



ASSESSMENT OF THE CONTENT OF HEAVY METALS IN PLANTS AND SOIL IN THE AREA OF THE TRZEBINIA MUNICIPALITY, POLAND. 3.LEAD

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Abstract

The aim of the article was to determine the content of heavy metals (lead) in soils and plants in areas heavily degraded by mining and processing industries. The study was conducted in the area of the municipality of Trzebinia, in the western part of the Małopolska province. Altogether 83 research areas were designated (one area of 25 m²) from which the plant material and soil samples were taken from the levels of 0-20 cm and 20-40 cm. The analysis of soil material was based on the determination of granulometric composition of the soil with the use of the Casagrande method modified by Prószyński [according to the industry standard (BN-78/9180-11), soil reaction in 1M KCl and in water with the use of the potentiometric method, electrolytic conductivity of the soil with the use of the conductometric method, content of organic matter in soil by its annealing using the modified Tiurin method, the total Pb content in the soil using the FAA method. The analysis of plant material was based on the determination of the total content of Pb in plants using the atomic absorption spectrometry. It was found that the mean lead content in the soil for the municipality exceeded the permissible concentrations, stated in national regulations (Journal of Laws 2002), of this element for farmlands. The research conducted on fallows of Trzebinia indicated a positive direction of the relationship between the lead content in the soil layer of 0-20cm and the content of the metal in plants present there. The results of the lead content in the plant material did not exceed the permissible content of the element in animal feed proposed by IUNG (Kabata-Pendias et al. 1993)

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

INTRODUCTION

Studies have shown that the lead content leads to negative consequences of toxicity of the element for plants that can manifest itself by shorter roots, wilting and browning of leaves and flowers. They are the result of abnormal mitosis, photosynthesis or the water management of the plant (Piskornik 1994, Piotrowska 2006). The accumulation of larger amounts of this element in the surface levels of the soil brings harmful consequences also for microorganisms resulting in slowing down organic matter mineralization (Janitor 1998). The excess of lead restricts the transport of zinc in plants and facilitates the uptake of cadmium (Gwóźdź and Kopyra 2003).. Plants largely accumulate it in the roots and that is because of its low mobility and the ability to transport both in plants themselves and in the soil (Samardakiewicz and Woźny 1987, Staszewski *et al.*, 2008, Ostrowska *et al.*, 2006). Soluble forms of the element most often occurs in acidic waters. The concentration in soil solutions is in the range of <math><1-60 \mu\text{g}/\text{dm}^3</math>. The process of collecting the element from the soil is passive and is slowed down by clay minerals, calcium and phosphorus fertilizers (Kabata-Pendias and Pendias 1999) . It is relatively easily absorbed from precipitation (Kabata-Pendias 1994 and 1998). There is a close relationship between its presence in plants and its presence in soils. The lead content has very uneven distribution in the levels of genetic soils (Petkowski 1995). National regulations (Journal of Laws 2002) set the following limits on the content of the element in (mg/kg) for industrial sites: 600, for farmlands: 100 and for protected areas: 50. In Poland, the mean content of lead in agricultural soils depends on the their mechanical composition and the pH and encompasses the range of 70-100 mg/kg. Lead is used in the production of ammunition, crystal glass, water pipes, printing fonts, paints, anti-corrosion materials, in the glass, ceramic and plastic industries (Gworek *et al.*, 2000, Paulo *et al.*, 2002, Bajda 2003, Manahan 2003). Contamination of soil and other elements of natural environment by this element is strictly anthropogenic and results from coal combustion, municipal sewage, paints, fertilizers, the metallurgical industry, etc. (Kabata-Pendias and Szeke 2012, Caussy 2003, Helios – Rybička *et al.*, 2004, Kusińska *et al.*, 2004).

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 a town in the Małopolska province (Figure 1), in the Chrzanowski county, the headquarters of the urban-rural community of Trzebinia. The municipality is entirely located in the Silesian-Cracow Upland which results in its very hilly character. The south-eastern part of the municipality belongs to the Cracow Upland which includes Tenczynek Prominence with Płaziński Block, the Krzeszowice Trench with the Dulowa syncline and the Ojców Plateau Paternity with Pagóry Myślachowickie. The north-western part covers the area of the Silesian Upland which includes *the Wilkoszyn* syncline with the Ciężkowice Hill and Przemsza Basin with Biskupi Bór Basin (Environment Programme 2013).



