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This study is a continuation of the investigation on the ^{210}Po emission to the atmosphere. For the identification of areas with elevated contents of this radionuclide, one lichen and one moss species were chosen. Both types of organisms were applied for contamination factor determination and mapping of regions with higher ^{210}Po activity concentration in the urban air. ^{210}Po concentration in lichen *Hypogymnia physodes* is an average of twice higher than in moss *Pleurozium schreberi*. The presented maps confirm higher local emission of pollutants enriched in ^{210}Po radionuclide. All regions with higher ^{210}Po activity concentration can be strongly linked with the release of the escaping of fly ashes from the local coal power plants and old type domestic central heating systems mostly used in loft buildings in the central part of Lodz city.

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ARTICLE TYPE

Use of moss and lichen species to identify ^{210}Po contaminated regions

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^{210}Po activity concentration in the urban air fluctuates as a result of natural ^{222}Rn radionuclide exhalation and technical activity especially linked with high temperature processes. Each year, an average 11GBq of ^{210}Po is released from local power plants into the urban air. During two months, about 180 samples in central Poland were collected. For ^{210}Po activity concentration, two common species of biomonitor were chosen: moss *Pleurozium schreberi* and lichen *Hypogymnia physodes*. For the same localization, ^{210}Po in lichen shows an average of twice the amount of activity concentration than in moss. In mosses, ^{210}Po concentrations in Lodz ranged from 41.5 Bq/kg to 258.0 Bq/kg, while in lichen it ranges from 74.2 Bq/kg to 670.9 Bq/kg. On the basis of the measured activity of ^{210}Po maps, radionuclides distribution has been prepared. For identified areas with higher concentrations of ^{210}Po program, Quantum Gis has been applied.

Introduction:

The urban air contains a whole range of radioactive elements of different natural and artificial origins. The dominant part of the natural isotopes is from radioactive series, mainly uranium-radium and thorium, which are transported to the atmosphere by resuspension of the soil process, or in result of industrial activity, especially high temperature processes^{1,2}. As a result of such technical activities, most of the radionuclides have been discharged in region of source. One of the most volatile and radiotoxic is the Polonium element.

Polonium has many radioactive isotopes, among the most important and most lasting, presented in the environment, being the ^{210}Po with a half-life of 138.4 days. ^{210}Po are products of the ^{238}U decay series and are released into the atmosphere via the decay of ^{222}Rn . The spontaneous diffusion of ^{222}Rn from the earth's surface into the atmosphere decays continuously to ^{210}Po through various other short-lived and long-lived radionuclides. In urban air, ^{210}Po activity concentration is also a result of common energetic coal combustion processes in power plants and domestic furnaces. As a result of combustion processes, ^{210}Po creates volatile compounds, and almost immediately adsorbs on the fines particles (especially those below 1 μm), which can easily penetrate the atmosphere despite the use of multi-level extraction or dedusting systems. Ash fractions of less than 1 μm are particularly dangerous as respiral fractions. Emitted exhaust gaseous and fine particles of fly ashes are mostly order magnitude enhancement in natural radionuclides in comparison with fossil fuels or surface soil in central Poland. The average activity concentration of ^{210}Po in escaping fly ash reported³ previously was even 1700 Bq/kg. In Lodz agglomeration, in result of coal combustion processes, about 11GBq of ^{210}Po and 0.9 GBq of ^{210}Pb per year are released into the atmosphere from three local power plants.

Lichens are symbiotic organisms composed of fungi (mycobionts) and green algae or cyanobacteria. Lichens and mosses obtain their nutrient supply directly from atmospheric deposition in result of effective biomonitor of environmental

contamination. Both of them, thanks to their morphological and physiological features, show a high ability to accumulate air pollutants (including toxic), also ^{210}Po . In Poland, the most spread and tolerance on presence of contamination are two organisms: moss *Pleurozium schreberi* and lichen *Hypogymnia physodes*. However, lichen are more sensitive on SO_2 and other pollutants, as a result, it is not possible to correct monitoring of ^{210}Po in regions of high contamination, named a lichen dessert. In general both biomonitor occur correlation between activity concentration of ^{210}Po and other radionuclides in the mass of the one-gram of the dry organism and activity in the urban air^{1,2}. This feature helped to identify the source of ^{210}Po emission.

