J. Elementol. 2009, 14(4): 729–736

CONCETRATION OF COPPER, ZINC, LEAD AND CADMIUM IN PLANTS CULTIVATED IN THE SURROUNDINGS OF ŻELAZNY MOST COPPER ORE TAILINGS IMPOUNDMENT

Agnieszka Medyńska, Cezary Kabała, Tadeusz Chodak, Paweł Jezierski

Institute of Soil Sciences and Environmental Protection
Wrocław University of Environmental and Life Sciences

Abstract

Regular monitoring of soil and plants in the surroundings of Żelazny Most tailings impoundment has been held since 1996. The results presented in this paper refer to potatoes and grains of cereals such as wheat, barley, triticale and oats, which are the most popular crops planted in that area in 2004-2006. The average content of heavy metals in 2006 in cereals and potatoes was approximately: Cu – 3.7 and 1.3 mg kg^{-1} of fresh mass; Zn – 20.6 and 3.5 mg kg^{-1}; Pb – 0.14 and 0.04 mg kg^{-1}; Cd – 0.055 and 0.011 mg kg^{-1}, respectively. All those concentrations are well below threshold limit values accepted in Poland. No significant differences in Cu, Pb and Cd concentrations between the tested cereals were found. Zinc concentration in wheat and oat was significantly lower than in barley and triticale. The copper ore tailings impoundment in Żelazny Most, although very large, at present has no negative impact on the quality of crops and species of cereals and pasture plants cropped in its surroundings.

Key words: tailings impoundment, trace elements, cereals, potato.

mgr inż. Agnieszka Medyńska, Institute of Soil Sciences and Environmental Protection, Wrocław University of Environmental and Life Sciences, 50-357 Wrocław, Poland, ul. Grunwaldzka 53

ZAWARTOŚĆ MIEDZI, CYNKU, OŁOWIU I KADMU W ROŚLINACH UPRAWNYCH W REJONIE SKŁADOWISKA ODPADÓW PO FLOTACJI RUD MIEDZI ŻELAZNY MOST

Abstrakt

W celu oceny ryzyka związanego z uprawą roślin konsumpcyjnych i paszowych na terenach znajdujących się pod wpływem składowiska odpadów po flotacji rud miedzi Żelazny Most, od 1996 r. prowadzony jest regularny monitoring jakości gleb i roślin uprawnych. W pracy przedstawiono zawartości Cu, Zn, Pb i Cd w ziarnie zbóż (pszenicy ozimej, jęczmienia ozimego, pszenżyta i owsa) i w bulwach ziemniaka, w latach 2004-2006. Stwierdzono następujące średnie zawartości metali (odpowiednio w ziarnie zbóż i w bulwach): Cu – 3,7 i 1,3 $mg \cdot kg^{-1}$ św. m., Zn – 20,6 i 3,5 $mg \cdot kg^{-1}$ św. m., Pb – 0,14 i 0,04 $mg \cdot kg^{-1}$ św. m. oraz Cd – 0,055 i 0,011 $mg \cdot kg^{-1}$ św. m. Nie stwierdzono istotnych różnic w zawartości Cu, Pb i Cd w ziarnie różnych gatunków zbóż. Zawartość Zn była istotnie niższa w pszenicy i owsie w porównaniu z pszenżytem i jęczmieniem. Nie stwierdzono przekroczenia dopuszczalnych zawartości pierwiastków śladowych, co świadczy o dużej skuteczności działań ograniczających negatywny wpływ składowiska na środowisko otaczających obszarów i warunki produkcji rolniczej.

Słowa kluczowe: pierwiastki śladowe, składowisko odpadów poflotacyjnych, zboża, ziemniak.

