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ASSESSMENT OF HEAVY METALS IN PLANTS AND SOIL IN THE TRZEBINIA MNICIPALITY, POLAND. 2.ZINC

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Abstract

The paper verified the hypothesis of the existence of the correlation between the content of zinc in soils and plants in the municipality of Trzebinia that is in the area which is highly degraded as a result of long term activity of mining and processing of local raw materials. In order to achieve the above, the total metal content in plant and soil material as well as the selected physicochemical properties of soil such as pH, electrolytic conductivity, organic matter content and granulometric composition were determined. 664 soil material samples and 332 plant material samples were collected in years 2010-2012 from 83 research plots located in fallow lands of the town of Trzebinia and in 10 village councils of the municipality. The results obtained of zinc content do not confirm the correlation between soil and plant. The disclosed concentration of the element is in line with indications of permitted levels of metal content in plants proposed by IUNG, which allows the use of plant material as animal feed. The mean content of zinc in the soils of the municipality is higher than the permitted level of national regulations. The claim that the soil of the municipality is contaminated with the element is eligible.

Keywords: heavy metals, zinc, soil, plant, fallow soil, pollution

INTRODUCTION

The problem of toxic presence of zinc in soils and plants of the municipality of Trzebinia is long-term and is the result of anthropogenic influence of human

on the environment. Plants relatively easily intake zinc in the metabolic and passive processes, mainly from the anthropogenic sources which include agriculture, combustion of coal and waste, metallurgical and glass industries as well as construction, but also natural sources cannot be ignored (Szteke, 2002, Broadley *et al*. 2007). Even insoluble or sparingly soluble zinc compounds can be absorbed by plants. Plants are not only sensitive to excess but also to the deficiency of the element. Susceptible species react at the content higher than 100 mg/kg of zinc in the soil, and the resistant ones at the content higher than 8000mg/kg (Kabata-Pendias and Szteke 2012). Reduced efficiency of photosynthesis and chlorosis may indicate an excessive amount of zinc in plants. Zinc indirectly affects the course of photosynthesis, the development of the root system, the formation of auxin and ribosomes, regulations of permeability of cell membranes and the resistance of plants to drought and diseases (Piskornik 1994, Pasławski 2002, Palazzo *et al*. 2003, Broadley *et al*. 2007). The element is characterized by high mobility, although it penetrates groundwaters in relatively small quantities (Kabata-Pendias and Piotrowska 1984). Soil solutions of zinc take the cationic, anionic or organic complex forms. Outside the soil environment, it adopts various forms – from free cations to suspended dust. For example, in the aquatic environment, it was found in the form of hydrated cations, colloidal organic compounds or soluble salts mainly sulfates and carbonates (Prasad 2002). The most susceptible to the accumulation of zinc is the part of the root rhizosphere. Most often it bonds with soluble organic compounds, particularly low molecular weight proteins which provide it with adequate transport capacity in the conditions of deficiency from old parts of plants to the growing ones (Kabata-Pendias 2002). The mean zinc content in the soil depends on its type and usage, and according to Terelak *et al*. (2000) for arable soils ranges from 0.5 to 5754 mg/kg. The standards of the content of the element according to (Journal of Laws 2002) for soils of protected areas are lower than 100 mg/kg, for uncontaminated soils fall into the range of 50-100 mg/kg, for soils of industrial areas are lower than 1000 mg/kg and for agricultural soils lower than 350 mg/kg. Overall, the mean zinc content in soils is classified at the level of 64 mg/kg (Kabata-Pendias and Mukherjee 2007).

FIELD AND LABORATORY METHODS

Methodology of laboratory and field research have been described in Petryk (2016).

