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# Sorption behaviour of neptunium in marine and fresh water bottom sediments in Far East area of Russia (Lake Khanka and Amur Bay)

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ARTICLE INFO ABSTRACT The concentration and sorption behavior of <sup>237</sup>Np on the bottom sediments of water bodies in the Far East region Keywords: <sup>237</sup>Np of Russia (Lake Khanka and Peter the Great Bay) were studied for the first time. The <sup>237</sup>Np concentrations vary Bottom sediments from  $1.06 \times 10^{-6}$  to  $4.43 \times 10^{-5}$  mBq g<sup>-1</sup> in the bottom sediments of Lake Khanka and from  $1.05 \times 10^{-4}$  to 2.52Lake Khanka  $\times 10^{-3}$  mBq g<sup>-1</sup> for Amur Bay. The experiment on the adsorption of Np on marine and lake sediment showed Peter the Great Bay that it is sorbed through complexation with silicates (albite, leucite). The Np sorption isotherm on marine Sea of Japan sediments is described by the Langmuir equation; the distribution coefficients (Kd) of Np vary from 57 to 588 mL

#### 1. Introduction

Sorption

Neptunium (Np) is of anthropogenic origin. As with other actinides, its main sources in the environment are nuclear accidents and global fallout. In addition,  $^{237}\!\mathrm{Np}$  (t $_{1/2}=2.14\times10^6$  years) is one of the main long-lived radionuclides in spent nuclear fuel and, in the long term, is considered to be one of the critical components of high-level waste (Yoshida et al., 2007; Petrov et al., 2017; Nilsson and Carlsen, 1989; Academy, 1974). This radionuclide can be highly mobile in the natural environment and exhibit significant radiotoxicity to mammals (Thompson, 2014). There are few studies focused on the migration of Np in the environment because it is contained in natural samples at low concentrations (less than  $\mu$ Bq kg<sup>-1</sup>) (Guérin et al., 2010) and is difficult to selectively extract. However, studying the behavior of Np in the environment (Townsend et al., 2022; López-Lora and Chamizo, 2019; Maher et al., 2013; Burns and Klingensmith, 2006) is crucial for evaluating the consequences of nuclear accidents and their impact on the environment.

Neptunium in the atmosphere (Efurd et al., 1982; Oldham et al., 2016; Lindahl et al., 2004), in marine waters (Holm A.AS and., 1987; Pentreath and Harvey, 1981) and its sorption on marine sediments (Higgo and Rees, 1986; Choppin and Wong, 1998; Efstathiou and

Pashalidis, 2017) resulting from global fallout activities post-1945 have been of interest to scientists since last century. Here, the Far Eastern region of Russia is chosen as the location of such a study for the first time. This region is of interest to researchers as it was significantly impacted by global fallout following nuclear weapons testing, as well as major radiation accidents in the vicinity (Romanova and Parker, 2002; Takano et al., 2001).

 $g^{-1}$ . For lake sediments, the isotherm is described by the Henry equation; the Kd value reaches 935 mL  $g^{-1}$ .

Sorption of Np on various clays is also the subject of many studies (Fröhlich, 2015; Semenkova et al., 2018), as clays are the main material used for constructing engineering barriers for the disposal of radioactive waste deep underground (Kaszuba and Runde, 1999). It was found that, on average, the sorption of Np increases with increasing pH up to 9 and then decreases due to the formation of negatively charged NpO<sub>2</sub><sup>+</sup>-carbonate species under ambient air conditions (observed on the example of kaolinite and Opalinus Clay) (Fröhlich, 2015). Furthermore, the sorption of Np(V) increased notably as the initial concentration of Np decreased. It was observed that the sorption of Np(V) on clays is higher in the presence of calcite. No apparent impact of ionic strength on the sorption of Np on clays was observed (Li et al., 2015).

This study aims to investigate the distribution of Np in marine and lake sediments in the Far East region of Russia in terms of concentration and depth. The adsorption mechanism of Np on these sediments was

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explored through sorption experiments to comprehend the behavior in both lake and marine ecosystems.

