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The influence of anthropogenically increased pH on the content and the mobility of nickel in arable soils in the surroundings of "Małogoszcz" cement plant

Abstract: The aim of the conducted research was the evaluation of the influence of increased pH on the content and mobility of nickel in arable soils in the surroundings of Małogoszcz Cement Plant. The physico-chemical properties of the investigated soils were determined by the methods commonly used in soil laboratories. The total content of Ni was determined after mineralization in the mixture of HF and $HClO_4$ acids, and the content of forms available for plants, after the extraction with DTPA solution, using ASA method. The investigated soils are characterized as loamy sands or sands (PTG 2008). These soils have the content of C-organic in the range of 10.3–24.2 g·kg^{-1} in the surface horizons and 8.3–20.3 g·kg^{-1} in the subsurface horizons. The pH values allow to classify these soils as alkaline. In all of the investigated soils calcium carbonate occurs. The values of total content of nickel were in the range of 1.47–2.82 mg·kg^{-1} in surface horizons and 1.80–2.45 mg·kg^{-1} in subsurface horizons, which allows to classify these soils as soil with natural nickel content. The content of Ni-DTPA were in the range of 0.06–0.26 mg·kg^{-1}. The sequential analysis of the obtained results indicates on significant statistically positive correlation between the total content of Ni and C-organic, which has the value of 0.648143 and between the content of Ni-DTPA and the content of fraction with ∅<0.002 mm, with the value of 0.581113 on p=0.05.

Key words: cement dust, soil, nickel

INTRODUCTION

The natural content of elements in soil environment depends mostly on their presence in parent material, erosion, soil-forming processes and texture (Czarnowska, 1996; Terelak and Piotrowska, 1997). The anthropopression has the influence on systematic increase of heavy metals content in soils. The emission of cement dusts by cement and lime industry significantly influences the environment. The range of emission of cement-lime dusts may be up to 8 km (Świercz, 2006). The deposition of dust depends on the type of technological process and the direction of prevailing winds (Kusza et al., 2009), and decreases with the distance from the emitter (Faber and Jakubczyk, 1976). Dobrzański et al., (1970) shows the highest content of $CaCO_3$ in the surface horizon of the soil. Long-term anthropopression leads to changes similar to those in over lime soils. The presence of calcium carbonate and pH of soil significantly influences the mobility of heavy metals. Nickel is an element with high mobility in the environment and liming is considered to be the main factor activating this element in soil. It is classified, along with Zn and Cu, as an element easily absorbed by roots and transported to aerial parts of plants, and it may be toxic for plants and non-toxic for animals (Cchaney and Oliver, 1996).

In 1974 the Małogoszcz Cement Plant in Świętokrzyskie province began production based on dry technology. It uses natural deposits of Jurassic limestone and marl. Cement-lime dusts from the cement plant in Małogoszcz are 84% of all dusts emitted in the district, according to GUS data (2004). Lafarge Cement Polska S.A., Małogoszcz Cement Plant along with KOSD S.A. in Kielce and "Bukowa" Lime Industry have negative influence on the state of the environment (Janus et al. 2003). The area of Małogoszcz municipality was classified to Podkielecka Area of Environmental Risk, listed among 27 such areas in the country (Janus et al., 2003).

The environment around the cement plant is regularly monitored. The results of the Factory Laboratory of Environmental Protection research shows that since 1998 the deposition norm of dusts, which is 200 g/m^2/year, have not been exceeded in neither measuring point within the protected area of the cement plant. In the year of 2000, the volume of dust fall in the mentioned measuring points remained in the range of 25 g/m^2 to 51 g/m^2, with overall dusts

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emission 427 mg. In previous years the emission of cement dusts was higher and varied from 1900 Mg/year to 800 Mg/year (Świercz, 2003). According to the Municipal Program of Environmental Protection for the years 2004–2011, the emission of dust spoilage from the Małogoszcz Cement plant (2003) was 283 Mg/year, where the share of cement-lime spoilage was 266Mg/year and the share of toxic and highly harmful contained (composed of Cr, Hg, Co and Ni) was 8.702 Mg/year.

