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Influence of Zn on different fractions of S in soil maintained under field capacity moisture regime

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Abstract : A laboratory investigation was conducted to study the effect of applied Zn on availability of various fractions of sulphur under field capacity moisture regime. The incubation study was conducted with 100 g soil with four levels of S (0, 5, 15 and 20 mg kg^{-1}) and Zn (0, 0.5, 1.0 and 2.0 mg kg^{-1}). Soil was sampled and analyzed at 10, 20, 30 and 60th day of the study period for SO_4-S, adsorbed S, organic S, total S and Zn. It was found that, irrespective of doses of Zn and S fertilizers, sulphate sulphur in soils tended to increase significantly with increase in the period of incubation. Addition of Zn fertilizer increases SO_4^{2-}-S content in soils. Adsorbed sulphur tended to increase significantly with increase in the period of investigation. However on the other hand, organic sulphur tended to decrease significantly with increase in the period of incubation. The decrease in organic sulphur with time is due to mineralization of this fraction of sulphur which is evidenced by the concomitant increase in sulphate and adsorbed sulphur in soils. Total S content slightly increased with increase in the dose of S addition. The increase in total S with added S fertilizer is due to incorporation of available S to the total sulphur pool in soil. Very little variation is recorded in non-sulphate sulphur in soils treated either with Zn or S fertilizer. Addition of Zn did not influence non-sulphate sulphur content in soils. Addition of sulphur fertilizer increased DTPA-extractable Zn in soils. The increment in available Zn is well marked when higher amount of S is added along with higher dose of Zn fertilizer.

Keywords : Fractions of S, S-fertilizer, Zn-fertilizer, available Zn.

Introduction

Sulphur is an element that occurs naturally in the environment and it is the 16th most abundant element in the earth crust, averaging 0.06 to 0.10%. Sulphur deficiency has become a major constraint in crop production in coarse textured soils[1]. Sulphur is essential for production of protein, fats and oils, promotes enzyme activity and helps in chlorophyll formation, improves root growth and grain filling resulting in vigorous plant growth and resistance to cold. Its deficiency causes interveinal chlorosis with a very distinct reddish colour of the veins and petioles[2]. Adoption of high yielding varieties, intensive cropping systems, continuous use of high analysis S-free fertilizers as well as restricted use of organic manures coupled with its leaching from root zone are largely responsible for increasing S deficiency in the soils[3]. The use efficiency of added S through external sources is also very low, being only 8 to10 percent[4]. In India, nearly 57 m ha of arable land suffers from various degrees of sulphur deficiency[5]. At present S deficiency in soils of Indian states varies from 5–83% with an overall mean of 41 precent[6]. In agricultural systems, where S inputs from fertilizer and atmospheric deposition are low, the release of S from organic forms is important for the supply of S to plants. Organic S is a valuable parameter for the estimation of the potential pool that makes plant-available S, especially following the addition of fresh organic matter to the soil.

The availability of nutrients in soil depends on soil characteristics especially soil pH. Fertilization and addition of acidifying amendments are common practices in high pH soils to enhance plant nutrient availability and improve plant performance. Elemental sulphur, when applied may increase the plant nutrient availability in the soil system since the micronutrient such as Zn is more available in acidic soil reaction. The acidifying function of S originates from its microbial oxidation to sulphuric acid over time. Therefore, transformation study was conducted to observe the effect of Zn on different fractions of sulphur in soil was undertaken in laboratory condition over a period of sixty days.

Experimental

Instrumentation :

(a) Electrical balance : Model No. PB 602-S (Monobloc inside), (b) Spectrophotometer : Spectrophotometer 104 (Systronics, Serial No. 1361), (c) Digital pH meter, Model No. 802 (Systronix), (d) Mechanical rotary shaker (MULTISPAN), (e) Electrical hot plate (Sisco make), (f) Muffle furnace (Avi Chem make).

Materials :

(a) Soil : 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, during the year 2012, (b) Water : Double distilled water was used for the experimentation purpose, (c) Filter paper : Whatman No. 1 filter paper.

