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VARIETY AS ONE OF THE FACTORS AFFECTING THE ACCUMULATION OF RISK ELEMENTS OF POTATO TUBERS

ZMIENNOŚĆ JAKO JEDEN Z CZYNNIKÓW WPŁYWAJĄCYCH NA KUMULACJĘ ZWIĄZKÓW POWODUJĄCYCH RYZYKO W BULWACH ZIEMNIAKA

Key words: potatoes, zinc, accumulation.
Słowa kluczowe: ziemniak, cynk, kumulacja.

Niezależnie od tego, że cynk pełni rolę ważną w życiowych funkcjach roślin i zwierząt, jego zwiększona zawartość, uwzględniając jego zachowanie w łańcuchu pokarmowym, może mieć negatywne skutki zdrowotne. W razie kumulacji cynku w ziemniakach – ważnej uprawy rolniczej – przy częstej ich konsumpcji stają się one ważnym źródłem tego metalu.

W prezentowanej pracy przedstawiono wrażliwość kilku odmian ziemniaka (Impala, Livera, Agria, Désirée) na zwiększoną zawartość cynku w glebach wykorzystywanych do ich uprawy (BT – piasek, VTP – gleba). Cynk był dodawany do podłoża w postaci roztworu $ZnSO_4 \cdot 7H_2O$: 5 wariantów do podłoża BT i 4 warianty do podłoża VTP w zróżnicowanych dawkach.

Po wykonaniu pomiarów zawartości cynku w poszczególnych wariantach i odmianach ziemniaka, najmniejszą zawartość zaobserwowano w odmianie Desiree (A2 = 10,849; B2 = 23,368; C2 = 40,443; D2 = 44,795 $mg \cdot kg^{-1}$ DW), w bulwie w podłożu VTP. Stwierdzono pozytywną korelację ($P < 0,01$) pomiędzy zawartością cynku w podłożu i kumulacją w bulwach oraz częściach naziemnych roślin.

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1. INTRODUCTION

Soil is a limited and irrecoverable natural source. In case of gradual degradation and its loss this source becomes in many parts of the world a limit of further development of human society. If the soil does not exist, also biosphere will be affected with harmful consequences for humankind [Hronec et al. 2002].

Heavy metals rank among basic groups of polluting substances that are monitored in various components of environment. Their content plants depends on concentration and migration heavy metals in soil, on physical and chemical traits of soil, availability of heavy metals (for potatoes heavy metals are set up as following: Cu > Zn > Cd > Pb > Ni > Cr) and on ability of plant to accumulate heavy metals (potatoes cumulate 2-fold more of Cd than wheat and 2.6-fold more than barley) [Otabong et al. 2001; Antanaitis, Antanaitis 2004].

Order of contamination rate of individual crops is as following: pea < cereals (grain < straw) < potatoes < sugar beat < alfalfa < maize < clover-grass. Monitored crops cumulate heavy metals in following order: Zn > Cd > Cr > Cu > Mn > Fe > Hg > Pb > As [Hronec et al. 2002].

Biological microelements (e.g. Cu, Zn, Mn, Co, Cr, etc.) as well as non-essential chemical elements (Cd, Pb, Hg, etc.) belong to heavy metals. Zinc ranks among important micronutrients under common conditions and fills important physiological and biochemical functions in plant and also in animal organisms. It becomes a foreign matter only when its concentration in environment exceeds exact limit. As one of essential elements for plants zinc is important for proper growth and development of plant tissues. It is an activator and stabilizer of many enzymes, it plays functional and structural roles in their reactions, participates in biosynthesis of proteins, affects an accumulation and transport of saccharides, affects synthesis of tryptophan. Although, more than 70 metaloenzymes containing Zn were identified, these present only small part of total zinc content in plant [Tomáš et al. 2000; 2007].

Mobility of zinc in soil and its availability for plants is affected by soil reaction, content of organic matter, texture of soil and bonds with some oxides (mainly aluminium, manganese and iron). Its availability by plants is significantly lowered in soil rich in phosphates. In alkali environment it is commonly absorbed mainly on humic acids [Kabata-Pendias, Pendias 2001].

