# Sulfur specification in bulk soil as influenced by long-term application of mineral and organic fertilizers

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## ABSTRACT

A field experiment established in 1962 on a luvisol derived from loess was chosen to investigate the effect of long-term application of farmyard manure, compost and sewage sludge, respectively, in two increments on inorganic and organic S fractions in bulk soil. Compared with mineral fertilizer, the high application rates of the different organic fertilizers (10 t farmyard manure (FYM2), 29 t compost (COM2), 7.44 t sewage sludge (SS2)/ha/year, respectively), resulted in an increase of the total S content in the bulk soil: 220 mg/kg (FYM2), 298 mg/kg (COM2), 277 mg/kg soil (SS2) as compared to the control (MIN) with 158 mg/kg soil. The sum of water soluble plus adsorbed S was significantly higher in the treatments with the high amount of compost (17.9 mg/kg soil) and sewage sludge (16.4 mg/kg) soil as compared to all the other treatments (10.0 to 13.1 mg/kg soil). The treatments with the high amounts of organic manures contained lower contents of ester sulfate and higher contents of C-bonded S as compared to the treatments with the low amounts, and vice versa.

**Keywords**: S binding forms; organic S; inorganic S; organic manure

Over the last decade sulphur (S) deficiency was recognized as a constraint to crop production all over the world (Scherer 2009). Reviewing crop responses to S fertilization Zhao et al. (1996) found that S had already become one of the most limiting nutrients for crop production in many European countries by the mid 1990s. Main reasons are the reduction of sulphur dioxide emissions from power plants and various industrial sources, the increasing use of high-analysis-low-S containing fertilizers, the decreasing use of S-containing fungicides and pesticides, high yielding plant varieties and intensive agriculture.

The most important S source for plants is sulfate ($SO_4^{2-}$) in the soil solution which is in equilibrium with $SO_4^{2-}$ adsorbed by Al and Fe oxides (Bohn et al. 1986). Because $SO_4^{2-}$ adsorption is pH dependent being strong at low soil pH, lime addition increases the amount of $SO_4^{2-}$ in soil solution. Further $SO_4^{2-}$ adsorption is declined in the presence of phosphate anions and therefore besides liming the application of P fertilizers may increase the soil $SO_4^{2-}$ desorption and subsequently availability of $SO_4^{2-}$. Sulfate may also precipitate as calcium, magnesium or sodium sulfate and occurs as a cocrystallized or coprecipitated impurity with $CaCO_3$ (Tisdale et al. 1993).

Although in most soils organic S accounts for 90% of total S or more relatively little is known about the chemical characteristics of organic S compounds (Wang et al. 2006). Traditionally two main groups can be distinguished, namely C-bonded S and HI-reducible S. A few other organic S forms – thought to be sulfonates and heterocyclic sulphur – also exist, but they are of comparatively minor importance (Kertesz and Mirleau 2004). Sulfamates may also be found in soils where S occurs in the form of $N\text{-}O\text{-}SO_3^-$ and $N\text{-}SO_3^-$. While C-bonded S primarily comprises the S-containing amino acids cysteine and methionine, HI-reducible S mainly consists of ester sulfate (C-O-S) and sulfamates (C-N-S) with ester sulfate dominating. The identity of ester sulfate and C-bonded S has recently been confirmed by an independent method, using X-ray near-edge spectroscopy. HI-reducible S accounts for 30 to 70% of the organic S, but values as high

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as 93% or as low as 18% were found (Tabatabai and Bremner 1972, Kowalenko and Lowe 1975). This high variation is the result of climatic factors, the nature of land use as well as the nature and amount of organic inputs. Lowe (1964) estimated that up to 58% of total soil S in Canadian soils occurred as C-bonded, while Morche (2008) found between 52 and 72% in a luvisol derived from loess in Germany.

