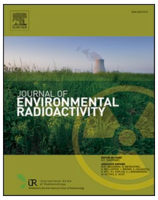
Journal of Environmental Radioactivity 232 (2021) 106569

Contents lists available at ScienceDirect

Journal of Environmental Radioactivity

journal homepage: http://www.elsevier.com/locate/jenvrad



Artificial radionuclides association with bottom sediment components from Mayak Production Association industrial reservoirs

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ARTICLE INFO

Keywords:
Artificial radionuclides
Sequential extraction
Sorption mechanism

ABSTRACT

About ten years have passed since the last published report in Russian on the speciation and distribution features of radionuclides in the bottom sediment of Production Association (PA) "Mayak" (further mentioned as Mayak) artificial reservoirs. Herein, the desorption parameters of ^{137}Cs, ^{90}Sr, ^{241}Am, and $^{238,239+240}$Pu and their association with bottom sediment components were investigated in two Mayak reservoirs (R-17 (decommissioned) and R-4 (still in use) with big differences in size, activity and water regime). It was established that ^{137}Cs and ^{90}Sr desorption from the R-17 bottom sediment reach constant values after 24 h, and the desorption degree is not dependant on pH but on ionic strength. Sequential extraction indicated that the main accumulation mechanism of ^{137}Cs is incorporation into the clay minerals. The maximum plutonium content was detected in the residual fraction of the R-17 bottom sediment, which could be associated with the effects of precipitation aging. In R-4, plutonium is equally distributed between residual and bound to organic matter fractions. The ^{241}Am is associated with carbonates in the R-17 bottom sediment and with organic matter in the R-4 bottom sediment and to lesser extent with iron-manganese oxides. The radionuclides are becoming less environmentally available with time since deposition.

1. Introduction

The mobility/availability of radionuclides in bottom sediments depend on their chemical speciation, i.e. adsorption/accumulation mechanisms, which in turn are determined by the radionuclide chemical properties and the physicochemical characteristics of the bottom sediments including mineralogical and chemical compositions. Bottom sediments act as a "geochemical barrier" in radionuclide migration processes as they readily sorb/accumulate various radionuclides. Determination of radionuclide desorption and leaching parameters for industrial reservoir sediments and sludge would permit one to radionuclide partitioning and to monitor its migration as well as determine the transfer probability between abiotic and biotic environmental components.

The industrial reservoirs at Mayak territory studied herein, R-4 and R-17, are characterized by unique radionuclide content compositions. About ten years have passed since the last published report on the speciation and desorption characteristics of radionuclides in the bottom sediment of these reservoirs. Thus, the dynamic changes in the distribution and mobility of radionuclides over time are of great interest.

Although Mayak investigations have focused on reservoirs and territorial areas, this work represents the first integrated approach to the study of radionuclide association with bottom sediment components based on literature data (Pavlotskaya et al., 1998; Strand et al., 1999; Skipperud et al., 2000, 2009; Stykalov, 2000, 2007; Slynchev, 2007; Levina, 2008; Stykalov and Simkina, 2008; Kenna, 2009; Andreev, 2013).

Previously, Stukalov and Simkina (2008) reviewed comprehensive reservoir investigations and studies from the 1950s to the 2000s on the desorption parameters of radionuclides in the bottom sediment from the R-17. In the first stages, experiments were performed with tap and distilled water, which showed that tap water more effectively washed out radionuclides by 5–15%. The total β-emitting radionuclide desorption reached the value 47–54%. In the 1970s, it was found that the desorption coefficient of ^{90}Sr was approximately an order of magnitude higher than that of ^{137}Cs indicative higher ^{90}Sr mobility compared with

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https://doi.org/10.1016/j.jenvrad.2021.106569
Received 16 March 2020; Received in revised form 9 February 2021; Accepted 23 February 2021

^{137}Cs. In 2008, as a result of the desorption experiment with natural water (pH 7.3), 7.2% of ^{137}Cs and 48.5% of ^{90}Sr were desorbed. Desorption by natural ground water nitrate solution (1.7 g/L by nitrate ions) was also performed, in which 13.2% of ^{137}Cs and 50.7% of ^{90}Sr were desorbed. The distribution coefficients of ^{137}Cs and ^{90}Sr for the nitrate solution were determined as 9700 ml/g and 1200 ml/g, respectively and 15,000 ml/g and 1400 ml/g, respectively for natural water. So the main conclusions have been made: the dependence of the ^{137}Cs and ^{90}Sr eluted activity on the desorbing solution portion serial number is described by a decreasing exponential form; transuranium elements are much less readily desorbed from the bottom sediment; during the experiments, a significant number of fixed (immobile) forms were determined (approximately 40–50% for ^{90}Sr and 90% for ^{137}Cs) (Stukalov and Simkina, 2008). These studies were carried out with the aim of safety assessment of radionuclide contaminated solutions storage in R-17 and served to monitor the spread of pollution. The mechanisms of desorption and radionuclide association with bottom sediment components have not been determined and the latest published data on the radionuclide desorption coefficients (or desorption percentage of initial activity) from R-17 were reported 10 years ago.

Sequential extraction tests provide information on partitioning of various radionuclides and therefore potential mobility and bioavailabilities. One of the most widely used protocols have been developed by Tessier et al. (1979) more than 30 years ago. The five functionally defined geochemical fractions are distinguished in this protocol: exchangeable, bound to carbonates (acid-soluble), iron-manganese oxides (reducible), bound to organic matter (oxidizable), and residual fraction. This method, which have been developed for heavy metal determination in soils, allows the study distribution of trace concentrations of metals when no direct spectroscopic methods could be applied. Since radiochemistry in radioecology is the science of trace amounts of metals, this technique is used to determine association with bottom sediments and indirectly assume and evaluate the physicochemical forms of radionuclides in bottom sediments. Unfortunately, we cannot apply other methods due to the very high radioactivity of the studied samples. Although there have been many adaptations and modifications to the Tessier method, the main fractions remain the same. Many attempts to modify the method in accordance with the studied objects, e.g. various types of bottom sediments and soils have been made. The used reagents are similar in terms of chemical properties, but they may increase the selectivity of extractable metals (McLaren et al., 1973; Kersten et al., 1986; Outola et al., 2009). The sequential extraction data depend on the reagents used, sample/solution contact time, mixing intensity, volumetric reagent-to-sample ratio, and bottom sediment mineral and structural characteristics (Fedotov et al., 2008).

