Metal bioavailability in northern low-salinity water: Case study of lakes in the Kola region, Russia

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Abstract

This paper presents metal speciation calculations that are based on mathematical modelling of chemical reactions in natural waters. Metal concentrations (Hg, Cd, Pb, Ni, Cu, Al, Sr) were determined, and their speciation in water were calculated for 22 water areas in the Kola region. Meanwhile, the accumulation of metals in fish organs and tissues was studied (e.g. whitefish). The biogeochemical activity of metals determines the proportions of labile and non-labile speciation in water. In the distribution zones of non-ferrous industry effluents, metal aqua-ions prevail; during the distribution, the proportions change in accordance with the metal activity. The bioavailability of metal speciation is estimated depending on aqueous geochemical conditions and, accordingly, the speciation of metals (in situ), based on the original studies of the lakes of the Kola region in northern Russia. The connection among the metal contents in fish and water has been identified using multidimensional scaling and redundancy analysis techniques. Using the example of natural conditions in northern low-salinity freshwaters, it is demonstrated that labile Cd, Pb, Ni, Cu, Al, and Sr are the species most bioavailable and able to penetrate fish; meanwhile, the organic complexes of Hg, Pb, and Al have a greater affinity to accumulation in the gills. This study demonstrates the need to correct the approved water quality standards in Russia, taking into account the high bioavailability of metals in northern low-salinity waters.

1. Introduction

The anthropogenic release of metals into the environment has sharply increased over the past century, which is associated with ever-increasing volumes of their production and, as a result, their dispersion in the environment (Nriagu 1996, Pacyna and Pacyna 2011, Bjerregaard and Andersen 2014). Metals enter as a part of the wastewater that originates from various industries, diffuse sources, and mineral rocks through leaching. Consequently, the enrichment factor of toxic elements in the surface waters of lakes has increased by an order of magnitude for lakes (Moiseenko et al 2019). Mankind has faced many new mass human and animal diseases, owing to the increased content and bioaccumulation of certain metals (Nordberg et al 2014). Moiseenko et al (2018) reported that high concentrations of metals in drinking water have led to bioaccumulation and disease in humans, which is indicated by the high metal content in fish. Non-essential trace elements, such as Cd, Hg, and Pb, are known to be highly toxic. Meanwhile, metals are components that are always present in nature in various concentrations. Many essential metals play important roles in the normal metabolic processes of living bodies at the microconcentration level. However, at high concentrations, they may also cause various diseases (Wood 2011, Davidson et al 2014).

Fish consume high concentrations of both toxic and essential elements in their bodies that impede many of their physiological functions (Wood et al 2012b, 2012a). Bioavailability is one of the key properties of elements that determine their penetration into fish; this property depends not only on the concentration of metals in water but also on their speciation, calcium content, humic acidity, pH, temperature, and ability to combine with other metals (Magalhaes et al 2015, Merrington et al 2016, Väänänen et al 2018).

Dissolved organic carbon (DOC) can inactivate many metals entering water by binding them to the
ligands of amino, fulvic, and humic acids, which reduces their bioavailability and toxicity for aquatic life (Ediagbonya et al. 2015). However, there are exceptions such as Hg, which has metalorganic complexes that accumulate more actively in fish (Gochfeld 2003, Magalhaes et al. 2015).

In Russia, only the total concentrations of metals in surface waters are controlled without taking into account the bioavailability and ecotoxicity of metals in various types of waters. Information on officially established water quality standards, such as the maximum permeation concentration (MPC) of metals in Russia (List of Fishery Standards 1999) as well as the Gide Line (GL) concentration for aquatic life in Western countries (US EPA 2004, CCME 2007, European Commission 2011), is based on experimental work performed in aquariums with test organisms. The principle of the experiments is that one metal corresponds with one type of organism (2–3 are possible). Experimental studies that determine the toxic properties of elements on test organisms provide information on the relative danger of the elements. However, the experimental parameters of water and the aquatic organism of concern have little in common with natural conditions and populations.

Currently, environmental authorities have announced the need to include methods for assessing the metal bioavailability in environmental regulations, including in Russia. However, until now, the same MPC standards have been used in Russia from the Arctic to the steppe regions, although the water varies greatly in salt composition, hardness, and DOC.

Water quality authorities are developing more effective methods for assessing pollution risk, particularly using the metal bioavailability index to assess the environmental risks of water metal pollution (Smith et al. 2015, Magalhaes et al. 2015, Tipping et al. 2015, Väännänen et al. 2018). Analytical measurements and modelling both play important roles in understanding speciation, whereas modelling is also needed for prediction. The calculated models (e.g. HD-MINTEQ, WHAM, NICA-Donnan, LMWOAs, HCh) are based on a general way in assessment of metals speciation and neglect of zonal features organic anions and their change in anthropogenic loads. For more realistic calculations, experimental research was made (Väännänen et al. 2018). Analytical measurements and modelling both play important roles in understanding speciation, whereas modelling is also needed for prediction.

Models of biotic ligands (e.g. biotic ligand model; BLM) have been developed based on the determination of elemental bioavailability. There are detailed models for research purposes and simplified models that are used for regulatory purposes (Smith et al. 2015). To some extent, these tools are already being used in Canada, the USA, and the EU (CCME (Canadian Council of Ministers of the Environment) 2007, US EPA 2007, European Commission 2011). In the EU, the adopted Water Framework Directive emphasises this trend by setting quality standards for Ni and Pb in their bioavailable concentrations (European Commission 2013).

However, the BLM is characterised by low efficiency for fresh, soft, and ultra-soft waters (Hoppe et al. 2015). In addition, model calculations and experimental results cannot consider the entire complex of geochemical conditions in natural waters nor polymetallic pollution, which refers to the conditions under which metals are generated and penetrate, that is, their pending bioavailability.

The purpose of the work was to perform the following:

- create a model for calculating the speciation of metals, based on the mathematical modelling of chemical reactions in natural waters and the fundamental laws of analytical and physical chemistry;
- determine the concentration of metals (Hg, Cd, Pb, Ni, Cu, Al, Sr) in water and use our model to calculate their speciation;
- assess the accumulation of metals in the fish (e.g. whitefish) and reveal the relationship between the bioaccumulation of these metals and their speciation in water;
- assess the bioavailability of metal speciation depending on the aquatic geochemistry and the metal speciation on the basis of the results of original studies (in situ) regarding lakes with low salinity water in the Kola region, north Russia.

2. Materials and methods

2.1. Objects of research

The objects of research were the subarctic lakes located in northwest Russia (Kola peninsula). Among all Arctic regions, this region is the most industrially developed, containing copper-nickel smelting and mining facilities. The largest lake among the investigated lakes is Imandra Lake, which consists of three parts (Bolshaya, Ekostrovskaya, and Babinskaya), connected by narrow straits. The remaining lakes constitute the catchment system of Imandra Lake (figure 1). Belonging to the postglacial period in terms of genesis, all lakes are oligotrophic with low-salinity water, which is typical for lakes in the Arctic zone.

These lakes differ according to the degree of anthropogenic influence and geochemical conditions. The ‘Severonickel’ facility has been polluting Lake Bolshaya Imandra for many years with heavy-metal-containing wastewater. The polluted waters spread to Ekostrovskaya Imandra. The catchment of lakes was exposed to air pollution emissions of sulphur dioxide and airborne metals.

Certain areas (22 lake areas) were identified for hydrochemical and fish studies. In these lake areas,
which differ in the level and extent of water pollution, the chemical composition of the waters and metal concentration has been determined, metal speciation has been calculated and measured, and metal content in the organs and tissue of fish has been determined. It should be emphasised that an examination was conducted within a specific area that included at least 10 water samples and 10 species of whitefish.

**2.2. Determination of chemical composition and metal concentration in water**

Water samples were taken into polyethylene bottles Nalgen®, the surface of which had no sorption properties. The bottles were thoroughly cleaned in the laboratory and rinsed with lake water twice before sampling. Water samples (20 ml) were taken separately to determine the metal concentrations. Samples were placed in dark containers, refrigerated (approximately + 4 °C), and, within a short period, transported to the laboratory for further analysis. For each lake, the examined area included 10–15 water samples (surface and bottom).

The chemical composition of the water—pH, electrical conductivity ($\chi$), Ca$^{2+}$, Mg$^{2+}$, K$^+$, Na$^+$, alkalinity, SO$_4^{2-}$, Cl$^-$, colour, organic matter content by permanganate oxidation, NO$_3^-$, NH$_4^+$, total nitrogen, PO$_4^{3-}$, total phosphorus, and Si were determined according to unified methods in...
accordance with the recommendations (Eaton et al 1992).

