The effect of different rates and forms of sulphur applied on changes of soil agrochemical properties

M. Skwierawska, L. Zawartka, B. Zawadzki

University of Warmia and Mazury in Olsztyn, Olsztyn, Poland

ABSTRACT

A three-year field experiment was conducted from 2000 to 2002 in North-East Poland. Each year three sulphur fertilization rates in the form of sulphate ($S\text{-}SO_4^{2-}$) and pure ($S\text{-}S^0$) sulphur were applied: 40, 80 and 120 kg/ha. In the soil horizon at the depth of 0–40 cm the triple rate of $S\text{-}SO_4^{2-}$ and $S\text{-}S^0$ depressed soil reaction. Acidification of soil caused by $S\text{-}SO_4^{2-}$ became evident already in the first year of the study while that resulting from $S\text{-}S^0$ application appeared as late as in the third year. The effect of sulphur on soil in the 40–80 cm horizon was irregular. As the sulphur rates increased and the duration of the experiment progressed, sulphates accumulated in soil. In the 0–40 cm soil layer, the increasing rates of sulphur tended to increase the content of $N\text{-}NH_4^+$. In most objects, the NPK + S fertilization, and especially the single $S\text{-}SO_4^{2-}$ treatment, caused an increase in $N\text{-}NO_3^-$ in both soil layers compared with the NPK fertilized object. The dose of 120 kg/ha $S\text{-}SO_4^{2-}$ caused a significant increase in the concentration of available phosphorus in soil in the 0–40 and 40–80 cm layers.

Keywords: soil; sulphur; sulphate; soil pH; nitrogen; available phosphorus; potassium

High content of sulphur in soil causes soil contamination and acidification. Besides, it is indirectly responsible for mobilization of phytotoxic chemicals, such as aluminium and some trace elements (Komarnisky et al. 2003).

Optimum sulphur fertilization helps plants to grow and develop properly and improves utilisation of nutrients. At present, there is a growing interest in sulphur as a component of fertilizers, especially in non-industrialised areas situated far from large cities, where deficient quantities of sulphur in plants are detected. Insufficient concentrations of sulphur reduce plant production in many parts of the world, and S deficit has been observed in soils and agricultural systems for the last ten years due to several factors: depressed emission of sulphur to atmosphere, low concentration of sulphur in most of mineral fertilizers, which does not balance the loss of sulphur caused by its uptake by crops, low level of organic fertilization and migration of sulphates to deeper soil horizons and groundwater (Zhao et al. 1999, Fismes et al. 2000, Scherer 2001, Blake-Kalff et al. 2003, McGrath et al. 2003, Walker and Dawson 2003, Matula 2004). Although sulphur is more and more often considered to be an important element in fertilizers and is referred to as 'the fourth macroelement', it must be remembered that excessive amounts of sulphur can be toxic to plants, soil and water.

The purpose of the present study has been to determine the effect of fertilization with increasing rates of sulphur applied in the form of sulphates and as elementary sulphur on the content of total sulphur, sulphate sulphur, ammonia and nitrate nitrogen, available phosphorus, available potassium and the soil pH in soil at the depths of 0–40 cm and 40–80 cm.

MATERIAL AND METHODS

A three-year field experiment was conducted from 2000 to 2002 in North-East Poland. The locality is distant from larger industrial plants which emit sulphur compounds, and lies far from any big cities. As a result, no changes in the concentration of sulphur in the soil were caused by human activity.

The trial was set up on Dystric Cambisols (FAO), of the granulometric composition of heavy loamy sand. The initial soil had the following properties: $pH_{(KCl)}$ = 5.30, mineral nitrogen 24.0, sulphate sulphur 4.10, available phosphorus 34.5 and potassium 110.0 mg/kg of soil. The annual rates of sulphate sulphur ($S\text{-}SO_4^{2-}$) and elementary sulphur ($S\text{-}S^0$) were: S_1 – 40, S_2 – 80 and S_3 – 120 kg/ha.

