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Quantification and Speciation of Trace Metals under Pollution Impact: Case Study of a Subarctic Lake

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Abstract: Monitoring the quantity and quality of metals in lake water is a major part of assessing water toxicity. A fundamental aspect of geochemical monitoring studies is the evaluation of the equilibrium distribution of metal speciation in water and the influence of environmental conditions on this process. It is important to understand the difference between the behavior of nanoparticles, dissolved particles, colloid particles, and suspended particles. This study involved environmental aquatic chemistry research and the assessment of the geochemical processes of metal speciation in an arctic lake in the metallurgical waste zone and other areas where natural processes prevail. Consecutive and parallel membrane filtration methods were used to compare the results of water analysis in Imandra Lake. The membrane pore sizes were 8, 1.2, 0.45, and 0.2 μm . The following filtrate characteristics were used: microfiltration-based mechanical suspension and oxidized contaminants ($>8, 1.2, 0.45, 0.2, 0.1 \mu\text{m}$), and ultrafiltration-based colloids, bacteria, viruses, etc. (less than 0.1 μm). Industrial effluents led to the formation of higher concentrations of elements (Ni, Cu, and Pb) in their labile forms. In the wastewater-mixing zone, the concentrations of most elements were evenly distributed in depth. In more distant areas, we found a significant increase in the concentration of elements in the near-bottom horizon in comparison with the surface water (Fe by more than three times). The obtained results showed that numerous elements had diverse distributions by speciation in the points located closer to the source of wastewater. This indicated the significant influence of the adsorption process on the system balance of elements such as Fe, Cu, and rare earth elements. The impact of the regional geochemical and anthropogenic speciation and the possible influence of climatic factors on the distribution of speciation were determined.

Keywords: metals; membrane filtration; Arctic lakes

1. Introduction

The pollution of aquatic ecosystems with metals is a serious global problem. In the past century, anthropogenic pollution of the environment significantly increased, associated with the increasing volumes of metal mining and their dispersion in the environment [1–3]. Mined and technologically enriched metals have toxic properties that are determined by their speciation in a water environment [2]. The regular evaluation of the content and features of the distribution of metals in natural waters is the main purpose of monitoring natural waters.

Speciation and bioavailability are determined by the chemical composition of water: the concentration of organic substances, pH, Eh, temperature, and competitive reactions of cations and anions [3–5]. Dissolved organic substances can inactivate metals in water by binding them with ligands, which reduces their toxicity and bioavailability for hydrobionts [4–6]. Some studies showed that biological systems are

threatened by nano-forms that can attach to the surface of organisms or be absorbed by them [6,7]. The study of the biogeochemical migration of elements, their speciation in the water environment, and their bioavailability in natural conditions provides grounds for the development of an adequate program for monitoring and evaluating the ecotoxicity of metals and their acceptable impact [8–10]. In global practice, environmental protection regulatory authorities specify the necessity of including tools for evaluating the speciation and bioavailability of metals in ecological regulations [5,8,9].

An important fundamental block in geochemical studies is the evaluation of the equilibrium distribution of metals in water and the influence of environmental conditions on the synthesis of these forms [4–6]. The differences between the behavior of nanoparticles, dissolved particles, colloid particles, and suspended particles must be understood. Dissolved forms are represented by ions and complexes of metals with non-organic ions or low-molecular organic compounds up to 0.05 μm in size. The colloid fraction is represented by particles 0.45–0.05 μm in size [1,7]. The particles that exceed the standard size of filter pores (0.45 μm) are defined as suspended particles [8–11].

Presently, the membrane filtration methods used for the analysis of natural waters are being quickly developed [11]. The development of new filter materials and filtration systems (nuclear, reverse osmosis, etc.) allows specialists to separate multi-component water systems into biological (viruses, bacteria, microplants, etc.), organic (macromolecules, simple organic acids, proteins, etc.), and non-organic (metal ions, complexes with nonorganic ligands, etc.) components of water [11,12]. The existing methods used for the analysis of natural water volumes are based on filters with 0.45 μm pores for the separation of the coarse fraction and 0.22 μm pores for ecological studies [11]. However, numerous studies [9–12] have been conducted with a set of membranes with different pore sizes and multistep filtration systems.

Membrane filtration is often combined with other methods of substances fractioning, as reviewed by [11,13,14]. The choice of membrane material and the size of pores is primarily determined by the aim of the study. The first stage of consecutive multistep filtration requires membranes with larger pores that subsequently decrease in size. This approach allows for obtaining fractions with differently sized substances and molecules. Further analysis of fractions by different physicochemical (e.g., inductively coupled plasma mass spectrometry), spectrophotometric, electrochemical, and other methods provides data on the distribution of metals and organic (humus) substances [14–18].

