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Andrzej KŁOS[1*], Zbigniew ZIEMBIK[1], Małgorzata RAJFUR[1]
Agnieszka DOŁHAŃCZUK-ŚRÓDKA[1], Zbigniew BOCHENEK[2], Jarle W. BJERKE[3]
Hans TØMMERVIK[3], Bogdan ZAGAJEWSKI[4], Dariusz ZIÓŁKOWSKI[2]
Dominik JERZ[1], Maria ZIELIŃSKA[1], Paweł KREMS[1] and Piotr GODYŃ[1]

THE ORIGIN OF HEAVY METALS AND RADIONUCLIDES ACCUMULATED IN THE SOIL AND BIOTA SAMPLES COLLECTED IN SVALBARD, NEAR LONGYEARBYEN

POCHODZENIE METALI CIĘŻKICH I RADIONUKLIDÓW ZAKUMULOWANYCH W PRÓBKACH BIOTY I GLEBY POBRANYCH NA SVALBARDZIE W POBLIŻU LONGYEARBYEN

Abstract: Heavy metals and radioactive compounds are potentially hazardous substances for plants, animals and humans in the Arctic. A good knowledge of the spatial variation of these substances in soil and primary producers, and their sources, is therefore essential. In the samples of lichen *Thamnolia vermicularis*, *Salix polaris* and *Cassiope tetragona*, and the soil samples collected in 2014 in Svalbard near Longyearbyen, the concentrations of the following heavy metals were determined: Mn, Ni, Cu, Zn, Cd, Pb and Hg, as well as the activity concentrations of the following: K-40, Cs-137, Pb-210, Pb-212, Bi-212, Bi-214, Pb-214, Ac-228, Th-231 and U-235 in the soil samples. The differences in the concentrations of the analytes accumulated in the different plant species and soil were studied using statistical methods. Sea aerosol was indicated as the source of Pb, Hg, Cs-137, Pb-210 and Th-231 in the studied area. A relatively high concentration of nickel was determined in the biota samples collected near Longyearbyen, compared to other areas of Svalbard. It was supposed that nickel may be released into the atmosphere as a consequence of the local coal mining around Longyearbyen.

Keywords: heavy metals, radioisotopes, biomonitoring, soil, Arctic regions

[1] Chair of Biotechnology and Molecular Biology, University of Opole, ul. kard. B. Kominka 6, 45-032 Opole, Poland, phone +48 77 401 60 42, email: aklos@uni.opole.pl, ziembik@uni.opole.pl, mrajfur@o2.pl, agna@uni.opole.pl
[2] Institute of Geodesy and Cartography, ul. Z. Modzelewskiego 27, 02-679 Warszawa, Poland, email: zbigniew.bochenek@igik.edu.pl, dariusz.ziolkowski@igik.edu.pl
[3] Norwegian Institute for Nature Research - NINA, FRAM - High North Research Centre for Climate and the Environment, PO Box 6606 Langnes, NO-9296 Tromsø, Norway, email: jarle.bjerke@nina.no, hans.tommervik@nina.no
[4] Department of Geoinformatics, Cartography and Remote Sensing, Faculty of Geography and Regional Studies, University of Warsaw, ul. Krakowskie Przedmieście 30, 00-927 Warszawa, Poland, email: bogdan@uw.edu.pl
[*] Corresponding author: aklos@uni.opole.pl

Introduction

Currently, the Arctic regions are an invaluable source of information regarding the influence of anthropopressure on the environment pollution level on a global scale. The changes of activity of the radioisotopes released as a consequence of the Fukushima nuclear power plant disaster in 2011 are an example of such an influence. Their presence in Svalbard's atmospheric aerosol was already detected a few days after the disaster [1]. These regions are also sensitive to the current climate changes [2]. Studies have been carried out for many years in Svalbard on the pollution of various environmental matrices: soil [3], water, such as water from cryoconites [4], atmospheric aerosol, such as the determination of PCBs in the air, and other matrices sampled for analyses in the area of Ny-Ålesund - Western Spitsbergen [5]. Biomonitoring studies are being applied more and more frequently, in order to assess the pollution level of ecosystems, and they include the determination of the pollution accumulated in living organisms. The studies also allow the determination of the sources of origin and direction of distribution of pollution. In the Arctic regions, various species of flora have been used in such studies, such as mosses, lichens and vascular plants [5-7], as well as fauna, including studies determining the accumulation of heavy metals and organic pollution in the anatomical parts of narwhals [8] and birds - *Larus hyperboreus* [9]. The assessment of historical changes is extremely import; it is carried out by various methods, including the long-term measurement of pollution accumulated in the defined matrices, or the analysis of the pollution accumulated in permafrost layers or bottom sediments, which can be age-dated. The determination of acidity and sulphate content in ice cores [10], analyses of mercury concentrations in lake bottom sediment cores sampled in Svalbard [11] and analyses of the bottom sediments from the Barents Sea [12] are relevant examples. An extensive study of the research carried out in the Svalbard Archipelago was presented in Kozak et al. [13]. The authors point out that the Arctic regions, which have no major local emission sources, are mainly under the influence of the emissions from Europe, North America and Siberia [7, 14]. Global sources of emission of Cd, Hg, Pb and radioisotopes, the paths of distribution to the Arctic regions, and their accumulation levels in various components of the Arctic ecosystems, have been described in the reports of the Arctic Monitoring and Assessment Programme [15, 16], but the low nickel content in the aerosol in Ny Ålesund (Svalbard) indicates negligible long transport of heavy metals like nickel to Svalbard [17]. However, coal fuelled electrical power plants in Longyearbyen, Barentsburg and Ny-Ålesund may also be a source of local air pollutants like SO_2 and heavy metals [18]. Another source of pollution is the wind-generated coal-mining pollution (e.g. heavy metals) released by thawing [19-21] and flushed down from the piles (acid mine drainage - AMD), which may injure local tundra vegetation [19]. These kinds of pollutants can be wind spread over the larger areas surrounding the mines and rock piles. Other sources of pollution might originate from sea bird colonies (bird cliffs) in the area [22]. The latter indicates that the seabirds (faeces) are acting as a vector for the movement of heavy metals between the marine and terrestrial ecosystems, which may contribute significantly to the spread of pollutants in the vicinities of such cliffs/colonies [22].

