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Sulphur fractionation in different soils: A review

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Abstract
Sulphur is an important nutrient that is required for better growth, protein synthesis, nutrient uptake, and oil formation in pants and its economic produce. The amount of sulphur availability in the soil is different in various soil types from acidic to alkaline, Red to laterite soils. S is a source received by the plants from Organic manure and Chemical fertilizers When applied to the soil mineralization process takes place which converts Organic form (96%) of S to inorganic form which is suitable for plant uptake in this process the conversion of elemental sulphur results in the formation of Sulphate fractions which are mostly uptake by plants. Hence knowledge about the fractionation of S in the soil is important to know how much quantity of fertilizers need to be added for better growth of the plant and also combined use of Organic + inorganic (mainly S related)amendments may be helpful in better increment in the fractionation of S. Extraction of S fractions from the soil is mainly estimated by the independent method and Sequence extraction method of the Sequence extraction method is a most cost-effective and time-consuming process that can estimate water-soluble, available, organic, inorganic and sulphate S except Residual Sulphur.

Keywords: Chemical fertilizers, mineralization, organic manures, sulphur fraction

Introduction
Sulphur is considered as an essential secondary macronutrient that is mainly required for the growth and development of plants rather than this it is also used for the functioning of protein synthesis, vitamins, oil formation, and other functions in the plant. In the present scenario, Sulphur is considered as 4th important nutrient required in soil for the growth of the plant next to Nitrogen, Phosphorus and Potassium as we have seen deficiency of Sulphur in soil have been increased drastically all over the global countries (Blair 2002, Zhao *et al.*, 2002) [4, 13]. At the time of the green revolution between 1960 - 1970, Some researchers have been found that about 70 kg S/ha has been deposited from the atmosphere (Mc Grath *et al.*, 2002) [17], and at present days it is less than 10 kg S/ha and this deficiency is more in India that to majorly in vertisols. Hence deficiency of these sulphur may result in a decrease in quality, quantity, and oil content of crops and -their produce, to overcome this deficiency Sulphur related fertilizers are added to soil, When these fertilizers are added to soil transformation of 'S' in the soil goes through Chemical, Biological, and Complex mineralogical processes. Sulphur in the soil is majorly taken up by the plant roots in Sulphate (SO_4^{2-}) form which is usually available in the water-soluble form or adsorbed form and also it depending upon mainly Characteristics of soil that may be the availability of iron oxides/hydroxide and pH (Curtin and Syers 1990; Syers *et al.*, 1987) [5, 23], Calcium carbonate (CaCO3) organic Matter and texture, etc., Knowledge about the different available forms of ' S ' in the soil plays a very crucial role for the better application of Sulphur related fertilizers to the soil. The traditional method for fractionation of ' S ' is a very costly and time- consuming process because of the loosely bounding of different forms of ' S '. Hence sequential extraction process of ' S ' fractionation is developed for performance

Available forms of sulphur in soil
1. Organic Sulphur
2. Inorganic Sulphur

Organic Sulphur: The form of sulphur present in soil may be either organic or inorganic form but mostly it is available in the organic sulphur form combined with the ' N ' and Carbon (Gajbhiye *et al.*, 2014) [11] when it comes to the peat soil mostly (100%) available sulphur is in organic form.

Again Organic Sulphur is divided into 2 forms.
1. Carbon bounded
2. e.g :- Sulphur of aminoacid
3. Non Carbon bounded
4. Phenolic Sulphates
5. Lipids
6. Choline Sulphates etc.,

Inorganic Sulphur: The available form of inorganic sulphur in soil is less but it is the immediate uptaking form in the roots of the plants. e.g:- Sulphate form SO - S, SO_4^{2-}

Fractionation of Sulphur

A) Water-soluble sulphur

Taking off 5 gm extracted soil in distilled water of 25ml in a ratio of 1:5 ratio and then shake it for 10 minutes, centrifuge and finally filtered.

