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Soil Chemistry

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SORPTION OF NICKEL IN SOILS OF AN AREA AFFECTED BY THE METAL INDUSTRY

Abstract: The analysed area was used for industrial activity for over 130 years. During that time many pollutants (including heavy metals) have been emitted by industrial plants and infiltrated into the soil. This article presents the properties of the soil from industrial sites located in Zielona Góra and analysis of its physical and chemical characteristics.

Heavy metals are considered one of the most serious threats to both humans and the environment. Contamination of industrial areas with heavy metals is a phenomenon observed worldwide [15, 22]. In addition to heavy metals such as lead and cadmium, which are very harmful to plants and animals, nickel is also prevalent, although it shows reduced harmfulness [14, 20].

The amount and type of contaminants affecting the soil depends mainly on the type and technology of the associated production methods. In the study area in Zielona Góra, welding technologies as well as painting and other technologies that could affect the increase of nickel content in the soil have been used [1, 3, 12, 16, 18].

As a result, the aim of this study was to determine the nickel content in the soil from an area affected by the local metal industry, as well as to investigate the factors affecting the accumulation of this metal into the soil.

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RESEARCH OBJECT DESCRIPTION

Industrial activities in the study area started in 1876, and included activities such as the production of agricultural machinery, steel structures such as industrial halls, bridges and railway stations. In 1886, the construction of railway freight and passenger carriages, tanks, mail carriages, refrigerated carriages, etc. was added. During the Second World War, the factory produced vehicles and equipment for the army including armored trains, cannon parts, military vehicles, submarine hulls and aircraft parts. After 1945 it produced rolling stock, freight carriages and locomotives, but also steel structures [4, 6]. Currently in the industrial area, rolling stock and steel structures are produced, and part of the area is used as depots and warehouses.

MATERIALS AND METHODS

The research site (about 11.5 ha) is located close to the city center of Zielona Góra, between Sulechowska, Dworcowa, Ludowa and Źródlana Streets. This area is surrounded by residential buildings (both single and multifamily); in the north, the area is bordered by green space (Fig. 1).

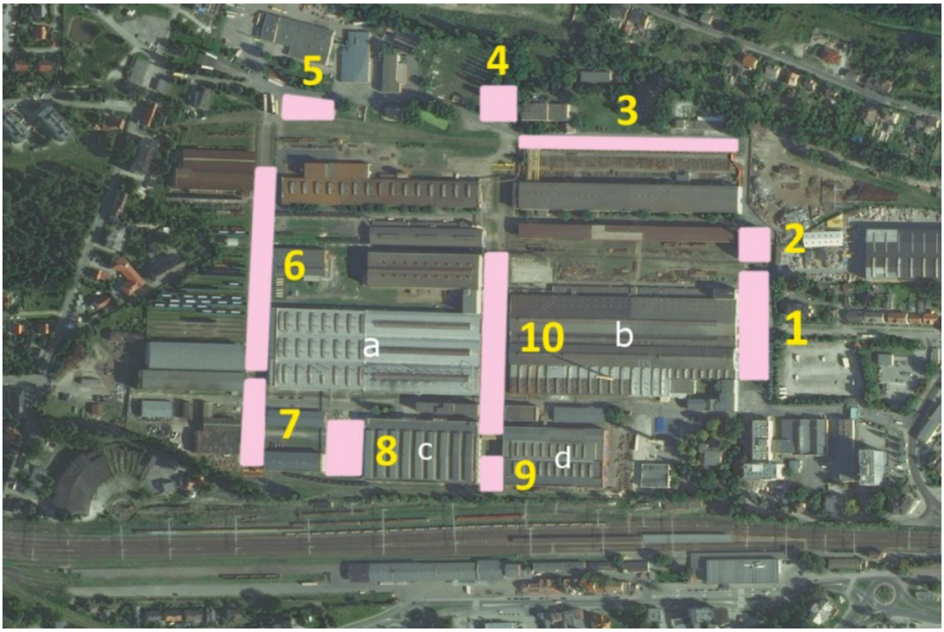


Fig. 1. Soil sampling sites (1–10). Halls with the highest manufacturing intensity are labeled a,b,c,d (based on www.maps.google.com).

Soil samples from 0–20 cm were taken in June 2009, 2010 and 2011 from the industrial area. Each sample was collected as a mixed one from 30 individual sampling points. The soil material was air-dried and sifted through a sieve with a mesh diameter of 2.0 mm.

