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MINERAL COMPOSITION OF FIELD-GROWN LETTUCE (*Lactuca sativa L.*) DEPENDING ON THE DIVERSIFIED FERTILIZATION WITH IODINE AND SELENIUM COMPOUNDS

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Abstract. The practice of simultaneous biofortification (enrichment) of plants with iodine (I) and selenium (Se) is based on solid grounds. Their low content in soils is the cause of an endemic deficiency of I and Se in several billion people worldwide. There is still no objective information as to the impact of I and Se interactions on mineral nutrition of plants. The study (conducted in 2012–2014), included soil fertilization of the lettuce cv. 'Valeska' in the following combinations: control, KI, KIO_3, Na_2SeO_4, Na_2SeO_3, KI + Na_2SeO_4, KIO_3 + Na_2SeO_4, KI + Na_2SeO_3, KIO_3 + Na_2SeO_3. I and Se were applied twice: before sowing and as top-dressing (each 2.5 kg $I·ha^{-1}$ + 0.5 kg $Se·ha^{-1}$) – a total dose of 5 kg $I·ha^{-1}$ and 1 kg $Se·ha^{-1}$ was used. Fertilization with Na_2SeO_4, KI + Na_2SeO_4 and KIO_3 + Na_2SeO_4 considerably reduced the dry matter yield of the plants – it also lowered the content of P, K, Mg, Ca, B, Zn and Cd in the lettuce. Fertilization with Na_2SeO_3, KI + Na_2SeO_3 and KIO_3 + Na_2SeO_3 had a less negative impact on dry matter yield than the use of Na_2SeO_4 – every year it affected the mineral content in the lettuce in a highly varied manner. Dry matter productivity of the plants after fertilization with KI and KIO_3 varied between the research years – in those plots, I content in lettuce was negatively correlated with the content of K, Mg, Ca, S, Na, B, Cu, Fe, Mn, Zn, Cd and Pb. Combined fertilization with KI and KIO_3 with Na_2SeO_4, and with Na_2SeO_3 reduced the negative correlation between I content (in the KI and KIO_3 plots) and the content of K, Mg, Ca, S, Na, B, Cu, Fe, Mn, Zn, Cd and Pb. After fertilization with Na_2SeO_4, Se content was positively correlated with Na content and negatively correlated with the content of Mg, Ca, Fe, Mn and Cd. Se content in the lettuce after fertilizing exclusively with Na_2SeO_3 was positively correlated with the content of P, K, Na, Mn, Mo and Zn. The changeable climatic conditions

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“disguised” the influence of fertilization with I and Se on the mineral composition of the lettuce plants.

Key words: macronutrients, micronutrients, plant nutrition, heavy metals,, mineral nutrition

INTRODUCTION

Selenium (Se) and iodine (I) are essential to the proper functioning not only of the thyroid but also the entire organism both in humans and animals [White and Broadley 2009, Niwińska and Andrzejewski 2014]. The cause of an endemic deficiency of these elements in human and animal populations is their low transfer from soils to plants – and thus to the first link of the food chain. Fertilization of soils with I and Se is the simplest way of increasing the content of these components in plants. This process is classified as an agrotechnical method of plant biofortification with mineral components [White and Broadley 2009].

Although the influence of I and Se on plants has been investigated for many years, only in Finland or Malawi there have been implemented nationwide programs for soil fertilization with Se [Eurola et al. 2003, Chilimba et al. 2012]. Widespread introduction of plant biofortification principles to agricultural practice is hindered by the fact that both these elements are not considered as an essential plant nutrients. For this reason, there need to be identified all the aspects of the effects and interaction of these elements with regard to soil medium and plants, including its chemical composition.

With the application of incremental doses of I to the soil (0, 4, 16, 36, 64 and 100 mg I·kg^{-1} of soil) in the form of KI, there were noted increases in the content of Mg, Ca, Cu and Mn, as well as a reduced Fe content in tomato plants [Hageman et al. 1942]. In five species of warm climate plants there were also found varying quantitative relations, i.e., coefficient values of positive or negative correlations between I and the content of: Ag, Au, Ca, Co, Cr Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, Zn, Cd and F in the plants studied [Rashed 1995]. In field cultivation of lettuce [Smoleń et al. 2011] as well as in spinach grown in pots I used prior to sowing (in the form of KI) had a synergistic effect on Mg uptake and an antagonistic one on P and Cu uptake. KI fertilization in a dose of 2 mg·I dm^{-3} of soil, as compared to the dose of 1 mg·I dm^{-3} of soil, resulted in an increased content of Na, Fe, Zn and Al, and a decreased content of P, S, Cu and Ba in spinach cultivated in a pot experiment [Smoleń and Sady 2011]. After a single presowing application of I, as well as with the application of continuous fertigation with I, there was noted an antagonistic impact of this element on Ca, Na and Zn uptake, and a synergistic effect on Fe uptake in spinach [Smoleń and Sady 2012].

In terms of the influence of Se on the mineral status of plants, Hawrylak-Nowak et al. [2015] determined that the content of N, P, K, Mg, Ca and S in the shoots of cucumber plants cultivated in hydroponics was basically constant, though it varied significantly depending on the dose (0, 2, 4, 6, 10, 20, 30, 40, 60 μM Se) of Se in the form of SeO_4^{2-} and SeO_3^{2-}. In the research by Çolak et al. [2014] there was recorded a varied influence of Se on the content of C, N, O, Se, S, P, Na, Mg, K, Ca, Mn, Fe, Co, Cu, Zn and Cl in the root and hypocotyl epidermal cells, and the cotyledon lower epidermal cells of the tomato seedlings. Moreover, the development of absorbing hairs in the roots of the tomato seedlings was decreased in parallel with the increasing Se concentrations in the nutrient solution.

In pioneering research on the simultaneous application of I and Se there was not found any significant impact of I fertilization on the Se content, nor of Se fertilization on the I content in spinach plants [Zhu et. al. 2004]. In hydroponic lettuce cultivation in an NFT system Smoleń et al. [2014] did not observe any significant influence of separate or combined application of KIO_3 and Na_2SeO_4 (applied to the nutrient medium or by foliar feeding) on the content of N, P, K, Ca, Mg, S, B, Cu, Fe, Mn, Mo and Zn in the leaves, or N, P, K, S, B. Cu, Mn, Mo and Zn in the roots. In the roots of lettuce cultivated on a nutrient medium containing 0.5 mg Se + 1.0 mg I·dm^{-3} the content of Ca, Mg and Fe decreased. Whereas in the literature there are no results of any research documenting the interaction effects of various chemical forms of I and Se on the mineral composition of plants grown in field conditions. Conducting such research is highly consequential for farming practice.