The choice of water as an indicator of certain changes in the environment is important. Arctic lakes are the most sensitive water objects in terms of geochemical peculiarities and regional technogenic impacts [19,20]. An example of such objects is Lake Imandra, which is affected by the waste flow from metallurgical and mining production [19]. The lake is located in a unique geochemical region of the Kola Peninsula [20]. The quantity of metals and metal speciation (complexes with organic compounds, solid particles, and free metal ions) in the lake's water depends on the pollution load and climatic conditions (air temperature, amount of precipitation, and wind load) [20–22].

The objective of this study was to evaluate the distribution of elements by speciation in a subarctic lake subject to the impacts of mining and metallurgic production in an area of severe and moderate pollution (along the spread of wastewater) and to assess the influence of geochemical factors and temperature conditions on the distribution of speciation.

2. Lake Characteristics and Experimental Methodology

2.1. Characteristics of the Lake and Sample Points

Lake Imandra was an ultra-fresh and oligotrophic Arctic lake. The concentration of total phosphorus was less than 2 $\mu\text{g/L}$; phosphates during the vegetation period were practically completely used in the production processes. Water transparency was about 8 m. The lake was characterized by a high saturation of the water with oxygen (up to the bottom) due to mountain ice-free rivers entering the lake. The watershed covers 12,300 km^2 ; the area of the lake is 880 km^2 . The lake consists of three parts connected by narrow straits (Figure 1).



Figure 1. Scheme of sampling points.

The high anthropogenic loads specific to the Kola Peninsula were due to the smelters that started in the 1940s and reached their peak in the 1980s. This led to serious changes in water chemistry: transparency decreased, metals concentrations increased, and the pH moved toward alkaline in comparison to the background. Due to the influx of salts, the ionic composition of the water changed. Technogenic sulfates in the ionic composition of the water dominated over hydro-carbonates. The pollution from the metallurgical enterprises increased the content of heavy metals, and especially that of Ni, Cu, and Zn [20,22].

Notably, the most severe heavy metal pollution of Lake Imandra was registered in 1970–1980 [3]. After 1990, the pollution from copper and nickel production decreased. The conducted studies showed that the influx of wastewater is currently much lower. Along with the spread of wastewater from Monche to Kumuzhiy (Figure 1), both the concentration of heavy metals and the content of ion forms decreased. Moiseenko et al. [20] studied the speciation of Ni and Cu as the main markers of the distribution of wastewater from copper–nickel enterprises.

We selected two samples points: the region of Monche bay (1) in the area of inflow of wastewater from a copper–nickel enterprise (6 km from the point of the wastewater emission, the Lake Imandra stretch) and the island Kumuzhiy, and (2) 80 km from the inflow of wastewater along the distribution of wastewater, Yorstrovskaya Imandra stretch, beyond the bay.

2.2. Sampling and Size Particles Fractionation

Water was sampled in polyethylene bottles for general assay and in separate bottles for the estimation of microelement content. The bottle material had no sorbing properties. Water samples were cooled down ($\sim 4^\circ\text{C}$) and quickly transported to the laboratory. Samples for the microelement

assay were acidified with HNO_3 (Fluka). Water was sampled with a Ruttner bathometer from two horizons: surface and near-bottom at the depth of 19 m (Monche) and 25 m (Kumuzhiy), respectively.

Samples were directly fractionated on site, as well as after their transportation to the laboratory. For the comparison of results and specification, syringe filter nozzles and a multistep tangential membrane filtration unit [16] were used. The membrane pore sizes were 8, 1.2, 0.45, and 0.2 μm (VLADiSART). The filter holder was Millipore (25 and 47 mm). The sample volume was 250 mL. The initial samples were consequently filtered through membrane filter holder (47 mm; Millipore) with an 8 μm membrane (VLADiSART) installed. The filtrate was filtered through 1.2, 0.45, and 0.2 μm (VLADiSART). Of the initial sample, 200–250 mL were successively passed through a membrane filter holder (47 mm; SWINNEX Millipore) with an installed 8 μm membrane (VLADiSART). The filtrate was then passed through a 1.2 μm membrane, then 0.45 and 0.2 μm (VLADiSART). A volume of 5 mL was discarded from each filtrate fraction for elemental analysis by inductively coupled plasma mass spectrometry (ICP-MS). At the multistep tangential membrane filtration unit, the sample was passed through the same set of membranes and we selected the solutions to be analyzed. The mass balance of all metals was monitored at each stage of fractionation. Notably, the results of metal fractionation with the syringe filter nozzles and the multistep tangential membrane system coincided. The syringe filter nozzle system allowed fractionation directly on site. Its usage becomes difficult if water turbidity increases compared with the water used during this study.