Particle size distribution was determined by the Casagrande-Proszynski areometer method. Texture classes were established according to the FAO procedure [7]. Hydrolytic acidity (HA) was determined by Kappen's method, total exchangeable bases (TEB) by the Pallmann method in 1 M ammonium acetate (pH 7,0), and pH in H_2O and 1M KCl by the potentiometric method. Total carbon (TC) and total organic carbon (TOC) content were quantified using a Shimadzu analyser, and the Ni content in *aqua regia* was determined using atomic absorption FAAS. Extracts in a*qua regia* (HCl + HNO_3 in a 3:1 ratio) were prepared according to PN-ISO 11466:2002 [19].

All statistical analyses were conducted using Statistica 10 for Windows. The basic statistical figures were defined together with correlations between soil condition indices at confidence levels of α=0.01 and 0.05.

RESULTS AND DISCUSSION

The particle size distribution of the soils located in the area affected by the metal industry is mostly sand. Only in sites no. 7 and 9 was loamy sand found. The skeleton content varied from 3.3 % (site No. 4) to 34.8 % (site No. 8). The highest content of particles >2 mm was noted in sites no. 3 and 5–9. The reason for this may be found in the method of land reclamation, where waste material such as slag was used in the past. Another factor demonstrating the validity of this thesis may be the high soil reaction detected in all analyzed soil samples (pH H_2O range from 7.1 to 8.2, pH KCl from 6,6 to 8.0). A high alkaline reaction has been noted in slag by many researchers [10, 17].

TABLE 1. PHYSICAL PROPERTIES OF TESTED SOIL

Sample		Soil fraction				pH	
		Sand 2–0.05 mm	Silt 0.05–0.002 mm	Clay <0.002 mm	Skeleton >2mm		
		%				H_2O	KCl
1	2009	94	5	1	8.7	7.1	6.6
	2010	95	4	1	8.2	7.1	6.6
	2011	94	6	0	9.6	7.1	6.6
2	2009	94	6	0	8.6	7.1	6.7
	2010	95	5	0	7.4	7.1	6.7
	2011	94	6	0	11.6	7.3	6.8

3	2009	94	6	0	12.3	8.0	7.9
	2010	93	7	0	13.3	7.4	7.3
	2011	94	6	0	12.1	7.7	7.4
4	2009	93	7	0	6.5	7.9	7.6
	2010	96	4	0	6.7	7.3	6.9
	2011	92	8	0	3.3	7.7	7.5
5	2009	92	8	0	18.3	7.8	7.5
	2010	93	7	0	17.5	7.2	7.1
	2011	93	7	0	17.3	7.5	7.3
6	2009	92	7	1	12.9	8.2	8.0
	2010	96	3	1	13.7	7.2	7.1
	2011	96	3	1	11.1	7.9	7.7
7	2009	89	11	0	20.4	8.0	7.7
	2010	91	9	0	17.9	7.1	7.0
	2011	90	10	0	16.3	7.2	7.0
8	2009	92	8	0	16.1	8.0	7.8
	2010	91	8	1	27.4	7.2	7.0
	2011	91	9	0	34.8	7.7	7.5
9	2009	86	14	0	31.4	7.7	7.3
	2010	94	6	0	16.2	7.3	7.2
	2011	91	9	0	18.4	7.5	7.3
10	2009	95	4	1	9.1	7.5	7.3
	2010	94	5	1	11.6	7.5	7.5
	2011	95	5	0	7.9	7.8	7.6

Low soil sorption capacity is due to particle size distribution, which at its maximum point reached less than 14 cmol kg^{-1} (Table 2). The content of organic matter varied dramatically (from 0.10 g kg^{-1} d.m. in site no. 2 to 103–104 g kg^{-1} d.m.in sites No. 8 and 9). Organic matter as well as soil reaction is reported as an important factor in heavy metal sorption (besides the clay content) [8, 11].

