



Assessment of Trace Metal Contamination and Water Quality of Surface Waters in the area surrounding the Lomonosov Diamond Deposit (NW Russia)

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Received: 29.03.2022, Revised: 27.05.2022, Accepted: 22.07.2022

Abstract

This article is devoted to the study of the impact of the development of the Lomonosov diamond deposit on the pollution of watercourses with trace metals. The high water cut of the exposed rock strata and the presence of groundwater require the constant pumping of wastewater into the filtration fields, and then to the nearby river. This work shows a significant contribution of discharge processes and drainage waters to the trace metal contents in the surface waters of the Zolotitsa river; an increase in the concentrations of Mg, Sr, Zn, Cu, Cd, As, and Se was noted. The seasonal variations of physicochemical parameters, the trace metal contents, as well as the total uranium and U isotope ²³⁴U, ²³⁸U, and ²³⁵U were analysed. Calculations of water quality indices (HMEI, HMPI, and HMTL) and public health risks (HI and CR) revealed a high level of pollution of certain sections of watercourses. Radiological studies of polluted rivers in the area showed a satisfactory situation. The results of this study can provide a basis for the subsequent monitoring of the impact of anthropogenic activities on nearby watercourses in the development of diamond deposits.

Keywords: trace metals, quality indices, health risk, radioactive pollution, Lomonosov diamond deposit.

INTRODUCTION

The impact of geochemical factors on the near-surface parts of the lithosphere creates prerequisites for the formation of environmental risks in certain areas (Rybakov et al., 2013; Legostaeva et al., 2021). The issues of surrounding the environmental safety of field developments are one of the most pressing concerns in the implementation of field development projects.

The Lomonosov deposit is the largest industrial diamond deposit in Europe, where the Arkhangelskaya and Karpinskogo-1 pipes are being fully developed (Soldatova, 2016; Yakovlev et al., 2020). Work on the extraction and processing of kimberlite ores at the deposit began in 2005 (Sheveleva & Shvartsman, 2012). The development of these pipes has been accompanied by the disruption of the lithological landscape, significant impacts on groundwater, and changes in the hydrological and hydrochemical characteristics of water bodies in the area surrounding the field (Zubkova et al., 2021). The development of the Lomonosov deposit pipes is accompanied by the need to constantly accumulate and dispose of wastewater with various compositions. This is due to the high water cut of the rock strata exposed during mining, the location of aquifers

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close to the surface, and the pressure character of groundwater. The water disposal system at the field is represented by a drainage contour of dewatering wells (DW) with a depth of up to 220 m and a dewatering capacity 120 m³/hour. Drainage water containing kimberlite ore is directed to sedimentation basins. The surface deposition of crushed kimberlite increases the likelihood of minerals reacting in the basins, resulting in an increase in dissolved solids in the storage water (Rollo & Jamieson 2006). Then, the drainage water flows to the surface fields of natural filtration (swamps), before running into the nearby river. The volume of wastewater disposal will constantly increase with the development of mining operations at the deposit, which will require the construction of additional sedimentation basins (Sheveleva & Shvartsman, 2012). Also, it was previously feared that the use of a system of water sinking wells would cause the formation of a powerful dispersion funnel, within which the depth of groundwater occurrence would significantly change, as well as leading to significant desalination of the aquifer in the field area (Shkil et al., 2016).

In addition to the impact on the environment during the discharge of drainage waters, air pollution by dust emissions from open pit mining and relatively local zones of technogenic soil pollution can also be observed (Zubkova et al., 2021). It should be noted that high risks from dust pollution and the drainage of drainage waters are associated with the mineral composition of rocks and groundwater, which contain a number of elements with highly toxic properties (Tl, As, Cd, and Hg) and high concentrations of trace metals (Cu, Zn, Pb, Ti, and V, among others) (Legostaeva et al., 2021). For example, there is an accumulation of Cr, Ni, Co, Ti, Si, Y, Nb, Li, Be, and Sr at the surface during work on the territories of the Udachninsky and Aikhalsky mining and processing plants (MPP) which are located within the Daldyn-Alakit diamond-bearing area in Western Yakutia (Eastern Siberia of Russia) (Legostaeva et al., 2021; Atroschenko, 2012). The direct mining and processing plant, located in the immediate vicinity of the Lomonosov deposit, does not pose as significant an environmental threat as sedimentation basins and the tailing dump (Sheveleva & Shvartsman, 2012).

The main technogenic load from the development of the Lomonosov field is experienced by water flowing near the Zolotitsa and Kepina rivers and their tributaries. Previous studies carried out in this area have shown that the discharge of drainage and processed waters more than doubled the water salinity of the Zolotitsa River, significantly changing the composition of river waters, namely from CaHCO₃ to Na-HCO₃-Cl-dominated compositions; there was also a significant increase in the trace metal contents of the waters (Malov, 2018). Increased Cd, Cr, Ni, Co, Ba, and V contents were also noted in the bottom sediments of the Zolotitsa river, which is reflected in the pollution indices of the bottom sediments (Geoaccumulation Index - Igeo: up to 1.1; Cd: up to 6.3; and enrichment factor - EF: up to 12.3) (Yakovlev et al., 2020).

It should be noted that the Zolotitsa river belongs to the water bodies of the highest category and has a special environmental status. Therefore, integrated monitoring studies of water bodies subjected to pollution from the diamond mining complex are highly important.

In the present work, we studied the trace metal contents in the surface waters of rivers adjacent to diamond deposits (the Lomonosov deposit and the V. Grib deposit) located in the Arkhangelsk region and part of the Arctic zone of Russia. This study reveals the impact of field development on the quality of nearby water bodies due to pollution by metals and radionuclides, as well as providing an assessment of the associated environmental risks.

MATERIALS AND METHODS

The overview map of the study area and location of the sampling points for surface waters are shown in Figure 1. The study area includes seven points located on the Zolotitsa river and its tributaries (T1, T2, T3, T4, T5, T6, and B3-1) and points located on the Kepina river and its tributaries (KB-1, KB-2, KB-3, KB-4, KB-5, and KB-6). Water sampling was carried out in May,

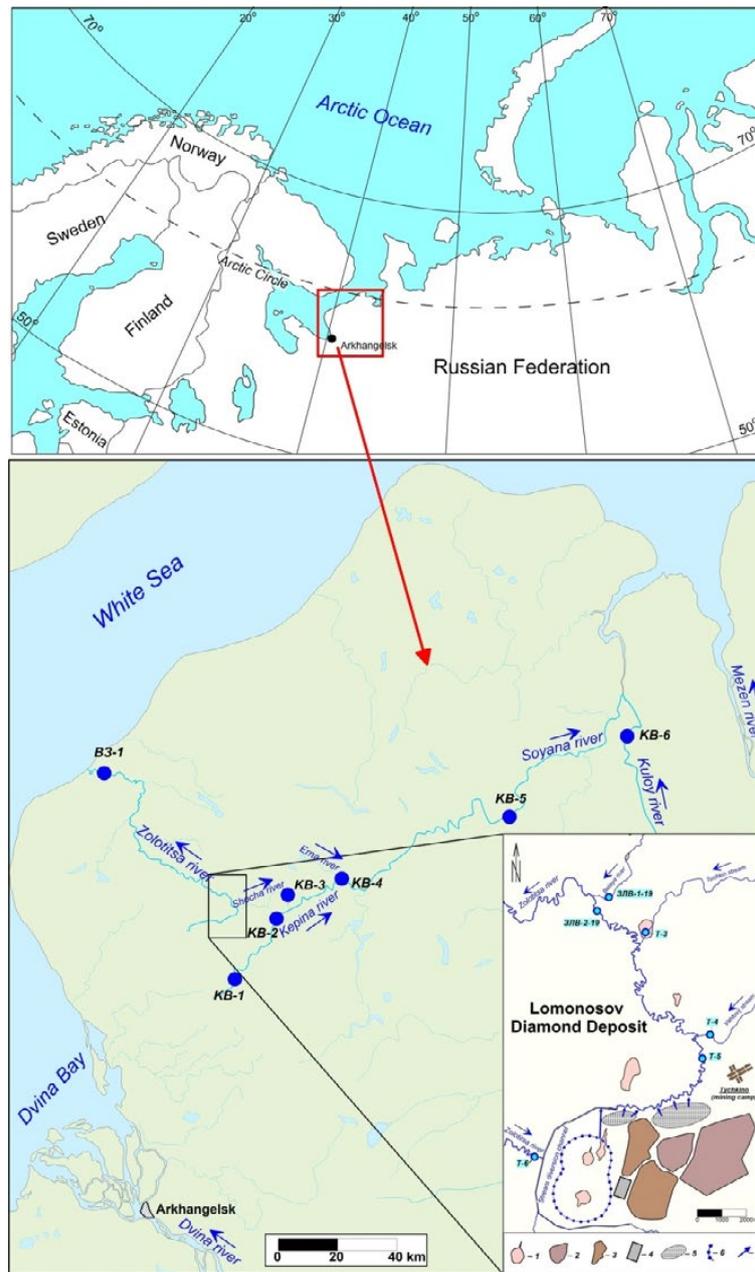


Fig. 1. Location of the study area and sampling points.

