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HEAVY METALS SOIL CONTAMINATION INDUCED BY HISTORICAL ZINC SMELTING IN JAWORZNO

ZANIECZYSZCZENIE GLEBY METALAMI CIĘŻKIMI ZWIĄZANE Z HISTORYCZNYM HUTNICTWEM CYNKU W JAWORZNIE

Abstract: The initial study of heavy metals (Cr, Cu, Ni and Mn) contamination was carried out on the 22 samples taken from 4 forest soil (podzol) profiles and 5 waste samples taken from 3 points of the historical zinc smelting area in Jaworzno, Southern Poland. XRD and pH analyses on the soil samples were done. The trace element concentrations were measured with the inductively coupled plasma optical emission spectrometry (ICP-OES) after mineralisation in concentrated HNO_3 (65 % Suprapur) and HCl (30 % Suprapur). Examined materials were ultra acidic to neutral, mostly very strong acidic. Total accumulations of trace elements in the soil varied from 21.91 to 119.32 mgCr, from 1.4 to 51.16 mgCu, from 2.15 to 36.16 mgNi and from 16.33 to 869.19 mgMn $\cdot$ kg^{-1}. In waste samples quantities of the same elements equalled 45.55–67.38 mgCr, 19.5–244.74 mgCu, 4.96–22.15 mgNi and 30.75–369.11 mgMn $\cdot$ kg^{-1}. Vertical distributions of examined metals were determined in each of soil profiles. The research revealed heavy metal pollution of studied soil. Influence of the historical smelter on the pollution is inferred, which changed soil environment to dangerous for humans, especially due to close proximity of abandoned industry to built-up and recreation areas as well as community gardens.

Keywords: zinc smelting, heavy metals, soil contamination

Introduction

Chromium, copper, nickel and manganese are natural and common components of the Earth's crust. The four elements account for 83 mgCr $\cdot$ kg^{-1}, 25 mgCu $\cdot$ kg^{-1},

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44 mgNi $\cdot$ kg^{-1} and 600 Mn $\cdot$ kg^{-1} of upper continental crust mass [1]. Natural and anthropogenic sources contribute to the presence of these elements in environmental compartments, such as air, water, soil and plant. The mentioned elements are known as microelements and they are essential in metabolic processes for plants and animals [2]. However, they may also appear toxic for living organisms if their concentrations in soil environment increase over maximum tolerable values [3–6].

From among number of factors controlling availability of trace elements in the soil environment [7, 8], these of the crucial importance are the pH value and oxidation--reduction potential.

Anthropogenic activities, such as ore mining and smelting, power industry, waste dumping sites, and transport, are thought to be sources of the heavy metals – Cr, Cu, Ni and Mn – pollution in the industrially changed environment [9–12]. The areas characterised by strong development of the present-day or historical mining and metallurgy production, constitute a hazard of the heavy metal contamination in many countries [13–16], also in the Jaworzno town vicinity [17–19]. The transfer of toxic elements from industrial wastes, soils, water and air to plants is of great concern *eg* [20], particularly in the surrounding of community gardens or agricultural area.

The aim of this study is to find out if an abandoned long time ago zinc smelting factory and its partly reclaimed waste heap left still recognisable imprint on local soil. Cr, Cu, Ni and Mn abundance is assumed as an indicator of former Zn processing effect, and inefficient coal combustion that powered smelting as most probable source of Cr, Cu, Ni and Mn immission to environment. Preliminary results on the concentration and distribution of the analysed metals in the soil are presented. Impacts of the metal contamination on the ecosystem have not been widely discussed.

Materials and methods

The scope of research is anthropogenic transformed area in the town of Jaworzno, located in the NE part of the Upper Silesian industrial region, Southern Poland. Many portions of the town have been mined for Zn-Pb ores since 12th century [21] and for coal since 18th century. Centuries-old mining and industrial activity has left numerous traces in the landscape of the town [22]. In the area of present study the exploitation resulted in founding the zinc smelter which started working in the 19th century. It was converted to zinc white (ZnO) plant afterwards and completely ceased in the middle 70's of the 20th century due to the concern of environmental pollution associated with outdated smelting technology [23]. Nowadays, the relics of the zinc historical metallurgic processes are tailings deposited on the old heap, situated in close vicinity of built-up area and community gardens (Fig. 1).