INTRODUCTION

Location of the copper industry in the Legnica – Głogów region decided about the economic structure and directions of regional development. Unfortunately, very intensive expansion of copper mining and smelting industry caused many adverse changes in natural environment (Dobrzański, Byrdziak 1995). Conditions of agricultural and forest production deteriorated as a result of air, soil and groundwater pollution (Czaban et al. 2007). Important sources of dust bearing heavy metals are impoundments containing tailings from copper ore enrichment. Fine-grained material can be blown away by wind from dry surfaces of an elevated impoundment, and transported to close surroundings as well as over very far distances. Such dust, having specific chemical composition, influences soils and plants in different ways, leading to disturbances in the life functions of soil microorganisms and cultivated plants.

Trace elements play a significant role in many metabolic processes in plant organisms, but at excessive concentrations, particularly in soluble forms and easily available to plants, can cause phytotoxic symptoms. Plant response to high contamination of soil and air with heavy metals is extremely variable and depends on many environmental factors (Kabata-Pendias, Pendias 1999, Turner 1994). Soluble and colloidal forms of heavy metals suspended in a soil solution are the most important for plant uptake, and the most important factors influencing their availability are their total concentration and soil reaction (Karczewska 2002).

Regular monitoring of soil and plant quality in the surroundings of the largest tailings impoundment located near Rudna, called Żelazny Most, has been held since 1996 with an aim of evaluating its impact on the environment and people's health (Angełow et al. 2000, Kabała et al. 2008, Medyńska et al. 2007). The purpose of the present study has been to asses the quality of potatoes and grain of various cereals cropped in an immediate vicinity of tailings pond, on the basis of the concentration of copper, zinc, lead, and cadmium analyzed in the years 2004-2006.

MATERIAL AND METHODS

The tailings impoundment called Żelazny Most is located in the agricultural area of three communities: Rudna, Polkowice and Grębocice in the Lower Silesia region, southwestern Poland. Soils in the surroundings of the impoundment are in general sandy in texture (prevailing sands and loamy sands), with a low or moderate content of organic matter, and nearly neutral soil reaction (Angełow et al. 2000). In 2004-2007, grain and tuber samples were taken in the phase of consumption ripeness from fields of the villages called Rudna (east of the impoundment) and Tarnówek (west of the impoundment). The quantity of samples of particular plants depended on the actual crop rotation and differed from year to year (Table 1). Four typical species of cereals (wheat, oat, barley, and triticale) and potatoes were chosen for the assessment. In accord with the reference methods, cereal grain was dried at 20ºC to *ca* 12% water content, and fresh (not dried) potato tubers were washed and peeled. Additionally, dry mass of samples was determined, after weight stabilization at 105ºC.

Plant samples were ignited at 450ºC and ash was dissolved with concentrated nitric acid. Concentration of copper and zinc in final extracts was measured with the FAAS technique, and concentration of lead and cadmium with the GF-AAS techniques. Accuracy of the measurements was controlled by inclusion of reference plant materials (NIST-RM 8412, IAEA-V-10) with a certified content of the analyzed trace elements.

The environmental risk caused by cadmium and lead to plants was assessed according to European Commission Regulation no 1881/2006 of 19th December 2006, which sets maximum levels of certain contaminants in foodstuff (Polish transcription in Dz.U. UE L364/5). Officially allowed threshold limit values (TLV) of lead and cadmium in potatoes are 0.10 $mg \cdot kg^{-1}$ of fresh mass. In cereals TLV of Pb is 0.20 $mg \cdot kg^{-1}$ and TLV of Cd is 0.10 $mg \cdot kg^{-1}$ (except wheat, where it is 0.20 $mg \cdot kg^{-1}$). Copper and zinc concentration in foodstuff is presently not regulated by the European Community. However, for an assessment of potential contamination with these elements, unofficial limit values established by the State Institute of Plant Cultivation,

Table 1

Range and mean concentrations of trace elements (mg·kg^{-1} of f.m.) in crops as compared to TLV (threshold limit value)

