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EFFECT OF ADDED ORGANIC MATTER AND SULPHUR ON TRANSFORMATION OF DIFFERENT FRACTIONS OF SULPHUR IN SOIL

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ABSTRACT
A laboratory investigation was conducted with three levels of S (0, 5, 15 and 20 mg kg^{-1} soil) and FYM (0, 0.5, and 1.0 % by weight of the soil) to study changes in different fractions of sulphur and organic carbon under field capacity moisture regime. Soils were sampled and chemically analyzed for SO_4 – S, adsorbed S, organic S, total S and organic carbon on 10, 20, 30 and 60th day of the incubation period. Results revealed that combined application of higher dose of sulphur and organic matter leads to accumulation of higher amount of inorganic S (12.87 to 16.66 mg kg^{-1}) in soil. Although, total S remained almost unchanged but organic sulphur decreased significantly (77.1 to 75.7 mg kg^{-1}) with increase in the period of incubation. Accumulation of non-sulphate-sulphur decreased (6.79 to 3.76 mg kg^{-1}) significantly with time. Oxidizable organic carbon also decreased (1.31 to 1.27 g $100g^{-1}$) significantly with the incubation period. The highest availability of inorganic S was recorded in soil which received 20 mg S and 10g FYM per kg soil. Results further pointed out that S mineralization is influenced by addition of organic matter as well as elemental sulphur.

INTRODUCTION

Sulphur is an essential macronutrient in plant growth and development. It is increasingly being recognized as the fourth major plant nutrient after nitrogen, phosphorus and potassium (Parakhia *et al.*, 2016). Sulphur supplying capacity is dependent on the status, forms and interrelationship with some important soil characteristics including organic matter content which affect its release and dynamics in soil (Reddy *et al.* 2001; Das *et al*. 2012). In soil, sulphur can be broadly grouped into four forms viz. Sulphate – S, organic S, total S and non-sulphate S (Pasricha and Sarkar, 2012). Sulphate is the most abundant form of inorganic S found in most soils as well as the main form available to plants (Zhou *et al*., 2005). Microbial oxidation of elemental S and mineralization of organic S were two major sources of soil SO_4 – S (Jaggi *et al*., 2005; Zhou *et al*., 2005). Organic sulphur in soil is a heterogeneous mixture of soil organisms and partially decomposed plants, animals and microbial residues and represents the majority of total S in most agricultural soils (Eriksen *et al*., 1998; Solomon *et al*., 2001). Organic sulphur is the main S binding form in soils (Scherer, 2009) and contributes up to 95% of total soil S in cultivated soils. Mineralization of organic S compounds and transformation into forms accessible to plants is catalyzed by enzyme sulphatase (Hayes *et al*., 2000). Organic carbon in soil is positively and significantly correlated with sulphur (r=0.554*) (Yurembram *et al*., 2015). The present study was therefore, conducted to monitor changes in different fractions of sulphur in presence and absence of added organic matter and elemental S conducted.

MATERIALS AND METHODS

A composite soil sample (0-15 cm depth) was collected from Sub Divisional Research Farm, Kandi, Murshidabad, WB (*Typic Haplaquept*), located at 23° 96' 27" N 88° 04' 96" E. The soil sample was air dried, powdered and passed through a 2 mm sieve. The experiment was conducted in controlled laboratory condition. Hundred gram air dried soil was taken in 100 ml polythene beaker for experimentation purpose. Elemental sulphur (97% S) and completely decomposed FYM (0.93% N, 0.48%P and 0.52% K) were mixed thoroughly as per treatments. Loss of moisture during incubation period was replenished on every alternate day by addition of distilled water. The treatments adopted for the experiment are as follows:

OM_0S_0	OM_1S_0	OM_2S_0
OM_0S_1	OM_1S_1	OM_2S_1
OM_0S_2	OM_1S_2	OM_2S_2

Where, OM_0 - No organic matter; OM_1 – Organic matter (FYM at 0.5% by weight of the soil); OM_2 – Organic matter (FYM at 1.0% by weight of the soil); S_0 – No sulphur; S_1 – S at 10 mg kg^{-1}; S_2 - S at 20 mg kg^{-1}

