Element specification in small lakes of the Kola Peninsula: geochemical and technogenic factors

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Abstract
This study focuses on metal speciation research in Arctic lakes with technogenic pollution and other areas where natural processes prevail (background lakes and lakes with marine influence). Element speciation in 75 lakes in the Kola Peninsula was investigated in 2014 and 2018 taking into account the influence of different geochemical factors. The geochemical features of lake water in the investigated regions are documented and discussed. Membrane filtration was used with the following features: mechanical suspension and oxidized contaminants (>8 µm, 1.2 µm) for lakes near smelters and those subject to marine effects; light suspension colloids (0.45–0.1 µm) for the natural waters of background lakes; low molecular weight complexes, inorganic ions, bacteria, and viruses (less than 0.1 µm) for identification of labile and non-labile components. It has been proven that the bioavailable speciation (unbound with organic components) is determined by the physicochemical properties of organic matter, such as zeta potential, molecular weight, and colloid stability. In conventional background lakes, Fe and Al complexes with humic substances dominate, and the most associative elements of the lanthanide/actinide group repeat the tendency of Fe. In lakes with a clear marine influence, the complexation potential of organic substances is reduced due to Na ions, which deactivate humic functional groups. Multivariate statistical methods showed significant differences between the selected gradations of lake waters and the genetic similarities and differences in the behavior of element speciation.

1. Introduction
An important fundamental block in geochemical research is the assessment of the equilibrium distribution of metal speciation in water and the influence of environmental conditions on this process. The anthropogenic impact on the environment has increased dramatically over the last century, and is associated with increasing volumes of extracted metals and their dispersal with atmospheric precipitation. Speciation and bioavailability are determined by the chemical composition of water, including the concentration of humic substances, pH, temperature, competitive reactions of cations and anions, and other factors. It is known that dissolved organic substances can inactivate metals in water by binding with them, which reduces their toxicity and bioavailability for hydrobionts (Bjerrregaard and Andersen 2007, Smith et al 2015, Cabrita et al 2017, Moiseenko et al 2018, Väänänen et al 2018). Some studies have shown that biological systems are threatened by ionic nanoforms that can attach to the surface of organisms or be absorbed by them (Phillips 1995, Ciffroy and Benedetti 2018). The study of biogeochemical element migration, speciation in water, and bioavailability under natural and anthropogenic conditions provides a base for the development of adequate programs for water monitoring and evaluation of the ecotoxicity of water. From a huge aspect, water protection regulation has manifested the necessity to include rules for assessment of metal speciation and bioavailability in monitoring systems (Väänänen et al 2018, Moiseenko 2019).

During periods of active technogenic pollution, the material balance of natural waters changes significantly, which leads to a change in the distribution of metals by speciation in comparisons of background layers. For example, the use of fossil fuels in the last
century has led to the formation of acid rain and acidification of water in Europe and North America (Demin 2012, Moiseenko et al 2013, Ma et al 2021). Dominance of sulfates and nitrates in technologically influenced water, as well as the presence of Ni and Cu ions, affect the fraction of labile/non-labile metal speciation (State Reports 2012, Moiseenko et al 2018b, Dinu et al 2020, Ma et al 2021). Therefore, the problem of water pollution is still valid in the current century, and it contributes to the relevance of assessing bioavailable forms of metals (their speciation and specification).

On the Kola Peninsula, there are lake waters with various physicochemical equilibrium features, including lakes with a high anthropogenic load (Cu–Ni smelters, nuclear power plants (NPPs)). Among the lakes that are remote from smelters (relative to wind rose diagrams), there are lakes with marine influence (according to Na balance and Cl), as well as those with possible contributions from various underlying geochemically active rocks. In addition, the concentration of labile metal speciation, which may be bioavailable, is often lower than the total metal content and may vary depending on several geochemical factors. The bioavailability of the elements is influenced by the physicochemical properties of the ions and the biogeochemical conditions of the environment (Bjerregaard and Andersen 2007, Cabrita et al 2017).