The purpose of the conducted research is to assess the sources of pollution: selected metals and gamma radionuclides in Svalbard, near Longyearbyen, and to compare the obtained results with the results of other studies carried out in Svalbard. It was supposed that marine aerosol is one of the pollution sources in the area investigated.

Materials and methods

Svalbard is a Norwegian archipelago in the Arctic Ocean comprising several islands, the largest of which is Spitsbergen. The archipelago borders the Greenland Sea from the west, the Barents Sea from the east and the Arctic Ocean from the north. The archipelago area is 62,924 km^2. Approximately 60% of the Spitsbergen area is covered by glaciers, the rest being mountains and seaside lowlands [23]. The perennial snow border goes from approximately 200 m above sea level in the south-east to approximately 800 m above sea level in the north, in West Spitsbergen. Flora vegetation occurs on only 6-7% of Svalbard's area. Plants grow mainly in the narrow strip along the coast, on the mountain slopes and in certain valleys. The plant vegetation period is very short, lasting a maximum of 90 days [23].

Samples of biota (mosses growing on experimental plots, lichens *Thamnolia vermicularis*, *Salix polaris* and *Cassiope tetragona*) and the surface layer of soil were taken for analysis during the period 03-07.08.2014. The sampling locations are marked in the map in Figure 1. Table 1 shows their geographical coordinates.

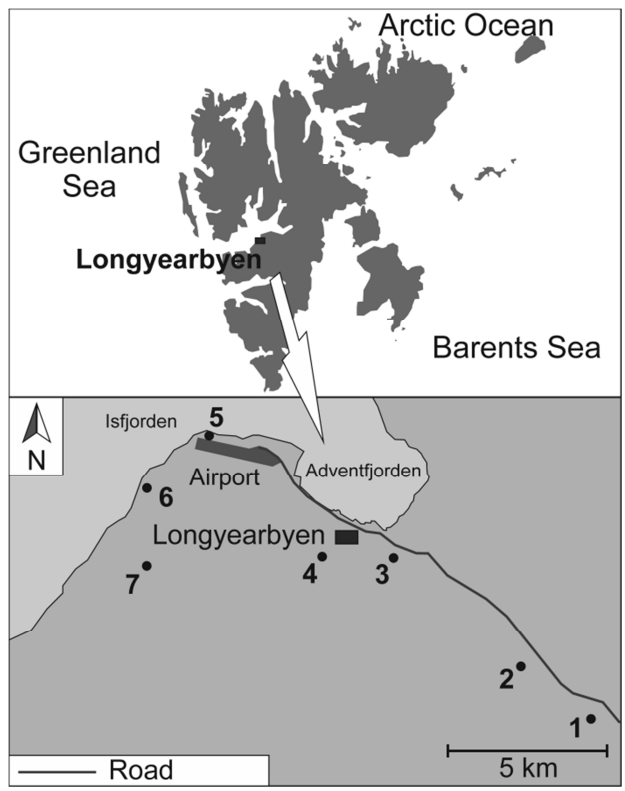

Fig. 1. Positions of sampling sites

After the manual removal of impurities and the drying of samples at 323 K, the collected material was stored in closed polyethylene containers.

Table 1

Geographical coordinates of the sampling sites

Site number	Latitude	Longitude
1	N 78° 10’ 26”	E 15° 56’ 28”
2	N 78° 11’ 15”	E 15° 50’ 53”
3	N 78° 12’ 53”	E 15° 42’ 23”
4	N 78° 12’ 56”	E 15° 36’ 31”
5	N 78° 14’ 58”	E 15° 26’ 14”
6	N 78° 14’ 02”	E 15° 19’ 52”
7	N 78° 12’ 38”	E 15° 20’ 33”

The 0.4 g of subsamples taken from homogenized material were mineralized in a mixture of nitric acid and hydrogen dioxide in a Speedwave Four microwave oven (Berghof, DE). Concentrations of Mn, Ni, Cu, Zn, Cd and Pb were determined via the FAAS method, using ICE 3000 (Thermo Electron Corporation, USA). To determine mercury concentrations in the plant samples, the AMA 254 analyser was utilized.

