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EFFECT OF SULPHUR FERTILISATION ON THE CONTENT OF MACROELEMENTS AND THEIR IONIC RATIOS IN POTATO TUBERS

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Abstract

Next to nitrogen, phosphorus, potassium and magnesium, sulphur plays an important role in plant metabolism and is considered to be one of the most important nutrients. As sulphur deficit in Polish soils has been increasing in the last few decades, research has been carried out in order to evaluate the impact of different sulphur rates and forms on the content of macroelements (N, P, K, Ca, Mg, S, Na) and their ratios in the Mila cultivar potato tubers. A strict, three-year field experiment was set up on Haplic Luvisol with acid reaction (5.3 pH_{KCl}), mean richness in available forms of phosphorus, potassium and magnesium but low in sulphur. The field experiments involved the sulphur application in doses of 20 and 40 kg S kg^{-1} in the form of sulphate (VI) (K_2SO_4 and $(NH_4)_2SO_4$) as well as in elemental form (Wigor S, containing 90% of pure sulphur and 10% of bentonite). Although potatoes represent the group of crops with low sulphur requirements, the research has clearly indicated that this component has definite impact on the content of macroelements in tubers. It was found that sulphur application, irrespective of its form and rate, compared with control sample generally increased the content of nitrogen, sulphur and magnesium in potato tubers, decreasing at the same time calcium content.

The effect of the form of sulphur fertilisers on the content of macroelements was not univocal. The values of all the ratios calculated (K^+:Mg^{+2}, K^+:(Ca^{+2}+Mg^{+2}) and (K^++Na^+):(Ca^{+2}+Mg^{+2})), except for K^+:Ca^{+2}, have generally decreased after sulphur application, which indicates positive changes in the nutritive value of potato tubers.

Key words: sulphur, fertilisation, potato tubers, macroelements, ionic rations.

INTRODUCTION

Owing to its specific physiological role in plant metabolism, sulphur is considered to be one of the key nutrients for plants (Haneklaus et al. 2000,

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SAHOTA 2006). Its deficit decreases plant yield and often leads to deterioration of the yield quality, which is determined by the content of minerals and their ratios (EPPENDORFER, EGGUM 1994, BLAKE-KALFF et al. 2003). At the turn of the 20^{th} and the 21^{st} century, data on sulphur deficit in Poland (SZULC 2008) and many other countries (STERN 2005, MORRIS 2007) was published. Symptoms of sulphur deficiency are observed not only in the plant species with high sulphur requirements but also in those which require relatively less S, including potato (*Solanum tuberosum* L.) (PAVLISTA 1995, KLIKOCKA 2004, SHARMA et al. 2011). Sulphur enhances starch synthesis in tubers, is a component of proteins and many enzymes, limits the content of nitrates and reducing sugars, which in turn improves the technological value of potato (EL-FAYOUMY, EL-GAMAL 1998, LALITHA et al. 2000). It increases the resistance of this species to environmental stresses and plays an important role in protecting the plants from pests and diseases (WALKER, BOTH 1994). KLIKOCKA (2005) demonstrated that induced sulphur fertilization increased potato resistance to infection with *Rhizoctonia solani* fungi. In regions polluted with sulphur compounds and with decreased soil pH, smaller infestation with Colorado potato beetle (*Lepti-notarsa decemlineata*) as well as an increased potato resistance to common scab (*Streptomyces scabies*) is observed (PAVLISTA 1995). The content of sulphur in potato tubers is on average between 0.7-2.0 g kg^{-1} and its uptake ranges from 18 to 40 kg ha^{-1} (KLIKOCKA 2004).

In Europe, potato tubers are the staple food in everyday diet. In the last decades, potato consumption has been growing steadily in countries where historically potatoes had hardly been grown at all, particularly in South-Eastern Asia (SHARMA et al. 2011). The consumption value of tubers is defined on the basis of the content of dry weight, starch and the content of respective macroelements. Maintaining the cation-anion balance is one of the major factors governing an adequate course of plant metabolism as well as the yield size and quality.

Sulphur plays a very important role in plant physiology. Moreover, its balance in agroecosystems has been disturbed, thus research has been carried out to evaluate the effect of varied sulphur rates and forms on the content of selected macroelements and their equivalent ratios in the Mila cultivar potato tubers.