The following filtrate characteristics were used: microfiltration-based: mechanical suspension and oxidized contaminants (>8 , 1.2, 0.45, 0.2, and 0.1 μm) and ultrafiltration-based: colloids, bacteria, viruses, etc. (less than 0.1 μm). Statistical analysis of the distribution of elements in suspended and dissolved conditions was performed based on the unified results of the filters with pore sizes: $>8 + 1.2 + 0.45 \mu\text{m}$; $0.2 + 0.1 \mu\text{m}$; and $<0.05 \mu\text{m}$.

The following parameters were determined for the samples: pH (Mettler Toledo ± 0.01), electric conductivity (Mettler Toledo ± 1), main cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+), Si, alkalinity (Alk), SO_4^{2-} , Cl^- , color (Col), organic matter content (OMC), total nitrogen (TN) and its forms (NO_3^- and NH_4^+), total phosphorus (TP), and PO_4^{3-} using chromatographic, spectrometric, and potentiometric methods; detailed techniques reflected in [17]. The analytical methods and obtained results of the chemical content of water were verified under strict in-house control with 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 ICP-AES (ICAP-61 Thermo Jarrell Ash, Institute of Problems of Microelectronic Technology and Superpure Materials RAS, Chernogolovka, Russia).

The element measurements were recorded with the following spectrometer parameters: an (radio frequency generator) RF generator with an output power of 1200 W, an angular nebulizer, a plasma-forming Ar flow rate of 18 L/min, an auxiliary Ar flow rate of 0.9 L/min, an Ar flow rate into the nebulizer of 0.6 L/min, an analyzed sample flow rate of 1.5 mL/min, 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 of each element. Element contents in the samples were calculated out using spectrometer software (ThermoSPEC, version 4.1). The detection limits of the various elements were: Li 0.5 mg/L; Si 0.05 mg/L; Na, Mg, Al, and Ca 0.01 mg/L; K, Zn, and S 0.15 mg/L; P 0.8 mg/L; Fe, Cu, Sr 0.003 mg/L; and Mn and Ba 0.0003 mg/L. The detection limits for ICP-AES measurements were calculated as follows: $\text{DLi} = \text{Ci} + 3\alpha$, where Ci is the mean content of an element of interest for measurement in control samples and α is the standard deviation of its determination in control samples. The accuracy of analyses was better than 5% for elements with $C > 5 \text{ DL}$ and did not exceed 20% for elements with $C < 5 \text{ DL}$. For most of the above elements analyzed, the concentrations were higher than 5 DL.

Contents 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, Tl, Pb, Bi, Th, and U in the samples were determined by ICP-MS

(X-7 ICP-MS Thermo Electron, Institute of Problems of Microelectronic Technology and Superpure Materials RAS, Chernogolovka, Russia). The measurements were conducted with the following spectrometer parameters: an RF generator with an output power of 1250 W, a PolyCon nebulizer, a plasma-forming Ar flow rate of 12 L/min, an auxiliary Ar flow rate of 0.9 L/min, an Ar flow rate into the nebulizer of 0.9 L/min, an analyzed sample flow rate of 0.8 mL/min, and a resolution of 0.8 mL/min. The following parameters were used for mass spectrum estimation: detector mode, double (pulse counting and analogous); scanning modes, survey scan and peak jumping. The detection limits for the ICP-MS measurements ($\leq 0.1\text{--}1$ ng/L for Cd, Ba, Y, Zr, Nb, REE, Hf, Pb, Th, and U; 1 ng/L for Ga, Ge, Rb, Sr, and Sb; ≤ 10 ng/L for Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, and As) were calculated as follows: $DLi = Ci + 3\alpha$. For elements with several isotopes, DL was used for the most abundant isotope. The accuracy of 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 were quantitatively determined using calibration solutions (High Purity Standards) with 5, 10, and 100 $\mu\text{g/L}$ of each element. Indium was used in all measurements as an internal standard. For Li, Al, V, Mn, Cu, Zn, and Ba, which were determined both by ICP-AES and ICP-MS, average values from the two methods were used.

To generalize the factual data, further theoretical analysis was based on the combined results of fractioning: up to $0.45\text{ }\mu\text{m}$ (suspended particles), $0.45 + 0.2 + 0.1 + 0.05\text{ }\mu\text{m}$ (compounds with high molecular weight), and $< 0.05\text{ }\mu\text{m}$ (true dissolved and low molecular fragments).

The obtained data were statistically processed using the software package Statistica Advanced 12. The methods of discriminant and canonical analysis were used.

2.3. Influence of Temperature on the Distribution of Elements by Speciation

The possible influence of the temperature on the distribution of the elements by speciation was evaluated based on the data on the chemical content of water obtained from databases of the previous years (1980 to present) and the data on local temperature fluctuations on the Kola Peninsula [23].

