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FORMS OF SULPHUR IN SOME BLACK SOILS OF VARANASI DISTRICT OF UTTAR PRADESH

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Fraction

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ABSTRACT

Information regarding sulphur (S) distribution in black soils of Varanasi district is meager. Therefore, present study was undertaken to assess the different forms of sulphur in black soils of Varanasi district, for this, 100 soil (0-15 cm depth) samples were collected by using global positioning system (GPS) from the Shahanshahpur village, Araziline block of Varanasi district, Uttar Pradesh. Analysis of soil samples revealed the presence of extractable sulphur (SO_4-S) in soils which ranged (mean) from 7 to 33 mg S kg^{-1} (15 mg S kg^{-1}) soil. The distribution pattern of sulphur was in the order of organic sulphur (40%) >non sulphate sulphur (30%)> adsorbed sulphur (16%) >heat soluble sulphur (11%)> 0.15% extractable available sulphur (3%). Perusal of the data shows positive and significant correlation between total sulphur, organic sulphur (r = 0.987), non sulphate sulphur (r= 0.601**) and heat soluble S (r= 0.803). Heat soluble S was also positively and significantly correlated with total S (r= 0.803**), organic sulphur (r= 0.764**) and non sulphate sulphur (r= 0.619**). The significant correlation amongst different forms of sulphur suggested an interrelated dynamic equilibrium in soils. Inferences drawn from the study on sulphur revealed that organic sulphur was determining factor in association with almost all the fractions of sulphur. Hence, organic matter thought to be good S-reservoir in these soils.

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1 Introduction

Black soils of Varanasi district of eastern Uttar Pradesh are formed under water-logged conditions and developed in the gangetic alluvium and fall under Vertisols (Chromusterts). Black soils popularly known as black cotton soils, categorised under Vertisols soil order in soil classification system are usually deep to very deep and prevails smectitic type clays. Slickensides or wedge-shaped peds, ≥ 30% clay, swell-shrink nature and microgilgai are the main features and/or characteristics of these soils with linear extensibility (LE) of 6.0 cm or more. This higher linear extensibility caused by smectitic clays sub-divide these soils in to vertic sub-group (Soil Survey Staff 2006). According to recent reports Vertisols show its presence in Indogangetic Plains of India (Ray et al., 2006). These soils are predominantly found in Maharashtra, Madhya Pradesh, and Gujarat except some parts of Rajsathan, Kerala and Jammu & Kashmir (Nair et al., 2006; Bhattacharyya et al., 2007; Mandal et al., 2012). These soils are poor in some available plant nutrients, especially nitrogen, phosphorus, sulphur and their calcareous nature adversely affects the availability of micronutrients. Varanasi district is located in the Indo-Gangetic plains and is the most productive region of the country. Imbalanced fertilization and mismanagement are the root causes of soil health deterioration in these black soils. Soils of the region are mostly used for vegetables and pulse growing purposes. Available nutrients in soils play pivotal role in determination of fertility status and sustainable productivity of the soils. Deficiencies of available major, secondary and micronutrients are widespread in soils of Varanasi district of eastern Uttar Pradesh (Tiwari et al., 2003).

Sulphur (S) is an essential nutrient for the plant growth and its metabolic activities. Its occurrence depends upon the parent materials and rocks from which soil is derived. Sulphur is a structural constituent of many co-enzymes and secondary plant products and acts as a functional group directly involved in metabolic reactions in plants. Further, it is an essential component for plant system which is present in soils in both organic and inorganic forms. Organic form particularly sulphate ester and carbon-bonded sulphur contributes approximately 75-90% of the total sulphur (Nguyen & Goh, 1992; Schmidt et al., 2012; Arvind and Rai, 2018). Widespread sulphur deficiencies in soils and crops have increased worldwide because of low input of S in the soil (Singh, 2001; Singh, 2002; Singh, 2006). This might became the cause of valuable yield reduction in many crops. Sulphur deficiencies in soils are generally attributed due to low in organic matter, coarse-textured, well drained, and subject to leaching etc (Kost et al., 2008). Conversion of natural ecosystems into agricultural lands for intensive cultivation severely depletes soil organic carbon pools (Kumar et al., 2013) which ultimately depletes the sulphur content of the soil. Since organic matter and plant residues are major sources of plant-available sulphur in the soil. Sulphur deficiency, to a tune of 50 percent in soils of eastern districts of Uttar Pradesh is reported by Singh et al. (2015). Similarly, wide spread crop sulphur deficiency have been reported in Madhya Pradesh state of India (Chibber, 2007). Further, Singh & Kumar (2012) and Singh et al. (2016) have been reported widespread sulphur and zinc deficiencies in the wheat growing alluvial soils of Araziline block of Varanasi district. Soil sulphur and its fractions can be an effective measure for the sulphur deficient areas for better management practices in future. No systematic effort yet has been made to diagnose the status and distribution of sulphur in black soils of the region. The present study was therefore, undertaken to study the above objective.

