

Original Research

## Geochemical Assessment of the Modern Sediments of a Lake in the North of Russia

Zakhar Slukovskii <sup>1,2,\*</sup>, Tatiana Shelekhova <sup>2</sup>

1. Institute of the North Industrial Ecology Problems of Kola Science Center of RAS, Academgorodok Str. 14a, Apatity, Russia; E-Mail: [slukovsky87@gmail.com](mailto:slukovsky87@gmail.com)
2. Institute of Geology, Karelian Research Centre of RAS, Pushkinskaya Str. 11, Petrozavodsk, Russia; E-Mail: [shelekh@krc.karelia.ru](mailto:shelekh@krc.karelia.ru)

\* **Correspondence:** Zakhar Slukovskii; E-Mail: [slukovsky87@gmail.com](mailto:slukovsky87@gmail.com)

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### Abstract

Core sediment (sapropel) samples were collected from Lake Okunozero, the Republic of Karelia, Russia, to assess the distribution of heavy metals and their main fractions, probable sources of pollution, and potential ecological and toxicological risks for the water body. Heavy metal concentrations were measured by the mass spectrometry method using an XSeries-2 ICP-MS. The sequential extraction of heavy metals from sapropel samples was performed using the scheme of Tessier. According to the Russian Interstate Standard (GOST), the sapropel of Lake Okunozero is suitable for use in agriculture. The exceedances of the regional background levels were detected only for Pb and Cd. In accordance with Pollution Load Index (PLI) and Potential Ecological Risk (RI), no ecotoxicological risk in researched sediments was found. A significant correlation between some investigated heavy metals was established. Most heavy metals were in the insoluble mineral phase (Mn et al.) or were associated with organic matter (Cu, Zn, Mo, Ni). Only Mn, Zn, Cd, and Pb were found in the available fraction from 13 to 24% of the total metal content in the sediments. Other metals were less associated with the available fraction.



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## Keywords

Small lakes; freshwater sediments; sapropel; heavy metals; a fraction of pollutants; Republic of Karelia

## 1. Introduction

The territory of Karelia is a land rich in lakes. Nearly 61 thousand lakes are registered in Karelia, most classified as small lakes with a surface area of no more than 1 km<sup>2</sup> [1]. Of great value is sapropel, which is formed in significant quantities at the bottom of Karelian lakes.

Sapropel (or Gyttia) is a type of fine-grained and loose freshwater sediment [2]. Usually, sapropel is formed in a relatively anoxic environment due to physicochemical and biochemical transformations of lake aquatic inhabitants with the participation of various mineral compounds and organic matter. The organic matter of sapropel, which may be autochthonous and/or allochthonous, comprises more than 15% of the total sediment mass [3]. The autochthonous organic matter is formed due to the death of plants and animals in the water and their deposition to the bottom. The allochthonous organic matter is the organic substance, which enters the waterbody from the surrounding catchment area.

The wide distribution of sapropel and the features of its chemical composition make these organic sediments an important natural resource that can be used in various economic sectors—agriculture, livestock and poultry, land reclamation, building material industry, medicine, drilling equipment, and the development of modern biotechnology [4]. Sapropel is very popular as a therapeutic mud, successfully used in medical practice to treat various diseases [5].

Earlier research on the stock valuation of sapropel was carried out in 215 small lakes of Karelia. The sediments of this raw material were revealed only in 164 lakes, the total square of which is 43 thousand m<sup>2</sup>, with total geological reserves and resources of about 33.4 million tons [6]. Most of the studied lakes suitable for the extraction of sapropel are located in the southern part of Karelia, where the infrastructure is more developed in comparison with other parts of the region. Thus, the extraction of sapropel in this area may be effective for the economy.

The researchers who studied sapropel for a long time, including Soviet and early Russian periods, evaluated only such parameters as the depth of lakes, the useful thickness of sapropel, ash content, pH, CaO, and Fe<sub>2</sub>O<sub>3</sub> concentrations, and other less common parameters. Many important indicators to assess perspectives of using the lake sapropel of Karelia were not researched. One such parameter is the content of heavy metals.

It is worth noting that the accumulation of heavy metals in sediments of small water bodies is one of the global problems for the European North of Russia [7-10]. Although the maximum concentrations of heavy metals are generally noted in the objects located near particular anthropogenic sources, there is a risk of contamination of objects located in background territories due to the factor of long-range transport of atmospheric pollutants [11, 12].

Any ecosystem, e.g., lake ecosystem, is a complex living mechanism with bound elements. In this sense, the sediments are not the final point of pollutant migration, because many organisms use sediments for living and eating [13]. The accumulation of heavy metals by living organisms is usual in conditions of anthropogenic impact [14, 15]. As a result of such accumulation, the degradation of

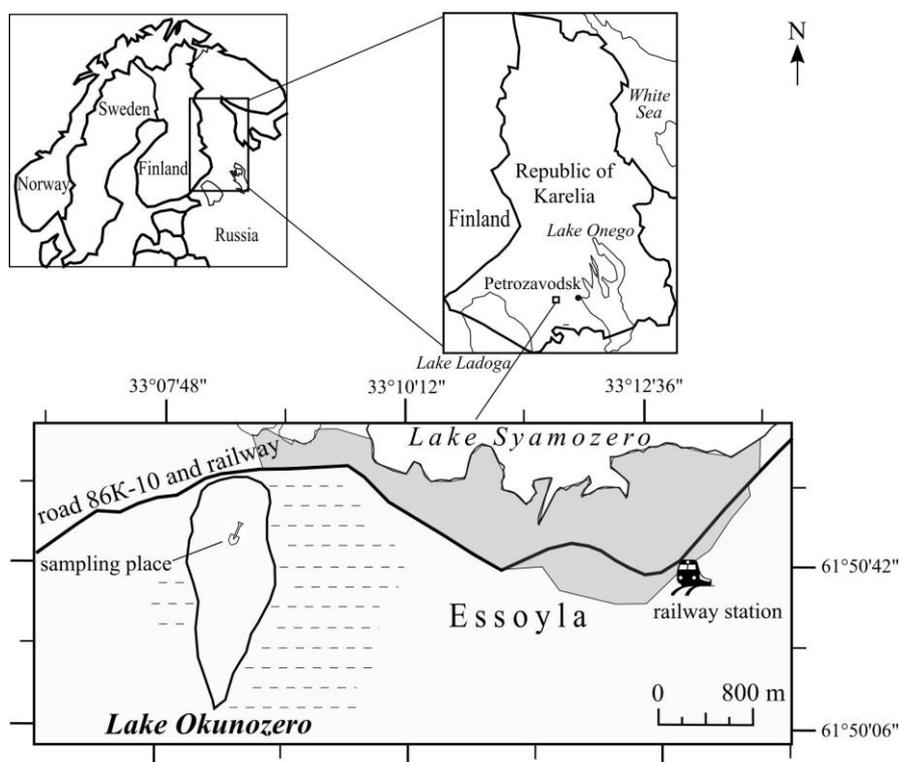
living tissues and the death of some individuals and even groups of organisms can occur. The role of Cu, Zn, and Mo as essential metals is widely known. However, the high concentrations of these elements, as well as Pb, Cd, Tl, and other toxic metals, migrating from different anthropogenic sources, are dangerous for many water organisms. Thus, the research on the biological availability of pollutants in sediments is a very important part of lake investigation [16].

