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ORIGINAL PAPER

COPPER AND ZINC CONCENTRATIONS IN PLANT AND ANIMAL RAW MATERIALS COLLECTED IN THE VICINITY OF THE ŻELAZNY MOST WASTE TREATMENT TAILINGS POND*

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Abstract

The study was carried out on the Cu and Zn content of plant material (wheat grain, hay and potato tubers) and animal food products (cow's milk, hen's eggs and chicken meat) collected in the vicinity of the Żelazny Most waste treatment tailings pond (Lower Silesia, Poland). The samples for the study accomplished in 2016-2018 were collected from the places located in the nearest vicinity of the tailings pond (6 farms within a distance shorter than 4 km – zone I) and those located further away (6 farms within a distance from 4 to 10 km from the tailings pond – zone II). Copper and Zn concentrations were measured on a Varian Spectra AA220 Fast Sequential atomic absorption spectrophotmeter. The mean values of Cu noted in wheat grain harvested in the years under investigation ranged from 3.87 to 5.27 mg kg^{-1} DM, while the maximum value was 6.97 mg kg^{-1} DM. The highest accumulation of Cu and Zn was in hay (max. 10.10 and 99.04 mg kg^{-1} DM, respectively), while the lowest values were noted in milk and eggs. The zinc content of cow's milk was found within the range from 2.64 to 4.01 mg kg^{-1} FM and the highest amount was 6.32 mg kg^{-1} FM. It was also found the mean Cu concentrations in poultry meat varied from 0.53 to 1.55 mg kg^{-1} FM and the maximum value was 3.50 mg kg^{-1} FM. No significant differences between zones I and II were observed ($p \le 0.05$). The current results are

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comparable with those obtained in 2007 and 2013. With only a few exceptions, the biomonitoring studies did not show that the levels of the two metals in the biological material tested exceeded data reported in the Polish and international literature. Nowadays, there is no reason to consider the Żelazny Most tailings pond to be an toxicological threat to the natural and agricultural environment regarding Cu and Zn, but its periodic biomonitoring is necessary due to the chemical properties of these two elements and their potential effect on some environmental factors.

Keywords: copper, zinc, biological raw materials, Żelazny Most tailings pond.

INTRODUCTION

The effects of mining industries on the environment have been studied extensively, but there is scarcity of data in the Polish literature on effects of the copper mining industry on the environment in the vicinity of mining sites, smelters or flotation waste tailings ponds containing high amounts of copper and zinc (PIESTRZYŃSKI 2007, KOTARSKA 2012). Copper is widely used by many industries. Next to silver, it is the best heat and electric conductor, commonly used as material for electric and electronic systems as well as construction materials, such as roof covers and installation systems, and also as glass dye or a catalyst. In addition, copper is a component of many alloys, including alloy steel, and it is added to silver and gold so as to improve their mechanical properties. Copper is also an indispensable microelement in plant, animal and human nutrition, although it can be toxic if used in abundance because it easily binds to proteins, especially low-molecular ones containing sulfur. The excess of this metal can result in growth retardation, bone diseases, anaemia or teratogenesis. In humans, excessive concentrations of Cu may result in Wilson's disease or idiopathic copper toxicosis (ICT). On the other hand, copper deficiency is likely to occur in regions exposed to S, Mo and Cd emissions, causing adverse effects on the metabolic processes in humans and animals, resulting in ischaemia, immunological and endocrine disorders (SZYCZEWSKI et al. 2009, HARADA et al. 2020). Like copper, zinc is commonly used by a number of industries and it is indispensable for the proper functioning of a human body. For instance, it is responsible for protein synthesis, cell growth and differentiation, proper functioning of such hormones as corticosteroids and insulin, growth and sex hormones. Moreover, an adequate zinc content is necessary for normal growth and skeletal condition, for maintaining an antioxidative barrier and inhibiting lipid peroxidation, protecting the body against X- and gamma rays, for reproductive functions and for many enzyme reactions. In addition, an adequate Zn content in the body has a positive impact on the central nervous system, properly regulated apoptosis and vitamin metabolism. However, too much Zn in the environment, especially in animal foodstuffs, can result in toxic effects. Zinc present in an animal body interacts in metabolic processes with other metals, such as Cu, Fe and Ca, affecting blood circulation and also resulting in mental disorders. It is quite likely that metabolic disturbances involving the metals indispensable for a human body induced by zinc can be a major cause of toxic effects in humans and animals. On the other hand, zinc deficiency caused by malnutrition or eating food with low Zn bioavailability, also due to ageing, certain diseases or deregulated homeostasis, is a far more common risk to human health than toxic effects of this element (Plum et al. 2010, Piontek et al. 2014). The purpose of the present study was to analyze copper and zinc accumulation in some food products of plant and animal origin originating from areas located in close vicinity of the Żelazny Most copper mining tailings pond.

