Paths of Air Pollutants Containing Radioactive Nuclides in the Suburban Area of Thessaloniki, Northern Greece

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ABSTRACT

The atmospheric behavior of [7]Be-aerosols in association with atmospheric pollutants was studied by using 1-ACFM Andersen type cascade impactors. The activity of [7]Be, a radionuclide of cosmogenic origin, determined by gamma-ray spectrometry (E_γ = 0.477 MeV), was largely associated with submicron aerosol particles in the accumulation mode (0.4–2.0 μm). The activity median aerodynamic diameter (AMAD) of [7]Be-aerosols ranged from 0.62 to 1.00 μm (average 0.80 μm). The geometric standard deviation, σ_g ranged from 1.87 to 2.50 (average 2.22). Low AMAD values of [7]Be-aerosols have been observed at locations characterized with relatively low pollution. Some dependency of AMADs on height from the ground surface varied from zero to 1201 m has also been observed with high AMAD values in zero height where the pollution was high and low AMAD values in high elevation where the pollution was low. In near marine environment where the airport is located, an area with additional pollution, the activity size distribution of [7]Be-aerosols was observed in higher size range of aerosol particles (0.82–0.90 μm).

Keywords: Aerosol Sampling and Transport; Air Pollution; Atmospheric Aerosols; Radioactive Aerosols; Air Samplers; Ambient Air; Urban aerosols.

INTRODUCTION

When a radioactive nuclide decays, electrons are stripped from the parent atom by its recoil, and decay products are formed as positive ions. These ions can attract liquid and even solid material and thus forming clusters of atoms or particles in the submicron region ranging from 0.001 to 0.01 μm. Air is permanently ionized by radiation from natural radioactivity of air, and by cosmic radiation which is consisted mostly of positively charged particles, 85% protons, 10% alpha particles and in smaller percentage stripped nuclei of heavier elements been positively charged, such as Fe, Co and Ni, etc. Production of an ion pair requires 35.6 eV if ionization is by alpha particles and 32.5 eV if by fast electrons. In the free atmosphere, the rate of production of small ions is in balance with the rate of neutralization by recombination, and the rate of attachment to condensation nuclei. Condensation nuclei are mostly the Aitken nuclei, which are submicrometer particles in the range of 0.005 to 0.01 μm.

In air containing water vapor, the positive ions are mostly hydrated protons, p^+ or H^+ $(H_2O)_n$, where n may be any number between 1 and 8. Negative ions are probably mostly hydrated O^- or OH^-. The formation of clusters of water molecules round ions is very rapid, but the clusters do not grow beyond about 0.001 μm (1 nm) diameter and remain as small ions until they become attached to condensation nuclei. They then become large ions. Large ions themselves can be classified in two size ranges. The nuclei mode (Aitken nuclei) centred on 0.01 μm (10 nm) is distinct from the accumulation mode, centred on 0.1 μm (100 nm). The number of particles in the nuclei mode is greater than the number in the accumulation mode, but their total surface area is less, and it is surface area which determines the probability of attachment of small ions to particles with diameter of order of 0.1 μm (100 nm) or less (Papastefanou and Bondietti, 1987; Papastefanou, 2009b). Thus, the large ions are mostly in the accumulation mode. The distinction between small and large ions is well established in atmospheric electricity. The existence of intermediate ions in the size range of 0.001 to 0.010 μm (1–10 nm) has been confirmed. If sulfate or nitrate vapors are present in air, molecules of them will dissolve in the water clusters, and these will then grow into the intermediate ion range.

A possible mechanism for formation of radiolytic nuclei is radiolysis of water, leading to formation of H_2O_2, which then oxidizes traces of SO_2 to give H_2SO_4. Addition of O_3 to the air also increased nuclei production, whereas addition of NO, a well-known radical scavenger, inhibited it.

The radionuclides ions in the atmosphere exist in two forms: (1) as "unattached clusters" with a diffusion

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equivalent diameter size ranging from 0.5 to 5 nm and (2) as "aerosols-attached clusters" with particle diameters varying between 5 and 3000 nm. Reported values of the diffusion coefficients in the literature range from 0.01 to 0.1 cm^2/s (Raabe, 1968; Porstendörfer and Mercer, 1979). Most of the previous studies on the diffusion coefficient did not consider the importance of the electrical charge of the radionuclide ions and the air humidity. Neutralization of radionuclide ions depends on their concentrations and on the humidity in air.