METHOD AND MATERIALS

Field experiments were performed from 2003 to 2005 at the Experimental Station of the Faculty of Agriculture of the University of Technology and Life Sciences in Bydoszcz, located at Wierzchucinek (53°26′ N, 17°79′ E). A mid-early cultivar of table potato called Mila was grown in *Haplic Luvisol* formed from till of very good rye complex. The III b soil valuation class soil was of acid reaction (pH_{KCl} – 5.3) and exhibited an average richness in the available forms of phosphorus, potassium and magnesium. The content of sulphate form (VI) $S\text{-}SO_4^{2-}$ was low (the mean of 9.4 mg kg^{-1}).

A strict fertilisation experiment was performed in 3 replicates. The experiment was set up as a single-factor experiment following the randomised block design. The area of the plot was 20 m^2, and for harvest - 16 m^2. The experimental factor involved the type of mineral fertilisation containing sulphur in the ionic or elemental form. The following fertilisation treatments were considered:

S_1 – 0 kg S ha^{-1};

S_2 – 20 kg S ha^{-1} in the form of ammonium sulphate (VI);

S_3 – 40 kg S ha^{-1} in the form of ammonium sulphate (VI);

S_4 – 20 kg S ha^{-1} in the form of potassium sulphate (VI);

S_5 – 40 kg S ha^{-1} in the form of potassium sulphate (VI);

S_6 – 20 kg S ha^{-1} in the form of Wigor S fertiliser;

S_7 – 40 kg S ha^{-1} in the form of Wigor S fertiliser.

Wigor S is a mineral fertiliser, containing 90% of elemental sulphur and 10% of bentonite.

Cultivation treatments and fertilisation were made in accordance with the agrotechnical guidelines for potato. Uniform mineral fertilisation was applied before sowing. Nitrogen was sown at the dose of 100 kg N ha^{-1} in the form of ammonium nitrate (for the treatments with ammonium sulphate (VI) balanced with the rate of nitre, considering the nitrogen introduced with sulphate). Phosphorus (25 kg P ha^{-1}) was sown in the form of triple superphosphate and potassium (120 kg K ha^{-1}) as 50% potassium salt, balancing the nutrient introduced into the treatments with potassium sulphate (VI). Prior to potato planting, FYM was applied at the dose of 30 t ha^{-1}.

For a more complete description of the weather conditions over the research period, the values of the Selyaninov hydrothermal coefficient (tab. 1) were calculated:

$$k = P/0.1\Sigma t,$$

where:

P – monthly precipitation sum (mm)

t – monthly daily air temperature sum >0°C.

In the region where the experiment was carried out precipitations are low (the annual average of about 450 mm) and demonstrated considerable variation in successive years, which has been reflected in the calculated values of the Selyaninov coefficient (Table 1). The highest temperature and the lowest precipitation were noted in the 2005 plant growing season. In all the months, except July, extremely dry or dry conditions were recorded. In 2003 and 2004, the mean values of the Sielianinow coefficient for the entire potato-growing season were higher than the long-term mean, although they varied much in respective months of the plant growing period.

Table 1

The Selyaninov hydrothermal coefficient values throughout the research period

Years	Months					Mean
	May	June	July	August	September	
2003	0.86	1.88	2.44	0.86	1.65	1.54
2004	2.29	0.64	1.33	0.94	1.82	1.40
2005	0.41	0.58	1.78	0.31	0.41	0.69
Mean 1949-2005	1.01	1.15	1.26	0.95	0.97	1.07

$K<0.4$ – extremely dry conditions, $0.4<K<0.7$ very dry, $0.7<K<1.0$ dry,
$1.0<K<1.3$ quite dry, $1.3<K<1.6$ optimal, $1.6<K<2.0$ quite moist, $2.0<K<2.5$ moist

After harvest, the following values were determined for the dry weight of potato tubers produced at the temperature of 105°C:

- the nitrogen content by the Kjeldahl method,
- phosphorus – by the colorimetric method with the use of ammonium molybdate, on a type DR-2000 colorimeter,
- magnesium – by atomic absorption spectrometry (AAS),
- calcium, potassium, sodium – by atomic emission spectrometry with the use of a flame photometer Flapho-4,
- total sulphur using the ICP OES method *(Inductively Coupled Plasma Optical Emission Spectrometry*) method mineralization in a mixture of concentrated acids: HNO_3 and $HClO_4$ (Khan 2012).

