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Dorota MODZELEWSKA[1], Agnieszka DOŁHAŃCZUK-ŚRÓDKA[1]
and Zbigniew ZIEMBIK[1]

# ASSESSMENT OF AIR CONTAMINATION WITH SELECTED RADIOISOTOPES NEARBY CEMENT PLANT USING MOSS BAG METHOD

## OCENA STANU ZANIECZYSZCZENIA POWIETRZA WYBRANYMI RADIOIZOTOPAMI W POBLIŻU CEMENTOWNI Z UŻYCIEM METODY WORECZKOWEJ

**Abstract:** Mining and processing industry represents a potential source of radioisotopes contaminating the nearest environment. In order to estimate conditions of the environment in the vicinity of cement plant moss bag biomonitoring method was used. The aim of the study was to assess the relationship between the extent of air pollution with $^{40}$K, $^{137}$Cs, $^{210}$Pb and the distance from the cement plant. The share of various radiation sources in the total $^{210}$Pb activity concentration in mosses after exposure was also analyzed. Sampling sites were located in the forest near Opole (PL), in a line and at different distances from the cement plant. In test two types of moss bags, exposed simultaneously in the same places, were used. In the studies, activity concentrations of gamma-radioactive isotopes were determined in samples of moss before and after the exposure. In investigations the gamma-spectrometer with a germanium detector was used. From the obtained results the Relative Accumulation Factors (*RAF*) were calculated. In order to assess the extent to which radionuclides activity depends on the distance from the cement plant, correlation coefficients were calculated. It is hard to estimate the trends of radionuclides activity concentration changes with distance from the cement plant due to substantial discrepancies in the results. No significant relationship of radionuclides deposition on the distance from the cement plant was noticed.

**Keywords:** Relative Accumulation Factor (*RAF*), radioisotopes, moss bag method, cement plant

## Introduction

For many years mining and processing industry significantly burden the environment. In the case of the Opole region (southern Poland) it is associated mainly with limestone mines and cement plants. They represent a potential source of radioisotopes that can spread over various distances. Cement plants use as feedstock limestone, marly

[1] Independent Department of Biotechnology and Molecular Biology, Opole University, ul. kard. B. Kominka 6a, 45–035 Opole, Poland, phone: +48 77 401 60 46, email: d.modzelewska92@gmail.com, agna@uni.opole.pl, ziembik@uni.opole.pl

limestone, marl and clay containing natural radionuclides that are released into the air under high temperature applied during the cement production process. The volatile isotopes $^{222}$Rn, $^{210}$Po and $^{210}$Pb are emitted in the gaseous form or as a precipitate and particulate matter, increasing radioactivity around these industrial plants [1–3].

To assess the air contamination from anthropogenic sources in the vicinity of industrial and urban areas the moss bag biomonitoring technique is frequently used. These method was introduced by Goodman and Roberts in the 80. of 20th century. Since then the moss bag method was repeatedly utilized to assess radioactive contamination near nuclear power plants, after nuclear weapon tests and after nuclear plants accidents [4–8].

The common application of mosses is mainly caused by their relative high efficiency in heavy metals and radioisotopes accumulation. Mosses do not have the epidermis and cuticle, which greatly facilitates the entry of contaminants into the cells. They have no roots, so they collect nutrients only from precipitation and dry deposition. It is assumed that concentration of chemical compounds in the mosses biomass corresponds to deposition from the air [9–11].

Mosses were used, among others, in assessment of radioactive pollution in the southern Poland areas [12–13]. Mosses *Ctenidium molluscum* were also used as radiodeposition bioindicators in north-east Italy [14]. In 1985–2004, in the Ural Mountains, radiodeposition of caesium was determined in the mosses *Hylocomium*, *Pleuroziumand Plerozium* [15]. Radiocaesium activity in the mosses *Pleurozium schreberi* and *Dicranum polysetum* was also studied by Horrill [16]. 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 [17]. Despite the fact that mosses and lichens are commonly used in monitoring programs, the amount of data regarding to transfer of radionuclides to these organisms is limited, in particular with regard to natural radionuclides [18].

The aim of the study was to assess the relationship between the extent of air pollution with radioisotopes: $^{40}$K, $^{137}$Cs, $^{210}$Pb and the distance from the cement plant.

