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Efficacy of various extractants in S fractionation in acid soils of Himachal Pradesh

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Abstract

In view of sulphur deficiency in soils of the Kangra valley of Himachal Pradesh a study was undertaken to evaluate the extracting ability of various extractants in releasing different forms of sulphur. The results obtained thereof are presented in this paper.

Additional keywords : Available sulphur, forms of sulphur.

Introduction

Sulphur deficiency in soils of the Kangra valley of Himachal Pradesh and response to applied S in raya (*Brassica juncea*) have been reported (Singh *et al.* 1976, Jaggi 1994). This situation, therefore, demanded a study on the amount of sulphur that could be extracted with different extractants. The extracted amount may be varying with respect of soil types and the most important is the kind of sulphur fractions and their proportionate contribution (Kanwar and Mudhar 1986). In view of this, a study on the contribution of S fractions to available S extracted by different extractants in Alfisols were undertaken. Such studies on the forms of sulphur in relation to their availability indices and uptake of S may help in selecting suitable soil S tests.

Materials and methods

Thirteen representative surface (0-22.5 cm) soils of the Kangra valley were collected from two agro-climatic zones viz. wet temperate zone and humid sub-tropical zone. The soils were analysed for various physical and chemical properties using standard laboratory procecures. Organic C (g/kg), free $CaCO_3$ (%) and CEC (cmol (p+) kg^{-1}) varied from 7.0 to 13.8, 8.4 to 17.8 and 6.9 to 11.4, respectively with their mean values of 10.3, 11.8 and 8.5. Similarly pH of the soils ranged between 5.3 and 7.1. The soils were loamy sand to sandy clay in surface texture.

Available S was determined using six extractants, namely 0.15% $CaCl_2$ (Williams and Steinbergs 1959), KH_2PO_4 (500 ppm-P) (Ensminger 1954), ammonium acetate-acetic acid (Bardsley and Lancaster 1960), 0.5*M* $NaHCO_3$ (pH 8.5) (Victor and Nearpass 1960), Morgan's reagent (Chesnin and Yien 1950) and water (Freney 1958). Total, non-sulphate and heat soluble forms of S were determined following the procedure outlined by Butter and Chenery (1959), Evans and Rost (1945), Fox *et al.* (1964), respectively. For estimating organic, sulphate and total water soluble forms, the method of Williams and Steinbergs (1959) was followed.

To quantify the different forms of S as determined by six extractants mentioned above, stepwise multiple regression equations were worked out (Snedecor and Cochran 1967).

Results and discussion

Available S by different extractants

The perusal of data indicated that all extractants used in this study differed in their capacity to extract available sulphur, but not to a large extent (Table 1). The maximum available S (ranging from 14.0 to 19.2 mg kg^{-1} with a mean value of 16.1) was extracted with KH_2PO_4. The highest extracability of this extractant could be attributed to the powerful replacing capacity of phosphate ions for sulphate, besides the fact that phosphate ions not only remove sulphur from readily soluble form but also from adsorbed and organic forms of sulphur. The adsorbed sulphate is in kinetic equilibrium with sulphate in solution and it may be replaced by another anion of greater co-ordinating ability in the order of hydroxyl > phosphate > sulphate = acetate > nitrate = chloride (Chao and Thomas 1963). The next in the order followed ammonium acetate-acetic acid, whose sulphur extractibility limits were from 12.8 to 17.1 mg kg^{-1} with an average value of 14.5 (Table 1). This may be ascribed to the fact that it solubilized some fraction of inorganic sulphur compounds from soils (Rehm and Caldwell 1968). The third in the descending order of extractability were 0.5 *M* $NaHCO_3$ and Morgan's reagent which were at par with each other. The mean values of available sulphur extracted by these two extractants were 13.9 and 13.8 mg kg^{-1}, respectively. The favourable extractability of sulphur by 0.5 *M* $NaHCO_3$ (pH 8.5) could be due to the fact that it extracted part of the adsorbed and organic sulphur being stronger extractants than the others (Kanwar and Mudhar 1986). Because of being weakly acidic, the extracting power of Morgans' reagent (NaOAC + HOAC) was restricted to be at par with 0.5 *M* $NaHCO_3$ (pH 8.5). Although the extractants with reasonable acidity are potential solubilizers of inorganic compounds of the soil. The average extractabilities of water and 0.15% $CaCl_2$ were 11.7 and 9.7 mg kg^{-1}, respectively (Table 1). The poor extraction capacity of 0.15% $CaCl_2$ is due to the fact that chloride ions are the weak competitors for adsorption sites (Chao 1964) and therefore, extract only free inorganic sulphates and a very small portion of the sulphates from the adsorption sites. Thus, the extractability of the reagents followed the order as KH_2PO_4 (500 ppm p) > ammonium acetate-acetic acid > 0.5 *M* $NaHCO_3$ (pH 8.5) > Morgans' reagent > water > 0.15% $CaCl_2$.

