Impact of geochemical surroundings on the distribution of ^{239,240}Pu in soil at the Baltic seaside

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In order to investigate ^{239,240}Pu specific activity distribution, in 1994, 1996 and 1999 sampling of beach sand and forest soil (0–5 cm) at Juodkrantė was performed. The sampling grid was composed in such a mannier that an about 5 km^2 area from the Baltic Sea to the Curonian Lagoon contained 100 sampling points. After the initial treatment of the samples and radiochemical analysis, plutonium isotopes ^{239,240}Pu and ^{242}Pu (the latter was used as a tracer) were identified by the alpha spectrometric method. The content of stable elements K, Fe, Mg, Mn, Cd, Sr, Ni, Cu, Co, Pb, Zn, Cr in the samples collected in 1996 was determined by the AAS method. Data analysis showed that there were some sites in the study area where Cd, Sr, Ni, Cu, Co, Pb levels were lower than the AAS sensitivity limit. The average values of ^{239,240}Pu specific activity in forest soil were found to be higher than those on the beach (Fig. 1). The higher level of ^{239,240}Pu specific activity in sand samples was observed in the surf zone and on the top of dunes than in the other sites of the beach. The following average values of ^{239,240}Pu specific activity were determined: 0.24 Bq/kg for sand opposite and beyond the dune; 0.37 Bq/kg for sand on the top of the dune; 0.26 Bq/kg at the surf zone. In the forest soil layer of 0–5 cm, ^{239,240}Pu concentration ranged from 0.09 to 2.40 Bq/kg. The obtained results are in agreement with the background values of the concentrations of stable elements and ^{239,240}Pu indicated in scientific literature. An analogous tendency of ^{239,240}Pu, Fe and Cu concentration change was observed (Figs. 3, 4). The dependence of ^{239,240}Pu specific activity on the organic matter content in the samples is described by the regression equation ^{239,240}Pu = 0.0087 org.m. + 0.3264.

Key words: plutonium isotopes, trace metals, sampling grid, beach sand, forest soil

INTRODUCTION

Plutonium was established by a group of American scientists [5, 7] in 1940 as a result of bombardment of uranium by deutons:

$$_{92}U^{238}\ (d, 2n)\ _{93}Np^{238} \xrightarrow{\beta^-} {}_{94}Pu^{238} \xrightarrow{\alpha} \quad (1)$$

Kennedy J. W., Seaborg G. T., Serge E., Wahl A. C. [5] ^{239}Pu, discovered another plutonium isotope:

$$_{92}U^{238}\ (n,\gamma)\ _{92}U^{239} \xrightarrow{\beta^-} {}_{93}Np^{239} \xrightarrow{\beta^-}$$

$$_{94}Pu^{239} \xrightarrow{\alpha} \quad (2)$$

Later, production of ^{239}Pu by this reaction was undertaken on an industrial scale [10]. On the whole, there are known 15 man-made plutonium isotopes which are all radioactive, and in nature natural plutonium isotopes practically do not exist. The role of separate artificial plutonium isotopes in nuclear technology, analytical chemistry and chemical investigations is not identical. ^{238}Pu is used as an isotopic source of energy for artificial Earth satellites and cosmic liners. ^{239}Pu and ^{241}Pu are mostly used for production of nuclear fuel and nuclear weapons. Besides, ^{239}Pu and ^{244}Pu are perspective for chemical investigations. Referring to aforementioned, the crash of satellites, accidents at nuclear power plants (NPP) or testing of nuclear weapons in the atmosphere can cause a release of plutonium isotopes to the environment on a global scale. Generally, ^{239}Pu, ^{240}Pu, ^{238}Pu, ^{241}Pu have got into the ecosystems of Lithua-

nia as a consequence of nuclear weapon trials in 1945–1980 (1820 nuclear blastings, 483 among them in the atmosphere), crash of the SNAP-9A satellite in 1964 and the accident at the Chernobyl NPP in 1986. Being long-lived, these plutonium isotopes once getting into the environmental systems, remain there for a hundred or thousand of years ($T_{1/2}$ of ^{238}Pu – 86.4 yr., ^{239}Pu – 24390 yr., ^{240}Pu – 6620 yr., ^{241}Pu – 14.4 yr.) [11, 8].