Reagents :

Potassium sulphate (K_2SO_4), calcium chloride ($CaCl_2$), barium sulphate ($BaCl_2.2H_2O$), potassium di-hydrogen phosphate (KH_2PO_4), sodium bicarbonate ($NaHCO_3$), hydrochloric acid (HCl), calcium acetate [$Ca(OAc)_2$], nitric acid (HNO_3), perchloric acid ($HClO_4$).

Soil sample preparation and analysis :

The composite soil sample was air dried, powdered, passed through a 2 mm sieve. The experiment was conducted in controlled laboratory condition. In 100 ml plastic beaker 100 g air dried soil, elemental sulphur (97% S) and zinc oxide (62% ZnO) were added as per treatment and mixed thoroughly. Loss of moisture was replenished on every alternate day through addition of distilled water. The treatments adopted for the experiment are as follows :

$S_0\ Zn_0$	$S_1\ Zn_0$	$S_2\ Zn_0$	$S_3\ Zn_0$
$S_0\ Zn_1$	$S_1\ Zn_1$	$S_2\ Zn_1$	$S_3\ Zn_1$
$S_0\ Zn_2$	$S_1\ Zn_2$	$S_2\ Zn_2$	$S_3\ Zn_2$
$S_0\ Zn_3$	$S_1\ Zn_3$	$S_2\ Zn_3$	$S_3\ Zn_3$

where, S_0 = No sulphur; S_1 = 5 mg kg^{-1}; S_2 = 15 mg kg^{-1}; S_3 = 20 mg kg^{-1}; Zn_0 = No Zn; Zn_1 = 0.5 mg kg^{-1}; Zn_2 = 1.0 mg kg^{-1} and Zn_3 = 2.0 mg kg^{-1}.

Altogether 16 sets of treatments with 3 replications were adopted for the experiment. The experiment was statistically designed (Completely Randomised Design) with three replications and soil samples were analyzed periodically on 10th, 20th, 30th and 60th day of the incubation to determine changes in different fractions of S and DTPA extractable Zn in the soils.

Methods followed :

Sulphate sulphur was extracted with 0.15% $CaCl_2$ extractant[7]. Adsorbed sulphur was calculated by deducting the values obtained with 0.15% $CaCl_2$ extractant from those with $Ca(H_2PO_4)_2$ extractant[8]. Organic sulphur was determined as the procedure given by Evans and Rost[9] and modified by Bardsley and Lancaster[10]. Total soil sulphur was determined by $HClO_4$ acid digestion[11]. Sulphur content in all the extracts was determined turbidimetrically[12]. The non-sulphate sulphur was calculated by subtracting organic and inorganic sulphur from total sulphur.

Results and discussion

Sulphate sulphur :

Irrespective of doses of Zn and S, sulphate sulphur in soils tended to increase significantly with increase in the period of incubation (Table 1). There is an increase in sulphate sulphur with dose of S and time of incubation period. The results find support of the earlier investigations carried out by earlier workers[13]. Furthermore, organic sulphur is mineralised with time which in turn increases SO_4^{2-}-S content in soil. The results of the present investigation are at par with the earlier works[14]. Addition of Zn make an spur in the activities of sulphur oxidizing microorganisms and encourage accumulation of sulphate sulphur in soils as it was found by earlier workers[1]. Critical analysis of the mean data in Table 1 revealed that the increment in sulphate sulphur is only 6.37 mg kg^{-1} in soil which is not treated with any source of S fertilizer. However, on the other hand, the increment in sulphate sulphur goes up to 14.88 mg kg^{-1} in soil which is treated with higher dose (20 mg kg^{-1}) of S fertilizer over 60 day period of incubation. Again, addition of Zn fertilizer increases SO_4^{2-}-S content in soil. This increase in sulphate sulphur is only 6.28 mg kg^{-1} on 10th day but the value is 6.65 mg kg^{-1} on 60th day of incubation when soil is treated with higher dose of Zn fertilizer. The result thus clearly pointed out that not only the doses of S and Zn fertilizers but also the time of its reaction is also a factor in accumulation of SO_4^{2-}-S in soils. The results of the present investigation find support of the earlier research works[15]. Stepwise regression analysis (Table 8) indicates that sulphate sulphur alone accounted for about 65.36% variation in total sulphur. Table 7 indicates that, sulphate sulphur is positively correlated to adsorbed S (r = 0.962**), organic sulphur (r = 0.523**) and total sulphur (r = 0.808**) and negatively correlated with non-sulphate sulphur.