Pavlotskaya et al. (1998) obtained abundant information about the R-10 bottom sediment forms; they reported the following geochemical fractions: exchangeable and easy to dissolve (1 M CH_3COONH_4), mobile (1 M HCl), acid-soluble (6 M HCl), and residual ($HF + H_2SO_4$) – these fractions are not common for the classic sequential extraction procedure, for example Tessier et al. (1979) or its adaptation. The highest ^{137}Cs content was detected in the residual fraction (average 68%), highest ^{241}Am content in the mobile fraction (68%) and highest plutonium content in the acid-soluble fraction (53%). The lowest ^{137}Cs content was detected in the exchangeable and mobile fractions (average 6 and 4%, respectively), lowest ^{241}Am content in the exchangeable and residual fractions (5 and 7%, respectively), and the lowest plutonium content in the exchangeable and mobile fractions (1 and 16%, respectively). In these investigations, the radionuclide association with bottom sediment components was identified by the special (not common) extracted fractions and in the reservoir where waste is not directly discharged. In R-10, radionuclides can only come in dissolved form in water due to natural overflow from R-4 (Pavlotskaya, 1998).

The maximum plutonium content was found in the bound to iron-manganese oxides (85%) and residual (13%) fractions from Ob' river bottom sediment (Western Siberia region) (Kenna, 2009); no plutonium was detected in the exchangeable or bound to organic matter fraction with ca. 1.5% bound to carbonates. For Asanov Swamp, which is close to Mayak site, Yenisei (Krasnoyarsk region), and the Techa river (Muslyumovo region) bottom sediments analysis showed the maximum plutonium contents in the bound to organic matter (35–75%) and residual (25–50%) fractions (Skipperud et al., 2000, 2009). See Supplementary Material for details.

All plutonium forms were precisely identified in several areas by the standard sequential extraction technique; however, these investigations were not in the Mayak territory and cascade reservoirs where waste is discharged. Pollution in the studied reservoirs is indirect.

The aim of this study is to determine the desorption parameters of ^{137}Cs, ^{241}Am, and $^{238,239+240}$Pu and their time dependence (since 2008) as well as to elucidate if sorption or other mechanisms dominate radionuclide interactions with bottom sediments at R-17 and R-4 by association with bottom sediment component determination. This is the first such study since 2008 that expands available data on radionuclide behavior after deposition in this evolving environment. In this study, we also collect and compare information from Russian sources that have not yet been internationally published.

2. Materials and methods

2.1. Study area

The Mayak Production Association located in the Chelyabinsk region was the first enterprise in the USSR to produce weapon-grade plutonium. As a result of production activities in 1949–1956, over 10^{17} Bq of radioactive waste was discharged into the Techa River. The upper reaches of the river were blocked by a dam cascade (Fig. 1) – "Techa Reservoir Cascade" – in 1956–1964 to prevent the further spread of deposited radioactive substances (Stukalov, 2000; Andreev, 2013). The discharge of liquid radioactive waste into the "Old Swamp" (R-17 reservoir) has been carried out from 1949 to 2018. At present, approximately 74 PBq of α-, β-, and γ-emitting radionuclides have accumulated in the reservoir, where most of the activity is concentrated in the bottom sediment. Reservoir R-17, which was used to store intermediate-level waste, is located in a natural lowland with later additional excavation. Nothing flows from the reservoir. The main dose-forming radionuclides are ^{90}Sr and ^{137}Cs (Stukalov, 2007). Specific activities in R-17 bottom sediments are: ^{137}Cs–$1.5 \cdot 10^5$ Bq/g; ^{90}Sr – $5.2 \cdot 10^4$ Bq/g; ^{241}Am–$5.27 \cdot 10^3$ Bq/g; ^{239,240}Pu – $4.5 \cdot 10^3$ Bq/g; ^{238}Pu – $6.2 \cdot 10^2$ Bq/g (Kuzmenkova et al., 2017). At present, the R-17 liquid radioactive waste storage has been decommissioned.

Reservoir R-4 is natural and, together with reservoirs R-3, R-10, and R-11, forms the Techa Reservoir Cascade (Fig. 1). Reservoirs R-3 and R-4 (Metlinsky Pond) existed before the formation of the Mayak Production Association. Currently, the reservoir is used as a repository of low-level radioactive waste. Waste has been discharged since 1972, before which the reservoir was replenished due to the overflow from R-3. Specific activities in R-4 bottom sediments are: ^{137}Cs–$1.7 \cdot 10^4$ Bq/g; ^{90}Sr – $3.5 \cdot 10^3$ Bq/g; ^{241}Am–$5.3 \cdot 10^2$ Bq/g; ^{239,240}Pu – $5.3 \cdot 10^0$ Bq/g; ^{238}Pu – $5.6 \cdot 10^0$ Bq/g (Kuzmenkova et al., 2017). The main dose-forming R-4 radionuclides are also ^{137}Cs and ^{90}Sr. However, the R-4 bottom sediment activity is an order of magnitude lower than that of R-17 (Kuzmenkova et al., 2017).

