Influence of the nitrogen-sulfur fertilizing on the content of different sulfur fractions in soil

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ABSTRACT

Precise field experiments were established at 3 sites with oilseed rape under different soil-climatic conditions in the Czech Republic (Humpolec, Hněvčeves and Uhříněves) in the years 2008–2010. In this experiment, four fertilizing treatments with increasing S rate were evaluated. The contents of bioavailable (S_W), adsorbed (S_{ads}), occluded (S_{ocl}), and hydroiodic acid (HI) reducible (S_{HI}) sulfur were measured. The contents of the fractions within the studied sites in the samples collected before fertilizers application were comparable. The S_W, S_{ads} a S_{ocl} contents did not exceed 10 mg S/kg. The S_{HI} contents differed depending on site and year. Fertilizing using S as $CaSO_4$ positively influenced the contents of S_W, S_{ads}, and S_{HI} in soil. Sulfur fertilizing had also the positive tendencies to increase the winter rape yields but the differences between studied treatments were not statistically significant.

Keywords: N-S fertilizing; bioavailable; adsorbed; occluded and estersulfate bounded sulfur; rape yield

Bioavailable sulfur deficiency in soils is an actual problem in the Czech Republic and in other European countries. It applies to the countries with a recent good sulfur supply as well (Eriksen 2004, Lehmann et al. 2008, Skwierawska et al. 2008, Balík 2009 and others).

It can be attributed to the (i) decrease of atmospheric emissions; (ii) less intensive application of mineral fertilizers together with changes of their composition; (iii) restriction of manure, and (iv) cropping of plants with high S uptake in crop rotation (e.g. rape) on a bigger area (Scherer 2001, Blair 2002, Pacyna 2005).

From the mentioned reasons it is clear that sulfur is becoming a limiting factor for the harvest and production quality (Eriksen et al. 2004). Therefore, it is necessary to pay attention to sulfur fertilizing and get more information about different sulfur fractions in soil to optimize fertilizers split doses.

Inorganic sulfur represents usually 5–10% from total S (Tisdale et al. 1993). It can appear in many different forms. The most important form for S uptake by plants is its bioavailable sulfate form (SO_4^{2-}). This form represents usually only about 1% of total S (Knauff 2000). Another form represents the sulfates adsorbed due to the weak bind on the surface of soil particles. These have a direct influence on the perseveration of sulfate balance with soil solution (McLaren and Cameron 1996). The most stable sulfur form is S occluded with carbonates, especially with calcium carbonate (Chen et al. 1997). The mentioned forms are possible to estimate using different sequential extraction methods, for example after Shan et al. (1997).

The content of organic sulfur ranges usually about 90% of total S in soil (Eriksen et al. 1998, Solomon et al. 2001) and includes (i) sulfur directly bound with carbon; (ii) sulfur indirectly bound with carbon, for example C-O-S and C-N-S bounds (Morche 2008) which can be approximately estimated using the extraction method according to Shan et al. (1992). This method can be also used for estimating some part of inorganic sulfur (Havlin et al. 2005). Both mentioned groups are potential sources of bioavailable sulfur.

The aim of this work is to evaluate different S forms in soils amended using different fertilizing systems in precise field experiments.

MATERIAL A METHODS

Precise field experiments were established at three sites with oilseed rape under different

Supported by the Ministry of Agriculture of the Czech Republic, Project No. QH81202.

Table 1. Characteristic of experimental fields

Site	Altitude (m)	Mean yearly rainfall (mm)	Mean yearly temperature (°C)	Soil type	Soil sort	pH ($CaCl_2$)
Uhříněves	295	575	8.3	luvisol	clayey	6.5
Hněvčeves	265	573	8.2	luvisol	silty loam	6.3
Humpolec	525	665	7.0	cambisol	sandy loam	5.1

soil-climatic conditions in the Czech Republic (Humpolec, Hněvčeves and Uhříněves) in the years 2008–2010 (except 2010 at Uhříněves site, where the plants were damaged due to strong frost in spring). The sites are characterized in Table 1.

For this experiment, four fertilizing treatments were evaluated. Addition of nitrogen (calcium ammonium nitrate – 27% N and calcium sulfate ammonium nitrate – 24% N, 6% S) at all treatments reached 200 kg N/ha. Treatment A was fertilized only with nitrogen, treatment B with 12.5 kg S/ha, treatment C with 25 kg S/ha and treatment D with 50 kg S/ha (Table 2). Each treatment was conducted in 4 replicates. Sulfur was applied in the form of $CaSO_4$ (as a component of N-S fertilizer Lovofert® – ammonium nitrate calcium sulfate). Fertilizers were applied in three split doses: (i) at the beginning of the spring vegetation; (ii) at the vegetation period BBCH 30-32, and (iii) at the vegetation period BBCH 50-52 (only nitrogen).