Adsorbed sulphur :

Irrespective of treatments, comparatively lower amount of adsorbed S than that of sulphate sulphur is accumulated in soils (Table 2). Adsorbed fraction of sulphur accounted for the smallest portion of the total sulphur[16]. Adsorbed sulphur tended to increase significantly with increase in the period of investigation and addition of S doses. This may be explained as mass action of sulphur which in turn increased adsorbed sulphur content in soil. The present finding is at par with earlier works[17]. Similar trend of results was also observed with the addition of Zn fertilizer. Combined application of S and Zn fertilizer increased adsorbed sulphur content in soils as it provides a favourable environment for S-oxidizing microorganisms which mineralize organic sulphur into available form and a part of which takes part in the adsorption process. Earlier workers found that combined application of S and Zn increases available sulphur content in soils[15]. The increase in adsorbed sulphur with the period of incubation is perhaps due to creation of more surface area in soil with the lapse of time. Results of earlier investigation support the present hypothesis[18]. The multiple regression equation (Table 8) showed that, 86.69% variation in total sulphur was attributable to the adsorbed sulphur. Again, adsorbed sulphur is positively correlated with available sulphur (r = 0.92604), organic sulphur (r = 0.7160*), total sulphur (r = 0.9310**) but negatively correlated with non-sulphate sulphur (r = –0.80462**) (Table 7).

Organic sulphur :

Result in Table 3 revealed that, organic sulphur tended to decrease significantly with increase in the period of incubation. The decrease in organic sulphur with time is due to mineralization of this fraction of sulphur which is evidenced by the concomitant increase in sulphate and adsorbed sulphur in soils (Tables 1 and 2). The present results corroborate the earlier findings[19]. Although organic sulphur decreased with increase in time but on the other hand, addition of S increased organic sulphur content in the soils. Highest organic S accumulation is due to accumulation of large amount of soil organic matter[20,21]. This trend of result is observed perhaps due to conversion of added inorganic S to organic form as well as due to consumption of available form of S by the microorganisms with subsequent conversion to organic form with the period of incubation. Data in Table 3 further pointed out that addition of Zn fertilizer had little effect on accumulation of organic S in soil. Higher dose of Zn addition slightly increased organic S content in soils over control at all the stages of incubation. The present hypothesis finds support of the earlier investigation[15]. Stepwise regression analysis (Table 8) indicates that inorganic sulphur (sulphate sulphur + adsorbed sulphur) accounted for about 75.02% variation in total sulphur. Inorganic forms of sulphur are the combination of sulphate (Table 1) and adsorbed sulphur (Table 2). Combined application of Zn and S fertilizers also showed increasing trend of organic S in soil.

Total sulphur :

No drastic change was observed in total sulphur content in soil treated with or without Zn and S fertilizers over 60 day period of incubation (Table 4). However, irrespective of Zn-fertilization, total S content slightly decreased with time. The decrease in total S with time is due to mineralization of total sulphur which is caused by the sulphur oxidising microorganisms. Sulphur transformations in soil are considered to result primarily from

Table 1. Changes in the amount (mg kg^{-1}) of sulphate sulphur in soils treated with and without Zn and S fertilizers

Treatments	Incubation period (days) 10					20					30					60				
	Z_0	Z_1	Z_2	Z_3	Mean	Z_0	Z_1	Z_2	Z_3	Mean	Z_0	Z_1	Z_2	Z_3	Mean	Z_0	Z_1	Z_2	Z_3	Mean
S_0	6.28	6.36	6.40	6.45	6.37	6.28	6.39	6.44	6.51	6.40	6.39	6.28	6.49	6.58	6.43	6.29	6.48	6.55	6.65	6.49
S_1	7.36	7.47	7.00	7.60	7.36	7.48	8.12	7.76	8.45	7.95	7.57	8.75	8.56	9.32	8.55	7.72	10.32	10.76	11.04	9.96
S_2	8.72	8.92	9.14	9.88	9.17	9.16	9.10	9.26	10.04	9.39	10.21	10.78	10.75	10.18	10.48	12.45	12.46	13.05	12.96	12.73
S_3	9.34	9.65	9.87	10.25	9.78	10.06	10.42	10.62	11.56	10.67	11.47	11.23	11.45	12.75	11.73	12.88	12.95	13.85	14.88	13.64
Mean	7.93	8.10	8.10	8.55	8.17	8.24	8.51	8.52	9.14	8.60	8.91	9.30	9.31	9.71	9.30	9.83	10.55	11.05	11.38	10.70
SEm (±)					0.014					0.016					0.061					0.022
CD (P = 0.05)					0.042					0.046					0.175					0.065
CV (%)					0.715					0.742					2.619					0.843