In the biota and soil samples, activity concentrations of gamma radioactive isotopes were determined. The measurements 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. The relative efficiency was 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 to 1836.06 keV. The geometry of the calibration source was Marinelli (447.7 ±4.5 cm^3) with a density 0.99 ±0.01 g/cm^3, containing Am-241, Cd-109, Ce-139, Co-57, Co-60, Cs-137, Sn-113, Sr-85, Y-88 and Hg-203. The measuring process and analysis of spectra were computer controlled with the use of GENIE 2000 software. The radiation spectrum was recorded day and night.

Quality control

Calibration of the spectrometer was performed with a standard solution from ANALYTIKA Ltd. (Czech Republic). The values of the highest concentrations of the models used for calibration (2 mg/dm^3 for Cd, 5 mg/dm^3 for Cu, Zn, Pb, 7.5 mg/dm^3 for Mn and 10 mg/dm^3 for Fe) were approved as the linear limits of the signal dependence on the concentration.

The instrumental detection limits (*IDL*), the instrumental quantification limits (*IQL*) for the spectrometer iCE 3500, and the concentrations of heavy metals in certified reference materials BCR-414 *plankton* and BCR-482 *lichen* (*Institute for Reference Materials and Measurements, Belgium*) were previously presented in Kłos et al. [24].

Statistical analyses

The concentrations of metals and activity concentrations of radioisotopes in the samples were determined, and the data was analysed using statistical methods. Since the concentration represents the amount of a selected substance in the total amount of all components, its analysis requires the application of appropriate mathematical methods [25-27].

Two approaches in compositional data analysis can be distinguished. The first is based on data analysis in the simplex sample space, and the second involves data transformation.

The distance d_a between compositional points **A** and **B**, with coordinates determined by the concentration vector of D components, is defined by the following relationship [25]:

$$d_a(c_A,c_B)=\sqrt{\sum_{j=1}^{D}\left(ln\frac{c_{Aj}}{g(c_A)}-ln\frac{c_{Bj}}{g(c_B)}\right)^2} \tag{1}$$

where $g(\boldsymbol{c})$ is the geometrical mean of concentrations.

An insight into the data structure can be delivered by cluster analysis methods. The hierarchical structure of a cluster can be determined using an agglomerative or a divisive method. For well differentiated point groups, regardless of the method used, the formation of similar structures is expected. In cluster structure determination, a dissimilarity matrix is used. This matrix determines the structure of distances between all pairs of data points. In the computations, the elements of the matrix were the distances between compositional points, calculated from Eq. (1). The relationships between the concentrations of elements were studied. The utilization of a classical correlation estimator in the statistical analysis of compositional data can lead to delusive conclusions [28]. This is a result of the relationship between the variance of a component concentration and its covariances with concentrations of the other components. An alternative method, appropriate for covariability estimation in compositional data, is based on variations matrix **T**. The elements t of this matrix are variances of x and y concentration logratios:

$$t_{xy}=\mathrm{var}\left(\ln\frac{\boldsymbol{c}_x}{\boldsymbol{c}_y}\right) \tag{2}$$

The variance of logratio is small when changes in both concentrations follow the same trend - that is, both values increase or decrease. The biggest logratio variance is observed when concentrations follow opposite trends. An increase in the values of one variable accompanied by a decrease in the values of the second one produces highly differentiated logratios. As a result, the biggest t value is observed. To distinguish between these two types of covariability, the terms ‘positive’ (an increase in both concentrations) and ‘negative’ (an increase in one concentrations and a decrease in the second) are used. The t values between these characteristic negative or positive covariabilities describe a random or non-linear relationship between concentrations. The intermediate values of randomly arranged data can be used in the assessment of the actual t classification [29].

To compare metals and radioisotope content, activity concentrations were recalculated to mass fraction c using the formula:

$$c=\frac{t_{1/2}M}{\ln 2\ N_A}a \tag{3}$$

where $t_{1/2}$ is the half-life of a radioisotope, M is its molar mass, N_A is the Avogadro number and a is the activity concentration.

In computations, the R language [30] and functions from the ‘cluster’ library [31, 32] and ‘compositions’ library [33, 34] were used.

Results

Figure 2 shows boxplots illustrating the heavy metal accumulation in biota and surface soil layer samples.

