IOŚ-PIB OCHRONA ŚRODOWISKA I ZASOBÓW NATURALNYCH
ENVIRONMENTAL PROTECTION AND NATURAL RESOURCES 2013
VERSITA VOL. 24, NO 2(56): 17–20
DOI 10.2478/oszn-2013-0009

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Risk of cadmium and lead transfer from the soil into seeds of chosen minor plants

Ryzyko migracji kadmu i ołowiu z gleby do nasion wybranych roślin rzadkich

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Keywords: cadmium, lead, soil contamination, buckwheat, amaranth, quinoa
Słowa kluczowe: kadm, ołów, zanieczyszczenie gleby, gryka, szarłat, komosa ryżowa

Abstract
The risk of Cd and Pb transfer from the soil into the seeds of different cultivars of buckwheat, amaranth and quinoa cultivated in field trial was investigated. Five cultivars from each pseudocereal, that is, buckwheat (Špačinská, Siva, Bamby, Aiva, Madawska), amaranth (Golden Giant, Rawa, Annapurna, Oscar Blanco, Koniz) and quinoa (Temuco, Quinua, Yulai, Carmen, Ccankolla) were analysed. Content of risky metals in soil and pseudocereal seeds was assessed by AAS. Pseudototal contents of metals determined in the soil extract by *aqua regia* were lower than the limit values given by Law No. 220/2004 with exception of Cd (the soil content was 40% higher than the hygienic limit). Contents of bioavailable forms determined in the soil extract by NH_4NO_3 (c = 1 mol•dm^{-3}) of all observed metals with exception of Pb were lower than hygienic limits. The determined content of bioavailable Pb forms was 2.3-fold higher than the hygienic limit. The limit value for Cd content was not exceeded in any buckwheat cultivar. The determined Pb content was in cv. Bamby at the level of hygienic limit, and in cv. Madawska twofold higher than the limit given by Foodstuff Codex of the Slovak Republic (FC SR). On the other hand, in seeds of nearly all the investigated amaranth and quinoa cultivars, higher Cd and Pb contents than the maximal allowed amounts in cereals according to FC SR were determined. The presented results indicate the serious risk of Cd and Pb accumulation by seeds of minor plants which are utilised in the production of functional foods.

Streszczenie
W pracy badano ryzyko migracji kadmu i ołowiu z gleby do nasion kultywarów gryki, szarłatu i komosy ryżowej uprawianych w eksperymencie polowym. Analizie poddano pięć kultywarów każdego pseudozboża, tj. gryki (Špačinská, Siva, Bamby, Aiva, Madawska), szarłatu (Golden Giant, Rawa, Annapurna, Oscar Blanco, Koniz) i komosy ryżowej (Temuco, Quinua, Yulai, Carmen, Ccankolla). Zawartości niebezpiecznych metali w nasionach pseudozbóż określono za pomocą metody AAS. Pseudo-całkowite zawartości metali określone w roztworze glebowym za pomocą wody królewskiej były niższe od wartości granicznych wynikających z Ustawy nr 220/2004 z wyjątkiem Cd (zawartość w glebie była wyższa o 40% w stosunku do dopuszczalnej wartości). Zawartość biodostępnych form określonych za pomocą NH_4NO_3 (c = 1 mol•dm^{-3}) dla wszystkich badanych metali były niższe od wartości dopuszczalnych z wyjątkiem Pb. Zawartość biodostępnych form Pb była 2,3-krotnie wyższa od wartości dopuszczalnej. Wartość graniczna zawartości Cd nie została przekroczona w żadnym kultywarze gryki. Zawartość Pb była na poziomie dopuszczalnym w odmianie Bamby oraz dwukrotnie przekraczała wartość graniczną wyznaczoną przez Kodeks Żywności Republiki Słowackiej (KŻ RS) w odmianie Madawska. Ponadto, stwierdzono zawartości Cd i Pb wyższe niż wartości dopuszczalne w zbożach ustanowione przez KŻ RS w nasionach prawie wszystkich kultywarów szarłatu i komosy ryżowej. Przedstawione wyniki wskazują na poważne zagrożenie akumulacji Cd i Pb w nasionach uprawianych pseudozbóż.

1. INTRODUCTION

The pollution of all environment components brings about many negative phenomena. The changes caused by their influence create the need to eliminate these reasons and to remedy the resulting damage. The atmosphere of the northern hemisphere was and still is contaminated by exhalants from energetics, transport, agriculture and, in particular, from industry.

