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Pb-210 ISOTOPE AS A POLLUTANT EMISSION INDICATOR

IZOTOP Pb-210 JAKO ZNACZNIK EMISJI ZANIECZYSZCZEŃ

Abstract: Passive biomonitoring using ^{210}Pb was used in the paper to evaluate pollutant deposition. Well-developed epiphytic foliose lichens *Hypogymnia physodes* growing on spruce branches were used in the studies. The samples of mosses *Pleurozium schreberi* and soil (raw humus) were collected from the area around the tree from which the samples of lichens were collected. The studies have shown that it is possible to identify dust emission sources using a radioactive lead isotope (^{210}Pb). The highest activity of ^{210}Pb was observed in areas with increased deposition of other pollutants, such as Ni, Cd, Cu and Pb, which may indicate that ^{210}Pb is one of the emission components.

Keywords: ^{210}Pb, pollutant emission indicator, passive biomonitoring

Introduction

Currently, classical technical monitoring of environmental pollution is increasingly being extended to include biomonitoring methods in which organisms showing measurable morphological, anatomical and physiological changes that occur as the result of physical and chemical changes in the environment are used. The biomonitoring methods can be passive (involving the analysis of changes in organisms living in their natural environment) and active (involving transplantation and exposure of organisms in the polluted environment). Mosses and lichens are the most frequently used biomonitors [1].

Mosses and lichens are good pollution accumulators, and that is why they are often used to assess atmospheric deposition of heavy metals and radionuclides. These plants, which have no root systems, collect large amounts of pollution, including radionuclides, which can be sorbed directly from atmospheric aerosol. These organisms, in the presence of moisture, also absorb substances from the soil, in which they grow. In the case of mosses, this is the main direction of transfer; mineral salts are absorbed from soil by rhizoids. Lichens, in turn, accumulate pollution by ions exchange between environment (water

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solution, with which they remain in contact) and the lichen cation-active layer (an extracellular structure). This process in water environment, due to acidification, increases solubility of certain substances in the soil [2].

Good accumulation of radionuclides in lichens was used, among others, to assess radionuclides pollution of environment around natural sources [3-6], uranium mines [7-10]. and artificial sources, *eg* near radioactive waste storage sites [11]. These studies confirmed the correlation between radionuclides concentration in lichens, which decreases as the distance from the source increases. The studies of proportions of different radionuclides, which can change due to, *eg* increase in anthropogenic radiation, often form the basis for assessment of the level, the source and the period of environment pollution.

The example of the use of lichens in assessing radionuclide pollution levels in urban areas is the monitoring program of Lublin, carried out during the period from October 1998 to March 1999 [12]. Epiphetic lichens (*Parmeliaceae*) transplanted from the areas with lower pollution levels were used in the studies. Slight increase of ^{137}Cs activity in lichens was detected. However, the activity of radium (^{226}Ra, $t_{1/2}$ = 1622 years) and thorium (^{232}Th, $t_{1/2} = 1.39 \cdot 10^{10}$ years), which are released to the atmosphere with exhaust gases, increased. The transplantation method was also applied to monitor the area around the uranium mine in Slovenia [7]. Lichens were used to monitor uranium pollution in the region of Kosovo [13] and polonium in the region of Yatağan in Turkey [14].

Mosses, similarly to lichens, are very good biosorbents, especially of the metal ions, including those radioactive. They were used, among others, in assessment of radioactive pollution of the southern Poland areas [15, 16]. Mosses *Ctenidium molluscum* were also used as radiodeposition bioindicators in north-east Italy [17]. In 1985-2004, in the Urals, radiodeposition of caesium was determined in the mosses *Hylocomium, Pleurozium*and *Plerozium* [18]. Radiocaesium activity in the mosses *Pleurozium schreberi* and *Dicranum polysetum* was also analysed by Horrill [19].

Both mosses and lichens have been used as biomonitors of ^{210}Po and ^{210}Pb atmospheric deposition in the vicinity of coal-fired power plants [20].

