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ORIGINAL PAPER

Net sulfur mineralization potential in Swedish arable soils in relation to long-term treatment history and soil properties

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Abstract The long-term treatment effect (since 1957–1966) of farmyard manure (FYM) application compared with crop residue incorporation was investigated in five soils (sandy loam to silty clay) with regards to the net sulfur (S) mineralization potential. An open incubation technique was used to determine accumulated net S mineralization (S_{AccMin}) and a number of soil physical and chemical properties were determined. Treatments and soil differences in S_{AccMin}, as well as correlations with soil variables, were tested with single and multivariate analyses. Long-term FYM application resulted in a significantly (p=0.012) higher net S mineralization potential, although total amounts of C, N, and S were not significantly (p<0.05) increased. The accumulated S mineralization differed significantly (p<0.05) between soils within this treatment. The measured soil variables were not significantly correlated to S_{AccMin}. Conclusively, different treatment histories influenced the quality (e.g., chemical composition) and cycling rate of the organic S pool, rather than its size.

Keywords Sulfur mineralization · Farmyard manure · Physical protection · Open incubation

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Introduction

Knowledge of soil sulfur (S) dynamics and availability to plants is increasingly important, as S deficiency in crops has been found worldwide (Scherer 2001). This is a result of decreasing S emissions (and thereby decreasing S deposition) in combination with increased use of high-analysis phosphorus (P) fertilizers, which contain virtually no S. Sulfur deficiency both limits crop yield and reduces its nutritional value (Rendig 1986) and, in case of wheat, its baking quality (Haneklaus et al. 1992). This is especially troublesome in organic farming systems, where mineral fertilizers and externally added nutrients in animal feed are often prohibited. Thus, the likelihood of S deficiency increases and an S deficient crop will provide insufficient levels of the S containing essential amino acids in animal feed. Consequently, there is a need for predicting and preferably controlling mineralization from organic S sources, such as farmyard manure (FYM), crop residues (CR), and the soil organic S pool. This need is not limited to organic farming systems, although S deficiency can easily be avoided by mineral S application in conventional farming, but in order to make this fertilization efficient, the farmer must know how much and when to apply.

Long-term FYM application leads to an increase in total soil S content and S mineralization (Knights et al. 2001; Sammi Reddy et al. 2001) and differences in S mineralization between soils are reported (Maynard et al. 1983; McLaren et al. 1985; Ghani et al. 1992). However, there is little published information about long-term effects of FYM application on net S mineralization in different soils. Moreover, the FYM/no FYM treatments previously studied have been refined to single out effects of FYM against the effects of mineral fertilizers, i.e., they have not been based on a realistic farming situation.

In this study, the long-term treatment effects on net S mineralization between plots designed to simulate a livestock farm with manure application and crop residue removal and plots simulating arable crop production (no manure and crop residues plowed under) were compared. Soil was collected from a set of long-term experimental sites in south and central Sweden that had the same treatments at all sites, with slight regional adaptations of fertilization levels and crop rotations based on climatic differences. The soil properties, fertilizer regimes, crop rotations, and crop yields of these experiments are well documented (Carlgren and Mattson 2001). A common open incubation technique was used to estimate net S mineralization and we measured soil pH, total amounts of C, N, and S, sulfate (soluble and adsorbed), amount of physically protected and unprotected organic S, and microbial activity (measured as anaerobic N mineralization). The results were tested statistically with single and multivariate analysis, with the purpose of determining differences in net S mineralization between treatments and soils, as well as evaluating the possibility of explaining the results by differences in the soil variables measured.

Materials and methods

Soils

Two experimental sites in southernmost Sweden, Fjärdingslöv (Fj) and Orup (Or), and three sites in south–central Sweden, Fors (Fo), Högåsa (Hö), and Vreta Kloster (VK), were used in this study. They are located from 54°24′ N (Fjärdingslöv) to 60°20′ N (Fors). The field experiments at these sites were initiated between 1957 and 1966 and are part of the same soil fertility experiment series (Carlgren and Mattson 2001), i.e., the field treatments are coordinated between the different sites. There are two main treatments: livestock production (with FYM application and removal of crop residues) and arable crop production (no FYM application, incorporation of crop residues). Within the main treatments, there are several subtreatments with different levels of mineral NPK fertilization (the same subtreatments are used in both main treatments) in a block design with two replicate plots (125 m^2 each) for each combination of main treatment and subtreatment. For this study, we used soil from one of the subtreatments (mineral N at normally recommended level, no PK) within both main treatments. Henceforth, the two treatments studied will be referred to as FYM (with farmyard manure application) and CR (with crop residue incorporation). A description of the treatments is presented in Table 1.

