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GEOPHYSICS

First Evidence for Concentrations of Transuranium Curium in the Yenisei Floodplain Ecosystem

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The long-term activity of the Mining–Chemical Plant (MCP) of the Federal Agency for the Atomic Energy of the Russian Federation (Rosatom) in Zheleznogorsk, Krasnoyarsk region resulted in pollution of the Yenisei River [1–4]. The radiochemical study of bottom sediments of the Yenisei River revealed in its channel segments concentrations of transuranium elements (^{238}Pu, ^{239,240}Pu, ^{241}Am) tens of times higher than the previously published data [1] and 100 times higher than the global background value. The previously performed determinations of concentrations of transuranium elements (particularly, ^{241}Pu and ^{237}Np) in bottom sediments have shown that their activity remains high over a distance as long as 200 km downstream from the MCP [3]. Occurrence of bottom sediment layers with anomalously high activity of transuranium elements (^{239,240}Pu up to 280 Bq/kg and ^{241}Pu up to 1430 Bq/kg) testifies to both a high migration ability of actinoids in the river ecosystem and ongoing discharge of technogenic radionuclides from the MCP [3]. The results of radiochemical analyses for transuranium elements have been obtained previously only for bottom sediments, floodplain soil, and hydrophytes of the Yenisei River [1–4]. No data are available for land plants in the Yenisei floodplain.

By analogy with the published data on concentrations of Cm isotopes (^{243,244}Cm) in the soil polluted as a result of the Chernobyl disaster [5–7] and taking into account the production of Cm in plutonium reactors [8], it may be expected that this element is contained in samples near the MCP. However, the data on pollution of the Yenisei floodplain with ^{243,244}Cm isotopes have not been available to date. Curium, a transuranium element with the highest atomic number 96 accessible in gram quantities, is formed by the successive capture of neutrons beginning from ^{239}Pu or heavier isotopes (^{242}Pu and ^{243}Am). ^{243}Cm and ^{244}Cm are rather long-lived isotopes with half-lives equal to 28.5 and 18.1 yr, respectively.

The objective of this study is to estimate the concentration of transuranium Cm in components of the Yenisei floodplain ecosystem near the MCP.

The ecosystem of the Yenisei floodplain was sampled during radioecological expeditions of the Institute of Biophysics, Krasnoyarsk in 2002–2003. The samples were taken close to the main radioactive sewage disposal of the MCP near Artamonovka Settlement at a distance of 88 km downstream from Krasnoyarsk. Cores of bottom sediments and floodplain soils were divided into layers, and the concentrations of radionuclides were analyzed in separate layers. The floodplain soils were sampled at places of blackberry (*Ribes nigrum*) growth. Samples of roots, stems, leaves, and berries taken for the analysis were dried. The specific activity of gamma-radiating nuclides (including ^{147}Cs and ^{241}Am) were measured at the Institute of Biophysics on a Canberra gamma spectrometer (United States) with a superfine Ge detector. The gamma spectra were processed with the CANBERRA GENIE-2000 software package (United States). In order to determine concentrations of alpha-radiating ^{238}Pu, ^{239,240}Pu, ^{241}Am, and ^{243,244}Cm, the radiochemical study of bottom sediments was carried out at the Center of Informational Processes and Technologies (GUP MosNPO Radon).

The dried samples were reduced to ash at 500°C for 7–8 h, up to the complete removal of traces of organic matter. Further, the incinerated samples were treated with concentrated nitric and fluoric acids (20 : 1 in volume) in a MLS 1200 mega laboratory microwave system (Milestone, Switzerland) equipped with vessels made of high-strength TFM Teflon.