Thus, this study aimed to give a detailed geochemical assessment of the modern sediments (sapropel) of Lake Okunozero, located in the South of Karelia, including identifying the main fractions of heavy metals in the studied sediments.

## 2. Materials and Methods

### 2.1 Study Area

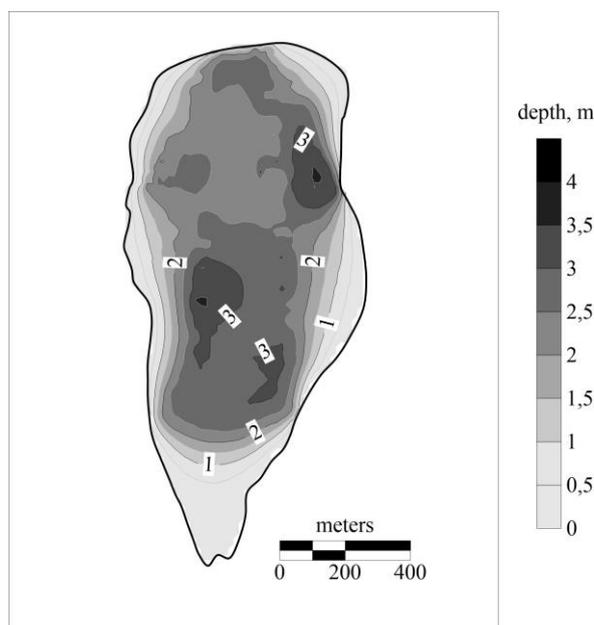
Lake Okunozero (61°50.665' N, 33°08.537' E) is a small water body with a surface area of 0.79 km<sup>2</sup> located nearby Essoyla village and about 60 km from Petrozavodsk, the capital of Karelia (Figure 1). The lake has an elongated shape and low swampy banks from the north to the south. The big marsh is adjacent to Lake Okunozero from the east. On the northern side the lake borders the regional motorway No 86K-10 and railway, connecting Petrozavodsk with the northern and western parts of Karelia.



**Figure 1** Location of the study are.

Lake Okunozero has a simple structure of depressions with the greatest depths in the central part. The lake average depth is 2.6 m, and the maximum depth is 3.5 m (Figure 2). The lake sediments are dark brown silt, which is named sapropel. This sapropel consists of 87% of organic matter. According to the Russian classification [6], sediments of Lake Okunozero belong to the organic type of sapropel, because this silt has more than 50% of organic matter. For this reason

sapropel Lake Okunozero can be used as therapeutic mud and fertilizer to produce adhesives, building materials, drilling fluids, and humates. The layer thickness of sapropel in Lake Okunozero reaches 4.4 m [17]. The average layer thickness of these sediments is 1.14 m.



**Figure 2** Bathymetric maps of Lake Okunozero.

## 2.2 Sampling

Fieldwork was carried out in April 2018. Samples were collected in the central part of the lakes (the accumulation zone) using the Limnos sampler from the ice sheet. Two cores (30 and 21 cm thick) of sediments were collected; each was divided into 2 cm and 5 cm layers immediately after sampling. The samples taken were assumed to be modern sediments that were probably formed in the last 100-150 years. A total of 17 samples were taken. Then, the samples were placed into plastic containers labeled and packed in a cooler bag. The samples were delivered to the laboratory, where the pH of the sediment was measured using a pH-420 millivoltmeter and an ESK-10610 glass combined electrode; then, the samples were placed in the refrigerator and kept at the temperature of 4°C.

## 2.3 Analytical Methods

For further study, the lake sediment samples were dried to an air-dry condition at room temperature and then to an absolutely dry condition in an oven at the temperature of 100°C. Laboratory tests were carried out in the Analysis Center of the Institute of Geology of the Karelian Research Center, Russian Academy of Sciences, in Petrozavodsk, Karelia, and at the Institute of Chemistry and Technology of Rare Elements and Minerals of the Kola Research Center, Russian Academy of Sciences, in Apatity, Murmansk Region.

For the analysis of the total content of Mn, Zn, Pb, Cr, Cu, Co, Ni, Cd, and Mo, sediment samples were decomposed with a mixture of strong acids (HF, HNO<sub>3</sub>, and HCl) in an open system. Sub-samples of 0.1 g each were used. The samples were placed in 50 ml Teflon glasses, 0.1 ml of a solution containing 8 ppb 161 Dy was added to monitor the chemical yield during the samples'

decomposition. Then, several drops of deionized water were added. Then, 0.5 ml of  $\text{HClO}_4$ , 3 ml of HF, and 0.5 ml of  $\text{HNO}_3$  were added and evaporated until intense white vapor was observed. The glasses were cooled, their walls were washed with water, and the solution was again evaporated to wet salts. Then, 2 ml of HCl and 0.2 ml of a 0.1 M solution of  $\text{H}_3\text{BO}_3$  were added and evaporated to a volume of 0.5–0.7 ml. The resulting solutions were transferred into polyethylene bottles and diluted with deionized water to 20 ml. The above procedure was repeated in Teflon glasses without samples to prepare blank samples. Blank samples and one standard (control) sample were decomposed with the analyzed samples.

