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THE EFFECT OF DIFFERENT FORMS OF SULPHUR ON ITS CONTENT IN PLANTS

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ABSTRACT

Background. In addition to N, P and K, S is a valuable plant nutrient that determines the size, and quality of harvested crop yields. Its deficiency leads to lower yields of plants and deterioration of their quality parameters.

Material and methods. The research was aimed to determine the effect of S fertilizer in various forms on the content of this component (S_{tot} and SO_4-S) in the dry matter (DM) of tested plant species: spring wheat (*Triticum aestivum* L.), white mustard (*Sinapis alba* L.), spring oilseed rape (*Brassica napus* L. var. *napus*), spring barley (*Hordeum vulgare* L.) and orchard grass (*Dactylis glomerata* L.). The study was performed based on a strict three-year pot experiment. The variable factor was S applied in seven different forms, plus the control – without S fertilization. The subject of the research were treatments: the control – without S fertilization (1); RSMS – sulphate-urea solution with addition of $Na_2S_2O_3{\cdot}5H_2O$ (2); $(NH_4)_2SO_4$ (3); K_2SO_4 (4); Na_2SO_4 (5); elemental sulphur (S-S°) (6); $CaSO_4{\cdot}2H_2O$ (7); H_2SO_4 (8).

Results. The highest content of total sulphur occurred in the vegetative and generative parts of spring wheat fertilized with sulphur in the form of RSMS. In barley and orchard grass, similar trends were found after the application of K_2SO_4, H_2SO_4 and $CaSO_4{\cdot}2H_2O$. The most favourable form of sulphur applied for the total sulphur concentration in the vegetative parts of white mustard and spring oilseed rape was RSMS, for white mustard seeds – S-S° and H_2SO_4, while for the generative parts of spring oilseed rape – K_2SO_4. Among the used forms of S nutrition, the largest impact on SO_4^{2-}-S content was exerted by this component application as RSMS (in spring wheat, white mustard seeds, spring barley grains), K_2SO_4 (straw of white mustard, seeds of spring oilseed rape) and S-S° (straw of spring barley, orchard grass).

Conclusion. Among the sulphur forms used, the largest amounts of total sulphur were found in the dry matter of the tested plants in which RSMS, K_2SO_4, H_2SO_4 and $CaSO_4{\cdot}2H_2O$ were used in cultivation. However, in the case of sulphate sulphur, this referred to the use of RSMS, K_2SO_4 and S-S°.

Key words: sulphate sulphur, sulphur fertilization, sulphur forms, sulphur total

INTRODUCTION

Besides nitrogen, potassium and phosphorus, sulphur performs important physiological functions in plant metabolism. Its deficiency leads to lower yields of plants and deterioration of their quality parameters (Podleśna, 2006; Bednarek *et al*., 2008; Podleśna, 2009). Despite its significance, until the early 1980s the important role of sulphur in plant production did not receive too much attention, which was mainly due to the fact that in most parts of Europe, sulphur balance was positive (Szulc *et al*., 2004; Barczak *et al*., 2011).

Lowering the sulphur deposit from the atmosphere and a decline in the quantity introduced along with mineral fertilizers have led to a shortage of this nutrient in crop production. Sulphur deficit in the

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environment of the plant growth was found in 73 countries of the world, including 18 countries in Europe (Szulc *et al*., 2004; Brodowska and Kaczor, 2007).

In such situation, it is feared that NPK fertilization used in accordance with the nutritional requirements of plants would not be fully balanced and sulphur deficit in the environment of plant growth may limit the utilization of other ingredients, in particular nitrogen (Barczak *et al*., 2011).

Therefore, the purpose of the study was to evaluate the fertilizing effect of S in various forms on the content of S_{tot} and SO_4-S in crops, especially for plants susceptible to sulphur deficiency in the environment.