## Materials and methods

In the studies moss of the species *Pleurozium schreberi* were used, due to their prevalence in the Poland and frequent use for contamination bioindication. About a month before an exposure, samples of moss were picked in the forests of the Karkonosze Mountains, an area not significantly polluted, at a minimum distance of about 100 m from the main roads.

In the laboratory, mosses were manually cleaned, carefully mixed together, air-dried and the initial activity concentrations of radionuclides such as $^{40}$K, $^{137}$Cs and $^{210}$Pb were determined using gamma-spectrometer. Then mosses were divided into 8 parts of 55 g each. All samples were packed in a plastic mesh net with mesh size of 1.5 × 1.5 cm, which was arranged in three-dimensional cylindrical boxes enabling uniform deposition efficiency of the analyzed elements from all directions. The test used two types of moss bags. In the A option, only mosses filled the volume of a bag, but in the B option, an additional plastic extender was located in the middle of the bag and mosses filled the space between it and bag walls. In Fig. 1 and 2 construction of the moss bags is shown.

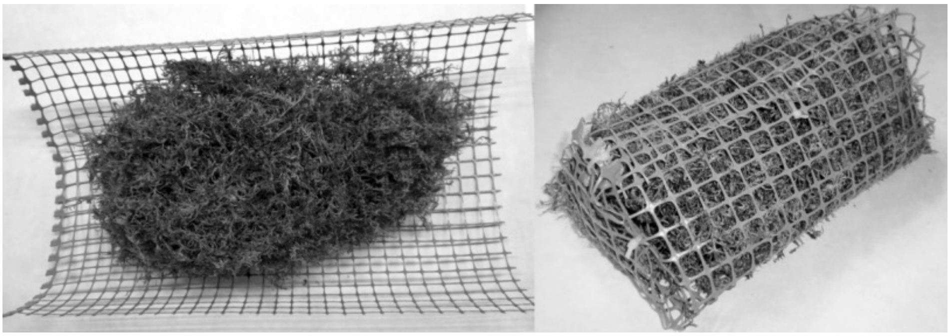

Fig. 1. Example of a moss bag, A option

Fig. 2. Example of a moss bag, B option

Moss bags were exposed in the study area between Chorula and Gorazdze villages, about 20 km far from Opole. The study area was located near the cement plant and limestone quarry connected by a conveyor transporting output from the quarry to the cement plant. For the study four sampling sites were selected. The first one was located about 100 m far from the road encompassing a cement plant and 200 m from a conveyor. Each subsequent sampling site was arranged about 400 m away from the previous and at the same distance from the conveyor as the first one. All samples were hanged in the branches of trees at a height of about 2 m. In each sampling site on the same tree two different options of moss bags were placed. After 98 days of field monitoring moss bags were collected and transported to the laboratory, in which they were treated in the same way like before the exposure.

The determination of radionuclide activity concentration in moss samples were 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, which covers an energy range from 59.54 keV to 1836.06 keV. The geometry of the


Fig. 3. Scheme of the study area

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 Marinelli of 450 cm$^3$, and it was filled with about 50 g of moss. The time of measurement was about 24 hours for all moss samples. Measuring process and analysis of spectra were computer controlled with the use of the software GENIE 2000.

The obtained results of radionuclide activity concentration in moss samples allowed to calculate the Relative Accumulation Factor (*RAF*), which values indicate an increase in analyte amount during exposition:

$$RAF = \frac{a_{1,i} - a_{0,i}}{a_{0,i}} \tag{1}$$

where: $a_{1,i}$ and $a_{0,i}$ are the activity concentration of the $i$-th radionuclide in mosses respectively after and before the exposure [Bq/kg d.m.]. On a *RAF* scale score 0 is no growth and 1 and 2 are respectively single and double amount increment of the analyte in the sample. For the *RAF* values, the maximum measurement uncertainties Δ*RAF* were calculated using the formula:

$$\Delta RAF = \sqrt{\left(\frac{a_{1,i}}{a_{0,1}^2}\,\Delta a_{0,i}\right)^2 + \left(\frac{1}{a_{0,i}}\,\Delta a_{1,i}\right)^2} \tag{2}$$

where: $\Delta a_{0,i}$ and $\Delta a_{1,i}$ are the measurement uncertainties of $i$-th radionuclide activity concentration in mosses respectively before and after their exposure [Bq/kg d.m.].