2 Materials and Methods

The Varanasi district lies between 25.14° and 25.23° N latitude and 82.56° and 83.03° E longitude, having an area of 1535 km^2 comprised of eight Vikas khand (block) with a total of 1,327 villages. The majority of soils of Varanasi fall under alluvial (Inceptisols). Some part of Varanasi district has black soils in Araziline block locally known as Karail (Vertisols).

2.1 Soil Sampling and Analysis

Altogether GPS based 100 surface soil samples (0-15 cm) were collected randomly from Shahanshahpur village of Araziline block, Varanasi district (Figure 1). The soil samples were air-dried, processed with wooden pestle and mortar and sieved by 2-mm sieve and reduced to final volume of 500 g each and were kept in labeled sample bottles for analysis.

Sulphur fractionation analysis was done by selecting different methods; value of total-S was estimated by the acid digestion (Johnson & Nishita, 1952); heat soluble sulphur (Williams & Steinbergs, 1969); available sulphur (0.15% $CaCl_2$) (Williams & Steinbergs, 1969) and adsorbed sulphur was calculated by deducting the values obtained with 0.15% $CaCl_2$ extractable S from those extracted with 500 ppm Ca $(H_2PO_4)_2$ (Fox et al., 1964). Non sulphate sulphur was computed by subtracting the sum of organic S (Evans & Rost, 1945) and available-S from the total S. Sulphur in all extracts was determined turbidimetrically (Chesnin & Yien, 1950) using UV-Visible spectrophotometer. Sulphur Availability Index (SAl) was calculated as per equation given by Donahue et al. (1977).

SAI= (0.4 x $CaCl_2$ extractable SO_4^{2-} in mg kg^{-1} soil) + % organic matter

Descriptive statistics of the available S and their fractions were obtained using data analysis in excel sheet. Simple correlation coefficients were derived to study the relationship among sulphur fractionation and SAI using SPSS 17.0 (SPSS Institute Inc., Chicago, IL, USA).

