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# Oxidation pattern of elemental sulphur as affected by levels of sulphur, organic matter and liming in a typical lateritic soil of West Bengal

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**ABSTRACT**

*Laboratory investigation was carried out to study the oxidation pattern of elemental sulphur as affected by levels of organic matter and liming in a typical acidic lateritic soil of Dhalla of Birbhum district of West Bengal. Results revealed that liming as well as organic matter favours the oxidation of elemental sulphur. The treatments comprised of three levels of sulphur (0, 50 and 100 mg kg$^{-1}$) as elemental sulphur, three levels of organic matter (0, 5 and 10 tons ha$^{-1}$) and two levels of lime (lime as per lime requirement and no lime) incubated at field capacity for 60 days. Under liming, the rate of oxidation increased with the increase of incubation period irrespective of levels of elemental sulphur and organic matter. It is interesting to note that the treatments that received organic matter along with elemental sulphur under non-limed condition resulted in a temporary crisis of $SO_4$-S up to 7 days of incubation and thereafter the rate of oxidation was faster with the increase in levels of organic matter and days of incubation. The oxidation of elemental sulphur under limed condition resulted in an increase of pH, although the treatments almost regain to its original pH values prior to completion of incubation period.*

***Key words*: Elemental sulphur, field capacity, lateritic soil, lime, organic matter, oxidation**

Sulphate is the primary source of sulphur taken up by most of the crops. Soil solution sulphate level determines the amount of sulphur accessible to a plant. The source of this solution sulphate is either from organic matter via the microbial pool or directly from animal residues, atmospheric inputs or fertilizer. Reduced forms of sulphur must first be oxidized in soils to the sulphate form before crops can use them. The oxidation of elemental sulphur ($S^0$), sulphide sulphur ($S^=$) and other inorganic sulphur compounds occurring in soils is thought to be biochemical in nature. The rate of oxidation in soils varies depending on the soil environmental conditions, characteristics of the sulphur sources and the microbial population in soils. The oxidation and reduction of inorganic sulphur compounds are of great importance to growing plants. In the first place, these reactions determine to considerable extent the quantity of sulphate present in soils at any one time. Since this is the form taken up by plants, the nutrient significance of sulphur oxidation and reduction is obvious. Second, the state of sulphur oxidation determines to a marked degree the acidity of a soil. As the red and lateritic soils of the region are acidic in soil reaction, therefore, the studies pertaining to oxidation of elemental sulphur under organic matter and limed and non-limed conditions have the special significance on sulphur nutrition to crops.

## MATERIALS AND METHODS

An experiment was conducted to study the oxidation pattern of sulphur contained in elemental sulphur at three levels of S *i.e.* 0, 50 and 100 mg S kg$^{-1}$ and three levels of organic matter as vermicompost @ 0, 5 and 10 tons ha$^{-1}$ under limed (as per lime requirement) and non-limed conditions in a typical acidic red and lateritic soil from April to June 2009. The surface (0-15 cm) soil samples were collected from Dhalla (Typic Ochraqualfs) under Illambazar block of Birbhum distrct of West Bengal, India. The soil was extremely acidic in soil reaction (pH 4.1) with high organic matter content (0.9%), medium cation exchange capacity (20 cmol (p$^+$) kg$^{-1}$), medium available sulphur (14 mg kg$^{-1}$) and sandy clay in soil texture. The sampling site was adjacent to Illambazar forest mainly dominated by Sal tree. Therefore, in spite of typical red and lateritic soil, extreme acidity, loose texture, the soil can somehow be reckoned as fertile soil with regards to organic matter, CEC and available sulphur. Twenty grams of processed soils (<2mm) were incubated in plastic cups under field capacity. Treatments were replicated thrice. The lime was added in case of limed treatments as per lime requirement (Shoemaker *et al*., 1961). Deionized water was added in plastic bottles from time to time to maintain desired moisture content throughout the incubation period. Soil samples were drawn at an intervals of 1, 7, 15, 30, 45 and 60 days. Samples were air-dried, powdered and the sulphate sulphur ($SO_4$-S) was extracted from the soil by 0.15% $CaCl_2$ extractant (William and Steinbergs 1959) and analysed turbidimetrically as per Chesnin and Yien (1951).