The most mobile form of zinc is Zn^{2+}. In acid soil environment zinc could be washed out into waters. Its solubility in alkali environment increases by formation of organic easily soluble complex compounds [Tomáš et al. 2007].

Adsorption of zinc is affected in acid environment by cation changeable capacity and in alkali environment the chemisorption is dependable on presence of organic ligands. In acid soil zinc dominates in form of Zn^{2+} a $ZnSO_4$, under alkali conditions $ZnHCO_3$, less Zn^{2+}, $ZnSO_4$ a $ZnCO_3$. Main compounds of zinc in soil solution are Zn^{2+}, $ZnCl^+$, $ZnOH^+$, $Zn(OH)_2$ and $ZnSO_4$ in neutral calcinated soil [Makovníková et al. 2006].

Non-controlled mining activities pose great environmental risk that is a problem especially in developed countries. Illegal mining has aftermath an occurrence of enormous amounts of wastes and various types of pollutants. Onyedika and Nwosu [2008] had evaluated accumulation of Cd, Pb and Zn in four typical agricultural crops cultivated in Nigeria in 6 localities of region with typical mining activity. Contents of heavy metals were in range from 0.02 to 0.140 mg Pb·kg^{-1} FW, from 0.820 to 2.84 mg Zn·kg^{-1} FW and from 0 to 1.91 mg Cd·kg^{-1} FW in potatoes, whereas influence of locality on the contents of these metals in crops was statistical non-significant.

Soil is the starting place of heavy metals to plants and afterwards into food chain. In case of risk of enter of heavy metals into food chain it is necessary to minimalize this risk. One possibility is the minimalization of risky metals input into plant production is application of sorbents amending not only soil reaction, but also soil content of organic matter. The most effective treatment in reducing of metal uptake by plant (Zn by 32–59%, Cd by 25–61%, Cu by 8–22% and Pb by 59–72%) was a combination of caustik, Humix and ground magnesite mineral into soil [Tomáš et al. 2006; Vollmannová et al. 2006; 2007]. Another way of utilization of soil contaminated by heavy metals is the orientation of crop rotation on cultivating of crops for technical purposes and the most radical treatment is mechanical removal of surface contaminated layer in order to dilute the remaining part by tillage on harmless, by norm tolerable level of heavy metals [Tomáš et al. 2007].

Potatoes belong to the most important foodstuffs and forage crops. Tubers are the only utilizable organs of potatoes. Their inner and outer quality is thus determining factor for all utilizable branches, while quality of potatoes including hygienic safety, is established by content of foreign matters in flesh. Heavy metals are significant inorganic contaminants entering the food chain.

2. MATERIAL AND METHODS

1. **Tested crop** – 4 cultivars of potatoes with different length of vegetation period: Impala, Livera, Agria, Désirée.
2. **Form of experiment:**

1) biological test (BT):
    - in BT germinated crown-capped parts of potato tubers were sown into containers with silicate sand,
    - zinc in form of water-soluble salt $ZnSO_4 \cdot 7H_2O$ was added on 18th day after BT establishment,
    - in individual variants (A1 – B1 – C1 – D1 – E1) graded doses Zn (0 – 75 – 150 – 225 – 300 mg·kg^{-1} sand) were applied,
    - content of Zn was assessed in potato biomass (harvest after 40 days after BT establishment) after mineralization of plant material with using of microwave digestion on MARS X-press (f-a CEM USA)**;** content of Zn was assessed at wavelength 213.9 nm by wet way method of AAS (AAS Varian DUO 240FS/240Z);

2) vegetation pot trial (VPT):
   - under model conditions VPT three potato tubers of 4 cultivars were sown into 25 kg containers with soil (soil : sand = 21 : 4),
   - zinc in form of water-soluble salt of $ZnSO_4.7H_2O$ was applied by establishing of VPT in gradual doses 0 – 100 – 200 – 300 $mg \cdot kg^{-1}$ soil) in variants A2 – B2 – C2 – D2,
   - content of Zn was assessed in fresh matter of potato tubers (harvest in consumers ripeness) and calculated on dry matter.