The content of macroelements was expressed in gram equivalents and the following ratios were calculated: K^+:Mg^{+2}, K^+:Ca^{+2}, K^+:(Ca^{+2}+Mg^{+2}) and (K^++Na^+):(Ca^{+2}+Mg^{+2}).

The results were statistically verified by the means of variance analysis in the split-plot design following the model compliant with the experimental design. To evaluate the significance of mean treatment differences the Tukey's range test at the probability of $P = 0.05$ was applied.

RESULTS AND DISCUSSION

The research showed that potato tubers contained most potassium (an average of 19.8 g kg^{-1}), slightly less nitrogen (13.0 g kg^{-1}) and considerably less phosphorus (3.17 g kg^{-1}), magnesium (1.71 g kg^{-1}), sodium (1.54 g kg^{-1}), total sulphur (1.26 g kg^{-1}) and calcium (1.29 g kg^{-1}) – Table 2. After sulphur application, analogously to the report by Skwierawska et al. (2008) from experiments on cabbage, onion and spring barley, a significant impact on the content of most of the macroelements in potato tubers was observed. As for nitrogen, sulphur and magnesium, after application of sulphur-containing fertilisers, generally there was a significant increase in their mean content

Table 2

Content of macroelements in potato tubers (g kg^{-1})

Years	Control	Form of fertilizer						Mean	$LSD_{0,05}$
		$(NH_4)_2SO_4$		K_2SO_4		Wigor S			
		dose of sulphur (kg S ha^{-1})							
	0	20	40	20	40	20	40		
	K_1	K_2	K_3	K_4	K_5	K_6	K_7		
The content of nitrogen									
2003	11.9	13.7	14.1	12.2	13.0	12.4	12.7	12.8	1.56
2004	12.0	11.1	12.5	12.2	12.7	12.2	11.7	12.0	0.67
2005	13.3	13.3	13.5	14.5	14.5	14.4	15.0	14.1	1.22
Mean	12.4	12.7	13.3	12.9	13.4	13.1	13.1	13.0	0.55
The content of phosphorus									
2003	3.23	3.33	3.53	3.50	3.27	3.40	3.40	3.38	0.21
2004	3.23	3.43	3.17	3.17	3.30	3.27	3.13	3.24	n.s.
2005	3.00	2.67	2.63	2.90	3.00	3.10	2.97	2.90	0.35
Mean	3.16	3.14	3.11	3.19	3.19	3.26	3.17	3.17	0.12
The content of potassium									
2003	21.0	21.7	21.3	21.0	20.7	21.0	20.4	21.0	n.s.
2004	19.5	20.5	20.3	20.5	21.0	20.8	19.5	20.3	0.78
2005	18.4	17.3	17.3	18.2	18.6	18.5	18.2	18.1	1.05
Mean	19.7	19.8	19.6	19.9	20.1	20.1	19.4	19.8	0.71
The content of calcium									
2003	1.46	1.65	1.50	1.41	1.05	1.20	1.01	1.25	0.52
2004	1.52	0.99	1.17	1.04	1.01	1.21	0.87	1.12	0.30
2005	1.90	1.43	1.37	1.33	1.40	1.40	1.40	1.46	0,39
Mean	1.63	1.36	1.35	1.26	1.15	1.27	1.09	1.29	0.19
The content of magnesium									
2003	1.43	2.02	1.49	1.66	1.86	1.62	1.75	1.69	0.236
2004	1.25	2.07	1.55	1.69	1.95	1.64	1.73	1.70	0.358
2005	1.56	2.02	1.64	1.74	1.97	1.62	1.75	1.76	0.320
Mean	1.41	2.03	1.56	1.70	1.92	1.63	1.74	1.71	0.058
The content of sodium									
2003	1.23	1.23	1.17	1.27	1.30	1.40	1.27	1.27	n.s.
2004	1.67	1.53	2.07	1.17	1.47	1.43	2.50	1.69	n.s.
2005	1.63	1.70	1.37	1.67	1.70	1.73	1.73	1.65	n.s.
Mean	1.51	1.49	1.53	1.37	1.49	1.52	1.83	1.54	n.s.
The content of total sulphur									
2003	0.83	1.31	1.28	1.14	1.19	1.18	1.36	1.19	0.078
2004	0.91	1.42	1.38	1.29	1.36	1.36	1.55	1.32	0.056
2005	0.90	1.40	1.37	1.23	1.30	1.30	1.47	1.28	0.064
Mean	0.88	1.38	1.34	1.22	1.28	1.28	1.46	1.26	0.062