S_0 = No sulphur; S_1 = Sulphur at 5 mg kg^{-1}; S_2 = Sulphur at 15 mg kg^{-1}; S_3 = Sulphur at 20 mg kg^{-1}

Z_0 = No zinc; Z_1 = Zinc at 0.5 mg kg^{-1}; Z_2 = Zinc at 1.0 mg kg^{-1}; Z_3 = Zinc at 2.0 mg kg^{-1}

Table 2. Changes in the amount (mg kg^{-1}) of adsorbed sulphur in soils treated with and without Zn and S fertilizers

Treatments	Incubation period (days) 10					20					30					60				
	Z_0	Z_1	Z_2	Z_3	Mean	Z_0	Z_1	Z_2	Z_3	Mean	Z_0	Z_1	Z_2	Z_3	Mean	Z_0	Z_1	Z_2	Z_3	Mean
S_0	3.07	3.17	3.13	3.30	3.17	3.07	3.20	3.33	3.40	3.27	3.07	3.43	3.40	3.63	3.46	3.07	3.80	3.77	3.90	3.79
S_1	3.37	3.87	4.40	4.07	3.93	3.87	4.33	4.50	4.30	4.25	4.60	4.47	4.63	4.77	4.62	4.63	4.83	5.47	5.13	5.02
S_2	4.27	4.33	4.77	5.10	4.62	4.67	4.80	4.97	5.28	4.93	5.20	5.40	5.43	5.67	5.43	5.67	5.75	5.84	6.08	5.84
S_3	5.53	5.73	5.97	6.80	6.01	6.07	5.90	6.50	7.27	6.44	5.90	6.57	6.47	6.97	6.48	6.33	6.92	7.33	7.90	7.12
Mean	4.06	4.28	4.57	4.82	4.43	4.42	4.56	4.83	5.06	4.71	4.69	4.97	4.98	5.26	4.97	4.92	5.33	5.60	5.75	5.40
SEm (±)					0.015					0.012					0.014					0.012
CD (P = 0.05)					0.043					0.036					0.042					0.036
CV (%)					1.367					1.075					1.184					0.925

S_0 = No sulphur; S_1 = Sulphur at 5 mg kg^{-1}; S_2 = Sulphur at 15 mg kg^{-1}; S_3 = Sulphur at 20 mg kg^{-1}

Z_0 = No zinc; Z_1 = Zinc at 0.5 mg kg^{-1}; Z_2 = Zinc at 1.0 mg kg^{-1}; Z_3 = Zinc at 2.0 mg kg^{-1}

Table 3. Changes in the amount (mg kg^{-1}) of organic sulphur in soils treated with and without Zn and S fertilizers

Treatments	Incubation period (days) 10					20					30					60				
	Z_0	Z_1	Z_2	Z_3	Mean	Z_0	Z_1	Z_2	Z_3	Mean	Z_0	Z_1	Z_2	Z_3	Mean	Z_0	Z_1	Z_2	Z_3	Mean
S_0	71.34	72.58	73.46	74.78	73.04	71.34	72.44	73.35	74.62	72.92	71.34	72.29	73.22	74.45	72.77	71.33	72.13	73.08	74.25	72.61
S_1	75.36	75.94	76.14	76.96	76.10	75.22	75.76	76.02	76.80	75.95	74.08	75.60	75.86	76.64	75.55	73.40	74.60	74.95	73.97	74.23
S_2	85.11	85.71	86.33	86.87	86.01	84.97	85.01	85.97	85.81	85.44	83.73	83.37	84.49	83.99	83.90	81.19	81.01	80.87	83.00	81.52
S_3	86.40	87.14	87.76	88.44	87.44	84.40	86.05	86.42	87.22	86.02	83.13	84.62	85.32	86.75	84.96	81.82	82.43	83.30	83.43	82.75
Mean	79.55	80.34	80.92	81.76	80.65	78.98	79.82	80.44	81.11	80.08	78.07	78.97	79.72	80.46	79.30	76.93	77.54	78.05	78.66	77.79
SEm (±)					0.492					0.470					0.461					0.501
CD (P = 0.05)					1.418					1.354					1.330					1.443
CV (%)					2.554					2.456					2.438					2.670

