Aquatic environment and anthropogenic factor effects on distribution of trace elements in surface waters of European Russia and Western Siberia

T I Moiseenko¹, M I Dinu¹, N A Gashkina¹ and T A Kremleva²

¹ Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, Kosygin str. 19, Moscow, 119991, Russia
² Tyumen State University, str. Lenin 25, Tumen, 625003, Russia

E-mail: moiseenko.ti@gmail.com

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Abstract

The distribution of trace elements of anthropogenic origin, especially toxic metals, is an environmental problem. We present the first results of research into the geochemistry of lake waters and metallic pollution in European Russia (ER) and Western Siberia (WS), based on a survey of 367 lakes from the tundra to the steppe zones. The content of more than 80 elements in the lake water was studied; the influence of airborne contamination and the geochemistry of water were estimated. We found that the concentrations of alkaline and alkaline-earth elements, as well as As, V, Co, U, Nb, Sb, increase with a change in the climatic gradient. This fact is explained not only by airborne contamination, but also by the geochemistry of lakes and the climatic factor (increased evaporation concentration). Anthropogenic eutrophication leads to an increase in the content of Fe, Sr, Mo, and acidification—Zn, Cd, Ni, Cu, and especially Pb. There are industry-specific influences: the waters of the northern regions of ER are enriched by Ni, Cd, As, Sb and especially Se because of the emissions from copper-nickel smelters. The oil and gas industry (WS) leads to increased concentrations of V, Pb and Mo in water. We assess the metallic pollution status of surface water in the Eurasian region of Russia using an enrichment factor (EF). In surface waters of ER and WS, metal concentrations do not exceed the maximum permissible concentration, but we have established higher concentrations of many elements in the background, including toxic ones. Prolonged low doses of toxic elements can be a potential hazard to ecosystems and humans. The results showed that from the northern to the southern regions the EF increases for most of the analyzed elements. It can be assumed that with climate warming the concentration of metals in these bodies of water will increase and this is dangerous for the environment.

1. Introduction

Understanding the distributions of trace elements (metals and metalloids) in nature and their increasing concentrations at a regional and global level is one of the topical challenges for the current environment. It is a proven fact that the anthropogenic input of trace elements into the environment has increased over the last century, which is associated with the production of continuously increasing volumes of metal and its release into the environment (Nriagu and Pacyna 1988, Nriagu 1996, Pacyna and Pacyna 2011, Bjerregaard and Andersen 2014, Moiseenko 2017). According to literary data, it was established that an important source of dispersion of As, Cd, Cu, In and Zn is the production of nonferrous metals, and fixed-site fuel burning sources contribute significantly to the release of Cr, Hg, Mn, Sb, Se, Sn, Ni ,V and Tl into the environment.

In the developed countries of Europe and North America, trace metal emissions have decreased over recent decades, while in the developing countries of South America and Asia the volumes of anthropogenic element releases of metals into the environment have
increased (Pacyna and Pacyna 2011). Many regions that are remote from industrial centers accumulate toxic metals in their environments. Increased concentrations of hazardous elements such as Hg, Cd and Pb are detected in the snow cover of Greenland and the Upper Arctic (AMAP Assessment 2002). Therefore, further studies of the effects of airborne pollution upon the enrichment of natural environments with trace elements are relevant. It should be noted that metals entering the environment are included in biogeochemical cycles and are accumulated in living organisms, including humans (Nordberg et al. 2014).

Surface waters are collectors for all kinds of pollutants and reflect changes in geochemical cycles of elements under the effect of human activities on a regional and global level. Even lakes situated far from direct sources of pollution are impacted by airborne contaminants (Skjelkvåle et al. 2001). Trace elements found in lake waters are the result of natural rock/soil/sediment leaching, erosion, and airborne pollution. Changes in migration processes and biogeochemical cycles of elements in lakes can cause eutrophication, salinization, and acidification.

The territory of Russia embraces different regions and climatic zones, from the tundra zones to the steppe. The processes of water chemical composition formation and anthropogenic loads vary (Moiseenko et al. 2018a). A higher density of population and industry concentration characterizes the territory of European Russia (ER). In the north of this region, copper and nickel smelting, apatite-nepheline and metallurgical, ore mining and processing plants are concentrated. In the central part, there is a large concentration of ferrous metallurgy enterprises. In the southern regions, agriculture and related industrial production is more widespread.

The source of release of metals into the environment of Western Siberia (WS) is from oil and gas production. Trace metals such as V, Ni, Fe, Al, Cu, Sr, Mn, Co, Mo, Cr, As, Mo, etc. are present in the oil produced in WS. These elements are found in organic and non-organic compounds of oils. Their total content does not exceed 0.02%–0.03% of the oil weight (Kiryushin et al. 2013). However, taking into account the volumes of production and input of crude oil and combustion products of associated petroleum gas, fuel oil and automotive fuels, the mass of microelements that gets into the environment is significant. Around the area with exploited oil fields and large centers of population, the content of heavy metals in snow increases (Kiryushin et al. 2013). In the northern taiga, a consistent increase in Fe, Mn, and Pb concentrations in snow has been recorded over the last ten years (State and Protection..., 2013–2017). This demonstrates that oil and gas production, both directly and indirectly through atmospheric emissions, results in the dispersion of metals and metalloids and the concentration of metals in the soils and waters of WS.

It should be noted that the population density in both regions is heterogeneous and increases from north to south, which increases the energy consumption and the level of pollution. The mean density of population in the northern regions of ER is 8.4 people km⁻², while in the southern regions it is 35 men km⁻². In WS, huge areas remain sparsely inhabited so far, and the mean density of population is 2 people km⁻². The distribution of population in the region is also nonuniform, and the density index varies within the range from 0.5 people km⁻² in the north up to 9.4 people km⁻² in the middle and southern parts of WS (ROSSTAT 2018). Agriculture, main traffic arteries, power stations and industry are developed in the southern regions, which inevitably results in larger releases of elements (National Atlas of Russia 2007).