Research was conducted on 4 forest soil profiles of the podzol, which has developed on the fluvio-glacial sediments, and 5 waste samples collected from 3 waste locations (Fig. 1). Each soil profile was divided into separate horizons, what gave 22 soil samples (Table 1). All soil and waste samples, about 2 kg weight each, were collected with small spade and stored in plastic sacks. Samples were collected in September of 2012.
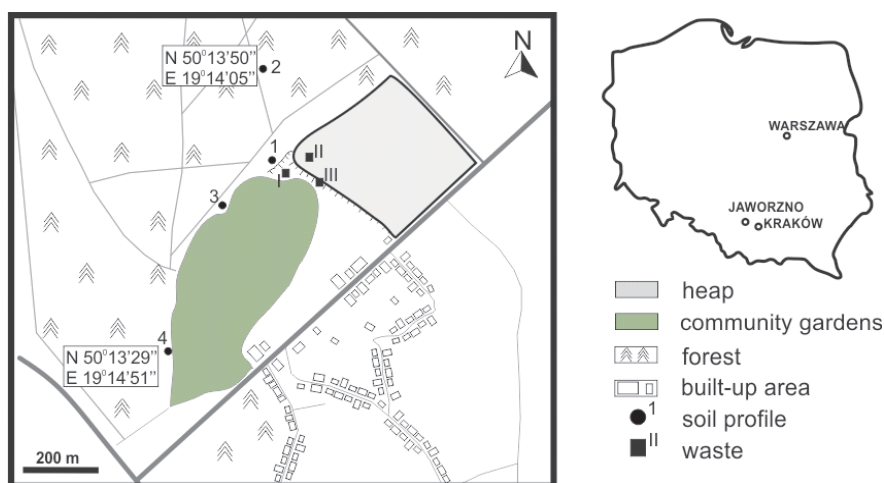
Fig. 1. Location of the study area and sampling sites in Jaworzno

Analyses were preceded by samples oven drying at 105 $^{\circ}$C to constant weight, sieving to 2 mm through a stainless steel sieve and milling into fine powder. Soil pH was determined using a 1 : 5 (*w/v*, g : cm^3) ratio of soil/waste and 1 mol · dm^{-3} KCl solution, with pH meter ELMETRON CP-315m.

The phase composition was provided by X-ray diffraction. The analysed material was manually ground in an agate mortar to grain size between 5 and 10 μm. Measurements were carried out in range from 2.5 to 65°2 Θ using 100 s time limit and 0.02°2 Θ step size. Generator settings were 45 kV and 30 mA. The divergence and antiscatter slits with 1/8° gap were applied. The XRD data were obtained at room temperature and were collected using a Panalytical X'Pert PRO MPD PW 3040/60 diffractometer with a Theta-Theta geometry and X'Celerator strip detector.

Results were processed by HighScore + computer programme of Panalytical company in combination with ICDD, PDF 4 + (version 2012) newest standard base. The mineralogical phase quantitative participations were automatically estimated with Rietvelda module of HighScore + programme.

Total contents of Cr, Cu, Ni and Mn were determined in the soil and waste samples. Samples were digested wet in closed system in a mixture of 6 cm^3 of concentrated nitric acid (65 % Suprapur) and 2 cm^3 of hydrochloric acid (30 % Suprapur). Digestion proceeded with the use of a Multiwave 3000 Microwave Digestion of Perkin Elmer, in two steps according to the program of mineralisation recommended by equipment provider – power: 1400 W, recovery time: 5 min, hold: 25 min in the first step, 10 min in the second, fan speed: 1 in the first step, 3 in the second. After mineralisation the samples were removed to measuring flasks (10 cm^3) with 1 % solution of Suprapur nitric acid.

