POLISH JOURNAL OF SOIL SCIENCE
VOL. XLVIII/1 2015 PL ISSN 0079-2985

DOI: 10.17951/pjss/2015.48.1.13

Soil Chemistry

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THE STATE OF SOIL CONTAMINATED WITH NICKEL IN THE FORMER SANITARY ZONE OF THE GŁOGÓW COPPER SMELTER

Abstract. Substances present in soils are of natural or anthropogenic origin. As a result of industrial activity, large quantities of potentially hazardous elements such as heavy metals are deposited in the environment. They may occur as unavailable (similar to the total form), or available for plants. The content of nickel in the soil from the former sanitary zone of the Głogów Copper Smelter does not exceed the Polish threshold values for industrial areas; however, its content may be influenced by other factors such as content of organic matter and soil reaction. In this article we present the results of the nickel pollution in the former sanitary zone of the Głogów Copper Smelter.

Nickel is one of the elements which is naturally present in the environment. It occurs in the form of organic compounds, ionic form (usually as Ni^{+}, Ni^{2+}, Ni^{3+}) and minerals in solid state [12, 13, 19, 20]. The average nickel content in natural soils varies between different soil types and can range from 5 mg kg^{-1} in sandy soils, through 11 mg kg^{-1} in medium-textured soils to 22 mg kg^{-1} in fine-textured soils [12, 13].Industrial activity is inextricably linked with the progress of civilization and prosperity. We should pay more attention to the fact that in previous years people were focused only on an increase in industrial efficiency, without considering its impact on the environment. Such behaviour leads to substantial

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deposition of potentially hazardous substances into the environment, particularly in the soil environment [28].

Many authors [2, 8] point out that land pollution is often caused by more than one pollutant. The main contamination from the Głogów Copper Smelter are SO_2, CO and metal-bearing dusts [14].

Soil has a buffer capacity depending on many factors, including: soil composition, content of organic matter and pH [6, 12, 13]. Also, the characteristic of a contaminant has significant meaning. Changes in environmental conditions may lead to the mobilization of inactive xenobiotics. Heavy metals available to plants may be incorporated into the food chain or can contaminate groundwater.

The aim of this paper is to present the state of soil contamination with nickel in the former sanitary zone of the Głogów Copper Smelter.

RESEARCH OBJECT DESCRIPTION

The Głogów Copper Smelter (GCS) is a part of the Copper Mining and Smelting Industrial Complex (KGHM) located in the northern part of the Lower Silesia province. The Głogów Copper Smelter includes two divisions – Głogów Copper Smelter I and II. Division I (based on the technology of smelting in shaft furnaces) was launched in 1971, while Division II (based on the slurry process), began producing copper in 1977 [24, 29].

The activity of copper smelting has affected the environment, and therefore, around all the plants emitting pollutants into the atmosphere, protective zones were set up. For the Głogów Copper Smelter, it was established in 1990, over an area of 2,840 ha. As a result of pro-environmental investments, the emission of pollutants has been reduced, which has contributed to a reduction in the area of protective zones. The one around the Głogów Copper Smelter decreased by 6% (to 2660 ha) in the year 2001 [14].

MATERIALS AND METHODS

The study took place in the former sanitary zone of the Głogów Copper Smelter (Lower Silesia Province, western part of Poland). The research site was selected in the SW (Żukowice) and NE (Bogomice) at a distance of up to 1 km from the GCS. The control site (Stypulów) was located about 15 km NW from the smelter. The location of the sites is shown in Fig. 1.

Soil samples were taken in June 2010 from all genetic horizons of the soil profile. Each sample was collected as a mixed one, representing material from the whole depth of the horizon. The soil material was air-dried and sieved through a sieve with a mesh diameter of 2.0 mm. With the material prepared this way, the following analyses were made:

– particle size distribution – using hydrometer method [21]

– pH – in H_2O and 1M KCl suspension (potentiometrically), soil/liquid – 1:2.5 [13]

– organic carbon – using Tiurin method [21]

– Ni – using atomic absorption spectrometry FAAS. Total content after mineralisation in aqua-regia [22], bioavailable form – after 1h mechanical shaking with 0.1M HCl and 1M HClAll the soil analyses were performed in triplicate. 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 α=0.05.