B) Available sulphur

The residue of soil that has been extracted from above water-soluble sulphur has been treated with 1% NaCl solution of 25 ml and then shaken immediately for 30 minutes and then centrifuge it and again filter the solution.

C) Inorganic sulphur

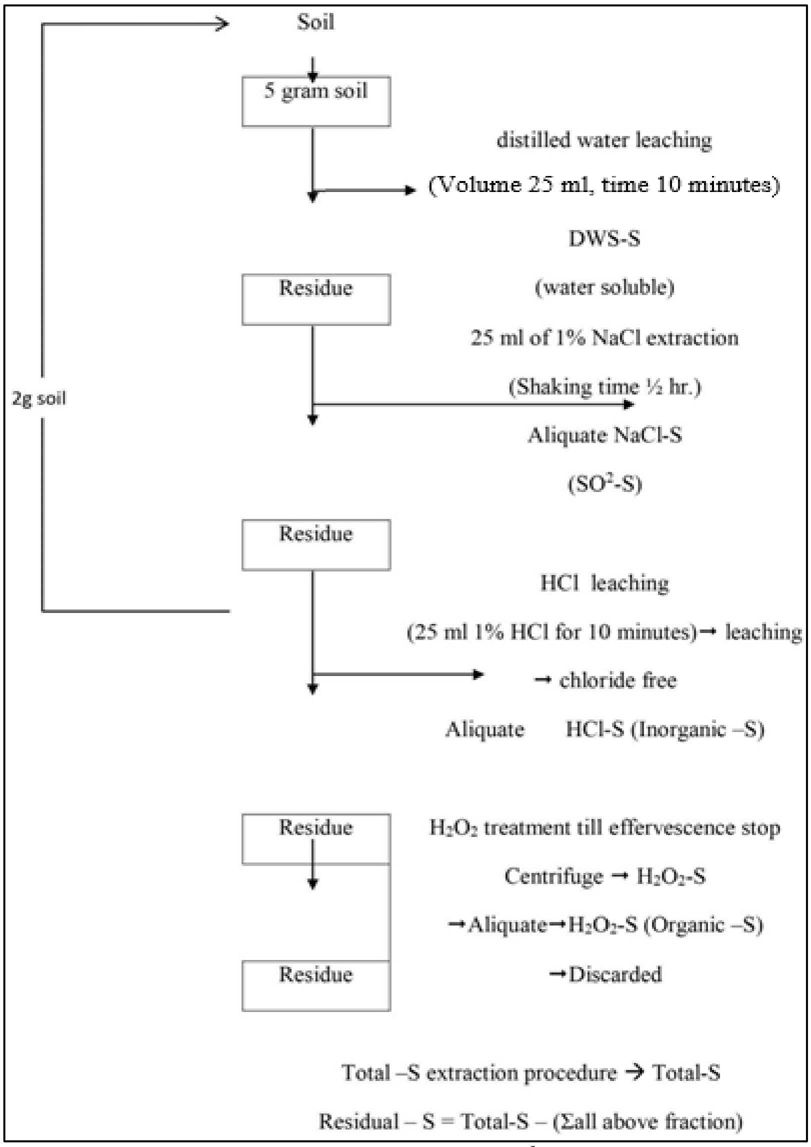
This inorganic sulphur has been extracted by the addition of 1% HCl solution of 25 ml to the previously extracted soil solution and then immediately shake it for about 10 minutes and centrifuge and finally filtered the solution. Then make the soil free of chloride by addition of distilled water and leaching it

D) Organic sulphur

Take the soil residue from above inorganic sulphur of HCl extracted and of this again take the 2-gram soil and oven-dried it and treat it with H2O2 up to the effervescence stops and again centrifuge and filter it.

E) Total sulphur

Total sulphur in soil was estimated by the acid digestion method. Take 5-gram fine ground soil and mix it with 3 ml 69% HNO3 and then heated it in the steam bath. Then again add the 3 ml of 60% HClO4 and 7 ml of H3PO4 and heat it in a sand bath at 190- 210°C up to the visible fumes and cool it and add 2 ml of 37% HCl and then again heat it to the white fumes visible. The digested mixture was transferred quantitatively and adjusted the volume to 100 ml using 1N HCl.