To identify the various fractions of heavy metals in the core samples subdivided into 5 cm layers, we used the method of sequential extraction of fractions of elements from soil samples [18], including the identification of the following:

- water-soluble fractions (reagent  $\text{H}_2\text{O}$ ),
- available (exchangeable) fractions (reagent  $\text{NH}_4\text{CH}_3\text{COO}$ ),
- fractions bound to Fe and Mn hydroxides (reagents 0.04 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 25%  $\text{CH}_3\text{COOH}$ ),
- fractions bound to organic matter (reagents 0.02 M  $\text{HNO}_3$  + 30%  $\text{H}_2\text{O}_2$  and 3.2 M  $\text{NH}_4\text{CH}_4\text{COO}$  in 20%  $\text{HNO}_3$ ),
- acid-soluble (residual) fractions (reagent  $\text{HNO}_3$ ),
- mineral (silicate) fractions are obtained by deducting the combined concentration of all the above fractions from the total concentrations.

All trace element content in the lake sediment samples was measured by the mass spectrometry method using an XSeries-2 ICP-MS instrument by Thermo Fisher Scientific. The results of the analysis of the collected samples and the reference sample showed that the measured concentrations in mg/kg (milligrams per kilogram) are characterized by a relative standard deviation (RSD) of 5.5–16.7%. Thus, the relative measurement error did not exceed the permissible values (15%) for the trace elements identified in the study. The authors presented a more detailed description of the sediment sample preparation method in the earlier studies [12, 19].

#### **2.4 Calculation of the PLI and RI Indices**

The Pollution Load Index (PLI) was used to determine the environmental quality of the sediment [20]:

$$PLI = (CF_1 * CF_2 * \dots * CF_n)^{1/n},$$

CF is the contamination factor (ratio of a metal concentration to a background metal concentration) and n is the number of metals.

Also, the Potential Ecological Risk index (RI), developed by Swedish scholar Håkanson [21], was calculated to assess the potential risks the metals pose. The RI was calculated for each metal as follows:

$$E_f^i = C_f^i * T_f^i,$$

$T_f^i$  represents the response coefficient for toxicity of an individual metal and  $C_f^i$  represents the contamination factor. The toxicity coefficient for Cu, Pb, and Ni is 5, for Cr is 2, and for Zn is 1 [22].

These values are associated with the potential negative impact of pollutants on biota. During development, they were tested in the study of lakes in Sweden [21].

Integrated RI values were calculated as follows:

$$RI = \sum E_i^f,$$

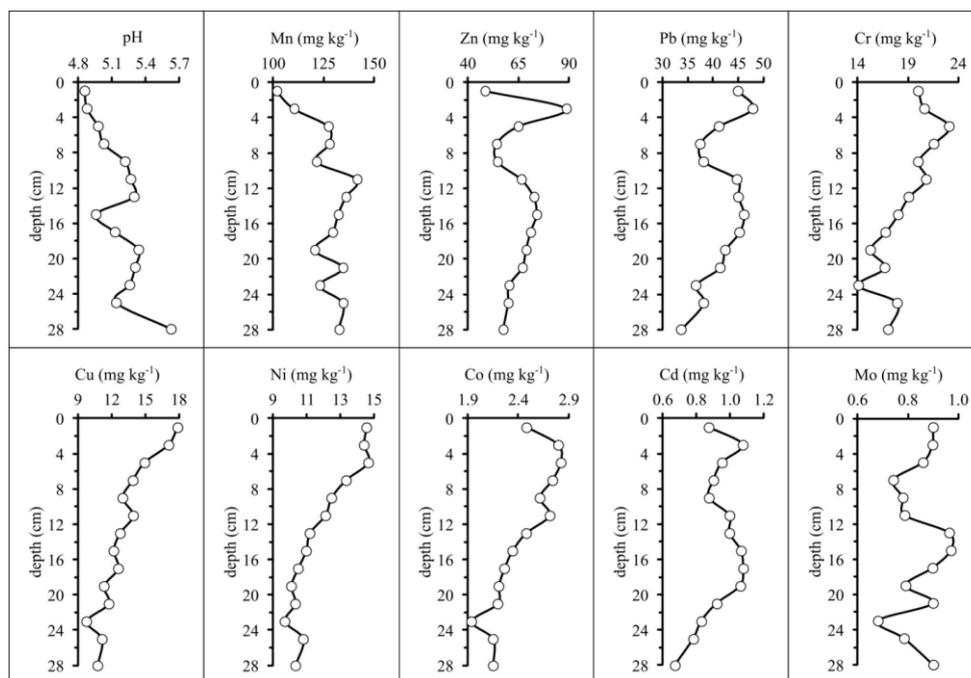
Statistical processing of the data was done using Microsoft Excel 2007. Figures illustrating the results were designed using Google Earth 7.1.8.3036, EasyCapture 1.2.0, and Inkscape 0.48.4.

### 3. Results and Discussion

#### 3.1 General Description of Sediment Geochemistry

The surface layers of sapropel in Lake Okunozero were characterized by an acid reaction with a pH between 4.86 and 5.63. pH values tended to grow with depth in the core samples (Figure 3), which is typical for organic lake sediments of Northern Russia. The growth of pH parameters can be related to the change in the total organic content of the lake. However, there are also other reasons for such dynamics. In addition, the slightly acidic reaction of the sediments of the studied lake may be due to the wetland (shown by dotted lines on the map (Figure 1)) near the waterbodies, as well as the influence of agricultural land in the area of the Essoyla village.