Elemental concentrations were determined using a graphite furnace method (GFAAS, Perkin-Elmer 5000 model, HGA-400, AAnalyst-800, Perkin-Elmer Corp., Norwalk, CT, USA) to determine atomic absorption. Hg was determined using atomic fluorescence (Merlin model). This work focused on the following elements— Cd, Pb, and Hg—as those receiving the greatest attention for ecotoxicology, as well as the elemental markers of pollution in the region— Sr, Al, Cu, and Ni. Standard solutions with appropriate concentrations for each element were formulated from 1000 ppm atomic absorption spectrometry (AAS) stock standards (Merk, Darmstadt, Germany). Quality control of measurements was carried out under tight internal laboratory control.

2.3. Metal speciation: a model and its verification

The speciation of elements in water samples was calculated using the software Mathcad (program name ‘Acidformmet’, Patent No. 2015–61770362015 (Dinu and Moiseenko 2015)). During the study, labile and non-labile speciations of metals were calculated. The calculations were based on modelling the material balance equations, mathematical expressions of equilibrium constants, electroneutrality equations, proton equilibria equations, and competing reactions.

Elemental concentration data and physical and chemical parameters of the aquatic environment from the hydrochemical database of lakes represent the initial data input into the software.

The reactions of the complex formation of metals with organic substances as well as inorganic complexes, such as sulphate, chloride, carbonate (hydrocarbonate), and hydroxy, were considered as the dominant reactions in the aquatic system. The most characteristic reactions occurring in a competitive environment were simulated for each metal (Ca, Mg, Sr, Fe, Al, Zn, Cd, Pb, Cu, Ni, Co, Cr, and Mn).

The proposed calculation algorithm contained the following four stages.

(i) Calculation of the acid-base equilibrium constants for humic organic substances based on experiments with samples separated from the waters of the region. This stage is necessary for the subsequent calculation of the equilibrium constants of metals with organic matter.

A possible mechanism of organic acid dissociation is the following: L—various functional groups, Rn-Rm—core of humic acids, Hk—possible degrees of acid dissociation

$\text{L} - \text{Rn} - \text{Rm} - \text{Hk} \rightarrow kH^+ + \text{L} - \text{Rn} - \text{Rm}^{-}$

The electrochemical simulation of acid-base equilibria was carried out by a coefficient fitting method taking into account the results of potentiometric titration ($\gamma$—activity coefficient, $m(i)$—titrant volume for given constants K, $V_e$—equivalent volume, and C—titrant concentration).

\begin{align}
    m(i) &= \frac{K_{1(i)} \cdot \frac{H(i)}{\gamma} + 2 \cdot K_{1} \cdot K_{2}}{(H(i))^{2} + K_{1} \cdot \frac{H(i)}{\gamma} + 2 \cdot K_{1} \cdot K_{2}} \\
    V(i) &= \frac{(H(i))^{2} - \text{Kw} \cdot V_0 - H(i) \cdot \gamma \cdot C \cdot m(i) \cdot V_e}{(H(i))^{2} - \text{Kw} + H(i) \cdot \gamma \cdot C} 
\end{align}

(1)

(ii) Conditional stability constants of metal and organic matter complexes were calculated using the experimental results of the assessment of acid-base equilibria and complexing and literature data (using the constants of stability of metals with inorganic ligands as competitive processes). Particular attention was given to assessing the competitive binding of Ca, Ni, and Co with organic ligands in the presence of other cations and inorganic anions. Spectrophotometric and electrochemical experimental methods were used to calculate the conditional constants of the stabilities of the complexes. For example, to determine the conditional constants of the stability of a complex by spectral methods, the following procedures were carried out: verification of the experimental data of a photometric study based on the optical absorption of solutions using the Lambert-Beer law; calculation of the absorbency (A) of the solution at known molar fractions (x); and determination of the absorbation coefficient (A) of all particles.

$\text{A} = x_{\text{CuI}} \cdot \frac{\text{Cu}}{\text{Cu} + x_{\text{Cu2}}} \cdot x_{\text{Cu2}} \cdot \frac{\text{Cu}}{\text{Cu} + x_{\text{Cu}} \cdot \text{CuCu} \cdot x_{\text{Cu}}} \cdot \text{CuCu}$

(2)

Next, the number of complexes in the system was estimated, and the conditional constants of binding the ligands with metal ions were calculated with changes in the metal content of the system.

(iii) The determination of the degree of binding a metal ion with its specific inorganic and organic anions within the presence of other cations and anions in the system completed the calculations of the computer program.

Schematically, the system is as follows:

$\text{M1} + \text{R1} - \text{R2} + \text{M2} + A_{(\text{neorg})} \rightarrow \text{Me1} - \text{R1} - \text{R2} - M1 - A_{(\text{neorg})} - + \text{R1} - \text{R2} - M2 \ldots$

where M—metal ions, R1-R2—organic ligands, $A_{(\text{neorg})}$—inorganic ligands.

An assessment of the change in the degree of metal binding to a specific ligand was based on a change in the molar fraction of the metal speciation in the system, where K is the corresponding stability constant of an individual complex,

\begin{align}
    \alpha ML(1) &= \frac{1}{(1 + L(2) \cdot K_2 + L(3) \cdot K_3 + L(4) \cdot K_4 + \ldots)} 
\end{align}

(3)
(iv) The model was verified by considering 70 lakes in the Kola Peninsula. To compare the obtained model calculations with natural experimental measurements in 2014–2018, the evaluation of the specification of elements in natural waters was performed.

During the experiment, the metal contents in the suspended (unfiltered) and dissolved fractions (filtered) were determined. They were subsequently separated into fixed and non-fixed groups with ion-exchange resin, strongly bound to the organic matter of natural waters (Dowex 50 W-X8, 50–100 mesh in Na + and H forms). Dowex fine-mesh resins are based on a microporous copolymer of styrene and divinylbenzene. This procedure is based on the ion exchange resin and solution component, that is, under labile and non-labile conditions, according to the selected ion exchange mechanism (Rodysushkin 1995). The labile speciation of elements was aqua-ionic, connected with inorganic (including mixed) metal complexes and also weakly complexed with organic matter (with a low conditional stability constant). Non-labile speciation included strong metal complexes with organic matter, mainly of humic nature.

2.4. Metal content in the organs and tissue of fish
The number of observed fish on each site varied but was usually 10 or more. Whitefish (Coregonus Lavaretus L.) is the most widespread species in the northern region of Russia. Notably, this species does not make long migrations, which allows us to connect the quality of the aquatic environment with the fish in this range. Fish sampling was carried out in the field in the same period, September, simultaneously with an examination of the hydrochemical conditions of their habitat. To minimise internal factors, such as fish maturation and aging, samples were taken in September of immature fish aged 4 + and 5 + . The metal contents in the muscle, liver, kidney, gills, and skeleton samples were analysed. The total number of samples of organs and tissues for the content of trace elements exceeded 1500.

Samples of fish organs and tissue for metal analyses were dried to a constant weight at 105 °C. Dry samples were prepared for analysis by wet digestion in ultrapure nitric acid (10 ml acid for 1 g of tissue). Metal contents in fish solution were also determined through AAS; meanwhile, Hg was determined using atomic fluorescence. Duplicate analyses were performed for quality control.

Considering that the metal contents of the sample were unequal in water and in the fish systems, their weighted average value was determined for 22 aquatic areas. Each of the samples underwent a large volume of measurements (>10), which significantly increased the accuracy and reliability of the results.

2.5. Statistical data processing
Mathematical data processing was performed using the package ‘Statistica’ version 12, from the company StatSoft, Inc. We were able to determine the significant environmental variables and explain most of the variation in the data, that is, to quantify the discrete contribution of the individual descriptors (Snuderl et al 2007).

We used multiple regression to understand the influence of environmental factors of metal speciation on the bioavailability. The metal content in the organ of concern (µg g⁻¹, dry weight) was considered as the dependent parameter, while the metal content in water (inorganic form and organic form, µg l⁻¹), pH, hardness (mg l⁻¹), and DOC (mg l⁻¹) were independent parameters. The adequacy of the dependencies was verified using the Durbin–Watson statistic (1951), in which the upper critical value for each dependency presented was exceeded (hypothesis of residual independence is true).

Additionally, multidimensional scaling Principle component analysis (PCA) (redundancy analysis; RDA) methods were used for the most demonstrative elements, Cu, Ni, Cd, Pb, and a model distribution was used for Hg, based on its speciation in water and accumulation in fish organs. This method identifies the affinities of elements in fish organs (dependent) to the most preferred elemental speciation (independent) in natural waters. RDA was first performed with many explanatory variables to ensure that no possible relationship was overlooked (Snuderl et al 2007).

