Pol. J. Environ. Stud. Vol. 22, No. 3 (2013), 909-914

*Original Research*

# Evaluation of Toxic Metal Bioaccumulation in a Reservoir of Flotation Tailings

**Małgorzata Śliwka[1]*, Agnieszka Baran[2]**, Jerzy Wieczorek[2]*****

[1]Department of Environmental Engineering and Mineral Processing,
Faculty of Mining and Geoengineering, AGH University of Science and Technology, Poland
[2]Department of Agricultural and Environmental Chemistry, Faculty of Agriculture and Economics,
University of Agriculture in Kraków, Al. Mickiewicza 21, 31-120 Kraków, Poland

*Received: 22 August 2012*
*Accepted: 11 February 2013*

### Abstract

Flotation tailings, formed mainly in copper mining, are the largest percentage of waste generated during the extraction of mineral resources. Polish copper mining deposits 100% of tailings in landfills. Flotation tailings, although there are many concepts of management, is unused. This waste contains a considerable amount of toxic metals that can pollute the natural environment near the reservoir of flotation tailings and accumulate in plant tissues.

The aim of our research was to evaluate the heavy metals concentrations in soils and their bioaccumulation in plant and mushroom tissues from a landfill.

**Keywords:** flotation tailings, copper mining, heavy metals, toxic metals, bioaccumulation

## Introduction

The research area was a reservoir of flotation tailings named Gilów and belonging to KGHM Polish Copper located in the municipalities Polkowice and Lubin. The landfill of flotation tailings is an artificially created reservoir. The area of the reservoir is 600 ha. Gilów is one of the largest unused waste landfills in Legnicko-Głogowski Okręg Miedziowy. Gilów was developed to deposit tailings from copper the processing plants ZG Lubin, ZG Rudna, and ZG Polkowice. The amount of waste deposited in the reservoir is estimated at 91.85 million Mg.

Gilów is subject to reclamation in the direction of the water and forestry sectors. Currently, unused landfill is covered with forest and autogenic plants. A major environmental problem is unused flotation tailings on grounds of high concentration of heavy metals. The unfavorable impact of flotation tailings on the natural environment is primarily pollution of groundwater and surface water, dust caused by wind erosion, and infiltration of supernatant water. Additionally, used waste disposal requires large areas of land. Dust emissions containing heavy metals have polluted soils and negatively affected the growth of vegetation [1-12]. Knowledge of physical, chemical, and ecotoxicological properties of flotation tailings is important for their management [13].

Our aim was to evaluate the heavy metals concentration in soils and their bioaccumulation in plant and mushroom tissues from the Gilów landfill.

*e-mail: sliwka@agh.edu.pl
**e-mail: Agnieszka.Baran@ur.krakow.pl
***e-mail: rrwieczo@cyf-kr.edu.pl

## Materials and Method

### Sampling of Soil and Plant Material

Our research area was the flotation tailings reservoir Gilów. The soil core sample was used for soil sampling.

Table 1. Selected properties of soil samples.

| Statistical parameters | pH | | Sainity | $CaCO_3$ | Organic matter |
|---|---|---|---|---|---|
| | $H_2O$ | KCl | $mS\cdot cm^{-1}$ | % | |
| Average | 8.14 | 7.96 | 0.26 | 4.42 | 1.59 |
| SD | 0.23 | 0.22 | 0.29 | 1.34 | 0.09 |
| Median | 8.12 | 7.98 | 0.14 | 5.00 | 1.50 |
| Minimum | 7.51 | 6.70 | 0.06 | 1.00 | - |
| Maximum | 8.63 | 8.23 | 1.26 | 5.00 | 3.30 |
| V% | 3 | 3 | 108 | 31 | 6 |

Soil samples for analyses were collected from 0-20 depth in points measured from the center of the Gilów area by from 0 to 1 km to the north, east, south, and west. The sample collection points were localized using a Garmin GPSap62s satellite receiver. Three samples were taken at each measuring point. Samples of vegetation (mushrooms, pine tree needles, monocotyledonous plants) and dicotyledonous plants were taken in measuring points. The total collected 61 soil samples and 44 plants samples.

