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Effect of levels of sulphur from various sources on sulphur transformations in onion growing soils

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Abstract
Sulphur (S) deficiency is widespread in Indian soils, and it has been emerging as a major limitation in Onion production. Onion being a sulphur loving crop, sulphur fertilisation to onion is important, and, therefore, to assess the supply of native sulphur from soil to onion crop requires an understanding about the effect of various sulphur fertilizers and their transformation in soils. With this view of understanding the soil S transformations, an incubation experiment was carried out for the period of 3 months in S deficient black soil (Vertic Ustropept) which was sandy loam in texture with available S content of 7 mg kg^{-1}. Ammonium sulphate, Single super phosphate, Gypsum and Elemental Sulphur were the four sources of sulphur applied at the levels of 0, 20 and 40 kg S ha^{-1} along with recommended doses of N, P and K (60:60:30 kg ha^{-1}) for onion. The treatments were laid out in CRD with 3 replications. The soil samples were analysed for different S fractions at fortnight intervals throughout the period of incubation. The mean values of different fractions of S namely total S ranged from 110.57 to 252.11 mg kg^{-1}, organic S ranged from 51.7 to 176.79 mg kg^{-1}, occluded S ranged from 32.57 to 66.54 mg kg^{-1}, Exchangeable S ranged from 3.56 to 12.57 mg kg^{-1}, Water soluble S ranged from 3.08 to 18.57 mg kg^{-1} and $CaCl_2$ extractable S ranged from 7.11 to 32.55 mg kg^{-1}. On an average, out of total sulphur, at 90 DAI, 4.95% got incorporated into water soluble sulphur, 4.07% into exchangeable sulphur, 10.45% into $CaCl_2$ extractable sulphur, 22.39% into occluded sulphur and 58.14% into organic sulphur. Comparing the sources of sulphur applied ammonium sulphate at both 20 and 40 kg S ha^{-1} and SSP @ 40 kg S ha^{-1} resulted in highly significant pattern on soil easily available sulphur fractions release over other sources.

Keywords: Sulphur, transformations, water - soluble sulphur, exchangeable sulphur

Introduction
Sulphur, a secondary major nutrient, is indispensable for the growth, production and quality of many sulphur loving crops. Onions are known for their affinity to sulphur which forms a chief constituent of secondary metabolites *i.e.* allin, cycloallin, thiopropanol and alkaloid (Allyl propyl disulphide) that governs taste, imparts pungency and medicinal properties to onion (Schnug, 1993; Raina and Jaggi, 2008) [12, 9]. Concerning fertilizer application, onion yield and quality is greatly influenced by inadequate supply of nutrients, particularly sulphur which is essential for building up of S containing amino acids viz., cystine, cysteine and methionine and also for proper vegetative growth, bulb development (Anwar *et al*. 2001) [1].

Before fertilizing, it is necessary to understand the sulphur transformations in soil to assess the sulphur releasing power of soils and S use efficiency by the crop. Hence, with this view of studying the soil sulphur fractions, the present incubation experiment was carried out with different sulphur sources and levels.

Materials and Methods
An incubation experiment was conducted for a period of 3 months with soils collected from Putthur, Narasipuram block, Coimbatore district which was found to be deficient in soil available sulphur with the value of 7.00 mg S kg^{-1} soil. The soil was sandy loam in texture, black coloured with neutral pH (7.15) and non-saline (0.19dSm^{-1}). The soil texture was analysed by following the international pipette method (Piper, 1966), pH by potentiometry (Jackson, 1973) [5] and EC by conductometry (Jackson, 1973) [5]. The collected samples were then air dried and passed through 2mm sieve. About 100g of soil was then filled in plastic cups of 250ml capacity. The ten treatments were laid out in CRD with 3 replications. The treatments from T_1 to T_{10} are control, RDF alone, Gypsum @ 20 and 40 kg ha^{-1} + RDF,