Recently, Dankelman *et al.* (2001) determined the neutralization rates of ^{218}Po ions in air by electron transfer process in "normal" environmental outdoor and indoor air with natural trace gases and found that is small and can be neglected under "normal humidity" (RH: 30–95%) and radionuclide concentrations.

Beryllium-7 is a relatively short-lived ($T_{1/2}$ = 53.3 days, τ = $1/\lambda$ = 77 days) naturally occurring radionuclide of cosmogenic origin which is formed by spallation processes of light atmospheric nuclei, such as carbon, nitrogen and oxygen, when they absorb protons and even neutrons of the primary component of cosmic rays (Bruninx, 1961, 1964; Silberberg and Tsao, 1973). Once ^7Be (inorganic ion) is formed in the troposphere, it rapidly associates primarily with submicron-sized aerosol particles (Bondietti *et al.*, 1987; Papastefanou, 2009a). Beryllium-7 in these fine aerosols may subsequently enter the marine as well as the terrestrial environment and vegetation via wet or dry depositional events. Following deposition, ^7Be will tend to associate with particulate material (particle-reactive element).

Beryllium-7 has come to be recognized as a potential tool in studying the description of environmental processes such as aerosol transit in the troposphere (Martell, 1980), aerosol deposition (Young and Silker, 1980), and aerosol trapping by above ground vegetation (Bondietti *et al.*, 1984). Beryllium-7 as well as other natural radionuclides like $^{212+210}Pb$, ^{22}Na, ^{35}S and $^{32+33}P$ participates in the formation and growth of the accumulation mode aerosols (0.07–2.0 μm diameter), which is a major reservoir of pollutants in the atmosphere. Following its production by gas-phase nuclear transformation, this isotope condenses on the aerosol population growing by condensation of non-radioactive species (e.g. H_2SO_4 or organics) and the fate of

^7Be will become the fate of the carrier aerosols (Bondietti *et al.*, 1988). On the behavior of ^7Be with atmospheric aerosols it was concluded from early aerosol studies that considerable coagulation occurred during migration from stratosphere and upper troposphere to ground level (Lockhart *et al.*, 1965; Gaziev *et al.*, 1966).

This paper summarizes results of an investigation regarding the aerodynamic size distribution of atmospheric aerosols in the context of ^7Be activity distributions and the influence of air pollutants on ambient aerosols in the suburban area of Thessaloniki, Northern Greece [40°38'N, 22°58'E].

INSTRUMENTATION AND SITING

The aerodynamic size distribution of ^7Be in atmospheric aerosols was achieved by using Andersen 1-ACFM cascade impactors. This 1-ACFM impactor involves a flow rate of 1.7 m^3/h (28.3 L/min or 1 ft^3/min) and eight atmospheric pressure stages for collecting aerosols above 0.4 μm (Fig. 1). The effective cutoff diameters (ECDs) of this impactor were as follows: 0.4, 0.7, 1.1, 2.1, 3.3, 4.7, 5.8 and 9.0 μm. The stainless steel plates supplied by the manufacturer were used for aerosol collection. Glass fiber filters were used as back up filters to collect particles below the 0.4 μm collection plate. Polycarbonate films can also be used as back up filters. The sampling device acts as a substitute for the human respiratory tract system as a particle collector, so that lung penetration by airborne particles can be predicted from sampling data. The sampling instrument should, therefore, classify the aerosol particles collected according to the aerodynamic dimension, which is the true measure of lung penetrability. The fraction of inhaled particles retained in the respiratory system and the site of deposition vary with size, shape and density and all the physical dimensions.