Research into the distribution of trace elements in water formation and anthropogenic loads in different regions are urgent in order to understand how concentrations of trace elements increase on a tranregional level and assess the effect of airborne contamination of aquatic environments. Metals are able to accumulate in living organisms, causing long-term genotoxic and carcinogenic effects when they are found in elevated concentrations in the aquatic environment (Hoffman et al. 2005, Nordberg et al. 2014). Even at relatively low concentrations, not exceeding the maximum permissible concentration (MPC), with long-term exposure metals accumulate in the bodies of fish and humans, causing diseases in fish living in the water and people using this water for drinking (Moiseenko et al. 2018b).

The aim of this paper is:
- To determine the distribution of trace elements in surface water in various climatic zones of ER and WS, from the tundra zone to the steppe zone;
- To identify the geochemical and anthropogenic effect on the water chemical composition formation;
- To assess of metallic pollution status of surface water in Eurasian region of Russia based on enrichment factor (EF).

2. Material and methods

2.1. Objects

This manuscript is the second step of large-scale research into surface waters chemistry in ER and WS. The layout of the sampling points, the basic methods used for studying and selecting lakes, taking samples and their chemical analysis are set forth in the study (Moiseenko et al. 2018a). In the article, attention is focused on research into lakes not subject to direct sources of contamination and, therefore, they reflect only the influence of airborne contamination with ingress of trace elements.

The selected lakes ranged from 0.4 km² to 20 km² in surface area with no direct sources of wastewater in their catchments. The sampling was carried out during...
autumn turnover (from late September for tundra lakes to late November for lakes of the steppe) to minimize the effect of interannual and seasonal variations. A total of 201 small lakes in ER along this transect were sampled from 2000 to 2005 and 166 samples of lake waters in WS from the Yamal and the Gydan Peninsulas to the Kurgan Region (forest steppe) were collected in 2011–2014.

Water samples were collected in plastic bottles without sorbing properties. In the field, the bottles were rinsed twice with lake water, then placed into dark containers and cooled to 4 °C. Water samples were transported to the laboratory as soon as possible (within 5–15 days) to determine the main hydrochemical parameters, as well as individually nonfiltrating sampling being acidified (not more than 15 ml) for the subsequent measurement of elements by the ICP method.

2.2. Determination of aquatic environment parameters
Chemical analyses were carried out using the techniques outlined in Standard Methods for the Examination of Water and Wastewater (Eaton et al 1992). According to the protocol, all samples were analyzed within 24 hours. Analyzed parameters included pH, conductivity (at 20 °C), alkalinity (Alk), \( \text{NH}_4^+ \), \( \text{PO}_4^{3-} \), Si, total N (TN), total P (TP), dissolved organic carbon (DOC) and colour. pH and conductivity (20 °C) were measured using a Metrohm pH meter, alkalinity by the Gran titration method, and organic matter content by the Mn oxidation method. Cations (Cat=Ca, Mg, K, Na) were measured using atomic absorption spectroscopy (flame), and anions (\( \text{SO}_4^{2-} \), \( \text{Cl}^- \), \( \text{NO}_3^- \)) were measured using ion chromatography, organic anion concentrations (an-) were determined based on the empirical relationship suggested by Oliver et al (1983). We used the ion balance, the anion charges (sum of \( \text{Cl}^- \), \( \text{SO}_4^{2-} \), \( \text{NO}_3^- \), \( \text{F}^- \), and \( \text{HCO}_3^- \)) and the cation charges (sum of \( \text{Ca}^{2+} \), \( \text{Mg}^{2+} \), Na\(^+ \), \( \text{NH}_4^+ \), K\(^+ \) and H\(^+ \)).

2.3. Determination of trace elements
Concentration measurements of Li, Na, Mg, Al, P, S, K, Ca, V, Mn, Fe, Cu, Zn, Sr, and Ba by ICP-AES (ICAP-61 Thermo Jarrell Ash, Institute of Problems of Microelectronics Technology and Superpure Materials RAS, Chernogolovka) were performed with a plasma-forming Ar flow rate of 18 L min\(^{-1}\), an auxiliary Ar flow rate of 0.9 L min\(^{-1}\), an Ar flow rate into the nebulizer of 0.6 L min\(^{-1}\), an analyzed sample flow rate of 1.5 m L min\(^{-1}\), and a plasma observation zone height of 14 mm. The integration time of the spectra during each run was 5 s. The element contents in aqueous solutions were determined by the quantitative method using calibration solutions (High Purity Standards, USA) of 0.5 and 10 mg L\(^{-1}\) of each element.

Concentration measurements of B, Li, Be, Al, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Ti, Pb, Bi, Th and U were performed by ICP-MS (X-7 ICP-MS Thermo Electron, Institute of Problems of Microelectronics Technology and Superpure Materials RAS, Chernogolovka). The main parameters were an RF generator output power of 1250 W, a Polyclon nebulizer, a plasma-forming Ar flow rate of 12 L min\(^{-1}\), an auxiliary Ar flow rate of 0.9 L min\(^{-1}\), an Ar flow rate into the nebulizer of 0.9 L min\(^{-1}\) and an analyzed sample flow rate of 0.8 mL min\(^{-1}\), and a resolution of 0.8 mL min\(^{-1}\). The detection limits were DL = Ci + 3\(\sigma\), where Ci is the mean content of an isotope of interest for measurements in control samples and \(\sigma\) is the standard deviation of its determination in control samples. For elements with several isotopes, DL was used for the most abundant isotope. The accuracy of the analyses was better than 10% for elements with C > 5 DL and did not exceed 20% for elements with C < 5 DL. For most elements analyzed, the concentrations were higher than 5 DL.

2.4. Statistical analysis
Statistical analysis was used to compare the mechanisms of distribution of elements in ER and WS and were performed by Statistica Advanced 12. We used statistical methods of cluster analysis and multidimensional scaling to assess the geochemical and anthropogenic features of the surface waters of the regions.

Cluster analysis allowed us to identify groups of elements related to each other by geochemical nature—the main and associated components of soil-forming rocks. We chose 21 elements, representatives of various geochemical groups.

Redundancy analysis (RDA) was used to determine significant environmental variables and to explain the majority of the variation in data, i.e. to quantify the discrete contribution of the individual descriptors (Filzmoser et al 2010, Narayanan et al 2015). The RDA analyses were first performed with many explanatory variables to ensure that no possible relationship was overlooked (Snuderl et al 2007). We chose independent (axial) physicochemical parameters—TOC, pH, TP, electrical conductivity, sulfates, as well as a significant number of dependent parameters (elements of different geochemical groups) to identify the affinity of elements for specific geochemical and anthropogenic parameters.

