EG0600052

Proceedings of the Environmental Physics Conference, 24-28 Feb. 2004, Minya, Egypt

ENVIRONMENTAL MONITORING IN SLOVAKIA USING NUCLEAR TECHNIQUES

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ABSTRACT

The contamination of the atmosphere of Slovakia by stable elements and also by radionuclides as ^{14}C, ^{7}Be, ^{210}Pb and ^{222}Rn were studied during the last decade using nuclear techniques. The main aims of this research were the better understanding of processes taking place in the atmosphere, the quantification of the atmospheric pollution and its trend, as well as the evaluation of the health risk from this pollution.

INTRODUCTION

The control of the atmospheric air quality is one of the most important tasks of the environmental protecting program. Atmospheric air is one of the basic components of the human environment. Cleanness of the air reservoir is a basic factor for the ecological balance and human health.

Among many pollutants heavy metals are the most toxic component for all living organisms. Heavy metals are presented in the atmosphere in organic and also in inorganic forms, in the form of dust and aerosols. They can be transported to large distances from the source (thermal power plant, chemical industry, transport, etc.) and where they fall out they have a very negative impact on the environment.

Systematically surveys of the atmospheric deposition of heavy metals are performed in several European countries every 5 years by means of the biomonitoring technique [1]. It is well established that the terrestrial mosses are among the most effective types of organisms for biomonitoring due to their biological features, widespread occurrence, and tendency to accumulate and retain pollutants. As distinct from higher plants the terrestrial mosses lack an advanced root system. This inhibits significant absorption of pollutants from the substrate and consequently their uptake results mainly from the ambient atmosphere. Moss surveys have several advantages over conventional deposition monitoring based on bulk precipitation, the sampling is simple and chemical analyses are much easier due to higher concentration and strongly reduced contamination problems.

From radioactive pollutants of the atmosphere the most significant are the natural ^{222}Rn with its daughters (^{218}Po, ^{214}Pb, ^{214}Bi, ^{214}Po, ^{210}Pb and ^{210}Po), ^{7}Be and ^{14}C as radionuclides of cosmogenic origine and case of ^{14}C also as products of nuclear bomb tests.

The concentration of these radionuclides in the atmosphere is not stable. We can observe daily and seasonal variations of the radon concentration in the surface layer of the atmosphere. These variations are explicitly attributed to the regular changes of the vertical atmosphere mixing rate during the day and during the year [2].

Identically the seasonal variations of the ^{7}Be, ^{210}Pb and ^{14}C concentrations in the atmosphere are observed as a result of transport processes in the atmosphere and of the alternation of annual cycles [3, 4, 5]. Moreover, the ^{14}C concentration in the atmosphere decreases because of the exchange processes between the atmosphere and the other reservoirs [5]. The decrease of ^{14}C in the atmosphere is reasonable influenced also by the dilution of the atmosphere with an inactive carbon, produced by combustion of the fossil fuel.

The concentrations of the atmospheric radionuclides and stable elements can vary substantially with location. Therefore their measurements on regional level bring always new knowledge about exchange processes in the atmosphere, about its contamination and knowledge of the population exposures.

In our contribution there is investigated the contamination of the atmosphere of Slovakia by stable elements. Further, the results of the long-term trends of the concentrations of some radionuclides in Bratislava atmosphere and ^{14}C also in Zlkovce atmosphere are presented. The complex view on daily and seasonal radon variations is provided finally.

SAMPLING SITES

The samples of mosses for a study of the atmospheric pollution by stable heavy metals were collected on 86 permanent plots situated in Slovakia at the intersections of 16 x 16 km pan-European network.

In the atmosphere the concentrations of ^{222}Rn, ^{210}Pb, ^{7}Be and ^{14}C were measured in industrial city of Bratislava (48° 9′ N, 17 ° 7′ E, 164 m a.s.l.) with 0,5 million inhabitants. For ^{14}C analysis also the samples of atmospheric CO_2 in Zlkovce (48° 29′ N, 17 ° 40′ E, 162 m a.s.l.) was collected. This station is situated approximately 60 km NE from Bratislava in a flat agricultural area. The nearest pollution source that can influence the ^{14}C concentration in the atmosphere is the nuclear power plant Jaslovske Bohunice, approximately 5 km WNW from Zlkovce.