We did not have data on the metal speciation at the chosen points for the whole period of monitoring, from 1985 to present. However, ElementPhasMigration (certificate 2017662509, Dinu M.I.) software was used to calculate the shares of labile and non-labile metal speciation during the years of the highest pollution (beginning of the 1990s) and during the current period of the ecosystem restoration. The software uses the mathematical modeling of chemical reactions occurring in natural water and is based on the main laws of analytical and physical chemistry: material balance equation, equilibrium constant, equations of electrical neutrality, equations of proton balance, and competing reactions.

The initial data comprised a significant number of physicochemical parameters of the environment (more than 10 metal ions, pH, content of organic and non-organic anions, etc.) and diverse mathematical tools were used for the consecutive calculation of the acidity constant of organic acids, conditional constants of complexes stability, the share of strong and weak acids in the system, etc. The software evaluated metal speciation depending on the physical and chemical parameters of the environment and provided the data on the balance speciation of a wide spectrum of elements in the system. The final stage of the calculations included the verification of results with the field data.

3. Results and Discussion

3.1. Chemical Composition of Water

The main physical and chemical parameters of water geochemistry for the two studied points are presented in Table 1. In general, the water in Lake Imandra is characterized by a low-alkaline medium and electric conductivity that is high for Arctic lakes (around $100\text{ }\mu\text{mho}$ and higher). This is associated with the influence of wastewater. In the area influenced by the industrial wastewater in Monche (point 1), the water was characterized by a high content of all elements, especially iron, manganese, and nickel. This water had insignificant variations in the chemical content (gross concentrations)

between the surface and near-bottom horizons, which indicated good interfusion and a dynamic factor impact on the flow of wastewater.

Table 1. Physicochemical parameters and element concentrations in samples (Al and Pb, µg/L; other elements, ng/L).

Parameters	Kumuzhiy		Monche	
	Surface	Near-Bottom	Surface	Near-Bottom
pH	7.29	7.22	7.14	7.06
Cond.	99	98	122	130
TOC	3.57	3.52	3.66	3.36
Ca+Mg	4820.88	4922.09	4826.08	4780.71
Al	12.1	18.9	17.9	13.5
Fe	8.9	29.2	14.7	14.9
Mn	8.3	10.7	17.8	15.1
Ni	3.9	4.4	9.3	9.7
Cu	2.7	5.8	5.3	4.8
Pb	<DL	0.41	<DL	0.12
Cs	18.7	22.8	24.6	21.5
Zr	9.1	13.4	9.9	10.3
Sb	90.4	110	81.7	77.1
Y	15.0	20.3	21.7	14.9
La	36.6	62.7	67.5	42.0
Ce	41.4	79.7	68.4	39.4
Pr	6.3	12.3	10.6	6.9
Nd	23.4	40.8	35.7	24.0
Sm	3.7	4.5	4.3	3.2
Gd	2.8	8.2	4.4	2.6
Dy	2.1	2.4	3.8	1.9
Er	0.84	1.6	1.4	1.2
Yb	0.85	1.2	0.8	<DL
W	133	146	164	166
Re	6.7	6.7	10.0	9.1
Tl	1.9	2.3	4.8	5.2
Th	1.0	1.3	0.9	<DL
U	33.5	45.3	52.4	46.2

The samples from Kumuzhiy (point 2), a more remote point, had a lower content of the majority of elements in comparison with point 1. We found a significant increase in the concentration of elements in the near-bottom horizon in comparison with the surface water (in some elements, by more than three times), along with a clear gradient of concentrations. Based on the total concentrations, we found that the associated rare earth metals show the same tendencies of distribution as iron and aluminum, which is discussed in detail below. The content of lanthanide elements was higher in the near-bottom water at point 2 with similar contents of these elements in the surface and near-bottom water at point 1. This is due to geochemical features (the prevalence of local laporite deposits) at point 2.

On average, according to the obtained results, the color of the water at the two points did not exceed 10 degrees. However, this parameter was higher in the area influenced by technogenic wastewater (point 1) as a result of the anthropogenic and geochemical impact. In turn, the concentration of organic substances in the water at the chosen points was low (around 2.5–3 mg O/L) and comparable with each other within the standard deviation of the method used. This indicated a low content of organic substances in this water.

3.2. Distribution of Elements by Speciation

A more detailed study of the content of elements in a larger number of fractions allowed us to obtain data on the distribution of elements by speciation in water from different geochemical locations.

Table 2. Cont.