MATERIAL AND METHODS

Description of the tailings pond

Żelazny Most is a post-flotation waste treatment tailings pond used by the Copper Ore Enrichment Company (ZWR) in the region of Polkowice, Lubin and Rudna (Low Silesia, Poland). Apart from the mining sites, two copper works (Głogów and Orsk) operate nearby. The Żelazny Most facility is one of the largest sites of this type in the world. The flotation process causes the formation of ground red rock, which accounts for 94% of the ore mined. The tailings pond has been steadily enlarged (Figure 1) and currently its total capacity is approximately 1 bln m^3. It is expected that amounts of the deposited effluents in the coming years will increase from 520 to more than 600 Tg. The presence of highly toxic elements in waste is considered very dangerous to both the natural environment and humans.

Baran et al. (2013*)* reported that Cu, Pb, Zn and Cd levels in the sediment samples collected from the Żelazny Most tailings pond amounted to 2610, 1132, 256 and 1.0 mg kg^{-1} DM, respectively. The Cu content of copper ore deposits ranged from 0.57 to 10.48%, while the zinc content was below 0.1%. Maximum Cu and Zn levels in the post-flotation effluents accounted for 0.21% and 90 mg kg^{-1} DM, respectively. Accumulation of these elements in the so-called gravitational concentrates reached 2.57-4.58% and 409-1672 mg kg^{-1} DM, depending on a site, Lubin, Rudna, Polkowice (Monography 2017). Although the effluents deposited in the Żelazny Most tailings pond are not a direct threat to the environment, the risk is likely to occur as a result of eolic processes, during which some metals, including Cu and Zn, can be emitted to the surrounding rural areas.

Area and research material

The measurements and analysis of Cu and Zn content included samples collected from 10 locations (12 farmsteads) around the tailings pond in the municipalities of Rudna, Polkowice and Grębocice (Figure 1). The farmsteads