The change in soil reaction caused by chemical reactions of acid components of these exhalants with the other components of atmosphere constitutes one of the global environmental problems. The destruction of organic and mineral soil components, the decreasing of basic cation concentration, the immobilization of nutrients, the decreasing of soil buffer capacity and the mobilisation of toxic elements are the main consequences of soil acidification. Cadmium and lead are risk elements with significant negative effects on all components of the environment, as well as on human health.

Cadmium, a by-product of zinc production, is one of the most toxic elements to which man can be exposed to at work or in the environment. Once absorbed, Cd is efficiently retained in the human body, in which it accumulates throughout life. Cd is primarily toxic to the kidney, but it can also cause prostate and renal cancer as well as bone demineralisation. Airborne Cd may impair lung function and increase the risk of lung cancer [Bernard 2008].

Lead is a toxic metal, too. As a result of many years of use in gas and paint production, lead can be found in many places. The most important lead sources in the environment include paints, dust, soil, drinking water and polluted atmosphere [Villalobos et al. 2009]. Lead exposure occurs mainly through the respiratory and gastrointestinal tracts. Lead toxicity affects the central and peripheral nervous systems, renal function and the cardiovascular system. Lead exposure also has been related to increased incidence of overall cancers, as well as stomach, lung and bladder cancer [Rousseau et al. 2007].

The aim of the work was to determine the risk of Cd and Pb transfer from the soil into the seeds of various cultivars of minor plants such as buckwheat, amaranth and quinoa.

2. MATERIAL AND METHODS

The field trial was realised in Plant Production Research Center in Piešťany. The soil from the grown locality was sampled by valid methods with pedogogical probe GeoSampler fy. Fisher. In each soil sample, the exchangeable reaction (pH/KCl), the contents of available nutrients (K, Mg, P) and mobile forms of Ca according to Mehlich II and content of humus by the Tjurin method were determined. Pseudototal content of risk metals including all of the forms besides residual metal fraction was assessed in a solution of *aqua regia*, and content of mobile forms of selected heavy metals in soil extract of NH_4NO_3 ($c = 1\ mol \bullet dm^{-3}$). The obtained results were evaluated according Law No. 220/2004. Five cultivars from each of the three types of pseudocereals, that is, buckwheat (Špačinská, Siva, Bamby, Aiva, Madawska), amaranth (Golden Giant, Rawa, Annapurna, Oscar Blanco, Koniz) and quinoa (Temuco, Quinua, Yulai, Carmen, Ccankolla), were analysed. All cultivars are registered in the EU. The plants were harvested when fully ripe. The pseudocereal seeds were manually separated, dried at 105°C to a constant weight (WTC Binder, Germany) and powdered (Fritsch Pulverisette, Germany). The content of risky elements was assessed after mineralisation by the dry way method of flame atomic absorption spectrophotometry (AAS) on apparatus AAS Varian AA Spectr DUO 240 FS/240Z/UltrAA. The amounts of risky elements in pseudocereals seeds were evaluated according to the Foodstuff Codex of the Slovak Republic (FC SR).

3. RESULTS AND DISCUSSION

Agrochemical characteristics, content of nutrients and heavy metals in soil from the field experiment are presented in Table 1. In the investigated soil the neutral till alkaline soil reaction, a medium humus supply, low P, sufficient K and very high Mg contents were determined. The P content was supplemented by use of NPK fertilisers.

Pseudototal contents of hazardous metals determined in the soil extract by *aqua regia* were lower than the limit values given by Law No. 220/2004 with exception of Cd, where the soil content was 40% higher in comparison to the hygienic limit.

Contents of bioavailable forms determined in the soil extract by NH_4NO_3 ($c = 1\ mol \bullet dm^{-3}$) of all observed metals with exception of Pb were lower than hygienic limits. The determined content of bioavailable Pb forms was 2.3-fold higher than the critical value for Pb content in relationship of agricultural soil and plant. Also, these results confirm that, in our conditions especially, Cd and Pb could be risky because of their transfer from the soil as the starting place of their entry into the human food chain.

The presented results showed that from the investigated buckwheat cultivars, Špačinská accumulated in groats the highest Cd amount and Bamby the lowest (Table 2).