For the analyses, fine (< 2 mm) topsoil (0–30 cm) samples of the spring vegetation beginning and from the BBCH 50-52 period were chosen. The samples were extracted using the following S-fractionation (Morche 2008): the soil sample was first extracted with demineralized water at 1:10 (w/v). After 30 min of shaking, each sample was centrifuged at 10 000 rpm for the duration of 10 min in order to get bioavailable sulfur (S_W). Following the centrifugation, the samples were extracted with 0.032 mol/L NaH_2PO_4 at the 1:10 (w/v) ratio. After 30 min of shaking, each sample was again centrifuged at 10 000 rpm for the duration of 10 min to get adsorbed sulfur (S_{ads}). The rest of the soil sample was extracted with 1 mol/L HCl. The extraction ratio was 1:20 (w/v). After 60 min of shaking, the samples were centrifuged for 10 min at 10 000 rpm to get occluded sulfur (S_{ocl}). For the HI-reducible sulfur (S_{HI}), the method after Shan et al. (1992 adapted by Morche 2008) was used.

RESULTS AND DISCUSSION

Precise field experiments with oilseed rape were established at three sites under different soil-climatic conditions in the Czech Republic in the years 2008–2010. Soil samples taken up before fertilizing and after adding the whole dose of S-fertilizers (vegetation period BBCH 50-52) were analyzed. In these samples, water extractable (bioavailable) sulfur (S_w), adsorbed sulfur (S_{ads}), occluded sulfur (S_{ocl}) and HI reducible sulfur (S_{HI}) was determined. Estersulfate bound sulfur (S_{es}) was subsequently calculated from these results. Regarding the fact that reached values did not fit the parameters of normal distribution, only basic statistical parameters were calculated. Table 3 mentions the different sulfur fractions amounts, estimated from the soil samples taken up before beginning of oilseed rape spring vegetation. The contents of the estimated fractions were comparable and the significant differences did not exceed the value of 0.5 (S_w); 0.4 (S_{ads}); 1.1 (S_{ocl}) and 7.7 (S_{HI}). For this reason it is possible to evaluate these sites as suitable for such experiments. It is also clear that the bioavailable S content was in very close range 4.1–6.8 mg S/kg (Table 3). This corresponds to the results of Matula

Table 2. Fertilizing of the experiment

Fertilizing treatment	1st rate (regeneration)	2nd rate (BBCH 30–32)	3rd rate (BBCH 50–52)	Total	
	(kg N/ha + kg S/ha)			(kg N/ha)	(kg S/ha)
A	80 + 0	80 + 0	40 + 0	200	0
B	80 + 12.5	80 + 0	40 + 0	200	12.5
C	80 + 25	80 + 0	40 + 0	200	25
D	80 + 25	80 + 25	40 + 0	200	50

Table 3. The contents of different S fractions in soils before fertilizing (mg S/kg)

Fraction	Hněvčeves			Humpolec			Uhříněves	
	2008	2009	2010	2008	2009	2010	2008	2009
S_W	6.3	6.2	6.3	4.1	4.4	4.5	6.3	6.8
S_{ads}	4.1	4.4	4.3	4.3	4.5	4.5	5.1	5.3
S_{ocl}	3.5	3.1	3.7	7.5	8.1	7.8	8.6	8.4
S_{in}*	13.8	13.7	14.3	15.9	17.0	16.8	20.0	20.5
S_{HI}	56.9	35.1	54.3	105.4	168.3	172.1	70.4	113.8
S_{es}**	43.1	21.4	50.0	89.5	151.3	155.3	50.4	93.3

*Σ $S_{W,}$ $S_{ads,}$ S_{ocl}, **calculated as $S_{es} = S_{HI} - S_i$

(2007), who estimated the range of bioavailable sulfur between 3.7 and 29.3 mg S/kg (estimated using 0.5 mol/L ammonium acetate) on 36 sites in the Czech Republic. A similar range was found for the S_{ads} and S_{ocl} values, where the contents reached 4.1–5.1 mg S/kg and 3.1–8.6 mg S/kg, respectively. The lowest contents of the bioavailable sulfur were always found at the Humpolec site. The contents of adsorbed sulfur were comparable at all sites and studied years.