The permanent experiment was established in a random block design and consisted of eight fertilization objects with four replications: (1) 0, (2) NPK, (3) NPK + $S_1\text{-}SO_4$, (4) NPK + $S_2\text{-}SO_4$, (5) NPK + $S_3\text{-}SO_4$, (6) NPK + $S_1\text{-}S^0$, (7) NPK + $S_2\text{-}S^0$, (8) NPK + $S_3\text{-}S^0$.

The NPK rates (Table 1) depended on the crop species and soil fertility.

The following fertilizers were applied after spring soil sampling: nitrogen – ammonium nitrate or ammonium sulphate, phosphorus – triple superphosphate, potassium – potassium chloride 60% or potassium sulphate, sulphur – potassium sulphate and, as a supplement, ammonium sulphate; in addition, elementary sulphur was applied on the objects where this form of sulphur was tested.

Soil samples were collected from each plot, at depths of 0–40 and 40–80 cm, prior to the establishment of the trials, after each harvest and before sowing of the consecutive crop. There was one exception to the routine – in spring 2001, due to a prolonged period of rains, soil samples were taken only from the 0–40 cm horizon. Air-dried soil was passed through a 1 mm mesh sieve. The soil samples were used to determine soil pH in 1 mol KCl (the ratio between soil and extraction 1:2.5); total sulphur (Butters and Chenery 1959) and $S\text{-}SO_4^{2-}$ with the turbidimetric method (the ratio between soil and extraction 1:3); $N\text{-}NO_3^-$ by colorimetry using phenyl disulphonic acid (the ratio between soil and extraction 1:5); $N\text{-}NH_4^+$ was determined using Nessler's reagent (the ratio between soil and extraction 1:5); available phosphorus and potassium was determined with Enger Riehm's method (DL) (the ratio between soil and extraction 1:50) (Panak 1997).

The results of the yields and chemical analysis of soil were processed statistically with the analysis of variance for a two-factor experiment in a random block design, using the form of sulphur as factor *a* and the rate of sulphur as factor *b*. Additional statistical analyses were performed with the software package Statistica 6.0 PL, to carry out the analysis of regression with Duncan's tests aiming at determining statistical differences between the sets of data.

Table 1. NPK rates applied in the trials

Crops	Year	N	P	K
		(kg/ha)		
Head cabbage	2000	200.0	52.5	180.0
Common onion	2001	160.0	60.0	183.0
Spring barley	2002	90.0	80.0	111.0

RESULTS AND DISCUSSION

Soil pH

In a three-year field experiment the influence of sulphate and elementary sulphur applied at different rates on changes in the soil pH was studied. After the first year of sulphur fertilization, at the soil depth of 0–40 cm (Table 2) a tendency towards soil acidification appeared, regardless of the form and rate of sulphur. However, when 120 kg $S\text{-}SO_4^{2-}$/ha was applied, the soil pH tended to be lower relative to the other fertilization objects. A similar relationship occurred in the 40–80 cm layer of soil (Table 2). The initial soil was poor in sulphur; that explains why the sulphur rates applied stimulated the crop yields and had no stronger influence on the physicochemical properties of the soil.

In spring 2001 the reaction determined in the soil horizon 0–40 cm ranged from 4.70 to 5.33 (Table 2). The object that received 120 kg of sulphate sulphur experienced a further drop in the soil pH during the following years of the trials. An addition of elementary sulphur meant that the soil pH increased relative to the control and $S\text{-}SO_4^{2-}$ fertilized objects. This may have resulted from the slower action produced by the former type of sulphur. Similar results were obtained by Motowicka-Terelak and Terelak (1998). In autumn 2001, after the onion harvest, the soil pH in the object fertilised with 120 kg $S\text{-}SO_4^{2-}$/ha decreased, which was similar to the effect obtained in the spring season. In the objects that received elementary sulphur, the soil pH was usually higher than in the other objects. No such relationship was observed for the samples taken at the depth of 40–80 cm (Table 2).