### Chemical Analysis of Soil and Plant Material

Basic physicochemical properties were assessed in the collected soil material: pH (by potentiometer in water and 1 $mol\cdot dm^{-3}$ KCl suspension), salinity (by conductivity), organic matter content (loss on ignition), and content of calcium carbonate (by Scheibler method) for each soil sample. Additionally, total content of heavy metals and their soluble forms were measured. In order to determine total heavy metals content, the soil material (2 g air-dried) was dissolved in the mixtures of $HNO_3$ and $HClO_3$ acids (3:2 v/v). Extraction of the soluble metal forms from the soil was conducted using static method through a single shaking of sediment samples with the solution at the sediment to solution ratio 1:10 and extraction time 1 h (1 mol $HCl\cdot dm^{-3}$). The contents of heavy metals in the plant material (2.5 g d.m) were assessed after dry digestion and dissolving the ashes in 10 $cm^3$ $HNO_3$ (1:3 v/v). The contents of Cu, Pb, Zn, Cd, and Ni in the obtained filtrates was assessed using inductively coupled plasma-atomic emission spectrometry (ICP-AES) on JY 238 ULTRACE apparatus (Jobin Von Emission).

Each sample of the soil material was analyzed in two replications. If the analysis results of those replications differed from one another by more than ±5%, another two analyses of that sample were conducted. Reference samples CRM023-050 – trace metals – sandy loam 7 (RT Corporation) (soil material) and BCR 129 (plant material) with known parameters was added to each series. A microsoft Excel 2007 spreadsheet and Statistica 10 package were used for analysis and presentation of the obtained results.

## Resultes and Discussion

The basic physicochemical parameters of soil samples were compared in Table 1. Tested samples were characterized by alkaline reaction: pH was from 7.51 to 8.63 in $H_2O$ and from 6.70 to 8.23 in KCl. Alkalinity of samples was determined by significant content of carbonate minerals in flotation tailings deposed (Table 1). Sediment samples showed a relatively low salinity. Electrolytic conductivity was in the range 0.06 to 1.26 $mS\cdot cm^{-1}$. This value is relatively low for a postindustrial area. Salinity in the waste tailings derived mainly from the processes of ore processing. Tested samples showed a low organic matter content. The average content of organic matter in flotation tailings was 1.59%.

The total content of heavy metals and their soluble forms in tested soil samples in 1 mol HCl are compared in Table 2. The total content of heavy metals was much more diversified in soil samples from Gilów. The greatest content variation was found for nickel and the lowest for lead: Ni > Cd > Cu = Zn > Pb (Table 2). The highest average content was observed for copper and the lowest for cadmium: Cu > Pb > Zn > Ni > Cd. The content of soluble form of metals in 1 mol HCl was formed by a series: Pb > Zn > Cu > Ni > Cd (Table 2). Distribution of heavy metals in soil at the landfill was shown in Table 3.

The total content of copper in tested samples ranged between 20.45 and 2,175.48 mg $Cu\cdot kg^{-1}$ d.m., on average 864.01 $mg\cdot kg^{-1}$ (Table 2). Such a copper content greatly exceeds the limits and classified the soil for the highest degree of contamination: V (by Kabata-Pendias et al. 1993) [14]. The content of copper showed very low solubility in 1 mol HCl, which represents 2% of the total content (Fig. 1).

The total content of lead ranged between 10.12 and 432.64 mg $Pb\cdot kg^{-1}$ d.m., average 195.39 $mg\cdot kg^{-1}$ (Table 2). Tested samples had a high content of lead, allowing us to classify the soil to contamination degree III. The solubility of lead was very high. The content of soluble forms of lead in 1 mol HCl was 98% of total content of lead (Fig. 1).

Cadmium is an element that occurs in small quantities in flotation tailings, usually not exceeding 1 mg $Cd\cdot kg^{-1}$. The total content of cadmium ranged between 0 and 0.18 mg

Table 2. The total content of heavy metals and their soluble forms in soil samples from the Gilów reservoir [mg·kg$^{-1}$ d.m.].