Samples of fresh matter were prepared by homogenisation of all potato tubers from individual containers. Content of Zn in potato tubers was assessed in mineralizates in four replications. Mineralization of samples was carried out in microwave MARS X-press (f-a CEM USA). Content of Zn was assessed at 213.9 nm by wet way method of AAS.

Soil taken from the area of Výčapy-Opatovce was used in containers. On the basis of gained agrochemical parameters this type of soil could be characterize as acid (pH/KCl = 5.25), with medium supply of humus (% hum. = 2.54, content of humus was assessed by method of Ťurin), medium content of phosphorus (P = 51.88 $mg \cdot kg^{-1}$), good content of potassium (K = 297.0 $mg \cdot kg^{-1}$) and high content of magnesium (Mg = 252 $mg \cdot kg^{-1}$) [Bielek 1996]. Content of calcium was 1356 $mg \cdot kg^{-1}$. Acid soil reaction with pH = 5.5 – 6.5 is optimal for potatoes cultivation and content of humus should be higher than 2% [Vokál et al. 2000]. Content of nutrients with exception of P is from standpoint of suitability of soil for potatoes cultivation convenient. Contents of nutrients (P, K, Ca, Mg) were determined by the method of Mehlich II, analytical method of the determination of contents of macroelements was flame atomic spectrometry (AAS).

Except for agrochemical characteristics the contents of heavy metals (HM) were assessed in soil: Zn, Cd, Pb, Cu, Ni in three various extraction reagents (Table 1):

1) by extraction with *aqua regia* pseudototal contents of HM were assessed and these include all forms except for residual fraction of metals (Law 220/2004);
2) by extraction with HNO_3 potentially releasable (mobilizable) forms of HM were assessed and these are utilized in local investigation of soil in SR (Act of MP SR 531/1994-540);
3) by extraction with NH_4NO_3 (c = 1 $mol \cdot dm^{-3}$) mobile forms of heavy metals were assessed (Law 220/2004).

Table 1. Content of heavy metals in $mg \cdot kg^{-1}$ in soil

Tabela 1. Zawartość metali ciężkich w glebie w $mg \cdot kg^{-1}$

Extraction reagent	Zn	Cd	Pb	Cu	Ni
Aqua regia	47.9	0.54*	14.0	22.1	9.9
Limit value	*100.0*	*0.4*	*70.0*	*60.0*	*40.0*
HNO_3 (c = 2 $mol.dm^{-3}$)	5.24	0.148	7.12	3.4	2.5
Reference value A_1	*40.0*	*0.3*	*30.0*	*20.0*	*10.0*
NH_4NO_3 (c = 1 $mol.dm^{-3}$)	0.09	0.022	0.195*	0.03	0.15
Critical value	*2.0*	0.1	0.1	1.0	1.5

Note: *exceeded limit/critical value.

On the basis of comparison with maximal acceptable contents according to valid legislative it could be stated an exceeding of limit value for Cd and critical value for Pb.

Analytical method of the determination of contents of risky elements was flame atomic spectrometry (AAS).

Two-factor analysis of variance ANOVA was used for statistical evaluation of results and program Statgraphics was used to process gained data.

3. RESULTS AND DISCUSSION

3.1. Biological test

The highest content of Zn in biomass by the highest applied dose (var. E1) was assessed in cultivar Livera (598.13 mg·kg^{-1} SH) and Zn content was 10-fold higher than in control variant A1 (E1/A1 = 9.76). The lowest content of Zn was assessed in cultivar Désirée in all variants and also the smallest increase of its content in variant E1 (E1/A1 = 7.04) (Table 2).