Monche (surface)							
	Kumuzhiy (near-bottom)						
	>8	8–1.2	1.2–0.45	0.45–0.2	0.2–0.1	0.1–0.05	<0.05
Al	7.93	0.00	0.00	0.00	0.00	0.94	9.97
Si	26.82	2.06	0.00	6.19	0.00	0.00	171.08
V	0.01	0.00	0.00	0.00	0.00	0.00	0.14
Fe	29.19	0.00	0.00	0.00	0.00	0.00	0.00
Ni	0.90	0.00	0.00	0.00	0.00	0.00	3.46
Cu	2.80	0.00	0.00	0.00	0.00	0.18	2.86
Ce	63.53	0.00	0.00	1.06	0.00	2.35	12.75
Sm	3.29	0.00	0.00	0.00	0.00	0.00	1.22
Gd	5.35	0.02	0.00	0.00	0.00	0.88	1.97
W	11.69	0.00	0.00	7.20	0.00	0.00	127.12
Re	0.00	0.00	0.00	0.00	0.00	0.00	6.71
Tl	0.34	0.00	0.00	0.00	0.00	0.00	1.93
U	9.00	0.00	0.00	0.00	0.00	0.00	36.24

For nearly all the studied components at the two points, there was a significant concentration in both the upper (up to 0.45 μm) and lower (<0.1 μm) ranges. Numerous publications have described similar tendencies in the distribution due to the prevalence of the adsorption processes or binding with low molecular weight ligands [20–25].

To analyze the data, we combined element speciation into major groups: suspended, highly molecular colloid, ion, and low molecular forms (see Materials and Methods). Element speciation groups are presented in Figure 2.

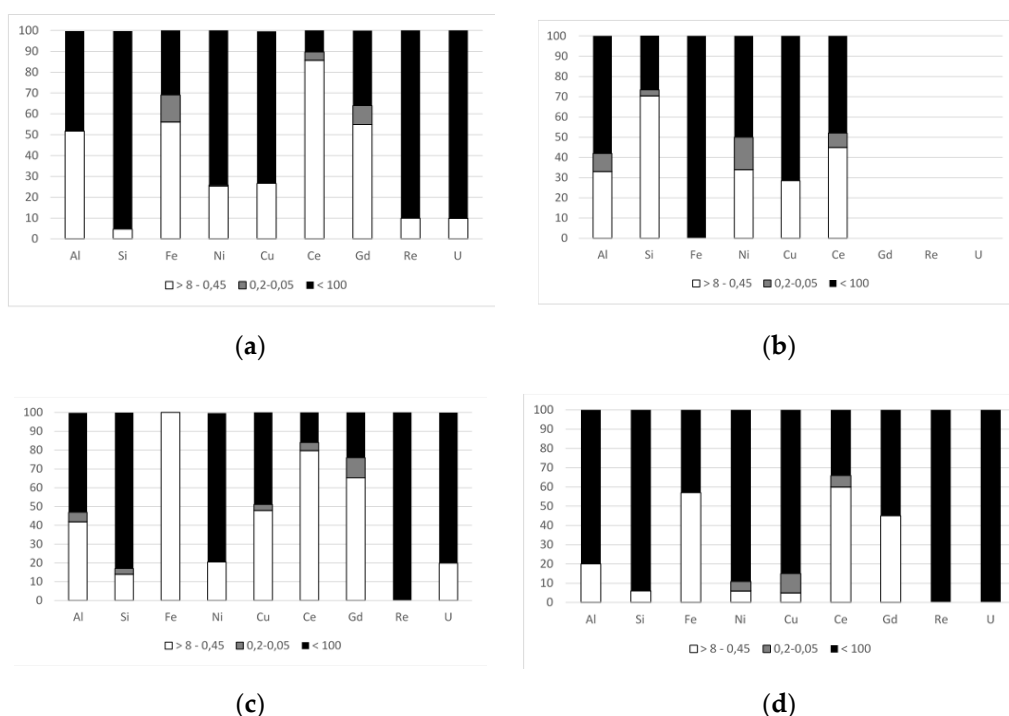


Figure 2. The content of elements by fractions (%): (a) Kumuzhiy (surface); (b) Kumuzhiy (near-bottom); (c) Monche (surface); (d) Monche (near-bottom).

The generalized data revealed some differences in the speciation of some chemical elements. The water from the Monche area contained suspended iron (near-bottom water) and low molecular complex compounds (surface water). The impact of suspended forms that prevail over the dissolved

forms occurs due to stronger technogenic and geochemical influences. Copper and nickel had a similar distribution in both surface and near-bottom layers at the specified point: dissolved forms with different molecular weights and, to a significantly lower extent, suspended particles. In the surface layer, aluminum and nickel were present in the form of highly molecular complexes ($0.2\text{--}0.05\text{ }\mu\text{m}$).

The highest content of suspended Si in the Monche area contributed to the adsorption and coagulation processes for some trace elements and transition metals. For example, nickel, copper, and cerium were better presented in this fraction than in the dissolved form.

