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AVAILABILITY OF HEAVY METALS IN SOIL OF DĄBROWA GÓRNICZA TO PLANTS

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DOSTĘPNOŚĆ DLA ROŚLIN METALI CIĘŻKICH ZAWARTYCH W GLEBACH NA TERENIE GMINY DĄBROWA GÓRNICZA

Gleby na terenie gminy Dąbrowa Górnicza charakteryzują się podwyższoną zawartością metali ciężkich. Najwyższe zawartości ołowiu przekraczają 650 mg/kg, kadmu 15 mg/kg i cynku 1000 mg/kg gleby. Próbki gleby z wybranych punktów podano analizie specjacyjnej według Tessiera w modyfikacji Kerstena i Forstnera. Z przeprowadzonych badań wynika, że na terenie Trzebiesławic stwierdzono najwyższe zawartości tych metali. Występują tutaj w formie silnie związanej i w znacznej części są związane ze skałami wapiennymi. Najwięcej form łatwo przyswajalnych występuje na terenie miasta Dąbrowa Górnicza. Najprawdopodobniej większość metali ciężkich w glebie pochodzi z zanieczyszczeń, które były emitowane przez przemysł głównie hutniczy.

W rejonie Błędowa występują głównie gleby piaszczyste, które charakteryzują się niską zawartością omawianych metali. Słabe własności sorpcyjne tych gleb sprawiają, że stosunkowo łatwo są ekstrahowane. Spośród badanych gleb na terenie Łęki stwierdzono silne związanie tych metali. Na szczególną uwagę zasługuje występowanie kadmu, który wbudowany jest w sieć krystaliczną minerałów.

Summary

Elevated content of heavy metals in soils is characteristic of the Dąbrowa Górnicza region. The highest concentrations of lead, cadmium and zinc exceed here 650, 15, and 1000 mg/kg of soil, respectively.

Samples of soil from selected sites underwent the speciation analysis with the use of the Tessier method, modified according to Kersten and Forstner. Results of the investigations proved the highest concentrations of these metals in the area of Trzebiesławice. They occur here in the strongly bound forms and, mainly, their occurrence is related to presence of limestone rocks. The greatest amounts of these metals in easily assimilable to plant forms occur within the area of the town of Dąbrowa Górnicza. The most probable source of most of these heavy metals in soils are here contaminants emitted by the industry, mainly by the metallurgy.

In the vicinity of the town of Błędów, mainly sandy soils occur, characteristic of which is low content of considered metals. Weak sorption capacities of these soils account for relatively good extractability of the three metals. In soils from the Łęka area, strong binding of these metals was confirmed. Occurrence of cadmium should be of special attention because this metal occurs as built in the crystal lattice of minerals.

INTRODUCTION

Dąbrowa Górnicza is a town of above one hundred-year history of industry development with predominance of metallurgy. Here, for many years, soils in almost whole area have been contaminated with wastes coming from numerous plants of any kind. The content of heavy metals in soil of greater part of the area exceeds admissible values but even their elevated concentrations not always mean their assimilability to plants. Their releasing from solid phase to soil solution, i.e. assuming forms assimilable to plants, depends on various soil properties such as pH value, content of organic matter, sorption capacity, grain composition, and on chemical form of occurrence of these metals [1–3, 5, 7, 8, 10].

Partly these metals occur as bound in minerals. In some soils, zinc is present in silicates: $ZnSiO_3$ and $ZnSiO_4$. Also, zinc ions can replace part of Fe^{2+} and Mg^{2+} ions in structure of such minerals as augite, hornblende or biotite.

From among three metals: cadmium, zinc and lead, cadmium is the most mobile element. Increase of soil acidity causes increase of this metal solubility. Instead, elevated pH causes formation of its weakly soluble compounds, e.g. carbonates. Adsorption of this metal on the soil colloids plays also a significant role in its availability to plants.

Studies on bioassimilation of heavy metals from soils have been carried out for years in various centers. The ability of plants to assimilate metals depends on several factors affecting metal binding strength, such as, for instance:

- acidification of soil solution,
- presence of buffering salts in solutions,
- presence of non buffering salts in solution,
- chelate formation in soil solutions.

By using different extractants, applied at consecutive steps of a serial extraction, one can obtain information on mobility of heavy metals. The extraction steps approximately show the gradual availability of forms of metals to plants: from the most available, extracted at the first step with water, to almost not assimilable, extracted at the last step with 1M nitric acid at high temperature.