The length of each collection period was 1 week. The samples were collected at different sites (locations) in the suburban area of the city of Thessaloniki, Northern Greece (40°38'N, 22°58'E), including rural areas, industrial areas, the airport area, high elevations and marine environment (Fig. 2). In this plan view, the direction of stream-lines of air masses that transfer air pollutants by the local wind blown, named "Vardaris", are also shown.
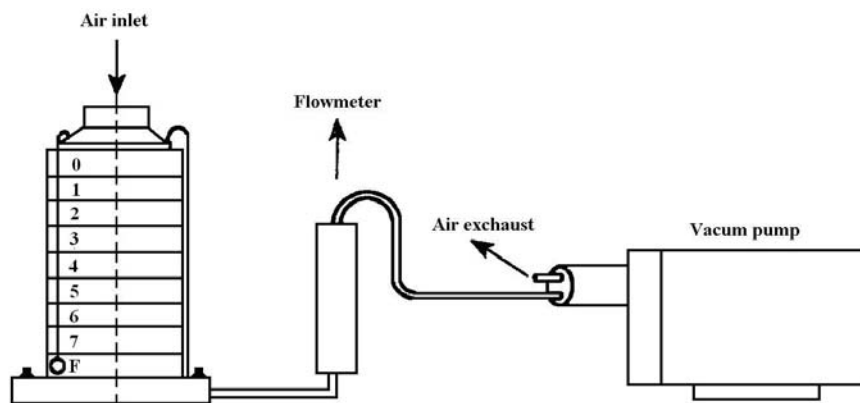

Fig. 1. A schematic diagram of an 1 ACFM Andersen type cascade impactor complete system for aerosol sampling.
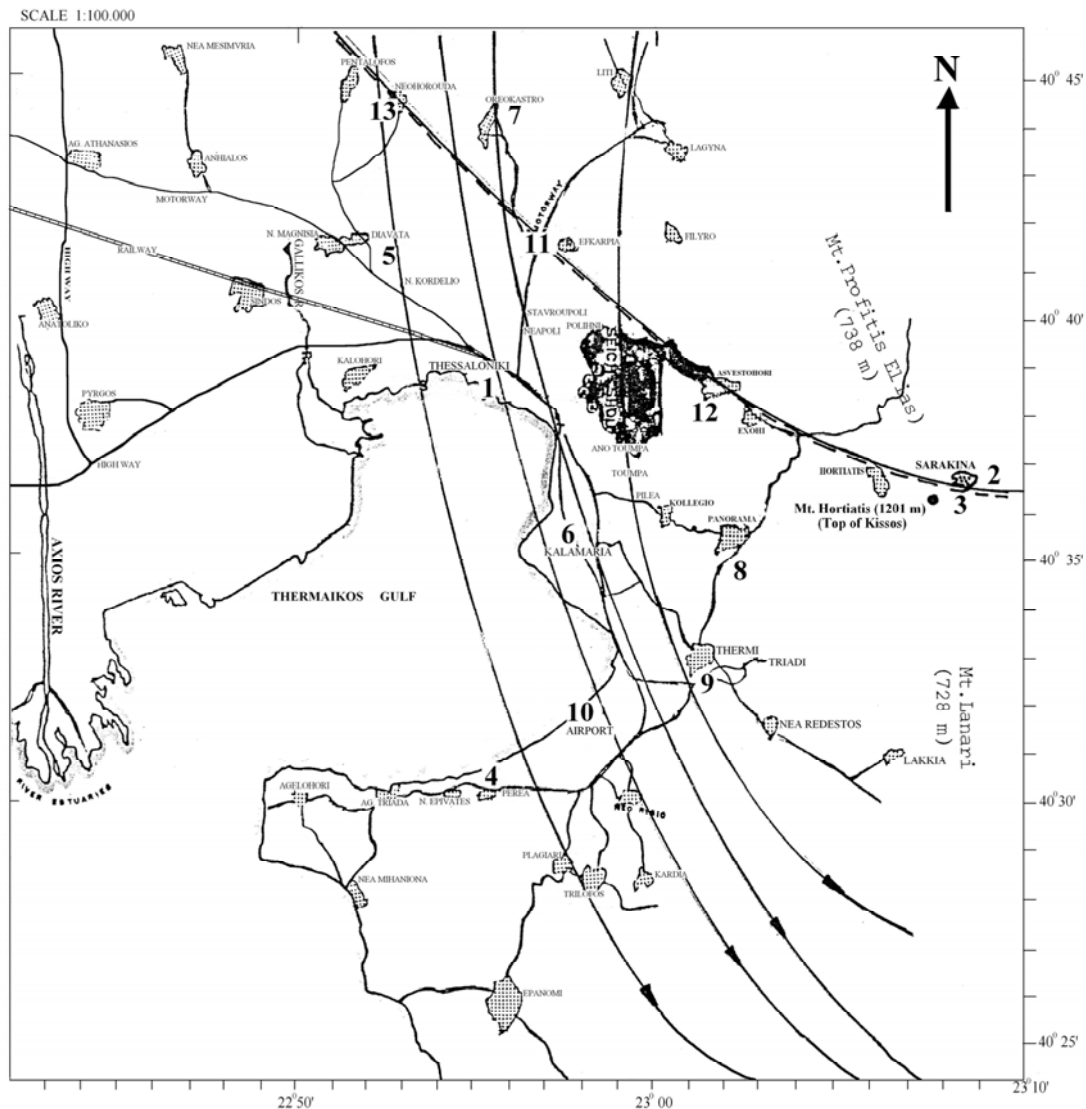
Fig. 2. A plan of the city of Thessaloniki, Northern Greece (40°N, 22°E) and the suburban area, showing the aerosol sapling location which are numerated according to Table 1, and the streamlines of air masses that transfer the air pollutants from North-West to South-East