The mosses and lichen have been widely used as bioaccumulation⁴, absorption⁵, localization⁶, release⁷, toxicity indicators of metals⁸ and radionuclides⁹ to the atmosphere and measured by various instrumental techniques¹⁰. ^{210}Po activity monitoring by use of lichen and mosses was applied previously in Turkey^{1,2,11}, Sweden¹², India¹³, Syria¹⁴ and in Poland¹⁵.

The aim of this work is to identify regions of higher ^{210}Po concentration in the urban air of Lodzan agglomeration after a heating period. Therefore, next to the standard alpha-spectrometric analysis, powerful visualization tools such as the Qantum Gis application¹⁶ have been applied.

Materials and methods

Sampling:

Lodz city is one of the most densely populated Polish and European cities. Samples were taken in Lodzian agglomeration consisting of Lodz and surrounding towns and Witow, Zawoja and Jamno village. There are huge environmental contrasts between these regions. Most samples were taken in Lodz city located in central Poland. In a city centrum, three coal power plants are located with a total power 2.6 GW. For comparison, samples were taken in regions surrounding the towns and villages.

About 180 of lichen and moss samples have been collected. Samples were taken out in February and March 2014, just after the cold winter season. The samples were taken just from trees, not from concrete or metal elements for a normalized living condition of the biomonitors. The samples were dried at room temperature for min 3 days, and after this the lichen thallus and mosses leaves were cleaned, fragmented and grinded in a mortar. Average 0.2 g of the green part of the leaves of the moss and top part of the lichen thallus samples were put into the Teflon container and filled with 50 ml of 1M HCl. After 24 hours of leaching, the solution was filtered. ^{210}Po present in the solution was separated by the spontaneous deposition on silver discs at 80°C by minimum 8h. Activity of ^{210}Po was determined using an alpha spectrometry system with a PIPS detector.

Accuracy:

Yield of polonium separation by this method has been calculated by use of IAEA reference materials: IAEA 300 and IAEA 434. Results are presented in Table 1.

Table 1. The ^{210}Po measured and certified activity in reference materials.

Code	^{210}Po measured activity [Bq/kg]	^{210}Po certified activity [Bq/kg]	Standard deviation %
IAEA 300 Marine sediment	340±18	340.5	-0.1
IAEA 434 Phosphogypsum	641±23	680.0 (on the base of ^{210}Pb)	5.6

As it is evident, good agreement between measured and certified value of activity has been obtained.

Results and discussion

The choice of moss and lichen species for analysis

In the forest located close next to village Witów, several species of mosses and lichens (mosses: *Pleurozium schreberi*, *Polytrichum commune*, lichens: *Hypogymnia physodes*, *Cladina rangiferina* (L.) Nyl.) have been collected. It allows for comparison the ^{210}Po activity concentration in different species. *Polytrichum commune* an accumulated more ^{210}Po (~154 Bq/kg), than *Pleurozium schreberi* (<100 Bq/kg). Among the lichens are also seen certain trends. *Hypogymnia physodes* an accumulated 273 Bq/kg, while *Cladina rangiferina* 164 Bq/kg at Witów region.

At a forest located close to Jamno village, results have shown the same trend, which confirms the accumulation ability of various indicator species.

Table 2. Activity concentration in lichen and mosses in a forest in the region small villages Witów and Jamno.

	^{210}Po activity concentration [Bq/kg]	
	Witów village	Jamno village
<i>Pleurozium schreberi</i>	91.6±6.2	69.8±4.5
<i>Polytrichum commune</i>	154±8	144±7
<i>Hypogymnia physodes</i>	273±9	205±8
<i>Cladina rangiferina</i>	164±8	No data

For further analysis of ^{210}Po commonly occurring moss *Pleurozium schreberi* and lichen *Hypogymnia physodes* have been selected. The relatively higher ^{210}Po activity concentration in biomonitor samples was typical in regions of polonium emission^{17,1,2,11}. In regions with higher source emission (the center of Lodz), the ratio of activity of ^{210}Po in samples of lichen relative to the activity in mosses at the same location ranged from 0.92 to 3, with an average ratio equal to 1.99 (Fig.1). Figure 1 confirms weak correlation ($r=0.73$) between ^{210}Po activity concentration in lichen and mosses samples at the same location. Therefore, lichen, as the better accumulator of this metal, is more useful for monitoring the activity of ^{210}Po in the urban air.