RESULTS AND DISCUSSION

Heavy metals monitoring

At the study of the atmospheric pollution by stable elements the mosses Pleurozium schreberi, Hylocomium splendes and Dicranum scoparium were used as bioaccumulators. In 86 moss samples were determined 44 elements (including most of heavy metals) by the epithermal and conventional activation analysis on IBR-2 reactor in JINR Dubna, supplemented with the atomic absorption spectrometry. The investigation showed the strong pollution of the examined areas of Slovakia by most of the heavy metals [6] in comparison with the limit values from Norway.

The region near the border between Slovakia, Poland and the Czech Republic is considered as the second "black triangle" of Central Europe with substantially higher concentrations of heavy metals than the first "black triangle" near the borders of the Czech Republic, Poland and Germany. The median of heavy metals in Slovakia for V, Cr, Ni, Cu, Zn, Pb, Cd and As, were compared with relevant data from similar areas of Europe [7]: Strongly elevated Pb values with compare even South Ural Mountans is evident. The Cd value is 1.5 to 9 times higher than in other Europens regions, only concentration of Zn is aproximetly equally. The evident effect of trans-boundary air pollutants was observed.

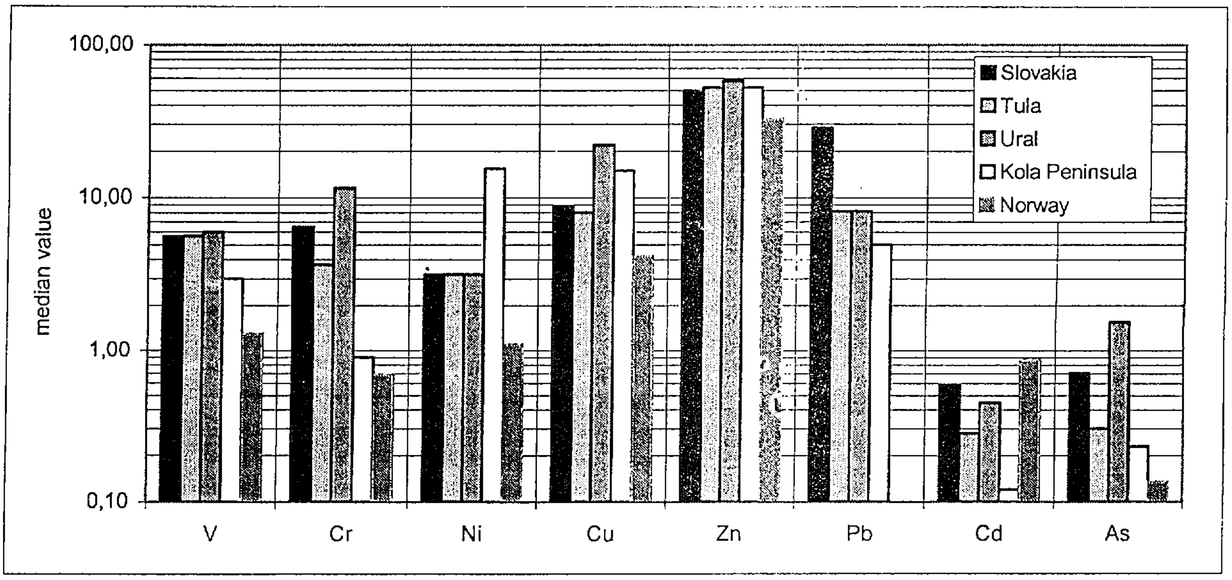
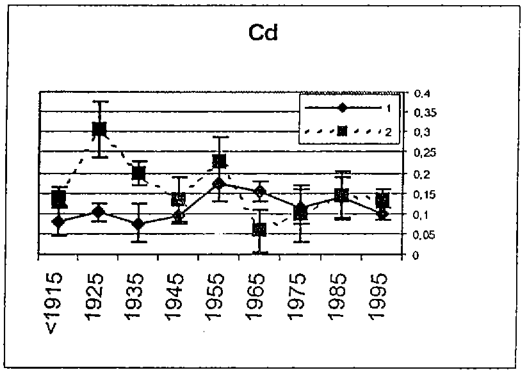


Fig. 1. Median value for some elements in mosses from different part of Europe

Very high level of contents of heavy metals we observed in region Central Spish. From metalgenetic aspect this region was the most important ore region in the Western Carpathian Mts and it is historically linked with exploitation and processing of non-ferrous metals. Since bronze period it had been the place of the exploitation of copper and later also ferrous ores. During the 19th century a small manufacture developed into a large industrial enterprise.

