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ORIGINAL PAPER

EFFECT OF SULPHUR AND NITROGEN FERTILIZATION ON THE SELENIUM CONTENT AND UPTAKE BY GRAIN OF SPRING WHEAT

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Abstract

The aim of the study was to evaluate the effect of nitrogen (N) and sulphur (S) fertilizer on the selenium content and selenium (Se) uptake in grain DM of spring wheat. A field experiment (2009-2011) was conducted on Cambisols (WRB 2007) in south-eastern Poland. The experiment included 2 variables: N fertilization (0, 40, 80, and 120 kg ha^{-1}) and S fertilization (0 and 50 kg ha^{-1}). The experiment showed a positive effect of nitrogen and sulphur fertilization on grain yield of spring wheat cv. Tybalt, with the highest yield obtained after the application of 80 kg N ha^{-1} (5.40 t ha^{-1}) and 120 kg N ha^{-1} (5.59 t ha^{-1}), which resulted in an average increase of 1.42 t ha^{-1} (34.7%) with respect to the control. S fertilization increased grain yield by 3.58%. the mean selenium content in the spring wheat grain was 0.085 mg kg^{-1} and the selenium uptake equalled 0.419 g ha^{-1}. The selenium content and uptake by grain DM increased significantly following the application of N at doses of 40 and 80 kg ha^{-1}: the content rose by 19.1% and 36.8%, respectively, and the uptake was 24.4% and 84.7% higher than in the control. Following the application of the nitrogen dose of 120 kg ha^{-1} no further statistically significant increase in the content and uptake of selenium in comparison with the application of the nitrogen dose of 80 kg ha^{-1}. The content of selenium and uptake of selenium by the grain following the application of sulphur at a dose of 50 kg ha^{-1} increased by 20.8% and 25.3%, respectively, in comparison with the control. A positive correlation was found between the content of selenium in grain and the selenium uptake by grain DM (r = 0.947).

Keywords: spring wheat, nitrogen, sulphur, selenium content in grain.

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INTRODUCTION

Selenium (Se) is a non-metallic element in Group VIa of the periodic table, between sulphur and tellurium, and with properties similar to both of these elements. In low concentrations it is an essential element for most animals, although it becomes toxic at higher levels. The recommended daily intake of selenium according to the World Health Organization (WHO) is 1 μg kg^{-1} per person per day. The daily intake of selenium by populations in European countries is 25-150 μg per day. A low selenium status in the human body may increase the risk of cardiovascular disease, cancer and other diseases induced by free radicals (Ducsay et. al 2009, Rayman 2000).

The two most abundant forms in which selenium occurs are elemental Se (Se^0) and the −2 oxidation state, as selenide (Se^{2-}), but under oxidizing conditions it may be present in the +4 oxidation state as selenite (SeO_3^{2-}) or in the +6 oxidation state as selenate (SeO_4^{2-}). Selenate minerals in well-aerated soils are generally more soluble than selenite minerals (Pilbeam et al. 2015). The natural content of selenium in soils worldwide ranges from 0.1 to 2.0 mg kg^{-1} DM and is below 0.5 mg kg^{-1} DM on average. Se-rich soils are mainly found in North America, Canada, Australia, Ireland and Israel, while areas poor in selenium include provinces of China, Finland, New Zealand and a considerable portion of Europe. Piotrowska (1984) reports that Polish soils contain selenium in levels ranging from 0.040 to 0.640 mg kg^{-1} DM, and the proportion of Se-poor soils is 70%.