The surface water in the Kumuzhiy area had nickel and copper prevailing in dissolved forms with different molecular weights. Trace elements, as well as iron ions, were primarily present in suspended form. In the near-bottom layer, iron was primarily present in dissolved forms with different molecular weights. Near-bottom water contained significant amounts of dissolved forms of copper and some trace elements. For nickel, the ratio of forms hardly changed.

The comparison of water from the two points showed that the content of the dissolved forms of transition metals was 10–15% higher in Kumuzhiy than in Monche. The distribution of elements by speciation was more variable in the Monche area, especially for trace elements and transition metals.

The changes in the physical and chemical parameters during fractioning (pH, electric conductivity, etc.) were indirect indicators of the content of a group of elements in a certain range. The obtained data showed that the specified parameters varied significantly, which indicated the differences in the distribution of elements by different speciation in the Monche and Kumuzhiy areas.

Consecutive membrane filtration revealed the most significant changes in the turbidity by more than one from 8 to $< 0.05\text{ }\mu\text{m}$ in the surface water in the Kumuzhiy area. The total Si content varied in the surface and near-bottom water at this point, from 150 to $250\text{ }\mu\text{m/L}$, respectively.

In general, water samples from Monche were characterized by higher turbidity, but there was no significant difference between the 8 and $< 0.05\text{ }\mu\text{m}$ fractions. The Si contents in the surface and near-bottom water were similar (around $450\text{--}475\text{ }\mu\text{m/L}$).

The water color values were higher in Monche ($10\text{--}11$ degrees) than in Kumuzhiy ($7\text{--}8$ degrees). In the former, this indicated a predisposition to the migration of transition metals in colloid form (from $0.45\text{ }\mu\text{m}$ to 100 kDa), and in the latter, in the suspended ($>8\text{ }\mu\text{m}$) or true soluble forms.

Cond and pH reflect the changes in the contents and degree of hydrolyzation of elements during the membrane fractioning. The most significant decrease in these parameters and, consequently, change in metal content, was observed in the surface water of Kumuzhiy, where the most significant changes in pH (more than 1.1) were recorded. This indicated the maximum concentration of elements in the largest and finest fractions (without gradual distribution by forms).

Due to insignificant variations in the specified parameters of the filtrate fractions in the Monche samples, the distribution of elements by six forms was more diverse. For example, the speciation of transition metals was concentrated in the colloid fraction with different molecular weights (range up to 0.45 and $0.45\text{--}0.1\text{ }\mu\text{m}$).

Multivariate statistical analysis of the discriminate and canonic analysis revealed significant differences in the content and specification of metals between Monche and Kumuzhiy (Figures 3 and 4). The surface–bottom distribution of elements was more evident in the Kumuzhiy samples. The differences were indicated by the following parameters (F not less 10): pH between the suspended and different colloid forms (>0.45 ; from 0.45 to $0.05\text{ }\mu\text{m}$) and the content of the copper and zinc in chosen fractions.

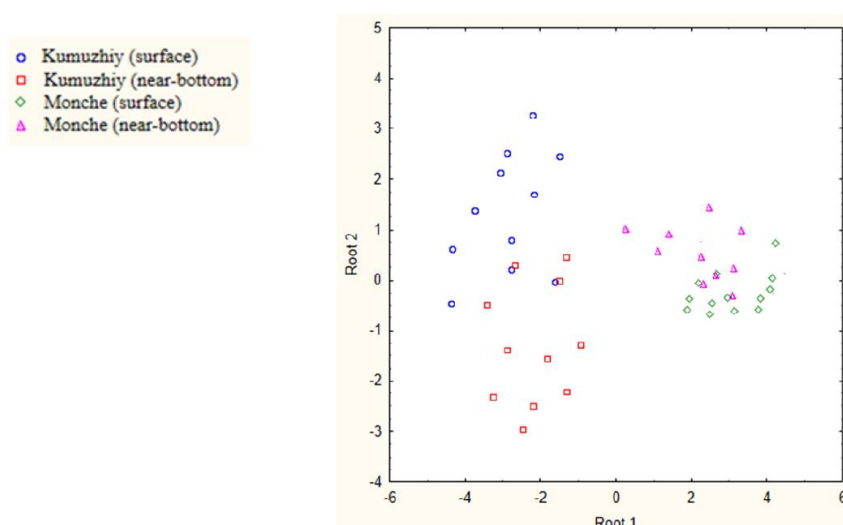


Figure 3. Discriminant analysis results for selected points.