Particularly after the Chernobyl catastrophe scientists began to strive for more extensive knowledge about the behavior of radionuclides and mechanisms controlling their migration, accumulation and spreading in different ecosystems. To date, about 95% of plutonium [2] from the atmosphere have settled down on the terrestrial and hydrological systems. Considering the plutonium ability to change the oxidation degree from 3 to 6, and its turn for the complexing or hydrolysis, the geochemical surroundings become the medium that influences the physico-chemical processes of plutonium in soil. Therefore, evaluation of the effect of geochemical surroundings on the aerial distribution of $^{239.240}$Pu in the upper (0–5 cm) forest soil and sand layer was among the goals of this research.

MATERIALS AND METHODS

The site studied in 1994, 1996 and 1999 was the zone between the Baltic Sea and Curonian Lagoon at the resort settlement of Juodkrantė. Free of local pollution sources, the research area included the beach, a pinery beyond the dunes and a pine forest. The sampling grid was 1000 × (5–30) m at the beach and 1000 × (200–500) m in the pine grove. Sampling of the upper layer (0–5 cm) of sand and forest soil was performed using a circular sampler 14 cm in diameter and 5 cm high. Thus, an investigative grid of 100 sampling points in an area of about 5 km^2 was composed. The samples were weighed, dried at room temperature and weighed again when a constant weight was achieved. Soil samples were ground mechanically and all fractions of a sample were included for analysis. The pH was measured in KCl extracts (10 g soil : 25 ml 1M KCl). Organic matter content was determined by loss on ignition at 550 °C for 12 hours. Measurement of stable elements was provided by flame AAS. For this purpose, 1 g of soil samples was wet digested in a HF : : HNO_3 (3 : 1) mixture and finally dry residue was dissolved in 2 ml of conc. HCl and diluted with distilled deionized water to 50 ml.

Radiochemical analysis of plutonium isotopes was based on the extraction of radionuclides from a sample by a mixture of acids, turning plutonium into the tetravalent state with $NaNO_2$, separation from admixtures on the anion exchange resin and final electrolytic deposition of plutonium on a stainless-steel disc at pH 2.2–2.4 in sodium sulphate solution. Alpha spectrometry was performed using a 450 mm^2 passivated ion-implanted silicon detector (α efficiency 20–25%). The chemical yield was determined using ^{242}Pu as a tracer. Alpha resolution 17 keV (FWHM), detection limit of the order of 10^{-3} Bq for $^{239.240}$Pu at a counting time of 86400 s.

RESULTS AND DISCUSSION

Average density values of collected sand samples varied from 1.020 g/cm^3 beyond the dune to 1.884 g/cm^3 in the surf zone, while the density values of forest soil samples were in the range of 0.300–0.970 g/cm^3. Also, as expected, organic matter content in sand samples was from 2.0 to 6.0 g/kg, and in forest soil samples it ranged from 6.0 to 479.3 g/kg. The pH values showed that from the samples of sand washed by the sea water to the samples at the top of dunes varied within 4.63–6.74, with the maximum values in the surf zone. The prevalent pH values of 3.16–3.80 were obtained in the forest soil samples, although at some sampling points the soil was more acidic (pH 2.50–2.98).

Trace metals were analytically detected in the following order: Cd>Sr>Ni>Cu>Co>Pb. Samples in which these metals were determined contained, mg/kg: Cd 0.9–1.9; Sr 3.9–53.9; Ni 3.9–28.1; Cu 0.8–11.4; Co 2.5–11.8; Pb 2.0–58.4. The concentrations (mg/kg) of other elements studied were as follows: Zn 7.8–104.0; Mg 53.0–4146; Mn 10.0–5690; K 5343–16474; Fe 725–21415. All results are in agreement with the values of separate elements in soil presented in [9].

