Differences in soil sulfur fractions due to limitation of atmospheric deposition

J. Balík[1], M. Kulhánek[1], J. Černý[1], J. Száková[1], D. Pavlíková[1], P. Čermák[2]

[1]*Faculty of Agrobiology, Food and Natural Resources, Czech University of Life Sciences in Prague, Prague, Czech Republic*
[2]*Central Institute for Supervising and Testing in Agriculture, Brno, Czech Republic*

ABSTRACT

The aim of this work was to estimate the changes in contents of different sulfur (S) fractions in soils under conditions of lowering inputs of S from emissions together with the influence of application of manure and mineral fertilizers. Soil samples from long-term field experiments were used for this purpose. The samples were taken from 10 sites from precise long-term field experiments with different soil-climatic conditions in the Czech Republic. The samples were analyzed using the following fractionation: (i) water soluble S (H_2O extracts), (ii) sorbed S (0.032M NaH_2PO_4 extracts) and (iii) S occluded with carbonates (1M HCl extract). Furthermore, the concentration of total S (S_{tot}) and organic S (S_{org}) was determined. Soil samples were taken in the years 1981 and 2007. During 26 years a decrease of S_{tot} by about 3–8%, water soluble S by 65–68% and sorbed S by 39–44% were observed in the topsoil of the evaluated soils. Furthermore, a low increase in the content of organic S was observed. The estimated ratio of S_{org} reached 78.7–80.9% from S_{tot} in the year 1981 and 87.7–89.8% in 2007. Farmyard manure (40 t/ha) applied every 4 years did not have a significant influence on S fractions and S_{tot} contents in soils; intensive S fertilizing increased S_{tot} and mobile S forms contents in soils. Very close correlations were obtained especially between S_{tot} and water soluble S and organic S.

Keywords: soil; S; long term stationary experiments; S-fractionation; fertilizing

Sulfur deficiency in plant nutrition is an actual problem in the Czech Republic (Matula 1999, Matula and Pechová 2005, Vaněk et al. 2008) and in other European states (Scherer 2001, Zhao et al. 2003, Yang et al. 2007, Lehmann et al. 2008). Agricultural and horticultural crops are more susceptible to sulfur deficiency. Sulfur deficiency can be attributed to the decrease of atmospheric emissions, less intensive application of mineral fertilizers together with change of their composition, restriction of manure and cropping of plants with high S uptake in crop rotation (e.g. rape) on bigger areas.

The total content of S in soil usually ranges between 0.01 and 0.1% (Stevenson and Cole 1999, Balík et al. 2007, Morche 2008). The main portion of total S in soils is bound in soil organic matter (Eriksen et al. 1998, Kertesz and Mirleau 2004, Yang et al. 2007).

Plant available S consists of: (i) soluble inorganic SO_4^{2-}, (ii) sorbed inorganic SO_4^{2-}, (iii) the portion of organic S in soil that is mobilized during vegetation periods.

Although it is possible to estimate the content of inorganic fractions using different extractants, a satisfactory method for estimating mobile organic S is currently not known. For the quantification of inorganic fraction the following extractants are used: H_2O, $CaCl_2$, $Ca(H_2PO_4)_2$, NaH_2PO_4, KH_2PO_4, $NaHSO_3$ (Zhao and McGrath 1994, Matula 1999, Hu et al. 2005, Lehmann et al. 2008). The SO_4^{2-} ions in soil solution and weakly sorbed SO_4^{2-} are estimated using water extracts (Prietzel et al. 2001). The P-containing extractants are used to release

---

Supported by the Ministry of Education, Youth and Sports of the Czech Republic, Project No. MSM 6046070901, and by the Ministry of Agriculture of the Czech Republic, Project No. QH 81202.

water soluble forms and sorbed S. The extractants on the Cl^- basis mobilize water soluble SO_4^{2-} (Hu et al. 2005). The $CaCl_2$ solution has a lower extraction power because of the formation of lowly soluble $CaSO_4$ (Matula 1999); therefore, the water extraction is more suitable. The number of studies for estimating mobile fractions in soils has increased after the restriction of S emissions. The results of Lehmann et al. (2008) showed that during 150 years on the Rothamsted (UK) site, the content of different S fractions varied according to S emissions.

The aim of our experiment was to estimate the changes in different S fractions in soils that were influenced by lowering S inputs from emissions. Furthermore, the influence of manure and mineral fertilization was assessed.

