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THE ASSESSMENT OF HEAVY METALS CONTENT IN TOTAL AND BIOAVAILABLE FORMS IN THE SOILS SURROUNDING CEMENTOWNIA CHELM S.A. IN CHELM, POLAND

Abstract: The study consisted in assessing the impact of the cement industry on the selected physicochemical properties and total and bioavailable content of heavy metals in soils located in the vicinity of the factory. The sampling points were located in the four transects to the east, west, north and south of the plant, at an increasing distance of 0 - 250 - 500 - 1500 and 2000 m. The soil samples were collected from the depth of 0-20 cm. The analysed soils were characterised by the significant presence of calcium carbonate, distributed evenly in all directions. Concentrations of heavy metals were characterised by high variation, depending on the direction and distance from the cement factory. The percentages of bioavailable forms of heavy metals in the general pool did not exceed 10%.

Key words: heavy metals, bioavailability, cement factory, soil contamination, industrial areas

INTRODUCTION

Heavy metals are natural components of the pedosphere, however, particularly in heavily industrialised areas, where large quantities of dust, waste and wastewater are by-produced, their concentration is increased (Kostecki *et al.* 2015; Plak *et al.* 2015; Jankiewicz, Adamczyk 2007). Cement production is one of the most dust-generating technological processes in industry. Produc-

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tion in the conditions of insufficient encapsulation of dust sources or inefficient de-dusting devices causes that clinker, cement, coal dust and ash are released into the atmosphere, soil and water and may lead to manifold damage to the environment. Primarily, the indicated substances have a very negative impact on the overall development of plants: layers of dust deposit on leaves, reducing the number of active stomata (Dąbkowska-Naskręt *et al.* 2006; Jaworska *et al.* 2010; Jaworska *et al*. 2013, Dąbkowska-Naskręt *et al.* 2013).

Prolonged dust fall may lead to a gradual progressive biological deactivation of soil, due to the depletion in types and quantity of species inhabiting the original population (Gołuchowska, Kusza 2010; Gołuchowska *et al.* 2012; Hua *et al.*, 2016 Mandre *et al.*, 1998) Moreover, the storage of waste, the drainage of domestic sewage of the crew, the drainage of cooling waters and the extraction of underground water intensifies an adverse impact of cement plants on the environment. The soil tested around cement factories displays high concentration of certain heavy metals, *e.g.* iron and calcium, which clearly decreases with increasing distance from plants (Asubiojo *et al.*, 1991; Ade-Ademilua Umebese 2007). An important aspect characterising the presence of heavy metals in soils and geochemical circulation is their bioabsorbability. A single speciation analysis was used in the study on the grounds that it is frequently only a limited percentage of total heavy metal content in soil that is absorbed by plants, or may migrate into groundwater, *i.e.* be active in geochemical circulation (Hlihor *et al.* 2009 Mocek *et al.* 2012). High concentration of heavy metals, especially in the bioavailable forms in the soils in the vicinity of industrial plants, seriously disrupts their natural geochemical cycle.

The aim of the study is to evaluate the impact of a given cement factory activity on the selected physicochemical properties of soils as well as total and bioavailable heavy metal content in the soils located in the vicinity of the cement plant.

Materials and Methods:

Chełm S.A. Cement Plant is located on the eastern outskirts of Chełm at a distance of 3.5 km from the city of the same name, counting approx. 70,000 residents. The immediate area of the plant is as follows:

to the north: railway line and the road Chełm - Dorohusk, Antonin residential area,

to the east: farmlands, village Ignatów,

to the south: open pit mine of chalk,

to the west: Polish rail lands, renovation company *Remur S.A.*

Three nature reserves, covering carbonate peat bogs with unique flora and fauna are located in close proximity to the north and east of the premises: *Brzeźno*, approx. 3.5 km, *Serebryskie Swamp*, approx. 2.5 km and *Roskosz*, approx. 5 km from the plant (Fig. 1). The total area of the plant is 4.2 km^2, including the surface of the open-cast mine of 3.19 km^2.