3. Results and discussion
3.1. Specificities of element distribution
The contents of trace elements in waters of ER and WS are shown in table 1. In spite of a great variability in the
Table 1. The median and limits of trace element concentrations (in brackets) in the water of lakes in various natural regions of the East European Plain (ER) and WS.

| Trace element | Tundra and forest tundra | Northern and middle taiga | South taiga and mixed forests | Forest-steppe and steppe |
|---------------|--------------------------|---------------------------|-------------------------------|--------------------------|
|               | ER (μg L⁻¹)               | WS (μg L⁻¹)               | ER (μg L⁻¹)                   | WS (μg L⁻¹)               |
| Al            | 54.0 (13.7–180)          | 19.9 (10.0–310)           | 55.0 (2.4–1010)               | 54.4 (7.8–230)           |
| Fe            | 50.0 (4.3–600)           | 57 (10–1474)              | 142 (2.8–3300)                | 125 (10–1134)            |
| Ti            | 1.79 (0.48–8.27)         | <0.6 (<0.6–4.8)           | 1.50 (0.94–3.30)              | <0.6 (<0.6–4.2)          |
| Mn            | 1.6 (0.2–18.0)           | 6.7 (1.1–26.1)            | 9.1 (0.3–125)                 | 5.0 (0.09–49.6)          |
| Ba            | 4.23 (2.24–10.9)         | 4.16 (2.6–26.8)           | 7.09 (3.3–37.1)               | 3.14 (0.71–48.9)         |
| Sr            | 11 (4–23)                | 4.70 (0.70–34.8)          | 23 (2–186)                    | 2.64 (0.51–222)          |
| Zr            | 0.05 (<0.02–0.15)        | 0.03 (<0.01–0.42)         | 0.34 (0.05–0.95)              | 0.05 (<0.01–0.39)        |
| Rb            | 0.56 (0.34–1.73)         | 0.37 (0.16–0.947)         | 1.60 (1.06–3.70)              | 0.50 (0.14–1.86)         |
| V             | 0.35 (<0.02–0.76)        | 0.11 (<0.01–0.4)          | 0.24 (0.09–1.73)              | 0.19 (<0.04–1.0)         |
| Zn            | 0.9 (0.2–4.7)            | 4.33 (1.94–20.0)          | 0.9 (0.2–25.0)                | 5.29 (1.30–100)          |
| Cr            | 0.2 (<0.1–0.5)           | 0.4 (<0.4–0.5)            | 0.2 (<0.1–1.3)                | <0.4 (<0.4–0.5)          |
| Co            | 0.29 (0.12–1.13)         | 0.07 (0.02–0.56)          | 0.42 (0.16–1.94)              | 0.07 (0.01–0.45)         |
| Ni            | 0.9 (<0.25–5.5)          | 0.93 (<0.2–2.78)          | 0.5 (<0.2–4.8)                | 0.68 (<0.2–16.3)         |
| Cu            | 0.7 (0.2–2.9)            | 2.58 (1.23–9.02)          | 0.6 (0.2–4.4)                 | 2.53 (0.76–5.90)         |
| Zn            | 0.10 (0.04–0.21)         | 0.04 (0.01–0.35)          | 0.13 (0.02–0.63)              | 0.06 (0.01–0.62)         |
| Nb            | 0.45 (0.11–0.65)         | 0.84 (0.32–4.14)          | 0.59 (0.18–1.40)              | 1.08 (0.28–5.12)         |
| Co            | 0.24 (0.07–0.62)         | 0.04 (0.02–0.17)          | 0.37 (0.13–4.10)              | 0.04 (0.01–0.12)         |
| Y             | 0.07 (0.02–0.10)         | 0.04 (0.01–0.29)          | 0.05 (0.02–0.23)              | 0.03 (0.01–0.21)         |
| Nb            | 0.01 (<0.01–0.02)        | <0.01                      | 0.01 (<0.01–0.02)             | <0.01 (<0.01–0.02)       |
| Ga            | 0.01 (<0.01–0.02)        | <0.02                      | 0.01 (<0.01–0.04)             | <0.02                    |
| Co            | <0.2 (<0.2–0.3)          | 0.06 (<0.04–0.19)         | 0.2 (<0.2–0.3)                | 0.07 (<0.04–0.19)        |
| Pb            | <0.1 (<0.1–0.16)         | 0.30 (0.11–3.39)          | <0.1 (<0.1–1.1)               | 0.45 (0.09–2.36)         |
| Th            | 0.01 (<0.01–0.03)        | 0.01 (<0.01–0.05)         | 0.01 (<0.01–0.03)             | 0.01 (<0.01–0.03)        |
| B             | <0.1                     | 13.5 (8.4–37.4)           | <0.1 (<0.1–1.3)               | 15.2 (7.9–156)           |
| Sc            | 0.04 (<0.1–0.8)          | <0.04                      | 0.8 (<0.1–3.0)                | <0.04                    |
| Pr            | 0.04 (<0.01–0.07)        | 0.01 (<0.004–0.08)        | 0.05 (0.02–0.18)              | 0.02 (0.003–0.056)       |
| Be            | <0.01 (<0.01–0.02)       | 0.01 (<0.01–0.19)         | 0.01 (<0.01–0.02)             | 0.01 (<0.01–0.02)        |
| Cs            | 9.45 (8.17–11.2)         | <0.01                      | 8.93 (8.04–15.6)              | <0.01 (<0.01–0.02)       |
| Sn            | 0.09 (0.00–0.32)         | <0.01 (<0.01–0.13)        | 0.15 (0.06–0.28)              | 0.01 (<0.01–0.11)        |
| U             | 0.03 (0.01–0.30)         | 0.04 (0.02–0.06)          | 0.02 (0.02–0.25)              | 0.03 (0.02–0.13)         |
| Br            | 8.7 (5.8–10.1)           | <8 (<8–150)                | 1.7 (0.5–9.4)                 | <8 (<8–305)              |
| As            | 0.1 (<0.1–0.3)           | 0.43 (0.10–1.56)          | 0.2 (<0.1–3.9)                | 0.46 (0.11–2.05)         |
| W             | 0.02 (<0.02–0.05)        | <0.01 (<0.01–0.02)        | 0.02 (<0.02–0.09)             | 0.01 (<0.01–5.28)        |
| Trace element | Tundra and forest tundra | Northern and middle taiga | South taiga and mixed forests | Forest-steppe and steppe |
|---------------|--------------------------|---------------------------|-----------------------------|-------------------------|
|               | ER | WS           | ER | WS           | ER | WS           | ER | WS           | ER | WS           |
| Mo            | 0.14 (0.04–0.32) | 0.93 (0.25–6.26) | 0.23 (0.08–0.46) | 0.69 (0.25–8.28) | 0.06 (<0.02–0.83) | 0.52 (0.32–3.80) | 0.14 (<0.02–0.71) | 1.28 (0.62–2.33) |
| Sb            | 0.04 (0.01–0.13) | 0.16 (0.12–0.27) | 0.07 (0.02–0.16) | 0.18 (0.10–0.49) | 0.05 (<0.01–0.17) | 0.14 (0.09–0.69) | 0.08 (<0.01–0.19) | 0.23 (0.16–0.38) |
| I             | 3.9 (1.9–25.3)   | not defined           | 3.0 (1.7–5.8)    | not defined           | 10.9 (2.8–31.9)   | not defined           | 71.5 (3.0–277)    | not defined           |
| Ag            | 0.02 (<0.01–0.06) | 0.04 (0.01–26.7)     | 0.10 (<0.01–0.19) | 0.04 (0.01–24.4)   | 0.01 (<0.01–0.07) | 0.02 (0.01–0.06)   | <0.01 (<0.01–0.06) | 0.05 (<0.01–2.06)   |
| Se            | 0.3 (0.1–0.7)    | <0.2                  | 0.3 (<0.1–0.5)    | <0.2                  | <0.1 (<0.1–1.0)   | <0.2                  | <0.1 (<0.1–1.7)    | <0.2                  |
| Cd            | 0.09 (<0.05–0.21) | 0.01 (<0.01–0.08)    | 0.05 (<0.05–0.61) | 0.02 (<0.01–0.11)   | 0.05 (<0.05–1.77) | 0.05 (0.01–0.40)   | 0.05 (<0.05–1.60) | 0.09 (0.07–0.13)   |
| Bi            | 0.01 (<0.01–0.03) | 0.45 (0.13–3.86)     | 0.01 (<0.01–0.13) | 0.53 (0.011–4.42)   | <0.01 (<0.01–0.02) | 0.38 (0.27–1.18)   | <0.01 (<0.01–0.02) | 0.30 (0.02–0.61)   |
| Re            | <0.01 (<0.01–0.08) | <0.01                 | 0.01 (<0.01–0.35) | <0.01                 | <0.01 (<0.01–1.67) | 0.96 (0.3–1.84)     | <0.01 (<0.01–2.06) | 2.38 (1.69–21.4)    |
concentrations of most trace elements in each climatic zone, there is a number of specificities. In the study (Moiseenko et al 2018a), an increase in Ca, Mg, Na, K contents from the northern to the southern regions is shown. The similar geochemistry is typical for all trace alkaline-earth and rare earth elements (Li, Rb, Cs, Sr, Be Ba). In general, the distribution of elements in waters for the zones of ER and WS increases for elements such as As, V, Co, U, Nb, Sb, with the change in the climatic gradient in the direction towards the more southern regions, which may be associated with an increased anthropogenic load and higher density of population in the southern provinces. The evaporation factor due to higher temperatures can be attributed to natural factors producing an effect resulting in an increase of trace element concentrations in the southern areas of these regions. An additional natural factor may be a marked zone-specific increase of rock leaching from North to South (Milanovsky 1987).