The total concentrations of the majority of heavy metals also varied in the studied sapropel core (Figure 3). For example, the total concentrations of Zn, Pb, Cr, Cu, Ni, Co, and Cd rose from the lower to upper layers, which is related to the anthropogenic influence on the lake, as these metals are indicators of the modern environmental transformations [10, 23-25]. Herewith, it can be associated both with the local anthropogenic sources, such as emissions from cars and trains, and with the long-range transport of heavy metals [26]. For instance, Pb is known to be a marker of the environmental influence of road transport due to using Pb additives for fuel from the 1930s [27, 28] and coal combustion at industrial enterprises and thermal power plants [29, 30]. Besides, Cd can also be a geochemical agent of long-range transport due to coal burning at industrial enterprises [23]. It is also known that metals can enter urban lakes and reservoirs near populated areas as part of dust. In the case of Lake Okunozero, this may be due to the activity of trains, cars and land development around the village. The closest large industrial and urbanized area to Lake Okunozero is the city of Petrozavodsk, where earlier studies of small lakes and rivers showed a significant level of heavy metal pollution [10]. On the other hand, the concentrations of Mn decreased in the lower layers and there was no dynamics of the distribution of Mo concentrations. It can reflect the natural origin of these metals in the researched sediments.



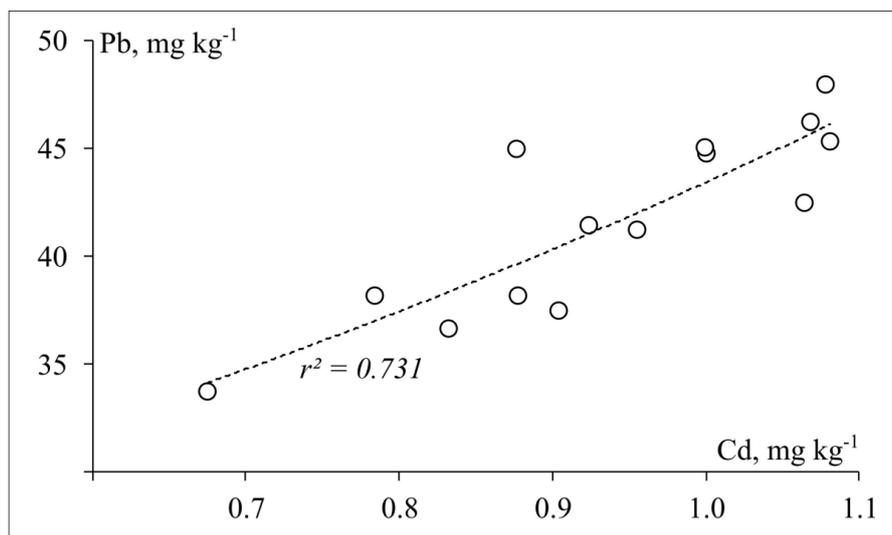
**Figure 3** Vertical distribution of pH and heavy metal concentrations in the core of sediments of Lake Okunozero.

Despite the slight growth of heavy metal concentrations in the core of modern sediments of Lake Okunozero, the average contents of Mn, Cr, Cu, Co, Ni, Zn, and Mo did not exceed the background level of these elements for the lakes of Karelia [31]. However, the average Pb and Cd content in the sapropel of Lake Okunozero exceeded the background level by 9.1 and 2.3 times, respectively (Table 1). Pb is the main pollutant in small lakes of Karelia, which was earlier shown in the examples of other water bodies in the region [32] and adjacent areas [9, 33]. Both metals (Pb and Cd) significantly correlated in the studied sediments (Figure 4). Similar patterns were previously noted in the sediments of lakes in other regions of Karelia.

**Table 1** Described statistics for heavy metal concentration in sapropel of Lake Okunozero and calculated environmental indexes.

	Cr	Mn	Co	Ni	Cu	Zn	Mo	Cd	Pb	PLI	RI
x	18.64	126.6	2.421	11.82	13.07	64.66	0.846	0.937	41.65	0.80	121.08
S	2.529	10.66	0.283	1.775	2.327	10.23	0.086	0.122	4.261	0.07	13.50
$x_{max}$	23.07	141.50	2.822	14.67	17.89	88.42	0.970	1.081	47.90	0.68	139.82
$x_{min}$	14.10	101.70	1.937	9.707	9.758	48.24	0.680	0.675	33.69	0.92	92.33
V, %	13.57	8.417	11.69	15.01	17.80	15.82	10.19	13.03	10.23	8.18	11.15
N	14	14	14	14	14	14	14	14	14	14	14
Standard	100.0	500.0	20.000	50.000	100.0	300.0	20.00	3.000	50.00	-	-
Background	17.99	436.70	6.100	24.75	32.50	95.10	1.970	0.410	4.590	-	-

**Note.** x – average, S – standard deviation,  $x_{max}$  – maximum value,  $x_{min}$  – minimum value, V - variation coefficient, N - number of samples, Standard - the Russian Interstate Standard (GOST), Background – mean content of elements for sediments of lakes of Karelia [31]. All numbers are given in mg/kg, except variation coefficient and index values.



**Figure 4** The relationship of Pb and Cd in sediments of Lake Okunozero, Karelia.

The general correlation analysis (Table 2) revealed the significant relationships in pairs Co-Cr, Cu-Ni, Ni-Cr, Ni-Co, Pb-Cd, Cu-Co, Cu-Cr, Cd-Zn, Pb-Zn, Cu-Mn, Pb-Cu, Pb-Mo, and Ni-Mn (all pairs are arranged in decreasing order of the module of the correlation coefficient). A negative correlation was established (pairs Cu-Mn and Ni-Mn). Thus, two geochemical associations were revealed in the modern layers of sapropel in Lake Okunozero: Co-Cr-Cu-Ni and Pb-Cd-Zn. The first association probably characterizes a local substance flow into the lake from the territory of Essoyla village and the area around it. The elements of the first association can also be related to railway and automobile emissions. The metals of the second association are usually the agents of long-range transport, evidenced by their close correlation in other previously studied water objects of the Karelia and Murmansk regions [7, 12, 32].

**Table 2** The Pirson’s correlation matrix of heavy metal concentrations from sapropel of Lake Okunozero, Karelia (The critical level of correlation significance:  $R_{crit} = 0.53$  for  $p < 0.05$ ).