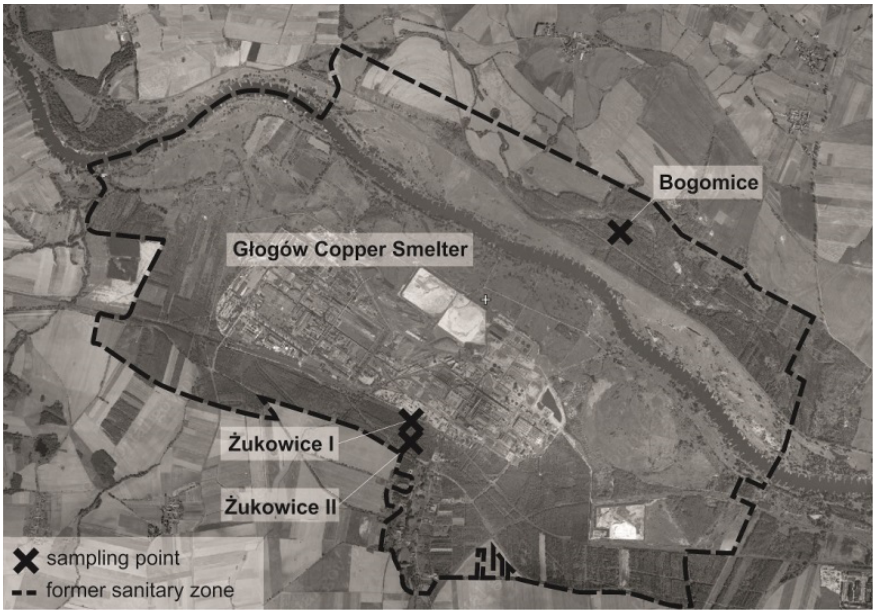

Fig. 1. Location of sampling sites in the protective forest of the GCS.

RESULTS AND DISCUSSION

The particle size distribution of the soils is mostly sandy loam (Żukowice II, Bogomice) and loamy sand (Żukowice I). The control site is mixed on loamy sand and sandy loam [14].

TABLE 1. PARTICLE SIZE DISTRIBUTION OF TESTED SOIL

Research site	Soil horizon	Depth, cm	Sand	Silt	Clay	Texture class (FAO 2006)
			2.0–0.05 mm	0.05–0.002 mm	< 0.002 mm	
Żukowice I	O	4÷0	-	-	-	-
	A	0÷20	74	25	1	loamy sand
	Bw	20÷25	79	19	2	loamy sand
	BwC	25÷32	75	22	3	loamy sand
	C1	32÷60	84	11	5	loamy sand
	C2	60÷85	83	12	5	loamy sand
	C3	>85	84	12	4	loamy sand
Żukowice II	O	2÷0	-	-	-	-
	ABw	0÷18	57	43	0	sandy loam
	Bw	18÷48	53	45	2	sandy loam
	BwC	48÷93	64	35	1	sandy loam
	C	>93	60	39	1	sandy loam
Bogomice	O	3÷0	-	-	-	-
	A	0÷23	50	44	6	sandy loam
	Bw1	23÷47	55	41	4	sandy loam
	BwCg	47÷59	65	32	3	sandy loam
	Cg	>59	76	20	4	loamy sand
Stypułów	Ap	0÷30	82	18	0	loamy sand
	Bv	30÷60	73	23	4	loamy sand
	C	60÷90	69	23	8	sandy loam
	Cg	>90	70	20	10	sandy loam

Nickel is an element that is naturally present in the environment; however, part of it gets into the soil as a result of human activity (e.g. burning of fuels, mining, smelting). Although it is not a highly toxic element, its excess is equally detrimental for plants, as well as animals and humans [7, 12, 14]. The total content of Ni in tested soils was highest in the Bogomice sampling location, the lowest in Żukowice I. The mean value for the area of the sanitary zone was nearly four times higher than the control site.

