ASSESSMENT OF ELEMENTAL AND RADIONUCLIDE CONTENT THROUGH ANALYSIS OF AEROSOL FILTERS FROM BRATISLAVA, SLOVAKIA

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Abstract

The 23 chemical elements (Na, Mg, Al, Cl, K, Ca, Ti, V, Cr, Mn, Ni, Cu, Zn, As, Br, Cd, In, Sb, I, Dy, W, Pb and U) and radionuclides ^{210}Pb, ^{7}Be, ^{40}K and ^{137}Cs were determined in low layers of atmosphere in Bratislava (Slovak Republic) using nuclear and related analytical techniques. The main goal of this study is to better understand the processes taking place in the atmosphere and the quantification of the atmospheric pollution and its trend. The aerosol particles from the atmosphere have been collected using nitro-cellulose filters with pore size of 0.85 μm. To determine the activities of radionuclides, air filters were measured by semiconductor HPGe detector in low level counting laboratory in Department of Nuclear Physics at Comenius University Bratislava. The content of 17 stable elements in filters was measured using neutron activation analysis at IBR-2 reactor in JINR Dubna, and 6 elements (Cr, Ni, Cu, Zn, Cd and Pb) were determined by AAS in Bratislava. The aerosol component of the atmosphere in Bratislava shows typical values of activity concentrations of ^{210}Pb, ^{7}Be, ^{40}K and ^{137}Cs for central European area. The obtained results confirm the decreasing trend of pollution by most of the heavy metals in Bratislava atmosphere, and they are compared with the contents of pollutants in atmosphere of other cities.

1 Introduction

Atmospheric aerosols are submicron particles, on which the elements of solid or liquid state present in the air are captured. Atmospheric aerosol particles are sorted according their size into:

(a) Aitken nuclei mode (from 0.003 to 0.07 μm, average 0.015 μm).
(b) Accumulation mode (from 0.07 to 2 μm, average 0.3 μm).
(c) Coarse mode (from 2 to 36 μm, average > 10 μm).

The aerodynamic size of aerosol determined the degree of biological effect on human organism. Atmospheric aerosol contains various elements including heavy metals. Also it has the radioactive component represented mainly by the radionuclides as ^{7}Be and ^{210}Pb. All of these parameters were determined and the results are discussed below.

Some heavy metals play important role in the nutrition of plants, animals or humans (Mn, V, Cr, Ni, Cu, Zn), but if they occur in excess, they may produce toxic effects. The others (Cd, Hg, Pb) are toxic even in very low contents. Heavy metals are released to the environment from a great number of sources like different industrial activities or combustion of fossil fuels. These elements are components of traffic emissions and into atmosphere are emitted in form of fine dust and aerosols. Velocity of dry deposition of heavy metals in atmospheric aerosols is usually less than 0.5 cm.sec^{-1} and medium residence time is supposed to be about 5 days [1]. Airborne soil particles, volcanic aerosols and forest fires contribute to natural emissions of trace elements. The current anthropogenic metal emissions are up to several orders of magnitude higher than natural contents [2].

In the low-level atmosphere contents of ^{210}Pb (half-life 22.3 years) and ^{7}Be (half-life 53.5 days) vary on level mBq.m^{-3}. The radionuclide ^{210}Pb is long-lived progeny of ^{222}Rn. It is interesting mainly from the radio-hygienic point of view, because it is classified in the group of high-toxic radionuclides. It is deposited in bones and here it constitutes the long-term source of alpha emitter ^{210}Po. The cosmogenic radionuclide ^{7}Be is used in studies of atmospheric transport processes and circulation. Considering that ^{7}Be has pure outdoor origin it is used as tracer in experiments

examining ingress of aerosols into buildings [3]. Its seasonal variations appear to show the effect of four factors [4]:

(a) Rate of exchange between the stratosphere and the troposphere.
(b) Rate of vertical mixing within the troposphere.
(c) Transport of air masses from middle latitudes into the high latitudes.
(d) Amount of rainfall.

In the past was present in the atmosphere the anthropogenic isotope ^{137}Cs, originated mainly from nuclear bomb tests and Chernobyl accident. Nowadays its contents are low (~ $\mu Bq.m^{-3}$). The content of the primordial radionuclide ^{40}K in low-level atmosphere is approximately 10-times higher than of ^{137}Cs. It is emitted into air via resuspension form the soil surface.