MATERIAL AND METHODS

The study was carried out based on a strict three-year pot experiment using throughout the experiment the soil material collected from the topsoil of lessive soil with a particle size of silt loam. The soil was characterized by a low level of available SO_4-S (12.0 $mg \cdot kg^{-1}$ soil). The experiment was established by means of a complete randomization. The variable factor was sulphur that was applied in seven different forms plus the control – without S fertilization. The subject of the research were treatments: the control – without S fertilization (1); RSMS – sulphate-urea solution with addition of $Na_2S_2O_3 \cdot 5H_2O$ (2); $(NH_4)_2SO_4$ (3); K_2SO_4 (4); Na_2SO_4 (5); elemental sulphur (S-S°) (6); $CaSO_4 \cdot 2H_2O$ (7); H_2SO_4 (8).

Sulphur fertilization was applied annually based on plant nutritional requirements (S – 0.012 $g \cdot kg^{-1}$ soil for cereals and orchard grasses and S – 0.024 $g \cdot kg^{-1}$ soil for spring oilseed rape and white mustard).

In the first year of the study, spring wheat (*Triticum aestivum* L.) of Ismena cv. and white mustard (*Sinapis alba* L.**)** of Borowska cv. were the test plant species. In the second year, spring oilseed rape (*Brassica napus* L. var. *napus*) of Sponsor cv. and spring barley (*Hordeum vulgare* L.) of Rataj cv. were grown. And in the third year, the test plants were barley (*Hordeum vulgare* L.) of Rataj cv. and orchard grass (*Dactylis glomerata* L.) of Bepro cv. Pots filled with 3 kg DM (dry matter) of soil were used for the experiments. In all experimental treatments, in each year, NPKMg fertilization was used in the amount consistent with the plants nutritional requirements (spring wheat, white mustard and spring barley: N – 0.14 $g \cdot kg^{-1}$ of soil, K – 0.075 $g \cdot kg^{-1}$ of soil, P – 0.038 $g \cdot kg^{-1}$ of soil, Mg – 0.015 $g \cdot kg^{-1}$ of soil; spring oilseed rape: N – 0.28 $g \cdot kg^{-1}$ of soil, K – 0.015 $g \cdot kg^{-1}$ of soil, P – 0.076 $g \cdot kg^{-1}$ of soil, Mg – 0.03 $g \cdot kg^{-1}$ of soil; orchard grass: N – 0.21 $g \cdot kg^{-1}$ of soil, K – 0.11 $g \cdot kg^{-1}$ of soil, P – 0.057 $g \cdot kg^{-1}$ of soil, Mg – 0.23 $g \cdot kg^{-1}$ of soil). Particular nutrients were administered in the following forms: N – NH_4NO_3, RSM, $(NH_4)_2SO_4$; P – $Ca(H_2PO_4) \cdot H_2O$; K – KCl, K_2SO_4; Mg – $MgCl_2 \cdot 6H_2O$. During the growing season, constant soil moisture was maintained at the level of 60% of the field water capacity.

Each experimental plant was grown in triplicate. The harvest of plants was carried out at the full maturity phase of wheat, barley, mustard, oilseed rape and in two cuts of orchard grass (Table 1). After harvesting, a statistical evaluation of yield was made. This evaluation was performed by means of a variance analysis for factorial experiments using Tukey's confidence intervals ($P < 0.05$) (Greń, 1974). The variable factor was the form of sulphur.

After harvesting and extracting the plant material using 2% CH_3COOH with the addition of activated carbon, the contents of sulphate sulphur was determined with nephelometry. Total sulphur was determined by the Butters-Chenery method (Butters and Chenery, 1959). Analyses of the plant material were performed in two replicates in averaged treatment samples. The tables show mean values.

RESULTS AND DISCUSSION

Fertilization of the test plants with the analysed forms of sulphur had an impact on the content of this element in plants. When determining the degree of plant nutrition with sulphur, various types of plant indicators can be helpful. Among them, the most frequently used are the following: the content of total sulphur, the content of SO_4-S, the N:S ratio, and the ratio of SO_4-S to S_{tot} (Mc Grath *et al*., 1996; Jackson, 2000). It is difficult to univocally determine which of the above indicators is the best. Its selection should be determined at first by a plant species, the sulphur supply status of which is to be evaluated (Mc Grath *et al*., 1996; Wielebski, 2011).