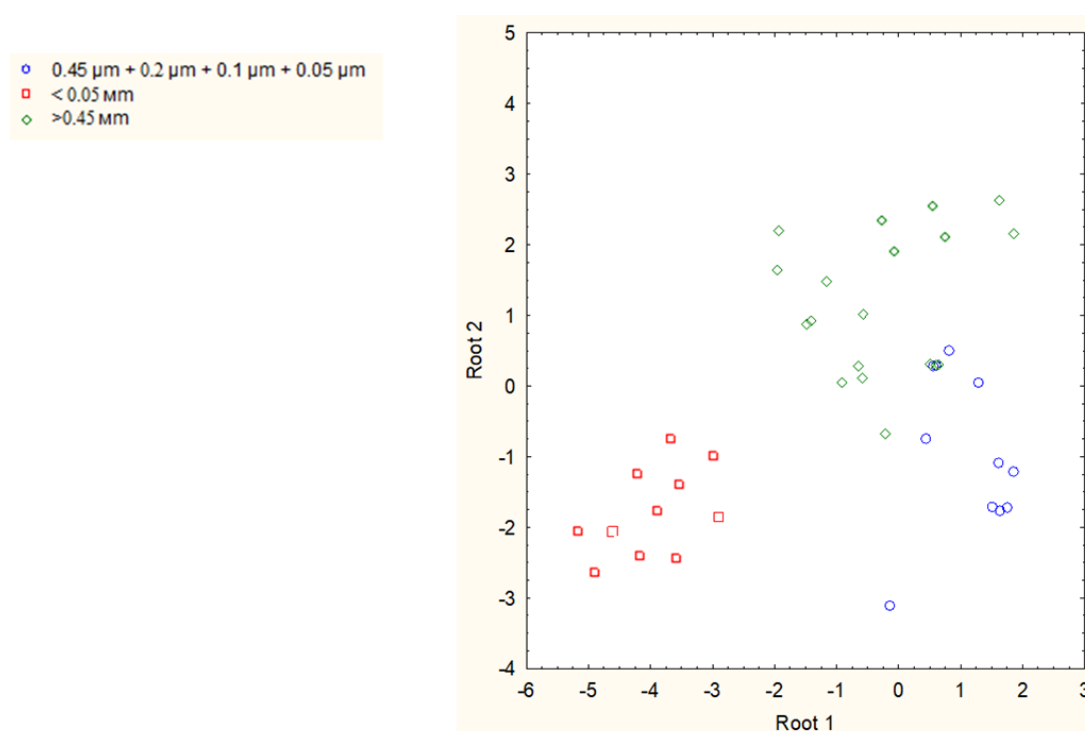


Figure 4. Discriminant analysis results for selected filtration diameters.

The conditional unification of the filtration-obtained forms into major groups provided particle size data: ion solution, colloids of different molecular weights, and suspended particles. The greatest impact on this distribution (F not less 10) was contributed by the suspended forms of iron and Si and dissolved forms of some heavy metals: zinc, aluminum, nickel, copper, etc.

3.3. Possible Impact of Geochemical Factors and Temperature on the Speciation of Elements

3.3.1. Geochemical Peculiarities

The content of siderophile elements associated with iron followed the same distribution, in general. At Monche, a similar distribution of elements was observed in the subgroup of nickel, molybdenum, and lanthanides. They are also presented in high molecular, low molecular, and dispersed forms.

In the near-bottom layer, the distribution shifted to the larger fractions. On average, a polluted point at Monche was characterized by an even distribution of the concentrations in the specified groups of elements in the fraction of surface and near-bottom water, indicating increasing turbidity and admixing.

At Kumuzhiy, the distribution of rare earth element components was similar to that of iron. The majority of the specified elements was present in a dispersed form or low molecular complexes.

Lithophylous elements mimicked the distribution of aluminum. From the point of view of geochemical distribution, elements from the lithophylous group were primarily present in the near-bottom water of the remote point in comparison with surface water (Kumuzhiy). The major speciation included the larger fraction or true solutions.

Chalcophylic elements, especially copper, were evenly distributed in the surface and near-bottom samples at Monche. The Kunuzhiy samples, clearer in terms of geochemistry, contained more dissociated elements bonded with organic substances in the near-bottom layer.

Geochemically, the region is characterized by the enrichment of elements with dissipated rare earth elements. During consecutive membrane filtration, large volumes of the specified elements were revealed, especially in the concentrated intermediate samples. The water in Monche that was located close to mountains was characterized by a two-fold higher content of rare earth elements due to the characteristics of the rocks.

3.3.2. Climatic Peculiarities

There is no consensus on the influence of temperature on the inflow and speciation of elements in natural water conditions. In combination with more important technogenic factors observed in the region, the obtained data should be treated as hypothetical. Sometimes, general tendencies can be found during the analysis of tendencies in the gross content of metals, temperature, and speciation.