In agricultural systems with low inputs from atmospheric deposition crops rely on the $SO_4^{2-}$ release from organic S forms in the soil (Eriksen and Mortensen 1999, Balík et al. 2009). These systems include those based on the use of organic fertilizers alone or in combination with low mineral fertilizer application, where mineralization of soil organic S was shown to contribute substantially to the S supply of plants. Organic S and thus S mineralization may be increased by long-term application of farmyard manure (Knights et al. 2001). However the plant availability of organic S depends on the microbial activity and the physical protection of soil organic sulphur caused by soil aggregation (Eriksen et al. 1995).

Organic materials such as sewage sludge and compost may be applied to agricultural land to improve the S supply of plants. However, investigations on their influence of long-term application on total soil S or inorganic and organic S fractions are scarcely available (Kulhánek et al. 2011).

A long-term field experiment initiated in 1962 at the University of Bonn, Germany, which includes the application of mineral and different organic fertilizers, provided a unique opportunity to study long-term effects of mineral and organic amendments on S content and S fractions in the soil. Therefore the objective of the present investigation was to determine the effect of different organic amendments (farmyard manure, compost, sewage sludge) as compared to mineral fertilizer application on total S, inorganic sulfate, ester sulfate and C-bonded S in the bulk soil.

## MATERIAL AND METODS

**Field experiment**. The long-term field experiment (randomized complete block design with four replicates) was established in 1962 at the experimental farm of INRES – Plant Nutrition (50°32'42''N, 6°59'14''E), University of Bonn, Germany. The soil is a luvisol derived from loess (17.8% clay, 76.3% silt, 5.9% sand) (World Reference Base for Soil Resources 2006).

Among a larger number of experimental treatments the following were selected for the present investigation: mineral fertilizer ($NH_4NO_3$ plus $CaCO_3$, KCl, $CaH_2PO_4$) [MIN], 9 t/ha and 18 t/ha farmyard manure [FYM1, FYM2], 14.5 t/ha and 58 t/ha compost from organic household waste [COM1, COM2] and 3.7 and 14.8 t/ha sewage sludge [SS1, SS2]. These amounts were applied every second year until 1997 to a root crop – cereal crop rotation. Since 1999, when the crop rotation was changed to root crop – cereal – cereal, organic fertilizers were applied every third year and the amounts were 9 and 18 t farmyard manure/ha, 30 and 120 t compost/ha and 5 and 20 t sewage sludge/ha. The amounts of organic fertilizers are based on a dry weight. Mineral fertilizer was applied according to the demand of the crop in the rotation.

The mean total S content of the organic fertilizers (based on dry matter) is 0.22% (farmyard manure), 0.12% (compost) and 0.67% (sewage sludge).

**Soil samples**. Soil samples were collected early in spring 2006 one year after the last application of organic fertilizers from the plough layer (0–30 cm) of each treatment. Ten 4-cm diameter cores were randomly taken from each of the four plots (24.5 $m^2$ each) of the corresponding treatments and bulked. Soil samples were air dried, ground and passed through a 2 mm sieve. For total S determination subsamples were ground to a fine powder. The most important soil parameters are shown in Table 1.

Table 1. Chemical soil characteristics

| | MIN | FYM1 | FYM2 | COM1 | COM2 | SS1 | SS2 |
|---|---|---|---|---|---|---|---|
| pH | 6.06 | 5.95 | 6.22 | 6.73 | 7.10 | 6.01 | 6.52 |
| $C_{tot}$ (g/kg) | 12.38 | 13.15 | 14.73 | 17.45 | 27.75 | 13.06 | 19.83 |
| $N_{tot}$ (g/kg) | 1.09 | 1.15 | 1.31 | 1.45 | 2.27 | 1.13 | 1.51 |
| C/N ratio | 11.36 | 11.43 | 11.24 | 12.03 | 12.22 | 11.56 | 13.13 |

