

CESIUM, AMERICIUM AND PLUTONIUM ISOTOPES IN GROUND LEVEL AIR OF VILNIUS

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Systematic observations of radionuclide composition and concentration in the atmosphere have been carried out at the Institute of Physics in Vilnius since 1963. Increases in activity concentration of radionuclides in the atmosphere were observed after nuclear weapon tests and the Chernobyl NPP accident. At present the radiation situation in Lithuania is determined by two main sources of radionuclides, forest fire and resuspension products transferred from highly polluted region of the Ukraine and Belarus. The activity concentrations of ^{137}Cs were measured in two to three days samples while plutonium and americium in monthly samples. The extremely high activity concentrations of ^{238}Pu , $^{239,240}\text{Pu}$, ^{241}Am determined in the atmosphere during the Chernobyl accident can be explained by transport of "hot particles" of different composition. Activity concentration in 1995–2003 of ^{241}Am and $^{239,240}\text{Pu}$ isotopes ranged from 0.3 to 500 and from 1 to 500 nBq/m³, respectively. $^{238}\text{Pu}/^{239,240}\text{Pu}$ activity ratio in measured samples differs from 0.03 to 0.45. A decrease in $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratio from 0.30 to 0.19 was observed in 1995–2003.

1 Introduction

The discovery of nuclear fission and the development of nuclear weapons and nuclear energy have caused significant releases of radionuclides into the environment. To evaluate the consequences of contamination, the information on total activity, activity concentration, and the physical chemical characteristics of released radionuclides is necessary. Following the Chernobyl accident, many measurements of gamma, beta and alpha emitters in aerosol samples were made in Vilnius [1]. However, the highly contaminated territories of the Ukraine and Belarus after the Chernobyl accident still remain potential sources of radioactive contamination not only because of resuspension but also as a result of the transfer of forest burning products. Half of the highly contaminated 30 km restricted Chernobyl zone is covered by forest. Two hundred forest fires occurred in this zone from 1992 to 1994, resulted in destruction of 2.4–3.9 10^3 ha of forest [2]. Activity concentration of ^{137}Cs in the Chernobyl zone in 1992 before and after these forest fires increased only by factor 5: however, the increase in activity concentration of ^{137}Cs by the factor 100 during forest fire was determined in Vilnius. Transport of combustion products after the forest and peat bog fires in Belarus resulted in the increase in the activity concentration of ^{137}Cs in Vilnius in 1996 and 2002. In addition, about 550 000 tons of firewood originated from local forests contaminated by radionuclides are annually utilized in 80 000 dwelling houses of rural settlements in Belarus. In contaminated territories, more than 600 wood-fire boilers are currently operated without flue gas filtration systems [3]. The emission of radiocesium from combustion of contaminated firewood can also

contribute to the radiological situation in Lithuania. The analysis of activity concentrations, meteorological situation, types of particle are important for understanding the sources and possible impact on given location.

2 Methods

Aerosols were sampled by pumping large volumes of air through perchlorovinyl filters. The ground level air samples were collected in the forested areas on the outskirts of Vilnius. Filters were exposed in a special building with blind walls at the height of 1 m above the ground. High volume samplers with flow rates from 2400 m³/h to about 6000 m³/h were used. The sampling was carried out continuously and monthly periods were covered completely. The radiochemical analyses were performed on monthly (total volume ~2.0 × 10⁶ m³) samples of aerosol ashes (about 30 g). For separation of Pu isotopes the TOPO/cyclohexane extraction and radiochemical purification using UTEVA resin were used [4], Am was separated after TOPO/cyclohexane extraction using TRU and TEVA resins (100–150 μm) [5]. Some separations of Pu isotopes from the samples were performed using the AG1–4 anion exchange resin (100–200 mesh). ²⁴²Pu and ²⁴³Am were used as tracers in the separation procedure. The alpha spectrometry measurements of Pu and Am isotopes deposited on a stainless steel disc were carried out with the Alphaquattro (Silena) spectrometer. The ²⁴⁰Pu/²³⁹Pu atomic ratio was determined by ICP–MS (ELEMENT-2). ¹³⁷Cs was determined by gamma-ray spectrometry using a high purity HPGe detector (resolution – 1.9 keV/1.33MeV, efficiency – 42%). Accuracy and precision of analysis were tested using reference materials IAEA-135, NIST SRM No 4350B and 4357 as well as in intercomparison runs, organized by the Riso National Laboratory, Denmark (mineral, sea and lake water matrices). Precision of ¹³⁷Cs measurements by gamma spectrometry was ≤ 7 % at 2σ, Pu ≤ 8 %, Am ≤ 10 %. For the determination of the radionuclides bound in aerosols, the Tessier sequential extraction method [6] was used.