At the Department of Nuclear Physics and Biophysics at the Faculty of Mathematics, Physics and Informatics it is long tradition of measuring the radioactivity of low-level atmosphere [5], [6], [7]. This study follows the preceding work.

2 Experimental

Using the sampler device with an air-flow rate of 30 $m^3.h^{-1}$ aerosol particles have been collected on the nitro-cellulose membrane filters (PRAGOPOR, pore size 0.85 μm, the collection efficiency approximately 100 %). The sampler device was situated at a height of 2.85 m above ground at the Meteorological Station near the Faculty of Mathematics, Physics and Informatics, Comenius University, Bratislava. The filters were changed every week and about 3000 m^3 of air was pumped through each sample. In September 2004 the new sampling device was launched and the volume of pumped air increased twofold.

After exposing the filters have been measured by a semiconductor HPGe detector (with a Be-window) placed in the low-background shield for determining radionuclides ^{7}Be and ^{210}Pb. In the case of ^{137}Cs and ^{40}K because of their very low contents two or more sets of samples were accumulated together to obtain flow volumes at least 10 000 m^3 level. These accumulated samples have been measured by a large volume HPGe detector with higher detection efficiency, than in the first case, placed also in low-background shielding.

Contents of stable elements were determined by NAA on reactor IBR-2, Dubna, Russia. Filters (~ 0.3 g) were packed in polyethylene foil bags for short-term irradiation. The used irradiation facilities are described in [8]. To determine the short–lived isotopes of Na, Mg, Al, Cl, K, Ca, Mn, Br, I and other, channel 2 (Ch2) was used (conventional NAA). Samples were irradiated for 5 min and measured twice after 3 – 5 min of decay for 5 – 8 min and 20 min, respectively.

Data processing was carried out using software developed in FLNP JINR, and element contents were determined on the basis of certified reference materials and flux comparators [8]. For short-term irradiation in Ch2 a comparator of Au (10 μg) was employed.

In addition the contents of Cr, Ni, Cu, Zn, Cd and Pb were determined using atomic absorption spectrometry at Institute of Geology at Faculty of Natural Sciences at Comenius University.

3 Results and Discussion

During the period from March 2001 to December 2004 the 111 sets of aerosol filters were sampled. Measured contents of ^{210}Pb and ^{7}Be over the term are presented in figure 1. The contents of ^{210}Pb ranged from 0.25 to 2.96 $mBq.m^{-3}$ with the average value 0.81 ± 0.02 $mBq.m^{-3}$. The contents of ^{7}Be ranged from 0.59 to 4.96 $mBq.m^{-3}$ with the average value 2.47 ± 0.08 $mBq.m^{-3}$. Both radionuclides show seasonal variations. ^{210}Pb reach higher values in autumn and winter months, what is attributed to frequent inversion conditions of the surface air layers [9]. The decrease of the ^{210}Pb content in warm spring and summer season is a result of the intensive air mixing. On the table 1 are compared activity contents of ^{210}Pb in four locations.

Tab. 1 Content of ^{210}Pb in low-level atmosphere for four locations

Location	Period	Content [mBq.m^{-3}]	Average [mBq.m^{-3}]
Bratislava (this paper)	2001 – 2004	0.25 – 2.96	0.81 ± 0.02
Neuherberg – Germany [10]	1994 – 1996	0.13 – 1.48	0.42
Belgrade – Serbia [11]	1985 – 1996	0.30 – 3.17	1.20 ± 0.48
El-Minia – Egypt [12]	1998 – 1999	0.11 – 0.82	0.37 ± 0.06

The variations of content of ^{7}Be behave almost inversely to the ^{210}Pb. The highest values of activity have been detected during spring and summer term. It is an effect of air-mass transport from stratosphere to troposphere. On the contrary in cold months these exchange processes are reduced and as a result the supply of ^{7}Be produced in higher layers of atmosphere declines. The measured content of ^{7}Be compared to other locations seems to be low (tab. 2), but it is a result of anticorrelation between the production of cosmogenic radionuclides and the sun activity. Monitored period 2001 - 2004 does not cover the entire 11-year sun cycle, but only the period with increased sun activity.