In the northern regions of ER, lake catchment areas are formed by magmatic rocks, the most resistant to leaching; crystalline Archean and Lower-Proterozoic outcrops form the Baltic Shield (Milanovsky 1987). In the northern regions of WS, a substantial part of the sedimentary rocks is in a frozen state, and the chemical and physical processes are significantly slowed (Khirenov 2011).

As and U content in lakes in the southern zones of WS are also considerably higher than those in the northern zones and higher than those in the respective zones of ER. High concentrations of U and Nb (about 1 μg L⁻¹) were detected in the southern taiga and forest-steppe zones of WS. In the opinion of scientists studying the contents of actinoids (especially with radioactive properties) in the selected region, the highest U content is detected in soil-forming rocks under the arid climate conditions of the southern regions of WS (Sukhorukov et al 2000), which is due to geochemical properties. Increased background As contents are typical for all types of soils in WS, but its content most significantly increases in the southern areas affected by anthropogenic factors.

Fe concentrations are highest in the taiga and forest regions due to the predominance of wetlands. The presence of humic and fulvic acids in aquatic environments and low pH values are the main factors contributing to an increase in Fe content. In the southern taiga and forest-steppe zones of WS, the content of carbonates in rocks grows, which results in an increase in the pH of waters. Fe is unable to be in a dissolved state in such conditions, and its content in waters decreases steeply (Moiseenko et al 2018a). The distribution of Mn and Ba is similar to that of Fe, their concentrations in waters of WS and ER are higher in the southern taiga and forest regions (except for steppe waters in ER). In WS, the greatest median contents of Fe in waters are typical for the southern taiga zone due to an increased influence of peatbogs.

Ni and Cu contents are characterized by high variations in each climatic zone. Ni content is higher in waters of the northern regions, which may be associated with the influence of smelting plants (Nornikel). In WS, an increased content of copper ions in waters is typical for all zones as compared with ER. This fact is stated by many researchers studying the composition of surface waters in WS (Babushkin et al 2007). The most probable explanation for it is a high affinity of this metal to organic ligands of humic origin, which is due to zonal functional specificities of organic compounds and a sufficient quantity of dissolved organic carbon in all waters of the zones in WS.

Al content is higher in northern waters where the soil-forming rock is made up of gneissic granite (ER) and quartz (WS) formations. It is well known that acid precipitation in this results in more intensive leaching of this element from the underlying rocks (Johansson et al 1995, Rodushkin et al 1995). In a dissolved state, Al may be present either with low or sufficiently high pH values, therefore, for example, a sufficiently high content of Al in the forest-steppe zone of WS is associated with the fact that there are lakes with a pH of 8–9.

