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Actinides and other radionuclides in sediments and submerged plants of the Yenisei River

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Abstract

The source of radioactive contamination of the Yenisei River floodplain, including contamination with actinides, is the Mining-and-Chemical combine (MCC), which has for many years been producing weapons-grade plutonium. Actinides have been detected not only in the soil and sediment of the river but also in the biomass of aquatic plants. The aim of our investigation was to assess the levels of actinides and other radionuclides in sediments and aquatic plants both near the MCC and at a considerable distance from it, down the Yenisei River.

Investigations of the Yenisei River sediment samples revealed high activity concentrations of actinides (Pu isotopes and ^{241}Am), which were 100 times higher than their global fallout levels. Sequential extraction of radionuclides from samples of sediments collected near the MCC showed that the amounts of extracted ^{241}Am were the largest (up to 98% of initial activity). It was found that aquatic plants of the Yenisei River collected both near the MCC discharge site and at a distance up to 200 km downstream contained several actinide isotopes. The aquatic moss, *Fontinalis antipyretica*, was found to contain higher levels of radionuclides than *Potamogeton lucens*. Leaves of *P. lucens* contained higher levels of radionuclides, including ^{239}Np, than stems. Sequential extraction of radionuclides from samples of aquatic plants showed that ^{239}Np levels in exchangeable and adsorption fractions of *P. lucens* biomass were higher than in the respective fractions of *F. antipyretica* biomass.

Keywords: Actinides in aquatic plants and sediments; Accumulation; Sequential extraction technique; Radiochemical and γ-spectrometric investigations; Yenisei River

1. Introduction

The Yenisei is one of the world's largest rivers, over 3000 km long, flowing into the Kara Sea. The Mining-and-Chemical combine (MCC) at Zheleznogorsk is situated on the east bank of the Yenisei River, 60 km downstream of the city of Krasnoyarsk. The Combine has been producing weapons-grade plutonium in uranium-graphite reactors since 1958, when the first reactor was started up. The irradiated uranium is reprocessed at the radiochemical plant to separate uranium, plutonium, and fission products. The reactor plant houses three reactors. Two of them used the Yenisei water as coolant, i.e. the water was taken from the river to remove heat from the core, passed through the reactor fuel channels, and returned to the Yenisei. Both of these reactors were shut down in 1992, but the third reactor is still working. It has been proposed to put it out of service in 2008–2010. This reactor also uses the Yenisei water as coolant for some channels and releases radionuclides of activation origin into the river.

Scientific expeditions revealed that the Yenisei River flood plain is contaminated with artificial radionuclides, including plutonium isotopes, within 200 km downstream of the plutonium complex [1,2]. Kuznetzov and his colleagues [3] reported that ^{239,240}Pu activity concentration in most of the samples of the Yenisei floodplain soil collected near the MCC did not exceed 10 Bq/kg, and in just one top layer it amounted to 17.8 Bq/kg. They also presented the data on levels of another actinide, ^{241}Am, in soil samples of the Yenisei floodplain: its maximal concentration activity, near the MCC, was just 4 Bq/kg and it was 1 Bq/kg at a distance of 24 km downstream of the MCC [3]. Levels of actinides were previously measured only in samples of the floodplain soil; no such measurements have been done in sediments.

Until 1997, little consideration had been given to radioactive contamination of components of the aquatic ecosystem. During the 1997–2004 expeditions, we collected samples of aquatic plants and animals from the river near the MCC;

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gamma-spectrometric and radiochemical analysis of the samples revealed a broad spectrum of long-lived and short-lived radionuclides [4]. Among the short-lived radionuclides the highest activity concentration in aquatic plants and animals was recorded for ^{239}Np. The Yenisei River continuously receives a wide range of radionuclides, both long-lived and short-lived, and, thus, the aquatic ecosystem of the Yenisei River is a unique environment that can be used to study the migration mechanisms of various radionuclides.