In the north of European Russia (ER), two large copper–nickel smelters are located in the western part of the Kola Peninsula—’Pechenganikel’ and ‘Severonikel’ and the emission of sulfur dioxide and metals has continued for more than 50 years. However, sulfur emissions have decreased substantially due to the modernization of production and purification of emissions in ER over the last 25 years (State Reports 2012). The enrichment of surface water by metals is a result of both natural processes and human activities. Within the Kola region rocks are represented mainly by granites and granitoids, strongly metamorphosed folded paragneisses, various amphibibolites, and intrusive rock complexes (Mitrofanov et al 2021).

The aim of this study was to investigate the metal speciation in Kola Peninsula lakes (75) subject to different anthropogenic loads and geochemical features, including background lakes, lakes near the Severonikel and Pechenganikel smelters and NPPs, lakes with direct marine influence, and lakes along a transect extending away from the smelter in 20–30 km intervals.

2. Methods

2.1. Sampling and general analysis

We investigated more than 70 lakes in 2014 and 2018, at different locations relative to the pollution source (see figure 1), for geochemical factors (sea influence, rock influence, and anthropogenic load). Notably, the colored circle on the map is the sampling range in this area (it can contain two to five lakes of similar location and genesis).

Water samples were collected in non-sorbing plastic bottles. In the field, the bottles were rinsed twice with lake water, filled, placed in dark contain-ers, and kept at 4 °C. The scheme of the sampling points, the principles of research, the water sampling methods, and chemical analyses are described in Moiseenko et al (2013). The total content of elements and their specification (suspension, colloids, inorganic ions and complexes with organic ligands), were determined in the sample (more detail information will be given later).

We used the following lake gradation: lakes without a direct pollution source (background lakes more than 200 km from the pollution source or isolated within the Khibiny Mountains), lakes near the pollution source (up to 20–30 km from NPPs or smelters), lakes successively removed from the pollution source (to assess changes in the protection provided by humic substances against pollution as the lake water progresses from polluted to conditionally background quality), and lakes with a clear marine influence (for the balance of Na and Cl relative to other ions, see figure 1, yellow points). Also, lakes by transect (every 20–30 km) from smelters to background site were considered.

In our analysis, all chemical elements were separated according to their geochemical properties: alkali, alkaline earth metals, chrome subgroup; lanthanides and actinides; Fe and Al ions, and other subgroups.

General sample analysis was performed to determine pH (Mettler Toledo ± 0.01), electric conductivity (Mettler Toledo ± 1), turbidity, main cations (Ca$^{2+}$, Mg$^{2+}$, K$^+$, Na$^+$), Si, alkalinity (Alk), SO$_4^{2-}$, Cl$^-$, color, organic matter (OM) content, total nitrogen and its forms (NO$_3^-$ and NH$_4^+$), total phosphorus, and PO$_4^{3-}$ evaluation. The verification of the analytical methods and the results obtained for the water chemical content was performed under strict in-house control using a unified system of standard solutions.

The concentrations of dissolved elements Li, Si, Na, Mg, Al, P, S, K, Ca, V, Mn, Fe, Cu, Zn, Sr, and Ba were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES) (ICAP-61 Thermo Jarrell Ash, Institute of Problems of Microelectronics Technology and Superpure Materials RAS, Chernogolovka).

The elemental measurements were taken using the following spectrometer parameters: a radio frequency (RF) generator output power of 1200 W, angular nebulizer, plasma-forming Ar flow rate of 18 l min$^{-1}$, auxiliary Ar flow rate of 0.9 l min$^{-1}$, Ar flow rate into the nebulizer of 0.6 l min$^{-1}$, analyzed sample flow rate of 1.5 ml min$^{-1}$, and a plasma observation zone height of 14 mm. The integration
time of the spectra during each run was 5 s. The elemental contents in aqueous solutions were determined quantitatively using calibration solutions (High Purity Standards, USA) of 0.5 and 10 mg l\(^{-1}\) of each element. The sample contents were calculated using the spectrometer software (ThermoSPEC, version 4.1). The detection limits of the various elements were: Li 0.5 mg l\(^{-1}\); Si 0.05 mg l\(^{-1}\); Na, Mg, Al, and Ca 0.01 mg l\(^{-1}\); K, Zn, and S 0.15 mg l\(^{-1}\); P 0.8 mg l\(^{-1}\); Fe, Cu, and Sr 0.003 mg l\(^{-1}\); and Mn and Ba 0.0003 mg l\(^{-1}\). The detection limits for ICP-AES measurements were calculated as follows: 