Despite the fact that mosses and lichens are commonly used in monitoring programs, data regarding transfer of radionuclides to those plants is limited, in particular with regard to natural radionuclides [21].

The objective of the studies is to use passive biomonitoring using ^{210}Pb to evaluate pollutant deposition.

Experimental

Well-developed epiphytic foliose lichens *Hypogymnia physodes* growing on spruce branches 1.0-1.5 m above the ground were used in the studies. The samples of mosses *Pleurozium schreberi* and soil (raw humus) were collected at the distance of approximately 3 m from the tree from which the samples of lichens were collected.

Samples were taken at 13 places in forests around Opole (south-western Poland) in an area of Bory Stobrawskie limited approximately by a 40 km × 20 km rectangle.

The material for measurements was prepared in the following steps:

1. collection of subsamples from the area of approx. 100 m^2,
2. impurities removal,
3. air drying, storage in paper bags,

4. drying at 105°C to constant mass,
5. mixing of subsamples, separation of subsample for measurement,
6. gamma spectrum measurement, subsample in Marinelli container 450 cm^3.

The measurement of radionuclide activity in plants and soils samples 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, Praha), which covers an energy range from 59.54 keV to 1836.06 keV. The geometry of the calibration source was a Marinelli container (447.7±4.5 cm^3), with density 0.99±0.01 g/cm^3, containing ^{241}Am, ^{109}Cd, ^{139}Ce, ^{57}Co, ^{60}Co, ^{137}Cs, ^{113}Sn, ^{85}Sr, ^{88}Y and ^{203}Hg. The geometry of sample container was a similar Marinelli of 450 cm^3. Time of measurement was 24 h for all of moss samples. Measuring process and analysis of spectra were computer controlled with the use of software GENIE 2000.

Results and discussions

The results of ^{210}Pb activity concentrations in the plants and soil samples in the Bory Stobrawskie area are given in Table 1. In this table Min is the lowest value in data, Ql is lower quartile, Median is median, Mean is arithmetic mean, Q3 is upper quartile, Max is the highest value, CV is variability of coefficient.

Table 1

Characteristics of ^{210}Pb activity concentrations in dry mass (d.m.) of the plants and soils samples collected in the Bory Stobrawskie area

	^{210}Pb radioactivity concentration						
	Min	**Q1**	**Median**	**Mean**	**Q3**	**Max**	**CV**
	[Bq/kg d.m.]						**[%]**
soil	18.8	28.6	42.1	66.8	98.0	173	78.6
lichen	121	423	545	520	644	1009	44.0
moss	88.2	167	401	349	435	620	49.1

The lowest activity concentration was observed in soil. In plants it was several times higher, particularly in lichen. Variability of ^{210}Pb activity was nearly two times higher in soil than in plants. The obtained data were used in calculations of parameters utilized in environmental biomonitoring (Enrichment Factor, Comparison Factor) and in geology (Geoaccumulation Index).

According to the definition of the Enrichment Factor (*EF*), the proportional share of the study analyte relative to the reference element in lichens or mosses and soil points out to soil as the source of its enrichment, *eg* [22-24]. EF is used to compare, usually with reference to aluminium or scandium concentrations, relative concentrations of analytes accumulated in lichens or mosses and soil.

$$EF = \frac{(a_i / a_{ref.})_{\text{lichens or mosses}}}{(a_i / a_{ref.})_{soils}} \tag{1}$$

where: a_i - the activity of the study analyte in lichens, mosses or soil, $a_{ref.}$ - the activity of the reference element in lichens or mosses and soil.

Enrichment Factors are calculated in relation to the total analyte concentration in soil, lichens or mosses, while lichens and mosses accumulate only bioavailable forms of these pollutants and bioaccumulation is affected by the chemical nature of compounds in which the study analytes occur (mainly the ability of these compounds to create ion forms) and the affinity of ion forms to sorption structures of lichens and mosses [25].