Choosing lettuce for the experiments was dictated by it belonging to model species used in some primary research [Dzida et al. 2012, Pitura and Michałojć 2012, Borowski et al. 2014, Sirtautas et al. 2014], including that in the area of biofortification with I [Blasco et al. 2010, 2012, 2011a, b] and Se [Ramos et al. 2010, Ríos et al. 2008, 2010].

The aim of the study was to evaluate the influence of I and Se fertilization (in their different chemical forms) on the mineral composition of lettuce heads grown in soil in field conditions.

MATERIAL AND METHODS

Plant material and treatments

A field study with the lettuce *Lactuca sativa* L. var. *capitata* cv. 'Valeska' was conducted at the Experimental Station (50°07'910 N, 19°84'764 E) of the University of Agriculture in Kraków, Poland. In 2012–2014 lettuce was grown during the spring season in different parts of the same field of the experimental station.

Seed was sown during the first ten days of March (in each research year) in a greenhouse, where seedlings were produced. On 18, 23 and 15 of April (fig. 1) in the subsequent years, seedlings were planted into soil in rows 30 cm apart, with 30 cm plant spacing.

Lettuce was cultivated in heavy soil (heavy clay: 24% sand, 23% silt and 53% loam). Each year, the chemical parameters of the soil prior to the cultivation of lettuce were within the following range (tab. 1): organic matter 2.33–2.56%, cation exchange capacity 2.33–2.56 cmol·kg^{-1}, saturation of the sorption complex with alkaline elements 85.8–92.7%, pH_{H_2O} 6.92–7.45, EC 0.10–0.1 mS cm^{-1}, Eh from +189.3 to +276.0 mV, $N\text{-}NH_4$ + $N\text{-}NO_3$ 8.4–13.4 mg·dm^{-3}, P 12.8–59.5 mg·dm^{-3}, K 139.1–190.4 mg·dm^{-3}, Mg 114.0–194.2 mg·dm^{-3}, Ca 1 211.0–2 089.3 mg·dm^{-3} and S 22.1–42.9 mg·dm^{-3}.

The study included soil fertilization with I and Se in the following combinations: 1) Control, 2) KI, 3) KIO_3, 4) Na_2SeO_4, 5) Na_2SeO_3, 6) KI+Na_2SeO_4, 7) KIO_3+Na_2SeO_4,

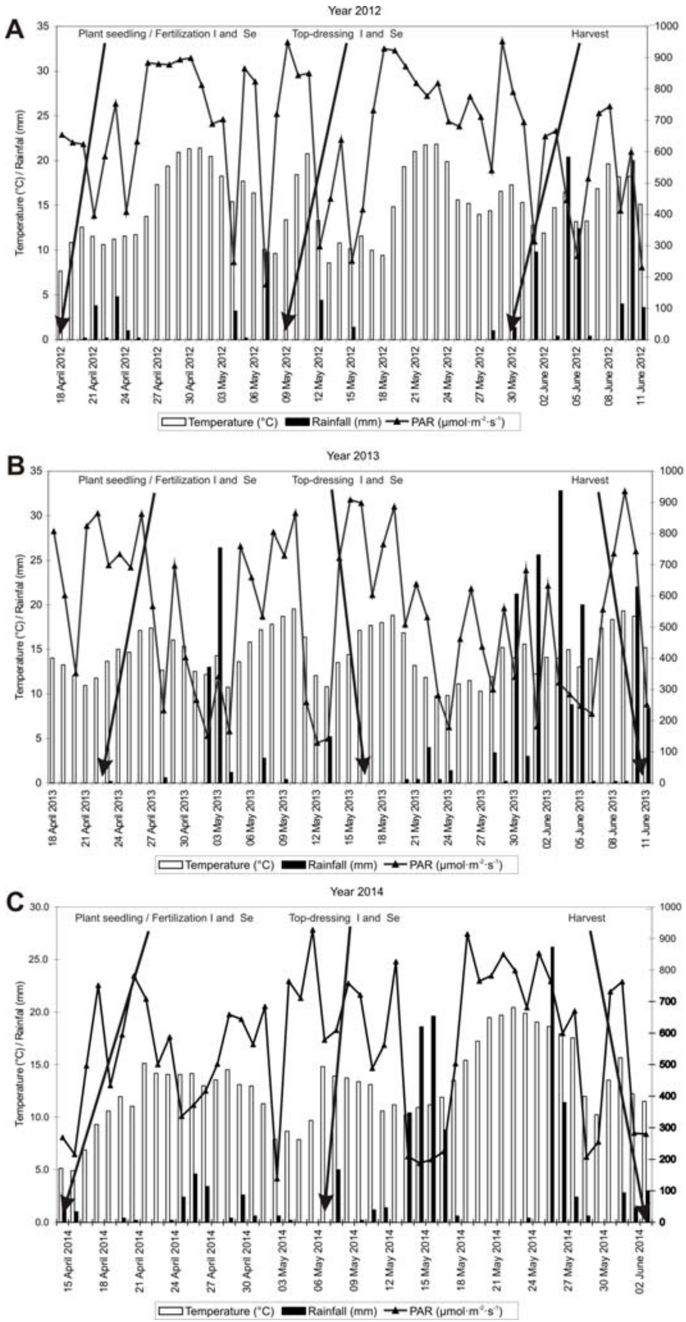

Fig. 1. Weather conditions in the lettuce cultivation period in 2012 (A), 2013 (B) and 2014 (C). The figure also shows the times marked for planting, presowing and top-dressing fertilization with I and Se, and for the harvest of lettuce

Table 1. Selected chemical properties of the 0–30 cm soil layer prior to the experiment in 2012–2014