The aim of the research was determination of content and mobility of nickel in arable soils with increased pH, from the surroundings of the Małogoszcz Cement Plant.

MATERIAL AND METHODS

The research material comprised arable soil samples from the surroundings of the Małogoszcz Cement plant located in Małopolska Upland. Agricultural lands of the municipality are characterized by medium-low value of agricultural quality. The soil samples were collected in August 2010. The research sections were located in various distance from the cement plant building on the edge or the cultivated fields: I – 700 m, II – 800 m, III – 850 m, IV – 1700 m, V – 2900 m, Vi –2200 m. The exact location of the research sections was determined by the use of GPS (Jaworska and Dąbkowska-Naskręt, 2011). The soil samples were collected from two depths (0–20 and 20–40 cm), where texture, pH, Corg, content of $CaCO_3$ were determined using common lab methods. Total content of Ni was determined after the mineralization process in teflon in the mixture of HF and $HClO_4$ acids, using Crock and Severson method (1980) and the content of forms available for plants after extraction in DTPA solution, according to Lindsay and Norvell procedure (1978), using ASA method. All designations were performed in 3 repetitions, but in this work the arithmetic means of the results are shown. Additionally control samples were analyzed. The obtained results were calculated using Statistica 10.0 software.

RESULTS AND DISCUSSIONS

The municipal area is dominated by agricultural lands, which are 64.4% of the whole area (9370 ha), where 7249 ha are arable lands (Janus et al. 2003). Agricultural lands of this region are characterized as of rather low agricultural quality. In the southern part of the municipality the most common are Rendzic Phaeozem (WRB, 2006) formed form chalk rocks with neutral or slightly alkaline reaction. In the central part (the surroundings of Małogoszcz and Leśnica) the most common are soils of good quality. They are more difficult for mechanical cultivation. The remaining areas are covered mostly by brown soils, leached and acidic, formed from sands (Janus et al. 2003).

TABLE 1. Granulometric composition of soils

Sample	Depth [cm]	Percentage of fraction with diameter [mm]		
		2–0.05	0.05–0.002	<0.002
Zakrucze I	0–20	83	12	5
	20–40	78	14	8
Zakrucze II	0–20	84	11	5
	20–40	91	6	3
Leśnica I	0–20	81	13	6
	20–40	86	11	3
Leśnica II	0–20	82	14	4
	20–40	82	12	6
Leśnica III	0–20	79	15	6
	20–40	79	17	4
Małogoszcz	0–20	72	24	4
	20–40	63	29	8

The investigated soil in agrotechnical categories were classified as sandy soils with texture of loamy sand and sands (PTG, 2008).The texture of the investigated soils is not much diversified (Table 1), and the content of fraction below >0.002 mm of ∅ diameter varied from 3 to 8% (Jaworska and Bartkowiak, 2011). In these soils the content of Corg in the range from 10.3 to 24.2 $g \cdot kg^{-1}$ in surface horizons and 8.3–20.3 $g \cdot kg^{-1}$ in subsurface horizons (Table 2). It may be connected to pH of dusts emitted from the cement plant, which was pH H_2O=11.82 (Kozłowski, 2012).

In all of the investigated soils the presence of calcium carbonate was detected. The content of $CaCO_3$ varied from 0.42 to 12.6% in surface horizons and from 0.38 to 0.84% in subsurface samples (Table 2). Significantly higher contents of $CaCO_3$ were in surface ho-