Crops	Crop part	Year 2004				Year 2005				Year 2006			
		Cu	Zn	Pb	Cd	Cu	Zn	Pb	Cd	Cu	Zn	Pb	Cd
Wheat	grain	2.8-3.3* 3.0**	10.8-14.0 12.8	0.15-0.19 0.17	0.03-0.04 0.03	2.2-4.0 3.4	13.8-25.1 19.4	0.15-0.19 0.17	0.05-0.08 0.06	3.3-6.2 4.1	17.0-23.0 18.5	0.14-0.19 0.16	0.05-0.08 0.06
TLV		20[a)]	50[a)]	0.20[b)]	0.20[b)]	20[a)]	50[a)]	0.20[b)]	0.20[b)]	20[a)]	50[a)]	0.20[b)]	0.20[b)]
Triticale	grain	2.6-3.9 3.1	15.6-26.2 19.5	0.08-0.17 0.14	0.02-0.2 0.07	2.7-4.0 3.4	18.9-20.1 19.5	0.15-0.17 0.16	0.05-0.08 0.06	3.2-5.3 3.9	16.5-37.2 25.6	0.12-0.18 0.15	0.05-0.07 0.06
Barley	grain	2.6-4.9 3.4	6.4-24.6 19.4	0.14-0.34 0.19	0.02-0.04 0.03	3.0-4.3 3.6	19.2-31.0 25.1	0.12-0.14 0.13	0.05-0.06 0.055	2.9-5.8 3.9	15.1-27.0 21.5	0.11-0.14 0.12	0.04-0.06 0.06
Oats	grain	-	-	-	-	-	-	-	-	2.5-3.5 3.0	8.7-21.3 16.8	0.11-0.16 0.14	0.05-0.08 0.06
TLV		20[a)]	50[a)]	0.20[b)]	0.10[b)]	20[a)]	50[a)]	0.20[b)]	0.10[b)]	20[a)]	50[a)]	0.20[b)]	0.10[b)]
Potato	tuber	0.6-1.1 0.8	2.3-3.1 2.8	0.06-0.09 0.07	0.038-0.-04 0.039	0.4-1.6 1.1	1.3-4.2 3.0	0.01-0.09 0.05	0.006-0.-02 0.013	1.1-1.7 1.3	2.8-4.4 3.5	0.014-0.084 0.04	0.007-0.018 0.011
TLV		10[a)]	20[a)]	0.10[b)]	0.10[b)]	10[a)]	20[a)]	0.10[b)]	0.10[b)]	10[a)]	20[a)]	0.10[b)]	0.10[b)]

Explanation:
*range of concentration
**arithmetic mean
[a)] TLV of Institute of Soil Science and Plant Cultivation, Puławy, Poland
[b)] TLV according to Commission Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs

Fertilization and Soil Sciences (Puławy, Poland) were taken. The limit values of zinc in potatoes were approximated at the level of 20 $mg \cdot kg^{-1}$ of fresh mass and 50 $mg \cdot kg^{-1}$ in cereals, and the limit values of copper were 10 and 20 $mg \cdot kg^{-1}$ of fresh mass, respectively

RESULTS AND DISCUSSION

The average levels of trace metals in 2006 in the analyzed cereals and potatoes were approximated at the level of: Cu – respectively – 3.7 and 1.3 $mg \cdot kg^{-1}$ of fresh mass; Zn – 20.6 and 3.5 $mg \cdot kg^{-1}$; Pb – 0.14 and 0.04 $mg \cdot kg^{-1}$; Cd – 0.055 and 0.011 $mg \cdot kg^{-1}$. Significant differences in concentrations of trace elements in cereals and potatoes depend mainly on the dry mass content, but could be also associated with plant species and variations, phase of plant growth, concentration of trace element in soil and the local climate (Bednarek et al. 2008, Gembarzewski 2000, Kabata-Pendias, Pendias 1999, Strączyński, Strączyńska 2007). No statistically significant differences in copper, lead and cadmium concentrations between the tested cereals were found. In 2004 higher concentrations of Cu and Pb were determined in barley than in wheat grain, contrary to 2006, when wheat grain contained more Cu and Pb than barley. It seems that the crucial factor is the location of particular crops in the consecutive years. However, no significant relation between the distance to the impoundment and concentration of Cu and Pb in plants or in soils was found. Among the determined trace metals, only zinc concentration in wheat grain was significantly lower in all the years (in a range from 12.8 to 19.4 $mg \cdot kg^{-1}$) than in barley and triticale grain (range: 19.4-25.6 $mg \cdot kg^{-1}$). Oat grain, which was analyzed only in 2006, contained less zinc than all the other cereals – on average 16.8 $mg \cdot kg^{-1}$. Zinc concentration in plant material, similarly to Cu and Pb, is not statistically related to the distance to the impoundment or to the metal concentration in soils.