Figure 1. Location of Trzebinia in the map of Poland

The geological structure of the municipality of Trzebinia has a direct impact on the diversity and size of mineral deposits located on its territory. Their exploitation for centuries shaped the directions of the development of the local industry. Only historical traces in the form of pits, heaps and closed mines remained in places of extraction of some of them, particularly conglomerates, zinc and lead ores. Other deposits, including limestone, clay minerals, dolomite

and coal may be exploited in the future (Kot-Niewiadomska 2013, Pęcowski 2013). The soils of the study area are of typological, species and water – humidity diversity resulting from a rich and complex foundation structure, built on limestone of Triassic and Jurassic. This foundation developed brown rendzina of complex skeletal structure and shallow thickness. In areas of intensive erosion processes, in particular on the peaks and slopes of the hills with a large drop, rendzinas of a small thickness and a poorly shaped soil profile were formed. In the eastern part of the municipality, in the belt of rural administrative units of Młoszowa and Karniowice, weathered brown earths were formed. Brown podzolic soils or endoeutric cambisols were created from glacial sands (Szuwarzyński and Orifice 1995). The economic development of the municipality of Trzebinia is determined by the natural resources. Their type and scope made the region of Trzebinia become a thriving centre of mining and processing industries. The economy of Trzebinia is notorious for water absorption, resources absorption, disorganized, organized and cross-border emission of pollutants into the atmosphere, a significant impact on the structure of soil as well as considerable production of municipal and industrial waste (Kot-Niewiadomska 2013).

FINDINGS AND DISCUSSION

The mean content of lead in the plants was 1.93 mg/kg. The mean content of lead in the soil at the depth of 0-20 cm was equal to 204.23 mg/kg. At the depth of 20-40 cm the mean lead content was 162.59 mg/kg (Table 1).

Table 1. Basic statistics of lead 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]	Pb	1.93	1.11	0.62	1.65	7.6
Heavy metals in soil 0-20 cm [mg/kg]	Pb	204.23	203.83	19.29	130.64	924.2
Heavy metals in soil 20-40 cm [mg/kg]	Pb	162.59	226.77	3.38	78.5	1367.6

The conducted analyses of the evaluation of lead content in the soil of the municipality of Trzebinia show the exceedance of permissible concentrations of the element according to (Journal of Laws 2002) determined for agricultural land (<100 mg/kg dry weight), both at the depth of 0-20 cm and of 20-40 cm. The claim that the municipality soils are contaminated with lead is fully eligible. Close proximity of the sampling points to the transportation routes in Piła Kościelecka also does not lead to the occurrence of the toxic range of metal con-

centration in the soil material. Jankowski *et al.* (2014) found a decrease in the mean lead content in the soil with the increase in the distance to the motorways. At the distance of one metre from the edge of the roadway the concentration amounted to 2.52 mg/kg, and at a distance of 15 metres it decreased to 1.64 mg/kg. The purview of contamination with heavy metals of the soils near roads was confined to the zone of 150 metres by Baran and Turski (1996). The mean concentration of lead in the street dust may be as high as 1000 mg/kg (Wierzbicka 1991). The mean lead content in the soil was higher than the ministerial standard (Journal of Laws 2002) of the permissible metal concentration for agricultural land (<100 mg/kg dry weight) in Czyżówka, in Lgota (in the 0-20cm layer three times as much, in the layer of 20-40cm twice as much), in Płoki (in the 0-20cm layer four times as much, in the layer of 20-40cm twice as much), in Psary (in the 0-20cm layer 3.5 times as much, in the layer of 20-40cm 3.7 times as much) and in the town of Trzebinia (in the 0-20cm layer twice as much, in the layer of 20-40 cm by 1.8 times as much). In Młoszowa and Myślachowice toxic content of the element was found in the soil layer of 0-20cm. The recorded mean lead content in the soils of Czyżówka should be associated with the activity of the “Siersza” power plant, industrial waste landfill of the energy industry and industrial waste dumping. In Lgota the content may result from the former mining activity of calamine ore in the “Katarzyna” mine shafts. The concentration of the element in the soils of Płoki can be influenced by the past exploitation activities of local raw materials, after which historical traces of the extraction of iron, calamine and lead can be observed in the area of the rural administrative unit. Similarly, in Psary toxic lead content can be explained by the impact of the effects of historical calamine ore mining whereas in the town of Trzebinia it results from numerous historical and active emitters of industrial pollution, including the activities of heating plants, metallurgical plants, coal mines and refineries that emit lead into the atmosphere. The particles of the metal can remain the longest among the other elements in the atmosphere, even up to 7-8 days (Panek 2000). The mean concentration of lead in the area of soil of Jedlicze S.A Refinery in the province of Podkarpackie reached the value of 26.6 mg/kg (Właśniewski *et al.* 2007). For Petkowski (1995) these are the heavy chemical, mining and processing industries which are the greatest source of lead emission. The researcher listed once active counties of Olkusz and Trzebinia and at present the counties of Upper Silesia as the noteworthy emitters of pollutants of the element. Also, Wierzbicka (1991) indicates the steel, copper and iron industries, cement production and mining of zinc ore as a potential source of industrial pollution with lead. To a limited extent the element enters the top layers of soil environment as a result of the element migration from natural minerals. High concentrations of the metal in the layer of humus soil in Młoszowa can be associated with an active landfill of agricultural waste. Kowicka (1997) sees the source of a small amount of lead in the surface layer of the soil in the use of fertilizers made from sewage