\[ DL_i = C_i + 3\sigma, \]

where \( C_i \) is the mean content of an element of interest for measurement in control samples and \( \sigma \) is the standard deviation of its determination in control samples.

### 2.2. Particle size fractionation and element speciation

In the experimental work, the metal contents, which were present in suspended (unfiltered), dissolved fractions (filtered), labile, and non-labile forms, were determined (Spivakov et al. 1994, Shkinev 2001). Speciation was subsequently separated into fixed and non-fixed states with ion-exchange resin, which was strongly bound to OM of natural waters (Dowex 50W-X8, 50–100 mesh in Na\(^+\) form). That is, the OM is conditionally labile and non-labile according to the selected ion-exchange resin (Moiseenko et al. 1997). The labile speciation of elements was aqua-ionic, connected with inorganic (including mixed) metal strong complexes, and metal weakly complexed with OM (with a low conditional stability constant). Non-labile speciation included strong metal complexes with OM that was mainly humic in nature.

During verification, a reliable correlation between the measured and calculated data was prepared (\( r^2 = 0.94, p > 0.0001 \)). This allowed us to use the results of mathematical modeling with confidence to calculate labile and non-labile metal speciation (Moiseenko et al. 2020).

Sample membrane fractionation was performed directly on-site and transported to the laboratory (a more detailed description is available in Dinu et al. 2020)). For comparison of the results of element specification analyses, syringe filter nozzles and multistep tangential membrane filtration units were used. The membrane pore sizes were: 8 \( \mu \)m, 1.2 \( \mu \)m, 0.45 \( \mu \)m, 0.2 \( \mu \)m, and 0.1 \( \mu \)m (SWINNEX Millipor, VLADiSART). A volume of 5 ml was discarded from

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**Figure 1.** Locations of the investigated lakes.
each filtrate fraction for ICP-MS elemental analysis. In the multistep tangential membrane filtration unit, the sample was passed through the same set of membranes, and the solutions were selected for analysis. The mass balance of all metals was monitored at each fractionation stage, and the average metal mass distribution did not exceed 15%.

2.3. OM analysis

Organic substances were isolated from the waters during freezing (or lyophilic drying) and were also investigated in situ in the sample. Dynamic light scattering technology was used to determine the zeta potential (colloid stability), molecular weight (MM), and size of the organic complexes (Malvern ZetasizerNano equipment). Additionally, IR spectrometry was used to confirm the functional groups, and chromatographic methods were used to assess the MM distribution.

2.3.1. Statistical analysis

The obtained data were statistically processed using Statistica Advanced 12 (Stat Soft, Inc, USA) using discriminant and canonical analyses (Parashar et al. 2008).

The significant variables were determined and used to explain most of the data variations by quantifying the discrete contributions of the individual descriptors. Canonical analysis, as the completion of the discriminant method, reliably showed the degrees of differences between the lakes in the proposed gradation. Additionally, multidimensional scaling principal component and classification analysis and redundancy analysis (RDA) were used for the most characteristic elements: Cu, Ni, Cd, and Pb.

3. Results

3.1. Geochemical factors

Water samples from lakes in areas far from the smelters, those near pollution sources, and those with a clear marine influence, were characterized by different geological features. In addition, we considered the features of the formation of equilibrium concentrations of elements in lakes along the transect ‘pollution source—background sites’.

Three dominant geological feature types were identified (based on the geological map of the Kola Peninsula, edited by the Kola Science Center).