The aim of our investigation was to assess the levels of actinides and other radionuclides in sediments and aquatic plants both near the MCC and at a considerable distance from it, down the Yenisei River.

2. Materials and methods

During the expeditions of 1997–2005, samples of sediment and aquatic plants were collected from the Yenisei River at different distances downstream of the MCC. Sediments were collected in the two main areas: near the MCC, at the village of B. Balchug (Core E15) and about 200 km downstream of the MCC, at the villages of Kazachinskoye (E17) and Zakharovka (E18) (Fig. 1). Sediments were collected from River branches with not more than 1 m of water above the sediments. The diameter of the sampler (made in Russia) is 11 cm and it can collect cores up to 1 m long. Each sediment sample was a 3-cm thick layer, except for the top sediment layer, which was 5–10 cm thick, depending on the core moisture content. In the laboratory, samples of sediments were dried; small stones and pieces of wood were removed.

The aquatic plants sampled were of two species: *Potamogeton lucens* (shining weed) and *Fontinalis antipyretica* (water moss). As control, we used samples of aquatic plants collected upstream of the MCC. In the laboratory, aquatic plants were cleaned, divided into species, and dried. In some cases, parts of the aquatic plant *Potamogeton lucens* (leaves and stem) were measured separately. For radiochemical and some γ-spectrometric investigations samples of sediments and aquatic plants were ashed at 500 °C. For the radiochemical analysis to determine the content of actinides in samples of aquatic plants, the ash was treated with the concentrated acids $(HNO_3 + HF)_{conc}$ (20:1, v/v) in an MLS 1200 mega microwave system (Milestone) equipped with high pressure TFM vessels.

Activity concentrations of γ-emitting nuclides in the sediment samples were measured on a "Canberra, USA" γ-spectrometer coupled to a GeHP hyperpure germanium detector. The γ-spectra were processed using the CANBERRA GENIE 2000 software (USA). Radiochemical determination of actinides (^{238}Pu, ^{239,240}Pu, ^{241}Pu, ^{241}Am) in sediment and plant samples was performed at the RPA RADON (Moscow) [2] and γ-spectrometric measurements of ^{241}Am and ^{239}Np—at the Institute of Biophysics (Krasnoyarsk). The chemical yield of the analyzed elements was controlled by introducing ^{242}Pu and ^{243}Am as tracers. Transuranic elements were concentrated and radiochemically purified in the ion-exchange column containing DOWEX 1 × 4, using solutions of mineral acids (HNO_3, HCl) and acid-alcohol solutions of various concentrations [5]. Plutonium and americium were deposited electrochemically from the solution on polished stainless discs, which then served as spectrometric sources. Concentrations of α-emitting plutonium and americium isotopes were determined with a "Canberra" α-spectrometric system (USA). The procedure of measuring ^{241}Pu in samples using a TRI-CARB 2550 TR/AB liquid scintillation counter (Canberra Packard) and the "SpectraDec" software is described in detail elsewhere [5,6].