Using the HCl extraction as a part of the fractionation should mobilize a major portion of S occluded with carbonates (Chen et al. 1997, Shan et al. 1997). In this case differences were observable between studied sites. The highest S_{ocl} contents were found at the Uhříněves site, where the values reached 7.5–8.6 mg S/kg and the lowest at Hněvčeves site, where they reached only 3.1–3.7 mg S/kg. Similar results were obtained by Balík et al. (2009), who estimated the average values of 7.2 mg S/kg (S_w), 5.2 mg S/kg (S_{ads}) and 9.9 mg S/kg (S_{ocl}) on 10 long-term non-fertilized sites in the year 2007.

The sum of the fractions S_w, S_{ads}, and S_{ocl} represents the so-called 'inorganic S' (S_{in}) (Morche 2008). Although the use of the extractants is not fully selective, it is possible to assume that most of the extracted S is inorganic S (Shan et al. 1992, Morche 2008). The observed values ranged between 13.7 and 20.5 mg S/kg.

The S_{HI} method should estimate the rate of organic sulfur bound with estersulfates. However, it is important to pay attention to the fact that using this method does not only estimate this S form. Sulfur dominates in estersulfate form, but it also estimates some ratio of inorganic sulfur (Havlin et al. 2005). Using the S_{HI} method estimates the whole content of inorganic sulfur (Morche 2008). Therefore, it is better to calculate estersulfate bound sulfur content like $S_{es} = S_{HI} - S_{in}$.

From Table 4 is clear that sulfur fertilizing influenced the amounts of almost all of estimated sulfur fractions. The differences were usually not statistically significant, but there are visible increasing tendencies with increasing S-fertilizer dose.

The lowest bioavailable sulfur content was always found on control sulfur non-amended treatment where the values reached about 5.7 mg S/kg. With the increasing S-dose the S_w content increased as well. The highest contents of bioavailable sulfur were found at the treatment fertilized with 50 kg S/ha. The average value of this treatment was 14.4 mg S/kg. Measured data correspond with the results published by Shan et al. (1997), who estimated the ratio of S_W between 5.8–44.4 in the pot experiments (13 soils) and 8.0–34.2 mg S/kg in the field survey (25 soils) with soils using different fertilizing systems.

Similar trends were observable for the S_{ads} values as well. Values between 5.0 and 5.6 mg S/kg were found in the year 2008, but the differences in 2009 and 2010 were obvious. Almost the same results were obtained by Balík et al. (2009), who observed an increasing trend of S_w and S_{ads} after a long term application of farmyard manure and farmyard manure together with NPK, where the part of N was added using ammonium sulfate. Shan et al. (1997) observed the S_{ads} range between 5.2 and 176 mg S/kg in a pot experiment and a closer range between 11.5 and 29.7 mg S/kg in the field survey.

Different fertilizing system probably did not have an influence on the content of sulfur occluded with carbonates. The increasing S_{ocl} trend with increasing S dose was observed only in the year 2010. Morche (2008) compared the changes in S_{ocl} contents after a long term usage of composts and mineral fertilizers. She gets in average about 16.0–16.3 mg S/kg higher contents at the soils

Table 4. The contents of different S fractions after S fertilizing (average from observed sites)

S fraction	Treatment	2008		2009		2010	
		(mg S/kg)	SD	(mg S/kg)	SD	(mg S/kg)	SD
S_w	A	6.0	0.9	5.5	0.6	5.5	1.1
	B	7.2	1.0	7.5	1.4	6.1	1.6
	C	7.9	2.9	11.0	6.7	9.4	1.4
	D	12.4	3.9	16.5	8.0	14.2	4.9
S_{ads}	A	5.0	0.5	4.9	0.7	4.1	0.8
	B	5.0	0.4	5.6	0.4	5.3	0.6
	C	5.1	0.5	6.7	1.3	6.2	1.0
	D	5.6	0.8	7.9	1.8	8.2	2.1
S_{ocl}	A	6.6	1.1	7.4	2.2	6.2	0.9
	B	6.3	1.0	6.8	1.3	6.2	1.5
	C	6.3	0.8	9.6	3.1	8.2	1.1
	D	7.1	1.2	8.3	2.5	8.5	0.8
S_{in}	A	17.6	1.3	17.9	0.7	15.8	1.2
	B	18.4	0.9	19.9	1.6	17.5	0.7
	C	19.4	2.1	27.3	1.3	23.7	1.5
	D	25.1	2.5	32.7	2.5	30.8	2.0
S_{HI}	A	103.7	8.3	100.9	13.9	113.3	7.6
	B	104.9	12.5	109.2	5.3	115.5	3.3
	C	110.4	15.1	111.4	6.9	123.2	3.6
	D	114.0	13.3	135.2	7.1	128.8	7.6
S_{es}**	A	86.1	7.2	83.0	8.5	97.5	4.3
	B	86.5	6.3	89.3	4.6	98.0	6.5
	C	91.0	9.8	84.1	5.1	99.5	6.5
	D	88.9	8.2	102.5	15.8	98.0	7.3

SD – standard deviation; **$S_{es} = S_{HI} - S_{in}$; A – 0 kg S/ha; B – 12.5 kg S/ha; C – 25 kg S/ha; D – 50 kg S/ha

amended with composts. Similar tendencies were observed for S_{ads} as well.