Parameter	Year 2012	Year 2013	Year 2014
pH_{H_2O}	6.72	7.45	7.19
EC (mS cm^{-1})	0.10	0.11	0.10
Eh (mV)	276.0	268.0	189.3
$N\text{-}NH_4 + N\text{-}NO_3$ ($mg \cdot dm^{-3}$)	13.4	12.7	8.4
P ($mg \cdot dm^{-3}$)	32.7	12.8	59.5
K ($mg \cdot dm^{-3}$)	181.4	139.1	190.3
Ca ($mg \cdot dm^{-3}$)	2 089.3	1 651.8	1 211.0
Mg ($mg \cdot dm^{-3}$)	194.2	182.8	114.0
Na ($mg \cdot dm^{-3}$)	8.6	23.5	2.9
S ($mg \cdot dm^{-3}$)	41.4	42.9	22.1
Organic matter (%)	2.33	2.56	2.33
Cation exchange capacity (CEC $cmol \cdot kg^{-1}$)	8.32	9.58	8.48
Saturation of the sorption complex with alkaline elements (%)	92.7	88.2	85.8

8) $KI+Na_2SeO_3$, 9) $KIO_3+Na_2SeO_3$. I and Se were applied twice: before planting seedlings and as top-dressing (in the first phase of formation of lettuce heads – the first ten days of May), in a total dose of 5 kg $I \cdot ha^{-1}$ and 1 kg $Se \cdot ha^{-1}$ (presowing and top-dressing of 2.5 kg $I \cdot ha^{-1}$ + 0.5 kg $Se \cdot ha^{-1}$), respectively. Fertilization with I and Se was performed using analytically pure reagents: KI and KIO_3 (P.O.Ch., Poland) as well as Na_2SeO_4 and Na_2SeO_3 (Sigma-Aldrich, Germany).

Presowing fertilization with I, Se and N, P, K was performed one day prior to lettuce planting (fig. 1). The dosages of P and K were calculated based on soil analysis results – the P and K content was supplemented to the levels optimal for lettuce, i.e., P-70 and K-200 (in $mg \cdot dm^{-3}$ of soil). At that time fertilization with N was applied as ammonium nitrate in a dose of 50 mg $N \cdot dm^{-3}$ soil, i.e., 50% of the N dose. Presowing fertilization with Mg, Ca and S was not performed, because their content in the soil covered the nutritional requirements of lettuce. The remaining 50% of N dose was applied at the same time as the top-dressing application of I and Se. After the top-dressing fertilization with I, Se and N, rain irrigation was applied to the plants in a dose of ca. 15 mm of rain.

The experiment was arranged in a split-plot design with four replications. Each experimental treatment was randomized in four replications, in 5 m × 1.5 m (7.5 m^2) plots. The total area used for the experiment was 270 m^2.

During harvest (30 May, 11 and 3 June in the subsequent years), the weight of the heads was measured for lettuce from sixteen plants from each plot/replication. For the purpose of the analysis, eight lettuce heads were collected from each replication.

Plant analysis

Washed and dried lettuce leaves (without the heart – contracted stem) were broken up in a mixer and dried at 70°C. After drying, the samples were ground with a variable speed rotor mill Pulverisette 14, FRITSCH using a 0.5 mm sieve. In order to determine the total content of P, K, Mg, Ca, S, Na, B, Cu, Fe, Mn, Mo, Zn, Cd and Pb, the milled lettuce samples were subjected to mineralization in 65% super pure HNO_3 [Pasławski and Migaszewski 2006], in a CEM MARS-5 Xpress microwave digestion system. The content of these elements was determined with the use of a high-dispersion spectrometer, ICP-OES from Prodigy Teledyne LeemanLabs.

Meteorological data

The most adverse climatic conditions for lettuce growing were observed in 2012 (fig. 1). In 2012, in relation to the years 2013–2014, there were recorded the lowest rainfall and the highest daily average temperature of air and PAR (photosynthetically active radiation). It was essential that in 2013 and 2014, a few days before the harvest of the lettuce, heavy rainfall occurred.

From the time of planting the lettuce in the field (the end of April) to its harvest (the end of May/beginning of June) the average daily PAR was 656.7, 537.8 and 562.4 $\mu mol \cdot m^{-2} \cdot s^{-1}$. Whereas the total amount of rainfall was 31.6, 203.8 and 132.2 mm for 2012, 2013 and 2014, respectively. The daily average air temperature for the whole of May was 15.6, 14.0 and 13.8°C for 2012, 2013 and 2014, respectively. For comparison, in the years 1971–2000 the monthly average precipitation total in the region of the research was: 50 mm in April, 74 mm in May and 94 mm in June [GUS (Central Statistical Office of Poland) of 2005]. On the other hand, in the years 1971–2000, the average monthly air temperature was: 8.0°C in April, 13.4°C in May and 16.2°C in June.

Data analysis

Due to the character of this publication, it contains the results of dry matter yield per hectare and the mean dry matter content in one lettuce head. These data were calculated on the basis of determination of dry matter in the lettuce (using the oven-drying method at 105ºC) as well as fresh matter yield per hectare and the weight of lettuce heads. The results of the fresh matter yield of the lettuce will be the subject of a separate publication [Smoleń et al. 2015].

The results obtained were statistically verified with the ANOVA module of the Statistica 8.0 PL suite for a significance level $P < 0.05$. Changes of any significance were assessed with the use of variance analysis. In instances of significant changes homogenous groups were determined on the basis of Tukey's test.

There were also calculated coefficients for the correlation between I and Se content and the content of P, K, Mg, Ca, S, Na, B, Cu, Fe, Mn, Mo, Zn, Cd and Pb in lettuce by using Pearson correlation analysis.