Table 2. Content of zinc in biomass of potatoes in, mg·kg^{-1} DM in BT

Tabela 2. Zawartość cynku w biomasie ziemniaka hodowanego w mg·kg^{-1} s.m.na podłożu BT

Cultivar	Anatomical part	Variant				
		A1	B1	C1	D1	E1
Impala	biomass	73.40	421.40	504.60	527.58	570.45
Livera	biomass	61.30	305.73	418.00	558.65	598.13
Agria	biomass	60.55	279.98	333.25	475.75	585.48
Désirée	biomass	61.28	96.75	141.25	242.36	431.58

On the basis of statistical processing of the results by method of regression and correlation analysis it could be anticipated that accumulation of Zn in biomass after application of higher doses of Zn than 300 mg·kg^{-1} would be increasing in the highest rate in cultivar Désirée (Fig. 1–4).

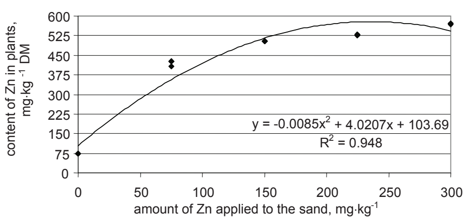

Fig. 1. Biological test, cultivar Impala

Rys. 1. Podłoże BT, odmiana Impala

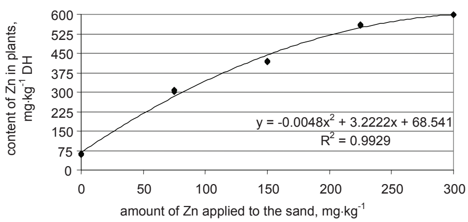

Fig. 2. Biological test, cultivar Livera

Rys. 2. Podłoże BT, odmiana Livera

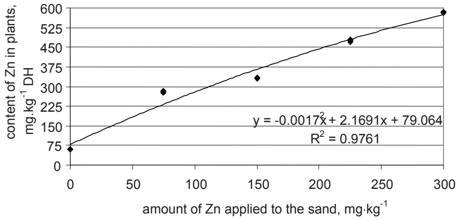

Fig. 3. Biological test, cultivar Agria

Rys. 3. Podłoże BT, odmiana Agria

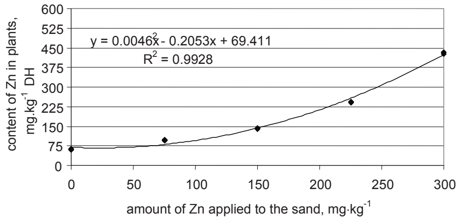

Fig. 4. Biological test, cultivar Désirée

Rys. 4. Podłoże BT, odmiana Desiree

Table 3. Analysis of Variance for ZN in leaves, Type III Sums of Squares

Tabela 3. Analiza wariancji dla zawartości cynku w liściach, typ III, suma kwadratów

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
MAIN EFFECTS	–	–	–	–	–
A: mg Zn·kg^{-1} sand	2.16309E6	4	540772.0	169.74	0.0000
B: variety	596153.0	3	198718.0	62.38	0.0000
RESIDUAL	229379.0	72	3185.82	–	–
TOTAL (CORRECTED)	2.98862E6	79	–	–	–

Note: All F – ratios are based on the residual mean square error.
– not applicable.

Table 4. Multiple Range Test for Zn in plants by content of applied Zn (BT) (Method: 95.0 percent LSD)

Tabela 4. Test Duncana dla zawartości cynku w roślinach w odniesieniu do zaaplikowanego Zn do podłoża BT. Metoda jednoczynnikowej wariancji 95% (najmniejszej istotnej różnicy)

mg Zn·kg^{-1} sand	Count	LS Mean	LS Sigma	Homogeneous Groups
0	16	64.1438	14.1108	X
75	16	275.963	14.1108	X
150	16	349.275	14.1108	X
225	16	451.087	14.1108	X
300	16	546.406	14.1108	X

Table 5. Multiple Range Test for Zn in plants by variety (BT) (Method: 95.0 percent LSD)

Tabela 5. Test Duncana dla zawartości cynku w roślinach w odniesieniu do zmienności podłoża BT. Metoda jednoczynnikowej wariancji 95% (najmniejszej istotnej różnicy)

Variety	Count	LS Mean	LS Sigma	Homogeneous Groups
Désirée	20	194.645	12.6211	X
Agria	20	347.0	12.6211	X
Livera	20	388.36	12.6211	X
Impala	20	419.495	12.6211	X

Results of analysis of variance confirmed that there is statistical significant difference in cumulating of Zn after application of various substances (P-Value = 0,000) also in accumulation between cultivars (P-Value = 0,000).