MIN – mineral fertilizer; FYM1 – 9 t/ha farmyard manure; FYM2 – 18 t/ha farmyard manure; COM1 – 14.5 t/ha compost; COM2 – 58 t/ha compost; SS1 – 3.7 t/ha sewage sludge; SS2 – 14.8 t/ha sewage sludge

**Sequential extraction – Procedure for sulphur speciation analysis**. Inorganic sulphur (water-soluble $SO_4^{2-}$ (a) and adsorbed $SO_4^{2-}$ (b)) were extracted using the sequential extraction method according to Freney et al. (1970) and Shan et al. (1997): (a) transfer 1 g of soil into a centrifuge tube; add 10 mL of distilled water; shake the soil suspension on a reciprocal shaker for 30 min; centrifuge at 12 000 g for 10 min; decant the supernatant into test tube without disturbing the soil at the bottom of the centrifuge tube. (b) add 10 mL of 0.032 mol/L $NaH_2PO_4$ to the residual soil in the centrifuge tube; continue as described above.

**Ester sulfate and C-bonded sulphur**. Organic S fractions were determined according to Shan and Chen (1995), modified by Morche (2008).

HI extraction: transfer 0.5 g of soil into a boiling flask; connect the boiling flask to a Johnson-Nishita digestion apparatus and add 15 mL reducing solution (a mixture of hydriodic, hypophosphoric and formic acid in the ratio 4:1:2); reflux the suspension gently for 1 h under nitrogen atmosphere. The $H_2S$ gas was trapped and converted to sulfate.

Ester sulfate was calculated from the difference between HI reducible S and total inorganic S.

C-bonded S is the difference between total S and HI reducible S.

Sulfur of all extracts from the sequential extraction was determined by anion chromatography and from HI extraction by ICP-OES (Chilly-Mazarin, France). All samples were filtered through a 0.45 µm cellulose acetate filter (M & N, Düren, Germany) before measuring.

**Total S**. Total S was measured using a CNS analyzer (Eurovector EUROEA, Wegberg, Germany).

**Statistical analysis**. Statistical analysis of the data was done by SPSS 17 (Chicago, USA). Means were compared using a one way ANOVA includin descriptives and test of homogeneity of variance. The differences between treatments were compared using the Tukey's test at a significance level of 0.05.

## RESULTS AND DISCUSSION

Total S content in bulk soil, which was influenced by long-term applications of organic fertilizers, ranged from 158 to 298 mg S/kg soil in different treatments (Figure 1). It was significantly highest in the treatments COM2 and SS2. In these treatments the mean S application, calculated per year, during the whole experimental period was 35 and 49 kg S/ha in COM2 and SS2, respectively, while in treatment FYM2 only 20 kg/S ha were applied. Therefore the variation of total soil S may be assumed to be dependent on the amount of S applied. However, organic manures are a variable matrix, since their composition is a product of many factors. We found that 47, 71 and 78% of the total S in farmyard manure, compost and sewage sludge, respectively, is organically bound. For this reason the extent of the increase of total S depends also on the type of the organic fertilizer, the share of organic S being highest with compost and sewage sludge. In both of these organic fertilizers only less than 30% of the total applied S is directly plant available. No such increase of total soil S was reported after 150 years supply of S containing mineral fertilizers (Knights et al. 2001), which may be traced back to the fact that with mineral fertilizers S is mainly applied as inorganic $SO_4^{2-}$ which is water soluble and therefore susceptible to leaching from surface soils into deeper soil layers. However, Nguyen and Goh (1990) showed that long-term application of superphosphate increased total soil S as compared to S free mineral fertilizer application. Therefore depending on the location and climatic conditions different results may be obtained.