over the three years of research in comparison with the control sample (K_1). Calcium was the only element on which sulphur had contrary impact.

Nitrogen was that component in potato tubers whose content was significantly modified by sulphur fertilisation. It is difficult, however, to state firmly which of the sulphur containing fertilises was most effective. The content of nitrogen in potato tubers was considerably affected by seasonal variations, thus it is difficult to define precisely, under field conditions, how significant the direct impact of sulphur was. In 2003, the significantly highest nitrogen content was recorded following the application of ammonium sulphate (VI) (K_2 and K_3); in 2004, such an effect was induced by potassium sulphate (VI) (K_5) and in 2005, it was caused by Wigor S (K_7). A more advantageous impact of elementary sulphur rather than the ionic one observed in the 2005 season (the third research year) was probably the result of the gradual release of the nutrient over time and a lower susceptibility to losses. That form requires biological oxidation and its impact depends on the activity of soil microorganisms (*Thiobacillus* sp.) (Aulakh 2003).

In general, the dose of 40 kg S ha^{-1}, as compared with that of 20 kg S ha^{-1}, stimulated a higher nitrogen content in potato tubers, although the differences were not always significant. Many authors (McGrath, Zhao 1996, Sud et al. 1996, Inal et al. 2003, Kaczor, Brodowska 2009, Barczak 2010) confirmed the positive influence of sulphur application on the plant protein synthesis and thus the nitrogen content in the yields.

The impact of sulphur fertilisation on the content of phosphorus and potassium in potato tubers was not unambiguous (Table 2). As for phosphorus, a significant increase in the content of that element, as compared with the control sample, was reported only in 2003 on plots K_3 and K_4; for potassium, it appeared on all the plots, except for K_7, in 2004. In 2005, after the application of ammonium sulphate (VI) at the doses of 20 and 40 kg S ha^{-1} (K_2 and K_3), a significant decrease was observed in the content of phosphorus and potassium in tubers in comparison with the control sample. According to Sawicka and Pszczółkowski (2004), the ionic composition of potato is genetically conditioned, despite being affected by high phenotypic variation depending on the impact of various environmental factors. Apart from fertilisation, another essential factor shaping the macroelements is the weather, especially the precipitation and temperature pattern during the vegetation period. A sufficient water supply alleviates the unfavourable impact of high temperatures. The years of field experiments were characterised by high variations in weather conditions (Table 1).

The elements whose content increased after the application of sulphur, in comparison with the control sample, were magnesium and sulphur. As for magnesium, by analogy to the results obtained by Brodowska, Kaczor (2009) for wheat and cocksfoot, a higher content of the element was recorded after the ionic rather than elemental form of sulphur. The sulphur content was more enhanced by the application of ammonium sulphate(VI) as well as

Wigor S than potassium sulphate(VI). Each research year, the tubers demonstrated higher concentrations of these macroelements in response to 40 kg S ha^{-1} in the form of potassium sulphate(VI) as well as Wigor S rather than after the use of 20 kg S ha^{-1} of these fertilisers. Out of the two ammonium sulphate(VI) doses applied, the magnesium content in tubers was significantly more favourably affected by 20 kg S ha^{-1}.

