



# Metals Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb in Aquatic Plants of Man-made Water Reservoir, Eastern Siberia, Russia: Tracking of Environment Pollution

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## ABSTRACT

The paper reports the results of research on the Bratsk water body (Russia), the hugest man-made reservoir in the world, using aquatic plants as bioindicators. This aquatic environment requires constant monitoring due to metal emissions by metallurgical, machine-building, and other industries. To that end, the accumulation capacities of *Myriophyllum spicatum* L., *Elodea canadensis* Michx., *Potamogeton pectinatus* L. and *Cladophora glomerata* L. were compared. The Ti, Cr, Mn, Fe, Ni, Cu, Zn, and, Pb contents in the plants were quantified with X-ray fluorescence. The calculated bioaccumulation indexes provided similar indicator characteristics of these species. The clustering analysis specified the spatial metal pollution in the reservoir. The aquatic plants sampled near industrial enterprises demonstrated the high concentrations: Ti (573-887), Cr (14-22), Mn (609-1080), Fe (9231-12724), Ni (8-11), Cu (51-103), Zn (35-45) and Pb (10-40) µg/g. The average concentrations in the samples collected away from emission sources were significantly lower: Ti (443-598), Cr (7-10), Mn (439-591), Fe (4575-6573), Ni (6-7), Cu (36-58), Zn (27-33) and Pb (6-9). While, they were several-fold higher than threshold values reported for the Lake Baikal plants: Ti – 6; Cr – 2-2.6; Ni – 1.9; Fe – 3-6.7; Mn – 1.5-2.6; Cu – 4; Zn – 1.2-2, and Pb – 7.3. In addition to industrial impacts, the sedimentation processes, coastal erosion, wood rotting and ore occurrences caused increasing in metal contents. Assessment of pollution through the pollution load index and the integration Nemerov index provided the classification of the environment of the Bratsk water reservoir as polluted one.

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## INTRODUCTION

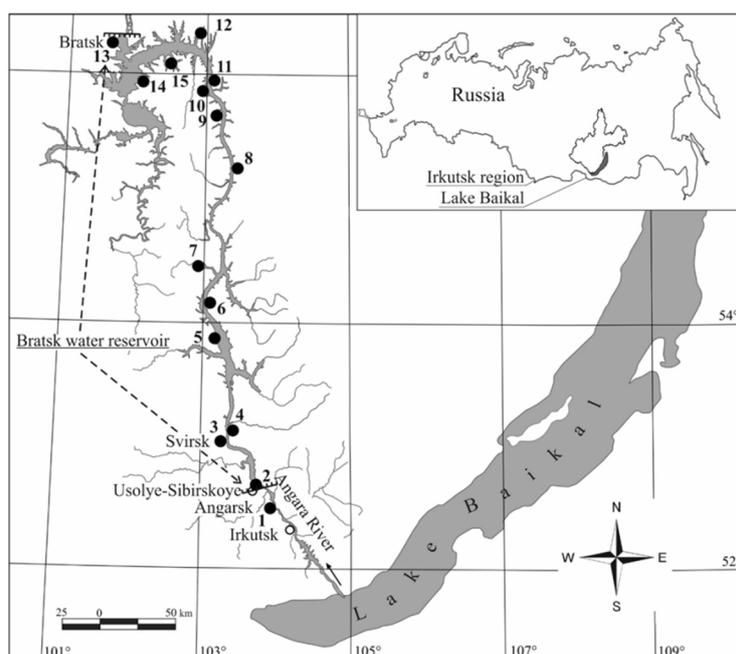
The examinations of water environment using some aquatic plants as bioindicators are widely recognized (Baldantoni & Alfani, 2016; Bonanno et al., 2017; Cegłowska et al., 2016; Costa et al., 2018; Favas et al., 2018; Genisel et al., 2015; Manasypov et al., 2018; Polechońska et al., 2018; Ruhela et al., 2019). Dwelling entirely or partly under the water, aquatic plants have a large area to capture elements from the environment (Favas et al., 2018). Both compounds dissolved in the water and suspended solids penetrate their tissues. After dying off, most of the vegetation remains at the bottom of the reservoir together with absorbed pollutants. In this way, these pollutants

