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EFFECTS OF SELENIUM ON MACRO- AND MICRONUTRIENTS AND SELECTED QUALITATIVE PARAMETERS OF OAT (*AVENA SATIVA* L.)

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ABSTRACT

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The article deals with the effect of foliar Se application on macro-and micro-elements and selected quantitative parameters (the content of ash, starch, and fat) in oat grains. The three-year experiments were carried out on Research and Breeding Station Vigl'aš – Pstruša in the years 2014, 2015, 2016. The used oat variety was Valentin. The experiment was performed by a block method within a parcel size of 10 square meters (8 x 1.25 m) with the span of rows amounting to 0.125 m in four replications. Alfalfa was grown as forecrop. A potato and wheat production area (III-C2) with a height of 375 m above the sea level. The experimental area is characterized by warm, slightly wet weather with an average annual temperature of 7.8 °C and average annual precipitations of 666 mm. Basic fertilizing was planned before the sowing in the form of 100 kg of Ammonium nitrate containing dolomite (27% N), 100 kg of 60% KCl (60% of K₂O), and100 kg of MAP (Monoammonium phosphate 12% N and 52% P₂O₅). Selenium was foliar applied in doses 25 g and 50 g Se per hectare in a solution form of sodium selenate (Na₂SeO₄). The harvest was realized by a small plot harvester in BBCH 91. The results of the experiments showed a statistically significant effect on microelements and most macroelements. Only sulfur content in oat grains was statistically significantly influenced by Se foliar treatment. The contents of ash, starch, and fat in oat grains were monitored, which showed statistically significant effect only in fat. Se content in grains showed a statistically significant effect only in fat. Se content in grains showed a statistically significant increase by both Se foliar treatments.

Keywords: selenium; macroelements; microelements; oat grain; quality

INTRODUCTION

Selenium is one of the essential mineral elements for human nutrition (White and Brown, 2010). The Se deficiency is associated with various diseases such as hypothyroidism, cardiovascular disease, a weakened immune system, male infertility, cognitive decline, and increased incidence of various cancers (Fairweather-Tait et al., 2011). Selenium is included in nearly 30 selenoproteins or selenoenzymes (Rayman, 2012). The level of selenium in the body depends on its concentration in the food. The selenium gets primarily to the food chain from the soils and drinking water. Its content in plants is a function of the conditions of the soil-plant system. The daily intake of Se varies geographically. Worldwide, it is estimated that over one billion people ingest Se below the recommended dose of 55 µg.day⁻¹ (Bañuelos, Lin and Broadley, 2017).

Selenium is chemically similar to sulfur (S) and the absorbed selenium replaces sulfur in some proteins of plants. The enzymes are unable to distinguish between Se and S until a critical value is reached after which Se becomes toxic to a plant (Ferri, Favero and Frasconi, 2007).

Macro- and microelements are significant for the growth and reproduction of plants, and their role in the human diet has been intensively investigated. Quantification and control of the mineral composition of food plants are therefore important factors for the sustainability of culture conditions which aims to increase the content of selected substances in plants (Combs, 2011).

Slovak soils are generally poor in selenium, which is related to its insufficient quantity in agricultural products. Content of selenium in the crops is constantly in the spotlight of the professional public. The biological value of grown food raw materials depends on a qualitative state of growing mediums – soils. Biogenic elements presented in the soils are taken by plants and thereby entering the food chain. Plants can receive the inorganic selenium added to the soil (in the form of selenate and selenite) and convert its part or all of it into the organic components. Agronomic biofortification through the application of fertilizers enriched with selenium is one of the possible ways of its content increasing in the soil. On the other hand, there is a potential danger of soil contamination. Due to the selenium content increasing in edible parts of a plant its combination with other biofortification approaches is promoted, such as foliar biofortification, i.e. selenium application directly to the plant (Graham et al., 2007). Foliar biofortification can provide a large-scale intake of minerals with antioxidant properties for human as well as an increase of certain biologically active substances as a result of their synergies (Hegedűsová et al., 2015).