| Statistical parameters | Pb | Cd | Cu | Zn | Ni |
|---|---|---|---|---|---|
| Total content | | | | | |
| Average | 200.18 | 0.07 | 864.01 | 53.13 | 9.85 |
| SD | 104.25 | 0.05 | 469.27 | 28.81 | 7.62 |
| Median | 200.40 | 0.08 | 897.13 | 51.85 | 8.50 |
| Minimum | 9.32 | 0.00 | 20.45 | 14.66 | 3.72 |
| Maximum | 436.47 | 0.18 | 2,175.48 | 227.67 | 59.90 |
| V% | 52 | 72 | 54 | 54 | 77 |
| Soluble form in 1 mol HCl·dm$^{-3}$ | | | | | |
| Average | 195.39 | 0.05 | 21.00 | 41.79 | 3.36 |
| SD | 102.95 | 0.05 | 11.44 | 17.89 | 1.85 |
| Median | 200.62 | 0.05 | 21.32 | 43.95 | 3.04 |
| Minimum | 10.12 | 0.00 | 0.62 | 4.21 | 0.28 |
| Maximum | 432.64 | 0.17 | 53.85 | 73.85 | 9.74 |
| V% | 53 | 93 | 55 | 43 | 55 |

Table 3. Distribution of heavy metals in soil at the landfill.

| Distance from the center of the Gilów area | Cu | Pb | Cd | Zn | Ni |
|---|---|---|---|---|---|
| km | mg·kg$^{-1}$ d.m. | | | | |
| 0-0.25 | 1062 | 1,089.6 | 0.08 | 52.3 | 8.54 |
| 0.25-0.5 | 842.4 | 241.8 | 0.06 | 63.4 | 6.78 |
| 0.5 -1 | 598.3 | 186.6 | 0.03 | 38.1 | 4.78 |

Cd·kg$^{-1}$ d.m., average 0.07 mg·kg$^{-1}$ in tested flotation tailings (Table 2). The content of cadmium was in the soil quality standards in all tested samples. The content of soluble forms of cadmium in 1 mol HCl was 71% of total content (Fig. 1).

The total content of zinc ranged from 14.66 to 227.67 mg Zn·kg$^{-1}$ d.m., average 53.13 mg·kg$^{-1}$ (Table 2) in the tested soil samples. The obtained values show an increase in the content of zinc in flotation tailings, which causes a risk for soil environment. The content of soluble forms of zinc in 1 mol HCl was 79% of total content (Fig. 1).

The total content of nickel ranged between 3.72 and 59.90 mg Ni·kg$^{-1}$ in tested sediment, average 9.85 mg·kg$^{-1}$ (Table 2). These values are regarded as natural for the soil. The content of soluble forms of nickel in 1 mol HCl was 34% of total content (Fig. 1).

The concentration of heavy metals in dry biomass of dicotyledomous plants, monocotyledonous plants, pine needles, and fungi are summarized in Table 4.

The heavy metals content in dicotyledonous plant dry biomass varied considerably and ranged from 3.55 to 159.62 mg Cu, from 0.60 to 28.28 mg Pb, from 21.99 to 105.38 mg Zn, from 0 to 0.24 mg Cd, and from 0.55 to 6.2 mg Ni·kg$^{-1}$ d.m. The highest average content was found for zinc and the lowest for cadmium: Zn > Cu > Pb > Ni > Cd (Table 4). The greatest variability of content was observed for Cd, in sequence for Cu, Pb, Ni, and Zn.

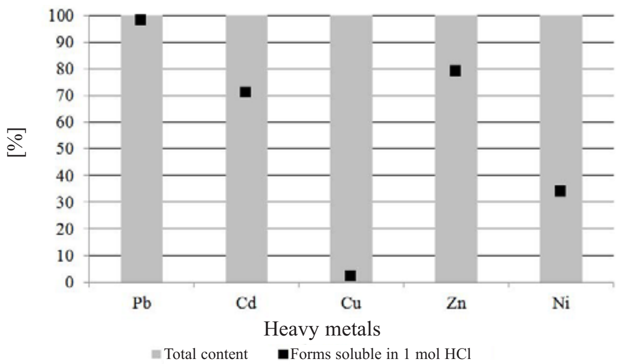


Fig. 1. The percentage content of the soluble form of metals in 1 mol HCl in comparison to the total content of metals in tested soil samples.