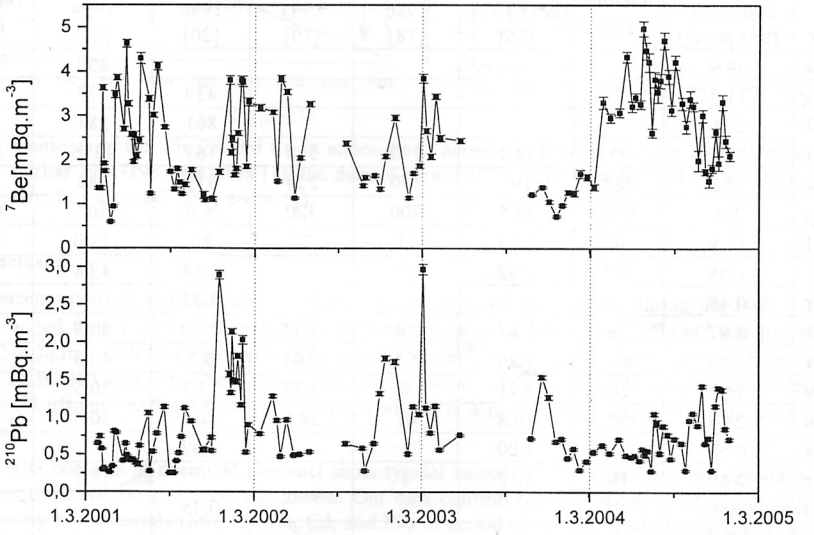

Fig. 1 Temporal variations of activity contents of ^{210}Pb and ^{7}Be in atmospheric aerosol

Tab. 2 Contents of ^{7}Be in low-level atmosphere for six locations

Location	Period	Content [mBq.m^{-3}]	Average [mBq.m^{-3}]
Bratislava (this paper)	2001 – 2004	0.59 – 4.96	2.47 ± 0.08
Neuherberg – Germany [10]	1994 – 1996	1.40 – 6.70	3.33
Granada – Spain [13]	1993 – 2001	1.50 – 7.60	4.45 ± 1.35
Monaco [14]	1997 – 2000	1.50 – 7.24	4.21
El-Minia – Egypt [12]	1998 – 1999	1.10 – 3.00	2.0 ± 0.09
Prague [15]	1986 – 2002	1.01 – 7.07	2.92

Using NAA at IBR-2 reactor in Dubna contents of 17 elements in 8 selected atmospheric aerosol samples were determined (Na, Mg, Al, Cl, K, Ca, Ti, V, Mn, As, Br, In, Sb, I, Dy, W and U). To complete the list of elements the atomic absorption spectrometry was used for measurements of Cr, Ni, Cu, Zn, Cd and Pb. The results are in the table 3. There is a comparison to other seven locations all over the world, too. Relatively low values comparing of Cl, Na and Br to the values from the coastal localities indicate the sea spray origin. The small contents of V, Ni and As can by attributed to weaker frequency of oil and coal combustion in the Bratislava compared to other locations. Oil combustion is practically the only source of V, while Ni can be emitted also from high quality steel production plants and Ni smelters [16]. Al, Ca and Ti are typically soil derived elements. Non-ferrous smelters are the sources of Zn, Cu, Cd and Pb. Cd and Pb are released into the environment also via fossil fuel combustion. The measured contents of almost all elements are lower in Bratislava comparing to other localities. It can be caused by the small number of sources of pollution. On the other side this location is typical with the high number of windy days per year.