Scientific hypothesis

We expect a significant effect of foliar Se application on macro-and micro-elements and selected quantitative parameters (the content of ash, starch, and fat) in oat grains.

MATERIAL AND METHODOLOGY

Small field nutritional experiments were carried out at the Research and Breeding Station Vígľaš – Pstruša in the last decade of March in the years 2014, 2015, 2016. The used variety of oat (*Avena sativa* L.) was Valentin. The experiment was realized with the soil type Luvisol Pseudogley. The experiment was performed by a block method within a parcel size of 10 m^2 (8 x 1.25 m) in four replications. The seeding rate represented 5 million of germinating grains per hectare with the span of rows amounting to 0.125 m. Alfalfa was grown as forecrop.

A potato and wheat production area (III-C2) with a height of 375 m above the sea level. An experimental area is characterized by warm, slightly wet weather with an average annual temperature of 7.8 °C and average annual precipitations of 666 mm.

The influence of Se salts foliar applied was monitored for qualitative changes in oat grains during the small field experiment. The agrochemical analysis of soil is stated in Table 1. Basic fertilizing was planned before the sowing in the form of 100 kg of Ammonium nitrate containing dolomite (27% N), 100 kg of 60% KCl (60% of K2O), and 100 kg of MAP (Monoammonium phosphate 12% N and 52% P2O5). 39 kg of Nitrogen, 49.8 kg of Potassium, and 22.9 kg of Phosphorus per hectare were applied by the used fertilizers. Selenium was foliar applied in doses of 25 g and 50 g Se per hectare in the solluted form of sodium selenate (Na₂SeO₄). The supplementary fertilization was realized by hand (dew machine STIHL). The spraying dose of solutions was 400 L.ha⁻¹. The application was planned during a growth phase of oat heading in BBCH 53 on 06 June 2014, 12 June 2015, and 07 June 2016. The experimental variants were the following:

Variants:

K – a control without foliar biofortification,

Se25 – an application of 25 g Se.ha⁻¹ in the form of an aqueous solution of sodium selenate in the stage of heading, **Se50** – an application of 50 g Se.ha⁻¹ in the form of an aqueous solution of sodium selenate in the stage of heading.

The harvest was realized by a small plot harvester in BBCH 91 (a growth staging scale of cereals – an over-ripe phase). Effect of fertilizing variants on Se content and selected Macro- and Micro – elements and content of ash, starch, and fat in oat grains were evaluated and analyzed

after the harvest. Soil and grain analyses were determined by common methods.

The samples were mineralized by a microwave decomposition method during the increased pressure with used reagents (hydrogen peroxide and concentrated nitric acid) in the following conditions:

Max. power: 800

Power: 100%

Ramp time: 20 minutes

Temperature: 170 °C

Hold 15 minutes.

The achieved mineralizate was poured into a volumetric bank and deionized water was added to the capacity of 25 mL.

Se content in wheat grains was determined by ICP-MS method (inductivelycoupled plasma mass spectrometry).

Principles of measurement:

- introduction of the measured solution into the high-frequency plasma, where the energy transfer processes from the plasma cause evaporation of the solvent, atomization, and ionization of the elements,
- extraction of ions from plasma via an interface with built-in ion optics and from the separation of ions in a mass spectrometer based on their mass to charge ratio,
- ion transfer through a mass filter (quadrupole) and from electron multiplier detection.

Equipment model: ICP-MS Agilent 7900, the country of origin is Japan.

Statistical analysis

The achieved experimental results were statistically evaluated by standard methods using the Statgraphics plus 5.1 statistical software (Rockville, USA). A multifactor ANOVA model was used for the individual treatment comparison at p = 0.05, with separation of the means by the *LSD* multiple-range test.

RESULTS AND DISCUSSION

Gluten-free plants and their products are the subject of interest for nutritionists, food technologists, and people with longlife gluten-free diet suffering from coeliac disease. Oat belongs to 27 grains gluten-free crops in the European Union, especially to the gluten-free cereals such as corn, buckwheat, amaranth, rice, teff, and quinoa. Popular gluten-free cererals (corn, rice, buckwheat) contain 2.8 μ g.100g⁻¹ of selenium on average and in less popular crops (amaranth, teff, and quinoa) the content of selenium content is 10.8 μ g.100g⁻¹ on average (**Rybicka et al., 2015**).