## RESULTS AND DISCUSSION

### Oxidation of elemental sulphur due to application of organic matter and lime in acidic lateritic soil

Results (Table 1) revealed that oxidation of elemental sulphur in general increased with increasing time of incubation irrespective of levels of organic matter and limed and non-limed conditions. The rate of oxidation was very slow at the beginning *i.e.* up to 7 days and thereafter very rapid up to 45 days and thereafter down trend of rate was observed under non-limed condition irrespective of levels of organic matter added in the form of vermicompost. The rate of oxidation at 0 level of organic matter application under non - limed condition was maximum i.e. 38.8 and 51.3 per cent respectively at 50 and 100 ppm levels of

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elemental sulphur up to 45 days of incubation. Almost similar pattern of oxidation was observed in case of organic matter applied @ 5 and 10 tons per hectare under non-limed condition where maximum oxidation (i.e. recovery of S as $SO_4^-$ S) 51.1 and 55.5 per cent at 50 and 100 ppm levels of elemental sulphur was recorded at 60 ad 45 days respectively. It is interesting to note that the treatments that received organic matter along with elemental sulphur resulted in a temporary crisis of $SO_4$-S up to 7 days thereafter the rate of oxidation is faster with higher levels of organic matter applied. Under liming, the rate of oxidation increased with the increase of incubation period irrespective of levels of elemental sulphur and organic matter. The maximum rate of oxidation under liming at 50 ppm levels of elemental sulphur *i.e.* 45.0, 57.7 and 64.1 per cent, respectively was observed on 45 days of incubation under no organic matter, and organic matter @ 5 and 10 t ha$^{-1}$. Similarly, in the treatments which received organic matter @ 0, 5 and 10 t ha$^{-1}$ along with 100 ppm elemental S, the maximum oxidation rate *i.e.* 51.9, 68.3 and 81.6 per cent, respectively was observed at 45 days of incubation at field capacity. Organic matter helped to invigorate the rate of oxidation and higher the rate of organic matter addition higher is the rate of oxidation.

**Table 1: Sulphur oxidization (%) from elemental sulphur due to levels of sulphur, organic matter and lime**

| **Elemental S (mg kg$^{-1}$)** | **Incubation period (Days)** | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **1** | | | **7** | | | **15** | | | **30** | | | **45** | | | **60** | | |
| **OM (t ha$^{-1}$)** | **0** | **50** | **100** | **0** | **50** | **100** | **0** | **50** | **100** | **0** | **50** | **100** | **0** | **50** | **100** | **0** | **50** | **100** |
| **Non-limed condition** | | | | | | | | | | | | | | | | | | |
| 0 | 5.4 | 5.7 | 6.2 | 5.8 | 5.1 | 3.2 | 8.2 | 15.0 | 17.9 | 11.4 | 37.4 | 49.2 | 10.4 | 38.8 | 51.3 | 8.6 | 36.6 | 47.5 |
| 5 | 7.2 | 7.9 | 8.2 | 5.4 | 7.9 | 9.3 | 11.0 | 18.2 | 21.1 | 12.1 | 48.6 | 53.3 | 11.3 | 46.2 | 50.2 | 12.3 | 45.5 | 51.1 |
| 10 | 8.6 | 9.2 | 9.9 | 4.9 | 4.3 | 5.8 | 13.5 | 23.3 | 28.9 | 13.9 | 51.3 | 58.5 | 11.9 | 50.3 | 55.5 | 14.2 | 48.5 | 54.6 |
| **Limed condition** | | | | | | | | | | | | | | | | | | |
| 0 | 5.7 | 6.6 | 8.1 | 9.5 | 19.9 | 27.4 | 12.1 | 43.3 | 47.4 | 11.9 | 45.5 | 51.1 | 11.4 | 45.0 | 51.9 | 11.0 | 41.0 | 47.9 |
| 5 | 8.2 | 8.9 | 9.1 | 12.3 | 27.9 | 38.1 | 13.5 | 55.5 | 66.3 | 13.0 | 59.9 | 71.0 | 12.7 | 57.7 | 68.3 | 11.4 | 55.5 | 66.6 |
| 10 | 8.9 | 9.2 | 10.1 | 12.9 | 33.3 | 41.4 | 14.8 | 60.5 | 72.6 | 13.5 | 63.3 | 79.9 | 13.8 | 64.1 | 81.6 | 12.0 | 60.6 | 72.2 |