In the third year of the trials (prior to barley sowing), the pH of soil at the depth of 0–40 cm increased in general in all the objects compared to the autumn of 2001. In all the objects treated with elementary and sulphate sulphur the soil pH was lower compared to the control objects. Sulphate sulphur was found to have produced a stronger effect on soil pH than elementary sulphur. Similar percentages were reported by Jaggi et al. (1999)

Table 2. Effect of different rates and forms of sulphur on macroelements content in the soil layers at depths of 0–40 and 40–80 cm, before and after experiment (mg/kg soil)

Horizon	Treatments	Before experiment							After experiment						
		pH	S total	$S\text{-}SO_4^{2-}$	$N\text{-}NH_4^+$	$N\text{-}NO_3^-$	P	K	pH	S total	$S\text{-}SO_4^{2-}$	$N\text{-}NO_3^-$	$N\text{-}NH_4^+$	P	K
0–40 cm	0	5.29	54.6	4.7	4.0	11.4	38.2	42.5	5.39	45.6	1.60	10.6	4.40	27.4	14.2
	NPK	5.31	54.8	4.0	4.8	11.1	39.1	34.5	4.50	45.6	1.10	14.2	4.50	37.5	102.1
	NPK + S_1-SO_4	5.30	58.2	5.2	4.7	12.2	39.3	35.0	4.86	50.3	5.30	17.2	2.90	47.7	106.6
	NPK + S_2-SO_4	5.31	57.9	4.0	5.8	11.0	39.0	36.0	4.39	45.2	9.70	16.8	4.10	40.3	107.1
	NPK + S_3-SO_4	5.30	53.6	4.8	4.7	10.4	38.2	34.6	4.36	57.6	12.5	14.5	7.10	49.2	64.1
	NPK + S_1-S^0	5.28	49.1	4.9	5.6	11.4	39.2	38.3	4.43	46.6	5.40	12.7	4.00	38.0	50.2
	NPK + S_2-S^0	5.30	58.5	4.0	5.8	11.4	39.5	42.7	4.61	51.7	9.60	11.6	5.40	39.3	99.6
	NPK + S_3-S^0	5.30	57.8	4.2	5.9	11.2	39.5	36.3	4.37	55.6	11.0	12.3	6.50	44.7	79.8
								$LSD_{0.05}$							
	a	NS	NS	NS	NS	NS	NS	NS	0.202	1.59	0.37	0.900	0.320	1.64	3.98
	b	NS	NS	NS	NS	NS	NS	NS	0.285	2.25	0.52	1.270	0.450	2.32	5.63
	a × b	NS	NS	NS	NS	NS	NS	NS	0.404	3.18	0.74	1.800	0.630	3.29	7.96
40–80 cm	0	4.74	19.9	3.7	1.2	3.9	32.0	30.1	4.55	24.4	2.1	2.00	2.70	36.7	12.7
	NPK	4.68	20.2	3.8	1.9	3.4	30.7	29.0	4.47	22.5	3.0	3.70	4.50	32.4	54.7
	NPK + S_1-SO_4	4.75	22.8	2.5	0.9	3.8	31.0	31.5	4.58	31.6	3.5	4.00	3.50	28.3	40.5
	NPK + S_2-SO_4	4.63	20.9	3.2	1.2	4.0	27.7	27.2	4.63	20.5	6.9	3.30	3.90	22.0	27.6
	NPK + S_3-SO_4	4.76	23.2	3.3	1.6	3.9	31.3	40.5	4.59	48.6	9.2	5.90	4.80	49.9	11.7
	NPK + S_1-S^0	4.74	22.3	3.7	1.8	3.8	29.8	26.5	4.60	21.3	5.3	2.50	6.80	32.2	24.3
	NPK + S_2-S^0	4.73	24.0	3.2	1.8	3.8	29.8	33.3	4.66	25.7	5.2	2.30	4.30	35.1	16.8
	NPK + S_3-S^0	4.76	19.5	3.2	1.9	4.1	32.0	26.5	4.54	43.5	7.3	3.10	5.20	41.3	13.2
								$LSD_{0.05}$							
	a	NS	NS	NS	NS	NS	NS	NS	NS	1.06	0.25	NS	0.150	2.25	2.48
	b	NS	NS	NS	NS	NS	NS	NS	NS	1.50	0.35	0.310	0.220	3.18	3.51
	a × b	NS	NS	NS	NS	NS	NS	NS-	NS	2.12	0.49	0.430	0.300	4.50	4.96