(**Source:** Azmi, N. Y. Seema and Manish, K., 2018) [1]

Fig 1: Sequential Extraction scheme for Sulphur

F) Residual sulphur

The residual sulphur cannot be measured or extracted by all sequential extractants, so this residual sulphur fraction was calculated by subtracting the total S and the sum of all fractions. After fractioning different extracts, sulphur in these extracts was estimated.

Figure: Sequential Extraction scheme for Sulphur (source: Azmi, N. Y. Seema and Manish, K., 2018) [1]

Review of Literature

Sulphur fractionation in different soils

Gajbhiye *et al.*, (2014) [11] experimented to know the sulphur fractions in soils of Lohara tahsil of Osmanabad district by collecting 180 samples in the year 2011-12 and reported that Sulphur content in black soil (vertisols) ranges between 544 - 3489 mg kg-1 and mean of 1862.14 mg kg-1. In inceptisols range of 430 - 2225 mg kg-1 and the average of 1448.34 mg kg-1 and Entisols it is of 381 - 1920 mg Kg-1 with an average of 906.12 mg Kg-1, At last, he said ' S ' fraction is more in vertisols due to the presence of clay particles in it and other two it is less due to different parent materials.

Misal, Nitin (2017) [19] experimented to know the Dynamics of sulphur fractions in calcareous soils of the Saurashtra region of Gujarat by collecting 169 surface soil samples (0-15 cm) from the year 2000 to 2010 and reported that total sulphur (710.88 - 693.4 ppm) and organic sulphur (625.13 - 607.82 ppm) were decreased and as of available sulphur(14.36 - 30.76 ppm), non-sulphate sulphur (24.92 - 66.63 ppm), sulphate sulphur (10.14 -19.09 ppm) and water-soluble sulphur (12.37 - 35.86 ppm) were shown the increase in amount. Among these non-sulphate, sulphate, and water-soluble shows the positive result as to available sulphur in all soil groups.

Sankhyan, N.K *et al.,* (2018) [10] as he conducted an experiment and studied at the Soil Science department on the vertical distribution of sulphur fractions on a long-term basis of fertilizer experiment in Palampur university by working on different combinations of fertilizers and amendments and reported that the application of 100% N, P, K results decrease of sulphur fraction amount of available sulphur (67%), Water soluble sulphur (70%), Heat soluble sulphur (34%), Organic sulphur (47%), and total sulphur (48%) were affected with continuous cropping and decrease in depth of sowing. and opposite to this 100% N, P, K + FYM shows a positive result in fractionation of sulphur.

Jintu Dutta *et al.*, (2013) [9] experimented on long term fertilizer experiment on maize-wheat cropping system in acid soils at Palampur which comprise 10 experiments from 1972-1981 and 11 treatments for 26 years from 1981-2007, and reported that ' S ' fractionation was increased with the usage of both combinations of organic amendments and chemical fertilizers and less fraction shown in the non-applicable sulphur amendment and show a positive impact on growth and yield of the maize-wheat cropping-system.

A. Basumatary *et al.*, (2018) [3] experimented to know the impact of sulphur fertilization on sulfur fractions distribution and use efficiency in black gram in subtropical acidic soil of Assam, India by applying different doses of 0,10,20,30,40 Kg S ha-1 and recommended dose of N, P, K as he reported that available ' S ' fractions were decreased with crop growth in control and recommended fertilizer treatment and he finds better Sulphur fractions in 10,20,30,40 kg S treatments and among these 20 kg S ha-1 shows the better result in fractionation and better yield.

Diwakar *et al.*, (2014) [7] experimented to know the transformation of S fractions under field conditions with Groundnut in alfisols of Karnataka by applying four levels of sulphur pf 0,15,30,45 Kg S ha-1 and 3 sources of elemental S, gypsum, and ammonium sulfate and reported that S fractions were increased in all treatments except no application of S treatment among these ammonium sulfate application shows the greater result of S fractions in comparison with both elemental S and gypsum. The lowest sulphur fractions were noticed in the treatments of elemental S.

