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Soil Bioavailability of Cadmium, Lead, and Zinc in the Areas of Zn-Pb Ore Mining and Processing (Bukowno, Olkusz)

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ABSTRACT

The study was performed to determine the bioavailable amounts of cadmium, lead, and zinc in the soils contaminated over the years of Zn-Pb ore mining and processing near Olkusz, Poland, and to identify the environmental risk (RAC) associated with the occurrence of the most mobile forms of these metals in the soil. The authors analyzed the topsoil samples for the basic physical and chemical parameters, as well as for total metal content (by *aqua regia* extraction), and for percentage of 1 M HCl^- and 1 M NH_4NO_3 – extractable fractions. The results were compared with the content of these metals in a common grass species, *Agrostis capillaris*. In the study region, the Cd, Pb, and Zn contents were (respectively, in $mg \cdot kg^{-1}$): 0.5–33.5, 2–529, and 4–7877. This means that in more than 24%, 30%, and 38% of samples, respectively, the metal content exceeded the limits defined by the Polish Environment Minister's Regulation of September 9, 2002, with nearly 24% of soil samples contaminated by all three metals. On the basis of the Environment Minister's Regulation of September 1, 2016, which is currently in force, and using the allowed limits for subgroup IV (industrial land), set at 15 $mg \cdot kg^{-1}$ for Cd, 600 $mg \cdot kg^{-1}$ for Pb, and 2000 $mg \cdot kg^{-1}$ for Zn, the analysis also found the excessive metal content in a considerable percentage of the topsoil samples (33%, 13%, and 38%, respectively). The content of the studied elements in a common grass species, *Agrostis capillaris*, was significantly higher than the so-called natural content. A strict association was found between the total Cd, Pb, and Zn content, and the potentially available 1 M HCl – extractable fraction. The environmental risk presented by the content of mobile Cd, Pb, and Zn forms, assessed in all the studied soil samples using Risk Assessment Codes (RAC), demonstrates very high environmental risk associated with Cd, high environmental risk connected with Zn, and moderate environmental risk related to Pb.

Keywords: zinc, lead, cadmium, bioavailability, bioaccessibility, soil, *Agrostis capillaris*, Bukowno.

INTRODUCTION

Bioavailability (understood as *phytoavailability*) of elements in the soil reflects the extent to which an element present in a potential source of contamination (in this case – in the soil) can enter into a plant organism or be absorbed by it (Newman, Jagoe, 1994). As reported by Migaszewski and Gałuszka (2016), bioavailability is a product of an element's geoavailability, physical dispersion, and chemical mobility, as well as the organism's exposure, biological characteristics, and individual sensitivity. Major factors affecting element absorption by plants include: the total content of potentially absorbable elements in the soil, the concentration and proportions of elements in soil water, movement of elements from the solid to the liquid phase, and subsequent uptake of elements by the roots and transport to the surface plant parts (Kicińska, Gruszecka-Kosowska 2016). The chemical composition of plants differs depending on their phase of growth, which affects the processes of element uptake from the soil or rock by the roots, and element and energy exchange with the atmosphere by the surface parts. Excessive amounts of elements, both those required for the plant growth and development (bioelements) and those with no fundamental metabolic role, may adversely affect the physiological processes, resulting e.g. in the changes in cytoplasmic membrane permeability (Larcher 2003). The micro- and macroelement uptake is also affected by the physical and chemical parameters of the soil, including: pH; structure and granularity; type and content of the colloidal fraction, mainly comprising Fe, Mn, and Al oxides and hydroxides; organic matter content; and content and characteristics of loamy minerals (Kicińska 2018, Kicińska, Bożęcki 2018). Soil microorganisms also play a significant role in element uptake from the soil, typically increasing element phytoavailability.