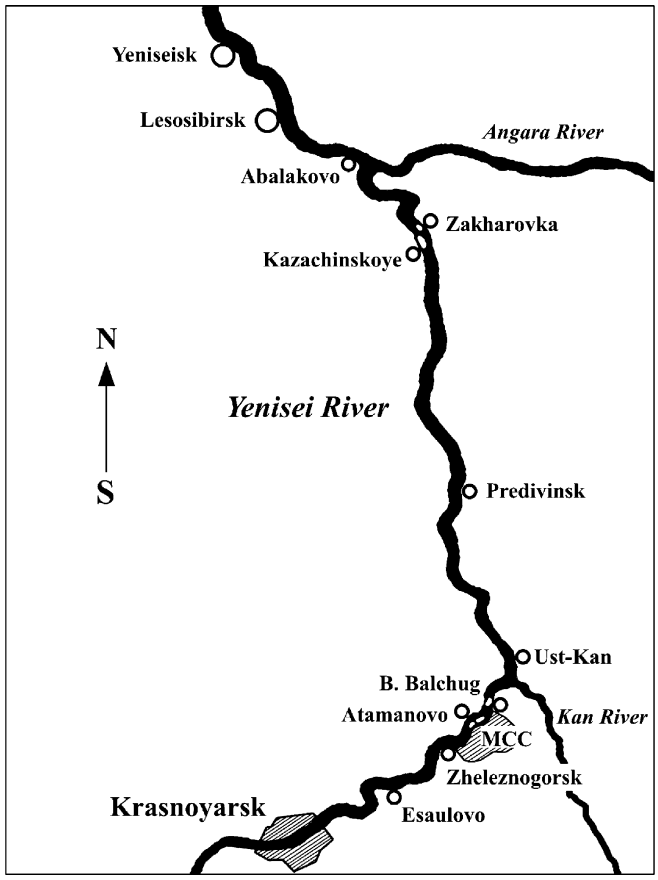

Fig. 1. Diagrammatic map of the south of the Krasnoyarsk Territory (Russia), showing settlements near which samples of sediments and aquatic plants were collected. Scale 1:2,000,000.

Sequential extraction technique proposed by Tessier and modified by Klemt et al. [7] was used to investigate sediment samples (Table 1). An abbreviated procedure was used to perform sequential extractions in aquatic plant samples and the obtained fractions were exchangeable and adsorbed fractions, organics, and mineral residue [8].

3. Results and discussion

3.1. Actinides in sediments

Gamma-spectrometric measurements showed that sediment samples contained isotopes of europium (^{152}Eu, ^{154}Eu, and ^{155}Eu), cesium (^{137}Cs and ^{134}Cs), and ^{60}Co. The distribution of

Table 1
Sequential extraction scheme for sediment samples

Fractions	Chemical reagent	Treatment	Phases with target ions
I	CH_3COONH_4 (1 mol/l)	24 h shaking	Exchangeable ions
II	CH_3COONH_4 (1 mol/l) + HNO_3 (1 mol/l) until pH = 5	Shaking to equilibrium	Carbonates
III	NH_2OH–HCl (0.2 mol/l) in CH_3COOH (25%)	3 h shaking	Oxides and hydroxides of iron and manganese
IV	H_2O_2 (35%) + HNO_3 (1 mol/l) up to 0.05 mol/l	3 h stirring at 85 °C	Organic matter
V	NaOH (0.2 mol/l)	40 min stirring at 80 °C	Amorphous silicates
VI			Residuals

Table 2
Activities of ^{137}Cs and actinides registered in some of the samples of the Yenisei River sediment

Sampling area, core no., and sediment layer	Radionuclides									
	^{137}Cs[a]		^{238}Pu[b]		^{239,240}Pu[b]		^{241}Pu[b]		^{241}Am[b]	
	Bq/kg	± (%)	Bq/kg	± (%)	Bq/kg	± (%)	Bq/kg	± (%)	Bq/kg	± (%)
B. Balchug, E15										
0–4 cm	2104	6	4.1	14	36	7	1430	8	48	6
22–25 cm	1600	6	7.4	11	98	6	433	7	35	8
Kazachinskoye, E17										
52–54 cm	527	6	≤0.4		10	8	4	70	5.2	9
Zakharovka, E18										
19–22 cm	427	6	2.9	22	280	8	254	8	45	10
37–40 cm	984	6	≤0.6		19	8	13	35	3	16

[a] Data of the Institute of Biophysics SB RAS (Krasnoyarsk).
[b] Data of RPA RADON (Moscow).

artificial radionuclides among sediment layers is described by a curve with one or two maxima in the lower and middle parts of the core. Gamma-spectrometry analysis also registered ^{241}Am in layers containing maximal levels of γ-emitting radionuclides (cesium and europium isotopes). Thus, our further research was focused on radiochemical investigations of the sediment layers that, as registered by γ-spectrometry, contained maximal levels of radionuclides, including ^{241}Am.

