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ASSESSMENT OF THE CONTENT OF HEAVY METALS IN PLANTS AND SOIL IN THE TRZEBINIA MUNICIPALITY, POLAND. 4.COPPER

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Abstract

The activity of steel and chemical industries, fertilizers and the development of transport mean that heavy metals (copper) in toxic quantities directly affect the condition of soil and natural ecosystems occurring in nature. The study concerned aimed at the assessment of the copper content in the soil samples and plant material from the area of the municipality of Trzebinia where the problem of the presence of toxic heavy metals in soils is long-term and is the result of anthropogenic human impact on the environment. 83 research areas were designated from which the plant material and soil samples were taken from the levels of 0-20 cm and of 20-40 cm. The copper content in the soil was determined by applying the FAA Method.

Additionally, in the soil samples the following were marked: granulometric composition, soil reaction in 1M KCl and in water, electrolytic conductivity and organic matter content. The content of the aforementioned element in the plant material was evaluated by applying the Atomic Absorption Spectrometry. The conducted research did not reveal any copper contamination of the soil in the municipality of Trzebinia (Journal of Laws 2002). The plant material did not exceed any IUNG standards of the content of copper in the animal feed. No correlation was found between the copper content in the top layer of the soil and the content of the metal in plants.

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

INTRODUCTION

Copper is a component of plant enzymes, including oxidases, and strengthens the resistance of plants to diseases and affects the permeability of cell membranes, photosynthesis and respiration as well as the course of other physiological processes. It is assimilated by active and passive plants, which, because of its limited ability to transport, accumulate it in large amounts in their roots. The growth of the root system and aboveground parts translate into an increase in the content of the element in the plant (Gwóźdź and Kopyra 2003, Boularbah *et al*. 2006). Also, in the soil, the metal has a low mobility, and this is due to the relationship with Fe and Mn hydroxides, clay minerals, sulfides, sulfates and carbonates (Spiak 1996). National regulations (Journal of Laws 2002) set the following limits on the content of the element in (mg/kg): for protected areas <30, for industrial areas <600, for agricultural land <150 where in Poland the mean copper content in agricultural soils according to Terelak *et al*. (2000) amounts to 6.6 mg/kg and ranges from 0.2 to 275 mg/kg. The soils of the intensive mining and metallurgical activities contain the greatest amount of the metal which interacts with such elements as Ca, P, K, N, as well as other trace metals such as Mn, Fe, Zn, Mo (Kabata-Pendias 1996, Dziadek and Wacławek 2005). It is used in the chemical and food industries, agriculture, metallurgy, electronics, medicine and cosmetics (Kabata-Pendias 1989). In water it takes the form of hydrated cations, compounds with organic colloids, as well as carbonates and sulfates. The excess or the increased amount of zinc, calcium and cadmium limits the copper intake (Piotrowska 2006).

FIELD AND LABORATORY METHODS

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

CHARACTERISTICS OF THE RESEARCH AREA

Trzebinia is the urban-rural municipality located in the western part of the Malopolska province. The location of the municipality determines its favourable rail and road transport conditions. The transport system establishes the perfect link of the municipality with the main towns/cities in the southern Poland connecting Upper Silesia and the Małopolska province (Figure 1).

Figure 1. Location of Trzebinia in the map of Poland

A strategic railway line from Krakow to Katowice connecting Chrzanów and numerous local factories and mines runs through the municipality (Environment Programme 2013). Historical sources indicate deposits of dolomite ore mined in the Bolęcin quarry in the 50s and 60s of the twentieth century. Their considerable quantities were discovered in the vicinity of Psary, in the northern part of Czyżówka, in Podkrystynów, in the Luszowskie Mountains and in the southern part of Bolęcin. For construction purposes Permian limestone (Karniowice travertine), Triassic (Gogoliński) and Jurassic limestone were utilised. Jurassic limestone, mined in the area of Młoszowa, was employed as building stone, aggregate and cement. Triassic limestone, mined in the area of Trzebinia, Psary and Płoki, served as building and pave stone. Permian limestone and Myślachowice conglomerates, mined in the area of Karniowice, Dulowa and Młoszowa were utilised as road aggregate and building stone (Molenda 1973). The total area of land in the municipality of Trzebinia amounts to 10 540 ha out of which fallow lands including green areas constitute 9.7%. Only 24.1% comprise the remaining agricultural land (Pęckowski 2013). In the town of Trzebinia, the presence of three groups that is area (urban agglomerations, industrial areas, mines, etc.), line (transportation lines and railways) and point (waste dumping and wastewater discharges, municipal waste landfill, etc.) of contamination sources of surface and groundwater was identified. The degradation of soil structure of the municipality is associated with the intense activity of entities in the mining, metallurgy, refining and energy sectors (Environment Programme 2013).