In order to get a chronological record of trace element pollution in the environment instrumental neutron activation analysis was used to determine content of 20 elements in 10-year-old segments of one hundred-old lime (covering practically the whole 20th century) originated from the area of Central Spish. Trees usually form visible annual rings. Samples



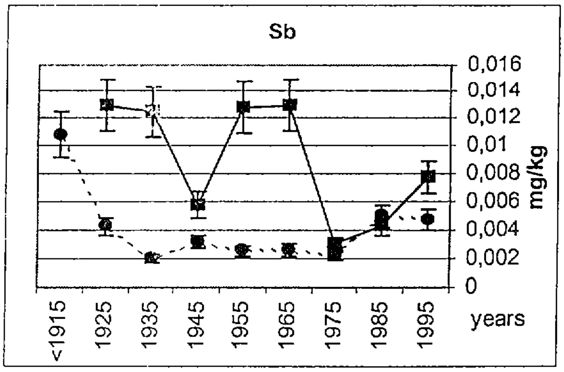


Fig. 2. Content (mg/kg) of Cd in 10-year-old lime segments from SW side (1st point) and from NW side (2nd point). Content of Sb in 10-year-old lime and spruce segments: Lime (dashed line) and spruce (full line) are added to the centre of decade.

were collected from two sides of a lime (SW 1st point and NW 2nd point) and from one side of a spruce. No correlation of elements was observed between two sides of the lime. Correlation of elements in relevant rings of two types of wood was not evident. Peaks of heavy metals are apparently mobile in the stem wood. Therefore the current locations of these peaks are not reliable markers for the dating of pollution events in forest environment. Radial distribution of heavy metals in wood rings should be cautiously used as a tool for chronological record of environmental pollution.

In the same time Geological Survey of Slovak Republic and Soil Science and Conservation Research Institute in Slovakia performed analyses 5200 samples of soil from territory Slovakia. In paper we compare spatial chemical distribution in atmosphere and soil. For example, minimum and maximum values for element Pb based on soil samples are incomparable wider than in mosses samples.

Table 1. Average, median, minimum and maximum value content of element Pb in moss and soil samples

Pb	Average	Median	Min. value	Max. value
Moss (86 samples)	33	28	9,7	109
Soil (5198 samples)	29	20	3	2122

It is connected with effect of accumulation of element in soil on valley and impact of wind to hill. If date from soil reflected contamination of environment of stable elements in during past time, but the date from mosses reflected contamination of environment for a determinate period. For example, mosses date shown (Fig. 3) decreasing the median values in last decade for Cd, Cu and Pb and for Zn. Elements Fe and Hg showed practically no change.