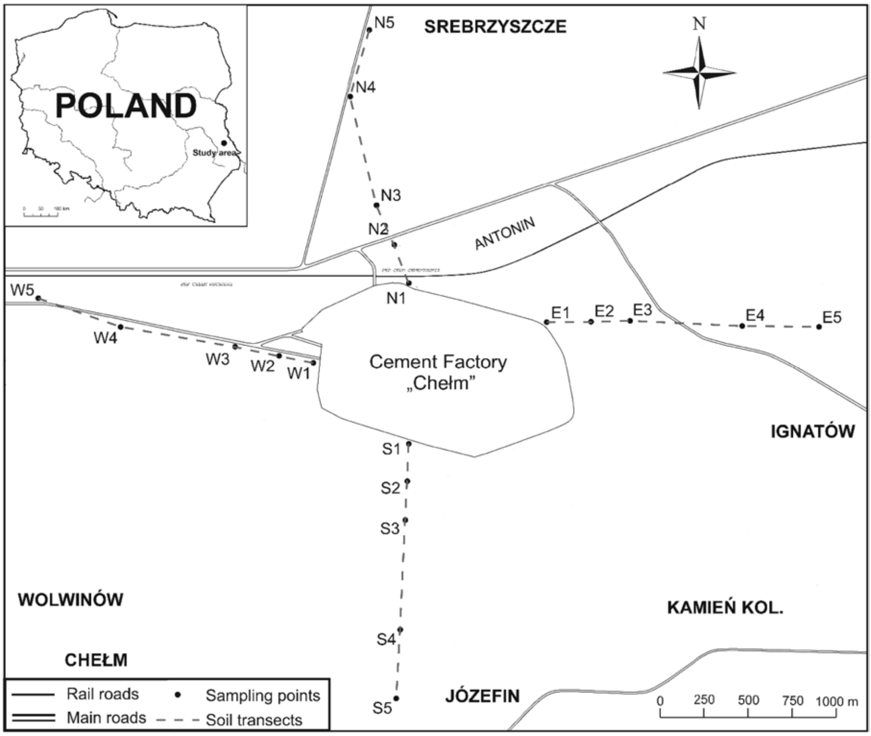

Fig. 1 Localization of the study area

The plant area covering the entire technological cycle, including infrastructure, amounts to 0.90 km2. A deposit of chalk called Chalk Mountain is a raw material base, exploited since 1926. Geological resources – balance deposits of chalk are around 386 million tons, which secures production for a period of 60 years. The average annual temperature is 7.3°C, with average values -2.9°C in winter, 7.1°C in spring, 17.3°C in summer, and 7.8°C in autumn. The average annual precipitation amounts to about 550 - 560 mm and is lower than the national average. About 40% of the annual precipitation falls in the summer months (June-August). The average annual wind speed reaches 3.8 m/s with prevailing south-west (16.4%), south-east (13.9%) and west (12.9%) winds (Kaszewski, Mrugała 2001).

There were four study transects located on the east, west, north and south off the plant. For each transect 5 samples were collected in 3 repetitions from the topsoils (0-20 cm), at distances of 0 - 250 - 500 - 1500 -2000 m from the plant (20 samples in total). Each transect included the samples that numbered in the following way: E1, E2, E3, E4, E5, corresponding to the distances from the cement plant. Analogous procedures were carried out in all other directions W1-5, N 1-5, S 1-5. The air-dried soil samples taken into analysis were sieved through a sieve with an aperture of 2 mm. The soil skeleton fraction (fragments of carbonate rocks) was separated. For further laboratory analyses the fine earth fraction (<2mm) was used and homogenized in a porcelain mortar.