CHARACTERISTICS OF THE RESEARCH AREA

The municipality of Trzebinia is located in the Małopolska province, in the northern part of the Chrzanów county (Figure 1). The whole area of the munici-

pality is located in the middle of two urban industrial agglomerations and these are Silesia and Katowice agglomeration in the west and Krakow agglomeration in the east. The municipality of Trzebinia spreads over 105 km2 and is home to approximately 34 thousand inhabitants. The municipality includes the town of Trzebinia and 10 rural administrative units i.e. Bolęcin, Czyżówka, Dulowa, Karniowice, Lgota, Młoszowa, Myślachowice, Piła Kościelecka, Płoki and Pisary. In the area of the municipality coal was dug out in the Siersza coal mine until the year 2000. Numerous traces of former open pit mines of ore were recorded in the region of Luszowskie Mountains, in Trzebionka, in Trzebinia, in the north part of Czyżówka between Psary, Płoki and Lgota. The origins of the extraction of these minerals dates back to the thirteenth century. Their excavation lasted until the early twentieth century. In the seventeenth and eighteenth centuries lead smelter and calamine roasting plant in Płoki were the main centre of the municipality whereas in the mid-nineteenth century Katarzyna and Trzebinia-Górka mines took over the place.



Figure 1. Location of Trzebinia in the map of Poland

Currently, traditional agriculture dominates in Trzebinia. The first records of crops in what is now the municipality Trzebinia date back to the fifteenth century. Rye, wheat, oats, millet, buckwheat and tartary buckwheat were cultivated. In some farms the cultivation of flax and hemp was reported. In the nineteenth century, a rapidly growing industry and housing development began to encompass an increasing amount of agricultural land. After the Second World War, farms of less than 2 hectares covered respectively 73% in Młoszowa, 68% in Myślachowice and 87% in Siersza of the total agricultural land (Kiryk 1994).

In the years 1976-1980 the state began the redemption of small farms. Since 1994 changes in agricultural land use of the municipality have been observed. The changes include a steady decrease in agricultural land, expansion of fallow land and wasteland, replacement of home gardens used for cultivating crops with lawns and ornamental shrubs (Curzydło 1995). The degradation of soil structure caused by heaps of steel, zinc, copper and lead waste; the former margle excavations, the stockpiles of coal wastes, flotation tailings, slags, dross and slag casting have a considerable impact on soil contamination with heavy metals (Environment Programme 2013).

FINDINGS AND DISCUSSION

The mean content of zinc in the plants was 71.75 mg/kg .The mean content of zinc in the soil at the depth of 0-20 cm was equal to 772.02 mg/kg. At the depth of 20-40 cm the mean zinc content was 643.45 mg/kg (Table 1).

Table 1. Basic statistics of zinc content in the soil and plants in the samples from the municipality of Trzebinia.

Parameter		Mean	SD	Min	Median	Max
Heavy metals in plants [mg/kg]	Zn	71.75	41.98	15.6	58.3	217
Heavy metals in soil 0-20 cm [mg/kg]	Zn	722.02	802.2	82.26	449.5	4594.04
Heavy metals in soil 20-40 cm [mg/kg]	Zn	643.45	877.41	28.79	294.6	5648.19

The content of zinc in the soils of the municipality of Trzebinia exceeded the national regulations (<350 mg / kg dry weight) according to Journal of Laws 2002). The activity of the Siersza Power Plant, the landfills of energy industry and industrial waste dumping in Czyżówka as well as the active agricultural landfills in Młoszowa may affect the toxic content of zinc in the soil material collected from the area of rural administrative units. The studies conducted in the framework of Monitoring of the Chemistry of Arable Soils in Poland (2012) confirmed the link between the agricultural use of contaminated sludge and the toxic concentration of zinc in the soil. Analyzing the content of trace elements in the soils around the Płock refinery, Biernacki and Livonian (1986) marked as appropriate for the petrochemical and refining the emission of dust containing heavy metals including zinc. Kabata-Pendias and Pendias (1999) gauged the amount of the annual deposition of lead and zinc to the soils from precipitation and metalliferous dust for lead at the level of 200 g/ha and for zinc at the level