The objective of the research was to determine the ability of heavy metals (zinc, cadmium and lead) in soils of the town of Dąbrowa Górnicza to pass to solution. The seven step serial extraction of these metals – starting from the weakest at the first stage (with distillated water) and finishing with the strongest one at the seventh stage (with nitric acid) – was applied.

METHODS

In the agricultural area of 5098 ha soils were sampled from the 0–20 cm layer of ground.

For the purpose of determination of the metals availability to plants, the speciation analysis of soil from selected sites of the region was performed.

The seven-step extraction of metals was applied to each sample [6, 9]:

0 – with distilled water,
I – with 1 M ammonium acetate,
II – with 1 M sodium acetate and 1 M acetate acid, pH 5,

III – with 0.1 M hydroxyloamine and hydrochloric acid and 0.001 M nitric acid, pH 2,
IV – with 0.1 M oxalate acid and 0.1 M ammonium oxalate, pH 3,
V – with hydrogen peroxide solution acidified with nitric acid to pH 2 and with 1 M ammonium oxalate added,
VI – with 1 M nitric acid at temperature 130°C.

The metals were determined by using AAS Perkins-Elmer apparatus.

For speciation analysis, different kinds of soils were selected: black degradaded soil, brown limestone soil, brown lixivated soil and pseudopodsol.

RESULTS AND DISCUSSION

The soil of Dąbrowa Górnicza region shows high heavy metals content. Zinc occurs in the highest concentrations – above 1000 mg/kg of this metal has been detected in Tucznawa and Trzebiesławice regions, and also in vicinity of the border with the town of Sławków (Fig. 1). Also in soils of Ząbkowice region above 1000 mg/kg of Zn was found. Toward east, the content of this element in soil decreases: the soil of Błędów area contains less than 100 mg/kg of Zn [11].

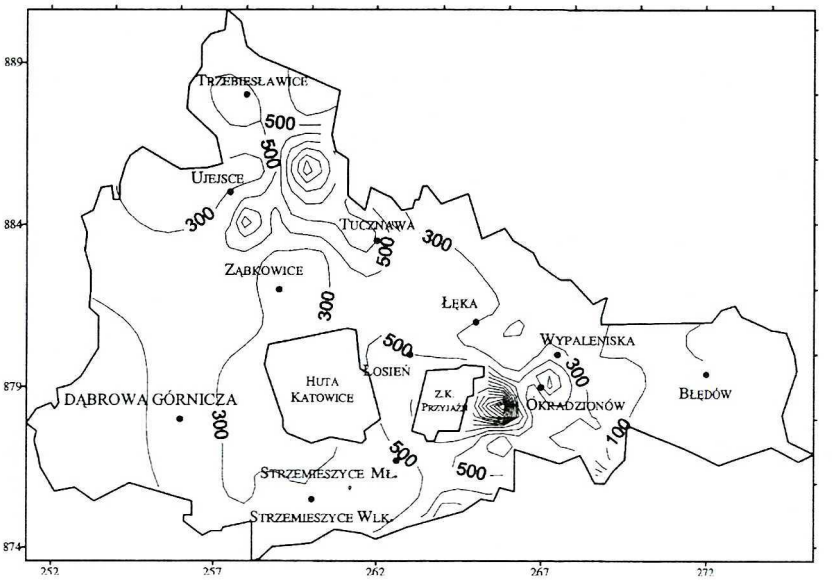

Figure 1. Content of zinc in soil

Average content of cadmium in soil in Poland does not exceed 1–2 mg/kg but soils near cadmium ore beds can contain even 300 mg/kg of Cd. In Dąbrowa Górnicza, the content of Cd is elevated. In the western part of the area, cadmium concentrations in soil exceed 8 mg/kg. In Tucznawa region they reached similar values. The highest contents of cadmium were in Trzebiesławice region: over 15 mg/kg. Only Błędów soils contained less than 2 mg/kg of Cd (Fig. 2).

The total content of lead in natural soils is between 2 and 200 mg/kg. Lead concentrations in soil of Dąbrowa Górnicza differed from this content considerably.

In western part of the area very high level of lead was observed – more than 350 mg/kg. Similarly to cadmium in Tucznawa and Trzebiesławice regions, here the soil contained over 650 mg/kg of lead (Fig. 3). The lowest content of lead, less than 50 mg/kg, was detectected in the eastern part of Okradzionów and in Błędów.