Some differences in trace element contents with regard to lake waters in the examined regions should be mentioned. High Bi concentrations were identified in waters of WS, which are typical for all zones and exceed the lead contents. This fact is explained by specificities of the water–rock geochemical equilibrium and depends on soil-forming rocks of WS (Shvartsev 1988). The Cd concentrations in waters of WS increase towards the southern regions, which may be associated with use for application of phosphate fertilizers (Cullen and Maldonado 2013). As for the regions of ER, the tendency is inverse, higher concentrations are found in waters of the northern regions, which may be associated with the effect of copper and nickel plants and the leaching of this element with acid precipitation, possibly, transboundary transport from contaminated Europe. The behavior of Cs is similar to that of Cd.

### 3.2. Assessment of tendency in the distribution of elements

The influence of geochemical and climatic factors on the formation of waters of the ER and WS lakes, including the anthropogenic contribution, were found. The chemical speciation of lake waters: concentration of macro- and micro-components, trace elements in waters of the regions of WS and ER, as well as primary physical-chemical parameters, were used for statistical analysis.

The fundamental property of the geochemical behavior of elements is their group distribution in underlying rocks subject to certain laws; therefore their migration into water systems is determined by generous laws. In order to identify the conjoined
Ingress of elements into water systems, correlation analysis and conformity analysis within the limits of the totality of all examined elements in overland waters were performed, which enabled us to identify the most general regularities of element migration. The assessment of reliable correlations was realized using sequential algorithms of the distance matrix and cluster analyses (figures 1(a) and (b)).

The correlation analysis showed a significant connection between specific groups of elements depending on their chemical properties, geochemical factors and anthropogenic factors. Cluster analysis enabled us to find a system of interacting sequential groups of elements.

Aluminum and iron. The selected elements, although they are not included in the same chemical
group (subgroup) or in a common geochemical family of elements, have similar physical-chemical features (hydrolyzability, complexity, adsorptive properties, sediment formation, etc) and conjointly are present in the composition of many natural formations. Besides strong correlations with each other, the elements show the composition of many natural formations. Besides group (subgroup), these elements similarly share physical-chemical features with Fe, Al, and Ni. The influence of lanthanoids and actinoids over subsequent subgroup formation with the participation of Fe and Al is identified for waters of WS, which conforms to the data on the composition of soil-forming rocks of the region.

Cluster analysis showed a bigger interaction between Fe and Al in forming element families for ER, as compared to WS. The Ni contribution to the formation of subfamilies is traced in waters of ER: geochemical rocks are enriched as Fe, Al, and Ni. The influence of lanthanoids and actinoids over subsequent subfamily formation with the participation of Fe and Al is identified for waters of WS, which conforms to the data on the composition of soil-forming rocks of the region.

The group of lanthanoids (cerium metals + yttrium metals) showed a positive correlation \((r > 0.9, p = 0.005)\) with those elements that are also included in the composition of iron-containing, aluminium-containing silicate, phosphate minerals and clays—such as Fe, Si, Be, Al, as well Cr, V, Ti. Because a wide variety of elements of this group are present in water samples from WS and, accordingly, their higher content and variations in soil-forming rocks, correlations of lanthanoids and organic matter are also typical for waters of WS.

The group of actinoids (Th + transuranium metals) showed positive correlations \((r > 0.9, p = 0.005)\) with alkaline-earth and alkali metals, sulfates, and phosphates. These elements are present together with the specified components in natural formations, such as molybdenite \(\text{MoS}_2\), galena \(\text{PbS}\), quartz \(\text{SiO}_2\), calcite \(\text{CaCO}_3\). In addition, a positive correlation \((r > 0.85, p = 0.005)\) is characterized for rare-earth metals and actinoids elements. Actinoid group metals are associated elements in natural minerals. Correlations of elements from this group with organic substances and transition metals are higher in waters of WS then other regions due to the structure of organic substances. Also, mean correlations are characterized for actinoids elements with water coloration and organic matter, especially in waters of ER.

Elements from the specified groups—lanthanoids and actinoids—also have significant correlations \((r > 0.95, p = 0.005)\) with each other because of uniform geochemical minerals formations (geo-chemical factor). Also, they have identical migration behavior under the effect of the physical-chemical conditions of the environment.

Chromium subgroup (Cr, Mo). These elements have correlations between themselves \((r > 0.95, p = 0.005)\), as specified above, as well as with elements from the groups of lanthanoids and actinoids and also with Fe, V, Ti. There is a positive correlation shown by elements from the subgroup with components such as Pb and some others, which, perhaps, is explained by the geochemical factors and technogenic processes. A significant correlation with Al and some other transition metals is traced for waters of ER, while that with Be and V is traced for waters of WS.

Group of alkali and alkaline-earth metals. As for these elements, correlation analysis showed significant correlations, due to some similarity of physical and chemical properties of these two groups, and with the basic parameters of water objects (alkalinity, \(\text{pH}\), conductivity) and some nonorganic anions that are contained in mineral sediments. In addition, positive correlations with sulfate ions were identified for ER \((r > 0.85, p = 0.005)\), which is associated with the abundance of sulfide-containing minerals in the mentioned territory. In the WS zone, correlations with alkalinity as a result of the formation of complex hydrocarbonates are found.

Pb has positive correlations with some elements that are contained in shared ore deposits such as Sb, Cd, Zn, Cu, Al and many of which have similar behaviors in the processes of leaching from soils and mineral formations. As for WS, correlations with organic matter, some lanthanoids and actinoids are identified. In the ER zone, there are correlations with anionic components and color.

The metalloid As is characterized by positive correlations with some aquatic environment parameters such as total alkalinity and content of alkali and alkaline-earth metals, which is the result of the influence of these factors on the specification of As in water. A positive correlation \((r > 0.5, p = 0.005)\) is traced also with sulfates, as well as Pb, which are primary and accompanied components in natural minerals.

In the ER zone, positive correlations \((r > 0.95, p = 0.005)\) between Co and Ni are identified, which is the result of an affinity between physical-chemical properties of ions and similar migration from natural minerals. These correlations did not exist in WS because of continuously low (below the detection limit) Co concentrations in water objects.

