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Distribution Features and Indicator Significance of Rare Earth Elements in River Waters of Southern Kamchatka

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Abstract : A study of the chemical composition of river waters in Kamchatka Krai revealed a complex interaction between natural (climate, geology, volcanism) and anthropogenic factors influencing the concentrations of dissolved rare earth elements (REEs). The analysis showed that economic activity in rivers subject to anthropogenic loads leads to increased REE concentrations and the emergence of specific anomalies. These findings highlight the need for further research to assess anthropogenic pollution of river ecosystems and develop effective measures for monitoring and managing water quality.

1 INTRODUCTION

Rare earth elements (REEs) are valuable indicators of anthropogenic impact on aquatic systems (Liu, 2022; Liu, 2024; Jiang, 2022; Jiang, 2024; Fu, 2024; Gao, 2023). Anomalies of elements such as gadolinium, lanthanum, and samarium in rivers and lakes, especially near cities, indicate point sources of pollution associated with human activities. Anthropogenic pollution of the hydrosphere with gadolinium, lanthanum, and samarium, associated with the use of contrast agents in MRI and the production of catalysts, has been recorded in rivers worldwide (Bau, 2011). Pronounced positive gadolinium anomalies in industrialized regions confirm the role of REEs as indicators of the ecological state of water bodies and make it possible to monitor the impact of human activities on aquatic systems (Bau, 2011).
When entering soil and water, REEs, being potentially toxic, can accumulate in the food chain and, ultimately, pose a risk to human health (Baranovskaya, 2024). Currently, there are no regulatory limits on the content of most dissolved REEs in natural waters, while REE concentrations near industrial discharges can reach significant levels (Kulaksız, 2013).

The aim of the work was to determine the concentrations and distribution patterns of rare earth elements (REE) in river waters subject to anthropogenic impact.

2 MATERIALS AND METHODS

2.1 Object of study

Kamchatka Krai was chosen for this study because, unlike many other regions of Russia and the world, it is characterized by a low population density and underdeveloped industry. Therefore, background concentrations of rare earth elements (REEs) in local rivers are likely close to natural levels, allowing for a more accurate identification and assessment of the contribution of anthropogenic pollution sources.
The study focused on rivers in Kamchatka Krai, each with varying degrees of anthropogenic pressure. The sample included rivers flowing through the densely populated southern part of the region and experiencing anthropogenic pressure, as well as those completely unaffected (the Bystraya River near the Malkinsky Plant, the Polovinka River, the Koryakskaya River, the Avacha River below the town of Yelizovo, the Kirpichny River, the Spokoiny Stream, the Zhirovaya River (source), and the

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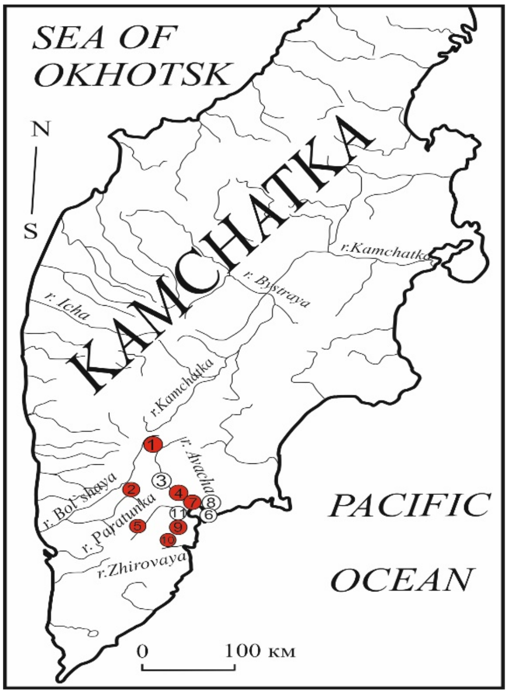
Paratunka River (the main channel of the Paramon River basin).

2.2 Research methods



Picture 1: The layout of the studied objects and sampling points of the rivers of Kamchatka: 1 – upstream Bystraya River, 2 – Bystraya River (main channel) , 3 – Koryakskaya River (A – anthropogenic impact), 4 – Avacha River upstream of Elizovo, 5 – Paratunka River, 6 – Polovinka River, 7 – Avacha River downstream of Elizovo, 8 – Kirpichny River, 9 – Spokoiny Creek, 10 – Zhirovaya River source, 11 – Paratunka River main channel of the Paramon River basin.