Ammonium sulphate @ 20 and 40 kg ha^{-1}+ RDF, Single super phosphate @ 20 and 40 kg ha^{-1}+ RDF and Elemental sulphur @ 20 and 40 kg ha^{-1}+ 0.5g *Thiobacillus sp.* + RDF, respectively. The different grades of sulphur sources were applied as per the treatments to the quantity of soil taken for incubation and mixed thoroughly. After mixing, required quantity of water was added to maintain the soil moisture at field capacity throughout the period of incubation (3 months). The soil samples were analysed for different S fractions following the standard protocol of Morche (2008) [7], at fortnight intervals throughout the period of incubation. The extracted sulphur fractions were then estimated turbidimetrically (Chesnin and Yien, 1950) [2]. The total sulphur was estimated using the method followed by Hesse, 1971 [4]. The results were statistically analysed using Aggress software at 5% level of significance.

Results

Water Soluble Sulphur: The water soluble sulphur fractions of soil ranged from 3.08 mg kg^{-1} in control to 18.57 mg kg^{-1} in AS @ 40 kg S ha^{-1}. The highest value of water soluble sulphur in soil was registered with the application of AS @ 40 kg S ha^{-1} + RDF (16.45,16.92,17.73,18.57,17.22 and 16.53 mg kg^{-1}) which was also on par with the application of AS @ 20 kg S ha^{-1} + RDF (15.36,15.89,16.58,17.55,16.23 and 15.42 mg kg^{-1}) and SSP @ 40 kg S ha^{-1} + RDF (14.58,15.43,16.22,17.21,16.05 and 15.11 mg kg^{-1}) at 15, 30, 45, 60, 75 and 90 DAI, respectively (Table.1). The lowest value of water soluble sulphur in soil was observed with control (6.75, 6.23, 5.25, 4.73, 3.54 and 3.08 mg kg^{-1}) which was on par with application of RDF alone (7.25, 6.54, 5.34, 5.06, 4.52 and 3.54 mg kg^{-1}) throughout the period of incubation. The releasing pattern of water soluble sulphur from soil had increased till 60 DAI and then slightly decreased up-to 90 DAI for all the sources and levels of sulphur applied. But, the trend seemed to be in contrast to treatments with the control and RDF alone applied lots which were decreasing throughout the period of incubation.

Table 1: Effect of sources and levels of sulphur on soil water soluble sulphur fraction (mg kg^{-1})

Treatments	15 DAI	30 DAI	45 DAI	60 DAI	75 DAI	90 DAI
T1	6.75	6.23	5.25	4.73	3.54	3.08
T2	7.25	6.54	5.34	5.06	4.52	3.54
T3	10.54	11.34	12.42	13.25	12.50	11.27
T4	12.25	12.72	13.45	14.21	13.23	12.53
T5	15.36	15.89	16.58	17.55	16.23	15.42
T6	16.45	16.92	17.73	18.57	17.22	16.53
T7	13.43	14.57	15.00	15.78	14.59	13.72
T8	14.58	15.43	16.22	17.21	16.05	15.11
T9	7.67	8.48	9.72	10.63	9.43	8.22
T10	8.38	9.25	10.63	11.42	10.24	9.43
Mean	11.27	11.74	12.23	12.84	11.76	10.89
SEd	0.2797	0.3	0.3102	0.3215	0.3173	0.2852
CD (0.05)	0.5834	0.6258	0.6471	0.6705	0.6618	0.5949

Exchangeable or adsorbed sulphur

The soil exchangeable sulphur fraction ranged from 3.56 mg kg^{-1} in control to 12.57 mg kg^{-1} in AS @ 40 kg S ha^{-1}. The highest value of soil exchangeable sulphur was recorded with the application of AS @ 40 kg S ha^{-1} + RDF (10.97, 11.19, 11.53,11.87, 12.57 and 12.21 mg kg^{-1}) which was also on par with the application of AS @ 20 kg S ha^{-1} + RDF (10.23, 10.69, 11.23, 11.66, 12.32 and 12.07 mg kg^{-1}) and SSP @ 40 kg S ha^{-1} + RDF (9.75, 9.95, 11.12, 11.45, 12.13 and 11.75 mg kg^{-1}) at 15, 30, 45, 60, 75 and 90 DAI, respectively (Table.2). This was then followed by the application of SSP @ 20 kg S ha^{-1} + RDF (9.24, 9.58, 9.89, 10.24, 10.78 and 10.52 mg kg^{-1}) throughout the period of incubation which was also on par with the application of gypsum at 40 kg S ha^{-1} + RDF (10.24 mg kg^{-1}) at 90 DAI alone. The lowest value of water soluble sulphur in soil was observed with control (5.45, 5.21, 4.63, 4.22, 3.78 and 3.56 mg kg^{-1}) which was on par with application of RDF alone (5.62, 5.43, 5.07, 4.75, 4.25 and 3.82 mg kg^{-1}) throughout the period of incubation. The releasing pattern of exchangeable sulphur from soil had increased till 75 DAI and then slightly decreased at 90 DAI for all the sources and levels of sulphur applied. But, the trend was decreasing throughout the period of incubation with control and RDF alone appllied lots.