The pH in 1 mol· l^{-1} KCl was measured using the potentiometric method in 1:2.5 soil: solution suspensions, content of organic carbon (OC) with the wet combustion method, $CaCO_3$ content by Scheibler's volumetric method, carbonate reactivity content with Loeppert and Suarez method, sum of exchangeable bases (TEB) (Ca, Mg, K and Na extracted from soil with 1M ammonium chloride and determined using the AAS technique), hydrolytic acidity (Hh) using the Kappen method (Nelson, Sommers 1996; Ostrowska *et al.* 1991). Cation exchange capacity (CEC) of soils was calculated as a sum of hydrolytic acidity (Hh) and total exchangeable bases (Ca, Mg, K, Na) – (TEB). Bioavailable forms of Cu, Cd, Cr, Pb, and Zn (denoted by dtpa) were sampled and extracted with the DTPA method, described by Lindsey and Norvell (1978). In order to measure the pseudo-total content of heavy metals (denoted by tot) the soil samples were dissolved with *aqua regia*, then the elements were determined using the AAS technique (ISO 11466:1995) Particle-size distribution was determined using the hydrometer method, modified by Casagrande and Prószyński and sieve method (Ryżak *et al.* 2009). Soil texture was determined according to the classification published by the United State Department of Agriculture (USDA 2006), with appropriate conversion made by the Polish Society of Soil Science (2009).

The statistical analysis was based on the correlations between the basic properties of the soil, and the content of total and bioavailable forms of heavy metals using Statistica 2011, StatSoft Inc.

RESULTS AND DISCUSSION

The texture of the fine earth fraction of tested soils in the area of Cementownia Chelm S.A. shows considerable variations (Table 1). Within the studied transects located to the east of the plant, a domination of sandy formations could be noted (sandy loam and loam sand, according to USDA). On the opposite side of the plant, the amount of finer fraction significantly increases and the soils were characterised by a particle size distribution of loam to silty clay. Loam dominated in the sampling points to the south, whereas in the immediate vicinity of the plant the dominating formation was silty clay loam. The most heterogeneous distribution was observed to the north of the cement plant, where formations such as silt loam, loamy sand and loam occurred.

TABLE 1. BASIC PROPERTIES OF THE SOILS AROUND THE CEMENT FACTORY

Transect	Teksture [USDA]	OC [g·kg^{-1}]	pH 1M KCl	$CaCO_3$ [g·kg^{-1}]	$CaCO_3$ react. [g·kg^{-1}]	$CaCO_3$ react. / $CaCO_3$	Hh [mmol(+)·kg^{-1}]	TEB [mmol(+)·kg^{-1}]	CEC [mmol(+)·kg^{-1}]	BS [%]
E1	loamy sand	7.7	8.2	35.7	6.4	0.18	9.8	660.6	670.4	99
E2	loamy sand	7.7	8.2	14.0	4.6	0.33	4.0	229.1	233.2	98
E3	sandy loam	42.5	7.7	85.9	18.1	0.21	2.4	417.6	420.0	99
E4	silt loam	51.6	7.8	481.0	44.0	0.09	2.4	624.0	626.5	99
E5	sandy loam	9.1	8.0	57.9	18.2	0.31	6.2	436.6	442.8	99
W1	silty clay	19.4	7.7	579.0	62.3	0.11	4.9	594.0	598.9	99
W2	loam	15.8	8.1	328.0	58.8	0.18	5.2	637.7	642.9	99
W3	silty clay	21.9	7.6	562.0	66.0	0.12	3.6	592.1	595.7	99
W4	loam	24.0	7.7	349.0	59.5	0.17	5.6	406.2	411.8	99
W5	clay loam	12.0	8.0	588.0	66.8	0.11	5.6	399.5	405.1	99
N1	loamy sand	9.1	8.0	67.2	8.8	0.13	6.4	436.4	442.8	99
N2	silt loam	35.8	8.0	570.0	52.5	0.09	7.2	428.1	435.3	98
N3	silt loam	41.6	7.9	255.0	48.5	0.19	6.4	405.8	412.2	99
N4	loam	11.5	7.9	153.0	49.0	0.32	5.6	380.2	385.8	99
N5	loamy sand	10.0	7.9	9.8	40.3	4.11	10.8	453.6	464.4	98
S1	silty clay loam	2.4	8.4	792.0	60.8	0.08	5.3	412.6	417.9	99
S2	loam	1.1	8.3	894.0	70.5	0.08	10.8	498.6	509.3	98
S3	loam	3.0	8.2	660.0	66.6	0.1	4.6	543.7	548.3	99
S4	loam	21.9	7.9	330.0	59.9	0.18	6.9	483.6	490.5	99
S5	loam	16.1	7.8	183.0	54.2	0.3	7.2	324.4	331.6	98