The highest content of S_{tot} in the straw of spring wheat was recorded in the treatment where RSM with the addition of sulphur was used (Table 2).

A similar situation occurred in the case of spring wheat grain. Also, generative parts of the species grown in the treatment fertilized with sulphur in the form of RSMS were characterized by the highest content of S_{tot}. An appropriate level of spring wheat supply in sulphur is extremely important. Deficiency of this nutrient decreases the quality of wheat flour by deterioration of its "baking value". This is due to the positive correlation between sulphur content in flour and dough elasticity (Mc Grath *et al.*, 1996). The problem concerns especially organic products which are not allowed to contain substances that increase the baking value of flour (Mc Grath *et al.*, 1996; Girma *et al.*, 2005).

Table 1. The effect of different forms of sulphur on plant yield (Kozłowska-Strawska *et al.*, 2018)

Treatment	First year of study		Second year of study		Third year of study	
	spring wheat	white mustard	spring oilseed rape	spring barley	spring barley	orchard grass
	g·pot^{-1} DM					
	Straw					first cut
Control	13.52	12.98	5.97	12.32	8.35	1.05
RSMS	15.70	21.50	30.03	22.12	23.18	1.33
$(NH_4)_2SO_4$	22.78	22.70	38.43	14.19	13.06	1.76
K_2SO_4	22.78	24.17	41.04	12.81	7.63	2.26
Na_2SO_4	22.33	24.38	41.46	16.52	14.49	1.84
S-S°	22.74	23.71	38.37	13.88	13.22	1.88
$CaSO_4·2H_2O$	22.88	22.19	38.56	15.26	12.93	1.68
H_2SO_4	23.17	23.98	38.28	15.94	13.17	1.66
$LSD_{0.05}$ S form	1.75	10.12	4.74	2.29	5.26	1.15
	Grain/seed					second cut
Control	10.79	0.11	X	3.22	2.79	1.75
RSMS	11.16	6.46	6.46	15.14	31.26	1.56
$(NH_4)_2SO_4$	17.91	5.18	16.85	12.72	17.84	3.82
K_2SO_4	17.15	5.64	12.66	11.43	10.71	4.54
Na_2SO_4	17.14	5.10	17.47	15.51	19.16	2.26
S-S°	17.09	5.14	13.63	12.59	16.22	4.30
$CaSO_4·2H_2O$	17.04	4.99	14.60	13.23	17.82	3.04
H_2SO_4	17.87	5.26	14.44	14.16	17.48	3.49
$LSD_{0.05}$ S form	2.53	5.26	6.25	1.09	4.38	3.76

X – no material

For white mustard straw, like for spring wheat, fertilization with sulphur in the form of RSMS had the most beneficial effect on the S_{tot} content. It was most probably related to the form in which sulphur was applied and the speed of its uptake from the soil. Seeds with the highest contents of this sulphur form were recorded in treatments in which elemental S and H_2SO_4 were used during cultivation. It was also confirmed by a study carried out by Bloem (1998). These authors emphasize that cabbage plant species accumulate much more sulphur in seeds than in straw.

Table 2. The total sulphur content in plants, g·pot^{-1}

Treatment	First year of study		Second year of study		Third year of study	
	spring wheat	white mustard	spring oilseed rape	spring barley	spring barley	orchard grass
			Straw			first cut
Control	0.45	0.76	0.97	0.53	1.04	3.00
RSMS	1.92	2.80	2.60	1.25	2.23	3.22
$(NH_4)_2SO_4$	0.75	1.41	2.21	1.29	2.17	3.45
K_2SO_4	0.82	1.66	1.93	1.37	2.31	3.90
Na_2SO_4	0.71	1.64	2.19	1.33	1.93	3.45
S-S°	0.67	1.11	1.58	1.35	2.09	3.71
$CaSO_4 \cdot 2H_2O$	0.59	1.21	2.03	1.27	1.92	3.79
H_2SO_4	0.76	1.28	2.52	1.28	1.83	4.00
Average	0.83	1.48	2.00	1.21	1.94	3.57
			Grain/seed			second cut
Control	0.69	0.25	X	0.77	1.03	3.98
RSMS	1.41	8.61	2.23	1.12	1.78	3.40
$(NH_4)_2SO_4$	0.91	8.51	2.38	1.06	1.38	3.17
K_2SO_4	1.01	8.39	2.70	0.92	1.86	3.47
Na_2SO_4	1.05	8.59	2.48	0.85	1.71	3.40
S-S°	1.04	8.98	2.38	1.15	1.52	3.54
$CaSO_4 \cdot 2H_2O$	1.01	8.35	2.46	1.24	1.45	3.54
H_2SO_4	1.02	8.97	2.35	1.34	1.69	3.48
Average	1.02	7.58	2.43	1.06	1.55	3.50