The main features of the lakes close to the smelters included Quaternary deposits represented by boulder sands and sandy loams up to 10 m thick. The underlying Quaternary rocks were represented by ultrabasic, basic, and intermediate lavas, tuffs, phyllites, dolomites, and quartzites. Basic minerals included quartz and sercite, and crystal lattice elements of the rock-forming minerals included: Al, Si, Fe, Mn, Co, Pb, Zn, Mg, Cr, Li, V, Na, Cs, Rb, and Ca. Secondary and impurity minerals, garnets, micas, hornblende, and chlorites include Mg, Fe, Ni, Cr, K, Mn, Al, Na, Ti, Li, Sr, Y, Ce, Ca, F, Y, Sr, U, W, Mo, Ga, Li, Zn, Sc, V, Be, B, Sn, Nb, Ta, Ti, Ta, Mo, W, U, Th, Bi, and P. Such conditions contributed to the formation of water that was resistant to acidification; nevertheless, many elements were present in bioavailable forms.

The lakes remote from the smelters (background lakes) were characterized by mica gneisses, garnet-biotite, and amphibolite gneisses. The main minerals here are feldspar, quartz, muscovite, biotite, hornblende, kyanite, and garnets. The elements that are contained in the crystal lattice of these rock-forming minerals are Si, Al, K, Ca, Na, Fe, Rb, Mg, Ti, Cr, Li, V, Mn, Cs, Sr, Y, Ce, Ba, TR, Y, Sr, U, W, Mo, Ga, Zn, and Sc. Secondary and impurity minerals here are apatite, zircon, and titanite that contain Ca, F, P, Cl, Mn, Fe, Sr, Th, U, Zr, Fe, etc. These lakes are the most vulnerable to acid deposition. But due to the distance from the smelters and their location close to the Khibiny Mountains, the influence of pollutants in these lakes is neutralized.

It was most difficult to identify the geological features of the lakes with sea influence, since these features were found in those lakes that are near pollutant sources as well as in those that are far from pollutant sources. Nevertheless, in the lakes with a predominant marine influence we noted the following geological features: these were mostly characterized by diorite and granodiorite. The main minerals here are plagioclase, K-feldspar, biotite, muscovite, quartz, hornblende, and clinopyroxene. Elements that are contained in the crystal lattice of these rock-forming minerals are Si, Al, Fe, Rb, Mg, Ti, Fe, Na, Li, Cr, V, Mn, Cs, Ca, Ti, Sr, Y, Ce, Ba, Y, Sr, U, W, Mo, Ga, Zn, and Sc. Also, there are apatite, zircon, and titanite minerals. These minerals contain Ca, F, P, Cl, Mn, Fe, Sr, Hf, Th, U, Tr, Zr, Fe, Y, Mn, Al, Ce, Sr, Na, Nb, Ta, Al, Mg, V, F, Zr, Sn, and Ti. The most varied content of rare-earth elements is typical for such a substrate and, in particular, elements of the subgroup (titanium, zirconium).

3.2. Physicochemical characteristics of lake waters

The selected lakes were characterized by various pH ranges: from slightly acidified (about 5.0) to alkaline (more than 8.0) (table 1 and suppl. 1 (available online at stacks.iop.org/ERL/16/065005/mmedia)). The content of cations and anions in these lakes depended on geochemical and anthropogenic influences.