The radiochemical method was used to determine actinides in several layers of Core E15, which had been collected near the MCC discharge site; in the sediment layer 22–25 cm down from the surface the registered activity of ^{239,240}Pu was 98 Bq/kg (Table 2). In the same layer, γ-spectrometric and radiochemical analyses registered a high level of ^{241}Am – 35 Bq/kg; ^{241}Pu in that layer amounted to 433 Bq/kg. However, in the top layer of that sediment core (0–4 cm), ^{241}Pu amounted to 1430 Bq/kg and ^{241}Am—to 48 Bq/kg. It is well known that ^{241}Am is a decay daughter of ^{241}Pu and the half-life of ^{241}Pu is 14.4 years. Evidently, the ^{241}Am of that top layer (which was 3–5 years old at the time of sampling) could not be the product of ^{241}Pu decay but was rather transferred from another part of the river. Such a high level of ^{241}Pu in the top layer of sediment can be indicative of fresh releases of actinides by the MCC.

Sediment samples collected at positions about 200 km downstream of the MCC also contained actinides. Even though the activities of γ-emitting radionuclides in the layers of sediments collected at the villages of Kazachinskoye and Zakharovka were several times lower than in the B. Balchug sediments, they still remained rather high (Table 2). The layer 19–22 cm of Core E18, collected at Zakharovka, contained the following levels of actinides: 280 Bq/kg for ^{239,240}Pu, 254 Bq/kg for ^{241}Pu, and 45 Bq/kg for ^{241}Am. Such high levels of ^{239,240}Pu, more than 100 times higher than the global fallout level [9], were previously reported for the MCC production area only [1]. The lower layer of Core 17, collected at Kazachinskoye, also contained actinides: 10 Bq/kg for ^{239,240}Pu and 5 Bq/kg for ^{241}Am (Table 2).

Thus, our investigations of the Yenisei River sediment samples revealed high activity concentrations of transuranic elements (^{238}Pu, ^{239,240}Pu, and ^{241}Am), which were several times higher than their global fallout levels. We were the first to measure ^{241}Pu in sediment of the Yenisei River and show that the levels of this actinide remain high as far as 200 km downstream of the MCC. The presence of high actinide levels (^{239,240}Pu – up to 36 Bq/kg and ^{241}Pu – up to 1430 Bq/kg) in the top layer can be indicative of fresh releases of actinides by the MCC.

Sequential extraction techniques are the most common method of studying radionuclide speciation in soils and sediments. Sequential extraction of radionuclides from samples of sediments collected near the MCC showed (Table 3) that

Table 3
Distribution of radionuclide (^{60}Co, ^{137}Cs, ^{152}Eu, ^{241}Am) forms among fractions of the sediment sample

Fractions	Radionuclides, Bq (%)			
	^{60}Co	^{137}Cs	^{152}Eu	^{241}Am
(I) Exchangeable ions	1.4 ± 0.4 (2.0 ± 0.5)	1.3 ± 0.5 (1.0 ± 0.4)	2.5 ± 0.5 (2.5 ± 0.5)	<MDA
(II) Carbonates	6.1 ± 0.4 (8.5 ± 0.6)	<MDA	12 ± 1 (12 ± 1)	0.55 ± 0.05 (10 ± 1)
(III) Oxides and Hydroxides of Iron and Manganese	5.8 ± 0.4 (8.0 ± 0.5)	3.1 ± 0.6 (2.5 ± 0.5)	5.5 ± 0.5 (5.5 ± 0.5)	0.33 ± 0.04 (6.0 ± 0.7)
(IV) Organic Matter	10.8 ± 1.4 (15 ± 2)	2.5 ± 0.3 (2.0 ± 0.2)	64 ± 4 (64 ± 4)	3.85 ± 0.28 (70 ± 5)
(V) Amorphous silicates	6.1 ± 0.4 (8.5 ± 0.5)	1.5 ± 0.3 (1.2 ± 0.2)	14 ± 1 (14 ± 1)	0.66 ± 0.11 (12 ± 2)
(VI) Residuals	41.8 ± 2.2 (58 ± 3)	116 ± 9 (93 ± 7)	2.0 ± 0.5 (2.0 ± 0.5)	0.10 ± 0.02 (1.9 ± 0.4)
Initial concentration per sample (Bq)	72 ± 6 (100%)	125 ± 3 (100%)	100 ± 2.7 (100%)	5.5 ± 1.7 (100%)