June, and October (the Zolotitsa river) and August (the Kepina river) of 2020.

The Lomonosov diamond deposit is located 90 km northeast of Arkhangelsk and consists of six kimberlite pipes: Arkhangelskaya, Karpinsky-1, Karpinsky-2, Pionerskaya, Lomonosovskaya, and Pomorskaya (Verzhak et al., 2008). Geologically, the field is located in the northern part of the East European platform. The upper structural stage is divided into the Riphean, Vendian, and Upper Paleozoic stages (Shirobokov, 1997; Kharkiv et al., 1995). The Vendian stage (V2) is represented by a layer of siltstones, mudstones, and sandstones which contain kimberlite pipes. The Upper Paleozoic stage includes carbonate rocks of the Middle Carboniferous (C2) and is represented by sandstones, limestones, and dolomite limestones, which, together with Quaternary deposits, overlap the pipes in the Lomonosov field. The Quaternary deposits are fluvioglacial, glacial, lacustrine, boggy, and alluvial deposits, in which the predominant rocks

are sand, loam, pebbles, sandy loam, and peat (Kutinov & Chistova, 2004). The diamondiferous kimberlite pipes are funnel-shaped in vertical section. The pipes are dated to the Upper Devonian-Middle Carboniferous (D3-C2) (Sablukov, 1987).

The V. Grib field (Verkhotinskoe field) is located 135 km northwest of Arkhangelsk and it is one of the largest diamondiferous kimberlite fields in the world. The kimberlite pipes break through weakly lithified sedimentary rocks of the Upper Riphean and Upper Vendian, overlain by a stratum of terrigenous-carbonate rocks of the Middle Carboniferous and loose Quaternary deposits. The vent part of the pipe is filled with tuff- and xenotophobrecias and kimberlite. The xenolith content reaches 40-50%. In terms of composition, xenolith is mainly represented by siltstones and mudstones (Bogatikov et al., 1999; Verichev et al., 2003). The kimberlites of the V. Grib pipe are also characterised by high magnesium contents, low alumina and alkalinity, and moderate titanium contents. According to the ratio of rock-forming components, the kimberlites of the V. Grib pipe and those of the Lomonosov deposit belong to rocks of the Mg-series and Al-Mg-series, respectively (Garanin et al., 2011). In terms of their moderate Cs, Rb, Ba, and Sr contents and the Zr / Nb ratio, the kimberlites of the V. Grib pipe are close to the kimberlites of South Africa and the rocks of the pipes of Yakutia, but they are less enriched in rare elements and rare earth elements (Garanin et al., 2011).

The Zolotitsa river crosses the territory of the Lomonosov diamond deposit from south to north (the length of the river is 177 km and the basin covers an area of 2010 km²) (Bednaruk, 2008). The Zolotitsa river is a salmon spawning ground in the White Sea basin, and therefore, it has a conservation status (Kalyuzhin, 2003). Indeed, the river valley is very sparsely populated. The channel of the Zolotitsa river in the development area of the diamond deposit was changed in connection with the construction of quarries, and the channel in this area is currently a technological channel for diverting streams, discharging groundwater, and diverting drainage water from drainage wells. The quarry waters are discharged and treated in peat-filtration fields before being discharged into the Zolotitsa river; these contain materials from kimberlites and host rocks in a suspended state (Malov, 2018). In addition, the Kepina river (the length of the river is 75 km and the catchment area is 1000 km²), which flows on the territory of the Soyansk State Natural Biological Reserve, is under the influence of dust pollution from the development of the Lomonosov diamond deposit and the V. Grib diamond deposit (the Verkhotinskoe deposit).

Water sampling for analyses of trace metals was carried out in disposable 50 ml test tubes made of polymeric material. The water was preliminarily filtered through a membrane filter with a pore size of 0.45 µm, and then acidified to a pH of less than 2 for conservation. For uranium isotope analyses, water was sampled into plastic canisters (20-25 L), acidified to a pH of 4, and uranium was then deposited on the activated carbon from the water, which was filtered and delivered to the laboratory.

Measurements of pH, Eh (oxidation-reduction potential - ORP), and salinity readings were carried out directly in water according to the operating instructions for the used measuring devices. The analysis of pH and Eh was carried out with a portable multiparameter pH / ORP meter HI 9126 (pH / ORP / T) (USA, Hanna Instruments) with a replaceable electrode for measuring pH and ORP. The measurements of salinity and water temperature were carried out with a conductometer MAPK-603/1 (Russia, VZOR).

The determination of the metal contents was carried out using atomic absorption spectroscopy; this method consists in the atomisation of the determined elements through heating by spraying the sample into a flame (Cu, Zn, Sr, Mg, and Fe) or heating it in a graphite furnace (Al, Cr, Mn, Co, Ni, Cd, Ba, Pb, V, As, and Se) The measurements were carried out on a ShimadzuAA-7000 atomic absorption spectrometer (Shimadzu, Japan) with flame and electrothermal atomizers. The measurement range of metal concentrations and their relative errors are shown in Table 1.

The determination of uranium concentrations was carried out according to a methodology

Table 1. Characteristics of the method used for measuring the concentration of metals.

| Element | Concentration range, mg/L | Relative error ±δ, % | Element | Concentration range, mg/L | Relative error ±δ, % |
|---------|---------------------------|----------------------|---------|---------------------------|----------------------|
| Al | 0.01...75 | 30 | Mg | 0.5...2500 | 11 |
| As | 0.01...50 | 30 | Mn | 0.005...50 | 15 |
| Ba | 0.05...500 | 29 | Ni | 0.002...10 | 14 |
| Cd | 0.0005...2.5 | 16 | Pb | 0.005...50 | 30 |
| Co | 0.005...12.5 | 30 | Se | 0.01...50 | 15 |
| Cr | 0.002...10 | 30 | Sr | 5.0...15000 | 15 |
| Cu | 0.001...2500 | 24 | V | 0.001...10 | 25 |
| Fe | 0.05...1000 | 22 | Zn | 0.005...5000 | 20 |

(Methods for measuring the volumetric activity of uranium isotopes, 2013) where, as a result of radiochemical preparation, uranium isotopes were deposited on a steel substrate. The substrate was then placed in the measuring chamber of the Progress-alpha spectrometer (Russia, Doza) and the semiconductor alpha-spectrometer MULTIRAD-AS (Russia, Amplitude).

Information on trace metal pollution in surface waters is highly important for assessing the impact of anthropogenic activities on these. The suitability of surface water resources for agricultural and drinking purposes was determined by considering the trace metal concentrations as indicators for assessing pollution and public health risks, namely defined by the Heavy Metals Evaluation Index (HMEI), Heavy Metals Pollution Index (HMPI), Heavy metal toxicity load (HMTL), as well as Non-carcinogenic (HI) and Carcinogenic health risks (CR).

The HMEI index helps to quickly assess the overall water quality in terms of trace metal contents (Prasanna et al., 2012). The HMPI is based on the spatial distribution of metals, depending on the amount of trace metal ions and their concentrations relative to acceptable levels according to water quality standards, and can be useful for identifying and quantifying trends in water quality (Chaturvedi et al., 2018; Mishra et al., 2018). The HMTL can evaluate the level of toxic metals in water and indicate when toxic metals should be removed to make the water safe for human use (Huang, 2021).

The measurable risk to public health was calculated to assess the potential risk by determining the intensity of exposure to metals, the level of their exposure, and the “metal dose-human response” relationship (Huang, 2021). The health risk assessment of each potentially toxic metal is based on a quantitative assessment of the level of risk and is expressed in terms of a carcinogenic (CR) or non-carcinogenic (HI) health risk (Ramadan, 2019). Two main risk factors for toxicity were assessed: the slope factor (SF) for characterising carcinogenic risks and reference dose (RfD) for characterising non-carcinogenic risks.

The HMEI index reflects the overall quality of water in relation to metals and is determined by the following formula (1):

$$HMEI = \sum_{i=1}^n \frac{HM_{Conc}}{HM_{MPC}} \tag{1}$$

where HM_{Conc} is the specified heavy metal concentration and HM_{MPC} is the maximum allowable metal concentration in water (Zakir et al., 2020). For this index, the threshold is 1.0, which means that $HMEI < 1.0$ is ‘Fit’ and the $HMEI > 1.0$ is ‘Unfit’ for domestic usage (Zakir et al., 2020). A more extended classification of water pollution levels: < 0.3 is ‘very pure’; $0.3 - 1.0$

is 'pure'; 1.0 – 2.0 is 'slightly affected'; 2.0 – 4.0 is 'moderately affected'; 4.0 – 6.0 is 'strongly affected'; and >6.0 is 'seriously affected' (Caerio et al., 2005; Haque et al., 2019).