Sampling was carried out in July 2024; the sampling locations are shown in Fig. 1. The main unstable parameters (pH, Eh, mineralization, temperature, color and odor) were measured directly at the sampling location using portable test kits (based on the M90 microprocessor and the portable Hach installation).

Water samples were analyzed at the Far Eastern Geological Institute, Far Eastern Branch of the Russian Academy of Sciences (FEGI FEB RAS) Collective Use Center. Samples were filtered through a 0.45-micron membrane filter using a vacuum pump and preserved with ultra-pure nitric acid immediately after collection. Fifty-five elements, including the entire REE group, were determined by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700x spectrometer, Agilent Techn., USA). Samples for macroion analysis were filtered and collected without acidification. Macrocations and macroanions were determined by ion chromatography on an LC-20 high-performance ion liquid chromatograph (Shimadzu, Japan). Hydrocarbons were determined using a Dosimat 765 titrator from Metrohm (Switzerland) with a division value of 0.002 ml.

Determination of organic carbon was performed by high-temperature oxidation (IR detection) using a TOC-V total organic carbon analyzer (Shimadzu, Japan).

The total mineralization of river water (∑i) was determined as the sum of the contributions of macrocomponents:

$$\sum i=[Na^+]+[K^+]+[Ca^{2+}]+[Mg^{2+}]+[SO_4^{2-}]+[Cl^-]+[HCO_3^-]$$

To interpret and analyze the data, a standard analysis of average statistical parameters was performed using the Microsoft Office 2013 software package.

The paper presents data only on dissolved forms of REE, normalized relative to REE concentrations in the standard post-Archean shale (PAAS) (Chudaev , 2016).

3 HYDROGEOCHEMISTRY

3.1 The main salt composition of the studied rivers

An analysis of the obtained data on the main salt composition showed that during the sampling period, the surface waters of all the studied rivers were fresh. However, water mineralization demonstrated significant variability (21.8-105.4 mg/L), with a predominance of low values, characteristic mainly of ultra-fresh waters. Low mineralization of river water during flood periods is explained by dilution by ultra-fresh atmospheric precipitation—a characteristic feature noted for many rivers, especially for small and clean rivers in the southern part of the Russian Far East. The spread of mineralization values during periods of maximum river discharge is explained by the increased role of precipitation, mineralized groundwater recharge, and anthropogenic load. The proportion of HCO_3^- ions in the waters of most rivers on the peninsula varies from 6.75 to 50.72 µg/L. Among cations in river waters, Ca ions dominate (0.66-16.4 mg/L). The magnesium content is lower (0.14-4.14 mg/l), as are the concentrations of sodium (0.12-6.67 mg/l) and potassium (0.1-0.9 mg/l). In terms of chemical composition, the waters of the studied rivers are primarily of the hydrocarbonate-calcium type, but hydrocarbonate-calcium-sodium and hydrocarbonate-calcium-sodium-magnesium waters are also found.

Sulfate ion levels range from 1.03 to 28.4 mg/L. Chloride ion levels in most Kamchatka rivers are insignificant, ranging from 0.29 to 3.56 mg/L. Elevated chloride levels are typically found in rivers located near the coast.

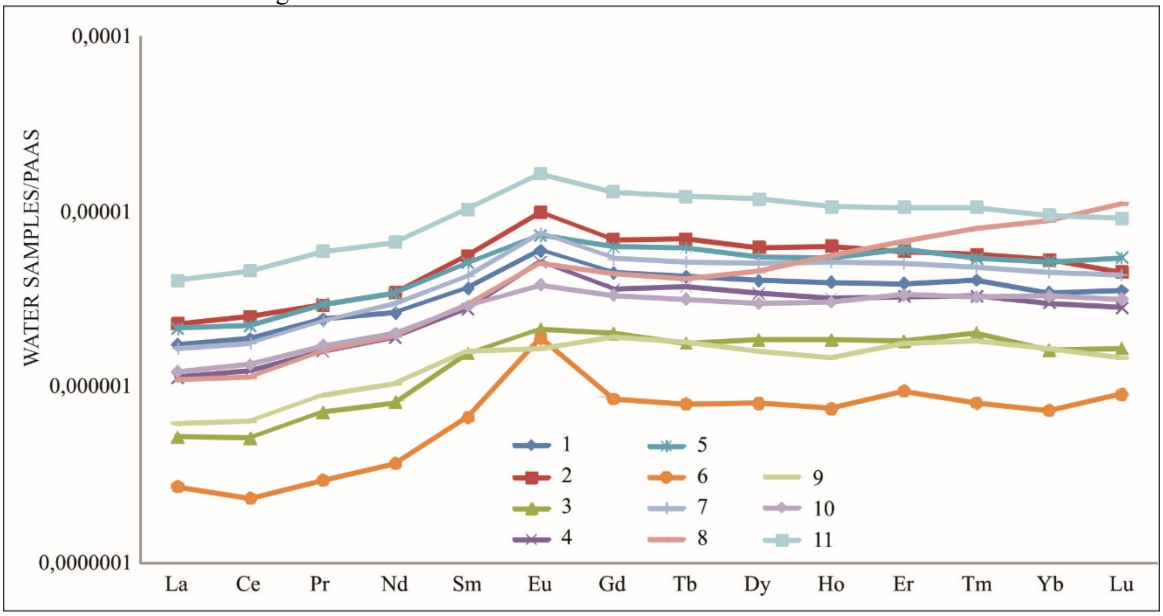
pH values are recorded in the range from 5.5 to 7.9. In most cases, the pH is close to neutral, which meets regulatory requirements for drinking water.