The analysed soils were characterised by the presence of calcium carbonate. Its content was spread evenly from the plant in all directions. To the east it ranged from 14.0 - 481.0 g·kg^{-1}, west 328.0 - 587.0 g·kg^{-1}, north 10.0 –

570,0 g·kg^{-1} and south 183.0 - 894,0 g·kg^{-1}. The ratio of active carbonate to the total content of calcium carbonate showed little variation in all directions and amounted to respectively; 0.09 – 0.33 to the east, 0.11 – 0.18 to the west, 0.09 – 4.1 to the north, and 0.08 – 0.3 to the south. The consequence of the presence of calcium carbonate in the soil was a high content of total calcium. To the east of the plant, the total content was in the range of 5.6 - 192.5 g·kg^{-1}with an average of 53.9 g·kg^{-1}, to the west 131.2 - 231.7 g·kg^{-1} with an average of 192.5 g·kg^{-1}, to the north 26.9 - 228.3 g·kg^{-1}with an average of 84.5 g·kg^{-1}and to the south 73.2 - 357.8 g·kg^{-1}with an average of 228.8 g·kg^{-1}. The percentage of forms available to plants in the total calcium pool did not exceed 1% (Table 2).

The pH of the tested soil was alkaline in all directions and was characterised by high pH in the range of 7.7 - 8.2 to the east, 7.6 - 8.1 to the west of the plant, 7.9 - 8.0 to the north and 7.8 - 8.4 to the south. So high pH levels around the plant result from former activities of the cement plant, as currently dust emissions have been significantly reduced. It can be therefore concluded that the soil accumulated pollution from the previous years. The soil values exceeding 7.0 pH indicate the evident anthropogenic effect of cement dust deposition on the soil surface. In the unaffected soils of the region, the pH values ranged from 5.4 to 6.5. It should be emphasized that calcium carbonate was detected in all samples. The research conducted by Dąbkowska-Naskręt (2014) in the vicinity of the Lafarge cement plant in Bielawa revealed that the soil had similar pH values.

The organic carbon content was also high. To the east of the plant it was in the range of 0.77 - 5.16%, to the west 1.20 - 2.40%, to the north 0.91 - 4.16% and to the south 0.11 - 2.19%. The large variability of organic carbon content resulted from the fact that in the designated transects some areas were soilless with no developed accumulation level. The analysed sorption capacity (CEC) displayed little variability and reached values from 233 to 670 mmol·kg^{-1}, and the degree of saturation of the sorption complex with basic cations was up to 99%. Almost complete saturation of the sorption complex with basic cations in all directions can be associated with the presence of calcium carbonate.

TABLE 2. STATISTICAL CHARACTERISTICS OF THE HEAVY METAL AND CALCIUM CONTENT OF THE SOILS AROUND THE CEMENT FACTORY

Transect	E		W		N		S	
	[mg·kg^{-1}]							
Total	Range	Mean/Std. dev.	Range	Mean/Std. dev.	Range	Mean/Std. dev.	Range	Mean/Std. dev.
Cu	3.2-26.5	14.8±11.2	5.06-12.9	8.3±5.0	2.8-29.2	11.4±10.3	2.1-18.8	6.5±7.4
Cd	0.1-0.4	0.2±0.2	0.0-0.3	0.1±0.1	0.1-1.54	0.7±0.6	0.0-0.1	0.1±0.0
Cr	1.3-5.41	3.8±1.6	1.6-11.1	4.5±4.0	1.8-5.2	3.2±1,3	1.6-2.8	2.1±0,6
Pb	4.3-55.3	27.5±22.4	2.7-20.2	9.3±7.1	5.1-38.8	20.3±12,5	7.1-25.7	14.7±9,3