Altogether nine sets of treatments with 3 replications were adopted for the experiment. The experiment was statistically designed (Completely Randomised Design). Soil samples were analyzed periodically on 10th, 20th, 30th and 60th day of the incubation to monitor changes in different fractions of S and organic carbon. Sulphate sulphur was extracted with 0.15 % $CaCl_2$ extractant (Williams and Steinbergs, 1959). Adsorbed sulphur was calculated by deducting the values obtained with 0.15% $CaCl_2$ extractant from those with $Ca(H_2PO_4)_2$ extractant (Fox *et al*., 1964). $CaCl_2$ extractable S and adsorbed S together are considered as inorganic S in the text. Organic sulphur was determined following the procedure of Evans and Rost (1945) and modified by Bardsley and Lancaster (1960). Total soil sulphur was determined by $HClO_4$ acid digestion (Chapman and Prat, 1961). Sulphur content in all the extracts was determined turbidimetrically (Chesnin and Yien, 1951). The non-sulphate sulphur was calculated by subtracting organic and inorganic sulphur from total sulphur. Organic carbon was estimated following the method of Walkley and Black (1934).

The physical, chemical and physico-chemical properties of the initial soil sample are bulk density 1.31 g cc^{-1}, water holding capacity 46.23%, pH 6.43, OC 1.1%, available N, P_2O_5 and K_2O are 196.5, 27.3 and 135.5 kg ha^{-1} respectively. Inorganic, organic and total sulphur content of the initial soil was 9.57, 72.93 and 88.42 mg kg^{-1} respectively.

RESULTS AND DISCUSSION

Inorganic Sulphur

Inorganic S (sulphate S and adsorbed S) increased significantly with the period of incubation (Table 1). Furthermore, irrespective of stages of sampling and S fertilizer additions, SO_4 – S increased with increase in the dose of organic matter applied to soil. Again, irrespective of organic matter additions and stages of incubation, S fertilization increased SO_4 – S in soil and the increment is more in soils treated with higher dose of sulphur fertilizer. The increase in SO_4 – S with time may be attributed to mineralization of organic sulphur in soil. Again, addition of higher dose of organic matter leads to accumulate higher amount of SO_4 – S in soil. The results of the present investigation find support of earlier works carried out by Reddy *et al*. (2002). Addition of S fertilizer also increased SO_4 – S in soil and this trend was observed throughout the incubation period. Ye *et al*., (2010) also pointed out that addition of S fertilizers increased inorganic S in soils. Results thus clearly pointed out that addition of organic matter or S fertilizer increased inorganic sulphur content in soils. Results of the present investigation corroborate the earlier findings carried out by Gharmakher *et al*. (2009). Multiple regression equation suggests that, about 60.46% variations in total sulphur content are attributable to the inorganic sulphur (Table 7).

Organic Sulphur

Organic sulphur was found to be decreased significantly with increase in the period of investigation (Table 2). The decrease is due to mineralization of organic sulphur in soil as described by Ye *et al*. (2010). It is more prominent in the soil treated with higher dose of organic matter. This is due to mineralization of sulphur from native as well as from added organic source. The present results find support of earlier investigation carried out by Jaggi *et al*. (2005) and Zhou *et al*. (2005). Addition of elemental sulphur did not affect the S mineralization pattern to a great extent. However, addition of higher dose of elemental S in absence of organic matter enhanced sulphur mineralization rate in soil. Organic matter acts as an energy source for S-oxidizing microorganisms which in turn make a spurt in their activities and increased the S-mineralization rate in soil (Gharmakher *et al*., 2009). Addition of elemental S did not enhance S-mineralization rate in the initial stage of incubation. This is because of the immobilization of added S by sulphur oxidizing organisms rendering comparatively lower amount of mineralizable S in soil. However, with time dead S-oxidizing microorganisms are decomposed and sulphur is released from the organic source. Similar hypothesis was reported earlier by Das and Saha (2003). Combined application of organic matter and elemental sulphur overshadowed the rate of S-mineralization which is taken place due to addition of only organic matter. Singh *et al*., (2006) also reported faster rate of S-mineralization due to addition of organic matter. Correlation studies of organic sulphur (Table 6) revealed that the organic sulphur is positively correlated with the sulphate sulphur (r=0.559*), adsorbed sulphur (r=0.895**) and total sulphur (r=0.990**) but negatively correlated with non-sulphate sulphur (r=-0.611*). Multiple regression equation suggests that, about 98.18% variations in total sulphur content are attributed by organic sulphur (Table 7).