Despite that zinc cumulates especially in roots of plants (and by higher concentration it is phytotoxic) [Tomáš et al. 2007] and in plant not very mobile (its lack could be manifested as chlorosis of young leaves) [Fecenko, Ložek 2000], by application of graded doses of Zn we observed the accumulation of this element in potato biomass. Under conditions of biological test statistically strong significant differences in accumulation of Zn were confirmed, only between cultivars Livera – Impala the differences were statistically non-significant, what suggest an influence of cultivar on accumulating of Zn even in first phases of potatoes growth.

High content of zinc in plant tissues inhibit the function of proteins containing other metals, which are substituted by zinc [Broadley et al. 2007; Malakouti et al. 2007]. Toxicity of zinc ions has probably the cause in its ability to form chelates with transporters of iron [Alloway, Ayres 1993]. Its excessive increased content affects transpiration, photosynthesis and enzymatic activity [Rout, Das 2003]. For toxic concentration is considered 150 to 200 mg $Zn \cdot kg^{-1}$ in dry matter of plant material [Sauerbeck 1989].

3.2. Vegetation pot trial

Hygienic safety of foodstuffs and nutritional value of tubers is important from the consumer's standpoint and is determined by chemical composition which finally forms foodstuff and raw material [Vokál et al. 2003]. For comparison to maximal acceptable content of Zn in potato tubers according to valid legislative (http://www.svssr.sk/) zinc content was assessed in fresh matter of potato tubers. Its content depends on rate of soil contamination with this element.

Content of zinc in potato tubers depends on rate of soil contamination by this element. Comparison of Zn accumulation in potato tubers after application of graded doses into soil showed that the highest increase of Zn content was after application 100 $mg \cdot kg^{-1}$ soil: B2/A2 – 2.2-fold average increase of Zn content in FW, C2/B2 = Ø 1.67-fold, D2/C2 = Ø 1.17-fold. Despite the fact that the highest content of Zn was assessed in all variants in cultivar Livera in comparison to control variant (B2/A2, C2/A2, D2/A2), content of Zn was the highest in individual variants in variety Impala and declined in order of cultivars Impala > Livera > Agria > Désirée (Tab. 6). Content of Zn exceeded limit value defined FC SR (10 $mg \cdot kg^{-1}$ FW) in 4^{th} variant besides cultivar Désirée. Increased content of nitrogen in soil results in increased uptake and accumulation of Zn in potatoes [Hlušek, Rop 1998] and its cumulating in tubers is influenced also by the way of cultivating (ecological vs. conventional) [Guziur et al. 2000].

Table 6. Content of zinc in various parts of plants and potato tubers in mg·kg^{-1} DM**/mg·kg^{-1} FW in VPT

Tabela 6. Zawartość cynku w różnych częściach rośliny i bulwie ziemniaka w mg·kg^{-1} s.m.**/ mg·kg^{-1} FW w podłożu VPT

Cultivar	Anat. part	Variant				Cultivar	Variant			
		A2	B2	C2	D2		A2	B2	C2	D2
Impala	tubers	16.00	30.18	52.19	63.39	Agria	11.22	24.79	42.56	49.70
	*tubers***	*2.75*	*5.81*	*9.58*	*11.93*		*2.40*	*5.31*	*9.13*	*10.29*
	peels	34.85	107.88	218.53	383.20		24.50	99.28	190.45	345.65
Livera	tubers	12.64	28.62	43.35	51.91	Désirée	10.85	23.37	40.44	44.80
	*tubers***	*2.45*	*5.77*	*9.38*	*10.76*		*2.34*	*5.01*	*8.48*	*9.64*
	peels	24.58	104.43	209.78	344.93		21.45	74.03	178.78	196.98
Limit value: 10.0 mg·kg^{-1}FW (Food Codex of Slovak Republic)										