### 2. Study location

Sediment cores were collected from Peter the Great Bay in the Sea of Japan and Lake Khanka (also known as Lake Xingkai) (Fig. 1). Lake Khanka is the largest fresh water reservoir in Northeast Asia, located on the border between China and Russia. The surface area of the lake ranges from 3940 to 5010 km<sup>2</sup>, depending on climatic conditions, with a length of 90 km and a width of 67 km. Lake Khanka is a shallow water reservoir with an average depth of 4.5 m, prevailing depths are 1–3 m and a maximum depth of 10.6 m (Matveev et al., 2020). Twenty-four rivers flow into the lake, and one (Sungacha River) flows out from Lake Khanka into the Ussuri River and then to the Amur River and finally to the North mouth of the Sea of Japan. Ussuri and Amur bays in Peter the Great Bay are located in the northwestern part of the Sea of Japan on the border of temperate and subtropical zones (Chernova et al., 2011). Amur and Ussuri bays are located on both sides of Vladivostok, which has a population of about one million and is heavily industrialized, resulting in relatively higher levels of pollution (Khristoforova et al., 2020). Geological, geochemical, ecological and other matters have been studied in prior works on the territory of Lake Khanka and Peter the Great Bay (Jiaojie et al., 2014; Sun et al., 2018; Polyakov et al., 2019). These studies have shown that Lake Khanka's sediments consist of sand varying in size, whilst Peter the Great Bay's sediments are organic compounds of varied decomposition levels. Since bottom sediments are the most important natural archive that records information about changes in the environment during the period of sedimentation, the sedimentation rate was estimated for both Lake Khanka and Peter the Great Bay. Recently, sedimentation rates determined in another study was estimated to be 1.6 mm  $y^{-1}$  in Lake Khanka and 0.43–0.5 mm  $y^{-1}$  in Peter the Great Bay (Kuzmenkova et al., 2023).

#### 3. Materials and methods

The sediment cores were sampled in Lake Khanka (the total length of the core is 28 cm) and Peter the Great Bay (the total length of the core exceeds 30 cm) in August 2021, using a modified percussion forcer boer (Grabenko and Bukin, 2022). The boer had a diameter of 110 mm. Four cores were taken, two from Lake Khanka from a depth of 3-4 m, one from Amur Bay and one from Ussuri Bay from a depth of 9-10 m, and were transported to the Institute of Chemistry, Far Eastern Branch of the Russian Academy of Sciences, Vladivostok. For radionuclide identification, the central part of the core measuring 4  $\times$  5 cm was sliced into segments of 0.50 cm for the cores from Lake Khanka and Ussuri Bay, and 1.0 cm for the core from Amur Bay. Sediment cores from the sea and from the lake have different thickness due to the fact that they are taken from different depths. Thus, for lake sediments, the core does not exceed 30 cm, so it is convenient to cut it into layers of 0.5 cm. In the case of marine sediments, the core exceeds 30 cm, so it is more convenient to cut it into 1 cm. Sediment deformation was minimal, and the adsorption of bottom sediments along the walls of the sampler was limited. Each segment of the samples was dried at a temperature of 105 °C for 8 h, then it was ground and reserved in a container. Part of the dried samples were packed and shipped to Xi'an AMS center for analysis of Np isotopes.

The sample (about 5 g) was weighed to a beaker and ashed at 450 °C for 10 h to eliminate any organic substances before being spiked with a  $^{242}$ Pu tracer (0.05 Bq). Next, the sample was leached with a 50 mL mixture of HNO<sub>3</sub> + HCl (in a 3:1 vol ratio) under heating at 150-200 °C on a hotplate. The leaching process was repeated until the sediment sample was completely dissolved and the resultant leachate was combined. Following dilution with H<sub>2</sub>O, NH<sub>3</sub> was added to adjust to pH 8–9. The co-precipitated Np with Fe(OH)<sub>3</sub> was subsequently separated from the solution through centrifugation. The precipitate was dissolved with HCl, and the valence states of Np and Pu were adjusted to Pu(IV) and Np (IV) by using KHSO<sub>3</sub> and HNO<sub>3</sub>. Next, the prepared sample solution was loaded onto a 2 mL TEVA column. Following rinsing with HNO<sub>3</sub> and