sludge and metallurgical waste. The increased accumulation of the metal in the soil inhibits organic matter decomposition. Terelak *et al.* (2000) tagged the concentration of lead in the soil layer of 0-20cm of agricultural land in the province of Podkarpackie in the range of 1.4 and 107.7 mg/kg. The mean lead content in agricultural soils in Poland is at the level of 13.6 mg/kg dry weight. (Terelak *et al.* 2000). In the study conducted by Gambuś (1993) the mean concentration of lead in the soils of the former province of Cracow did not exceed 28.4 mg/kg dry weight. Terelak *et al.* (1995) determined the geochemical background of lead of agricultural soils in Poland at 14 mg/kg dry weight whereas Czarnowska (1996) suggested the amount of 9.8 mg/kg dry weight. The extreme lead content in the range of 2000-3000 mg/kg (Jędrzejczyk and Rostańki 2001) was determined in the soil of zinc heap in Katowice-Welnowiec as well as in the heaps of Bolesławiec near Olkusz in the range of 1650-3000 mg/kg (Abramowska 2006). The presence of the highest concentrations of lead in the soil layer of 7-14cm in the opinion of Weber (1995) may be caused by disorders in natural formation of soil profiles arising from construction works and reclamation treatments. These disorders may also facilitate penetration of large amount of heavy metals into the soil up to the depth of 70cm. In all rural administrative units lead had a significantly higher range of content and a higher mean content in the soil material than in the plant material. It was, therefore, considerably more accumulated in the soil than in the plants. The lack of vegetation contamination with heavy metals in the municipality of Trzebinia despite exceeding the permissible content levels of Cd, Pb, Zn in the soil according to national regulations (Journal of Laws 2002), which refer to agricultural lands, can be justified by the gradation of metals mobility, by the development stage of plants as well as by the defence mechanisms limiting the intake of metals from the soil to the plant (Czerwinski 1977). A notable difference in concentration of the element in the plants and in the soil is discernible especially in Psary. Soil is the main source of lead for plants (Rejmer 1997) as the element penetrates mainly through the root system (Cyra and Pajdzik 1995). The lead content in plants is also influenced by its immission from atmospheric dust (Ciepał 1992). According to Kabata-Pendias and Pendias (2002) from 73% to 95% of the total metal concentration in the grass vegetation originates from precipitation. Comparing the obtained lead contents with the literature data of Kabata-Pendias and Pendias (1999) it can be noted that the test plants contain this element in amount which does not exceed the critical content enabling their growth. According to the Regulation of the Minister of Agriculture and Rural Development (2012a) the maximum permissible concentration of lead in animal feed is ≤ 10 mg/kg dry weight. Given the fact that the determined concentrations of this element are 5 times lower than the permissible value, all the harvested plants meet these requirements. Plants on the contaminated sites may contain very large quantities of this metal. Lead concentration in the grass in the area of mines and mineral deposits in the UK was in the range of 63–232 mg/kg

dry weight, whereas in the area of activity of the steel industry in Canada varied between 229 and 2714 mg/kg dry weight and in Sweden the lead content along the transport routes came to the range of 67–950 mg/kg dry weight (Kabata-Pendias and Pendias 2002). Very similar concentrations of lead were determined in the grass of the ecologically threatened area in the vicinity of Żyraków (Dębicki county), where the lead content ranged from 0.71 to 5.98 mg/kg dry weight. (Gambuś *et al.* 1999). Lead content in the greensward in the area of the copper industry activity averaged 1.11 mg/kg dry weight. (Dobrzański *et al.* 2003). Biernacka and Wójcik (1998), who studied the effect of the antropogenisation of environment on lead content in grass vegetation, found the presence of this element in the grass in Roztocze (5.42 mg/kg dry weight), Łomża (1.87 mg/kg dry weight), in the vicinity of the steel plant in Dąbrowa Górnicza (17.05 mg/kg dry weight). The positive direction of the relationship between lead content in soil and plants was shown (Table 2).