Tab. 3 Contents of stable elements [ng.m^{-3}] in atmosphere for eight locations

	Bratislava 2001/2005 (this paper)	**Vienna** [17]	**Bily Kriz** 1993/1994 [16]	**Antwerp** 1986 [18]	**Lund** 1993 [19]	**Detroit** 1996 [20]	**Singapore** 1994 [21]	**Kyoto** [17]
Na	99.9						802	
Mg	11.5					439	177	
Al	231					861	281	
Cl	79.1	35	11.1	190	514	163	1376	260
K	158	280	191	170	224	313	280	360
Ca	228	970	53.5	300	320	2630	303	620
Ti	11.8	30	7.13	21	20	86	33.0	67
V	1.05	11	2.32	13		8.58	4.08	9
Cr	0.45				21.6	2.73		
Mn	4.97	19	5.87	10	8.37	45.2	8.63	26
Ni	0.59	6.3	1.26	6.1	2.08	8.2	4.68	9.1
Cu	5.90	20	4.71	8	4.57	13.7	20.5	15
Zn	23.6	50	50.8	41	28.5	103	30.5	88
As	0.52		4.00			2.07		
Br	2.49	16	4.12				16.1	9
Cd	0.098					0.45		
In	0.002							
Sb	0.83					1.81		
I	1.15							
Dy	0.017							
W	0.36					0.24		
Pb	34.2	83	28.7	110	19.8	21.5	33.8	44
U	0.018							

Figure 2 shows decreasing trend of air pollution by heavy metals in Bratislava since the year 1981. The emissions of Pb have decreased, reflecting the shift from leaded to unleaded gasoline. The next reason of this positive trend is the decline of the industry production in Slovak Republic after the year 1989. The emissions of pollutants were reduced via application of more strict requirements in the environmental legislative, too.

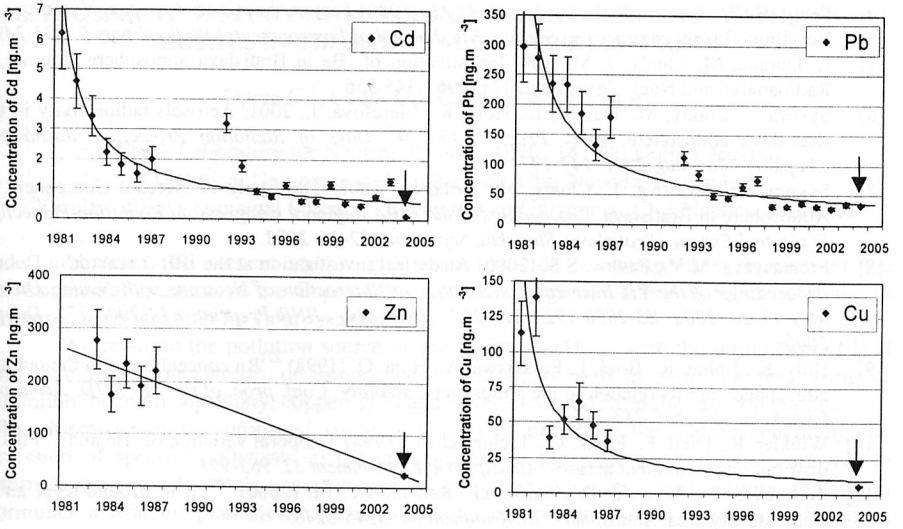

Fig. 2 Contents of Cd, Pb, Zn and Cu in atmospheric aerosol in Bratislava since 1981. The data of period 1981-1987 are from [1]; the data of period 1992 – 2003 for Cd and Pb are from [22]. Our data are marked by arrow (↓).

4 Conclusion

The concentrations of radionuclides ^{210}Pb and ^{7}Be in low-level atmosphere during the 2001 - 2004 period ranged from 0.25 to 2.96 mBq.m^{-3} with the average value 0.81 ± 0.02 mBq.m^{-3} and from 0.59 to 4.62 mBq.m^{-3} with average value 2.05 ± 0.05 mBq.m^{-3}, respectively. Both radionuclides show typical seasonal variations. The radioactivity concentrations of ^{137}Cs and ^{40}K are near the detection limit, ~ 0.4 μBq.m^{-3} and ~ 0.5 μBq.m^{-3}, respectively. It is a reason why only a few data have been evaluated.

The contents of chemical elements show typical values for European area and comparing to other locations are most of them the lowest. Our data confirm the decreasing trend of atmospheric pollution by heavy metals (Mn, Cu, Zn, Cd, and Pb) in period of last 20 years. In the future we are planning to realise the long-term irradiation for determination of the additional elements. The obtained data may be useful as a reference level for comparison with the future measurements of pollution by heavy metals in Bratislava's atmosphere.

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