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STUDY OF THE EXCESSIVE Pb-210 CONTENT IN SOIL

BADANIE ZAWARTOŚCI NADMIAROWEGO Pb-210 W GLEBIE

Abstract: The aim of the study was the analysis of soil contamination in the area in vicinity of metalworking plants located in the district Opole-Metalchem (PL). Pb-210 was used as pollution indicator because its increased concentration of activity may indicate the presence of other contaminants in the studied area. On the base of the obtained results, the activity concentration of the excessive lead was calculated. Its biggest value was observed in soil in a forest area. In areas with increased excessive lead content also elevated values of Cs-137 activity concentrations were recorded. Atmospheric source of Pb_{ex} and Cs-137 deposition was supposed.

Keywords: pollution indicator, Pb-210, soil contamination

Introduction

Industrial metalwork is one of the major sources of environmental pollution. It deals with the treatment of ores, obtaining pure metals, creating specific shapes of metal pieces and production of alloys [1]. The result of these processes is emission of a number of substances harmful to the environment and to human health [2]. One of these processes is welding, in which dust is released which contains, for example, iron oxides, manganese oxides, magnesium oxides, zinc, lead and volatile products, including sulfur oxides and carbon monoxide [3]. These substances can be dangerous for human health causing, among others, damage in neural system or induce asthma [4].

Lead and zinc alloys are one of the most important raw materials for welding. They may pose a significant threat to the health of workers and to environment. Excess amount of lead can stop production of heme and it can change routes of important biochemical processes in living organisms [5].

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Lead release during activity of various works is followed by its accumulation in soil, and then also in plants [6]. Lead accumulates in the surface layers of soil rich in humus, because it is easily incorporated into organic matter [7]. Availability of lead for living organisms depends on its chemical form in soil. Easily leached from the surface layers of soil are chlorides, nitrates, acetates, while the lead oxides are practically insoluble in water, hence immobile [8].

Lead, in particular the isotope Pb-210, may be an indicator of pollution of industrial origin. Detection of pollution is possible because its activity concentration consists of the autogenous (of natural origin) and the allogeneic (anthropogenic) part. Significant amounts of the allogeneic lead in a sample likely indicates deposition of undesired environmental pollutants [9].

The vapors produced during metallurgical processes contain, besides lead, many other heavy metals. Among them chromium, copper, lead, manganese, nickel, zinc, iron or cadmium can be listed [4–16].

In Opole-Metalchem district in the late 80. and 90. of 20th century was located great industrial center with several welding plants. The symbol of those times was Metalurgic-Chemical Plant “Metalchem” in which armaments was produced. Several thousand people were employed there and they had a housing estate specially built for them. Up to now in this area there are many welding, galvanizing and tinning works. Due to their waste production the periodic analyses of water, soil and air, are desired.

In 2013 an analysis of heavy metals content in the Odra River was carried out [17]. The object of this study was the 8.5 km section of the river, which ran among others, by Metalchem. The biggest heavy metals concentration was found in water sample collected at the river harbor on the Metalchem estate. It could be a result of the continuous pollutant rinsing from machines moored there. These are old, rusty barges and ships used formerly in transport of steel and welded structures. But it is possible that contaminants were washed out from upper soil layers by atmospheric and ground water. Determination of actual pollution sources is critical for selection of appropriate mitigation strategies which would limit impact of contaminants on environment and life quality of local population.

The aim of the study was estimation of soil contamination in the area of Metalchem. In the study Pb-210 was used as an index of pollution. The isotope Pb-210 is a natural radioactive isotope and represents the disintegration series of radioactive uranium U-238. This radionuclide may also be artificially introduced into the environment by human activities. The difference between concentrations of allogenic and autogenous Pb-210 can be regarded as a measure of total contamination of the site.

Materials and methods

The soil samples were collected at 6 places located in the south east direction from the area occupied by metalworking companies (Fig. 1).