X – no material

McGrath *et al*., (1996) suggest that for winter oilseed rape harvested at the flowering stage, S_{tot} concentration is accepted as the best indicator informing about the plant supply in sulphur. The N:S ratio in leaves is considered less useful, because there is a linear correlation with the seed yield, hence there is no possibility to set up any critical values. Under conditions of intensive nitrogen fertilization and sulphur deficiency, the N:S ratio isclearly decreased, which results from an increase in non-protein nitrogen content in a plant. It contributes to a decrease in yields and deterioration of its qualitative parameters (Kaczor and Zuzańska, 2010; Wielebski, 2011). The straw from spring oilseed rape grown in the second year of the experiment was characterized by the highest S_{tot} content in the treatment where sulphur was introduced as RSMS. Application of H_2SO_4 had also a beneficial effects on the quantity of S_{tot}. The situation was slightly different in the case of spring oilseed rape seed. Considering the generative parts of the plant, the highest quantity of S_{tot} was recorded in the treatment where S was introduced in the form of K_2SO_4. High content of S_{tot} in the straw of barley grown in the second and third years of the study was found after the application of S in the form of K_2SO_4. Depending on the year of the study, the grain contained an increased S_{tot} amount after the introduction of $CaSO_4{\cdot}2H_2O$ and H_2SO_4 (2^{nd} year of the experiment) and after introducing sulphur as RSMS and K_2SO_4 (3^{rd} year of the study). It was also confirmed by results obtained by Kaczor and Łaszcz--Zakorczmenna (2003), who emphasize a clear increase in S_{tot} content in the straw and grain of spring barley fertilized with sulphur. Meanwhile Inal *et al*., (2003) indicate that S concentration in a plant may be an excellent reflection of sulphate availability in soil. In the case of the first cut of orchard grass, a sharp rise in S_{tot} was reported after fertilizing the plants with sulphur in the forms of K_2SO_4 and H_2SO_4. For comparison, in the second cut, the highest content of S_{tot} characterized plants from the control object (S_0) while, mean sulphur concentration for Polish grasses is considered to be 2.1 $g{\cdot}kg^{-1}$ DM (Motowicka--Terelak and Terelak, 2000). Among the introduced sulphur forms, the use of this component in the form of elemental S and $CaSO_4{\cdot}2H2O$ had the most beneficial impact on the content of S_{tot}. An adequate supply of orchard grass in sulphur is essential for the quality of harvested yields of this crop. Under conditions of insufficient plant supply in sulphur, the inhibition of protein synthesis and reduction in the content of sulphur amino acids occurs. Limiting the protein synthesis also results from the disruption in the nitrate reductase functioning. In the absence of sulphur, the activity of this enzyme is considerably diminished, which in turn promotes an excessive accumulation of non-protein nitrogen forms, in particular nitrates. This has a great impact on the forage value of grasses (Kaczor and Zuzańska, 2009; 2010).

Fertilization of the test plants using the analysed forms of sulphur also affected the content of SO_4-S in plants (Table 3). It is often emphasized in the literature (Brodowska and Kaczor, 2007; Kozłowska--Strawska and Badora, 2013) that the content of SO_4-S in dry matter of plants clearly increases as a result of their better supply in this nutrient. This problem is especially important in view of intensifying crop production and increased plant demand for sulphur (Bednarek *et al*., 2008). As in the case of S_{tot}, the highest contents of SO_4-S have been shown by the vegetative and generative parts of spring wheat, for which sulphur fertilizer was used in the form of RSMS.