TABLE 2. THE RESULTS OF SOIL Ph, CARBON AND Ni CONTENT

Research site	Soil horizon	Depth, cm	pH		TOC $g{\cdot}kg^{-1}_{d.m.}$	Ni, mg kg^{-1} d.m.		
			H_2O	KCl		0,1 M HCl	1 M HCl	Total
Żukowice I	O	4÷0	6.2	5.8	-	-	10.6	23.6
	A	0÷20	6.6	5.9	9.40	0.30	1.80	8.54
	Bw	20÷25	6.8	6.3	6.60	0.17	2.40	8.89
	BwC	25÷32	5.1	4.4	1.30	0.13	2.10	6.97
	C1	32÷60	6.1	4.7	2.90	-	2.50	6.74
	C2	60÷85	6.2	5.1	1.20	-	1.80	9.14
	C3	>85	6.4	5.4	1.60	-	3.70	14.8
Żukowice II	O	2÷0	6.9	6.6	-	0.03	7.30	23.2
	ABw	0÷18	8.0	7.4	13.8	0.16	1.11	12.6
	Bw	18÷48	8.0	7.6	12.0	0.11	1.01	11.3
	BwC	48÷93	8.1	7.5	14.3	-	1.58	19.5
	C	>93	8.0	7.5	18.6	-	1.76	21.7
Bogomice	O	3÷0	7.0	6.5	-	-	1.77	12.1
	A	0÷23	5.1	4.1	14.3	0.14	1.92	21.7
	Bw1	23÷47	5.7	4.7	28.6	0.27	1.54	24.3
	BwCg	47÷59	6.0	4.6	6.30	0.24	1.53	21.8
	Cg	>59	5.6	4.5	9.80	0.42	1.26	21.6
Min.	-	-	5.10	4.10	1.20	0.13	1.26	6.74
Max.	-	-	8.10	7.60	28.6	0.42	3.70	24.3
Mean*	-	-	-	-	9.15	0.24	2.03	14.3
S. deviation*	-	-	-	-	8.18	0.24	1.34	8.34
S. error*	-	-	-	-	0.74	0.03	0.12	0.76
Stypułów	Ap	0÷30	7.5	7.4	13.8	-	1.10	4.35
	Bv	30÷60	6.9	5.0	1.40	-	0.95	3.97
	C	60÷90	6.0	4.5	1.60	-	0.80	3.65
	Cg	>90	4.8	3.9	0.40	-	1.20	2.93
Min.	-	-	4.8	3.9	0.40	-	0.80	2.93
Max.	-	-	7.5	7.4	13.8	-	1.20	4.35
Mean	-	-	-	-	4.30	-	1.01	3.73
S. deviation	-	-	-	-	4.82	-	0.79	2.90
S. error	-	-	-	-	0.44	-	0.07	0.26

* counted only for mineral horizons.

Nickel is a component of urease, so it is responsible for urea nutrition [15]. According to Mengel et al. [19] a high level of nickel in soils can disturb nutrient uptake and can be a cause of chlorosis and necrosis. Jadia et al. [9] and Maheshwari and Dubey [18] pointed out a decrease in seed germination in environments polluted with nickel. Singh [26] noted that nickel is toxic for plants at concentrations above 50 mg kg^{-1} d.m.

It is known that there are elements in the soil environment in the form most commonly associated with the various fractions of the soil, which has been shown repeatedly using sequential extraction [7, 10]. The content of chemical compounds is directly related to soil texture, reaction and organic matter content [6, 7, 12, 13]; however, statistical analysis showed no significant correlation (α=0.05) between the content of any form of nickel and soil properties in the sites located in the former sanitary zone. A highly significant correlation was found between the total content of Ni and soil reaction in the control site (r = 0.994; α=0.01).