The contents of studied heavy metals in the prepared solution were determined using atomic emission spectrometer ICP-OES Optima 7300 Dual View Perkin Elmer. Each

soil sample was analysed in two replications. If the results of these replications differed one from another by more than 5 %, another two analyses of that sample were conducted.

Results and discussion

The main focus of this study is to give initial information about the contents of Cr, Cu, Ni and Mn in soil and distribution pattern of the metals in soil profiles. Examined forest soil (podzol) developed on the Pleistocene glacial rocks, mainly sand or clay, whereas the waste under study is the material left over after the metallurgical process of Zn and ZnO production.

The pH values measured in the soil varied from 3.85 to 7.59, with median 5.55. The pH value detected for waste material in 1 mol $\cdot$ dm^{-3} KCl solution ranges from 2.83 to 4.28, with median 3.15. It can be concluded that examined materials are ultra acidic to neutral, mostly very strong acidic. According to Kabata-Pendias and Pendias [2], Cr, Cu, Ni and Mn are highly soluble in the acidic soil environment with pH value between 2 and 4.

Mineralogical characterisation of soil profiles and waste materials

Crystalline phases in the topsoil are mainly represented by low-temperature quartz with the highest reflex $d_{110} = 3.343$ Å and P3$_2$21 space group (80–98 wt.%). The other minerals identified in this part of soil profile are kaolinite, mica or illite and chlorites. K-feldspars and plagioclases occur there as the accessory minerals. In some samples, larger concentrations of mullite phase (6–15 %) were recognised, accompanied by iron oxides (magnetite, hematite) and rarely akermanite from melilite group. The jarosite- -alunite family phases were also documented, which might form by replacing iron sulphides.

The eluvial zone is characterized by similar assemblage of rock-forming minerals and occurring in the same proportion as in the topsoil. The additional phases that appear there are dolomite and trace substances closely related to melilite (akermanite-gehlenite group).

The samples from the illuvial zone can be divided into two types: clayey (samples 1e and 3f) and sandy (samples 2e, 2f and 4d, 4e). In the first type an increase in participation of the clay minerals to over 30 wt.% and the feldspars to 5–7 wt.% is observed. The most frequent clay mineral – kaolinite (about 18 wt.%) is accompanied by mica/illite (12–14 wt.%) and chlorite close to klinochlorite (~10 wt.%). The second type consists of phases similar to those described for elluvial zone with a little addition (3–4 wt.%) of material closely related to microcline. Quartz dominates in both types.

The representation of the jarosite-alunite group phases in diffraction pattern informs about possible oxidation of the iron sulphide minerals in the soil. These sulphides might originate in ore-bearing dolomites, the main source of zinc for Zn-smelting, which naturally have included quantity of iron minerals in their composition.

Apart from natural components of the soil, the mullite, melilite and iron oxides have been identified, which are considered to be anthropogenic. As they are typical

high-temperature minerals, their occurrence can be derived from processes set during Zn-ores smelting.

Phase composition of collected waste is comparable to that in illuvial zone of clayey soil samples; quartz (> 60 wt.%) is there accompanied by clay minerals – mainly kaolinite (~25 wt.%), illite, mica and chlorite (< 10 wt.%). Moreover, Ca and Fe sulphates – gypsum (~2 %), rozenite (~3 %), and phases from alunite-jarosite series (4 % in total) were found in sample I. In material of the sample II, with mineralogical composition similar to that mentioned before, jarosite content is elevated to ~6 %. The III waste sample differs from others because of dolomite (25 %), calcite (~2 %) and hematite (~2 %) presence. It is probable that this material is enriched with ore-bearing dolomite (Zn ore host rock) which contains sizable amount of iron oxides.

Cr, Cu, Ni and Mn contents in soil and waste

Total heavy metal contents in the soils from study area ranged as follows: 21.91–119.32 mgCr · kg^{-1}, 1.40–51.16 mgCu · kg^{-1}, 2.15–36.16 mgNi · kg^{-1} and 16.33–869.19 mgMn · kg^{-1}, with geometrical means 63.67 mg · kg^{-1}, 8.62 mg · kg^{-1}, 6.13 mg · kg^{-1} and 71.78 mg · kg^{-1}, respectively (Table 1).