Plants take up Se as selenate or selenite ions or as organic Se compounds such as selenomethionine, thus the availability of these Se forms in soils affects uptake of this element. Uptake of selenate has been known for some time as an active process. The SeO_4^{2-} ion shares at least one high-affinity carrier with the sulphate (SO_4^{2-}) ion, and as a consequence high availability of sulphate in the rooting medium reduces its uptake (Pilbeam et al. 2015). Selenium content in vegetable-based foods is influenced by climate and soil conditions, particularly soil pH, redox potential, the quantity of organic matter, and activity of soil microbes. Hence the content of this micronutrient in plants may range from trace amounts to even 1,000 mg kg^{-1} (Hartikainen 2005). In crop plants it usually ranges from 0.006 to 0.3 mg kg^{-1} and generally does not exceed 1 mg kg^{-1}. However, plants of the *Cruciferae* and *Liliaceae* families, with high sulphur requirements, contain even 2-5 times more selenium than cereals. Grains and grain products are an important source of selenium in the human diet. They meet about 70% of the daily selenium requirement in China, 40-50% in India, and 18-24% in Great Britain. Selenium content in the grain of cereals is highly varied, ranging from 10 to even 3,000 μg kg^{-1} DM (Hawkesford, Zhao 2007). Zhu et al. (2009) report that Canada and USA produce wheat with the highest content of Se in the grain, while Se content in rice is highest in the USA and India. In Slovakia the mean selenium content for wheat grain is 0.029 mg kg^{-1} DM, for barley 0.023 mg kg^{-1} DM, and for rye 0.015 mg kg^{-1} DM (Ducsay et al. 2007). A study by Korol et al. (1992) found that the mean selenium content in the grain of Polish cereals was below 0.1 mg kg^{-1}.

Nitrogen and sulphur are both important constituents of protein, and adequate supply of both nutrients is important for optimum crop yield (Klikocka et al. 2016, Dostálová et al. 2015). Fertilizers containing S, N and Se interact at many levels, as the uptake and assimilation of NO_3, SO_4^{2-} and Se_4^{2-} have much in common and there are many common products of N and S and Se metabolism in plants (Pilbeam et al. 2015).

The aim of the study was to evaluate the effect of nitrogen and sulphur fertilizer on selenium content and selenium uptake by grain DM of spring wheat.

MATERIAL AND METHODS

A field experiment was carried out in 2009-2011 in Malice, south-eastern Poland (50°42’ N, 23°15’ E), in a randomized split-plot design with four replications. The experiment was conducted on Cambisols (WRB 2007) consisting of light silty sand (sand 68%, silt 31%, clay 1%). The soil was slightly acidic (pH = 5.6), with high available P content, medium content of K and Mg, and low S and Se content (Table 1). Total precipitation during the growing season (March-August) in 2009 was 349.1 mm, which was 18.3 mm less than the long-term average (1971-2005: 367.4 mm). In the 2010 and 2011 growing seasons precipitation exceeded the long-term average by 76.0 and 47.2 mm, respectively. In 2009 particularly high levels of precipitation were observed in May (102.6 mm) and June (124.4 mm), while July was dry (24.2 mm). In 2010 it was particularly rainy in May (98.2 mm), July (143.5 mm) and August (86.1 mm), while rainfall in June was optimal (62.9 mm). In 2011 the precipitation distribution was optimal during the period from April to June, but July and August were very rainy (148.0 and 133.6 mm). The air temperature sums in the analysed growing seasons (March-August) were higher than the long-term average (1971-2005: 2,553°C), by 99°C in 2009, 162°C in 2010 and 28°C in 2011. In general, in each month of the analysed years the air temperature exceeded the long-term average (Figure 1).

The subject of the experiment was the Tybalt variety of spring wheat (*Triticum aestivum* L.) fertilized with different doses of nitrogen (0, 40, 80 and 120 kg N ha^{-1}) and sulphur (0 and 50 kg S ha^{-1}). The area of each plot was 30 m^2 (5 m × 6 m). The first application of nitrogen (as 34% ammonium nitrate) at a rate of 40.0 kg N ha^{-1} was made before sowing (between 28 March and 5 April, depending on the year). In the combination of 80 and 120 kg N ha^{-1} the second N application was made during the beginning of shooting (BBCH 30-31). In the combination of 120 kg N ha^{-1} the third N

Table 1

Chemical characteristics of soil (spring before sowing, layer 0-25 cm)