The five sites chosen from the experimental series represented a range of soil textures, from sandy loam to silty clay (Table 2). Soil samples (ten per plot) were collected in the fall 2005 (postharvest) from the plough layer (0–20 cm). Since we had no intention to upscale our results to field scale, samples from the two field replicates within each treatment were combined into one composite sample. This gave a total of ten bulk samples from the five sites. The soil was stored in closed plastic bags at +2°C until the start of the laboratory incubations.

Table 1 Fertilization and crop rotation in the two field treatments selected for this study (Carlgren and Mattson 2001)

	FYM		CR	
	South	South–central	South	South–central
Mineral N (kg N ha^{-1} $year^{-1}$)	100	82	100	82
Mineral S as $MgSO_4$[a] (kg S ha^{-1} $rotation^{-1}$)	84	84	84	84
FYM[b] (t ha^{-1} $rotation^{-1}$, fresh weight)	20	30	0	0
Crop residues	Removed	Removed	Incorporated	Incorporated
Crop rotation	**Barley**	Barley	**Barley**	Barley
	Ley 1 (1 cut)	Ley 1 (2 cuts)	Oil seed	Oats
	Winter wheat	Ley 2 (1 cut)	Winter wheat	Oil seed
	Sugar beet	**Winter wheat**	Sugar beet	**Winter wheat**
		Oats		Oats
		Winter wheat		Winter wheat

Bold text in the crop rotation marks the crop that was grown in the season before sampling, except at the Fors site where sampling followed the second winter wheat in the rotation

[a] Applied in spring the year after barley since 1998

[b] Applied in autumn after winter wheat in southern sites and after Ley 2 in south–central sites

Table 2 Soil texture and soil classification

Soil	Texture	Sand (%)	Silt (%)	Clay (%)	Classification
Fj	Sandy loam	55.1	25.9	19.1	Oxyaquic Hapludoll[a]
Fo	Silt loam	28.3	54.9	16.9	Udic Haploboroll[a]
Hö	Sandy loam	75.4	17.3	7.4	Humic Dystrocrept[b]
Or	Sandy loam	60.2	29.0	10.8	Aquic Haploboroll[a]
VK	Silty clay	8.1	49.1	42.9	Oxyaquic Haplocryoll[b]

Percentages represent means of the two treatments (FYM and CR) at each site

[a] Soil taxonomy (Carlgren and Mattson 2001)

[b] Soil taxonomy (Kirchmann et al. 2005)

Incubation

The soil in each plastic bag was thoroughly mixed and sieved at ≤2 mm. Thereafter, a subsample for soil characterization was withdrawn and air-dried. Another three subsamples of fresh soil, equivalent to about 30 g oven-dry soil, were withdrawn and carefully mixed with 20 g of glass beads (Ø 2 mm), giving three replicates for each soil/field treatment combination. The soil/bead mixture was put in Plexiglas tubes (Ø 40 mm, height 15 cm) equipped with a drainage hole on the side and a silicon rubber stopper at the bottom, covered with glass wool and a 1-cm-thick layer of quartz sand. A small wad of glass wool was put on top of each soil/bead column to avoid surface disturbance during irrigation and leaching events. To avoid contamination, all materials used (tubes, glass wool, quartz sand, and beads) were acid-washed (1% HNO_3) and carefully rinsed in deionized water prior to filling.

To obtain a similar moisture level in all soils, 20 ml of deionized water was allowed to pass through each tube before a suction of 10 kPa was applied. The tubes were then covered with punctured aluminum foil to avoid rapid drying and kept in darkness at +18°C. Every 7 days, water loss due to evaporation was determined gravimetrically and an equivalent amount of deionized water was added. After 2 weeks of preincubation, the tubes were first leached with 5×20 ml of 0.016 M KH_2PO_4 to remove dissolved plus adsorbed sulfate (SO_4^{2-}) and then with 5×20 ml of "rainwater" (ion concentrations in micromoles per liter: K^+ 5, Na^+ 60, Ca^{2+} 15, Mg^{2+}10, NH_4^+ 60, NO_3^- 30, and Cl^- 145) to wash out excessive phosphate and obtain a realistic salt concentration in the soil solution. As before, a suction of 10 kPa was applied to restore the moisture level.