The concentrations of macroelements were determined in the oat grains. In the present study, the variation in the minerals (Ca, K, Mg, and P) that are essential for good preventive nutrition of humans (Harmankaya, Özcan and Gezgin, 2012; Rayman, 2012) are evaluated and discussed. Metabolic pathways of sulfur and nitrogen are influenced by assimilation of selenium in plants. A recent study was focused on influence of selenium treatment on nitrogen and sulfur secondary metabolites with expected health benefits (Malagoli et al., 2015).

In Table 2 the results of macroelements N, P, K, Ca, Mg are stated, showing statistically nonsignificant influence,

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but the Se25 foliar application confirmed a statistically significant effect increasing of sulfur content 1.00 g.kg⁻¹. The same tendencies are confirmed by a two-year experiment with maize grains, where a statistically nonsignificant effect on macronutrients N, P, K, Ca and Mg contents were signed (Wang, et al., 2013). By contrast, a two-year experiment showed the results, in which Se foliar application at 50 g Se ha⁻¹ confirmed statistically significant decrease of S, K, Ca in garlic (Põldma et. al, 2011). Interesting results were achieved in the maize experiments, where contents of macronutrients in aerial parts of maize depended on a selenium concentration in the nutrient solution. Selenium at concentrations of 50 and

100 μ mol.dm⁻³ caused a significant increase in phosphorus and calcium. Potassium significantly increased at the presence of 25 μ mol Se·dm⁻³, while decreasing under the influence of 100 μ mol Se·dm⁻³. The presence of selenium in the medium did not have a significant influence on magnesium. An excessive concentration of selenium affected the plant growth. A lower selenium concertration 5 μ mol.dm⁻³ stimulated the process of root elongation positively, but higher doses of selenium concentration 50 and 100 μ mol.dm⁻³ decreased not only a root tolerance index but also dry mass accumulation. Thus, from the above mentioned, it might mean that selenium in solution at high doses causes the disturbance of plant mineral balance.

Table 1 Agrochemical soil characteristics determined before the trial establishment.

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Soil analyses	2014	2015	2016
pH/KCl	6.12	5.65	6.62
Nan (mg.kg ⁻¹)	10.2	12.4	10.5
P Mehlich III (mg.kg ⁻¹)	57.5	77.5	33.8
K Mehlich III (mg.kg ⁻¹)	207.2	237.5	125.0
Se-total content (HF + HNO ₃ + HCl) (mg.kg ⁻¹)	0.21	0.20	0.21

Dose Se ⁶⁺	Dose Se ⁶⁺ Nutrient content (g.kg ⁻¹), mean of years 2014, 2015, 2016					
(g Se.ha ⁻¹)	Ν	Р	K	Ca	Mg	S
0	18.4 ±0.7a	3.28 ±0.23a	8.00 ±2.81a	0.57 ±0.20a	1.51 ±0.18a	0.91 ±0.06a
25	18.0 ±1.0a	3.20 ±0.37a	8.33 ±3.00a	0.55 ±0.18a	1.47 ±0.10a	$1.00 \pm 0.02b$
50	17.8 ±0.4a	$3.06 \pm 0.33a$	8.00 ±2.81a	0.53 ±0.14a	1.53 ±0.16a	0.93 ±0.08a
LSD0,05	0.6	0.26	2.39	0.14	0.12	0.05

Note: 0 - 0.0 g Se.ha⁻¹; 25 - 25 g Se.ha⁻¹; 50 - 50 g Se.ha⁻¹; the values in the columns with different letters are significantly different from each other at p < 0.05.