	<i>Cr</i>	<i>Mn</i>	<i>Co</i>	<i>Ni</i>	<i>Cu</i>	<i>Zn</i>	<i>Mo</i>	<i>Cd</i>
Mn	-0.094							
Co	<b>0.942</b>	-0.165						
Ni	<b>0.884</b>	<b>-0.531</b>	<b>0.861</b>					
Cu	<b>0.744</b>	<b>-0.609</b>	<b>0.772</b>	<b>0.921</b>				
Zn	-0.036	0.106	0.160	-0.047	0.093			
Mo	0.134	0.026	0.112	0.100	0.289	0.434		
Cd	0.128	-0.067	0.362	0.144	0.320	<b>0.718</b>	0.319	
Pb	0.231	-0.208	0.380	0.309	<b>0.572</b>	<b>0.657</b>	<b>0.561</b>	<b>0.856</b>

### 3.2 Assessment of Pollution and Main Fraction of Elements

All studied element contents did not exceed the Russian Interstate Standard (GOST) No. 54000-2010 developed to assess the sapropel quality as organic fertilizer. According to this document (metal concentration values are given in Table 1), the sapropel of Lake Okunozero is suitable for use

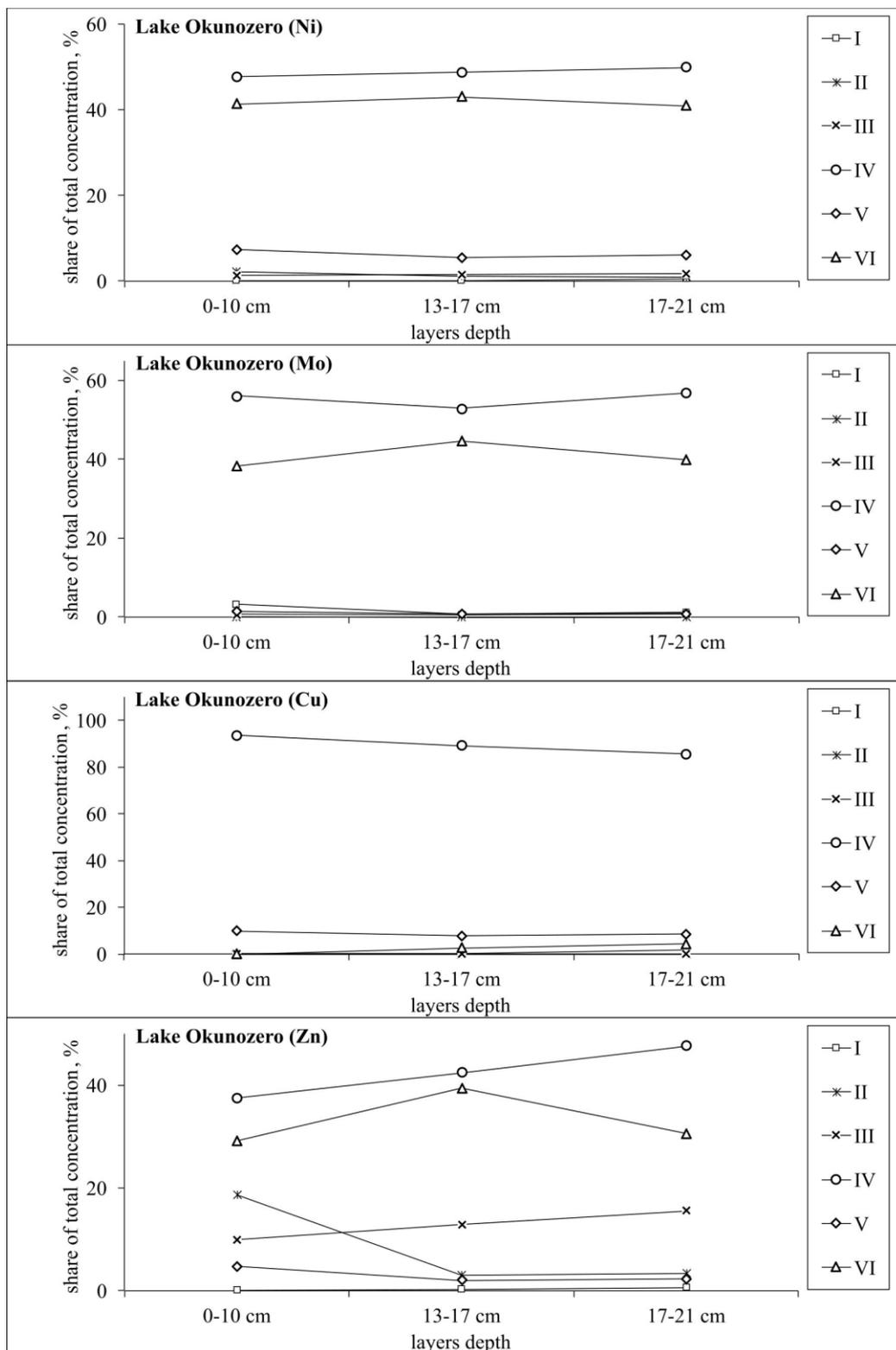
in agriculture. However, before extracting sapropel, it is necessary to investigate its other parameters, which are also described in the GOST. On the other hand, there are no norms of such dangerous metals as V, Sb, Tl, W, and Bi for sapropel in these standards, although the concentrations of these elements frequently exceeded the background levels in upper layers of modern lake sediments, which is related to the long-range transport of heavy metals [25]. According to different research, the emissions from the factories of other regions of Russia (Murmansk and Leningrad regions, St. Petersburg), Finland, Sweden, Germany, and Poland reach the territory of Karelia [34-37]. Studies show that the range of transport of emissions from metallurgical plants in the Murmansk region is hundreds of kilometers. This can be seen from the increased concentrations of Ni and Cu in the modern sediments of small lakes in the background regions of the North of Russia [12].