Element	Types of soil analyses	2009	2010	2011
pH in 0.01 mol L^{-1} $CaCl_2$	potentiometrically using a Methrohm 605 pH-meter	5.6	5.7	5.8
($g\ kg^{-1}$)				
C – total	combustion with LECO EC-12®, model 752-100	9.2	8.9	7.7
N – total	by the Kjeldahl's method	0.9	0.9	0.7
($mg\ kg^{-1}$)				
P – available	extracted by double lactate and determined by the colorometric method – Egner Riehm DL method. PN-R-04023:1996	54.5	53.5	48.3
K – available	extracted: see phosphorus, determined by the photometric method. PN-R-04022:1996	88.6	85.2	79.6
Mg – available	extracted by 0.0125 m L^{-1} $CaCl_2$ and determined by AAS. PN-R-04020-1994	34.8	33.7	35.1
S – total	by ICP-AES, mineralization with HNO_3 + $Mg(NO_3)_2$	102.8	86.3	72.0
S-SO_4	extracted by 0.025 m L^{-1} KCl and determined on an ion-chromatograph	14.2	12.6	10.3
Se – total	determination in *aqua regia* soil extracts with electrothermal or hydride-generation by AAS	0.167	0.164	0.162

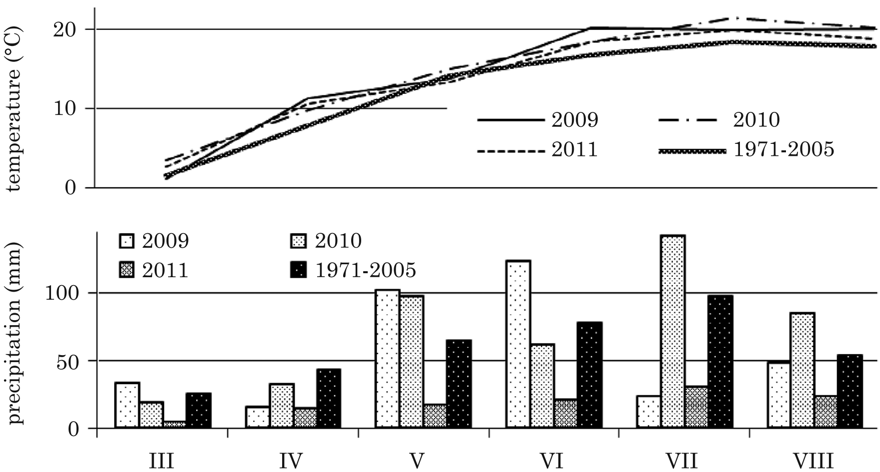

Fig. 1. The mean air temperature (°C) and sums of rainfall (mm) in the years 2009-2011 and the long-term averages for 1971-2005 (Zamość Research Station)

application was made during the heading (BBCH 55-59). First dose of sulphur was applied before sowing (40 kg S ha^{-1}) in the form of kieserite – $MgSO_4 \times H_2O$ (as 15.1% Mg, 20.0% S), and the second (10 kg S ha^{-1}) as foliar application in the form of *magnesium sulphate* heptahydrate ($MgSO_4 \times 7H_2O$); 10.2% Mg, 12.8% S or 32% SO_3; 3.2% SO_3 solution in 100 L of water per 300 L water per ha in the beginning of shooting (BBCH 30-31).

More detailed data on fertilization with other elements and protection of the spring wheat plants against pests in the experimental stand can be found in Klikocka et al. (2016).

Grain yield (at 11% moisture content) was calculated after the harvest (BBCH 92) from each plot. The total selenium content (g kg^{-1} DM) in the dry matter (DM) of the grain was determined by ICP-MS method (PN-EN ISO 17294-2:2006). Selenium uptake by the grain was calculated as the product of selenium content in the spring wheat grain and the grain yield.

Analysis of variance was performed by Snedecor's *F*-test. Significance of differences was calculated using Tukey's test (p = 0.05) followed by post-hoc analysis. The statistical software Excel 7.0 and Statistica (StatSoft Polska '97) were used for the analysis.