High pH values were characteristic of waters near smelters (smelters and NPPs). This is associated with the influence of geochemical high buffer properties of rocks. Here, alkalinity values are more than 200 and may reach 1000 μeq l⁻¹. Near the smelters, the maximum contents of the main polluting components are turbidity, Ni, and Cu (in concentrations of 147 and 11 μeq l⁻¹, respectively, maximum value), with the existing maximum
| Type of lake          | Geological features                                                                 | pH  | Cond (µS cm\(^{-1}\)) | Alk (µeq L\(^{-1}\)) | SO\(_4^{2-}\) | NO\(_3^{-}\) | CI\(^{-}\) | Color, Pt/Co | Turbidity, farm. | COD\(_{lab}\) (mg l\(^{-1}\)) | MM (kDa) | Zeta potential (mV) | Size (nm) |
|----------------------|--------------------------------------------------------------------------------------|-----|------------------------|-----------------------|-------------|------------|----------|-------------|------------------|------------------|------------|-------------------|-----------|
| Background lakes     | Mica gneises, garnet-biotite and amphibolite gneises, granites of various types (weak buffering properties) | 4.8–7.0 | 18–32 | 0–161 | 1.0–3.9 | 0–2 | 1.2–4.4 | 14–121 | 0–10 | 3.3–16 | 1400–3500 | -- | 19.8 to --25.8 | 1980–4500 |
| Near smelters        | Quaternary deposits represented by boulder sands and sandy loams (high buffering capacity) | 7.9–8.5 | 97–120 | 189–354 | 25–55 | 4.2–5.0 | 2.5–5.2 | 6–14 | 5–14 | 100–100 | 500–1000 | -- | 2 to --10 | 200–900 |
| Near the nuclear power plant | Mica gneises, garnet-biotite and amphibolite gneises, granites of various types (weak buffering properties) | 5.6–7.8 | 25–350 | 159–483 | 1.2–2.2 | 6–10 | 0.7–6.37 | 11–58 | 2–10 | 2.3–11 | 1000–4000 | -- | 2.6 to --9.8 | 300–876 |
| Lakes with sea influence | Michasen, biotitice, diorite and granodiorite (sufficient buffering properties) | 5.9–6.7 | 22–53 | 36–122 | 1.4–5.1 | 0–2 | 2.4–10 | 13–69 | 2–17 | 3.4–11 | 850–2100 | 0.5 to --10.1 | 1560–2340 | 5.6–24.1 |
| From pollution source to background lakes | Mixed rock types: along the coastline it is a buffer type; across land it is a more vulnerable type of rock | 6.5–8.1 | 22–97 | 47–300 | 2.0–31 | 0–4.0 | 1.5–3.3 | 7–66 | 3–45 | 2.1–11.0 | 250–1800 | -- | 2 to --22.5 | 200–2500 |

Table 1. Main features of lake water components (min–max/aver.).
permissible concentrations (MPC) of Cu and Ni ions in water of 200 and 20 µg l\(^{-1}\). \(\text{SO}_4^{2-}\) is released into the environment with industrial emissions and was higher, 60–65 mg l\(^{-1}\). \(\text{NO}_3\) in the waters near the NPPs was dominant. In the same lakes, there were high concentrations of Fe and trace elements and accompanying Fe elements.

**Lakes unaffected by the impacts from smelters or NPPs** are located close to the Khibiny Massif. As mentioned above in section 3.1, their geological buffering properties are not high and the water alkalinity content was approximately 150–160 µeq l\(^{-1}\). Also, compared to other types of lakes, levels of Cu and Ni were much lower, with slightly lower levels of Fe and associated elements. In these lakes, the dominant role of rocks in the water formation was found, as discussed in the literature (Henriksen et al 1998).

Table 1 shows that in **water lakes along the transect** from the smelters (more than 40 lakes), there is a marked difference between the minimum and maximum element contents, especially for metal ions such as Cu, Ni, and Fe. The content of organic substances also varied by more than 100 times (color), which is associated both with natural enrichment factors of waters with allochthonous OM and with changes in the qualitative and quantitative composition of organic substances as a result of pollution. It can be assumed that a significant contribution to the inorganic components of water occurs through \(\text{SO}_4^{2-}\), Cu, and Ni ions in equilibrium forms in water.

We conditionally identified the waters of lakes *‘with sea influence’* based on the balance of Na and Cl. This identification is suitable both for lakes near smelters and for lakes at some distance from them (figure 1).

Nevertheless, the following chemically significant features of the component composition for equilibria in these lakes were found:

- the high content of Cl (up to 10 mg l\(^{-1}\)) compared to other lakes,
- the content of OM here is higher than for lakes with direct technogenic impact,
- a rather diverse water composition of trace elements due to the underlying rocks.

Notably, the increased Na and Cl content in lakes with marine influence (see table 1) contributed to a decrease in the complexation of heavy metals with organic substances because of the obvious salt effect. This effect was most pronounced for coastal lakes close to the smelter.