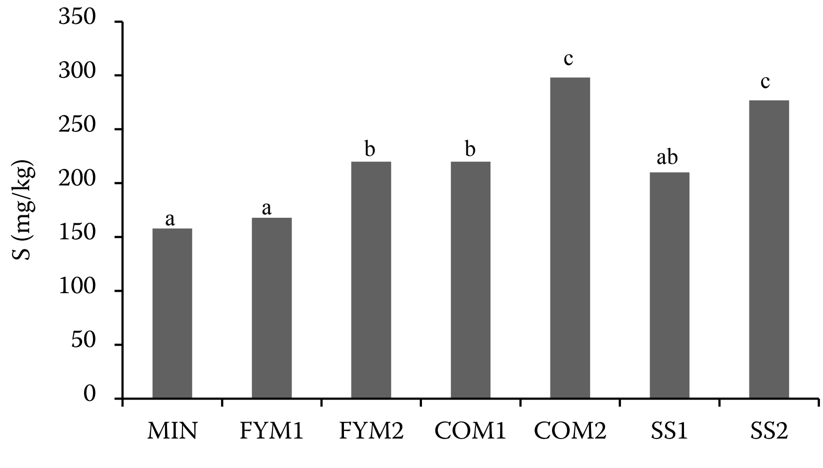


Figure 1. Total S content of bulk soil under different fertilizer treatments (values with the same letters are not significantly different). MIN – mineral fertilizer; FYM1 – 9 t/ha farmyard manure; FYM2 – 18 t/ha farmyard manure; COM1 – 14.5 t/ha compost; COM2 – 58 t/ha compost; SS1 – 3.7 t/ha sewage sludge; SS2 – 14.8 t/ha sewage sludge

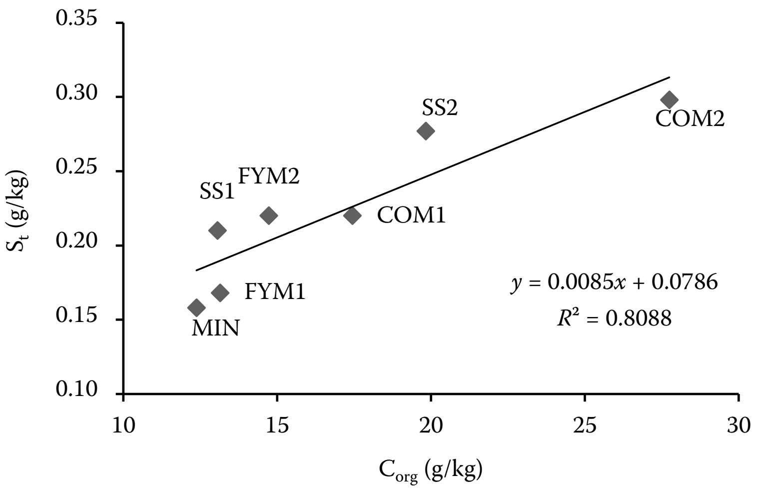


Figure 2. Correlation between $C_{org}$ and total S (St). MIN – mineral fertilizer; FYM1 – 9 t/ha farmyard manure; FYM2 – 18 t/ha farmyard manure; COM1 – 14.5 t/ha compost; COM2 – 58 t/ha compost; SS1 – 3.7 t/ha sewage sludge; SS2 – 14.8 t/ha sewage sludge

Because we found a significant correlation between soil organic carbon and total organic S ($R^2$ = 0.81) (Figure 2) we conclude that an increase of soil organic C is a prerequisite for an increase of total soil S and changes in total S are proportional to the quantities of organic S applied.

Based on the total S content of the control S sequestration amounted to 14.0 kg S/ha/year in COM2 and 11.9 kg S/ha/year in SS2, while 1.0, 6.2, 6.2 and 5.3 kg S/ha/year were sequestered in plots supplied with FYM1, FYM2, COM1 and SS1, respectively. In field trials of Yang et al. (2007) the application of NPKS fertilizer did not result in S sequestration although the S input was higher as compared to farmyard manure. However, it should be taken into consideration that S applied as sulfate in form of NPKS fertilizers is taken up by plants in high amounts and therefore no increase in total soil S may be observed. Furthermore we assume that sulfate applied with mineral fertilizers is more prone to leaching and that S sequestration depends on both the fertilizer type and the S application rate.