The values of PLI calculated for all metals and their background levels were between 0.68 and 0.92, and the mean PLI value was 0.80 (Table 1). Despite slight PLI growth from the lower to upper layers of the sapropel core, this parameter indicated the low pollution level of Lake Okunozero's ecosystem. Studies of sediments of small lakes in the background areas of the North of the Republic of Karelia and the south of Murmansk region showed that such PLI values were typical for clean water bodies located far from large cities and industrial areas [25]. The contaminated lakes in urban areas of the North of Russia were characterized by PLI values from 2 to 9 [7]. Sediments of lakes in the cities of Murmansk, Petrozavodsk, and Monchegorsk were the most polluted in terms of the heavy metals content and the anthropogenic load. Similar results were obtained after calculating the RI-index, using data from Cr, Ni, Cu, Zn, and Pb. In the sapropel of Lake Okunozero, the values of RI were between 92.3 and 139.8, and the mean RI value was 121.1 (Table 1). Usually, RI levels lower than 150 shows a low ecological risk [21]. Thus, calculated indexes also illustrated that the sapropel of Lake Okunozero is safe to use. However, the extraction of lake sapropel should be carried out only after a complete environmental assessment of the water body and an assessment of the possible consequences for the biota of the lake from its extraction. Also, the authors do not take responsibility to state that using sapropel in agriculture or medicine can be a panacea. It is worth carrying out additional work to determine the exact benefits of sapropel from the studied lake for people.

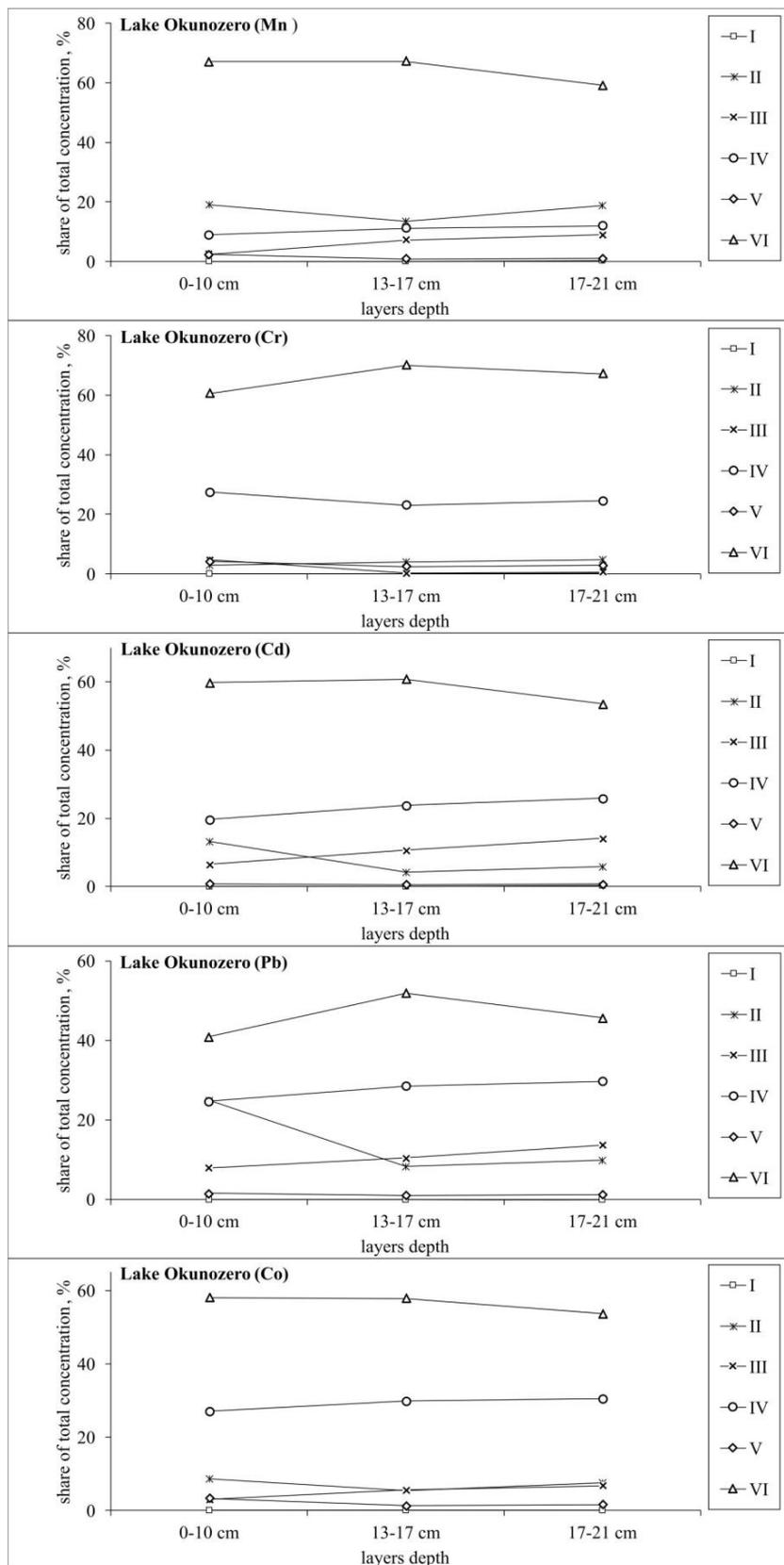
The main fractions of heavy metals in sediments of water bodies are clay and silt particles, organic matter, carbonate minerals and hydroxides of Fe and Mn [7, 38-40]. On the other hand, a significant part of heavy metals can be included in the crystal structure of natural minerals (sulfides, aluminosilicates, etc.). However, many metals often partially or sometimes completely occur in an available form, which allows them to become agents of secondary water pollution from contaminated sediments [16]. In this case, as well as in the close relationship of heavy metals with organic matter in lake sediments, pollutants are most dangerous for the ecosystem and its inhabitants.

Fraction analysis of heavy metals in sapropel from Lake Okunozero revealed that metals, such as Cr, Mn, Co, Cd, and Pb, were predominantly in the stable phase (Figure 5 and Figure 6), especially Mn (from 59 to 67% of the total content of the metal), Cr (61-70%) and Cd (54-61%). In addition, Cu was barely associated with the mineral phase of the researched sediments – there was only from 0 to 4% of the total Cu concentration. However, the predominant fraction of Cu in the sediments of Lake Okunozero was the organic phase. Moreover, Mo, Ni, and Zn were also associated with the

organic matter (37-57% of the total content), while Mn, Co, Cr, Cd, and Pb were less associated (9-30%) with this phase.