3. Results

3.1. Chemical composition of water and metal speciation
For the convenience of data interpretation, the results of chemical measurements were grouped into four large bodies of water (tables 1 and 2). The northern part of Lake Imandra (Bolshaya Imandra) is subject to the greatest anthropogenic impact. This area has a higher conductivity and concentration of technogenic sulphates and a higher concentration of phosphorus than what is observed under natural conditions. Along with increased conductivity, the concentrations of Ni and Cu are the highest in this reach, as a result of the influence of the wastewaters from the ‘Severonickel’ plant. The percentage of elements in inorganic (labile) form is higher, reaching up to 90% for Ni and up to 70% for Cu. Higher concentrations of Al and Sr are also characterised for this part of the lake; the percentage of inorganic Al does not exceed 50%, and concentration of labile Sr is more than 90%.

Ekostrovskaya and Babinskaya Imandra are subject to the indirect influence of anthropogenic loading owing to the spread of the diluted wastewater stream from Bolshaya Imandra. These water bodies also have a higher conductivity and concentration of sulphates compared with their natural characteristics; meanwhile, the contents of Ni and Cu, including their inorganic forms, are almost lower than those in Bolshaya...
Table 1. Median and limits of variation (within brackets) of hydrochemical parameters of the water bodies under study.

| Parameter      | Bol'shaya Imandra | Iokostrovskaya and Babinskaya Imandra | Lakes Pirenga and Okhtozero | Lake Chuna |
|----------------|--------------------|---------------------------------------|-----------------------------|------------|
| pH             | 7.31 (6.89–7.62)   | 7.27 (6.85–7.44)                      | 7.22 (7.04–7.29)            | 6.89 (6.04–7.29) |
| Conductivity, $\mu$Scm$^{-1}$ | 112 (99.5–128)    | 91.2 (55.3–112)                       | 41.2 (31.2–47.1)            | 25.0 (19.3–27.0) |
| Ca, mg l$^{-1}$ | 3.8 (3.2–4.6)      | 3.8 (3.2–4.0)                         | 3.4 (2.7–3.6)               | 2.2 (1.8–2.5)  |
| Mg, mg l$^{-1}$ | 1.1 (1.0–1.3)      | 1.1 (1.0–1.1)                         | 1.2 (0.80–1.3)              | 0.76 (0.63–0.85) |
| Na, mg l$^{-1}$ | 16.5 (14.3–20.2)   | 6.0 (5.7–6.3)                         | 2.8 (2.0–3.1)               | 1.2 (1.1–1.4)  |
| K, mg l$^{-1}$  | 2.4 (1.8–3.6)      | 1.3 (1.2–1.4)                         | 0.94 (0.74–1.3)             | 0.33 (0.27–0.39) |
| Alkalinity, meq l$^{-1}$ | 362 (321–443)    | 283 (270–290)                         | 262 (183–296)               | 110 (106–158) |
| $\text{SO}_4$, mg l$^{-1}$ | 26.3 (19.6–32.4)  | 18.5 (8.34–25.5)                      | 5.39 (3.95–5.83)            | 2.81 (2.59–4.62) |
| $\text{Cl}$, mg l$^{-1}$ | 5.2 (4.7–7.4)     | 2.2 (1.9–2.3)                         | 1.0 (0.90–1.2)              | 0.95 (0.65–1.1)  |
| Hardness, mg l$^{-1}$ as CaCO$_3$ | 26.5 (22.9–31.4)  | 25.0 (20.0–28.1)                      | 10.5 (6.00–18.5)            | 9.96 (8.28–12.1) |
| $\text{DO}$, mg l$^{-1}$ | 9.5 (7.0–18.5)    | 10.5 (6.0–18.5)                       | 30 (5.0–30.5)               | 27 (14–34)  |
| TP, µP l$^{-1}$ | 3.69 (3.53–4.58)   | 3.67 (3.28–4.45)                      | 4.66 (4.36–4.71)            | 3.79 (3.51–4.45) |
| $\text{pH}$     | 29 (17–76)         | 13 (4.5–36)                           | 6.5 (4.5–6.5)               | 4.0 (4.0–8.0)  |

Table 2. Median and limits of variation (within brackets) of metal concentrations and its forms ($\mu$g/L—in numerator, %—in denominator) in the water bodies under study.

| Metal      | Bol'shaya Imandra | Iokostrovskaya and Babinskaya Imandra | Lakes Pirenga and Okhtozero | Lake Chuna |
|------------|--------------------|---------------------------------------|-----------------------------|------------|
| Cd         | 0.05 (<0.05–0.36)  | 0.10 (<0.05–0.16)                     | 0.10 (<0.05–0.11)           | 0.08 (<0.05–0.13) |
| $\text{Cd}_{\text{org}}$ | 0.05 (0.05–0.31) 90.0 | 0.07 (0.05–0.15) 90.0                 | 0.09 (0.05–0.10) 91.4       | 0.07 (0.05–0.11) 87.0 |
| $\text{CaCO}_3$ | 0.01 (0–0.05) 10.0 | 0.01 (0–0.03) 10.0                    | 0.01 (0–0.01) 8.6           | 0.01 (0–0.01) 13.0 |
| Pb         | 0.15 (0.10–0.30)   | 0.35 (0.20–0.55)                      | <0.1 (<0.1–0.18)            | <0.1 (<0.1–0.60) |
| $\text{Pb}_{\text{org}}$ | 0.12 (0.06–0.23) 76.5 | 0.26 (0.16–0.43) 76.5                 | <0.1 (0–0.14)               | <0.1 (0–0.34)  |
| $\text{Al}$ | 71.0 (19.0–175)    | 31.5 (14.5–157)                       | 26.0 (20.0–37.5)            | 32.0 (17.0–41.0) |
| $\text{Al}_{\text{org}}$ | 22.3 (6.18–43.7) 31.1 | 18.2 (4.28–41.8) 29.5                 | 8.34 (5.39–12.6) 32.1       | 6.60 (3.40–15.9) 20.0 |
| $\text{Sr}$ | 49.9 (12.8–135) 68.9 | 16.2 (10.2–115) 70.5                 | 17.7 (14.6–25.0) 67.9       | 25.2 (13.6–30.4) 80.0 |
| $\text{Sr}_{\text{org}}$ | 29.0 (1.55–5.58) 5.0 | 2.93 (1.40–3.78) 5.0                 | 3.08 (1.22–3.65) 4.5        | 0.39 (0.15–0.71) 3.0 |
| $\text{Ni}$ | 10.1 (6.15–28.8)   | 5.05 (1.80–13.2)                      | 0.80 (0.65–1.00)            | 1.65 (1.00–2.40) |
| $\text{Ni}_{\text{org}}$ | 6.27 (4.76–25.0) 72.7 | 2.90 (1.04–9.89) 65.0                 | 0.33 (0.27–0.44) 42.1       | 0.88 (0.47–1.39) 51.5 |
| $\text{Cu}$ | 2.91 (1.39–3.87) 60.0 | 1.73 (0.82–3.09) 57.0                 | 0.49 (0.42–0.61) 65.1       | 0.73 (0.44–1.12) 48.5 |
| $\text{Cu}_{\text{org}}$ | 4.90 (3.85–7.20) 3.35 | 3.35 (2.00–6.40) 27.1 | 0.80 (0.65–1.00) | 1.55 (1.00–2.00) |

Imandra, whereas the concentrations of Al and Sr were only slightly decreased.

Lake Pirenga and Lake Okhtozero lie at a considerable distance from industrial areas; therefore, their waters have nearly natural parameters, such as low conductivity and salt content. Greater colour and DOC concentration indicate the influence of a wetland of the drainage system compared with Lake Imandra. The contents of Pb, Ni, and Cu are lower here because of the remoteness of the area location from the industrial centres. Owing to the increased content of organic matter, the proportion of the organic (non-label) forms of these elements increases.
Lake Chuna is surrounded by mountainous terrain (Chuna-tundra), and the drainage is composed of crystalline rocks. Consequently, these waters show the lowest water conductivity and DOC as well as lower Sr content. The concentration of the majority of metals was also lower in comparison with other examined lakes. The exception is the slightly higher concentrations of Ni and Cu compared with those of the Pirengskiy Lakes, which results from the airborne emissions of the ‘Severonickel’ smelter.