The soils were then incubated for 95 days under the same conditions as during the preincubation. Every 2 weeks, the tubes were leached with 5×20 ml of "rainwater" to remove the SO_4^{2-} that had formed. Toward the end of each leaching event, a suction of 10 kPa was applied to restore the moisture level.

At the end of the incubation period, the tubes were leached with 5×20 ml of 0.016 M KH_2PO_4 to ensure all SO_4^{2-}, which had formed during the incubation, were removed. The leachates were filtered (Millipore filter; pore diameter 0.45 µm) and refrigerated until the sulfate content was analyzed by anion chromatography with an IC Dionex ICS-90 equipped with an AG14A guard column and an AS14A analytical column.

Soil analyses

All extractions and analyses were made on triplicate samples.

Basic soil characteristics

The pH of the soils was determined on 5 ml soil mixed with 25 ml deionized H_2O, shaken for 5 min and then left for at least 2 h before pH measurement. Water-soluble sulfate (SO_4^{2-}-H_2O) was determined by mixing 5 g soil with 25 ml of deionized water and shaking end-over-end for 60 min before centrifugation (4,600×*g*, 30 min) and Millipore filtration (0.45 µm). The extracts were refrigerated until analyzed by anion chromatography, as described above. Soluble plus adsorbed sulfate (SO_4^{2-}-KH_2PO_4) was determined by the same procedure as for soluble sulfate, but with 0.016 M KH_2PO_4 as an extractant instead of water. The difference in SO_4^{2-} concentration between the two extracts was regarded as adsorbed SO_4^{2-} (SO_4^{2-}-Ads; Tabatabai 1996). Total S in the soils was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) after digestion with HNO_3/$HClO_4$ (volume ratio 10:1). Total C and N were determined with a CHN analyzer (Leco CHN-932).

To estimate the microbial activity of soils, the N mineralization potential (N_{PotMin}) was determined by anaerobic incubation according to the method suggested by Drinkwater et al. (1996). Subsamples for this purpose were taken from the field-moist soil and preincubated under similar conditions (watered every 7 days, but not leached) as the soil incubated for determining net S mineralization.

Physically protected S

Physically protected S was determined by ultrasonication and extraction in acetylacetone, according to the method originally proposed by Keer et al. (1990) and later modified by Eriksen et al. (1995a, b). The procedure followed the description in Eriksen et al. (1995a), except for the following modifications:

- The initial extraction of inorganic and easily dissolved organic S was made with 0.016 M KH_2PO_4 instead of HCl.
- All extractions were sequential, i.e., each soil sample was extracted in three steps:
    1. Inorganic and easily dissolved organic S (Sol-S), 0.016 M KH_2PO_4
    2. Organic nonprotected S (Org-S_{ND}), 0.2 M acetylacetone
    3. Organic protected S (Org-S_D): ultrasonication (1,800 J ml^{-1}) in 0.2 M acetylacetone

For the ultrasonication in step 3, a Sonics & Materials Inc. VCX 500, equipped with a 19-mm tip, was used. Each step was repeated twice before moving on to the next step. The two extracts from each step were combined and diluted to 100 (KH_2PO_4 extract) or 200 ml (acetylacetone extracts) with deionized water. The extracts were filtered (0.45 µm Millipore filter) and refrigerated until analysis. All extracts were analyzed for total-S by ICP-AES (the acetylacetone extracts were digested by concentrated HNO_3 prior to analysis).

Statistical analyses

One-way analyses of variance, paired *t* tests, and single regression analyses were done with MINITAB release 15.1. In the statistical analyses, the bulked soil samples from the five sites were treated as replicated observations for the two treatments FYM and CR. As the field replicates were combined into composite samples, soils from the same site were not tested against each other, except for accumulated S mineralization (S_{AccMin}).

One of the purposes of this study was to investigate the relationship between the measured soil variables and net S mineralization. Due to the large number of variables measured, a multivariate analysis of the variance by partial least squares regression (PLS) was performed. This analysis was made with SIMCA-P version 11.0. For PLS, explanatory variables, in this case the measured soil variables, are used to explain the variance of the response variable (S_{AccMin}) and the components are rotated in multidimensional space to maximize the degree of explanation.