FINDINGS AND DISCUSSION

The mean content of copper in plants was 3.45mg/kg. The mean content of copper in the soil at the depth of 0-20cm was equal to 19.73mg/kg. At the depth of 20-40cm the mean copper content was 15.51mg/kg (Table 1).

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

Parameter		Mean	SD	Min	Median	Max
Heavy metals in plants [mg/kg]	Cu	3.45	1.39	1.36	3.06	7.46
Heavy metals in soil 0-20 cm [mg/kg]	Cu	19.73	23.76	2.6	13	177.4
Heavy metals in soil 20-40 cm [mg/kg]	Cu	15.51	20.49	1.3	9.9	135

The mean content of copper in soil did not exceed the permissible concentrations for agricultural land (<150 mg/kg dry weight). The conducted evaluation took into account the recommendations included in the (Journal of Laws 2002). The past exploitations of raw materials such as clay, chemical and building materials in Bolęcin or travertine and coal in Karniowice or calamine ore in Lgota or raw building materials in Młoszowa or coal and calamine ore in Myślachowice or calamine ore in Psary or iron, lead and calamine in Płoki do not currently affect the content of the metal in the soil. The remains of the former and contemporary activity of metallurgical plants, coal mines, excavation of clay and limestone, cement plants, heating plants and refineries do not result in toxic levels of the metal in the soil of the town of Trzebinia. It should be recognized that the soils of the rural administrative units of the element. Augustyn *et al*. (2003) determined the copper content of the soil in the garden allotments in the area of Bielawa in the range of 17.5 and 37.6 mg/kg. In Poland, the mean content of the metal in agricultural soils can reach the value of 6.5 mg/kg (Kabata-Pendias i Pendias 1999). Soils containing natural concentrations of the metal are dominant in the Malopolska province; however, the content of copper soils ranges from 0.7 to 14.3 mg/kg dry weight. (Rogóż 2003). Polish soils according to Kabata-Pendias and Pendias (2001) ranged from 2.2 to 211 mg/kg dry weight. The excessive accumulation of the element in soils applies mainly to the areas of high dominance of te mining and metallurgy industries and intensive agricultural production as well as the areas affected by atmospheric dust from agglomerations (Wierzbicka 1995, Baran and Turski 1996, Kowicka 1997, Czamara and Czamara 2008). The extreme copper concentration amounting to 5000 mg/kg was determined in arable topsoil of sanitary protection zones of the Metallurgical Plant in Głogów (Roszyk and Szerszeń 1988).This value is nearly fifteen times lower than the permissible content of the element in plants for animal feed (50 mg/kg dry weight) proposed by IUNG (Kabata-Pendias *et al*. 1993), which indicates that all of the tested plants meet the required criteria. According to Kabata-Pendias and Pendias (2002) the mean concentration of copper in Polish grass adds up to 5.5 mg/kg dry weight. Wybieralski and Maciejewska (2001) reported the mean content of 11.5 mg/kg dry weight in the grass near Szczecin. Maciejewska *et al*. (2007) conducted research along the local roads on the way from Szczecin to Poznań. They noted the concentration of copper in the grass in the range of 2.7-8.8 mg/kg . The analyses carried out by Gambuś *et al*. (1999) in the city of Tarnow revealed the Cu content in the grass in the range of 1.61-7.29 mg/kg dry weight, with the mean at the level of 3.96 mg/kg dry weight. The obtained results of the mean content of the metal in the soil material particular do vegetation is contaminated copper. The statistical analyses did not confirm any correlation between the copper content in the soil and in the plant (Table 2).

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

Heavy metal	Spearman correlation coefficient	P-value	Direction of the relationship	Power of the relationship
Cu	-0.094	0.396	---	---

