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CONTAMINATION OF POTATO TUBER (*Solanum tuberosum* L.) BY NICKEL AND COPPER

ZANIECZYSZCZENIE NIKLEM I MIEDZIĄ BULW ZIEMNIAKA (*Solanum tubersosum* L.)

Abstract: The content of toxic microelements is one of the hygienic-toxicological factors of the foodstuffs quality. Lead, mercury, arsenic and cadmium belong to the most important toxic elements. Also the essential elements (minor ones – Fe, Zn or trace elements – Cr, Cu, Ni, Se) occurring in higher concentrations could have toxic effects. Copper and nickel belong to the essential elements, intake of which organisms have to take from food in certain amount, in order to provide its important biological functions. Most of foodstuffs contain less than 10 mg Cu $\cdot$ kg^{-1} (potatoes 0.3–0.1 mg $\cdot$ kg^{-1}), the nickel content in fruit, cereals and foodstuffs of animal origin (except some sea animals) is very low – hundredths to decimals mg $\cdot$ kg^{-1} (potatoes 0.01–0.26 mg Ni $\cdot$ kg^{-1}).

Keywords: potatoes, heavy metals, contaminations

Potatoes belong among staple food of global citizens. Furthermore, they have dimensional and saturating functions in human nutrition, they are also the source of mineral matters and vitamins (B_1, B_2, C, folic acid). Nowadays potatoes are cultivated in the area ca 19.5 mil. hectares, while China is the greatest producer (Table 1).

Table 1

The greatest producers of potatoes in 2006–2007 [1]

Potatoes producers	[ton]	Potatoes producers	[ton]
1. China	72,000,000	6. Germany	1,162,400
2. Russian Fed.	3,727,982	7. Poland	1,036,900
3. India	2,500,000	8. Belarus	818,501
4. Ukraine	1,946,240	9. Netherlands	677,700
5. USA	1,909,750	10. France	668,082

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At the beginning of 90ties in Slovakia there was continuous decline of cultivation acreage and the absolute minimum was recorded in 2006, with the acreage declined on 18.400 hectars and reproducing areas declined even on 760 ha. In 2007 the cultivation areas have remained on last-year values, but minimally have increased the reproducing areas (ca by 200 ha) [2].

The important factor for producers and consumers of potatoes is besides the tubers yield also external and inner quality, including its food safety, which is given also by the content of foreign substances in flesh. Heavy metals are important inorganic contaminants entering into food chain.

Regular long-termed survey of heavy metals in different international projects has showed on important increase of their concentration in soil, especially in city and industrial areas. Soil is also starting place of their enter into the plants and afterwards into food chain. Enhanced contents of heavy metals in food chain can affect significant health consequences. Obviously, hazardous ones are metals, which are accumulated in human body [3].

The occurrence of toxic elements and of chemical substances in the environment, in raw materials of plant and animal origin causes the consequence worse total hygienic quality of chosen foodstuffs, what is reflected in final point on bad health conditions of the consumer [4].

So the best solution is to prevent food chain from contamination in the beginning. If the soil contamination had originated, it is possible to monitor it or to try to eliminate its consequences [5].

The influence of heavy metals on the environment is emphasized by their persistence. The occurrence of heavy metals in plants is connected with their presence in soils [6].

Biologically essential microelements belong among heavy metals (eg Cu, Zn, Mn, Co, Cr, etc.) as well as many non-essential chemical elements (Cd, Pb, Hg, etc). They occur in soils in various concentrations, oxidation degrees and in bonds. Their risks lie in ecotoxicity and in accumulation in biotic and abiotic environmental components. Toxic ones are also biological essential microelements, when exceeding certain concentration.

The most hazardous are those elements having relative low presence in ecosystems and low border of toxicity. Metals, unlike of organic substances which have been degrading in the environment by influence of continuous activity of bacteria and fungi, by chemical degradation, are resistant to these processes and even in some cases soil microorganisms and bacteria in waters enable toxic metals to enter into complexes with organic compounds and thus change or even multiply their toxicity. It is necessary to deal with negative influence of risky elements in connections with emission situation (atmospheric gradients) [7].

Content of heavy metals in plants depends on their concentration and transfer in soil. Their transport is dependable mainly on physical and chemical soil properties [8]. The mobility or immobility of heavy metals are influenced by following parameters: soil reaction, organic matter, mineral composition, the content of oxides Fe and Mn [9].