Table 2: Effect of sources and levels of sulphur on soil exchangeable sulphur fraction (mg kg^{-1})

Treatments	15 DAI	30 DAI	45 DAI	60 DAI	75 DAI	90 DAI
T1	5.45	5.21	4.63	4.22	3.78	3.56
T2	5.62	5.43	5.07	4.75	4.25	3.82
T3	7.98	8.34	8.76	9.43	9.78	9.51
T4	8.23	8.54	9.25	9.76	10.45	10.24
T5	10.23	10.69	11.23	11.66	12.32	12.07
T6	10.97	11.19	11.53	11.87	12.57	12.21
T7	9.24	9.58	9.89	10.24	10.78	10.52
T8	9.75	9.95	11.12	11.45	12.13	11.75
T9	6.25	6.68	7.27	7.64	8.12	7.82
T10	6.87	7.15	7.53	7.86	8.32	8.11
Mean	8.06	8.28	8.63	8.89	9.25	8.96
SEd	0.1949	0.2098	0.2191	0.2246	0.23	0.2251
CD (0.05)	0.4066	0.4376	0.457	0.4685	0.4797	0.4695

$CaCl_2$ extractable Sulphur

The soil $CaCl_2$ extractable sulphur fraction ranged from 7.11 mg kg^{-1} in control to 32.55 mg kg^{-1} in AS @ 40 kg S ha^{-1}. The highest value of soil $CaCl_2$ extractable sulphur was observed with the application of AS @ 40 kg S ha^{-1} + RDF (26.22, 27.58, 28.35, 29.25, 31.03 and 32.55 mg kg^{-1}) which was also on par with the application of AS @ 20 kg S ha^{-1} + RDF (23.52, 24.22, 25.76, 26.75, 29.25 and 30.15 mg kg^{-1}) and SSP @ 40 kg S ha^{-1} + RDF (22.56, 23.23, 25.63, 26.52, 27.88 and 29.10 mg kg^{-1}) at 15, 30, 45, 60, 75 and 90 DAI, respectively (Table.3). This was then followed by the application of SSP @ 20 kg S ha^{-1} + RDF (21.73, 22.12, 23.73, 24.23, 25.89 and 26.47 mg kg^{-1}) throughout the period of incubation which was also on par with the application of gypsum at 40 kg S ha^{-1} + RDF (25.79 mg kg^{-1}) at 90 DAI alone. The lowest value of soil $CaCl_2$ extractable sulphur in soil was observed with control (9.00, 8.53, 8.25, 8.22, 7.76 and 7.11 mg kg^{-1}) which was on par with application of RDF alone (9.53, 8.92, 8.68, 8.51, 7.93 and 7.45 mg kg^{-1}) throughout the period of incubation. The soil $CaCl_2$ extractable sulphur fractions had shown a constant increase throughout the period of incubation for all the sources and levels of sulphur applied. But, the trend was decreasing throughout the period of incubation with control and RDF alone applied lots.