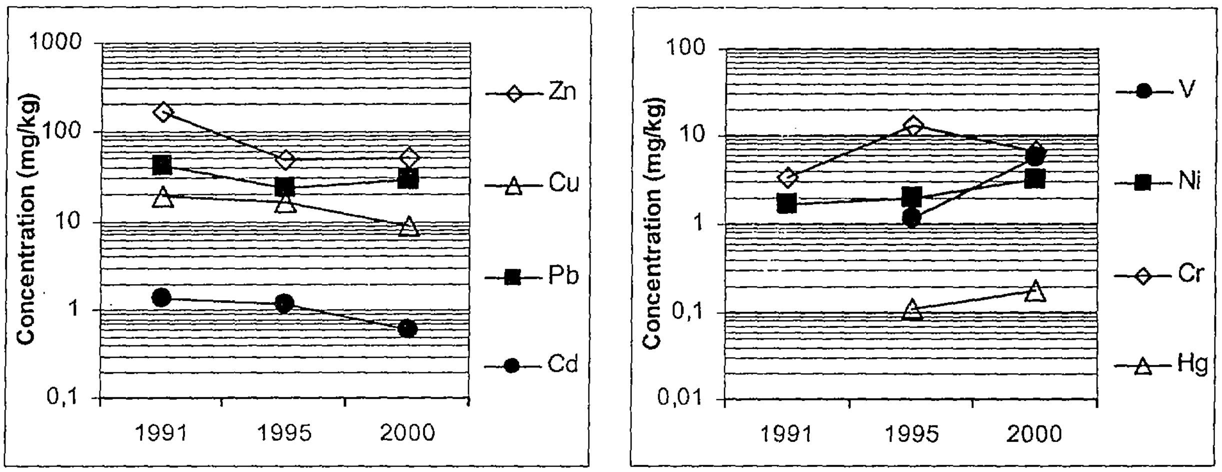


Fig. 3. Temporal changes of heavy metals content in Slovakia mosses

During the same period concentration of such elements as Ni and V increased by ~50 %. This reflects falling-off the production of steel and non-ferrous metals in Slovakia and decrease in using leaded gasoline. The main source of increase of nickel and vanadium in air is gradually growing combustion of heavy oil and products of its refining.

Monitoring of ^{222}Rn

For the measurement of ^{222}Rn the air was sucked at a height of 1.5 m above the ground surface. The radon activity concentration was continuously monitored using the large volume scintillation chamber with frequency of 12 data per day [8].

^{222}Rn in the surface layer of the atmosphere in Bratislava has been monitored continuously since 1991. The extensive set of data allows to study the average daily courses of the ^{222}Rn concentration for individual months and different years and to map long – term trends of the ^{222}Rn activity concentration in the atmosphere.

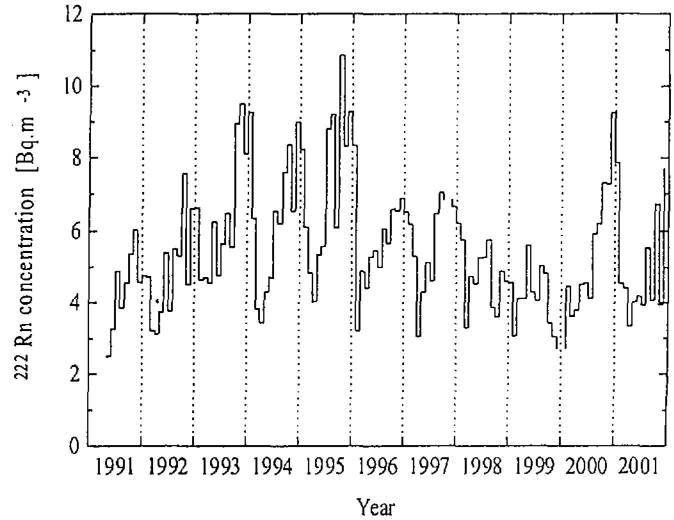


Fig. 4. The monthly mean values of the ^{222}Rn activity concentration in the surface layer of the atmosphere in Bratislava.

The monthly means of the radon activity concentration for the years 1991 – 2001 are shown in the Fig. 4. The spring minima and maxima occurring in various months of the second half – year can be seen in the annual ^{222}Rn courses for all the years. However, the individual years differ from each other quite considerably. The amplitudes of the annual courses vary from 3.1 Bq.m^{-3} (1995) to 1.2 Bq.m^{-3} (1999). The years 1996 – 1999 show a decreasing trend of these amplitudes, predominantly as a consequence of the decreasing of the radon activity in the year's maxima. Simultaneously, a shift of the year's maxima from the late autumn and winter months towards the summer months is observed.

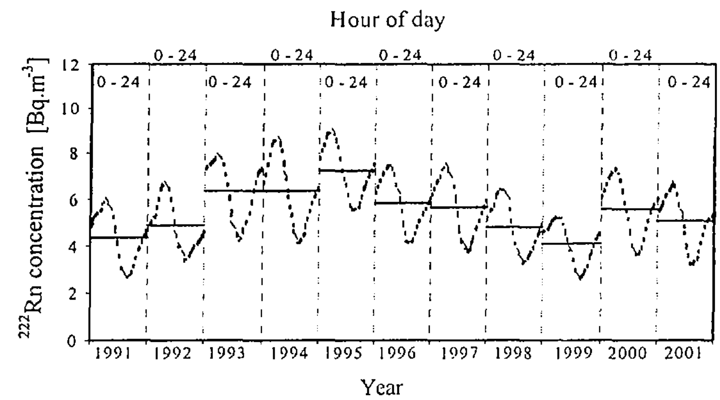


Fig. 5. The mean annual values (solid lines) and the mean diurnal courses (dotted curves) of the ^{222}Rn activity concentration in the Bratislava atmosphere.