Confirming results of Eriksen et al. (1995) between 2.5 and 3.7% of total soil S was inorganic (Table 2). Total inorganic S, composed of water soluble $SO_4^{2-}$ and adsorbed $SO_4^{2-}$, which is generally believed to be the immediate source for plants, ranged between 10.0 and 17.9 mg/kg soil (Figure 3). It was significantly higher in the treatments COM2 and SS2. $H_2O$-extractable $SO_4^{2-}$ varied between 7.6 and 12.2 mg S/kg soil. According to Castellano and Dick (1990) low levels of $SO_4^{2-}$ in the soil solution are observed during winter and spring due to leaching and low S mineralization rates associated with low temperatures. Therefore we suppose that the low contents in our investigations must be linked to the date of soil sampling, which was early in spring. $SO_4^{2-}$ adsorption in soils is strongly pH dependent and increases with decreasing pH from 7 to 4. For this reason our low amounts of adsorbed $SO_4^{2-}$ (2.5 to 5.7 mg S/kg soil) may be the result of the high pH values, ranging between 6.0 and 7.1 (Table 1).

In contrast to C and N, which is also associated with a heterogeneous mixture of plant residues and microorganisms, the effect of long-term application of organic manure on soil organic S, being the main S fraction in soil, was barely investigated in the past (Yang et al. 2007). In our investigations total organic S ranged between 144.9 (MIN) and 280.1 mg S/kg soil (COM2) (Figure 4). As expected, total organic S increased with the increasing input rates of each organic fertilizer. The increase was highest with compost and less pronounced with farmyard manure. However, these differences cannot be attributed solely to varying supply of organic S with the different organic fertilizers. They are in part a consequence of differences in decompos-

Table 2. Inorganic and organic S as % of total soil S

| | MIN | FYM1 | FYM2 | COM1 | COM2 | SS1 | SS2 |
|---|---|---|---|---|---|---|---|
| Inorganic S | 3.74 | 2.98 | 2.47 | 2.81 | 2.85 | 2.64 | 3.44 |
| Organic S | 96.26 | 97.02 | 97.53 | 97.19 | 97.15 | 97.36 | 96.56 |

MIN – mineral fertilizer; FYM1 – 9 t/ha farmyard manure; FYM2 – 18 t/ha farmyard manure; COM1 – 14.5 t/ha compost; COM2 – 58 t/ha compost; SS1 – 3.7 t/ha sewage sludge; SS2 – 14.8 t/ha sewage sludge

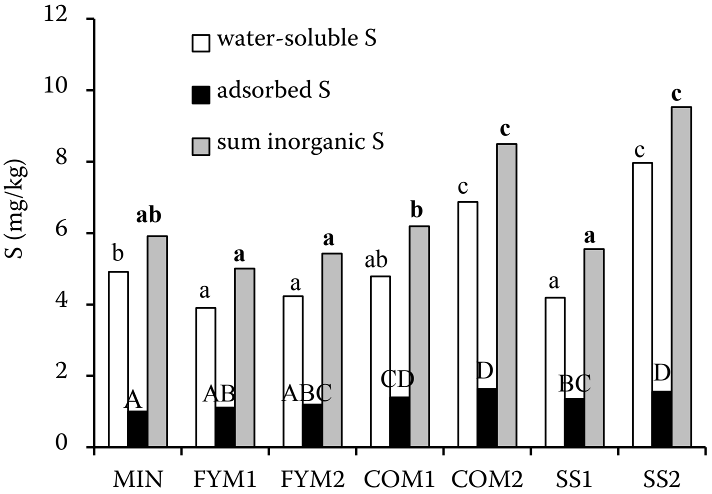


Figure 3. Inorganic S content of bulk soil under different fertilizer treatments (values with the same letters are not significantly different). MIN – mineral fertilizer; FYM1 – 9 t/ha farmyard manure; FYM2 – 18 t/ha farmyard manure; COM1 – 14.5 t/ha compost; COM2 – 58 t/ha compost; SS1 – 3.7 t/ha sewage sludge; SS2 – 14.8 t/ha sewage sludge