Results

Soil characterization and anaerobic N mineralization

The pH and sulfate data are presented in Table 3. In agreement with earlier studies (Curtin and Syers 1990), adsorbed sulfate was only detectable in soils with pH less than 6 (Or and Hö). The pH dependency of adsorbed sulfate was reflected in a significant negative correlation ($R^2=0.72$, $F=20.2$, $p=0.002$). As the initial sulfate content was removed from the columns before incubation, only the initial amount of adsorbed sulfate was used in the single and multivariate regression analyses of correlation with accumulated S mineralization. The initial amount of adsorbed sulfate was then assumed to reflect the capacity of the soil to adsorb sulfate, which could be an important factor affecting the inherent net S mineralization potential of the soil (see "Discussion").

Table 3 Soil pH and sulfate concentration

Soil/treatment	pH-H_2O	SO_4^{2-}-H_2O (mg kg^{-1} soil)	SO_4^{2-}-KH_2PO_4 (mg kg^{-1} soil)	SO_4^{2-}-Ads[a] (mg kg^{-1} soil)
Fj FYM	6.89±0.17	0.99±0.03	0.75±0.05	0[b]
Fj CR	6.91±0.11	1.00±0.07	1.07±0.03	0.07
Fo FYM	7.34±0.03	1.92±0.01	1.61±0.02	0[b]
Fo CR	7.50±0.05	1.43±0.06	1.46±0.08	0.03
Hö FYM	5.91±0.01	2.90±0.18	4.45±0.08	1.55
Hö CR	6.20±0.01	3.02±0.21	5.03±0.29	2.01
Or FYM	5.64±0.02	1.99±0.03	4.95±0.02	2.96
Or CR	5.98±0.08	1.58±0.01	3.01±0.21	1.44
VK FYM	6.88±0.01	2.19±0.03	1.85±0.03	0[b]
VK CR	6.87±0.03	1.72±0.00	1.56±0.09	0[b]

Mean ± SD (*n*=3)

[a] SO_4^{2-}-Ads is calculated by subtraction of SO_4^{2-}-H_2O from SO_4^{2-}-KH_2PO_4

[b] Slightly negative values (−0.17 to −0.34) were obtained, probably due to sample variation and differences in precision in the analytical methods. In these cases, the adsorption is set to zero

Total C, N, and S are presented in Table 4, along with corresponding C/N/S ratios and N mineralization potential. All soils had a C/S ratio <100, which should result in a net mineralization of S, according to earlier studies (Tabatabai and Chae 1991; Sammi Reddy et al. 2002; Eriksen 2005). The total S content ranged between 190 and 390 mg S kg^{-1} soil, which is in general agreement with the amounts previously found in agricultural soils (Tabatabai 1996). No significant ($p<0.05$) differences were detected between the treatments, although N mineralization potential was higher in FYM than in CR for all soils.

Physically protected S

The results from the extraction of physically protected S are presented in Fig. 1. The amount of extracted S varied widely between the soils (12–80% of total soil S), and although the ratio Org-S_D to Org-S_{ND} was similar in all soils, ranging between 0.9 and 2.7, there was a difference

Table 4 Total S, C, and N, C/N/S ratios, and N mineralization potential

Soil/treatment	S (mgkg^{-1} soil)	C (gkg^{-1} soil)	N (gkg^{-1} soil)	C/N/S	N_{PotMin} (mgkg^{-1} soil)
Fj FYM	226±2	16.83±0.09	2.03±0.01	75:9:1	9.8±0.7
Fj CR	192±4	12.87±0.02	1.70±0.00	67:9:1	7.9±0.7
Fo FYM	392±5	22.53±0.03	2.30±0.01	58:6:1	6.7±0.9
Fo CR	373±3	20.30±0.02	1.90±0.01	54:5:1	2.9±0.1
Hö FYM	228±2	19.90±0.02	1.90±0.00	87:8:1	16.2±1.6
Hö CR	233±3	21.87±0.06	2.07±0.01	94:9:1	14.2±1.4
Or FYM	258±4	22.60±0.12	2.27±0.01	88:9:1	8.4±0.7
Or CR	263±5	20.63±0.06	2.30±0.01	78:9:1	7.6±2.0
VK FYM	351±3	20.43±0.04	2.40±0.00	58:7:1	9.7±0.1
VK CR	320±3	18.27±0.08	2.27±0.01	57:7:1	5.2±1.0

Mean ± SD (n=3)

associated with soil texture. The clayey soils (Fj, Fo, and VK) averaged around a ratio of 2, whereas the more coarse-grained soils (Hö and Or) averaged around 1.