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are re-involved in the biogeochemical cycles in the water system. Toxic components are released into the environment and again contribute to its total contamination. However, not all aquatic species are capable to accumulate chemical elements in significant quantities (Narayan et al., 2020). So, *Paspalum repens* macrophyte was not suitable for biomonitoring examinations, since the differences between the compositions of the samples collected in polluted and non-polluted places were insignificant (Narayan et al., 2020). On the contrary, *Ceratophyllum demersum* has been selected to assess metal pollution in some Polish rivers due to significant accumulations of Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Rb, Ti, V and Zn (Polechońska et al., 2018). The species *Apium nodiflorum* was preferred for monitoring the Mediterranean rivers (Baldantoni & Alfani, 2016). The accumulation of copper and zinc by *Elodea canadensis* was described in (Cegłowska et al., 2016), and the long-term exposure of high metal levels on the biomass growth has been revealed. Therefore, before monitoring, the environment, it is important to choose suitable plants with indicator properties. Hence, comparative studies of the elemental compositions of some plants are required. The wide-spreading and simplicity of sampling of bioindicator species, as well as uncomplicated sample preparation for analysis, should be taken into account (Baldantoni & Alfani, 2016).

The other markers are sometimes used while assessing quality of the water environment, e.g. chemical compositions of bottom sediments or water. However, some difficulties occur in such studies. The water compositions change quickly over time, so, it is not worth researching pollution using only chemical data for water samples (Lomartire et al., 2021). Likewise, the chemical compositions of bottom sediments are sometimes not representative as a result of the upper layer offset together with pollutants by the water flow (Perks et al., 2017; Schubert et al., 2012). Therefore, the authors (Hagger et al., 2008; Lomartire et al., 2021; Pham, 2017) considered macrophytes as preferable markers of environmental contamination.

The Bratsk fresh-water reservoir (BR) occupies a huge area. It appeared after flooding vast land areas as a result of the construction of the hydroelectric power station on the Angara River in 1961. It is situated in the Irkutsk region (Eastern Siberia), Russia (Fig. 1). Its water area is over 5000 square km, and its extent, counting from the backwater site (near Usolye-Sibirskoye town,



**Fig. 1.** Map of the Bratsk water reservoir with industrial centers and sampling points of the water and plants

Fig. 1) is over 500 km. Lake Baikal bearing the purest water with outflowing Angara River makes up the source of natural water in the BR. However, some geochemical and anthropogenic factors change this mother aquatic system.

The industrial and agricultural enterprises of the Irkutsk region discharge harmful metals into the reservoir with waste waters and air emissions, such as Cr, Mn, Fe, Ni, Cu, Zn Hg, and Pb. Only mercury contamination was the main target of environmental monitoring of the Bratsk water body for several decades (Azovsky et al., 2010; Koval et al., 1999; Pastukhov et al., 2019; Perrot et al., 2010). At the same time, hundreds of thousand people live on the reservoir shore, in close proximity to the sources of emissions. The report (State report 2016) underlines the rise of respiratory diseases, illnesses of stomach, cardiovascular system and cancer. With this in mind, the assessment of the environmental state will raise awareness to ensure the proper life quality of people. This artificial reservoir, like many others, is subjected to the combined impacts of factors of both natural and anthropogenic origin. The peculiar temperature regime, currents, wave processes and water level regulation distinguish it from any natural reservoir. The pollution of such water bodies is also specific and requires to be studied.

The article focuses on determining the Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb contents in some aquatic plants of the Bratsk water reservoir and on examining metal variations depending on their locations. For this, it was necessary to compare the accumulative capacities of some aquatic plants and to select suitable species as bioindicators. The spatial distribution of metals should be specified and the factors affecting the content changes should be identified. Moreover, the elemental composition of water samples will be studied.

## MATERIALS AND METHODS

The Siberian platform, hosting the Bratsk reservoir, encompasses the rocks of different geological ages, including sandstones, argillites, siltstones, carbonate rocks, ore minerals and others. Tectonic and exogenous processes are responsible for the metals entry into the environment (Kuskovskii et al., 1999). Constant seismic activity causes releasing chemical elements into the reservoir zone. Abundant sedimentary materials enter the water due to exogenous processes like abrasion, erosion, landslides and weathering (Kuskovskii et al., 1999). The regional climatic conditions intensify exogenous processes, especially in warm seasons. The climate is sharply continental: the summer period is short and hot, with rich precipitation. The long winter is quite dry and frosty. The average temperature in January is - 23 to - 25 °C, reaching - 50 °C. In July, it is above +17 °C, maximum + 35 degrees and above that (State report 2016).