RESULTS AND DISCUSSION

Analysis of the results showed a significant beneficial effect of nitrogen and sulphur fertilizer on the grain yield of spring wheat and on the content and uptake of selenium in the grain. No interaction was found between increasing application rates of N and S for grain yield or for content and uptake of selenium. However, the addition of sulphur to each nitrogen dose independently increased yield and the content and uptake of selenium. This type of yield-increasing factor, in this case fertilizer, signals the additive effect of sulphur, also known as Mitscherlich's law. In general the additive interaction of nutrients is manifested when there is a constant increase in weight (or yield) as a result of application of the second factor (Grzebisz 2009).

The highest grain yield was found after application of 120 kg N ha^{-1} (5.59 t ha^{-1}) and a little lower in the case of 80 kg N ha^{-1} (5.40 t ha^{-1}) with the increase compare to the control respectively, by 1.51 t ha^{-1} (37.0 %) and 1.32 t ha^{-1} (32.4 %) – Figure 2. The literature devotes much attention to the beneficial effect of nitrogen fertilization on grain yield (Klikocka et. al 2016). Fertilization with sulphur improved the grain yield and the mean increase amounted 3.58% compare to NPK fertilization (Figure 2). In a study by Podleśna (2013), sulphur fertilization of winter wheat at a rate of 60 kg S ha^{-1} led to an 11% increase of grain yield. In another study of Potarzycki et al. (2015) sulphur fertilization of winter wheat at a dose of 25 kg S ha^{-1} led to

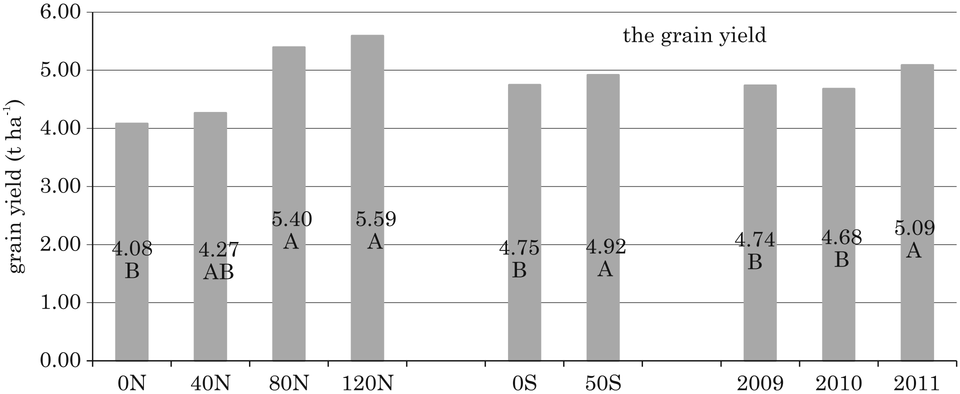

Fig. 2. Effect of nitrogen and sulphur fertilization as well as the study year on the grain yield of spring wheat. Values in the columns with different letters differ significantly ($P < 0.05$)

from 6 to 12% increase of grain yield, depending on the form of applied sulphur fertilizer.

The mean selenium content in the spring wheat grain was 0.085 mg kg^{-1}. Selenium content in the grain increased significantly following the application of N at doses of 40 and 80 kg ha^{-1}, by 19.1% and 36.8%, respectively, as compared with the control. There was no further statistically significant increase in the content of selenium following the application of 120 kg N ha^{-1} as compared with the application of 80 kg N ha^{-1} (Table 2, Figure 3). Nitro-

Table 2

Effect of nitrogen and sulphur fertilization on the selenium content in spring wheat grain DM