Calculations and natural measurements of metal speciation showed great similarity in the elemental distribution of the organic and inorganic components in the waters of the examined lakes (table 2). As mentioned above, labile forms are represented to a greater extent by the aqua-ionic compounds of metals (inorganic complexes of metals) as well as the weakly metal complexes with organic matter. In turn, the non-labile speciation of metals comprises the most strongly complexing of metal with organic matter (mainly humic).

The proportions of metal compounds in organic matter and in aqua-ions are different and are determined by the properties of the metal and the close physicochemical characteristics of the waters. In all the examined lakes, almost 90% of Cd is characterised by the migration of labile speciation. Sr non-label speciation demonstrates nearly the same percentage of concentration. For Pb and Ni, the percentage of labile speciation with respect to the non-labile speciation is also high (over 70%); meanwhile, the content of labile Cu ions is lower (approximately 60%). Al features a predominance of complexes with organic matter.

Note that the variability of the geochemistry of the natural waters is small; these water bodies are characterised as oligotrophic and low-salinity freshwater (with the exception of the polluted Lake Imandra); therefore, the proportion of metal speciation within the region varies and is determined by the nature of the elements. Bolshaya Imandra exhibited the greatest amounts of labile ions, in contrast to the non-labile speciation in the other areas.

3.2. Metal content in fish
The metal concentrations in the fish of the examined water lakes are presented in table 3, whereby the concentration of Hg in the water was below the analytical limit. This element accumulates in the kidneys, liver, and muscles of the fish in all the examined lakes, particularly where organic matter is highly concentrated—Lake Pirenga and Lake Okhtozer.

The Cd content is the highest in fish kidneys, as the kidney can be considered as the ‘acceptor’. Cd accumulates in extremely high concentrations in the kidneys of fish in the waters with the lowest salinity, Lake Chuna. Lakes are located in the Chuna Tundra mountains and are subject to the influence of acid deposition from the Severonickel smelter. Let us emphasise that the concentrations of Cd in the waters of Lake Chuna in most samples were very low. Despite the fact that the wastewater from the Severonickel smelter is distributed in Lake Bolshaya Imandra, the Cd content in all fish systems was lower than that in the fish from Chuna Lake, which can be explained by the higher water salinity or competition with other elements.

Pb accumulates in the gills and kidneys of fish from various water systems in similar amounts. The effects of the predominant bioaccumulation of this element in fish in low-salinity waters are also shown.

The Al content in all organs is observed in the fish from Bolshaya Imandra, which receives wastewater from metallurgical and mining production. To a greater extent, Al accumulates in the gills, as found here. However, in rare cases, its content in fish kidneys can reach abnormally high values (up to 500–950 µg g⁻¹, dry weight).

Ni and Cu are markers of the anthropogenic impact of Cu–Ni production. Ni accumulates in the kidneys of fish from Lake Imandra. The fish from Lake Imandra and Lake Chuna are characterised by an abundance of Cu in the liver, owing to the increased contents of these elements in the respective waters.

The presented results show that the bioaccumulation of elements in fish occurring in various organs and tissue depends not only on the concentration of metals in water but also on the number of related exogenous and endogenous factors.

4. Discussion

4.1. The influence of geochemical factors and metal speciation on bioavailability
The concentration of labile metals in the aquatic environment, which may be bioavailable, is often lower than the total content of metals and may vary depending on the influence of a number of geochemical factors. The bioavailability of the elements is influenced by the nature of the ion and the conditions of the aquatic environment, which affect the metal speciation (Amde et al 2017, Bjerregaard and Andersen 2014, Liu et al 2017).

Existing modern models that are used to calculate the metal speciation (e.g. HD-MINTEQ, WHAM, NICA-Donnan, LMWOAs, MITEQ2, and PHREEQC, HCh) are quite universal in assessing the effect of pH, the content of major ions. But the characteristics of the composition of the organic substance (strength and degree of dissociation, coordination number of the complexing agent, etc) and changes in the buffer capacity of the system as a whole under specific zonal conditions, the calculation is not adapted (Koopal et al 2001, Tipping 2002, Dudal and Gérard 2004, Shvarov 2015, Gustaffson 2016). For example, models for the binding of humic substances (Dudal and Gérard 2004, Tipping et al 2015) in soil and swamp waters have been developed to calculate the interaction of organic matter, the main sources
During verification, a reliable correlation between the measured and calculated data (r² = 0.94, p > 0.0001) was obtained, which indicates the justification of using the calculated data.

Figure 2 shows an example of the convergence of the measurement results and model calculations for Cd; similar dependencies were obtained for all the studied elements. This allowed us to use the results of mathematical modelling with confidence to calculate the labile and non-labile speciation of metals.

The proportions of speciation in the waters of the Kola lakes are specific for each metal but are similar in all the studied areas. The quantities of labile metals (averaged data) were calculated as follows:

\[
\text{Sr} (\sim 95\%) > \text{Cd} (\sim 90\%) > \text{Pb} (\sim 76\%) > \text{Ni} (\sim 42\% - 77\%) > \text{u} (\sim 60\%) > \text{Al} (\sim 30\%)
\]

The parameters of water chemistry in the studied areas were characterised by relatively low salinity and contents of the main cations (except Bol’shaya Imandra), which is typical for northern soft waters. Based on these data, we can conclude that the content of the labile elements of various metals was determined primarily by the nature of the ion. However, within

### Table 3. Median and limits of variation (within brackets) of metal concentrations (µg/g dry weight) in the organs and tissues of whitefish caught from different water bodies under study.

| Metal | Bol’shaya Imandra | Iokostrovskaya and Babinskaya Imandra | Lakes Pirenga and Okhtozero | Lake Chuna |
|-------|-------------------|--------------------------------------|-----------------------------|------------|
| Hg    | 0.014 (0.004–0.490) | 0.071 (0.010–0.145) | 0.036 (0.023–0.058) | —         |
| Hg    | 0.095 (0.030–0.568) | 0.152 (0.063–0.578) | 0.214 (0.073–0.713) | —         |
| Hg    | 0.058 (0–0.480)     | 0.161 (0.019–0.503) | 0.123 (0.006–0.382) | —         |
| Hg    | 0.021 (0.005–0.160) | 0.105 (0.010–0.171) | 0.101 (0.019–0.170) | —         |
| Hg    | 0.010 (0.001–0.400) | 0.046 (0.002–0.111) | 0.015 (0.006–0.033) | —         |
| Cd    | 0.12 (0–1.16)       | 0.07 (0–1.09)         | 0.13 (0–0.76)         | 1.06 (0.48–1.49) |
| Cd    | 0.24 (0.01–2.09)    | 0.45 (0.03–1.88)      | 0.78 (0.16–3.02)      | 2.79 (0.52–7.27) |
| Cd    | 1.91 (0.08–16.3)    | 3.17 (0.24–10.1)      | 3.76 (0.76–19.3)      | 27.1 (14.1–38.3) |
| Cd    | 0.004 (0–0.038)     | 0.01 (0–0.39)         | 0.13 (0–0.35)         | 0.01 (0–0.10) |
| Cd    | 0.005 (0–0.088)     | 0.03 (0–0.24)         | 0.03 (0–0.44)         | —         |
| Pb    | 0.20 (0–1.23)       | 0.11 (0–0.70)         | 0.08 (0.01–0.44)      | 0.24 (0.02–3.70) |
| Pb    | 0.06 (0–8.41)       | 0.06 (0.01–0.40)      | 0.07 (0.01–0.97)      | 0.06 (0.03–2.22) |
| Pb    | 0.16 (0–1.93)       | 0.11 (0.01–7.27)      | 0.13 (0–1.21)         | —         |
| Pb    | 0.07 (0–0.81)       | 0.08 (0–0.27)         | 0.04 (0–0.10)         | —         |
| Pb    | 0.08 (0–1.32)       | 0.14 (0.03–0.86)      | 0.09 (0.03–0.15)      | —         |
| Al    | 36.5 (3.26–533)     | 11.4 (2.92–55.9)      | 31.3 (4.34–96.9)      | 20.2 (7.57–32.8) |
| Al    | 19.1 (2.76–112)     | 9.61 (3.74–43.1)      | 8.91 (3.75–46.8)      | 8.68 (4.69–65.8) |
| Al    | 15.9 (3.45–147)     | 22.5 (2.87–59.2)      | 23.2 (8.08–540)       | 31.0 (13.5–75.4) |
| Al    | 4.70 (0.68–39.0)    | 1.91 (0.88–5.71)      | 4.61 (0.89–17.5)      | 3.03 (1.13–9.66) |
| Al    | 14.4 (2.90–123)     | 11.4 (3.04–41.2)      | 40.7 (5.94–77.3)      | 12.5 (5.75–34.2) |
| Sr    | 168 (96.9–254)      | 149 (103–207)         | 161 (53.7–216)        | 57.6 (37.6–64.6) |
| Sr    | 3.64 (1.26–57.3)    | 1.98 (0.83–16.1)      | 1.61 (0.32–9.86)      | 0.51 (0.05–2.77) |
| Sr    | 5.40 (1.81–830)     | 6.27 (0.75–20.6)      | 5.85 (1.72–17.9)      | 2.39 (0.83–28.2) |
| Sr    | 11.0 (0.60–47.4)    | 3.57 (0.55–20.6)      | 9.15 (0.72–32.3)      | 3.30 (0.17–7.10) |
| Sr    | 654 (363–1088)      | 521 (362–783)         | 676 (274–1112)        | 217 (152–267)  |
| Cu    | 2.69 (0.33–8.86)    | 2.02 (0.77–3.12)      | 0.80 (0.18–8.77)      | 0.55 (0.37–1.20) |
| Cu    | 1.23 (0.33–8.86)    | 1.43 (0.45–5.41)      | 0.44 (0.09–0.82)      | 0.18 (0.07–0.64) |
| Cu    | 7.21 (1.73–27.9)    | 6.58 (2.69–27.9)      | 1.48 (0.60–2.48)      | 3.22 (1.02–5.29) |
| Cu    | 0.67 (0.04–3.80)    | 0.92 (0.27–1.91)      | 0.52 (0.05–1.45)      | 0.12 (0.09–0.18) |
| Cu    | 1.92 (0.41–8.17)    | 4.34 (0.77–6.87)      | 1.46 (0.12–13.3)      | 0.25 (0.13–0.39) |
| Cu    | 2.71 (1.10–15.8)    | 1.78 (0.89–7.04)      | 1.50 (0.91–3.66)      | 2.88 (1.91–9.23) |
| Cu    | 30.5 (8.42–249)     | 31.7 (3.03–145)       | 19.6 (11.5–55.1)      | 81.0 (9.00–245) |
| Cu    | 6.06 (1.66–11.0)    | 5.60 (2.09–32.0)      | 2.91 (2.18–9.68)      | 10.6 (5.38–43.4) |
| Cu    | 0.78 (0.51–2.80)    | 0.87 (0.49–1.33)      | 0.65 (0.43–1.93)      | 1.07 (0.48–1.55) |
| Cu    | 2.72 (0.75–4.53)    | 1.08 (0.38–5.87)      | 0.54 (0.26–1.19)      | 0.84 (0.53–1.18) |
the 22 water areas studied, there was some variability in salt content, organic matter, and metal concentration (see table 1), which was reflected in the proportion of the elemental speciation. The highest variability of the speciation in water was observed for Ni, and the concentration of labile Ni was higher in the polluted parts of the lake (see table 2).