S_0 = No sulphur
S_1 = Sulphur at 5 mg kg^{-1}
S_2 = Sulphur at 15 mg kg^{-1}
S_3 = Sulphur at 20 mg kg^{-1}

Z_0 = No zinc
Z_1 = Zinc at 0.5 mg kg^{-1}
Z_2 = Zinc at 1.0 mg kg^{-1}
Z_3 = Zinc at 2.0 mg kg^{-1}

Table 4. Changes in the amount (mg kg^{-1}) of total sulphur in soils treated with and without Zn and S fertilizers

Treatments	Incubation period (days) 10					20					30					60				
	Z_0	Z_1	Z_2	Z_3	Mean	Z_0	Z_1	Z_2	Z_3	Mean	Z_0	Z_1	Z_2	Z_3	Mean	Z_0	Z_1	Z_2	Z_3	Mean
S_0	87.94	87.54	88.40	89.60	88.37	87.94	87.47	88.26	89.94	88.24	87.61	87.25	88.13	89.33	88.08	87.94	87.14	88.01	89.10	87.93
S_1	91.62	92.92	93.92	93.42	92.97	91.49	92.76	93.80	93.32	92.84	91.36	92.64	93.71	93.29	92.75	91.22	92.52	93.57	93.24	92.64
S_2	101.52	102.45	103.45	104.42	102.96	101.38	102.30	103.33	104.28	102.82	101.26	102.17	103.20	104.19	102.71	101.13	102.02	103.02	104.06	102.56
S_3	104.23	105.46	105.96	108.89	106.14	104.10	105.30	105.81	108.78	106.00	103.99	105.15	105.69	108.65	105.87	103.85	104.99	105.54	108.47	105.71
Mean	96.33	97.09	97.93	99.08	97.61	96.22	96.96	97.80	98.96	97.48	96.05	96.80	97.68	98.87	97.35	96.03	96.67	97.54	98.72	97.24
SEm (±)					0.501					0.422					0.462					0.598
CD (P = 0.05)					1.444					1.216					1.331					1.722
CV (%)					2.131					1.798					1.971					2.553

S_0 = No sulphur
S_1 = Sulphur at 5 mg kg^{-1}
S_2 = Sulphur at 15 mg kg^{-1}
S_3 = Sulphur at 20 mg kg^{-1}

Z_0 = No zinc
Z_1 = Zinc at 0.5 mg kg^{-1}
Z_2 = Zinc at 1.0 mg kg^{-1}
Z_3 = Zinc at 2.0 mg kg^{-1}

Table 5. Changes in the amount (mg kg^{-1}) of non-sulphate sulphur in soils treated with and without Zn and S fertilizers

Treatments	Incubation period (days): 10					20					30					60				
	Z_0	Z_1	Z_2	Z_3	Mean	Z_0	Z_1	Z_2	Z_3	Mean	Z_0	Z_1	Z_2	Z_3	Mean	Z_0	Z_1	Z_2	Z_3	Mean
S_0	7.25	5.43	5.41	5.07	5.79	7.02	5.44	5.14	4.94	5.64	6.73	5.10	5.02	4.67	5.38	6.36	4.73	4.61	4.30	5.00
S_1	5.53	5.64	6.38	4.79	5.59	4.92	4.55	5.52	3.77	4.69	5.11	3.82	4.66	2.56	4.04	5.47	2.77	2.39	3.10	3.43
S_2	3.42	3.49	3.21	2.57	3.17	2.58	3.39	3.13	3.15	3.06	2.12	2.62	2.53	4.35	2.91	1.82	2.80	3.26	2.02	2.48
S_3	2.96	2.94	2.36	3.40	2.92	3.57	2.93	2.27	2.73	2.88	3.49	2.73	2.45	2.18	2.71	2.82	2.69	1.06	2.26	2.21
Mean	4.79	4.38	4.34	3.96	4.37	4.52	4.08	4.02	3.65	4.07	4.36	3.57	3.67	3.44	3.76	4.12	3.25	2.83	2.92	3.28
SEm (±)					0.664					0.661					0.445					0.761
CD (P = 0.05)					1.906					2.035					2.037					2.216
CV (%)					60.67					65.63					47.67					93.65

