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EFFECT OF IODINE FERTILIZATION AND SOIL APPLICATION OF SUCROSE ON THE CONTENT OF SELECTED HEAVY METALS AND TRACE ELEMENTS IN SPINACH

Sylwester Smoleń, Włodzimierz Sady
University of Agriculture in Kraków

Abstract. Iodine is not an essential nutrient for plants. Side-effects of its application on mineral nutrition of plants have not yet been thoroughly documented. The aim of the study was to evaluate the influence of soil application of iodine and sucrose on accumulation of heavy metals and trace elements in spinach. In 2009–2010, a pot experiment was carried out with spinach *Spinacia oleracea* L. 'Olbrzym zimowy' cv. cultivated on mineral soil. The research included diverse combinations with pre-sowing iodine fertilization (in the form of KI) and soil application of sucrose: 1) – control (without iodine fertilization and sucrose application), 2) – 1 mg I dm^{-3} of soil, 3) – 2 mg I dm^{-3} of soil, 4) – 1 mg I + 1 g sucrose dm^{-3} of soil and 5) – 2 mg I + 1 g sucrose dm^{-3} of soil. In spinach as well as soil after its cultivation the content of 29 elements was determined by ICP-OES technique, including: Ag, As, Be, Bi, Cs, Dy, Er, Eu, Hg, Ho, In, Li, Lu, Ni, Pb, Pr, Sb, Sc, Sm, Sn Sr, Tb, Th, Ti, Tl, Tm, V, Y and Yb. A significant influence of iodine fertilization as well as its interaction with sucrose was found in respect of: Li, Ni, Pb, Sr, Ti, Y, V, Ag, Lu, Sc, Tb, Th, Yb, Dy and Sn level in spinach leaves. Fertilization with iodine only (in both tested doses) contributed to a significant increase in V, Sc and Th as well as reduced Ag content in spinach when compared to the control plants. Application of the higher iodine dose (2 mg I dm^{-3} of soil) resulted in greater accumulation of Pb and Sn in spinach as well as lowered Sr concentration in comparison to plants treated with 1 mg I dm^{-3}. Simultaneous application of iodine (in both doses) and sucrose decreased spinach content of: Li, Ni, Pb, Sr, Y, V, Sc, Tb and Yb when compared to the control object as well as plants fertilized only with iodine. In the case of Li, Y, V, Sc and Tb, a stronger influence was found for sucrose applied together with the higher dose of I. Obtained decrease in Sr, Y, Sc and Tb accumulation in spinach (after iodine and sucrose application) correlated with lower soil content of these elements.

Key words: iodine, heavy metals, trace elements, sucrose, spinach

Corresponding author – Adres do korespondencji: Sylwester Smoleń, Department of Soil Cultivation and Fertilization of Horticultural Plants, University of Agriculture in Kraków, Al. 29 Listopada 54, 31-425 Kraków, Poland, e-mail: ssmolen@ogr.ar.krakow.pl

INTRODUCTION

Plants with increased iodine content (biofortified with iodine) can become an additional source of this element both in human diet as well as in fodder for livestock [White and Broadley 2005, 2009, Yang et al. 2007, Zhao and McGrath 2009]. Iodine has not been shown an essential plant nutrient. For that reason, development of agronomic rules for iodine application requires thorough investigation on its influence on plant growth and metabolism. The recognition of iodine effect on plant mineral nutrition needs particular attention as previous preliminary studies revealed synergistic or antagonistic I action on the uptake of mineral nutrients and heavy elements by plants [Smoleń et al. 2011a, 2011b, 2011c]. Iodine fertilization in the form of KI reduced P content in leafy vegetables such as spinach and lettuce [Smoleń and Sady 2011a, Smoleń et al. 2011a], while increased its accumulation in carrot storage roots [Smoleń et al. 2011b, 2011c]. In the studies with field cultivation of lettuce, both foliar and soil application of I contributed to higher level of Mg, Ca, Mn and Cd as well as reduced P, Cu and Zn concentration in leaves [Smoleń et al. 2011a]. Additionally, diverse influence of iodine dose, form and method of its application was revealed in reference to K, S, Na, B, Fe, Mo, Al and Pb accumulation in lettuce. Results of field experiments with carrot cultivation indicated an increase in P, Zn Cd and Pb content (synergistic influence) as well as reduced level of Cu in storage roots due to soil fertilization with iodine. In the available literature no information can be found on iodine interaction on the uptake of trace elements by plants.