Places No.1 and 3 were located on a meadow not far from the nearby forest. Place No. 2 was located in this forest. The remaining sampling sites were located in cornfield. The soil samples were collected from the depth of 0–15, 15–30 and 0–30 cm. The

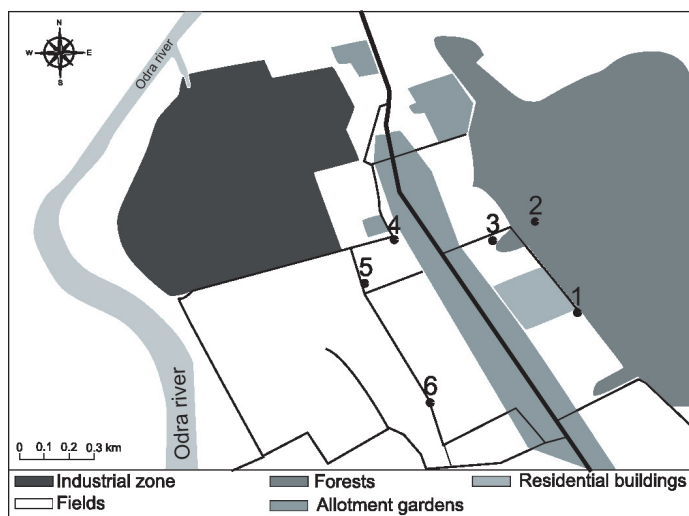


Fig. 1. Localization of sampling sites

collected samples were dried to constant mass at 105 °C, then sieved through a sieve ($d = 2.0$ mm) and analyzed for activity of gamma ray emitting radionuclides.

The measurements of activity concentrations was carried out by means of a gamma-spectrometer with a germanium detector HPGe (Canberra) of high resolution: 1.29 keV (FWHM) at 662 keV and 1.70 keV (FWHM) at 1332 keV. Relative efficiency: 21.7 %. Energy and efficiency calibration of the gamma spectrometer was performed with the standard solutions type MBSS 2 (Czech Metrological Institute, Prague, CZ) which covers an energy range from 59.54 keV to 1836.06 keV.

Geometry of calibration source was Marinelli (447.7 ± 4.5 cm³) with density 0.99 ± 0.01 g/cm³, containing Am-241, Cd-109, Ce-139, Co-57, Co-60, Cs-137, Sn-113, Sr-85, Y-88 and Hg-203. Geometry of samples container was Marinelli, 450 cm³. Measuring process and analysis of spectra were computer controlled with use of the software GENIE 2000.

Results and discussion

In soil samples Cs-137, Pb-210, Bi-214 and Pb-214 radionuclides were determined. Table 1 contains characteristics of distribution of radionuclides specific activity concentration in the samples collected from the sites. Maximum (max), minimum (min) values, lower quartiles (Q_1), upper quartiles (Q_3), mean values (\bar{x}), medians (Q_2) and standard deviations (s).

The lowest difference in activity concentrations was observed for Bi-214 in upper soil layer. Similarly, the Pb-214 isotope was rather uniformly distributed in the investigated area. Concentration of this isotopes somewhat increased in deeper soil layer. Mean concentration of Bi-214 and Pb-214 in the surface layer of soil were several times lower than the average activity in the deeper layer.

Table 1

The maximum (max), minimum (min) and mean (\bar{x}) values of activity concentrations of the determined radionuclides. Additionally the values of standard deviation (s), median (Q_2), lower (Q_1) and upper (Q_3) quartiles are shown

Layer thickness	Radio-nuclide	Min	Max	\bar{x}	s	Q_1	Q_2	Q_3
		Bq/kg d.m.						
0–15	Bi-214	9.11	10.8	0.65	9.53	9.65	9.92	9.11
	Pb-214	7.43	11.7	1.77	9.48	9.82	11.7	7.43
	Cs-137	78.3	524	174	84.5	97.3	172	78.3
	Pb-210	11.1	104	33.8	21.3	30.4	45.8	11.2
15–30	Bi-214	7.54	20.2	5.83	8.48	9.98	17.9	7.54
	Pb-214	8.21	23.2	6.13	9.98	11.0	16.7	8.21
	Cs-137	18.3	102	31.2	35.4	42.1	70.2	18.3
	Pb-210	2.38	35.6	12.8	14.1	23.5	31.4	2.38
0–30	Bi-214	7.12	23.4	11.5	6.19	8.01	8.76	12.2
	Pb-214	7.47	23.3	12.2	5.76	9.19	10.1	12.6
	Cs-137	39.2	233	97.6	72.7	50.1	72.7	112
	Pb-210	14.4	41.4	25.2	9.51	19.1	25.3	27.3

The activity concentrations of Pb-210 and Cs-137 were significantly higher in the surface soil layer, reaching 104 Bq/kg d.m. and 524 Bq/kg d.m., respectively. The range of activity concentration changes was the biggest for Cs-137 (446 Bq/kg) in upper soil layer. The same difference for Pb-214 was lower (93 Bq/kg), but it was much bigger than the differences for Bi-214 and Pb-214.