The HMPI measures the impact of each individual trace metal on the overall water quality. The HMPI index is calculated using the formula (2):

$$HMPI = \frac{\sum_{i=1}^n (Q_i \times W_i)}{\sum_{i=1}^n W_i} \quad (2)$$

where, Q_i is the sub-index of the i th metal parameter, W_i is the unit weight of the i th parameter reflecting its relative importance, and n is the number of parameters considered. The sub-index (Q_i) is calculated with the following Eq. (3):

$$Q_i = \frac{C_i}{S_i} \times 100 \quad (3)$$

where C_i is the concentration of the i -th trace metal ($\mu\text{g/L}$), and S_i is the maximum standard allowable concentration of the i -th trace metal (data from the guidelines of the World Health Organization (WHO, 2017), Table 2).

The unit weight (W_i) of the metal concentration parameter is calculated using Eq. (4):

$$W_i = \frac{k}{S_i} \quad (4)$$

where k is a proportionality constant equal to 1 (Wanda et al., 2012). The critical (threshold) value of the HMPI index for drinking water is 100 (Prasad & Bose, 2001). However, for moderate water pollution by trace metals, a modified scale with three levels is used: low (HMPI <15), medium (HMPI 15–30), and high (HMPI >30) (Edet & Offiong, 2002).

The HTML index evaluates the trace metal contents in water that cause toxic effects on the human body (Saha & Paul, 2018, Zakir et al., 2020). This index is calculated using Eq. (5):

$$HMTL = \sum_{i=1}^n C_i \times HIS_i \quad (5)$$

where C_i , mg/kg is the content of trace metals in the test water and HIS_i is the general hazard level of individual metals (Table 3). The hazard level of an individual trace metal was assigned by the Toxic Substances Agency and the Disease Registry. The hazard ratings for each metal are found in the toxicology profiles of the Priority Hazardous Substances List (ATSDR, 2019). The HIS hazard level is categorised based on the frequency of occurrence of the metal, its toxicity level, and the likelihood of contact with humans. For these studies, a modified classification of waters was introduced depending on the level of HMEI values: 0–100, low toxicity; 100–300, moderate toxicity; 300–500, high toxicity; 500–1000, very high toxicity; above 1000, extremely high toxicity.

Human exposure to metals occurs in three ways: direct ingestion, inhalation, and absorption through the skin. The most important pathways for the entry of metals into the body are through ingestion of water and absorption through the skin. The absorbed human dose is calculated as chronic daily intake (ADD) and refers to the dose of the contaminant per kilogram of human

Table 2. Values of the parameters of metals required for calculating water pollution indices and human health risks.

| Element | C_i , $\mu\text{g/L}$ | HIS_i | K_p | RfD_{ing} | RfD_{derm} | SF, mg/L |
|---------|-------------------------|----------------|-------------------|---------------------------|----------------------------|-------------------|
| Mg | - | 0 | $1 \cdot 10^{-3}$ | - | - | - |
| Fe | 300 | 0 | $1 \cdot 10^{-3}$ | 700 | 140 | - |
| Sr | - | 0 | $1 \cdot 10^{-3}$ | 600 | 120 | - |
| Al | 200 | 685 | $1 \cdot 10^{-3}$ | 1.3 | 0.07 | - |
| Mn | 500 | 797 | $1 \cdot 10^{-3}$ | 24 | 0.96 | - |
| Ba | 700 | 800 | $1 \cdot 10^{-3}$ | 70 | 14 | - |
| Zn | 3000 | 913 | $6 \cdot 10^{-4}$ | 300 | 60 | - |
| V | - | 648 | $1 \cdot 10^{-3}$ | 1 | 0.01 | - |
| Cr | 50 | 895 | $2 \cdot 10^{-3}$ | 3 | 0.08 | 0.5 |
| Ni | 20 | 993 | $2 \cdot 10^{-4}$ | 20 | 0.8 | 1.7 |
| As | 10 | 1676 | $1 \cdot 10^{-3}$ | 0.3 | 0.12 | 1.5 |
| Cu | 2000 | 805 | $1 \cdot 10^{-3}$ | 40 | 8 | - |
| Se | 10 | 775 | $1 \cdot 10^{-3}$ | 5 | 2.2 | - |
| Co | 100 | 1011 | $4 \cdot 10^{-4}$ | 0.3 | 0.06 | - |
| Cd | 3 | 1318 | $1 \cdot 10^{-3}$ | 0.5 | 0.03 | 15 |
| Pb | 10 | 1531 | $1 \cdot 10^{-4}$ | 1.4 | 0.42 | 0.0085 |

weight per day that is absorbed through ingestion or through the skin (USEPA, 2013; Kumar et al., 2019). The exposure estimates for each trace metal were calculated using the methodology recommended by the United States Environmental Protection Agency (USEPA) using Eqs. (6) and (7):

$$ADD_{\text{ing}} = \frac{C_i \times IR \times EF \times ED}{BW \times AT} \quad (6)$$

$$ADD_{\text{derm}} = \frac{C_i \times SA \times K_p \times ET \times EF \times ED \times CF}{BW \times AT} \quad (7)$$

where ADD_{ing} ($\mu\text{g/kg day}$) and ADD_{derm} ($\mu\text{g/kg day}$) are the average daily doses through ingestion and dermal absorption of water, respectively (Kumar et al., 2019, Saha & Paul, 2018). In Eqs. (6) and (7) C_i is the concentration of the HMs ($\mu\text{g/L}$), IR is the ingestion rate (2.0 L/day), EF is the exposure frequency (350 days), ED is the exposure duration (30 years), BW is the body weight (70 kg), AT is the average time (10950 days), SA is the exposed skin area (18000 cm^2), K_p is the skin adherence factor (Table 3), ET is the exposure time (0.58 h/day), and CF is the conversion factor (0.001).

The calculation of non-carcinogenic risks was determined by calculating the hazard coefficient (HQ) according to the USEPA (2013) method following Eq. (8):

$$HQ_{\text{ing/derm}} = \frac{ADD_{\text{ing/derm}}}{\text{RfD}_{\text{ing/derm}}} \quad (8)$$

where RfD_{ing} и RfD_{derm} are the ingestion and dermal reference doses ($\mu\text{g/kg-day}$), respectively (Table 3), HQ_{ing} is the hazard quotient through ingestion, and HQ_{derm} is the hazard quotient through dermal absorption (Kumar et al., 2019; Naveedullah et al., 2014; Iqbal & Shah, 2013; Wu et al., 2009).

The HI is the cumulative potential non-carcinogenic risk to human health caused by the

presence of heavy metals in water (Zakir et al., 2020). It was calculated from the USEPA recommendation for water ingestion and dermal water absorption using Eq. (9):

$$HI_{ing/derm} = \sum_{i=0}^n HQ_{ing/derm} \quad (9)$$

To assess the potential non-carcinogenic risks to public health caused by exposure to various trace metals present in water, the threshold was set at 1.0. This means that at HI 1.0, there may be non-carcinogenic health risks to the local population (Mohammadi et al., 2019).

The incremental lifetime cancer risk ($CR_{ing/derm}$) was calculated due to exposure to a potential carcinogen metal (Cr, Ni, Cd, As, Pb). Potential carcinogenic risk possibilities (developing cancer over a lifetime) were calculated by multiplying together the ADD and slope factor (SF, mg/kg day Table 3) (USEPA, 2004, Kumar et al., 2019). To calculate the CR for each carcinogen, the following equation was used (Eq. 10):

$$CR_{ing/derm} = ADD_{ing/derm} \times SF \quad (10)$$

The SF values for carcinogenic metals were taken from the California Office of Environmental Health Hazard Assessment (OEHHA, 2020). The sum of the CR of oral and skin exposure to carcinogens was considered when calculating the total CR (ΣCR). The acceptable range for ΣCR is 1.0×10^{-6} to 1.0×10^{-4} , and values $>10^{-4}$ indicate a high likelihood of human cancer (USEPA, 2014; Mohammadi et al., 2019).

RESULTS AND DISCUSSION

In general, the pH value of the samples varies ranged from 6.86 to 7.68, which was in line with the WHO recommendation for drinking water (pH values should be in the range of 6.5-8.5 units). For the Zolotitsa river, lower pH values were observed mainly in the spring, which was probably due to the influence of melted snow water. The more alkaline environment of surface waters was determined in October. For the most polluted sampling sites (T5 and T2), significant changes in pH relative to the T6 point were not observed, so it can be concluded that there was no significant influence of quarry and groundwaters from the Lomonosov diamond deposit on the pH parameter. Higher pH values were determined for the tributaries of the Kepina river (KB-3 and KB-4) for a series of KB samples. In general, the pH values for the investigated waters were within the acceptable range. So, according to the requirements for the quality of water for discharge from the Long Lake Containment Facility (Ekati Diamond Mine in Canada), it was noted that all water discharges from production should have a pH from 6.0 to 9.0 (Rollo & Jamieson, 2006). Groundwater located on the territory of the investigated field was in the pH range of 7.8 to 9.2 units (Shkil et al., 2016).