RESULTS AND DISCUSSION

The I and Se compounds used in this research had a significant impact on dry matter yield per hectare and the mean dry matter content in one lettuce head (figs 2 A, B), and also on the content of P, K, Mg, Ca, S, Na (figs 3 A–F), B, Cu, Fe, Mn, Mo, Zn, Cd and Pb (figs 4 A–H) in the lettuce. However, during each year of the research there was observed a varied influence of each combination of fertilization with I and Se on these parameters. Additionally, for each of the combinations studied, the coefficients of correlations between the content of I as well as Se (variable *x*) and the content of P, K, Mg,

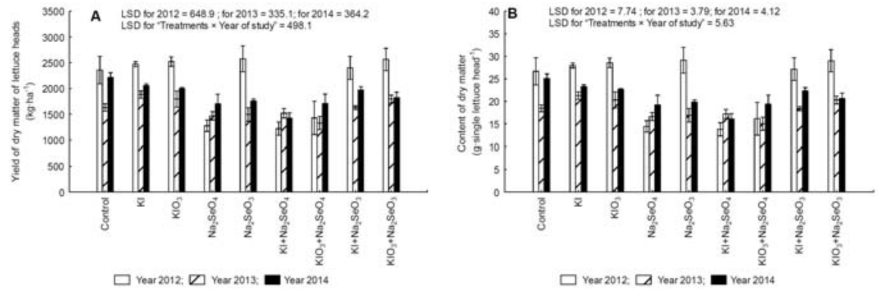

Fig. 2. The effect of I and Se fertilization on the dry matter yield of lettuce heads (A) and the content of dry matter in a single lettuce head (B). Bars indicate standard error (n = 4)

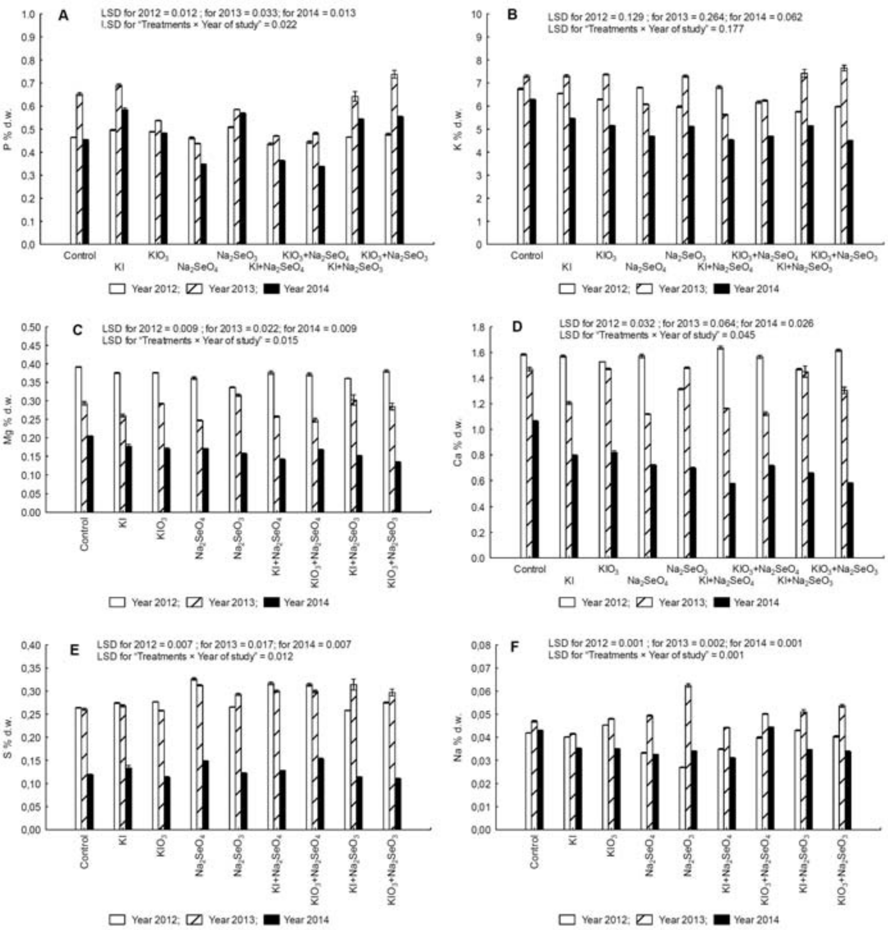

Fig. 3. The content of P (A), K (B), Mg (C), Ca (D), S (E) and Na (F) in lettuce. Bars indicate standard error (n = 4)