The sizes of the Sol-S (R^2=0.67, F=16.5, p=0.004) and the S_{ND} (R^2=0.62, F=12.9, p=0.007) pools were weakly but significantly positively correlated with the C/S ratio of the total soil. For S_{Res}, the correlation with the C/S ratio was significant but negative (R^2=0.77, F=26.5, p=0.001). The differences between treatments were small, except for the Orup soil where a larger amount of Org-S_{ND} was extracted in the FYM treatment, although this difference could not be statistically tested due to the use of composite sampling.

Net S mineralization

One of the tubes containing Fj CR soil material clogged during incubation and was removed from the experiment after 42 days. Due to this, the accumulated net S mineralization of Fj CR after day 42 was based on only two samples. Moreover, the variation between the two remaining tubes was large, probably due to one of them being close to clogging and was therefore likely to become anaerobic. Thus, the incubation results for this soil/treatment combination were uncertain and were excluded from the statistical analyses; they are presented for demonstration purposes only.

The accumulated net S mineralization after 95 days of incubation ranged between 3.5 and 5.6 mg S kg^{-1} soil (Fig. 2; Table 5), corresponding to 1.0–2.5% of total soil S. The mineralization rate was relatively constant during the entire incubation period, as shown by the linear increase in accumulated S mineralization (Fig. 2).

Generally, the FYM treatment displayed a higher (df=26, F=7.27, p=0.012) accumulated S mineralization than the CR treatment. Within sites, this difference was undetectable; however, within the FYM treatment, net S mineralization in the Högåsa soil was significantly (p<

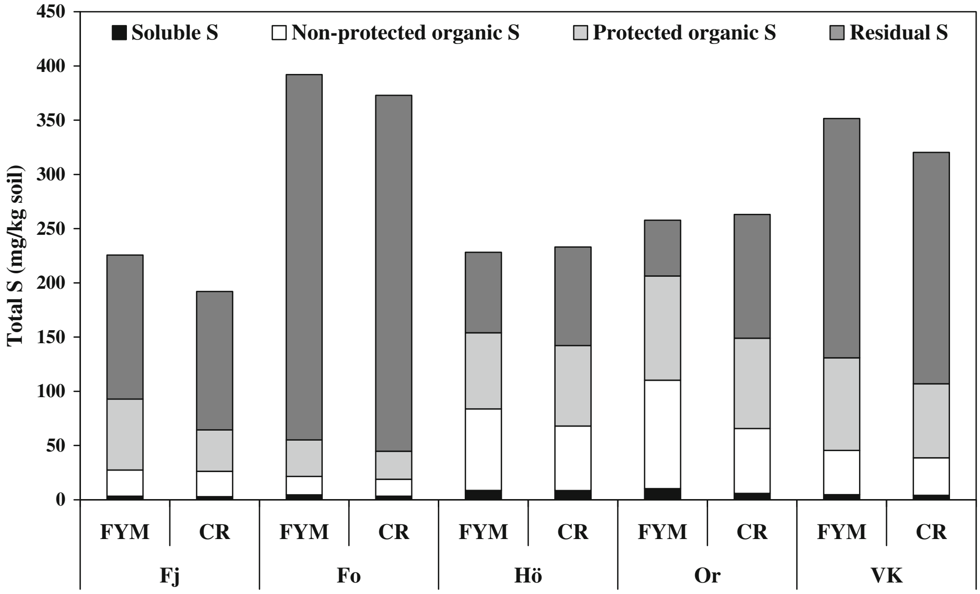

Fig. 1 Total S in the different pools of soil S according to the acetylacetone/ultrasonic dispersion method (see text)