Relationship between activity concentrations of the radionuclides determined in upper and lower soil layers is shown in the graphs (Figs. 2–5). In these figures the straight line shows equal values of the radionuclide activity concentrations in both layers. Comparison of Bi-214 and Pb-214 activity concentrations indicates rather similar amounts of these radioisotopes in upper and lower ground layers (Figs. 2–3).

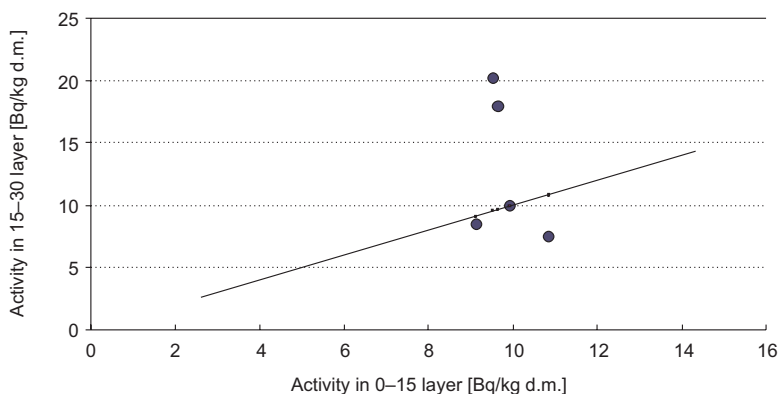


Fig. 2. Relationship between the activity concentrations of Bi-214 in upper and lower soil layer

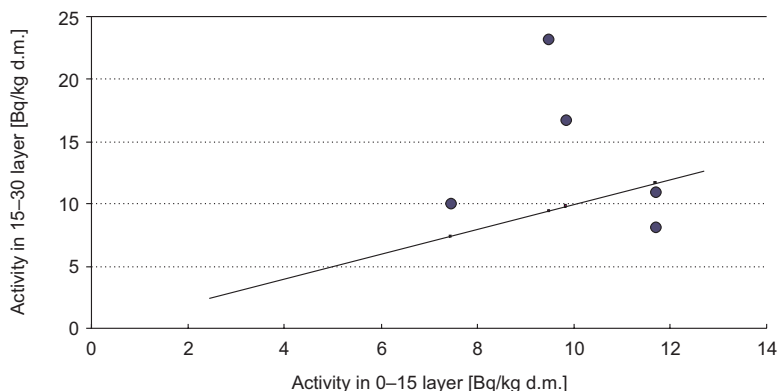


Fig. 3. Relationship between the activity concentrations of Pb-214 in upper and lower soil layer

While crops cultivation the soil layers are periodically mixed with each other as the result of ploughing. Even if mineral fertilizers supply some amounts of radionuclides, soil layer mixing in a seasonal cycles homogenizes its composition. But in opposite to Bi-214 and Pb-214, content of the Cs-137 radioisotope was considerably bigger in upper layer than in the lower. The biggest amounts of this radioisotope appeared in environment as the result of the nuclear tests carried out in 50. and 60. of 20th century [18–20]. The investigated region was additionally contaminated by Cs-137 after the explosion in Chernobyl Nuclear Power Plant in 1986 [21, 22]. Considerable amount of radiocesium was released to atmosphere as a result of the tsunami caused breakdown in Fukushima Daiichi Nuclear Power Plant in 2011 [23, 24].

In atmosphere Cs-137 was transported over long distances from contamination sources. The isotope falls down on ground surface from which it can be again blown to atmosphere. At present horizontal redistribution of Cs-137 is mainly a result of aeolian processes, though other mechanisms like forest or steppe fires should be also considered [25].