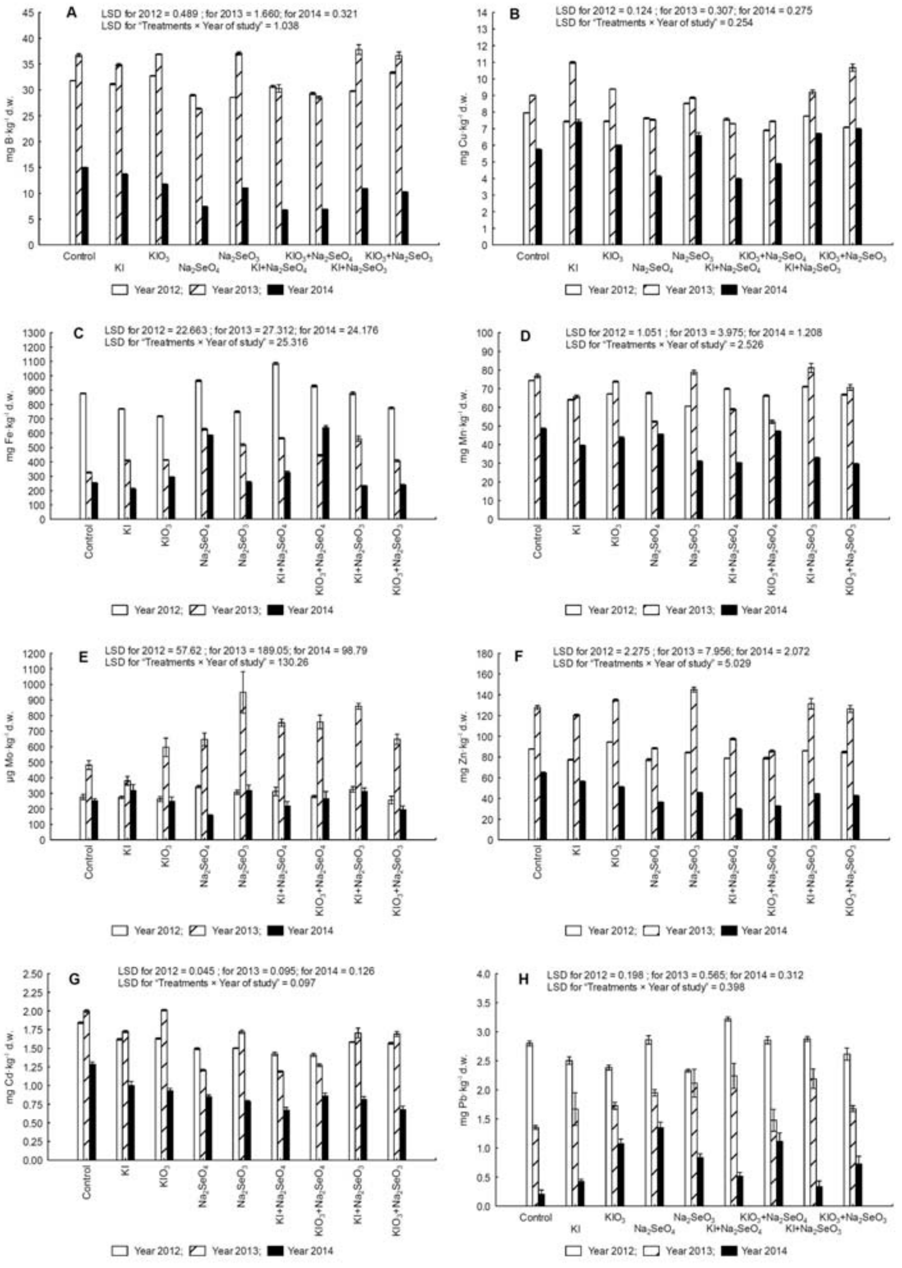

Fig. 4. The content of B (A), Cu (B), Fe (C), Mn (D), Mo (E), Zn (F), Cd (G) and Pb (H) in lettuce. Bars indicate standard error (n = 4)

Table 2. Coefficients of the correlation between the iodine content and the content of macro- and microelements and heavy metals in lettuce

Element content in lettuce (variable *y*)	Iodine content in lettuce (mg I·kg^{-1} d.w.) (variable *x*)								
	treatments/correlation coefficient r (n = 12)								
	control	KI	KIO_3	Na_2SeO_4	Na_2SeO_3	KI + Na_2SeO_4	KIO_3 + Na_2SeO_4	KI + Na_2SeO_3	KIO_3 + Na_2SeO_3
P % d.w.	0.61*	0.21	-0.31	-0.26	-0.68*	-0.37	-0.51	-0.69*	0.37
K % d.w.	0.50	-0.71*	-0.67*	-0.13	0.17	-0.83*	-0.68*	-0.77*	-0.04
Mg % d.w.	-0.18	-0.88*	-0.97*	0.10	0.71*	-0.84*	-0.96*	-0.16	-0.47
Ca % d.w.	0.03	-0.92*	-0.94*	0.04	0.52	-0.81*	-0.95*	-0.36	-0.43
S % d.w.	0.12	-0.89*	-0.95*	-0.36	0.55	-0.64*	-0.76*	-0.56	-0.26
Na % d.w.	0.61*	-0.80*	-0.85*	-0.84*	-0.32	0.01	0.63*	-0.69*	0.09
mg B·kg^{-1} d.w.	0.25	-0.83*	-0.87*	-0.33	0.42	-0.60*	-0.73*	-0.58*	-0.25
mg Cu·kg^{-1} d.w.	0.29	-0.21	-0.59*	-0.40	0.54	-0.62*	-0.56*	-0.74*	0.20
mg Fe·kg^{-1} d.w.	-0.41	-0.85*	-0.88*	0.34	0.82*	-0.87*	-0.74*	0.01	-0.57
mg Mn·kg^{-1} d.w.	0.20	-0.88*	-0.84*	0.18	0.39	-0.74*	-0.95*	-0.51	-0.27
µg Mo·kg^{-1} d.w.	0.38	0.24	-0.20	-0.71*	-0.27	0.16	0.18	-0.83*	0.28
mg Zn·kg^{-1} d.w.	0.50	-0.49	-0.66*	-0.56	0.17	-0.41	-0.62*	-0.69*	-0.04
mg Cd·kg^{-1} d.w.	0.25	-0.81*	-0.76*	-0.03	0.51	-0.74*	-0.82*	-0.46	-0.25
mg Pb·kg^{-1} d.w.	-0.24	-0.86*	-0.91*	0.10	0.66*	-0.79*	-0.95*	-0.17	-0.56

* – Pearson’s correlation analysis ($p < 0.05$ considered significant)

Table 3. Coefficients of the correlation between the selenium content and the content of macro- and microelements and heavy metals in lettuce

Element content in lettuce (variable *y*)	Selenium content in lettuce (mg Se·kg^{-1} d.w.) (variable *x*) treatments/correlation coefficient r (n = 12)								
	control	KI	KIO_3	Na_2SeO_4	Na_2SeO_3	KI + Na_2SeO_4	KIO_3 + Na_2SeO_4	KI + Na_2SeO_3	KIO_3 + Na_2SeO_3
P % d.w.	-0.64*	0.61*	0.69*	-0.40	0.82*	-0.45	-0.45	0.95*	0.98*
K % d.w.	-0.27	-0.32	0.39	-0.53	0.80*	-0.96*	-0.63*	0.81*	0.73*
Mg % d.w.	0.70*	-0.94*	-0.48	-0.75*	0.18	-0.96*	-0.97*	-0.09	-0.13
Ca % d.w.	0.44	-0.90*	-0.16	-0.69*	0.47	-0.95*	-0.95*	0.16	-0.03
S % d.w.	0.28	-0.70*	-0.19	-0.27	0.42	-0.77*	-0.72*	0.44	0.36
Na % d.w.	-0.77*	-0.51	0.10	0.71*	0.99*	-0.03	0.70*	0.63*	0.82*
mg B·kg^{-1} d.w.	0.05	-0.54	0.06	-0.31	0.57	-0.72*	-0.68*	0.46	0.37
mg Cu·kg^{-1} d.w.	-0.04	0.24	0.48	-0.23	0.40	-0.75*	-0.50*	0.71*	0.94*
mg Fe·kg^{-1} d.w.	0.88*	-0.94*	-0.75*	-0.91*	-0.20	-1.00*	-0.81*	-0.32	-0.45
mg Mn·kg^{-1} d.w.	0.18*	-0.62*	0.11	-0.81*	0.62*	-0.87*	-0.98*	0.37	0.34
µg Mo·kg^{-1} d.w.	-0.56	0.43	0.74*	0.43	0.90*	0.10	0.29	0.92*	0.91*
mg Zn·kg^{-1} d.w.	-0.38	-0.06	0.38	-0.00	0.80*	-0.50	-0.57	0.66*	0.70*
mg Cd·kg^{-1} d.w.	0.04	-0.56	0.26	-0.61*	0.49	-0.88*	-0.81*	0.29	0.36
mg Pb·kg^{-1} d.w.	0.72	-0.83*	-0.57	-0.74*	0.13	-0.90*	-0.96*	-0.08	-0.24

* – Pearson's correlation analysis ($p < 0.05$ considered significant)

Ca, S, Na, B, Cu, Fe, Mn, Mo, Zn, Cd and Pb (variable *y*) assumed extremely dissimilar values (tabs 2, 3).