Fig. 1. Sampling sites for two sediment cores in Khanka Lake (left) and two marine sediment cores from Amur Bay and Ussuri Bay (right).  $\bigcirc$  sampling points for bottom sediments used for sorption experiments;  $\bigcirc$  sampling points for bottom sediments used for measuring <sup>237</sup>Np concentration;  $\bigcirc$  sampling point for bottom sediments used for measuring <sup>237</sup>Np concentration by (Zhang et al., 2022).

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HCl, Np and Pu were eluted from the column. Chemical yields of Pu and Np in all analyzed samples ranged from 60% to 90%. The  $^{237}$ Np in the separated sample solution was measured using ICP-MS/MS (Agilent 8800). A quality control sample was analyzed for each sample to ensure quality control. The method's full details have been reported elsewhere (Xing et al., 2022).

Elemental analysis of bottom sediments was conducted using a Shimadzu EDX-800HS energy-dispersive X-ray fluorescence spectrometer after pressing 200 mg of sample material into a boric acid substrate. The measurement time for each area of the Ti–U, C–Cs definitions was 200 s with a 10 mm collimator. The method's relative error ranged between 1 and 5%, depending on the element being determined.

Mineral composition of the sediments was measured by full-profile X-ray diffraction analysis using powder preparations on a Rigaku Ultima-IV X-ray diffractometer (Cu-K $\alpha$ , D-Tex-Ultra detector, scanning area 3–65° 2 $\Theta$ ). Detailed X-ray patterns of the sediment's layers might be found in the supplementary material.

The marine sediment collected from 0 to 3 cm depth and lake sediment from 0 to 3.5 cm depth were used for sorption experiments. A  $^{237}$ Np solution (the chemical matrix was distilled water) was mixed with the sediment by addition of 0.03 L distilled water to 5 g sediment sample. The initial concentration of  $^{237}$ Np was  $1.22 \times 10^{-5}$  mol L<sup>-1</sup> (75 Bq mL<sup>-1</sup>). At certain time intervals: e.g., 30 min, 1, 1.5, 3, 6, 24, 168 h and up to 5 months, a small fraction (0.5 mL) of supernatant was taken. The samples were continually mixed on a shaker with a rate of 150 rpm in between sampling events. The concentration of  $^{237}$ Np in solutions was measured with liquid scintillation spectrometry (Quantulus GCT 6220) for 30 min in alpha/beta discrimination mode after adding 5 mL of Gold Star scintillation cocktail (detection limit is 0.05 Bq). Blank samples were also measured for quality control. The typical uncertainty of the measurement was 0.2 cpm (0.003 Bq)

The degree of sorption (*S*, %) and the distribution coefficient of the radionuclide between the solid and liquid phases (*Kd*, mL g<sup>-1</sup>) were calculated using the following formulas:

$$S = \frac{I_0 - I_e}{I_0 - I_{bkg}} \times 100\%$$
(1)

$$K_d = \frac{S}{1-S} \times \frac{V}{m} \tag{2}$$

where  $I_{bkg}$  is the count rate of the background,  $I_0$  is the count rate of the

initial solution and  $I_e$  the count rate of the equilibrium solution; V (mL) is the volume of the solution and m (g) is the mass of the sediment.

Water samples were obtained from the locations in Lake Khanka and Amur Bay where sediments had been collected. Analysis of element composition was performed using ICP-MS.

The two sediment samples were leached with deionized water and the leachate was analyzed for major elements. The measurements were conducted three months after adding water to the sediment. Three types of solutions were measured: 1) sediments with distilled water; 2) collected water from the site without sediments; and 3) sediments with collected water. Collected water with and without sediments was measured to understand what elements are washed out from sediments. Both collected and distilled water were measured to understand the impact of ionic strength on  $^{237}$ Np sorption.