Researchers (Cachada et al. 2014) increasingly highlight the distinction between bioaccessibility and bioavailability. Bioaccessibility depends on environmental factors, including soil properties, while bioavailability depends on the characteristics of living organisms (ISO 17402, 2008). Bioaccessibility is determined using chemical methods, whereas bioavailability is determined in biological tests. The operationally defined bioavailable or bioaccessible fraction of metals is identified by extraction using chelating agent solutions (e.g. EDTA, DTPA) (Kicińska 2011) or 1 M solutions of hydrochloric acid or ammonium nitrate (Karczewska, Kabała 2010). Identifying the amounts of metals that are bioaccessible to living organisms, especially in heavily contaminated land, is an important area of research.

One example of an area with a high content of trace elements is undoubtedly the Olkusz Ore-Bearing Region (OOB) where Zn-Pb ores occur (Cabała 2009, Kicińska, Gruszecka–Kosowska 2016). Ore-bearing minerals in the OOB are found in ore-bearing dolomites, in two forms – sulfide (as primary minerals: ZnS, PbS, FeS_2) and oxide (as secondary minerals, termed calamines) (Sass-Gustkiewicz 1997). Centuries of mining and processing of Zn-Pb ores, containing galena and smithsonite, among other minerals, caused large areas of soil and crops to become permanently contaminated. The subject has been broadly covered in Polish literature (Kayzer *et al.* 2011; Szarek-Łukaszewska 2009, Gruszczyński *et al.* 1990; Gorlach, Gambuś 1995; Kicińska-Świderska 2004; Trafas *et al.* 2006; Pająk *et al*. 2012; Stefanowicz *et al*. 2014). Multiple publications on the subject focused on determining the total content of metals (Zn, Pb, and Cd in particular), while the research on metal bioavailability remains scarce (Gruszecka-Kosowska, Kicińska 2017). Polish Environment Minister's Regulations of September 9, 2002 (Journal of Laws: Dz.U. 165, 2002) and of September 1, 2016 (Dz.U. 2012, item 1395), of which the latter is currently in force, list heavy metals among substances presenting an environmental risk, and set the maximum allowed limits for the content of 10 of these metals, including Zn, Cd, and Pb, in the topsoil of land in each use category (Regulation, 2016). The present paper reports the findings from a study performed to: (1) determine the total and bioavailable amounts of Cd, Pb, and Zn in soils contaminated over years of Zn-Pb ore mining and processing near Olkusz, Poland, and (2) estimate the environmental risk (RAC) associated with the occurrence of the phytoavailable forms of these metals in the soil. In order to accomplish these objectives, the authors analyzed and compared the metal content in soil and plant samples, collected in 2010 and 2016. The soil samples were collected from the topsoil, corresponding to the "A" horizon. Total metal content was analyzed with wet extraction in *aqua regia*, while the bioavailable fraction was determined by means of extraction in 1 mol·dm^{-3} HCl and 1·mol dm^{-3} NH_4NO_3 solutions. The obtained results were compared to the content of these metals in a grass species commonly occurring in the Olkusz region, *Agrostis capillaris*.

STUDY AREA

For the study, the authors selected the Olkusz Ore-Bearing Region, an area of approx. 1200 km^2, located to the north-west of Kraków, where Zn-Pb ores are found. It is represented on the "Olkusz" 1:25 000 topographic map, with a surface area of 83 km^2 The Zn-Pb ores found in Triassic dolomites have a hydrothermal origin, and the OOB deposit itself is of the Mississippi Valley type (MVT). The MVT deposits have a simple mineral composition, with the polymorphic forms of Zn, Pb, and Fe sulfides. Their complex geological structure is the result, among other factors, of tectonic movements that caused the outcrops of these deposits to become exposed to exogenous factors.

This resulted in the presence of oxidized forms of ores (Cabała 2011), as well as the formation of local geochemical dispersion halos of elements such as Zn, Pb, and Cd in the soils (Sass-Gustkiewicz *et al.* 2001, Trafas *et al.* 1990).