Results revealed that in general, 30 days of incubation will be required to achieve the maximum rate of oxidation of elemental sulphur under non-limed condition irrespective of levels of organic matter and elemental sulphur in the present set up of experiment. Whereas 45 days of incubation is required to attain the maximum rate of oxidation under limed condition irrespective of levels of organic matter and elemental sulphur in the present set up of experiment under consideration. Almost similar pattern of oxidation was observed in case of organic matter applied @ 5 and 10 tons per hectare under non-limed condition where maximum oxidation (*i.e.* recovery of S as $SO_4^-$ S) 51.1 and 55.5 per cent at 50 and 100 ppm levels of elemental sulphur was recorded at 60 ad 45 days respectively. Liming favours the rate of oxidation of elemental sulphur at both levels (i.e. 50 and 100 ppm) of soil-sulphur inoculation.

The pattern of sulphur oxidation differed markedly with elemental sulphur during the incubation period. Elemental sulphur oxidises in the soil to produce sulphuric acid by the action of bacteria, *Thiobacillus thiooxidans*. The rate of oxidation of sulphur to sulphuric acid depends primarily upon temperature, moisture and oxygen availability. Several workers have reported the rate of oxidation of elemental sulphur in soils (Quispel *et al*., 1952, Singh *et al*., 1997). High acidity in soil accelerates the rate of weathering, but usually decreases the rate of oxidation of the sulphur to sulphate (Rasmussen, 1961). It is interesting to note that oxidation of sulphur with added elemental sulphur in soil was more under liming. The per cent recovery of sulphate-sulphur as a result of oxidation was more with higher dose (*i.e.* 100 ppm S) than lower dose (50 ppm S) of sulphur addition under limed and non-limed condition. Generally, liming of acid soils increases both the rate of oxidation of applied sulphur and the mineralisation of organic sulphur (Fox *et al.,* 1964). Fenster (1965) reported that the rate of sulphur oxidation increased during the first two weeks. In fact, the actual amount of sulphate – sulphur recovered by extraction decreased with time during the last periods of incubation. Other researchers (Rudolfs, 1922, Fenster, 1965) also have observed decrease in sulphate recovery with time after few weeks of sulphur-soil incubation studies. Whether this effect is the result of gaseous losses, precipitation of insoluble sulphate containing compounds, biological assimilation or the consequence of some other mechanism is not known. The soil organic matter in the form of vermicopost favoured the oxidation of elemental sulphur under consideration. Soil organic fraction can serve either as a source or a sink for sulphur. Usually, the organic fraction is considered to be a source of sulphur for crop plants (Walker *et al*., 1959).

**Effect of oxidation of Elemental sulphur on soil reaction**

It is interesting to note that the oxidation of elemental sulphur under non-limed condition resulted in decrease of pH irrespective of levels of sulphur addition (Table 2). However, the decrease in pH was temporary one and last for about a month and there after it increased. Although within the time span of the incubation study i.e. up to 60 days, the treatments almost recovered to the nearer of its original pH values. But the addition of organic matter in the form of vermicompost @ 5 and 10 t ha$^{-1}$ along with elemental sulphur @ 50 and 100 ppm under non-limed condition resulted a slight increase up to 60 days of incubation.