Soil redox potential (Eh) as well as pH level are known to remarkably influence the content of easily available forms of mineral nutrients, heavy metals and trace elements in soil environment [Fuge and Johnson, 1986, Calmano et al. 1993, Chuan et al. 1996]. The rate of iodine desorption is strongly dependent on Eh value of soil. Studies conducted by Muramatsu et al. [1996] revealed that after 60-day soil incubation with 5 g dm^{-3} soil dose of glucose (laboratory test), a decrease in soil Eh from positive (app. +580 mV) to negative values (app. -200 mV) was noted. Decreased Eh value observed after introduction of sugars in soil could have been caused by H_2 production from mentioned compounds due to its decomposition by soil microorganisms [Yamane and Sato 1968]. In the mentioned work by Muramatsu et al. [1996], the reduction in Eh value was related to increased rate of iodine desorption in soil. Prior to the study shown in the present paper, a trial 13-day laboratory incubation with 5 g dm^3 of soil dose of sucrose and glucose was carried out on soil subsequently used for spinach cultivation. Sucrose application contributed to a significant decrease in Eh values from +238.5 to -116.3 mV, while glucose – to the level of -66.7 mV (detailed data not published).

Basing on results of their own studies, Muramatsu et al. [1985, 1989] ranked plant organs in respect of iodine distribution in the following order: the highest amounts of this element are accumulated in older leaves, significantly less in younger leaves, while the smallest content of I is noted in fruits and seeds. Generally, leafy vegetables, including spinach, are characterized by significantly higher ability to accumulate iodine when compared to root crops [Asperer and Lansangan 1986]. Additionally, spinach is classified into a group of vegetables with high rate of heavy metal uptake [Salariya et al. 2003]. For that reason, it is particularly important to determine to what extent iodine fertilization and soil application of sucrose (decreasing soil redox potential) change soil content of easily available forms of heavy metals and trace elements as well as affect its uptake and accumulation in spinach plants.

The aim of the work was to determine the influence of iodine fertilization (in diverse doses) and soil application of sucrose on the uptake of selected heavy metals and trace elements by spinach plants.

MATERIAL AND METHODS

Spinach (*Spinacia oleracea* L.) 'Olbrzym zimowy' c.v. was cultivated in the 2009–2010 in containers sized 60 × 40 × 20 cm, placed in the unheated plastic tunnel. The containers were filled with silt loam (35% sand, 28% silt and 37% clay) with mean content of organic matter: 2.76% and the following concentrations of the available nutrient forms soluble in 0.03 M acetic acid: N ($N\text{-}NO_3$+$N\text{-}NH_4$) 58.7 mg, P 39.3 mg, K 73.3 mg, Mg 151.5 mg, Ca 1245.2, S 17.2, Na 6.8 and Cl 0.0 mg in 1 dm^{-3} soil. Soil $pH_{(H2O)}$ was 6.97, the oxidation – reduction (redox) potential of the soil (Eh): 326.7 mV, while soil salinity (electrical conductivity – EC): 0.31 mS cm^{-1}. The content of available forms of nitrogen, phosphorus and potassium was supplemented before the cultivation to the following levels: 100 mg N, 60 mg P and 160 mg K dm^{-3} of soil using calcium nitrate, potassium phosphate and potassium sulfate. Plants in all containers were irrigated with the same amount of tap water.

In the study, various combinations with pre-sowing fertilization with iodine (in the form of KI) and soil application of sucrose were applied including: 1) – control (without iodine and sucrose application), 2) – 1 mg I dm^{-3} of soil, 3) – 2 mg I dm^{-3} of soil, 4) – 1 mg I + 1 g sucrose dm^{-3} of soil and 5) – 2 mg I + 1 g sucrose dm^{-3} of soil. Iodine and sucrose were applied pre-sowing in the form of water solutions using 1 dm^{-3} of solution per 1 container.

The experiment was carried out according to randomized method in three replications. Each replicate (*i.e.* one container) consisted of 4 rows with 10 plants per row. Seed sowings were performed with 20 seeds in a row on 20^{th} and 23^{rd} March in the subsequent years. After germination the plants were singled out leaving 10 seedlings in one row (40 plants per one container). Spinach was harvested on 28^{th} April 2009 and 4^{th} May 2010.

Each year, shredded plant material (spinach leaves) was dried at 70°C and mineralized in 65% super pure HNO_3 (Merck no. 100443.2500) in a CEM MARS-5 Xpress microwave oven [Pasławski and Migaszewski 2006]. In mineralized plant material, concentration of 29 elements including: Ag, As, Be, Bi, Cs, Dy, Er, Eu, Hg, Ho, In, Li, Lu, Ni, Pb, Pr, Sb, Sc, Sm, Sn Sr, Tb, Th, Ti, Tl, Tm, V, Y and Yb was determined by ICP-OES technique with the use of a Prodigy Teledyne Leeman Labs USA spectrometer. In both years of the study concentration of all 29 elements in soil collected after the harvest (extracted with 1 mol HCl) was assessed using ICP-OES method.

Prior to the experiment, organic matter concentration in soil was determined with Tiurin method modified by Oleksynowa. The content of N-mineral ($N\text{-}NH_4$, $N\text{-}NO_3$), P, K, Mg, Ca, S, and Na was determined after extraction with 0.03 mol CH_3COOH

[Nowosielski 1988]. Nitrogen level was estimated by FIA technique [PN-EN ISO 13395:2001, PN-EN ISO 11732:2005 (U)], while P, K, Mg, Ca, S, and Na were assessed using ICP-OES method.