MATERIAL AND METHODS

Topsoil (0–30 cm) samples from stationary long-term field experiments were used for the experiment. The experimental sites are owned by the Central Institute for Supervising and Testing in Agriculture (CISTA) Brno, Czech Republic. Samples from the years 1981 and 2007 were chosen. The stationary experiments on 10 sites with different soil-climatic conditions in the Czech Republic were established in the years 1966–1977. Basic agrochemical characteristics of the soil samples before establishing the experiments are presented in Table 1. Periodic crop rotation was used during the experiments (Table 2).

Three fertilization treatments were chosen: (i) control – not fertilized, (ii) farmyard manure, (iii) farmyard manure + mineral NPK fertilizing (Table 3). Each treatment was conducted in 6 replicates and then mixed together to get one representative soil sample from each treatment. The samples were always taken after the harvest of winter wheat in the years 1981 and 2007.

Fine soil was used for the analysis (< 2 mm). 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. Following the centrifugation, the samples were extracted with 0.032M 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. The rest of the soil sample was extracted with 1M HCl. The extraction ratio was 1:20 (w/v). After 60 min of shaking, the samples were centrifuged 10 min at 10 000 rpm.

Total concentrations of S in soils were determined in the digests obtained by the following decomposition procedure: Aliquots (0.5 g) of air-dried soil samples were decomposed in a digestion vessel with a mixture of 8 ml of concentrated nitric acid, 5 ml of hydrochloric acid, and 2 ml of concentrated hydrofluoric acid. The mixture was heated in the Ethos 1 (MLS GmbH, Germany) microwave-as-

Table 1. Agrochemical characteristics of the soils in the year of the experiments establishment

Site	Soil type	pH (KCl)	Nutrients-Mehlich 2 (mg/kg)				Content (%)		Texture classes (%)				
			P	K	Mg	Ca	N_{tot}	C_{ox}	< 0.001	0.001 –0.01	0.01 –0.05	0.05 –0.25	0.25 –2 mm
Horažďovice	cambisol	6.2	79	172	155	1648	0.12	0.80	6.70	13.7	16.6	18.8	44.0
Chrastava	cambisol	5.3	42	144	125	1425	0.08	0.99	10.5	17.8	56.1	13.8	1.80
Jaroměřice	haplic luvisol	6.1	73	201	199	2413	0.12	1.03	18.1	20.7	38.5	14.1	8.70
Krásné Údolí	cambisol	6.2	50	135	155	2134	0.14	1.09	5.90	16.6	20.5	25.6	21.4
Libějovice	haplic luvisol	5.7	79	150	105	1685	0.14	0.88	10.8	16.9	16.1	19.3	37.0
Lípa	cambisol	6.6	68	135	82	2075	0.13	0.99	7.90	17.8	24.5	20.9	28.9
Uherský Ostroh	haplic luvisol	6.9	63	293	165	3820	0.12	1.06	17.3	14.8	26.4	30.4	11.5
Pusté Jakartice	haplic luvisol	6.7	70	108	76	2142	0.12	0.97	10.1	18.0	61.8	8.70	1.50
Sedlec	chernozem	7.4	95	270	196	4501	0.12	1.34	16.2	16.0	40.9	23.9	3.10
Žatec	chernozem	7.3	91	265	277	4001	0.17	1.53	21.7	16.5	26.6	24.0	11.2

Table 2. Crop rotations on the different sites

Year	1	2
1	oat – alfalfa	oat – clover
2	alfalfa	clover
3	winter wheat	winter wheat
4	silage maize	potatoes
5	winter wheat	winter wheat
6	spring barley	spring barley
7	sugar beet	potatoes
8	spring barley	spring barley

1 – Uherský Ostroh, Pusté Jakartice, Sedlec, Žatec; 2 – Horažďovice, Chrastava, Jaroměřice, Krásné Údolí, Libějovice, Lípa

sisted wet digestion system for 33 min at 210°C. After cooling, the digest was quantitatively transferred into a 50 ml Teflon® vessel and evaporated to dryness at 160°C. The digest was then dissolved in a 3 ml nitric and hydrochloric acid mixture (1:3), transferred into a 25 ml glass tube, filled up with deionized water, and kept at laboratory temperature until measurement. The certified reference material RM 7003 Loam was applied for the quality assurance of analytical data.

The concentrations of S in soil digests and extracts were determined using optical emission spectroscopy with inductively coupled plasma (ICP-OES) with axial plasma configuration, Varian, VistaPro, equipped with autosampler SPS-5 (Australia). Operating measurement wavelength for ICP-OES was 180.7 nm for S. Measurement conditions were: power 1.2 kW, plasma flow 15.0 l/min, auxillary flow 0.75 l/min, nebulizer flow 0.9 l/min.