4.2. Penetration of metals in fish and bioaccumulation

In freshwater systems, bioavailability is controlled by competition with other cations for complex formation on the surface of the gill epithelium (Fortin et al 2010, Gandhi et al 2011, Mykolenko et al 2018). We understand that in natural waters, along with the penetration of metals from water through the gill apparatus and skin, elements are also absorbed by food. As a rule, invertebrates that fish feed on live freely in polluted waters and also accumulate metals. This indirect path is determined by similar patterns regarding the influence of geochemical environmental conditions on living organisms, primarily by the speciation of metals.

The most common approach for determining the bioavailability of free metal ions is to consider their active penetration. Therefore, a number of models calculate the penetration of labile metals (free ion activity model), which depends on the parameters of the aquatic environment (Smith et al 2015, 2018). These models combine chemical speciation with the process of cation competition for biotic ligands, in which the mixture of metals and the additive properties of metal toxicity are considered (Magalhaes et al 2015, Perez and Hoang 2017).

In our results, the variability of geochemical conditions was not significant; therefore, the proportions of labile and non-labile speciation were similar for a given metal in different lakes but significantly different for different metals. There are a number of issues concerning the applicability of BLM to fresh, soft, and ultra-soft waters. For example, half of the approximately 1 500 lakes and rivers examined in Sweden were outside the BLM calibration in terms of pH, DOC, and particularly, carbonate alkalinity. When testing the three different BLM of Cu toxicity available today, large and statistically significant differences among the model results were obtained. The greatest difference in the calculated predicted concentrations without toxic effects was obtained for low-hardness water (Hoppe et al 2015).

Fish are good indicators of the pollution level due to heavy metals in the aquatic ecosystem and their impact on human health. During the period of severe pollution (1980–1990 years) of the Kola lakes, there were mass fish diseases (e.g. nephrocalcitos, lipid liver degeneration, cirrhosis, anaemia, and scoliosis). The accumulation of heavy metals in fish has been correlated with the aetiology of many diseases (Moiseenko and Kudryavtseva 2001). More recent studies have shown that the prevalence of disease in the population in the region is caused by the consumption of drinking water with increased concentrations of metals in soft and ultra-soft waters. The transport of heavy metals from drinking water into humans and its effect manifested as liver and kidney diseases demonstrates a close relationship between fish and human pathology (Moiseenko et al 2018).
In recent decades, pollution of Lake Imandra has decreased, and high concentrations of metals in the water have not been detected. Gashkina et al (2020) explored the fish response of metal bioaccumulation to reduced toxic loads by metals in long-term-contaminated Lake Imandra. Fish diseases were not observed; however, there was a change in the metabolism of both essential and non-essential elements. This phenomenon is explained by the adaptation of fish populations to the presence of long-term water pollution by metals and the regulation of the processes of absorption and removal of not only toxic but also essential elements.

4.3. Features of different metal accumulations in fish

Low calcium concentrations in Arctic lakes cause organisms to be more vulnerable to metals. Unlike in experiments, in natural conditions, many accompanying factors increase or decrease the penetration ability of hazardous substances. We used multiple regression to understand the influence of environmental factors and metal speciation on bioavailability and penetration (in situ). The metal content in the examined organ (µg g⁻¹ dry weight) was used as a dependent parameter, while metal content in water (inorganic and organic form, µg l⁻¹), pH, hardness (mg l⁻¹), and DOC (mg l⁻¹) were used as variables. In our studies, the variability of geochemical conditions was not significant; therefore, the proportions of labile and non-labile speciations were similar for a particular metal in different lakes but significantly different for different metals.

4.3.1. Mercury.

The global effects of Hg transfer to the Arctic regions are widely known (AMAP/UNEP 2013). As early as the 1990s, the enrichment of a variety of hazardous elements, including Hg, in the northern chesmohere was noted (Norton et al 1990). The accumulation of Hg in freshwater fish in the northern regions has been demonstrated (Gochfeld 2003).

Our studies revealed a reliable correlation between the accumulation of Hg in fish organs and the DOC content in water and low pH values.

\[
\text{Hg}_{\text{gills}} = 0.0075 \times \text{DOC} - 0.089 \\
\times \text{pH} + 0.627, r = 0.651 \tag{5}
\]

\[
\text{Hg}_{\text{skeleton}} = 0.0036 \times \text{DOC} - 0.123 \times \text{pH} \\
+ 0.0059 \times \text{Hardness} + 0.744, r = 0.632. \tag{6}
\]

The Hg content in gills likely reflects the deposition of methyl–organic complexes on the gills, whereas the accumulation of Hg in the skeleton indicates the internal metabolism and accumulation of this element in bone tissue, as a result of prolonged exposure of fish to increased doses of methyl–organic complexes. The effect of water enrichment with organic matter on the degree of Hg penetration into fish was demonstrated in this study. Moiseenko and Gashkina (2016), performing studies in the European territory of Russia (from tundra to steppe zones), also revealed a correlation between high concentrations of Hg in fish liver and DOC content in water.

To assess Hg speciation and its contribution to bioavailability, the following conditional modelling was carried out. We do not have data on the Hg content in water owing to its low concentrations (below the detection limit of our device, approximately 0.01 µg l⁻¹). However, according to our data on the content of this element in fish organs, Hg may reach a concentration of 0.7 µg g⁻¹ dry weight. Based on the literature (Gochfeld 2003) and our data, we can say that the role of organic speciation of this element (up to 99% connection with aqueous humic substances) is important in terms of penetration.

We conducted a conditional simulation, assuming that the level of element concentration in water fluctuates near 0.01 µg l⁻¹ (the maximum level for determining the element concentration by the indicated methods, with a maximum error of 20% and organic matter constitutes 97%–99% of the total matter. Next, multidimensional scaling (RDA) was carried out, which revealed a reliable affinity for the Hg-organic anion in all organs of fish (figure 3).