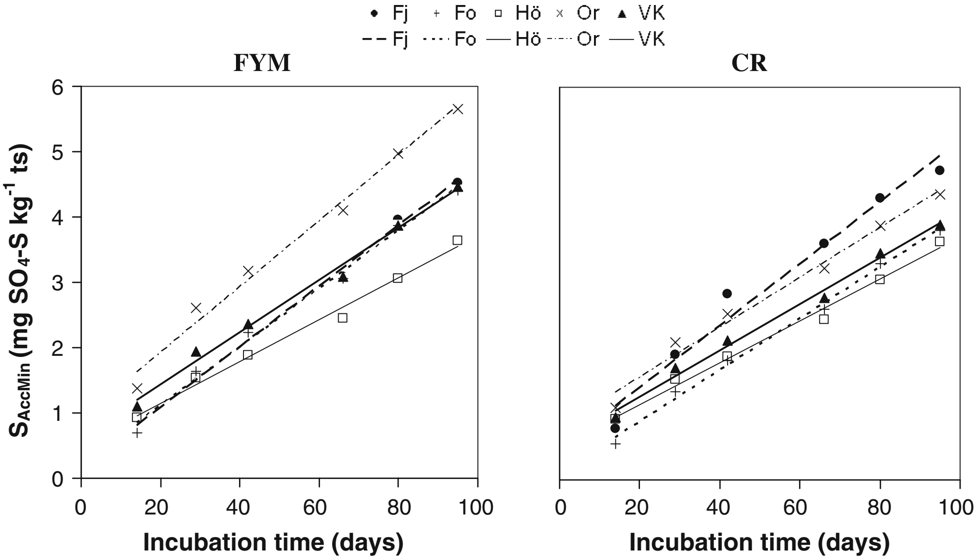

Fig. 2 Accumulated S mineralization during 95 days of incubation, with linear regression fits (R^2 values are presented in Table 5)

0.05) lower than in all the other soils, except for Vreta Kloster. The Orup soil had the highest mineralization rate in the FYM treatment, although this difference was only significant ($p<0.05$) with respect to Fors and Högåsa. Within the CR treatment, there were no significant differences between the soils for net S mineralization. The single regression analyses revealed no correlation between any of the soil variables studied and accumulated net S mineralization.

Multivariate analyses

The results of the PLS analysis are presented in Fig. 3 and the statistics for the model are shown in Table 6. As the first PLS regression did not return any significant components (see Table 6), the data were examined for outliers by plotting *t* versus *u* scores, normal probability for residuals, observation risks, and distance to model for both *X* and *Y* variables (plots not shown). It was concluded that Or FYM was a potential outlier and when this soil was removed from the model, two significant components were identified, explaining 84% of the variance in the soil (*X*) variables and 61% of the variance in S_{AccMin} (*Y*; Table 6). The resulting loading scatter plot is shown in Fig. 3. In a PLS plot, variables close to each other have a strong positive relationship, variables at a 180° angle are strongly negatively related, and a 90° angle indicates no relationship. The further away a variable is from the origin, the higher its explanatory power. Thus, it appeared that sulfate adsorption, easily soluble S, total C, and C/N ratio were negatively related to net S mineralization (S_{AccMin}), whereas total N was positively related. From both single and multivariate analyses, it appeared that total S, residual S, the N/S ratio, silt content, and pH had little explanatory power with respect to the accumulated net S mineralization in these soils.

Table 5 Total accumulated S mineralization (S_{AccMin}) after 95 days of incubation with R^2 values for the linear regressions displayed in Fig. 2

Soil	FYM		CR	
	S_{AccMin}[a] (mgkg^{-1} soil)	R^2	S_{AccMin}[a] (mgkg^{-1} soil)	R^2
Fj	4.5ac±0.1	0.98	4.7±1.4	0.78
Fo	4.4a±0.1	0.98	3.8d±0.2	0.99
Hö	3.6b±0.2	0.96	3.5d±0.4	0.95
Or	5.6c±0.4	0.95	4.4d±0.5	0.94
VK	4.5abc±0.6	0.93	3.9d±0.0	0.99

Different lowercase letters denote significant differences at $p<0.05$ between soils within a treatment (no significant differences were found between treatments within soils)

[a] Means ± SD ($n=3$), for Fj CR $n=2$

Discussion

Long-term treatment effects on S pools and cycling rates

The design of the Swedish long-term fertility field experiments used in this study gives the unique opportunity to investigate differences and similarities between different kinds of soils in combination with different treatment effects. In this study, we focused on the long-term effects on soil S dynamics of farmyard manure application versus crop residue incorporation at five sites. We found that the FYM treatment had resulted in an increased net S mineralization potential, even though the organic matter content (total C, N, and S) was not elevated in comparison with the CR treatment. Previously published results from long-term field experiments have also shown the positive effect of FYM on S mineralization, but then in combination