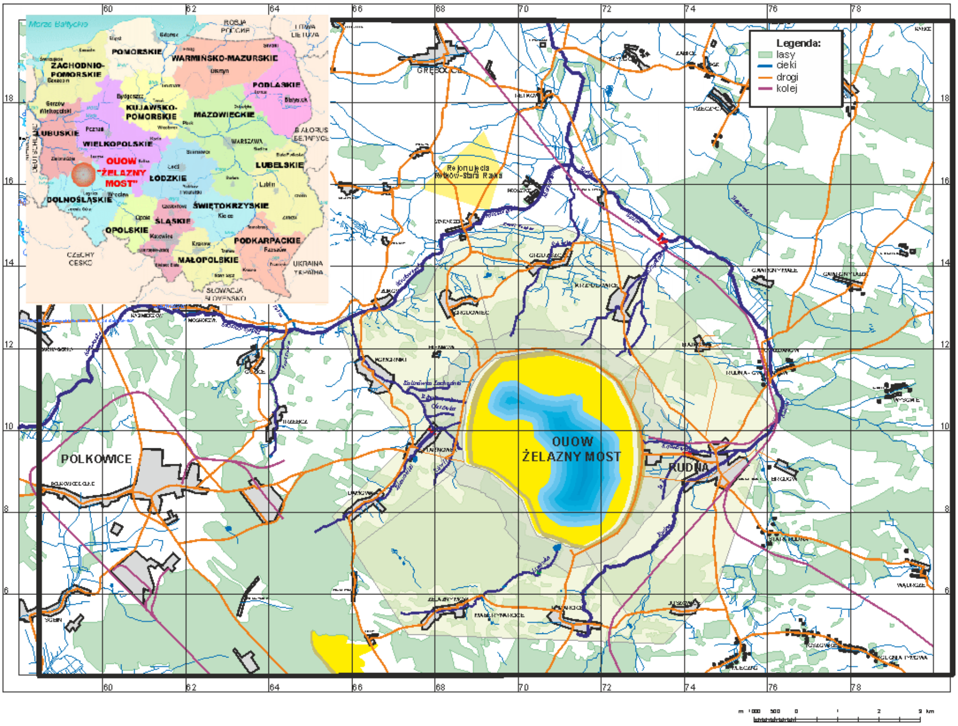

Fig. 1. Location of the Żelazny Most waste treatment tailings pond (Low Silesia)

located within a distance of less than 4 km from the crown of the tailings pond were allocated to zone I (Dąbrowa, Pieszkowice, Rudna, Rynarcice and Żelazny Most), while those located further away (4 -10 km) were allocated to zone II (Grodziszcze, Mleczno, Orsk, Proszyce and Studzionki). Copper and zinc content was studied in dry grasses (hay), wheat grains and potato tubers (unpeeled, cleaned) and also in cow's milk, hen's eggs and chicken meat (pectoral muscle without skin). The cows from the analyzed farms graze on natural meadows in spring/summer period and are given hay harvested on farm as fodder in winter. The laying hens were kept in free range systems. The samples for the studies were collected in October 2016, 2017 and 2018.

Analytical techniques

The samples were collected on the farms selected for the study, after which they were prepared for analyses. Wheat grains and grasses were dried, while potato tubers, cow's milk and chicken muscles were bio-lyophilized. Hen's eggs were boiled and the eggshells were removed. The material was then mineralized in a Multiware microwave, using concentrated nitric acid (15,2 mol L^{-1}). Copper and Zn levels in the solutions were measured on a Varian Spectra AA220 Fast Sequential atomic absorption spectrophotmeter (Australia). Ceritified reference materials (CRMs) were used for qualitative verification of Cu and Zn determinations in the plant material: Tea leaves (certificate no. INTC-TL-1, Institute of Nuclear Chemistry and Technology in Warsaw, Poland) and Hay powder (certificate no. BCR-129, EC – Institute for Reference Materials and Measurements (IRMM) in Geel, Belgium). Bovine liver (certificate no. BCR-185R, EC – IRMM in Geel, Belgium) was used for the samples containing the material of animal origin (milk, egg, meat).

Statistical analysis

The results were presented as minimum, maximum and mean values with a standard deviation obtained for a period of three years (2016-2018). Before analyses, all data were screened for normality using the Shapiro-Wilk test assuming normal distribution. Results are given in the dry matter – DM (grain, hay) and fresh matter – FM (potato, milk, egg, meat). The Duncan's test was used for statistical analysis of the differences observed between zones I and II. The data are presented as average values, accompanied by standard deviation and minimum and maximum values. Significant differences were declared at $p \leq 0.05$.

RESULTS AND DISCUSSION

Tables 1, 2 and 3 show Cu and Zn content in the plant materials. Slight differences in Cu accumulation were observed in fodder and agricultural products destined for animal consumption (grass, wheat and potatoes). The mean values of Cu noted in wheat grain harvested in the years under investigation ranged from 3.87 to 5.27 mg kg^{-1} DM, while the maximum value was 6.97 mg kg^{-1} DM. In comparison, the Cu content of hay (dry grasses) was higher and averaged from 4.71 to 7.40 mg kg^{-1} DM, while the maximum value reached 10.1 mg kg^{-1} DM. The copper content of potato tubers was markedly lower and averaged from 1.26 to 1.59 mg kg^{-1} FM, while the maximum value amounted to 2.57 mg kg^{-1} FM, which was 4-fold lower than the levels found in hay. No significant differences in the mean Cu content were found between zones I and II in samples collected in the three consecutive years (Table 4). This may suggest that dust from the beach around the tailings pond did not affect Cu accumulation in the analysed raw materials, which had also been confirmed by the results of similar studies carried out in 2007 and 2013 on Cu levels in wheat grain and potatoes. However, the results of the research conducted in 2016-2018 showed significantly lower Cu levels in hay (Kołacz et al. 2014).