The interaction of the amount of heavy metals in soil affect the amount of heavy metals absorbed by plants [10].

Copper belongs among elements which are essential for man, but on the other hand they are potentially toxic. Deficit of copper in human body is very rare. It is relatively frequent industrial exposure to steams of copper or dust aerosols from the standpoint of toxicity, but numerous observations of health state of workers have not detected any symptoms of chronic damages of organism.

Copper is essential element for plants. It has obvious importance in metabolic processes of the plants, because its content in plant tissues is very low and does not reach the concentrations of zinc and manganese. The copper ions form complexes with proteins and other biopolymers in plant tissue. Copper content in plants is ranging from 1 to 50 $\mu g \cdot g^{-1}$ of dry matter of tissue. Toxic effects of copper for plants can occur when the concentration is enhanced in soil after the application of fungicides.

Copper can be concentrated in mineral soil fraction, more rich are the soils containing the oxides of manganese or the mixtures rich in organic compounds. The copper content in soil is very variable. The greatest range of values is in brown soil on chalk sandstone, terraces and slopes and on non-limestone niveau deposits. Balanced set of values is gained in chernozem illimerized on loesses and in meadow soils on lime deposits.

Nickel is in line of crust composition on the 24th place, so it is not the element with abundance occurrence. Nickel is the essential element for plants and some animals.

For its low absorbing from digestive system nickel is similarly as zinc, manganese and chromium (besides Cr^{VI}) relatively less toxic. The most important consequence mostly of long-timed work-related exposure of nickel is the incidence of man's lunge cancer, nasal cavity and rarely larynx. From the standpoint of carcinogenic effects compounds of nickel sulfide and oxide are the most dangerous ones [11].

Concentration range of nickel in soils varies widely and often is in range from 1 to 300 $mg \cdot kg^{-1}$. Average values are in a range 30–80 $mg \cdot kg^{-1}$. Also extreme high contents of nickel can occur (100–7000 $mg \cdot kg^{-1}$) [12]. When nickel is present in high concentration in soil, then it is toxic for plants.

On the basis of the highest and the lowest content of four most hazardous risky elements – cadmium, mercury, lead and arsenic the scale of contamination line had been done by [13] by eight crop species, while potatoes were set on the fourth place.

Material and methods

Soil. Soil samples were taken from the site Stara zem with the acreage 62.5 ha, located in cadastre area of Imel village, between the flows of Nitra and Zitava rivers. Localisation coordinates of the site are 47°54.221′ of northern latitude and 18°10.123′ eastern longitude. Bonitation soil-ecological unit of this area is 0040001, soil type: black chernozem – carbonated, soil type: light-sandy.

Plant. The tested crop was potatoes tuber (*Solanum tuberosum* L.) in six cultivars: Volumia, Adora (very early), Vivaldi, Liva, Courage (early), Victoria (late). Potatoes were harvested in the ripeness of consuming.

The sampling sites determination (soil, plant) was done by covering of borders of the key site by raster, their distances inside the site presented sampling sites. Site borders were gained with navigation apparatus GPS MAP 60 Cx GARMIN (GPS). After data transfer about position and above sea level into the program OziExplorer the borders were adapted and covered by raster with density of lattice of 6 seconds. Sampling places with the accuracy ±2 meters were determined with GPS. The site borders were defined by 149 points, their above sea level ranged from 105.8 to 118.0 ma.s.l. Sampling sites and varieties of potatoes are presented in Figure 1.

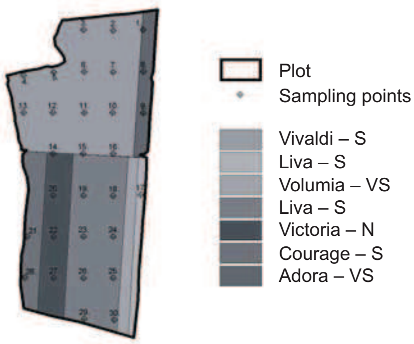

Fig. 1. Sampling sites and the potatoes varieties

After localization of sampling point we had done taking of the soil in this place by valid methods from two horizons (A: 0–0.2 m; B: 0.3–0.45 m) with pedological sampler GeoSampler fy. Fisher.