Transect	E		W		N		S	
Zn	21.5-66.0	41.4±20.9	5.7-36.3	19.85±12.3	12.7-42.6	30.9±11.2	5.6-21.8	11.7±6.7
Ca*	5.6-192.5	54.0±78.2	131.2-231.7	192.5±52.3	26.9-228.3	84.5±88.5	73.2-357.8	228.8±121,6
dtpa	[mg·kg-1]							
Cu	0.2-0.5	0.4±0.1	0.2-0.3	0.3±0.0	0.2-2.0	0.6±1.8	0.2-0.4	0.3±0.1
Pb	0.4-4.2	2.2±1.3	0.2-1.3	0.6±0.5	0.3-3.1	1.5±0.8	0.2-1.9	0.8±0.7
Zn	0.3-2.7	1.2±1.0	0.4-2.2	1.2±1.0	0.3-1.8	1.2±1.0	0.5-1.7	0.8±0.5
Ca	3.7-77.5	23.6±30.8	64.5-85.6	76.9±10.2	2.8-87.1	37.0±32.1	36.1-99.5	73.5±29.2
	$(C_{dtpa}/C_{tot})\cdot 100\%$							
Cu	0.8-10,4	2.3±4.0	1.9-5.8	3.1±1.6	2.9-9.1	5.7±2.5	2.2-10.8	4.1±3.1
Pb	7.4-9.4	7.6±0.9	1.9-10.1	6.0±3.1	6.1-8.0	7.2±0.7	2.6-7.4	5.7±1.8
Zn	0.8-5.2	3.0±1.9	3.2-9.4	6.3±2.6	0.9-8.7	3.9±2.8	2.9-9.1	6.7±2.5
Ca	0.03-1.0	0.5±0,4	1.1-8.6	2.2±3.0	0.7-3.4	1.3±1.4	1.2-8.2	4.4±2.9

* [g·kg-1]

The basic statistical data on the content of heavy metals can be found in Table 2. The analysed soils, surrounding Cementownia Chelm S.A. do not show contamination with heavy metals. General content of heavy metals (Cd, Cu, Cr, Pb, Zn) does not exceed permissible concentration values, set by the Regulation of Minister of Environment on soil quality standards and ground quality standards, Dz.U. [Official Journal] 02.165.1359 dated. 04.10.2002). The limit values for concentration of heavy metals in the soil, for industrial, fossil land and communication areas are as follows: Cd: 6-20 $g\cdot kg^{-1}$; Cu: 200-1000 $g\cdot kg^{-1}$; Cr: 150-800 $g\cdot kg^{-1}$; Pb: 200-1000 $g\cdot kg^{-1}$; Zn: 300-3000 $g\cdot kg^{-1}$.