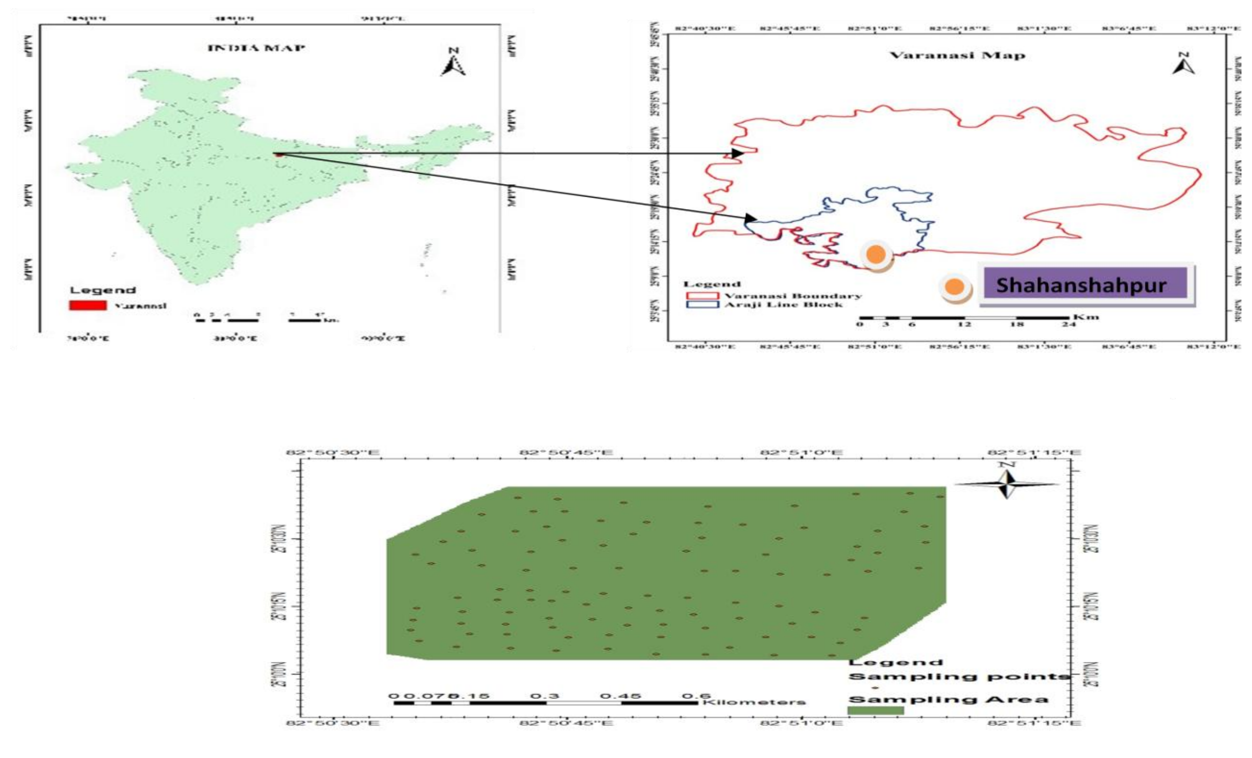

Figure 1 Sampling site of the study area, Shahanshahpur village in Araziline block of Varanasi district

3 Results and Discussion

3.1 *Available sulphur status*

Generally, available or plant available sulphur refers to the soluble and easily extractable sulphur utilized by the plants. It is a pool of sulphate S from mineral and oragnic sources which can be extracted by a suitable extractant (0.15% $CaCl_2$ solution or any other extractant like 500 ppm solution of KH_2PO_4) and the amount extracted is significantly correlated with plant growth. The available S status in surface soils ranged from 7 to 33 mg kg^{-1} with a mean of 15.52 mg S kg^{-1} soil (Table 1). Of the total samples 26, 48 and 26% samples were found under low, medium and high categories, respectively. Most of the soil samples were tested as medium in available S (Table 1). Since, determination of available sulphur provides an estimate of the soils's sulphur fertility status which ultimately considered to be plant available.

3.2 Different forms of sulphur

3.2.1 Total S

Total soil sulphur is usually distributed among several fractions viz. organic S, non-sulphate sulphur and plant available sulphur (inorganic sulphur). As a matter of fact, total sulphur content is positively associated with the organic matter content which acts as a sulphur reservoir in the soil. The mean value of total sulphur and percent distribution of sulphur are presented in table 1 and figure 2, respectively. Mean value of total sulphur was found 352 mg S kg^{-1} soil (Table 1) and this lower value might be associated with lower amounts of organic carbon. It is established that soil organic carbon largely controls by regulating the binding capacity of SO_4-S. As shown in table 2, total sulphur maintained a significant positive association with organic S, heat soluble S and non-sulphate S. Such relationship suggests that sulphur exists in a state of dynamic equilibrium in these soils. Total S content indicates the reserve pool of this element in soils, may be attributed due to the presence of clay and some extent of organic carbon in these soils. Total S exhibited a significant positive correlation (Table 2) with organic sulphur (r= 0.987**) and heat soluble sulphur (r= 0.803**). It is established that soil texture largely controls S-status by regulating the leaching losses of soluble SO_4^{2-} as reported earlier (Sarkar et al., 2007; Borkotoki & Das, 2008; Kour & Jalali, 2008; Paul & Mukhopadhyay, 2009; Chattopaddhyay & Ghosh, 2009; Basumatary et al., 2010). The close correlations suggest that the contents and the stocks of sulphur in the soils are controlled by the humification processes. Existence of similar relationship among various fractions of S was also reported by Basumatary et al. (2008).