2.2. Samples

Two bottom sediment samples from Mayak reservoirs R-17 and R-4 were investigated. Sampling stations for both reservoirs were located in the reservoir coastal zone — 1.5 m from the coastline. Sampling was taken using a bucket-type sampler from a boat. The sampler catches bottom sediments no deeper than 5 cm. A surface layer was selected in both reservoirs. R-17 bottom sediment was sampled near the place of radioactive waste discharge at 2.5 m depth; R-4 bottom sediment was

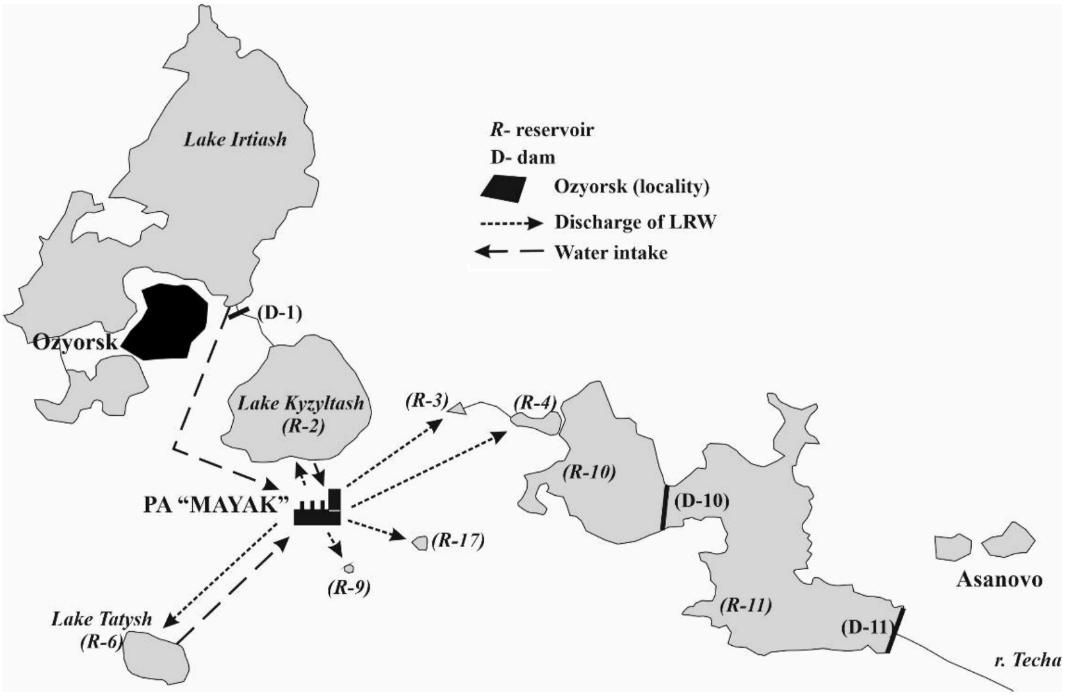


Fig. 1. Map of Techa Reservoir Cascade near Plant Mayak.

sampled at the channel mouth flowing from R-3 at a depth of ~2 m. The site heterogeneity and representativeness of these samples cannot be interpolate to the all reservoirs sediments.

Reservoir R-17 is small, with a water surface area of 0.13 km^2, water volume of 0.36 million m^3, maximum depth of 6.5 m, and an average depth of 2.8 m. The reservoir salt composition (Stukalov, 2000) includes $NaNO_3$ at 17.14 g/L; $NaHCO_3$ at 0.52 g/L; Na_2SO_4 at 0.71 g/L; and NaCl at 0.29 g/L. Reservoir R-4 is 10 times larger, with a water surface area of 1.3 km^2, water volume of 3.8 million m^3, and maximum depth of 3.5 m. Reservoir R-4 is characterized by the following salt composition: $NaNO_3$ at 1.8 g/L; $NaHCO_3$ at 0.4 g/L; Na_2SO_4 at 1.67 g/L; and NaCl at 0.1 g/L.. The water in R-4 is exchanged completely throughout the year due to natural overflow into the next cascade reservoir, R-10 (Kuzmenkova et al., 2017; Slyunchev et al., 2007).

All samples were air dried, and stones and large organic particles (roots, leaves, etc.) were removed from the sediment. Then, the samples were dried at 80 °C and homogenized. The analyzed mass was small, 0.05–0.1 g, because the bottom sediment had high radionuclide specific activity.

2.3. Standards and reagents

Spectrometric measurements were performed using a GR 3818 semiconductor γ-spectrometer with a Canberra high-purity (HPGe) detector (USA). The efficiency coefficients were 0.015 for ^{137}Cs and 0.13 for ^{241}Am. The efficiency of the γ-spectrometer was determined by calibrating the instrument of known activity standards (^{137}Cs and ^{241}Am). The specific activity of the radionuclides was measured in the standard geometries. Energy spectra measurements depended on the activity but did not less 10,000 s, and ^{137}Cs and ^{241}Am activities were calculated from the net full energy peaks 661.7 keV and 59.3 keV, respectively, using the "Genie 2000" spectrometric analysis software package. The analytical error of γ-spectrometry did not exceed 2%. Reference materials were standart solutions containing ^{137}Cs and ^{241}Am. Minimum detectable activity depended on the measurement time but did not exceed 0,5 Bq. Sample measurement and subsequent ^{90}Sr activity determination were performed using liquid scintillation spectrometry (Tri-Carb 2700 TR). To trace the chemical yield, the samples were spiked with ^{85}Sr (MDA did not exceed 0,8 Bq). Anion exchange resin AB-17 × 8 (0.315–1.25 mm grain size) was used for plutonium separation. The alpha-activities of Pu isotopes ($^{238,239+240}$Pu) were measured with the spectrometer ORTEC Alpha-Ensemble-2 with detector ENS-U900 type UL-TRA-AS with a vacuum chamber and a pulse analyzer. A solution of 10 μL of ^{236}Pu (0.3 Bq) in 2 mol/L HNO_3 was added as a tracer for chemical yield control. During radiochemical procedures the blank solutions containing all reagents without any activities was prepared and measured.