a – form of sulphur; b – dose of sulphur; a × b – interaction; NS – no significant difference and Zhou et al. (2002). The biggest depression in the soil pH was recorded in the objects fertilized with 120 kg S-SO_4^{2-}/ha. With time, increasing rates of S-S^0 caused strong acidification of soil. The soil sampled at the depth of 40–80 cm was characterised by even soil pH except for the object fertilized with 120 kg S-SO_4^{2-}/ha. After the barley harvest (Table 2), in the 0–40 cm soil horizon, an addition of sulphur caused further depression in the soil pH, which was particularly evident when the triple rate of sulphur was applied. At the depth of 40–80 cm, neither the rate nor the form of sulphur had any effect on the modification of the soil pH relative to the control and NPK-fertilized objects (Table 2).

During the three years of the experiment, sulphate and elementary sulphur addition had a significant effect on changes in the soil pH at the depth of 0–40 cm (Table 2). The rate of 120 kg S-SO_4^{2-}/ha and S-S^0 caused a significant decline in the soil pH compared to the control object. At the deeper layer of soil (40–80 cm) the soil pH was in general more even and lower than in the topsoil layer in the analogous objects.

An analysis of differences with Duncan's test showed some statistically significant differences between the objects during the three years of the trials. The most conspicuous was the object that received the triple dose of sulphate sulphur, in which the average soil pH was the lowest and significantly different from the other fertilized objects.

Rate 120 kg S-SO_4^{2-}/ha and S-S^0 depressed soil pH in the 0–40 cm soil horizon. Acidification of soil caused by S-SO_4^{2-} became evident already in the first year of the trials, while that produced by S-S^0 did not occur until the third year. The influence of sulphur on soil pH at the depth of 40–80 cm was irregular.

Sulphur

Prior to the establishment of the field experiment, the content of total sulphur in soil was uniform all over the field, including both 0–40 and 40–80 cm layers (Table 2). At the depth of 40–80 cm the content of total sulphur was about 2.5-fold lower than in the more superficial layer of 0–40 cm. Once the experiment was terminated, both soil horizons were determined to contain significantly higher amounts of total sulphur, having received a single and triple rate of S-SO_4^{2-} as well as a single and triple rate of elementary sulphur compared to the NPK object. In the remaining objects, the content of total sulphur was on a similar level to that determined in the NPK object.

After the trials, the objects that were fertilized with sulphur were observed to have a drastically lower concentration of total sulphur in the soil sampled at the depth of 0–40 cm (a 16% decrease) whereas the soil sampled at the 40–80 cm depth was found to contain elevated total sulphur concentration (from 11 to 36%) compared to soil samples taken in spring 2000.

The S-SO_4^{2-}content in soil depended on the rate and form of sulphur applied as well as on the duration of the experiment (Table 2). Higher sulphur rates tended to result in higher concentration of sulphates in soil as compared to the lower fertilization doses. In autumn 2000 and 2001 (after the harvest of sulphidic crops), the accumulation of S-SO_4^{2-} in both soil layers (Table 2), after single- or double-dose fertilization treatments was similar to or lower than in the NPK object. The double rate of S-SO_4^{2-} applied in autumn 2001 was an exception as it actually increased the content of S-SO_4^{2-} in soil at the depth of 0–40 cm.

Once the field trials were terminated, the content of sulphates in soil sampled at 0–40 cm of depth (Table 2) under the influence of the fertilization rate equalled 40 kg S-SO_4^{2-}/ha and S-S^0 remained on a level that was comparable to that determined before the experiment. By increasing the fertilization rates, the content of sulphates in soil was considerably raised. It was demonstrated that accumulation of sulphates in soil sampled at both depths tended to be higher in spring than in the autumn of the previous year, especially after the application of S-S^0.