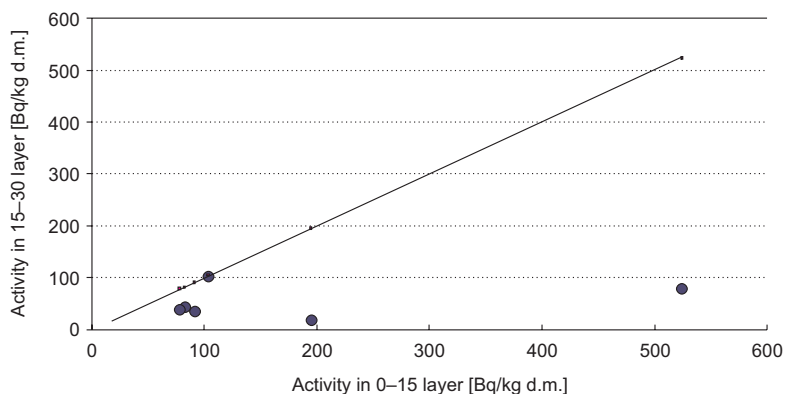


Fig. 4. Relationship between the activity concentrations of Cs-137 in upper and lower soil layer

Vertical distribution of Cs-137 in soil reflects these mechanism. The plot in Fig. 4 shows significantly bigger Cs-137 activity concentration in upper than in lower soil layer. Though cesium is transported from soil depth to surface by plants [26, 27], increased concentration of this radioisotope in the upper layer of disturbed soil justifies fallout from atmosphere as its source.

The Pb-210 radioisotope is member of the radium decay series, like Bi-214 and Pb-214. But its distribution in soil is different than that of the latter radionuclides. An increased content of this radionuclide is observed in the surface layer of the soil (Fig. 5), similarly like for Cs-137. This relationship supposes deposition of this radionuclide from atmosphere.

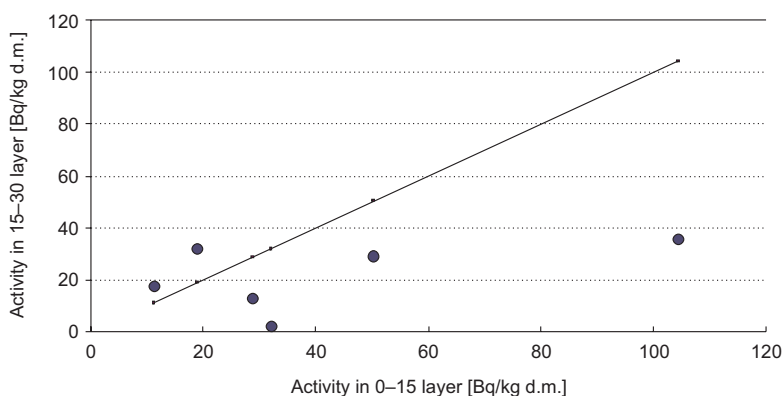


Fig. 5. Relationship between the activity concentrations of Pb-210 in upper and lower soil layer

Two different sources of Pb-210 can be distinguished – autogenous and allogenic. Autogenous component originates from decay of Pb-210 parent radionuclides in radium series. The relatively stable ancestor of Pb-210 is Ra-226 with half-life time 1602 years. A measure of its concentration in system is activity concentration of its short living daughters, *ie* Pb-214 and Bi-214, and then the more stable Pb-210. The allogenic component of Pb-210 appears with dust transported from distant sources, and can be regarded as the excessive lead closely associated with industrial pollutants. Presence of the two Pb-210 components enables calculation of the excessive lead content as the difference between activity concentrations of total Pb-210 and Ra-226. Further analysis was based on content of the excessive lead in soil samples. The Ra-226 activity concentration was calculated from Pb-214 and Bi-214 activity concentrations using the formula (Eq. 1):

$$a_{\text{Ra-226}} = \frac{a_{\text{Pb-214}} + a_{\text{Bi-214}}}{2} \quad (1)$$

where a is the activity concentration of radionuclide in the soil [Bq/kg d.m.].

Activity concentration of the excessive lead Pb_{ex} in the sample was calculated from Equation 2.

$$a_{\text{Pb}_{\text{ex}}} = a_{\text{Pb-210}} - a_{\text{Ra-226}} \quad (2)$$

where: $a_{\text{Pb}_{\text{ex}}}$ – activity concentration of the excessive lead in soil sample [Bq/kg d.m.].

The calculated lead content of the anthropogenic origin (Pb_{ex}) in the surface soil layer was significantly higher than its content in the deeper soil layer (Fig. 6). This observation confirms atmospheric deposition of Pb_{ex} .