2.4. Desorption experiments

Four solutions were prepared to determine the parameters of radionuclide leaching just from the R-17 bottom sediment (Table 1). A 0.1 g sample of sediment was placed in a 50 ml vial and the investigated solution was brought to the mark of 45 ml. Mixing was carried out on a shaker at 155 rpm. Every 1, 3, 5, 24 h and then every day, an aliquot of 1.5 ml was taken; then centrifuged for 20 min at 21,000 rpm to remove

Table 1
Characteristics of investigated solutions.

Solution composition	pH	Ionic strength	Concentration, mol/L
Sodium carbonate (Na_2CO_3)	11.1	0.3	0.1
Model water (composition similar to groundwater in investigated area)[a]	8.1	0.018	[$NaHCO_3$] = $4.6 \cdot 10^{-3}$ [$CaSO_4$] = $1.4 \cdot 10^{-3}$ [$MgSO_4$] = $2.0 \cdot 10^{-3}$ [KCl] = $2.0 \cdot 10^{-4}$
Acetate buffer solution (CH_3COONa + CH_3COOH)[b]	5.6	6.66	[Na^+] = 6.63 [$CH3COO^-$] = 6.68
Acid (HNO_3)	3.0	$1 \cdot 10^{-3}$	$1 \cdot 10^{-3}$

[a] Prepared according to standard procedure (Heber, 1994) relative to pH (8.0–8.4).

[b] Prepared according to standard procedure (State quality standard 42-0072-07).

bottom sediments microparticles that could be get to aliquot; pH values were monitored after each aliquot selection. The solution was separated from the precipitate in a volume of 1.4 ml after centrifuging and was measured on a γ-spectrometer. After determining the gamma activity, a 1.3 ml aliquot of the solution was poured into 6 ml of liquid scintillator and the total α-β activity was measured using a liquid scintillation counting. The sediment remaining after centrifugation was also measured on a gamma spectrometer to calculate the distribution coefficients. After a week, the entire vial with the sediment was centrifuged (20 min; 8000 rpm), replaced with a new portion of the investigated solution, and the experiment to study desorption was repeated.

Acetate buffer solution was prepared according to the standard procedure (State quality standard) as follows: 108.8 g of CH_3COONa was dissolved in 100 ml of water, heated to 35 °C to completely dissolve sodium acetate. After cooling the resulting solution, 20.0 ml of anhydrous acetic acid was slowly added, mixed and the volume of the solution was brought to 200.0 ml with deionized water.

The bottom sediment initial activity was measured for each sample before experiments for γ-emitting radionuclides, and the α-/β-emitted radionuclide initial activities were taken from previous experiments (Kuzmenkova et al., 2017). Desorption percentage was calculated by the following equation for comparable data:

$$K_{\text{desorption}} = 100\% \cdot A_{\text{aliquot}}\ [\text{Bq/mL}] \,/\, A_{\text{initial}}\ [\text{Bq/g}] \tag{1}$$

Distribution coefficients were calculated for each i portion of the desorption solution by the equation

$$Kd = \frac{S_{i-1} - C_i \cdot V}{m \cdot C_i}, \tag{2}$$

where S_{i-1} – radioactivity of bottom sediment sample for previous desorption solution (i-1), Bq;

C_i – radionuclide concentration of i portion of strippant, Bq/mL;
V – volume of the one desorption solution portion, mL;
m – sample mass, g.

The desorption percentage for each aliquot was determined only once. The experimental error includes a statistical count error (instrument error) of 0.2–2%, detection efficiency of 2.5–4.5%, and a volume measurement error of 1–3%. The sample was sufficient to determine the standard deviation and calculate the errors according to the three sigma rule.

2.5. *Sequential extraction scheme*

The sequential extraction of radionuclides from R-17 and R-4 bottom sediments was performed according to the method reported by Tessier et al. (1979). Three identical 0.05 g samples of each sediment were taken to estimate statistical errors. The ratio of precipitate: the solution was 1:20 by weight. After each fraction was centrifuged in an Eppendorf tube (21000 rpm for 10 min), the solutions were removed to clean tubes and further used to separate and concentrate plutonium isotopes. A water-soluble fraction was added before the five standard Tessier fractions by preparing a model water solution relative to the reservoirs at pH 8.0–8.4 (Heber, 1994).

For Fraction 1 (F1, exchangeable), the sediment was extracted at room temperature for 1 h with 1 ml of 1 M $MgCl_2$ at pH 7.5. After shaking at 160 rpm the solution was centrifuged. Stirring of a mixture of the F1 residue and 1 ml of 1 M CH_3COONa with CH_3COOH (pH 4.7) at room temperature for 3.5 h shaking (160 rpm) and left overnight provide Fraction 2 (F2, bound to carbonates). The solution was then centrifuged and separated. For Fraction 3 (F3, bound to iron-manganese oxides), the residue from F2 was leached at 96°C with 1 ml of 0.04 M $NH_2OH \cdot HCl$ adjusted by 25% CH_3COOH v/v to obtain the resulting pH of 2.1. For Fraction 4 (F4, bound to organic matter), the solid-to-liquid ratio was 1:40 as hydrogen peroxide is a strong oxidizing agent and decomposes upon heating, therefore 1 ml is not enough for the extraction procedure. The interaction between hydrogen peroxide and the sediment was extremely active, and thus the leaching of this fraction was performed in three steps. To the residue from F3 2 ml of 30% H_2O_2 adjusted to pH 1.8 with 0.02 M nitric acid was added. The sediments were left for a day to react, then heated to 85 °C for 2 h. The sample was then centrifuged to collect the supernatant, and the experiment was repeated. The interaction was less active the second time, and thus the sediments were left for 30 min until the reaction completes, afterwards heated again to 85 °C for 3 h, and centrifuged after cooling. At the third step, 0.6 ml of 3.2 M CH_3COONH_4 in 20% HNO_3 v/v was added, and the mixture was diluted with water up to 2.5 ml, stirred at room temperature for 30 min, and combined with the previous solutions. For Fraction 5 (F5, residual), the residue from F4 was dissolved in a concentrated HF–HCl–HNO_3 acid mixture.