Obtained results were statistically verified by ANOVA module of Statistica 8.0 PL program for significance level P < 0.05. Changes of any significance were assessed with the use of variance analysis. In case of significant changes homogenous groups were determined on the basis of Duncan test.

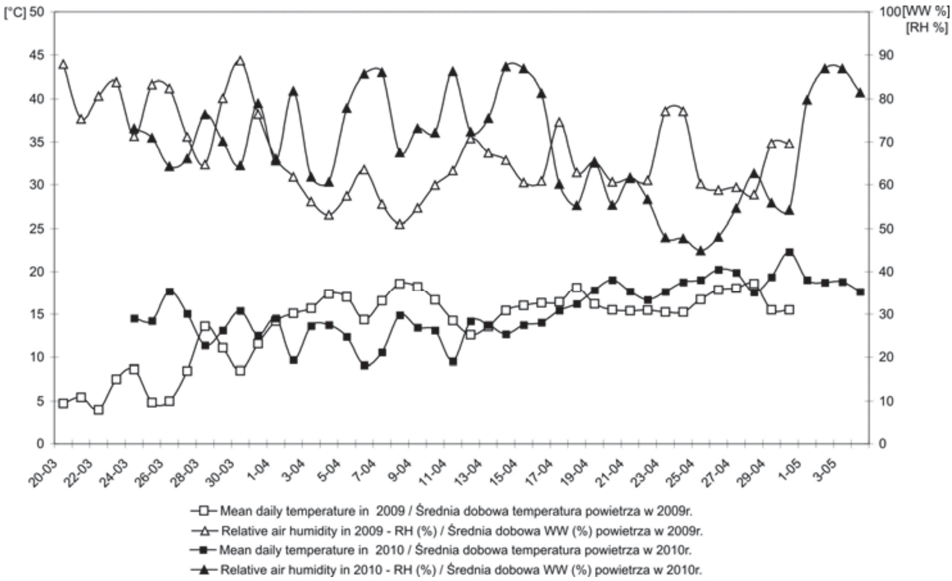

Fig. 1. Mean daily temperature and relative air humidity during spinach cultivation in a foil tunnel in both years of the study

Ryc. 1. Średnia dobowa temperatura i wilgotność względna powietrza w okresie uprawy szpinaku w tunelu foliowym

Meteorological data. During spinach cultivation (2009 and 2010) the course of mean daily temperature and relative humidity remained at a comparable level (fig. 1). Mean daily temperature and air humidity throughout spinach cultivation were respectively: 13.7°C and 67.4% RH in 2009 while 15.5°C and 68.8% RH in 2010.

RESULTS AND DISCUSSION

Mineral content of spinach and soil. Results of iodine determination in spinach plants are discussed in a separate publication [Smoleń and Sady 2011b]. Iodine fertilization together with soil application of sucrose significantly influenced the content of: Li, Ni, Pb, Sr, Ti, Y, V, Ag, Lu, Sc, Tb, Th, Yb, Dy and Sn in spinach (tab. 1–4). It should be however mentioned that the range of mentioned effect was specific both for iodine fertilization as well as interaction between I and sucrose application. No statistically relevant influence of tested factors was found in respect to the accumulation of Bi, In, Sb and Tm in spinach as well as the soil content of soluble in 1 mol HCl forms of: Ni, Pb, V, Ag, Bi, Er, Hg, In, Th, As, Dy, Sb and Sn. In all tested combinations, the level of Be, Cs, Er, Eu, Hg, Ho, Pr, Sm and Tl in spinach as well as soil concentration of Cs after cultivation were below limits of its detection using ICP-OES spectrometer.

After analyzing the effect of iodine fertilization (in both doses, irrespective of sucrose application) in comparison to the control, a significant increase of V, Sc and Th as well as reduction in Ag content in spinach were found (tabl. 1–3). The mentioned relations were not, however, reflected by soil content of these elements – application of iodine only (when compared to the control) did not affect the concentration of V, Sc, Th and Ag in soil samples extracted with 1 mol HCl.

A statistically significant effect in respect of applying diverse iodine doses (combinations no. 2 and 3) was revealed in the case of Pb, Sr and Sn content in spinach leaves (tab. 1 and 4). A higher dose of iodine, in comparison to 1 mg I dm^{-3} of soil, contributed to greater accumulation of Pb and Sn as well as reduced level of Sr in spinach plants. A tendency was also observed (although not statistically significant) of increased content of Dy and Sb due to introduction of higher iodine dose – 2 mg I dm^{-3} (tab. 1 and 4). Obtained changes in Pb, Sr, Sn, Sb and Dy concentration in plants were not related with the soil level of its forms soluble in 1 mol HCl. Application of various I doses (without sucrose addition) did not affect the concentration of Pb, Sr, Sn, Sb and Dy in soil. The revealed lack of correlation between soil and plant content of these elements may arise from using a relatively strong extractant (1 mol HCl) for analyzing soil samples. Results of the determination of mineral content in soil treated with strong extractants usually weakly correlate with the concentration of respective elements in plants [Westerman 1990].