Table 4. Heavy metal contents in plant and fungi biomass [mg·kg$^{-1}$ d.m.].

| Statistical parameters | Cu | Pb | Cd | Zn | Ni |
|---|---|---|---|---|---|
| Dicotyledonous plants (n = 9) | | | | | |
| Average | 46.72 | 10.45 | 0.06 | 55.38 | 2.89 |
| SD | 55.61 | 8.59 | 0.10 | 34.97 | 2.12 |
| Median | 23.18 | 8.42 | 0.01 | 38.54 | 2.11 |
| Minimum | 3.55 | 0.60 | 0.00 | 21.99 | 0.55 |
| Maximum | 150.6 | 28.28 | 0.24 | 105.4 | 6.20 |
| V% | 119 | 82 | 163 | 63 | 73 |
| Monocotyledonous plants (n = 10) | | | | | |
| Average | 46.72 | 12.82 | 0.06 | 72.05 | 3.69 |
| SD | 55.61 | 18.98 | 0.43 | 42.99 | 3.16 |
| Median | 35.02 | 6.44 | 0.03 | 54.56 | 2.99 |
| Minimum | 3.81 | 0.64 | 0.00 | 21.65 | 0.50 |
| Maximum | 177.25 | 63.14 | 1.40 | 136.50 | 9.66 |
| V% | 104 | 148 | 199 | 60 | 86 |
| Pine tree needles (n = 15) | | | | | |
| Average | 55.71 | 4.53 | 0.04 | 55.2 | 1.75 |
| SD | 47.13 | 3.27 | 0.08 | 16.41 | 1.01 |
| Median | 47.63 | 2.98 | 0 | 52.44 | 1.48 |
| Minimum | 3.48 | 2.26 | 0 | 37.04 | 0.32 |
| Maximum | 130.64 | 11.84 | 0.32 | 105.78 | 3.22 |
| V% | 85 | 72 | 230 | 30 | 58 |
| Fungi (n = 10) | | | | | |
| Average | 39.68 | 13.02 | 0.55 | 90.5 | 2.52 |
| SD | 39.77 | 10.22 | 0.48 | 35.48 | 1.05 |
| Median | 26.42 | 9.74 | 0.52 | 93.17 | 3.08 |
| Minimum | 7.38 | 2.84 | 0 | 45.94 | 0.52 |
| Maximum | 111.16 | 31.38 | 1.28 | 147.74 | 3.54 |
| V% | 100 | 79 | 88 | 39 | 42 |

Contents of individual elements in monocotyledonous plant biomass ranged between 3.81 to 177.27 mg Cu, from 0.64 to 63.14 mg Pb, from 21.00 to 136.50 mg Zn, from 0.50 to 9.66 mg Ni, and from 0.00 to 1.40 mg Cd·kg$^{-1}$ d.m. The greatest diversity of content in monocotyledonous plant biomass was found for cadmium, the smallest for zinc (Table 4). The greatest average content in test material was observed for zinc and the lowest for cadmium: Zn > Cu > Pb > Ni > Cd.

The content of the analyzed elements in the needles of pine trees was in the range between 3.48 to 130.64 mg Cu, from 2.26 to 11.84 mg Pb, from 0 to 0.32 mg Cd, from 37.04 to 105.78 mg Zn, and from 0.32 to 3.22 mg Ni·kg$^{-1}$ d.m. The greatest average content was for copper: 55.71 mg, the lowest for cadmium: 0.04 mg·kg$^{-1}$ d.m, by a series: Cu > Zn > Pb > Ni > Cd. The greatest diversity of content in pine tree needles was found for cadmium, the smallest for zinc (Table 4).

The considerable variation of heavy metals content was found in mushrooms. The content of copper ranged from 7.38 to 111.16 mg, for lead from 2.84 to 31.38 mg, for cadmium from traces to 1.28 mg, for zinc from 45.94 to 147.74 mg, and for nickel from 0.52 to 3.54 mg·kg$^{-1}$ d.m. Zinc was distinguished by the highest average content and cadmium the lowest (Table 4). The greatest variation was observed for copper concentration and the smallest for zinc: Cu > Cd > Pb > Ni > Zn.