## 4. Results

The concentrations of  $^{237}Np$  determined in the sediment cores from the southern part of Lake Khanka and Ussuri Bay in the Japan Sea (Fig. 2) are remarkably low. They range from  $1.05 \times 10^{-4}$  to  $2.52 \times 10^{-3}$  mBq g<sup>-1</sup> (with an average value of  $5.12 \times 10^{-4}$  mBq g<sup>-1</sup>) in Ussuri Bay, and from  $2.55 \times 10^{-6}$  to  $4.43 \times 10^{-5}$  mBq g<sup>-1</sup> (with an average of  $1.27 \times 10^{-5}$  mBq g<sup>-1</sup>) in Lake Khanka. For marine sediments, a peak is present at a depth of 19.5 cm with an activity concentration of  $25.2 \times 10^{-4}$  mBq g<sup>-1</sup>. Contrastingly, two peaks can be observed in the lake sediments, one at a depth of 1.5 cm (3.87  $\times 10^{-5}$  mBq g<sup>-1</sup>) and another at 9 cm (4.43  $\times 10^{-5}$  mBq g<sup>-1</sup>), respectively.

Notably, the distribution of Np-237 closely matched that of Pb-210 and Cs-137 in Lake Khanka (Kuzmenkova et al., 2023). However, an additional peak indicating a release was observed in the distribution of Np-237 in marine sediments. The confirmation of our results' accuracy was achieved through the use of previously determined sedimentation rates, allowing a comparison with existing data.

The results (Table 1) show that the concentrations of Mg in sea water is hundreds of times greater than that in lake water, with concentrations of Ca and Sr also tens of times higher. Concentrations of Al, Ba, Mn and Th are comparable in both seawater and lake water. Other element concentrations are relatively low. The fourth column for both lake and marine sediments in Table 1 shows the difference between collected water composition with and without sediments.

The elemental analysis of the bottom sediments was carried out for



Fig. 2. Activity concentrations of <sup>237</sup>Np in the sediments cores: a) marine; b) lake water.

Table 1

Analytical results of elements in lake and seawater as well as the water leachate of the sediment by ICP-MS.

