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Hanna JAWORSKA[1] and Halina DĄBKOWSKA-NASKRĘT[1]

TOTAL CONTENT OF MERCURY IN THE SOILS OF THE SURROUNDINGS OF LAFARGE-CEMENT PLANT IN MALOGOSZCZ

CAŁKOWITA ZAWARTOŚĆ RTĘCI W GLEBACH W OTOCZENIU ZAKŁADÓW CEMENTOWYCH „LAFARGE" W MAŁOGOSZCZY

Abstract: The aim of this research was to determine the total content of mercury in soils in the surroundings of "Lafarge" – Cement Plant in Malogoszcz. "Lafarge" factory is the source of emission of alkaline dusts. Soil samples were taken from six sites located in the various distances from the "Lafarge" factory. The content of mercury in soils was analyzed using AMA 254 spectrometer.

Investigated soils are classified as light soils with medium content of organic matter. The results of studies showed that soil samples in the vicinity of the source of dust emission had high pH and higher content of $CaCO_3$. It is caused by the continuous emission of alkaline dust from the factory. The content of mercury in tested soil samples was below the natural average content of mercury in mineral soils in Poland. Emission of cement dust from the "Lafarge" – Cement Plant does not influence the content of mercury in the investigated soils.

Keywords: cement dust, soils, mercury, alkalisation

Malogoszcz cement plant is a part of "Lafarge" Cement Company and is located in Malogoszcz, 35 km south-west from Kielce. Geographically this area is classified as Malopolska Upland [1]. This area is built from Jurassic limestone and Cretaceous sandstones. The cement plant started production in 1974 on the basis of its own natural resources – limestone and Jurassic marls from the quarry located 1 km from the factory. The factory produces clinker using dry method and there are four cement production lines. Cement manufacture requires very high temperatures, above 1400 ^{o}C and as a fuel different waste materials, often rich in heavy metals, are used for combustion [2, 3]. During the cement production a significant emission of gases and dusts occurs. Gases and dusts are captured by electrostatic precipitators and their effectiveness decide on pollution of the environment even excessive alkalization of surrounding soils and they

[1] Department of Soil Science and Soil Protection, University of Technology and Life Sciences in Bydgoszcz, ul. Bernardyńska 6, 85–029 Bydgoszcz, Poland, phone: +48 52 374 95 12, email: hjawor@.utp.edu.pl

are often the source of heavy metals even at the distance over 15 km [4]. Dusts emitted by a cement industry contain metals, including mercury. The mercury content in raw materials used for cement production as well as in fuels of different origin and composition, may significantly affect its concentration in the flue gases and the quantity of emission of this metal [4]. Mercury has the highest ability to release in the environment. It has high mobility due to the easy transition into various chemical forms, especially in the volatile form (Hg^0). Moreover, it is an element with one of the highest accumulation factor and the most toxic for living organisms [5]. High toxicity of mercury decided to treat it as a problem of global importance [6, 7].

The aim of the present study was to determine the level of total content of mercury in soils in the surroundings of "Lafarge" – Cement Plant in Malogoszcz.

Material and methods

The study has been done on soils sampled from the fields (arable soils) located in various distances from the "Lafarge" – Cement Plant in Malogoszcz (Table 1).

Table 1

Localizationof the research sites

Sampling site	Layer [cm]	Coordinates	Distance from the cement plant [m]
Zakrucze I Zakrucze I	0–20 20–40	50°49′48.31″ N 20°17′01.53″ E	800
Zakrucze II Zakrucze II	0–20 20–40	50°49′53.99″ N 20°17′00.53″ E	850
Lesnica I Lesnica I	0–20 20–40	50°49′54.12″ N 20°15′17.13″ E	700
Lesnica II Lesnica II	0–20 20–40	50°50′15.50″ N 20°14′31.35″ E	1700
Lesnica III Lesnica III	0–20 20–40	50°48′57.69″ N 20°15′09.14″ E	2900
Malogoszcz Malogoszcz	0–20 20–40	50°48′57.69″ N 20°17′09.06″ E	2200

Soil samples were taken from six sites, from two layers (surface) (0–20 cm) and (subsurface) (20–40 cm). In the dried and sieved material (∅ below 2 mm) the following soil properties were determined: pH in H_2O and in 1 mol · dm^{-3} KCl solution potentiometrically, the content of $CaCO_3$ – with the volumetric method by Scheibler, C-organic – according to Tiurin method. Texture was determined with the Casagrande areometric method, modified by Proszynski. Interpretation of the texture results was performed according to PTG (2008) classification [8]. The total content of mercury was determined in solid samples by atomic spectrometry method using AMA 254 mercury analyser [9]. Analyses were performed in three replications. The reliability of the results of the total Hg content was confirmed on the basis of certified reference material

TILL-3 and S-VM analysis. The results of Hg content are the arithmetical mean of three replicates with a standard deviation below 5 %.