Although the copper level in soils in the immediate surroundings of the impoundment is elevated (Angełow et al. 2000, Kabała et al. 2008), concentrations of this metal in crops cultivated in this area did not diverge from mean values presented by Gembarzewski (2000). However, the Cu content in cereals from the nearest vicinity of the impoundment is at least 20% higher than Cu concentrations in crops cultivated on poor, sandy soils prevailing in the nearby counties. The copper level in potato tubers (in consecutive years from 0.8 to 1.3 $mg \cdot kg^{-1}$ of fresh mass) was higher then average values presented by Kabata-Pendias and Pendias (1999) – 0.7 $mg \cdot kg^{-1}$ of fresh mass, but similar to those determined in southeastern Poland, where Mikos-Bielak et al. (1996) reported 0.6-1.3 $mg \cdot kg^{-1}$ of fresh mass.

Although zinc concentrations in soils in the surroundings of the impoundment were no higher than in other areas (Angełow et al. 2000), the

content of this metal in the examined cereals, like that of Cu, was *ca* 15-20% higher than the average reported from this region (KUCHARZEWSKI et al. 2002). The determined Zn concentrations did not diverge from average Polish and European values presented by KABATA-PENDIAS and PENDIAS (1999) and are significantly lower than those presented by WŁAŚNIEWSKI (2002) from the Rzeszów region. Zinc amounts in potato tubers (in a range from 2.8 to 3.5 $mg \cdot kg^{-1}$ of fresh mass) were similar to those determined in two regions of southeastern Poland (BEDNAREK et al. 2006, MIKOS-BIELAK et al. 1996), and lower than the average in the Lower Silesia region (KUCHARZEWSKI et al. 2002).

Lead concentration in soils surrounding Żelazny Most impoundment is relatively low, despite rather high pH values and organic matter content (ANGEŁOW et al. 2000), which may explain low concentrations of the element in cereal grain (0.08-0.34 $mg \cdot kg^{-1}$ of fresh mass). These amounts of Pb are much lower than found in cereals cultivated on contaminated soils near a copper smelter (BOJARSKA, BZOWSKI 1998, STRĄCZYŃSKI, STRĄCZYŃSKA 2007) and significantly lower than the average content in cereals reported from this part of the Lower Silesia region. Lead concentrations in the analyzed potato tubers (0.01-0.09 $mg \cdot kg^{-1}$ of fresh mass) were similarly lower than the mean 0.41 $mg \cdot kg^{-1}$, measured in potatoes cultivated on polluted areas of the Lower Silesia region (STRĄCZYŃSKI, STRĄCZYŃSKA 2007) but somewhat higher than in the Lublin region of southeastern Poland (BEDNAREK et al. 2006).

Concentration of cadmium in the analyzed cereal grain was in the range from 0.02 to 0.20 $mg \cdot kg^{-1}$ (average 0.055 $mg \cdot kg^{-1}$). These values, after recalculation per dry mass, are similar to those presented by KABATA-PENDIAS and PENDIAS (1999) from the entire area of Poland, and by BEDNAREK et al. (2008) from the Lublin region, but significantly lower than reported from the Rzeszów region (WŁAŚNIEWSKI 2000). Similarly, the contamination of potato tubers with cadmium was very low, with the metal contents in the range from <0.01 to 0.04 $mg \cdot kg^{-1}$ of fresh mass, which was close to results presented by KUCHARZEWSKI et al. (2002) and WŁAŚNIEWSKI (2000).

