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AIR POLLUTION STUDIES IN OPOLE REGION, POLAND, USING THE MOSS BIOMONITORING TECHNIQUE AND NEUTRON ACTIVATION ANALYSIS

BADANIE ZANIECZYSZCZENIA POWIETRZA W REGIONIE OPOLA Z UŻYCIEM BIOMONITORINGU ORAZ NEUTRONOWEJ ANALIZY AKTYWACYJNEJ

Summary: Biomonitoring of multielement atmospheric deposition using terrestrial moss is a well-established technique in Europe. In October 2006 30 moss samples of *Hylocomium splendens* and *Pleurozium schreberi* were collected around the town of Opole, capital of the agricultural Opole Region, situated between two industrial regions of Poland: the Silesia-Krakow region in the east and the Legnica-Glogow Copper Basin in the west. A total of 34 elements including a number of toxic metals and rare earths were determined by instrumental neutron activation analysis using epithermal neutrons at the IBR-2 reactor of FLNP JINR. The interpretation of the obtained results points to pronounced contamination of the sampled area with element pollutants such as As, Sb, V, Ni, Mo, *etc*. at levels similar to those in the neighboring industrial regions. It is an evidence of regional atmospheric transport of pollutants in addition to local pollution sources.

Keywords: air pollution, moss biomonitoring, neutron activation analysis

Moss is the most effective type of organism for biomonitoring of metals from the atmosphere because of its ability to accumulate and retain chemical substances, including trace elements. Mosses have only a rudimentary root system, so the uptake of elements comes mostly from the atmosphere. Nowadays the moss biomonitoring technique is widely used all over the Europe as a method to evaluate atmospheric deposition of metals [1, 2].

The presence of heavy metals in atmospheric deposition within the Polish territory had been previously studied for some specific locations [3-5] including the largest industrial regions the Silesia-Krakow Industrial Region and Legnica-Glogow Copper Basin [6]. In 2006 moss samples were collected throughout the territory of the mainly agricultural Opole Region situated between these two studied industrial regions.

These samples were analyzed by multielement instrumental epithermal neutron activation analysis, previously successfully used by one of the authors in similar studies in Russia, Norway, Romania, Northern Serbia and Bosnia, Macedonia [7-12] and several other countries.

The primary task of the present study was to quantitatively characterize the deposition of trace elements, including some toxic metals, over the agricultural Opole Region and to assess the atmospheric transport of pollutants to this region from the strongly contaminated neighboring regions. The results of this study will be submitted to the Coordination Center of the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops (ICP Vegetation) [13].

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Study area

The Opole Region is located in the central part of Silesia, in the south-west part of Poland, with an area of 9,412 square kilometers and a population of 1,055,000. It borders in the east with the Silesia-Krakow Industrial Region, with the southern part of the Severomoravský Region of the Czech Republic in the south-west, and in the west with Lower Silesia with the Legnica-Glogow Copper Basin.

The south of the region is mountainous, but three quarters of the territory are lowlands (about 160 metres above sea level in the town of Opole situated in the centre of the region) with the Oder River valley crossing the region from north-west to south-east. Forests cover 26.2% of the region (mostly pine forests) and 62% of the area is fertile soil used for agriculture.

Sampling

Samples of the two moss species *Pleurozium schreberi* (more than 85% of all collected samples) and *Hylocomium splendens* were collected during October 2006 at 30 sites located 5 to 18 km from the center of the town. The sampling was carried out in accordance with the strategy of the European moss survey programme [13].

Samples were collected at least 300 m from main roads, villages and industries, at least 100 m from local roads and houses. The sampling points were situated in forests gaps or clearings, at least 3 m away from the nearest trees to reduce influence from the forest canopy. On each site 5÷10 subsamples were collected within a 50×50 m area to make the moss samples representative. Sampling and sample handling was performed using polyethylene gloves and collected material was stored in paper bags.

The sampling network is shown in Figure 1.