It is worth to mention that iodine fertilization of spinach plants decreased arsenic content in spinach plants. Concentration of As in plants treated with higher dose of iodine (2 mg I dm^{-3} soil) was below the limit of detection by ICP-OES technique (tab. 4). However, simultaneous application of iodine and sucrose (in comparison to fertilization with iodine only) contributed to greater accumulation of As in spinach plants.

In both tested combinations with iodine and sucrose application (in comparison to the control as well as plants treated only with iodine) a statistically significant decrease in the content of Li, Ni, Pb, Sr, Y, V (tab. 1) as well as Sc, Tb and Yb (tab. 3) was found in spinach. In the case of Li, Y, V, Sc and Tb, higher I dose applied with sucrose (2 mg I + 1 g sucrose dm^{-3}) exerted a stronger influence in this aspect. In comparison to other tested combinations, a tendency was revealed to reduce Ti accumulation in spinach plants due to simultaneous application of iodine and sucrose (combination no 4 and 5). Leaves of spinach treated with iodine and sucrose in a dose of 2 mg I + 1 g sucrose contained the lowest amount of V, Lu, Sc and Dy when compared to other combinations used in the study (tab. 1, 3 and 4). Obtained decrease in the concentration of Sr, Y, Sc and Tb in spinach correlated with reduced content of these elements in soil. No such relations were observed for Li, Ni, Pb, V and Yb. Application of a milder extractant (e.g. 0.03 mol acetic acid) than 1 mol HCl used in the study would perhaps allow to

Table 1. Content of Li, Ni, Pb, Sr, Ti, Y and V in spinach leaves and soil after spinach cultivation (means from 2009–2010)
Tabela 1. Zawartość Li, Ni, Pb, Sr, Ti, Y i V w liściach szpinaku oraz w glebie po uprawie szpinaku (średnie z lat 2009–2010)

	Combinations (iodine and sucrose doses per 1 dm^3 of soil) Kombinacje (dawki jodu i sacharozy na dm^3 gleby)	Li	Ni	Pb	Sr	Ti	Y	V
Content of elements in spinach ($mg \cdot kg^{-1}$ d.w.) Zawartość pierwiastków w szpinaku ($mg \cdot kg^{-1}$ s.m.)	1) control – kontrola	0.67 c	1.07 b	0.71 c	45.8 c	20.8 b	0.14 c	0.60 c
	2) 1 mg I	0.66 c	1.06 b	0.51 b	46.1 c	20.0 ab	0.14 c	0.61 cd
	3) 2 mg I	0.68 c	1.08 b	0.68 c	44.3 b	20.5 ab	0.15 c	0.64 d
	4) 1 mg I + 1 g sucrose – sacharoza	0.59 b	0.99 ab	0.42 a	42.9 a	18.0 a	0.12 b	0.54 b
	5) 2 mg I + 1 g sucrose – sacharoza	0.54 a	0.90 a	0.46 a	42.5 a	17.9 a	0.11 a	0.48 a
	test *F* for content of elements in spinach test *F* dla zawartości pierwiastków w szpinaku	*	*	*	*	*	*	*
Content of elements in soil ($mg \cdot dm^{-3}$) Zawartość pierwiastków w glebie ($mg \cdot dm^{-3}$)	1) control – kontrola	0.58 b	2.87	25.4	21.2 b	5.87 c	5.97 c	6.53
	2) 1 mg I	0.56 ab	2.78	25.4	21.3 b	5.45 bc	5.69 abc	6.27
	3) 2 mg I	0.52 a	2.85	25.5	20.5 b	5.45 bc	5.78 bc	6.32
	4) 1 mg I + 1 g sucrose – sacharoza	0.53 ab	2.70	24.8	18.6 a	5.18 ab	5.45 ab	6.05
	5) 2 mg I + 1 g sucrose – sacharoza	0.51 a	2.66	24.5	19.0 a	4.99 a	5.32 a	5.89
	test *F* for content of element in soil test *F* dla zawartości pierwiastków w glebie	*	n.s. – n.i.	n.s. – n.i.	*	*	*	n.s. – n.i.

Means followed by the same letters are not significantly different for P < 0.05 – Średnie oznaczone tymi samymi literami nie różnią się istotnie dla P < 0,05.
Test *F*: * – means are significantly different – średnie różnią się istotnie.
n.s. – not significant – n.i. – brak istotnego zróżnicowania.