Copper concentrations in the examined cereal grain and potato tubers did not exceed approximately 20% and 13% (respectively) of the appropriate threshold limit values (TLV), and zinc concentrations – 51% and 18% of TLV according to KABATA-PENDIAS et al. (1989). Moreover, cadmium concentrations did not exceed approximately 70% and 39% (respectively), and lead concentrations – 85% and 70% of TLV set in Commission Regulation (EC) no 1881/ /2006. Trace metal concentrations in all the tested plant samples were lower than threshold limit values. It means that there are no restrictions for consumption or pasture use of cereals and potatoes planted in the surrounding of tailings impoundment Żelazny Most.

Several technologies of waste stabilization on drying surfaces had been tested during the nearly 25 years of exploitation of the impoundment to avoid dusting. The presently used technology of tailings stabilization with asphalt

emulsion reduces dust emission by 95% as compared to the emission reported in the initial phase of the impoundment exploitation (Dobrzański, Byrdziak 1995). Also the regular soil quality monitoring in the vicinity of the impoundment confirms decreasing emission of metal-bearing dust (Kabała et al. 2008, Medyńska et al. 2007). The results of our investigation on quality of crops confirm good efficiency of all the actions undertaken in order to reduce the negative impact of the copper ore tailings impoundment on the environment and conditions of agricultural production.

CONCLUSIONS

1. Copper, zinc, lead, and cadmium concentrations in all the tested samples of cereal grain and potato tubers cropped in the surroundings of tailings Żelazny Most impoundment were similar to concentrations reported from other regions of Poland and did not exceed the threshold limit values for edible plants.

2. No significant differences in copper, lead, and cadmium concentrations in grain were found among the four tested cereal species. Zinc concentration in wheat and oat grain was significantly lower than in triticale and barley grain.

3. No significant statistical relation was found between trace metal concentrations in cereal grain or potato tubers and metal contamination in soils or the distance to the tailings impoundment.

REFERENCES

Angełow Z., Chodak T., Kabała C., Kaszubkiewicz J., Szerszeń L. 2000. *Oddziaływanie zbiornika odpadów poflotacyjnych Żelazny Most na otaczające środowisko glebowe [Effect of Żelazny Metal tailnings impoundment on the surrounding soil environment].* Rocz. AR Pozn., Rol., 56: 327-339. (in Polish)

Bednarek W., Tkaczyk P., Dresler S. 2006. *Zawartość metali ciężkich jako kryterium oceny jakości bulw ziemniaka [Content of heavy metals as a criterion for quality evaluation of potato tubers].* Ann. UMCS, Sect. E, 61: 121-131. (in Polish)

Bednarek W., Tkaczyk P., Dresler S. 2008. *Zawartość metali ciężkich jako kryterium oceny jakości ziarna pszenicy ozimej [Content of heavy metals as a criterion for quality evaluation of winter wheat].* Acta Agroph., 12: 315-326. (in Polish)

Bojarska K., Bzowski Z. 1998. *Występowanie ołowiu w ziarnie pszenicy i glebach ornych przylegających do strefy sanitarnej huty miedzi Głogów [Presence of lead in wheat grain and in arable soils adhacent to the sanitary zone of Głogów copper works].* Zesz. Nauk. Kom. „Człowiek i Środowisko" PAN, 21: 247-254. (in Polish)

Czaban S., Fiałkiewicz W., Kabała C. 2007. *Potential impact of tailings pond on crop and forest production*. In: *Environmental modelling and simulation.* J. Wilson (ed.), Acta Press, Honolulu, 41-47.

