Haplustalf	55.2	33.7	11.1	8.4	5.7	9.3	0.40
Rajar	Typic Ustochrept	5.1	84.4	10.5	8.3	7.2	14.1	0.34
Mardan	Vertic Ustochrept	13.0	41.6	45.3	8.2	15.5	8.2	1.17
Manschra	Typic Eutrochrept	23.0	44.1	32.8	8.2	16.6	1.4	0.95
Abbotabad	Typic Haplaquent	16.5	47.5	36.0	8.3	14.3	1.2	0.77
Charsada	Aeric Haplaquent	33.0	37.5	29.4	7.9	9.8	4.1	1.03
Wazirabad	Udic Haplustalf	80.9	11.6	7.5	8.2	6.8	0.4	0.52
Balkasar	Udic Haplustalf	63.0	19.3	17.6	8.2	10.0	3.0	0.56
Dhamman	Typic Camborthid	72.3	6.5	21.5	8.4	6.3	7.0	0.22

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Table 2. Amount of different sulphur fractions found in the experimental soils

Soil	Sulphur forms			Sulphur extracted by		
	Total	Inorganic	Organic	CaCl ₂	NaCl	NaHCO ₃
	----- (mg S/kg) -----			----- (mg S/kg) -----		
Dhamman	65.6	1.9	63.7	10.0	36.7	11.0
Missa	125.7	3.8	121.8	9.7	28.6	27.6
Pacca	83.5	5.6	77.9	12.7	27.4	3.3
Rasulpur	159.0	21.0	137.0	12.9	38.8	19.0
Sultanpur	492.9	21.0	471.0	9.1	16.5	23.1
Nabipur	51.6	6.1	45.4	15.8	27.4	19.4
Bhalwal	115.5	7.3	122.8	15.2	37.6	51.9
Hafizabad	182.0	70.5	111.5	72.5	88.0	109.8
Lyallpur	125.7	12.9	112.7	34.6	50.1	71.1
Haripur	413.5	19.3	394.2	26.2	59.7	42.0
Peshawer	198.6	4.2	194.4	16.2	31.6	10.7
Shahpur	162.8	5.3	157.5	76.8	78.0	44.1
Tharpal	77.0	29.4	37.5	10.8	64.2	72.9
Warsak	283.6	45.5	238.1	60.7	29.8	38.5
Balkasar	42.6	1.9	40.7	9.6	24.7	9.9
Guliana	77.1	3.7	73.4	13.0	29.8	14.8
Gujranwala	101.4	4.2	97.2	13.8	47.5	28.3
Pindorian	330.4	82.3	248.1	16.2	53.7	35.5
Rajar	97.6	5.3	92.3	15.3	21.4	21.1
Mardan	492.8	8.4	484.4	13.7	29.2	9.2
Mansehra	123.2	7.4	115.8	13.1	37.0	8.5
Meranshah	212.7	82.3	130.4	85.5	102.6	65.6
Abbotabad	15.6	3.5	12.2	121.3	14.8	14.5
Charsadha	176.9	12.4	164.5	14.1	15.5	7.9
Wazirabad	31.1	7.2	23.3	13.5	22.6	8.5
Palkasar	57.3	6.6	50.6	14.7	36.6	19.0
Dhamman	51.3	12.5	38.5	9.9	20.2	4.5

Table 3. Range and mean values for various S forms and different soil physical and chemical properties (n = 27)

<i>Property</i>	<i>Range</i>		<i>Mean</i>
	<i>Minimum</i>	<i>Maximum</i>	
pH	7.76	9.10	8.26
OM(%)	0.17	2.15	0.68
CaCO ₃ (%)	Traces	17.70	5.17
CEC (me/100g)	3.0	16.6	9.8
S fractions			
Total (mg S / kg)	15.6	492.9	162.1
Inorganic (mg S / kg)	1.9	82.3	18.2
Organic (mg S / kg)	12.2	484.4	144.0
CaCl ₂ Ext. (mg S / kg)	9.1	85.4	23.3
NaCl Ext. (mg S / kg)	16.5	88.0	39.6
NaHCO ₃ Ext. (mg S / kg)	3.3	109.8	29.7

Table 4. Simple correlation coefficients for soil properties and various S forms (n=27)