Direction and magnitude of changes in the content of SO_4-S in the dry matter of spring wheat therefore depended primarily on the S form and status of the plant supply in this nutrient, and to a lesser extent, on the analysed part of the plant. Similar conclusions were also drawn in the study by Brodowska and Kaczor (2007), who emphasized that better plant supply in S is associated with an increase in SO_4-S content in their dry matter. In contrast to the spring wheat, higher SO_4-S contents were recorded in the straw of white mustard from treatments where Na_2SO_4 and K_2SO_4 were used, as well as in seeds of plants grown in treatments with RSMS application. The positive effect of Na_2SO_4 on S content in white mustard pods was also reported in the research by Filipek-Mazur and Gondek, (2005), who found that a higher content of this element can be detected in plants after fertilization of white mustard using Na_2SO_4, rather than after S application in the form of $(NH_4)_2SO_4$. In spring oilseed rape straw grown in the second year of the study, the application of S in the form of H_2SO_4 had the most beneficial effect on the contents of SO_4-S. In the discussed treatment, the amount of SO_4-S was 1.1–9 times higher than values found in plants from the other experimental treatments.

Table 3. The SO_4-S content in plants, g·pot^{-1}

Treatment	First year of study		Second year of study		Third year of study	
	spring wheat	white mustard	spring oilseed rape	spring barley	spring barley	orchard grass
	Straw					first cut
Control	0.02	0.04	0.19	0.18	0.05	X
RSMS	0.66	0.52	1.00	0.66	0.79	X
$(NH_4)_2SO_4$	0.18	0.84	1.60	1.00	0.75	0.71
K_2SO_4	0.23	1.02	1.40	0.94	0.90	0.75
Na_2SO_4	0.18	0.92	1.56	0.99	0.68	0.64
S-S°	0.22	0.34	0.92	1.02	1.01	0.91
$CaSO_4·2H_2O$	0.06	0.48	1.38	0.88	0.70	0.76
H_2SO_4	0.12	0.55	1.71	1.13	0.66	0.70
Average	0.21	0.59	1.22	0.85	0.70	0.75
	Grain/seed					second cut
Control	0.69	X	X	0.07	0.11	0.05
RSMS	1.41	3.00	0.14	1.06	0.73	0.30
$(NH_4)_2SO_4$	0.91	2.50	0.26	0.07	0.09	0.57
K_2SO_4	1.01	2.40	0.28	0.13	0.11	0.64
Na_2SO_4	1.05	2.10	0.14	0.07	0.08	0.59
S-S°	1.04	2.40	0.17	0.08	0.11	0.73
$CaSO_4·2H_2O$	1.01	2.50	0.24	0.07	0.08	0.73
H_2SO_4	1.02	2.60	0.18	0.06	0.08	0.60
Average	1.02	2.50	0.20	0.20	0.17	0.53

X – no material

The content of SO_4-S in spring rapeseed markedly increased after $(NH_4)_2SO_4$ and K_2SO_4 application. This is very important for the growth and development of spring oilseed rape. Plants insufficiently supplied with sulphur are characterized with a number of symptoms of this element deficit. Chlorosis and deformation of the leaf blade (spoon-like shape) can be seen on leaves. Discoloration of flowers, a reduction in the amount of oilseed rape pods and seeds in pods, also occurs. In addition, plants grow more slowly and take the characteristic shape (Bednarek *et al*., 2008; Podleśna, 2009). Considering the vegetative parts of the spring barley grown in the second year of the experiment, S fertilization in the forms of Na_2SO_4, $(NH_4)_2SO_4$ and elemental S had the greatest impact on the increase in SO_4-S content. For the grain of this test plant species, RSMS application appeared to be the most advantageous. After administration of that S form, the content of SO_4-S in dry matter of plants from that treatment was about 8–17-fold higher as compared to the values found in crops cultivated in other experimental treatments. The content of SO_4-S in spring barley straw grown in the subsequent year of the study was clearly increased after K_2SO_4 and elemental S introduced. The highest content of SO_4-S occurred in the spring barley grain, for growing of which RSMS was used. In the first cut of orchard grass, high SO_4-S content was recorded after the application of elemental S. Referring to the second cut, plants for growing of which elemental S and $CaSO_4 \cdot 2H2O$ was used were characterized by the highest concentrations of that S form. This is important for the quality of the yields. An adequate supply of grasses in suphfur favours the protein synthesis and reduces interference in the functioning of nitrate reductase (Kaczor and Zuzańska, 2009).