Dobrzański J., Byrdziak H. 1995. *Wpływ polskiego przemysłu miedziowego na środowisko naturalne [Influence of the Polish copper industry on natural environment].* Zesz. Probl. Post. Nauk Rol., 418: 391-398. (in Polish)

GEMBARZEWSKI H. 2000. *Stan i tendencja zmian zawartości mikroelementów w glebach i roślinach z pól produkcyjnych w Polsce [Status and tendecies in modification of the content of micronutrients in soils and crops from production fields in Poland].* Zesz. Probl. Post. Nauk Rol., 471: 171-179. (in Polish)

KABAŁA C., MEDYŃSKA A., CHODAK T., JEZIERSKI P., GAŁKA B. 2008. *Zmiany zawartości miedzi i arsenu w glebach wokół składowiska odpadów po flotacji rud miedzi w 12-letnim cyklu badań monitoringowych [Fluctuations in the content of copper and aresnic in soils around a copper tailinigs impoundment during a 12-year monitoring research cycle].* Rocz. Glebozn., 59: 81-88. (in Polish)

KABATA-PENDIAS A., GAŁCZYŃSKA B., DUDKA S. 1989. *Baseline zinc content of soil and plants in Poland*. Environ. Geochem. Health, 11: 19-24.

KABATA-PENDIAS A., PENDIAS H. 1999. *Trace elements in soils and plants*. CRC Press, Inc., Boca Raton, Florida.

KARCZEWSKA A. 2002. *Metale ciężkie w glebach zanieczyszczonych emisjami hut miedzi – formy i rozpuszczalność [Heavy metals in soils polluted by emissions from copper works – forms and solubility].* Zesz. Nauk. AR Wroc., 432: 159 ss. (in Polish)

KUCHARZEWSKI A., NOWAK L., DMOWSKI Z., MARKOWSKA J. 2002. *Zawartość metali ciężkich i siarki w ziemniakach na Dolnym Śląsku [Content of heavy metals and sulphur in potatoes in Lower Silesia].* Zesz. Probl. Post. Nauk Rol., 489: 491-497. (in Polish)

MEDYŃSKA A., KABAŁA C. CHODAK T. 2007. *Zmiany zawartości miedzi, cynku i kadmu w glebach użytkowanych rolniczo i glebach leśnych wokół składowiska odpadów po flotacji rud miedzi [Changes in the content of copper, zinc and cadmum in agriculturally used soils and forest soils around a copper tailings impoundment].* Zesz. Nauk. Uniw. Zielonogórskiego, 133: 301-309. (in Polish)

MIKOS-BIELAK M., BUBICZ M., WARDA Z. 1996. *Zawartość Cu, Mn, Zn i Fe w bulwach ziemniaków pochodzących z regionu środkowo-wschodniej Polski [Content of Cu, Mn, Zn and Fe in potato tubers from the central-eastern part of Poland].* Zesz. Probl. Post. Nauk Rol., 434(1): 323-328. (in Polish)

PIOTROWSKA M. 1998. *Wpływ źródła zanieczyszczenia gleby ołowiem na jego zawartość w roślinach uprawnych [Effect of a source of soil contamination with lead on lead content in crops].* Zesz. Nauk. Kom. „Człowiek i Środowisko" PAN, 21: 63-67. (in Polish)

STRĄCZYŃSKI S., STRĄCZYŃSKA S. 2007. *Zawartość ołowiu w wybranych gatunkach roślin uprawianych w rejonie oddziaływania hutnictwa miedzi [Content of lead in some plant species cropped in an area affected by the copper industry].* Zesz. Probl. Post. Nauk Rol., 520 (1): 257-265. (in Polish)

TURNER A.P. 1994: *The response of plants to heavy metals.* In: *Toxic metals in soil-plant system.* ROSS S.M. (ed.), John Wiley & Sons Ltd., London, 153-182 pp.

WŁAŚNIEWSKI S. 2000. *Wpływ czynników środowiskowych na fitoprzyswajalność metali ciężkich w warunkach gleb lessowych regionu podkarpackiego [Effect of environmental factors on phytoavailability of heavy metals in lessive soils in Podkarpacie].* Zesz. Probl. Post. Nauk Rol., 471 (2): 1197-1206. (in Polish)