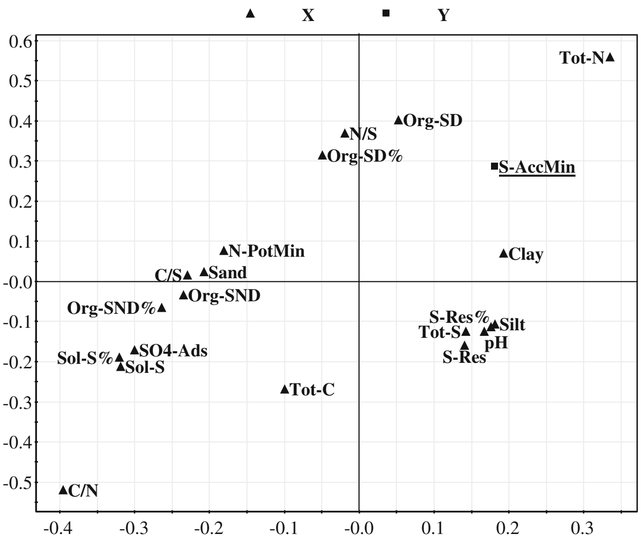

Fig. 3 Loadings scatter plots for the partial least squares regression. Variables denoted as described in the text, with the addition of the following: Sol-S%, Org-SND%, Org-SD%, and S-Res%, all of which refer to the percentage of total S found in the respective fraction. Variance in the *X* variables (soil variables) is used to explain the variance in the *Y* variable (S_{AccMin})

with increased organic matter and total S contents (Knights et al. 2001; Sammi Reddy et al. 2001). However, the comparison in those cases was made with treatments with only mineral fertilizer input. In the present study, the incorporation of crop residues in the CR treatment possibly provided a similar amount of organic matter input as the FYM application, but of different quality and composition. Our results thus provide new information in that higher net S mineralization potential with FYM application is not simply an effect of increased pool size, but can be attributed to differences in quality of the organic matter source. Since there were no significant differences between the two treatments in physical protection of organic S or total amounts of S and SO_4^{2-}, the most likely explanation for the increased S mineralization rate is that the FYM application has resulted in a general stimulation of the microbial activity, as the tendency toward increased anaerobic N mineralization also suggests. In support of this, Knights et al. (2001) found that S mineralization was more closely correlated with microbial biomass C than with soil organic S. Contradictingly, Hö FYM had the lowest net S mineralization rate, but the highest potential N mineralization (Table 4). Thus, all the differences in potential S mineralization found in this study cannot be explained by differences in general microbial activity and it is the diverging behavior of Or FYM and Hö FYM that is most intriguing in this study. These sites were similar with respect to the measured soil variables. Both sites had coarse-grained soils (Table 2) with relatively low pH (Table 3) and had a higher sulfate adsorption capacity (Table 3) and a lower Org-S_D/Org-S_{ND} ratio compared with the other soils. According to Eriksen et al. (1995b), only the nonprotected S pool (Org-S_{ND}) is directly available for microbial turnover. Therefore, a larger amount of S in this pool means that more S is available for mineralization. In support of this statement, Orup FYM had the largest Org-S_{ND} pool. However, also Högåsa FYM had a relatively large portion of soil S in this pool. Moreover, no statistical evidence for a relationship between this pool and the net S mineralization was identified.

The most reasonable explanation for the high mineralization potential in Orup FYM and low mineralization potential in Högåsa FYM would be differences in organic matter quality and/or relative abundance of microbial functional groups. However, these differences should be small, as all sites were part of long-term field experiments with similar treatment histories for the past 40–50 years, and the presampling crops at all sites were cereals. Furthermore, the mineralization patterns of Orup CR and Högåsa CR did not differ from each other or the other soils; thus, it was not an effect of the inherent properties of the soil or preexperimental treatment history. One possibility is that regional differences in the microbial community have led to different responses to the FYM treatment. Cho and Tiedje (2000) have shown that geographical distances correlate with genetic distances of bacterial strains in soils. However, it is unclear whether the genetic differences also influence the functionality of the microbial community to the degree observed here. It is also possible that the low net S mineralization rate in Hö FYM is simply an effect of that the soil microbes for some reason are more S limited in this soil, and therefore, the immobilization rate is higher than in the other soils, giving a low net (but plausibly high gross) flow. Further studies are necessary to verify or reject these speculations.