S_0 = No sulphur; Z_0 = No zinc
S_1 = Sulphur at 5 mg kg^{-1}; Z_1 = Zinc at 0.5 mg kg^{-1}
S_2 = Sulphur at 15 mg kg^{-1}; Z_2 = Zinc at 1.0 mg kg^{-1}
S_3 = Sulphur at 20 mg kg^{-1}; Z_3 = Zinc at 2.0 mg kg^{-1}

Table 6. Changes in the amount (mg kg^{-1}) of DTPA extractable Zn in soils treated with and without Zn and S fertilizers

Treatments	Incubation period (days): 10					20					30					60				
	Z_0	Z_1	Z_2	Z_3	Mean	Z_0	Z_1	Z_2	Z_3	Mean	Z_0	Z_1	Z_2	Z_3	Mean	Z_0	Z_1	Z_2	Z_3	Mean
S_0	0.123	0.319	0.537	1.065	0.511	0.125	0.325	0.553	1.036	0.510	0.126	0.345	0.572	1.112	0.539	0.126	0.353	0.607	1.164	0.563
S_1	0.125	0.328	0.558	0.996	0.502	0.127	0.345	0.575	1.052	0.525	0.128	0.367	0.593	1.128	0.554	0.131	0.386	0.625	1.193	0.584
S_2	0.127	0.337	0.581	1.042	0.522	0.128	0.352	0.594	1.086	0.540	0.129	0.376	0.613	1.135	0.563	0.132	0.398	0.646	1.205	0.595
S_3	0.128	0.364	0.602	1.122	0.554	0.129	0.382	0.635	1.152	0.575	0.133	0.404	0.668	1.168	0.593	0.136	0.429	0.694	1.224	0.621
Mean	0.126	0.337	0.570	0.806	0.460	0.127	0.351	0.589	1.082	0.537	0.129	0.373	0.612	1.136	0.562	0.131	0.392	0.643	1.197	0.591
SEm (±)					0.018					0.010					0.010					0.010
CD (P = 0.05)					0.013					0.011					0.013					0.012
CV (%)					3.52					2.90					3.43					2.88

S_0 = No sulphur; Z_0 = No zinc
S_1 = Sulphur at 5 mg kg^{-1}; Z_1 = Zinc at 0.5 mg kg^{-1}
S_2 = Sulphur at 15 mg kg^{-1}; Z_2 = Zinc at 1.0 mg kg^{-1}
S_3 = Sulphur at 20 mg kg^{-1}; Z_3 = Zinc at 2.0 mg kg^{-1}

microbial activity which involves processes of mineralization, immobilization, oxidation and reduction[22]. Irrespective of doses of Zn addition increased total sulphur content in soils. Similar finding has been reported by earlier workers[23]. Practically, no significant effect of Zn fertilization is recorded on changes of total S accumulation in soils. Thus it is clear from the results that although Zn fertilization has little effect on total S content but had some effects on distribution of different inorganic and organic fractions of S in soil. Total sulphur maintained a significant positive association with all the forms of sulphur. Such relationship suggests that S exists in a state of dynamic equilibrium in the soils[24]. Similar relationship among various forms of sulphur was reported earlier[25,26]. The stepwise multiple regression analysis (Table 8) indicates that, about 98.18% variations in total sulphur were attributable to the combined effect of sulphate sulphur, adsorbed sulphur and organic sulphur. Correlation study (Table 7) of total sulphur with different fractions of sulphur found significantly positive relationship with sulphate sulphur (r = 0.808**), adsorbed sulphur (r = 0.931**), organic sulphur (r = 0.901**) but negatively correlated with non-sulphate sulphur (r = –0.734*).