When calculating the Enrichment Factor values, the analyte studied was compared to the activity of ^{137}Cs, as the reference element, in lichens or mosses and soil. Although ^{137}Cs is an anthropogenic isotope which was especially intensively introduced into the environment in the 50s and 60s of the last century as the result of nuclear tests carried out in the atmosphere as well as during Chernobyl nuclear power plant accident in 1986, at the moment it is not migrant in nature [26].

Calculated values of ^{210}Pb Enrichment Factor in the study area are shown in Figure 1.

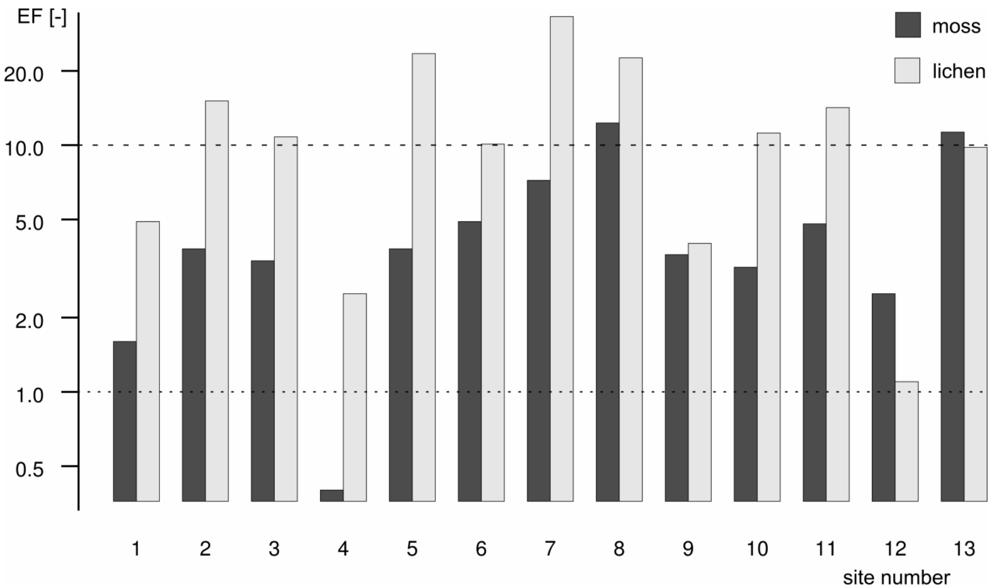

Fig. 1. Calculated values of ^{210}Pb Enrichment Factor in the study area

According to the definition of *EF*, the proportional share of the analyte studied relative to the reference element in lichens or mosses and soil (*EF* = 1) points out to soil as its source. However, the authors argue that the values of *EF* < 10 constitute the background and on their basis it is difficult to evaluate the source of analytes accumulated in lichens or mosses, which may be soil or distant emission sources. We may consider the migrant nature when *EF* > 10 [25]. The *EF* > 10 was found in several places (Fig. 1), which may suggest the migrant nature of ^{210}Pb in these areas.

However, given that in calculation of *EF* only the total content of elements in soil and the bioavailable forms of these analytes in lichens or mosses is taken into account, the obtained results were verified by determining the comparative activity being a difference between the activity concentrations of the radionuclide in mosses and lichens relatively to the mean value of this radionuclide in lichens and mosses.

$$a_{i(comp.)} = \frac{a_{i(lichen)} - a_{i(moss)}}{\frac{a_{i(lichen)} + a_{i(moss)}}{2}} \tag{2}$$

The obtained comparative activity $a_{(comp.)}$ results are shown in Figure 2.