RESULTS AND DISCUSSION

The Czech Republic was known as an important S emitting country from the 1950s to the beginning of the 1990s. For example in the year 1991, the emissions in Prague region reached 394 kg S/ha, in the north Bohemian region 484 kg S/ha and in the rest of the Czech Republic they reached almost 100 kg S/ha (Tlustoš et al. 2001). New technologies of thermal power plant desulfurization significantly decreased SO_2 emissions. Therefore, dry + wet deposition is currently approximately 15–30 kg S/ha. It is possible to deduce that this change could significantly influence the total content of S in soils and its different fractions (Zhao et al. 2003).

Table 1 summarizes the agrochemical characteristics of the soils from different sites at the beginning of the long-term field experiments. Ten of the chosen sites represent well different soil-climatic conditions in the Czech Republic. These soils are usually loamy and the pH ranges between acidic and neutral values. In these long-term experiments stabile crop rotation was performed (Table 2). In this study, 3 treatments were chosen. The control treatment was not fertilized. Quality farmyard manure was periodically applied to treatments 2 and 3. Based on manure analysis in the last 10 years, it is possible to deduce that S input is approximately 8 kg/ha year (Table 3), which also corresponds to the results of Eriksen et al. (1998). Ammonium sulfate and simple superphosphate application before sowing to treatment 3 added high amounts of mineral S (99.2 kg S/ha year).

The plant material was not archived in the previous years of experiment. It is thus problematic to estimate S export through harvest. Zhao et al.

Table 3. Design of the experiment

No.	Treatment	Description	Average yearly S dose added with fertilizers (kg S/ha)
1	control	con	0
2	farmyard manure[1]	$FYM_{(+Ca)}$	8
3	farmyard manure + NPK[2] in mineral fertilizers	$FYM_{(+Ca)}$ + NPK	8 + 91.2

[1] 40 t farmyard manure/ha is periodically applied to the root crops (potatoes, sugar beet) in the crop rotation. The average farmyard manure dose is 10 t/ha year

[2] the amount of farmyard manure is same with the treatment 2. The average yearly dose of nutrients is: 69 kg N/ha, 50 kg P/ha, 59 kg K/ha. The nitrogen is applied together with the soil preparation in the ammonium sulfate form; to the fertilizing during vegetation nitrochalk is used. The source of phosphorus is simple granulated superphosphate (7.5% P). Potassium is applied in the potassium salt (50% K). The application of liming was effected by $pH/CaCl_2$ value and soil-climatic conditions at treatments 2 and 3

(2003) estimated that S ratio originating from the atmosphere accounted for 60–78% of total S uptake with harvest of winter wheat during maximal atmospheric deposition (year 1970). Therefore, we can assume that in our experiments this factor dominated between 1970 and 1995. From the exactly registered harvest results, from the different sites and average S uptakes from the literature, the yearly uptake of S was estimated to 13.1 kg S/ha at the control treatment, 14.0 kg S/ha at the $FYM_{(+Ca)}$ treatment and 22.0 kg S/ha at the $FYM_{(+Ca)}$ + NPK treatment. Higher contents (approximately by 1/3) of S due to intensive fertilization with mineral S form were calculated at the treatment 3.

Tables 4 and 5 summarize S contents using the fractionation of the soil samples from the years 1981 and 2007. The contents of plant available S (S_{H_2O}), exchangeable sorbed S ($S_{NaH_2PO_4}$) and occluded S (S_{HCl}) were estimated after Morche (2008). The content of organic S (S_{org}) was calculated as a difference between total S (S_{tot}) and sum of mineral S (S*). A decrease of total S content in soils was observed in time. Average contents observed at the control treatment were 221 mg S/kg in the year 1981 and 204 mg S/kg in 2007. Similar decreasing trends were observed at the treatment 2 (from 216 mg S/kg to 210 mg S/kg) and 3 (from 235 mg S/kg to 219 mg S/kg). The contents of S_{tot} ranged in dependence on the site and treatment between 133 and 334 mg S/kg in 1981 and between 105 and 321 mg S/kg in 2007. These soils follow similar S_{tot} trends as most European soils. Similar results in other European experiments were published also by Zhao et al. (2003), Lehmann et al. (2008) or Morche (2008).