The content of available nutrients (P, K, Ca, Mg) in soil was determined by the Mehlich II method, the content of nitrogen by Kjeldahl method, for the agrochemical characteristics of soil we also determined: % humus, active and exchangeable form of pH (pH/H_2O; pH/KCl).

In soil samples various forms of **nickel** and **copper** were assessed in the following extracts:

– in extract of *aqua regia* – determination of pseudototal content of heavy metals – includes all their forms except of residual fraction of metals

– in soil extract HNO_3 ($c = 2$ mol $\cdot dm^{-3}$) – determination of so-called potential mobilizable forms of heavy metals in soil,

– in soil extract NH_4NO_3 ($c = 1$ mol $\cdot dm^{-3}$) – determination of mobile forms of heavy metals

Plant material was collected from the same sites as the soil.

Copper and nickel content were determined in potato tubers mineralized by dry way with AAS method on atomizer Pye Unicam SP9.

Results and discussion

The content of nutrients determined in the soil samples ranged from 1050–5250 mg N $\cdot$ kg^{-1}, 45.1–636.4 mg P $\cdot$ kg^{-1}, 146.5–647.5 mg K $\cdot$ kg^{-1}, 800–22,450 mg Ca $\cdot$ kg^{-1},

Table 2

Contents of nutrients and of humus in soil taken from 2 soil horizons (A, B)

Sampling site	Nutrients content [mg · kg^{-1}]										% Hum.	
	N		P		K		Ca		Mg			
	A	B	A	B	A	B	A	B	A	B	A	B
1	3938	6475	117.7	121.4	359.0	399.0	3790	3950	46.4	39.2	2.28	2.35
2	5250	4900	127.5	114.4	146.5	156.5	1575	1955	19.5	17.2	1.64	1.21
3	1225	1400	68.4	86.7	298.0	209.5	22450	23350	74.0	85.4	1.92	2.06
4	2275	2800	265.7	310.7	632.0	608.5	1235	1510	29.0	34.0	1.92	1.92
5	2100	2100	165.3	147.8	376.5	355.0	3655	3645	50.7	46.6	2.78	2.49
6	1575	2100	182.1	146.9	238.0	232.5	2615	2055	29.4	24.4	2.28	1.85
7	1925	2100	138.7	145.1	373.5	589.5	2180	2530	29.0	40.4	2.56	2.63
8	1925	1750	90.1	95.5	282.0	342.5	16075	15925	111.7	110.3	2.35	2.99
9	2450	4025	100.7	112.9	427.0	501.0	3630	3685	37.3	38.5	3.06	2.70
10	4025	2975	94.9	103	287.5	302.0	2005	1725	48.5	42.2	2.70	2.99
11	4025	4025	131.6	247.3	387.5	317.5	4660	5240	47.1	49.5	3.37	2.93
12	2975	4550	169.3	262.3	366.0	372.5	4295	4665	64.5	78.5	2.49	3.15
13	3500	3413	231.4	196.1	647.5	466.0	1985	2260	53.9	59.4	3.45	3.30
14	4375	5075	87.1	70.4	203.5	288.0	25400	29800	198.0	212.0	2.42	3.30
15	4375	3500	125.2	146.6	321.0	355.5	5635	5505	36.9	36.4	2.85	2.99
16	3500	3325	165.5	127.9	334.5	414.0	5525	6000	48.2	55.7	3.34	2.71
17	3850	4025	145.7	155.3	297.0	268.0	3360	3720	78.1	80.9	3.77	3.77
18	4550	4025	329.6	337.8	327.0	340.0	5625	5690	46.0	49.1	2.35	2.21
19	4725	4375	240.9	202.9	361.5	331.5	10675	13080	80.2	95.7	2.92	2.85

Table 2 contd.

Sampling site	Nutrients content [mg · kg^{-1}]										% Hum.	
	N		P		K		Ca		Mg			
	A	B	A	B	A	B	A	B	A	B	A	B
20	3500	4025	233.3	218.7	420.0	362.5	3715	3350	40.0	34.5	2.63	2.06
21	2800	3675	636.7	568.6	604.0	640.5	800	920	31.5	38.7	3.01	2.05
22	2975	3150	156.1	124.5	218.5	217.5	1540	1530	41.5	41.0	2.35	2.27
23	2100	875	167.9	173.4	384.5	395.5	6600	7475	86.7	92.8	3.45	3.45
24	1050	1050	347.8	353.8	402.5	386.5	6265	5910	53.7	51.8	2.71	2.64
25	1400	1400	248.7	210.1	360.5	449.0	1860	1795	55.6	53.4	3.08	2.86
26	2450	3850	140.9	130.9	245.5	280.0	2050	2435	43.4	48.6	3.08	2.86
27	3325	4200	45.1	42.5	189.5	136.5	20880	16500	77.5	59.6	2.71	3.67
28	5250	350	266.7	359.4	228.5	422.0	1220	1420	32.4	42.1	1.78	1.92
29	1750	3150	126.2	127.5	246.5	208.5	965	950	24.9	28.4	1.49	1.35
30	1750	3850	129.8	139.1	455.5	493.5	4780	4075	77.8	70.5	3.34	3.34