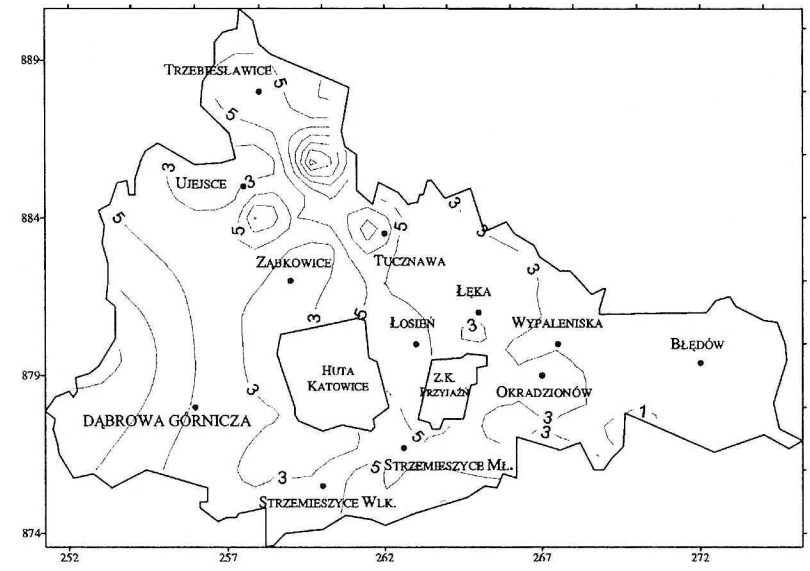

Figure 2. Content of cadmium in soil

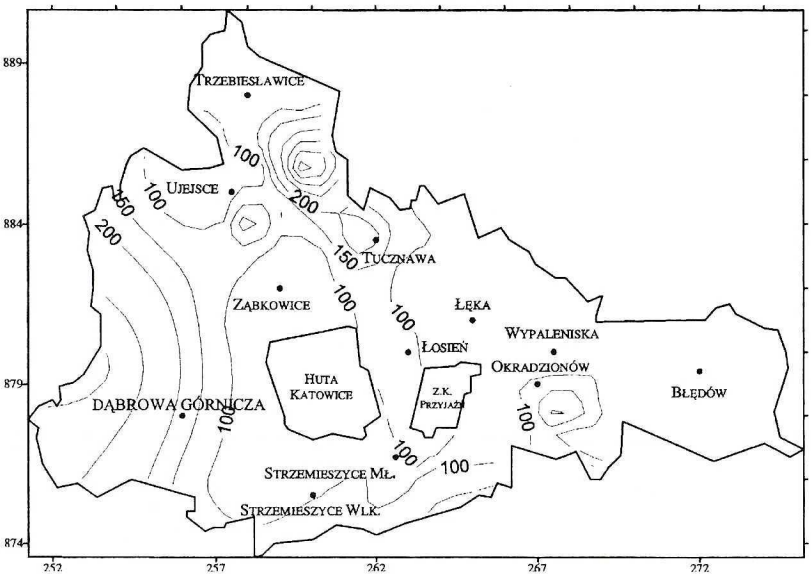

Figure 3. Content of lead in soil

The high contents of heavy metals in soils show potential hazard to growing plants and to consumers. In soils these metals occur in various minerals and in various chemical compounds, differing with their water solubility, and, consequently, also with availability of their soluble salts to plants.

The results proved existence of different chemical forms of zinc, cadmium and lead in the investigated area. The lowest amounts of zinc were found in Błędów and in northern part of Łęka environs. Most of metals in soil occur here in weakly soluble form (extractable at II through IV steps of the extraction, Tab. 1, Fig. 4). Similar regularity was observed in Trzebiesławice area (also II through IV steps). Soils in Błędów and Łęka represented degraded black and brown soils, limestone soils were in Tucznawa. In these soils metals occur as very hard to dissolve carbonates. Only extractions at pH equal to 3 or 2 cause passing these metals to solution. In the western part of the region, situation is different because easier to dissolve forms of the metals were detected there. Of the studied metals, cadmium was the element deciding on the soil pollution in Dąbrowa Górnicza.

