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## HEAVY METALS IN SOIL FROM COAL MINE DUMP IN GLIWICE

### METALE CIĘŻKIE W GLEBIE Z HAŁDY POGÓRNICZEJ W GLIWICACH

**Abstract:** The aim of this work was to carry out investigation on heavy metal content: Cu, Zn, Mn, Pb, Ni, Cd and Fe in samples of soil collected from the coal mine dump in Gliwice and evaluation of their bioavailability. Each sample was subjected to sequential extraction according to Tessier's method. Five fractions were separated: I – exchangeable; II – carbonate; III – bound to Mn and Fe oxides; IV – bound to organic matter and V – residue. The content of Cu, Zn, Mn, Pb, Ni and Fe in particular fractions was analysed by atomic absorption spectrometry (AAS) with flame atomization, whereas Cd by AAS with electrothermal atomization.

On the basis of carried out experiments it was found that in examined samples of soil the contents of metals are higher than admissible values and also higher than geometric mean reported for this region. The greatest amounts of heavy metals have been found in oxide, organic and residue fractions, in forms less available for plants. Smaller amounts were determined in more available exchangeable and carbonate fractions. It is advisable to monitor such deposits as coal mine dumps, due to the potential threat for the environment.

**Key words:** heavy metals, sequential extraction, soil

Coal mine tailings in Gliwice, in Pszczyńska street, have been deponed near the former mine and the coke plant in Gliwice. Additionally, this area is prone to dusts settlement from the coal combustion in the coke plant, as well as the products of car exhaust emissions from outlet of high street.

Heavy metals can be leached from the heaps of deponed material to surface and groundwater, and then contaminate arable soil from which they can be accumulated by plants growing on them. In this way they can be hazardous also to people.

Heavy metals in trace amounts are necessary for proper functioning of life forms, participating in many important metabolic processes, but both their excess and deficiency can turn out to be toxic, therefore monitoring their concentration in the environment is important. Heavy metals can be accumulated in different organs of alive

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organisms but effects of their action can appear after many years. Their presence causes the enzymatic disorders the most often. Damaging the root system, slowing down the growth of plants, appearance of chlorosis and necrosis are the most frequent symptoms of heavy metals contamination. In the forest soil heavy metals are accumulated mostly in the forest litter, and in the arable soil mostly in humus layer [1, 2].

## Materials and methods

### Sampling of soils

5 soil samples were collected from the Gliwice dump: 3 samples were taken from the side of the former coke plant (samples No. 3, 4 and 5), and 2 samples were taken from the other side of the dump, eg from the side of Pszczynska street (samples No. 1 and 2). For comparison of results two samples were collected from the allotment in the center

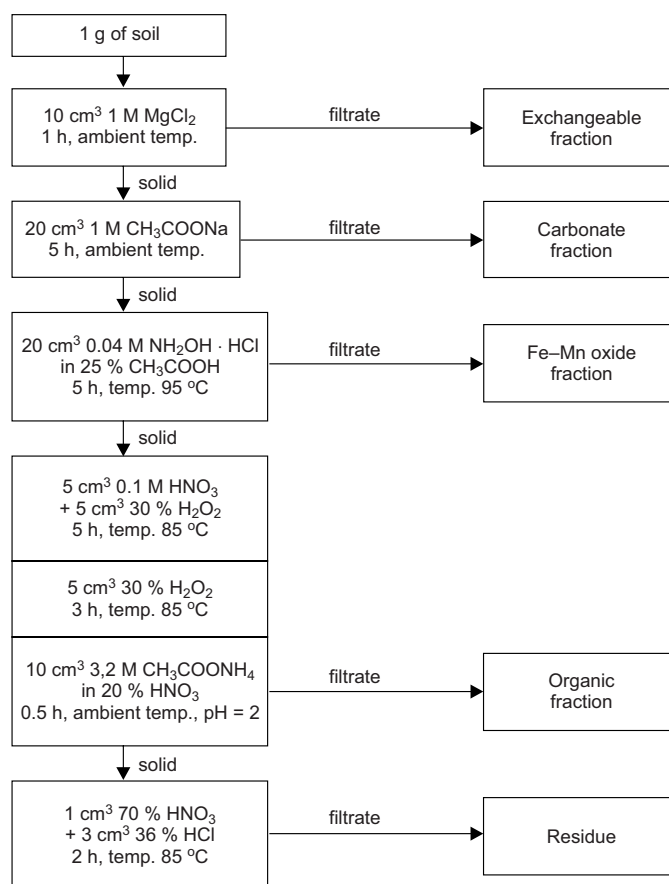


Fig. 1. Flow diagram of the Tessier's method of sequential extraction of heavy metals from the soil [3]

of Gliwice (sample No. 6) and from the unpolluted area near Zawada village in the Małopolskie province (sample No. 7).