19.5–198.0 mg Mg · kg^{-1}. Exact values for individual sampling sites and A and B horizons are shown in Table 2. The gained results showed that soil had high phosphor content, low magnesium content and high content of potassium.

According [14], potatoes require soil with humus content over 2 %. All samples of soils with the exception of sampling sites 2, 3, 4, 28, 29 (Table 2) correspond to this requirement. The soil reaction should be in the range between values from pH 5.5 to 6.5, high and stabile yields of potatoes are reached when keeping the soil reaction in weakly acid area (pH 6.7) [15]. Assessed values of active form pH ranged from 6.44 to 8.70 and of exchangeable form pH ranged from 5.26 to 7.90 (Fig. 2), so it is neutral to weakly alkaline reaction, but it need not to lead to reduced production from the standpoint of potatoes cultivation.

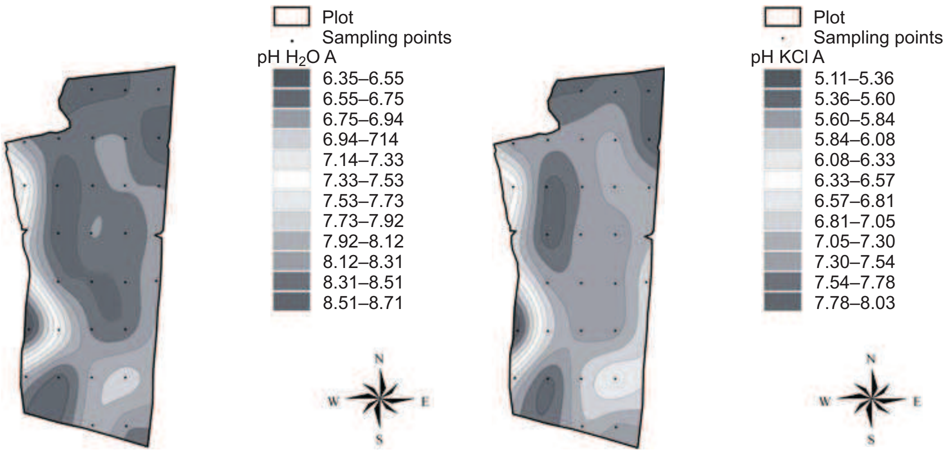

Fig. 2. Izoline maps illustrating values of pH/H_2O and pH/KCl of soil taken from A horizon

The contents of Cu and Ni in soil [mg · kg^{-1}] assessed in different extracts are presented in Table 3. The highest value determined in the extract of *aqua regia* is for Ni in A horizon 22.2 mg · kg^{-1} and B horizon 20.8 mg · kg^{-1}, for Cu 27.6 mg · kg^{-1} (in both horizons). In soil extract HNO_3 the highest content of Ni is 7.5 mg · kg^{-1} (A horizon) and 7.8 mg · kg^{-1} (B horizon), the highest content of Cu 14.6 mg · kg^{-1} (A horizon) and 12.1 mg · kg^{-1} (B horizon). In soil extract NH_4NO_3 the highest Ni content is 0.195 mg · kg^{-1} (A horizon) and 0.220 mg · kg^{-1} (B horizon), the highest content of Cu 0.175 mg · kg^{-1} (in both horizons). When the higher content of risky elements in soil occur, than their limit values, it can not mean their transfer into cultivated crops, but when the limit is exceeded this factor is significant. In contrary their content in soil below limit values will not guarance that the plants cultivated on this soil will contain tolerable amount. That is why from the hygienic standpoint it is determining, if these elements accumulate in edible parts used for consume [7].