According to reported data [25–30], the air temperature tends to increase 1–1.5 °C, especially in spring and autumn, which might affect the rate of system recreation, in general. A study of the Kola Peninsula [18] highlighted an average increase in the air temperature from the end of the 1980s until the beginning of the 1990s to the present time by 2 °C. Some fluctuations in temperature were noted.

At the beginning of the 1990s, higher concentrations of some elements were registered in Lake Imandra. Some decreases in the concentration in the 2000s coincided with the changes in temperature (1 °C decrease) with a significant correlation ($R = 0.97$). Figure 5 shows some consistency between the temperature increase and pollution growth in certain years. We also attempted to distribute the elements by speciation.

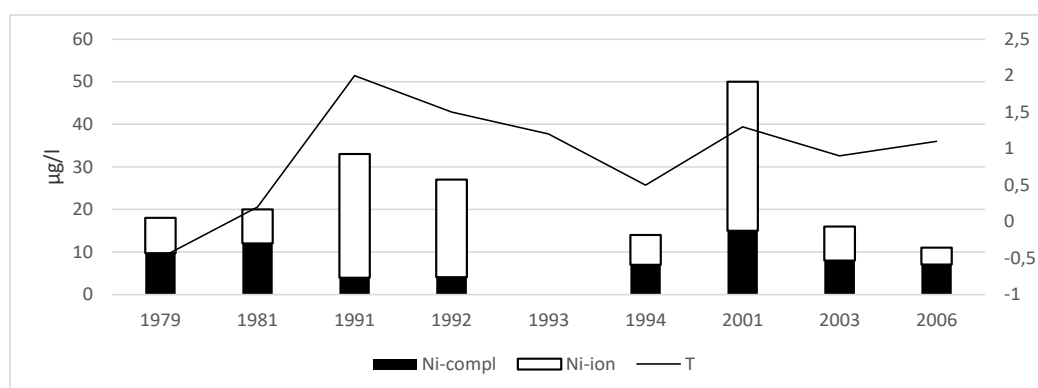


Figure 5. Temperature trend and change in labile and non-labile forms of Ni.

The calculated evaluations of the labile and non-labile forms by year also revealed synchronization in the temperature changes and gross content of labile speciation. As an example, we studied the content and speciation (labile/stable) of nickel ions as the main technogenic pollutant of the region.

The obtained data indicated a set of technogenic and climatic factors that cumulatively influenced the coexisting speciation.

To verify the calculations, the obtained data were compared with the published literature on the natural changes in the speciation of elements based on the ion exchange distribution. We found that during the years with maximum anthropogenic load, the share of labile forms in Lake Imandra significantly increased (Figure 5). For nickel and copper, the labile speciation was 80%; for zinc, it was 100% [15]. More than 80% of nickel, up to 85% of copper, and around 60% of zinc at Monche were labile. At Kumuzhiy, these levels were 15–20% lower due to a lower content of organic substances.

4. Conclusions

An important fundamental block in geochemical studies is the research of metal equilibrium distribution in water by speciation and the influence of geochemical conditions on metal fractioning by speciation. Understanding the differences in the behavior of nanoparticles, dissolved forms, colloids, and suspended particles plays a crucial role in the assessment of the bioavailability and toxicity of elements.

Here, we proposed a multistep system of water filtration through a set of filters from 8 to 0.05 μm . The theoretical labile and non-labile speciation of the elements were calculated. The effects of wastewater from copper and nickel mining on the subarctic Lake Imandra was studied at two chosen points along the flow (10 and 60 m from the source). We studied six speciations of elements in the surface and near-bottom water of the lake.

The obtained results showed that numerous elements had diverse distributions by speciation at the point located closer to the source of wastewater. This indicated a significant influence of adsorption processes on the system balance of elements, such as iron, copper, and rare earth elements. The prevalence of the impact of suspended, over the dissolved, forms was significant in the near-bottom layer due to greater technogenic and geochemical influences. Copper and nickel showed a similar distribution in the surface and near-bottom water at the specified point: the dissolved forms with different molecular weights and some suspended forms.

In the surface water at the remote point, the dissolved forms of nickel and copper with different molecular weights prevailed. Trace elements and iron ions were in suspended forms. In natural water, rare earth elements prevailed with particle sizes of 1.2–0.1 μm . A high content of dissolved forms of some transition and trace elements was revealed. The ratio of nickel speciation did not change along the depth. At this point, a high variability of element distribution by speciation was observed, especially for trace and transition metals.

Climate warming may have impacted the speciation of metals based on the comparison of temperature conditions and the distribution of metals in labile and non-labile forms (in the historical, compared with the calculated, data). The observed tendency of the share of labile forms to increase during warm periods indicates a correlation between the temperature and activation of geochemical processes with the formation of labile speciation, which was confirmed by the available published data.

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