The distribution of elements by form (% and concentrations of unstable (non-labile) speciation) is shown in figures 2 and 3. As indicated in section 2.2, we used data from different-sized component specification (from suspension to ionic forms), as well as conditional separation of element speciation into bioavailable (labile) and fixed by OM (non-labile) fractions.

According to the data in figure 2, the most diverse distributions among different-sized speciation were typical for the waters of lakes with a marine influence and lakes near smelters. The distribution of elements by speciation in the waters of background lakes showed the geochemical influence of rocks on both elements and different-sized component speciation.

Figure 3 shows a division of Fe, Ni, and Cu by labile and non-labile contents. It can be said that the complexation of Ni ions with humic substances prevails in more polluted lake waters, while Fe ion complexation prevails in less polluted and background waters. The speciation distribution of Cu ions is more complex.

### 3.3. Properties of OM

The main characteristics of the organic substances are presented in table 1 and figure 3 (additional scale). We found changes in the zeta potential from significant negative values (high stability colloid) to close to zero values (unstable colloid state) (McDonald et al 2004, Wolthers et al 2008). These changes are typical for lakes on transect ‘lakes close to smelters—background lakes’. Significant changes in the MM of OM present in lake waters that are influenced by technogenic effects and decreases in colloid size can be illustrated by the following scheme:

\[
\text{H-OOC-X1-R1-R2-X2H} \rightarrow \text{R1-COO}^- + \text{nH}^+ + \text{-R2-X2H} + \text{-R1 X1COO}^- + \text{-R2 X2}^- \]

where X1 and X2 are fragments of humic substances with a reduced MM and size.

### 4. Discussion

#### 4.1. Lakes with a direct pollution source

Lakes located close to the smelter or NPP (less than 20–30 km) were characterized by increased concentrations of Ni ions (up to 150 µg l\(^{-1}\), with an existing MPC of 20) and Cu (up to 15 µg l\(^{-1}\) as well as \(\text{SO}_4^{2-}\) ions (up to 65 mg l\(^{-1}\)). Also, in conditions of increased turbidity (compared to other types of lakes), most of the alkali and alkaline earth metals migrate in suspension.

Previous studies (Singh et al 2000, Millero 2001, Moisenecko et al 2013) considered these Arctic lakes and our data do not contradict their findings. Higher contents of these components are critical for the distribution equilibrium speciation of other elements. It should be noted that the organic substances in these waters are characterized by a low MM and low strength of the formed colloids; the colloid size does not exceed 1 µm. Similar results for the reactions of humic organic substances to the external influences of inorganic acids, UV, and temperature based on experimental data were obtained (Drozdova et al 2020). The pH values in lakes near the smelters were more than 7 (with a maximum of 8.5), while in those near
the NPPs, the pH values were slightly lower. In addition, near the NPPs, concentrations of Ni and Cu ions that exceeded the MPC were not detected, and the concentrations of sulfate and nitrate ions were high. Therefore, anionic influences prevail in these lakes.

According to the Le Chatelier–Brown principle, Ni ions predominantly bind with organic ligands; therefore, other metal ions with similar complexing abilities (and lower concentrations) become bioavailable (e.g. Cu, Pb, and chromium). Because of the pH value > 7.0 and increased turbidity and, as a result of industrial production, Al and Fe ions are common and are not strongly associated with organic substances under these conditions (the zeta potential is close to zero, which indicates colloid instability).

The main explanation for this instability is the low MM of the colloid and the ability of metals to form
larger coagulates with a greater size and bioavailability (Forstner 1986, Gupta et al 2013, Jamali et al 2016).

Under such physicochemical conditions, the binding percentage of Fe and Al ions to organic substances is reduced in comparison with the waters of other lake types.

Elements of chromium groups are also characterized by complexing capacity under high anthropogenic loads (Monteiro et al 2016). Mn in such conditions has a high capacity to form suspensions. The affinity of these elements to an organic substance is: Fe > Al > Ni > Cu > Pb = Zn > La > Ce > Co.