Table 2. Content of Ag, Be, Bi, Cs, Er, Eu, Hg and Ho in spinach leaves and soil after spinach cultivation (means from 2009–2010)
Tabela 2. Zawartość Ag, Be, Bi, Cs, Er, Eu, Hg i Ho w liściach szpinaku oraz w glebie po uprawie szpinaku (średnie z lat 2009–2010)

	Combinations (iodine and sucrose doses per 1 dm^3 of soil) [1] Kombinacje (dawki jodu i sacharozy na dm^3 gleby) [1]	Ag	Be	Bi	Cs	Er	Eu	Hg	Ho
Content of elements in spinach ($\mu g \cdot kg^{-1}$ d.w.) Zawartość pierwiastków w szpinaku ($\mu g \cdot kg^{-1}$ s.m.)	1) control – kontrola	381.9 b	<2.0	320.3	<1.75	<3.0	<1.3	<2.5	<5.0
	2) 1 mg I	346.7 ab	<2.0	504.8	<1.75	<3.0	<1.3	<2.5	<5.0
	3) 2 mg I	333.1 a	<2.0	542.8	<1.75	<3.0	<1.3	<2.5	<5.0
	4) 1 mg I + 1 g sucrose – sacharoza	335.7 a	<2.0	183.1	<1.75	<3.0	<1.3	<2.5	<5.0
	5) 2 mg I+1 g sucrose – sacharoza	305.2 a	<2.0	637.2	<1.75	<3.0	<1.3	<2.5	<5.0
	test *F* for content of elements in spinach test *F* dla zawartości pierwiastków w szpinaku	*	-	n.s. – n.i.	-	-	-	-	-
Content of elements in soil ($\mu g \cdot kg^{-1}$) Zawartość pierwiastków w glebie ($\mu g \cdot kg^{-1}$)	1) control – kontrola	8.7	341.6 c	90.4	<0.35	849.3	292.3 c	6.38	722.3 c
	2) 1 mg I	6.6	325.2 abc	69.0	<0.35	787.0	278.8 abc	4.13	685.3 bc
	3) 2 mg I	1.5	327.6 bc	82.4	<0.35	813.4	282.1 bc	5.75	692.5 bc
	4) 1 mg I + 1 g sucrose – sacharoza	4.3	310.9 ab	140.9	<0.35	749.7	265.7 ab	1.75	646.7 ab
	5) 2 mg I + 1 g sucrose – sacharoza	<1.0	305.7 a	92.0	<0.35	725.6	260.2 a	1.75	626.9 a
	test *F* for content of elements in soil test *F* dla zawartości pierwiastków w glebie	-	*	n.s. – n.i.	-	n.s. – n.i.	*	n.s. – n.i.	*

[1] – See table 1 – Opis jak w tabeli 1.
"<" – Element level in samples were below the limits of its detection on the ICP-OES spectrometer – Oznacza, że zawartość pierwiastków w próbach była niższa od limitu ich detekcji na spektrometrze ICP-OES.

Table 3. Content of In, Lu, Pr, Sc, Sm, Tb, Th, Tl and Yb in spinach leaves and soil after spinach cultivation (means from 2009–2010)
Tabela 3. Zawartość In, Lu, Pr, Sc, Sm, Tb, Th, Tl i Yb w liściach szpinaku oraz w glebie po uprawie szpinaku (średnie z lat 2009–2010)

	Combinations (iodine and sucrose doses per 1 dm^3 of soil) [1] Kombinacje (dawki jodu i sacharozy na dm^3 gleby) [1]	In	Lu	Pr	Sc	Sm	Tb	Th	Tl	Yb
Content of elements in spinach ($\mu g \cdot kg^{-1}$ d.w.) Zawartość pierwiastków w szpinaku ($\mu g \cdot kg^{-1}$ s.m.)	1) control – kontrola	237.6	7.05 b	<10.0	49.0 c	<30.5	52.9 bc	256.7 a	<25.0	19.1 b
	2) 1 mg I	301.9	7.16 b	<10.0	51.8 cd	<30.5	57.5 c	541.3 b	<25.0	20.2 b
	3) 2 mg I	292.5	7.36 b	<10.0	52.6 d	<30.5	51.2 bc	548.5 b	<25.0	19.6 b
	4) 1 mg I + 1 g sucrose – sacharoza	217.8	6.32 b	<10.0	43.9 b	<30.5	42.8 ab	247.1a	<25.0	16.6 a
	5) 2 mg I + 1 g sucrose – sacharoza	321.7	5.07 a	<10.0	39.9 a	<30.5	32.5 a	421.5 ab	<25.0	16.1 a
	test *F* for content of element in spinach test *F* dla zawartości pierwiastków w szpinaku	n.s. – n.i.	*	-	*	-	*	*	-	*
Content of elements in soil ($\mu g \cdot kg^{-1}$) Zawartość pierwiastków w glebie ($\mu g \cdot kg^{-1}$)	1) control – kontrola	365.9	99.0 b	3299.8 c	59.8 b	1366.9 c	210.9 b	1310.4	213.0 b	470.9 c
	2) 1 mg I	319.9	95.0 ab	3140.9 abc	58.9 b	1305.6 abc	204.3 ab	1248.2	176.5 ab	449.0 abc
	3) 2 mg I	353.0	95.4 ab	3186.8 bc	59.3 b	1320.9 bc	202.9 ab	1275.0	215.1 b	454.3 bc
	4) 1 mg I + 1 g sucrose – sacharoza	328.9	90.4 a	3010.9 ab	55.4 ab	1250.1 ab	191.0 a	1220.4	151.3 a	428.1 ab
	5) 2 mg I + 1 g sucrose – sacharoza	306.9	88.1 a	2922.9 a	53.3 a	1221.2 a	191.1 a	1188.9	126.8 a	419.0 a
	test *F* for content of element in soil test *F* dla zawartości pierwiastków w glebie	n.s. – n.i.	*	*	*	*	*	n.s. – n.i.	*	*