2.6. *Determination of plutonium in each fraction and sample*

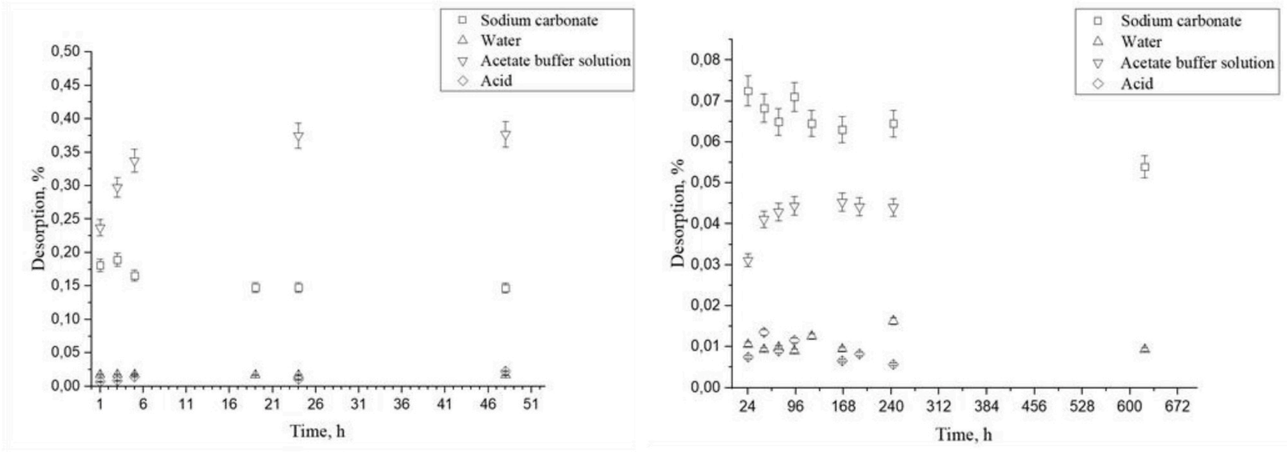
Anionite AB-17 × 8 resin was used to separate plutonium from the bottom sediment. To do this the resulting solutions after sequential extractions were evaporated to wet salts and dissolved in 7.5 M HNO_3. To stabilize plutonium in tetravalent state, crystalline $NaNO_2$ was added to the stock solution, and the mixture was heated at 150 °C for 5 min then left until nitrogen dioxide emission ceased. The resulting solution was passed through a preconditioned anionite column, and then the column was washed sequentially with 7.5 M HNO_3, 9 M HCl, again 7.5 M HNO_3, and distilled water. Plutonium were eluted from the column by hydroxylamine hydrochloride heated up to 40 °C. The plutonium was coprecipitated with CeF_3 on a Resolve filter (Eichrom Technologies, ACW17 VBS) for α-spectrometry measurements.

3. Results

3.1. *Desorption experiments*

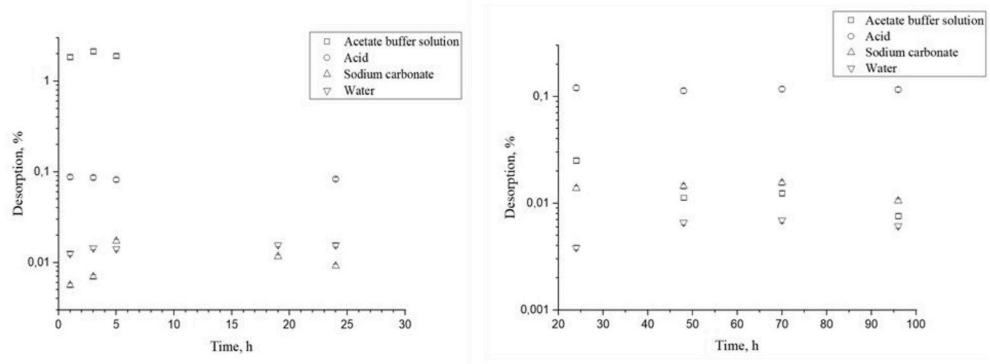
First, desorption experiments with R-17 bottom sediment were performed – resulting in only ^{137}Cs and ^{90}Sr detection. The time-dependent desorption percentages were determined for all portions of ^{137}Cs solutions (solution change once per week) and are shown in Fig. 2. For all four solutions, ^{137}Cs desorption became constant after 24 h in the first desorption cycle. For the second cycle, the changes in desorption with time was different. In the buffer and acid solutions, desorption ended after 94 h, in water after 160 h, and in the sodium carbonate solution after 24 h. The ^{90}Sr desorption data (Fig. 3) show that in both cycles, desorption ended after 24 h. It was determined that steady-state condition on the first stage of desorption reach within first 24 of the reaction. In the first cycle, there may be a washout of physically adsorbed radionuclides, which is less significant in subsequent cycles, but we cannot state this for sure, since there may be many processes during desorption. In the second cycle, mixing with solutions caused desorption of radionuclides. In general, the desorbed ^{90}Sr was higher than that of ^{137}Cs.

Distribution coefficients were calculated. The smallest distribution coefficients were obtained in the buffer (27 ml/g) and sodium carbonate (21 ml/g) solutions, which indicates that ^{137}Cs more readily desorbs from the bottom sediment in these solutions compared with in the others. In contrast, the distribution coefficient was the highest in water (9250 ml/g), indicating its inefficiency for ^{137}Cs desorption. This value correlates with the data obtained by Stukalov and Simkina in 2008 (15,000 ml/g). Distribution coefficient in nitric acid solution was 3800 ml/g. Despite the low percentage of desorption (<1%), each sample is highly radioactively contaminated in terms of absolute activity (10^5 Bq/g^{137}Cs; 10^4 Bq/g^{90}Sr), which allowed us to calculate thousandths of a percent.