Table 1. Extractability of available S (mg kg^{-1}) by different extractants

S. No.	Location	0.15% $CaCl_2$	KH_2PO_4 (500 ppm-P)	0.5M $NaHCO_3$ (pH 8.5)	Ammonium acetate-acetic acid	Morgan's reagent	Water
1.	Alampur	8.5	14.1	12.1	13.2	12.1	10.5
2.	Baijnath	9.5	15.2	13.2	13.8	13.5	11.5
3.	Dadh	9.2	17.2	13.8	15.8	13.2	10.2
4.	Dheera	9.7	16.6	12.6	14.9	13.9	11.0
5.	Gaggal	11.3	17.8	15.2	16.2	16.1	13.0
6.	Guler	9.8	15.8	14.0	13.2	14.0	11.0
7.	Jawalamukhi	8.5	14.0	12.0	13.6	12.1	10.5
8.	Khaira	9.3	15.1	13.0	14.1	13.1	11.3
9.	Malan	11.3	19.0	17.0	17.1	16.0	13.6
10.	Kangra	9.2	15.2	13.0	13.6	13.0	11.2
11.	Palampur	8.5	14.2	12.5	12.8	12.1	11.0
12.	Ranital	11.3	19.2	17.6	16.8	16.1	13.8
13.	Shahpur	10.2	16.6	14.2	13.9	14.5	13.1
	Mean	9.7	16.1	13.9	14.5	13.8	11.7

Forms of S

Organic sulphur content in these soils (Table 2) varied from 88 to 176 mg kg^{-1} (48.4-68.5 per cent of the total sulphur) with a mean value of 128.5. High organic sulphur in these soils is possibly due to the rich organic carbon status (7.0 to 13.8 g kg^{-1}). A prolonged spell of cool temperature from November to March is responsible for slow mineralization of sulphur resulting in accumulation of most of the sulphur in organic form. Added to that an appreciable amount of sulphur in sulphate form is lost through leaching and run off induced by high annual rainfall (2500-3000 mm) and sloping topography. The amount of 0.15% $CaCl_2$ extractable S was in the narrow range of 8.5 to 11.2 mg kg^{-1} constituting only 3.2 to 6.0% of total S (4.5% on mean basis). Very low percentage of this fraction is due to the fact that plants absorb sulphur in sulphate form and additionally much more of it is lost through leaching and run off. Tripathi and Singh (1992) observed organic and sulphate form of sulphur in the range of 65 to 228 and 5.5 to 21.0 mg kg^{-1} of soil, respectively, in some soil groups of Himachal Pradesh.