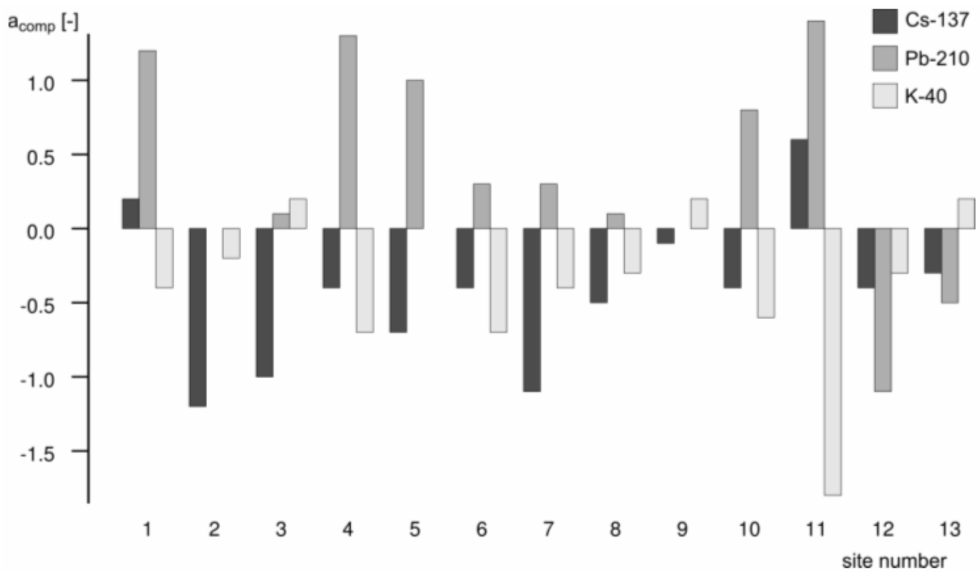

Fig. 2. Calculated values of the comparative activity in the study area

In the study area, $a_{(comp.)} > 0$ was found only for ^{210}Pb isotope, with the exception of sites No. 12 and 13. In the case of artificial ^{137}Cs isotope and natural ^{40}K isotope, the calculated values of $a_{(comp.)}$ were smaller than zero, which suggests that soil is the source of these radionuclides. This observation also justifies the possibility of using ^{137}Cs isotope as the reference element when calculating the Enrichment Factor.

In order to interpret the results of $a_{(comp.)}$ calculations, it was assumed, as suggested in the papers [25], that $a_{(comp.)}$ values exceeding 0.62 indicate the migrant, not caused by translocation from soil, nature of pollutants deposited in the studied area. The places where the above-mentioned relation is true are shown on the map (Fig. 4).

On the base of obtained measurement results, calculations used in geology, *ie* Geoaccumulation Index (I_{geo}) [27], were also carried out

$$I_{geo} = \log_2\left(\frac{a_i}{1.5GB}\right) \tag{3}$$

where *GB* is geochemical background of the analysed element.

The multiplier value of 1.5 reflects natural variations in the content of a given radionuclide in the environment, with low anthropogenic impact, caused by minor differences in geological structure.

The Geoaccumulation Index measurement results are shown in a box plot (Fig. 3) where static parameters of the obtained calculation results are marked.