Table 3: Effect of sources and levels of sulphur on soil $CaCl_2$ extractable sulphur fraction (mg kg^{-1})

Treatments	15 DAI	30 DAI	45 DAI	60 DAI	75 DAI	90 DAI
T1	9.00	8.53	8.25	8.22	7.76	7.11
T2	9.53	8.92	8.68	8.51	7.93	7.45
T3	19.05	20.05	21.32	22.12	23.55	24.65
T4	19.43	20.46	21.77	22.35	24.56	25.79
T5	23.52	24.22	25.76	26.75	29.25	30.15
T6	26.22	27.58	28.35	29.25	31.03	32.55
T7	21.73	22.12	23.73	24.23	25.89	26.47
T8	22.56	23.23	25.63	26.52	27.88	29.10
T9	18.22	19.30	20.05	21.22	22.00	22.98
T10	18.73	19.56	20.69	21.73	22.28	23.63
Mean	18.80	19.40	20.42	21.09	22.21	22.99
SEd	0.465	0.4866	0.5129	0.5412	0.569	0.5869
CD (0.05)	0.97	1.0151	1.0699	1.1289	1.1869	1.2242

Occluded or precipitated sulphur

The soil occluded sulphur fraction ranged from 32.57 mg kg^{-1} in control to 66.54 mg kg^{-1} in AS @ 40 kg S ha^{-1}. The highest value of soil available sulphur was observed with the application of AS @ 40 kg S ha^{-1} + RDF (65.74, 65.98, 66.45, 67.56, 67.25 and 66.54 mg kg^{-1}) which was also on par with the application of AS @ 20 kg S ha^{-1} + RDF (61.12, 61.54, 62.37, 63.42, 63.15 and 62.57 mg kg^{-1}) and SSP @ 40 kg S ha^{-1} + RDF (58.45, 58.87, 59.35, 60.44, 60.24 and 59.41 mg kg^{-1}) at 15, 30, 45, 60, 75 and 90 DAI, respectively (Table.4). This was then followed by the application of SSP @ 20 kg S ha^{-1} + RDF (53.12, 53.68, 54.65, 55.45, 55.23 and 54.80 mg kg^{-1}) throughout the period of incubation. The lowest value of soil available sulphur in soil was observed with control (35.21, 34.87, 34.45, 33.76, 33.43 and 32.57 mg kg^{-1}) which was on par with applications of RDF alone (36.56, 36.32, 35.57, 35.21, 34.67 and 34.21 mg kg^{-1}) throughout the period of incubation, Elemental sulphur + RDF + 0.5g *Thiobacillus sp*. @ 20 (40.21, 40.57, 41.43, 42.65, 42.34 and 41.62 mg kg^{-1}) and 40 kg S ha^{-1} (42.78, 42.95, 43.57, 44.86, 44.54 and 43.73 mg kg^{-1}) till 45 DAI. The soil occluded sulphur fractions had shown a constant increase till 60 DAI for all the sources and levels of sulphur applied and then slightly decreased up-to 90 DAI. But, the trend was decreasing throughout the period of incubation with control and RDF alone appllied lots.

Table 4: Effect of sources and levels of sulphur on soil occluded sulphur fraction (mg kg^{-1})

Treatments	15 DAI	30 DAI	45 DAI	60 DAI	75 DAI	90 DAI
T1	35.21	34.87	34.45	33.76	33.43	32.57
T2	36.65	36.32	35.57	35.21	34.67	34.21
T3	45.67	45.90	46.73	47.81	47.53	46.51
T4	49.25	49.78	50.42	51.84	51.51	50.63
T5	61.12	61.54	62.37	63.42	63.15	62.57
T6	65.74	65.98	66.45	67.56	67.25	66.54
T7	53.12	53.68	54.65	55.45	55.23	54.80
T8	58.45	58.87	59.35	60.44	60.24	59.41
T9	40.21	40.57	41.43	42.65	42.34	41.62
T10	42.78	42.95	43.57	44.86	44.54	43.73
Mean	48.82	49.05	49.50	50.30	49.99	49.26
SEd	1.1926	1.1857	1.1981	1.2232	1.2146	1.2069
CD (0.05)	2.4877	2.4732	2.4991	2.5516	2.5337	2.5176