Variations of the average values of $^{239.240}$Pu specific activity showed different levels of this radionuclide accumulation in the upper layer (0–5 cm) of forest soil (Fig. 1). Stripe 5, which was situated

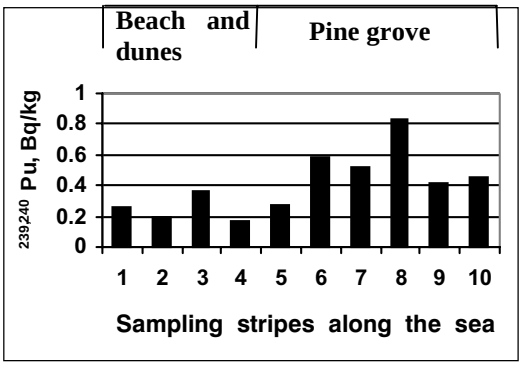

Fig. 1. Distribution of average $^{239.240}$Pu concentrations (Bq/kg) in soil at Juodkrante in summer, 1999.
1 pav. Vidutinių ^{239,240}Pu koncentracijų (Bq/kg) pasiskirstymas dirvožemyje ties Juodkrante 1999 m. vasarą.

before the pineries, according to the $^{239.240}$Pu concentration level could be attributed to the beach area, where the mean value of $^{239.240}$Pu specific activity does not exceed 0.24 Bq/kg. Analysis of this sample series showed the highest $^{239.240}$Pu content at the top of the dunes (section 3) where the mean value of $^{239.240}$Pu concentration reached 0.37 Bq/kg with variation limits between 0.09 and 0.80 Bq/kg. At the foot of a dune from the both sides (sections 2, 4) $^{239.240}$Pu maximum concentration values were 0.41 and 0.30 Bq/kg and the average concentration 0.20 and 0.17 Bq/kg, respectively. A rather high $^{239.240}$Pu concentration was obtained in the surf zone samples (section 1); it ranged in the interval of 0.08 and 0.48 Bq/kg with the mean 0.26 Bq/kg value. Peculiarities of $^{239.240}$Pu distribution pattern in the beach zone show that marine aerosol formation and its transport with air masses could probably influence plutonium spreading processes. Presence of a submicron film with an abundance of radionuclides and other pollutants on the surface of open water reservoirs due to the rough sea as aerosols from foam and spray are transported further inland or fall down near the sea. Dynamic changes of the air stream because of a sudden increase of the surface roughness can be attributed to an increase in plutonium concentration on the top of the dune. The land roughness magnitude was in the order of 10^2–10^4 higher than that of the Sea surface, moreover, wind velocity decreases in 1.4–1.7 times when air masses reach land [1], therefore, the dunes become as a specific barrier to a great extent detaining the further transport of marine air masses. Such a constrained slowdown of air masses favours larger amounts of marine aerosols containing $^{239.240}$Pu falling down on the dune. Significantly higher $^{239.240}$Pu concentrations were determined in the forest soil of pine backwoods with rich vegetation and litter humus in soil (section 8); they varied between 0.09 and 2.40 Bq/kg, mean 0.83 Bq/kg. The mean value 0.50 Bq/kg of $^{239.240}$Pu with variation limits between 0.17–2.10 Bq/kg was observed in soil of section 6. Samples of section 7 contained from 0,08 to 0.92 Bq/kg of $^{239.240}$Pu. The present work suggests that the lower plutonium mobility depending on the higher level of humus in the upper forest soil layer (0–5 cm) causes a higher $^{239.240}$Pu specific activity (Fig. 2). On the other hand, $^{239.240}$Pu concentrations in the upper soil layer of the study region are close to the data of other investigators [3, 6], and the results fall in the indicated background values of $^{239.240}$Pu 0.10–

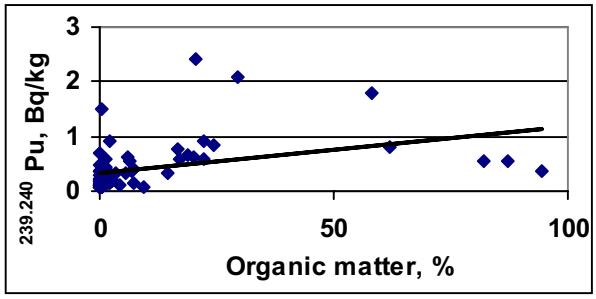

Fig. 2. Relationship between $^{239.240}$Pu specific activity and the percentage of organic matter in samples
2 pav. ^{239,240}Pu savitojo aktyvumo ir procentinio organinių medžiagų kiekio ryšys.