The observed changes of the annual radon courses can indicate the lowering of the stability of the surface layer of the atmosphere in autumn and winter months in the mentioned period in comparison to the previous years.

The average annual course of the ^{222}Rn activity concentration calculated on the basis of all the continual measurements in years 1991 – 2000 reaches the maximum in months from October to January (6.9 Bq.m^{-3}) and the minimum in April (3.9 Bq.m^{-3}).

The long – term trend of the average annual ^{222}Rn activity concentrations is shown in Fig. 5. For individual years, there are presented also average radon daily courses.

The average annual radon activity concentrations vary from 4.1 Bq.m^{-3} (in 1999) to 7.2 Bq.m^{-3} (in 1995). The average radon activity concentration in years 1991 – 2000 is equal to 5.6 Bq.m^{-3}. The highest radon concentration in 1995 is caused by the high amplitude of average daily wave in this year (1.7 Bq.m^{-3}) and also by high average value of the radon concentration during a day (5.6 Bq.m^{-3}). In 1999 the minimum of the average daily wave is equal 2.6 Bq.m^{-3} and its amplitude is equal only to 1.2 Bq.m^{-3}. In investigated period, the highest amplitude of average daily wave was observed in 1994 (2.3 Bq.m^{-3}).

The average daily wave of the ^{222}Rn activity concentration (Fig.6) obtained as the mean of all data from years 1991 – 2000 reaches a maximum between 4 and 6 a. m. (7.1 Bq.m^{-3}) and a minimum between 2 and 4 p. m. (4 Bq.m^{-3}). The ^{222}Rn activity concentration reaches its average daily value equal to 5.6 Bq.m^{-3} at about 10 a.m. and at 9 p.m.

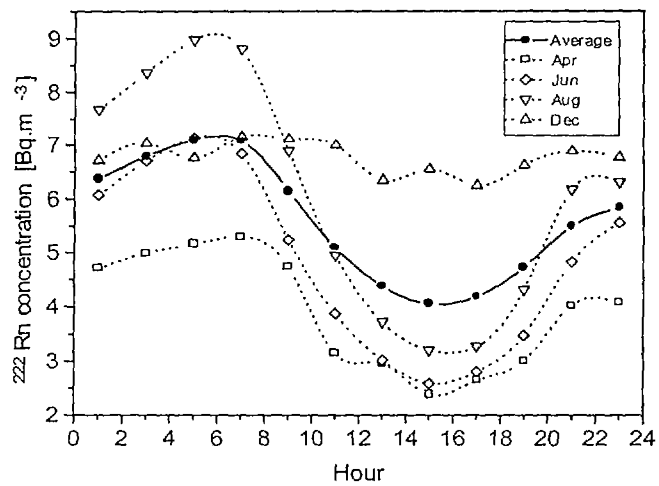


Fig. 6. The mean diurnal courses of the ^{222}Rn activity concentration in Bratislava atmosphere (years 1991 - 2000).

Also the average daily courses of the ^{222}Rn activity concentrations for individual months have a form of waves with the maximum in the morning hours and with the minimum in the afternoon. The maximal amplitudes of the daily waves are reached in the summer months from June till August (2.2 – 2.9 Bq.m^{-3}). In this part of the year also the lowest afternoon ^{222}Rn activity are reached (~3 Bq.m^{-3}). The amplitudes of the daily waves are very small at the end of autumn and during winter months (0.5 – 0.7 Bq.m^{-3}). The detailed analysis of the daily ^{222}Rn courses was carried out in our previous work. There was shown also that the amplitudes of the daily waves are in proportion to the intensity of the global solar radiation [9].