S mineralization and correlation with soil variables

The net S mineralization potential, as measured by sulfate production during an open incubation, could not be easily

Table 6 Explanation of variance for explanatory (*X*) and response (*Y*) variables and significance of the two first components in the PLS analyses

	PLS including all samples	PLS excluding Or FYM	
Component	1	1	2
X variance explained (%)	57	65	19
Y variance explained (%)	23	34	27
Significance[a]	ns	–	–

– significant component, *ns* nonsignificant component

[a] A component is considered significant when the cross-validation of the model is <0.05

predicted or explained by any of the soil variables measured. No significant correlations were determined in the single regression analyses. Some interesting correlations between different soil variables where, however, found. For example, the size of the residual organic S pool was negatively correlated with the C/S ratio. Since the C/S ratio in soil organic matter generally decreases with age (Zhao et al. 1996), this supports the proposal that S_{Res} consists of older more recalcitrant material (Eriksen et al. 1995b) and thus provides a limited short-term contribution to S mineralization. In the clayey soils, the residual insoluble S pool (S_{Res}) comprised a large portion (up to 88% in Fo CR) of total S, which, in combination with a larger portion of the extractable organic S in the physically protected pool, could partly explain why the mineralization rate was low in these soils (compared with earlier studies and with the Or soil in this study). However, the net S mineralization in all soils was at the lower end of the range reported from similar open incubation studies (Maynard et al. 1983; McLaren et al. 1985; Ghani et al. 1992; Knights et al. 2001; Pamidi et al. 2001; Sammi Reddy et al. 2001), and the main explanation is perhaps the relatively low incubation temperature.

In the multivariate analysis (Fig. 3), there was an indication of negative correlations between net S mineralization potential and the variables sulfate adsorption, easily soluble S, total C, and C/N ratio. The first two variables are obviously related and the negative correlation between either of these variables and S_{AccMin} suggests that S mineralization takes place via the biochemical mineralization pathway, i.e., by sulfatases released specifically to mobilize S bound to organic compounds via C–O–S bonds (McGill and Cole 1981). The release of sulfatases is controlled by available sulfate and is thought to play a role mainly where S is scarce for the microbes (i.e., where the C/S ratios are high). There is also a connection between the negative correlation of S_{AccMin} with either total C or C/N ratio and the positive correlation with total N. These relationships indicate that microbiological S mineralization (McGill and Cole 1981) is important in these soils. Sulfur mineralized through the microbiological pathway is a result of microbial C utilization and is important in soils where S is abundant relative to C (and to some extent N). In most of the soils investigated, the C to S ratios were within the 57–85 range normally found in microbial biomass (Scherer 2001), which means that there will be a surplus of S after respiration is accounted for. Thus, it is likely that the microbiological pathway is responsible for most of the S mineralization in these soils, although on the microscale, there will be sites where S availability is low and sulfatases contribute substantially to the mineralization.

Orup FYM did not fit the multivariate model for predicting net S mineralization with the soil variables measured in this experiment. Therefore, it appeared as if some other variable(s) were controlling S mineralization in Orup FYM, and if this/these variable(s) is/are identified, it could perhaps explain and predict the net S mineralization of the other soils more precisely as well.

Concluding remarks and future research

Long-term FYM application resulted in a significantly higher net S mineralization potential compared to the CR treatment and also some significant differences *between* FYM treated soils. However, as with previous studies within this field (e.g., Kirchmann et al. 1996; McGrath and Zhao 1996; Shan et al. 1997; Pamidi et al. 2001; Riffaldi et al. 2006; Wang et al. 2006), the results from this work did not elucidate the reasons behind differences in net S mineralization potential of different soils. The basis for this is probably that our understanding of the mechanisms behind S cycling patterns is still rudimentary and the methods used are too crude to provide explanations for the observations made. Future S research on the soils investigated in this study should focus more on the mechanistic aspects of the mineralization patterns and delve deeper into the nature of organic S in the soils. The latter can be achieved by S X-ray absorption near edge structure spectroscopy (Prietzel et al. 2003; Solomon et al. 2003; Prietzel et al. 2007; Schroth et al. 2007). With this technique, the chemical speciation of organic and inorganic sulfur can be determined. Quantification of the gross processes of S cycling and uptake should also form an important step forward. Turnover rates of different S pools and, thus, gross S mineralization can be followed by isotopic labeling with ^{35}S (Ghani et al. 1993; Eriksen 1997a, b; Eriksen 2005; Nzigueba et al. 2005, 2006). In addition, the significance of measured accumulated net S mineralization should be tested through comparison with actual plant uptake of S from the soil. More research is also necessary regarding the microbial community composition and functionality, probably starting with arylsulfatase measurements. However, as S research on these soils will continue, the results from this experiment will serve as an important knowledge base.

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