| Element  | Dist. water + Lake sed.                                       | Lake water                                      | Lake water + Lake sed.                                       | Diff.   | Dist. water + Marine sed.                                    | Marine<br>water                                    | Marine water + Marine sed.                        | Diff.  |
|----------|---|---|--|---|--|--|---|--|
|          | Concentration, mg $L^{-1}$                                    |   |  |   |  |  |   |  |
| Ca<br>Mg | $\begin{array}{c} 2.00 \pm 0.17 \\ 0.81 \pm 0.07 \end{array}$ | $22 \pm 2 \\ 3.89 \pm \\ 0.33$                  | $\begin{array}{c} 26.0 \pm 2.2 \\ 8.72 \pm 0.74 \end{array}$ | $\begin{array}{c} 4.00\pm0.34\\ 4.83\pm0.41\end{array}$ | $\begin{array}{c} 4.00 \pm 0.34 \\ 10.3 \pm 0.9 \end{array}$ | $\begin{array}{c} 381\pm32\\ 578\pm90 \end{array}$ | $\begin{array}{l} 396\pm34\\ 424\pm85\end{array}$ | $\begin{array}{c} 15.00\pm1.3\\ -154\pm23 \end{array}$ |
| Si       | $\textbf{2.74} \pm \textbf{0.21}$                             | $\begin{array}{c} 1.69 \pm \\ 0.13 \end{array}$ | $\textbf{3.74} \pm \textbf{0.28}$                            | $\textbf{2.05} \pm \textbf{0.15}$                       | $\textbf{6.75} \pm \textbf{0.51}$                            | $0.37\pm0.03$                                      | $1.22\pm0.09$                                     | $\textbf{0.85}\pm\textbf{0.06}$                        |
| Al       | $0.63\pm0.06$   | < 0.01  | $0.23\pm0.02$  | $0.22\pm0.02$   | $2.04\pm0.2$   | < 0.01   | $0.09\pm0.01$                                     | $0.08\pm0.01$  |
| Fe       | $1.36\pm0.14$   | < 0.01  | $\textbf{0.87} \pm \textbf{0.09}$                            | $\textbf{0.86} \pm \textbf{0.09}$                       | $2.85\pm0.29$  | < 0.01   | $1.66\pm0.17$                                     | $1.65\pm0.17$  |
| Sr       | < 0.01  | $0.06 \pm$                                      | $0.07\pm0.01$  | 0.01 $\pm$  | $0.03\pm0.003$   | $3.41 \pm 0.34$                                    | $3.46\pm0.35$                                     | 0.05 $\pm$   |
|          |   | 0.01  |  | 0.001   |  |  |   | 0.005  |
|          |   | Concentratio                                    | n, $\mu g L^{-1}$  | ·   |  |  |   |  |
| Ba       | $16.0 \pm 1.6$  | $17.0\pm1.7$                                    | $\textbf{38.0} \pm \textbf{3.8}$                             | $21.0\pm2.1$  | $7.0\pm0.7$  | $\textbf{7.0} \pm \textbf{0.7}$                    | $23.0\pm2.3$                                      | $16.0\pm1.6$   |
| Mn       | $97.0\pm9.7$  | $\textbf{2.0} \pm \textbf{0.2}$                 | $4.0\pm0.4$  | $\textbf{2.0} \pm \textbf{0.2}$                         | $17.0\pm1.7$   | $\textbf{2.0} \pm \textbf{0.2}$                    | $21.0\pm2.1$                                      | $19.0 \pm 1.9$   |
| Zn       | $23.0\pm2.3$  | $\textbf{4.0} \pm \textbf{0.4}$                 | $6.0\pm0.6$  | $\textbf{2.0} \pm \textbf{0.2}$                         | $20.0\pm2.0$   | $296\pm30$   | $40.0\pm4.0$                                      | $-256\pm26$  |
| U        | $0.08\pm0.01$   | $\begin{array}{c} 0.18 \pm \\ 0.02 \end{array}$ | $0.77\pm0.8$   | $\textbf{0.59} \pm \textbf{0.06}$                       | $0.38\pm0.04$  | $1.42\pm0.14$                                      | N/D <sup>a</sup>                                  | -  |
| Th       | $0.17\pm0.01$   | <0.01   | $0.05\pm0.004$   | $\begin{array}{c} 0.04 \ \pm \\ 0.003 \end{array}$      | $0.31\pm0.02$  | <0.01  | $0.13\pm0.01$                                     | $0.12\pm0.01$  |

<sup>a</sup> Not Detected.

investigation the effect of the elemental composition on sorption (Table 2). Only the surface layer of sediments was taken, since the elemental composition remains consistent throughout the entire core length (Fig. 3). In any incident occurring on the Earth's surface, the surface horizon will be the initial site of impact, therefore assessing its sorption properties as a geochemical barrier to Np is of utmost significance (Assinder, 1999). <sup>237</sup>Np serves as an additional marker for dating bottom sediments. Its application facilitates determining the date of release, consequently enabling the calculation of sedimentation rates.

It is shown that the neptunium peaks in the sediment column do not correlate with the elemental composition of the sediments. Therefore, the physicochemical properties of neptunium itself and the sedimentation process are of most importance.

X-ray phase analysis showed that the bottom sediments of the Sea of Japan are approximately half quartz (SiO<sub>2</sub>), one-fifth albite (Na [AlSi<sub>3</sub>O<sub>8</sub>]), and small amounts of dolomite (CaMg[CO<sub>3</sub>]<sub>2</sub>), halite (NaCl), magnesioferrite (MgFe<sub>2</sub>O<sub>4</sub>) and hematite (Fe<sub>2</sub>O<sub>3</sub>) (Fig. 4). The bottom sediments of Lake Khanka consist of 80% quartz and albite, and small amounts of leucite (K[AlSi<sub>2</sub>O<sub>6</sub>]) and dolomite (Fig. 5). The occurrence of halite in marine sediments suggests the leftover sea salt after the sediment dried up. Lake sediments, on the other hand, do not contain halite or chlorine according to elemental analysis.

