Introduction

Over the last two decades sulphur (S) deficiency has been recognized as a constraint to crop production all over the world (Scherer, 2001). Reviewing crop responses to S fertilization Zhao et al. (1996) already found that S has become one of the most limiting nutrients for crop production in many European countries.

In mineral arable soils total S varies between 0.02 and 0.2 % and is composed of inorganic and organic forms and is cycled between these forms via mobilization, mineralization and immobilization.

While S applied in combination with mineral fertilizers is mobile in soils and therefore prone to leaching, S applied with organic fertilizers might reduce leaching and thereby increase the overall S-use efficiency in crop rotations. In soils organic S occurs mainly in two primary forms as ester sulphates (C-O-S) and carbon bonded S (C-S). Both fractions contribute differently to S mineralization and thus to the nutrition of plants (Ghani et al., 1991). However, little is known about the influence of (in-)organic fertilization on the proportions of ester sulphates and carbon-bonded S.

Our long-term field experiment, which includes the application of mineral fertilizer and different organic fertilizers provided an unique opportunity to study long-term effects of organic amendments on total S and the distribution of different inorganic and organic S forms.

Material and Methods

Soil samples

Soil samples were collected from the topsoil layer of the field experiment (randomized complete block design with four replicates), established in 1962 at the experimental farm of INRES - Plant Nutrition, University of Bonn, Germany, on a luvisol derived from loess, following a cereal-root crop sequence.

The treatments selected were: S free mineral fertilizer according to the demand of the crop= control (MIN), 5 t and 10 t farmyard manure ha^{-1} $year^{-1}$ (FYM1 and FYM2), 7.25 t and 29 t compost from organic household waste ha^{-1} $year^{-1}$ (COM1 and COM2) and 1.86 t and 7.44 t sewage sludge ha^{-1} $year^{-1}$, respectively (SS1 and SS2). Until 1997 organic fertilizers (amounts are based on dry weight) were applied every second year. Since 1999 they were applied every third year and the amounts were changed to 3.33 and 6.66 t farmyard manure ha^{-1} $year^{-1}$, 10 and 30 t compost ha^{-1} $year^{-1}$ and 1.67 and 3.3 t sewage sludge ha^{-1} $year^{-1}$. The application rate of mineral fertilizers was kept at the same level. Since 1999 the crop sequence was cereal-cereal-root crop.

Sulphur analysis

Water-soluble and adsorbed: sequential extraction (Shan et al., 1997); ester sulphate = HI reducible S - (water-soluble S + adsorbed S): HI extraction (Shan and Chen, 1995); carbon-bonded sulphur: subtracting the inorganic sulphur (water-soluble and adsorbed) plus ester sulphate from total sulphur; total S: Elemental Analyser, Eurovector EUROEA.

Results and Discussion

Total S concentrations in bulk soils ranged from 99 mg to 263 mg S kg^{-1} soil (Table 1). Compared to the control long-term application of the high amounts of compost and sewage sludge resulted in significantly higher total S concentrations. The other organic fertilizer treatments did not show any significant impact on total S. Our study demonstrates that the accumulation of total S after long-term application depends on the fertilizer type, the amount applied as well as on the S content. Changes of total S in soil have been found to be proportional to the amount of organic residues added (Larson et al, 1972). According to Gutser and Tucher (2000) the mean total S content of farmyard manure, compost and sewage sludge is 0.45 kg, 0.30 kg and 1.25 kg 100 kg^{-1} dry matter, respectively. Accordingly, we applied between 22.5 and 147 kg S ha^{-1} every year. However, all the organic manures applied in our field experiment are a variable matrix, since their composition and therefore their S content is a product of many factors.

Treatment	MIN	FYM1	FYM2	COM1	COM2	SS1	SS2
Total soil S (mg kg^{-1})	116.3^{ab}	130.3^{ab}	143.6^{ab}	148.3^{b}	262.8^{c}	98.7^{a}	231.0^{c}

Table1: Influence of long-term application of a mineral and different organic fertilizers on total soil S (different subscripts denote significant differences at the 5 % level; ANOVA)

Inorganic S is generally much less abundant than organically bound S. According to Table 2, in our investigations inorganic S ranged from 4.9 % to 15.6 % of the total soil S. Interestingly, the addition of the high amount of the different organic fertilizers resulted in a lower proportion of inorganic S of the total S pool. Therefore we assume that the addition of carbon tends to increase the amount of SO_4^{2-} that is bound in organic forms. Despite the very different forms and amounts of S applied for about 45 years, the proportions of organic and inorganic S only vary in a rather small range. Obviously, soil and site characteristics are more important for this partitioning than quality and quantity of S fertilization.