Table 2. Relative abundance of different forms of S in soils (mg kg^{-1}) of the Kangra valley

S. No.	Location	Total sulphur	Organic sulphur	Non-sulphate sulphur	Sulphate sulphur	Heat soluble sulphur	Total, water soluble sulphur
1.	Alampur	186	104 (55.9)	73.5 (39.5)	8.5 (4.6)	16.1 (8.7)	17.0 (9.1)
2.	Baijnath	204	130 (63.7)	64.3 (31.6)	9.5 (4.7)	17.2 (8.4)	17.6 (8.6)
3.	Dadh	238	160 (67.2)	68.8 (28.9)	9.2 (3.9)	18.8 (7.9)	19.1 (8.0)
4.	Dheera	196	100 (51.0)	86.3 (44.0)	9.7 (4.9)	17.2 (8.8)	17.4 (8.9)
5.	Gaggal	242	158 (65.3)	72.7 (30.0)	11.3 (4.7)	18.4 (7.6)	19.6 (8.1)
6.	Guler	208	112 (53.8)	86.2 (41.4)	9.8 (4.5)	17.6 (8.7)	16.8 (8.1)
7.	Jawalamukhi	182	88 (48.4)	85.5 (46.9)	8.5 (4.7)	15.9 (8.7)	16.6 (9.1)
8.	Khaira	202	118 (58.5)	74.7 (37.0)	9.3 (4.6)	16.0 (7.9)	17.2 (7.6)
9.	Malan	260	176 (67.7)	72.7 (28.0)	11.3 (4.3)	18.2 (7.0)	19.8 (7.6)
10.	Kangra	192	108 (56.3)	74.8 (39.0)	9.2 (4.8)	16.2 (8.4)	16.8 (8.8)
11.	Palampur	268	168 (62.7)	91.5 (34.1)	8.5 (3.2)	16.6 (6.2)	17.8 (6.6)
12.	Ranital	188	92 (48.9)	84.7 (45.0)	11.3 (6.0)	18.2 (9.7)	22.1 (11.8)
13.	Shahpur	248	170 (68.5)	67.8 (27.3)	10.2 (4.1)	16.8 (6.7)	19.2 (7.7)
	Mean	216.5	128.5 (59.0)	77.2 (36.4)	9.7 (4.5)	17.2 (8.0)	18.2 (8.4)

Figures in parentheses indicate respective percentage of S fractions of the total S.

Non-sulphate sulphur (compounds of lower oxidation state) forming insoluble compounds of Al, Fe, Ba and Ca were found to range from 64.5 to 91.5 mg kg^{-1} with an average value of 77.2. This fraction constituted 27.3 to 46.9% of total S with a mean value of 36.4%. Relatively high average composition of this fraction is due to its genetic origin from the parent rock such as granite, gneiss, quartzite and schist. In these rocks sulphur exists as sulphides and other intermediate products. In an earlier study the content of non-sulphate sulphur was found to be in the range of 30.3 to 159.4 mg kg^{-1} (Singh *et al.* 1976).

Total water soluble fraction, in addition to sulphate fraction, includes a part of easily releasable organic sulphur. In the present study the total water soluble sulphur is 8.2 mg kg^{-1} (varying from 16.6 to 22.1 mg kg^{-1} which constituted 8.4% of the total sulphur) (Table 2). Karwasra (1968) reported the variation in this form of sulphur from 3.3 to 68.5 mg kg^{-1} in tea soils of Palampur.

Table 3. Stepwise regression analysis of S availability indices in relation to their forms