The limit value for Cd content in cereal grain was not exceeded in any buckwheat cultivar. The most sensitive buckwheat cultivars for Pb intake were Bamby and Madawska. The determined Pb content was in cv. Bamby at the level of hygienic limit, and in cv. Madawska twofold higher than the limit value given by FC SR. On the other hand, in seeds (nearly of all investigated amaranth cultivars), high contents of Cd and Pb were determined (Table 3). Only in cv. Rawa the determined Cd and in cv. Golden Giant the Pb contents were lower than the hygienic limits given by the legislation. From the tested amaranth cultivars, Annapurna was able to accumulate the highest Cd and Pb amounts. In the seeds of cv. Annapurna, the hygienic limit given by the FC SR for Cd exceeded by 100% and for Pb by 170%.

Also, all observed quinoa cultivars accumulated very high Cd and Pb amounts in seeds (Table 4). With the exception of Cd content in seeds of cv. Yulai (where the determined Cd content was at the level of hygienic limit), in seeds of all cultivars the hygienic limits for Cd and Pb given by the legislation were exceeded. The highest Cd content was determined in seeds of cv. Temuco and the highest Pb content was determined in cvs. Carmen and Ccankolla (higher than the hygienic limits by 90% and 180% respectively).

Heavy metals can enter into the environment due to various human activities, and in high concentrations can disrupt the natural terrestrial ecosystem [Yadav et al. 2009]. In high concentrations, all risky metals have a strong toxic effect and are considered to be dangerous environmental pollutants [Chehregami et al. 2005]. Many authors present a phytotoxic influence of different heavy metals on plants [Dan et al. 2008]. Some of the risky metals such as As, Cd, Hg or Pb are not essential, but other metals

Table 1. Agrochemical characteristics, content of nutrients ($mg \bullet kg^{-1}$) and heavy metals ($mg \bullet kg^{-1}$) in soil from locality Piešťany

Agrochemical characteristics	**pH (H2O)**	**pH (KCl)**	**Cox (%)**	**humus (%)**					
	8.17	7.25	1.39	2.39					
Nutrients	**N**	**K**	**Ca**	**Mg**	**P**				
	3145	295.49	3802.55	327.41	26.77				
Heavy metals	**Zn**	**Cu**	**Mn**	**Fe**	**Cr**	**Cd**	**Pb**	**Co**	**Ni**
Aqua regia	74.2	25.2	670	2192.0	32.6	0.98	26.2	13.8	44.6
Limit value	150	60	-	-	70	0.7	70	15	50
NH_4NO_3 ($c = 1\ mol \bullet dm^{-3}$)	0.09	0.09	0.45	0.18	0.04	0.04	0.23	0.15	0.17
Critical value	2	1	-	-	-	0.1	0.1	-	1.5

Limit value for heavy metal content in the soil extract by *aqua regia* – Law No. 220/2004

Critical value for heavy metal content in the soil extract by NH_4NO_3 ($c = 1\ mol \bullet dm^{-3}$) – Law No. 220/2004

Table 2. Content of observed heavy metals in buckwheat groats ($mg \cdot kg^{-1}$ dm)

Buckwheat cultivar	Content of observed heavy metals ($mg \cdot kg^{-1}$ dm)	
	Cd	Pb
Špačinská	0.09 ± 0.030	0.1 ± 0.016
Siva	0.06 ± 0.012	0.1 ± 0.013
Bamby	0.05 ± 0.080	0.2 ± 0.010
Aiva	0.08 ± 0.010	0.1 ± 0.029
Madawska	0.06 ± 0.010	0.4 ± 0.045
limit (FC SR)	0.1	0.2

Average values ± standard deviation
FC SR = Foodstuff Codex of the Slovak Republic

Table 3. Content of observed heavy metals in amaranth seeds ($mg \cdot kg^{-1}$ dm)

Amaranth cultivar	Content of observed heavy metals ($mg \cdot kg^{-1}$ dm)	
	Cd	Pb
Golden Giant	0.11 ± 0.017	0.18 ± 0.024
Rawa	0.08 ± 0.288	0.29 ± 0.013
Annapurna	0.2 ± 0.010	0.54 ± 0.007
Oscar Blanco	0.1 ± 0.011	0.25 ± 0.005
Koniz	0.14 ± 0.007	0.34 ± 0.007
limit (FC SR)	0.1	0.2

Average values ± standard deviation
FC SR = Foodstuff Codex of the Slovak Republic

Table 4. Content of observed heavy metals in quinoa seeds ($mg \cdot kg^{-1}$ dm)