Total Sulphur

Irrespective of treatments, total sulphur decreased slightly with

Table 1: Changes in the amount (mg kg^{-1}) of inorganic sulphur in soils treated with and without organic matter and S fertilizer

Treatments	Incubation period (days)															
	10				20				30				60			
	OM_0	OM_1	OM_2	Mean	OM_0	OM_1	OM_2	Mean	OM_0	OM_1	OM_2	Mean	OM_0	OM_1	OM_2	Mean
S_0	9.76	9.97	11.38	10.37	9.75	11.12	12.82	11.23	9.77	12.55	14.37	12.23	9.77	13.29	16.02	13.02
S_1	12.56	12.86	13.29	12.90	13.73	14.09	14.46	14.09	14.88	15.46	15.62	15.32	16.61	16.90	17.70	17.07
S_2	14.83	15.30	15.92	15.35	15.77	16.20	17.05	16.34	16.37	17.48	17.64	17.16	18.42	18.84	20.68	19.31
Mean	12.38	12.71	13.53	12.87	13.08	13.80	14.78	13.93	13.67	15.16	15.88	15.00	14.93	16.34	18.13	16.66
SEm (±)				0.20				0.36				0.03				0.04
CD (P=0.05)				0.59				1.08				0.10				0.12
CV (%)				2.70				4.54				0.42				0.42

OM_0 – No organic matter; OM_1 – Organic matter (FYM at 0.5% by weight of the soil); OM_2 – Organic matter (FYM at 1.0% by weight of the soil); S_0 – No sulphur; S_1 – S at 10 mg kg^{-1}; S_2 – S at 20 mg kg^{-1}

Table 2: Changes in the amount (mg kg^{-1}) of organic sulphur in soils treated with and without organic matter and S fertilizer

Treatments	Incubation period (days)															
	10				20				30				60			
	OM_0	OM_1	OM_2	Mean	OM_0	OM_1	OM_2	Mean	OM_0	OM_1	OM_2	Mean	OM_0	OM_1	OM_2	Mean
S_0	69.35	69.89	70.76	70.00	69.14	69.51	70.31	69.65	68.96	69.23	70.02	69.40	68.85	69.02	69.75	69.21
S_1	75.56	76.26	78.01	76.61	75.14	76.01	77.72	76.29	74.96	75.85	77.54	76.12	74.45	74.94	76.14	75.18
S_2	83.39	84.52	86.09	84.67	83.13	84.15	85.87	84.38	82.86	83.74	85.42	84.01	82.44	82.26	83.36	82.69
Mean	76.10	76.89	78.29	77.09	75.80	76.56	77.97	76.78	75.59	76.27	77.66	76.51	75.25	75.41	76.42	75.69
SEm (±)				1.90				1.16				1.27				1.60
CD (P=0.05)				5.67				3.45				3.79				4.80
CV (%)				4.29				2.62				2.89				3.66

OM_0 = No organic matter; OM_1 = Organic matter (FYM at 0.5% by weight of the soil); OM_2 = Organic matter (FYM at 1.0% by weight of the soil); S_0 = No sulphur; S_1 = S at 10 mg kg^{-1}; S_2 = S at 20 mg kg^{-1}

Table 3: Changes in the amount (mg kg^{-1}) of total sulphur in soils treated with and without organic matter and S fertilizer

Treatments	Incubation period (days)															
	10				20				30				60			
	OM_0	OM_1	OM_2	Mean	OM_0	OM_1	OM_2	Mean	OM_0	OM_1	OM_2	Mean	OM_0	OM_1	OM_2	Mean
S_0	87.32	88.68	89.17	88.39	87.18	88.45	89.02	88.22	87.04	88.30	88.81	88.05	86.85	88.19	88.53	87.86
S_1	96.27	96.93	97.43	96.88	96.43	96.09	97.20	96.57	96.26	95.94	97.04	96.41	96.17	95.52	96.85	96.18
S_2	104.55	104.95	105.47	104.99	104.36	104.77	105.23	104.79	104.21	104.51	105.05	104.59	104.03	104.22	104.69	104.31
Mean	96.05	96.85	97.36	96.75	95.99	96.44	97.15	96.53	95.84	96.25	96.97	96.35	95.68	95.98	96.69	96.12
SEm (±)				1.28				1.13				0.95				1.09
CD (P=0.05)				3.81				3.32				2.82				3.24
CV (%)				2.29				2.03				1.70				1.96