Combinations		Se content in dry matter of grain (mg kg^{-1})			Mean	Relatively (%) 1 = 100
		2009	2010	2011		
1	N0	0.111	0.029	0.046	0.062*a**	100.0
2	N40	0.141	0.031	0.054	0.075*a*	121.0
3	N80	0.148	0.035	0.062	0.082*a*	132.3
4	N120	0.119	0.065	0.084	0.089*a*	143.5
5	N0S50	0.138	0.034	0.052	0.075*a*	121.0
6	N40S50	0152	0.040	0.065	0.086*a*	138.7
7	N80S50	0.157	0.082	0.074	0.104*a*	167.7
8	N120S50	0.142	0.086	0.098	0.109*a*	175.8
Mean (S)	0S	0.130	0.040	0.062	0.077*B*	100.0
	50S	0.147	0.061	0.072	0.093*A*	120.8
Mean (N)	0N	0.125	0.032	0.049	0.068*C*	100.0
	40N	0.147	0.036	0.060	0.081*B*	119.1
	80N	0.153	0.059	0.068	0.093*A*	136.8
	120N	0.131	0.076	0.091	0.099*A*	145.6
Mean (*Y*)		0.139*A*	0.050*C*	0.067*B*	0.085	-

* Values in the columns with different letters differ significantly ($P < 0.05$). Small letters mark the differences for objects, capital letters mark differences for means.

gen aids the remobilization of selenium in wheat plants, hence the suggestion that application of N and Se together at the heading phase may increase the grain Se content (Govasmark and Salbu, 2011). These authors proposed that sulphate-free fertilizers should be used to prevent competition between sulphate and selenate for their uptake and translocation, although this would not be appropriate if wheat grain yield was to be depressed by the shortage of sulphur. The content of selenium in the grain following the application of sulphur at a dose of 50 kg ha^{-1} increased by 20.8% in comparison with the control. Selenium content in the grain of Polish cereals was studied by Korol et al. (1992), who showed that the mean content of this element was under 0.1 mg kg^{-1}, while the mean selenium content in the grain of spring wheat was 0.066 mg kg^{-1}. In Slovakia, the mean content of selenium in wheat was 0.029 mg kg^{-1} DM (Ducsay et al. 2007).

Selenium uptake by spring wheat grain in the control was 0.245 g ha^{-1} (Table 3). Similar uptake of selenium by winter wheat grain was noted by Ducsay and Ložek (2006), and by spring wheat by Ducsay et al. (2009). Selenium uptake by the grain DM increased significantly after the application of N at a dose of 40 and 80 kg ha^{-1}, by 24.4% and 84.7%, respectively, as compared with the control. There was no further statistically significant increase in selenium uptake following the application of 120 N kg ha^{-1} as compared to the application of 80 kg N ha^{-1} (Table 2, Figure 3).

The uptake of selenium in the grain DM following the application of S at a dose of 50 kg ha^{-1} increased by 25.3% in comparison with the control. Selenium is taken up by means of sulphate transporters and therefore sulphate has long been known as a strong inhibitor of selenite uptake. The addition of

Table 3

Effect of nitrogen and sulphur fertilization on the selenium uptake by spring wheat grain DM

Combinations		Se uptake (g ha^{-1})			Mean	Relatively (%) 1 = 100
		2009	2010	2011		
1	N0	0.418	0.115	0.201	0.245*a**	100.0
2	N40	0.571	0.122	0.241	0.311*a*	126.9
3	N80	0.798	0.175	0.353	0.442*a*	172.4
4	N120	0.647	0.354	0.464	0.488*a*	199.2
5	N0S50	0.537	0.133	0.240	0.303*a*	123.7
6	N40S50	0.631	0.170	0.309	0.370*a*	151.0
7	N80S50	0.687	0.436	0.404	0.569*a*	232.2
8	N120S50	0.812	0.482	0.571	0.622*a*	253.9
Mean (S)	0S	0.609	0.192	0.315	0.372*B*	100.0
	50S	0.712	0.305	0.381	0.466*A*	125.3
Mean (N)	0N	0.478	0.124	0.221	0.274*C*	100.0
	40N	0.601	0.146	0.275	0.341*B*	124.4
	80N	0.833	0.306	0.379	0.506*A*	184.7
	120N	0.730	0.418	0.518	0.555*A*	202.6
Mean (*Y*)		0.660*A*	0.248*C*	0.348*B*	0.419	-

* Values in the columns with different letters differ significantly ($P < 0.05$). Cf. under Table 2