Whereas total contents of the same elements in collected waste samples were comprised in different scopes and ranged as follows: 45.55–67.38 mgCr · kg^{-1}, 19.5–244.74 mgCu · kg^{-1}, 4.96–22.15 mgNi · kg^{-1} and 30.75–369.11 mgMn · kg^{-1}, with geometrical means 56.06 mg · kg^{-1}, 38.10 mg · kg^{-1}, 6.13 mg · kg^{-1} and 71.78 mg · kg^{-1}, respectively (Table 2).

The geometrical means of Ni and Mn accumulation are higher in the topsoil than in the tailings, but those of Cr and Cu are the exact opposite.

The geometrical means calculated for the topsoil samples were compared to corresponding values reported by Kabata-Pendias and Pendias [2] for topsoils of the Polish podzols. And medians obtained for the topsoil were correlated with the medians determined by Pasieczna [24] for topsoils in Silesia-Cracow region. The data taken from reference materials [2, 24] were used as regional baseline concentrations. Levels of metal concentrations in the examined topsoil are, except Mn, elevated compared to the baseline values. The Ni contents scarcely exceed mentioned baseline parameters. But the chromium and copper contents are strongly increased, 4–8-fold and 3-fold higher than the baseline concentrations, respectively. Our results are supported by previous research on the Ni contamination of soils in the Olkusz Zn-Pb mining area and in the vicinity of the Tadeusz Sendzimir Steelworks in Krakow [25].

Contents of metals (Cr, Cu, Mn and Ni) in soil seem to be dependent on the distance from the former Zn-smelter. The highest contents of Cu, Ni and Mn were detected close to heap (profile 1), while the lowest ones of Cu, Ni (profiles 2 and 4) and Cr (profile 4) were found in the outermost locations. The highest chromium amount was reported from the profile 2 (for profile localisations see Fig. 1). Similar lateral distribution of heavy metals (Cr, Cu, also Pb, Zn, Cd and As) was observed in other areas impacted by former Zn-smelting *eg* [13, 26].

Table 1

Total heavy metal contents in sampled soils (n = 22)

Soil profile	Sample	Depth [cm]	Cr	Cu	Ni	Mn
			[mg · kg^{-1} d.m.]			
1	1a	0–2	107.27	45.49	22.89	673.57
	1b	2–8	97.24	51.16	21.66	340.80
	1c	8–16	71.97	9.74	3.60	35.40
	1d	16–30	62.11	4.85	3.42	32.45
	1e	30–60	85.94	24.30	36.16	869.19
2	2a	0–4	119.32	9.15	5.11	61.96
	2b	4–28	81.85	21.30	6.70	77.05
	2c	28–38	102.65	5.04	3.23	33.65
	2d	38–43	96.98	3.08	3.02	31.43
	2e	43–53	96.14	3.80	4.02	36.15
	2f	53–70	75.54	2.47	3.91	31.90
3	3a	0–2	40.57	21.78	7.66	163.64
	3b	2–10	47.32	38.62	16.72	185.18
	3c	10–20	65.58	24.00	6.79	32.21
	3d	20–28	54.37	2.03	2.15	21.28
	3e	28–40	26.98	1.40	2.64	16.33
	3f	40–65	56.72	5.06	8.71	34.38
4	4a	0–2	24.33	12.21	7.86	166.78
	4b	2–8	21.91	10.82	8.53	132.50
	4c	8–18	62.55	5.63	3.44	40.91
	4d	18–30	61.77	5.63	4.23	79.20
	4e	30–73	79.56	4.10	4.40	60.99
Geometric mean			63.67	8.62	6.13	71.78
Median			68.78	7.39	4.75	50.95
Relative standard deviation [%]			26.81	14.29	8.30	214.25
Geometric mean for studied topsoil			**53.62**	**21.84**	**11.17**	**191.73**
Median for studied topsoil			**47.32**	**21.78**	**8.53**	**166.78**
Reference materials						
Median for topsoils in South Poland*			**6**	**7**	**5**	**224**
Geometric mean for Polish podzol topsoils**			**12**	**8**	**8**	**240**

Explanations: n – number of analysed samples; * median for topsoils (0–0.3 m) according to geochemical map of Southern Poland (sheets: Slawkow, Olkusz, Nowa Gora, Myslachowice, Chrzanow, Dabrowa Gornicza, Strzemieszyce, Jaworzno and Libiaz) (after 24); ** geometric mean of trace element contents in topsoils of the Polish podzols (after 2).