Sorption kinetics of <sup>237</sup>Np on bottom sediments. Experiments were conducted on the sorption kinetics of Np on bottom sediments at pH

| Tal | ble | 2 |
|-----|-----|---|
|-----|-----|---|

Analytical results of elemental composition in bottom sediments.

| Element | Elemental composition <sup>a</sup> , % | Elemental composition <sup>a</sup> , % |  |  |  |  |  |
|---------|--|--|--|--|--|--|--|
|         | Lake sediments (0–3.5 cm) <sup>b</sup> | Marine sediments (0–3 cm) <sup>b</sup> |  |  |  |  |  |
|         |  |  |  |  |  |  |  |
| Si      | 64.6                                   | 48.7                                   |  |  |  |  |  |
| Cl      |  | 2.3                                    |  |  |  |  |  |
| Al      | 15.2                                   | 20.9                                   |  |  |  |  |  |
| Fe      | 4.8                                    | 12.2                                   |  |  |  |  |  |
| K       | 5.5                                    | 4.4                                    |  |  |  |  |  |
| Na      | 3.7                                    | 3.9                                    |  |  |  |  |  |
| Ca      | 3.4                                    | 1.9                                    |  |  |  |  |  |
| Ti      | 1.0                                    | 1.1                                    |  |  |  |  |  |
| Mg      | 0.7                                    | 2.3                                    |  |  |  |  |  |
| Ва      | 0.5                                    | 0.6                                    |  |  |  |  |  |
| S       | 0.1                                    | 1.2                                    |  |  |  |  |  |
|         |  |  |  |  |  |  |  |

<sup>a</sup> The relative error did not exceed 5%.

<sup>b</sup> Compositions of other layers are in the supplementary material.

values ranging from 4 to 12. The required pH values were adjusted only once using NaOH and  $HClO_4$  solutions, and measured during the experiment (Figs. 6 and 7).

In general, marine sediment exhibited a higher adsorption of  $^{237}$ Np compared to lake sediment. At a pH of approximately 6, 25% of Np was adsorbed on marine sediments, while only 5% was adsorbed on lake sediments (Fig. 8).

At a pH of approximately 8, the adsorption of Np in marine sediment decreased from 75% to 42% over a 5-month period since the start of the experiment (Fig. 9). In contrast, Np sorption in lake sediments remained stable at approximately 18%.

The dashed lines in Figs. 8 and 9 represent the average sorption value during the experiment.

Dependence of <sup>237</sup>Np sorption on the pH value of the aqueous phase. A low sorption of <sup>237</sup>Np on marine sediments (less than 20%) was observed at pH < 4, then the sorption of Np increased from ~10% to 90% as pH increased from 4 to 12 (Fig. 10).

Sorption isotherm of <sup>237</sup>Np on bottom sediments of the Sea of Japan and Lake Khanka. The <sup>237</sup>Np sorption isotherm on marine sediments at pH around 7 is described by the Langmuir equation (Fig. 11). Kd varies from 57 mL g<sup>-1</sup> to 588 mL g<sup>-1</sup> with maximum adsorption  $1.04 \times 10^{-4}$  mol g<sup>-1</sup>. For lake sediments, the isotherm is described by the Henry equation (y = 0.94-1.67x). The Kd value reaches 935 mL g<sup>-1</sup>.

### 5. Discussion

 $^{237}\mathrm{Np}$  level in bottom sediments of the Sea of Japan and Lake Khanka.