The content of S_{H_2O} reached 22.6 mg S/kg at the control treatment in 1981 and was only about 7.20 mg S/kg in 2007, which represents only a fraction of 32% (Figure 1). Similar trends were obtained at the treatments 2 and 3 where it accounted for 33% and 35%, respectively. The measured results varied on the majority of sites (except Žatec) between 4–9 mg S/kg. This corresponds with the results of Balík et al. (2006) in other soil-climatic

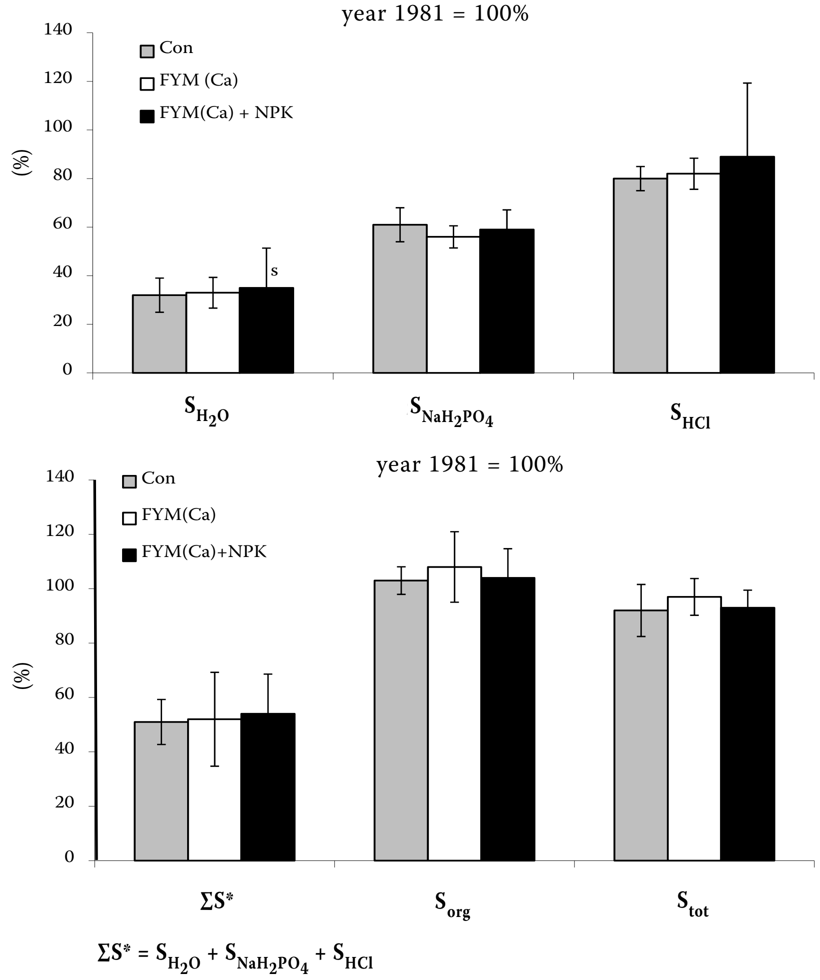

Figure 1. The average ratio (in %) of different S fractions in soils in the samples of the year 1981 compared to 2007