Total heavy metal contents in sampled waste (n = 5)

Waste loca-tion	Sample	Depth [cm]	Cr	Cu	Ni	Mn
			[mg · kg^{-1} d.m.]			
I	Ia	0–10	45.55	20.77	13.11	30.75
	Ib	10–90	54.72	19.50	14.40	42.50
	Ic	90–120	67.38	22.40	4.96	40.73
II		10	60.76	36.14	15.75	101.56
III		50	54.24	244.74	22.15	369.11
Geometric mean			**56.06**	**38.10**	**6.13**	**71.78**
Median			**54.72**	**22.40**	**14.40**	**42.50**
Relative standard deviation [%]			7.27	88.22	5.52	128.53

Explanations: see Table 1.

Vertical distribution of examined metal contents in soil is presented in profiles (Fig. 2). Most of the soil profiles exhibits decreasing contents of nickel and copper with
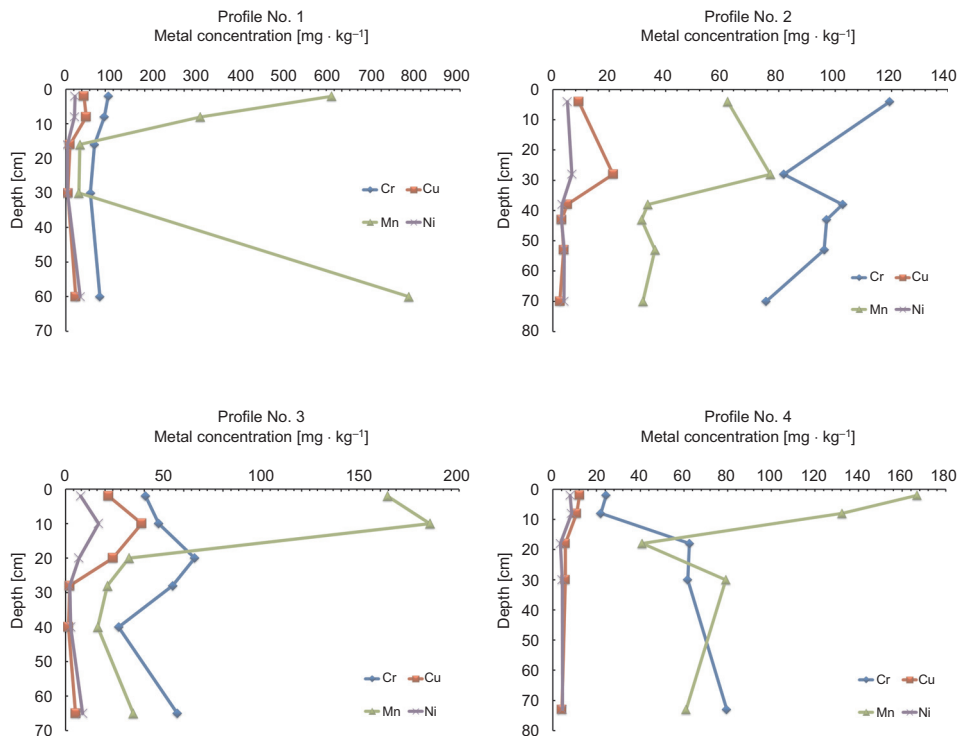
Fig. 2. Vertical distribution of heavy metal contents [mg · kg^{-1}] in studied soil profiles

depth (except profile 2), followed by little enrichment close to bedrock in case of profiles 1 and 3.

Cr distribution similar to that of Cu and Ni is presented only in profile 1 as non-monotonic decrease of Cr level with depth can be observed in profile 2. On the other hand, an increase of Cr content with depth is reflected in profile 4. The biggest enrichment of chromium near the bedrock is seen in profile 3, where Cr concentration can also be considered as growing with depth.