Silicon content in the studied samples varied widely: from 0.04 mg/L to 10.7 mg/L, indicating heterogeneity in the geochemical processes influencing its concentration. Organic carbon concentrations ranged from 0.04 mg/L to 10.7 mg/L. Kamchatka river waters are quite heterogeneous in terms of organic matter content: the average organic carbon content is 4.1 ± 0.4 mg/L.

3.2 Rare earth elements

A geochemical study of anthropogenic-impacted river waters in Kamchatka Krai has revealed patterns in the distribution of dissolved rare earth elements (REEs). REE concentrations in the studied samples varied widely, from 0.065 µg/L to 1.09 µg/L, with an average of 0.4 µg/L and a median of 0.34 µg/L.

In all the rivers studied, a clear dominance of light rare earth elements (LREE) over heavy rare earth elements (HREE) is evident, with LREE constituting, on average, 77.6% of the total REE (∑REE). This distribution is typical of surface waters and is due to the complex interaction of chemical weathering processes, soil formation, and the mineralogical composition of the parent rocks within the drainage basins.



Picture 2: The concentration of REE`s in the river waters of Kamchatka normalized to PAAS . Samples : 1 – upstream Bystraya River, 2 – Bystraya River (main channel) , 3 – Koryakskaya River (A – anthropogenic impact), 4 – Avacha River upstream of Elizovo, 5 – Paratunka River, 6 – Polovinka River, 7 – Avacha River downstream of Elizovo, 8 – Kirpichny River, 9 – Spokoiny Creek, 10 – Zhirovaya River source, 11 – Paratunka River main channel of the Paramon River basin.

A comparison of the obtained data with global background values indicates that, in general, the studied waters of Kamchatka Krai are depleted in REE: the average content of total REE (0.4 µg/L) is almost half the world average for river waters (0.745 µg/L) (Gaillardet, 2002). However, at the same time, an anomalously high content of yttrium is noteworthy - 0.161 µg/L, which is 4 times higher than the world background. This geochemical composition is likely associated with intense weathering of basic or alkaline igneous rocks, such as basalts and nepheline syenites, rich in minerals such as xenotime and gadolinite. In addition that is observed low fractionation (Lan/Ybn = 0.337).

3.3 Standardized REE

Rare earth element (REE) distribution profiles in the studied river waters, normalized to post-Archean shale (PAAS), generally exhibit a uniform pattern. However, two samples stand out as reflecting specific anthropogenic impacts. The Kirpichnaya River sample is characterized by a noticeable accumulation of heavy REE, while the Polovinka River sample exhibits the lowest REE concentrations and a pronounced europium anomaly. The La/Ybn ratio (0.12-0.83) indicates a relative depletion of heavy lanthanides in the waters and a connection with volcanic rocks as the main source. The negative cerium anomaly (Ce/Ce* = 0.83-0.96), caused by the oxidation of Ce^{3+} and its removal from the aquatic environment, is a typical feature of surface waters in the Russian Far East and is associated with high pH, abundance of suspended matter and possible seasonal changes.

It is noteworthy that there is a predominance of positive europium anomalies (Eu/Eu* = 1.12-3.39) compared to a single negative one (Eu/Eu* = 0.94), which is not typical for surface waters and may be an indicator of hydrothermal influence or technogenic input of europium.