The influence of I on the uptake of macro- and micronutrients as well as trace elements may be dependent on multiple factors: the form, dose and mode of I application, the soil and substratum type or the culture medium in hydroponics, climatic conditions during the raising process, and genotypical (varietal) differences in plants in terms of their preference of mineral nutrients uptake from soil [Hageman et al. 1942, Rashed 1995, Smoleń and Sady 2011, 2012 Smoleń et al. 2011, Blasco et al. 2012]. The influence of Se fertilization on the mineral composition of plants also depends on the same factors as in the case of I [Çolak et al. 2014, Hawrylak-Nowak et al. 2015].

Smoleń et al. [2014] did not demonstrate any interactions of I and Se (in the form of KIO_3 and Na_2SeO_4), applied by foliar feeding or to the nutrient medium, with the mineral composition of lettuce grown in hydroponic culture. Only in the roots there was recorded a decreased content of Ca, Mg and Fe, after lettuce cultivation on a nutrient medium with an addition of 0.5 mg Se + 1.0 mg I·dm^{-3}. Apart form this information, there is no data in the literature on the interaction of I and Se affecting the chemical composition of plants.

After cultivation in the conditions of dry and hot weather, in 2012 lettuce plants were characterized by a definitely higher content of Mg, Ca (figs. 3 C, D), Fe and Pb (figs 4 C, H) than in 2013 and 2014 – years with optimum and excessive rainfall volumes, respectively, during the cultivation of the plants in the field (fig. 1). In 2014 lettuce was characterized by the lowest content of K, Mg, Ca, S (figs 3 B, C, E), B, Cu, Fe, Mn, Zn Cd and Pb (figs 4 A, B, C, D, F, G, H) in relation to plants grown in 2012 and 2013. It needs to be underlined that in the control as well as in combinations with the application of I (both KI and KIO_3) and Na_2SeO_3 alone or simultaneously, higher values of dry matter yield (kg·ha^{-1}) and the content of dry matter in one lettuce were found in 2012 than in 2013 and 2014. That was not registered for the application of fertilization with Na_2SeO_4 alone or together with KI or KIO_3.

SeO_4^{2-} (selenate) and SO_4^{2-} (sulfate) ions can be actively transported in plants by the same transport proteins, that is high-affinity sulfate transporters [Li et al. 2008, Zhu et al. 2009]. In our research in 2013 and 2014, there was observed a highly negative effect of the application of Na_2SeO_4 (separately and in combination with KI or KIO_3) on the uptake of P, K, Mg, Ca (figs 3 A, B, C, D), B, Zn and Cd (figs 4 B, F, G), but not S. Importantly, in 2012 the negative effect of Na_2SeO_4, KI + Na_2SeO_4 and KIO_3 + Na_2SeO_4 on the uptake of P, K, Mg, Ca, B, Zn and Cd was not observed, or was less significant than in 2013 and 2014. It should be emphasized that in the plot fertilized exclusively with Na_2SeO_4 the Se content was positively correlated with Na content and negatively correlated with the content of Mg, Ca, Fe, Mn, and Cd (tab. 3).

With combined application of KI + Na_2SeO_4, KIO_3 + Na_2SeO_4, Se content was negatively correlated with much larger amounts of certain elements (than while applying Na_2SeO_4 alone), that is with: K, Mg, Ca, S, B, Cu, Fe, Mn and Cd. Only in this aspect did there manifest the close connection, presented by Zhu et al. [2009], between the uptake of SeO_4^{2-} and S by plants. In our opinion, the negative correlation between Se content and the content of K, Mg, Ca, S, B, Cu, Fe, Mn and Cd resulted, rather, from the effect of additional application of KI or KIO_3 with Na_2SeO_4, than from the interaction of I with Se (tab. 3). We draw this conclusion because after fertilization exclusively with KI or KIO_3, I content in the lettuce was negatively correlated with the content of K, Mg, Ca, S, Na, B, Fe, Mn, Cd, and Pb, and further, Cu and Zn, but only after the application of KIO_3 (tab. 2). Neither did combined application of KI + Na_2SeO_4 and KIO_3 + Na_2SeO_4 change the negative relations between I content and said elements in the lettuce. It should be noted that after the application of KI + Na_2SeO_4 the coefficient values of the correlation between I content and the content of Ca, S, B, Mn Cd, and Pb were not that high (in relation to KI fertilization), but they still came out negative. An exception in the plot fertilized with KI + Na_2SeO_4 was the emergence of a negative interrelation between the I and Cu content in lettuce (r = -0.62). In the case of combined fertilization with KIO_3 + Na_2SeO_4, the coefficients of the correlation between I content and the content of Na and Cu (in comparison to KIO_3 application) were reduced – for Na they even had a positive value r = 0.63.

Fertilization with KI + Na_2SeO_3 and KIO_3 + Na_2SeO_3, in relation to the application of KI or KIO_3 (differently to applying KI + Na_2SeO_4 and KIO_3 + Na_2SeO_4), diametrically changed the coefficient values of the correlation between the iodine content and the content of K, Mg, Ca, S, Na, B, Cu, Fe, Mn, Zn, Cd and Pb in the lettuce (tab. 2). Only with fertilization with KI + Na_2SeO_3, in comparison to KI, the iodine content in the lettuce remained in a significantly negative correlation with the content of K, Na and B (less expressed in the case of Na and B), and additionally with Cu content.