### Methods of analysis

Dried off to the state air dry the samples of soils (< 0.75 mm) were subjected to Tessier's method of the sequential extraction. Applied procedure and used reagents are described in Fig. 1. For each sample six replicates have been analysed. Content of Cu, Zn, Mn, Pb, Ni and Fe in each fraction have been determined using the FAAS spectrometer, Carl Zeiss Jena while Cd by the ETAAS technique. Additionally a pH of each soil solution was determined according to the Polish Standard PN-ISO 10390:1997.

### Results and discussion

Content of metals in each fraction of sequential extraction of soil samples has been gathered in Table 1. Percentage of individual metals in fractions of the examined soil samples has been shown in Fig. 2–8, whereas in Table 2 total contents of determined metals, being a sum of values obtained for each fraction and the pH of the corresponding soil solutions have been presented.

On the basis of carried out analyses, it was found that copper in examined samples is present mainly in the forms associated with organic matter. Amounts below limit of detection of analytical technique were observed in the exchangeable fraction while in the carbonate fraction small amounts of copper were found. In four samples collected from the dump the amount of copper was higher than the natural level (according to IUNG, Pulawy) and the threshold limit values (according to the Dutch List) [4]. In the soil from the side of the former coke plant the obtained values were even 1.5–2 times higher than in the samples collected from the side of Pszczynska street.

Contents of zinc distribute relatively evenly among four last fractions, but the contribution of this element into the oxide fraction is the greatest. The content of zinc in other fractions of soils varies among samples. Small amounts of zinc were found in the exchangeable fraction. Two last fractions obtained from soil samples from the side of coke plant contained much higher amount of Zn than other samples. In all samples of soil from the dump the contents of zinc were higher than the natural level (according to IUNG) and exceeded threshold limit values (in soil 4 and 5 even twice) (according to the Dutch List).

In the examined soil the greatest amount of manganese appeared in the oxide and carbonate fraction, constituting essentially about 80 % of the total content. The smallest amounts of manganese were found in the exchangeable fraction. In the soil samples collected from the side of the coke plant the content of Mn was about 1.5 times greater than in the samples collected from the side of Pszczynska street.

It was found that the content of lead in particular fractions differed considerably for each sample. Significant amount of Pb was found mainly in organic fraction (except samples No. 5 and 6) and in residue (the greatest amount in the sample No. 5).

Table 1  
Content of metals in each fraction of sequential extraction of soil samples