**Figure 5** Share of different fractions of heavy metals (Ni, Mo, Cu, Zn) in sediments of Lake Okunozero. Note: I – water-soluble fractions, II – available fractions, III – fractions associated with hydrated oxides Fe, IV – fractions associated with organic matter, V – acid-soluble (residual) fractions, VI – mineral (stable) phase.



**Figure 6** Share of different fractions of heavy metals (Mn, Cr, Cd, Pb, Co) in sediments of Lake Okunozero. Note: I – water-soluble fractions, II – available fractions, III – fractions associated with hydrated oxides Fe, IV – fractions associated with organic matter, V – acid-soluble (residual) fractions, VI – mineral (stable) phase.

Four metals (Mn in the whole sediment core and Zn, Cd, and Pb in 0-5 cm of the layer of the studied core) were in the available fraction from 13 to 24% of the total metal content in the sediments. Cr, Ni, and Co were less associated with the available fraction, and Mo and Cu were not bound to this phase. Considering that Cd and Pb are the most dangerous toxic metals, their potential mobility in sapropel is a prerequisite for the migration of Cd and Pb in the trophic pyramids (sediment – benthos – fish) of the studied lake and similar ones. Also, the metals bound to the organic matter of the sediments can easily enter living organisms as many aquatic species feed on detritus, accumulating at the bottom of the lakes. Zn (9-16%), Cd (6-14%), and Pb (8-14%) were most closely bound to Fe compounds in comparison with other researched metals.

All metals were weakly associated with the water-soluble fraction. Such data was obtained even in the uppermost layers of sediments that border the lake water. Therefore, the secondary pollution of the aquatic environment of Lake Okunozero is only possible when the physicochemical conditions in the water body change. Generally, it may depend on the redox potential (Eh) values and pH parameters of the upper layers of sediments.

#### **4. Conclusions**

The research of ecological and geochemical characteristics of the modern sediments of Lake Okunozero, located in the southern part of the Republic of Karelia (Russia), showed a tendency towards increased concentrations of Pb, Cr, Zn, Cd, Sb, Cu, Ni, and Co in the upper layers of sediments compared to the lower layers. Nevertheless, median concentrations of all metals except for Pb and Cd (41.7 and 0.94 mg/kg, respectively) did not exceed the regional geochemical background. At the same time, variations of Mo and Mn concentrations indicated the prevalence of natural factors in accumulating these elements in the water body. The correlation analysis identified special geochemical associations of heavy metals (Co-Cr-Cu-Ni and Pb-Cd-Zn). They showed the influence of local (motorways and railways, urbanization) and global (long-range transport of pollutants) sources of pollution on the lake's ecosystem. The dynamics of Pb and Cd in the studied sediments of Lake Okunozero were similar to the behavior of these metals in other small lakes in the North of Russia, which indicated the global contribution of both metals to the pollution of the aquatic environment in this area. The analysis of fractions of heavy metals in the sediments of Lake Okunozero revealed the significant role of insoluble phases (mineral and associated with the organic matter). Metals, such as Cu, Mo, Ni, and Zn, were most bound to the organic matter. At the same time, Pb, Cd, and Zn were highly associated with the available fraction, the analysis of which is important in terms of understanding the potential of secondary pollution. Close attention should be paid to these three metals in further studies of Lake Okunozero.

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## Author Contributions

Zakhar Slukovskii – conceived and designed study, collected the data, performed the analysis, wrote the paper, prepared illustrations, received funding. Tatiana Shelekhova – collected the data, take part in proofreading, received funding.

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## Competing Interests

The authors have declared that no competing interests exist.

## References

1. Filatov NN, Kukharev VI. Lakes of Karelia (In Russian). Petrozavodsk: Karelian Research Centre of RAS; 2013.
2. Strakhovenko VD, Taran OP, Ermolaeva NI. Geochemical characteristics of the sapropel sediments of small lakes in the Ob'-Irtys interfluvium. *Russ Geol Geophys*. 2014; 55: 1160-1169.
3. Stankevica K, Klavins M, Rutina L. Accumulation of metals in sapropel. *Mater Sci Appl Chem*. 2012; 26: 99-105.
4. Blečić A, Raičić B, Dubljević R, Mitrović D, Spalevic V. Application of sapropel in agricultural production. *Agric For*. 2014; 60: 243-250.
5. Gomes C, Carretero MI, Pozo M, Maraver F, Cantista P, Armijo F, et al. Peloids and pelotherapy: Historical evolution, classification and glossary. *Appl Clay Sci*. 2013; 75: 28-38.
6. Mikhailov VP, Aminov VN. Mineral resources base of Republic of Karelia (In Russian). Petrozavodsk: 2006.
7. Guzeva A, Slukovskii Z, Dauvalter V, Denisov D. Trace element fractions in sediments of urbanised lakes of the arctic zone of Russia. *Environ Monit Assess*. 2021; 193: 378.
8. Moiseenko TI, Megorskii VV, Gashkina NA, Kudryavtseva LP. Water pollution effect on population health in an industrial northern region. *Water Resour*. 2010; 37: 194-203.
9. Rognerud S, Hongve D, Fjeld E, Ottesen RT. Trace metal concentrations in lake and overbank sediments in southern Norway. *Environ Geol*. 2000; 39: 723-732.
10. Slukovskii Z. Geochemical indicators for paleolimnological studies of the anthropogenic influence on the environment of the Russian Federation: A review. *Water*. 2023; 15: 420.
11. Hosono T, Alvarez K, Kuwae M. Lead isotope ratios in six lake sediment cores from Japan archipelago: Historical record of trans-boundary pollution sources. *Sci Total Environ*. 2016; 559: 24-37.
12. Slukovskii Z, Medvedev M, Mitsukov A, Dauvalter V, Grigoriev V, Kudryavtzeva L, et al. Recent sediments of arctic small lakes (Russia): Geochemistry features and age. *Environ Earth Sci*. 2021; 80: 302.
13. Moiseenko TI. Impact of geochemical factors of aquatic environment on the metal bioaccumulation in fish. *Geochemistry Int*. 2015; 53: 213-223.