Linear correlation coefficients were calculated to assess the linear relationship between radionuclides *RAF* and the distance from the cement plant. It was computed using the “correlation coefficient” function in Excel.

The share of various radiation sources in the total $^{210}$Pb activity concentration in mosses after exposure was also analysed. Excessive lead activity concentration $a_e$ was calculated from the formula:

$$a_e = a_{1,\text{Pb-210}} - a_{0,\text{Pb-210},m} - a_{1,\text{Bi-214}} \quad (3)$$

where: $a_{1,\text{Pb-210}}$ and $a_{1,\text{Bi-214}}$ are the activity concentration of the respectively $^{210}$Pb and $^{214}$Bi in moss after exposure and $a_{0,\text{Pb-210,m}}$ is the mean value of $^{210}$Pb activity concentration in moss before exposure.

## Results and discussion

All tested radionuclides were determined in all samples before and after exposure.

Table 1

Activity concentration $a_{1,i}$ [Bq/kg d.m.] of radionuclides in moss before exposure with measurement uncertainties $\Delta a_{1,i}$ [Bq/kg d.m.]

| Sample number | I | | II | | III | | IV | |
|---|---|---|---|---|---|---|---|---|
| | $a_{1,i}$ | $\Delta a_{1,i}$ | $a_{1,i}$ | $\Delta a_{1,i}$ | $a_{1,i}$ | $\Delta a_{1,i}$ | $a_{1,i}$ | $\Delta a_{1,i}$ |
| $^{40}$K | 282 | 33 | 62 | 11 | 94 | 27 | 79 | 22 |
| $^{137}$Cs | 31 | 2 | 18 | 1 | 14 | 2 | 17 | 2 |
| $^{210}$Pb | 436 | 132 | 204 | 51 | 323 | 118 | 230 | 90 |

The mean initial activities of radionuclides in mosses were:
a) 129 ± 23 Bq/kg d.m. of $^{40}$K,
b) 20.0 ± 1.4 Bq/kg d.m. of $^{137}$Cs,
c) 298 ± 98 Bq/kg d.m. of $^{210}$Pb.

Radionuclides concentration activities for all samples after exposure in both options are presented in Table 2.

Table 2

Activity concentration $a_{1,i}$ [Bq/kg d.m.] of radionuclides in moss after exposure with maximum measurement uncertainties $\Delta a_{1,i}$ [Bq/kg d.m.]

| Distance from the cement plant | 100 m | | 500 m | | 900 m | | 1300 m | |
|---|---|---|---|---|---|---|---|---|
| | $a_{1,i}$ | $\Delta a_{1,i}$ | $a_{1,i}$ | $\Delta a_{1,i}$ | $a_{1,i}$ | $\Delta a_{1,i}$ | $a_{1,i}$ | $\Delta a_{1,i}$ |
| A option | | | | | | | | |
| $^{40}$K | 220 | 31 | 196 | 32 | 221 | 30 | 211 | 20 |
| $^{137}$Cs | 35.2 | 2.5 | 30.6 | 2.4 | 51.6 | 2.8 | 36.7 | 1.5 |
| $^{210}$Pb | 588 | 129 | 500 | 138 | 679 | 142 | 549 | 102 |
| B option | | | | | | | | |
| $^{40}$K | 211 | 32 | 162 | 27 | 166 | 32 | 178 | 23 |
| $^{137}$Cs | 30 | 2.4 | 27 | 2.0 | 31.7 | 2.7 | 22.0 | 1.5 |
| $^{210}$Pb | 587 | 144 | 495 | 122 | 490 | 138 | 410 | 102 |

In all samples post-exposure activities of $^{40}$K, $^{137}$Cs and $^{210}$Pb were higher than mean pre-exposure activities. Relationship between the calculated *RAF* values and distance from the plant are shown in Fig. 4, 5.