In another study it has been reported that in Xingkai Lake, located in the northern region of Lake Khanka, where Np-containing particles enter via river flow, the concentrations of  $^{237}\rm Np$  range from  $2\times10^{-5}$  to 21.9  $\times10^{-4}$  mBq g^{-1} (Zhang et al., 2022) (Fig. 1). These concentrations are approximately ten times higher than the observed levels of  $^{237}\rm Np$  in the sediment core gathered in the lake's central region during this study.

Elemental and mineralogical composition of bottom sediments from the Sea of Japan and Lake Khanka. The sediment elemental and mineralogical composition is crucial for this study to ensure their consistency throughout the core. It's essential to note that neptunium's behavior is linked to its chemical properties and not impacted by the sediment's composition. Furthermore, the values obtained from elemental analysis can be relied upon when determining the phase composition. The presence of Cl in marine sediments is probably due to the remains of dried sea salt; therefore, it is absent in lake sediments.



Fig. 3. Distribution of the major elements along the sediments cores: a) marine; b) lake water.



Fig. 4. Mineralogical composition of marine bottom sediments.



Fig. 5. Mineralogical composition of lake bottom sediments.



Fig. 6. Variation of pH in solution over time of adsorption experiment of Np on marine sediment.

Previous studies conducted by other groups in this region have determined that the migration rate of chromium (Cr), nickel (Ni), copper (Cu), zinc (Zn) and lead (Pb) in bottom sediment from both freshwater and seawater decreases in reverse proportion to the increase in pH. The accumulation of these metals in sediments from the liquid medium follows the order:  $Pb \gg Mn > Ni > Cu > Zn > Fe \gg Cr$ . By analyzing the elemental composition of the coastal soil of Lake Khanka, it was found that the concentration of certain heavy metals exceeds the normal levels, which enhances the migration of metals into the water and their accumulation in Lake Khanka bottom sediments (Tokar et al., 2023).

Sorption kinetics of  $^{237}$ Np on bottom sediments. A high adsorption of  $^{237}$ Np on marine sediments compared to lake sediment was observed. This may be attributed to the higher presence of iron in marine sediments, on which Np can precipitate owing to reduction of Np(V) to high



Fig. 7. Variation of pH in solution over time of adsorption experiment of Np on lake sediment.



**Fig. 8.** Kinetics of Np sorption on bottom sediments of Lake Khanka and the Sea of Japan at pH 6. Both dependency curves have been highlighted in grey to illustrate the minimal scattering of points for each type of sediments.



**Fig. 9.** Kinetics of Np sorption on bottom sediments of Lake Khanka and the Sea of Japan at pH 8. Only values for lake sediments are located within the grey-shaded area, since a decrease in sorption is observed for marine sediments.



Fig. 10. pH dependence of Np sorption on sediment.



Fig. 11. Sorption isotherm of Np on bottom sediments of the Sea of Japan and Lake Khanka.

particle active Np(IV).

Considering the kinetic dependence at pH 6, it is noticeable that the sorption equilibrium could be quickly established within 1 h. Desorption of Np on marine sediments at pH 8 is probably due to the changed pH during adsorption process. During the experiment, the pH of the solution decreased gradually from its initial value of pH 8 to pH 6 (Fig. 6). The decrease in Np adsorption may be attributed to the desorption of Np on the sediment, consequent to the reduction in pH of the solution to pH 6.

It is difficult to ascertain the exact sorption kinetics of Np, since its behavior can change depending on factors such as the mineral composition and the presence of oxygen. For instance, Np is more effectively sorbed onto magnetite under anaerobic conditions compared to aerobic ones, meanwhile, the sorption of Np on hematite appears to be similar, regardless of the presence of oxygen (Nakata et al., 2002), (Nakata et al., 2004).

**Dependence of** <sup>237</sup>Np sorption on the pH value of the aqueous phase. An increase in Np adsorption on bottom sediments was observed with an increase in pH (Fig. 10). The sorption curve represents the typical S-type for Np (Li and Kaplan, 2012).

The sorption maxima for both kinds of sediments at pH > 10 can be attributed to the formation of carbonates or NpO<sub>2</sub>(OH) (Petrov et al., 2017).