The stainless steel collection plates of the impactor as well as the back up filters used as plane radioactive sources were measured for ^{7}Be activity ($E_\gamma = 0.477$ MeV) by γ-ray spectrometry using a high resolution (1.9 keV at 1.33 MeV ^{60}Co), high efficiency (42%), low-background high purity Ge coaxial-type detector. Uncertainty in counting of ^{7}Be activity was varied from 10% to 20%. Less than 3 mg of particulate material on any impactor stage was collected in each sampling, thus overloading ($\geq$10 mg on any stage) was excluded. A typical γ-ray spectrum of a glass fiber air filter obtained by a Ge detector, in which the 0.477 MeV γ-ray peak of ^{7}Be is clearly shown in Fig. 3.

RESULTS

A typical plot of the activity size distribution of ^{7}Be versus aerodynamic diameter (D_p) is represented in Fig. 4.

This distribution was selected from twelve measurements performed over an almost 1-year period (26 August 1993 to 5 August 1994). Atmospheric aerosol size distribution appears to follow a trimodal distribution expected for condensation-derived aerosols with the following mode ranges: the Aitken nuclei mode ranges from 0.003 to 0.07 μm (average 0.015 μm), the accumulation mode ranges from 0.07 to 2.0 μm (average 0.3 μm) and the coarse mode ranges from 2.0 to 36.0 μm (average 10.0 μm) (NRC, 1979; Papastefanou, 2009b). Beryllium-7 aerosols are accumulation mode aerosols as it is evident from the plot of Fig. 4 (Papastefanou, 2009a).

A summary of experimental data regarding the ^{7}Be size distribution of atmospheric aerosols in the suburban area of Thessaloniki, Northern Greece [40°38'N, 22°58'E] is presented in Table 1 for 12 measurements carried out from August 1993 through August 1994. The activity median aerodynamic diameter (AMAD) varied from 0.62 to 1.00 μm
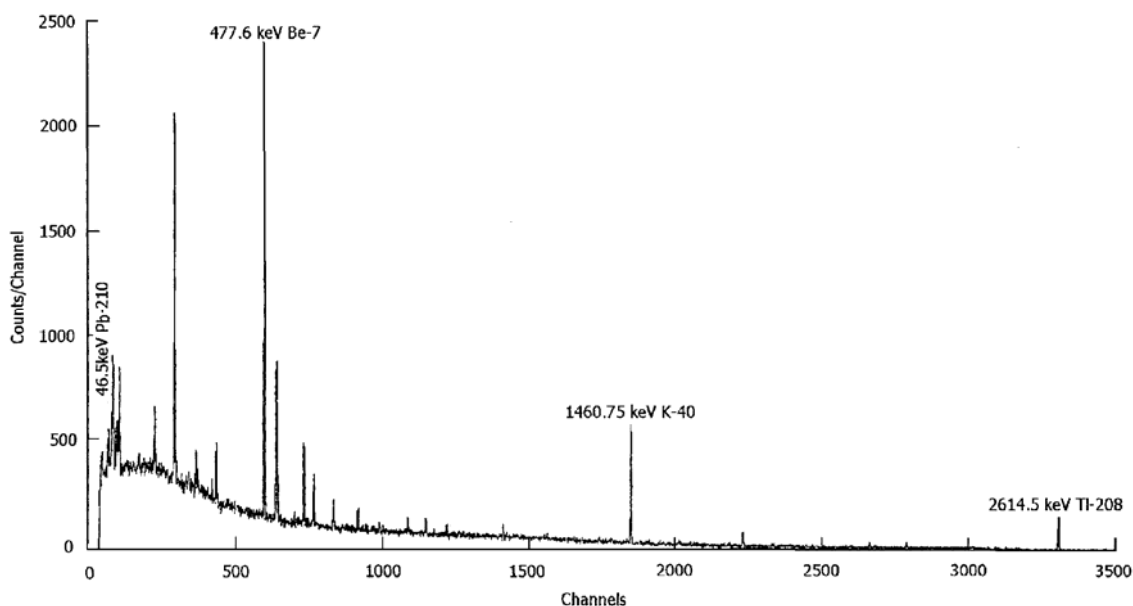
Fig. 3. Plot of a γ-ray spectrum of an atmospheric aerosol sample (air filter) obtained by a Ge detector.
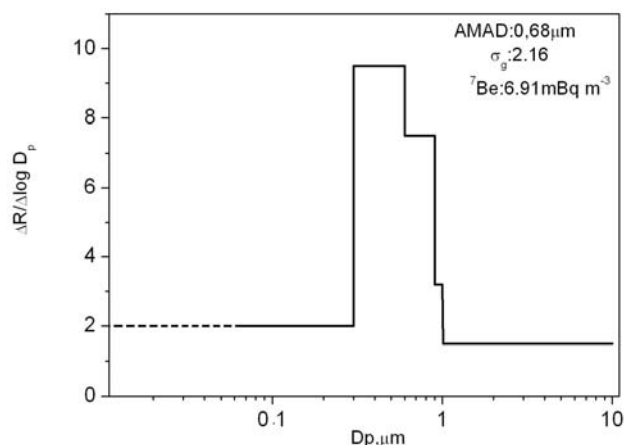