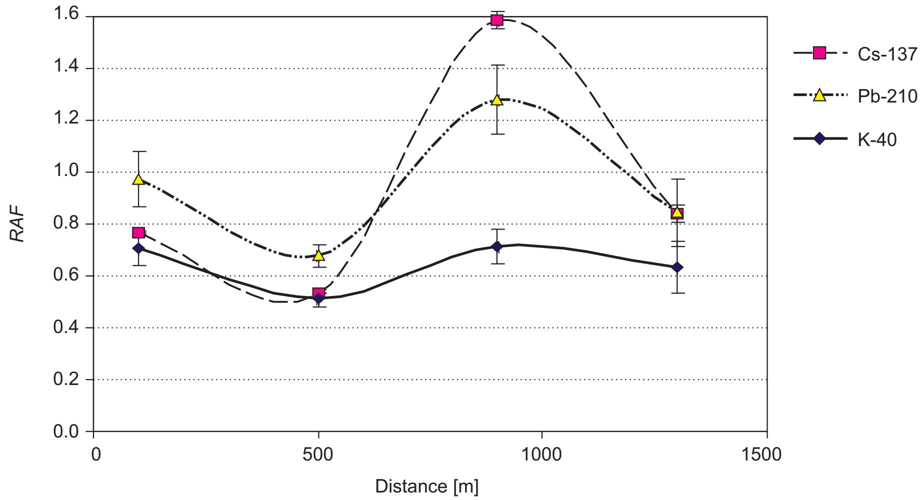


Fig. 4. *RAF* values for $^{40}$K, $^{137}$Cs and $^{210}$Pb in moss bags A options

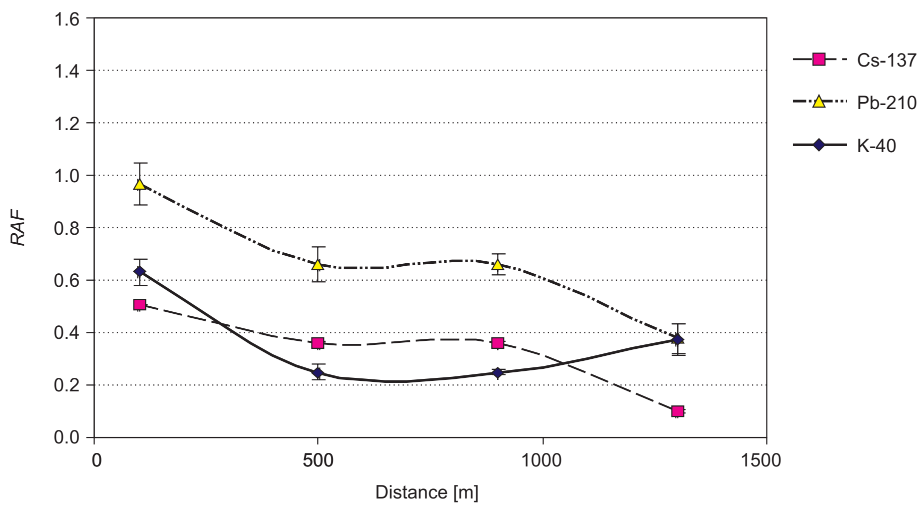


Fig. 5. *RAF* values for $^{40}$K, $^{137}$Cs and $^{210}$Pb in moss bags B options

In A option, the biggest $^{137}$Cs and $^{210}$Pb activity concentration increases were observed at a distance of 900 m from the cement plant. The activity concentrations ratios were respectively 1.6 and 1.3. It does not coincide with B option, for which it was reached at a distance of 100 m from the cement plant, respectively with ratios 0.5 and

1.0. Similar differences in the *RAF* values in both options is observed for the smallest activity concentration increase of these radioisotopes, but in distances of 500 m (A variant) and 1300 m (B variant). Due to the divergence in trends between options it is difficult to determine relationship between activity concentration and distance. In opposite, the increase in $^{40}$K activity concentration in both options is almost constant in all sampling sites.

In order to confirm the preliminary observations linear correlation coefficients were calculated. Correlation coefficients between the radionuclides *RAF* and the distance from the cement plant are:

– $^{40}$K in A option – 0.03 and in B option – 0.55,
– $^{137}$Cs in A option – 0.36 and in B option – 0.93,
– $^{210}$Pb in A option – 0.10 and in B option – 0.95.

These results showed a total lack of correlation between the studied variables in A option and both partial and almost complete correlation in B option. This observation confirmed lack of ability to assess the trends of radionuclides activity increases with the change in the distance from the cement plant. Studies concerning such relationship require additional data.

In Fig. 6 the shares of autogenous (natural lead) and allogeneic (excessive lead) [19] are illustrated.