Notably, in the results of the present study, the DOC content variations were insignificant, and there were no sources of water pollution with Hg in the Kola region. The accumulation of Hg in fish is associated with transboundary atmospheric transfer to the northern regions and its inclusion into biogeochemical cycles. It has also been demonstrated that lower pH contributes to the activation of Hg bioavailability. Biogeochemical reactions alter Hg, transforming it into the most toxic form, methylmercury (MMHg), which primarily accumulates in the gills. MMHg is highly toxic and poses a serious problem for a number of European countries due to mercury accumulation in freshwater fish (Moiseenko and Gashkina 2016).

4.3.2. Lead.

Pb, owing to its high similarity in penetration to that of Ca, is being absorbed by the gills of freshwater fish through the apical Ca channel and transferred by the basolateral Ca, adenosine triphosphatase (Wood 2001). It was shown that the Kola waters contain low concentrations of this element, and Pb varies considerably, exhibiting no relation to the stream of industrial wastewater. For the most part, it is present in lakes in labile speciation (over 70%). Its contents in the gills, kidneys, muscles, and skeleton are correlated with each other, confirmed by a reliable relationship with the total content in water (r > 70, p = 0.001). This indicates that Pb is a bioavailable species and
Figure 3. RDA-ordination diagram for model system (Hg in water, Hg in fish): points indicate dependent variables, vectors indicate the independent variables.

accumulates in all organs, dependent on the total concentration in water ($r > 80, p = 0.05$).

Previous studies on Pb bioaccumulation in a number of water reservoirs in the European area of Russia have shown that among organs, Pb accumulates in the largest quantities in the kidneys of fish; among fish species, in perch and whitefish living in the less mineralised waters of the North (Moiseenko 2015), which is consistent with the data obtained.

RDA confirmed the close connection between the contents of Pb in labile speciation in water and the concentrations of the elements in the organs and tissues of fish (figure 4). The data obtained show that when water is contaminated with Pb, it penetrates into all organs, with labile speciation exhibiting the highest penetrating power.

4.3.3. Cadmium.
Cd metabolism is closely related to essential elements; especially Zn. Cd can replace Zn in many vital enzymatic reactions, leading to their stoppage and inhibition (Brzoska and Moniuszko-Jakoniuk 2001). Wood (2001) suggested that the primary mechanism of Cd toxicity may be associated with the inhibition of Ca transfer by proteins; in fact, hypocalcaemia is the most common hypothesis to explain the acute toxic effects of Cd.

This paper provides examples of the influence of labile metal speciation on its bioavailability, which is reflected in the reliable relationships between the Cd content in the gills and that in the kidneys of fish with its ionic form and inverse proportionality to water hardness.

$$
\begin{align*}
\text{Cd}_{\text{gills}} &= 2.84 \times \text{Cd}_{\text{inorg}} + 0.66 \times \text{pH} - 0.040 \\
&\quad \times \text{Hardness} - 3.76, \quad r = 0.763
\end{align*}
$$

$$
\begin{align*}
\text{Cd}_{\text{kidney}} &= 6.32 \times \text{pH} - 0.94 \\
&\quad \times \text{Hardness} - 19.3, \quad r = 0.749
\end{align*}
$$

The data of Cullen and Maldonado (2013) show that labile Cd has the highest bioavailability, which corresponds to our data. It has been shown that this element is mainly targeted to the kidneys of fish (Moiseenko and Gashkina 2018). RDA also showed high affinity to this element in labile speciation to fish (figure 4), which indicates the active accumulation of this element, even at low elemental concentrations in water.

Satarug et al (2010) showed that small doses of Cd lead to accumulation in human lungs, kidneys, and adrenal glands, causing renal pathology. Similar patterns are commonly demonstrated for the population of the Kola region, which consumes low-salinity water.
with slightly increased Cd concentrations (Moiseenko et al 2018). Water hardness is worth highlighting separately. A reliable inverse relationship between the Cd content in the gills, liver, kidneys, skeleton of trout of the Kola region, and Ca concentration in water has been established. Owing to the significant importance of water hardness to the bioavailability of this metal in Canada, the GL standard (CCME (Canadian Council of Ministers of the Environment) 2007) depends on water hardness. For example, when the content of \( \text{CaCO}_3 \) (mg l\(^{-1}\)) in water reaches as high as 60, the allowable content of Cd is 0.2 \( \mu \text{g l}^{-1} \); at higher \( \text{CaCO}_3 \) contents, these values increase. Therefore, the bioavailability of Cd is determined by both its concentration in the water, characteristic of its ionic form, and the hardness of the water, determined by the Ca content. In our studies, the water hardness was in the range of 6–31 mg l\(^{-1}\).

4.3.4. Aluminium.

Similar regularity was found for Al; its content in the gills was dependent on the labile metal content in water. Our field data show great influence on the bioaccumulation of labile speciation of this element as well as inverse correlation with water hardness.

\[
\text{Al}_{\text{gills}} = 1.61 \times \text{Al}_{\text{org}} - 0.36 \times \text{Al}_{\text{org}} + 74.0 \times \text{pH} - 2.35 \times \text{Hardness} - 469, \ r = 0.650. \tag{9}
\]

Figure 4. RDA-ordination diagram for model system: points indicate dependent variables, vectors indicate the independent variables.

The major consequences of fish exposure to aluminium are as follows: impaired respiratory function, violation of ion and osmoregulation due to the deposition of aluminium on the gill surface, intercellular accumulation of Al, etc (Wilson 2012). Our studies and the revealed dependences exemplified by natural water reservoirs show a correlation with the inorganic forms of this element, which dominate in aquatic environments.

4.3.5. Strontium.

Sr is predominantly found in labile speciation in water, a characteristic of the alkaline earth group (Boyer et al 2018). Sr can replace calcium in metabolic processes, leading to bone base pathologies (Martín del Campo et al 2019). Notably, the highest Sr content in fish was found in the Bolshaya Imandra areas, which are affected by effluents from ore-enrichment and processing plants. Fish from lakes with high Sr concentrations in water are characterised by bone tissue pathologies such as scoliosis and osteoporosis, which are manifested in the backbone curvature and absence of normal cranium calcification (Moiseenko and Kudryavtseva 2001). In these studies, the maximum Sr was accumulated in the bone base of fish from the Bolshaya Imandra areas. Our studies have confirmed that its accumulation in the kidneys depends on the concentration of the
The content of Sr in the liver and muscles is much lower than that in the bone base. However, with respect to the 'normal values', the high level of Sr accumulation is noted. With increasing levels in water, Sr accumulates in all systems of fish (Moiseenko and Kudryavtseva 2001).

4.3.6. Nickel.
This element is found in high concentrations in the water of the lakes of the Kola region, owing to the activities of the 'Severonickel' non-ferrous-metals processing facility. Fish kidneys have been demonstrated to contain the greatest accumulating ability with respect to Ni. This leads to the development of fibroelastosis and nephrocalcinosis as anthropogenically determined fish endemic pathologies, as indicated by Moiseenko and Kudryavtseva (2001).

This study has shown that the Ni content in the gills is determined by the organic speciation of this element. It is possible that its organic form is retained in the gills, whereas the labile speciation penetrates the body and accumulates in the kidneys. The highest inorganic nickel content is typical for the contaminated waters of Bolshaya Imandra. As the effluent of contaminated water spreads, the content of labile speciation decreases to 50% of its total concentration, owing to complex formation processes.

\[ \text{Sr}_{\text{kidney}} = 0.142 \times \text{Sr}_{\text{inorg}} - 1.49, \quad r = 0.61. \]  

\[ \text{Ni}_{\text{gills}} = 0.676 \times \text{Ni}_{\text{org}} - 0.058 \times \text{DOC} + 1.68, \quad r = 0.64 \]  

\[ \text{Ni}_{\text{kidney}} = 0.504 \times \text{Ni}_{\text{org}} + 3.76, \quad r = 0.69. \]  

For labile Ni, RDA revealed the highest affinity to all organs, except gills. Meanwhile, the natural correlation between the non-labile speciation of Ni and metal content in gills is confirmed by the reliable affinity. The results indicate the contribution of sulphate- and hydroxo-inorganic complexes of Ni (figure 5).

4.3.7. Copper.
Cu is characterised by a high complex formation ability (McGeer et al 2002). The accumulation of Cu in fish increases when copper is present in labile speciation, that is, in low-mineralised and anthropogenically acidified waters. In the presence of humic acids of allochthonous origin, Cu is inactivated and its accumulation in fish decreases (Fortin et al 2010).