The results show that with regard to solubility of the metals two regions can be distinguished: one, Błędów and the western part of the town of Dąbrowa Górnicza, from the soils of where most of metals are extractable by using 0.1 M oxalate and 0.1 M ammonium oxalate mixture, and the second, Łęka and Trzebiesławice areas, where cadmium is present in weakly soluble forms – more than 90% of it could be extracted with hot nitric acid only (Fig. 5). Similar situation occurs for limestone soils, from which 92% of metals were to extract in nitric acid solutions only, what means poor availability of the heavy metals in these soils to plants. Lead occurred in much higher amounts, as extractable, at I and II steps of the extraction.

In the Łęka area, where brown soils prevail higher amounts of lead, extractable at I and II steps, occur. Only small part is of worse solubility. In contaminated soils, affected by human activity, lead occurs in easier soluble forms. We can, with high probability, determine the origin of lead present in soil of the western part of Dąbrowa Górnicza.

The reaction (pH) of soil solution has the highest influence on the three metals solubility in this solution [4]. In soils with high pH, the amount of each released heavy metal increases with the increasing number of an extraction step.

The analysis of soils from the vicinity of zinc and lead smelter showed that the extraction of 1 mg/kg with acetate ammonium solution was 3.4% of the total content of lead, and 9.3% of total content of zinc and cadmium in these soils [5].

The applied extraction of heavy metals, in spite of its seven stages, does not guarantee full efficacy. In the same soil, particular heavy metals display different susceptibility to mobilization. Extraction of the studied metals from soil with HNO_3 resulted in passing of 100% of lead, 86% of zinc and 70% of cadmium to solution [8]. Among the used extractants, only distilled water had lower extraction strength than roots of plants. It can be observed that other reagents remove more metals from soils than plants. In general, water-soluble metals are available to plants, but when the metals are soluble in stronger extractants they, in soil, can become available to plants too, for example in the case of soil higher acidification [1, 4].

Table 1. Exraction of cadmium, lead and zinc from soil

Metal	Locality	Steps extracion						
		0^0	I^0	II^0	III^0	IV^0	V^0	VI^0
		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Zn	Błędów	0.85	12.00	27.88	10.20	30.32	8.024	45.4
	Trzebiesławice	<0.05	8.142	31.52	16.06	42.35	90.72	34.155
	Łęka	<0.05	2.288	21.74	9.355	47.00	7.22	62.9
	Dąbrowa Górnicza	1.004	23.82	81.00	42.9	102.5	64.36	154.0
Cd	Błędów	<0.05	0.744	0.668	<0.25	0.27	0.294	0.51
	Trzebiesławice	<0.05	0.84	0.808	<0.25	0.27	20.54	5.525
	Łęka	<0.05	0.606	0.808	<0.25	0.27	0.47	25.25
	Dąbrowa Górnicza	<0.05	2.58	3.4	0.62	1.19	0.482	1.04
Pb	Błędów	<0.05	2.41	9.206	<0.25	15.41	2.12	8.01
	Trzebiesławice	<0.05	1.646	11.216	3.13	22.37	2.024	10.07
	Łęka	<0.05	<0.1	4.594	<0.25	40.35	1.004	25.035
	Dąbrowa Górnicza	<0.05	13.33	82.04	6.565	243.25	10.16	43.5