The redox potential (ORP) is the ability of water to oxidize pollutants (Al-Samawi & Al-Hussaini, 2016). The redox potential for most of the studied samples was negative and generally varied from -34.2 mV to 12.5 mV. This indicates a transitional state of the redox environment of surface waters and the effect of groundwater with a predominant reduction potential. In general, the aquatic environment is characterized as anoxic in which the denitrification reaction occurs (Al-Samawi & Al-Hussaini, 2016). The lowest Eh values for the Zolotitsa river were determined during the autumn period. Point T5 was especially prominent in May and October, potentially indicating an increased discharge of groundwater from the Lomonosov diamond deposit during periods of snow melt and rain. The tributary of the Kepina river (KB-4) was also characterised by the most negative redox potential values. This situation is typical for groundwater, where there are low-valence metals (Fe^{2+} , Mo^{4+} , Mn^{2+} , V^{4+} , U^{4+}), as well as hydrogen sulfide (Goncharuk,

2010).

The mineralisation of the investigated surface waters varied over a wide range from 35.7 to 299.8 mg/L, without exceeding the permissible value (above 1000 mg/L) established by the WHO (2017). The lowest contents of water-soluble salts in the Zolotitsa river were determined during the spring period (35.6-51.8 mg/L), probably due to the effect of dilution by snowmelt waters. The maximum water salinity was observed (69.5-196.7 mg/L) during the drier summer period. It should be noted that for the Zolotitsa river, for all studied seasons the maximum values were determined for sampling point T5, where water is discharged upstream during the development of the field. At the sampling point, located before the river flows into the channel (T6), the salinity values were 1.9-2.0 times lower than those at the T5 sampling point. This indicates the discharge of a large amount of mineral water-soluble components into the channel, which was also confirmed by the high TDS values for sampling point T2, located downstream of the river point T5. In another series of samples (KB-1 to KB-6), high values were determined for KB-6 (299.8 mg/L) due to the inflow of groundwaters with high salinity into the Kuloy river. In general, the mineralisation of the Kepina river increased downstream, possibly highlighting both the influence of its tributaries with increased mineralisation (KB-3 and KB-4) and the influence of the development of the Lomonosov and Grib diamond deposits. According to literature data, the surface waters of the Arctic region have a salinity of 10-30 mg/L and are classified as fresh and ultrafresh (Dauvalter, 2019). However, the studied watercourses contain a greater amount of groundwater with increased mineralisation. Thus, it was previously shown that in this territory, low-mineralised (about 140 mg/L) groundwaters occurred in the uppermost part of the sedimentary cover, while groundwaters with a salinity of 210-850 mg/L were present in the lower zone of active water exchange (Shkil et al., 2016). It is noted that over 10 years of operation, the open pit waters of the Arkhangelskaya pipe have had dry residues in the range of 214-560 mg/L, with an average value of 400-450 mg/L (Shkil et al., 2016).

Dumps of host rocks containing high concentrations of metals are susceptible to weathering and erosion by rain and melt waters. As a result of these processes and the diversion of the drainage waters of the mining and processing plant, metals can be transferred to the Zolotitsa river through wastewater. The kimberlite rocks of the deposit have a high experienced a degree of chemical weathering, and therefore, almost all of the source material consists of the clay mineral saponite (Karpenko, 2008). Thus, during mining, this material enters the quarry waters and forms a finely dispersed suspension, which has a low sedimentation rate and forms a dense sediment (Malov, 2004). As a result, drainage water discharged to peat-filtration fields also contains a significant amount of saponite. Apparently, the pumped-out pit water is not completely purified by filtration through the peat massif, since an increased content of Mg (the main element of saponite) was noted in the bottom sediments of the Zolotitsa river from the northern border of the mining complex to the village of Tuchkino (Yakovlev et al., 2020). In addition, fine particles of saponite that make up the dumps, create dust with a high content of trace elements when dried, which has an adverse effect on forest ecosystems (Sheveleva & Shvartsman, 2012).

Seasonal studies of the contents and distribution of metals showed (figure 3, table 3) that for the studied surface waters, two groups of metals can be distinguished: 1) with minimum trace metal contents in May (typical for Mg, Fe, Sr, V, Se, and Cd), with a tendency for Al, Mn, and Ba, and 2) with maximum contents in May (typical for Ni (up to 7.8 µg/L) and Pb (up to 0.26 µg/L), with a tendency for Zn (up to 14.6 µg/L), Cr (up to 10.8 µg/L), and Cu (up to 0.94 µg/L). The reduced metal contents during the spring period were associated with the melting of the snow cover and, consequently, the effect of dilution of river waters. The increased concentrations of Ni, Pb, as well as Zn, Cr, and Cu in May was of interest, and this phenomenon applied both to the Zolotitsa river and to its tributaries (T1, T3, and T4). This effect was probably also associated with snow melting. However, during the winter period, these trace metals accumulated in the

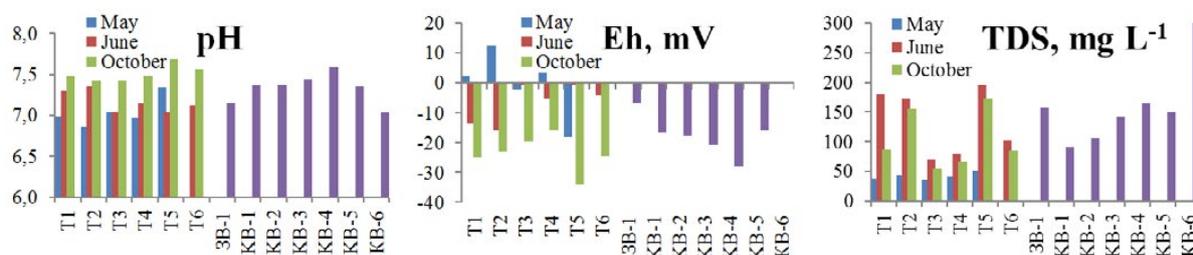


Fig. 2. Physical and chemical properties of surface waters near the Lomonosov diamond deposit

Table 3. The metals contents ($\mu\text{g/L}$) in surface waters near the Lomonosov diamond deposit

| | Mg | Fe | Sr | Al | Mn | Ba | Zn | V | Cr | Ni | As | Cu | Se | Co | Pb | Cd |
|----------------------------------|-------|------|--------|-------|------|------|------|-------|------|-----|-------|------|-------|------|-------|-------|
| $\mu\text{g/L}$ | | | | | | | | | | | | | | | | |
| Zolotitsa river (May) | | | | | | | | | | | | | | | | |
| T1 | 3890 | 171 | 11.3 | 38.9 | 8.7 | 11.4 | 2.7 | 0.47 | 9.9 | 7.8 | 2.36 | 0.94 | <0.01 | 0.11 | 0.12 | <0.01 |
| T2 | 2056 | 247 | 26.6 | 69.1 | 29.6 | 10.2 | 8.2 | 0.35 | 7 | 5.4 | 0.1 | 0.81 | <0.01 | 0.1 | 0.088 | <0.01 |
| T3 | 3763 | 283 | 16.0 | 52.0 | 39.4 | 15.3 | 5.8 | 0.25 | 6.2 | 7.1 | 0.13 | 0.9 | <0.01 | 0.14 | 0.081 | <0.01 |
| T4 | 4519 | 124 | 16.8 | 33.2 | 29.4 | 10.2 | 5.7 | 0.21 | 4.9 | 6.1 | <0.01 | 0.64 | <0.01 | 0.04 | 0.258 | <0.01 |
| T5 | 2322 | 262 | 33.2 | 57.4 | 26.6 | 9.4 | 14.6 | 0.67 | 10.8 | 6.7 | <0.01 | 0.64 | <0.01 | 0.1 | 0.12 | <0.01 |
| Zolotitsa river (June) | | | | | | | | | | | | | | | | |
| T1 | 11452 | 463 | 147.2 | 85.4 | 54.1 | 35.7 | 4.3 | 8.63 | 3.33 | 1.7 | 2.28 | 0.5 | 0.25 | 0.17 | 0.05 | 0.01 |
| T2 | 11188 | 479 | 145.2 | 104.1 | 57.6 | 19.5 | 14.2 | 9.12 | 3.6 | 1.8 | 2.49 | 0.73 | 0.2 | 0.21 | 0.06 | 0.084 |
| T3 | 11361 | 550 | 35.5 | 58.2 | 41.2 | 20.5 | 13.5 | 5.65 | 1.75 | 1.7 | 2.88 | 0.57 | 0.22 | 0.14 | 0.08 | 0.047 |
| T4 | 13491 | 457 | 30.1 | 46.2 | 66.2 | 16.5 | 9.5 | 5.42 | 1.63 | 2.4 | 2.18 | 4.1 | 0.33 | 0.12 | 0.02 | 0.121 |
| T5 | 11163 | 392 | 173.4 | 99.6 | 50.3 | – | 8.6 | 10.39 | 3.53 | 1.3 | 2.78 | 0.74 | 0.21 | 0.16 | 0.05 | 0.207 |
| T6 | 5211 | 560 | 95.4 | 203.9 | 62.8 | 26.0 | 6.7 | 8.74 | 3.18 | 1.3 | 2.09 | 0.57 | 0.13 | 0.23 | 0.1 | 0.031 |
| Zolotitsa river (October) | | | | | | | | | | | | | | | | |
| T1 | 10754 | 280 | 24.0 | 23.7 | 15.7 | 22.3 | 0.5 | 0.12 | 0.57 | 0.4 | 0.01 | 0.18 | 0.06 | 0.06 | 0 | <0.01 |
| T2 | 7269 | 465 | 120.1 | 75.2 | 33.1 | – | 2.7 | 0.99 | 1.85 | 0.5 | 0.01 | 0.16 | 0.1 | 0.1 | 0.067 | <0.01 |
| T3 | 6930 | 465 | 25.5 | 49.4 | 29.3 | 34.4 | 1.4 | 1.26 | 0.7 | 0.5 | 0.11 | 0.1 | 0.04 | 0.08 | 0 | <0.01 |
| T4 | 8227 | 306 | 24.9 | 26.5 | 18.3 | – | 1.5 | <0.01 | 0.41 | 0.4 | 0.01 | 0.12 | 0.02 | 0.05 | 0.009 | 0.027 |
| T5 | 7275 | 461 | 142.6 | 83.4 | 29.4 | – | 0.8 | 0.92 | 1.63 | 0.4 | 0.01 | 0.19 | 0.11 | 0.09 | 0.034 | <0.01 |
| T6 | 3909 | 660 | 91.1 | 157.8 | 35.8 | 47.9 | 2.2 | 2.14 | 1.54 | 0.5 | 0.08 | 0.17 | 0.1 | 0.12 | 0.092 | <0.01 |
| Kepina river | | | | | | | | | | | | | | | | |
| KV-1 | 17390 | 503 | 24.7 | 55.1 | 20.1 | 15.9 | 7.5 | 10.58 | 4.75 | 3.7 | 1.83 | 0.8 | 0.24 | 0.15 | 0.12 | <0.01 |
| KV-2 | 20351 | 460 | 18.6 | 31.1 | 7.7 | 21.9 | 5.8 | 9.52 | 4.92 | 3.8 | 1.64 | 0.81 | 0.35 | 0.13 | 0.08 | <0.01 |
| KV-3 | 15737 | 440 | 69.7 | 55.6 | 11.4 | 64.4 | 5.1 | 9.58 | 4.65 | 3.2 | 1.84 | 0.66 | 0.20 | 0.14 | 0.08 | <0.01 |
| KV-4 | 15284 | 463 | 94.4 | 30.3 | 12.5 | 79.5 | 15.0 | 7.27 | 6.81 | 4.9 | 2.63 | 0.88 | 0.29 | 0.16 | 0.13 | <0.01 |
| KV-5 | 15418 | 582 | 437.5 | 64.8 | 11.2 | – | 8.3 | 5.66 | 4.62 | 4.2 | 2.29 | 0.73 | 0.35 | 0.17 | 0.11 | <0.01 |
| KV-6 | 12060 | 1431 | 1699.5 | 95.7 | 45.9 | – | 9.9 | 5.71 | 4.23 | 8.1 | 3.61 | 0.98 | 0.45 | 0.42 | 0.07 | <0.01 |
| ZV-1 | 11321 | 893 | 192.4 | 162.6 | 73.0 | 17.5 | 15.6 | 8.42 | 6.09 | 3.6 | 2.89 | 0.93 | 0.18 | 0.22 | 0.23 | <0.01 |