The lack of such a correlation between the copper concentration in the bedrock of the Beskidy Mountains and in the moss (*Polytrichum formosum*) was also noted by Panek [2000]. On the other hand, the analyses carried out by Niesiobędzka *et al*. (2005), Broadley *et al*. (2007), Kabata-Pendias and Szteke (2012), Yan *et al*. (2012) and Remon *et al*. (2013) show a relationship between the concentration of zinc, cadmium and lead in soil material and plant material. No such a relationship for copper might result from high content of zinc which in view of Kabata-Pendias and Szteke (2012) reduces the intake by plants. The legitimacy of the assertion is confirmed by the fact that in the soils of the municipality of Trzebinia zinc reached the highest mean content (71.75 mg/kg) among the monitored elements. The lack of correlation might result from its low content in the soil. No correlation was found between the copper content in plants and in the soil at the level of 20-40 cm (Table 3). The presence of the highest concentrations of copper in the soil layer of 0-20 cm in the opinion of Weber (1995) may be caused by disorders in natural formation of the soil arising from previous reclamation treatments or from displacement of soil layers during e.g. construction works. The most important, perhaps, is the fact that the main mass of roots of herbaceous plants, especially grasses, grows in the top layer of the soil. The decisive factor could be the high value of organic matter and the soil pH in the top layer of the soil which forming a barrier immobilizing the metal in the soil solution hampered the transport of the elements from the lower layers of the soil to plants.

Table 3. The relationship between the copper 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
Cu	-0.113	0.311	---	---

A correlation between soil pH and the content of Cu in the soil layer of 0-20cm (Table 4) and of 20-40cm (Table 5) was found. The noted relationships and slightly acidic soil influenced the toxic concentrations of metals in the soils of the municipality, their accumulation and immobilization in the upper layers of the soil (in the case of cadmium, lead and zinc in Psary, and copper in Lgota and Dulowa also at a depth of 20-40 cm), small mobility of metals between soil solution and vegetation, and consequently low accumulation of the elements in the plant material.

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

pH	Spearman correlation coefficient	P-value	Direction of the relationship	Power of the relationship
in H_2O	0.275	0.012	positive	weak
in KCl	0.254	0.02	positive	weak

The results obtained by (Lityński and Jurkowska 1982, Moraghan and Mascani 1991) underpin the significant impact of soil factors, especially soil pH on solubility, migration, bioassimilability and bioavailability of metals including copper in the soil, and therefore on their content in plants.

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

pH	Spearman correlation coefficient	P-value	Direction of the relationship	Power of the relationship
in H_2O	0.206	0.061	---	---
in KCl	0.268	0.014	positive	weak

It must be concluded that the low acidity of the soil of the municipality of Trzebinia reduced leaching of metals into the soil profile which justifies a downward trend of the element content with the depth increase. They were concentrated in a greater amount in the top layer. This, also, might have been influenced by the intensity of soils cultivation in the municipality. Kobierski *et al*. (2011), Kabata-Pendias (2004), Boligłowa (1998) as well as Trafas and Eckes (2003) observed an increase in the concentration of heavy metals in the upper soil levels with the increase in industrialization and intensification of agricultural activity. A correlation between organic matter content in the soil and the content of Cu in the analysed soil layer of 0-20cm (Table 6) and of 20-40 cm (Table 7) was found.

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

Heavy metal	Spearman correlation coefficient	P-value	Direction of the relationship	Power of the relationship
Cu	0.521	<0.001	positive	strong

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

Heavy metal	Spearman correlation coefficient	p-value	Direction of the relationship	Power of the relationship
Cu	0.614	<0.001	positive	strong

It was shown that the higher the content of organic matter in the soil, the higher the pH of the soil. The increase in organic matter content and in pH reduces the mobility of metals between soil solution and a plant, increases their concentration in the soil environment and reduces the accumulation of metals in plants. In turn, low humus content and acidic soil increases the mobility of elements in the soil solution and its fitoavailability for plants (Gębski 1998, Spiak 1998, Kabata-Pendias and Pendias 1999, Łabętowicz and Rutkowska 2001, Terelak and Tujaka 2003, Mercik 2004, Martyn and Niemczuk 2009).

CONCLUSIONS

In the study area, no contamination of the soil with copper was found both at the depth of 0-20cm and of 20-40cm. No correlation was found between the copper content in the soil layer of layer 0-20cm and the content of the metal in plants. The obtained results of the copper content in the plant material, analysed according to the guidelines for animal feed proposed by IUNG, did not exceed the recommended standard. In Młoszowa, Karniowice, Myślachowice, Piłą Kościelecka, Płoki, Psary and in the town of Trzebinia, a decline in the metal content with the depth of the soil profile is noted. The effects of historical industrialisation of the Trzebinia region district are visible to this day and are reflected in the state of soil contamination with heavy metals of the area. There is a need to restore biological and utility value of the soils of the municipality for either agricultural or recreational purposes. Gradually public awareness of ubiquitous environmental degradation and pollution with substances containing trace elements is increasing (Preżdo and Nowakowski 1995, Alloway and Ayres 1999). It manifests itself in a rapidly growing number of specialised publications, in countless ongoing research projects, in the presence of environmental issues in the public discourse on national and international level and in ad hoc social campaigns.

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