CONCLUSIONS

The highest content of S_{tot} occurred in the vegetative and generative parts of spring wheat fertilized with sulphur in the form of RSMS. In barley and orchard grass, similar trends were found after the application of K_2SO_4, H_2SO_4 and $CaSO_4 \cdot 2H_2O$. The most favourable form of sulphur applied for S_{tot} concentration in the vegetative parts of white mustard and spring oilseed rape was RSMS, for white mustard seeds – elemental S and H_2SO_4, while for generative parts of spring oilseed rape – K_2SO_4.

The greatest influence on the content of SO_4 -S was exerted by the use of this component in the form of RSMS (in the straw and grain of spring wheat, white mustard seeds, and spring barley grains), K_2SO_4 (straw of white mustard), as well as elemental S (straw of spring barley, the first and second cut of orchard grass).

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WPŁYW RÓŻNYCH FORM SIARKI NA ZAWARTOŚĆ TEGO SKŁADNIKA W ROŚLINACH

Streszczenie

Siarka obok azotu, fosforu i potasu jest cennym składnikiem pokarmowym roślin, który decyduje nie tylko o wielkości, ale również jakości plonów roślin uprawnych. W związku z tym, celem podjętych badań była próba określenia wpływu siarki pochodzącej z różnych źródeł na zawartość tego składnika ($S_{og.}$ i S-SO_4) w suchej masie badanych gatunków roślin: pszenicy jarej (*Triticum aestivum* L.), gorczycy białej (*Sinapis alba* L.), rzepaku jarego (*Brassica napus* L. var. Napus), jęczmienia jarego (*Hordeum vulgare* L.) i kupkówce pospolitej (*Dactylis glomerata* L.). Badania przeprowadzono w oparciu o ścisłe trzyletnie doświadczenia wazonowe. Czynnikiem zmiennym była siarka użyta w siedmiu różnych formach. Badania obejmowały obiekt kontrolny – bez nawożenia siarką (1) oraz obiekty traktowane związkami siarki: RSMS – roztwór saletrzano-mocznikowy z dodatkiem $Na_2S_2O_3 \cdot 5H_2O$ (2); $(NH_4)_2SO_4$ (3); K_2SO_4 (4); Na_2SO_4 (5); siarka elementarna (S-S°) (6); $CaSO_4 \cdot 2H_2O$ (7); H_2SO_4 (8). Najwyższą zawartością $S_{og.}$ charakteryzowały się wegetatywne i generatywne części pszenicy jarej nawożonej siarką w postaci RSMS. W przypadku jęczmienia i kupkówki pospolitej podobne tendencje stwierdzono po zastosowaniu K_2SO_4, H_2SO_4 i $CaSO_4 \cdot 2H_2O$. Najkorzystniejszą formą nawożenia siarką w przypadku zawartości siarki całkowitej w wegetatywnych częściach gorczycy białej i rzepaku jarego było stosowanie RSMS, dla nasion gorczycy białej – siarki elementarnej i H_2SO_4, natomiast dla generatywnych części rzepaku jarego – użycie K_2SO_4. Wśród zastosowanych form nawożenia siarką największy wpływ na zawartość S-SO_4 wywarło stosowanie tego składnika w postaci RSMS (w przypadku pszenicy jarej, nasion gorczycy białej i ziarna jęczmienia jarego), K_2SO_4 (słoma gorczycy białej, nasiona rzepaku jarego) i siarki elementarnej (słoma jęczmienia jarego, kupkówka pospolita).

Słowa kluczowe: formy siarki, nawożenie siarką, siarka ogółem, siarka siarczanowa