Table 4. The content of different S fractions, year 1981

Site	Treatment	S_{H_2O}	$S_{NaH_2PO_4}$	S_{HCl}	S*	S_{org}	S_{tot}
		(mg S/kg)					
Horažďovice	Con	14.4	6.10	12.4	32.9	187	219
	$FYM_{(+Ca)}$	15.6	7.10	15.2	37.9	170	208
	$FYM_{(+Ca)}$ + NPK	21.5	6.70	18.2	46.4	162	208
Chrastava	Con	41.2	16.0	21.7	79.3	244	323
	$FYM_{(+Ca)}$	35.7	13.0	19.5	68.5	229	297
	$FYM_{(+Ca)}$ + NPK	40.1	15.0	23.7	79.0	239	318
Jaroměřice	Con	18.9	7.50	8.27	34.7	228	262
	$FYM_{(+Ca)}$	19.3	7.40	9.13	35.8	172	207
	$FYM_{(+Ca)}$ + NPK	31.4	8.50	10.9	50.7	211	262
Krásné Údolí	Con	29.8	11.0	16.9	57.4	227	284
	$FYM_{(+Ca)}$	22.2	9.00	16.1	47.3	231	279
	$FYM_{(+Ca)}$ + NPK	25.5	9.00	25.1	59.6	215	274
Libějovice	Con	21.3	5.60	10.6	37.4	171	209
	$FYM_{(+Ca)}$	20.5	5.60	10.5	36.5	187	223
	$FYM_{(+Ca)}$ + NPK	24.9	6.60	13.9	45.5	175	221
Lípa	Con	18.3	9.40	11.4	39.1	147	186
	$FYM_{(+Ca)}$	19.1	8.70	10.8	38.6	120	159
	$FYM_{(+Ca)}$ + NPK	18.3	8.30	11.6	38.2	108	146
Ostroh	Con	14.1	5.40	10.7	30.2	134	164
	$FYM_{(+Ca)}$	15.4	5.80	8.90	30.0	124	154
	$FYM_{(+Ca)}$ + NPK	21.3	6.30	8.80	36.4	134	170
Pusté Jakartice	Con	19.2	6.40	8.40	33.9	99.2	133
	$FYM_{(+Ca)}$	16.7	5.80	7.30	29.8	104	133
	$FYM_{(+Ca)}$ + NPK	20.1	7.30	7.00	34.4	149	183
Sedlec	Con	24.0	8.30	14.7	47.1	187	234
	$FYM_{(+Ca)}$	22.2	9.00	11.2	42.4	168	210
	$FYM_{(+Ca)}$ + NPK	32.2	9.70	10.7	52.6	181	234
Žatec	Con	24.6	9.60	9.20	43.4	149	192
	$FYM_{(+Ca)}$	27.5	9.20	10.3	47.0	245	292
	$FYM_{(+Ca)}$ + NPK	38.5	9.00	11.1	58.6	275	334
Average of the sites	Con	22.6	8.50	12.4	43.5	177	221
	$FYM_{(+Ca)}$	21.4	8.10	11.9	41.4	175	216
	$FYM_{(+Ca)}$ + NPK	27.4	8.70	14.1	50.1	185	235

$S^* = \Sigma\ S_{H_2O} + S_{NaH_2PO_4} + S_{HCl}$

conditions in the Czech Republic and it confirms the need for S application through mineral fertilizers for sulfur-intensive crops. It is also necessary to mention that S analyses using ICP-OES estimate total extractable S and the ratio of total S with mineral S ranges between 50 and 90% (Kotková et al. 2008). The content of exchangeable sorbed S also decreased through the 26 years of experiment

Table 5. The content of different S fractions, year 2007

Site	Treatment	S_{H_2O}	$S_{NaH_2PO_4}$	S_{HCl}	S*	S_{org}	S_{tot}
		(mg S/kg)					
Horažďovice	Con	4.55	3.80	13.7	22.0	197	219
	FYM$_{(+Ca)}$	4.18	3.30	14.5	22.0	174	196
	FYM$_{(+Ca)}$ + NPK	7.49	3.40	9.00	19.9	179	199
Chrastava	Con	5.87	8.20	14.8	28.9	159	188
	FYM$_{(+Ca)}$	4.93	5.80	13.6	24.3	200	224
	FYM$_{(+Ca)}$ + NPK	8.37	6.00	12.7	27.0	253	280
Jaroměřice	Con	5.85	5.90	7.20	19.0	158	177
	FYM$_{(+Ca)}$	5.29	4.50	6.50	16.3	198	214
	FYM$_{(+Ca)}$ + NPK	7.05	5.00	7.40	19.4	178	197
Krásné Údolí	Con	9.55	4.70	10.8	25.1	265	290
	FYM$_{(+Ca)}$	8.12	4.50	10.8	23.3	233	256
	FYM$_{(+Ca)}$ + NPK	13.5	6.60	13.6	33.6	224	258
Libějovice	Con	4.90	2.60	7.50	15.0	155	170
	FYM$_{(+Ca)}$	5.68	4.00	12.3	21.9	178	200
	FYM$_{(+Ca)}$ + NPK	6.08	3.50	8.30	17.9	170	188
Lípa	Con	6.44	5.50	10.3	22.3	120	143
	FYM$_{(+Ca)}$	5.26	4.70	6.90	16.9	88.0	105
	FYM$_{(+Ca)}$ + NPK	6.88	4.20	10.0	21.0	97.0	118
Ostroh	Con	4.91	3.70	6.60	15.2	118	134
	FYM$_{(+Ca)}$	4.66	3.60	7.50	15.7	125	140
	FYM$_{(+Ca)}$ + NPK	7.84	4.90	8.00	20.7	178	199
Pusté Jakartice	Con	5.94	3.90	5.20	15.0	115	130
	FYM$_{(+Ca)}$	7.14	3.90	7.40	18.5	175	193
	FYM$_{(+Ca)}$ + NPK	8.88	4.10	8.10	21.1	160	181
Sedlec	Con	6.67	5.20	7.60	19.5	251	270
	FYM$_{(+Ca)}$	6.47	5.30	9.30	21.1	235	256
	FYM$_{(+Ca)}$ + NPK	11.0	5.90	28.2	55.1	215	270
Žatec	Con	17.6	8.20	15.5	41.3	280	321
	FYM$_{(+Ca)}$	19.1	6.20	9.00	34.3	284	318
	FYM$_{(+Ca)}$ + NPK	17.6	7.30	9.80	34.8	266	301
Average Of the sites	Con	7.20	5.20	9.90	22.3	182	204
	FYM$_{(+Ca)}$	7.10	4.60	9.80	21.4	189	210
	FYM$_{(+Ca)}$ + NPK	9.50	5.10	11.5	27.0	192	219