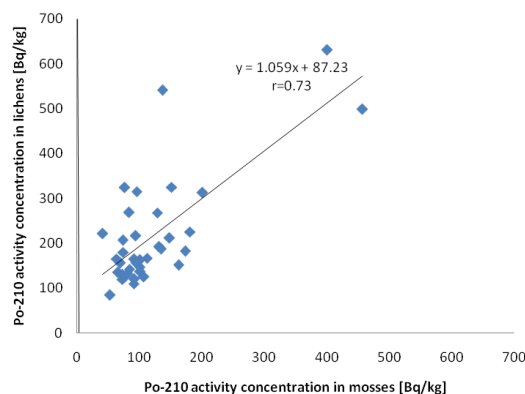


Fig. 1. The ^{210}Po activity concentration in lichen *Hypogymnia physodes* and in moss *Pleurozium schreberi* at the same sampling site.

Difference of ^{210}Po activity in various parts of biomonitors body.

To understand the absorption mechanism, radionuclide was analyzed separately in different parts of the biomonitor. In this study, statistically significant differences between ^{210}Po activity concentration in various parts of moss body and in different sizes of lichen thallus has been analyzed.

Lichen shows an intercellular absorption of the metals¹⁸ through an exchange process, thus lichens are perfect accumulators of the metals. Because of no root system, lichen can uptake metals from the atmosphere and then efficiently transport it in the whole thallus. Local insolation, presence of SO_2 and other stressed compounds can change dramatically the rate of growth and reduce the lichen population.

Table 3. ^{210}Po activity concentration in relation to size of lichen *Hypogymnia physodes*

Code sample	small thallus [Bq/kg]	large thallus [Bq/kg]
10	121±5	203±10
12	168±7	244±7
Z4	153±6	471±16

On the other hand, large thallus of the lichen seems to be an efficient tool for the absorption of pollutants by wet and dry precipitation from the atmosphere. For *Hypogymnia physodes* two sized samples, sampling at the same location has been analyzed. It means that the same species can exhibit differences in their accumulation properties depending on its diameter.

Brancher thallus of lichen body can accumulate on average 50% more polonium than a small part of lichen body (Table 3).

Table 4. ^{210}Po activity in various moss *Pleurozium schreberi* body parts.

Code sample	pincers [Bq/kg]	stem [Bq/kg]	leave [Bq/kg]
W4	786±16	415±12	125±8
J1	737±19	373±10	69.8±3.5
J2	847±28	226±9	144±6

Mosses do not have epidermis and cuticle, therefore metal ions can easily penetrate the cell wall. Mosses do not have a proper root system, but have threadlike rhizoids only as an anchor to substrate. Mosses absorb water and nutrients mainly through their leaves. It is well known that the transport of minerals between segments, and parts of the moss body is limited because of lack of vascular tissue. Mosses accumulate metals in a passive ion exchange¹⁸ (Szczepaniak and Biziuk, 2003). In this study significant difference (t-test, $p < 0.005$) in ^{210}Po activity concentration between three moss body parts has been measured. The concentration of ^{210}Po in the pincers system is several times higher, compared with stem and leaves. Similar results were noted for the root system of orchid *Cymbidium aloifolium* (Lo) Swartz¹⁹. The main reason for the higher concentration of ^{210}Po in the different parts of the plant might be the artificially produced fallout radionuclide, which occurred in the past. It should be noted that ^{210}Po activity in the surface soil is an order of magnitude lower. The average activity of ^{210}Po in the top soil is equal to 29.1 ± 1.5 Bq/kg. Polonium content in soil can not be a reason for a higher radionuclide activity concentration in pincers system of the analysed *Pleurozium schreberi* species presented in Table 4. This data confirms absorption of radionuclide directly from the atmosphere, by dry and wet precipitation of the pollutants. Escaped fly ashes released from technical activities seems to be the main source of the highest ^{210}Po activity concentration measured in the biomonitors in Lodzian agglomeration.