Table 5. Bioaccumulation factor values (BCF).

| Plant matter | Cu | Pb | Ni | Zn | Cd |
|---|---|---|---|---|---|
| Dicotyledonous plants | 0.054 | 0.053 | 0.295 | 1.042 | 0.857 |
| Monocotyledonous plants | 0.062 | 0.066 | 0.375 | 1.356 | 3.114 |
| Mushrooms | 0.050 | 0.072 | 0.279 | 1.786 | 8.667 |
| Pine needles | 0.061 | 0.023 | 0.171 | 1.034 | 0.473 |

Bioaccumulation factors were calculated to assess the degree and direction of movement of heavy metals in plant and fungi samples. The bioaccumulation factor value determined the ability of plants for elements uptake from soil, and informs us about movement of these elements from soil solution to plants [15-18]. Values of bioaccumulation factor (BCF) were presented in Table 5. The biggest value of BCF was shown for fungi and the lowest for pine tree needles. It also showed that monocotyledonous plants accumulated more toxic substances than dicotyledonous plants. It also found that plants accumulated zinc and cadmium easier than the other metals (Table 5).

The high content of some metals is one of the important problems arising during soil reclamation and management of flotation tailings. It significantly exceeded the limits of copper and lead content in tested soil samples [8, 9]. Most metals are unavailable for plants due to high pH. Chemical pollution that is easily dissolved is activated by rain and passes into the soil. Erosion processes may cause activated chemical components that lead to concentration of hydrogen ions and increased acidification. In presented research we showed that acidification promotes activation of further quantities of chemical components. The content of soluble forms of metals increased on account of acidification. This mechanism provides a large mobility of heavy metals in reservoirs of flotation tailings and their high risk on the natural environment [6, 10, 19-21]. It may be very promising to use an innovative biotechnological method for more efficient biological reclamation of a reservoir of flotation tailings [22, 23].

## Conclusions

Research allows us to formulate the following conclusions:

1. A large part of samples showed exceeding permissible levels of cooper and lead content (in 33% samples) in Gilów Reservoir. The content of other metals in the studied samples was within acceptable limits.
2. Chemical analysis of plant (dicotyledonous plants, monocotyledonous plants, pine tree needles) and mushroom materials showed increased content of heavy metals. Increased content of copper was found in 52% of samples, increased content of lead was found in 32% of samples, and increased content of zinc was found in 25% of tested samples. The increased content of metals qualifies plants for industrial use [14].
3. The highest contents of zinc, cadmium, and lead were found in mushrooms. The highest content of copper was found in pine needles, and the highest content of nickel was found in monocotyledonous plants.
4. The bioaccumulation factor showed low capacity of plants for heavy metals uptake from tested soil. The cause of this is low content mobility from soils containing tailings. The low mobility of metals may result from high pH of tested flotation tailings.

## Acknowledgements

Research was supported by the AGH - University of Science and Technology, Faculty of Mining and Geoengineering, Department of Environmental Engineering and Mineral Processing "Badania Statutowe," No. 11.11.100.482 (in 2012).

## References

1. ANGEŁOW Z., CHODAK T., KABAŁA C., KASZUBKIEWICZ J., SZERSZEŃ L. The impact of tailings reservoir "Iron Bridge" on the surrounding soil environment. Volume of Uniwersity of Life sciences in Poznan. **CCCXVII**, 328, **2000** [In Polish].
2. BOGDA A., CHODAK T. Some physical properties and mineral content of flotation tailings from "Gilow" reservoir. Advances of Agicultural Science Problem Issues, **418**, 415, **1995** [In Polish].
3. BARAN A., JASIEWICZ CZ., KLIMEK A. Plants response to toxic zinc and cadmium content in soil. Proc. ECOpole, **2**, (2), 417, **2008** [In Polish].
4. KASZUBKIEWICZ J., KOWAŁKO D. Modification of tailings deposits, from the point of their reclamation, through the addition of various mineral components. Mining and Geology, **1/272**, 73, **2006** [In Polish].
5. SZCZEPOCKA A. Criteria for assessing soil pollution by heavy metals. Scientific Papers SGSP. Warszawa, **32**, 18, **2005** [In Polish].
6. LEWIŃSKI J. Management and utilization of flotation tailings in KGHM Polska Miedź S.A. Technical and ecological problems of copper ore mining. Lubin [In:] VII Conference of Sozology. Problems of enviromnental protection around the landfill "Żelazny Most". Publishing of PPGSMiE PAN, Kraków, 30-32, **1995** [In Polish].
7. ŁUSZCZKIEWICZ A. A concept of management of flotation tailings of Polish copper industry. Journal of the Polish Mineral Engineering Society, **1**, 25, **2000**.