$S^* = \Sigma\, S_{H_2O} + S_{NaH_2PO_4} + S_{HCl}$

duration. Contents in the year 2007 decreased to 61% at the treatment 3 (Figure 1). From the results of Prietzel et al. (2001) it is clear that the SO_4^{2-} sorption intensity strongly depends on soil pH value and increases with increasing acidity. This was not verified in our experiments. With liming, the OH^- ion displaces the SO_4^{2-} from the sorption sites on the Fe and Al oxides and the

Table 6. The ratio (in %) of the different S fractions compared to the S_{tot} content in soils

Treatment	S_{H_2O}	$S_{NaH_2PO_4}$	S_{HCl}	S*	S_{org}	S_{tot}
Year 1981						
Con	10.2	3.9	5.6	19.7	80.3	100
$FYM_{(+Ca)}$	9.90	3.7	5.5	19.2	80.9	100
$FYM_{(+Ca)}$ + NPK	11.7	3.7	6.0	21.3	78.7	100
Year 2007						
Con	3.5	2.5	4.9	10.9	89.1	100
$FYM_{(+Ca)}$	3.4	2.2	4.6	10.2	89.8	100
$FYM_{(+Ca)}$ + NPK	4.3	2.3	5.3	12.3	87.7	100

$S^* = \Sigma\, S_{H_2O} + S_{NaH_2PO_4} + S_{HCl}$

sorption values of sulfates are underestimated (Evans 1986). In our experiment, lower contents at the treatment 2 (limed on some sites) compare to the treatment 1 were calculated, but the differences were not significant. Therefore, we can only speculate about some trends without significant relevance. The sorption could as well decrease due to increased sorption of organic anions after farmyard manure application. Other works are not uniform in this question. Although Haque and Walnsley (1973) estimated a positive correlation between the sorption of SO_4^{2-} and organic matter, Singh and Johnson (1986) obtained a negative correlation. The results of Kaiser and Zech (1996) show that organic acids anions block the sorption sites on hydrated Fe and Al oxides. Furthermore, the increasing concentration of phosphorus anions in soil solution decreases SO_4^{2-} sorption (Bohn et al. 1986). Therefore, application of phosphorus fertilizers increases the mobility of SO_4^{2-}. We cannot quantify how these factors influenced our experiments, although at the treatment 3, intensive phosphorus and S fertilization was performed. Our measured values correspond well with the results of Scott (1976), who found similar value in Australian soils, but are higher than Schnug's (1988) results from northern Germany.

Using the HCl extraction as a part of the fractionation should mobilize a major portion of S occluded with carbonates (Shan et al. 1992, Chen et al. 1997).

From the data presented in Tables 4 and 5 it is clear that high S contents on the Sedlec and Žatec sites were not found, which was previously expected (based on the soils characteristics). The values of pH/KCl were 7.3 (Žatec) and 7.4 (Sedlec). Calcium contents (Mehlich 2) were 4001 mg Ca/kg (Žatec) and 4501 mg Ca/kg (Sedlec). On the other hand, on the Chrastava site (acidic soils); the highest S_{HCl} contents were obtained. Therefore, using HCl does not selectively estimate only S occluded with carbonates. That confirms the results of Morche (2008); the data on occluded S obtained from this extraction are thus overestimated. From the comparison of the data from 1981 and 2007 a decrease of occluded S is apparent. The values of this fraction in the year 2007 reached only 80–89% from the year 1981.