The manganese behaviour is also complicated. Profiles 3 and 4 demonstrate huge depletion of Mn content with depth, while profile 2 shows little growth of Mn quantity in subsoil, and profile 1 reveals strong Mn enrichment close to the bedrock.

According to Ullrich et al [13], distribution pattern exhibited by heavy-metal contents decreasing from topsoil to subsoil generally indicates a non-lithogenic source of the contamination, while higher metal concentrations found at lower depths may reflect the influence of underlying parent rocks or result from downward migration of contaminants related to historic human activity. Evaluating possible reasons of elevated Cr, Cu, Ni and Mn it is important to remind about acidic soil reaction measured for studied soil, which is responsible for heavy metals mobility in environment [2].

Strong correlations are found between studied metals content in soil samples, *eg* Mn and Cu (r = 0.65), Ni and Cu (r = 0.75), Ni and Mn (r = 0.95), while the correlations between Cr and other studied metals are rather weak (r = 0.19–0.24). The strong correlation coefficients between Ni *versus* Cu and Ni *versus* Mn may indicate genetic relations of these elements to industrial processes.

The smelter emissions, as well as dust wind-blown from factories, tailings and smelter slag dumps are obviously the main point sources of soil pollution [27]. But role of the smelting-related fuel combustion as a source of soil contamination must not be underestimated. About 10–20 % of ash particles are released to the atmosphere because of coal combustion related to mineral processing [2]. The metal contents in the coal ashes are higher than average concentrations in the Earth's crust: 10–1000 mgCr, 50–150 mgCu, 50–10000 mgNi and 200–1200 mgMn $\cdot$ kg^{-1} what results in large Cr, Cu, Ni and Mn contamination in coal-ash dumps [28] and adjacent sediments [29]. Likewise, high quantities of Ni and Cr could be released to soils during a fast burning of sulphides. Superiority of Cr compared with Ni observed in such soils [30] may document a combined impact of coal combustion and metal smelting processes. Effect of coal burning on the increase of chromium contents in atmosphere and soil is also noted in the vicinities of several power plants in southern Poland [31].

It is reasonable to conclude that metal contamination of the topsoil results from the atmospheric deposition of particles emitted by Pb/Zn smelter. Smelting, converting and fire-refining of base metal concentrates can generate considerable volumes of dust and gases which now are usually passed through electrostatic precipitators to remove almost all of the entrained particulate matter. But in the past, even in 1970's, industrial fumes was not enough purified. And the former, low efficient smelter in Jaworzno needed 18 kg of coal to get 1 kg of clear zinc [32].

Conclusions

The vertical distribution pattern of Cr, Ni, Mn and Cu contents in studied profiles suggests an anthropogenic origin of soil contamination. High concentrations of analysed metals together with occurrence of man-made high-temperature phases point to smelting-related fuel combustion as a possible source of the metals in soil. Lateral dispersal of the metals, from the highest concentrations detected close to heap to the lowest found in the outermost profiles enables locating the former Zn-smelter in the positive anomaly center.

The soil is still polluted by hazardous trace elements (HTEs) even though the Zn smelting and the ZnO production became closed more than forty years ago. Contents of chromium, copper and nickel in the examined topsoil are up to 8-fold elevated compared to the baseline values, and strong acidity at the site activates Cr, Cu, Ni and Mn high solubility. Thus, soil environment has been changed to dangerous for humans, especially due to close proximity of abandoned industry to built-up and recreation areas as well as community gardens.

Sequential extraction of trace elements should be done in the next step of the research to precise heavy metals behaviour in the soil. Potential harm of the pollutants to eco-environment and human health in the vicinity of the zinc historical industry area in Jaworzno should also be examined in greater detail.