Analysis

Neutron activation analysis (NAA) was performed in the Frank Laboratory of Neutron Physics, Dubna, Russia. In the laboratory the samples were carefully cleaned from needles, leaves, soil particles and only the green, green-brown shoots representing the last three years growth were analyzed, after being air-dried to constant weight at 30÷40°C for 48 hours. The samples were neither washed nor homogenised. Previous surveys based on NAA in moss biomonitoring have shown that samples of about 300 mg are large enough to be used without homogenization [14].

For short-term irradiation samples of about 300 mg were pelletized in simple press-forms and heat-sealed in polyethylene foil. For epithermal neutron activation analysis samples prepared in the same manner were packed in aluminum cups for long-term irradiation.

Table 1

Flux parameters of irradiation positions [15]

Irradiation position	Neutron flux density, $[n \cdot cm^{-2} \cdot s^{-1}] \cdot 10^{12}$		
	Thermal ($E = 0 \div 0.55$ eV)	Resonance ($E = 0.55 \div 10^5$ eV)	Fast ($E = 10^5 \div 25 \cdot 10^6$ eV)
Ch1 (Cd-screened)	0.023	3.3	4.2
Ch2	1.23	2.9	4.1

The samples were irradiated in the IBR-2 fast-pulsed reactor, in channels equipped with a pneumatic system. The neutron flux characteristics are shown in Table 1.

Two kinds of analyses were performed: to determine short-lived radionuclides (Cl, Ca, V, Mn) the samples were irradiated for 3 minutes in the second channel (Ch2) and to determine elements associated with long-lived radionuclides (Na, Sc, Cr, Fe, Co, Ni, Zn, As, Se, Rb, Mo, Sb, Cs, W, Th, U) samples were irradiated for 100 hours in the cadmium-screened Ch1.