Organic Sulphur

The soil organic sulphur fraction ranged from 51.70 mg kg^{-1} in RDF alone applied lot to 176.79 mg kg^{-1} in ES @ 20 kg S ha^{-1}. The higher amount of organic sulphur was registered with the application of elemental sulphur (176.79, 174.54, 171.41, 167.97, 168.56 and 170.03 mg kg^{-1}@ 20 kg S ha^{-1} and 174.01, 172.32, 169.12, 165.91, 166.59 and 167.21 mg kg^{-1} @ 40 kg S ha^{-1}) and gypsum (164.08, 161.80, 158.39, 155.20, 154.56 and 156.25 mg kg^{-1} @ 20 kg S ha^{-1} and 158.96, 156.84, 153.76, 150.70, 149.33 and 150.02 mg kg^{-1} @ 40 kg S ha^{-1})

and were also on par throughout the period of incubation (Table.5). The lowest values were observed with control (54.16, 56.28, 58.28, 60.64, 63.43 and 65.73 mg kg^{-1}) and application of RDF alone (51.70, 53.96, 58.28, 60.64, 63.43 and 65.73 mg kg^{-1}) throughout the period of incubation and were on par. The trend seemed to be constantly decreasing throughout the period of incubation for all the sources and levels of sulphur applied whereas, in contrary, the trend was constantly increasing for the control and RDF alone applied lots.

Table 5: Effect of sources and levels of sulphur on soil organic sulphur fraction (mg kg^{-1})

Treatments	15 DAI	30 DAI	45 DAI	60 DAI	75 DAI	90 DAI
T1	54.16	56.28	58.28	60.64	63.43	65.73
T2	51.70	53.96	56.47	58.29	60.74	63.23
T3	164.08	161.80	158.39	155.20	154.56	156.25
T4	158.96	156.84	153.76	150.70	149.33	150.02
T5	131.02	129.20	125.82	122.49	121.16	122.09
T6	122.97	120.87	118.66	115.68	115.03	115.52
T7	145.72	143.50	140.36	138.12	137.59	138.64
T8	138.98	137.08	132.46	129.33	128.94	130.16
T9	176.79	174.54	171.41	167.97	168.56	170.03
T10	174.01	172.32	169.12	165.91	166.59	167.21
Mean	131.84	130.64	128.47	126.43	126.59	127.89
SEd	3.232	3.1951	3.1338	3.0768	3.076	3.0965
CD (0.05)	6.7418	6.6648	6.5369	6.4181	6.4163	6.4591

Total Sulphur

The soil total sulphur ranged from 110.57 mg kg^{-1} in control to 252.11 mg kg^{-1} in ES @ 40 kg S ha^{-1} (Table.6). The studies on total sulphur revealed that, all the sources and levels of sulphur applied were on par and superior to the control and RDF alone treated lots, throughout the period of incubation. The soil total sulphur contents had shown a constant increase throughout the period of incubation for all the treatments of the experiment including control and RDF alone applied lots.

Table 6: Effect of sources and levels of sulphur on soil total sulphur fraction (mg kg^{-1})

Treatments	15 DAI	30 DAI	45 DAI	60 DAI	75 DAI	90 DAI
T1	110.57	110.84	111.14	111.57	111.94	112.05
T2	110.75	110.93	111.37	111.82	112.11	112.25
T3	247.32	247.43	247.62	247.81	247.92	248.19
T4	248.12	248.34	248.65	248.86	249.08	249.21
T5	241.25	241.54	241.76	241.87	242.11	242.30
T6	242.35	242.54	242.72	242.93	243.10	243.35
T7	243.24	243.45	243.63	243.82	244.08	244.15
T8	244.32	244.56	244.78	244.95	245.24	245.53
T9	249.14	249.57	249.88	250.11	250.45	250.67
T10	250.77	251.23	251.54	251.78	251.97	252.11
Mean	218.78	219.04	219.31	219.55	219.80	219.98
SEd	5.305	5.3112	5.3155	5.3218	5.3265	5.3312
CD (0.05)	11.066	11.0789	11.088	11.1011	11.1109	11.1206