Strong statistical relation between the amount of applied zinc into soil and its content in fresh matter (Impala: P-value = 6.247·10^{-11}; Livera: P-value = 1.102·10^{-8}; Agria: P-value = 2.337·10^{-9}; Désirée: P-value = 1.641·10^{-7}), or in dry matter of potato tubers was evaluated in all cultivars of potatoes (Fig. 5–8).

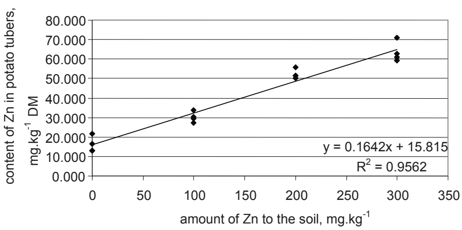

Fig. 5. VPT, cultivar Impala

Rys. 5. Podłoże VPT, odmiana Impala

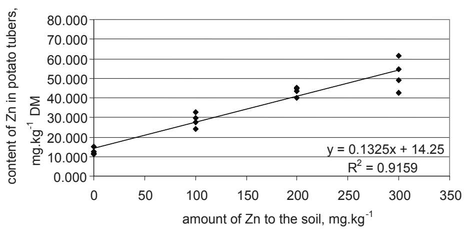

Fig. 6. VPT, cultivar Livera

Rys. 6. Podłoże VPT, odmiana Livera

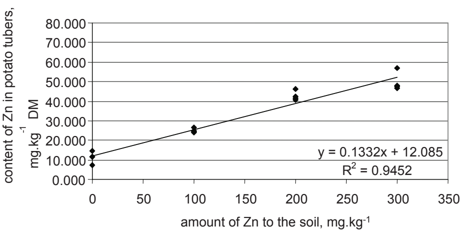

Fig. 7. VPT, cultivar Agria

Rys. 7. Podłoże VPT, odmiana Agria

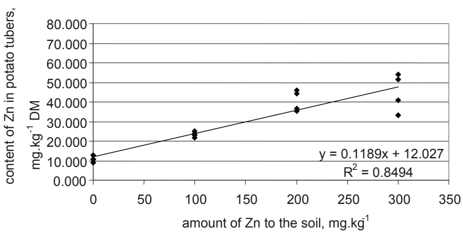

Fig. 8. VPT, cultivar Désirée

Rys. 8. Podłoże VPT, odmiana Desiree

Also positive statistically strong significance was confirmed between Zn applied into soil and its accumulation in potato peels (Impala: P-value = $2.184 \cdot 10^{-9}$; Livera: P-value = $8.118 \cdot 10^{-10}$; Agria: P-value = $3.540 \cdot 10^{-10}$; Désirée: P-value = $8.286 \cdot 10^{-6}$).

Horigughi and Nishihara [1981] compared the contents of Zn, Mn, Cu and Fe in potato peels and peeled potato tubers. Content of zinc was higher by 9%, manganese by 4.3%, copper by 43.9% and content of Fe more than 5-fold higher in peel than in peeled tuber. Our results (Tab. 5) confirmed their findings about higher accumulation of mentioned heavy metals in peels, while the most significant difference even 6-fold higher was evaluated in variant D2.

Table 7. Analysis of Variance for potato tubers, Type III Sums of Squares
Tabela 7. Analiza wariancji dla bulwy ziemniaka, typ III, suma kwadratów

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
MAIN EFFECTS	–	–	–	–	–
A: mg $Zn \cdot kg^{-1}$ soil	15372.7	3	5124.23	246.40	0.0000
B: variety	996.22	3	332.073	15.97	0.0000
RESIDUAL	1185.39	57	20.7963	–	–
TOTAL (CORRECTED)	17554.3	63	–	–	–

Note: All F – ratios are based on the residual mean square error.
– not applicable.