Degryse, Fien, *et al.*, (2013) [6] reported that deficiency of Sulphur has been increased due to using of sulphur-free fertilizers and decreasing in atmospheric inputs. Hence use of sulphur fertilizers is increased as this sulphur is in sulphate form and elemental sulphur form thus it has very little transformation and application cost and has a low leeching effect. Here elemental sulphur is available to plants after it has been transferred into sulphate form and these sulphates are immobilized into organic matter and final result of mineralization makes sulphate available this whole process makes the availability of sulphur to plants.

Scherer H.W *et al.*, (2012) [21] investigate sulphur fractions in particle size separates as influenced by long-term application of mineral and organic fertilizers as he conducted an experiment from 1962 by long term application of FYM, Compost, Sewage and Sludge respectively and compared the inorganic fraction of S and organic Sulphur fractions in mineral fertilizers of particle size of <0.002 mm, 0.002-0.02 mm, 0.02-2 mm respectively. This application of Compost, Sewage, and Sludge shows the highest total S contents in soil Among particle sizes <0.002 mm has the more amount of total soil S. As particle size increases water-soluble S and adsorbed sulphate has a negative effect.

Mehdi Karimixarchi *et al.*, (2014) [18] said that Incorporation and Transformation of Elemental Sulphur in High PH soils of Malaysia as a part of his experiment he wants to quantify different S fractions and also known about how elemental S amendments are affecting the S dynamics in Bintang series soils. From his experiment, he reported that the application of 1 g elemental S Kg-1 has been successfully oxidized and has been converted to both sulphur forms as organic sulphur and inorganic sulphur. whereas inorganic water-soluble S has shown the dominant forms of S as of near about 65% of overall S and at the final report he found that organic form of S was more as of near to 96% of total S. As of said elemental S has efficient work in enhancing soil nutrient availability majorly of micronutrients.

Balik. J *et al.*, (2009) experimented to know the difference in soil S fractions due to limitations of atmospheric depositions as a part of this he applied lowering inputs of S, and together with applied manures and mineral fertilizers as a part of these, he collected soil samples from 1981 - 2007 of long term field experiments in the Czech Republic region of 10 sites that have various soils as well as various climatic conditions. As of these, he analyzed samples with Water-soluble S, Sorbed S and S occluded with carbonates then determine total and organic S from his experiment he knows that total S decreased by (3- 8%), Water soluble S(65 - 68%) and Sorbed S by(39 - 44%) as this he also finds the slight amount of organic S content was increased. Application of 40 t FYM for every 4 has no significant role in S fractionation.

Azmi N.Y *et al.*, (2018) [1] described a new technique for sequential Fractionation of Soil Sulhur as a part these he said that sequential Fractionation of soil sulphur has been developed for long term experiment in RAU research farm, Pusa and the result shows that as compared to independent fractions all the fractions except Residual S has been increased with increased fertility level and the same increment followed in addition of organic manures with different fertilizers levels as total S contributed very little by the organic S, distilled water-soluble S, inorganic S. Where in Residual S extracted from sequential process shows negative result whereas in non sulphate S extracted from traditional method shows the negative result. As of final Sequential extraction of S shows better results than independent extraction is time-consuming and costly and among all fractions, Sulphate-S and organic S have the most important fractions is related to crop production.