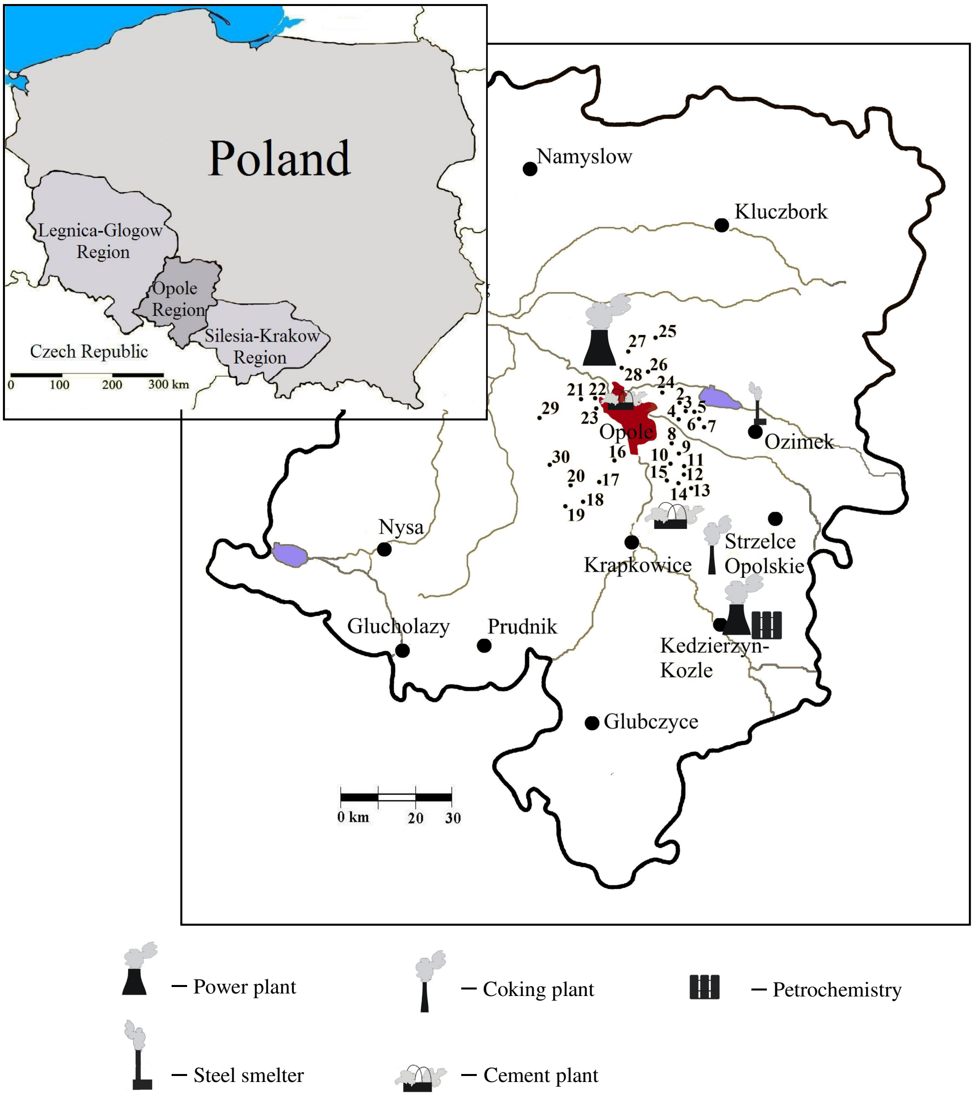

Fig. 1. Study area - the Opole Region and neighboring industrial regions

After irradiation gamma-ray spectra were recorded twice for each irradiation using a high-purity Ge detector: the first one after decay periods of 2÷3 minutes for 5 minutes, the second one for 20 minutes, 9÷10 minutes following the short irradiation. In case of long irradiation, samples were repacked into clean containers and measured after 4÷5 days for 45 minutes and 20÷23 after days for 3 hours.

Quality control (QC)

The QC of NAA results were ensured by analysis of reference materials: trace and minor elements in lichen IAEA-336 (International Atomic Energy Agency), IAEA-SL-1 (Trace elements in lake sediment) and SRM-1633b (Constituent elements in coal fly ash, US NIST-National Institute of Standards and Technology), SRM-2709 (Trace elements in soil).

Table 2

Comparison of the results obtained in the present study with neighboring industrial regions [μg/g]

Element	Opole Region			Silesia- Krakow Industrial Region [6]			Legnica- Glogow Copper Basin [6]		
	Median	Min	Max	Median	Min	Max	Median	Min	Max
Na	198	82	536	-	-	-	-	-	-
Cl	462	161	1045	183	66	715	226	123	537
K	8352	5740	17260	-	-	-	-	-	-
Ca	4870	2785	11660	-	-	-	-	-	-
Sc	0.23	0.076	1.14	0.18	0.06	0.55	0.13	0.03	0.63
Ti	140	37	909	-	-	-	-	-	-
V	2.8	1.1	11.7	3.5	1.5	8.1	2.5	1.1	8.1
Cr	2.8	1.5	9.1	3.3	1.2	98	1.5	0.8	13.1
Mn	236	37	882	125	39	410	222	70	896
Fe	813	240	3086	943	302	4515	357	147	845
Co	0.5	0.2	1.1	0.2	0.1	0.7	0.3	0.1	1.5
Ni	2	0.8	4.9	2.3	1.4	7.6	1.8	0.1	3.5
Zn	64	26	125	118	56	877	45	31	110
As	0.89	0.3	3.12	0.37	0.03	2.85	0.61	0.25	6.04
Se	0.24	0.07	0.61	0.43	0.13	0.79	0.33	0.22	0.77
Br	2.43	1	5	1.22	0.08	5.85	1.3	0.91	2.85
Rb	21	9	37	27	4	50	22	2	45
Sr	22	12	54	9	0.5	34	7.3	0.7	339
Mo	0.22	0.06	0.53	-	-	-	-	-	-
Sb	0.36	0.13	0.68	0.39	0.15	3.05	0.25	0.16	0.79
I	1.4	0.4	5.4	0.9	0.21	1.78	1.11	0.35	2.68
Cs	0.45	0.12	1.25	0.79	0.16	3.1	0.41	0.16	1.3
Ba	42	12	97	19	7.2	85	10	5.5	79
La	0.88	0.46	4.32	2.1	0.05	14	0.5	0.14	1.6
Ce	1.9	0.9	9.3	5.6	0.7	43	1.1	0.2	3.7
Sm	0.14	0.06	0.72	-	-	-	-	-	-
Tb	0.018	0.009	0.115	0.016	0.005	0.053	0.012	0	0.085
Yb	0.06	0.02	0.41	0.04	0.01	0.32	0.03	0.01	0.18
Hf	0.18	0.06	1.74	0.12	0.03	1.45	0.09	0.01	0.58
Ta	0.03	0.01	0.19	0.02	0.01	0.07	0.02	0.01	0.13
W	0.2	0.14	0.65	0.32	0.01	3.99	0.19	0.02	0.62