Fig. 4. Aerodynamic size distribution of ^{7}Be-aerosols in different location in the suburban area of Thessaloniki, Northern Greece (size range in μm).

Table 1. Experimental data for ^{7}Be-aerosols in different locations in the suburban area.

Date	Location	R (^{7}Be) (mBq/m^3)	% in Size Range					AMAD (μm)	σ$_g$
			<0.4	0.4–0.7	0.7–1.1	1.1–2.1	2.1–9.0		
1993									
26 August	2 Sarakina	6.91	22.15	29.93	21.46	13.26	13.20	0.68	2.16
6 September	3 Mt. Hortiatis	7.38	27.98	26.91	30.40	8.47	6.24	0.62	2.24
13 October	4 Perea	9.10	12.12	29.44	25.29	14.18	18.98	0.82	1.88
15 December	5 Industrial Area	4.04	22.05	16.24	25.32	20.05	16.34	0.84	2.50
1994									
3 February	6 Kalamaria	6.16	13.28	19.17	25.02	22.35	20.18	1.00	2.31
23 February	7 Oreokastro	3.98	14.96	16.32	28.94	22.40	17.88	0.64	2.24
18 March	8 Panorama	5.92	19.18	24.19	16.16	25.19	15.28	0.97	2.34
12 April	9 Thermi	10.55	19.09	19.89	18.12	30.28	12.62	0.87	2.27
6 May	10 Airport	8.47	12.63	25.95	24.27	23.41	13.72	0.90	2.09
13 June	11 Efkarpia	7.78	23.45	24.53	20.20	20.20	11.63	0.74	237
1 July	12 Asvestohori	9.44	32.02	19.74	22.85	17.28	8.11	0.63	2.39
5 August	13 Neohorouda	10.38	23.30	31.16	26.70	18.84	–	0.64	1.87

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(average 0.80 μm) and the geometric standard deviation (σ_g) varied from 1.87 to 2.50 (average 2.22). The AMAD and σ_g calculations were made by plotting the cumulative distributions on log-normal probability paper. The filter radioactivity, R is expressed in mBq/m³ of air sampled.

DISCUSSION

In a rural region of Sarakina village (site No. 2, Fig. 2), height 250 m , 50 km distant from the city of Thessaloniki, beyond the Mt. Hortiatis (1201 m height), under quite clear (without significant pollution) atmospheric conditions and a relatively dry (precipitation free) climate, the activity median aerodynamic diameter (AMAD) of ⁷Be-aerosols was found to be 0.68 μm, i.e. significantly lower than the mean AMAD (0.90 μm) as determined by eleven measurements carried out at the center of the city of Thessaloniki (site No. 1, Fig. 2). The AMAD of ⁷Be-aerosols at that area was varied between 0.80 and 1.20 μm (Papastefanou and Ioannidou, 1995).