The OOB region has a large diversity of land formations and large amplitude of elevation. The current land formation is dominated by gentle slopes and rather small differences in the relative elevation. Natural land formation has been largely modified by human activity associated with ore mining and processing, which results in the presence of observable heaps, terraces, and pits. Nearly one-third of the OOB area is used for the extraction of filling sand. Agriculture is heavily restricted due to the differences in the production potential of the soil, fragmented land ownership, and relatively high availability of jobs in the industry and services. The soil cover is much diversified due to the diversity of bedrocks, dominated by limestone, dolomites, loesses, sands, and clays. Typologically, the soils in the study are mainly brown earth soils (39%), podsols and luvisols (24%), and rendzina soils (20%). The soil cover predominantly comprises the soils allocated to the land use classes V and VI, with some class IV soils. A large share of agricultural land has been allocated for industrial use or road infrastructure, which additionally restricts direct access to the fields. More than 10% of arable land is uncultivated (Smreczak et al. 2015).

The soil contamination with Zn, Pb, and Cd is mainly caused by the mining and metallurgical industry. The major industrial plant, which emits particulate matter contaminating the soil, is the "Bolesław" Mining and Metallurgical Plant, one of the largest producers of zinc as well as zinc and lead concentrate in Poland. Historically, the plant was also involved in ore mining in the "Bolesław" mine (decommissioned in 1998), the "Olkusz" mine (decommissioned in 2003), and the "Pomorzany" mine (still active). One considerable environmental concern in the area is the subsequent release of large amounts of particulate matter containing heavy metals from poorly secured storage yards, heaps and sedimentation tanks (Kicki 1997; Sroczyński 1997). Other concerns include the contaminant reemissions from uncovered ground and mining byproducts (Dmuchowski *et al.* 2011, Gruszecka-Kosowska, Kicińska 2017).

MATERIAL AND METHODS

The samples (n = 79) for analysis of total heavy metal content and bioavailable fraction content were collected from the topsoil, corresponding to the A horizon. The sampling sites were mainly located on arable land (Figure 1). After air-drying, the samples were thoroughly mixed, homogenized, and dried at 105°C, and subsequently used in the chemical analyses.

Total Cd, Pb, and Zn content in the soil

The total Cd, Pb, and Zn content in the soil was analyzed by extraction in a mixture of concentrated HNO_3 and HCl (65% HNO_3 + 38% HCl, at a 1:3 ratio), with a solid-to-solution ratio of 1:10 (PN-ISO 11466: 2002). The total metal content was determined by ICP-MS, using an Agilent 7500CE device.

Bioavailability of Zn, Pb, and Cd in the soil

The bioavailable fraction of Zn, Pb, and Cd was extracted from the soil using two chemical methods to determine the so-called easily soluble fraction, and the amount available to plants. Metal extraction from the soil samples using a 1 M solution of ammonium nitrate was performed as per Gryschko et al. (2005), and extraction using a 1 M solution of hydrochloric acid was performed in accordance with the ISO 19730:2008 procedure, as described by Pasieczna and Lis (1995).

Testing the content of easily soluble heavy metal forms in the soil by extraction in 1 M ammonium nitrate

In order to determine the amount of easily soluble forms of the elements in the collected soil samples, extraction using 1 M NH_4NO_3 was performed. The amount extracted using this procedure is not equal to the fraction absorbable by plants (Gryschko et al., 2005), but may be considered to be accessible to plants. According to Gryschko et al. (2005), this method of extraction can be used in the environmental studies estimating the risk for the soils contaminated with metals.