References

[1] Taylor SR, McLennan SM. Planetary Crusts, Their Composition, Origin and Evolution. Cambridge: Cambridge University Press; 2009.
[2] Kabata-Pendias A, Pendias H. Biogeochemia pierwiastków śladowych. Warszawa: PWN; 1999.
[3] Senesi GS, Baldassarre G, Senesi N, Radina B. Chemosphere. 1999;39(2):343-377. DOI: 10.1016/S0045-6535(99)00115-0.
[4] Sivakumar S, Subbhuraam CV. Ecotoxicol Environ Saf. 2005;62(1):93-98. DOI: 10.1016/j.ecoenv.2004.08.006.
[5] Ippolito JA, Ducey T, Tarkalson D. Soil Sci. 2010;175(12):586-592. DOI: 10.1097/SS.0b013e3181fe2960.
[6] Nádaská G, Lesný J, Michalík I. Hungar Electronic J Sci Environ Eng. 2012;ENV-100702-A:1-16.
[7] Rogival D, Scheirs J, Blust R. Environ Pollut. 2007;145(2):516-528. DOI: 10.1016/j.envpol.2006.04.019.
[8] van den Brink N, Lammertsma D, Dimmers W, Boerwinkel M-C, van der Hout A. Environ Pollut. 2010;158(1):245-251. DOI: 10.1016/j.envpol.2009.07.013.
[9] Szyczewski P, Siepak J, Niedzielski P, Sobczyński T. Pol J Environ Stud. 2009;18(5):755-768.
[10] Cai Q, Long M-L, Zhu M, Zhou Q-Z, Zhang L, Liu J. Environ Pollut. 2009;157(11):3078-3082. DOI: 10.1016/j.envpol.2009.05.048.
[11] Kopittke PM, Asher CJ, Kopittke RA, Menzies NW. Environ Pollut. 2007;150(2):280-287. DOI: 10.1016/j.envpol.2007.01.011.
[12] Singh RP, Tripathi RD, Sinha SK, Maheshwari R, Srivastava HS. Chemosphere. 1997;34(11):2467-2493. DOI: 10.1016/S0045-6535(97)00087-8.
[13] Ullrich SM, Ramsey MH, Helios-Rybicka E. Appl Geochem. 1999;14(2):187-196. DOI: 10.1016/S0883-2927(98)00042-0.
[14] Audry S, Schäfer J, Blanc G, Jouanneau JM. Environ Pollut. 2004;132(3):413-426. DOI: 10.1016/j.envpol.2004.05.025.
[15] Chojnacka K, Chojnacki A, Górecka H, Górecki H. Sci Total Environ. 2005;337(1-3):175-182. DOI: 10.1016/j.scitotenv.2004.06.009.

[16] El Hamiani O, El Khalil H, Lounate K, Sirguey C, Hafidi M, Bitton G, Schwartz C, Boularbah A. J Hazard Mater. 2010;177(1-3):755-761. DOI: 10.1016/j.jhazmat.2009.12.096.

[17] Cabala J, Sutkowska K. Prace Nauk Inst Górn Polit Wroc. 2006;117(32);13-22.

[18] Chrastný V, Vaněk A, Teper L, Cabala J, Procházka J, Pechar L, Drahota P, Penížek V, Komárek M, Novák M. Environ Monit Assess. 2012;184(4):2517-2536. DOI: 10.1016/j.jhazmat.2009.12.096.

[19] Vaněk A, Chrastný V, Komárek M, Penížek V, Teper L, Cabala J, Drábek O. J Geochem Explor. 2013;124:176-182. DOI: 10.1016/j.gexplo.2012.09.002.

[20] Vaněk A, Chrastný V, Teper L, Cabala J, Penížek V, Komárek M. J Geochem Explor. 2011;108(1):73-80. DOI: 10.1016/j.gexplo.2010.10.006.

[21] Molenda D. Górnictwo kruszcowe na terenie złóż śląsko-krakowskich do połowy XVI wieku. Wrocław: Ossolineum; 1963.

[22] Sutkowska K, Teper L. Przegl Górn. 2012;68(2):70-77.

[23] Pakuła L. Rozwój i zmiana struktury przemysłu (1945–1994). In: Jaworzno: zarys dziejów w latach 1939-1990. Zawistowski J, editor. Kraków: Krajowa Agencja Wydawnicza; 1996:153-190.