<i>Property</i>	<i>Correlation coefficient (r)</i>					
	<i>S Forms</i>			<i>S extracted by</i>		
	<i>Total S</i>	<i>Inorganic S</i>	<i>Organic S</i>	<i>CaCl₂</i>	<i>NaCl</i>	<i>NaHCO₃</i>
Inorganic-S	0.37	—	—	—	—	—
Organic-S	0.93	0.20	—	—	—	—
CaCl ₂ Ext.	0.18	0.60	0.07	—	—	—
NaCl Ext.	0.14	0.65	0.02	0.77	—	—
NaHCO ₃ Ext.	0.43	0.61	0.01	0.65	0.80	—
CEC	0.07	-0.42	0.16	-0.12	-0.17	-0.26
pH	-0.04	-0.01	-0.03	0.23	0.04	0.03
CaCO ₃	0.11	-0.12	0.13	-0.25	-0.26	-0.20
OM	0.44	-0.03	0.46	0.19	0.21	0.06

A coefficient of 0.38 and 0.49 is required for significance at 0.05 and 0.01 probability level respectively

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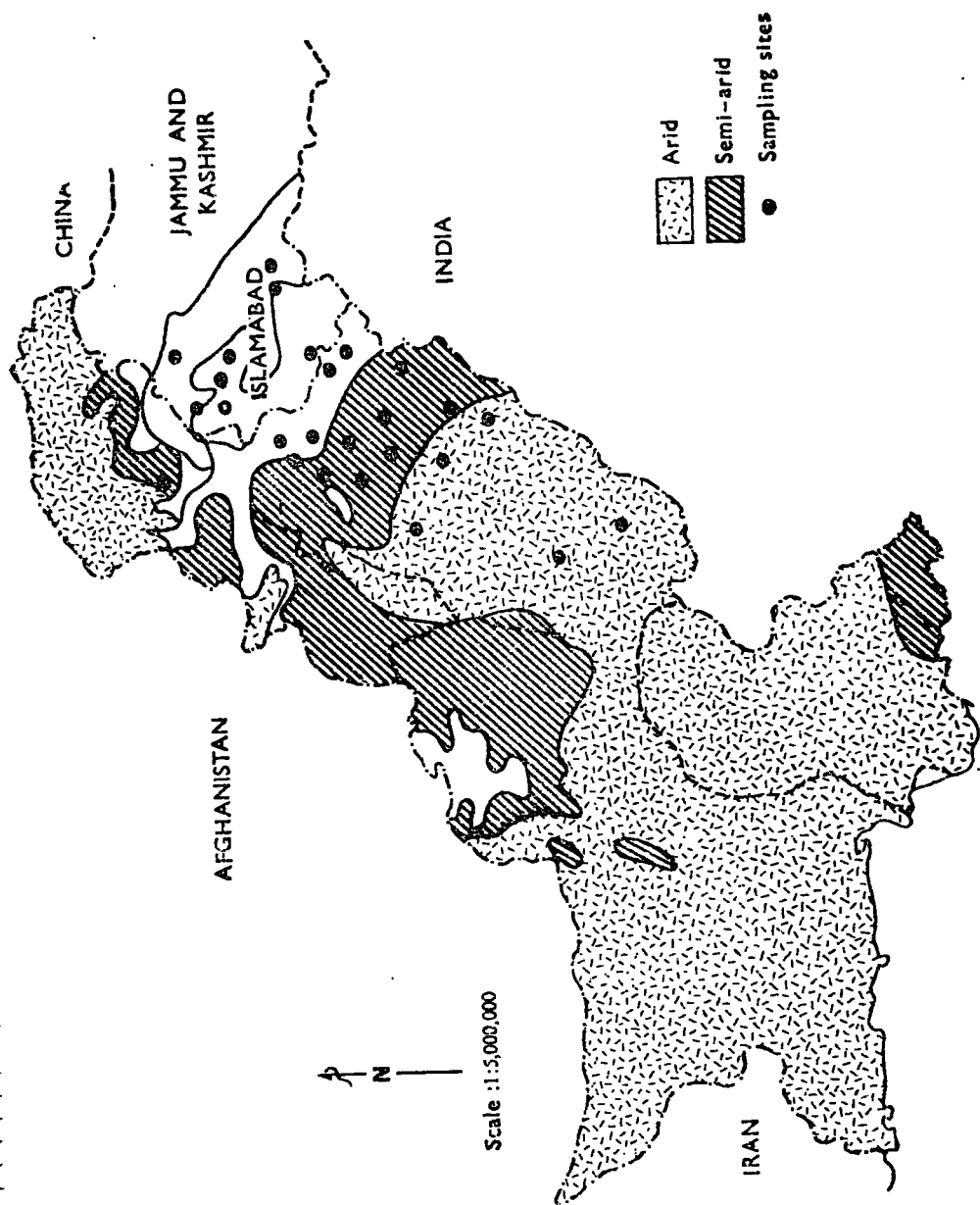


Fig. 1. Map of Pakistan showing sampling sites