Table 3 Influence of foliar Se application on content of Cu, Fe, Mn, Z	In in oat grains.
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Dose Se ⁶⁺	Nutrient content (n	ntent (mg.kg-1), mean of years 2014, 2015, 2016			
(g Se.ha ⁻¹)	Cu	Fe	Mn	Zn	
0	5.39 ±0.85a	95.2 ±24.7a	42.4 ±7.3a	58.3 ±10.5a	
25	4.99 ±1.39a	98.0±31.6a	40.7 ±9.0a	58.0 ±10.8a	
50	5.38 ±0.91a	129.0 ±67.1a	$41.7 \pm 10.4a$	54.3 ±7.0a	
LSD _{0,05}	0.89	37.5	7.5	8.0	

Note: 0 - 0.0 g Se.ha⁻¹; 25 - 25 g Se.ha⁻¹; 50 - 50 g Se.ha⁻¹; the values in the columns with different letters are significantly different from each other at p < 0.05.

Table 4 Influence of Se foliar application on content of ash, starch and fat in oat grains.
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Dose Se ⁶⁴	Dose Se ⁶⁺ Content (%), mean of years 2014, 2015, 2016			
(g Se.ha ⁻¹)	ash	starch	fat	
0	3.98 ±1.13a	39.4 ±1.7a	3.72 ±0.26ab	
25	$4.10 \pm 1.48a$	39,1 ±1.7a	3.58 ±0.39a	
50	4.13 ±0.94a	39.9 ±2.4a	$4.01 \pm 0.43b$	
LSD _{0,05}	1.0	1.6	0.31	

Note: 0 - 0.0 g Se.ha⁻¹; 25 - 25 g Se.ha⁻¹; 50 - 50 g Se.ha⁻¹; the values in the columns with different letters are significantly different from each other at p < 0.05.

Table 5 Effect of foliar Se application on Se content in oat grains.

Dose Se ⁶⁺ Se content (mg.kg ⁻¹)					
(g Se.ha ⁻¹)	2014	2015	2016	Average of years	
0	<0.03a	<0.03a	<0.03a	<0.03a	
25	$0.35 \pm 0.02b$	0.13 ±0.05b	$0.36 \pm 0.08b$	0.28 ±0.12b	
50	$0.56 \pm 0.11c$	$0.25 \pm 0.06c$	$0.53 \pm 0.07c$	0.45 ±0.16c	
LSD0,05	0.13	0.08	0.12	0.12	

Note: 0 - 0.0 g Se.ha⁻¹; 25 - 25 g Se.ha⁻¹; 50 - 50 g Se.ha⁻¹; the values in the columns with different letters are significantly different from each other at p < 0.05.

The result is the increase of high amount of calcium and phosphorus in root shoot tissue (Hawrylak-Nowak, 2008).

Selenium foliar application showed a statistically nonsignificant effect on the content of microelements Cu, Fe, Mn, and Zn in oat grains (Table 3). Three-year average values of microelement contents after Se foliar application were Cu 4.99, 5.38 mg.kg⁻¹, Fe 98.0, 129.0 mg.kg⁻¹, Mn 40.7, 41.7 mg.kg⁻¹ and Zn 58.0, 54.3 mg.kg⁻¹. In experiments with maize grains according to **Wang et al.** (2013) Se soil and foliar applications did not confirm statistically significant influence on monitored microelements (Fe, Mn, Cu, Zn).

Se is a microelement influencing a proper function of organism, but with a negative effect in dosage. It means that selenium disposes with a very interesting property, where the main sign is a very thin line between dietary deficiency and toxicity (Kieliszek and Błażejak, 2013). Recent experiments have been focused on tracking the selenium content in selected crops intented for human consumption. A consumption of selenium affected products becomes the main source of selenium in human nutrition (Chen et al., 2002; Hawkesford and Zhao 2007; Lyons, Stangoulis and Graham, 2004; Ramos et al., 2010; Schiavon et al., 2013).