Table 4: Changes in the amount (mg kg^{-1}) of non-sulphate sulphur in soils treated with and without organic matter and S fertilizer

Treatments	Incubation period (days)															
	10				20				30				60			
	OM_0	OM_1	OM_2	Mean	OM_0	OM_1	OM_2	Mean	OM_0	OM_1	OM_2	Mean	OM_0	OM_1	OM_2	Mean
S_0	8.21	8.82	7.03	8.02	7.87	7.82	5.89	7.19	7.44	6.52	4.42	6.13	6.50	5.88	2.76	5.05
S_1	8.15	7.81	6.13	7.36	7.56	5.99	5.02	6.19	6.42	4.63	3.88	4.98	5.11	3.68	3.01	3.93
S_2	6.33	5.13	3.46	4.97	5.46	4.42	2.31	4.06	4.98	3.29	1.99	3.42	3.17	3.12	0.65	2.31
Mean	7.56	7.25	5.54	6.79	6.96	6.08	4.41	5.82	6.28	4.81	3.43	4.84	4.93	4.23	2.14	3.76
SEm (±)				1.90				1.81				1.94				1.98
CD (P=0.05)				5.67				5.39				5.77				5.89
CV (%)				48.74				54.09				69.52				91.21

Table 5: Changes in the amount (g 100g^{-1}) of oxidizable organic carbon in soils treated with and without organic matter and S fertilizer

Treatments	Incubation period (days)															
	10				20				30				60			
	OM_0	OM_1	OM_2	Mean	OM_0	OM_1	OM_2	Mean	OM_0	OM_1	OM_2	Mean	OM_0	OM_1	OM_2	Mean
S_0	1.11	1.26	1.52	1.30	1.11	1.25	1.50	1.29	1.11	1.24	1.49	1.28	1.10	1.22	1.45	1.26
S_1	1.12	1.27	1.53	1.31	1.12	1.26	1.51	1.30	1.12	1.25	1.50	1.29	1.11	1.23	1.47	1.27
S_2	1.14	1.29	1.55	1.33	1.14	1.29	1.54	1.32	1.13	1.28	1.52	1.31	1.12	1.26	1.50	1.29
Mean	1.12	1.27	1.53	1.31	1.12	1.27	1.52	1.30	1.12	1.26	1.50	1.29	1.11	1.24	1.47	1.27
SEm (±)				0.063				0.032				0.026				0.044
CD (P=0.05)				0.047				0.039				0.035				0.037
CV (%)				3.85				3.32				3.48				3.55

increase in the period of investigation (Table 3). This slight decrease in total sulphur content may be attributed due to sulphur oxidizing microorganisms which mineralize the total sulphur and make an increase in the inorganic form of sulphur. Again, addition of organic matter helps to accumulate total S in soil. Results in Table 3 further showed that addition of higher dose of inorganic sulphur leads to accumulate comparatively higher amount of total sulphur in soil. The results of the present investigation are at par with earlier work carried out by Sharma and Jaggi, (2001). Correlation studies revealed that, total sulphur is positively correlated with the sulphate sulphur (r= 0.607*), adsorbed sulphur (r=0.905**), organic sulphur (r=0.990**) but negatively correlated with non-sulphate sulphur (r=-0.600*) (Table 6). Furthermore, stepwise

Table 6: Coefficient of correlation among different fractions of Sulphur and OC

	Sulphate S	Adsorbed S	Organic S	Total S	Non Sulphate	
Sulphate S	1					
Adsorbed S	0.74*	1				
Organic S	0.55*	0.89**	1			
Total S	0.60*	0.90**	0.99**	1		
Non Sulphate S	-0.88**	-0.80**	-0.61*	-0.60*	1	
Organic C	0.19	0.39	0.22	0.15	-0.52*	1

Table 7: Coefficient of correlation between total sulphur and different sulphur fractions as affected by different treatments under S x OM interaction