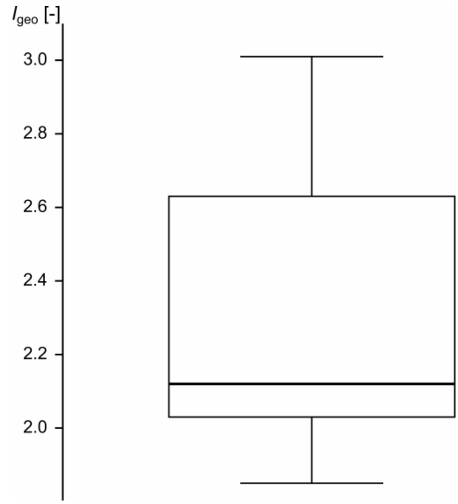

Fig. 3. Geoaccumulation Index box plot

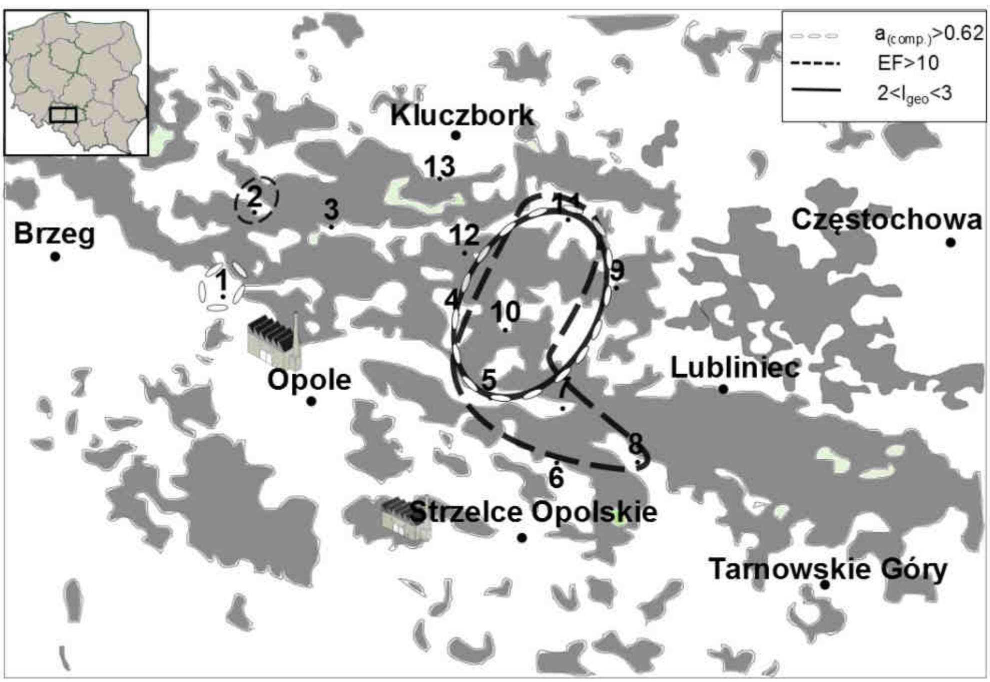

Fig. 4. The map showing ^{210}Pb deposition sites in the study area

The Geoaccumulation Index makes it possible to distinguish seven classes of the environment quality - from unpolluted to extremely polluted [27].

Taking into account the maximum value of this Index which does not exceed 3, it may be assumed that the places where the highest Geoaccumulation Index values were recorded fall into Class 3. Thus, it may be concluded that the study areas are moderately to heavily polluted. The areas with the highest I_{geo} values are shown in Figure 4.

The area highlighted in the map (Fig. 4) is characterised by increased ^{210}Pb radionuclide deposition, which may suggest the migrant nature of this isotope in the studied areas. The location of two cement plants which may be the emission source is marked on the map. Minerals and raw materials used in the cement industry contain natural radionuclides. Due to high cement production process temperatures and the scale of cement production, significant releases of radionuclides, including ^{222}Rn, ^{210}Po and ^{210}Pb, can be expected [28]. Given the predominance of south-westerly winds, such a distribution of ^{210}Pb in the studied area is justified.

The highest deposition was observed in areas of increased deposition of other pollutants [25], which may indicate that ^{210}Pb may be one of the emission components.

Conclusions

- The studies have shown that it is possible to identify dust emission sources using a radioactive lead isotope (^{210}Pb).
- The highest activity of ^{210}Pb was observed in areas with increased deposition of other pollutants, such as Ni, Cd, Cu and Pb, which may indicate that ^{210}Pb is one of the emission components.
- As it is possible to use ^{210}Pb as an indicator of dust emitted by fossil fuel burning sources, utilization of this isotope in biomonitoring studies is recommended.