[24] Pasieczna A. Gospod Surowcami Min. 2008;24(2/2):67-82.

[25] Gambuś F. Nikiel w glebach i koniczynie województwa krakowskiego. In: Chrom, nikiel, glin w środowisku – problemy ekologiczne i metodyczne. Kabata-Pendias A, editor. Wrocław: Ossolineum; 1993:135-139.

[26] Bi X, Feng X, Yang Y, Qiu G, Li G, Li F, Liu T, Fu Z, Jin Z. Environ Int. 2006;32(7):883-890. DOI: 10.1016/j.envint.2006.05.010.

[27] Ettler V, Křibek B, Majer V, Knésl I, Mihaljevič M. J Geochem Explor. 2012;113:68-75. DOI: 10.1016/j.gexplo.2011.08.001.

[28] Hajarnavis MR, Bhide AD. Indian J Environ Health. 2003;45(4):293-298.

[29] Equeenuddin SM, Tripathy S, Sahoo PK, Panigrahi MK. J Geochem Explor. 2013;124:230-237. DOI: 10.1016/j.gexplo.2012.10.010.

[30] Strzyszcz Z, Bzowski Z. Zawartość chromu i niklu w węglach kamiennych, a wielkość depozycji tych metali w północno-wschodniej części woj. Katowickiego. In: Chrom, nikiel, glin w środowisku – problemy ekologiczne i metodyczne. Kabata-Pendias A, editor. Wrocław: Ossolineum; 1993:93-98.

[31] Nowak B, Kwapuliński J. Ocena możliwości zanieczyszczenia niklem i chromem powietrza oraz gleb wokół elektrowni węglowych. In: Chrom, nikiel, glin w środowisku – problemy ekologiczne i metodyczne. Kabata-Pendias A, editor. Wrocław: Ossolineum; 1993:117-121.

[32] Leś-Runicka M. Co tydzień (Jaworzno). 1998;16:45.

ZANIECZYSZCZENIE GLEBY METALAMI CIĘŻKIMI ZWIĄZANE Z HISTORYCZNYM HUTNICTWEM CYNKU W JAWORZNIE

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Abstrakt: Przeprowadzono wstępne badania zanieczyszczenia metalami ciężkimi (Cr, Cu, Ni i Mn) w 22 próbkach pobranych z 4 profili leśnych gleb bielicowych oraz 5 próbkach odpadów pohutniczych pobranych z 3 punktów w rejonie historycznego hutnictwa cynku w Jaworznie (południowa Polska). Wykonano pomiary pH oraz analizy XRD. Zawartość pierwiastków śladowych oznaczono, stosując optyczny spektrometr plazmowy (ICP-OES) po wcześniejszym zmineralizowaniu próbek w stężonym HNO_3 (65 % Suprapur) i HCl (30 % Suprapur). Badane materiały miały odczyn od ekstremalnie kwaśnego do obojętnego, w większości bardzo kwaśny. Całkowita zawartość pierwiastków śladowych w badanych glebach wahała się w szerokim zakresie: od 21,91 do 119,32 mgCr, od 1,4 do 51,16 mgCu, od 2,15 do 36,16 mgNi i od 16,33 do 869,19 mgMn · kg^{-1}. W materiale odpadowym zawartości badanych pierwiastków wynosiły: 45,55–67,38 mgCr, 19,5–244,74 mgCu, 4,96–22,15 mgNi i 30,75–369,11 mgMn · kg^{-1}. W badaniach określono również pionową zmienność zawartości metali w poszczególnych profilach glebowych. Wykryte zawartości metali ciężkich świadczą o silnym zanieczyszczeniu gleb. Wskazano na dawną działalność hutniczą jako na źródło tego zanieczyszczenia, które może stanowić zagrożenie dla mieszkańców, ze względu na bliskie sąsiedztwo zamkniętej huty z obszarami zabudowanymi i rekreacyjnymi oraz ogrodami działkowymi.

Słowa kluczowe: hutnictwo cynku, metale ciężkie, zanieczyszczenia gleby