The average ratio of the content of nitrogen to sulphur (N:S) in potato tubers was 10.5:1 (Table 3). In all the plants fertilised with sulphur, in comparison with the control sample, its ratio was narrowed. This change was due to a higher increase in the content of sulphur rather than nitrogen in tu-

Table 3

Expressed in gram equivalents ionic ratios of macroelements in potato tubers

Years	Control	Form of fertilizer						Mean	$LSD_{0.05}$
		$(NH_4)_2SO_4$		K_2SO_4		Wigor S			
		dose of sulphur (kg S ha^{-1})							
	0	20	40	20	40	20	40		
	K_1	K_2	K_3	K_4	K_5	K_6	K_7		
N:S									
2003	14.3	10.5	11.0	10.7	10.9	10.5	9.3	11.0	1.86
2004	13.4	7.9	9.1	9.5	9.3	9.0	7.5	9.4	2.21
2005	14.8	9.5	9.9	11.8	11.2	11.1	10.2	11.0	3.20
Mean	14.2	9.6	10.0	10.7	10.5	10.2	9.0	10.5	0.69
K:Mg									
2003	4.55	3.16	4.39	3.93	3.42	4.00	3.58	3.86	0.102
2004	5.04	2.87	4.04	3.76	3.32	3.91	3.47	3.77	0.218
2005	3.77	2.24	3.18	3.28	2.96	3.55	3.20	3.17	0.147
Mean	4.45	2.76	3.87	3.66	3.23	3.82	3.42	3.60	0.169
K:Ca									
2003	7.37	6.73	7.30	7.61	10.12	9.02	10.35	8.36	0.83
2004	6.93	10.87	8.87	10.31	10.64	8.88	11.46	9.71	0.55
2005	5.09	6.25	6.36	7.09	6.98	6.95	7.14	6.55	n.s.
Mean	6.46	7.95	7.51	8.34	9.25	8.28	9.65	8.21	0.36
K:(Mg+Ca)									
2003	2.80	2.22	2.74	2.58	2.56	2.76	2.66	2.62	0.055
2004	2.88	2.26	2.78	2.75	2.53	2.71	2.66	2.65	n.s.
2005	2.16	1.64	2.12	2.22	2.08	2.34	2.18	2.11	n.s.
Mean	2.61	2.04	2.55	2.52	2.39	2.60	2.47	2.46	0.147
(K+Na):(Mg+Ca)									
2003	3.08	2.43	3.00	2.84	2.83	3.07	2.95	2.92	0.063
2004	3.29	2.54	3.26	3.03	2.83	3.03	3.24	3.03	n.s.
2005	2.48	1.92	2.41	2.59	2.40	2.71	2.53	2.43	n.s.
Mean	2.95	2.30	2.89	2.82	2.69	2.94	2.91	2.79	0.163

bers after fertilisation. Many reports (Janzen, Bettany 1984, McGrath, Zhao 1996, Kaczor, Brodowska 2009) point to a strong interaction between nitrogen and sulphur as the elements indispensable for the synthesis of sulphur amino acids used in protein synthesis. At the same time, the N:S ratio in the indicator plant parts facilitated the determination of the sulphur fertilisation requirements in plants (Withers et al. 1995, Blake-Kalff et al. 2003, Grant et al. 2003). As for potato, according to Klikocka (2004), a typical N:S value is about 12:1. Krzywy et al. (2002) found an optimal ratio between sulphur and nitrogen in plants grown for animal feed around 15-16:1.

There was a significantly negative effect of sulphur, both in the ionic and elemental form, on the content of calcium in potato tubers. The mean differences between the sulphur non-fertilised plot (K_1) and the fertilised ones were 16.6% (K_2), 17.2% (K_3), 22.7% (K_4), 29.4% (K_5), 22.1% (K_6) and 33.1% (K_7). The negative impact of sulphur fertilisers on the content of calcium in tubers was evident, especially in 2004 and 2005, when on all the plots fertilised with sulphur there was a significant decrease in the content of that nutrient, in comparison with the control sample. A particularly high decrease in the content of calcium in tubers was the result of the application of 40 kg S a^{-1} of Wigor S containing the elemental form of sulphur (K_7).

So far, sodium has been shown as an indispensable nutrient for just a few plant species. Its physiological role is less known than that of potassium; in literature there are some studies of the impact of sulphur fertilisation on its content in yields of crops. In the current study, there was no significant impact of sulphur fertilisers on the content of sodium in potato tubers.