snow cover due to anthropogenic activities in the diamond mining area (burning coal and diesel fuel). In general, it can be noted that maximum concentrations for most metals were observed during the drier summer period due to the concentration effect: Mg (up to 13491 $\mu\text{g/L}$), Fe (up to 560 $\mu\text{g/L}$), Sr (up to 173 $\mu\text{g/L}$), Al (up to 204 $\mu\text{g/L}$), Mn (up to 66.2 $\mu\text{g/L}$), Se (up to 0.33 $\mu\text{g/L}$), Co (up to 0.23 $\mu\text{g/L}$), and Cd (up to 0.207 $\mu\text{g/L}$); a partial trend was also observed for Ba (up to 35.7 $\mu\text{g/L}$), Zn (up to 14.2 $\mu\text{g/L}$), V (up to 10.4 $\mu\text{g/L}$), and As (up to 2.88 $\mu\text{g/L}$).

Downstream of the confluence of the Zolotitsa river into the technological channel (for sampling points T2 and T5) an increase in the concentrations of Mg (up to 11188 $\mu\text{g/L}$), Sr (up

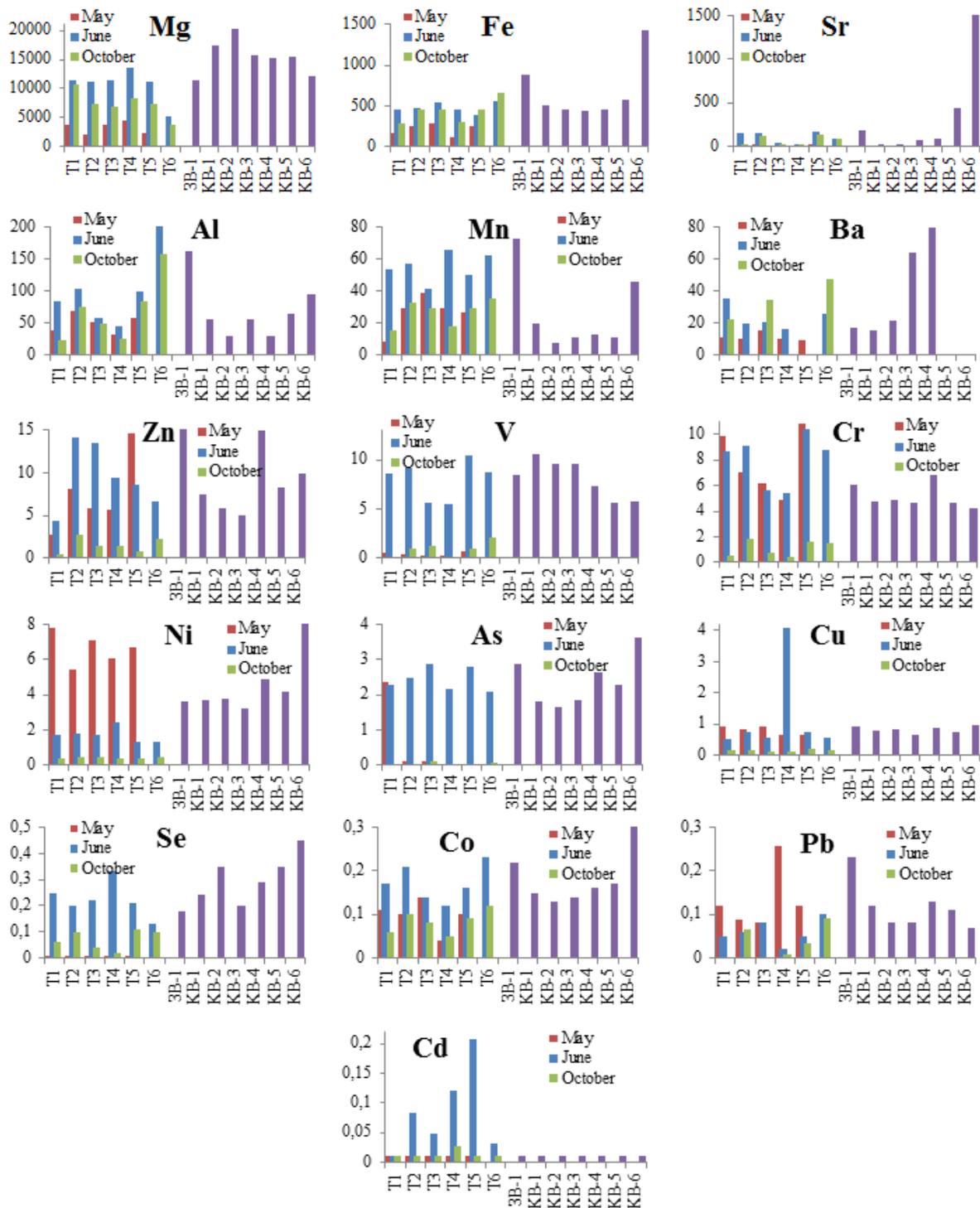


Fig. 3. The metals contents ($\mu\text{g/L}$) in surface waters near the Lomonosov diamond deposit

to 173 $\mu\text{g/L}$, Zn (up to 14.6 $\mu\text{g/L}$), Cu (up to 0.73 $\mu\text{g/L}$), and Cd (up to 0.207 $\mu\text{g/L}$), as well as a partial increase of As (up to 2.78 $\mu\text{g/L}$) and Se (up to 0.20 $\mu\text{g/L}$), can be noted relative their concentrations at point T6, which is located upstream of the river section that is subjected to anthropogenic impacts. The increase in the concentrations of these metals at points T2 and T5 relative to point T6 was especially marked during the summer. This was most likely due to the discharge of technological and groundwaters from a diamond deposit containing waste

kimberlite rocks (high-magnesian saponite), which contain Mg (9.83%), Cu (29 mg/kg), and Zn (149 mg/kg) in high concentrations (Yakovlev et al., 2020). The elevated Cd contents were likely related to the infusion of dissolved enclosing rocks (V2) with a Cd concentration of 2.71 mg/kg into river waters. Local increases in the concentrations of Cd (up to 2.6 ppm), Mg (up to 1.4%), as well as Ca (up to 1.2%), Ti (up to 0.27%), Cr (up to 80 ppm), and V (up to 42 ppm) in the bottom sediments of the Zolotitsa river in the area of drainage water discharge from filtration fields have also been reported by (Yakovlev et al., 2020). The analysis of surface waters at the Long Lake Containment Facility (Ekati Diamond Mine, Canadian Arctic) also showed an excess of As (up to 9 µg/L) and Cd (up to 0.69 µg/L) concentrations relative to the Water Quality Guidelines of National Office for Guidelines and Standards (NGSO) (Rollo & Jamieson, 2006).