### 3.3. Impact of aquatic environment on distribution of elements

The elemental composition of surface waters is formed under the influence of natural factors having an effect on the water chemical composition (climatic, lithological, morphometrically, hydrological, biological, etc), as well as anthropogenic factors contributing to
changes in geochemical migration and the behavior of elements in water systems. The determination of the affinity of chemical elements to basic physical-chemical parameters enables us to make assumptions about the possible mechanisms of the formation of their chemical composition under the effect of natural and anthropogenic factors. X-ray diffraction analysis demonstrated different responses from trace elements to the basic physical-chemical parameters of waters such as pH, TOC, TP, SO$_4$, Cond (figures 2(a), (b)). The distribution of these parameters per zone is described in the study (Moiseenko et al 2018a).

Alkali and alkaline-earth metals, which are characterized by a high affinity to electrical conductivity in the zones of WS and ER, are found. While the organic matter concentration has an effect upon the contents of Fe and Al ions in the waters of ER, the pH serves as the determining factor in waters of WS. Such a tendency is also typical for other transition metals such as Cu, Pb, Cd, Zn. This is

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**Figure 2.** RDA-ordination diagrams (connection between chemical components of ER (a) and WS (b) lakes): axes are independent variables (factors) that determine the behavior of other components; points are dependent variables that have an affinity for general physicochemical parameters.
explained by higher contents of the metals in waters of WS, which forms an increased redox potential in the system and, consequently, a greater effect of the pH upon the metal–organic matter equilibrium.

While Co and Ni ions have a certain affinity to sulfates and the pH in the zone of ER, it may be explained by technogenic and natural factors, an affinity to the pH system is identified for the WS zone, as has been explained earlier.

Representatives of lanthanoids and actinoids, as accompanying elements, repeat the dependences of Fe and Al for waters of WS. However, U shows an affinity to sulfates, like alkali metals, as regards the waters of ER, which may be explained by the industrial specificities of the region. As has an obvious affinity to phosphorous in the ER zones. This is regular from the point of view of anthropogenic impact.

In recent years, anthropogenic acidification and eutrophication of waters has been a general phenomenon affecting the water quality. Accordingly, we have analyzed the behavior of trace elements for three groups of lakes such as anthropogenically acidified lakes, lakes with a high content of humic acids and eutrophic lakes (table 2).

Natural humic lakes are numerous in humid areas of ER and especially WS. These lakes are characterized by a high level of water color (>100°Pt-Co) according to the respective classification (Håkanson and Boullion 2001)) and a low value of pH (pH ≤ 6), which is associated with a high concentration of humic acids. Based on the stability constants calculated for metal complexes with humic substances discharged from tundra and taiga soils in ER and WS, it is shown that binding of elements by humic substances is limited by the quantity and quality of organic substances, as well as the quantity of iron (Moiseenko et al. 2012). In ER and WS, the natural processes of gleying are accompanied by the extraction in large amounts of both Fe and Al (table 2). In tundra and forest, Sb concentrations in lake water increase really significantly, while in tundra and northern and middle taiga—Zn and As.

Acidified lakes are characterized by a high sulfate content (especially in ER), low colour (<30°Pt-Co) and low pH (<6). In tundra and taiga, such lakes account for 6.9% in ER and 17.2% in WS (Moiseenko et al 2018a). Under the conditions of water acidification, migration and water enrichment with elements may intensify (Nelson and Campbell 1991, Johansson et al 1995, Moiseenko and Gashkina 2011). In contrast to WS, in more industrially-developed ER, sulfate leaching from the catchment and acidic water of these lakes leads to increased trace element migration and more high concentrations of Zn, Ni, Cu and especially Pb in water (table 2). The low pH of the water of acidified and humic lakes (especially lakes at higher latitudes) reduces the migration of Mo, Sr.

Eutrophic and hypertrophic lakes are characterized by a high total phosphor content (>35 μg l−1 according to the respective classification (OECD 1982)). The biogeochemical cycles of Mn are enhanced while eutrophication of the lakes is apparent, while in WS this is true only for lakes of southern areas. In eutrophic and hypertrophic lakes of ER, water is enriched with Mn and to some extent with Fe, Sr due to an increase in watershed humification. At the same time, water of such lakes in WS is significantly enriched only with Mo. It is noteworthy that Cd concentrations significantly increase in water of eutrophic and hypertrophic lakes in the more southern areas.

3.4. Anthropogenic impact assessment via enrichment factors and criticality to human and ecosystem well-being

The variety of factors that have an effect on the migration activity of elements complicates the assessment of the anthropogenic contribution to water enrichment. The geochemistry of lake waters integrally reflects the cumulative effect produced by intensified water migration under specific aquatic environment conditions, and the anthropogenic contribution. Perelman (1982) proposed to use a water migration coefficient characterizing the ability of elements to leach. This coefficient is calculated as the ratio between the element content in the mineral composition of waters (salt composition) of a water object (%) and the content of the same element in rocks (%) forming the water catchment area.

In the study (Moiseenko and Gashkina 2007), the water migration coefficient for a number of elements was calculated. Among trace elements with high migration rates (coefficient from 1 to 100), there are elements such as Re, Cd, Mo, Ag, As, Se, Bi, Sb. The contents of these elements are very low in the earth’s crust, but they are present in increased concentrations in water as compared to those in rocks. As is shown, these elements actively spread into the environment as a result of fuel burning and the operations of industrial smelting plants (Pacyna and Pacyna 2011).

The EF, as an effective method for assessing the level of pollution for soils (Krisha et al 2013, Ghazaryan et al 2017), lake sediments (Ryan and Windom 1988, Wang et al 2015) or the aquatic environment (Soto-Varela et al 2015, Ediagbonya et al 2015, Barbiery 2016), is used more widely, and is calculated as the following ratio:

\[
EF = \frac{\text{Me}}{\text{Al}}\text{sample: } \frac{\text{Me}}{\text{Al}}\text{rock, where: }
\]

\(\text{(Me/Al)}\) sample is the ratio between the metal being analyzed (Me sample) and the reference metal (Al sample), and \(\text{(Me/Al)}\) rock is the ratio Me/Al in the background rock.