of 709 g/ha. The geochemical background of agricultural land in Poland for zinc was determined in the range of 7-40 mg/kg dry weight by Terelak *et al*. (1995) whereas Czarnowska (1996) suggested the range of 5-59 mg/kg. The extreme zinc content at the level of 5500mg/kg (Jędrzejczyk and Rostański 2001) was determined in the soil of zinc heap in Katowice-Wełniowiec as well as in the heaps of Bolesławiec near Olkusz: the range of 4000-8000mg/kg (Abramowska 2006). In urban soils of Bydgoszcz, Dąbkowska-Naskręt and Różański (2009) also noted a decline in the zinc content with the depth of the soil profile. The decline in the metal content with the increase in depth and the accumulation of zinc in the top layers of soil was confirmed in the studies by Smal *et al*. (2000) and Kawałko (2000). The average concentration of copper in plants amounted to 3.45 mg/kg dry weight. It is lower than the guidelines of IUNG for vegetation intended for animal feed (50 mg/kg dry weight).The claim that the community soils are contaminated with zinc is fully eligible. In agricultural soils of the Małopolska province, the mean content of zinc adds up to 79.2 mg/kg dry weight. For Poland this value is equal to 32.4 mg/kg dry weight. (Terelak *et al*. 1995). In the study conducted by Gambuś (1993) mean concentration of the metal in the soil of the former province of Cracow was set at 87.1 mg / kg dry weight. According to Kabata-Pendias and Pendias (2002) Polish grass contains around 12–72 mg/kg dry weight of zinc with the mean content of the element coming up to 30 mg/kg dry weight. Niesiobędzka and Krajewska (2007) examined the content of the metal in plants along the fast transport routes in Warsaw and in its surroundings. According to them, the content of zinc ranged between 75.57 and 340.83 mg/kg dry weight with the mean at the level of 165.56 mg/kg dry weight.

No significant correlation between the zinc content in soil and plants was disclosed. (Table 2)

Table 2. The relationship between the zinc content in the soil (0-20 cm) and in the plant

Heavy metal	Spearman correlation coefficient	p-value	Direction of the relationship	Power of the relationship
Zn	0.049	0.661	---	---

The reason for such discrepancies in test results is that the uptake of metals by plants is affected by numerous factors. In response to the contamination with heavy metals of the soil, plants can also develop adaptive mechanisms to achieve a certain level of tolerance by adjusting, for example, to the excessive content of trace elements in the soil solution, as exemplified by metallophytes and hyperacummulators (Baranowska-Morek 2003, Słysz and Wierzbicka 2005, Bidar *et al*. 2007). According to Siwek (2008) plant organisms evolved a variety of defence strategies. The plant avoids the uptake of metals by retaining them

in the root zone and in the root itself by mineral salts of phosphorus, preventing the transport of metals to the above ground part of the plant (Cieśliński 1997). There was no correlation between the zinc content in plants and in the soil layer of 20-40 cm (Table 3). Gałuszka (2007) reported that the type of use of soil can also affect the mobility and availability of metals for plants. The properties of elements are also affected by the content of clay minerals, hydroxides, organic matter (Spiak 1998, Gębski 1998, Kośla 1999), the activity of the bacterial flora, electrolytic conductivity and granulometric composition of soil as well as by the course of interactions between metals (Alloway 1999, Kabat-Pendias and Pendias 1999, Gambuś and Rak 2000, Gworek *et al*. 2000, Drozd *et al*. 2002, Zawadzki and Fabijańczyk 2005, Świercz and Sykała 2009, Kaszubkiewicz and Kawałko 2009, Ovečka *et al*. 2014).

Table 3. The relationship between the zinc content in the soil (20-40 cm) and in the plant

Heavy metal	Spearman correlation coefficient	p-value	Direction of the relationship	Power of the relationship
Zn	0,04	0,722	---	---

The revealed correlations with the positive direction of the relationship between the soil pH and the heavy metals content in the soil layers of 0-20cm (Table 4) and of 20-40cm (Table 5). Kabata-Pendias and Pendias (1979) found a proportional relationship between the decrease in the solubility of zinc connections and the increase in soil pH. On the other hand, in the framework of Monitoring of the Chemistry of Arable Soils in Poland (2012) it was stated the decrease in the mobility of cadmium and lead in the soil and their fitoavailability plants caused by the increase in pH occurred as a result of adsorption, occlusion or precipitation of sparingly soluble metal salts. According to Jackowska (1997), Godzik (1999) and Gawroński (2002), cadmium and copper are mostly immobilised in the soil environment in the form of carbonates and phosphates.