Testing the content of potentially available metal forms in the soil by extraction in 1 M hydrochloric acid

The procedure for extracting elements from the soil using a hydrochloric acid solution had

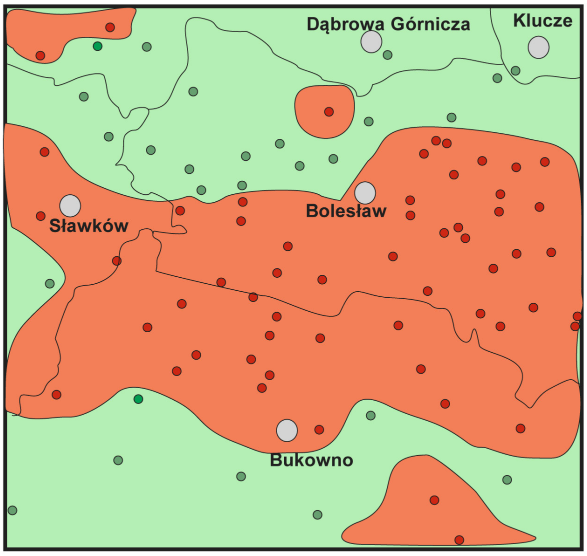

Figure 1. Location of sampling points where (red color) and no (green color) exceeded permissible Cd, Zn and Pb content in the surface soil level, according Regulation of Ministry of Environment (2002).

previously been used in the studies at the National Geology Institute – National Research Institute in order to determine the amount of mobile element forms from contaminants or deposit weathering processes (Lis, Pasieczna 1995). In this procedure, metals are extracted from the soil using a 1 M solution of HCl (HCl/H_2O, 4:1 v/v), with a solid-to-solution ratio of 1:10, and the suspension is then heated at 90°C for 1 hour.

Environmental risk (RAC)

The environmental risk was estimated using the RAC coefficient. It is based on the amount of metals in exchangeable and carbonate-bound forms (Rodríguez *et al*. 2009), and reflects the amount of metal cations with the potential to enter the food chain. Depending on the percentage of the two fractions (exchangeable and carbonate, determined by extraction in 0.11 M CH_3COOH at 22°C for 16 hours), 5 risk levels are identified, from low to very high (Jain 2004; Singh *et al*. 2005).

Total Cd, Pb, and Zn content in grasses

The Cd, Pb, and Zn content in *Agrostis capillaris* grasses was tested in the samples collected in spring of 2016 in an area near Olkusz corresponding to the soil sample collection area. After drying at 60°C, the plant material underwent extraction in a mixture of 65% HNO_3 and 38% H_2O_2 (Kicińska-Świderska 1999). The concentrations of Cd, Pb and Zn in the extracts were determined with ICP-MS using an Elan 6100 system at the accredited AGH UST geo-hydrochemical laboratory in Kraków (certificate no. AB1050), with precision of 10^{-5} mg/dm^3.

Test quality control

During the soil sample analyses, in order to ensure consistent readings and minimize matrix effects, all tests were performed in the presence of ^{45}Sc, ^{89}Y, and ^{159}Tb, used as an internal control, in the amount of 1 mg·dm^{-3}, introduced simultaneously with the sample. Quality control was performed both for the sample preparation process, and for the operating parameters of the device (ICP-MS). For each sample series, certified reference material BCR-701 or the laboratory reference material was analyzed. Additionally, the accuracy of the chemical test results was verified by means of the double sample analysis (approx. 6% of all samples). For each series, a blank sample and a reagent blank were used as well.

The soil contamination in the Olkusz area was determined by comparing the total metal content found in the soil samples against the maximum allowed limits specified by the Environment Minister's Regulation of September 9, 2002, which was in force at the time of soil sample collection, and the currently applicable Environment Minister's Regulation of September 1, 2016.

RESULTS AND DISCUSSION

Total Cd, Pb, and Zn content in the soil

The Cd, Pb, and Zn levels found in the soil of the OOB region were as follows (respectively, in mg·kg^{-1}): 0.5–33.5, 5–529, and 22–7877 (Table 1). This means that in 24–38% of all samples (depending on the specific element), the metal content exceeded the limits defined by the Polish Environment Minister's Regulation of September 9, 2002 (Figure 1), with nearly 24% of soils contaminated by cadmium, lead, and zinc simultaneously.