Table 4
Results of radiochemical and γ-spectrometric analysis of samples of aquatic plants from the Yenisei River (value ± S.D.)

Sample, position, and distance from the MCC (downstream)	^{239,240}Pu (Bq/kg)	^{238}Pu (Bq/kg)	^{239}Np (Bq/kg)
Atamanovo, 5 km			
Potamogeton lucens (stem)	0.6 ± 0.1	0.12 ± 0.04	370 ± 30
P. lucens (leaves)	1.2 ± 0.2	0.06 ± 0.03	800 ± 40
Zakharovka, 194 km			
P. lucens (leaves)	0.4 ± 0.1	≤0.1	30 ± 6
Atamanovo, 5 km			
Fontinalis antipyretica	4.1 ± 0.6	0.5 ± 0.13	1490 ± 60

Table 5
Distribution of the actinide ^{239}Np among chemical fractions of biomass of the Yenisei River aquatic plants

Plant	Fraction I (Bq)	Fraction II (Bq)	Fraction III (Bq)	Fraction IV (Bq)
Potamogeton lucens (leaves)	0.52 ± 0.13 (17%)	0.61 ± 0.12 (19%)	0.56 ± 0.16 (17%)	1.5 ± 0.1 (47%)
Potamogeton lucens (stems)	0.3 ± 0.05 (18%)	0.42 ± 0.12 (25%)	0.65 ± 0.17 (39%)	0.3 ± 0.1 (18%)
F. antipyretica	0.22 ± 0.08 (10%)	0.41 ± 0.03 (19%)	1.54 ± 0.15 (71%)[a]	

Notes: The ^{239}Np of the exchangeable fraction (I) was extracted by placing plant biomass in a 1 M solution of CH_3COONH_4 for 24 h. The ^{239}Np of the adsorption fraction (II) was extracted by placing plant biomass into a 0.2 M solution of H_2SO_4 for 20 min. The ^{239}Np bound by organic matter (fraction III) and mineral residue (fraction IV) of the plant biomass was separated by "wet combustion", using H_2O_2 (30%) and a HNO_3 solution (0.1 M) [8].
[a] Fraction III + fraction IV (Bq).

the amounts of extracted ^{152}Eu and ^{241}Am were the largest (up to 98% of initial activity), then followed ^{60}Co (42%), and, last, ^{137}Cs (7%). The largest amounts of the radionuclides are extracted from such fractions as organics, sesquioxides and hydroxides, and amorphous silicates. Exchangeable fractions contain not more than 2% of total radionuclides. The results of extraction of ^{241}Am from the sediment samples shows that the largest amounts of the ^{241}Am are extracted from organics (70%).