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References

[1] Szczepaniak K, Biziuk M. Aspects of the biomonitoring studies using mosses and lichens as indicators of metal pollution. Environ Res. 2003;3:221-230. DOI: 10.1016/S0013-9351(03)00141-5.
[2] Kłos A, Rajfur M, Wacławek M. Application of lichens for the determination of precipitation pH by the exposure method. In: Pawłowski L, Dudzińska M, Pawłowski A, editors. Environ Eng. London: Taylor&Francis Group; 2007:505-512.
[3] Biazrov LG. Lichens as indicators of radioactive contamination. J Radioecol. 1993;1:15-20.
[4] Loppi S, Malfatti A, Sani M, Whitehead NE. Lichens as biomonitors of geothermal radionuclide pollution. Geothermics. 1997;26(4):535-540. DOI: 10.1016/S0375-6505(97)00005-9.
[5] Mathews KM. The use of lichens in a study of geothermal radon emissions in New Zealand. Environ Pollut. 1981;A24:105-116. DOI: 10.1016/0143-1471(81)90072-6.
[6] Santos PL, Gouvea RC, Dutra IR. Lead-210 in vegetables and soils from an area of high natural radioactivity in Brazil. Sci Total Environ. 1993;138:37-46. DOI: 10.1016/0048-9697(93)90403-S.
[7] Thomas PA, Gates TE. Radionuclides in the lichen-caribou-human food chain near uranium mining operations in northern Saskatchewan, Canada. Environ Health Perspectiv. 1999;107(7):527-537. DOI: 10.1289/ehp.99107527.

[8] Boileau LJR, Beckett PJ, Lavoie P, Richardson DHS. Lichens and mosses as monitors of industrial activity associated with uranium mining in northern Ontario, Canada. Environ Pollut. 1982;B4:69-84.

[9] Fahselt D, Wu TW, Mott B. Trace element patterns in lichens following uranium mine closures. Bryologist. 1995;98(2):228-234.

[10] Jeran Z, Byrne AR, Batic F. Transplanted epiphytic lichens as biomonitors of air-contamination by natural radionuclides around the Zirovski vrh uranium mine Slovenia. Lichenologist. 1995;27(5):373-385. DOI: 10.1006/lich.1995.0035.

[11] Thomas RS, Ibrahim SA. Plutonium concentrations in lichens of Rocky Flats environs. Health Phys. 1995;68(3):311-319. DOI: 10.1097/00004032-199503000-00002.

[12] Chibowski S, Reszka M. Investigation of Lublin town environment contamination by radionuclides and heavy metals with application of Parmeliaceae lichens. J Radioanalytic Nuclear Chem. 2000;247(2):443-446. DOI: 10.1023/A:1006798828071.

[13] Guogang J, Belli M, Sansone U, Rosamilia S, Gaudino S. Concentration, distribution and characteristics of depleted uranium (DU) in the Kosovo ecosystem: A comparison with the uranium behavior in the environment uncontaminated by DU. J Radioanalytic Nuclear Chem. 2004;260(3):481-494. DOI: 10.1023/B:JRNC.0000028206.70671.70.

[14] Uğur A, Özden B, Saç MM, Yener G, Altmbaş Ü, Kurucu Y, Bolca M. Lichens and mosses for correlation between trace elements and ^{210}Po in the areas near coal-fired power plant at Yatağan, Turkey. J Radioanalytic Nuclear Chem. 2004;259(1):87-92. DOI: 10.1023/B:JRNC.0000015811.68036.69.

[15] Dołhańczuk-Śródka A, Ziembik Z, Wacławek M, Hyšplerová L. Transfer of cesium-137 from forest soil to moss Pleurozium schreberi. Ecol Chem Eng S. 2011;18(4):509-516. http://tchie.uni.opole.pl/freeECE/S_18_4/DolhanczukSrodkaZiembik_18%28S4%29.pdf.

[16] Ziembik Z, Dołhańczuk-Śródka A, Majcherczyk T, Wacławek M. Illustration of constrained composition statistical methods in the interpretation of radionuclide concentrations in the moss Pleurozium schreberi. J Environ Radioactiv. 2013;117:13-18. DOI: 10.1016/j.jenvrad.2012.04.002.

[17] Giovani C, Nimis PL, Bolognini G, Padovani R, Usco A. Bryophytes as indicators of radiocesium deposition in Northeastern Italy. Sci Total Environ. 1994;157:35-43. DOI: 10.1016/0048-9697(94)90563-0.