The measured concentration of heavy metals was generally characterised by high variability with respect to the direction and distance from the cement factory in question. Their largest accumulation was not observed in the immediate distance to the factory either. It should be noted, however, that it was not the rule. Such a situation was quite typical of movement of the soil material associated with wind or water erosion (Li *et al.* 2014; Paluszek 2010). The comparison of the content of heavy metals on the analysed surfaces sampled from different directions was noticeably variable. Average cadmium content was the highest in the axis of the north direction, and the lowest in the south, and followed the sequence N>E>W>S. The content of lead and zinc followed the sequence E>N>S>W copper: E>N>W>S and chromium W>E>N>S. A single speciation analysis applied in the study, involving the separation of forms available to plants, showed that heavy metals were present in relatively low-mobility forms. Despite the presence of chromium and cadmium in total, these two elements were not observed in plant-available forms. The percentage share of forms available to plants in the general pool of other elements did not exceed 10%. Low hydrolytic acidity values and more than 95% degree of saturation of basic cations resulted in strong binding of heavy metals and consequently low participation of forms available to plants in a pool of total content of heavy metals. The influence of alkaline pH on immobilisation of heavy metals is confirmed by other authors (Chaun *et al.* 1996; Kogbara *et al.* 2012). Exceptions are Pb, Ni and Cu, which at above pH 7 increase the contribution of mobile forms (Brümmer, Herms 1983; Ashworth, Alloway 2008). The studied soils adjacent to the cement plant are characterized by alkaline pH and the highest contribution of mobile lead forms (10%) of all heavy metals examined. It is worth noting that the zinc contribution is anomalous and similarly to lead, in the alkaline pH it shows a significant contribution of mobile forms (9.4%) of total lead content. Increased metal solubility at low pH is to be expected because of cation exchange processes involving hydrogen, decreases in negative (pH-dependent) charge on oxides and organic matter, and dissolution of precipitates (Alloway 1995). These processes would appear to have been important in controlling the solubility of Cd, Zn, and Ni, and relatively high solubility (3 – 3.5%) was observed for these elements at low pH (4 – 5). At 6-7 pH, the solubility of these metals was significantly reduced. Indeed, Cd and Zn solubility remained low up to the maximum pH (7.7). The increasing solubility of Pb, Cu, and Ni at increasing pH was less expected (Ashworth, Alloway 2008). The application of wastes of different origin and composition as a fuel in cement manufacturing causes an increase in the content of metals such as lead and zinc in soils in the vicinity of the cement plant. The concentrations of plant-available DTPA-extractable Pb in the studied soils were high due to high alkalinity caused by the cement dust. Based on metal extractability with DTPA, it was also concluded that plant-available zinc and copper concentrations in the soils affected by cement particles were below the recommended limits due to their alkalization (Fertillizers recommendation, 1985). Dąbkowska-Naskręt (2013; 2014) also reported low level of heavy metals in the available forms. The high pH value generally restricted the mobility of heavy metals and influenced the accumulation of heavy metals in various levels for both general and plant available forms (Chaun *et al.*, 1996; Kabata-Pendias, Pendias, 1999), which was observed in the studied samples.

One of the factors to estimate level of pollution is an Enrichment Factor (EF). Enrichment Factor (EF) of an element in the studied samples was based on the standardisation of a measured element against a reference element. A reference element is often the one characterised by low occurrence variability, such as the most commonly used elements: Al, Fe, Ti, Si, Sr, K, etc., (Duzgoren-Aydin, 2007; Sezgin *et al.*, 2003). The EF calculation is expressed below as:

$$EF= \frac{\left[\frac{Cx}{Cref}\right]_{sample}}{\left[\frac{Cx}{Cref}\right]_{background}}$$

where, C_x is the concentration of the element of interest

C_{ref} is the concentration of reference element for normalisation. In this study, the background level of different soils is chosen on the basis of Kabata-Pendias (1999) and Czarnowska (1996).

EF values less than 5.0 are not considered significant, because such small enrichments may arise from differences in the composition of the local soil material and reference soil used in EF calculations (Sezgin *et al.*, 2003). However, there is no accepted pollution ranking system or categorisation of degree of pollution on the enrichment ratio and/or factor methodology. Five contamination categories are recognised based on the enrichment factor: EF < 2 states deficiency to minimal enrichment, EF = 2-5 moderate enrichment, EF = 5-20 significant enrichment, EF = 20-40 very high enrichment and EF > 40 extremely high enrichment (Duzgoren-Aydin *et al.*, 2006; Sezgin *et al.*, 2003). Enrichment factors of heavy metals have been calculated for each soil sample relative to the background values of Abundance of chemical elements in the continental crust, choosing Fe as the reference element.