3 Results and Discussion

After the Chernobyl accident a great amount of radioactive substances was emitted to the atmosphere. Measurements carried out in many countries showed differences not only in the ratio of contaminating radionuclides but also in their speciation. Depending on the distance from Chernobyl and transport peculiarities, the contamination contained different proportions of condensed material and fuel components. An increase in radionuclide concentrations was registered in Vilnius on 26 April 1986. Two maxima of ¹³⁷Cs concentrations were observed: on 28–29 of April with 8200 mBq/m³ and on 30 April 8 h 42' – 14 h 30' with 27900 mBq/m³. The highest activity concentrations of ^{239,240}Pu, ²³⁸Pu, and ²⁴¹Am were also determined in aerosol samples collected on 30 April 8 h 42' – 14 h 30'.

Extremely high activities of ^{239,240}Pu found in sample collected on 30 April 1986 can be explained by the presence of “hot particles” of 0.37–22.2 μm size and, among them, “hot particles” of 0.7–2 μm containing the alpha emitting radionuclides (²³³U, ²³⁴U, ²³⁵U, ²³⁸Pu, ²³⁹Pu, ²⁴⁰Pu, ²⁴¹Am, ²⁴²Cm, ²⁴⁴Cm) [1]. This analysis was performed without replicate because of a limited amount of available filter material when radiochemical analy-

ses on Am and Pu nuclides were performed. Despite the fact of high density of fuel particles and our strong opinion that they could not be transported over long distances, the “hot particles” were found widely over the world. The presence of “hot particles” in Vilnius atmosphere was determined using radiography. Sequential extraction indicated two fractions of Am and Pu in aerosol samples and an increase in the amount of Pu and Am associated with organic matter by a factor of 10 in the most active samples. The possible explanation of these findings could be the formation of carbonaceous particles of lower density and different structure during the fire of the damaged reactor, which provided the long distance transport of plutonium isotopes.

In recent years, the Chernobyl-origin radionuclides have been detected in the Lithuanian atmosphere. A considerable ^{137}Cs concentration in the atmosphere was registered on 31 August – 1 September 1992 (up to $300\ \mu\text{Bq}/\text{m}^3$) and on 6–7 September ($190\ \mu\text{Bq}/\text{m}^3$). It should be noted that extensive forest fires in the 30-km exclusion zone of the Ukraine during May – August 1992 resulted in release of radionuclides into the atmosphere. Additional analyses of the situation, namely of the air mass trajectories, allowed identification of this sample as due to transfer of resuspended particles after a dust storm. In 1996 the maximum concentration of ^{137}Cs was observed in April. The mean monthly concentration was $25.9\ \mu\text{Bq}/\text{m}^3$, but in two days samples, it increased up to $253\ \mu\text{Bq}/\text{m}^3$ (09. 04. 1996). The comparatively high percentage of water-soluble (about 63%) and exchangeable (about 20%) ^{137}Cs was found in this sample originated from forest fires. The last event of transport of products of forest fires was registered 6–9 September 2002 after extensive fire in the forests and peat-bogs of Belarus (Fig. 1). Speciation of radionuclides in the atmospheric aerosols was investigated, and compared with that determined in 1996 and after the Chernobyl accident (Fig. 2). The high solubility was characteristic of cesium aerosols transported to Lithuania after forest fires in the Ukraine and Belarus. 30% of ^{137}Cs was associated with particles $>0.2\ \mu\text{m}$ and 20% of this amount was found in the exchangeable fraction. It should be noted that about 90 % of water-soluble ^{137}Cs was present in anionic form in samples of September 2002, contrary to other analyzed samples where cesium was found to be Cs^+ (Fig. 3). In addition, ultrafiltration indicated that 60% of ^{137}Cs passed through 100, 50, 30, 10 and 5 kDa filters (Fig. 4). The presence of low molecular weight, organically bound ^{137}Cs can be suggested. However, it is rather difficult to explain the origin of organically bound cesium because the formation of com-

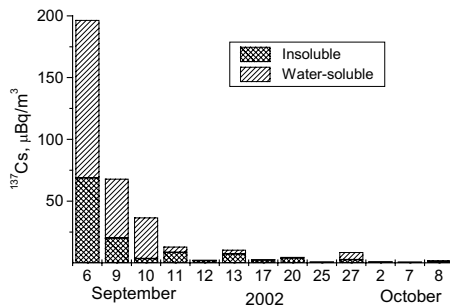


Fig. 1. Activity concentration and speciation of ^{137}Cs in aerosol samples in 2002 in Vilnius.