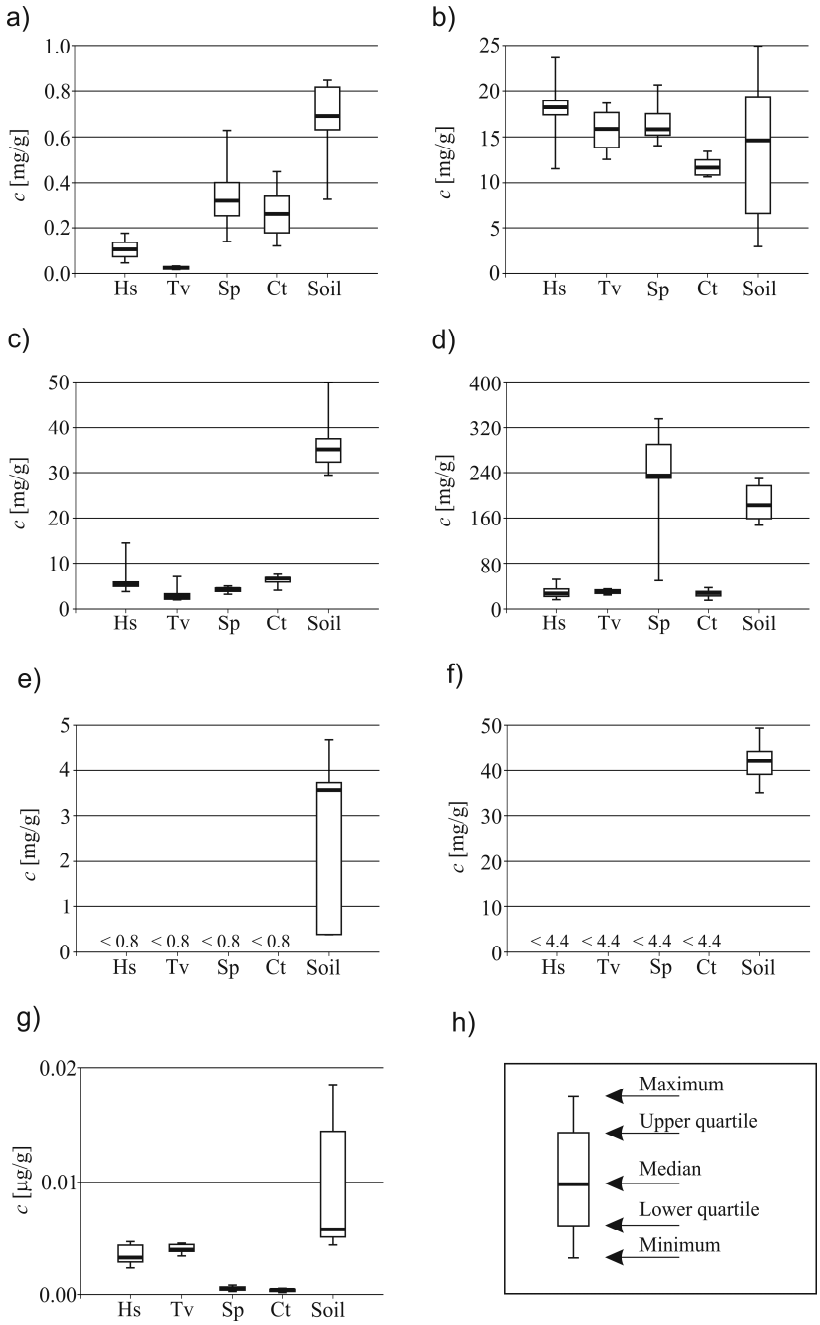

Fig. 2. Concentrations of heavy metals: a) Mn, b) Ni, c) Cu, d) Zn, e) Cd, f) Pb and g) Hg accumulated in the samples of mosses (Hs), *Thamnolia vermicularis* (Tv), *Salix polaris* (Sp), *Cassiope tetragona* (Ct) and soil; h) graph description

Special attention should be paid to the relatively high concentrations of manganese and zinc accumulated in *Salix polaris* and the concentrations of mercury in mosses and lichens, which are one order of magnitude higher compared to vascular plants.

Table 2 contains a summary of the analyses of the activity concentrations of radionuclides, accumulated in the surface layer of soil collected in 7 measurement locations and in the samples of *Salix polaris* and *Cassiope tetragona* (mixed samples from 7 measurement locations). The table contains mean, minimum and maximum values, as well as measurement uncertainty $\Delta^m X$ [%] defined for the analysed samples.

Table 2

The mean activity concentrations *a* of radionuclides accumulated in the soil and in the averaged samples of *Salix polaris* (Sp) and *Cassiope tetragona* (Ct). The figures in brackets show the minimal and maximal activity concentration values and Δ^m is the measurement uncertainty

Isotope	Soil		Sp		Ct	
	***a* [Bq/kg^{-1}]**	**$\Delta^m X$ [%]**	***a* [Bq/kg]**	**$\Delta^m X$ [%]**	***a* [Bq/kg]**	**$\Delta^m X$ [%]**
K-40	584 (485-674)	< 4.1	495	14	172	20
Cs-137	27.9 (12.7-57.0)	< 3.6	5.5	47	1.4	93
Pb-210	76 (44-108)	< 47	-	-	-	-
Pb-212	30.0 (25.6-31.3)	< 4.4	-	-	-	-
Bi-212	19 (15-22)	< 22	-	-	-	-
Bi-214	21.6 (18. 6-25.1)	< 6.6	23.0	31	23.8	16
Pb-214	23.2 (20.3-26.7)	< 4.9	-	-	18.6	20
Ac-228	33.3 (27.0-36.1)	< 4.7	-	-	6.3	73
Th-231	7.8 (5.6-12.7)	< 20	-	-	35.2	89
U-235	3.4 (2.5-4.4)	< 42	-	-	-	-

The table contains only the determination results for which measurement uncertainty $\Delta^m X$ did not exceed 100%. In total, the activities of 10 radionuclides were determined; they were part of the following radioactive decay series: uranium-actinium (U-235, Th-231), thorium (Ac-228, Pb-212, Bi-212), uranium-radium (Pb-214, Bi-214, Pb-210), natural K-40 and artificial Cs-137.

Discussion

In order to compare the heavy metal concentrations accumulated in the selected biota species and soil, the results of research carried out in other regions of Svalbard were collected.