In general, the form of sulphur applied did not affect the content of macroelements and their ionic ratios. Sulphur in the elemental form does not dissolve in water; hence there is a lower risk of sulphur loss by leaching in light soils. On the other hand, it must undergo biological oxidation with participating *Thiobacillus* genus bacteria to sulphate form (VI), (available to plants), which makes sulphur in the elemental form act more slowly than in the ionic form. The process of that microbiological transformation depends on many factors, e.g. on the soil properties, particularly its biological activity, on the level of fertiliser sulphur fragmentation as well as on precipitation and temperature (Aulakh 2003). Their pattern in each growing season was different (Table 1), which excluded any firm statement as to which sulphur forms had the strongest impact on the content of macro elements in potato tubers.

Variations in weather conditions in respective research years caused bigger differences between the mean content of the nutrients in potato tubers in successive years than the differences due to fertiliser sulphur. Analogously to the report by Klikocka (2004), it was found that the content of macroelements in potato tubers was influenced more by the year-related hydrothermal conditions than by sulphur fertilisers. As for nitrogen, calcium and magnesium, the highest concentrations were noted in the driest year 2005, when – in all the months of the plant growing season, except for July

– the precipitation was lower then the long-term mean. With that in mind, it seems that sulphur fertilisation effectiveness in the accumulation of those elements, nitrogen in particular, including protein nitrogen, is higher in years with lower precipitation than in those plant growing seasons when the rainfall conditions are similar to the long-term mean.

Although the content of macroelements in crop yields is generally well-known, significantly less information is available on ratios between these nutrients, in particular, about the impact of sulphur fertilisation on their values. The ratios of macroelements determining the ionic equilibrium in potato tubers grown either for human consumption or animal feed can determine their nutritive value.

As a result of sulphur fertilisation, the values of $K^{+}:Mg^{+2}$, $K^{+}:(Ca^{+2}+Mg^{+2})$ and $(K^{+}+Na^{+}):(Mg^{+2}+Ca^{+2})$ ratios generally decreased in comparison with the control sample, whereas the value of the $K^{+}:Ca^{+2}$ ratio increased. These particular changes in quantitative ratios were caused by sulphur fertilisation, which in turn led to changes in the content of respective nutrients, especially magnesium and calcium, in potato tubers.

The ionic equilibrium of a plant is one of the major factors determining the quality of crop yields because an excessive intake of specific cations or anions limits the concentration of other, frequently valuable macro- and microelements. Many authors claim that a high content of potassium decreases whereas that of calcium and magnesium enhances the nutritive value of the yields of plants grown either for animal feed or for human consumption (Krzywy et al. 2002). In practice, animal feed more often has an excess rather than a deficit of potassium. What is especially undesirable is an excessively wide quantitative ratio of univalent cations to divalent ones in animal feed for ruminants, which as a result of hypomagnesemia can lead to grass tetany in cattle. Thus, the reported changes in the values of $K^{+}:Mg^{+2}$, $K^{+}:(Ca^{+2}+Mg^{+2})$ and $(K^{+}+Na^{+}):(Ca^{+2}+Mg^{+2})$ are beneficial because they are caused by a significant increase in the amount of magnesium in potato tubers owing to sulphur fertilisation. The calcium content plays an important role in maintaining the equilibrium between univalent and divalent ions, which – like magnesium - can show an antagonistic effect towards potassium.

Drawing on the present research, it may be stated that sulphur fertilisation generally has a favourable influence on the content and the quantitative ratios of macro elements in potato tubers. However, developing final conclusions is not easy due to lack of significance of the differences.

CONCLUSIONS

1. It was found that sulphur fertilisation, irrespective of its form and dose, has generally increased the content of nitrogen, sulphur and magne-

sium in potato tubers, decreasing the content of calcium in comparison with the control sample.

2. The application of 40 kg S·ha^{-1} in the form of potassium sulphate(VI) as well as Wigor S in each of the research years stimulated a higher content of sulphur and magnesium in potato tubers than the rate of 20 kg S·ha^{-1}.

3. The values of K^+:Mg^{+2}, K^+:(Ca^{+2}+Mg^{+2}) and (K^++Na^+):(Ca^{+2}+Mg^{+2}) ratios in potato tubers following an application of sulphur generally decreased in comparison with the control sample, which is considered to be a positive tendency for the nutritive value of tubers.

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