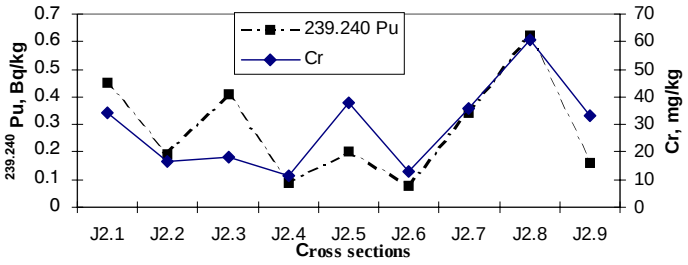

Fig. 3. Changes in $^{239.240}$Pu specific activity and chromium content
3 pav. ^{239,240}Pu savitojo aktyvumo ir chromo kiekio kaita.

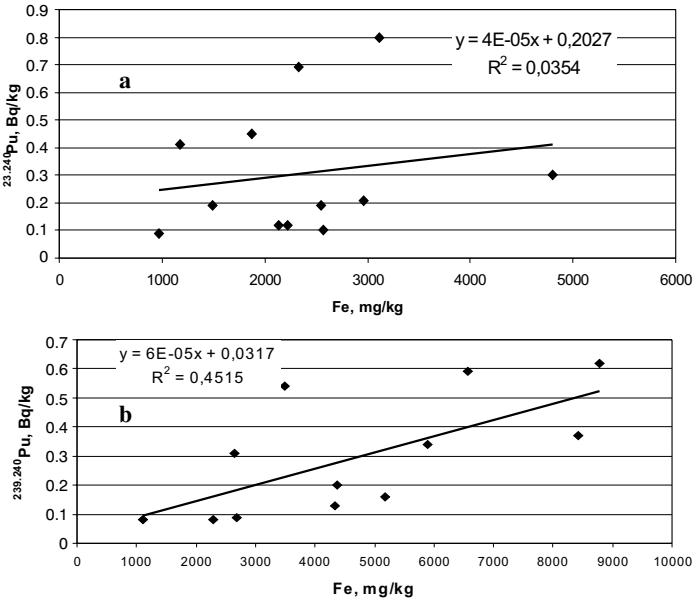

Fig. 4. $^{239.240}$Pu specific activity as a function of iron content (*a* – beach sand, *b* – pine grove soil)
4 pav. ^{239,240}Pu savitasis aktyvumas kaip geležies kiekio funkcija (*a* – paplūdimio smėlis, *b* – pušynėlių dirvožemis)

7.00 Bq/kg in the soil surface [4]. A significant feature in the variation of the $^{239.240}$Pu activity and chromium amount among different sampling sites is the similarity in trends for both substances, and this similarity in behavior is illustrated for the second sampling section (Fig. 3). $^{239.240}$Pu geochemical surroundings with chromium and iron can influence the behavior of this radionuclide due to the formation of insoluble compounds with humic acids by ions of Fe^{2+}, Cu^{2+}, Cr^{2+} or the ability of Fe^{3+}, Al^{3+} to form stable, insoluble in water complexes with fulvic acids. Analysis of the data on $^{239.240}$Pu activity distribution all over the sampling grid and changes in the Fe concentration in sampling sites indicated a tendency of iron content to influence the $^{239.240}$Pu activity level. Calculations gave a slight direct correlation between the $^{239.240}$Pu activity and total iron content in the study area (Fig. 4).

This work is an initial approach to the investigation of the influence of geochemical surroundings of $^{239.240}$Pu distribution in the upper soil layer by means of analysis and comparison of $^{239.240}$Pu specific activity and content of macro- and microelements in this medium. The necessity of further research in this field is evident.