In 1985, in the south-west part of Spitsbergen, near the Polish Polar Station (Hornsund), the following heavy metals were determined: Ni, Cu, Zn Cd and Pb, in 16 species of mosses, including *Hylocomium splendens* [35]. Heavy metals were also determined in the samples of soil, algae, lichen and vascular plants near the Polish Polar Station. The samples were collected for research in 2011 [7]. During the period 1987-1995, analyses of heavy metals in various biota elements were carried out in western Spitsbergen (Bellsund area) [36, 37]. Heavy metals were also determined in various environment samples collected in 1988 in the area of western Spitsbergen (Bockfjorden). Samples of *Cassiope tetragona*, among others, were collected for analysis [38]. In 2001, soil samples were collected during research in the area of Billefjorden [39]. Concentrations of heavy metals and PHAs were determined in the 20 cm surface layer of the soil.

Table 3 contains a summary of the mean (median [7]) values of metal concentrations determined in *Hylocomium splendens*, *Thamnolia vermicularis*, *Salix polaris*, *Cassiope tetragona* and in the soil; the data was presented in the articles referenced. The table includes the mean content of mercury in samples of *Thamnolia vermicularis* collected for analysis in 2005 and 2007 from the islands located between Canada and Greenland: Devon Island and Ellesmere Island [40].

Table 3

Mean concentrations [μg/g] of heavy metals accumulated in samples of mosses (Hs), *Thamnolia vermicularis* (Tv), *Salix polaris* (Sp), *Cassiope tetragona* (Ct) and soil

Matrix	Mn	Ni	Cu	Zn	Cd	Pb	Hg	References
Hs	-	3.6	6.1	24	0.7	6.5	-	[35]
	48	-	8.5	45	0.7	24.9	-	[37]
Tv	9.5	-	3.0	45	0.7	6.4	-	[36]
	10	-	2.9	35	0.8	11.7	-	[37]
	-	-	-	-	-	-	0.18	[40]
Sp	65	-	8.1	108	3.8	-	-	[36]
	105	-	5.9	175	1.1	2.2	-	[37]
	210	3.4	5.6	160	1.1	0.3	0.02	[7]
Ct	107	4.1	10.7	33.5	0.2	1.6	0.14	[38]
Soil	440	20	25	54	0.2	11	0.04	[7]
	14	0.6	0.5	3.3	0.01	1.6	-	[39]

The results presented in Table 3 confirm the data contained in Figure 2 - the good bioaccumulation characteristics of *Salix polaris* in terms of Mn and Zn, but also cadmium, which is illustrated by the determination results of this metal in the *Salix polaris* samples collected in western Spitsbergen [36, 37].

Comparison of the data presented in Figure 2 and Table 3 allows the statement that the samples collected near Longyearbyen contain relatively high nickel concentrations > 10 μg/g. According to the current research results, the main source of nickel in Svalbard is the rock waste, mined along with coal and stored on the surface. For example, in 2004, an analysis was conducted of the heavy metal concentration in the soil surface layer and plants collected near the dumps formed during coal mining, located approximately 10 km from Longyearbyen (Bjørndalen). Samples were collected along the transects: parallel and perpendicular to the dumps, with a length of 200 and 110 m, respectively. The metals were extracted from the soil with 25% acetic acid. The mean values of Ni concentration in the samples of surface soil (A horizon) ranged from 5.1 to 63.7 μg/g, whereas in plants: *P. arctica*, *L. confusa* and *P. concinna*, the mean Ni concentrations ranged from 5.7 to 27.9 μg/g [21]. The samples collected near the Polish Polar Station also contain high concentrations of Ni (min. 11 μg/g, max 26 μg/g); however, in the samples of *S. polaris* collected in the area, Ni concentrations did not exceed 7.0 μg/g [7]. Another potential source of nickel is pollution emitted from the Kola Peninsula, where mines and industrial plants processing this metal, among others, are located [41, 42], although the distance might be too great to influence the areas on Svalbard, since there are steep gradients of deposition of nickel to mosses and lichens around the Cu-Ni smelters [42, 43]. However, one more potential source of nickel near Longyearbyen should be highlighted, namely aviation emission. Samples for analysis were collected near the airport and along the take-off and landing strip (Fig. 1). Nickel superalloys are used in the construction of aircraft engines.

As a consequence of friction and high temperature, Ni may be released into the atmosphere [44, 45]. Higher concentrations of Ni in the atmosphere near airfields have been confirmed by the results of studies carried out in Incheon, South Korea [46]. However, the Longyearbyen airport is situated in the vicinity of the coal mining deposits of Mine no. 3 (Gruve 3), so the site here could be influenced by coal mining as well.