The experiments of McGeer et al (2002) showed that, like Cu content in water, the addition of organic chelates sharply reduced the effect of the bioaccumulation of Cu in the gills and liver of rainbow trout, that is, its bioavailability. Thus, in coloured and humus-rich waters, the bioavailability of
Cu for fish is reduced. This phenomenon was clearly evident in the study of fish from the Kola north lakes.

\[
\text{Cu}_{\text{gills}} = 0.95 \times \text{Cu}_{\text{inorg}} + 2.95 \times \text{pH} - 0.20 \\
\times \text{Hardness} - 0.059 \times \text{DOC} - 15.2, r = 0.73,
\]

(13)

\[
\text{Cu}_{\text{liver}} = 5.47 \times \text{Cu}_{\text{inorg}} - 3.03 \times \text{Hardness} \\
- 0.93 \times \text{DOC} + 106, r = 0.62,
\]

(14)

\[
\text{Cu}_{\text{skeleton}} = 0.57 \times \text{Cu}_{\text{inorg}} - 0.08 \times \text{Hardness} \\
- 0.097 \times \text{DOC} + 3.84, r = 0.81.
\]

(15)

Under our conditions, the content of non-labile Cu is only slightly less than that of the inorganic form. It also confirms More active accumulation of labile speciation of Cu in the ‘acceptor’ organ, the liver, is typical for low-mineralised waters and low concentration of Ca, which is confirmed by the direct correlation with the Cu ion content in water and reverse correlation with water hardness. Accordingly, the content of organic matter is also inversely related—higher content of humic substances corresponds to more active processes of complex formation and smaller labile Cu proportion. Cu content in organs is characterised by a statistical proximity to its labile speciation (figure 5). Aqua-ionic and hydrated speciation play a predominant role in the statistical affinity for Cu.

A study of the bioaccumulation of Cu in fish in the areas of influence of Cu–Ni-containing wastewater at different distances showed that as the Cu content in water increased to 8–10 µg l\(^{-1}\), the accumulation of Cu increased in the liver and kidneys. At higher concentrations in water, a significant decrease in the copper content of liver was observed, which is explained by the pathological degeneration of this organ involving the destruction of enzyme systems due to toxic effects (Moiseenko and Kudryavtseva 2001).

5. Conclusion

The growing volumes of metals entering freshwater require new approaches to assess the danger of their accumulation to aquatic life and human health. The bioavailability of elements for fish and their predominant bioaccumulation were demonstrated, exemplified by the soft lake waters of the Kola region. Elemental bioavailability depends on the nature of the metal and the aquatic environment, which affects the metal speciation. The global scientific community has paid the most attention to such dangerous elements as Hg, Cd, and Pb. In the waters of the studied areas, the Hg content was very low, whereas the accumulation of this element in the organs and tissue of fish indicated contamination of this region by Hg. With respect to Cd, the main target function is the kidneys of fish. RDA demonstrated a high affinity of labile Cd to all the organs of the fish, which indicates the active accumulation of this element, even at extremely low concentrations in water. Pb is mostly represented by labile speciation (over 70%) in lakes. In water, Pb is in bioavailable form and accumulates in all body systems of fish, dependent on the total concentration in water. RDA confirmed the close relationship between the contents of the labile form of Pb in organs and tissues and its penetrability.

The accumulation of Al in the gills was found to be dependent on the labile metal content in water. Sr in water was found to be predominantly in labile speciation, which is a characteristic of the alkaline earth group. Accompanying Ca, this element was found to accumulate in the greatest amount in the skeleton but was also found in other organs of fish.

Ni and Cu are markers of water contamination from wastewater and air emissions from non-ferrous metallurgy facilities. Here, Ni had the higher variability, in which the concentrations of its labile forms increased in polluted water bodies. RDA revealed the highest affinity to labile Ni for all organs except gills. Cu is characterised by high complex-formation ability. The accumulation of Cu in fish increased under conditions in which Cu is present in the ion speciation, that is, in anthropogenically acidified waters. In soft waters, there was more active accumulation of labile Cu in the ‘acceptor’ organ, the liver.

In general, it can be argued that the ionic speciation of the majority of the elements is more active for most elements, in terms of their bioavailability in low-salinity water. However, it should be noted that exceptions include the penetration of methylmercury as a bioavailable speciation. Nevertheless, for the gills of fish, a higher accumulation of several non-labile elements (e.g. Pb, Al, and Cu) was revealed, which can possibly be explained by the gills serving as an organ barrier, preventing toxic elements from penetrating the fish. Thus, studies on subarctic lakes showed a higher risk of soft water pollution by metals, due to their low hardness and high bioavailability of heavy metals for aquatic life. This requires a correction of the adopted MPC standard by at least a factor of three for the surface water of circumpolar areas.

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References

Amde M, Liu J, Tan Z and Bekana D 2013 Transformation and bioavailability of metal oxide nanoparticles in aquatic and terrestrial environments. A review Environ. Pollut. 230 250–7

Arctic Monitoring and Assessment Programme (AMAP), UNEP Chemicals 2013 Technical background report for the global mercury assessment Arctic Monitoring and Assessment Programme, ed Norway/UNEP Chemicals Branch (Geneva: AMAP) p 263

Bjerregaard P and Andersen O 2014 Ecotoxicology of metals - sources, transport, and effects in the ecosystem Handbook on the Toxicology of Metals, ed G F Nordberg, B A Fowler and M Nordberg (New York: Academic) pp 79–100

Boyer A, Ning P, Killey D, Klukas M, Rowan D, Simpson A J and Passeport E 2018 Strontium adsorption and desorption in wetlands: role of organic matter functional groups and environmental implications Water Water Res. 133 27–36

Brezosa M M and Moniuszko-Jakoniuk J 2001 Interaction between cadmium and zinc in the organism Food Chem. Toxicol. 39 967–80

CCME (Canadian Council of Ministers of the Environment) 2007 A Protocol for the Derivation of Water Quality Guidelines for the Protection of Aquatic Life (Winnipeg: National Guidelines and Standards Office)

Cullen J T and Maldonado M T 2013 Biogeochemistry of CCME (Canadian Council of Ministers of the Environment) 2007 Substances in the Field of Water Policy. 2013/39/EC Directives 2000/60/EC and 2008/105/EC as Regards Priority for the Water Framework Directive.

Dinu M I 2015 Chapter 5 – Influence of Humus substances and their biospheric properties Earth-Sci. Rev. 199–216

Dinu M I 2017 Formation of organic substances of humus nature and their biopspheric properties Geochem. Int. 55 911–26

Dinu M I and Moiseenko T I 2015 Certificate for a computer program «ACIDFORMMET» 2015-617036

Duda T and Gérad G 2004 Accounting for natural organic matter in aqueous chemical equilibrium models: a review of the theories and applications Earth-Sci. Rev. 66 199–216

Durbin J and Watson G S 1951 Testing for serial correlation in least squares regression II Biometrika 38 159–79

Eaton A, Arnold E, Archie A E, Rice E W and Clesceri L S 1992 Standard Methods for the Examination of Water and Wastewater 17th edn (Washington, D.C: American Public Health Association (APHA))

Ediagbonya T F, Nemna E E, Nwachukwu P C and Teniola O D 2015 Identification and quantification of heavy metals, anions and colloids in water bodies using enrichment factors Environ. Anal. Chem. 2 146

European Commission 2011 Common Implementation Strategy for the Water Framework Directive. Technical Guidance for Deriving Environmental Quality Standard. (Brussels: European Communities)

European Commission 2013 Directive 2013/39/EC Amending Directives 2000/60/EC and 2008/105/EC as Regards Priority Substances in the Field of Water Policy. 2013/39/EC (Brussels: European Commission)

Fortin C, Couillard Y, Vigneault B and Campbell P G C 2010 Determination of free Cd, Cu and Zn concentrations in lake waters by in situ diffusion followed by column equilibration ion-exchange Aquat. Geochem. 16 151–72

Gandhi N, Diamond M L, Hujibregts M A I, Guinée J B, Peijnenburg W J G M and Van De Meent D 2011 Implications of considering metal bioavailability in estimates of freshwater ecotoxicity: examination of two case studies Int. J. Life Cycle Assess. 16 774–87

Gashkina N A, Moiseenko T I and Kudryavtseva L P 2020 Fish response of metal bioaccumulation to reduced toxic load on long-term contaminated Lake Imandra Ecotoxicol. Environ. Saf. 191 110205

Goechfeld M 2003 Case of mercury exposure, bioavailability and absorption Ecotoxicol. Environ. Saf. 56 174–9