After fertilization exclusively with Na_2SeO_3, Se content in the lettuce was significantly and positively correlated with the content of P, K, Na, Mn, Mo and Zn (tab. 3). With Na_2SeO_3 fertilization, the significant correlation between the content of Se and P may result from the synergetic effect of SeO_3^{2-} ions on the uptake of HPO_4^{2-} ions through the roots. SeO_3^{2-} and HPO_4^{2-} ions are actively transported in plants by the same transport proteins, that is high-affinity phosphate transporters [Li et al. 2008, Zhu et al. 2009]. In a study of Altansuvd et al. [2014] the total concentration of Se was significantly correlated with the available P. Soil soluble Se and the soil–plant transfer factor for Se were not affected by P fertilization. In our research, combined fertilization with KI + Na_2SeO_3 and KIO_3 + Na_2SeO_3, in relation to application of Na_2SeO_3 alone, caused a significant lessening of the correlation of the content of Se and Mn, and the formation of a vital and positive interrelation between the content of Se and the Cu; r = 0.71 and 0.94 (for KI + Na_2SeO_3 and KIO_3 + Na_2SeO_3, respectively).

It is worth noting that in relation to the control, in the years 2012–2014 fertilization with Na_2SeO_3, KI + Na_2SeO_3 and KIO_3 + Na_2SeO_3 had a multifarious effect on the content of the studied elements in lettuce (figs 3 A–F and figs 4 A–H). In essence, these fertilization combinations did not have such a negative impact on the mineral composition of the plants as fertilizing with Na_2SeO_4, KI + Na_2SeO_4 and KIO_3 + Na_2SeO_4.

The results of our research unambiguously indicate that with the deficit rainfall volume and consecutive heat waves in 2012, the effect of the toxic action of Na_2SeO_4 was intensified (when applied separately and combined with KI and KIO_3), the primary and measurable result of which was a significant reduction of dry matter yield per hectare and a drop of the dry matter content in a single lettuce head. It is curious that it did not translate into some spectacular imbalances of the mineral composition of the plants in 2012, which occurred in 2013 and 2014 – after plant cultivation under moderate and higher than optimum rainfall volumes. That may have been caused by reduced uptake of water by the roots, and thus of mineral nutrients from the soil in 2012. It seems, however, that it was a more complex problem. In 2012, in comparison to the period 2013–2014, there may have occurred a weakening of the flushing (transport) of the characterized elements in the soil, due to which the plants could have absorbed them in greater amounts – this applies to Mg, Ca (figs 3 C, D), Fe and Pb (figs 4 C, H). Perhaps there also ensued a nutrient concentration effect in the lettuce owing to a lower leaf water content. Hence dry matter yield per hectare and the dry matter content in a single lettuce head (figs 2 A, B) were highest in 2012, except for the combinations of Na_2SeO_4, KI + Na_2SeO_4 and KIO_3 + Na_2SeO_4. Thus, the climatic conditions (the drought and the heat spells in 2012, as compared to the period 2013–2014) 'disguised' the effect of fertilization with I and Se on the mineral composition of the lettuce plants.

I in the form of iodides (I^-) is more easily absorbed by plants than iodate ions (IO_3^-), but at the same time the toxicity of I^- ions is greater than that of IO_3^- ions – this was discovered in cultures of lettuce [Blasco et al. 2010, Blasco et al. 2011a, b], rice [Kato et al. 2013], tomato and spinach [Gonda et al. 2007] or Chinese cabbage [Hong et al. 2012]. In studies of Blasco et al. [2012], I applied in the form of IO_3^- (in concentrations of 0, 20, 40, 80 μM) was less toxic for plants and caused less severe imbalances in the macro- and micronutrients content in lettuce than application of I in the I^- form.

As regards Se, selenates (VI) (SeO_4^{2-}) are generally more easily absorbed, but they are also more damaging to plants than selenates (IV) (SeO_3^{2-}) if plans are cultivated in soil [Kopsell and Kopsell 2007]. There are available results of research in this area documenting opposite relations that indicate easier uptake and higher toxicity for lettuce plants in soilless culture of the SeO_3^{2-} form than SeO_4^{2-} [Ríos et al. 2008, 2010, Ramos et al. 2010]. Ramos et al. [2010] and Ríos et al. [2010] have demonstrated lower dry matter productivity of lettuce plants after the application of SeO_3^{2-} than SeO_4^{2-}. In hydroponic corn culture, the SeO_3^{2-} form, as compared to SeO_4^{2-}, caused a reduction of the leaf area, dry matter of whole plants and seeds, and the number of seeds [Longchamp et al. 2015]. Interestingly, the total Se content in whole corn plants, roots and grains was higher after fertilization with SeO_3^{2-} than SeO_4^{2-}, but in the leaves Se content was higher after the application of SeO_4^{2-} than SeO_3^{2-}. In the research of Hawrylak-Nowak et al. [2015] cucumber plants cultivated in hydroponics showed higher sensitivity to SeO_3^{2-} than to SeO_4^{2-} – importantly, the total Se content in the shoots was lower with the application of SeO_3^{2-} than SeO_4^{2-}. The disparities between these authors with respect to the preferences of uptake and toxicity of SeO_3^{2-} over SeO_4^{2} arise not so much from specific differences, but chiefly from growing the plants in different conditions – soil, soilless techniques or hydroponics. In soil, selenate(IV) (SeO_3^{2-}) is less bioavailable to plants than is selenate(VI) (SeO_4^{2-}), because the former is more strongly adsorbed by Fe oxides and/or hydroxides [Zhu et al. 2009].

Our research has unambiguously demonstrated that the form SeO_4^{2-} showed higher toxicity for plants than SeO_3^{2-} – essentially in terms of dry matter yield per hectare and the average dry matter content in a single lettuce head (figs. 2 A, B). In the cases of application of I dose five times higher than that of Se, there were not observed any differences between KI and KIO_3 in terms of dry matter productivity in the plants. In each of the years it was at levels higher, lower than or identical to the control. This could seemingly indicate an absence of toxic effects of I compounds on the plants. However, the results of negative correlation of the Se content with the content of K, Mg, Ca, S, Na, B, Cu, Fe, Mn, Zn, Cd and Pb in the lettuce (tab. 2), discussed above, unambiguously indicate a negative impact of I on the mineral composition of the plants. Negative but not translating explicitly in each of the years of the research into plant yield (dry matter yield or dry matter content in lettuce heads). Estimating the content of the selected elements in lettuce heads, it needs to be stressed that fertilization exclusively with KI or KIO_3, in relation to the control, caused a significant lowering of the Mg, Fe, Mn and Cd content in 2012, and the content of K, Mg, Ca, Na, Mn, Zn and Cd in 2014 (figs 3A–F, figs 4 A–H). With the other elements, in the years 2012–2014 there was obtained a very different and highly varied influence of KI and KIO_3 on the degree of accumulation of the macro- and microelements, and heavy metals in the lettuce.