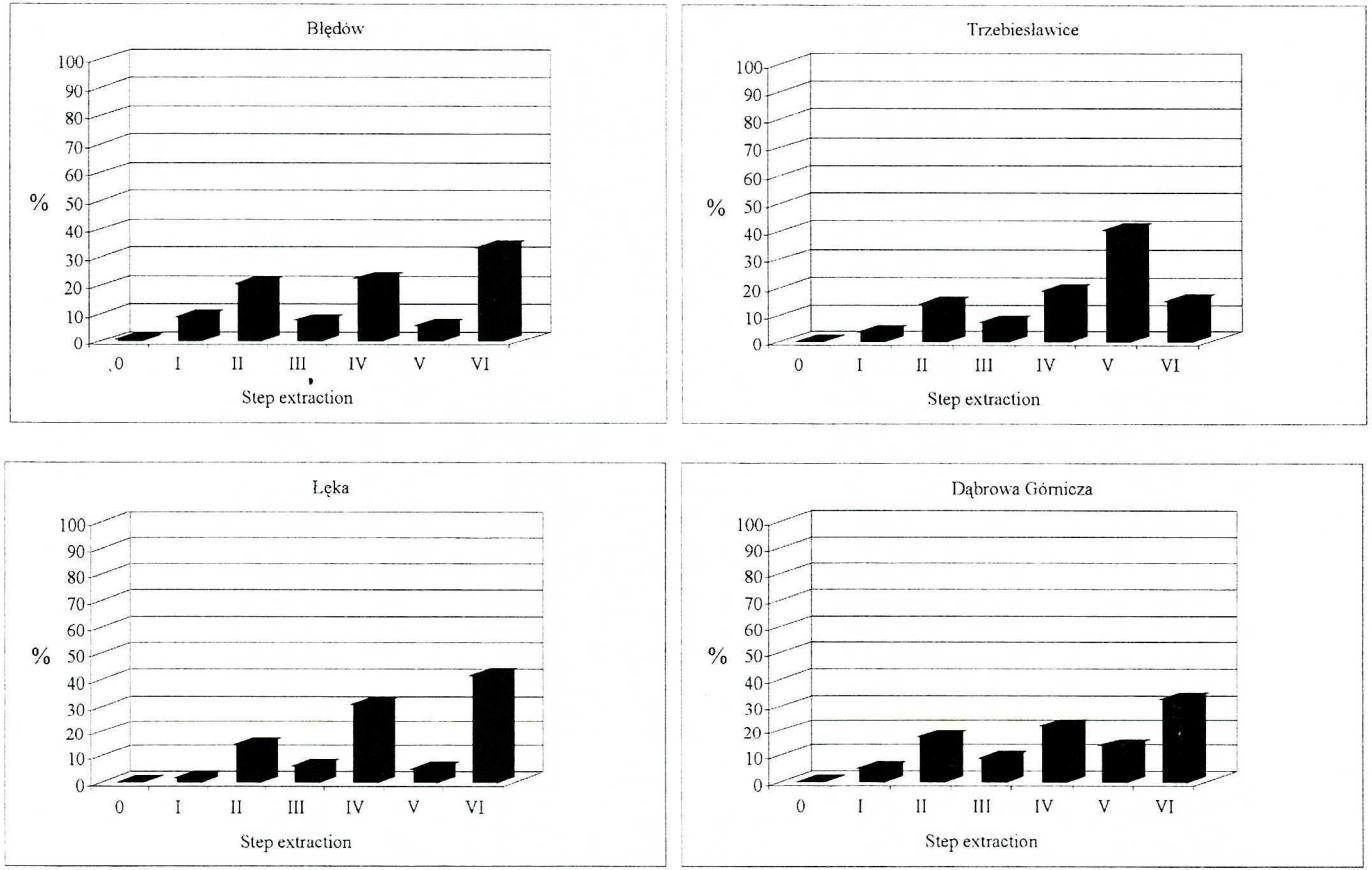

Figure 4. Zinc content in the extracts

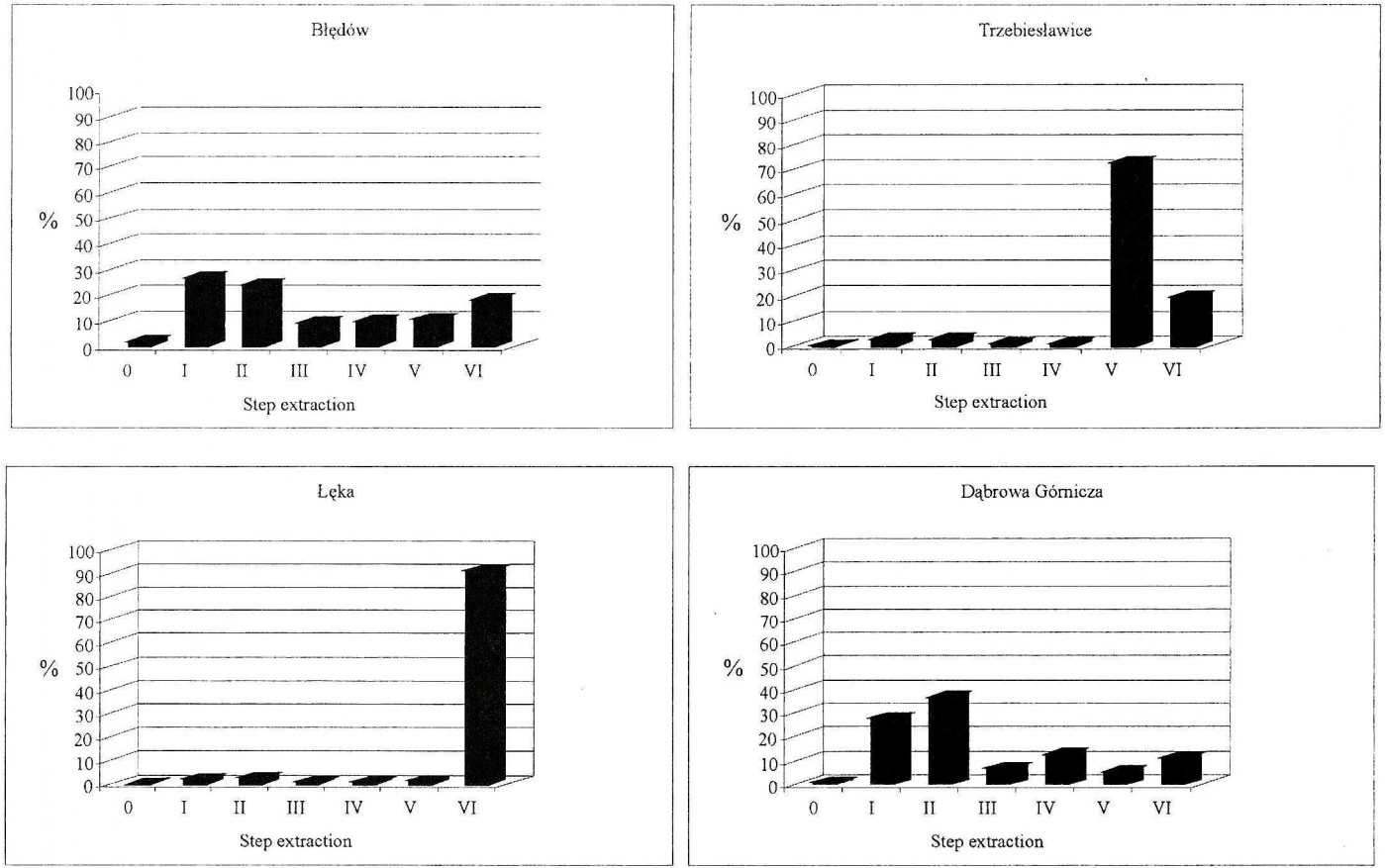

Figure 5. Cadmium content in the extracts

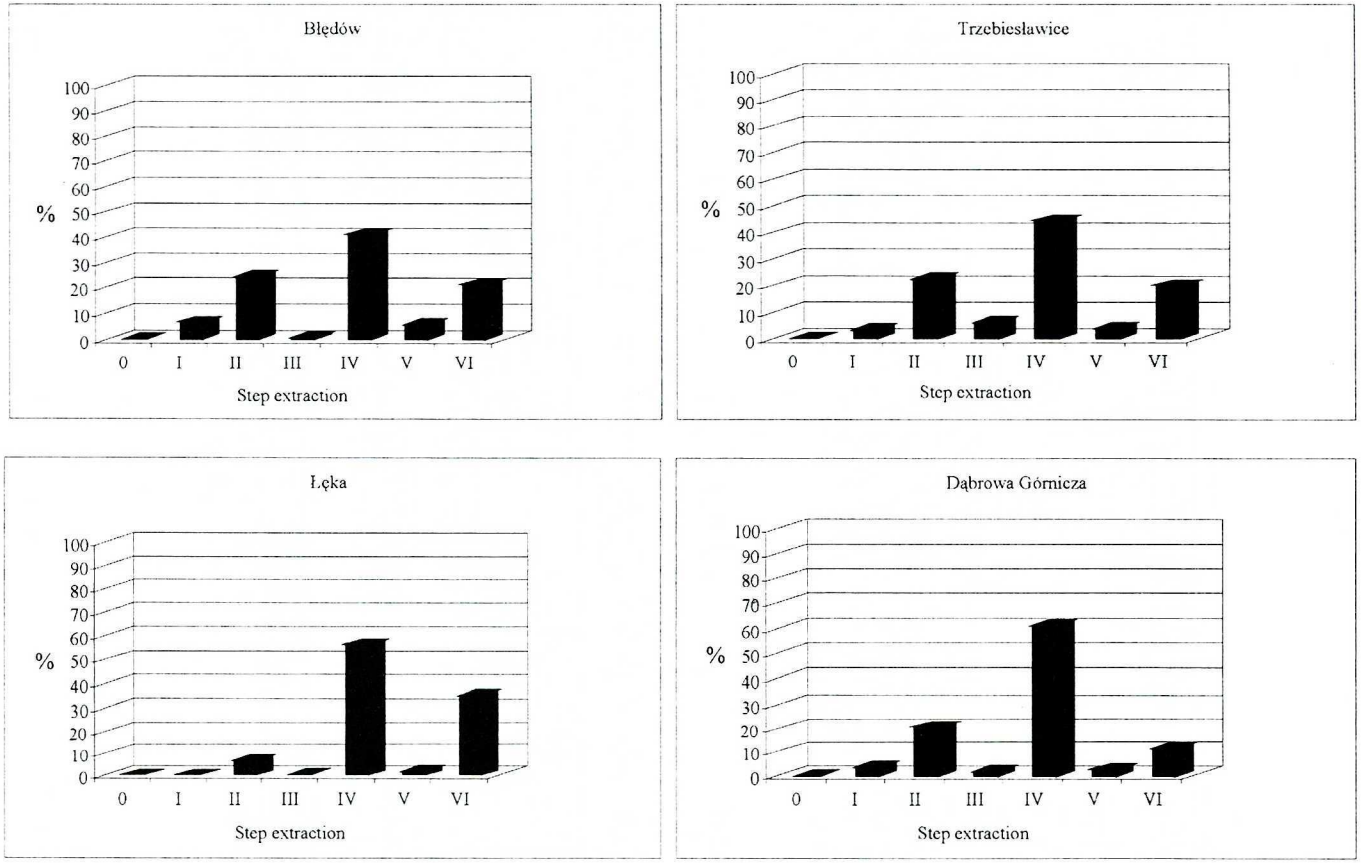

Figure 6. Lead content in the extracts

REFFERENCES

[1] Czułdzijan Ch., S. Karweta, Z. Facek: *Tjażełyje mietałły w poczwach i rastiejach*, Ekołogiczieskaja Kooperacja, Bratisława 1988.

[2] Gambuś F.: *Metale ciężkie w wierzchniej warstwie gleb i w roślinach regionu krakowskiego*, Zesz. Nauk AR w Krakowie, Rozprawa habilitacyjna, nr 176 (1993).

[3] Gambuś F., M. Rak: *Wpływ własności gleby na rozpuszczalność związku kadmu*, Zesz. Probl. Nauk Rol., **472**, 251–257 (2000).