On the basis of the Environment Minister's Regulation of September 1, 2016, which is currently in force, and using the allowed limits for subgroup II (arable land, orchards, permanent meadows and pastures, ponds, ditches, garden plots), set at 2, 250, and 300 mg·kg^{-1}, respectively, for Cd, Pb, and Zn, the analysis showed that the limits for this land category were exceeded in 33% of samples with regard to Cd, 13% for Pb, and 38% for Zn.

The present findings are consistent with the data published by other authors (Trafas *et al.* 1990, Kicińska-Świderska 1999, Sass-Gustkiewicz et al. 2001, Cabała 2009, Szarek-Łukaszewska 2009, Pająk et al. 2015). Cabała (2009), studying areas with a history of ore mining and processing in Bukowo, Sławków, and Strzemieszyce, found soil Cd, Pb, and Zn content reaching (in mg·kg^{-1}): 153, 16,659, and 27,147. According to Szarek-Łukaszewska (2009), the Zn content in former mine sites and wild vegetation areas within the OOB region reaches up to 7.75%. Similarly high metal levels were also reported by the research team led by Sass-Gustkiewicz (2001), who found soil levels of Zn locally reaching up to 10% by weight, Pb levels exceeding 1%, and Cd levels up to 193 mg·kg^{-1}.

Bioavailable Cd, Pb, and Zn forms in OOB area soils

The amounts of bioavailable metal forms extracted using 1 M ammonium nitrate were: between <0.01 and 6.3 mg/kg for Cd, <0.1–65.5 mg/kg for Pb, and 0.6–634 mg/kg for Zn (Table 2). Conversion of the results into the percentage share of these forms in the total content of each metal (for 79 samples) shows that this share is above 47% for Cd, 19% for Pb, and slightly above 33% for Zn. Considerably larger amounts of bioavailable elements were extracted from the OOB soils using 1 M hydrochloric acid. The content of the bioavailable fraction of Cd in soils from the Bukowno area ranged between 0.1 and 27.7 mg/kg; for Pb, the values were between 1.3 and nearly 485 mg/kg; and for Zn, between 1 and 7599 mg/kg – all values were multiple times higher than those found using ammonium nitrate extraction. For all samples, the fraction accounted for nearly 73% of total Cd content, over 90% for Pb, and 89% for Zn.

A strict association was found between the total content of the analyzed heavy metals, and the potentially available, 1 M HCl – extractable fraction. The calculated linear correlation coefficients (at $\alpha \leq 0.05$) were 0.99 for Cd, Pb, and Zn (Figure 2). No such association was found for the 1 M NH_4NO_3 – extractable fraction.

The above-mentioned findings indicate a large variation in results depending on the particular method that is used to extract the bioavailable fraction, which may consequently affect the estimation of environmental risk, i.e. exposure of living organisms to the metals, and potential for movement of these metals into deeper soil layers.

Table 1. Statistical evaluation of the total content of Cd, Pb and Zn in the upper layer of soils from the Olkusz region

Element	Limit* (a/b)	Min. – Max.	Median	Average± SD	Sample above upper limit (in %), according: a/b
	(mg·kg^{-1})				
Cd	4.0/2.0	0.5 – 33.5	0.5	2.9±4.9	24/33
Pb	100/250	2.0 – 529.0	30.0	90.1±116.6	30/13
Zn	300/300	4.0 – 7877.0	124.0	499.7±1043.6	38/38

* limit value for agricultural soils according to:
a – Regulation of Minister of Environment (2002),
b – Regulation of Minister of Environment (2016).