14. Demirak A, Keskin F, Silim M, Nedim O, Dilek Y, Priit B, et al. Bioaccumulation and health risk assessment of heavy metals in European eels taken from Lakes K yoc ğiz (Turkey) and V rtsj rv (Estonia). *Environ Sci Pollut Res*. 2022; 29: 1620-1633.
15. Rainbow PS, Hildrew AG, Smith BD, Geatches T, Luoma SN. Caddisflies as biomonitors identifying thresholds of toxic metal bioavailability that affect the stream benthos. *Environ Pollut*. 2012; 166: 196-207.
16. L pez DL, Gierlowski-Kordesch E, Hollenkamp C. Geochemical mobility and bioavailability of heavy metals in a lake affected by acid mine drainage: Lake hope, Vinton County, Ohio. *Water Air Soil Pollut*. 2010; 213: 27-45.
17. Shelekhova TS, Tikhonova JS, Lazareva OB. Environmental dynamics and evolution of lake Okun' in South Karelia (based on micropaleontological data). *Trans Karelian Res Cent Russ Acad Sci*. 2021; 4: 134-152. Available from: <http://journals.krc.karelia.ru/index.php/limnology/article/view/1319>.
18. Tessier A, Campbell PG, Bisson M. Sequential extraction procedure for the speciation of particulate trace metals. *Anal Chem*. 1979; 51: 844-851.
19. Slukovskii ZI, Svetov SA. Geochemical indicators of technogenic pollution of bottom sediments of small rivers in an urbanized environment. *Geogr Nat Resour*. 2016; 37: 32-38.
20. Suresh G, Ramasamy V, Meenakshisundaram V, Venkatachalapathy R, Ponnusamy V. Influence of mineralogical and heavy metal composition on natural radionuclide concentrations in the river sediments. *Appl Radiat Isot*. 2011; 69: 1466-1474.
21. H kanson L. An ecological risk index for aquatic pollution control. A sedimentological approach. *Water Res*. 1980; 14: 975-1001.
22. Guo W, Liu X, Liu Z, Li G. Pollution and potential ecological risk evaluation of heavy metals in the sediments around Dongjiang Harbor, Tianjin. *Procedia Environ Sci*. 2010; 2: 729-736.
23. Dauvalter V, Kashulin N. Chalcophile elements (Hg, Cd, Pb, As) in Lake Umbozero, Murmansk Province. *Water Resour*. 2010; 37: 497-512.
24. Chaharlang BH, Bakhtiari AR, Mohammadi JF. Geochemical partitioning and pollution assessment of Ni and V as indicator of oil pollution in surface sediments from Shadegan wildlife refuge, Iran. *Mar Pollut Bull*. 2016; 111: 2247-2259.
25. Kuwae M, Tsugeki NK, Agusa T, Toyoda K, Tani Y, Ueda S, et al. Sedimentary records of metal deposition in Japanese alpine lakes for the last 250 years: Recent enrichment of airborne Sb and In in East Asia. *Sci Total Environ*. 2013; 442: 189-197.
26. Wan D, Han Z, Yang J, Yang G, Liu X. Heavy metal pollution in settled dust associated with different urban functional areas in a heavily air-polluted city in North China. *Int J Environ Res Public Health*. 2016; 13: 1119.
27. Escobar J, Whitmore TJ, Kamenov GD, Riedinger-Whitmore MA. Isotope record of anthropogenic lead pollution in lake sediments of Florida, USA. *J Paleolimnol*. 2013; 49: 237-252.
28. Thomas VM. The elimination of lead in gasoline. *Annu Rev Energy Environ*. 1995; 20: 301-324.
29. McConnell JR, Edwards R. Coal burning leaves toxic heavy metal legacy in the Arctic. *Proc Natl Acad Sci USA*. 2008;105: 12140-12144.
30. Pacyna JM, Pacyna EG. An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. *Environ Rev*. 2001; 9: 269-298.

31. Slukovskii ZI. Background concentrations of heavy metals and other chemical elements in the sediments of small lakes in the south of Karelia, Russia. *Vestnik of MSTU*. 2020; 23: 80-92. doi: 10.21443/1560-9278-2020-23-1-80-92.
32. Medvedev A, Slukovskii Z, Novitcky D. Heavy metals pollution of small urban lakes sediments within the Onego Lake catchment area. *Polish J Nat Sci*. 2019; 34: 245-256.
33. Johansson K, Andersson A, Andersson T. Regional accumulation pattern of heavy metals in lake sediments and forest soils in Sweden. *Sci Total Environ*. 1995; 160: 373-380.
34. Bränvall ML, Bindler R, Emteryd O, Renberg I. Four thousand years of atmospheric lead pollution in northern Europe: A summary from Swedish lake sediments. *J Paleolimnol*. 2001; 25: 421-435.
35. Dauvalter V. Influence of pollution and acidification on metal concentrations in Finnish Lapland Lake sediments. *Water Air Soil Pollut*. 2010; 85: 853-858.
36. Keinonen M. The isotopic composition of lead in man and the environment in Finland 1966–1987: Isotope ratios of lead as indicators of pollutant source. *Sci Total Environ*. 1992; 113: 251-268.
37. Virkutyte J, Vadakojte S, Sinkevičius S, Sillanpää M. Heavy metal distribution and chemical partitioning in Lake Saimaa (SE Finland) sediments and moss *Pleurozium schreberi*. *J Chem Ecol*. 2008; 24: 119-132.
38. Förstner U. Sediments—Resource or waste. *J Soils Sediments*. 2004; 4: 3.
39. Li X, Shen Z, Wai OW, Li YS. Chemical forms of Pb, Zn and Cu in the sediment profiles of the Pearl River Estuary. *Mar Pollut Bull*. 2001; 42: 215-223.
40. Moore F, Nematollahi MJ, Keshavarzi B. Heavy metals fractionation in surface sediments of Gowatr bay, Iran. *Environ Monit Assess*. 2015; 187: 4117.