(a) (b)

Fig. 2. ^{137}Cs desorption kinetics of the (a) first and (b) second cycle solutions.



(a) (b)

Fig. 3. ^{90}Sr desorption kinetics of the (a) first and (b) second cycle solutions.

3.2. Desorption of α-emitting radionuclides

Fig. 4 shows the kinetics of ^{241}Am desorption by the buffer solution.

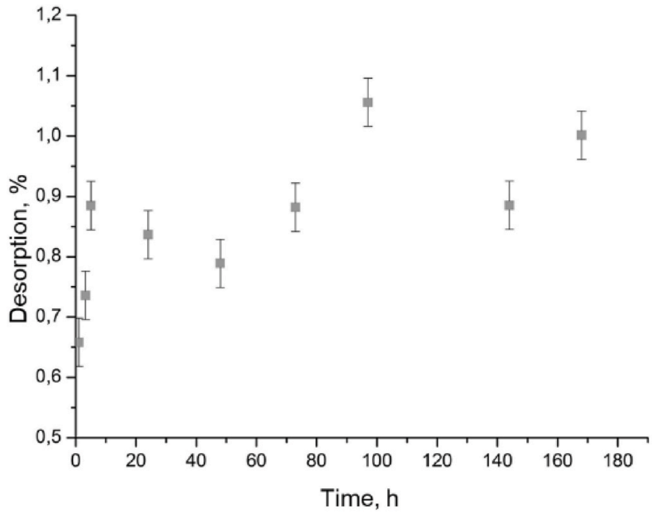


Fig. 4. ^{241}Am desorption by first acetate buffer solution.

^{241}Am was found only in the first solution indicative the washing of ^{241}Am from the sediment. The calculated desorption values error was quite large, and thus it was impossible to confirm the ^{241}Am desorption. There were no other α-emitting radionuclides detected in the other investigated solutions (sodium acetate, acid, water) or the second solution of acetate buffer as confirmed by LSC spectrometry.

3.3. Distribution of caesium, americium, and plutonium isotopes in sequentially extracted fractions

The desorption experiments showed that ^{137}Cs content in the water-soluble fraction was less than one percent of the total activity; α-emitting radionuclides (^{241}Am and $^{238,239+240}$Pu) were not detected in this fraction. The maximum ^{137}Cs content (up to 95%) was detected in the residual fraction (Fig. 5).

The sequentially extracted plutonium isotopes showed the same fraction behavior (Fig. 5) with different distributions for the R-4 and R-17 bottom sediments, like for ^{137}Cs and ^{241}Am. The association of radionuclides with bottom sediment components in each fraction was considered.

4. Discussion

Compared to the 1970s, in 2008 studies, the concentrations of ^{137}Cs

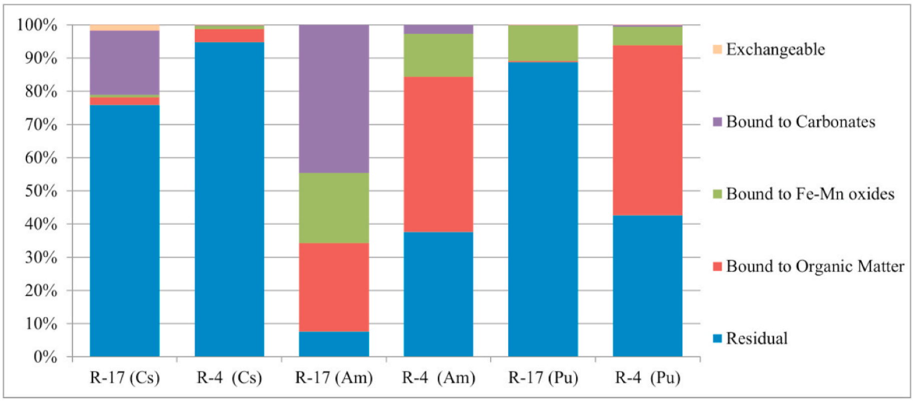


Fig. 5. ^{137}Cs, ^{241}Am and $^{238,\ 239,\ 240}$Pu percentage distributions in fractions from R-17 and R-4 bottom sediments.

and ^{90}Sr in mobile forms has clearly decreased (Stukalov and Simkina, 2008). Thus, the fact that just a part of ^{137}Cs that was absorbed by ion exchange can migrate and desorb (Orlova, 1974) may indicate a change in the form over time. We assume, that if pH does not have an effect, a solution that is most suitable for the environment at pH = 8.6 for the studied reservoirs can be used to decontaminate the sediments since the smallest change in pH affects the cells of organisms living in the reservoir. The absence of radionuclide desorption as a function of pH also supports an assumption regarding the desorption mechanism. The monovalent ^{137}Cs cation sorption is most likely characterized by the ion exchange mechanism. The ionic strength of the buffer solution is higher than that of the other solutions used (Table 1); therefore, assuming ion exchange, the highest desorption should occur in the acetate buffer solution, which was experimentally confirmed. Additionally, it is possible to assume complexation of ^{90}Sr with acetate anions. A high CH_3COO^- concentration contributes to reactions with Sr^{2+} cations because of the characteristics of bivalent strontium chemistry. The ^{137}Cs K_d values obtained for water ($9 \cdot 10^3$) from the desorption experiments completely correlated with the range described by Strand et al. (1999) for the bottom sediment of R-10, which follows R-4 in the Techa Reservoir Cascade ($9 \cdot 10^3$–$3 \cdot 10^4$).