The permissible limit for the Cu content of plant material for animal

Table 1

Copper and zinc concentration in wheat grain (mg kg^{-1} DM)

Statistics	2016		2017		2018	
	Cu	Zn	Cu	Zn	Cu	Zn
Zone I						
$\bar{x}$	4.60	32.90	5.27	34.81	4.84	36.13
Min.	3.83	20.75	3.83	28.60	3.07	30.89
Max.	5.91	48.18	5.91	41.63	6.36	45.12
SD	0.74	9.55	0.89	4.38	1.21	5.50
Zone II						
$\bar{x}$	3.87	31.91	4.39	29.25	5.10	33.69
Min.	2.84	21.23	3.75	23.66	4.15	23.12
Max.	4.81	50.05	5.85	35.32	6.97	40.33
SD	0.77	11.35	0.81	4.74	1.06	6.38

Table 2

Copper and zinc concentration in hay (mg kg^{-1} DM)

Statistics	2016		2017		2018	
	Cu	Zn	Cu	Zn	Cu	Zn
Zone I						
$\bar{x}$	6.76	23.48	5.61	32.23	5.73	30.04
Min.	3.55	18.52	4.05	24.11	4.28	20.21
Max.	10.10	26.71	8.30	46.30	6.36	55.60
SD	2.39	3.54	1.67	8.02	0.81	12.92
Zone II						
$\bar{x}$	5.31	17.17	4.71	33.03	7.40	29.22
Min.	3.86	9.84	2.91	14.12	4.60	18.10
Max.	8.69	26.20	8.46	94.04	10.08	39.49
SD	1.77	6.69	2.20	30.45	1.81	7.84

fodder is 25 mg kg^{-1} (Assessment... 1993*)*. Since 2006, the threshold content of this element in food products has not been regulated in the EU law (Commission Regulation 2006). The data literature show big differences in the Cu content of plant raw materials, food products and animal foodstuffs (Jastrzębska et al. 2010, Bost et. al. 2016). Also, Kabata-Pendias and Szteke (2012) reported that the mean Cu content of wheat was 2.21 and its level in potatoes was 0.79 mg kg^{-1} FM. According to Elmadfa and Muskat (2003), these values correspond to 4.59 and 0.9 mg of Cu kg^{-1} FM, respectively. Significant differences in the Cu content of potatoes were reported by others (Dobrzański et al. 2016). The values for hay and grasses (Nicholson et al. 1999,

Table 3

Copper and zinc concentration in potato tubers (mg kg^{-1} FM)

Statistics	2016		2017		2018	
	Cu	Zn	Cu	Zn	Cu	Zn
Zone I						
$\bar{x}$	1.25	2.91	1.39	3.64	1.59	2.02
Min.	0.97	2.60	0.82	2.73	1.12	1.53
Max.	1.62	3.63	2.57	5.23	2.03	2.89
SD	0.22	0.40	0.62	0.92	0.43	0.47
Zone II						
$\bar{x}$	1.31	3.23	1.26	3.69	1.28	2.37
Min.	0.85	1.93	0.71	2.48	0.91	1.77
Max.	1.72	3.26	1.63	4.90	1.77	2.93
SD	0.34	1.21	0.38	0.96	0.31	0.50

Kucharczyk, Moryl 2010) were found within the range of 4.2 to 8.0 mg kg^{-1} DM. On the other hand, excessive microelement content in a diet of ruminants can have toxic effects. High levels of this element in feed also negatively affect the absorption of other nutrients, which can lead to oxidative stress, lipid peroxidation and increased secretion of many enzymes considered to be antioxidants (Kupczyński et al. 2017).

The zinc content of wheat grain averaged from 29.25 to 36.13 mg kg^{-1} DM and the highest values were found in 2016 (max. 50.05 mg kg^{-1} DM). The content in hay ranged from 17.17 to 33.03 mg kg^{-1} DM and the highest value of 94.04 mg kg^{-1} DM was found in 2017. The zinc content of potato tubers averaged from 2.02 to 3.69 mg kg^{-1} FM and the highest concentration was 5.23 mg kg^{-1} FM. No significant differences were found between zones I and II (Table 4). The analysis of the results obtained in 2007 and 2013 showed similarities in the Zn content of grain, hay and potatoes (Kołacz et al. 2014), which may indicate stabilized levels of this elements in plant raw materials.