Radionuclides ^{242}Pu and ^{143}Pm were introduced into samples as spikes to control the chemical yield of the analyzed elements. The application of eluent chromatography at the final stage of analysis was a specific fea-

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Activity of ^{137}Cs and transuranium elements in samples from the ecosystem of the Yenisei River floodplain, Bq/kg

Material	^{137}Cs[1]	^{238}Pu[2]	$^{239,240}Pu$[2]	^{241}Am[2]/^{241}Am[1]	$^{243,244}Cm$[2]
Bottom sediments[3]					
layer 0–4 cm	413 ± 25	5.9 ± 1.0	41 ± 4	4.0 ± 0.4/8.1 ± 2.0	3.6 ± 0.4
layer 22–25 cm	1600 ± 100	7.4 ± 0.8	98 ± 7	35 ± 3/7 ± 3	21.4 ± 2
Floodplain soil[3]					
layer 0–5 cm	690 ± 40	1.2 ± 0.4	13.7 ± 1.0	2.6 ± 0.2/14 ± 3	1.7 ± 0.4
layer 5–12 cm	1060 ± 60	1.2 ± 0.4	15.6 ± 1.0	5.9 ± 1.5/17 ± 4	1.1 ± 0.5
Blackberry					
roots	33 / 730 ± 60	0.1 / 2.1 ± 1.0	0.42 / 9.3 ± 2.1	0.3/0.5 / 6.9 ± 0.5/12 ± 4	0.08 / 1.8 ± 0.5
stems	22 / 875 ± 80	<3.2	<2.5	0.15/0.32 / 5.8 ± 1.6/13 ± 8	0.02 / 0.9 ± 0.5
leaves	48 / 440 ± 24	<1.0	0.4 / 3.5 ± 1.5	0.3/<20 / 3.1 ± 0.6/<20	0.05 / 0.5 ± 0.2
berries	40 ± 3 / 1040	<4.0	0.1 / 2.5 ± 1.5	<21/15 ± 3 / –	0.03 / 0.7 ± 0.3

Note: (1) Gamma spectrometry data, Institute of Biophysics, Krasnoyarsk; (2) radiochemical data, MosNPO Radon, Moscow; (3) dry samples of bottom sediments and soil. Blackberry samples: results for dry and ash samples are shown in the numerator and denominator, respectively.

ture of the new method proposed for determination of transuranium elements. Thereby, radionuclide ^{143}Pm is used as a reference point for Cm and Am peaks in the chromatogram. In this process, Pm is eluated between Cm and Am, partly overlapping each nuclide [9]. Thus, we rule out the necessity to use ^{243}Am and other isotopes, which may be contained in the sample, as marks of chemical yield of alpha-radiating radionuclides.

The ion-exchange chromatography on a column filled with Dowex 1 × 4 anionite was used for separation and purification of plutonium. Macrocomponents and the main portion of interfering radionuclides were eluated successively with 7.5 M HNO_3 (U, Po, Pa) and 9 M HCl (Th); Pu was eluated from column with 0.36 M HCl with addition of H_2O_2. The final purification of Pu was performed by extraction with 0.2 M TTA (tenoyltrifluoracetone) in toluene from 1 M HNO_3 solution. After decomposition of organic residues, Pu was precipitated electrochemically from an ammonium oxalate-chloride solution at pH = 2.2–2.5 on polished stainless steel discs that subsequently served as sources for alpha spectrometry.

Transuranium elements (Am and Cm) were concentrated from a filtrate obtained at the first stage by the successive precipitation of oxalates and iron hydroxide. Further removal of Fe and U from the specimen was carried out by filtration through a column in 9 M HCl. The ultimate purification was performed by extract chromatography on the column filled with a stationary phase (a mixture of dialkyl carbamoylmethylphospine oxide and tributyl phosphate) represented by TRU resin (Eichrom Ind. Inc., United States) and by the subsequent eluation from the column with 4 M HCl. After a concentration of eluates by boiling and breakdown of organic remains, Am and Cm were precipitated electrochemically from ammonium oxalate–chloride solution at pH = 2.2–2.5 on polished stainless steel discs that subsequently served as sources for alpha spectrometry. ^{143}Pm also precipitated on discs in the course of this procedure. To determine chemical yield, the activity of ^{143}Pm on the discs was preliminarily measured with a gamma spectrometer.