Gustaffson J 2016 Visual MINETEQ Version 3.1. http://vmineteq.lwr.kth.se/download/

Hoppe S, Gustaffson J P, Borg H and Breitholtz M 2015 Evaluation of current copper bioavailability tools for soft freshwaters in Sweden Ecotoxicol. Environ. Saf. 114 143–9

Koopal L K, Willem H, Riemsdijk W H and Kinniburgh D G 2001 Humic matter and contaminants. General aspects and modeling metal ion binding Pure Appl. Chem. 73 2005–16

List of Fishery Standards 1999 Maximum Permissible Concentrations (MPC) and Approximate Safe Levels of exposure (ASLE) of Toxic Substances for Fishery Water Basins: 1999 (VNIRO, Moscow) (in Russian)

Liu Y, Du Q, Wang Q, Yu H, Liu J, Yu, T. Ch, and Lei J 2017 Causal inference between bioavailability of heavy metals and environmental factors in a large-scale region Environ. Pollut. 226 370–8

Magalhães D, Marques M, Baptista D, Forsin D and Buus D 2015 Metal bioavailability and toxicity in freshwaters Environ. Chem. Lett. 13 69–87

Martin-del-campo M, Sampedro J, Flores-Cedillo M L, Rosales-Ibáñez R and Rojo I. 2019 Bone regeneration induced by strontium folate loaded biohybrid scaffolds Molecules 24 1660

McGeer J C, Szebedinszky C, Mcdonald D G and Wood C M 2002 The role of dissolved organic carbon in moderating the bioavailability and toxicity of Cu to rainbow trout during chronic waterborne exposure Comp. Biochem. Physiol. C: Toxicol. Pharmacal. 133 147–60

Merrington G, Peters A and Schlekat C E 2016 Accounting for metal bioavailability in assessing water quality: a step change? Environ. Toxicol. Chem. 35 257–65

Moiseenko T I 2015 Impact of geochemical factors of aquatic environment on the metal bioaccumulation in fish Geochim. Int. 53 213–23

Moiseenko T I, Dinu M I, Gashkina N A and Kremenleva T A 2019 Aquatic environment and anthropogenic factor effects on distribution of trace elements in surface waters of European Russia and Western Siberia Environ. Res. Lett. 14 065010

Moiseenko T I and Gashkina N A 2016 Bioaccumulation of mercury in fish as indicator of water pollution Geochim. Int. 54 485–93

Moiseenko T I and Gashkina N A 2018 Biogeochemistry of Cadmium: anthropogenic dispersion, bioaccumulation, and ecotoxicity Geochim. Int. 56 798–811

Moiseenko T I and Kudryavtseva L P 2001 Trace metal accumulation and fish pathologies in areas affected by mining and metallurgical enterprises in the Kola Region, Russia Environ. Pollut. 114 285–97

Moiseenko T I, Morgunov B A, Gashkina N A, Megorskiy V V and Pesiakov A A 2018 Ecosystem and human health assessment in relation to aquatic environment pollution by heavy metals: case study of the Murmansk region, northwest of the Kola Peninsula, Russia Environ. Res. Lett. 13 065005

Mykolenko S, Liedienov V, Kharytonov M, Makieieva N, Kulitish T, Queralt M E, Hidalgo M, Pardini G and Gispert M 2018 Presence, mobility and bioavailability of toxic metal (oids) in soil, vegetation and water around a Pb-Sb recycling mining and metallurgical enterprises in the Kola Region, Russia Environ. Pollut. 285–97

Mykolenko S, Liedienov V, Kharytonov M, Makieieva N, Kulitish T, Queralt M E, Hidalgo M, Pardini G and Gispert M 2018 Presence, mobility and bioavailability of toxic metal (oids) in soil, vegetation and water around a Pb-Sb recycling mining and metallurgical enterprises in the Kola Region, Russia Environ. Pollut. 285–97

Nordberg G F, Fowler B A and Nordberg M (eds) 2014 The role of dissolved organic carbon in moderating the bioavailability and toxicity of Cu to rainbow trout during chronic waterborne exposure Comp. Biochem. Physiol. C: Toxicol. Pharmacal. 133 147–60

Pesiakova A A 2018 Ecosystem and human health assessment in relation to aquatic environment pollution by heavy metals: case study of the Murmansk region, northwest of the Kola Peninsula, Russia Environ. Res. Lett. 13 065005

Passeport E 2018 Strontium adsorption and desorption in wetlands: role of organic matter functional groups and environmental implications Water Water Res. 133 27–36

Peijnenburg W J G M and Van De Meent D 2011 Implications of considering metal bioavailability in estimates of freshwater ecotoxicity: examination of two case studies Int. J. Life Cycle Assess. 16 774–87

Popp J C, Szebedinszky C, Mcdonald D G and Wood C M 2002 The role of dissolved organic carbon in moderating the bioavailability and toxicity of Cu to rainbow trout during chronic waterborne exposure Comp. Biochem. Physiol. C: Toxicol. Pharmacal. 133 147–60

Rogers E H, Churchill D A, Hanton N and Lloyd D R 1990 The history of atmospheric deposition of Cd, Hg and Pb in North America: evidence from lake and peat bog sediments Acidic Precipitation. Sources, Deposition and Caution Interactions, ed A L Lindberg, A L Page and S A Norton (New York: Springer) pp 73–101
Nriagu J O 1996 A history of global metal pollution Science 272 223–4
Pacyna J M and Pacyna E G 2011 An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide Environ. Rev. 9 269–98
Perez E and Hoang T 2017 Chronic toxicity of binary-metal mixtures of cadmium and zinc to Daphnia magna Environ. Toxicol. Chem. 99 1–11
Rodyushkin V, 1995. Candidate’s Dissertation in Geography (Inst. Ozerovedeniya, St. Petersburg, 1995) (in Russian)
Satarug S, Garrett S H, Sens M A and Sens D A 2010 Cadmium, environmental exposure, and health outcomes Environ. Health Persp. 118 82–190
Shvarov Y 2015 A suite of programs, OptimA, OptimB, OptimC, and OptimS compatible with the Unitherm database, for deriving the thermodynamic properties of aqueous species from solubility, potentiometry and spectroscopy measurements Appl. Geochem. 55 17–27
Smith K S, Balistrierib L S and Todd A S 2015 Using biotic ligand models to predict metal toxicity in mineralized systems Appl. Geochem. 57 55–72
Snuderl K, Simonic M, Mocak J and Brodnjak-Voncina D 2007 Multivariate date analysis of natural mineral waters Acta Chimica Slovenica (ACS) 54 33–39
Tipping E 2002 Cation Binding by Humic Substances (New York: Cambridge University Press) p 512
Tipping E, Lofs S and Stockdale A 2015 Metal speciation: modeling and measurement Environ. Chem. 15 115–30
U.S. EPA 2004 National Recommended Water Quality Criteria. Report 4304T EPA/600/4-91/002 (Springfield, VA: EPA)
U.S. EPA 2007 National Recommended Water Quality Criteria. Report 4304T EPA/600/4-91/002 (Springfield, VA: EPA)
Vääänänen K, Leppänen M T, Chen X and Akkanenaa J 2018 Metal bioavailability in ecological risk assessment of freshwater ecosystems: from science to environmental management Ecotoxicol. Environ. Saf. 147 430–46
Wijdevelda A J, Schipper C A and Heimovaara T J 2018 Variation in the availability of metals in surface water, an evaluation based on the dissolved, the freely dissolved and Biotic Ligand Model bioavailable concentration Catena 166 260–70
Wilson R W 2012 Aluminium Homeostasis and Toxicology of Non-Essential Metals, ed C M Wood, A P Farrel and C J Brauner (New York: Academic) pp 67–123
Wood C M 2001 Toxic responses of the gill Target Organ Toxicity in Marine and Freshwater Teleosts, ed D Schlenk and W H Benson (London: Taylor and Francis) pp 1–89
Wood C M 2011 An introduction to metals in fish physiology and toxicology: basic principles Homeostasis and Toxicology of Essential Metals-Fish Physiology, ed C M Farrell, A P Brauner and C J Wood (San Diego: Elsevier) pp 1–51
Wood C M, Farrell A P and Brauner C J (eds) 2012a Fish Physiology: Homeostasis and Toxicology of Essential Metals, vol 31A (New York: Academic) p 520
Wood C M, Farrell A P and Brauner C J (eds) 2012b Fish Physiology: Homeostasis and Toxicology of Non-Essential Metals, vol 31B (New York: Academic) p 507