In both highly acidic and highly alkaline conditions, similar behavior

is observed in the sorption of Np on marine and lake bottom sediments. While, at neutral and slightly alkaline medium, a difference in behavior of <sup>237</sup>Np is observed for two types of sediment. Generally, there is a higher sorption of Np on marine sediments in comparison to lake sediments. This variation in behavior is likely caused by differences in the composition of the two types of sediments. Sea bottom sediments contain iron oxides such as magnesioferrite, hematite and magnetite. The sorption of <sup>237</sup>Np onto iron oxides is a crucial geochemical process that impacts the migration of radionuclides from nuclear waste in nearsurface zones. An order of goethite > ferrihydrite > hematite, magnetite for Np adsorption was reported (Li and Kaplan, 2012). Even small amounts of iron oxides in the sediment can greatly impact Np sorption (Semenkova et al., 2018). Carbonates, specifically dolomite, present in the system can further affect sorption and lead to its reduction (Li and Kaplan, 2012). Presumably, <sup>237</sup>Np is adsorbed by marine and lake sediments primarily through complexation with silicates such as albite and leucite.

# 6. Conclusions

For the first time, Np concentrations have been established for the Far East region of Russia. Ultra-low concentrations of  $^{237}\text{Np}$  were observed in the sediment cores from Peter the Great Bay  $(1.05\times10^{-4}$  to  $2.52\times10^{-3}$  mBq g $^{-1})$  and Lake Khanka  $(2.55\times10^{-6}$  to  $4.43\times10^{-5}$  mBq g $^{-1})$ .

The sorption of Np(V) on clays was found to be higher in the presence of calcite (Fröhlich, 2015). We have found that sorption of Np in the environment is strongly influenced by complexation with silicates. Presumably, the obtained sorption values are linked to an increased amount of silicates. The bottom sediments of the Sea of Japan consist of following silicates: 55% quartz (SiO<sub>2</sub>) and 20% albite (Na[AlSi<sub>3</sub>O<sub>8</sub>]), while the bottom sediments from Lake Khanka consist of 80% quartz and albite and also contain leucite (K[AlSi<sub>2</sub>O<sub>6</sub>]).

The sorption kinetics of Np showed that equilibrium is reached in 1 h on marine sediments, whereas low sorption is observed on lake sediments. In the event of an accidental release of Np into the environment, it would be sorbed much more rapidly by marine sediments than lake sediments. The typical sorption curves of Np as a function of pH are observed for both types of sediments. This correlates well with existing data and confirms the correctness of the experiment. The results on the concentration of heavy metals in collected water and bottom sediments indicate that Mg, Al, Fe and Mn are likely to be washed out of bottom sediments and, presumably, have an additional effect on sorption.

Np distribution coefficients on marine and lake sediments were evaluated. The  $^{237}\rm Np$  sorption isotherm on marine sediments is described by the Langmuir equation. Kd varies from 57 mL g $^{-1}$  to 588 mL g $^{-1}$  with maximum adsorption  $1.04\times10^{-4}$  mol g $^{-1}$ . For lake sediments, the isotherm is described by the Henry equation. The Kd value reaches 935 mL g $^{-1}$ . These constants are planned to be used for thermodynamic modelling of Np behaviour in the environment for the study locations.

It is supposed that in the case of radiation accidents and Np release into environment in an ionic form, it will not be quickly sorbed on sediment. Our studies show that only a small fraction of Np binds to suspended matter containing silicates at pH values typical for investigated marine and fresh water conditions (pH 6–8). Thus, the most part of Np will be accessible to biota. The behavior of Np released in the solid form (e.g., as a part of hot particles) should be investigated in addition.

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#### Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Kuzmenkova Natalia reports financial support was provided by Russian Science Foundation. Hou Xiaolin reports financial support was provided by National Natural Science Foundation of China. Co-author is an assocaited editor in Journal of Environmental radioactivity.

#### Data availability

Data will be made available on request.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvrad.2023.107334.

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