Discussion

Easily available S fractions in soil

The easily plant available S fractions in the soil include the water soluble sulphur, adsorbed sulphur and $CaCl_2$ extractable sulphur. The results on mean values of soil easily available sulphur fractions revealed that, among all the easily available soil sulphur fractions, water soluble sulphur and exchangeable sulphur had gradually increased till 60 DAI and then slightly decreased up-to 90 DAI irrespective of sources and levels of sulphur applied (Fig.1). Whereas, the mean values of $CaCl_2$ extractable sulphur showed a constant increase throughout the period of incubation. These observations were in accordance with the findings of earlier co-workers Clarson and Ramaswami (1990) [3] who reported that there was an increasing trend observed in available sulphur with increasing levels of applied sulphur and time of incubation. From the results of present investigation, it is confirmed that S fertilisation definitely increases soil available S fractions up-to the application of 40 kg S ha^{-1}. This was in line with the findings of Khalid *et al.*, 2012 [10]. However, the significantly highest amount of soil easily available S fractions were registered with the application of AS @ both 40 and 20 kg S ha^{-1} which was then followed by SSP @ 40 kg S ha^{-1}. At 90 DAI, almost similar fractions of AS at both 40 and 20 kg S ha^{-1} and SSP @ 40 kg S ha^{-1} (21%, 23.38% and 25.2% of the total sulphur, respectively) got incorporated into the soil easily available sulphur fractions. Higher S release in AS treated plots might be due to relatively higher solubility of AS as compared to SSP, Gypsum and Elemental Sulphur (Scherer, 2001) [12]. Hence, Ammonium sulphate can be found effective in promptly alleviating crop S deficiency when applied in time (Withers *et al.*, 1995) [15]. On the other hand, S availability from gypsum to plants is primarily controlled by its sparingly soluble nature (Wen *et al.*, 2003) [14]. The poor results with the application of elemental sulphur might be due to the requirement of time for sulphur mineralisation by the S oxidising bacteria added. Karimizarchi *et al.*, 2014 also discussed that, pertaining to elemental sulphur, S immobilisation is the predominant process at the beginning of S oxidation which is then followed by sulphur mineralisation and sulphates production as inorganic soluble sulphur forms.

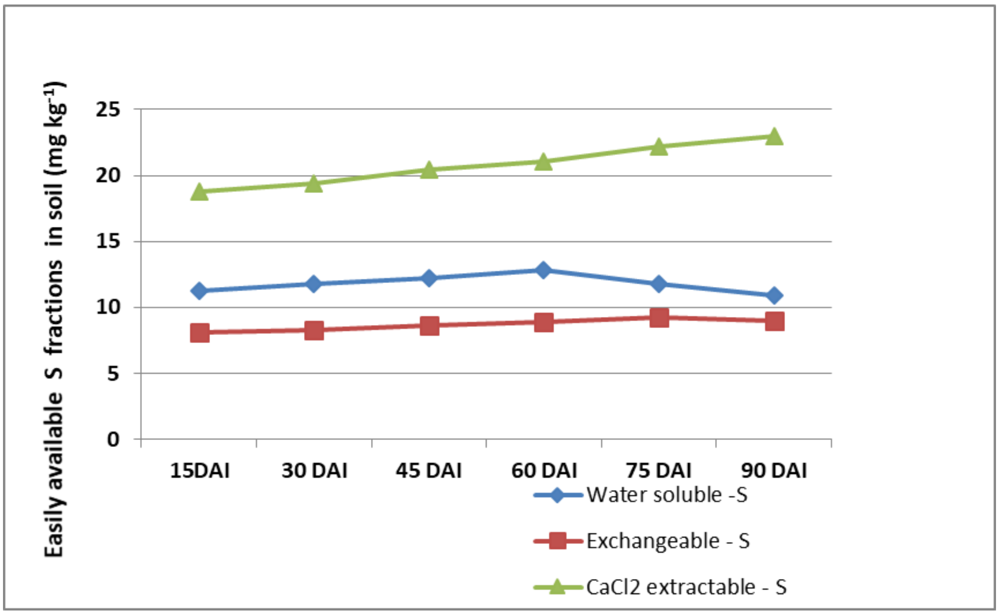

Fig 1: Easily available sulphur fractions distribution during different periods of incubation (mg kg^{-1})