Au	0.002	0.001	0.008	0.003	0.001	0.015	0.002	0	0.024
Th	0.22	0.06	1.3	0.17	0.06	0.59	0.13	0.08	0.45
U	0.1	0.02	0.51	0.1	0.01	0.24	0.08	0.02	0.99

Ele-ment	Czech Republic [16]			Northern Norway [14]		
	Median	Min	Max	Median	Min	Max
Na	-	-	-	-	-	-
Cl	-	-	-	-	-	-
K	-	-	-	-	-	-
Ca	-	-	-	2820	1680	5490
Sc	-	-	-	0.052	0.009	0.22
Ti	-	-	-	23.5	12.4	66.4
V	1.52	0.57	5.86	0.92	0.39	5.1
Cr	1.88	0.38	7.66	0.55	0.1	4.2
Mn				256	22	750
Fe	401	176	1850	209	77	1370
Co				0.202	0.065	0.654
Ni	1.95	0.56	10.2	1.1	0.1	6.6
Zn	35	19.4	149	26.5	7.9	173
As	0.29	0.07	1.4	0.093	0.02	0.505
Se	-	-	-	0.33	0.05	1.3
Br	-	-	-	4.5	1.4	20.3
Rb	-	-	-	7.7	1.3	51.5
Sr	-	-	-	15.8	3.6	43.3
Mo	-	-	-	0.135	0.065	0.7
Sb	-	-	-	0.033	0.004	0.24
I	-	-	-	2.5	0.6	41.7
Cs	-	-	-	0.072	0.016	0.88
Ba	-	-	-	17.1	5.6	50.5
La	-	-	-	0.189	0.045	2.56
Ce	-	-	-	0.342	0.095	4.61
Sm	-	-	-	0.33	0.05	1.34
Tb	-	-	-	0.003	<0.002	0.03
Yb	-	-	-	-	-	-
Hf	-	-	-	-	-	-
Ta	-	-	-	0.01	<0.01	0.07
W	-	-	-	0.13	0.01	1.23
Au	-	-	-	-	-	-
Th	-	-	-	0.033	0.004	0.24
U	-	-	-	0.015	0.001	0.138

Results and discussion

Median values and ranges for the elements studied are presented in Table 2, along with corresponding data from similar studies in the neighboring Silesia-Krakow Industrial Region, Legnica-Glogow Copper Basin, and Severomoravský Region of the Czech Republic [16]. For comparison with a pristine territory corresponding data for the Northern Norway [14] are shown in the bottom part of the Table. The Norwegian values are from ICP-MS and are based on nitricacid solutions, possibly leaving out fractions of the elements contained in silicate minerals (soil particles).