Elevated REE concentrations and enrichment in heavy REEs are also noted, particularly in the Paratunka River and the main channel of the B. Paramon River, which may indicate the influence of hydrothermal processes, mineralization, or underground sources. A pronounced positive Eu anomaly in the Kirpichnaya River sample may be related to reducing conditions or the influence of igneous rocks.

Furthermore, gadolinium (Gd: 1.03-1.11) and samarium (Sm: 1.05-1.18) anomalies were detected in the Koryakskaya River and Spokoiny Stream, further indicating the potential impact of economic activity on water quality. The presence of these anomalies, along with other identified REE distribution patterns, suggests the introduction of anthropogenic substances into water bodies. The use of gadolinium as a contrast agent in medical procedures and samarium in industrial production can lead to their accumulation in wastewater and, consequently, to anomalous concentrations in natural water bodies, particularly near populated areas or industrial zones. Analysis of such REE anomalies provides valuable information for assessing the extent of pollution and identifying potential sources of anthropogenic impact on aquatic ecosystems.

The Paratunka River sample (main channel) is characterized by high concentrations of REEs, particularly HREEs, and a flat profile increasing toward Lu. A pronounced positive Eu anomaly in this sample is characteristic of industrial discharges. Thus, the REE profiles in these samples reflect the specificity of anthropogenic sources, such as industrial emissions or municipal wastewater, which lead to elevated concentrations of certain REEs, particularly Eu, and enrichment of the water with HREEs, thereby confirming that REEs are indicators of anthropogenic processes.

4 RESULTS AND DISCUSSIONS

The chemical composition of river waters in Kamchatka Krai is influenced by a complex array of natural factors, including climate, topography, soil cover, and the geological structure of drainage basins. Active volcanic and hydrothermal activity in the region significantly impacts the overall mineralization and chemical component ratios in the water. Furthermore, anthropogenic impacts also play a significant role in shaping the composition of surface waters.

A study of dissolved REE concentrations in Kamchatka rivers revealed a wide range of values (0.065 µg/L to 1.09 µg/L), reflecting the influence of both natural and anthropogenic factors. The observed homogeneity of REE distribution profiles indicates the general composition of the drainage basin rocks, while elevated concentrations in rivers indicate the influence of anthropogenic activity. Overall, the content of dissolved REE in natural river waters in southern Kamchatka is low (up to 0.4 µg/L); however, under the influence of anthropogenic loads or natural anomalies, concentrations can increase sharply (up to 1.09 µg/L).

Analysis of REE distribution profiles revealed both general patterns typical of surface waters in the Far East (Vakh , 2017; Pavlova , 2020) and anomalies indicating potential anthropogenic impact. The anomalously high yttrium content is likely due to intense weathering of igneous rocks in the region. Furthermore, positive europium anomalies, as well as gadolinium and samarium anomalies recorded in individual rivers, suggest the influence of economic activity, particularly industrial and municipal wastewater.

Thus, the study of rivers in southern Kamchatka Krai allows us to conclude that, despite the predominant influence of natural factors, anthropogenic impacts have a significant impact on the composition and concentration of REEs in the region's water bodies. The data obtained highlight the need for further comprehensive research to thoroughly assess the extent of anthropogenic pollution in Kamchatka's river ecosystems and develop effective water quality monitoring and management strategies that take into account both natural and anthropogenic sources of pollution.

5 CONCLUSION

Rare earth elements (REEs) are currently the focus of natural water researchers, driven by their promising role as geochemical indicators. Studying the distribution patterns of REEs in water bodies is essential for monitoring and interpreting various environmental processes. Realizing this potential requires a thorough understanding of the behavior and fractionation of REEs in aquatic environments. REEs can exist in various forms—dissolved, colloidal, and nanoparticle—which determines their mobility and accessibility to biota.

When rare earth elements enter soil and water, they can become hazardous to health by accumulating in the bodies of animals and plants. They easily enter the food chain and accumulate in the body, overcoming the blood-brain and embryonic barriers (Baranovskaya, 2024). Although standards for the content of these elements in natural waters have not yet been established, high concentrations of REEs are often found near industrial facilities (Vakh , 2014; Dantas, 2015). Conducting studies of the content and composition of dissolved REEs is an important step in assessing the ecological state of water bodies and identifying potential pollution zones, as well as subsequently developing methods for monitoring and controlling the spread of REEs in the environment. Research aimed at identifying the content and composition of dissolved REEs in Kamchatka rivers is important for understanding the current ecological state of water resources and identifying areas with potential pollution. These data are necessary for the further development of effective methods for monitoring and controlling the spread of REEs in nature.

GRATITUDE

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