Influence of wind on ^{210}Po distribution

The distribution of ^{210}Po activity concentration in biomonitors depends on ^{210}Pb and artificial discharging of pollutants from the domestic heating systems or from local coal power plants²⁰ (Bem, et al., 2002) enhanced in ^{210}Pb and ^{210}Po radionuclides. The samples were taken just after the snow layer disappeared, in a period of low natural ^{210}Pb production from ^{222}Rn radionuclide exhaled from the ground and maximal ^{210}Pb and ^{210}Po emission from energetic coal combustion. The wind rose for Lodz suggests north-west and west, and rarely an east direction of the wind. In conclusion most contaminations emitted mostly from point sources, are preferably moved in these directions.

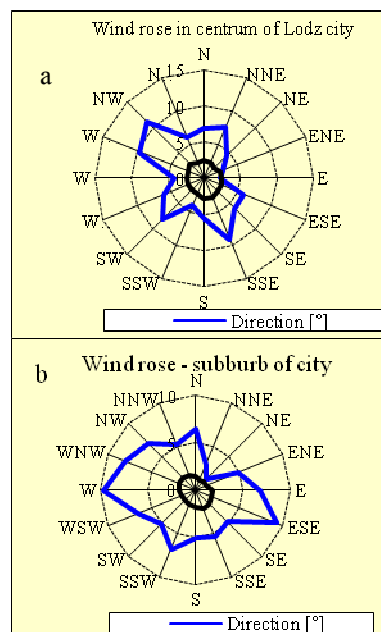


Fig. 2. Wind rose for a) Lodz city centrum and b) suburb area.

The carried analysis confirmed the correlation between the ^{210}Po activity concentration in mosses and lichens depending on the distance from the emission source. In this study there have been several regions found with a higher ^{210}Po activity concentration. Localization each of them suggest energetic coal combustion as the dominant ^{210}Po origin. For easy indication²¹ of such regions, contamination factor F_p for moss or F_h for lichen have been applied.

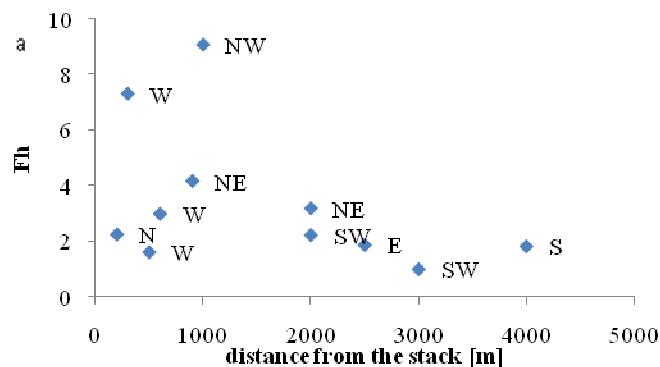
$$F_p = \frac{A_{xp}}{A_{Txp}} \quad \text{and} \quad F_h = \frac{A_{xh}}{A_{Txh}} \quad (1)$$

Where:

A_x - ^{210}Po activity concentration in samples of *Pleurozium schreberi* (p) or *Hypogymnia physodes* (h), taken in city centre,

A_{Tx} - ^{210}Po activity concentration in samples of both biomonitors (p) and (h), sampling in the forest, far (about 10 km) from antropogenic activity

Contamination factor F_p for *Pleurozium schreberi* moss fluctuate from 1.07 to 8.78 with an average 2.45. For *Hypogymnia physodes* lichen F_h obtain value between 0.95 and 9.06 with an average of 3.00.



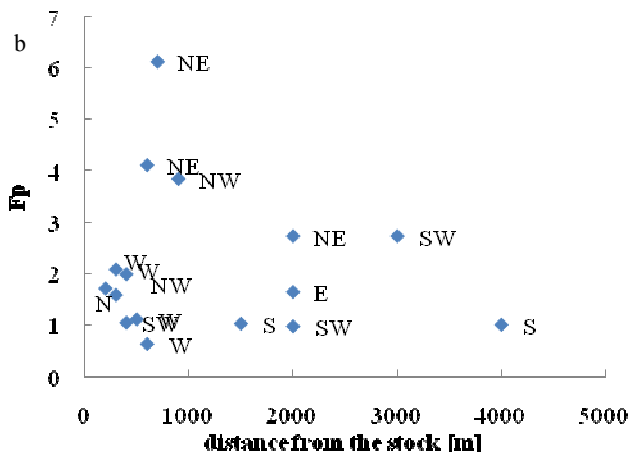


Fig. 3 Contamination factors for a) *Hypogymnia physodes* and b) *Pleurozium schreberi* in distance from the coal power plant stack.