Table 8. Multiple Range Test for Zn in potato tubers by content of applied Zn (VPT). Method: 95.0 percent LSD
Tabela 8. Test Duncana dla zawartości cynku w bulwach ziemniaka w odniesieniu do zaaplikowanego Zn do podłoża VPT. Metoda jednoczynnikowej wariancji 95% (najmniejszej istotnej różnicy)

Appl.	Count	LS Mean	LS Sigma	Homogeneous Groups
0	16	12.6777	1.14007	X
100	16	26.7386	1.14007	X
200	16	44.6381	1.14007	X
300	16	52.4476	1.14007	X

Table 9. Multiple Range Test for Zn in potato tubers by variety (VPT). Method: 95.0 percent LSD
Tabela 9. Test Duncana dla zawartości cynku w bulwach ziemniaka w odniesieniu do zmienności podłoża VPT. Metoda jednoczynnikowej wariancji 95% (najmniejszej istotnej różnicy)

Variety	Count	LS Mean	LS Sigma	Homogeneous Groups
Désirée	16	29.8639	1.14007	X
Agria	16	32.0683	1.14007	XX
Livera	16	34.13	1.14007	X
Impala	16	40.4398	1.14007	X

On the basis of our results it could be stated that there was statistically strong significant difference in accumulation of Zn after application of various doses (P-Value = 0,000) also in accumulation among cultivars (P-Value = 0,000). Statistically significant differences in accumulation of Zn were evaluated between cultivars Désirée – Livera, Désirée – Impala, Agria – Livera and Agria – Impala. Statistically non-significant differences were between cultivars Désirée – Agria and Agria – Livera.

Our results partly correspond to the results cited by Hlušek et al. [1998], who found out that content of zinc almost was not dependent on cultivar, but the influence of locality was the most important factor.

4. CONCLUSION

Varietal dependence is one of the most important factors affecting quality of potatoes, their resistance against diseases and, as our results suggest, also against the entry of risky elements from soil. Also zinc by its high concentration could rank among risky elements.

Content of zinc in biomass (BT) was highest in cultivar Impala in variants A1 – C1, where we evaluated also the highest increase of Zn content in comparison to control variant (B1/A1 = 5.74; C1/A1 = 6.87). In variants with applied higher content of Zn its concentration in biomass significantly increased in cultivar Livera in variant D1 on 558.65 $mg \cdot kg^{-1}$ DM (D1/A1 = 9.11), and in variant E1 on 598.13 $mg \cdot kg^{-1}$ SH (E1/A1 = 9.76). The lowest content of Zn was assessed in biomass of cultivar Désirée (var. A1 – E1: 61.28 – 96.75 – 141.25 – 242.36 – 431.58 $mg \cdot kg^{-1}$ DM).

Similarly the highest content of Zn in all variants in cultivar Impala was assessed in fresh matter of potato tubers (VPT) also in potato peels (flesh: A2 → D2: 2.75 → 11.93 $mg \cdot kg^{-1}$ FW; peel: A2 → D2: 34.85 → 383.20 $mg \cdot kg^{-1}$ DW) and the lowest content was in potato tubers of cultivar Désirée (flesh: A2 → D2: 2.345 → 9.64 $mg \cdot kg^{-1}$ FW; peel: A2 → D2: 21.45 → 196.98 $mg \cdot kg^{-1}$ DW).

Strong positive correlation (P-value < 0.01) was confirmed between amount of Zn applied into cultivation substrate and its accumulation in biomass (BT) also in tubers and peels of potatoes (VPT). In biological test similarly also the influence of cultivar on ability of accumulation of zinc by plant, statistically non-significant were only differences between cultivars Impala and Livera (BT) and between cultivars Désirée – Agria and Agria – Livera (VPT).

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