The spectrometric measurements designed for the calculation of concentrations of alpha-radiating Pu, Am, and Cm isotopes were carried out on a Canberra alpha-spectrometric complex (United States). These isotopes cannot be separated reliably with alpha spectrometry because of similar energies of alpha radiation: ^{243}Cm (5742 keV, 11.5%; 5785 keV, 73.3%; and 5993 keV, 5.6%) and ^{244}Cm (5763 keV, 23.6%; 5805 keV, 76.4%). Therefore, the summary concentration of $^{243,244}Cm$ is given in this paper.

The gamma spectrometric measurements have shown that samples of bottom sediments and floodplain soils contain europium isotopes (^{152}Eu, ^{154}Eu, and ^{155}Eu), cesium isotopes (^{137}Cs and ^{134}Cs), and ^{60}Co; ^{241}Am was detected occasionally. Thus, the list of technogenic gamma-radiating radionuclides in our samples corresponds to the set of radionuclides analyzed previously [1–4]. Results of both gamma spectrometry and radiochemical study show that the layers with maximal activity of gamma-radiating Cs and Eu isotopes reveal the highest concentrations of Pu and Am isotopes [3]. Therefore, we focused our attention in the process of

further research on the radiochemical study of particular layers of bottom sediments, which stand out by the maximal activity of radionuclides (including ^{241}Am) detected by gamma spectrometry, e.g., the bottom sediment layer cored at a depth of 20–25 cm from the surface. Additionally, we carried out the radiochemical study of samples from the surface layer (0–4 cm).

As follows from the table, the maximal activity of ^{239,240}Pu and ^{241}Am in the surface layer of the bottom sediment core is 41 and 4 Bq/kg, respectively. The radiochemical analysis yielded similar concentrations of ^{243,244}Cm and ^{241}Am. The bottom sediment layer at a depth of 22–25 cm with the highest concentrations of gamma-radiating radionuclides is also characterized by maximum concentrations of all transuranium elements. However, the ^{239,240}Pu concentrations in this layer increased 2.4 times in comparison with the surface layer of bottom sediments, while the ^{241}Am and ^{233,244}Cm concentrations increased 9 and 6 times, respectively. The ^{233,244}Cm concentration in the deep layer of bottom sediments amounts to 21.4 Bq/kg (table). Concentrations of all studied transuranium elements in floodplain soils are lower than those in bottom sediments. In floodplain soils, the highest ^{239,240}Pu and ^{241}Am concentrations (15.6 and 5.9 Bq/kg, respectively) were recorded in layer 5–12 cm. At the same time, the ^{243,244}Cm concentration is only 1.7 Bq/kg, which is two times lower than that in the surface layer of bottom sediments. According to the published data on Cm concentrations in samples of soils affected by radioactive fallout after the Chernobyl APS disaster, the maximal activity of ^{243,244}Cm (10 Bq/kg) was recorded in Belarus [5]. The Cm concentration in soils of Finland and Poland is much lower (0.25 Bq/kg) [6, 7]. Therefore, our data on maximum concentrations of Cm isotopes (21.4 Bq/kg) in bottom sediments of the Yenisei River is two times higher than the available data on maximum Cm concentrations in soil samples from the Chernobyl disaster area.