Table 4. The relationship between the pH value and the content of zinc in soil (0-20 cm)

pH	Spearman correlation coefficient	p	Direction of the relationship	Power of the relationship
in H_2O	0.465	<0.001	positive	average
in KCl	0.542	<0.001	positive	strong

The increase in soil pH causes precipitation of sparingly soluble metal ions in the soil solution which are immobilized in the soil environment as a result of being bound by the buffer system of the soil. The transport of metal ions from the soil solution to the above ground parts of plants is impeded the higher their bioavailability and bioassimilability by plants are (Kabata-Pendias and Pendias 1979, Blake and Gouldinga 2002, Karczewska 2002, Gawronski 2002, Zielinski 2003, Mercik 2004, Dziadek and Wacławek 2005, Węglarzy 2007, Martyn and Niemczuk 2009, Chrzan *et al*. 2009, Świercz and Sykała 2009, Burzyńska 2009).

Table 5. The relationship between the pH value and the content of zinc in soil (20-40 cm)

pH	Spearman correlation coefficient	p	Direction of the relationship	Power of the relationship
in H_2O	0.369	0.001	positive	average
in KCl	0.498	<0.001	positive	average

The observed, for the soils of the municipality of Trzebinia, correlations with the positive direction of the relationships between the content of organic matter and heavy metals in the soil, both in the layer of 0-20cm (Table 6) and in the layer of 20-40 cm (Table 7). An increase in humus content, oxides of iron, aluminium and manganese, clay minerals in the soil as well as its sorption capacity and the use of fertilizers, for example, liming treatment reduce the solubility of metals in the soil solution and their bioavailability to plant organisms. Dicotyledonous plants show a higher level of intake of heavy metals than grass or cereal plants (Czerwińska 1977, Gondek and Kopec 2005).

Table 6. The relationship between the content of organic matter and zinc in soil (0-20 cm)

Heavy metal	Spearman correlation coefficient	p	Direction of the relationship	Power of the relationship
Zn	0.509	<0.001	positive	strong

The soils of the town of Trzebinia, especially in the humus layer, were grossly contaminated with the metal, presumably in connection with the activity of historical as well as active emitters of industrial pollutants including metallurgical plants, coal mines, cement plants, heating plants and refineries Biernacki and Livonian (1986).

Table 7. The relationship between the content of organic matter and zinc in the soil (20-40 cm)

Heavy metal	Spearman correlation coefficient	p	Direction of the relationship	Power of the relationship
Zn	0.598	<0.001	positive	strong

CONCLUSIONS

1. Zinc content in the soil material at both levels concerned that is 0-20 cm and 20-40 cm is higher than the acceptable national regulations (Journal of Laws 2002) set for agricultural land. It must therefore be concluded that the soils of the municipality of Trzebinia are contaminated with the metal.
2. The contamination of soils of the municipality of Trzebinia with zinc is associated with long-term activities of mining and processing of local raw materials and industrial and agricultural activity carried out in the areas of the municipality.
3. The obtained results of zinc content in soil and plant material as well as conducted statistical analyses do not confirm correlation between the concentration of the element in the above ground parts of plants and in the soils of the municipality of Trzebinia. High content of organic matter and soil pH value presumably affected the suppression of transport of the element from the soil to the plants.
4. The obtained results of zinc content in plant material show the possibility of the use of vegetation from fallow lands of the municipality of Trzebinia as animal feed in livestock farming. The concentration of the element in the above ground parts of plants did not exceed the permissible content of the element in animal feed proposed by IUNG.

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