The partitioning of ^{137}Cs, ^{241}Am, and $^{238,239+240}$Pu from the bottom sediments from the two reservoirs were analyzed. ^{137}Cs is one of the dose-forming radionuclides and is easily detectable at low extraction percentages. ^{241}Am, the only α-emitting radionuclide detected during the desorption experiments, is relatively bioavailable by hydrobionts. Plutonium has a complex redox behavior, and thus its migration is of great interest in radioecology. The first three fractions – water-soluble, exchangeable, and bound to carbonates – are the most mobile and biologically accessible. Therefore, the radionuclide contents in these fractions are the most important for contamination risk assessments.

The maximum of ^{137}Cs in the residual fraction indicates the possible incorporation of ^{137}Cs into clay mineral structures, the destruction of which is achieved by strong acids. The partitioning of ^{137}Cs and ^{241}Am (Fig. 5) from the bottom sediments of the two reservoirs differed in the carbonate and organic matter fractions, which can be explained by the differences in sediment compositions. It was reported before that the bottom sediment of the R-17 reservoir is mostly, ca. 90%, consists of inorganic substances (50% feldspar, 40% quartz particles as soil-filling materials, and hydrated-slurry pulps from chemical and metallurgical production waste) (Stukalov and Simkina, 2008), 9% of organic residues with destroyed structures (detritus), and 1% of organic residues with preserved structures (algae, plant organs, zooplankton). The R-4 reservoir species diversity is notably richer than that of the R-17 reservoir (Pryakhin et al., 2016), which could account for the large amount of ^{241}Am in the fraction bound to organic matter.

The behavior of plutonium in the environment and changes to its form may arise from several simultaneous processes, for example, sorption in combination with reduction reactions at the water-mineral phase boundary or in solution due to precipitation (Duff, 2001). Plutonium in environmental samples is poorly soluble (Rai et al., 1980). The plutonium solubility/complexation and mobility in natural water vary greatly; plutonium is more easily adsorbed and less soluble in the +3 and + 4 states due to the high charge of the ions as compared with valencies of V and VI, which are represented by the PuO_2^+ and PuO_2^{2+} ions (Duff, 2001).

According to the Tessier method the association of radionuclides with bottom sediment components in each fraction was considered by the following paragraphs.

4.1. Exchangeable (F1)

For the investigated reservoirs, the low ^{137}Cs content and absence of ^{241}Am and plutonium in this fraction confirm the low possibility of the transfer of these radionuclides from the sediment to water. However, even at a low content of ^{137}Cs in the exchangeable fraction (1.0% of the total ^{137}Cs activity), the resulting solution has a specific activity of 365 Bq/mL and is thus radioactively contaminated. Exchangeable cations are held by weak electrostatic interactions, and their behavior is determined by ion exchange processes in the sample. A medium change in ionic composition or decrease in solution pH leads to the mobilization of exchange ions (Fedotov et al., 2008). This fraction is physicochemically mobile and biologically available.

4.2. Bound to carbonates (F2)

For the studied R-17 bottom sediment sample, 11.0% of the detected ^{137}Cs contained in the fraction bound to carbonates; in contrast, the R-4 sediment content in this fraction was less than 1%. The largest ^{241}Am content (32.7%) was found in the R-17 sediment. The complexation of ^{241}Am with carbonates is characteristic of its chemistry, and the formation of many ^{241}Am carbonate complexes is known (Silva, 2012). A maximum ^{241}Am content in the carbonate fraction has been reported by many studies (McDonald et al., 2001; Bunzl et al., 1995). It is likely that the minimum amounts of ^{241}Am and plutonium found in the R-4 samples were due to the low carbonate content of the R-4 bottom sediment.

The sequential extraction results depend on many factors among which the composition of the studied bottom sediment is the most important. Carbonate content (calcite, dolomite) of about 10% yielded high plutonium (30%) and ^{241}Am (50%) contents in this fraction (Schultz et al., 1998). In contrast, a minimal plutonium concentration in the fraction bound to carbonates is expected for sediments containing little or no carbonates (Kenna, 2009). In some sequential extraction techniques, this fraction is also called acid-soluble (Ure et al., 1993; Rauret et al., 1999). Metals that co-precipitate with carbonates and those adsorbed on the surface of compounds recovered in the following stages are recovered in this fraction. Metals are extracted from the sample at a pH close to 5. The metal content may depend on the composition of the bottom sediment; namely, it varies depending on the amount of carbonate minerals (Fedotov et al., 2008; Sheppard et al., 1992).

4.3. Bound to iron and manganese oxides (F3)

Significant ^{241}Am activities were found in this fraction (15.4% for R-17 and 13.1% for R-4). The highest ^{241}Am activity is usually observed in fractions associated with carbonates, iron-manganese oxides, and bound to organic matter. On average, the ^{241}Am in the fractions bound to iron-manganese oxides and organic matter was distributed equally. The contents may differ due to the chemical composition of the soil and the predominance of various components.

The plutonium content results obtained in this fraction for R-17 (≈10%) and R-4 (≈5%) bottom sediments agree with the results reported by Bunzl et al. (1999), who showed that in mineral soils (gray forest soils samples from southern Germany) with 1190 mg/kg manganese and 7.4% organic matter, approximately 10% of the detected plutonium was in the fraction bound to iron-manganese oxides. In contrast, for soils with a high organic matter (95%) and low manganese (68 mg/kg) content (podzolic Al–Fe soil from the taiga of northern Finland), the presence of plutonium in the iron-manganese oxide fraction was approximately 5%.

This fraction is easily reducible, and manganese oxides, amorphous iron, and aluminum oxides are extracted here. These compounds are difficult to mobilize physicochemically, and thus they have a medium bioavailability. The reducible soil material consists of iron and manganese oxides, which are known for the fixation of trace amounts of metals (Jenne, 1968). Iron-manganese oxides are not stable under reducing conditions. The iron-manganese oxide extraction is carried out at a low pH of 2, which indicates the low bioavailability of the radionuclides associated with the extracted metals.