Slowly available S fractions in soil

The slowly available sulphur fractions include occluded sulphur and organic sulphur out of total sulphur. Over time these fractions slowly release sulphates and serve as soil sulphur reserve pool. The soil occluded and organic fractions were the greater parts compared to that of all available sulphur fractions. An increasing trend was observed in soil occluded sulphur till 60 DAI and then decreased for all the sources and levels of sulphur applied (Fig.2). The mean values of occluded sulphur were in line with the findings of Sankaran, 1989. The organic sulphur fractions showed a decreasing trend throughout the period of incubation for all the sources and levels of sulphur applied. The highest organic sulphur values were recorded with the application of elemental sulphur and gypsum which might be due to the slow mineralisation rate in-case of elemental sulphur (Karimizarchi *et al.*, 2014) and sparingly soluble nature in case of gypsum (Khalid *et al.*, 2012) [10].

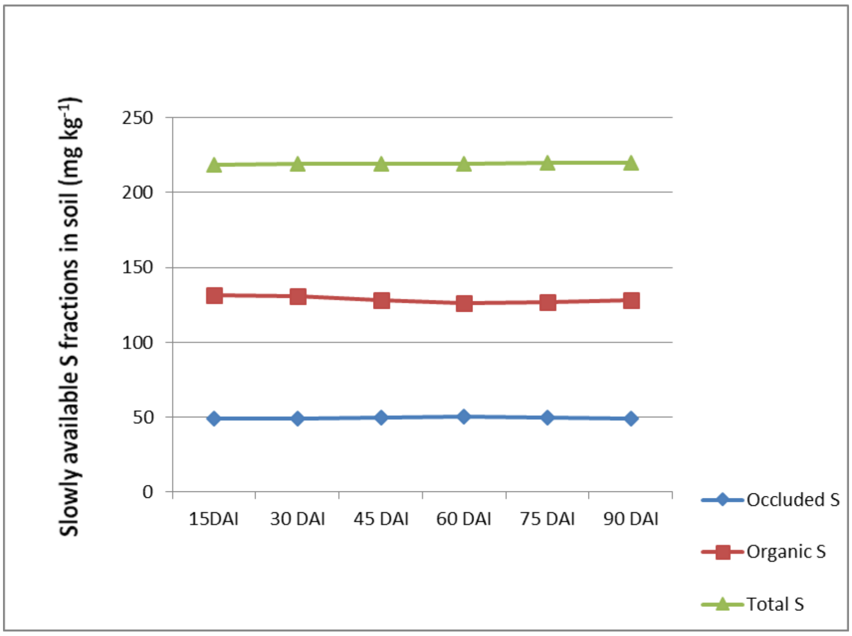

Fig 2: Slowly available sulphur fractions and total sulphur distribution during different periods of incubation (mg kg^{-1})

Total Sulphur

With regards to total sulphur, the trend seemed to be significantly increasing over the control and RDF alone applied lots for all the treatments which were on par, throughout the period of incubation (Fig.3). These results are in line with the findings of Thirunavukarasu, 2014 [13].

Conclusion

The present investigation concludes that with the application of different sulphur sources at two levels of 20 & 40 kg S ha^{-1}, there always occurred an increase in the soil available sulphur fractions (water soluble, exchangeable and $CaCl_2$ extractable sulphur) and soil occluded sulphur at higher rate. Hence, sulphur fertilisation to a sulphur deficient soil can increase soil available sulphates and soil occluded sulphur to enhance onion production. The soil sulphur fractions were in the ascending order of adsorbed sulphur < water soluble sulphur < $CaCl_2$ extractable sulphur < occluded sulphur < organic sulphur out of total sulphur. Concerning to sulphur sources, ammonium sulphate at both 20 and 40 kg S ha^{-1} and SSP @

40 kg S ha^{-1} registered the significantly highest soil available sulphur fractions statistically. Considering the cost of source and environmental safety, ammonium sulphate being cheaper than SSP, it is concluded that application of ammonium sulphate @ 20 kg S ha^{-1} can be recommended to enhance the Soil available sulphur fractions and yield of onion grown in such sulphur deficient soils reducing environmental pollution at lower levels.

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