According to Kabata-Pendias and Pendias [12, 13] the nickel in an acidic environment occurs frequently in the ion form of Ni^{2+} and can migrate in the environment (the acidic environment also increases its mobility). A relatively high pH suggests that contamination introduced into the soil has been adsorbed and will not migrate into the soil profile. Kabata-Pendias and Pendias [12] reported the phytoavailability of nickel drops at pH> 6, but Hooda [7], based on other authors, suggests a pH limit of 6.9. The reaction of tested soils is slightly acidic and neutral (Bogomice, Żukowice I, Stypułów). Samples taken in Żukowice II showed an alkaline reaction (tab. 2). Similar pH values were found by other researchers [25]. The difference in the pH within a short distance (Żukowice I and II) is caused by the disproportionate use of lime during soil reclamation in the sanitary zone. Soil reaction is not the only factor influencing the sorption in soil – the other is the content of organic matter. The content of organic carbon was greater mainly in the top horizons (tab. 2), while the smallest content was found in Stypułów. Sites located in the former sanitary zone are located in the Odra Valley, characterized by various pedogenesis and anthropogenic impact (agriculture, industry, reclamation) [17]. The control site is used as a set-aside field.

A high content of organic matter reduces the availability of heavy metals for plants [5] through the creation of organic complexes [30]. This is a result of sorption [6, 27]; however, the process is not irreversible – in appropriate conditions adsorbed metals can be re-released into the environment. According to Gąszczyk et al. [4] nickel is quite easily adsorbed in sandy soils (Pb> Cu> Zn ≥ Cr> Ni> Co> Cd) and loess (Pb> Cu> Cr> Zn> Ni> Co> Cd). On the one hand this causes a potential threat to the environment, on the other it enables the use of methods based on extraction to remove it from the soil.

The mobility of heavy metals is determined by a series of physico-chemical and biological mechanisms. The total content of heavy metals in contaminated soils cannot be used as an indicator of environmental risk. A real threat can be presented only by the indication of mobile forms of xenobiotics, which may be difficult as there are no uniform standards for extractants. According to Polish Law [11], the limit of nickel content for industrial and traffic areas is up to 300 mg kg^{-1} d.m. The content of nickel in the soil from the former sanitary zone of the Głogów Copper Smelter does not exceed those values; however, there are no threshold values for the mobile form of any heavy metal.

CONCLUSIONS

1. The main factor influencing the content of heavy metals in the tested area seems to be the content of organic matter, which, despite the soil reaction, may absorb much higher amounts of nickel (Bogomice) than in soils with higher pH (Żukowice II).

2. The content of nickel in the soil from the former sanitary zone of the Głogów Copper Smelter does not exceed Polish threshold values for industrial areas, which is established up to 300 mg kg^{-1} d.m.

3. Nickel occurs in the soil solution, and it may also be weakly absorbed by a soil mineral fraction. The mineral fraction of tested soils showed similar quantities of nickel on tested sites (for both the sanitary zone and the control site), which was confirmed by extraction of weak acids (0,1 M HCl and 1 M HCl).

4. The difference in the amount of nickel in the sanitary zone and the control site indicates the anthropogenic enrichment of soil. A similar nickel concentration throughout the profile may indicate a long-term deposition of pollutants in the area.

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STAN ZANIECZYSZCZENIA GLEB NIKLEM W STREFIE OCHRONY HUTY MIEDZI GŁOGÓW

Obecne w glebie związki chemiczne mają pochodzenie naturalne lub antropogeniczne. Jako efekt działalności przemysłowej, do atmosfery emitowane są znaczne ilości zanieczyszczeń, w tym metali ciężkich. Zanieczyszczenia obecne w środowisku mogą być związane trwale z materiałem glebowym, część z nich jest jednak dostępna dla roślin. W artykule przedstawiono wyniki zanieczyszczenia niklem terenów strefy ochronnej Huty Miedzi Głogów. Badania wykazały, że zawartość niklu nie przekraczała wartości granicznych, wg obowiązujących w Polsce standardów dla gleb stref przemysłowych. Zawartość niklu może być jednak modyfikowana przez zawartość materii organicznej oraz pH.