Furthermore, it should be noted that in some cases, at the sampling point T6, upstream of the river flowing into the technological channel, the concentration of metals such as Fe, Al, Ba, Co, and Pb was higher than for points T5 and T2. It is likely that these metals are present in the river waters due to the dissolution of minerals upstream and in the channel; downstream, their concentration in the water decreases due to dilution by technological and groundwaters, as well as by the waters of streams flowing into the river. However, it is also worth noting that some streams flowing into the Zolotitsa river were characterised by relatively high contents of some trace metals (T4, T3, and T1). Thus, in the Vakhtovy stream (sampling point T4), a high concentration of Cu was observed in June, and for the Belaya river and Tuchkin stream (T1 and T3), an increased concentration of Ba was noted during the autumn period.

The metal contents in the Zolotitsa river at sampling point B3-1, located closer to the river mouth, slightly differed from points T2, T5, and T6; increased Fe, Mn, Zn, Pb, and Al concentrations were measured relative to points T2 and T5. The conducted studies of the content of metals in the waters of the Kepina river (KB-1, KB-2, and KB-5) showed that higher concentrations of Mn were observed relative to the Zolotitsa river, but the Mn and Cd contents were lower. The tributaries of the Kepina river (KB-3 and KB-4) were characterised by increased Ba contents. The sampling point KB-6 was located on the Kuloy river and exhibited high Fe, Sr, Ni, Se, and Co concentrations.

Correlation coefficients were calculated for the obtained data on the content of metals in the Zolotitsa and Kepina rivers (Figure 4). As can be seen from Figure 4 for three seasons (Zolotitsa River), the overall picture of correlations was different. The least significantly correlated pairs of metals were identified for the Zolotitsa river in May (correlation coefficient from 0.8 and higher): Pb-As, Fe-Co, As-V, As-Cr, Cr-V, Zn-Sr and Fe-Al. A large number of correlations with As were determined precisely in the spring (for As, correlation coefficients above 0.7 with Ni and Cu are shown). This is probably due to the melting of snow containing combustion products of coal and oil products. The following correlation coefficients were determined in June: Fe-Pb, Al-Co, Mg-Se, Ni-Se, Cu-Se, Ni-Cu, Cr-Sr, Cr-V and V-Sr. Metal pairs were different for May and June, only the Cr-V pair was common for both months. In autumn, the largest number of correlating pairs of metals (Fe-Pb, Al-Pb, Mn-Pb, Pb-Cr, Pb-Se, Pb-Co, Fe-Co, Al-Co, Mn-Co, V-Co, Co-Se, Se-Sr, Cr-Se, Cu-Se, As-Ba, Mn-Ni, Zn-Ni, Ni-V, Cr-Sr, Mn-Cr, Fe-V, Al-V, Mn-V, Fe-Mn, Mn-Al and Fe-Al), where metals Fe, Co, Mn, Ni, Se, Cr, V, Pb and Al were bonded. The reason may be the leaching of metals from the soil during heavy autumn precipitation and additional discharge of drainage water.

For the Kepina river, where the selection was made in August, the following correlations were revealed: Fe-Co, Co-Sr, Co-Al, Co-Mn, Co-Ni, Co-As, Cu-Co, Co-Se, Se-Fe, Se-Sr, Ni-Se, Cu-Ni, Cu-As, Fe-As, As-Sr, Mn-As, Ni-As, Fe-Ni, Sr-Ni, Mn-Ni, Ba-Cr, Zn-Cr, Fe-Mn, Mn-Sr, Al-Mn, As-Sr and Fe-Sr. The main bound metals in the Kepin river were Fe, Co, Mn, Ni, Se, As, Cu and Sr. It should be noted that many pairs of metals (Fe-Co, Co-Al, Co-Mn, Co-Se, Se-Sr, Mn-Ni, Fe-Mn, Mn-Al) correlated in the Zolotitsa river (October) and the Kepina river (August).

The results of the calculations of the indices of water quality and health risks of the population

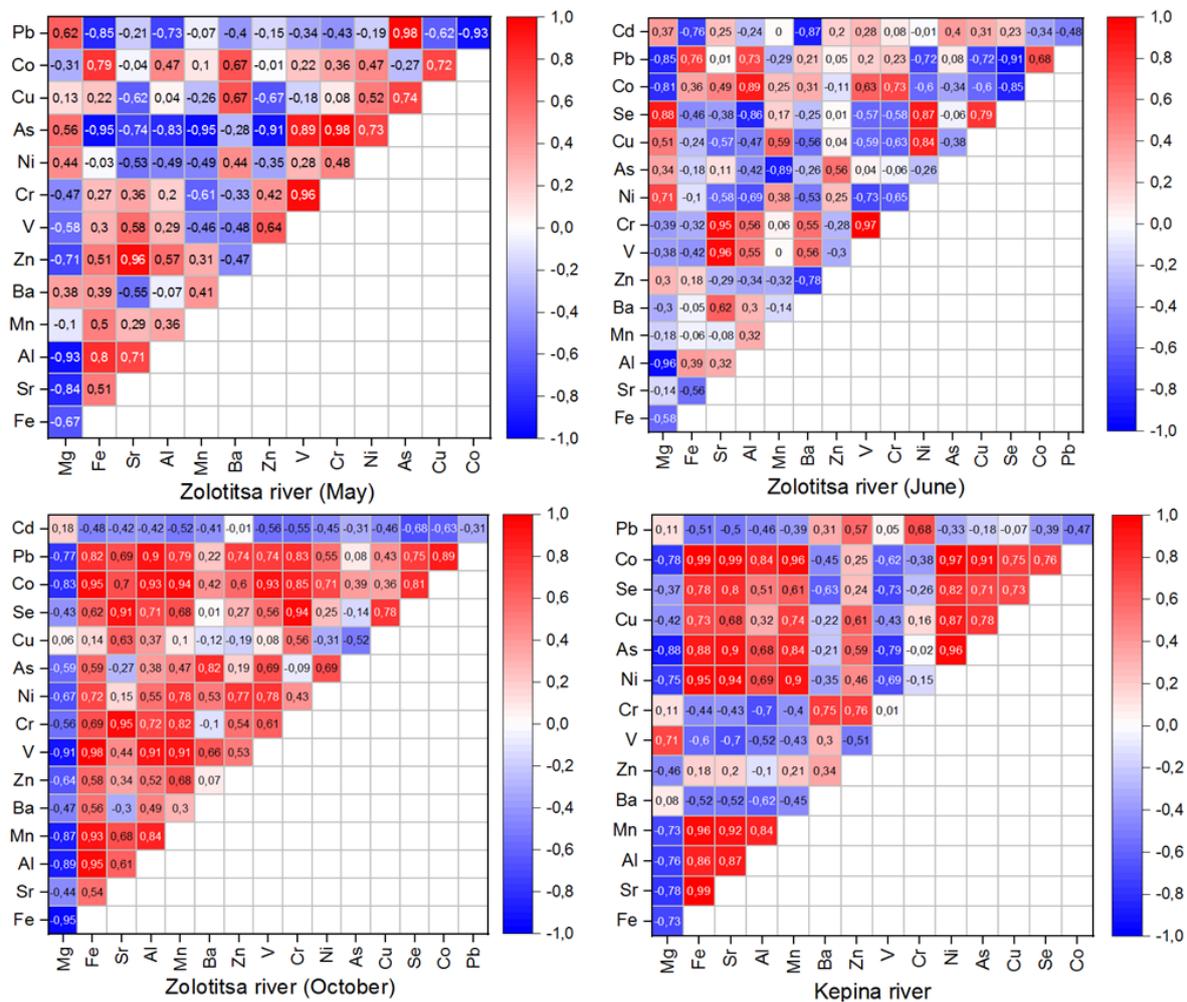


Fig. 4. Correlation coefficients between metals in the water of the Zolotitsa and Kepina rivers.

are presented in Figure 5. The graphs differ significantly from each other, indicating different degrees of influence of the contents of individual trace metals, depending on the selected indices. For example, the HMEI index was most influenced by the Fe content, while a less significant effect was manifested by Al, Ni, and As (figure 5a). For the Zolotitsa river, the highest values of the HMEI index were determined during the summer period (up to 3.4 at point T6) and the waters were classified as “Moderately affected”. In turn, the waters closer to the river mouth (B3-1) with an HMEI index = 4.6 was characterised as “Strongly affected”. In the spring, the waters of the Zolotitsa river and its tributaries had an index of 0.7-1.1 and the waters were generally referred to as “Pure”. The waters in the Kepina river and its tributaries (KB-1 to KB-5, with HMEI values = 2.2-2.9) were also referred to as “Moderately affected”. However, at point KB-6 (the Kuloy river), the HMEI index values reached 6.3, corresponding to a level of “Seriously affected”.