4.2. Lakes without direct pollution source (background conditions)

Background condition lakes were characterized by remoteness from the smelter (at least 200 km) or were protected from technogenic influence by the Khibiny Ridge (figure 1). Their organic content was quite high, which reduced metal competition for ligands. The pH values were slightly low, the alkalinity was equal to 0, and the MMs of the organic substances were high (not less than 1000 kDa). According to our results (table 1 and figure 2), the predominant distribution of Fe and Al is either in suspended large particles (oxides, silicates), or in the large colloids with a high MM and a stable negative charge.

In background condition lakes, alkali and alkaline earth metals were characterized by soluble speciation in comparison with lakes with a direct pollution source because the conditions for suspended matter formation were less favorable. The contents of Ni and Cu were not as high as those in other lake types, and the degree of Cu binding with OM ligands was high. Because of the low Ni concentrations, in this case, the percentage of Ni-inorganic complexes was higher. The associative elements of the U and lanthanum subgroups showed similarities in the distribution of elements such as Fe, Al, and Zn (Nifant’eva et al 1999, 2001). The associative elements of the U and lanthanum subgroups showed similarities in the distribution of the main elements of Fe, Al, and Zn (Nifant’eva et al 1999, 2001).

For ions in the Zn, La, and U subgroup, various forms of compounds were found, which indicated the formation of organic and inorganic complexes containing hydrated metal ions in the structure. The evidence of strongly negative zeta potential values (less than 10 mV) is characteristic of OM in these lakes. The results of IR studies show the presence of several cations in the structure.

We found the contribution of the labile forms of Cd and Ni to the general equilibrium of the system. Furthermore, we found non-labile contents of Fe and Al. The main anions affecting the forms of metals in these lakes are OM. Alkalinity was decisive in the formation of equilibrium elemental forms for these types of lakes. At
alkalinity equal to 0, the content of inorganic hydroxyl complexes of transition metals was minimal. The content of carbonate and bicarbonate complexes was also minimal, and the proportion of precisely ionic (labile) forms increased.

The data facilitated the construction of the following series of activity of metal in complexation:

When pH < 6 Fe ≥ Al > Y > Pb > Zn > Cu > Sc > Ni > Co > Cd and pH > 6 Cu > Fe > Al > Sc > Co > Ni > Zn > Pb > Y > Cd.

Figure 5. RDA of selected lake types: (a)—lakes close to the source of pollution, (b)—background lakes, c—lakes with a sea effect.
4.3. Changing metal speciation with increasing distance from the Cu–Ni smelter pollution source

The most obvious change in the physicochemical properties of organic substances was found along the transect from the pollution source. According to figure 3 and table 1, the colloid stability varied from −5 mV to −20 mV. The MM also gradually increased from 300 to more than 1000 kDa, symmetrically with the size of the organic colloid.

An increase in the MM of organic substances at a distance from smelters significantly increased the proportion of Fe and Al complexes with humic substances in comparison with the unstable high molecular complexes of Ni ions. Cu ion associations were not as clear, but they still repeated the behavior of Fe, increasing the proportion of non-labile organic compounds in the background lakes.

The concentration of Zn organic complexes (and Zn subgroup elements) in water upon removal from the pollution source decreased sharply. Pb was characterized by varying degrees of complexation with OM. Y, like other transition metals, was derived from industrial activity waste (elements accompanying production). On removal from the smelter, the percentage of organic complexes declined, indicating a transition to natural contents.

4.4. Lakes with possible marine influence

For the indicated lakes, the locations were found both at a distance from smelters and in the background or heavily polluted locations. They were characterized by increased Na and Cl ion content, which formed terminal (salt) fragments on humic substances. In other words, electrochemical salt formation prevailed over the formation of chemical complexes. Colloids were stable, which was indicated by either positive (more than +20 mV with the contribution of Na ions) or strongly negative (about −20 mV with the contribution of Cl ions) colloid zeta potentials. The MM was closer to 1000 kDa, which is typical for a large colloid with electrochemical coagulation (closer to 1.2 µm). These features did not contribute to the maximum complexation of Al and Fe ions (figure 2), the forms of which shifted toward larger particles. Depending on other geochemical features of the waters (rocks, remoteness, and proximity to the smelter), the gross contents of Fe, Ni, Cu, and their contribution to the equilibrium of the system changed and a similar effect in sea waters and waters of lakes with marine influence was considered (Nriagu and Pacyna 1988, Hirose 2006, Djae et al. 2017). Nevertheless, despite the OM content (in five lakes, the color value is more than 60), the contribution of bioavailable forms of almost all elements to the system equilibrium was high.