[4] Jones A.K., M.S. Johnson, R.M. Bell: *The movement of metals in reclaimned metal contaminated land*, Dep. of the Environment, Report on the Working Party on The Disposal of Sewage Sludge to Land, Standing Technical Committee Report N 5, London 1977.

[5] Karweta S.: *Oddziaływanie na rośliny i gleby niektórych pierwiastków toksycznych (cynku i ołowiu) emitowanych do powietrza atmosferycznego przez hutnictwo metali nieżelaznych*, Praca doktorska AR Kraków 1974

[6] Kersten M., U. Forstner: *Assessment of metal mobility in dredged material and mine waste by water chemistry and soil speciation*, Chemistry and Biology of Solid Waste, Dredged Material and Mine Tailings. Springer-Verlag, Berlin Heidelberg, 214–237 (1988).

[7] Miechówka A., J. Niemyska-Łuszczuk, R. Mazurek, K. Sołek-Podwika: *Wpływ odczynu gleby na zawartość Zn, Pb, Ni i Cd w roślinach wybranych użytków zielonych Pogórza Wielickiego i Podhala*, Zesz. Probl. Nauk Rol., **456**, 421–426 (1995).

[8] Niemyska-Łuszczuk J.: *Wpływ składu granulometrycznego i odczynu na zawartość przyswajalnych form metali ciężkich*, Zesz. Probl. Nauk Rol., **418**, 459–464 (1995).

[9] Tessier A., P.G.C. Campbell, M. Bisson: *Trace Metal Speciation in Yamashe and St. Francois River (Quebec)*, Canadian Journal of Earth Sciences, **17** 128–139 (1980).

[10] Tułupow P.E., L.I. Żurawlewa: *Ispozowanije kisłowych wytjażesk dla opriedielenija nałowogosookierżanija tjażełych mietałłow w poczwach*, Trudy I-ła eksperimentalnoj meteorologii, Wypusk 14, Moskwa Giedrometeoizdał 1987.

[11] Wyżgolik B.: *Skażenie metalami ciężkimi gleb gminy Dąbrowa Górnicza*, Środowisko i Rozwój, WSEiA Bytom, **1-2** 109–116 (2000).

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