The area around Opole is characterized with the highest median for seven elements: As, Cl, Co, Mn, Sc, Th and U. Arsenic and antimony are mainly associated with coal combustion. Near Opole there is a large conventional power plant “Opole” - the most important source of electricity for the region. Additionally, there are local industrial power plants, heat and water generating plants. In villages around Opole people heat their houses using coal. The most likely source of As and Sb could be fly ash from coal burning. Local abnormalities in distribution of As could be connected with pesticides or wood preservatives using by farmers and forest government (most of sampling sites were situated in forests and some nearby fields).

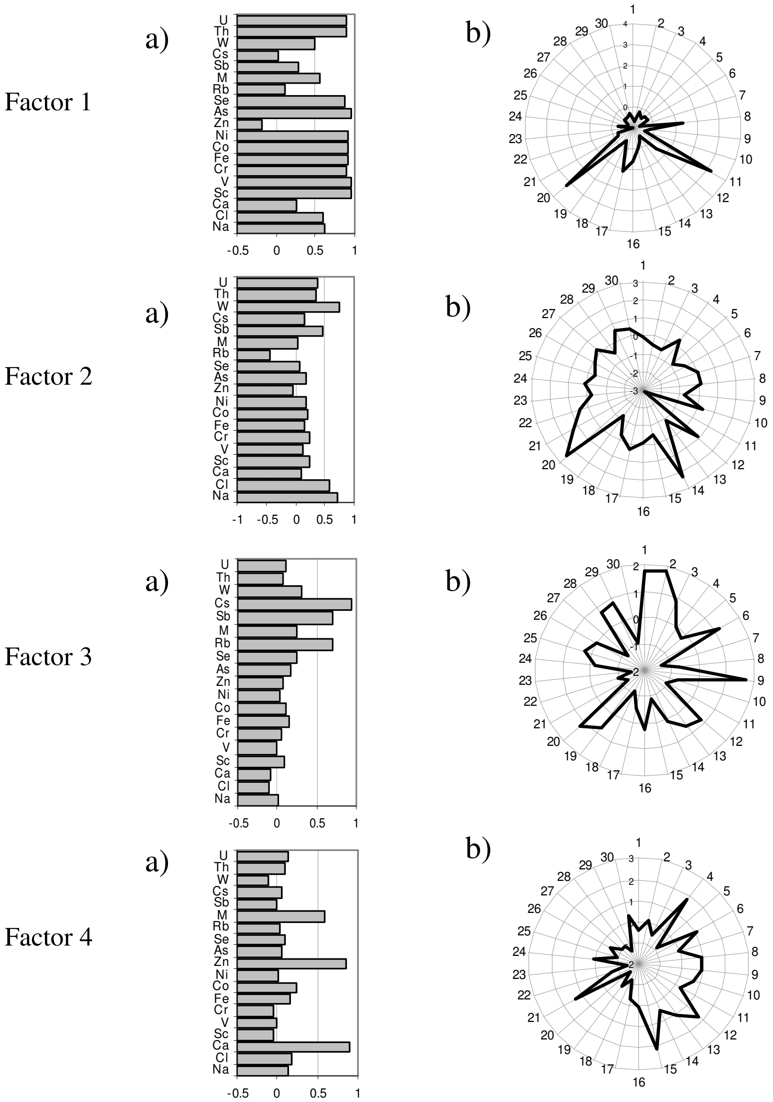

Fig. 2. Factor loadings (a) and factor scores (b) of individual sampling sites

Molybdenum is emitted by a metallurgical plant in the town of Ozimek in the east of Opole.

Zinc may arise from cement plant dust or from marble and limestone mines. As follows from [17], elevated concentrations of Zn may originate from long-range atmospheric transport of this contaminant from the Pardubicky district of the Czech Republic, to the south of the Opole Region.

Vanadium and nickel most probably originate from petrochemical emissions associated with the chemical industrial enterprises situated in the south-east part of the Opole Region. A coke plant situated in the same area produces various kinds of coke, coke-oven gas and carbon derivatives: tar, crude benzene and ammonium sulfate. Nickel may also originate from long-range atmospheric transport both from neighboring industrial regions of Poland and the Czech Republic.