Patra *et al.*, (2012) [20] experimented to know about the status of available sulphur in West Bengal from the surface and subsurface soils of red and lateritic soils, and as a part of this, he collected 67 soil samples from each surface and sub-surface of 4 districts in West Bengal of Birbhum, Bankura, Burdwan and Purulia under red and laterite soils has been chosen and find the Sulphur availability index has been ranged from 13 - 73% and of avg 45.2% in surface soils and Subsurface soils it is range from 40-66% and avg of 56.5%. The available Sulphur content of different districts ranged between 0.5-219.5 mg Kg-1 with avg of 29.5 mg Kg-1 in surface soils and Sub-surface soil, which ranges between 0.5-68.4 mg Kg-1 and avg of 18.7 mg Kg-1. Z.Y.Hu *et al.*, (2004) conducted an experiment to know about the Sulphur fractionation in calcareous soils and bioavailability to plants and reported after collecting 64 calcareous soil samples that have varying amounts of CaCO3 in 10 provinces of China and reported that the organic form of S was predominant of S fractions near about 77% of total S present and amount of adsorbed S is to be negligible and amount of water-insoluble sulphate and immobilized correlate with CaCO3 and it is accountable for 0.03-40.3% and mean of 11.7% that these CaCO3 precipitated with Sulphate in calcareous soil may be partially available to plant-based on PH.

G.S. Sutaria *et al.*, (2016) [22] conducted an investigation to study sulphur fractions in soils of Rajkot district, Gujarat and he collected from 14 talukas in Rajkot of 280 (0-15 cm) surface soil samples and analyzed different available forms of S in soil and chemical properties of these samples and reported that these soils are alkaline that it has high pH and this pH is negatively correlated with the non sulphate and total S, EC, and Organic carbon has a positive effect on the all Sulphur forms having an exception in non sulphate sulphur in term of EC and available S in Rajkot dist., soils were low to medium.

Lavanya K.R. *et al.,* (2019) [16] along with her group members conducted an experiment to know about the Sulphur fractionation studies in soils of long-term fertilizer experiment under finger millet + Maize Cropping sequence and as a part of her field experiment from(1986-2016) She has replicate 11 treatment for 4 times in RCBD and collected soil samples at 5 years interval and studied fractions of that soil S.These fraction of S are in the order of Organic>residual>inorganic>water soluble>avilable forms and over 30 years of the experiment there is the gradual increase in fractionation of S in cropping cycles un all the treatments. As with all treatments that which does not apply S has decreased the sulphur availability. Different treatments that have 100% N, P, K+ FYM+lime,100% N, P, K+FYM, and 150% N, P, and K have shown slow fractions, and when applied recommendations of SSP as P fertilizer shows the better result in S fractionation.

Kajal D Bhoyar *et al.*, (2019) [14] along with her group members experimented to know the status of different S forms under intensively soybean growing soils of savner tehsil, district Nagpur and experiments were carried out between 2017-18 as she takes 50 samples that consist of 25 samples of surface 0-20 cm) and 25 samples of Sub-surface soil(20-40 cm) from 25 fields after harvesting of soybean in five locations and she reported that total S present between the range of (293-455 mg Kg-1) in surface soil and as of in sub-surface soil it ranges between(286-442 mg Kg-1). Organic S ranges between (213.24-312.24 mg Kg-1) in surface soil and (208.35-299.12 mg Kg-1) in sub-surface soil. As of final all Sulphur forms have a positive relationship with Organic carbon, available N, P, K, and E.C having a correlation that is positive with the Sulphate sulfur.

S. Kour *et al.*, (2010) [15] experimented to know about the amount of S available in the cultivated locations of an intermediate mid-hill zone of the Jammu region in India and they reported that the availability of total S ranged between 193-774 mg Kg-1. Non-sulphate S and Organic S were higher in the contribution that has 46.71% and 49.05% respectively of total S and inorganic sulphate S had the least contribution (0.93-11.98%), Water soluble S of
(2.21 -14.82%) adsorbed S (7.15-50.26%). All S forms have a positive correlation due to the presence of clay particles except the absorbed S form.

Conclusion

Sulphur is the major macronutrient that is essentially required for plant growth and sulphur is available in both organic S forms and inorganic S forms in the soil that plants majorly taken in inorganic form. Here requirement of S is essential for various activities in plants and knowing about the fractions of S in the soil is important for the required application of S to the soil. Fractionation of S is mostly variable in different soils as it depends upon the amounts of applied organic and also inorganic amendments for long time application as it shows the better result when applied the S related fertilizers.

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