Table 1 Summary statistics for soil sulphur fractions and sulphur availability index of Black soils of Varanasi

Sulphur forms	Minimum	Maximum	Mean	Kurtosis	Skewness
Total sulphur	151	608	352	-1.294	0.178
Organic sulphur	18	414	194	-1.326	0.209
Non sulphate S	96	211	142	-0.244	0.605
Adsorbed S	26	139	76	1.1278	1.035
$CaCl_2$ extractable S	7	33	15	-0.383	0.667
Heat soluble sulphur	26	77	53	-0.739	-0.196
Sulphur availability index	3	14	7	-0.312	0.667

Table 2 Correlation amongst different S fractions

	Total	Organic S	SO_4-S	Heat-soluble S	Adsorbed S	Non sulphate S
Total S	1					
Organic S	0.987**	1				
SO_4-S	0.030	0.048	1			
Heat-soluble S	0.803**	0.764**	-0.009	1		
Adsorbed S	0.071	-0.071	-0.346**	-0.011	1	
Non sulphate S	0.601**	0.468**	-0.280**	0.619**	0.767**	1

* and ** denote significant at 5% and 1% level, respectively

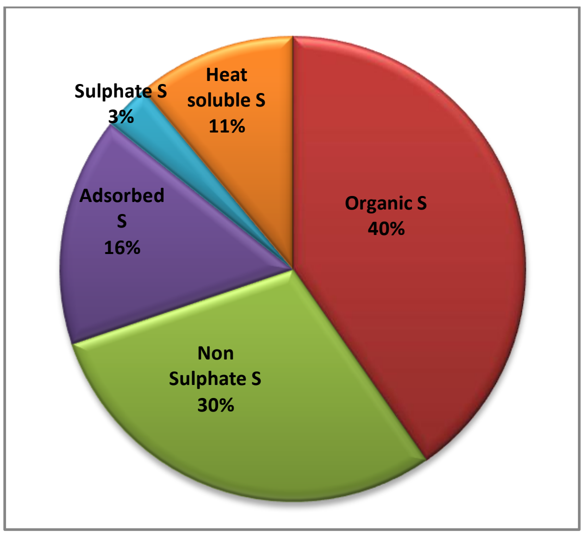

Figure 2 Distribution of sulphur in black soils of Varanasi

3.2.2 Organic S

Organic sulphur is a part of S containing organic compounds (proteins, cystein, cystine, methionine etc.) contributed mainly due to the leaflitter, animal wastes, crop residues, etc. Some researchers compute the value of organic sulphur indirectly by simply deducting available S from total S which inflates the figures of organic S (95% in Inceptisols of West Bengal) as any non-sulphate sulphur also gets included in the organic S fraction (Das et al 2006). The mean organic sulphur content of the soil was found 194 mg S kg^{-1} soil. Organic S maintained a significant and positive relationship with all forms of S except SO_4-S and adsorbed S (Table 2) suggesting a dynamic equilibrium among them (Tripathi & Singh 1992; Chattopddhyay & Ghosh 2009). Organic sulphur also correlated positively with heat soluble S (r= 0.764**). The organic S was found to be the dominant fraction in soils and accounted for 40% followed by non sulphate S (30%), adsorbed S (16%) and heat soluble S (11%) of total S in these soil samples. Possible explanations for the distribution of the organic sulphur fraction might be difference in microbial ecology from upper to lower depths in the soil, the sulphate ester constitutes the major fraction in surface soils (Stickland et al., 1987; Dhamala et al., 1990); generation of sulphate esters would be consisted with the sulphate flux variation in surface soil (Mac Laren et al., 1985). Decomposition and humification of organic sulphur compounds inherited from plants residues is directly linked with the soils and consequently mineralized and generates sulphates used for plant and microbial uptake (Stevenson, 1982). However, organic sulphur is a more dominant fraction of total S in temperate regions than in warmer climates.

3.2.3 Non sulphate S

This fraction consists primarily of occluded/precipitated S and which can vary from less than 5 to over 50% of total S. Its distribution pattern is generally reverse of organic S. Non sulphate S was computed by subtracting the sum of organic S and sulphate S from the total S. It is mostly made up of SO_4^{2-} occluded on carbonates (Evans & Rost 1945) or insoluble S compounds of Fe and Al in soil which remain unextractable even after removal of organic carbon and SO_4-S (Balanagoudar & Satyanaranyana, 1990). The results revealed that non-sulphate S content varied from 96 to 211 mg kg^{-1} with a mean of 142 mg S kg^{-1} soil (Table 1) and it constituted about 30% of total S. In Assam soils, this fraction formed 11-17% of total S (Borkotoki & Das 2008). In three agroclimatic regions of Jammu region, non-sulphate S formed 30% of total S in the temperate zone, 45% in interediate zone and 53% in the sub-tropical zone (Kour & Jalali 2008).