The sum of the fractions S_{H_2O}, $S_{NaH_2PO_4}$ and S_{HCl} represents the so-called 'inorganic S' (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). Due to the significant restriction of atmospheric depositions during the last 20 years

Table 7. The values of the correlation coefficients between S_{tot} content and the different S fractions contents in soils (n = 30)

	1981				2007			
	S_{H_2O}	$S_{NaH_2PO_4}$	S_{HCl}	S_{org}	S_{H_2O}	$S_{NaH_2PO_4}$	S_{HCl}	S_{org}
Correlations with S_{tot}	0.811	0.685	0.622	0.987	0.720	0.558	0.373	0.993
P-value	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01	≤ 0.01

in the Czech Republic the ratio of inorganic S decreased by 50% (Figure 1). Intensive S fertilization (treatment 3) led to increased contents of inorganic S in soil (27 mg S/kg) in the year 2007. The ratio of different fractions (in %) from the total S content is mentioned in Table 6. Similar to the results of Chapmann (2001), organic S is the major fraction. It accounted for 78.7–80.9% from S_{tot} in the year 1981 and 87.7–89.8% in 2007. The experimentally estimated data in the year 2007 are close to the data presented by Kertesz and Mirleau (2004), who published a ratio of 95%. From the comparison of the results from 1981 and 2007, the content of inorganic S fractions decreased during 26 years. While the ratio ranged between 9.9 and 11.7% in the year 1981, it was only between 3.4 and 4.3% in 2007. The ratio of S occluded with carbonates ranged between 5.5–6.0% in the year 1981 and between 4.6–5.3% in 2007. Similar results (6.9% from total S) were mentioned also by Chen et al. (1997). Our results are significantly lower then the values from Roberts and Bettany (1985) for calcareous soils in Canada. The decreasing content of inorganic S was probably influenced by decreasing inputs and with elutriation losses. The content of S_{org} did not change. That corresponds also with a stable C_{ox} content. The average value of C_{ox} was 1.02% at the control treatment in the year 1981 and 1.04% in 2007, at the treatment $FYM_{(+Ca)}$ 1.04% in 1981 and 1.07% in 2007 and at the treatment $FYM_{(+Ca)}$ + NPK the content decreased from 1.15% in 1981 to 1.09% in 2007.

The values of correlation coefficients between different S fractions with S_{tot} are presented in Table 7. It is necessary to point out, that the high values were partly influenced by the evaluation of the long-term field experiments, where the closer relation can be expected. For both sets of samples a close relations between S_{H_2O} and S_{tot} were found. That indirectly confirms the usefulness of the S_{H_2O} extraction for S fertilizing optimization. The close relations between S_{org} and S_{tot} were influenced by the procedure of S_{org} estimation.

REFERENCES

Balík J., Pavlíková D., Tlustoš P., Černý J., Jakl M. (2007): The fluctuation of copper content in oilseed rape plants (*Brassica napus* L.) after the application of nitrogen and sulphur fertilizers. Plant, Soil and Environment, *53*: 143–148.

Balík J., Pavlíková D., Tlustoš P., Sýkora K., Černý J. (2006): The fluctuation of molybdenum content in oilseed rape plants after the application of nitrogen and sulphur fertilizers. Plant, Soil and Environment, *52*: 301–307.

Bohn H.L., Barrow N.J., Rajan S.S.S., Parfitt L. (1986): Reactions of inorganic sulfur in soils. In: Tabatabai M.A. (ed.): Sulfur in Agriculture. Agronomy Monography 27. ASA, CSSA and ISSSA, Madison, 233–249.

Chapmann S.J. (2001): Sulfur forms in open and afforested areas of two Scottish peatlands. Water, Air, and Soil Pollution, *128*: 23–39.

Chen B., Shan X.Q., Shen D.Q., Mou S.F. (1997): Nature of the HCl-soluble sulfate in the sequential extraction for sulfur speciation in soils. Fresenius' Journal of Analytical Chemistry, *357*: 941–945.

Eriksen J., Murphy M.D., Shung E. (1998): The soil sulphur. In: Schung E. (ed.): Sulphur in Agroecosystems. Kluwer Academic Publishers, Dordrecht, 39–73.

Evans A. jr. (1986): Effects of dissolved organic carbon and sulfate on aluminium mobilization in forest soil columns. Soil Science Society of America Journal, *50*: 1576–1578.

Haque I., Walmsley D. (1973): Adsorption and desorption reversibility in a variety of forest soils. Journal of Environmental Quality, *18*: 419–426.

Hu Z.Y., Zhao F.J., McGrath S.P. (2005): Sulphur fractionation in calcareous soils and bioavailability to plants. Plant and Soil, *268*: 103–109.

Lehmann J., Solomon D., Zhao F.J., McGrath S. (2008): Atmospheric SO_2 emissions since the late 1800s change organic sulfur forms in humic substance extracts of soils. Environmental Science and Technology, *42*: 3550–3555.