[1] – See table 1 – Opis jak w tabeli 1.
"<" – See table 2 – Opis jak w tabeli 2.

Table 4. Content of As, Dy, Sb, Sn and Tm in spinach leaves and in soil after spinach cultivation
Tabela 4. Zawartość As, Dy, Sb, Sn i Tm w liściach szpinaku oraz w glebie po uprawie szpinaku

	Combinations (iodine and sucrose doses per 1dm^3 of soil) [1] Kombinacje (dawki jodu i sacharozy na dm^3 gleby) [1]	As	Dy	Sb	Sn	Tm
Content of elements in spinach (µg·kg^{-1} d.w.) Zawartość pierwiastków w szpinaku (µg·kg^{-1} s.m.)	1) control – kontrola	223.9	236.0 c	349.5	0.12 a	3.0
	2) 1 mg I	3.3	214.2 ab	329.9	0.60 a	0.4
	3) 2 mg I	<3.0	233.9 bc	457.3	1.43 b	10.4
	4) 1 mg I + 1 g sucrose – sacharoza	273.4	218.3 abc	438.3	0.35 a	9.2
	5) 2 mg I + 1 g sucrose – sacharoza	12.5	203.4 a	605.1	0.47a	5.0
	test *F* for content of element in spinach test *F* dla zawartości pierwiastków w szpinaku	-	*	n.s. – n.i.	*	n.s. – n.i.
Content of elements in soil (mg·kg^{-1}) Zawartość pierwiastków w glebie (mg·kg^{-1})	1) control – kontrola	2.88	1.16	0.11	3.74	0.062 b
	2) 1 mg I	2.85	1.12	0.08	4.13	0.057 ab
	3) 2 mg I	2.85	1.14	0.09	3.52	0.057 ab
	4) 1 mg I + 1 g sucrose – sacharoza	2.65	1.09	0.08	3.20	0.055 a
	5) 2 mg I + 1 g sucrose – sacharoza	2.64	1.06	0.06	3.22	0.054 a
	test *F* for content of element in soil test *F* dla zawartości pierwiastków w glebie	n.s. – n.i.	n.s. – n.i.	n.s. – n.i.	n.s. – n.i.	*

[1] – See table 1 – Opis jak w tabeli 1.
"<" – See table 2 – Opis jak w tabeli 2.
For spinach content of As, Sb and Tm means are from 2009, for Dy and Sn – means from 2010; – the level of As, Sb and Tm in 2010 as well as Dy and Sn in 2009 were below the limits of its detection by ICP-OES technique. Obtained results of soil mineral analysis are means from 2009–2010.
Dla zawartości w liściach szpinaku: As, Sb, Tm średnie z 2009 r., dla Dy, Sn średnie z 2010 r.; – zawartość As, Sb, Tm w 2010 and Dy, Sn w 2009 r. była poniżej limitu detekcji. Zawartość pierwiastków w glebie stanowi średnią z lat 2009–2010.

determine the total content of Li, Ni, Pb, V and Yb forms (speciations) in soil. As a consequence, it would likely result in obtaining a better correlation with its level in spinach. In the study conducted by Smoleń et al. [2010] a higher value of correlation coefficient was found for the relation between soil content of elements extracted by 0.03 mol CH_3COOH (rather than 1 mol HCl) and plant accumulation of: Al, B, Ba, Cd, Mn, Ni and Zn in spinach, while: Al, B, Ba, Cd, Cr, Fe, Li and Ti in lettuce plants.

In the available literature no information can be found which would enable to explain diverse influence of iodine (depending on additional sucrose application) on the level of Sr, Y, Sc and Tb in soil. It is likely that simultaneous application of iodine and sucrose affected processes conducted by soil microorganisms (or its growth) and/or redox reactions taking place in soil. The latter ones could have specifically altered the solubility of Sr, Y, Sc and Tb (due to changes in oxidation rate, speciation etc.) and, as a consequence, the level of its forms available to plants.