4.4. Bound to organic matter (F4)

The percentage of ^{241}Am in this fraction was approximately equal to that in the fraction bound to iron-manganese oxides for the R-17 bottom sediment, whereas a predominant amount was detected in this fraction for the R-4 sediment. Fifty percent of bound-to-organic-matter plutonium was detected for the R-4 bottom sediment.

This fraction is also called the oxidizable fraction. Stable organic compounds, sulfides, and salts of humic acids and fulvic acids are extracted at a 1:40 wt ratio by double hydrogen peroxide extraction, then acidified with nitric acid to pH 2. The fraction is biologically difficult to access and physicochemically difficult to mobilize. ^{137}Cs is not characteristically bound to organic compounds in the bottom sediment (Mori et al., 2017). It is known that the plutonium content in this fraction directly depends on the sediment organic matter content (Torres et al., 1984; Kim et al., 1989; Livens et al., 1987). Lucey et al. (2004) showed that at an organic matter content of approximately 1.5%, the plutonium content was 15%, and with a decrease in organic matter, the plutonium content decreases as well.

4.5. Residual (F5)

The maximum ^{137}Cs and plutonium contents were found in the residual fraction. This indicates the isomorphic substitution of sodium and potassium by ^{137}Cs in the crystalline clay minerals. This plutonium distribution can be explained by precipitation aging—irreversible structural changes occur in the sediment from the moment of formation, including recrystallization/transformation into a stable form, thermal and chemical hardening, and particle agglomeration (Shapiro et al., 1950). Haire et al., in 1971 shows: "The results showed that the freshly precipitated material consisted of small, primary particles that are essentially amorphous. After sufficient aging in an aqueous medium, the material became crystalline". This fact explains the different plutonium distribution in the residual fraction of the sequential extraction of two reservoirs bottom sediments. Since in R-17 the waste has been discharged since 1949, and in R-4 since 1972, and the reservoir R-4 is a flow-through, and therefore a more dynamic system. This fraction is physicochemically immobile and biologically unavailable.

By analyzing the association of ^{137}Cs, ^{241}Am, and $^{238,239+240}$Pu with the bottom sediment components of two reservoirs, different contents were found in the studied fractions. For ^{137}Cs, the contents in the residual fractions were similar to most other bottom sediments, for example, from Lake Uruskul (90%) located near the Mayak territory (Levina, 2008). ^{137}Cs quickly integrates into crystalline clay minerals, and plutonium is adsorbed by amorphous compounds on the surface of mineral particles (Pavlotskaya, 1993). The ^{137}Cs and ^{241}Am distribution correlations obtained in this work are similar for both bottom sediments (R-4 and R-17) with R-10 bottom sediments (Pavlotskaya et al., 1998), but for plutonium, only the content in the R-4 bottom sediment was in agreement with R-10. Reservoir R-10 is the next after R-4 in the Techa Reservoir Cascade.

All of these plutonium results in the literature correlate with the R-4 results in the present study. The distribution in the bound to organic and residual fractions is similar to that in the Asanov Swamp pond and Techa river bottom sediments (Muslyumovo region), and the absence of plutonium in the exchangeable fraction resembles the Yenisey river bottom sediment (Krasnoyarsk region). This distribution and difference between the R-17 and R-4 bottom sediment fractions can be explained by composition. The high organic matter content in the R-4 sediment results in distributions similar to other radioactive-contaminated investigated reservoirs in the region. In contrast, the R-17 bottom sediment distribution indicates a large number of inorganic compounds.

After analysis of the literature data, we can conclude that plutonium in the bottom sediment of Chelyabinsk region reservoirs, in particular, the Mayak lakes, is mainly present in fractions associated with organic matter and iron-manganese oxides. The content in the residual fraction (25–50%) is also significant. A comparison of the present sequential extraction results to literature data from experiments where the bottom sediment compositions were determined precisely by physicochemical methods according to sequential extraction procedure was carried out, and thus we can attempt to indirectly determine the compositions of the studied bottom sediments. This finding can be useful for bottom sediment composition determination. The forms of the studied radionuclides in the R-4 bottom sediment matched those determined in other reservoirs around Mayak (Skipperud et al., 2000, 2009; Pavlotskaya et al., 1998).

5. Conclusion

Studies have shown that after 10 years, the percentage of ^{137}Cs and ^{90}Sr desorption has significantly reduced and the probability of changes in association with bottom sediment components of the studied radionuclides is minimal.

The ^{137}Cs and ^{90}Sr desorption processes depend more on the solution composition and ionic strength. Radionuclide desorption did not exceed 1%. The desorption kinetic parameters were also determined. The first washout occurred over 24 h for ^{137}Cs and ^{90}Sr in all the studied solutions; in the second cycle desorption solution, the time required for ^{137}Cs desorption to complete was from 24 to 160 h, whereas that for ^{90}Sr was still 24 h. The α-emitting radionuclide desorption was not detected.

Using the Tessier technique, most ^{137}Cs (up to 95%) content was found in the residual fraction for both reservoirs. This may indicate that the main ^{137}Cs sorption mechanism is incorporation into the structure of clay minerals. ^{241}Am sorption occurred by complexation, mainly with carbonates (R-17 bottom sediment) and organic matter (R-4 bottom sediment) and less with iron-manganese oxides. The maximum plutonium content was detected in the residual fraction of the R-17 bottom sediment, which could be associated with the effects of precipitation aging. In the R-4 sediment, plutonium was mainly found in the bound to organic matter and residual fractions.

Sequential extraction results depend on many factors and can be interpreted in different ways. However, the presence of ^{137}Cs and plutonium in a biologically unavailable and physicochemically immobile fraction indicates their low bioavailabilities and low probabilities of desorption upon changes to the chemical composition of the water.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the Russian Science Foundation [grant number 19-73-20051].

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvrad.2021.106569.

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