Results and discussion

The analysis of granulation of soil samples taken from soils adjacent to “Lafarge” – Cement Plant indicates that their texture is corresponding to a granulometric group of loamy sand, sand, loam and sandy loam (Table 2). In terms of agricultural criteria they are qualified to light soils with the content of sand fraction in the range of 78–84 %, silt fraction 11–17 % and colloidal clay (∅ < 0.002 mm) 4–8 % [8]. Texture of the investigated soils indicates that they exhibit low buffer properties and are very vulnerable to pollution [10], however calcium carbonate from cement dust might affect these properties.

Table 2

Physicochemical properties of studied soils

Sample	Layer [cm]	Percentage of fraction with diameter [mm]			C-organic [g · kg^{-1}]	$CaCO_3$ [%]	pH	
		2–0.05	0.05–0.002	< 0.002			H_2O	KCl
Zakrucze I	0–20	83	12	5	11.0	1.05	8.31	7.73
	20–40	78	14	8	10.8	0.38	8.07	7.53
Zakrucze II	0–20	84	11	5	8.3	1.26	7.84	7.61
	20–40	91	6	3	10.3	0.8	7.90	7.87
Lesnica I	0–20	81	13	6	16.3	0.42	7.93	7.42
	20–40	86	11	3	10.3	0.38	7.95	7.14
Lesnica II	0–20	82	14	4	18.4	0.42	6.40	5.82
	20–40	82	12	6	12.8	0.38	5.61	4.40
Lesnica III	0–20	79	15	6	12.0	0.42	5.66	4.84
	20–40	79	17	4	18.9	0.38	6.40	5.62
Malogoszcz	0–20	72	24	4	24.2	0.84	7.57	7.09
	20–40	63	29	8	20.3	0.84	7.75	7.15

The pH of investigated soils varied from acidic to alkaline. Soil pH was in the range of 5.61–8.31 (pH_{H_2O}) and exchangeable acidity pH_{KCl} was in the range of 4.40–7.87 (Table 2). In the investigated samples predominate soils with neutral and alkaline pH, which should be attributed to a long-term impact of cement dust emission, which caused the alkalization of soils [11]. The highest values of pH have soil samples taken from the closest neighborhood of the cement plant, and the lowest – the outermost soils. Similar relation between soil pH and the distance from the cement plant was observed by other authors [11–13]. The change of pH in soils to alkaline range is mostly caused by the dominant component of cement dust – calcium carbonate [14]. The content of calcium carbonate in investigated soils was in the range of 0.38–1.26 % (Table 2). Higher content of calcium carbonate in soil samples was detected in 0–20 cm a layer compared to 20–40 cm layer. The highest content of $CaCO_3$ (1.26 %) was found in the sample from

Zakrucze I, which is located 850 m from the cement plant. The highest content of $CaCO_3$ in the top layer of soil and in the neighborhood of the factory was also observed by other authors [15, 16]. With the increasing distance from the emission source, the $CaCO_3$ content decreased. In the investigated soil samples located closest to the emitter the highest pH and significant additions of $CaCO_3$ was found. A similar relationship between the change of pH and accumulation of $CaCO_3$ content is not confirmed by Dobrzanski et al [14] in their study. Organic carbon content in surface layers ranged from 8.3 to 24.2 $g \cdot kg^{-1}$ and in subsurface layers from 10.3 to 20.3 $g \cdot kg^{-1}$ (Table 2) in studied soils.

Physical and chemical properties of soils, their texture, pH and the content of C-organic have a direct impact on the content of mercury [17].

The total content of mercury in the investigated soils was in range of 12.32–51.6 $\mu g \cdot kg^{-1}$ in surface samples and 7.14–36.30 $\mu g \cdot kg^{-1}$ in subsurface samples (Table 3).The content of this element in surface layers in 83 % (ie 4 samples) of analyzed samples was higher than the content in subsurface layers.