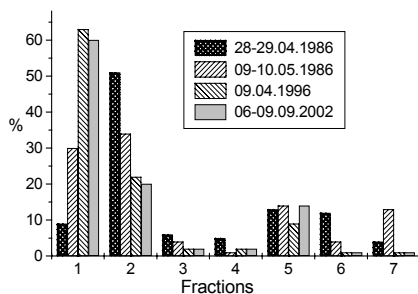


Fig. 2. Fraction distribution of ^{137}Cs in aerosol samples collected in Vilnius (1-water-soluble), 2-exchangeable (1 M NH_4Cl), 3-carbonates, 4-oxides, 5-organic, 6-acid-soluble, 7-residue)

plexes between cesium and organic ligands is very weak. Nevertheless, the association of ^{137}Cs with organic substances of the molecular weight of 800 was found in soil solutions of the samples collected within the 10 km Chernobyl zone in 1994 [7]. Our results obtained during the forest fire sampling indicated that during fires a great amount of sub-micronic ($<0.2\ \mu\text{m}$) aerosol carriers of ^{137}Cs was formed. In separate aerosol samples collected in a highly contaminated Briansk region (Russia) during the active fire experiment over 40 % of water-soluble and exchangeable submicron aerosol particles of ^{137}Cs of 0.1-0.4 μm contributed to the total aerosol [8]. On the other hand the heating of highly contaminated Chernobyl soil indicated insignificant losses of ^{137}Cs below 900°C (less than 2%) and repeated heating did not increase the losses [9]. It means that ^{137}Cs associated with biomass (e.g. grass, fir needles, moss, peat) contributes mainly to the radioactive aerosol generated during forest fire. These results were confirmed by experiments carried out in different laboratories. It was shown that about 95% of fine particles forming during combustion of contaminated biomass had the size of 0.1-0.4 μm [3]. Experiments with burning of fir needles indicated formation of aerosol particles of ^{137}Cs in the range of 0.62 – 0.72 μm below $600\text{-}700^\circ\text{C}$ [10]. Moreover, the formation of particles smaller than 0.7 μm was found in burning products of needles and grass. However, the data on the integral airborne activity concentrations and deposition flux of radionuclides indicated that only 2 – 5% of released ^{137}Cs contributed to the deposition to the soil. The large

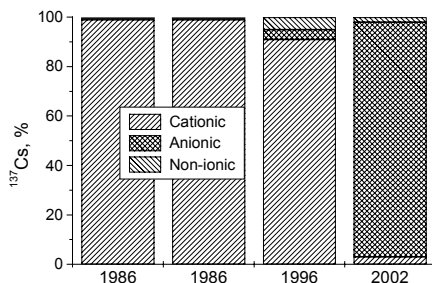


Fig. 3. Speciation of ^{137}Cs in water-soluble fraction of aerosol samples in Vilnius

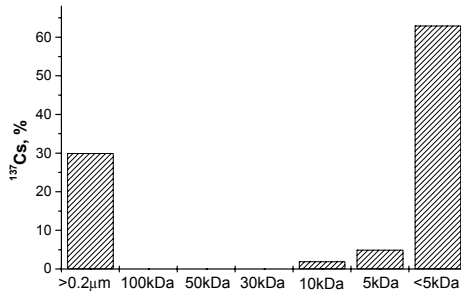


Fig. 4. ^{137}Cs retained (%) by 0.22 µm membrane filter (Millipore), Omegacell of 100 kDa, 50 kDa, 30 kDa (Filtron) and Amicon centrifugal filters Centricon Plus-80 with Ultracel-PL membrane of 10 kDa and 5 kDa (Millipore)

variations observed in the size distribution, chemical composition and content of elements in the aerosol generated in different forest fires were attributed to the combustion conditions (object, temperature, humidity and intensity of fire) [11].

Thus, emission of cesium to the atmosphere can take place during combustion of biomass but not by heating contaminated soil. In addition, the temperature regime of forest fires and perhaps burning of grass can affect the speciation of ^{137}Cs towards more available and complex forms and can affect the circulation of ^{137}Cs in the environment. On the other hand, the increase in temperature up to 900°C probably facilitates a clay interlayer collapse or may cause clay mineral degradation, resulting in fixation of ^{137}Cs [9].

The measurements carried out on aerosol samples collected in Vilnius in 1995–2003 indicated the presence of alpha emitting radionuclides. The activity concentrations of $^{239,240}\text{Pu}$ and ^{241}Am ranged from 1 to 500 and from 0.3 to 500 nBq/m³, respectively.