TABLE 2. CHEMICAL PROPERTIES OF TESTED SOIL

Sample		TEB	CEC	TC	TOC	Ni
		cmol kg^{-1} d.m.		g kg^{-1} d.m.		mg kg^{-1} d.m.
1	2009	2.42	3.67	16.0	1.00	47.0
	2010	2.10	3.35	16.0	0.90	50.0
	2011	6.25	7.52	19.1	1.10	22.0
2	2009	3.51	4.91	25.0	0.30	18.0
	2010	4.96	6.36	24.6	0.10	8.0
	2011	2.94	4.41	25.5	0.30	20.0

3	2009	4.86	5.63	30.5	2.70	19.0
	2010	4.68	5.66	35.6	1.90	18.0
	2011	6.19	7.04	44.8	3.40	17.0
4	2009	4.35	5.58	23.4	0.30	13.0
	2010	5.56	6.93	29.5	0.60	16.0
	2011	5.44	6.80	22.7	0.20	9.0
5	2009	4.44	5.79	52.0	50.7	17.0
	2010	5.17	6.55	37.5	37.1	18.0
	2011	5.17	6.54	62.0	61.6	12.0
6	2009	6.20	7.20	30.5	29.4	29.0
	2010	4.10	5.22	25.9	25.7	31.0
	2011	4.51	5.6	21.8	21.3	14.0
7	2009	4.81	5.84	39.6	39.3	36.0
	2010	5.71	7.48	65.7	65.6	57.0
	2011	4.69	5.69	45.7	45.4	33.0
8	2009	5.48	6.31	46.2	45.4	45.0
	2010	4.23	5.70	75.5	75.0	78.0
	2011	3.16	4.14	104	104	74.0
9	2009	4.92	6.87	104	103	48.0
	2010	4.68	5.86	38.6	38.1	50.0
	2011	6.42	7.78	51.6	51.0	59.0
10	2009	4.35	5.08	22.9	22.2	45.0
	2010	5.95	6.65	23.5	23.2	43.0
	2011	3.52	4.37	20.2	19.2	58.0
Min.		2.10	3.35	16.0	0.10	8.0
Max.		6.42	7.78	104	104	78.0
Mean		4.69	5.88	39.3	29.0	33.5
S. deviation		1.10	1.12	22.8	30.0	19.5
S. error		0.04	0.04	0.76	1.00	0.65

TEB – total exchangeable bases, CEC – cation exchange capacity, TC – total carbon, TOC – total organic carbon.

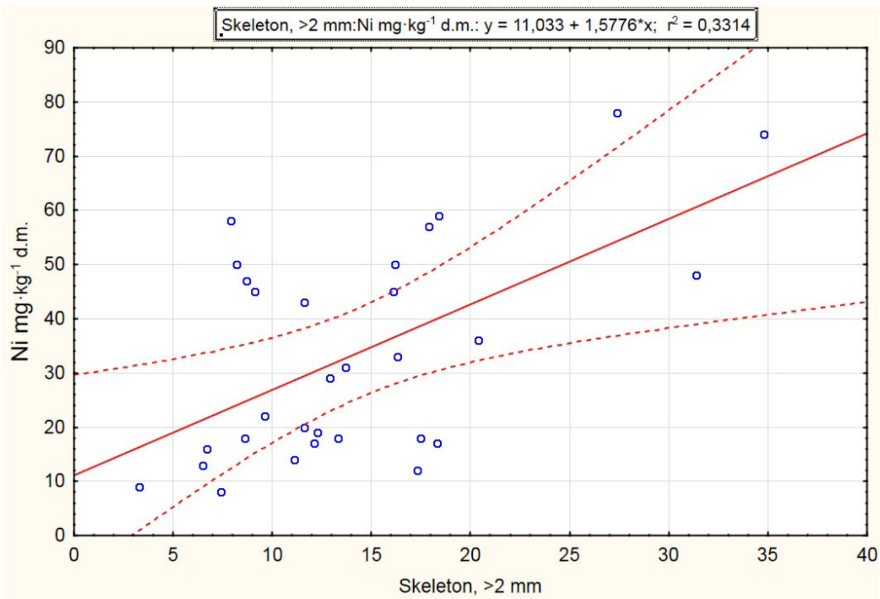
The total content of nickel in the tested soils varied from 8.00 mg kg^{-1} d.m. (site No. 2) to 78.0 mg kg^{-1} d.m. (site No. 8), but differences in the nickel content were found even within one research site. According to Polish Law [13], the content of nickel in tested samples does not exceed the threshold values for industrial soil. The mean content of nickel is slightly above the threshold value designated for green areas; however, it is not unusual for the soil of Zielona Góra (Greinert et al. have noted the maximum nickel content of urban soil of Zielona Góra to be 46.8 mg kg^{-1} d.m [9]). The primary content of heavy metals in soils depends mainly on the type of bedrock and soil-forming factors; however, the total content of heavy metals can change under the influence of meteorological and anthropogenic factors [14]. Many authors indicate that the measure of the accumulation of heavy metals for most soils corresponds to the particle size distribution (especially the content of the clay fraction), sorption capacity, soil reaction and the content of organic matter [2, 5, 14, 21].