Qualitative parameters in oat grains (ash, starch, and fat) after foliar applications were studied. The achieved values of these parameters are ash 4.10, 4.13%, starch 39.1, 39.9%, and fat 3.58, 4.01%. A statistically significant influence on selected qualitative parameters was achieved only between foliar Se applications. The statistically non-significant effect was shown between the control variant (without Se treatment) and variants with Se foliar treatment (Table 4). Similar results were described in the experiment according to Havrlentová et al. (2013), where the qualitative parameter was β-D-glucan. A statistically significant difference was found between 2 variants of 5 by hulled oat. The application of fertilizers with selenium at naked oat grains was statistically non-significant. Other experiments with tomatoes showed interesting results in qualitative parameters, where foliar application of selenium had a positive effect on the increase of total polyphenol. The influence of Se biofortification on the content of vitamin C and carotenoids was not detected. Selenium foliar fertilization in dosage 150 g.ha⁻¹ is suitable way of tomato fruits enriching in polyphenols, without the negative effect on other antioxidants content (Andrejiová et al., 2019).

Foliar application of Se is usually more efficient than soil application whenever the element is prone to be sorbed into soil particles (Arthur, 2003), which is the case of Oxifact, Oxisols have positively charged surfaces that retain many anions (Lopes and Guimarães Guilherme, 2016), including selenite and selenate, thus decreasing the availability of soil apsoil-applied is interaction is especially strong for selenite, when compared with selenate. Irrespective of the form, in both cases (i.e., Se selenite or Se-selenate), since soil particles might absorb Se, the foliar application requires smaller doses and are more efficient (Fernandes Boldrin et al., 2013; de Oliveira et al., 2018; Zhu et al., 2009). Se, best acceptable in the form of Na₂SeO₄ (Eurola et al., 1990), is primarily transported into the chloroplast. SeO4-2 then activates ATP-sulphurylase and forms of APSe by being reduced to selenite. This results in the production of amino acids, such as selenocysteine and selenomethionine. Selenium increases the content of amino acids, particularly isoleucine (**Duma and Karklina, 2008**). Selenomethionine can be methylated to dimethylselenid through evaporation in the plant. It is particularly difficult and not easy to determine the levels of Se in the plant (**Brown and Shrift, 1982**), as well as determine whether Se is essential for plant microelements. However, there is evidence that a higher content of Se (depending on the concentration of sulphur) has a positive impact, not only on levels of amino acids but also on plant growth and multiplication (Ferri, Favero and Frasconi, 2007; Mora et al., 2015; Pennanen, Xue and Hartikainen, 2002; White and Broadley, 2009; White et al., 2007).

As expected, the Se content showed a statistically significant increase in oat grain after Se foliar treatment, as it is confirmed in Table 5. The average of years 2014 - 2016 in Se treatments were 0.28 ± 0.12 mg.kg⁻¹ and 0.45 ± 0.16 mg.kg⁻¹. Our achieved results of contents are comparable to multiple experiments (Aspila, 2005; Galinha et al., 2012; Ventura, 2008) with a positive effect on Se content in crops and vegetables after different application doses of selenium (Galinha et al., 2012; Ventura, 2008).

Selenium is an essential mineral element for the wellbeing of animals and a beneficial element for plants. However, excess Se can be toxic to both animals and plants. There is considerable interest in understanding how plants acquire and accumulate Se, not only to facilitate appropriate dietary Se intakes for animal and humans, which often requires Se biofortification of edible crops but also to remediate the land contaminated anthropogenically by an excess of Se and to appreciate the ecology of native plants inhabiting seleniferous soils.

CONCLUSION

This study monitored the effect of Se foliar application on macro- and microelements and selected qualitative parameters in oat grains. In most cases a statistically nonsignificant effect of Se treatment on macroelements and microelements content in oat grains was found. The only sulfur amount increased 1.00 ± 0.02 by foliar Se application in sodium selenate form in a dose of 25 g Se.ha⁻¹.

Qualitative parameters (ash, strarch, and fat) showed a statistically significant effect in fat content on both variants with Se treatment. Se contents in oat grains proved a statistically significant increase in both foliar Se applications, where the highest amount of Se 0.45 ± 0.16 was achieved on variants treated in dose of 50 g Se ha⁻¹.

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