As mentioned in the beginning, the Arctic area is also a source of information regarding the distribution of radionuclides. During the period 2000-2002, in the area of Kongsfjorden (western Spitsbergen), studies were conducted on the activity of radionuclides accumulated in the soil and bird excrement [47], as well as in a separated surface soil layer [48]. It was determined that the activity concentration of certain radionuclides accumulated in bird excrement, including artificial Cs-137 and natural K-40, are higher than those found in the surface soil layers which result in the increase of surface activity in birds' habitat areas. The mean activities of Cs-137 and K-40 in bird excrement were 78 and 365 Bq kg^{-1}, respectively, while the equivalent values in the 3 cm layer of surface soil were 35 and 283 Bq kg^{-1}. The mean activities of Cs-137 and K-40 were 151 and 499 Bq kg^{-1} in the organic component of the soil, due to the better sorption characteristics. A small increase in the natural radionuclide activity can also be observed in the mining waste storage areas [49]. For Cs-137 and K-40, the results included in Table 2 do not differ considerably from those presented above, which illustrates the fairly even distribution of anthropogenic Cs-137 in particular. In 2001, in the 0-3 cm surface soil layer in Longyearbyen, the activity concentration of Cs-137 was < 0.7 Bq/kg, and 706 Bq/kg for K-40 [50]. In comparison, in the area of the Opole Anomaly (south-western Poland), the activity concentration of Cs-137 in surface layers of woodland soils, measured in 2007, locally exceeded 1,000 Bq kg^{-1} [51]. Compared to European countries, low artificial radionuclide pollution levels were observed in Svalbard, which was also confirmed by other authors, such as Gwynn et al. [52]. It should be mentioned that, at the beginning of the 1980s (before the Chernobyl accident), the Cs-137 mean activity concentration in *Salix polaris* was 27 Bq/kg. This was 5 times higher than in the samples collected for this study in the Longyearbyen vicinity (see Table 2). The high Cs-137 activity concentration was the result of nuclear weapons testing [50].

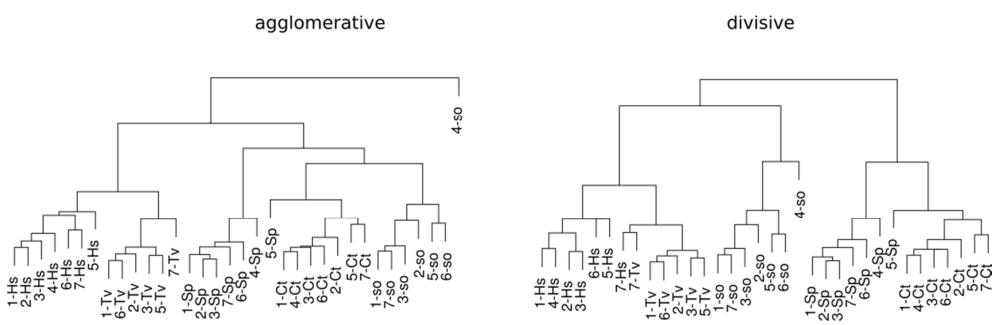

Fig. 3. Structures of hierarchical dendrograms produced by agglomerative and divisive algorithm on the base of dissimilarity matrix composed of distances between pairs of compositional points in simplex space

In our study, the relationships between the concentrations of metals in the samples were studied. Figure 3 shows the structures of hierarchical dendrograms, relating to the content of Mn, Ni, Cu, Zn, Cd, Pb and Hg in biota and soil samples. The branches in the dendrogram are described by sampling point number and biota type ('Hs' for mosses, 'Tv' for *Thamnolia vermicularis*, 'Sp' for *Salix polaris*, and 'Ct' for *Cassiope tetragona*), or 'so' for soil.

Both agglomerative and divisive algorithms produced similar dendrograms. Their structures suggest the crucial role of the sample type in cluster formation. Each type of biota and soil tends to create its own group of points, regardless of the sampling point location. This observation assumes different expositions of plants for element deposition or selective metal sorption from the background soil. This conclusion points to the possibility of plant and soil utilization in selective biomonitoring in the Arctic regions.

In the estimation of concentration covariability, the elements of the variation matrix were used. Positive covariabilities were calculated for Ni/Zn accumulated in mosses, Mn/Cu accumulated in *Thamnolia vermicularis*, Mn/Zn and Cu/Zn accumulated in *Salix polaris* and Ni/Cd accumulated in the soil. A negative correlation was determined for Zn/Hg accumulated in mosses. Taking into account the different preferences of metal sorption of the plant species examined (Fig. 3), it is difficult to explain the positive correlation between the metal concentrations accumulated within them. The negative correlation between Zn and Hg accumulated in the soil suggests different sources of these metals.

In the soil samples, the activity concentrations of radioisotopes were determined and then their mass concentrations were calculated (Eq. (2)). A positive covariability between concentrations was found for the following radioisotope pairs: Cs-137/Th-231, Cs-137/Pb-210, Th-231/Pb-210, Ac-228/Bi-212 and Pb-212/Bi-212.

Cs-137 is an artificial radioisotope, which was released into the atmosphere mainly after tests of nuclear weapons carried out in the 1950s and 60s, and accidental leakages from nuclear facilities or waste dumps, such as the malfunction at the Chernobyl NPP in 1986 [53-56]. Its half-life is 30.1 years. Currently this radioisotope circulates between components of the environment and its transport in the atmosphere comprises redeposition processes [57, 58]. Th-231, with a half-life of 25.5 hours, should be regarded as a representative of its long-living ancestor, U-235 (half-life $7 \cdot 10^8$ years). The same relationship between Cs-137 and either Th-231 or U-235 could be expected. However, contrary to Th-231, concentrations of Cs-137 and U-235 were not related in a linear way.