High anthropogenic pressure on urban and industrial soil may result in heavily modified chemical composition and the physical properties of the soil. This may result in changes in the parameters responsible for the content of nickel. The statistical analysis indicated two major factors affecting the level of nickel in the test soil (Tabale 3, Fig. 2).

TABLE 3. THE CORRELATION MATRIX OF NICKEL AND PHYSICO-CHEMICAL PROPERTIES OF SOILS

Soil fraction				TEB	CEC	TC	TOC	pH	
Sand	Silt	Clay	Skeleton					H_2O	KCl
-0.342	0.266	0.270	0.578**	-0.232	-0.228	0.482**	0.605**	-0.096	-0.024

** highlighted coefficients are significant at $p < 0.01$; N=30.



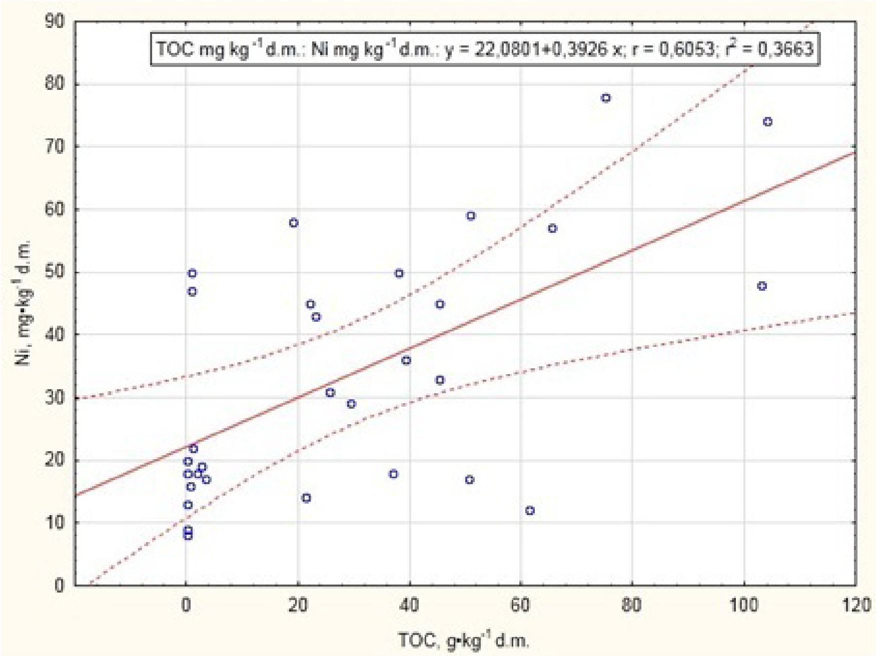


Fig. 2. The correlation between the nickel content in soil, soil skeleton and TOC.

The first factor was the particle size distribution. The nickel content in the soil was highly significantly dependent on the percentage of skeletal parts (r = 0.578; α=0.01). There was no relationship between the nickel content in the tested soils and other soil fractions (sand, silt and clay).

A highly significant correlation between the contents of total carbon and the contents of nickel, and between the total organic carbon and nickel content has been found. The correlation coefficient measured using α=0.01 was r = 0.482 and r = 0.605 (for Ni-TC and Ni-TOC, respectively). There was no relationship between the nickel content and soil sorption properties.

CONCLUSIONS

1. Soil affected by industrial activity is often characterized by an increased content of heavy metals. The example of the sites from Zielona Góra showed that nickel content in industrial soils is higher than average for urban soil in the city. Main factors affecting the accumulation of nickel were the content of soil skeleton and the organic matter content.

2. The reasons for this may be found in attempts at reclamation of these areas in the past (where the soil has been enriched with slag and lost its homogeneity) and long-term deposition of pollutants (which, because of the heterogeneity of the soil under anthropogenic pressure, can migrate into the profiles).