8. PACYNA J., ZWOŹDZIAK J., ZWOŹDZIAK A. Impact of copper metallurgy on the degree of heavy metal contamination of natural environment. Advances in Agricultural Science, **5/81**, 132, **1981** [In Polish].
9. PORĘBSKA G., OSTROWSKA A. Heavy metal accumulation in wild plants: implications for remediation. Pol. J. Environ. Stud., **8**, (6), 433, **1999**.
10. SĘKARA A., PONIEDZIAŁEK M., CIURA J., JĘDRSZCZYK E. Zinc and copper accumulation and distribution in the tissues of nine crops: implications for phytoremediation. Pol. J. Environ. Stud., **14**, (6), 829, **2005**.
11. WERNO M. The landfill "Gilów." Monograph KGHM Polska Miedź S.A. Lubin. pp. 797-798, **1996** [In Polish].
12. ŻYLIŃSKA-DUSZA R., JAWORSKI A., LEWIŃSKI J., MIZERA A. Processing of copper ores and the natural environment. Monograph. KGHM Polska Miedź S.A., Lubin. pp. 763-764, **1996** [In Polish].
13. ALEKSANDER-KWATERCZAK U., MAZUREK M., WARDAS M. The use of physicochemical and biological quality elements for the determination of aquatic environment quality as shown by the example of watercourses in the surroundings of the Żelazny Most flotation tailings pond. Pol. J. Environ. Stud., **18**, (2B), 56, **2009**.
14. KABATA-PENDIAS A., MOTOWICKA-TERELAK T., PIOTROWSKA M., WITEK T. Assess the degree of soils and plants pollution by heavy metals and sulfur. Framework guidelines for agriculture. Puławy IUNG, series **P(53)**, 20, **1993** [In Polish].
15. CIARKOWSKA K., HANUS-FAJERSKA E. Remediation of soil-free grounds contaminated by zinc, lead and cadmium with the use of metallophytes. Pol. J. Environ. Stud., **17**, (5), 707, **2008**.
16. GRUCA-KRÓLIKOWSKA S., WACŁAWEK W. Metals in environment. Part. II. Impact of heavy metals on plants. Chemistry-Didactics-Ecology-Metrology, **11**, (1-2), 41, **2006** [In Polish].
17. GRZEBISZ W., DIATTA J. B., BARŁÓG P. Extraction of heavy metals by fibrous plants from soil contaminated by copper metallurgy. Advances of Agicultural Science Problem Issues, **460**, 68, **1998** [In Polish].
18. JASIEWICZ CZ., ANTONKIEWICZ J. Extraction of heavy metals by plants from soils contaminated with heavy metals. Part. II. Hemp seed. Advances of Agicultural Science Problem Issues, **472**, 331, **2000** [In Polish].
19. KROLAK E. Accumulation of Zn, Cu, Pb and Cd by dandelion (*Taraxacum officinale* Web.) in environments with various degrees of metallic contamination, Pol. J. Environ. Stud., **12**, (6), 713, **2003**.
20. SĘKARA A., PONIEDZIAŁEK M., CIURA J., JĘDRSZCZYK E. Cadmium and lead accumulation and distribution in the organs of nine crops: implications for phytoremediation. Pol. J. Environ. Stud., **14**, (4), 509, **2005**.
21. SZCZEPOCKA A. Criteria for assessing soil pollution by heavy metals. Scientific Papers SGSP. Warszawa. **32**, 18-20, **2005** [In Polish].
22. WIERZBICKA M. The impact of heavy metals on plants. Polish Society of Naturalists them. Copernicus. Kosmos, **44**, 640, **1995** [In Polish].
23. DOBROWOLSKI J.W., WĄCHALEWSKI T., SMYK B., BARABASZ W. Experiments on the influence of laser light on some biological elements of natural environment. Environmental Management and Health, **8/4**, 136, **1996**.
24. DOBROWOLSKI J.W., RÓŻANOWSKI B. The influence of laser light on accumulation of selected macro-, trace-and ultra elements by some plants, Menegenund Spurenelemente, Friedrich-Schiller-Universitat, Jena., **18**, 147, **1998**.