The examined samples were collected at fifteen sites in July and August of 2015, starting from the lower river and further upstream. They were selected in different reservoir bays and close to some towns and settlements (Fig. 1, Table 1).

The sampling points 1 and 13 are located in the towns with population of about 200 thousand people, and with diverse industries (Table 1). The titanium deposit was discovered 66 km southwest off Angarsk, P. 1 (Vladykin & Alymova, 2019). The points 2 and 3 are represented by dangerous sources of metal emission in not big towns, some of them located in the coastal zone. The sampling point 4 belongs to an industrial area due to its proximity to emission sources. The sampling points from 5 to 15 were selected at different distances from polluting industries (Table 1). The locations 5, 7-10, 12, 14, and 15 are the reservoir bays, surrounded by coniferous forests and meadow-steppe landscapes. The sites 6 and 11 are situated in the residential zone with man-made activities as harvesting, farming and fishing. Some iron ore deposits and copper occurrences lay close to the points 11, 12, 14 and 15.

The water samples were taken with the Ocean Test 110A bathometer at depth 0.6 m. After filtration through the disposable membrane filters (0.45 microns), water samples were placed in the clean polyethylene containers of 15 mL volume. Then, these samples were acidified with

nitric acid (ultrapure Merk) and delivered to the laboratory to be stored in a refrigerator. Four plant species were chosen from BR. No published data are available on the species dominating there. Preliminary plant sampling in several bays showed that the Canadian waterweed (*Elodea canadensis* Michx.), fennel-leaved pondweed (*Potamogeton pectinatus* L.), Eurasian water-milfoil (*Myriophyllum spicatum* L.) and alga (*Cladophora glomerata* L.) were identified more often than the other species. Herewith, the first three species are the submerged plants (macrophytes). They grew near the shoreline at different depths. The samples were taken from area of 2 to 4 square meters. In the sites, where the plants were visible above the water surface, sampling proceeded relatively easily. Macrophytes and alga were manually pulled out of the water. But in the places, where the phytomass was under the water, sampling was “blind”. Mixed species were net-dragged to the shore where the plants were sorted. The aquatic plants of interest were left for further processing, and the remaining species were rejected. Not all plants to be examined were found at each sampling site. Only *M. spicatum* and *Cl. glomerata* were present at all fifteen locations. *E. canadensis* was collected only at eleven sites, and *P. pectinatus* was found at twelve sites. The samples of combined green parts (leaves, stems, and flowers) were analyzed.

After sampling, the plants were rinsed with the reservoir water to delete some mineral particles and hydrobionts. However, it is impossible to clean completely their tissues from the tiniest particles of sedimentary material, because they are strongly fixed in the pores of the plants. Further, the plants were air-dried in gauze pouches for seven to ten days. The dried material was delivered to the laboratory.

The metal concentrations were measured in the water samples by inductively coupled plasma mass spectrometry (ICP-MS), using the high-resolution mass spectrometer Element-2 (Thermo Finnigan, Bremen, Germany) with double focusing. The calibration solutions were prepared as the diluted multi-element standard solutions CLMS-1, 2, 3 (SPEX, USA). The signal fluctuations were monitored during the spectrum recording using an internal standard Rh with the final concentration of 2 µg/L. The spectra were recorded at low (LR-300) and medium (MR-4000) nominal mass resolution M/DM, depending on the available overlaps of extraneous masses in the spectrum regions. All solutions were prepared in the deionized water purified using the Simplicity-185 (18 Mom) device. The instrumental drift was checked by repeated analysis of one of the multi-element standards every ten samples to be determined. The accuracy was controlled with the standard solution IQC-26 (NIST, USA). The limits of the detection method were as follows, µg/L: Ti 0.07, Cr 0.04, Mn 0.11, Fe 0.8, Ni 0.06, Cu 0.05, Zn 0.36 and Pb 0.03.