In some samples the activity ratio of $^{238}\text{Pu}/^{239,240}\text{Pu}$ was found to be close to the Chernobyl ratio. The determination of $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratio confirmed the presence of the Chernobyl derived plutonium (Fig. 5). The activity concentrations of actinides in monthly samples could not be traced back via the backward trajectories precisely; however, the transport from contaminated territories was obvious. The atomic ratio of $^{240}\text{Pu}/^{239}\text{Pu}$ in samples collected in April 1996 and September 2002 was found to be 0.229 and 0.185, respectively. The high plutonium activities and atomic ratios were detected in

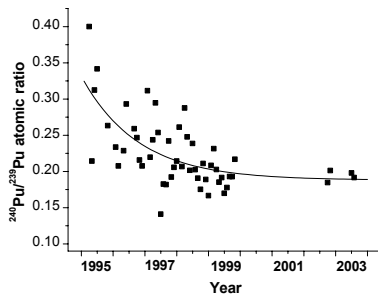


Fig. 5. $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratio in monthly aerosol samples in 1995–2003

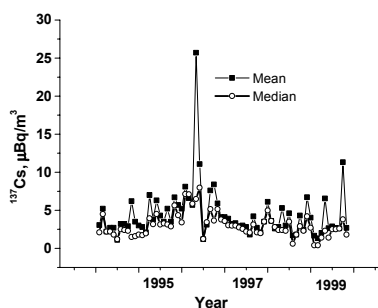


Fig. 6. Mean and median activity concentrations of ^{137}Cs in aerosol samples in 1994-1999 samples collected during periods with high frequencies of air transport from contaminated regions.

In order to evaluate a possible transport of alpha emitting radionuclides from the Chernobyl restricted zone the size distribution of aerosol particles and the speciation of Pu and Am in aerosol and in soil samples were measured in samples collected in the 30-km Chernobyl zone. The size distribution of ^{137}Cs , ^{241}Am and $^{238, 239, 240}\text{Pu}$ differed from 4 to 8 μm [12]. Speciation and size distribution of radionuclides determined in these samples indicated that they originated from resuspension. We suppose that resuspended soil can be the source of aerosol particles carrying plutonium with high activity.

It was reported that pure fuel particles of the size $< 5 \mu\text{m}$ can not be transported outside the 10 km of the Chernobyl zone [13]. An estimation of the size distribution of “hot particles”, unfortunately rather approximate, indicated the possible presence of particles of 2–0.5 μm in the aerosol samples with very high specific alpha activity ($> 10^5 \text{ Bq/cm}^3$). It is obvious that these particles can be transported over long distances and can cause the increase in the activity ratio and the activity concentration of plutonium. It should be noted that an obvious decrease in $^{239}\text{Pu}/^{240}\text{Pu}$ atomic ratio from 0.30 to 0.19 (mean values) was observed in 1995-2003. It can be interpreted as the result of decrease in the amount of the Chernobyl originated plutonium in the environment but the variations of the cesium activity concentrations showed a different behavior in the environment (Fig. 6). This observation can be explained by the effect of forest fires and possibly by emission of radiocesium from the combustion of contaminated firewood.

4 Conclusions

Transport of forest fire products from highly contaminated regions of the Ukraine and Belarus is responsible for an increase in activity concentrations of ^{137}Cs in the atmosphere and in the bioavailable (water-soluble and exchangeable) fraction of this nuclide. Forest fires affect the circulation of ^{137}Cs in the environment and could be considered as a possible mechanism of redistribution of radioactive contamination from one region to another.

The presence of “hot particles” and their heterogeneous distribution in aerosol samples collected in Vilnius during the Chernobyl accident could result in the high activity

concentrations of ^{238}Pu , $^{239,240}\text{Pu}$ and ^{241}Am determined in aerosol samples in 1986. High activity $^{238}\text{Pu}/^{239,240}\text{Pu}$ and $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratios found in some samples can be attributed to the transfer of resuspended submicronic particles from highly contaminated region after the Chernobyl accident.

Different behavior of plutonium isotopes in comparison with cesium ones was observed. The atomic ratio of $^{240}\text{Pu}/^{239}\text{Pu}$ in aerosol samples collected after forest fires in Vilnius was close to the global fallout (0.229 and 0.185). Moreover, the clear decrease in $^{240}\text{Pu}/^{239}\text{Pu}$ atomic ratio down to the global fallout value was determined in 1995-2003.

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