4.5. Statistical results and electrochemical modeling

Despite the numerous disparate parameters characteristic of natural systems, statistical methods have made it possible to reveal the logic behind the formation of element speciation in the selected waters.

Multivariate statistical methods of discriminant and canonical analysis revealed significant differences in the content and metal specification in lake waters with different anthropogenic loads (figure 3). The differences were provided by the following parameters (F not less than 10): organic properties (molecular mass, zeta potential), suspended and different colloid forms (above 0.45; from 0.45 to 0.05 µm), and Fe, Al, and Ni labile or non-labile speciation.

We have chosen parameters that determine the metal speciation in the Kola Peninsula, including the possibility of formation of coarsely dispersed forms (turbidity), obvious technogenic influence (sulfate ions), electrostatic forces’ influence due to marine lakes (zeta potential), and the influence of OM and natural factors (MM) (figures 4–5).

Lakes with direct anthropogenic impact are characterized by the affinity of elements for sulfate ions, which are genetically close to turbidity, for many elements in soluble forms (some of the non-labile metals), including Al, Fe, Cu, MM affinity, and zeta potential.

In contrast to these lakes, background waters are characterized mainly by a high role of natural OM and geochemical solid components (natural silicates and oxides). Most of the soluble elemental forms, such as Fe, Al, Zn, and Pb, have an affinity for MM, which determines the equilibrium in the system. For larger forms, an affinity for turbidity and the zeta potential was revealed, which is explained by the humic component of water and their protection properties.

In waters with sea influence, we proved an essential role of electrochemical processes in the distribution of elements by forms and, for waters near the source of pollution, the affinity of anthropogenic Pb, Ni, and Cu ions for sulfate ions. This indicates the possibility of the dominance of ionic metals, regardless of the OM content.

5. Conclusions

Research and analyzed literature data have shown the influence of several environmental factors affecting the distribution of element speciation in the lakes of the Kola Peninsula with different technogenic loads. The defining quality indicators of element speciation (besides metal content and OM concentration) are the qualitative characteristics of humic substances (MM, zeta potential, colloid size), the contribution of geochemical factors (buffer or granite rocks, proximity to the sea), and location from the pollution source.

Multivariate statistical methods of discriminant and canonical analysis revealed significant differences in the metal content and specification between clear and non-clear (near smelters) lake waters and lakes with different geochemical features (figure 3). The differences can be explained by the following
parameters (F not less 10): organic properties (MM, zeta potential), suspended and different colloidal forms (>0.45; from 0.45 to 0.05 µm), and Fe, Al, Ni, labile or non-labile elements speciation.

Lakes with direct anthropogenic impact are characterized by the affinity of Ni and Cu (suspended speciation) for sulfate ions, which are close to turbidity; for many elements in soluble speciation (non-labile speciation of metals), including Al, Fe, and Cu, the affinity for molecular mass (MM) and zeta potential of organic acids was characterized.

In contrast to these lakes, background waters are characterized mainly by a high proportion of natural OM and geochemical solid components (natural silicates and oxides). Most of the soluble forms of elements, such as Fe, Al, Zn, and Pb, have an affinity for MM, which determines the system equilibrium. For larger forms, an affinity for turbidity and the zeta potential was revealed, which is explained by the humic component of organic substances.

In waters with marine influence, the essential role of electrochemical processes in the elemental distribution, as well as the affinity of anthropogenically sourced Pb, Ni, and Cu ions for sulfate ions (for waters near the pollution source) has been proven. This indicates the possibility of the dominance of ionic forms of metals, regardless of the OM content.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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