Kaiser K., Zech W. (1996): Nitrate, sulfate, and biophosphate retention in acid forest soils affected by natural dissolved organic carbon. Journal of Environmental Quality, *25*: 1325–1331.

Kertesz M.A., Mirleau P. (2004): The role of soil microbes in plant sulphur nutrition. Journal of Experimental Botany, *55*: 1939–1945.

Kotková B., Balík J., Černý J., Bazalová M. (2008): Crop influence on mobile sulphur content and arylsulphatase activity in the plant rhizosphere. Plant, Soil and Environment, *54*: 100–107.

Matula J. (1999): Use of multinutrient soil tests for sulphur determination. Communications in Soil Science and Plant Analysis, *30*: 1733–1746.

Matula J., Pechová M. (2005): Influence of gypsum treatment on extractability of nutrients from soils. Plant, Soil and Environment, *51*: 368–375.

Morche L. (2008): S-Flüsse und räumliche Veränderungen anorganischer und organischer Schwefelfraktionen im Boden sowie deren An- und Abreicherung in der Rhizosphäre landwirtschaftlicher Kulturpflanzen unter partiellem Einsatz des Radioisotops ^{35}S. [Dissertation.] Rheinischen Friedrich-Wilhelms-Universität, Bonn.

Prietzel J., Weick C., Korintenberg J., Seybold G., Thumerer T., Treml B. (2001): Effects of repeated $(NH_4)_2SO_4$ application on sulfur pool in soil, soil microbial biomass, and ground vegetation of two watersheads in the Black Forest/Germany. Plant and Soil, *230*: 287–305.

Roberts T.L., Bettany J.R. (1985): The influence of topography on the nature and distribution of soil sulfur across a narrow environmental gradient. Canadian Journal of Soil Science, *65*: 419–434.

Scherer H.W. (2001): Sulphur in crop production – invited paper. European Journal of Agronomy, *14*: 81–111.

Schnug B. (1988): Quantitative und qualitative Aspekte der Diagnose und Therapie der Schwefelversogung von Raps (*Brassica napus* L.) unter besonderer Berücksichtigung glucosinolatermer Sorten. [Habilitationnsschrift.] Agrawissenschaftliche Fakultät der Universität Kiel.

Scott N.M. (1976): Sulphate contents and sorption in Scottish soils. Journal of the Science of Food and Agriculture, *27*: 367–372.

Shan X.Q., Bin C., Long-Zhu J., Yan Z., Xiao-Ping H., Shi-Fen M. (1992): Determination of sulfur fractions in soils by sequential extraction, inductively coupled plasma-optical emission spectroscopy and ion chromatography. Chemical Speciation and Bioavailability, *4*: 97–103.

Singh B.R., Johnson D.W. (1986): Sulfate content and adsorption in soils of two forest watersheds in southern Norway. Water, Air, and Soil Pollution, *31*: 847–856.

Stevenson F.J., Cole M.A. (1999): Cycles of Soil – Carbon, Nitrogen, Phosphorus, Sulfur, Micronutrients. John Wiley and Sons Inc., New York, 427.

Tlustoš P., Pavlíková D., Balík J., Száková J. (2001): Sulphur cycle in the soil and in the environment. In: 7th International Conference Reasonable Use of Fertilizers Focused on Sulphur in Plant Production, Czech University of Life Sciences Prague, 20–26. (In Czech)

Vaněk V., Balík J., Šilha J., Černý J. (2008): Spatial variability of total soil nitrogen and sulphur content at two conventionally managed fields. Plant, Soil and Environment, *54*: 413–419.

Yang Z., Singh B.R., Hansen S., Hu Z., Riley H. (2007): Aggregate associated sulfur fractions in long-term (> 80 years) fertilized soils. Soil Science Society of America Journal, *70*: 163–170.

Zhao F.J., McGrath S.P. (1994): Extractable sulphate and organic sulphur in soils and their availability to plants. Plant and Soil, *164*: 243–250.

Zhao F.J., Knights J.S., Hu Z.Y., McGrath S.P. (2003): Stable sulfur isotope ratio indicates long-term changes in sulfur deposition in the Broadbalk experiment since 1845. Journal of Environmental Quality, *32*: 33–39.

Received on May 22, 2009

Corresponding author:

Prof. Ing. Jiří Balík, CSc., Česká zemědělská univerzita v Praze, Fakulta agrobiologie, potravinových a přírodních zdrojů, Kamýcká 129, 165 21 Praha 6, Česká republika
phone: +420 224 382 732, e-mail: balik@af.czu.cz