Soil content of easily available forms of iodine as well as mineral nutrients, heavy metals and trace elements is primarily related to pH and redox potential of soil [Fuge and Johnson, 1986, Calmano et al. 1993, Chuan et al. 1996]. Addition of significant amount of sugars into soil results in a drastic decrease of Eh values (soil redox potential) which is related to the development of soil microorganisms – these relations were revealed by Muramatsu et al. [1996]. In the present study a relatively weak effect of simultaneous application of iodine and sucrose was observed in reference to soil pH and Eh of soil (detailed data published previously [Smoleń and Sady 2011a]). Values of pH and Eh (mV) in soil in individual combinations of the study were: 1) pH 6.78 and +336.7 mV, 2) pH 6.79 and +338.3 mV, 3) pH 6.75 and +341.8 mV, 4) pH 7.05 and +330.1 mV, 5) pH 6.94 and +337.2 mV, respectively. Lack of effect of sucrose on soil Eh could have resulted from measuring redox potential in soil after spinach cultivation – approximately 40 days after sucrose application. It is worth to mention that in both years of the experiment white fungal filaments appeared on soil surface approximately 10 days after sucrose application. Detailed description of the effect of sucrose application on soil microflora as well as physico-chemical properties of soil and nitrogen metabolism of spinach plants are presented in a separate publication [Smoleń and Sady 2011b]. It should be additionally mentioned that noted changes in soil pH and Eh did not affect the level of easily available forms of P, K, Mg, Ca, S and Na (soluble in 0.03 mol CH_3COOH) as well as B, Cu, Fe, Mn, Mo, Zn, Al, Ba, Cd, Ce, Co, Cr and La (extracted using 1 mol HCl) in soil after spinach cultivation [Smoleń i Sady 2011a].

On the basis of the present as well as previous studies [Smoleń and Sady 2011a, Smoleń et al. 2011a, 2011b, 2011c] it can be stated that iodine influence on the uptake of mineral nutrients, heavy metals and trace elements by plants depend on numerous factors, including: iodine form, dose and method of application but also is affected by conditions of crop cultivation and genotypic variation of plants in the preference (capacity) towards particular speciations of elements taken from soil.

Among all the elements classified as heavy metals, European regulations provide maximum levels only for Cd and Pb in *Brassica* and leafy vegetables [Commission Regulation (EC) No 466/2001]. In the case of lead, the limit of its content is set on the level of 0.3 mg Pb kg^{-1} f.w. In the present study, Pb content in spinach did not exceed the maximum level and was in the range of 0.42–0.71 mg Pb kg^{-1} d.w. (tab. 1), after recalculation: 0.03–0.06 mg Pb kg^{-1} f.w.

One of the most toxic elements included in the study, apart from mercury, is thallium. As far as relatively high content of thallium is appearing in soils, a potential risk for humans can arise at levels around 1 mg kg^{-1} [Małuszyński 2009]. It should be underlined that Hg and Th content in spinach remained below the limits of its detection by ICP-OES technique (tab. 2 and 3).

In the previous studies on the range of influence exerted by agronomic factors on mineral nutrition of plants, rarely have heavy metals and trace elements included in our work been analyzed. Each of these minerals (Ag, Be, Bi, Cs, Dy, Er, Eu, Ho, In, Lu, Pr, Sb, Sc, Sm, Sn, Sr, Tb, Th, Tm, Y and Yb) is characterized by diverse physico-chemical properties and mobility in soil-plant system [Kabata-Pendias and Pendias 1999, Tyler and Olsson 2001]. Its deleterious effect on human and livestock is poorly recognized particularly in the aspect of its intake (introduction to the food chain) due to excessive accumulation in consumed plants. What is better understood is the negative impact of some speciations of these elements (e.g. Sb, Be, Sn) on organisms resulting from environment contamination with a special emphasis on air pollution [Chmielnicka 2002].

As far as physiological (natural) levels of Ag, Be, Bi, Cs, Dy, Er, Eu, Ho, In, Lu, Pr, Sb, Sc, Sm, Sn, Sr, Tb, Th, Tl, Tm, Y and Yb in plants are concerned, it can be stated that the content of: Ag, As, Li, Ni, Pb, Sb and V in spinach leaves presented in this work is recognized as a physiological level [Kabata-Pendias and Pendias 1999]. The determined content of Ag, As, Bi, Li, Ni, Pb, Sb, Sc, Sn, Sr and V in spinach fell within the average range characteristic for vascular plants [Kabata-Pendias and Pendias 1999]. Additionally, accumulation of Li, Ni, Pb, Sr, Ti, Y and V in spinach (tab. 1) was up to several dozen times higher than of other tested elements (tab. 2–4).