REFERENCES

[1] Abidemi O.O.: Nigerian J. Ap.p Sci. Environ. Man., **15,** 2, 2011.
[2] Al-Khashman O.A.: Atm. Environ., **38**, 39, 2004.
[3] Amza G., Cicic D.T., Rontescu C., Apostolescu Z., Pica D.: Proc. 4th IASME/WSEAS Int. Conf. Energy & Environment, 65, 2011.
[4] Borkowski W., Fedorowicz C., Kapała J., Koziorowski A., Łuczkiewicz Z., Rutkowski H.: Zastal 1945–1985. Wyd. Zaodrzańskie Zakłady przemysłu Metalowego im. M. Nowotki ZASTAL, Zielona Góra, 1985.
[5] Chłopecka A.: IUNG, Seria R., 1994.
[6] Eckert M.: Zastal 1876–1976. Wyd. Wyższa Szkoła Pedagogiczna, Zielona Góra, 1980.
[7] FAO Guidelines for Soil Description. Rome, 2006.
[8] Fleming M., Tai Y., Zhuang P., Mc Bride M.B.: Environ. Poll., **177**, 90, 2013.
[9] Greinert A., Fruzińska R., Kostecki J.: Urban soils in Zielona Góra. [In:] Technogenic Soils of Poland (Eds.) P. Charzyński, P. Hulisz, R. Bednarek, Toruń, Polish Society of Soil Science, 2013.
[10] Greinert A.: Studia nad glebami obszaru zurbanizowanego Zielonej Góry. Zielona Góra, Oficyna Wydawnicza Uniwersytetu Zielonogórskiego, 2003.
[11] Gustafsson J.P., Tiberg C., Edkymish A., Berggren Kleja D.: Environ. Chem., **8**, 485, 2011.
[12] Järup L.: Oxford J. Medicine, British Medical Bulletin **68**, 1, 2013.
[13] Rozporządzenie Ministra Środowiska z dnia 9 września 2002 r. w sprawie standardów jakości gleby oraz standardów jakości ziemi. 2002.165.1359.
[14] Kabata-Pendias A., Pendias H.: Trace Elements in Soils and Plants. CRC Press LLC Boca Raton, 2001.
[15] Li X., Liu L., Wang Y., Luo G., Chen X., Yang X., Hall M.H.P, Guo R., Wang H., Cui J., He X.: Geoderma, **192**, 2013.
[16] Matusiak, J.: Biul. Inst. Spawalnictwa, **48**, 5, 2009.
[17] Negim O., Eloifi B., Mench M., Bes C., Gaste H., Motelica-Heino M., Le Coustumer P.: Soil Sediment Cont. Int. J., **19,** 2, 2010.
[18] Nwachukwu M.A., Feng H., Alinnor J.: Int. J. Environ. Sci. Tech., **7**, 2, 2010.
[19] PN-ISO 11466:2002: Jakość gleby – Ekstrakcja pierwiastków śladowych rozpuszczalnych w wodzie królewskiej. Warszawa, 2002.Turski R., Baran S.: Degradacja, ochrona i rekultywacja gleb. Wyd. AR w Lublinie, Lublin, 1995.
[20] Wilkens B.J., Loch J.P.G.: Water Air Soil Poll., **96**, 1, 1997.
[21] Zhong X-l., Zhou S-l., Zhuc Q., Zhaod Qi-G.: J. Haz. Mat., **198**, 1, 2011.

SORPCJA NIKLU W GLEBACH W STREFIE ODDZIAŁYWANIA PRZEMYSŁU METALURGICZNEGO

Na obszarze badań działalność przemysłowa prowadzona była przez ponad 130 lat. W tym czasie na terenie przemysłowym emitowanych było wiele zanieczyszczeń (w tym także metali ciężkich), z których część została zdeponowana w glebie. Celem badań było określenie zawartości niklu na terenie zakładu przemysłowego metalowego oraz zbadanie czynników wpływających na jego zawartość w glebie. W pracy zaprezentowano właściwości gleb terenu przemysłowego zlokalizowanego w Zielonej Górze oraz zależność pomiędzy właściwościami fizyko chemicznymi a zawartością niklu. W porównaniu do metali ciężkich, takich jak ołów i kadm, które wykazują dużą szkodliwość wobec roślin i zwierząt, nikiel charakteryzuje się mniej szkodliwym działaniem. Ilość zanieczyszczeń mających wpływ na glebę zależy od rodzaju i sposobu prowadzenia procesu produkcji. Na terenie badań stosowane były podczas produkcji procesy spawania oraz malowania, które mogły mieć wpływ na zawartość niklu w glebie.