A positive covariability between concentrations of Cs-137 and Pb-210 (with a half-life of approx. 22 years) was observed, as well as for the Th-231 and Pb-210 pair. This result suggests a similar origin of Cs-137, Th-231 and Pb-210. Since Cs-137 is deposited from the atmosphere, the main load of the other radioisotopes also originates from this source.

The radioisotopes Ac-228, Pb-212 and Bi-212 belong to the same decay series. These are rather short living isotopes, with half-lives of 6.2 hours, 11 hours and 61 minutes, respectively. Because the time between sample collection and determination exceeded a few months, the actual activity concentrations of the radionuclides were close to those in radioactive equilibrium state. The measurement results can be used in the estimation of more stable parent radioisotope concentrations. Among the long living ancestors of Ac-228 is Ra-228 (half-life 5.8 years) and the grandparent of the series, Th-232 (half-life $1.4 \cdot 10^{10}$ years).

For Cs-137 and Bi-212, a negative concentration covariability was observed. This result could be due to the action of a specific combination of different factors. However, a reasonable explanation of the observation cannot currently be formulated.

It is quite difficult to explain the positive covariability between the Cu and Bi-214 concentrations. Furthermore, a similar relationship should be observed for Pb-214, but this was not noticed. Unfortunately, this observation remains to be interpreted.

In the soil, a positive covariability (at a confidence level of 0.02) was found between mercury and Cs-137, Th-231, and Pb-210 concentrations. A positive covariability between Cs-137 and Pb was also observed, but at a confidence level of 0.05.

Figure 4 presents a graph of Cs-137 spatial distribution. In the map, the diameters of the circles are proportional to the logarithm of Cs-137 mass fraction in the soil samples. The 'X' symbols show the positions of former coal mine pits. An outlined trend can be observed of a decrease in the Cs-137 content of the soil with increasing distance from the coast.

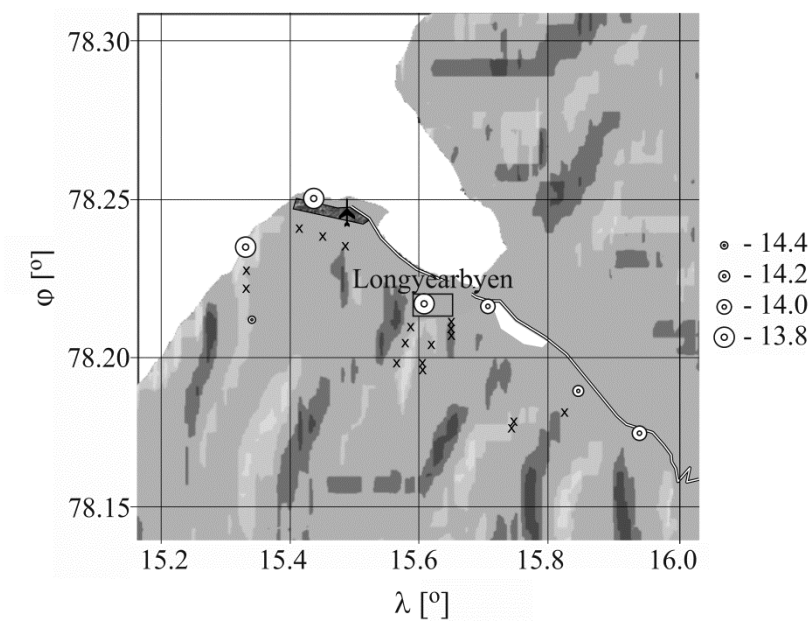

Fig. 4. Distribution of Cs-137 concentrations determined in soil samples collected in Longyearbyen vicinity. The data are presented in logarithm scale

Additionally, the results of the *t* parameter interpretation were compared to the results of the linear regression application.The graphs illustrate the linear relationships between the activity concentrations of Pb-210 and Th-231 vs. Cs-137 (Fig. 5) and Pb and Hg vs. Cs-137 (Fig. 6) in the surface soil layer. Because of the artificial origin of Cs-137 and its incidental release into the atmosphere, this radioisotope was selected as a reference material. In 2001, the activity concentration of Cs-137 in the sea water close to Svalbard was

approx. 2.3 Bq/m^3 [50]. The points in the graphs are numbered to correspond with the sampling point numbers.

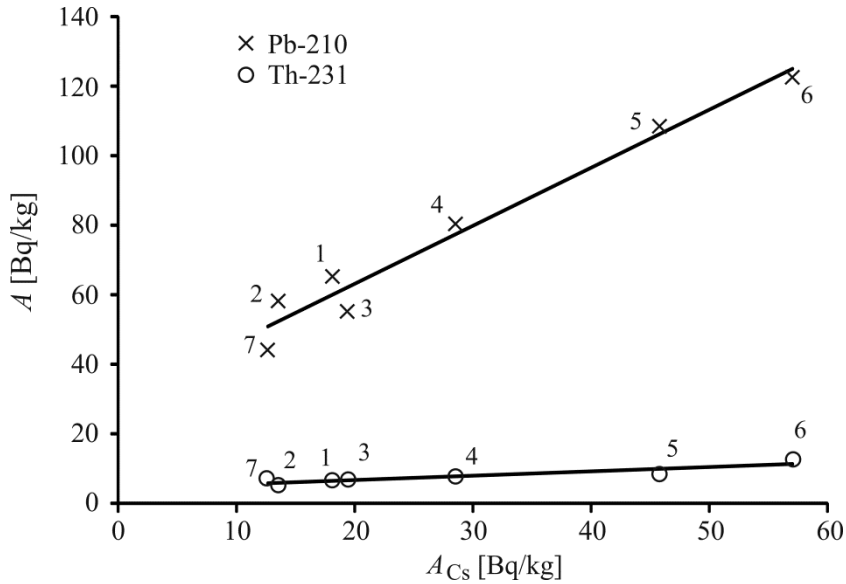

Fig. 5. Relationship between Cs-137 and Pb-210, Th-231 activity concentrations in surface soil samples collected in Longyearbyen region