The accumulation of sulphates in soil (at both depths) occurred in the third year of the experiment in all the NPK + S fertilized objects. The actual content of sulphates in soil depended on a sulphur fertilization rate and was the highest following the application of 120 kg S. The use of elementary sulphur as a fertilizer in the first and second year of the trials did not affect the concentration of S-SO_4^{2-} in soil. Nonetheless, in the third year the concentration of S-SO_4^{2-} became uniform in all the sulphur-fertilized objects, irrespective of the form of sulphur used. This suggests that elementary sulphur is gradually oxidized, which was also confirmed by Wen et al. (2001).

The levels of sulphates in soil sampled at both depths throughout the three years of the trials are verified by the results of the calculations on the significance level of differences in the concentration of sulphates in soil, derived from the Duncan's test. Analysis of the results of this statistical assay enabled us to discover that fertilization with 80 and 120 kg S/ha caused increased S-SO_4^{2-} accumulation in soil compared to the NPK and control objects.

In general, NPK + S fertilization, especially if applied at the rate of 120 kg S/ha, caused an increase in the content of organic sulphur in soil, at both 0–40 and 40–80 cm depths, as compared to NPK-fertilized objects. As the rates of sulphur rose and the duration of the experiment progressed, accumulation of sulphates in soil was observable. The effect of sulphate sulphur fertilization on increasing content of S-SO_4^{2-} in soil at the depth of 0–40 cm was evident already in the first year of the trials, whereas the influence of elementary sulphur became noticeable as late as in the third year of the experiment. Such a tendency did not occur in the soil layer sampled at the depth of 40–80 cm.

Nitrogen

The soil sampled in spring each year from the depth of 0–40 cm (Table 2) was observed to have experienced increased accumulation of N-NH_4^+ compared to the soil collected in autumn the previous year. Higher rates of sulphur tended to result in increased levels of N-NH_4^+ in soil after harvest compared to lower ones. This tendency was particularly evident in the second and third year of the trials. In the deeper layer of soil (40–80 cm) modifications in the content of N-NH_4^+ in soil did not reveal any regularity (Table 2).

Concentrations of N-NO_3^- in soil sampled at 0–40 cm are presented in Table 2. Autumn soil sampled from that layer of the NPK + S fertilized objects accumulated less nitrates than soil sampled in the following spring. On the other hand, soil taken from the deeper layer (40–80 cm) contained more nitrates than soil sampled at the same depth in the previous autumn (Table 2).

During the whole period of trials, no constant and unambiguous correlations were observed between the form and rate of sulphur on the one hand and the concentration of nitrates on the other hand. However, it was noticed that in most objects the NPK + S fertilization, especially the single S-SO_4^{2-} treatment, contributed to raised N-NO_3^- levels in both soil layers as compared with the NPK fertilized objects.

The above relationships were reflected in the calculations of the significance of differences in the concentration of nitrates in soil, performed with the Duncan's test.

Soil sampled at 0–40 cm accumulated more N-NH_4^+ under the effect of increased sulphur rates. In the deeper soil layer (40–80 cm) modifications in the concentration of N-NH_4^+ revealed no unanimous tendency. In most objects, the NPK + S fertilization, especially that in the form of a single S-SO_4^{2-} rate, contributed to increased concentration of N-NO_3^- in both soil layers compared to the NPK fertilized objects.

Phosphorus

During the whole duration of the field trials, the results demonstrating the effect of fertilization with different forms and rates of sulphur on the content and transfer of available phosphorus in soil were inconsistent (Table 2). Only one rate, namely 120 kg S-SO_4^{2-}/ha initiated mobilization and migration of phosphorus in soil throughout the whole period of the field trails.

The available references contain diverse interpretation of the influence of sulphur on the dynamics of available phosphorus in soil. The differences stem from changes in soil pH, competition among sulphate ions, mineralization of phosphorus organic forms (Jaggi et al. 2005) as well as liberation of aluminium and iron ions, which bind fewer phosphate ions by reacting with sulphates. Besides, the presence of free sulphur acid in sulphur-rich soils creates favourable conditions for the release of phosphorus from compounds that are hardly soluble (Gądor and Motowicka-Terelak 1986).