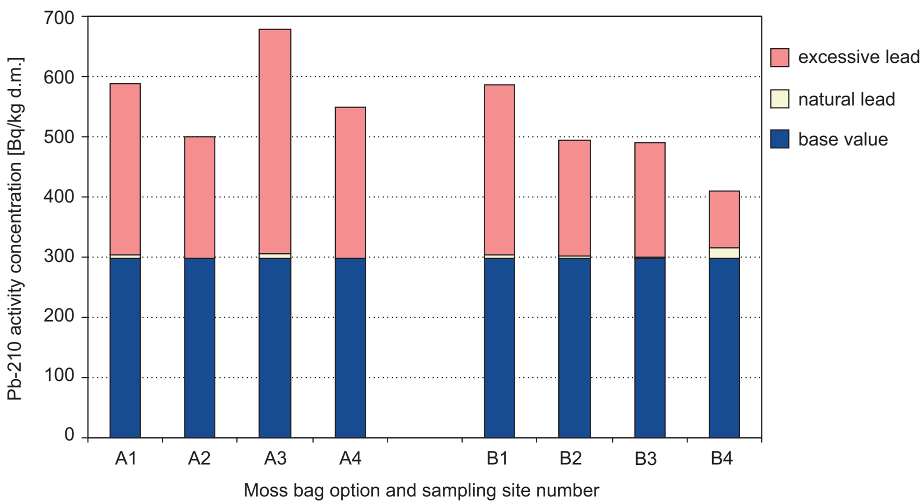


Fig. 6. The share of various sources of $^{210}$Pb in his total activity

The $^{210}$Pb activity concentration in moss after exposure is associated primarily with allogeneic component, representing the excess lead introduced into the environment due to human activity. A possible source of this radioisotope is the nearby cement plant. Minerals, raw materials and fuels used in the cement industry contain natural radionuclides. Due to the high temperatures during a cement production and large scale of the process, a significant release of radionuclides, including $^{222}$Rn, $^{210}$Po or $^{210}$Pb to the atmosphere can be expected [1].

# Conclusions

Substantial discrepancies of results in options disabled description of the relationship between increase in activity concentration of $^{40}K$, $^{137}Cs$ and $^{210}Pb$ in mosses and the distance from the cement plant. No significant linear dependence in radionuclides deposition on the distance from the cement plant was observed.

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## OCENA STANU ZANIECZYSZCZENIA POWIETRZA WYBRANYMI RADIOIZOTOPAMI W POBLIŻU CEMENTOWNI Z UŻYCIEM WORECZKOWEJ METODY

Samodzielna Katedra Biotechnologii i Biologii Molekularnej
Uniwersytet Opolski

**Abstrakt:** Przemysł wydobywczy i przetwórczy stanowi potencjalne źródło izotopów promieniotwórczych zanieczyszczających najbliższe środowisko. W celu oceny stanu środowiska w okolicy cementowni zastosowano metodę woreczkową z mchami. Celem doświadczenia było zbadanie zależności pomiędzy stopniem zanieczyszczenia powietrza $^{40}$K, $^{137}$Cs i $^{210}$Pb a odległością od cementowni. Przeanalizowano również udział różnych źródeł promieniowania w sumarycznej aktywności $^{210}$Pb w mchach po ekspozycji. Punkty pomiarowe zlokalizowane były w lesie niedaleko Opola, w jednej linii i w różnych odległościach od cementowni. W badaniu wykorzystano dwa typy woreczków wywieszone jednocześnie w tych samych miejscach. Zmierzono aktywność izotopów gamma-promieniotwórczych w próbkach mchów przed i po ekspozycji, wykorzystując gamma spektrometr z detektorem germanowym. Z uzyskanych wyników wyliczono względne współczynniki akumulacji (*RAF*). Chcąc ocenić w jakim stopniu aktywność radionuklidów zależy od odległości od cementowni, wyznaczono współczynniki korelacji liniowej. Ze względu na znaczną rozbieżność wyników w wariantach trudno jest ocenić trend wzrostu aktywności radionuklidów wraz ze zmianą odległości od cementowni. Nie zauważono wyraźnych zależności wielkości depozycji radionuklidów od odległości od cementowni.

**Słowa kluczowe:** względny współczynnik akumulacji (*RAF*), radioizotopy, metoda woreczkowa, cementownia