TABLE 2. Physicochemical properties of soils

Sample	Depth [cm]	Corg [$g \cdot kg^{-1}$]	$CaCO_3$ [%]	pH	
				H_2O	KCl
Zakrucze I	0–20	11.0	1.05	8.31	7.73
	20–40	10.8	0.38	8.07	7.53
Zakrucze II	0–20	10.3	1.26	7.84	7.61
	20–40	8.3	0.80	7.90	7.87
Leśnica I	0–20	16.3	0.42	7.93	7.42
	20–40	10.3	0.38	7.95	7.14
Leśnica II	0–20	18.4	0.42	6.40	5.82
	20–40	12.8	0.38	5.61	4.40
Leśnica III	0–20	18.9	0.42	5.66	4.84
	20–40	12.2	0.38	6.40	5.62
Małogoszcz	0–20	24.2	0.84	7.57	7.09
	20–40	20.3	0.84	7.75	7.15

TABLE 3. Total and plant available forms of Ni of analyzed soils

Sample	Depth [cm]	Ni-total [mg·kg^{-1}]	Ni-DTPA [mg·kg^{-1}]	Ni-DTPA Ni-total
Zakrucze I	0–20	2.82	0.11	0.04
	20–40	2.42	0.26	0.11
Zakrucze II	0–20	1.47	0.19	0.13
	20–40	1.85	0.25	0.14
Leśnica I	0–20	2.72	0.11	0.04
	20–40	1.90	0.09	0.05
Leśnica II	0–20	2.67	0.10	0.03
	20–40	2.10	0.14	0.14
Leśnica III	0–20	2.51	0.09	0.08
	20–40	1.80	0.11	0.11
Małogoszcz	0–20	2.80	0.06	0.04
	20–40	2.45	0.10	0.13

rizons from the sampling point Zakrucze I and II located 800 m and 850 m from the emitter respectively. The total contents of nickel fell in the range from 1.47 to 2.82 mg·kg^{-1} in surface horizons and from 1.80 to 2.45 mg·kg^{-1} in subsurface horizons (Table 3).

This Ni content was higher in surface horizons, except for one research point (Table 3, Fig. 1), which is the result of susceptibility of nickel to from complexes with organic matter as mobile chelates, also in neutral and alkaline reaction (Kabata-Pendias and Pendias, 2001). Research conducted by Arasimowicz (2009) indicates predominant share of nickel connected to organic substance in soil, and sorption of nickel by mostly in mineral soils iron and manganese hydroxides. Statistical analysis of the obtained results indicates statistically significant positive correlation between the total content of nickel and the content of Corg, which is 0.648143 with $p<0.05$. Similar dependency was confirm in the research of Sady and Smoleń (2004). Low accumulation of Ni in the surface samples suggests its origin from dusts, which contain of nickel, emitted by the company (Janus et al., 2003). Interesting, is the10 times lower total content of Ni in the investigated soils, compared to the results presented by Kusza et al. (2009) for soils located in the surroundings of the Odra Cement Plant. In the research conducted by Świercz (2005), total content of Ni in soils in the surroundings of the Małogoszcz Cement Plant, are significantly higher, compared to those present only in organic horizons of forest soils. The results obtained for soils located around the Bielawy Cement Plant (Dąbkowska-Naskręt et al., 2011), part of Lafarge group, are similar to results shown in this paper. These contents do not exceed the geochemical background (McGrath, 1995; Czarnowska, 1996; Kabata-Pendias and Pendias, 2001), which allows to classify them, in accordance with general guidelines for agricultural soils, as soils with natural nickel content (Kabata-Pendias et al., 1993). These soils may be used for horticultural and agricultural cultivation.