S. No.	Dependent variables (Extractant used)	Equations in steps	R² (Variations explained)
1.	0.15% $CaCl_2$	1. 0.4846+0.5063** (TWS)	0.5330
		(0.1182)	
		2. -4.2359+0.3851** (TWS) +0.4049* (HSS)	0.5480
		(0.1614) (0.1496)	
		3. -5.3113+0.2402** (HSS)+0.2358 (TWS)+0.557* (OS)	0.7312
		(0.0916) (0.1012) (0.0146)	
2.	KH_2PO_4	1. -1.3206+1.5627** (SS)	0.6978
	(500 ppm-P)	2. -4.3024+0.4786 (TWS)+0.9716** (SS)	0.7253
		(0.1679) (0.2623)	
		3. -5.2875+0.9411 (SS)+0.4068 (TWS)+0.1548 (HSS)	0.7452
		(0.2748) (0.1744) (0.0996)	
		4. -5.299+0.9398 (SS)+0.2627 (TWS)+0.111(HSS)+0.0283* (OS)	0.7777
		(0.2623) (0.1121) (0.0812) (0.0108)	
3.	0.5M $NaHCO_3$	1. 1.0005+1.5597** (SS)	0.6025
	(pH 8.5)	(0.2016)	
		2. -2.7696+0.2601 (TWS)+1.4531** (SS)	0.6311
		(0.0858) (0.1982)	
		3. -2.7001+0.2113 (TWS)+1.2501 (SS)-0.1715 (HSS)	0.6452
		(0.0762) (0.1498) (0.1264)	
		4. -1.-243+0.1149 (TWS)+1.6546 (SS)+0.0176 (OS)+0.2323 (HSS)	0.6953
4.	Ammonium	1. 1.0852+1.3845** (SS)	0.6689
	acetate-acetic acid	(0.3598)	
		2. -4.3371+0.8950** (SS)+0.5929* (HSS)	0.7211
		(0.2623) (0.1679)	
		3. 5.8700+1.0857** (SS)+0.3555 (TWS)-0.6541 (HSS)	0.7698
		(0.3367) (0.1560) (0.3707)	
		4. 6.6027+1.1058 (SS)+0.8400 (TWS)-0.7428 (HSS)+0.0068 (OS)	0.7749
		(0.3498) (0.1568) (0.3986) (0.0012)	

5.	Morgan's reagent	1. 0.0223+1.4205* (SS) (0.3202)	0.7028
		2. -0.7170+0.0697** (HSS)+1.3735** (SS) (0.0216) (0.2877)	0.7211
		3. 0.9776+0.0718 (HSS)+1.3761 (SS)+0.00146* (OS) (0.0204) (0.1970) (0.00042)	0.7849
6.	Water	1. 1.1446+1.0833** (SS)	
		2. 6.1634+1.4026** (SS)-0.4730 (HSS) (0.5801) (0.2871)	0.8698
		3. 5.800+1.0867** (SS)+0.3600** (TWS)-0.6641(HSS) (0.4464) (0.0954) (0.3329)	0.8782
		4. 6.5829+1.1060** (SS)+0.3392** (TWS)-0.7390 (HSS)+0.0072(OS) (0.4355) (0.1172) (0.3915) (0.0022)	0.8928

SS = Sulphate sulphur, TWS=Total water soluble sulphur, HSS= Heat soluble sulphur, OS=Oganic sulphur

* Significant at 5% level; **Significant at 1% level.

Contribution of different forms to available S

The contribution of sulphate form to available sulphur extracted by KH_2PO_4 (500 ppm-P), 0.5 *M* $NaHCO_3$ (pH 8.5), ammonium acetate-acetic acid, Morgan's reagent and water were 69.8, 60.3, 66.9, 70.3 and 62.9, respectively (Table 3). Similarly water soluble form contributed 53.3, 2.8, 2.9, 4.9 and 0.8% to the available sulphur extracted by 0.15% $CaCl_2$, KH_2PO_4 (500 ppm-p), 0.5 *M* $NaHCO_3$ (pH 8.5), ammonium acetate-acetic acid and water, respectively (Table 3). In tea soils of the state, sulphate and water soluble fractions contribute 62.0 and 61.5 per cent of available S extracted by 0.5 *M* $NaHCO_3$ (pH 8.5) and ammonium acetate-acetic acid, respectively (Sharma 1989).

It is evident from the table 3 that the heat soluble sulphur did not contribute significantly in most of the cases. Out of six extractants heat soluble fraction contributed significantly only to two extractants i.e. 0.15% $CaCl_2$ (R^2 = 51%) and Morgan's reagent (R^2 = 1.8%). Organic sulphur was found to contribute 18.3, 3.3, 5.0, 6.4 and 1.5% in the available pool extracted by 0.15% $CaCl_2$, KH_2PO_4 (500 ppm-P), 0.5*M* $NaHCO_3$ ammonium acetate-acetic acid, Morgan's reagent and water, respectively.

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