Table 2. The contents of Cd, Pb and Zn bioaccessible forms in soil from Olkusz area

Element	Metal bioavailable forms			
	soluble in 1M NH_4NO_3	soluble in1 M HCl	soluble in 1M NH_4NO_3	soluble in 1 M HCl
	min. – max. [mg·kg^{-1}]		average [as % of total content]	
Cd	<0.01–6.3	0.1–27.7	47	73
Pb	<0.1–65.5	1.3–485.1	19	90
Zn	0.6–634	1.0–7599	33	89

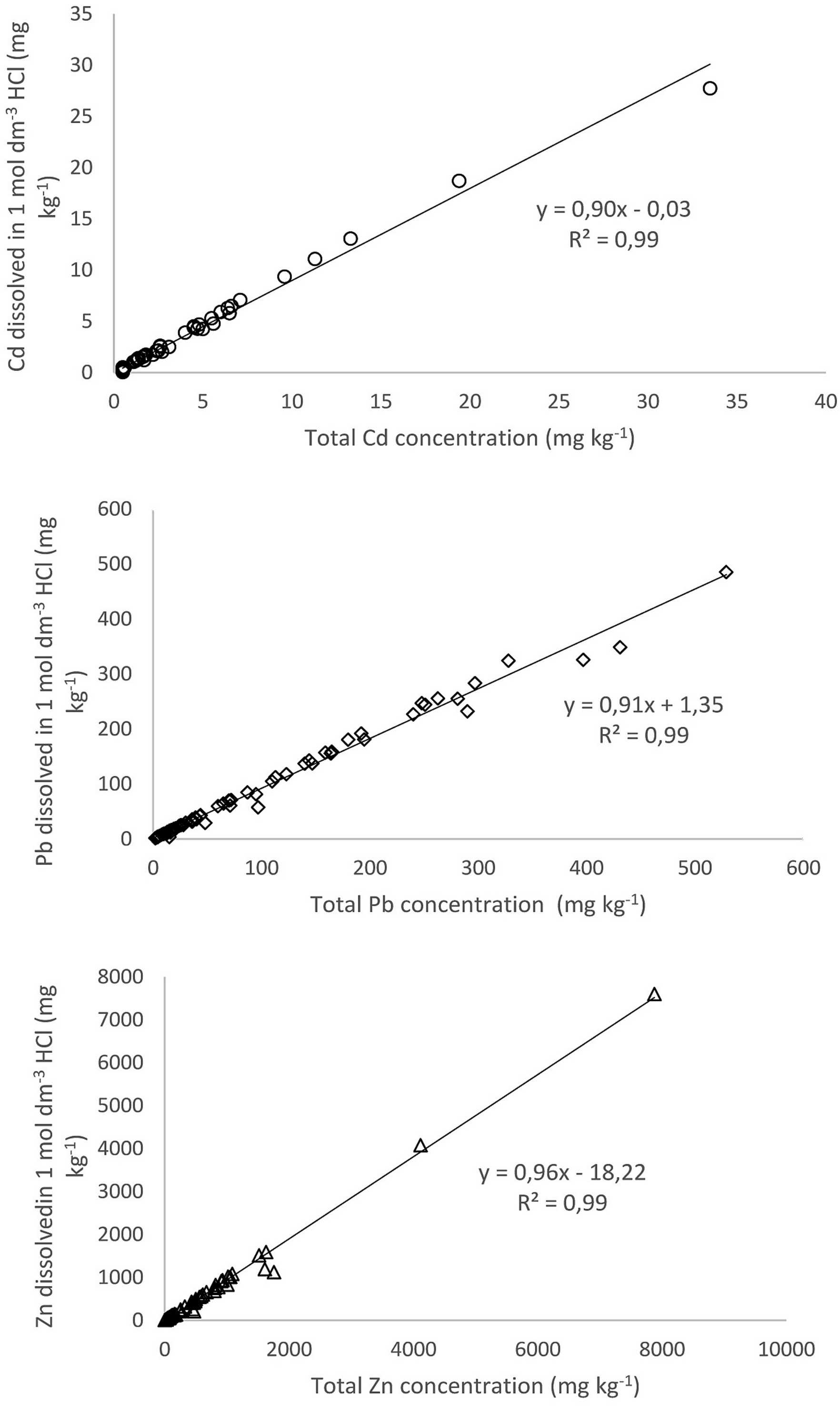

Figure 2. Relationship between total content of Cd, Pb and Zn and their bioaccessible fractions extracted with 1 mol dm^{-3} HCl

A comparison of the present results with those obtained almost 20 years ago by Kicińska-Świderska (1999) and those found in 2014 by Gruszecka-Kosowska and Kicińska (2017) demonstrated that the share of bioavailable forms of Zn has significantly increased in recent years (by up to 40%).