Non-sulphate sulphur :

Result in Table 5 revealed that contribution of non-sulphate sulphur to total sulphur is next to organic sulphur. Similar findings were also found by earlier workers[27]. It is true that in some soils, contribution of non-sulphate sulphur may account for upto 66.85% of the total sulphur[28]. This is perhaps due to the rapid oxidation of organic matter and mineralization of sulphur under arid condition but in the present investigation, the contribution of non-sulphate S to total S hardly exceeds 7.0 percent. Non-sulphate sulphur remains as unextractable after the removal of organic carbon (H_2O_2 extractable) and SO_4^{2-}-S and is mostly made up of sulphate-occluded in and adsorbed on the carbonates of soils[9]. Data in Table 5 showed very little variation in non-sulphate sulphur in soils treated either with Zn or S fertilizer. Addition of Zn did not influence non-sulphate sulphur content in soils. Soil treated with higher dose of sulphur along with higher dose of Zn is found to decrease non-sulphate sulphur particularly at the later stage of incubation. The observed result is perhaps due to formation of soluble ZnS. Thus it is clear from the results that Zn and S fertilization had little effect on content as well as transformation of non-sulphate sulphur in soils. The multiple regression equation (Table 8) showed that, about 54.01% variation in total sulphur was attributable to the non-sulphate sulphur. On the other hand non-sulphate sulphur is negatively correlated with all the fractions of sulphur.

DTPA extractable Zn :

Irrespective of S and Zn fertilizers addition DTPA extractable Zn increased significantly in soils. However, addition of different doses of Zn alone had little effect on accumulation of DTPA extractable Zn in soils. But, S fertilization changed Zn accumulation pattern in soil. Addition of sulphur fertilizer increased DTPA extractable Zn in soil. Acidification of soil through elemental sulphur application may have increased plant micronutrient availability[29]. It is also noteworthy to mention that with increase in the dose of S fertilizers DTPA extractable Zn is found to increase with the period of incubation. The increment in available Zn is well marked when higher amount of S is added along with higher dose of Zn fertilizer. The increase in DTPA extractable Zn due to combined application of Zn and S fertilizers is perhaps due to creation of favourable environment which maintain more amount of Zn in available form as $ZnSO_4$. The

Table 7. Coefficient of correlation among different fractions of sulphur and Zn under different treatment combinations

	Sulphate S	Adsorbed S	Organic S	Total S	Non-sulphate S	Zn
Sulphate S	1					
Adsorbed S	0.926**	1				
Organic S	0.523*	0.716*	1			
Total S	0.808**	0.931**	0.901**	1		
Non-sulphate S	–0.846**	–0.804**	–0.640*	–0.734*	1	
Zn	0.274	0.319	0.283	0.307	–0.312	1

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

Table 8. Multiple regression equation of total sulphur and different fractions of sulphur as affected by different treatments combination

Parameters	Regression equation	Coefficient of determination (R^2)
Total sulphur vs Available sulphur, adsorbed sulphur and organic sulphur	$Y = 23.11126 + 0.272492X_1 + 1.703348X_2 + 0.789324X_3$	0.981879**
Total sulphur vs Sulphate sulphur	$Y = 78.30034 + 1.693872X_1$	0.653648**
Total sulphur vs Adsorbed sulphur	$Y = 76.19161 + 3.613688X_2$	0.866942**
Total sulphur vs Inorganic sulphur	$Y = 76.98433 + 1.198904X_3$	0.750268**
Total sulphur vs Organic sulphur	$Y = 0.1833 + 1.370728X_4$	0.81287**
Total sulphur vs Non-sulphate sulphur	$Y = 103.4293 - 2.46842X_5$	0.540129*
	Significant at → **1% level	
	*5% level	

Y_1 = Total sulphur; X_1 = Sulphate sulphur; X_2 = Adsorbed sulphur; X_3 = Organic sulphur; X_4 = Inorganic sulphur; X_5 = Non-sulphate sulphur.

results find support of earlier investigation[15]. Correlation study of Zn with different fractions of sulphur showed a non-significant relationship (Table 8).

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