Soil	Fraction	Mean value $\pm$ SD [ $\mu\text{g/g}$ ] n = 6									
		Cu	Zn	Mn	Pb	Ni	Cd	Fe			
1	Exchangeable	< 0.4	3.74 $\pm$ 0.27	3.71 $\pm$ 0.16	4.10 $\pm$ 0.23	6.80 $\pm$ 0.09	—	8.42 $\pm$ 0.17			
	Carbonate	5.43 $\pm$ 0.41	45.09 $\pm$ 0.99	81.40 $\pm$ 2.77	< 4	14.80 $\pm$ 0.31	(0.39 $\pm$ 0.04) $\cdot 10^{-1}$	63.75 $\pm$ 1.48			
	Oxide	10.47 $\pm$ 0.40	57.78 $\pm$ 1.95	142.83 $\pm$ 2.52	< 4	9.75 $\pm$ 0.49	0.88 $\pm$ 0.10	3588 $\pm$ 70			
	Organic	22.95 $\pm$ 2.23	16.65 $\pm$ 0.79	13.04 $\pm$ 0.61	17.93 $\pm$ 1.38	3.64 $\pm$ 0.35	(0.46 $\pm$ 0.05) $\cdot 10^{-1}$	1276 $\pm$ 63			
	Residue	7.59 $\pm$ 0.68	30.79 $\pm$ 0.82	33.55 $\pm$ 1.91	8.24 $\pm$ 0.22	6.71 $\pm$ 0.46	0.26 $\pm$ 0.03	12530 $\pm$ 637			
2	Exchangeable	< 0.4	6.80 $\pm$ 0.16	6.05 $\pm$ 0.04	11.05 $\pm$ 0.57	< 0.4	—	8.41 $\pm$ 0.11			
	Carbonate	< 0.8	77.20 $\pm$ 1.75	114.59 $\pm$ 3.32	12.39 $\pm$ 1.02	3.80 $\pm$ 0.22	(0.43 $\pm$ 0.02) $\cdot 10^{-1}$	76.43 $\pm$ 4.22			
	Oxide	< 0.8	88.82 $\pm$ 2.42	148.77 $\pm$ 8.88	< 4	7.34 $\pm$ 0.19	1.29 $\pm$ 0.13	2616 $\pm$ 58			
	Organic	22.16 $\pm$ 0.75	32.79 $\pm$ 1.62	11.72 $\pm$ 0.30	13.40 $\pm$ 0.89	1.45 $\pm$ 0.07	(0.95 $\pm$ 0.05) $\cdot 10^{-1}$	991 $\pm$ 14			
	Residue	7.65 $\pm$ 0.26	39.48 $\pm$ 1.81	41.39 $\pm$ 1.76	3.29 $\pm$ 0.23	13.87 $\pm$ 0.30	2.12 $\pm$ 0.05	8442 $\pm$ 401			
3	Exchangeable	< 0.4	5.66 $\pm$ 0.19	5.79 $\pm$ 0.07	3.54 $\pm$ 0.10	< 0.4	—	9.15 $\pm$ 0.17			
	Carbonate	1.39 $\pm$ 0.04	3.64 $\pm$ 0.33	12.62 $\pm$ 1.20	< 4	6.48 $\pm$ 0.30	< 0.08 $\cdot 10^{-1}$	16.54 $\pm$ 0.47			
	Oxide	< 0.8	78.84 $\pm$ 1.34	266.50 $\pm$ 3.09	15.02 $\pm$ 1.29	12.28 $\pm$ 0.24	1.63 $\pm$ 0.14	3762 $\pm$ 60			
	Organic	54.93 $\pm$ 2.41	108.79 $\pm$ 1.66	87.71 $\pm$ 1.12	47.76 $\pm$ 2.40	18.42 $\pm$ 0.99	0.24 $\pm$ 0.01	15659 $\pm$ 554			
	Residue	6.08 $\pm$ 0.13	29.93 $\pm$ 1.14	20.45 $\pm$ 1.02	3.74 $\pm$ 0.17	12.39 $\pm$ 0.61	0.79 $\pm$ 0.12	6611 $\pm$ 301			
4	Exchangeable	< 0.4	5.34 $\pm$ 0.25	4.82 $\pm$ 0.08	13.22 $\pm$ 0.18	< 0.4	—	4.38 $\pm$ 0.17			
	Carbonate	4.51 $\pm$ 0.20	35.67 $\pm$ 1.41	176.57 $\pm$ 3.13	8.87 $\pm$ 0.44	4.46 $\pm$ 0.16	(0.36 $\pm$ 0.04) $\cdot 10^{-1}$	260 $\pm$ 14			
	Oxide	1.24 $\pm$ 0.05	88.02 $\pm$ 1.39	209.30 $\pm$ 4.74	37.31 $\pm$ 1.04	10.58 $\pm$ 0.32	0.84 $\pm$ 0.08	3535 $\pm$ 57			
	Organic	37.29 $\pm$ 0.61	56.91 $\pm$ 1.64	20.19 $\pm$ 0.59	32.68 $\pm$ 0.60	5.39 $\pm$ 0.25	0.47 $\pm$ 0.01	2871 $\pm$ 38			
	Residue	13.96 $\pm$ 0.30	96.01 $\pm$ 3.38	56.47 $\pm$ 0.91	24.09 $\pm$ 0.55	16.26 $\pm$ 0.27	1.27 $\pm$ 0.04	11923 $\pm$ 271			

Table 1 contd.