Lanthanide elements are known to pose serious harm for human health but poisoning with them do not give specific symptoms. In general, accumulation of lanthanides in plants is reduced along with increasing atomic number. Additionally, lanthanides with even atomic numbers occur more frequently than those of odd atomic numbers according to the Oddon-Harkins rule [Kabata-Pendias and Pendias 1999]. In the present study, however, this ratio was disturbed for all tested lanthanides (Pr, Sm, Tb, Dy, Ho, Er, Tm, Yb and Lu). The most common reason of such an observation is changes in physicochemical properties of soil affecting the oxidation state of these elements [Kabata-Pendias and Pendias 1999].

CONCLUSIONS

A significant influence of iodine as well as its interaction with sucrose were observed on the content of: Li, Ni, Pb, Sr, Ti, Y, V, Ag, Lu, Sc, Tb, Th, Yb, Dy and Sn in spinach leaves.

Fertilization with iodine only (in the dose of 1 and 2 mg I dm^{-3}) contributed to greater accumulation of V, Sc and Th as well as reduced Ag level in spinach leaves when compared to the control plants.

Application of higher iodine dose (in comparison to 1 mg I dm^{-3}) resulted in a significant increase of Pb and Sn level (additionally in Sb and Dy – without statistical significance) as well as reduction of Sr concentration in spinach.

Simultaneous application of iodine (in both doses) and sucrose (1 g dm^{-3}) led to a significantly lower plant content of Li, Ni, Pb, Sr, Y, V, Sc, Tb and Yb when compared to the control as well as plants fertilized only with iodine. In the case of Li, Y, V, Sc and Tb treatment with higher dose of iodine and sucrose (2 mg I + 1 g sucrose dm^{-3}) revealed a stronger interaction in this aspect.

A decrease in Sr, Y, Sc and Tb accumulation in spinach (due to simultaneous application of iodine and sucrose) was related with reduced concentration of these elements in soil.

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WPŁYW NAWOŻENIA JODEM I DOGLEBOWEJ APLIKACJI SACHAROZY NA ZAWARTOŚĆ WYBRANYCH METALI CIĘŻKICH I PIERWIASTKÓW ŚLADOWYCH W SZPINAKU

Streszczenie. Jod nie jest jednak składnikiem pokarmowym roślin. Jego uboczny wpływ na gospodarkę mineralną roślin nie został dobrze udokumentowany. Celem badań było określenie oddziaływania jodu oraz doglebowej aplikacji sacharozy na zawartość metali ciężkich i pierwiastków śladowych w szpinaku. W latach 2009–2010 przeprowadzono doświadczenie wazonowe z uprawą szpinaku *Spinacia oleracea* L. ‘Olbrzym zimowy’ na glebie mineralnej. Badaniami objęto zróżnicowane kombinacje z przedsiewnym nawożeniem jodem (w formie KI) i doglebową aplikacją sacharozy: 1) – kontrola (nienawożona jodem i bez aplikacji sacharozy), 2) – 1 mg I dm^{-3} gleby, 3) – 2 mg I dm^{-3} gleby, 4) –

1 mg I + 1 g sacharozy dm^{-3} gleby i 5) – 2 mg I + 1 g sacharozy dm^{-3} gleby. W szpinaku oraz w glebie po uprawie oznaczono zawartość 29 pierwiastków: Ag, As, Be, Bi, Cs, Dy, Er, Eu, Hg, Ho, In, Li, Lu, Ni, Pb, Pr, Sb, Sc, Sm, Sn Sr, Tb, Th, Ti, Tl, Tm, V, Y, Yb techniką ICP-OES. Stwierdzono istotny wpływ nawożenia jodem oraz istotną interakcję aplikacji tego pierwiastka z sacharozą na zawartość: Li, Ni, Pb, Sr, Ti, Y, V, Ag, Lu, Sc, Tb, Th, Yb, Dy i Sn w szpinaku. Nawożenie samym jodem (w obydwu dawkach) w porównaniu z kontrolą powodowało istotne zwiększenie zawartości V, Sc, Th oraz obniżenie zawartości Ag w szpinaku. Wyższa dawka jodu w porównaniu do aplikacji 1 mg I dm^{-3} gleby powodowała istotne zwiększenie zawartości Pb i Sn oraz obniżenie zawartości Sr w szpinaku. Łączna aplikacja jodu (w obydwu dawkach) i sacharozy w porównaniu do kontroli i nawożenia roślin samym jodem powodowała istotne zmniejszenie zawartości Li, Ni, Pb, Sr, Y, V, Sc, Tb i Yb w szpinaku – w odniesieniu do Li, Y, V, Sc, Tb wyższa dawka jodu aplikowana łącznie z sacharozą wykazała w tym aspekcie silniejsze oddziaływanie. Obniżenie zawartości Sr, Y, Sc i Tb w szpinaku (wskutek połączonej aplikacji jodu i sacharozy) było skorelowane ze zmniejszoną zawartością tych pierwiastków w glebie.

Słowa kluczowe: jod, metale ciężkie, pierwiastki śladowe, sacharoza, szpinak

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