In calculating the HMPI index for the studied waters, the greatest influence was exerted by the As, Ni, and Cd contents, and to a lesser extent by Fe, Cr, and Al (figure 5b). For all studied water samples, the values of the HMPI index were below the critical value (HMPI <100) and were at a low level (HMPI <15). According to the data obtained, the greatest degree of water pollution was observed during the summer period, where the maximum value of the index (HMPI = 9.0) was recorded in the Zolotitsa river at sampling point T5, located downstream

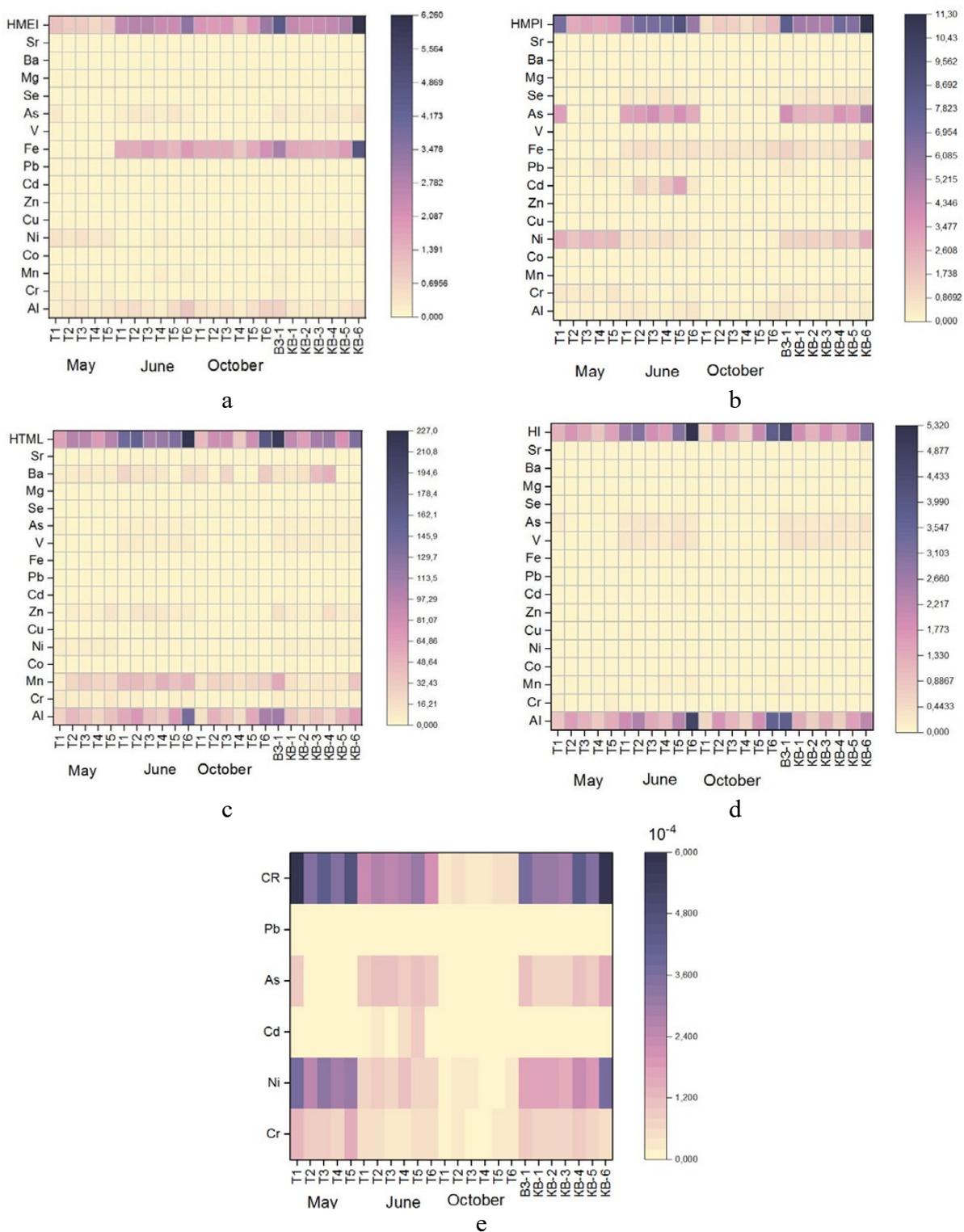


Fig. 5. Health risk of trace metals and quality indices of surface waters of the rivers near the field named after M.V. Lomonosov: a) heavy metal evaluation index; b) heavy metal pollution index; c) heavy metal toxicity load; d) non-carcinogenic health risk; e) carcinogenic health risk

of the technological channel. In autumn, pollution of the Zolotitsa river and its tributaries was minimal (HMPI values from 0.8 to 2.2). The highest value of the index (HMPI = 11.3) was determined for the Kuloy river (KB-6). The Kepina river and its tributaries were characterised by HMPI values similar to those of the Zolotitsa River in summer, and it can be noted that the Kepina river tributary KB-4 (Erna river) contributes to an increase in the metal concentrations in the Kepina river downstream.

The Al and Mn contents had the greatest influence on the HTML index value for the studied waters, and to a lesser extent - Ba and Zn (figure 5c). The assessment of water quality in the Zolotitsa river using the HTML index showed that the maximum toxicity of waters was observed in summer; the index values varied from 110 to 226, corresponding to a level of “moderate toxicity”. However, the highest toxicity was determined for point T6, due to the increased Al contents in the river water upstream of the process channel. The minimum seasonal values of the toxicity index for the Zolotitsa river and its tributaries were determined during the autumn period. The toxicity of water in the Kepina river and its tributaries varied from 65 to 133, corresponding to “low” and “moderate toxicity” levels, while the tributaries with sampling points KB-3 and KB-4 contributed to the general toxicity of the Kepina river.

The values of the non-carcinogenic risk index for public health (HI) for the studied water bodies depend to the greatest extent on the concentrations of Al, and to a lesser extent on As and V. Therefore, the distribution pattern of the non-carcinogenic risk values was similar to the distribution of the HTML index values (figure 5d). In general, the waters of the Zolotitsa and Kepina rivers and their tributaries pose a low risk of non-cancerogenic effects through dermal contact (HI_{derm} values from 0.06 to 0.44). However, when the test water was consumed as drinking water, a low risk was noted in a few cases: in May in the Vakhtovy stream (T4), and in October in the Belaya river (T1) and Vakhtovy stream (T4). For the Zolotitsa river and its tributaries, the HI index varied from 0.59 to 5.31 with higher values in summer. The highest non-carcinogenic risk was recorded at point T6, upstream of the technological channel.

The calculation of carcinogenic risks (CR) is related to the Pb, As, Cd, Ni, and Cr contents in water (fig. 5e). For the studied surface waters, the prevailing factor in the formation of the CR index was the concentration of Ni, and to a lesser extent, the influence of Cr and As. In general, the CR index for all studied water bodies was higher than the threshold and, therefore, it can be concluded that the high carcinogenic effects were directly caused by the consumption of this water. The pollution of the studied waters with trace metals in terms of CR is significantly different from the indices considered earlier. The highest CR index values for the Zolotitsa river, as well as its tributaries, were observed in the spring and could reach values of $3.87 \cdot 10^{-4}$, indicating a significant CR for the population. In October, Ni concentrations decreased, leading to a decrease in CR values ($0.19 \cdot 10^{-4}$ to $0.26 \cdot 10^{-4}$). The water in the Kepina river and the tributaries flowing into it were characterised by increased values of CR in summer and varied from $1.63 \cdot 10^{-4}$ to $3.99 \cdot 10^{-4}$. In terms of CR, the water in the Kuloy river (KB-6) in August was similar to that of the Vakhtovy stream (T1) in spring.

The disturbance of the soil cover during the development of diamond deposits is a catalyst for the geochemical processes of matter migration; moreover, the processes of water migration are most pronounced, leading to the accumulation or dispersion of the most mobile trace elements, the removal of nutrients, salinisation, soil leaching, and a sharp disruption of the ecological balance. Changes in the chemical composition of watercourses are reflected in the biogeochemical parameters of the ecosystems of the northwestern region as a whole, increasing the concentration of chemical elements, primarily in edicator plants (Legostaeva et al., 2021).