[18] Nifontova M. Current contents of ^{90}Sr and ^{137}Sr in the moss-lichen cover of Piedmont and Mountain Landscapes of the Northern Urals. Russian J Ecol. 2003;34(1):47-51. DOI: 10.1023/A:1021867122150.

[19] Horrill AD. Natural and Semi-Natural Pasture Ecosystems and Their Importance in the Context of Environmental Contamination. London, New York: Elsevier; 1990:231-237.

[20] Sert E, Uğur A, Özden B, Saç MM, Camgöz B. Biomonitoring of ^{210}Po and ^{210}Pb using lichens and mosses around coal-fired power plants in Western Turkey. J Environ Radioactiv. 2011;102:535-542. DOI: 10.1016/j.jenvrad.2011.02.005.

[21] Dragović S, Janković Mandic L. Transfer of radionuclides to ants, mosses and lichens in semi-natural ecosystems. Radiation Environ Biophys. 2010;49:625-634. DOI: 10.1007/s00411-010-0319-8.

[22] Varrica D, Aiuppa A, Dongarra G. Volcanic and anthropogenic contribution to heavy metal content in lichens from Mt. Etna and Vulcano island (Sicily). Environ Pollut. 2000;108:153-162. DOI: 10.1016/S0269-7491(99)00246-8.

[23] Prudêncio MI. Biogeochemistry of trace and major elements in a surface environment (volcanic rock, soil, mosses, lichens) in the S. Miguel Island, Azores, Portugal. J Radioanalytic Nuclear Chem. 2007;271:431-437. DOI: 10.1007/s10967-007-0227-9.

[24] Popovic D, Todorovic D, Frontasyeva M, Ajtic J, Tasic M, Rajsie S. Radionuclides and heavy metals in Borovac, Southern Serbia. Environ Sci Pollut Res. 2008;15:509-520. DOI: 10.1007/s11356-008-0003-6.

[25] Kłos A. Porosty w biomonitoringu środowiska (Lichens in Environmental Biomonitoring). Studia i Monografie; Opole: Opole University; 2009.

[26] Dołhańczuk-Śródka A, Majcherczyk T, Ziembik Z, Smuda M, Wacławek M. Spatial ^{137}Cs distribution in forest soil. Nukleonika. 2006;51(Suppl.2):69-79.

[27] Al-Haidarey MJS, Hassan FM, Al-Kubaisey ARA, Douabul AAZ. The geoaccumulation Index of Some Heavy Metals in Al-Hawizeh Marsh. Iraq. E-J Chem. 2010;7:157-162. DOI: 10.1155/2010/839178.

[28] Bem H. Radioaktywność w środowisku naturalnym (Radioactivity in Natural Environment). Łódź: PAN; 2005.

IZOTOP Pb-210 JAKO ZNACZNIK EMISJI ZANIECZYSZCZEŃ

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Abstrakt: W pracy zastosowano biomonitoring pasywny, z wykorzystaniem ^{210}Pb, do oceny depozycji zanieczyszczeń. Do badań wykorzystano dobrze wykształcone epifityczne porosty listkowate *Hypogymnia physodes*, porastające gałęzie świerka. Wokół drzewa, z którego pobrano próbki porostów, pobierano próbki mchów *Pleurozium schreberi* oraz gleby - próchnicy nadkładowej. W prowadzonych badaniach stwierdzono, że możliwa jest identyfikacja źródeł emisji pyłu przy wykorzystaniu radioaktywnego izotopu ołowiu - ^{210}Pb. Największe aktywności ^{210}Pb zaobserwowano na terenach o zwiększonej depozycji innych zanieczyszczeń, np. Ni, Cd, Cu i Pb, co może wskazywać, że ^{210}Pb jest jednym z komponentów emisji.

Słowa kluczowe: ^{210}Pb, znacznik emisji zanieczyszczeń, pasywny biomonitoring