Table 2. The relationship between the lead 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
Pb	0.39	<0.001	Positive	average

The results obtained are acknowledged by Brüggemann’s (1999) research. He describes a disproportionate increase in the content of heavy metals in plants in the relationship to their concentration in soil solution. The metal content in plants is not related only to their contents in the soil, but is determined by many factors. The reason for such discrepancies in the 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 hyperaccumulators (Baranowska-Morek 2003, Słysz and Wierzbička 2005, Bidar *et al.* 2007). According to Siwek (2008) plant organisms evolved a variety of defence strategies. A plant avoids 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 parts of the plants (Cieśliński 1997). High values of the soil factors, especially the soil pH and the organic matter content, immobilize some metals in the soil, thus limiting the transport of cadmium and lead from the soil environment to plants. It must be assumed that the high soil pH and the organic matter content limited the transport of cadmium and lead from the soil environment to vegetation. There was no correlation between the lead content in plants and in the soil layer of 20-40 cm (Table 3). This can be

connected to the disclosed decline in content of the elements with the increasing depth in most of the rural administrative units in question in the municipality of Trzebinia. 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 the plants. 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.

Table 3. The relationship between the lead 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
Pb	0,214	0,052	---	---

Many studies (Lityński and Jurkowska 1982, Moraghan and Mascani 1991) indicate that soil factors, especially the soil pH, have a significant influence on solubility, migration and fitoavailability of lead in soil and, consequently, on its content in plants (Maciejewska and Kotowska 1992, Niemyski-Łukaszuk 1995). The denoted value of the soil pH in the municipality of Trzebinia leads to the conclusion that these soils can be described as slightly acidic. 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) suggest that an increase in soil pH results in an increase in the content of sparingly soluble metal ions in the given soil layer.

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

pH	Spearman correlation coefficient	p-value	Direction of the relationship	Power of the relationship
in H ₂ O	0.301	0.006	positive	average
in KCl	0.384	<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 the layer of 20-40 cm (Table 7) as well as between the organic matter content influenced the vegetation contamination with heavy metals and the higher accumulation of the elements in the soil material than in the plant material.

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

pH	Spearman correlation coefficient	p-value	Direction of the relationship	Power of the relationship
in H ₂ O	0.35	0.001	positive	average
in KCl	0.458	<0.001	positive	average

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

Heavy metal	Spearman correlation coefficient	p-value	Direction of the relationship	Power of the relationship
Pb	0.376	<0.001	positive	average

The presented relationships indicate the existence of high impact of organic matter content on the soil pH (Wiater 2008, Kwiatkowska-Malina and Maciejewska 2009, Józefowska 2009), and thereby on the immobilization of heavy metals in the soil layers concerned, on precipitation of sparingly accessible metal ions to plants, on limiting their bioavailability for plants, on obstruction of the transport of metals from the soil environment to the above ground parts of plants and thereby on reducing the fitoavailability of ions of the elements.

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

Heavy metal	Spearman correlation coefficient	p-value	Direction of the relationship	Power of the relationship
Pb	0.535	<0.001	positive	strong

CONCLUSIONS

The research results obtained allowed to put forward the following conclusions:

1. Considering the study results of the mean content of lead in the soil for the municipality of Trzebinia, it must be stated that they exceeded the permissible concentrations of the element according to national regulations (Journal of Laws 2002) for agricultural lands, both at the depth

- of 0-20cm and of 20-40cm. The claim that the soil of the municipality is contaminated with the element is eligible.
2. The research carried out on fallow lands in the municipality of Trzebinia showed the positive direction of the relationship between the lead content in the soil layer of 0-20cm and the content of the metal in plants.
 3. The obtained results of soil contamination with lead indicate its connection with the industrial, agricultural, mining and processing of local raw materials deposits activities carried out in the past in the rural administrative units of the municipality.
 4. The obtained results of the lead content in the plant material did not exceed the permissible content of the element in animal feed proposed by IUNG (Kabata-Pendias *et al.* 1993). It is therefore concluded that vegetation of fallow lands of the municipality of Trzebinia can be used as animal feed for animals.
 5. The pH of the soil significantly determined the content of heavy metals in the study soils. It must be assumed that the high values of soil factors, especially pH and organic matter, reduced the transport of metals, especially cadmium and lead from the soil environment to the plants.
 6. The measured contents of heavy metals in plant material do not constitute an unequivocal reflection of the level of soil contamination with heavy metals, however, they can serve as a supplement to the traditional analysis of soil samples.

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