The total uranium contents in the studied samples of surface waters of the Zolotitsa river and its tributaries varied from $0.11 \cdot 10^{-6}$ to $3.72 \cdot 10^{-6}$ g/L (figure 6a). Based on the chemical and radiological toxicity of uranium, the approximate value of the total uranium contents in drinking water was 0.03 mg/L (WHO, 2017; Nuccetelli et al., 2012), and it can thus be concluded

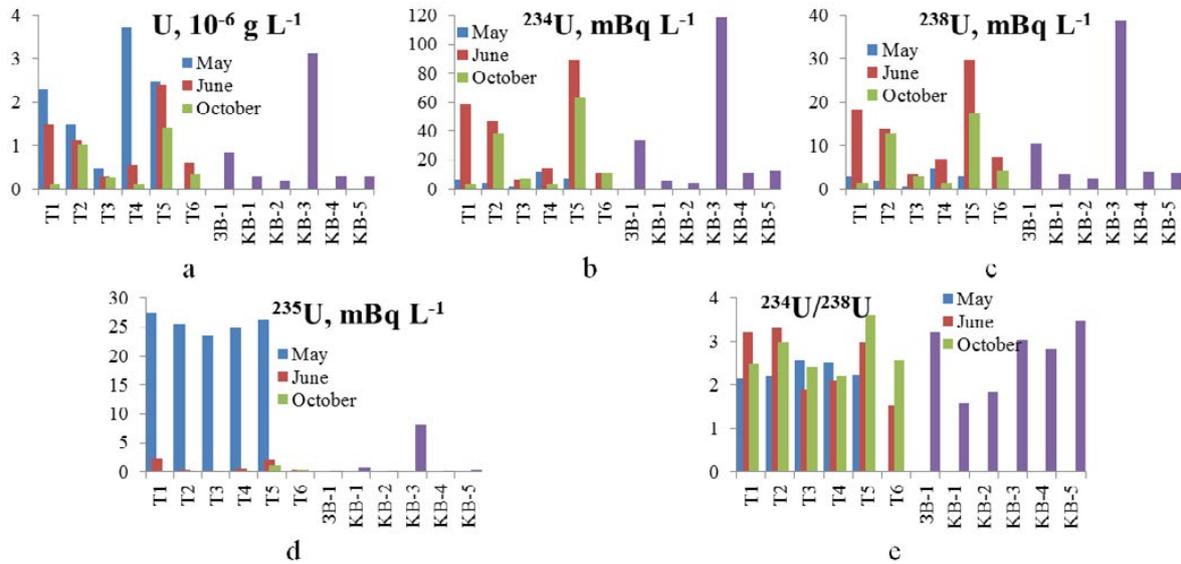


Fig. 6. Radioecological characteristics of surface waters near the Lomonosov diamond deposit: a) total concentration of uranium isotopes; b) concentration of ^{234}U ; c) concentration of ^{238}U ; d) concentration of ^{235}U ; e) ratio of the activities of ^{234}U and ^{238}U

that the radiological situation is satisfactory. The study of the seasonal variations of the total uranium contents showed that the concentrations of this element were at a maximum during the spring period, and the lowest contents were determined during the autumn. The highest value of uranium concentrations was revealed in spring in the waters of the Tuchkin brook (T4), which was probably associated with the accumulation of uranium in the snow due to lithogenic dust during the development of the diamond deposit in winter. In general, the pollution of the waters of the Zolotitsa river with uranium was distinguished, since there was an increase in its contents after the infusion of technological and groundwaters into the river. For the Kepina river and its tributaries, the highest uranium content was determined for the KB-3 tributary (Shocha river), which is explained by the groundwater input to the river, and the influence of dusty rock particles delivered by winds from the kimberlite deposit.

The radioactivity of natural uranium is mainly due to the isotopes ^{238}U and ^{234}U (Nuccetelli et al., 2012). The determination of the uranium isotope ^{234}U , ^{238}U , ^{235}U contents in the studied waters (figures 6b, 6c, 6d) revealed a similar nature of the local and seasonal distributions of ^{234}U and ^{238}U : during the drier summer period, the concentrations of these isotopes were at a maximum for the Zolotitsa river and its tributaries, and a sharp increase in ^{234}U and ^{238}U was observed downstream of the river's confluence with the technological channel (T5). The concentrations of ^{235}U were maximal in spring, while these concentrations varied slightly depending on the sampling site. For the Kepina river and its tributaries, the highest concentrations of the three uranium isotopes were determined for the Shocha river (KB-3). The investigation of groundwater from dewatering wells in 2006 and 2012 showed that the activity of uranium isotopes U^{234} and U^{238} reached 0.23 Bq/L and 0.08 Bq/L, respectively (Shkil et al., 2016).

The transition of uranium from rocks into a fluid phase is often accompanied by a disruption of the natural radioactive equilibrium of ^{234}U and ^{238}U , leading to the partitioning of ^{234}U into the fluid. This is explained by the weaker bonding of ^{234}U isotopes with the structure of minerals and its easier diffusion to the surface of mineral grains and cracks (Borylo & Skwarzec, 2014). The lower the value of the $^{234}\text{U} / ^{238}\text{U}$ ratio, the higher the rate of chemical dissolution of rocks in comparison with the rate of their radioactive decay (Shkil et al., 2016). The average values

of the activity coefficient of the $^{234}\text{U} / ^{238}\text{U}$ ratio were in the range 1.0 - 2.1 for river water, 0.5 - 9.0 for groundwater, and 1.1 - 5.1 for sea water (Borylo & Skwarzec, 2014). The concentration ratio of uranium isotopes $^{234}\text{U} / ^{238}\text{U}$ in the studied water bodies varied from 1.53 to 3.62 (figure 6e). These values indicate a significant inflow of groundwater into the rivers and tributaries. Groundwaters in the study area had $^{234}\text{U} / ^{238}\text{U}$ values ranging from 2 to 7 (Shkil et al., 2016). In general, it is difficult to determine the time of the year in which the highest values of the isotope ratio were recorded. Higher values of $^{234}\text{U} / ^{238}\text{U}$ for the sampling point T5 relative to T6 allow us to conclude that groundwater and drainage waters are infused due to the development of the field. An increase in the $^{234}\text{U} / ^{238}\text{U}$ ratio downstream was observed when considering the values of the uranium isotope ratio for the waters of the Kepina river. This can be explained by the inflow into the river of tributaries (KB-3 and KB-4) feeding on groundwater with a higher isotope ratio.

CONCLUSION

As a result of the studies carried out, it can be concluded that one of the main tasks of the activities of the diamond mining plant at the Lomonosov deposit is the systematic monitoring of the state of environmental components. In particular, attention should be paid to the drainage system and the discharge of highly mineralised wastewater into the Zolotitsa river. The obtained results show that the activity of the mining and processing plant for the extraction of diamonds significantly affects the pollution of the Zolotitsa river with metals.

It was determined that the physicochemical indicators of the rivers exposed to anthropogenic impacts are within the normal range. However, there was a sharp increase in salinity (up to 171 mg/L) and a decrease in the redox potential (up to -34.2 mV) in the sections of the Zolotitsa river located downstream of the discharge point of drainage and industrial waters.

Seasonal studies of the metal contents allowed the identification of a group of metals with minimum concentrations in the Zolotitsa river in May (Mg, Fe, Sr, V, Se, Cd, Al, Mn, and Ba), associated with the process of water dilution during snow melting. Metals (Ni, Pb, Zn, Cr, and Cu) were also identified at maximum concentrations in the river in May. It was probably associated with anthropogenic activity in the territory of diamond mining in winter and the accumulation of these metals in the snow, followed by its melting. An increase in the concentrations of the metals Mg (up to 11188 µg/L), Sr (up to 173 µg/L), Zn (up to 14.6 µg/L), Cu (up to 0,73 µg/L), and Cd (up to 0.207 µg/L), as well as As (up to 2.78 µg/L) and Se (up to 0.20 µg/L) was found downstream of the confluence of the Zolotitsa river into the technological channel. It can be explained by the high contents of saponite in waste waters coming from filtration swamps.

Calculations of the indices of water quality and health risks of the population showed different results. For the most polluted river sections, the values of the HMPI index were at a “low” level, the HMTL index revealed “moderate toxicity” and the HMEI index was at the “seriously affected”. Level and the values of the HI and CR indices were above the threshold, indicating high non-carcinogenic and carcinogenic risks. It was shown that the indices in the study area are mainly influenced by the Fe, Ni, As, Cd, and Mn contents in water.

Radiological studies of polluted rivers showed a satisfactory situation. An increase in the uranium content (up to $2.4 \cdot 10^{-6}$ g/L) was noted after the infusion of technological and ground waters into the Zolotitsa river. The study of seasonal variation showed the maximum uranium content in the spring (up to $3.7 \cdot 10^{-6}$ g/L). The ratio of uranium isotopes $^{234}\text{U} / ^{238}\text{U}$ varies in the range of 1.53 – 3.62, which indicates the infusion of groundwater into the rivers under study.

ACKNOWLEDGMENTS

The authors thank Kosyakov D.S. and Kozhevnikov A.Yu. for the opportunity to use

equipment of the Core Facility Centre 'Arktika', Northern (Arctic) Federal University.

GRANT SUPPORT DETAILS

The reported study was funded by the grant of the President of Russian Federation for young scientists MK-4298.2022.1.5. Study of uranium isotopic composition was carried out under the grant of the Russian Science Foundation No 20-77-10057.

CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of the manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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