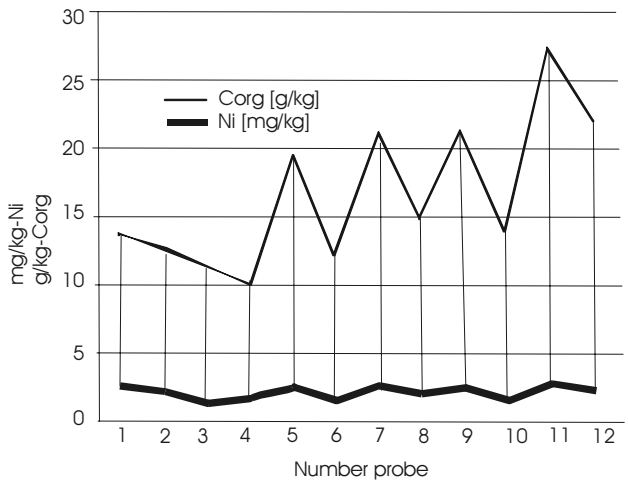

FIGURE 1. Total content of nickel and Corg

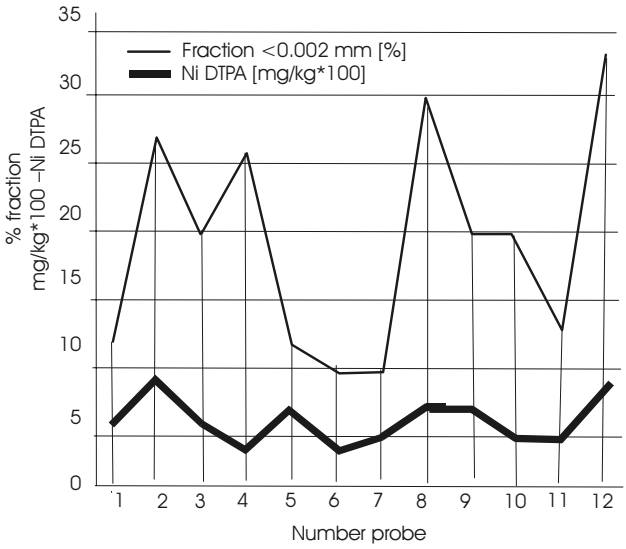

FIGURE 2. Content of Ni-DTPA and fraction ∅ 0.002 mm

The content of DTPA extracted forms of nickel were in range from 0.06 to 0.26 mg·kg^{-1} (Table 3).A slightly higher content of available Ni in soils was observed in the subsurface horizons. The movement of soluble forms of this element carries out in accordance with the prevailing direction of water movement, which is effected of climate conditions, and is related to decreasing pH. With the increase of acidity, the solubility of Ni increases. Its sorption by Fe and Mn hydroxides increases with the decrease of acidity (Lis and Pasieczna, 1995).

Determination of Ni- DTPA content in soils indicates its availability to plants. It is taken generally in proportion to its concentration in soil (Panwar et al. 2002. pH, texture, and most of all the content of fraction with ∅<0.002 mm are the factors which have

significant impact on the content and the mobility of nickel (Perlak, 2000; Weng et al., 2004; Rooney et al., 2007), which is shown in statistical analysis of the obtained results (Fig. 2). A statistically significant positive correlation between the content of Ni-DTPA and the content of fraction with ∅<0.002 mm which is 0.581113 with $p<0.05$ was determined. In the investigated soil samples the content of bio-available forms of Ni is in range from 0.78 to 2.17% of the total content and its average share is 8.31%. These values are below values recognized as toxic and relatively low (Latosińska and Gawdzik, 2011).

Due to the texture of the investigated soils, and the presence of Ni in the dusts emitted by the cement plant, it is necessary to control its content in the cultivated soils surrounding the cement plant.

CONCLUSIONS

1. The total content of nickel were ranged from 1.47 to 2.82 mg·kg^{-1} in surface horizons and from 1.80 to 2.45 mg·kg^{-1} in subsurface horizons, which allows to classify them as soils with natural nickel content.
2. The content of DTPA extracted forms of nickel ranged from 0.06 to 0.26 mg·kg^{-1}. Slightly higher content of available Ni in soils was observed in subsurface horizons. These values are below toxic level.
3. Statistical analysis of the obtained results indicates on statistically significant positive correlation between the total content of nickel and the content of Corganic (which is 0.648143) and between the content of Ni-DTPA and the content of fraction with ∅<0.002 mm (which is 0.581113 with $p<0.05$).
4. Detected total content of nickel and its mobile forms in the investigated soils does not exclude these soils from agricultural use.

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