To determine the background values used for EF calculations, various approaches were used: the local background value of metal concentration in the deep layers of bottom sediments, for soils—the local background value of metal concentration in the C horizon. Average values for the Earth’s crust (crust) are often used as background values. Al, Ti and Fe Sc, Th, Fe are...
Table 2. The average values of concentrations of elements in various types of lakes (acidified, humic, eutrophic and hypertrophic and other lakes) in various natural regions of ER and WS.

| Natural zone                  | Type of lake | Al (μg l⁻¹) | Fe (μg l⁻¹) | Mn (μg l⁻¹) | Sr (μg l⁻¹) | Zn (μg l⁻¹) | Ni (μg l⁻¹) | Cu (μg l⁻¹) | Pb (μg l⁻¹) | As (μg l⁻¹) | Mo (μg l⁻¹) | Sb (μg l⁻¹) | Cd (μg l⁻¹) |
|-------------------------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| European Russia               | Acidified   | 47.7        | 49.5        | 2.80        | 5.47        | 1.93        | 1.67        | 1.11        | 0.5         | 0.42        | 0.11        | 0.24        | 0.10        |
|                              | Humic       | 80.1        | 305         | 2.90        | 9.10        | 2.30        | 1.40        | 2.16        | 0.3         | 0.35        | 0.16        | 0.32        | 0.07        |
|                              | Eutrophic   | —           | —           | —           | —           | —           | —           | —           | —           | —           | —           | —           | —           |
|                              | Other       | 56.9        | 117         | 3.06        | 11.5        | 1.74        | 1.64        | 0.81        | 0.1         | 0.35        | 0.21        | 0.07        | 0.09        |
|                              | Acidified   | 95.8        | 70.5        | 8.83        | 8.07        | 2.59        | 1.22        | 0.96        | 0.3         | 0.27        | 0.08        | 0.09        | 0.07        |
| Northern and middle taiga     | Humic       | 219         | 777         | 22.4        | 21.3        | 2.47        | 1.05        | 0.90        | 0.2         | 0.84        | 0.12        | 0.08        | 0.07        |
|                              | Eutrophic   | 77.3        | 539         | 40.7        | 41.2        | 1.95        | 0.65        | 0.78        | 0.1         | 0.33        | 0.35        | 0.39        | 0.09        |
|                              | Other       | 63.2        | 173         | 11.6        | 27.1        | 1.57        | 0.80        | 0.80        | 0.1         | 0.38        | 0.27        | 0.07        | 0.05        |
|                              | Acidified   | 5.03        | 190         | 7.26        | 127         | 6.22        | 0.88        | 0.71        | 1.4         | 0.37        | 0.23        | 0.06        | 0.03        |
| Mixed forests                | Humic       | 137         | 242         | 23.8        | 27.7        | 1.30        | 0.44        | 1.01        | 1.1         | 0.65        | 0.50        | 0.04        | 0.01        |
|                              | Eutrophic   | 72.4        | 299         | 39.5        | 73.6        | 2.03        | 0.54        | 0.74        | 0.3         | 0.75        | 0.10        | 0.06        | 0.05        |
|                              | Other       | 22.9        | 86.5        | 17.6        | 58.7        | 1.65        | 0.40        | 0.72        | 0.1         | 0.56        | 0.15        | 0.06        | 0.02        |
|                              | Acidified   | —           | —           | —           | —           | —           | —           | —           | —           | —           | —           | —           | —           |
| Forest-steppe and steppe      | Humic       | —           | —           | —           | —           | —           | —           | —           | —           | —           | —           | —           | —           |
|                              | Eutrophic   | 4.15        | 40.8        | 1.77        | 104         | 3.98        | 2.13        | 1.80        | 0.7         | 1.15        | 0.22        | 0.05        | 0.52        |
|                              | Other       | 17.8        | 57.7        | 1.43        | 101         | 5.59        | 1.92        | 1.24        | 0.7         | 1.08        | 0.18        | 0.12        | 0.11        |
| Western Siberia               | Acidified   | —           | —           | —           | —           | —           | —           | —           | —           | —           | —           | —           | —           |
|                              | Humic       | —           | —           | —           | —           | —           | —           | —           | —           | —           | —           | —           | —           |
|                              | Eutrophic   | 53.8        | 56.9        | 180         | 787         | 15.1        | 0.10        | 4.57        | 0.4         | 3.85        | 0.98        | 0.28        | 0.08        |
|                              | Other       | 48.6        | 24.5        | 88.6        | 355         | 18.7        | 0.36        | 5.67        | 0.5         | 3.80        | 1.49        | 0.23        | 0.09        |

Note: The entries in bold indicate the average concentrations of elements in those types of lakes in which they are significantly higher than in other lakes, and entries in bold italics significantly lower (with the signification level $p < 0.05$) in each of the natural areas under consideration.
used as reference elements (Ryan and Windom 1988, Ediagbonya et al 2015, Wang et al 2015, Barbier 2016). In addition, these studies specify the enrichment level assessment scale, from a moderate enrichment level (2–5) up to an extremely high enrichment level (>40). It was proposed to use the EF for assessment of the anthropogenic Cd ingress into water objects, which is calculated as the ratio between the cadmium to aluminium ratio of the object being investigated and the same ratio for the Earth’s crust: EF = Cd:Al x/Cd:Al crust (Cullen and Maldonado 2013).

According to the obtained findings, the Cd to Al ratio of natural water objects can vary from one to ten; if this ratio is more than ten, then there is an anthropogenic contribution. At the present time, as regards the world’s rivers, it is equal on average to 15 and may rise to 100 and more.

We used this approach and calculated the EF for the lake waters being investigated (figure 3). At the first stage, we calculated the percentage content of elements in the waters based on the sum of all salts present in the waters. We used Al as the reference element.

We analyzed the set of elements based on the work by Pacyna and Pacyna (2011). Its elements are spread in the environment as a result of anthropogenic activity. The EF is high enough for many elements, which is difficult to explain by only anthropogenic contribution. The natural specificity of regions is also reflected in the variability of this parameter for many elements. The analysis of the results shows that the general tendency for practically all elements is increasing the EF from the northern towards the more southern regions of ER and WS.