ability among the organic residues. While sewage sludge, for example, has a large pool of potential mineralizable S, compost (with a higher C/S ratio) encourages microbiological immobilization of S. According to Wang et al. (2006) total organic S in soil is highly significantly correlated with total soil organic carbon, indicating a close association between C and S. Confirming results of Eriksen and Mortensen (1999) we also found that build up of organic C ($C_{org}$) (Table 1) was followed by a similar build-up of organic S. The correlation between both parameters is highly significant ($R^2$ = 0.80).

Ester sulfate accounted for 36.3 to 51.6% of total organic S, which is in the same range as reported by Eriksen et al. (1995). The absolute amounts ranged from 74.9 (FYM1) to 150.6 mg S/kg soil (COM2) (Figure 4). According to Eriksen (1996) the accumulation of ester sulfate reflects the incorporation of high amounts of inorganic S, being highest with the high compost application. Thus we assume that S is stored as ester sulfate as a response to a high $SO_4^{2-}$ supply. However, with time and further S cycling a large proportion of ester sulfate is distributed to the C-bonded S pool, which is less affected by the $SO_4^{2-}$ concentration of the soil and varies with fluxes in the microbial biomass. C-bonded S varied between 63.4 (MIN) and 150.9 mg S/kg soil (SS2). Unlike ester sulfate, its content was higher after long-term farmyard manure and sewages sludge applications. In systems where $SO_4^{2-}$ is minimally available C-bonded S dominates, because its presence is related more to soil C levels than to S. A high proportion of C-bonded S was also reported for New Zealand soils (Nguyen and Goh 1990) which may be attributed to its return via animal excreta in farmyard manure.

In general, our study indicates that the type as well as the amount of fertilizer applied strongly influences total S content as well as inorganic and organic S fractions of soils. Overall, the absolute amount and the share of different inorganic and organic S forms reflect soil type, site specific conditions and fertilizer history.

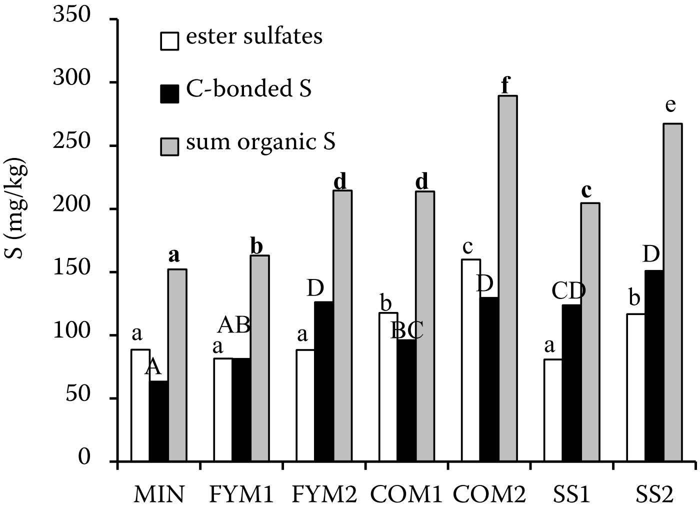


Figure 4. Organic S content of bulk soil under different fertilizer treatments (values with the same letters are not significantly different). MIN – mineral fertilizer; FYM1 – 9 t/ha farmyard manure; FYM2 – 18 t/ha farmyard manure; COM1 – 14.5 t/ha compost; COM2 – 58 t/ha compost; SS1 – 3.7 t/ha sewage sludge; SS2 – 14.8 t/ha sewage sludge

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