The permissible Cu content of fodder is 100 mg kg^{-1} (Assessment... 1993). The standard for this element in food products has not been regulated since 2006 (Commission Regulation 2006). The literature data show different

Table 4

Cumulative data of Cu and Zn levels in plant materials (n=18)

Zone	Wheat grain (mg kg^{-1} DM)		Hay (mg kg^{-1} DM)		Potato tubers (mg kg^{-1} FM)	
	Cu	Zn	Cu	Zn	Cu	Zn
I	4.68^{a}±0.87	34.60^{a}±6.56	6.03^{a}±1.72	28.59^{a}±9.59	1.41^{a}±0.45	2.86^{a}±0.91
II	4.45^{a}±0.98	31.63^{a}±7.75	5.80^{a}±2.17	26.47^{a}±18.77	1.28^{a}±0.33	3.10^{a}±1.04

^{ab} – means in the column with different superscripts differed significantly at $p \le 0.05$

levels of Zn in raw materials, fodder and plants destined for food production. Kabata-Pendias and Szteke (2012) reported the mean values of 9.4 (wheat) and 2.8 mg kg^{-1} FM (potato), while Elmadfa and Muskat (2003) reported that 26.9 and 3.47 mg kg^{-1} FM were natural Zn content in these raw materials. The values reported by many authors for hay were found within the ranges from 17 to 41 mg kg^{-1} (Nicholson et al. 1999, Kucharczyk, Moryl 2010). The copper and Zn concentrations in raw materials and plant products are likely to be affected by their accumulation in soil, agrotechnical treatments and metallurgic industry (Chojnacka et al. 2005, Khan et al. 2008, Medyńska et al. 2009).

Tables 5, 6 and 7 show the Cu and Zn content of animal food products. Copper levels in cow's milk averaged from 0.044 to 0.098 mg kg^{-1} FM and the

Table 5

Copper and zinc concentrations in cow's milk (mg kg^{-1} FM)

Statistics	2016		2017		2018	
	Cu	Zn	Cu	Zn	Cu	Zn
Zone I						
$\bar{x}$	0.044	3.99	0.092	3.39	0.098	2.66
Min.	0.032	2.77	0.063	2.14	0.069	1.63
Max.	0.057	6.32	0.156	4.43	0.111	2.80
SD	0.046	1.51	0.019	0.55	0.022	1.04
Zone II						
$\bar{x}$	0.059	4.01	0.094	3.41	0.096	2.64
Min.	0.034	2.40	0.057	2.91	0.073	1.33
Max.	0.153	6.24	0.112	4.45	0.132	4.34
SD	0.049	1.52	0.017	0.57	0.019	1.02

Table 6

Copper and zinc concentrations in hen's eggs (mg kg^{-1} FM)

Statistics	2016		2017		2018	
	Cu	Zn	Cu	Zn	Cu	Zn
Zone I						
$\bar{x}$	1.09	12.30	0.41	11.60	0.97	12.10
Min.	0.84	10.28	0.28	9.53	0.79	9.82
Max.	2.11	16.22	0.49	13.40	1.23	13.81
SD	0.50	2.03	0.10	1.31	0.16	1.40
Zone II						
$\bar{x}$	0.74	12.93	0.43	11.98	0.95	12.45
Min.	0.66	8.79	0.28	10.47	0.88	10.80
Max.	0.85	23.6	0.56	13.60	1.06	14.02
SD	0.08	5.67	0.09	1.16	0.07	1.08

Table 7

Copper and zinc concentrations in chicken meat (mg kg^{-1} FM)