**Table 2: Changes in soil pH due to oxidation of elemental sulphur due to levels of sulphur, lime and organic matter**

| Elemental S (mg kg$^{-1}$) | Incubation period (Days) | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **OM (t ha$^{-1}$)** | **1** | | | **7** | | | **15** | | | **30** | | | **45** | | | **60** | | |
| | **0** | **50** | **100** | **0** | **50** | **100** | **0** | **50** | **100** | **0** | **50** | **100** | **0** | **50** | **100** | **0** | **50** | **100** |
| **Non-limed condition** | | | | | | | | | | | | | | | | | | |
| 0 | 4.87 | 4.63 | 5.02 | 4.71 | 4.87 | 4.71 | 4.69 | 4.77 | 5.05 | 4.49 | 4.75 | 4.67 | 4.14 | 4.62 | 4.55 | 4.53 | 4.96 | 4.78 |
| 5 | 4.84 | 4.92 | 4.77 | 4.83 | 4.75 | 4.67 | 5.19 | 5.25 | 5.41 | 4.70 | 4.89 | 4.62 | 4.46 | 4.77 | 4.69 | 4.85 | 5.04 | 4.92 |
| 10 | 4.92 | 4.71 | 5.16 | 4.84 | 4.74 | 4.85 | 5.25 | 5.32 | 5.32 | 4.78 | 5.16 | 4.88 | 4.35 | 4.76 | 4.79 | 4.88 | 5.37 | 5.20 |
| **Limed condition** | | | | | | | | | | | | | | | | | | |
| 0 | 8.22 | 8.00 | 7.90 | 7.87 | 7.71 | 7.73 | 7.96 | 8.29 | 8.30 | 8.05 | 7.94 | 7.92 | 7.81 | 7.73 | 7.67 | 8.10 | 7.92 | 7.77 |
| 5 | 8.06 | 8.11 | 8.06 | 7.71 | 7.74 | 7.80 | 8.43 | 8.46 | 8.27 | 8.00 | 7.96 | 7.93 | 7.69 | 7.30 | 7.89 | 8.01 | 7.89 | 7.80 |
| 10 | 7.92 | 8.03 | 8.03 | 7.82 | 7.77 | 7.75 | 8.40 | 8.43 | 8.36 | 8.00 | 7.99 | 7.95 | 7.90 | 7.77 | 7.81 | 7.92 | 7.72 | 7.81 |

But the oxidation of elemental sulphur under limed condition resulted in an increase of pH rather than non-limed condition oxidation under consideration. However, the increase in pH gradually decreased slightly up to 60 days of incubation. The decrease in pH was temporary one and last for about a month and there after it increased. Although within the time span of the incubation study i.e. up to 60 days, the treatments almost recovered to the nearer of its original pH values. But the addition of organic matter in the form of vermicompost @ 5 and 10 t ha$^{-1}$ along with elemental sulphur @ 50 and 100 ppm under limed condition resulted in a slight decrease up to 60 days of incubation.

Liming favours the increase in pH at the beginning up to seven days, and thereafter tends to decrease irrespective of all the levels of sulphur addition (i.e. 50 and 100 ppm) and the sulphur sources (i.e. elemental sulphur or pyrites) up to fifteen days onwards as a result of oxidation of sulphur. Again a trend of increase in pH was observed after thirty days on wards as a result of reduction of sulphur from higher oxidation state to lower oxidation state. The probable reaction pathway may be cited as:

$$\underset{\text{(sulphate)}}{H_2SO_4} \xrightarrow[-H_2O]{2H} \underset{\text{(sulphite)}}{H_2SO_3} \xrightarrow[-H_2O]{2H} \underset{\text{(sulphoxylate)}}{HS(OH)O} \xrightarrow{2H} \underset{\text{(s-hydrate)}}{H_2S(OH)_2} \xrightarrow[-H_2O]{} \underset{\text{(suphide)}}{H_2S}$$

At the end of the incubation study, the pH of all treatments converge towards neutrality (i.e. within the pH range of 6.5 to 7.5) may be due to the buffering capacity of the soil, precipitation of insoluble sulphates and the active assimilation of biological agents (Rudolfs, 1922).

Since sulphur oxidation is an acidifying process and for every sulphur atom oxidized, two hydrogen ions result. Theoretically, one pound of elemental sulphur, when completely oxidized to sulphuric acid, will neutralize three pounds of pure calcium carbonate. In soils, however, the effect of sulphur oxidation on soil pH is quite variable. Differential oxidations in different soils with variable buffering capacities make it practically impossible to make exact predictions of pH change.

Oxidation pattern of elemental sulphur revealed that liming as well as organic matter favours the oxidation of sulphur compounds in acidic red and lateritic soils of the region. Based on the outcome of the present study it can strongly be recommended to apply sulphur fertilizers, lime and organic matter along with other fertilizers in soils on regular basis so that the deficiency of sulphur in soils can be avoided and balanced plant nutrition will be maintained.

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