Monitoring of ^{7}Be and ^{210}Pb

Aerosol particles in the atmosphere have been collected using the nitro-cellulose filters with the collection efficiency of approximately 100 %. After exposing in a sampler device the filters have been measured by a semiconductor HPGe detector with a beryllium window placed in the low-background shield.

During monitoring period from March 2001 to April 2003 68 sets of nitro-cellulose filters were sampled. Measured concentrations of ^{210}Pb and ^{7}Be over the term are presented in Fig. 7. The concentrations of ^{210}Pb ranged from 0.27 to 2.93 mBq.m^{-3} with a mean value 0.87 ± 0.02 mBq.m^{-3}. The concentrations of ^{7}Be ranged from 0.46 to 4.42 mBq.m^{-3} with a mean value 2.14 ± 0.04 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 [10]. The decrease of the ^{210}Pb concentration in warm spring and summer season is a result of intensive air mixing. The concentration of ^{7}Be behaves almost inversely to the ^{210}Pb concentration. 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.

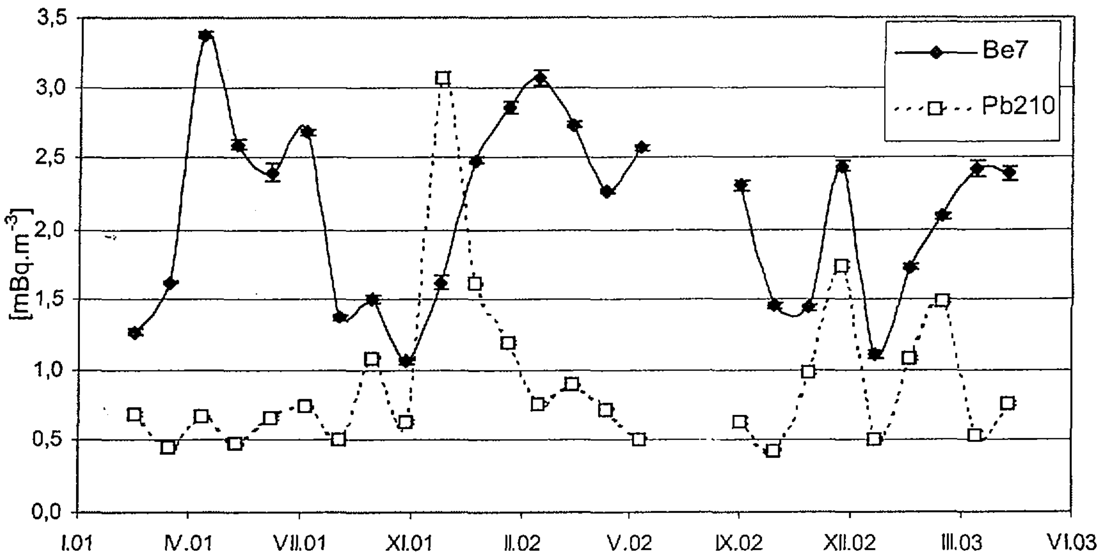


Fig. 7. Monthly means of air activity concentrations of ^{7}Be and ^{210}Pb.

Monitoring of ^{14}C

For the carbon isotope measurements in the atmosphere the monthly large-volume samples of atmospheric CO_2 have been continuously collected at a height of 15 m above the ground surface by the dynamic absorption of CO_2 in NaOH solution [11]. Further CH_4 was prepared from the sample for filling the low-level proportional counter, which was used for the counting of the ^{14}C decays [12]. Results are presented as Δ^{14}C values and they were obtained from δ^{14}C values by the correction on the isotopic fractionation.

The ^{14}C activity has been measured in atmospheric CO_2 in Bratislava and Zlkovce stations since 1987 [13]. In Fig.8 the courses of the annual mean Δ^{14}C measured in both localities are shown. For a comparison, the dashed line in Fig.1 shows the long-term trend of annual mean of Δ^{14}C in background air over Europe.

Before 1994 [14] the annual mean values of Δ^{14}C in the atmospheric CO_2 collected in Bratislava were on average about 50 % lower and at Zlkovce about 20 % in comparison with the Δ^{14}C background level. At that time Δ^{14}C at Zlkovce were about 50 ‰ higher than in Bratislava. In this period in Bratislava, very low and sometimes even negative monthly mean Δ^{14}C values were measured mainly in January and February evidently as a consequence of the high input of ^{14}C free fossil fuel CO_2 into the atmosphere (Suess effect). According to the expectation, the Suess winter minima of Δ^{14}C were not as distinct at Zlkovce as they were in Bratislava, although they were also identified.