The effect produced by elementary sulphur depended on the rate of its oxygenation in soil and its dose. This is proven by that fact that the concentration of available phosphorus in soil increased as late as in the third year of our experiment and only in the object fertilized with 120 kg S-S^0/ha. Our findings are confirmed by Germida and Janzen (1993) as well as by Watkinson and Lee (1994). Lindemann et al. (1991) found no increase in available phosphorus in soil following fertilization treatments with elementary sulphur, even though the soil pH was lowered and the amount of the sulphate form in soil increased. According to Jaggi et al. (2005), addition of elementary sulphur improves the availability of phosphorus in cultivated soils, irrespective of the soil initial pH.

The computation of the level of significance of the differences performed with the Duncan's test showed statistically significant differences between particular objects during the three years of the experiment. The object fertilized with triple dose of sulphate sulphur was the most distinct as the average content of available phosphorus determined in its soil was the highest and significantly different from the values established in the other fertilization objects.

The application of 120 kg S-SO_4^{2-}/ha caused a significant increase in the content of available phosphorus in soil in the 0–40 and 40–80 cm layers. All rates of elementary sulphur as well as those of 40 and 80 kg/ha of sulphate sulphur produced only an increasing tendency in the soil concentration of phosphorus. The effect of elementary sulphur on mobilization of phosphorus in soil revealed itself as late as in the third year of the experiment.

Potassium

In autumn, after the cabbage harvest, the use of higher S-SO_4^{2-} rates, especially those of 80 and 120 kg/ha, significantly depressed the content of available potassium relative to the NPK object and analogous objects fertilized with elementary sulphur. In the 40–80 cm soil layer (Table 2), in general, addition of sulphate or elementary sulphur significantly decreased the content of potassium in soil compared to the NPK object.

After the onion harvest (autumn 2001), at the depth of 0–40 cm, sulphur fertilization (in one case 120 kg S-S^0) caused a large decrease in the potassium concentration in soil relative to the NPK object. In the 40–80 cm soil layer (Table 2), the rate of 120 kg S-SO_4^{2-}/ha as well as all the rates of elementary sulphur depressed the concentration of available potassium in soil relative to the NPK object.

NPK fertilization after the barley harvest, either with or without sulphur, caused a very significant increase of available potassium content in the 0–40 cm soil layer. In the objects that received 40 or 80 kg S-SO_4^{2-} or 80 kg S-S^0/ha the soil was considerably enriched in this form of potassium whereas in the remaining objects the modifications in the amounts of available potassium were irregular. The deeper soil layer (40–80 cm) was characterised by a considerably lower concentration of available potassium than the 0–40 cm soil layer. There was a very clear tendency towards decreasing potassium concentrations in soil after the application of higher rates of either form of sulphur, especially those with 120 kg S-SO_4^{2-} and S-S^0/ha.

During the three years of the experiment, in the 0–40 cm soil layer (Table 2), when higher doses of sulphate sulphur were applied, the concentration of available potassium in soil was observed to have decreased. In contrast, as a result of the application of elementary sulphur the soil became richer in available potassium. In the 40–80 cm soil layer, application of higher rates of sulphur (in either of the forms) depressed the concentration of available potassium in soil compared to the NPK fertilized object (Table 2). The elementary form of sulphur caused a small albeit significant depression in the soil content of available potassium compared to sulphate sulphur.

When the data underwent the Duncan's test of significance levels, it was determined that fertilization with an additional dose of sulphur tended to result in significant modifications in the amounts of available potassium versus the NPK object. In one case (40 kg S-SO_4^{2-}/ha) the differences were not significant.

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Corresponding author:

Dr. Ing. Małgorzata Skwierawska, University of Warmia and Mazury in Olsztyn, Department of Agricultural Chemistry and Environmental Protection, ul. Oczapowskiego 8, 10-718 Olsztyn, Poland
e-mail: gosus1@wp.pl