Quinoa cultivar	Content of observed heavy metals ($mg \cdot kg^{-1}$ dm)	
	Cd	Pb
Temuco	0.19 ± 0.004	0.44 ± 0.051
Quinua	0.14 ± 0.006	0.4 ± 0.010
Yulai	0.09 ± 0.014	0.33 ± 0.007
Carmen	0.12 ± 0.004	0.56 ± 0.011
Ccankolla	0.16 ± 0.006	0.56 ± 0.008
limit (FC SR)	0.1	0.2

Average values ± standard deviation
FC SR = Foodstuff Codex of the Slovak Republic

such as Co, Cu, Fe, Mn, Mo, Ni and Zn are necessary for plant development and metabolism [Pagliano 2006].
The consumption of these plants or derived products can be risky also for humans [Friesl et al. 2006]. Seeds of plants are the main source of human food production and the input material for another crop production. Quality of seed is reflected in its chemical composition, and thus in the mineral content including trace elements and risky metals [Cakmak 2008; White & Broadley 2009].
From the aspect of Cd and Pb intake, the buckwheat groats seem to be the safest, and quinoa seeds the most risky, for human consumption or food preparation (Fig. 1 and 2).
Since the P-values in the ANOVA (Table 5) are greater than 0.05, there is no statistically significant relationship between the observed risky elements in seeds and in soil at 95.0% or higher confidence level.

Table 5. Relationship between the risky metal content in soil and in seeds of the investigated plants (P-value ANOVA Simple Regression)

Plant	Cd in soil vs. in seeds (*P-value*)	Pb in soil vs. in seeds (*P-value*)
Buckwheat	0.1343	0.5699
Amaranth	0.0879	0.9106
Quinoa	0.8805	0.6341

4. CONCLUSION

The presented results indicate the serious risk of Cd and Pb accumulation by seeds of minor plants which are utilised in functional food production. Despite the fact that content of mobile Cd forms and pseudototal Pb content in soil of the field experiment were lower than the limit values given by Law No. 220/2004, the determined amounts of Cd and Pb especially in amaranth and quinoa seeds were higher than the maximal allowed amounts in cereals according to the foodstuff Codex of the Slovak Republic. It is therefore necessary to permanently monitor soil as well as plant content of risky heavy metals and to apply measures for the minimalisation of risky metal input into the human food chain.

ACKNOWLEDGEMENTS

This contribution is the result of the project implementation: Centre of excellence for white-green biotechnology, ITMS 26220120054, supported by the Research & Development Operational Programme funded by the ERDF.

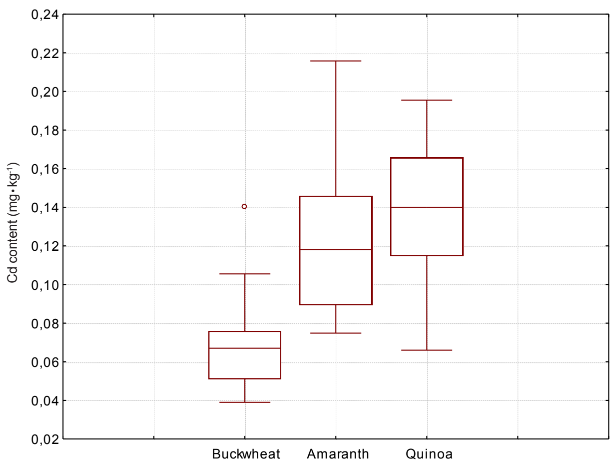

Figure 1. Average values of Cd ($mg \cdot kg^{-1}$).

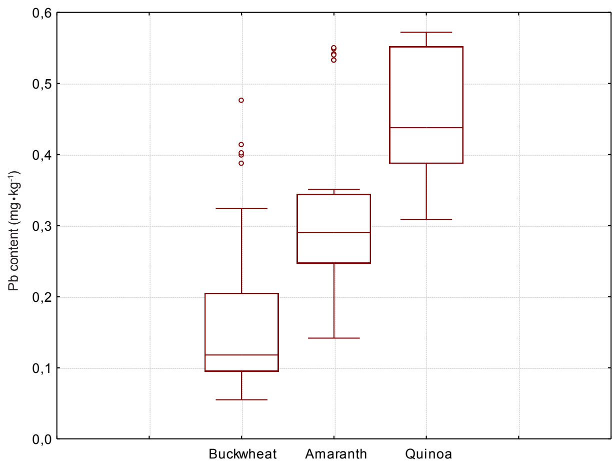

Figure 2. Average values of Pb ($mg \cdot kg^{-1}$).

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