It is worth emphasizing that in comparison to the control, in none of the research years was there observed any significant increase of K and Na content in the lettuce after fertilization with KI and KIO_3 as well as Na_2SeO_4 and Na_2SeO_3, respectively – with the exception of Na with Na_2SeO_3 fertilization in 2013 (figs 3 B, F). That could have been caused by the application of low doses of K and Na introduced to the soil together with KI, KIO_3, Na_2SeO_4 and Na_2SeO_3. With KI and KIO_3 application, K dose was about 748 g $K \cdot ha^{-1}$, and with using Na_2SeO_4 and Na_2SeO_3 Na dose was about 139 g $Na \cdot ha^{-1}$.

As for the very results of determination of the I and Se content in lettuce, they are the subject of another publication of the same team of authors [Smoleń et al. 2015]. Within the three years of the study the content of I and Se stayed within the following ranges for individual combinations no. 1–9: 1) 1.13–1.61, 2) 4.00–7.67, 3) 2.89–5.45, 4) 0.99–1.79, 5) 1.39–1.86, 6) 3.40–5.35, 7) 2.64–5.34, 8) 4.05–5.06, 9) 4.24–4.77 mg $I \cdot kg^{-1}$ d.w. and 1) 1.32–7.57, 2) 1.68–2.18, 3) 1.87–4.07, 4) 38.03–219.19, 5) 3.68–34.82, 6) 33.94–148.05, 7) 37.79–157.35, 8) 4.05–31.62, 9) 2.11–21.27 mg $Se \cdot kg^{-1}$ d.w. [Smoleń et al. 2015].

CONCLUSIONS

Application of Na_2SeO_4 alone or together with I (KI and KIO_3) caused a reduction of the dry matter yield as well as the content of P, K, Mg, Ca, B, Zn and Cd in the lettuce – peaking in the conditions of dry and hot weather in 2012.

Treatment with Na_2SeO_3 (applied separately and in combination with I) had a less negative impact on dry matter yield per hectare and dry matter content in lettuce heads than respective use of Na_2SeO_4.

In the three-year period of the research, plots with Na_2SeO_3 application had a highly varied influence on the content of P, K, Mg, Ca, S, Na, B, Cu, Fe, Mn, Mo, Zn, Cd and Pb in the lettuce.

Fertilization with KI and KIO_3 combined with with Na_2SeO_3, diminished the negative relation (illustrated by a correlation) between the I content (in KI and KIO_3 plots) and the content of K, Mg, Ca, S, Na, B, Cu, Fe, Mn, Zn, Cd and Pb in the lettuce.

The Se content in the lettuce after fertilization with Na_2SeO_3 alone was positively correlated with the content of P, K, Na, Mn, Mo and Zn.

The climatic conditions (the drought and the heat spells in 2012 as compared to the period 2013–2014) 'disguised' the influence of fertilization with I and Se on the mineral composition of the lettuce plants.

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SKŁAD MINERALNY ROŚLIN SAŁATY (*Lactuca sativa* L.) GRUNTOWEJ W ZALEŻNOŚCI OD ZRÓŻNICOWANEGO NAWOŻENIA ZWIĄZKAMI JODU I SELENU

Streszczenie. Prowadzenie równoczesnej biofortyfikacji (wzbogacenia) roślin w I i Se jest uzasadnione. Niska ich zawartość w glebach jest przyczyną endemicznego niedoboru I i Se u kilku miliardów ludzi na świecie. Wciąż brak jest obiektywnych informacji na temat wpływu interakcji I i Se na gospodarkę mineralną roślin. Badania (przeprowadzone w latach 2012–2014) obejmowały nawożenie doglebowe jodem i selenem sałaty odmiany Valeska z uwzględnieniem następujących kombinacji: kontrola, KI, KIO_3, Na_2SeO_4, Na_2SeO_3, KI + Na_2SeO_4, KIO_3 + Na_2SeO_4, KI + Na_2SeO_3, KIO_3 + Na_2SeO_3. Jod i selen były aplikowane dwukrotnie: przedsiewnie i w nawożeniu pogłównym (po 2,5 kg $I \cdot ha^{-1}$ + 0,5 kg $Se \cdot ha^{-1}$) – zastosowano całkowitą dawkę 5 kg $I \cdot ha^{-1}$ i 1 kg $Se \cdot ha^{-1}$. Nawożenie Na_2SeO_4, KI + Na_2SeO_4 i KIO_3 + Na_2SeO_4 powodowało silne ograniczenie wielkości plonu suchej masy roślin – wpływało również na obniżenie zawartości P, K, Mg, Ca, B, Zn i Cd w sałacie. Nawożenie Na_2SeO_3, KI + Na_2SeO_3 i KIO_3 + Na_2SeO_3 miało mniej negatywny wpływ na plon suchej masy niż stosowanie Na_2SeO_4 – rokrocznie miało one bardzo zróżnicowany wpływ na zawartość składników mineralnych w sałacie. Produktywność suchej masy roślin po nawożeniu KI i KIO_3 było zmienne w latach badań – w tych obiektach zawartość jodu w sałacie była negatywnie skorelowana z zawartością K, Mg, Ca, S, Na, B, Cu, Fe, Mn, Zn, Cd i Pb. Łączne nawożenie KI i KIO_3 z Na_2SeO_4 oraz z Na_2SeO_3

zmniejszało negatywną korelację pomiędzy zawartością jodu (w obiektach KI i KIO_3) a zawartością K, Mg, Ca, S, Na, B, Cu, Fe, Mn, Zn, Cd i Pb w sałacie. Po nawożeniu Na_2SeO_4 zawartość selenu w sałacie była dodatnio skorelowana z zawartością Na oraz negatywnie skorelowana z zawartością Mg, Ca, Fe, Mn i Cd. Zawartość selenu w sałacie po nawożeniu wyłącznie Na_2SeO_3 była dodatnio skorelowana z zawartością P, K, Na, Mn, Mo i Zn. Zmienne warunki klimatyczne „maskowały" wpływ nawożenia I i Se na funkcjonowanie gospodarki mineralnej roślin sałaty.

Słowa kluczowe: makroskładniki, mikroskładniki, żywienie roślin, metale ciężkie, żywienie mineralne

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