TABLE 3. ENRICHMENT FACTOR (*EF)* OF HEAVY METALS IN SOILS AROUND THE CEMENT FACTORY

	EF									
	Cu		Cd		Cr		Pb		Zn	
Transect	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
E	0.2-0.8	0.5	0.2-0.6	0.3	0.0-0,05	0,04	0.2-1.3	0.7	0.3-0.8	0.4
W	0.3-1.0	0.6	0.1-0.2	0.2	0,0-0,1	0,06	0.2-0.5	0.3	0.1-0.3	0.2
N	0.3-1.3	0.6	0.3-4.7	1.8	0,0-0,1	0,05	0.4-1.3	0.9	0.2-0.7	0.5
S	0.3-1.1	0.6	0.1-0.3	0.2	0,0-0,1	0,05	0.5-2.0	1.1	0.2-0.3	0.3

The analysis of EF value indicates that the content of heavy metals in all tested directions is on the level described as "*states deficiency to minimal enrichment*" (Table 3). Only at one point on the research plot, to the north of the plant, is there a slight enrichment of cadmium. Based on the analysis of the value of EF indicator and the distribution of its values in different directions it can be concluded that the activity of the cement factory does not significantly affect the enrichment of the soil in heavy metals in the vicinity of the cement plant.

In contrast, the activity of Cementownia Chelm S.A. significantly affects the physicochemical properties of the soil around the facility. The works of many authors confirm that the manufacturing process of cement, as well as the acquisition of raw materials cause changes in properties of soil around the plant (Ahiamadjie *et al*. 2011; Mandre *et al.* 1998). A clear alkalinisation of the investigated soils is associated with precipitation of alkaline dust present in pollution resulting from the technological process used in the cement factory and the presence of calcium carbonate, introduced to the ground levels from bedrock – the deposits of chalk.

TABLE 4. CHOSEN CORRELATIONS BETWEEN SOIL PARAMETERS (SIGNIFICANT AT P<0.05)

	Cu-tot	Cd-tot	Cr-tot	Pb-tot	Zn-tot	Fe-tot	Ca-tot	Cu-dtpa	Pb-dtpa	Zn-dtpa	Ca-dtpa
2,0-0,05							**-0,83**				**-0,90**
0,05-0,002							**0,71**				**0,79**
<0,002							**0,72**				**0,75**
OC		**0,47**									
pH											
$CaCO_3$							**1,00**				**0,97**
$CaCO_{3\ react.}$							**0,79**				**0,84**
Hh						**-0,47**		**0,47**			
TEB											
CEC											

The results of the statistical analysis are shown in Table 4. The correlation coefficients between the basic properties of the soil, and the content of total and bioavailable forms of heavy metals were calculated. It was shown that among the assayed elements only calcium strongly correlated with granulometric fine fractions and with the content of the total and reactive calcium carbonate. Moreover, there was a weak correlation between the content of cadmium in the form of total and organic carbon. Many authors indicate the strong connection between the content of heavy metals and the finest fractions of soil or humus. The studied soils adjacent to the cement plant showed no such relationship (Brümmer, Herms 1983; Ashworth, Alloway 2008, Alloway 1995).

CONCLUSIONS:

1. The total content of Cu, Cd, Cr, Pb and Zn in soils around Cementownia Chelm S.A. did not exceed the limit values described in the Polish regulations.

2. The spatial distribution of heavy metals in the soils along the studied transects showed no clear trends, and the concentrations were evenly distributed in all directions from the plant.

3. The levels of the values designated for the tested points enrichment factor (EF) were low, which was characteristic for a lack of anthropogenic enrichment, and was arranged in the following, increasing order: Pb>Cd>Cu>Zn>Cr.

4. The presence of calcium carbonate in soils significantly affects the change of their properties, including pH and ion exchange in sorption complex.

Low hydrolytic acidity values and more than 95% of saturation with basic cations results in strong binding of heavy metals and consequently a small proportion of forms available to plants in a pool of heavy metals total content.

5. The soils adjacent to the inconvenient production facilities, which include cement factory, should be subjected to continuous geochemical monitoring.

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