In highland, height 1201 m (site No. 3, Fig. 2), at theTop of Kissos, 50 km distant from the city of Thessaloniki, the AMAD of ⁷Be-aerosols was found to be 0.62 μm, which is comparable to that of the rural area (site No. 2, Fig. 2), reflecting clear atmospheric conditions. At sites No. 2 and No. 3 of Fig. 2, SO_2 concentrations in air were significantly low as compared with corresponding values at the city center of Thessaloniki (site No. 1, Fig. 2) according to the measurements of the Laboratory of Atmospheric Physics, Aristotle University of Thessaloniki (Zerefos, 1994, personal communication).

In a coastal area of Thermaikos Gulf (site No. 4, Fig. 2), at Perea village, near the Airport (site No. 10, Fig. 2), 25 km distant from the city of Thessaloniki, under atmospheric conditions of the marine environment, the AMAD of ⁷Be-aerosols was found to be 0.82 μm and shifted to higher particle size range. This was due to the air masses transported air pollutants by the local wind blown from NW to SE on one hand and on the other hand to the pollutants of traffic of aircrafts particularly during landing and/or take off.

Sites where the AMAD values of ⁷Be-aerosols were varied between 0.62 and 0.74 μm were located on a line with direction from NW to SE (see the dotted line in Fig. 2). That line crosses the direction of the stream-lines from NW, where the industrial area (sites No. 5, Fig. 2), the main source in producing air pollutants, to SE (sites No. 4 and 10 up to the sites No. 9 and 8, including the site No. 6, in the suburban area, Fig. 2). Below the dotted line, the AMAD values of ⁷Be aerosol were varied between 0.82 and 1.00 μm, that is significantly higher than that observed above the dotted line where the AMAD values varied between 0.62 and 0.74 μm.

It is concluded that the AMAD in the activity size distribution of ⁷Be-aerosols in ambient air is shifted to large particle sizes in the presence of air pollutants. Removal of small aerosol particles in the submicron size range of the activity size distribution either by scavenging or by deposition of particles on any surface may result in a depletion of small particles in the activity size distribution.

Subsequent ⁷Be condensation on all aerosols effectively enriches large particles in the activity size distribution.

The radioactive aerosol is only generated by attachment and there is no nucleation, in contrast to the surface aerosol (nucleation + attachment) (Hopke, 1991). Freshly produced ⁷Be should attach to an existing aerosol or coagulate with other nuclei during its lifetime, as mean attachment half-lives are of the order of a minute less (Porstendörfer and Mercer, 1980; Porstendörfer *et al*., 2000; Grundel and Porstendörfer, 2004).

Furthermore, the ⁷Be activity size distribution was associated with a small size range of aerosol particles with AMAD 0.62 μm at height 1200 m, and with AMAD 0.68 μm at height 250 m showing a dependency of the AMAD of ⁷Be-aerosols on height. In marine environment, zero height, the ⁷Be activity size distribution was associated with relatively higher size range of aerosol particles (sea-spray) with AMAD 0.82 μm, thus confirming the dependency of the AMAD of ⁷Be-aerosols on height.

CONCLUSIONS

The atmospheric behavior of ⁷Be-aerosols in association with atmospheric pollutants was studied in the suburban area of Thessaloniki, Northern Greece (40°N, 22°E). The activity of ⁷Be, a radionuclide of cosmogenic origin, was largely associated with submicron aerosol particles in the accumulation mode (0.4–2.0 μm). The activity median aerodynamic diameter (AMAD) of ⁷Be-aerosols ranged from 0.62 to 1.00 μm (average 0.80 μm). The geometric standard deviation, σ_g ranged from 1.87 to 2.50 (average 2.22). Low AMAD values of ⁷Be-aerosols have been observed at locations characterized with relatively low pollution. Some dependency of AMADs on height from the ground surface varied from zero to 1201 m has also been observed with high AMAD values in zero height where the pollution was high and low AMAD values in high elevation where the pollution was low. In near marine environment where the airport is located, an area with additional pollution, the activity size distribution of ⁷Be-aerosols was observed in higher size range of aerosol particles (0.82–0.90 μm).

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