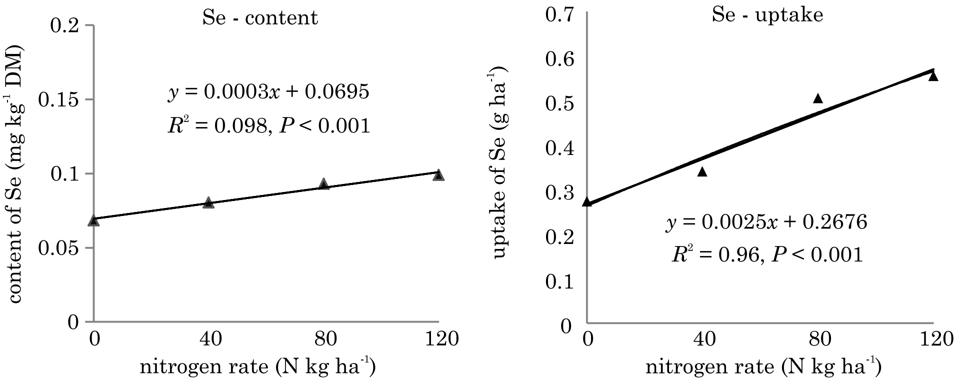

Fig. 3. The effect of nitrogen fertilization on the selenium content and uptake by grain of spring wheat (n = 4)

sulphate ions to soil desorbs selenate, but less effectively than the addition of phosphate desorbing selenite or selenate (SINGH et al. 1981). High salt content in soil generally lowers sorption of selenate and selenite, and the competitive ability of anions for selenite adsorption sites seems to follow the order: phosphate > silicate > citrate > molybdate > bicarbonate/carbonate > oxalate > fluoride > sulphate (BALISTRIERI, CHAO 1987). However, the competition between SO_4^{2-} and SeO_4^{2-} for uptake means that increased availability of selenate caused by desorption would not necessarily be apparent in terms of plant selenate uptake. It was noted in a study on wheat that when selenium was supplied as selenate there was more accumulation of selenium in the grain when the NPK fertilizer used was chloride-based rather than sulphate-based, but when selenite was applied, the accumulation of selenium in the grains was greater when the NPK fertilizer was sulphate-based (SINGH 1991). This effect can be explained by the competition between anions for uptake. High concentrations of sulphate would competitively inhibit the uptake of selenate, so even if the desorbed selenate was not leached from the soil quickly, it might not be taken up by the plants. Furthermore, most soils in Europe are no longer well loaded with sulphur due to the lower deposition of atmospheric sulphur dioxide from pollution (KLIKOCKA et al. 2005, 2015). For this reason, the use of sulfur fertilizers is recommended in plant cultivation. Analysis of the effect of sulphur with increasing application doses of nitrogen revealed that, despite the lack of statistically confirmed interactions, the most favourable values for the grain yield as well as the content and uptake of selenium by grain DM were found in the combination of 80 and 120 kg N ha^{-1} applied with 50 kg S ha^{-1}. It should also be noted that these increases following the nitrogen application at 120 kg ha^{-1} relative to lower application doses were less favourable than in the case of 80 kg N ha^{-1} with respect to 40 kg N ha^{-1}. This phenomenon can be explained by the law of diminishing returns (Mitscherlich's law) (GRZEBISZ 2009).

The grain yield and the content and uptake of selenium were also modified by the weather. The most favourable weather conditions for grain yield were in 2011 (quite wet). In 2009 (a fairly dry year) the meteorological conditions during the growing period of spring wheat had a significant beneficial effect on the content and uptake of selenium. Ducsay and Ložek (2006) also observed a variable effect of the weather on grain yield of winter wheat and on the selenium content and uptake by grain.

No significant correlations were found between the grain yield of spring wheat and the content and uptake of selenium. On the other hand, a high correlation coefficient was obtained between the content and uptake of selenium ($r_{n=24} = 0.947$, $P < 0.01$). As the content of available sulphur is low in Polish and European soils, a lower dose of nitrogen with addition of sulphur should be recommended in agricultural practice. Nitrogen and sulphur application did not reduce the selenium content in spring wheat grain; in fact, it led to an increase in its content and uptake by grain DM.

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