3.2.4 Adsorbed S

The 500 ppm Ca $(H_2PO_4)_2$ solutions extracts the SO_4^{2-} ions from the exchange complex of soil and contains both exchange complex adsorbed SO_4^{2-} and S in soil solution. Thus the adsorbed S can be obtained by deducting the values of available S (0.15% $CaCl_2$ extractable SO_4-S) from that of $Ca(H_2PO_4)_2$ extractable S. It was accounted for the 16% of the total S and ranged from 26 to 139 mg kg^{-1} with a mean of 76 mg S kg^{-1} soil (Table 1), this may be attributed due to non-displacement of adsorbed SO_4^{2-} under medium rainfall in Varanasi which restricts the leaching loss of SO_4^{2-} ions in lower layers. The adsorbed SO_4^{2-} had a highly significant positive correlation with non-sulphate S (0.767**) (Table 2). When compared with $CaCl_2$, the higher observed extractability of $Ca(H_2PO_4)_2$ is most likely due to the phosphate solution being able also to extract a portion of the labile soil organic S (Zhao & Macgrath 1994). Similar relationship among various fractions of S was also reported by Basumatary et al. (2008). However, contribution of subsoils to plant S uptake cannot be ignored in good grainage conditions (Hue & Cope, 1987). For this reason, an extractant containing phosphate which can adsorb sulphate is preferred.

3.2.5 Sulphate S

This form of S (0.15% $CaCl_2$ extractable SO_4-S) is used as an index of S availability in many soils for plant growth and subsequently reductions in yield and S uptake in crops in many soils caused by variation in this form. This form of S contributed about 3% total S and ranged from 7 to 33 mg kg^{-1} with mean of 15 mg S kg^{-1} soil (Table 1). However, this form of sulphur was negatively correlated with non sulphate S and adsorbed S and result was opposite to general expectations. $CaCl_2$ extraction appears to be a less soil dependent measurement (Ketterings et al., 2011), also reflecting well the changes in soil available S in soils having a high pH. Analyses of S in $CaCl_2$ soil extracts, in general provide a measure of soil inorganic S, because $CaCl_2$ extracts mostly SO_4-S (Zhao & Macgrath, 1994). However, extractable organic S is regarded as plant available S as it is readily mineralized to SO_4-S (Anderson et al., 1992). In general, S in $CaCl_2$ soil extracts provides a measure of soil inorganic S, because $CaCl_2$ extracts mostly SO_4-S (Goh & Tsuji, 1979). However, results revealed that available S was fall under medium category. Moreover, two compartments of the ecosystems are involved in the sulphur retention viz. sulphur assimilation by the plant uptake and incorporated in the vegetation biomass and the soil cover.

3.2.6 Heat soluble sulphur

This form of S constituted about 11% of the total S and is an indicator of the mineralizable S present in the soil. The heat soluble sulphur content was comparatively larger than available S or sulphate S. It exhibited a range from 26 to 77 mg kg^{-1} with a mean of 53 mg S kg^{-1} soil (Table 1). Heat soluble S was positively and significantly correlated with total S, organic S and non-sulphate S which indicates that almost all forms of S had contributed towards heat soluble S. It is a matter of fact that heating of soil may liberate greater amount of S covalently bonded to organic matter (Aderichin, 1960).

In general, organic sulphur had positive association with almost all the fractions of sulphur (except adsorbed and available S) and hence, organic matter could be thought of as a good S-reservoir in the soils (Borkotoki & Das 2008). Conversely, available S and adsorbed sulphur had negative or very low positive correlations with all forms of sulphur. This might be due to the presence of H^+ and OH^- ions on soil complex, where SO_4^{2-} ions are attracted to H^+ ions with the formation of insoluble compounds of S.

Conclusion:

It is concluded from the present investigation that the intensively crop growing cultivated black soils of Varanasi showed medium sulphur status. The relationship studies between different forms of sulphur revealed that, in general, organic sulphur had positive association with almost all the fractions of sulphur (except adsorbed and available S) and hence, organic matter could be thought of as a good S-reservoir in the soils.

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Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this research paper.

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