In the tundra and forest-tundra zones of ER, non-ferrous plants are located. This resulted in higher EF values for Ni, Cd, As, Sb, and especially Se. The contents of other trace elements are also increased, which may be a consequence of the input of elements by acid precipitation. In the zones of WS from tundra to taiga, the greatest EF for Pb, V, As, Sb and especially Mo were found. It should be noted that the occurrence of oil fields is typical for WS, as a consequence of which oil constantly leaks towards the surface. As is well known, oil contains a great number of elements,
particularly V, As, Sb, Mo, etc (Kiryushin et al. 2013). Oil is subject to biodegradation in the environment, while metals take part in the biogeochemical cycling, which is reflected in the geochemistry of surface waters. Also, oil gas is burned here, a consequence of which is that trace elements are dispersed (Kiryushin et al. 2013). The causes of high values of EF for V in the middle taiga are associated with the most intensive development of oil fields and oil gas burning in this very climatic zone.

In the southern taiga and forest-steppe zones of ER and WS, there are very high values for most metals being analyzed, while the enrichment coefficient values are recorded for many elements in the southern taiga of WS. Here we find the highest density of population, an agglomeration of agricultural and industrial facilities, and the network of main traffic arteries is developed. It is obvious that the high EF values for Pb, Se, Se, As, as well as Ni and Mo, are explained by these factors. In the southern regions of WS, higher concentrations of Pb and Mo, and especially V, are traced. As for the forest-steppe zone of ER, these are Mn, Zn, Mo, Ni, As. Higher factor values related to the enrichment of waters with many elements in the southern regions may be explained by a number of factors: (1) a higher anthropogenic load in the southern regions, (2) an enhanced concentration due to vaporization, as well as (3) the occurrence of carbonate rocks in the more southern regions as compared to the Earth’s crust, which clearly proves the EF for Li, as a representative of the alkali element group. Some elements such as Mn, Cu, and Fe have higher enrichment factor values in waters of WS due to waterlogging and involvement of humic substances in metal speciation.

We analyzed the concentrations of metals (see table 1) as compared with the MPC or guideline concentration for aquatic lift (GLC) which are accepted in various countries (Väänänen et al. 2018), including Russia. This is evidence that airborne contamination does not lead to heavy water pollution, but contributes to an increase in surface concentrations of many elements. Our investigations showed that the use of the EF for assessment of the anthropogenic signal is effective.

Metals and nonmetals are characterized by the accumulation in living organisms at significantly higher concentrations than in natural water, which leads to long term negative consequences for humans and animals. The literature reflects studies on the ecotoxicity of metals (Seiler et al. 1994, Hoffman et al. 2005, Nordberg et al. 2014). In the literature, it has been found that many human diseases are associated with the excessive accumulation of elements in living organisms, including humans: Cd, Pb, V, As, Ni, and others have carcinogenic and gonadotoxic properties. Despite the fact that many elements (Cu, Zn, Se, As and others) in microscopic quantities are necessary for living organisms, their excess in the body stimulates a number of disorders and negatively affects the immune, cardiovascular, excretory and other systems. In recent years, new toxicological properties of elements have become widely known. The growth of such elements as Pt, Rh, Pd, Ga, and Ir has been noted due to the wide development of the electronic industry (Nordberg et al. 2014). Even small doses of metals can accumulate and stimulate pathology. The article (Moiseenko et al. 2018b) showed that while concentrations of metals (Ni, Pb, Cd, Cu) in drinking water are quite low according to the accepted standards in Russia, they still cause high rates of diseases in the human population.

The studies carried out in the Eurasian region of Russia over vast areas reflected global trends in the state of the environment and the impact of airborne pollution on surface waters. It has been proven that elements such as Pb, Cd, As, Se, V, Ni have significantly higher IF values compared to the background. The enrichment factor for such elements may increase to from 100 to 1000 (figure 3), indicating the growing influence of the anthropogenic dispersion of elements in the modern biosphere.

Significantly higher IF values are found in the ER and WS in the southern regions. It may be presumed that with climate warming the processes of the enrichment of waters with trace elements will increase.

### 4. Conclusion

The anthropogenic input of trace elements into the environment has risen sharply over the past century, which is associated with continuously increasing volumes of metal production. The content of trace elements in small lakes without any direct pollution sources reflects the geochemical conditions of water catchment areas and airborne contamination. Water enrichment with trace elements was investigated in the two large regions of Russia (ERussia and WS). In general, the distribution of elements in overland waters shows an increase in alkaline and alkaline-earth elements, as well as As, V, Co, U, Nb, and Sb, towards the more southern regions, which may be associated with an increasing anthropogenic load and some natural factors such as higher evaporation and leaching. Humic acids present in aquatic environment and low pH values are the primary factors contributing to an increase in Fe content. The Al content is higher in the northern waters, where the underlying rock is formed by gneissoid granite (ER) and quartz (WS) formations and acid rains. High concentrations of V, U, and Nb are identified in the southern taiga and forest-steppe zones of WS, which is associated with the oil and gas production in the region. Anthropogenic eutrophication leads to an increase in Fe, Sr, and Mo content, and acidification (Zn, Cd, Ni, Cu and especially Pb). Ingress of Fe, Al, and As is increased in
waterlogged catchment areas.

The absolute concentrations of trace elements in the water of the lakes investigated, including toxic ones, do not exceed the established water quality standards (MPC or GLC). For the assessment of the anthropogenic contribution, the EF was used as a more sensitive indicator of the anthropogenic signal. Studies of such vast expanses of waters of lakes distant from industrial centers showed the influence of global and regional dispersion of metals in the Eurasian region. It has been proven that elements such as Pb, Cd, As, Se, Sb, V, Ni have significantly higher IF values compared to background values. This indicates a growing distribution of elements in the environment. The main property of metals and metalloids, even in very low concentrations in the environment, is that they can accumulate in living organisms at significantly higher concentrations, causing long-term genotoxic and carcinogenic effects. The studies carried out in the Eurasian region of Russia over vast areas have reflected global trends in the state of the environment, and were critical regarding further airborne pollution. They showed the influence of the climate gradient on increasing the concentrations of elements, which is important for predicting the effect of possible climate warning on the behavior of elements.

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ORCID iDs

T I Moiseenko © https://orcid.org/0000-0003-2875-1693

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