The content of Ni assessed in potato tubers after their mineralization by dry way method is the highest one in the sample from sampling site no. 7 (0.1223 mg · kg^{-1} of

Table 3

Nickel and Copper content in soil [mg · kg^{-1}] assessed in various extracts

Sampling site	*Aqua regia*				HNO_3				NH_4NO_3			
	Ni		Cu		Ni		Cu		Ni		Cu	
	A	B	A	B	A	B	A	B	A	B	A	B
1	21.8	15.2	12.2	11.2	5.4	5.7	7.6	7.8	0.100	0.100	0.080	0.090
2	11.4	12.2	8.6	7.6	3.0	2.9	4.4	4.1	0.085	0.080	0.075	0.075
3	19.0	17.8	10.0	10.2	6.5	6.7	5.7	5.9	0.120	0.140	0.115	0.110
4	11.2	14.0	12.6	16.4	2.9	3.6	10.8	10.9	0.095	0.095	0.175	0.175
5	18.0	16.4	14.2	13.4	5.7	5.2	10.0	9.0	0.125	0.110	0.085	0.070
6	12.6	14.0	11.0	9.2	3.1	3.1	6.8	5.9	0.115	0.100	0.075	0.060
7	17.8	18.4	21.2	14.2	5.7	5.7	8.6	8.4	0.090	0.095	0.070	0.055
8	18.6	20.4	9.2	13.6	6.0	6.0	8.2	8.3	0.100	0.110	0.070	0.070
9	17.8	18.0	12.4	12.4	7.4	7.3	7.8	7.7	0.135	0.145	0.080	0.085
10	16.6	15.4	13.4	10.6	6.7	5.5	7.5	6.2	0.100	0.085	0.060	0.075
11	19.6	14.6	12.4	11.4	7.0	7.2	8.3	8.1	0.135	0.155	0.095	0.100
12	16.6	19.6	13.4	16.2	5.5	6.7	9.7	11.3	0.120	0.170	0.085	0.120
13	17.6	17.8	15.8	15.2	6.1	6.1	11.2	10.6	0.125	0.085	0.115	0.085
14	11.8	20.6	8.8	12.4	6.1	7.7	7.4	8.6	0.110	0.140	0.095	0.125
15	20.6	19.4	13.2	12.8	7.5	7.5	7.8	7.9	0.135	0.150	0.110	0.100
16	19.6	20.0	13.4	14.4	6.7	6.8	7.7	7.7	0.135	0.160	0.055	0.065
17	19.2	20.0	27.6	27.2	7.4	7.6	11.8	12.1	0.170	0.220	0.065	0.080
18	11.2	12.2	13.8	22.2	6.2	6.3	9.0	9.0	0.135	0.125	0.065	0.060
19	22.2	20.8	26.4	27.6	6.9	6.9	11.6	11.1	0.165	0.180	0.080	0.070

Table 3 contd.

Sampling site	*Aqua regia*				HNO_3				NH_4NO_3			
	Ni		Cu		Ni		Cu		Ni		Cu	
	A	B	A	B	A	B	A	B	A	B	A	B
20	19.6	14.4	18.8	20.2	5.0	3.8	8.2	6.2	0.115	0.110	0.055	0.055
21	10.6	9.6	20.8	13.8	3.4	3.5	14.6	9.9	0.130	0.110	0.055	0.075
22	6.6	11.8	5.6	10.6	4.2	4.3	6.8	7.0	0.105	0.095	0.040	0.025
23	17.0	19.2	17.4	17.0	7.5	7.8	11.9	11.7	0.195	0.170	0.110	0.075
24	19.2	18.8	13.6	24.4	7.2	7.2	10.5	10.2	0.155	0.170	0.085	0.080
25	15.8	16.8	25.6	25.6	6.6	6.5	10.1	10.0	0.125	0.135	0.050	0.050
26	14.2	12.4	19.6	19.2	4.9	5.1	7.1	7.4	0.130	0.135	0.050	0.060
27	15.8	14.4	16.4	18.2	5.8	6.1	6.5	6.6	0.155	0.155	0.075	0.070
28	7.0	11.4	12.8	22.2	3.0	3.8	7.3	9.0	0.095	0.095	0.060	0.060
29	3.4	9.0	3.8	7.6	3.0	3.1	3.9	4.1	0.105	0.070	0.035	0.030
30	15.2	12.8	13.0	11.0	7.2	7.3	9.0	9.1	0.155	0.170	0.090	0.085