The metal contents in the plants were determined using X-ray fluorescence spectrometry. First, the air-dried plant material was grinded in the hand grinder and then in an agate mortar. The weight of 0.5 g of the powder was put into a steel cylinder, the dozed amount of boric acid was added, and the specimen was pressed as a pellet under load of 16 ton on the boric acid substrate. The  $K\alpha$ -line of Ti, Cr, Mn, Fe, Ni, Cu, Zn and Pb  $L\beta$ -line intensities were measured with X-ray wavelength spectrometer S4 Pioneer, Bruker, Germany. Analytical precision, defined as the relative standard deviation for three replicate determinations, ranged from 2 to 25 %, depending on the concentration levels. The values of limits of quantification (LoQ), defined from plant CRMs with minor contents, were, µg/g: Ni (2), Cr and Pb (3), Cu (6), Ti, Zn and Mn (10) and Fe (50). Plant CRM, Canadian pondweed EK-1 produced at the Vinogradov Institute of Geochemistry (IGC), Russia (Catalogue of CRMs, 2013), was used to test the trueness of XRF results. The errors of Ti, Mn and Fe determinations were, respectively, within 7, 3 and 2 % of the certified values. These were 9, 9 and 8 % for Ni, Cu and Zn, respectively. The discrepancy in Cr determination was 12 %. Accuracy for lead could not be estimated, as the XRF result was less than LoQ, while the information value in EK-1 was 1.1 µg/g. Additionally, XRF results were compared with the data of atomic absorption spectrometry (AAS). Each plant sample of 100 mg was decomposed in an ANCON-AT autoclave with a mixture of nitric and hydrofluoric acids and hydrogen peroxide for 3 hours at the temperature of 180° C. The measurements were

performed on Perkin Elmer-403 and Perkin Elmer-503 spectrometers. Recoveries between two methods results amounted to (%) 82-87 (Ti, Cr, Mn, Ni and Pb) and 92-97 (Cu, Fe and Zn). Significant discrepancies between the results could be caused by both the errors in plant decomposition in AAS, and errors, made at the preparation stage of artificial samples for XRF. The plant XRF technique has been described in detail in paper (Chuparina & Azovsky, 2016).

Statistical analyses were performed using PASW Statistics 10.0 software and MS Excel 2010. These programs are convenient for effective analysis of the acquired data, their processing and visualization. The normality of the data distribution was checked according to the Shapiro-Wilk's  $W$ -test and the homogeneity of variances by the Levene's test. Since some parameter distributions deviated from normality ( $p < 0.05$  for most elements; the variation coefficients of element contents  $CV$  are 24-135 %), tests of nonparametric statistic were applied. The Kruskal-Wallis test (one-way ANOVA on ranks) was used to evaluate the significance of the differences between plant species and between the water and plant groups collected in different habitats. Wilcoxon signed rank criteria was also usable. For a pair comparison of the studied groups, Mann-Whitney test was applied (independent samples). Probability level  $p$  was 0.05 in all tests. Spearman's rank correlations were computed to investigate the connections among metal concentrations in the water and between plants. The element concentrations were processed by complete-linkage clustering algorithm and the Manhattan distance method to reveal the similar sample groups and show visibly the differences between them.

To assess the aquatic plants as potential bioindicators the bioaccumulation factors ( $BF$ ), reflecting the element concentrations ratio in the plants ( $C_p$ ) to ambient water ( $C_w$ ) (Ahmad et al., 2016) were calculated as:  $BF = C_p/C_w$ . The good accumulative capacities are pointed by the values of  $BF$ , exceeding  $10^3$ .

The total pollution load index ( $PLI$ ), which characterizes the contamination degree of any area by several metals simultaneously, was estimated as:

$$PLI = \sqrt[n]{CF_1 * CF_2 * \dots * CF_n},$$

where  $CF_i$  – individual contamination factor for the element (Hakanson, 1980) as  $C_i/C_o$ , where  $C_i$  – the element content in the water and plant under study;  $C_o$  – threshold concentration of the same element in the water and plant from a background location. Based on the obtained  $PLI$  values and the categories of this index, proposed by the authors (Tomlinson et al., 1980), the sampling sites were compared with each other and assigned to different groups depending on the contamination degree. The characteristic of the environment state is performed according to the proposed classification (Tomlinson et al., 1980):  $PLI$  is close to 0 – state of medium is perfect;  $PLI$  value is up to 1 – baseline of pollutants;  $PLI$  is above 1 – polluted medium.