Calcium is most probably coming from mining based on marble and limestone, building and road stone, gravel and sand.

The reason for the high Cl contamination is not very obvious. Geographical distribution and wind directions suggest that the source of this pollution could be dust from the cement plants, petrochemical industries or coke plants.

Principal component analysis has been applied to identify and characterize different pollution sources. Graphical presentations of factor loadings and factor scores of individual sampling sites are given in Figure 2. Four factors explain eighty-five percents of the total variance.

Factor 1 is responsible for 52% of total variance and includes Na, Cl, Sc, V, Cr, Fe, Co, Ni, As, Se, Mo, Th and U (Fig. 2a). This factor has a typical crustal composition. Contribution from coal fly ash from power plant operating on lignite and also from houses in settlements heating by lignite combustion, could explain high concentrations of As, Th, and U. The source of Sc, V, Fe, Co, and Ni could be a metallurgical plant located in Ozimek, east of Opole. Atmospheric transport from neighboring industrial regions probably also contributes to the high amounts of elements characterized by factor 1. Rather high factor loadings for As and Sb point to the presence of fly ash in addition to the solely geogenic material.

Factor 2 (12%) is characterized by the highest loadings of Na, Cl and W.

Factor 3 (12%) includes Rb, Sb and Cs. Rb are natural and essential components of mosses, while Rb is only essential for plants, so it is connected with the effect of forest vegetation, Cs as well. Sb is typical industrial component.

Factor 4 (11%) has high loadings for Ca, Zn and Mo. The highest factor scores correspond to the points 12, 15 and 21(cement plant dust or from marble and limestone mines), point 4 - metallurgical plant in the town of Ozimek situated east of Opole.

Conclusions

This is the first attempt to assess the atmospheric deposition of toxic metals and other trace elements within the Opole Region. The study adds this region to the European moss network. A comparison with the neighboring industrial regions where similar studies have been conducted in the past, shows that the level of toxic elements in moss collected in the agricultural Opole Region are practically the same. Aside from the local industries, the origin of pollutants from the neighboring strongly industrial areas is obvious. Further detailed moss surveys in Opole Region on a larger scale will fill more gaps in the atmospheric deposition map for Europe.

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BADANIE ZANIECZYSZCZENIA POWIETRZA W REGIONIE OPOLA Z UŻYCIEM BIOMONITORINGU ORAZ NEUTRONOWEJ ANALIZY AKTYWACYJNEJ

Streszczenie: Biomonitoring zanieczyszczeń atmosferycznych z wykorzystaniem mszaków jest techniką rozpowszechnioną w Europie. W październiku 2006 r. zebrano 30 próbek mchów: *Hylocomium splendens* i *Pleurozium schreberi* z terenu wokół miasta Opole, stolicy rolniczego województwa opolskiego. Obszar ten leży pomiędzy dwoma regionami o charakterze przemysłowym: regionem śląsko-krakowskim na wschodzie oraz

Legnicko-Głogowskim Okręgiem Miedziowym na zachodzie. W sumie 34 pierwiastki, w tym również metale toksyczne oraz metale ziem rzadkich, zostały wykryte metodą instrumentalnej neutronowej analizy aktywacyjnej wykorzystującej epitermalne neutrony z reaktora IBR-2 w FLNP JINR. Interpretacja uzyskanych wyników wskazuje na wyraźne zanieczyszczenie badanego obszaru przez takie pierwiastki, jak As, Sb, V, Ni, Mo itd., na poziomie zbliżonym do zanieczyszczenia sąsiednich obszarów przemysłowych. Dowodzi to wpływu transportu zanieczyszczeń pomiędzy regionami, powiązanego ze źródłami lokalnymi.

Słowa kluczowe: zanieczyszczenia powietrza, biomonitoring, neutronowa analiza aktywacyjna