Contamination factor for both biomonitors fluctuate with distance from the power plant stack. Depending on the wind, the maximum rose of ^{210}Po activity concentration that was obtained for a distance of about one km, and then decreases. Because of the presence of lichen in the desert, it was not possible to verify ^{210}Po presence in all directions around the local power plants. For better visualization of the ^{210}Po content in the air an easy map has been prepared.

Maps of ^{210}Po activity concentration in Lodzian agglomeration

Both biomonitors show maximal concentrations in regions of coal power plants that are located close to large urban settlements and in the region of Old Town (Fig.4 and 5). In this region contamination factors F_p and F_h were equal even 9.1 (activity concentration equal 671 ± 23 Bq/kg), 8.8 (457 ± 21 Bq/kg). Lower activity concentration was determinate in the suburb of the Lodz city. In this region maximal contamination factors F_p and F_h produced values of 5.1 (379 ± 15 Bq/kg) and 1.7 (112 ± 4 Bq/kg). The lowest activity concentration were measured from samples taken out from deep forests located next to small villages. These results were applied as a natural background of ^{210}Po content in the biomonitors.



Fig. 4 Map of F_p in lichen (*Pleurozium schreberi*) in Lodzian agglomeration.

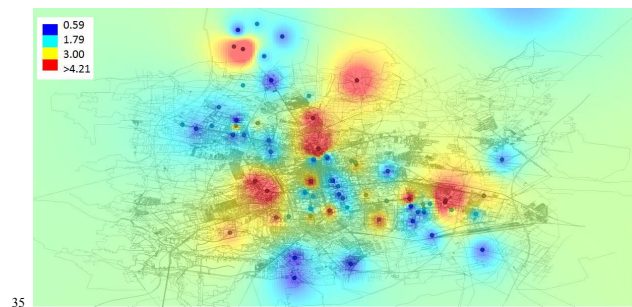


Fig. 5 Map of F_h in the moss (*Hypogymnia physodes*) in Lodzian agglomeration.

In this study significant differences in concentrations in power plant region and suburb have been observed (t-test, $p < 0.001$). In the suburb region activity of ^{210}Po is lower than the fluctuations between radionuclide concentrations. Both biomonitors at the sampling points could be in connection with various ecological conditions and individual lichen and moss predisposition. The uncertainty of presented results doesn't exceed 5%. The presented maps (Fig. 4 and 5) suggest the presence of local pollution emission sources. The prevailing winds influence on local distribution of fine escaping fly ashes and dilution of ^{210}Po activity concentration.

Both maps were elaborate in Quantum Gis application in version 1.8.0 (Lisboa). For visualization apply layer three: with a map of the city, map of the sampling points and interpolation results. The calculated ^{210}Po contamination factors were visualized by interpolation methods based on Inverse Distance Weighting (IDW).

In the next step of this study correlation between ^{210}Po and other natural, as well as artificial radionuclides, will be analyzed.

Conclusion

This study is a continuation of the investigation on the ^{210}Po emission to the atmosphere²². For the identification of areas with elevated contents of this radionuclide, thus identify local sources of its emission method of biomonitors has been applied. For ^{210}Po activity concentration analysis, one lichen and one moss species were chosen. Both types of organisms were applied for contamination factor determination and mapping of regions with higher ^{210}Po activity concentration in the urban air.

^{210}Po concentration in lichen *Hypogymnia physodes* is an average of twice higher than in moss *Pleurozium schreberi*. However, *Hypogymnia physodes* as a more suitable biomonitor could not be found in most pollutant regions, therefore the highest ^{210}Po concentration couldn't be analyzed.

The presented maps confirm higher local emission of pollutants enriched in ^{210}Po radionuclide. All regions identify with higher ^{210}Po contaminations can be strongly linked with the release of the escaping of fly ashes from the local coal power plants and old type domestic central heating systems mostly used in loft buildings in the central part of Lodz city.

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