The integration Nemerov index ( $NPI$ ), displayed in the works (Benhaddya et al., 2019) in water samples investigations and by (Baldantoni et al., 2018; Polechońska et al., 2018) for aquatic plants, was also used to assess the quality of the environment:

$$NPI = \sqrt{\frac{\left(\frac{1}{n} \sum_{i=1}^n \frac{c_i}{c_0}\right)^2 + \left(\frac{c_i}{c_0}\right)_{\max}^2}{2}},$$

where  $c_i$  and  $c_0$  are the  $i$ -metal concentration in studied sample and reference one, respectively;  $n$  – number of metals (in this paper  $n=8$ ).

$NPI$  values mean in the water examination:  $NPI \leq 1$  – water is not contaminated;  $1 < NPI < 2$  – slightly contaminated;  $2 < NPI < 3$  – moderately contaminated;  $NPI > 3$  – severely contaminated (Benhaddya et al., 2019). This parameter is informative both for the each location in particular

**Table 1.** Characteristics of the sampling points

Sampling points	Place name coordinates	The nearest source of metals distance, km
<b>Industrial areas</b>		
P.1	Angarsk town 52°39'01"N 103°53'57"E	oil refining - 11 cement production - 3.8 catalyst industry - 8 heavy-machinery – 20 titanium deposit - 66
P.2	Usolye-Sibiskoye town 52°55'18"N 103°40'12"E	chemical enterprise - 15 ferroconcrete production- 17 mining equipment - 20 agricultural complex - 17
P.3	Svirsk town 53°07'03"N 103°20'33"E	river port - 0.6 battery manufacturing - 3.2 equipment repair - 3.3
P.4	Location near Svirsk town 53°31'5"N 103°22'3"E	20 km downstream coal pit – 9 to the west
P.13	Bratsk town 56°17'49"N 101°42'39"E	pulp and paper mill - 1.1 aluminum smelter - 9 machine-building plant - 28 ferroalloy production - 10
<b>Non-industrial areas (bays)</b>		
P.5	Tal'kino 53°51'28"N 103°10'38"E	Svirsk – 85; Bratsk - 288
P.7	Kada 54°24'43"N 103°3'59"E	Svirsk – 143; Bratsk - 233
P.8	Podvolochny 55°11'54"N 103°23'21"E	Svirsk – 235; Bratsk - 160
P.9	Karahun 55°34'19"N 103°6'20"E	Svirsk – 277; Bratsk - 121
P.10	Ozernaya Balya 55°50'04"N 102°56'34"E	Svirsk – 307; Bratsk – 95
P.12	Kezhma-Volokovaya 56°16'04"N 102°52'44"E	Svirsk – 346; Bratsk – 74 iron ore mining – 85
P.14	Ermakovka 55°55'16"N 102°0'5"E	Bratsk - 40 iron, copper deposits - 6 -31
P.15	Kezhma-Naratayskaya 56°3'24"N 102°27'8"E	Bratsk – 56 iron deposits – 5-31
<b>Non-industrial areas (settlements)</b>		
P.6	Ust'-Uda 54°10'15"N 103°2'0"E	Svirsk – 122; Bratsk - 250
P.11	Shumilovo 55°56'55"N 103°0'41"E	Svirsk – 320; Bratsk – 90 iron ore mining – 96

and for the complex of areas, demonstrating the combined influence of several pollutants on the natural environment. It is convenient tool for ecological study of territories with different loads.

## RESULTS AND DISCUSSION

Table 2 provides the initial analytical data – metal contents in the water samples, showing the differences between habitats. The last line of the table yields the metal contents in pure water of Lake Baikal (Grachev, 2002; Vetrov et al., 2013).