Soil	Fraction	Mean value $\pm$ SD [ $\mu\text{g/g}$ ] n = 6							
		Cu	Zn	Mn	Pb	Ni	Cd	Fe	
5	Exchangeable	< 0.4	3.01 $\pm$ 0.14	5.78 $\pm$ 0.27	8.69 $\pm$ 0.45	< 0.4	—	7.97 $\pm$ 0.26	
	Carbonate	3.95 $\pm$ 0.13	49.86 $\pm$ 2.46	180.23 $\pm$ 8.23	8.41 $\pm$ 0.52	2.83 $\pm$ 0.12	(0.30 $\pm$ 0.02) $\cdot 10^{-1}$	373 $\pm$ 36.7	
	Oxide	2.84 $\pm$ 0.04	74.62 $\pm$ 2.12	189.75 $\pm$ 7.37	6.16 $\pm$ 0.23	9.08 $\pm$ 0.32	1.42 $\pm$ 0.08	3044 $\pm$ 72	
	Organic	35.37 $\pm$ 0.85	59.30 $\pm$ 2.97	26.62 $\pm$ 1.14	5.61 $\pm$ 0.45	4.40 $\pm$ 0.20	0.26 $\pm$ 0.01	2710 $\pm$ 188	
	Residue	13.35 $\pm$ 0.60	108.67 $\pm$ 1.74	66.02 $\pm$ 1.17	30.06 $\pm$ 1.19	16.60 $\pm$ 0.23	0.83 $\pm$ 0.03	14018 $\pm$ 144	
6	Exchangeable	< 0.4	22.92 $\pm$ 0.98	34.98 $\pm$ 0.46	10.80 $\pm$ 0.28	6.40 $\pm$ 0.24	—	8.52 $\pm$ 0.41	
	Carbonate	2.40 $\pm$ 0.14	10.57 $\pm$ 0.50	15.91 $\pm$ 1.19	< 4	13.16 $\pm$ 0.25	(0.52 $\pm$ 0.05) $\cdot 10^{-1}$	21.47 $\pm$ 1.06	
	Oxide	< 0.8	25.04 $\pm$ 1.18	144.18 $\pm$ 6.01	< 4	4.98 $\pm$ 0.22	1.27 $\pm$ 0.04	1274 $\pm$ 23	
	Organic	< 0.8	14.88 $\pm$ 0.67	25.25 $\pm$ 1.17	< 4	8.07 $\pm$ 0.36	(0.54 $\pm$ 0.05) $\cdot 10^{-1}$	1388 $\pm$ 50	
	Residue	0.68 $\pm$ 0.03	7.07 $\pm$ 0.35	15.45 $\pm$ 1.10	< 2	2.86 $\pm$ 0.14	(0.31 $\pm$ 0.02) $\cdot 10^{-1}$	931 $\pm$ 40	
7	Exchangeable	< 0.4	3.60 $\pm$ 0.19	7.27 $\pm$ 0.17	4.92 $\pm$ 0.24	< 0.4	—	6.15 $\pm$ 0.14	
	Carbonate	2.56 $\pm$ 0.15	21.59 $\pm$ 0.57	130.31 $\pm$ 2.32	4.27 $\pm$ 0.29	< 0.8	(0.11 $\pm$ 0.02) $\cdot 10^{-1}$	32.40 $\pm$ 1.03	
	Oxide	1.82 $\pm$ 0.08	41.40 $\pm$ 0.93	212.65 $\pm$ 4.66	< 4	5.03 $\pm$ 0.18	0.70 $\pm$ 0.05	1422 $\pm$ 36	
	Organic	18.56 $\pm$ 0.91	19.34 $\pm$ 0.63	10.59 $\pm$ 0.44	15.17 $\pm$ 1.00	< 0.8	0.23 $\pm$ 0.01	1015 $\pm$ 37	
	Residue	4.30 $\pm$ 0.12	19.81 $\pm$ 0.33	34.13 $\pm$ 1.09	5.47 $\pm$ 0.30	10.10 $\pm$ 0.40	(0.47 $\pm$ 0.04) $\cdot 10^{-1}$	4709 $\pm$ 119	