The S_{in} ($S_W + S_{ads} + S_{ocl}$) content confirmed the above mentioned tendencies. Calculated values ranged between 15.8 and 32.7 mg S/kg, whereas the lowest contents were always estimated at control sulfur non-fertilized treatment (A) and the highest at the treatment fertilized using 50 kg S/ha (D).

The highest S_{HI} amount was observed at D treatment and the lowest at A treatment. There, in contrast of inorganic sulfur fractions, outstanding differences between studied treatments were found. Values between 32.8 and 97.7 mg S/kg were found at the Hněvčeves site and values between 107.5 and 198.3 mg S/kg were even found at the Humpolec site.

From the results it is clear that the increase of S_{HI} content was caused by the parallel estimating of the S_{in} fraction. After calculating the estersulfate bound S content ($S_{HI} - S_{in}$) it is obvious, that using different fertilizers did not probably influence the content of S_{es} in soil. A signifficant S_{es} increase was observed only at treatment D in the year 2009. The values of S_{es} found corresponds to the results of Shan et al. (1997) who got the S_{es} range between 41 and 205 mg S/kg in pot experiments and between 61 and 274 mg S/kg in a field survey.

The aim of our experiment was also to evaluate the yields of oilseed rape (Table 5). There were no statistically significant differences between the studied treatments. Despite that, it is possible to assume that S-fertilizing using $CaSO_4$ S-form

Table 5. The yield of oilseed rape seeds at 12% moisture

Site	Treatment	2008		2009		2010	
		(t/ha)	SD	(t/ha)	SD	(t/ha)	SD
Hněvčeves	A	3.93	0.18	3.79	0.41	6.84	0.68
	B	4.21	0.14	4.13	0.07	6.88	0.88
	C	4.03	0.26	4.08	0.16	6.85	0.66
	D	4.33	0.14	4.31	0.19	7.02	0.85
Humpolec	A	3.06	0.18	3.17	0.05	2.70	0.11
	B	3.27	0.18	3.27	0.11	4.00	0.12
	C	3.15	0.13	3.27	0.14	3.59	0.11
	D	3.25	0.15	3.06	0.07	4.48	0.12
Uhříněves	A	3.65	0.21	4.69	0.37	–	–
	B	3.49	0.26	5.08	0.17	–	–
	C	3.59	0.14	5.41	0.07	–	–
	D	3.64	0.16	5.29	0.13	–	–

SD – standard deviation; A – 0 kg S/ha; B – 12.5 kg S/ha; C – 25 kg S/ha; D – 50 kg S/ha

positively influenced the oilseed rape yield. There are visible tendencies: the seed yields on non-S-fertilized treatments are usually the lowest and at the treatment fertilized using the highest S dose (50 kg S/ha) the highest yields were obtained. The highest yields were reached in the year 2010, where we got a range between 6.84 and 7.02 t of oilseed rape seed per ha at the Hněvčeves site. The least favourable was the year 2008, where we got the highest yields at the Hněvčeves site as well, but the values ranged only between 3.93 and 4.33 t/ha. The lowest yields were usually found at the Humpolec site, where are the worst soil-climatic conditions for oilseed rape cropping.

From our experiment is possible to conclude following facts: the S_w content ranged between 4.1 and 6.8 mg S/kg, the S_{ads} between 4.1 and 5.3 mg S/kg, the S_{ocl} between 3.1 and 8.6 mg S/kg and the S_{HI} between 35.1 and 175 mg S/kg.

The N-S fertilizer application (with the increasing S dose) increased the S_w and S_{ads} contents. The contents of S_{ocl} and S_{es} were probably not influenced by the chosen fertilizers.

The highest oilseed rape yields were always found at the Hněvčeves site and the lowest yields were usually observed at the Humpolec site.

Increasing S dose led usually to an increase of oilseed rape seed yield, but the differences between the observed treatments were not statistically significant.

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Received on June 24, 2010

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