It is evident, that the composition of the reservoir water is different from the background of Baikal water: the Ti content is higher 13, Cr -3, Mn – 70, Fe – 52, Ni – 4 , Cu – 6, Zn –

**Table 2.** ICP-MS results of the water samples

Site	Metal content, µg/L							
	Ti	Cr	Mn	Fe	Ni	Cu	Zn	Pb
1	0.99 <sub>0.60</sub>	0.19 <sub>0.10</sub>	9.9 <sub>3.0</sub>	43.0 <sub>12.0</sub>	0.24 <sub>0.09</sub>	1.41 <sub>0.56</sub>	2.29 <sub>0.92</sub>	0.10 <sub>0.05</sub>
2	0.67 <sub>0.40</sub>	0.29 <sub>0.14</sub>	7.7 <sub>2.3</sub>	20.3 <sub>6.1</sub>	0.33 <sub>0.13</sub>	2.17 <sub>0.86</sub>	2.18 <sub>0.87</sub>	0.21 <sub>0.10</sub>
3	0.31 <sub>0.19</sub>	0.15 <sub>0.08</sub>	8.7 <sub>2.6</sub>	14.3 <sub>4.3</sub>	0.35 <sub>0.14</sub>	0.73 <sub>0.29</sub>	1.48 <sub>0.59</sub>	0.35 <sub>0.18</sub>
4	0.19 <sub>0.11</sub>	0.08 <sub>0.04</sub>	10.3 <sub>3.1</sub>	5.2 <sub>1.6</sub>	0.35 <sub>0.14</sub>	0.49 <sub>0.19</sub>	2.04 <sub>0.81</sub>	0.21 <sub>0.18</sub>
5	0.26 <sub>0.16</sub>	0.11 <sub>0.06</sub>	7.6 <sub>2.3</sub>	6.3 <sub>1.9</sub>	0.27 <sub>0.11</sub>	0.39 <sub>0.15</sub>	0.92 <sub>0.36</sub>	0.16 <sub>0.08</sub>
6	0.44 <sub>0.26</sub>	0.11 <sub>0.06</sub>	3.2 <sub>1.0</sub>	4.2 <sub>1.3</sub>	0.34 <sub>0.14</sub>	0.57 <sub>0.23</sub>	1.09 <sub>0.43</sub>	0.23 <sub>0.12</sub>
7	0.34 <sub>0.20</sub>	0.09 <sub>0.05</sub>	3.1 <sub>0.9</sub>	4.4 <sub>1.3</sub>	0.28 <sub>0.11</sub>	0.64 <sub>0.26</sub>	1.13 <sub>0.45</sub>	0.13 <sub>0.07</sub>
8	0.11 <sub>0.07</sub>	0.11 <sub>0.06</sub>	2.8 <sub>0.8</sub>	5.3 <sub>1.6</sub>	0.24 <sub>0.10</sub>	0.53 <sub>0.21</sub>	1.26 <sub>0.50</sub>	0.10 <sub>0.05</sub>
9	0.38 <sub>0.23</sub>	0.10 <sub>0.05</sub>	5.3 <sub>1.6</sub>	9.4 <sub>2.8</sub>	0.37 <sub>0.18</sub>	0.97 <sub>0.38</sub>	1.43 <sub>0.57</sub>	0.33 <sub>0.17</sub>
10	0.16 <sub>0.10</sub>	0.15 <sub>0.08</sub>	2.9 <sub>0.9</sub>	3.5 <sub>1.0</sub>	0.30 <sub>0.12</sub>	0.58 <sub>0.23</sub>	1.50 <sub>0.60</sub>	0.24 <sub>0.12</sub>
11	0.20 <sub>0.12</sub>	0.10 <sub>0.05</sub>	5.3 <sub>1.6</sub>	6.4 <sub>1.9</sub>	0.33 <sub>0.13</sub>	0.53 <sub>0.21</sub>	1.52 <sub>0.61</sub>	0.05 <sub>0.03</sub>
12	0.32 <sub>0.19</sub>	0.09 <sub>0.05</sub>	1.8 <sub>0.5</sub>	3.7 <sub>1.1</sub>	0.27 <sub>0.11</sub>	0.63 <sub>0.25</sub>	1.27 <sub>0.50</sub>	0.32 <sub>0.16</sub>
13	0.41 <sub>0.24</sub>	0.20 <sub>0.10</sub>	9.0 <sub>2.7</sub>	15.2 <sub>4.6</sub>	0.52 <sub>0.20</sub>	1.37 <sub>0.55</sub>	5.5 <sub>2.2</sub>	0.42 <sub>0.21</sub>
14	0.26 <sub>0.16</sub>	0.14 <sub>0.07</sub>	4.2 <sub>1.3</sub>	14.8 <sub>4.4</sub>	0.30 <sub>0.12</sub>	0.70 <sub>0.28</sub>	1.65 <sub>0.61</sub>	0.36 <sub>0.10</sub>
15	0.31 <sub>0.19</sub>	0.11 <sub>0.06</sub>	1.7 <sub>0.5</sub>	11.4 <sub>3.4</sub>	0.38 <sub>0.15</sub>	0.72 <sub>0.29</sub>	0.96 <sub>0.38</sub>	0.25 <sub>0.13</sub>
*	0.04	0.07	0.13(1.5)	0.38(1.3)	0.15(0.08)	0.21	3.2 (0.4)	<0.02