As noted above, floodplain soil samples were taken from places of blackberry (*Ribes nigrum*) growth. Therefore, it was reasonable to expect the input of technogenic nuclides from soil into plants. We analyzed roots, stems, leaves, and berries. The table shows concentrations of transuranium elements and ^{137}Cs in the different parts of the plants. The results pertain to both the dry biomass and the ash of plants. The ^{241}Am concentration was estimated by gamma spectroscopy and alpha spectroscopy with radiochemical separation of this radionuclide. It should be noted that the radiochemical study provides a higher accuracy in the measurement of ^{241}Am, but a smaller charge of biomass (up to 10 g) is used. In the gamma spectrometric determination of ^{241}Am, the total charge (tens and hundreds of grams of biomass) is used, but uncertainty may reach 50%. As was expected on the basis of determination of radionuclides in soils, the plants also contain the same list of transuranium elements (Pu, Am, and Cm isotopes). Since the radiochemical study and alpha spectrometry were carried out for ash samples, the maximum concentrations of all transuranium elements per ash biomass unit in blackberry roots amounts to 9.3 Bq/kg for ^{239,240}Pu, 6.9 Bq/kg for ^{241}Am, and 1.8 Bq/kg for ^{243,244}Cm. Concentrations of transuranium elements in stems and leaves are almost two times lower. The specific ^{243,244}Cm activity is 0.5–0.9 Bq/kg of ash. Concentrations of ^{239,240}Pu and ^{243,244}Cm in berries are equal to 2.5 and 0.7 Bq/kg of ash, respectively. Occurrence of ^{241}Am in berries is corroborated only by the gamma spectrometric results pertaining to large charges of dry biomass. Thus, the ^{243,244}Cm isotopes are recorded in all parts of blackberry, and no significant differences are observed in the distribution of Cm isotopes in various parts of the plant.

To estimate intensity of transition of radionuclides from the soil layer into the plant, the available literature recommends using a transition coefficient (TC) equal to the ratio of radionuclide concentration (Bq/kg) in biomass of plant (or its separate parts) to the radionuclide concentration (Bq/kg) in soil. We calculated TC for various radionuclides based on the assumption that the main fraction of radionuclides is delivered from the 5- to 12-cm layer of the soil. Data on dry biomass of plants and soils were used in the calculations. The results showed that the TC of ^{137}Cs varies from 0.02 to 0.045 for all elements of plant. The maximal TC of ^{239,240}Pu and ^{241}Am for blackberry are 0.026 and 0.05, respectively. The maximal TC of ^{243,244}Cm is 0.073 for stems and 0.027 for berries. The TC of ^{239,240}Pu for berries is 0.006, which is several times lower than that of ^{243,244}Cm. According to [10], a TC of ^{137}Cs for leaves and stems of raspberry bushes (*Ribes idaeus*) sampled within the 30-km zone around the Chernobyl APS varies from 0.41 to 0.02 depending on the sampling period [10], a TC of ^{239,240}Pu for raspberry bushes varies in a narrow range (0.003–0.006). However, TC of Pu isotopes for other plants may reach 0.04 [10]. We do not know the data on Cm isotopes and their TC in plants. Our results indicate that Cm may accumulate in black berries more intensely than Pu.

Thus, we detected for the first time the transuranium ^{243,244}Cm isotopes in bottom sediments, floodplain soil, and in blackberry (*Ribes nigrum*) from the floodplain of the Yenisei River. The highest concentrations of Cm isotopes detected in bottom sediments of the Yenisei River amounts to 21.4 Bq/kg of dry mass, which is two times higher than the published data on the maximum Cm content in soil samples taken from the Chernobyl disaster area. Blackberry is growing on the radioactively polluted soils also contains Pu, Cm, and Am isotopes. The maximum concentrations of all transuranium elements per ash biomass unit are recorded in the blackberry roots: $^{239, 240}$Pu 9.3 Bq/kg, ^{241}Am 6.9 Bq/kg, and ^{243,244}Cm 1.8 Bq.kg. The maximal coefficient of

^{243,244}Cm transition from soil into plant is 0.073 for roots and 0.027 for berries. The TC of ^{239,240}Pu for berries is 0.006, which is several times lower than for ^{243,244}Cm. Thus, ^{243,244}Cm isotopes are detected in all parts of blackberry. Moreover, they can accumulate more intensely than Pu isotopes.

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