3.2. Actinides in aquatic plants

It can be inferred from the published work of the MCC specialists [3] that the MCC continues releasing the cooling water into the Yenisei River. The Yenisei is reported to receive the following radionuclides of activation origin: ^{24}Na, ^{32}P, ^{46}Sc, ^{51}Cr, ^{54}Mn, ^{58}Co, ^{59}Fe, ^{64}Cu, ^{65}Zn, ^{95}Zr, etc. The parts of the river near the MCC and downstream of it are abundant in submerged macrophytes, which accumulate artificial radionuclides. Aquatic plants that we collected for our investigations contained many radionuclides typically found in MCC effluents. It should be noted that ^{24}Na, ^{46}Sc, ^{51}Cr, ^{54}Mn, ^{58}Co, ^{60}Co, ^{65}Zn, ^{76}As, ^{239}Np and cesium, cerium and europium isotopes were found in the plants analyzed. Levels of ^{137}Cs in the plants collected at the MCC discharge site reached 350 Bq/kg. The plant samples collected upstream of the MCC discharge site contained only one artificial radionuclide, ^{137}Cs, with the activity levels not exceeding 2 Bq/kg [4].

It was found that aquatic plants of the Yenisei River collected both near the MCC discharge site and at a distance up to 200 km downstream contained several actinide isotopes (Table 4). The aquatic moss, *F. antipyretica*, was found to contain higher levels of radionuclides than *P. lucens*. Leaves of *P. lucens* contained higher levels of radionuclides, including ^{239}Np, than stems.

We estimated the strength of ^{239}Np binding by plant biomass using sequential extraction techniques [8]. The neptunium of the exchangeable fraction (I) was extracted by placing plant biomass in a 1 M solution of CH_3COONH_4 for 24 h. The ^{239}Np of the adsorption fraction (II) was extracted by placing plant biomass into a 0.2 M solution of H_2SO_4 for 20 min. The neptunium contained in the biomass following those treatments was considered as strongly bound to plant structures. The neptunium activities bound by organic compounds (fraction III) and mineral residue (fraction IV) of the plant biomass were separated by "wet combustion", using H_2O_2 (30%) and a HNO_3 solution (0.1 M) [8]. Mineral residue is an inorganic skeleton, which mainly consists of silicon compounds (BioSilicon [10]) with trace amounts of insoluble sulfides (such as FeS) and oxides (such as Fe_3O_4).

The data presented in Table 5 show that in the water moss, *F. antipyretica*, the larger part of ^{239}Np is strongly bound to biomass cell structures (71% is found in the organic and mineral fraction) and the smaller part – 29% – is extracted from the exchangeable and adsorption fractions. For the shining weed, *P. lucens*, the amount of ^{239}Np found in the exchangeable and adsorption fractions is somewhat higher – 36–43% and, hence, fractions III and IV contain less ^{239}Np – 57–64%. Sequential extraction of radionuclides from samples of aquatic plants showed that ^{239}Np levels in exchangeable and adsorption fractions of *P. lucens* biomass were higher than in the respective fractions of *F. antipyretica* biomass.

4. Conclusion

1. Investigations of the Yenisei River sediment samples revealed high activity concentrations of actinides (Pu isotopes and ^{241}Am), which were 100 times higher than their global levels. We were the first to measure ^{241}Pu in sediment of the Yenisei

River and show that the levels of this actinide remain high as far as 200 km downstream of the MCC. The presence of high actinide levels (^{239,240}Pu – up to 36 Bq/kg and ^{241}Pu – up to 1430 Bq/kg) in the top layer can be indicative of fresh releases of actinides by the MCC. Sequential extraction of radionuclides from samples of sediments collected near the MCC showed that the amounts of extracted ^{241}Am were much larger (up to 98% of initial activity) than those of ^{60}Co (42%) and ^{137}Cs (7%).

2. It was found that aquatic plants of the Yenisei River collected both near the MCC discharge site and at a distance up to 200 km downstream contained a wide range of artificial radionuclides, including actinides. The aquatic moss, *F. antipyretica*, was found to contain higher levels of radionuclides than *P. lucens*. Leaves of *P. lucens* contained higher levels of radionuclides, including ^{239}Np, than stems. Sequential extraction of radionuclides from samples of aquatic plants showed that ^{239}Np levels in exchangeable and adsorption fractions of *P. lucens* biomass were higher than in the respective fractions of *F. antipyretica* biomass.

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