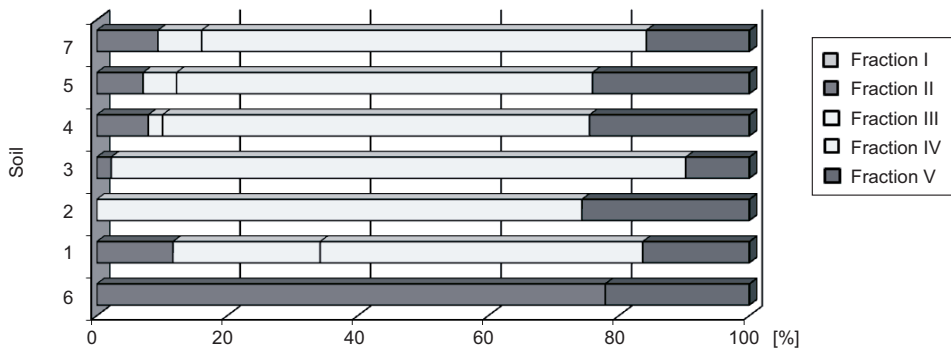


Fig. 2. Percentage of copper in fractions for every soil

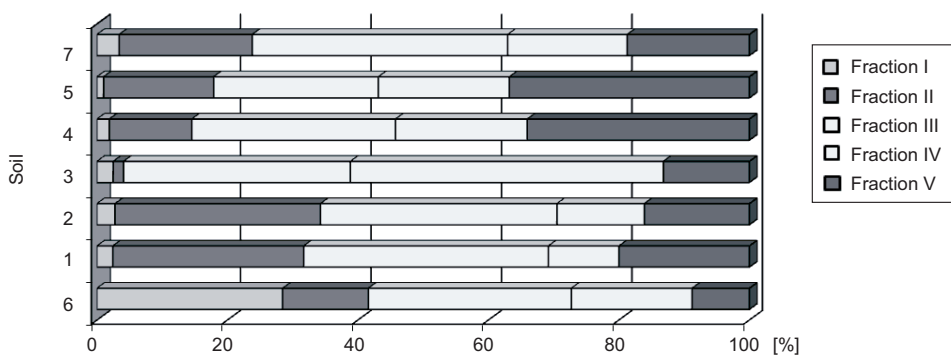


Fig. 3. Percentage of zinc in fractions for every soil

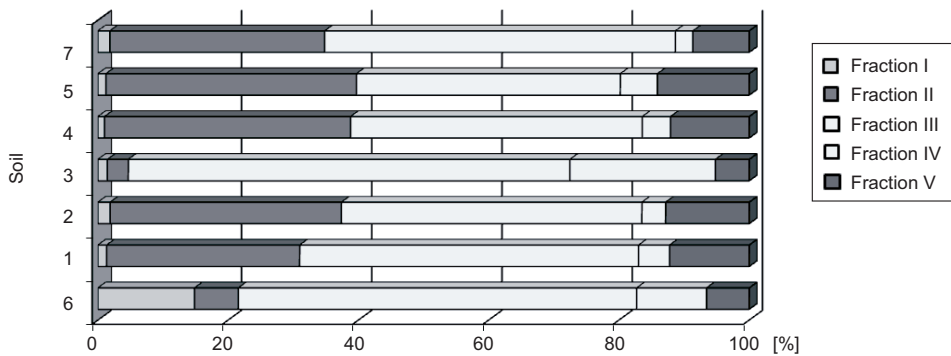


Fig. 4. Percentage of manganese in fractions for every soil

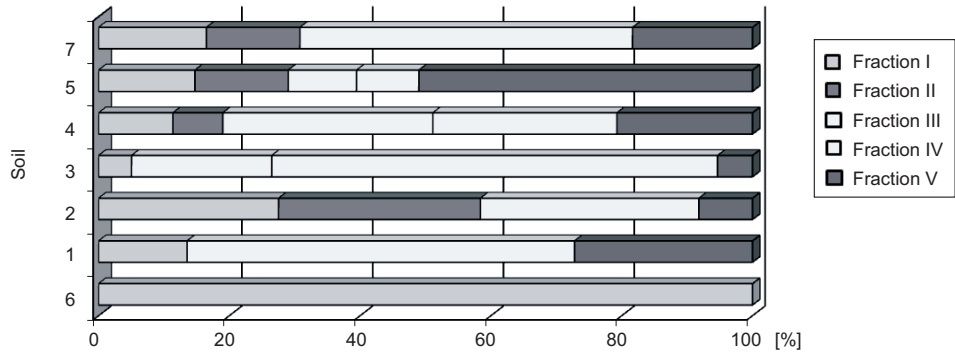


Fig. 5. Percentage of lead in fractions for every soil

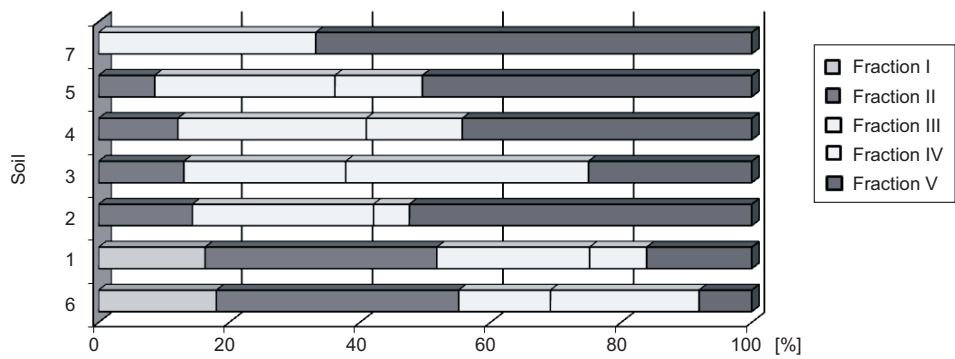


Fig. 6. Percentage of nickel in fractions for every soil

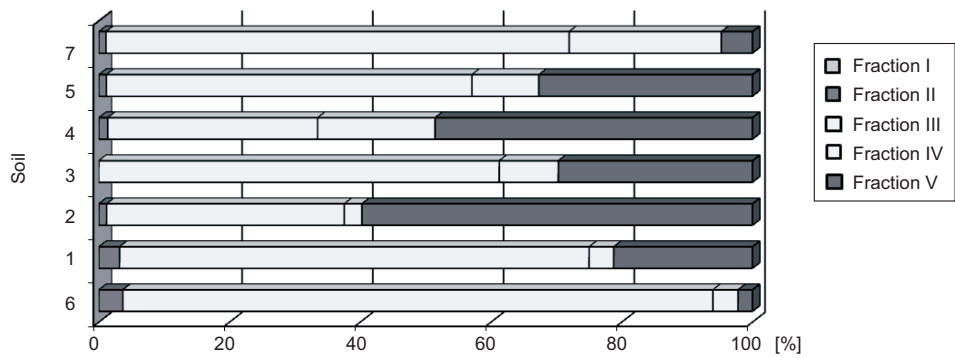


Fig. 7. Percentage of cadmium in fractions for every soil

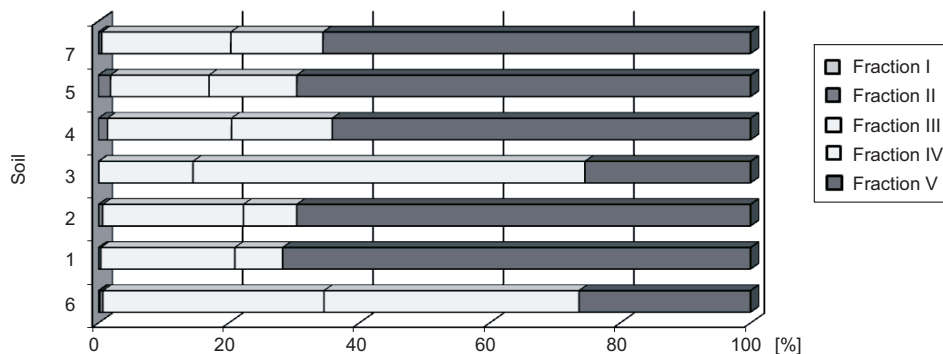


Fig. 8. Percentage of iron in fractions for every soil

Relatively great amount of lead is found in exchangeable fraction. In the samples No. 3 and 4 the content of lead was higher than the natural level (according to IUNG), and in the sample No. 4 an admissible amount was also exceeded (according to the Dutch List).

Table 2

Total content of heavy metals in  $\mu\text{g/g}$  of the soil in all examined fractions and corresponding pH values

Soil	Element [ $\mu\text{g/g}$ ]							pH
	Cu	Zn	Mn	Pb	Ni	Cd	Fe	
1	46.44	154.05	274.53	30.27	41.70	1.23	17466	5.5
2	29.81	245.09	322.52	40.13	26.46	3.55	12133	5.0
3	62.40	226.86	393.07	70.06	49.57	2.66	26058	5.3
4	57.00	281.95	467.33	116.17	36.69	2.62	18593	5.5
5	55.51	295.46	468.40	58.93	32.91	2.54	20153	5.2
6	3.08	80.48	235.77	10.80	35.47	1.41	3551	3.5
7	27.24	105.74	394.95	29.33	15.13	0.99	7185	4

In examined soil samples nickel was found mainly in the oxide fraction, organic fraction and residue. Significant amounts were analysed also in the carbonate fraction. In the samples No. 1 and 6 the great amount of nickel was found also in the exchangeable fraction, what perhaps is connected with the presence of manganese which causes immobilization of nickel in the soil [4]. All examined samples of the soil had the natural content of nickel.