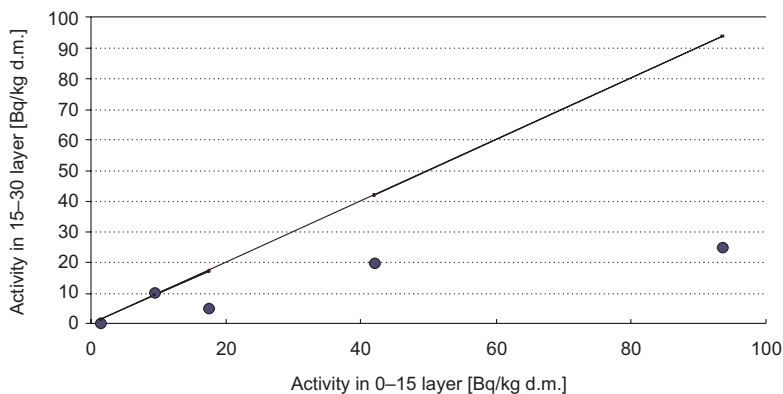


Fig. 6. Relation between the activity of Pb_{ex} in soil layers

The biggest activity concentration of Pb_{ex} was calculated in place No. 2 (32.2 Bq/kg d.m.), being the forest area. At the places No. 1 and No. 6 the activity concentrations were about half lower than at the place No. 2. In other samples Pb_{ex} activity concentration did not exceed 7.5 Bq/kg d.m.

In Fig. 7 relationship between activity concentrations of Pb_{ex} and Cs-137 in upper soil layer is shown. The straight line in the plot shows linear approximation of relationship between these parameters. Parameters of the line in the plot were calculated using the least square method.

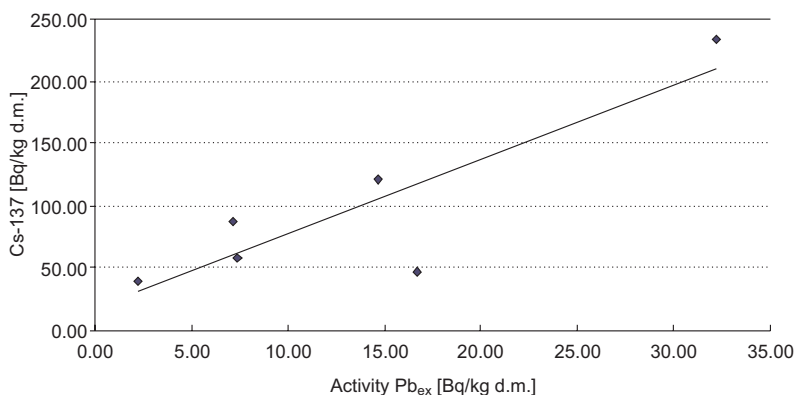


Fig. 7. Relation between the Cs-137 and the Pb_{ex} activity concentrations in upper soil layers

Well outlined linear relationship between Pb_{ex} content and Cs-137 activity concentration could be observed in Fig. 7. The calculated correlation coefficient was 0.87. Such a high correlation coefficient indicates a decisive influence of the local weather conditions on the accumulation of pollutants of atmospheric origin in a certain location. Though the investigated area was not big, atmospheric deposition of pollutants was highly differentiated. Inhomogeneity of soil pollution could be also a result of horizontal transport of fine matter which was floated with rain water or water from melted snow. Secondary pollutants deposition could be much more inhomogeneous than the initial pattern of atmospheric precipitation.

Conclusions

The gamma spectrometric method analysis allowed determination of two Pb-210 isotope components, the allogenic (Pb_{ex}) and autogenous, in soil samples. Because in upper soil layer contents of Pb_{ex} and Cs-137 were well correlated, the atmospheric origin of allogenic lead can be supposed.

The excessive lead is a good indicator of the local pollution related to dry or wet atmospheric deposition. It can be used for estimation of distribution pattern of contaminants in an area. The allogenic lead can be used also as an indicator of pollution transport from distant sources.

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BADANIE ZAWARTOŚCI OŁOWIU NADMIAROWEGO W GLEBIE

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Abstrakt: Celem badań była analiza zanieczyszczenia gleby w rejonie zakładów metalurgicznych w dzielnicy Opole-Metalchem. Jako wskaźnika użyto Pb-210, ponieważ podwyższona jego aktywność może wskazywać na obecność innych zanieczyszczeń na badanym terenie. Na podstawie uzyskanych wyników obliczono aktywność ołowiu nadmiarowego. Największe jego aktywności zaobserwowano w glebie na terenie leśnym. W miejscach z podwyższoną aktywnością ołowiu nadmiarowego odnotowano także wyższe wartości aktywności Cs-137.

Słowa kluczowe: wskaźnik, Pb-210, zanieczyszczenie gleby