\* - Baikal Lake (Vetrov et al., 2013; Grachev, 2002 - in the parentheses);

Analysis error is presented as the subscript

7 and Pb 14 times. When the sites under industrial exposure (p. 1-4 and 13) were compared with the places, not affected by such influences (rest points), using the Kruskal-Wallis ANOVA, significant differences were revealed between the two groups in the contents of Ti, Cr, Mn, Fe, Cu and Zn (H varied as 4.65-8.06;  $p = 0.004-0.031$ ). The contents of Ti and Fe are highest in the samples in point 1 (near Angarsk town), caused by heavy machinery production. Besides, the titanium ore deposit (Table 1) is the source of these metals. Considerable Cu and Cr abundances, being detected close to Usolye-Sibirskoye town (P. 2), could be caused by chemical and mining equipment manufacturing; high Ni, Zn and Pb contents in the point 13 (Bratsk town) are due to ferroalloys production and machine building. High lead measured near Svirsk town in the points 3 and 4 is caused by battery production. The average metal content in the sample under industrial activity was, µg/L: Ti 0.51, Cr 0.18, Mn 9.1, Fe 19.6, Ni 0.36, Cu 1.2, Zn 2.7 and Pb 0.29. For second group, the average contents of most elements in the water were significantly lower than in the first group: Ti 0.28, Cr 0.11, Mn 3.8, Fe 6.9, Ni 0.31, Cu 0.63, Zn 1.27 and Pb 0.20 µg/L. However, even without any emissions, the reservoir water is dirtier relative to the reference Lake Baikal water. It is enriched with suspended substance due to the continuous abrasion and wave processes (Karnaukhova, 2008). The other factors are also the case, e.g. municipal wastes and geological sources like mineral deposits and fault zones.

Spearman's rank correlations ( $p < 0.05$ ) demonstrate the relations between the metal contents in the water and plant samples. Metal contents in all plant species strongly correlated with those in the water samples (R coefficient values 0.73-0.83). This means, that elements are actively consumed by the plants from aquatic surroundings. Furthermore, the composition of accumulator-plants reflects the ambient water composition, thus creating the prerequisites to apply them for environment state assessment.

Table 3 presents the XRF results for 53 plant samples of different species. The element contents vary widely in these plants, both between different species and within the same species.

So, the minimum and maximum values change in *E. canad.* from 2.4 (Zn) and 3 (Ni) to 10-16 times (Ti, Mn, Fe and Pb). The order of accumulation of metals in *E. canadensis* with respect to