CONCLUSIONS

1. Joint analysis of samples using alpha and AA spectrometries followed by radiochemical analysis allowed us to obtain information on the level of contamination of sand and forest soil (0–5 cm) at Juodkrantė with $^{239.240}$Pu and to determine the amount of Mg, K, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb, Sr, Cd on this territory.

2. Differences in the values of $^{239.240}$Pu concentration in the upper layer of sand and forest soil were evident: 50% of the forest soil samples contained 0.08–0.90 Bq/kg and some samples 2.4 Bq/kg; in 70% of sand samples the $^{239.240}$Pu concentration was from 0.08 to 0.52 Bq/kg.

3. A conditionally high level of $^{239.240}$Pu concentration in a surf zone and on the top of the dune was observed, with variation limits 0.22–0.80 Bq/kg and 0.09–1.50 Bq/kg, respectively.

4. Preliminary results showed a tendency of an analogous course of change in the $^{239.240}$Pu specific activity and the amount of iron and chromium in the research area.

5. In the samples studied, $^{239.240}$Pu specific activity as a function of organic matter content can be described by the regression equation: $^{239.240}$Pu = 0.0087 org. m. + 0.3264.

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GEOCHEMINĖS APLINKOS ĮTAKA ^{239,240}PU PASISKIRSTYMUI PAVIRŠINIAME DIRVOS SLUOKSNYJE BALTIJOS PAJŪRYJE

S a n t r a u k a

1994, 1996 ir 1999 m. buvo renkami paplūdimio smėlio ir pušyno dirvožemio (0–5 cm) bandiniai ties Juodkrante. Bandinių paėmimo tinklelis sudarytas taip, kad ~5 km^2 plote nuo Baltijos jūros iki Kuršių marių buvo 100 bandinių paėmimo taškų. Po bandinių pradinio apdorojimo bei radiocheminės analizės alfa spektrometrinės analizės metodu buvo identifikuojami plutonio izotopai ^{239,240}Pu ir ^{242}Pu, pastarasis buvo įdedamas į bandinį radiocheminio

išskyrimo efektyvumui įvertinti. 1996 m. bandiniuose AA spektrometru nustatytas ir stabilių elementų K, Fe, Mg, Mn, Cd, Sr, Ni, Cu, Co, Pb, Zn, Cr kiekis. Duomenų analizė parodė, kad tiriamajame plote yra vietų, kuriose Cd, Sr, Ni, Cu, Co, Pb kiekis mažesnis už AAS jautrio slenkstį. ^{239,240}Pu savitojo aktyvumo vidutinės vertės pliažo zonoje mažesnės negu miško dirvožemyje (1 pav.). Pažymėtina, kad ^{239,240}Pu savitasis aktyvumas jūros vandens skalaujamoje zonoje ir kopų viršūnėje yra didesnis negu kitose pliažo vietose. Pliažo zonoje, išskyrus vandens skalaujamą juostą bei kopų viršūnes, taip pat pušynėlio ir kopų pradžioje vidutinė ^{239,240}Pu savitojo aktyvumo vertė buvo ne didesnė negu 0,24 Bq/kg. Kopos viršūnėje vidutinė ^{239,240}Pu savitojo aktyvumo vertė gauta 0,37 Bq/kg, o jūros vandens skalaujamoje juostoje 0,26 Bq/kg. Pušyno dirvožemio paviršiniame 0–5 cm sluoksnyje ^{239,240}Pu koncentracija buvo nuo 0,09 iki 2,40 Bq/kg. Gauti rezultatai atitinka mokslinėje literatūroje nurodomas cheminių elementų ir ^{239,240}Pu koncentracijų fonines vertes. Analizuojant gautus rezultatus pastebėta ^{239,240}Pu, Fe ir Cr koncentracijų panašaus kitimo tendencija (3, 4 pav.). ^{239,240}Pu savitojo aktyvumo verčių kitimo priklausomybė nuo organinių medžiagų kiekio bandiniuose aprašoma regresijos lygtimi: ^{239,240}Pu = 0,0087 org.m. + 0,3264.

Raktažodžiai: plutonio izotopai, žymėtieji metalai, bandinių rinkimas, paplūdimio smėlis, miško dirvožemis