Parameters	Regression equation	Coefficient of determination (R^2)
Total sulphur vs. sulphate sulphur, adsorbed sulphur and organic sulphur	$Y = 11.08955168 + 0.311776344 X_1 - 0.014455189 X_2 + 1.079204261 X_3$	0.985949238**
Total sulphur vs. Sulphate sulphur	$Y = 74.34191503 + 2.417926371 X_1$	0.369355318*
Total sulphur vs. Adsorbed sulphur	$Y = 67.13411513 + 5.346859219 X_2$	0.8202631**
Total sulphur vs. Organic sulphur	$Y = 10.23483991 + 1.126572193 X_3$	0.981822554**
Total sulphur vs. Inorganic sulphur	$Y = 67.56718556 + 1.97490037 X_4$	0.604649962*
Total sulphur vs. Non-sulphate sulphur	$Y = 107.1990693 + -2.030056033 X_5$	0.360701451*

Y = Total sulphur; X_1 = Sulphate sulphur; X_2 = Adsorbed sulphur; X_3 = Organic sulphur; X_4 = Inorganic sulphur; X_5 = non-sulphate sulphur

multiple regression analysis revealed that, about 98.59% variations in total sulphur is attributable to the sulphate sulphur, adsorbed sulphur and Organic sulphur combinedly (Table 7).

Non-Sulphate Sulphur

Irrespective of organic matter additions and stages of sampling, comparatively lower amount of non-sulphate sulphur is accumulated in soils treated with higher dose of S fertilizer (Table 4). Accumulation of non-sulphate sulphur decreased significantly with the period of incubation. It remains as unextractable after the removal of organic carbon (H_2O_2 extractable) and SO_4 – S and is mostly made up of sulphate-occluded in and adsorbed on the carbonates of soils (Evans and Rost, 1945). However, interestingly, higher amount of non-sulphate sulphur is accumulated in soil treated with lower dose of S fertilizer. Addition of lower amount of sulphur fertilizer leads to accumulate S in inorganic forms (Table 1). Thus, it is clear from the results (Table 4) that added sulphur is occluded in or adsorbed on insoluble S compounds of Fe and Al which remains unextractable after removal of $SO_4^{=}$ - S (Balanagoudar and Satyanarayana, 1990). Addition of organic matter decreased non-sulphate sulphur in soil. However, accumulation of non-sulphate sulphur increased with the period of incubation. Furthermore, comparatively lower amount of non-sulphate sulphur is accumulated in soil treated with higher dose of organic matter. Addition of higher dose of organic matter encourages proliferation of the activities of S-oxidizing microorganisms which in turn convert higher amount organic S in inorganic form (Chen *et al.,* 2001). Data in Table 4 thus leads to conclude that addition of organic matter decreased non-sulphate sulphur in soils. This is because of the activities of S-oxidizing organisms which not only releases sulphate sulphur from the added organic source but also from native source present in the soil. The present results are in agreement with earlier works of Przybulezwska *et al.* (2004). Correlation studies (Table 6) of non-sulphate sulphur found significant negative correlation with sulphate sulphur (r=-0.883**), adsorbed sulphur (r=-0.80367**), organic sulphur (r=-0.611*) and total sulphur (r=-0.600*). Multiple regression analysis revealed that, about 36.07% variations in total sulphur is attributable to the non-sulphate sulphur (Table 7).

Organic Carbon

Irrespective of doses of S fertilizer additions and stages of sampling, comparatively higher amount of oxidizable organic carbon is accumulated in soils treated with higher dose of organic matter (Table 5). It is obvious that addition of higher amount of organic matter definitely promote accumulation of higher amount of oxidizable organic carbon in soil. However, oxidizable organic carbon significantly decreased with time in soils treated with both the doses of organic matter. The decrease in organic carbon with the increase in period of investigation is due to mineralization of organic carbon and loss of carbon in the form of CO_2 from soil system. Similar trend of results is also observed earlier by Basumatari *et al.* (2008). Results in Table 5 further revealed that addition of either dose of S fertilizer had little effect on accumulation of oxidizable organic carbon in soils. Correlation studies (Table 6) revealed that oxidizable organic carbon is negatively correlated with non-sulphate sulphur (r=-0.527*).

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