Table 3

Total Hg contents in soils

Sample	Layer [cm]	Hg [$\mu g \cdot kg^{-1}$]
Zakrucze I	0–20	13.00
	20–40	17.28
Zakrucze II	0–20	14.15
	20–40	9.09
Lesnica I	0–20	12.32
	20–40	7.14
Lesnica II	0–20	23.52
	20–40	16.64
Lesnica III	0–20	34.50
	20–40	36.30
Malogoszcz	0–20	51.60
	20–40	31.23

The highest content of mercury was found in surface layer of soil from Malogoszcz – 51.60 $\mu g \cdot kg^{-1}$ and the lowest in subsurface layer of soil from Lesnica I – 7.14 $\mu g \cdot kg^{-1}$. The contamination of soil with mercury on industrial areas concerns mostly the surface layer, because this metal hardly migrates to deeper soil horizons [18]. Similar regularity was found in the investigated soils. This element is not usually washed out to deeper layer of soil, which is related to a large sorption of mercury by soil organic matter [5, 19]. The main factors that increase sorption of mercury are pH and organic matter [19, 20]. The highest content of mercury in the investigated soils corresponded to the high content of C-organic (Table 2 and 3). Natural content of mercury in soils is difficult to determine, but it is assumed it corresponds to a range of 50–300 $\mu g \cdot kg^{-1}$ [7, 20]. Average mercury content in mineral soils does not exceed 100 $\mu g \cdot kg^{-1}$ [7]. The results show that in investigated samples, Hg content was below the average content of this element in non contaminated soils [20]. Similar regularities were observed by Kusza et al [21], who investigated soils formed from chalk marl, which had alkaline pH. Also during the research carried on cultivated soils in the surroundings of "Lafarge" Cement Plant in Bielawy higher total content of Hg in surface layers was observed which could be the result of absorption of this metal by organic substances and clay minerals. Thus, the total content of Hg in soils near Malogoszcz Cement Plant was below the natural, geochemical background level for this element in mineral soils of Poland [13].

Investigated soils poor in soil colloids, were not contaminated with mercury. Thus, Malogoszcz Cement Plant has no significant influence on the total content of mercury in nearby soils. However, elevated level of Hg in surface layers (0–20 cm) compared with subsurface layer (20–40 cm) in the most studied sites is the evidence of some changes in soil environment caused by the dust emission.

Conclusions

1. Physicochemical analysis of soils located in the surroundings of Malogoszcz Cement Plant allow to qualify them as highly vulnerable soils with content of organic carbon in the range of 8.3–24.2 $g \cdot kg^{-1}$ (0–20 layer) and 10.3–20.3 $g \cdot kg^{-1}$ (20–40 layer) and with pH_{H_2O} in the range of 5.66–8.31 (0–20 layer) and 5.61–8.07 (20–40 layer).

2. Emission of cement dusts from Malogoszcz Cement Plant caused the increase of $CaCO_3$ content and the alkalization of soils.

3. Total content of mercury in the analyzed soil material was in range of 7.14–51.6 $\mu g \cdot kg^{-1}$ and in all samples studied did not exceed the content seemed to be natural for this metal.

4. Emission of cement dust from the Lafarge – Cement Plant in Malogoszcz does not cause the increase of total mercury content in the surrounding soils.

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CAŁKOWITA ZAWARTOŚĆ RTĘCI W GLEBACH OKOLIC ZAKŁADÓW CEMENTOWYCH „LAFARGE" W MAŁOGOSZCZY

Katedra Gleboznawstwa i Ochrony Gleb
Uniwersytet Technologiczno-Przyrodniczy w Bydgoszczy

Abstrakt: Celem badań było określenie całkowitej zawartości rtęci w glebach sąsiadujących z Zakładem Cementowym „Lafarge" w Małogoszczy. Zakłady są źródłem emisji pyłów cementowych o charakterze alkalicznym. Próbki glebowe pobrano z sześciu punktów z głębokości 0–20 cm i 20–40 cm w różnej odległości od cementowni. Całkowitą zawartość rtęci oznaczono za pomocą spektrometru AMA 254.

Badane gleby można zaliczyć do kategorii gleb lekkich o średniej zawartości C-organicznego. W wyniku przeprowadzonych badań stwierdzono, że próbki gleb w pobliżu źródła emisji wykazują większe wartości pH i zawartości $CaCO_3$. Jest to spowodowane stałą emisją pyłów alkalicznych. Zawartość całkowita rtęci w badanych próbkach glebowych była mniejsza od naturalnej średniej zawartości rtęci w glebach mineralnych Polski. Emisja zanieczyszczeń z Cementowni Małogoszcz nie spowodowała zwiększenia całkowitej zawartości rtęci w badanych glebach.

Słowa kluczowe: pyły cementowe, gleba, rtęć, alkalizacja