The greatest amount of cadmium was found in the oxide fraction and in the residue. Small amounts are observed in the organic fraction, and trace amounts in the carbonate fraction. The cadmium content in the exchangeable fraction was not analysed due to the interferences coming from  $\text{MgCl}_2$  presence. In all soil samples from the dump, cadmium contents were higher than the natural level (according to IUNG) and exceeded



the thresholds limit values (in soil 2, 3, 4 and 5 even 3–4 times) (according to the Dutch List and PIOŚ [Polish State Inspectorate of Environmental Protection]).

It results from conducted experiments that about 60 % of total content of leachable iron is present in residue (except sample 3 and 6), the rest part of iron was found in the oxide fraction and smaller amount associated with organic matter. Much lower amounts of iron were analysed in carbonate and exchangeable fractions. The content of iron in the soil from the side of the coke plant is about two times higher than in samples from the side of Pszczynska street.

## Conclusions

The content of analysed elements in all examined samples of the soils varies significantly but obtained results are within the range of concentrations published for the soils coming from Poland and the Silesia province. It is worth underlying that the total amounts of analysed elements are higher than the geometric mean for Silesia. The sum of the content of elements in four fractions the most easily accessible for plants, for samples coming from the dump is 4–5 times higher than average values for Silesia for copper, 2 times higher than average for zinc, up to 2 times higher for lead, over 2 times higher for nickel and about 2 times higher for cadmium [6].

Samples collected from the side of the coke plant contained greater amount of iron (2–5 ×), copper (more than 2 ×), manganese (1.5 × or more), lead (more than 2 ×) and cadmium a little bit more. Amounts of remaining elements: of zinc and nickel were similar in samples collected on both sides of the dump.

Comparing the results with those obtained for samples collected from the allotment in Gliwice and from the unpolluted area from Malopolska province, it was found that the content of iron was 3 times smaller, zinc over 2 times smaller, copper about 4 times smaller. The content of remaining elements did not differ markedly from their content in the soil from the dump. It is noticeable that content of zinc and the manganese in exchangeable fraction in the soil No. 6 (from allotment) was 5 times greater than in other samples, what can correlate with fertilizing this soil and its acidity.

High contents of heavy metals in samples of the soil coming from the dump in Gliwice show the constant need for monitoring of their amount, due to the possible leaching of elements to groundwater, uptake by plants, being the part of the food chain, at the end of which is the human being.

It seems to be advantageous to protect area adjacent to the dump by planting hyper accumulating plants or trees which can be used for fitoremediation of contaminated areas.

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### METALE CIĘŻKIE W GLEBIE Z HAŁDY POGÓRNICZEJ W GLIWICACH

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**Abstrakt:** Celem pracy było zbadanie zawartości metali ciężkich: Cu, Zn, Mn, Pb, Ni, Cd i Fe w próbkach gleby z hałdy w Gliwicach oraz określenia ich biodostępności. Dla każdej próbki gleb przeprowadzono frakcjonowanie sekwencyjne metodą Tessiera, podczas której zostaje wydzielonych 5 frakcji metali: frakcji I wymiennej, frakcji II związanych z węglanami, frakcji III związanych z tlenkami, frakcji IV związanych z materią organiczną oraz frakcji V pozostałości. Zawartość Cu, Zn, Mn, Pb, Ni i Fe w poszczególnych frakcjach oznaczono za pomocą absorpcyjnej spektrometrii atomowej z atomizacją w płomieniu, a zawartość kadmu za pomocą absorpcyjnej spektrometrii atomowej z elektrotermiczną atomizacją.

Z przeprowadzonych badań wynika, że w badanej glebie znajdują się duże zawartości oznaczanych metali, często większe niż dopuszczalne, oraz większe od średnich geometrycznych dla tego terenu. Największe ilości metali ciężkich występują we frakcji tlenkowej, organicznej i w pozostałości, a więc w formach mało dostępnych dla roślin. Małe ilości występują w formach biodostępnych czyli we frakcji wymiennej i węglanowej. Pomimo to monitoring takich miejsc powinien być prowadzony, gdyż stanowią one potencjalne zagrożenie ekologiczne.

**Słowa kluczowe:** metale ciężkie, ekstrakcja sekwencyjna, gleba