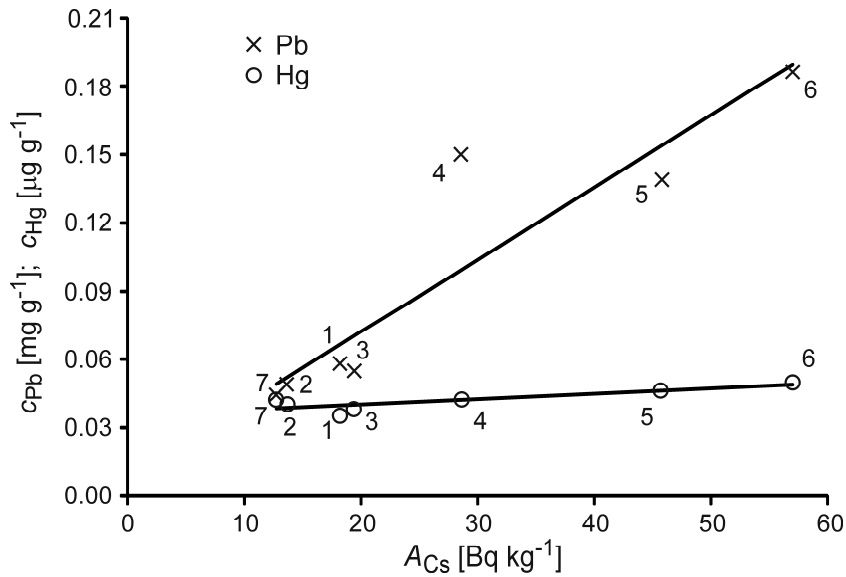

Fig. 6. Relationship between Cs-137 activity concentrations and Pb, Hg concentrations in surface soil samples collected in Longyearbyen region

The linear relationships shown in Figures 5 and 6 are described by the following formulas and determination coefficients: R^2: Pb-210/Cs-137: $y = 1.66 \cdot x + 29.5$, $R^2 = 0.966$, Th-231/Cs-137: $y = 0.124 \cdot x + 4.36$, $R^2 = 0.840$, Pb/Cs-137: $y = 0.0032 \cdot x + 0.0087$, $R^2 = 0.850$, Hg/Cs-137: $y = 0.0002 \cdot x + 0.0355$, $R^2 = 0.706$. The critical R^2 value for $\alpha = 0.05$ is 0.569.

Considering the location of the sampling places illustrated in the map (Fig. 1), a decrease in Cs-137, Pb-210, Th-231, Pb and Hg concentrations with increasing distance from the shoreline can be concluded. The exception is the 7th location, which is separated from the sea by a range of hills. Considering the fact that the primary emission and deposition of Cs-137 has not occurred on a global scale since the failure at the Fukushima NPP, it is clear that the only source of proportional deposition of Cs-137, Pb-210, Th-231, Pb and Hg in Longyearbyen is sea aerosol. Similar relationships were observed for halides (Cl, Br, I) accumulated in the surface soil layers in northern Norway [59]. The concentrations of halides decreased exponentially with increasing distance from the shoreline, indicating marine aerosol as their source. This source was also confirmed by the results of a study conducted in Norway, in which halide concentrations in mosses, taken along several transects perpendicular to the shoreline, were determined [60].

Conclusions

The studies carried out over many years have proved that the Arctic regions are exposed to pollution caused by anthropopressure. The transfer of pollution on a global scale takes place through the atmosphere and surface waters.

The studies carried out in Svalbard near Longyearbyen showed that, in the studied area, one of the sources of anthropogenic pollution is sea aerosol, which is confirmed by the linear correlations between concentrations of Cs-137, Pb-210, Th-231, Pb and Hg in the soil surface layer. Concentrations of these analytes decrease with increasing distance from the coastline. It was also proved that nickel, accumulated in relatively large quantities in biota samples - mosses, lichen *Thamnolia vermicularis*, *Salix polaris* and *Cassiope tetragona* - may be released into the atmosphere as a consequence of local coal mining around Longyearbyen, among other things.

The statistical assessment of the results and their visualisation as a dendrogram show that the studied plant species accumulate heavy metals in different ways, both in comparison to one another and to the surface soil layer. No statistical interrelations were found which confirm the influence of local emissions on the accumulation of heavy metals in the studied plants. Positive correlations were found in the concentration pairs Ni/Zn accumulated in mosses, Mn/Cu accumulated in *Thamnolia vermicularis* and Mn/Zn and Cu/Zn accumulated in *Salix polaris.*

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