Statistics	2016		2017		2018	
	Cu	Zn	Cu	Zn	Cu	Zn
Zone I						
$\bar{x}$	1.55	5.38	0.75	7.44	0.53	7.49
Min.	0.58	3.79	0.24	5.30	0.35	5.65
Max.	3.50	6.20	1.63	10.49	0.64	9.07
SD	1.16	0.97	0.51	1.85	0.11	1.45
Zone II						
$\bar{x}$	1.19	7.58	0.67	7.34	0.70	7.51
Min.	0.56	2.40	0.30	4.92	0.54	5.55
Max.	2.52	18.40	1.35	9.32	0.81	10.24
SD	0.76	6.06	0.41	1.80	0.09	1.65

highest amount (0.156 mg kg^{-1} FM) was found in 2017. The copper content of whole egg (white and yolk) averaged from 0.41 to 1.09 mg kg^{-1} FM, with the maximum of 2.11 mg kg^{-1} FM in 2016. The content of this metal in chicken meat was found within the ranges from 0.53 to 1.55 mg kg^{-1} FM, with the highest value of 3.50 mg kg^{-1} FM. Allowed copper concentrations in eggs, milk and chicken meat are not regulated in the EU law (Commission Regulation 2006). The literature data show big differences in the Cu content determined in milk, eggs or chicken meat. Kabata-Pendias and Szteke (2012) reported an average Cu content of 0.02, 0.56 and 1.44 mg kg^{-1} FM, respectively. Other authors (Elmadfa, Muskat 2003) reported 0.1 in milk, 0.5-2.3 in eggs and 3.0 in chicken meat (mg kg^{-1} FM).

Table 8 shows no significant differences between zones I and II. Comparison with the results obtained in similar studies conducted in 2007 and 2013 demonstrates similar Cu levels found in milk and eggs (Kołacz et al. 2014), which may implicate stable concentrations of this element in animal raw materials and food products, although they were three-fold lower in 2013 than the mean values observed in 2016-2018. These effects may be attributed to specific chicken rearing conditions and feeding systems (Hashish et al. 2012, Vincevica-Gaile et al. 2013, Fu et al. 2014).

On average, the Zn content of cow's milk was found within the range of 2.64 to 4.01 mg kg^{-1} FM, and the highest concentration was 6.32 mg kg^{-1} FM. The mean values of Zn noted in whole eggs ranged from 11.60 to 12.93 mg kg^{-1} FM, with the maximum value of 23.60 mg kg^{-1} FM. The average Zn concentration in poultry meat varied from 5.38 to 7.58 mg kg^{-1} FM and the maximum value was 18.40 mg kg^{-1} FM. No significant differences between zones I and II were observed (Table 8).

The zinc concentrations in eggs, milk and meat are not specified in the

Table 8

Cumulative data of Cu and Zn levels in the material of animal origin (mg kg^{-1} FM, n=18)

Zone	Cow's milk		Hen's eggs		Chicken meat	
	Cu	Zn	Cu	Zn	Cu	Zn
I	0.080^{a}±0.030	3.25^{a}±1.17	0.83^{a}±0.42	11.98^{a}±1.54	0.94^{a}±0.83	6.78^{a}±1.71
II	0.082^{a}±0.034	3.36^{a}±1.18	0.71^{a}±0.24	12.45^{a}±3.22	0.85^{a}±0.53	7.47^{a}±3.54

^{ab} – means in the column with different superscripts differed significantly at $p \leq 0.05$

EU standards for food products (Commission Regulation 2006). The literature data show some differences in the Zn content of animal products (Dobrzański et al. 2005, Szkoda et al. 2011), but it is well-known that such discrepancies are caused by the presence of this element in the environment and animal foodstuff and by food processing technologies (Kabata-Pendias, Szteke 2012, Bubel et al. 2013).

Similar Zn levels in milk and eggs were observed in 2007 and 2013 (Kołacz et al. 2014*)*, which may suggest that the content of this metal has remained at a stable level in the raw materials and animal food products from farms located in the close vicinity of the Żelazny Most tailings pond.

CONCLUSIONS

The results of the present study show moderate accumulation of Cu and Zn in plants and animal raw materials in the vicinity of the Żelazny Most waste treatment tailings pond, despite high levels of elements, especially Cu and Zn, in the mining deposits. Influence of environmental factors may cause food contamination with potentially toxic elements, and this is an issue of high importance regarding consumer safety. The Żelazny Most post-flotation waste pond is not a toxicological threat to agriculture, livestock and natural environment in terms of Cu and Zn emissions, but its periodic biomonitoring is necessary in order to exclude any toxic effects of the two metals on food and the environment in the future.

Conflict of interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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