Table 4

The content of Ni and Cu in tubers of potatoes [mg · kg^{-1}] fresh mater

Sampling site	Variety	Ni	Cu	Sampling site	Variety	Ni	Cu	Sampling site	Variety	Ni	Cu
1	Adora	0.029	0.088	11	Vivaldi	0.042	0.085	21	Courage	0.059	0.121
2	Vivaldi	0.016	0.065	12	Vivaldi	0.016	0.110	22	Victoria	0.020	0.105
3	Vivaldi	0.031	0.118	13	Vivaldi	0.040	0.078	23	Liva	0.073	0.178
4	Vivaldi	0.029	0.104	14	Victoria	0.019	0.142	24	Liva	0.021	0.099
5	Vivaldi	0.016	0.090	15	Vivaldi	0.018	0.084	25	Liva	0.025	0.148
6	Vivaldi	0.018	0.095	16	Vivaldi	0.025	0.118	26	Liva	0.015	0.078
7	Vivaldi	0.122	0.064	17	Liva	0.014	0.102	27	Victoria	0.041	0.063
8	Adora	0.044	0.073	18	Liva	0.015	0.117	28	Courage	0.021	0.112
9	Adora	0.018	0.085	19	Liva	0.017	0.114	29	Liva	0.032	0.095
10	Vivaldi	0.015	0.059	20	Victoria	0.016	0.095	30	Liva	0.030	0.090

fresh matter), content of Cu is the highest one in the sample from sampling site no. 23 (0.178 mg · kg^{-1} fresh matter). Results of assessment are presented in Table 4. None of the contents of Ni and Cu was higher than legislative limits. The highest acceptable amounts defined by Foodstuffs Codex of Slovak Republic are for Ni 0.5 and for Cu 3.0 mg · kg^{-1} of fresh matter [16].

Conclusions

The advantage of using of navigation system GPS by samples taking is the accuracy with which it is possible from the same sampling site to take repeatedly soil samples and plant material with certain time period and also after some years with minimal deviation and thus to observe possible changes and trends in contents of key elements, respectively possible contamination of soil.

Soil samples from the site located on cadastre area of Imeľ village do not contain enhanced contents of heavy elements Ni and Cu, the limit value for pseudototal content was not exceeded (Ni 40 mg · kg^{-1}, Cu 30 mg · kg^{-1}), for mobile forms (Ni 1.5 mg · kg^{-1}, Cu 1.0 mg · kg^{-1}) [17] and for potential mobilizable forms (Ni 10 mg · kg^{-1}, Cu 20 mg · kg^{-1}) [18]. It could be concluded that these soils are not contaminated.

Assessed contents of Ni and Cu in tubers of potatoes taken from the same sampling sites are lower than the highest acceptable amounts defined in Foodstuffs Codex SR. From the standpoint of the content of these two metals is the cultivation of the potato tuber in key locality without any risk. For the total evaluation of the safety it is very important to monitor also the contents of others risky metals which can often have not only antagonistic, but also synergic effect.

Acknowledgement

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ZANIECZYSZCZENIE NIKLEM I MIEDZIĄ BULW ZIEMNIAKA (*Solanum tubersosum* L.)

Abstrakt: Zawartość toksycznych mikroelementów jest jednym z ważnych parametrów jakości żywności. Ołów, rtęć, arsen i kadm należą do najważniejszych toksycznych pierwiastków. Mikroelementy (Fe, Zn, Cr, Cu, Ni, Se) występujące w dużych stężeniach również mogą mieć działanie toksyczne. Miedź i nikiel zaliczane są do mikroelementów, które organizm wchłania z pożywienia w ilościach niezbędnych do podtrzymania wielu procesów biologicznych. Większość pokarmów zawiera Cu w ilości nie przekraczającej 10 mg $\cdot$ kg^{-1} (ziemniaki 0,3–0,1 mg $\cdot$ kg^{-1}). Zawartość niklu w owocach, płatkach zbożowych i pokarmach pochodzenia zwierzęcego (z wyjątkiem niektórych zwierząt morskich) jest bardzo mała – od setnych do dziesiątych mg $\cdot$ kg^{-1} (ziemniaki 0,01–0,26 mg $\cdot$ kg^{-1}).

Słowa kluczowe: ziemniaki, metale ciężkie, zanieczyszczenie