Environmental risk (RAC)

The environmental risk presented by the content of exchangeable and carbonate-bound Cd, Pb, and Zn forms (Ure et al. 1993), assessed in all the studied soil samples using Risk Assessment Codes (RAC), demonstrates very high en-

Tab. 3. Risk Assessment Code index for Surface soil sample form Olkusz area

Element	Form extracted by 0.11 M CH_3COOH [$mg \cdot kg^{-1}$]	% of total content	RAC
Cd	0.1–6.2	22–93	Very high risk
Pb	0.4–75.4	7–28	Medium risk
Zn	1.0–271.5	25–51	High risk

no risk <1% metal concentration in carbonate and exchangeable fractions (%)
low risk 1–10%
medium risk 11–30%
high risk 31–50%
very high risk >50%

vironmental risk associated with Cd, high environmental risk connected with Zn, and moderate environmental risk related to Pb (Table 3). This classification was due to the fact that the amount of Cd, Pb, and Zn forms extracted using 0.11 M CH_3COOH reached up to 93% of the total content for Cd, 28% for Pb, and 51% for Zn.

Cd, Pb, and Zn content in grasses

The content of Cd, Pb, and Zn found in the surface parts of the common bent (*Agrostis capillaris*) was as follows (respectively, in $mg \cdot kg^{-1}$): 0.2–9.8, 7–284, and 95–1574. The highest concentrations of Cd (9.8 $mg \cdot kg^{-1}$) and Zn (1574 $mg \cdot kg^{-1}$) were found in the immediate vicinity of the "Bolesław" industrial plant in Bukowno, while the highest Pb levels (284 $mg \cdot kg^{-1}$) were found in the grass near the former "Olkusz" mine. Over the past 20 years, the Cd levels in the species decreased by as much as 87%, and the Zn levels – by 52%. Compared to the data from 1994, the amount of the element increased by nearly 6% (Kicińska-Świderska 1999, Kicińska, Gruszecka-Kosowska 2016). The levels of these elements in the considered common grass species significantly exceeded the so-called natural content (Kabata-Pendias, Pendias 1999), established for Poland at 0.05–0.6, 0.4–4.5, and 12–72, respectively, for Cd, Pb, and Zn. In most habitats, the identified levels also exceeded the concentrations considered toxic, i.e. 5–30 $mg \cdot kg^{-1}$ for Cd, 30–300 for Pb, and 100–400 for Zn (Kabata-Pendias, Pendias 1999).

Despite these high metal levels, no macroscopic changes were found in the plant appearance, and their development and the appearance of surface parts were normal *in situ*. This indicates that the species has developed and maintained a tolerance to high concentrations of these metals. It can also suggest that some of the metals identified were deposited on the plants as particles were carried by wind from unsecured slag heaps and waste tanks.

CONCLUSION

The legal restrictions and regulations introduced over the past 20 years to enhance environment protection significantly contributed to an improvement of environmental conditions, e.g. in the vicinity of the mining and metallurgical industrial plant near Olkusz, Poland. These changes resulted in diminished concentration of pollutants in the soil. Nonetheless, the total content of heavy metals in the region, especially Cd, Pb, and Zn, remains high. The excessive content of easily soluble forms of Cd, Pb, and Zn, found in some of the analyzed samples, demonstrates a risk of their penetration not only into groundwater, but also into plants, including grasses such as the common bent, consumed by multiple animal species. The present study demonstrated that the amount of bioavailable metal forms found depends on the extraction method used, which must be kept in mind during any assessment of risk for metal-contaminated areas.

Furthermore, "new" sources of metal emissions were found in the Olkusz region, namely the unsecured or poorly secured waste tanks and slag heaps.

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