Treatment	MIN	FYM1	FYM2	COM1	COM2	SS1	SS2
Inorganic S	11.3	9.7	8.2	11.7	4.9	15.6	4.6
Organic S	88.7	90.3	91.8	88.3	95.1	84.4	95.4

Table 2: Inorganic and organic S in % of total soils S

Total inorganic S ranges between 11.7 mg kg^{-1} soil and 17.9 mg kg^{-1} soil (Table 3) and consists mainly of water-soluble sulphate. Because of the high pH values (6.0-7.1) of the plots sulphate adsorption is low. In almost all treatments the adsorbed proportion is a highly stable.

Treatment	MIN	FYM1	FYM2	COM1	COM2	SS1	SS2
H_2O soluble SO_4-S (mg kg^{-1})	9.19^{a}	8.10^{a}	9.07^{a}	8.42^{a}	12.21^{b}	7.55^{a}	11.51^{b}
Adsorbed SO_4-S (mg kg^{-1}	$3,89^{b}$	3.59^{b}	3.72^{b}	4.00^{b}	5.69^{d}	2.47^{a}	4.85^{c}
Total inorganic S	13.08	11.69	12.79	12.42	17.90	10.02	16.42

Table 3: Influence of long-term application of different organic fertilizers on inorganic soil S

The organic S pool is dominated by ester sulphate (Table 4). The enrichment of this fraction is highest in COM2 (155.9mg S kg^{-1}) and SS2 (115.86 mg S kg^{-1} soil). Carbon-bonded S ranges between 18.7 mg S kg^{-1} soil (SS1) and 98.9 mg S kg^{-1} soil (SS2) with the highest amounts in

COM2 and SS2. In the case of COM and SS, the higher doses cause a superproportional increase of carbon bonded S, whereas for FYM the proportion stays stable (37-38 %). This indicates that the kind of fertilizer and the amount applied strongly influences soil organic S fractions. Overall, the absolute amount and the share of different inorganic and organic S forms reflects soil and site specific conditions as well as fertilizer history.

Treatment	MIN	FYM1	FYM2	COM1	COM2	SS1	SS2
Ester sulphate S (mg kg^{-1})	81,5[ab]	73.8[a]	82.0[ab]	106.0[bc]	155.9[d]	69.9[a]	115.8[cd]
Carbon bonded S (mg kg^{-1}	21.7[a]	44.8[b]	48.8[b]	29.9[ab]	89.0[c]	18.7[a]	98.9[c]

Table 4: Influence of long-term application of different organic fertilizers organic soil S

References

Ghani A, McLaren RG, Swift RS (1991) Sulphur mineralisation in some New Zealand soils. Biol Fertil Soils 11, 68-74

Gutser, R Tucher von S (2000) Zur Schwefelwirkung von Wirtschafts- und Sekundärrohstoffdüngern. VDLUFA-Schriftenreihe 53, 48-63

Larson WE, Clapp CE, Pierce WH, Mocharan VB (1972) Effect of increasing amounts of organic residues on continuous corn: II: organic carbon, nitrogen, phosphorus, and sulfur. Agron. J. 64, 205-208

Scherer HW (2001) Sulphur in crop production - invited paper. Eur. J. Agron. 14, 81-111

Shan, X, Chen B (1995) Determination of carbon-bonded sulfur in soils by hydriodic acid reduction and hydrogen-peroxide oxidation. Fresen J Anal Chem 351, 762-767

Shan X, Chen B, Zhang T-H, Li F-L, Wen B, Quian J (1997) Relationship between sulfur specification in soils and plant availability. Sci Total Environm 199, 237-246

Zhao FJ, Hawkesford MJ, Warrilow AGS, McGrath SP, Clarkson DT (1996) Response of two wheat varieties to sulphur addition and diagnosis of sulphur deficiency. Plant Soil 181, 317-327