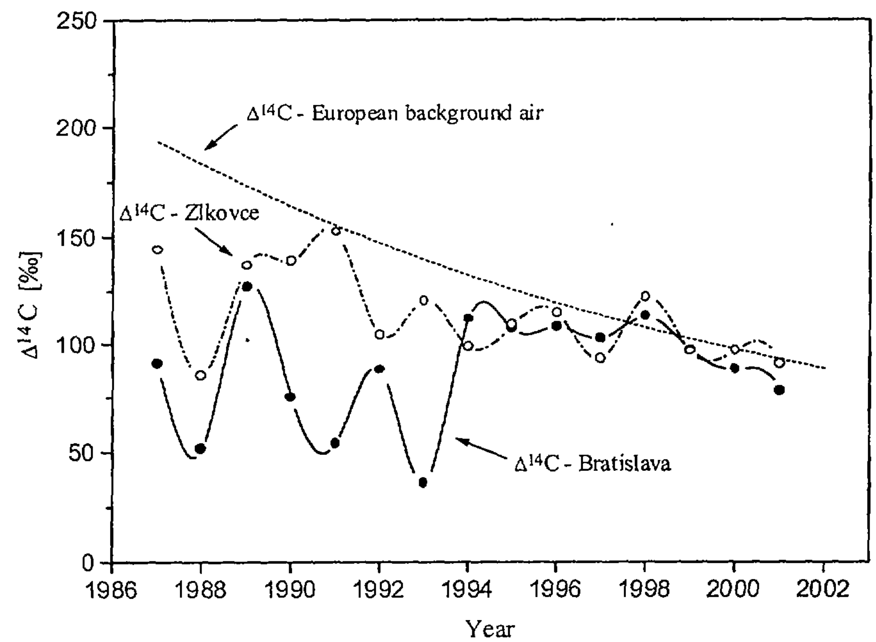


Fig. 8. The annual mean values of the $\Delta^{14}C$ in the atmospheric CO_2 in Bratislava and at Zlkovce. The dashed line represents the long-term of the annual mean $\Delta^{14}C$ in the background air over Europe.

Since 1994 there were no longer such marked differences in annual mean $\Delta^{14}C$ values between the two stations. This could be explained by the decreasing of the fossil fuel CO_2 emissions in Slovakia after 1990 and their stabilization after 1994 [15, 16]. In 2001 the annual mean $\Delta^{14}C$ reached the value approximately 8 % only above the $\Delta^{14}C$ natural level.

CONCLUSION

a. Information about the air pollution status in different parts of the Slovakia is essential for a better understanding of environmental stresses. Biomonitoring technique allows monitoring the heavy metals atmospheric deposition with a very high spatial resolution.

b. By the continual monitoring we obtained the extensive set of radon data in Bratislava atmosphere covering the time period of 1991 – 2000. The average annual radon activity concentrations varied from 4.1 to 7.2 $Bq.m^{-3}$. In the years 1996 – 1999 the decreasing of the average annual radon concentration was observed.

c. The mean air activity concentrations of ^{210}Pb and ^{7}Be in surface atmosphere are 0.87 ± 0.02 $mBq.m^{-3}$ and 2.14 ± 0.04 $mBq.m^{-3}$, respectively. Both radionuclides show seasonal variations. ^{7}Be maxima occur in spring and summer and ^{210}Pb reach higher values in autumn and winter.

d. A high variability of the annual mean $\Delta^{14}C$ in the atmospheric CO_2 was observed at two not very distant stations until 1993. In this period the annual mean values of the $\Delta^{14}C$ in heavily polluted atmosphere of Bratislava were about 50 % lower and at Zlkovce about 20 % lower compared to $\Delta^{14}C$ in European background air. In 2001 reached the value approximately 8 % only above the $\Delta^{14}C$ natural level. The observed $\Delta^{14}C$ behavior in the atmosphere provides an unique evidence of the decrease of fossil fuel CO_2 emissions into the atmosphere

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