Table 3. XRF results of aquatic plants, collected in the Bratsk reservoir

Site	Plant species	Metal concentration, µg/g dry weight							
		Ti	Cr	Mn	Fe	Ni	Cu	Zn	Pb
1	<i>M. spicat.</i>	1039 <sub>62</sub>	19 <sub>5</sub>	1224 <sub>62</sub>	11380 <sub>460</sub>	8 <sub>3</sub>	62 <sub>14</sub>	39 <sub>10</sub>	9 <sub>4</sub>
1	<i>P. pect.</i>	1057 <sub>63</sub>	19 <sub>5</sub>	538 <sub>38</sub>	11620 <sub>464</sub>	7 <sub>3</sub>	113 <sub>17</sub>	45 <sub>11</sub>	13 <sub>6</sub>
1	<i>E. canad.</i>	1030 <sub>62</sub>	16 <sub>4</sub>	289 <sub>30</sub>	9650 <sub>390</sub>	9 <sub>4</sub>	50 <sub>11</sub>	50 <sub>13</sub>	7 <sub>3</sub>
1	<i>C. glomer.</i>	680 <sub>68</sub>	19 <sub>4</sub>	590 <sub>41</sub>	18320 <sub>740</sub>	9 <sub>4</sub>	129 <sub>20</sub>	48 <sub>12</sub>	14 <sub>6</sub>
2	<i>M. spicat.</i>	693 <sub>69</sub>	18 <sub>5</sub>	835 <sub>58</sub>	8664 <sub>607</sub>	9 <sub>4</sub>	68 <sub>15</sub>	25 <sub>9</sub>	8 <sub>4</sub>
2	<i>P. pect.</i>	730 <sub>73</sub>	24 <sub>5</sub>	670 <sub>47</sub>	10360 <sub>420</sub>	8 <sub>3</sub>	92 <sub>36</sub>	39 <sub>10</sub>	9 <sub>4</sub>
2	<i>E. canad.</i>	808 <sub>81</sub>	20 <sub>5</sub>	1949 <sub>97</sub>	12010 <sub>480</sub>	12 <sub>5</sub>	70 <sub>15</sub>	35 <sub>10</sub>	6 <sub>3</sub>
2	<i>C. glomer.</i>	780 <sub>78</sub>	22 <sub>5</sub>	716 <sub>50</sub>	10780 <sub>424</sub>	9 <sub>4</sub>	128 <sub>20</sub>	61 <sub>15</sub>	48 <sub>8</sub>
3	<i>M. spicat.</i>	713 <sub>71</sub>	17 <sub>4</sub>	1420 <sub>70</sub>	7260 <sub>510</sub>	13 <sub>5</sub>	43 <sub>10</sub>	24 <sub>9</sub>	11 <sub>5</sub>
3	<i>P. pect.</i>	1050 <sub>63</sub>	33 <sub>9</sub>	867 <sub>61</sub>	15850 <sub>635</sub>	12 <sub>5</sub>	109 <sub>41</sub>	55 <sub>14</sub>	26 <sub>6</sub>
3	<i>E. canad.</i>	822 <sub>82</sub>	12 <sub>3</sub>	864 <sub>62</sub>	8720 <sub>610</sub>	10 <sub>4</sub>	107 <sub>17</sub>	58 <sub>14</sub>	47 <sub>8</sub>
3	<i>C. glomer.</i>	959 <sub>96</sub>	26 <sub>5</sub>	372 <sub>26</sub>	14430 <sub>580</sub>	10 <sub>4</sub>	125 <sub>19</sub>	58 <sub>14</sub>	104 <sub>10</sub>
4	<i>M. spicat.</i>	582 <sub>58</sub>	16 <sub>4</sub>	502 <sub>35</sub>	7010 <sub>490</sub>	8 <sub>3</sub>	77 <sub>16</sub>	23 <sub>9</sub>	10 <sub>5</sub>
4	<i>P. pect.</i>	710 <sub>71</sub>	18 <sub>5</sub>	346 <sub>25</sub>	8380 <sub>590</sub>	9 <sub>4</sub>	177 <sub>26</sub>	29 <sub>9</sub>	12 <sub>6</sub>
4	<i>C. glomer.</i>	334 <sub>33</sub>	12 <sub>3</sub>	450 <sub>32</sub>	7510 <sub>525</sub>	6 <sub>3</sub>	68 <sub>15</sub>	29 <sub>9</sub>	23 <sub>6</sub>
5	<i>M. spicat.</i>	320 <sub>32</sub>	9 <sub>3</sub>	497 <sub>35</sub>	4656 <sub>326</sub>	9 <sub>4</sub>	26 <sub>11</sub>	24 <sub>9</sub>	8 <sub>4</sub>
5	<i>P. pect.</i>	410 <sub>41</sub>	6 <sub>3</sub>	550 <sub>38</sub>	5060 <sub>355</sub>	8 <sub>3</sub>	49 <sub>10</sub>	26 <sub>9</sub>	5 <sub>2</sub>
5	<i>E. canad.</i>	390 <sub>39</sub>	9 <sub>3</sub>	730 <sub>51</sub>	4590 <sub>320</sub>	10 <sub>4</sub>	63 <sub>12</sub>	32 <sub>10</sub>	9 <sub>4</sub>
5	<i>C. glomer.</i>	500 <sub>50</sub>	6 <sub>3</sub>	403 <sub>28</sub>	5700 <sub>400</sub>	7 <sub>3</sub>	38 <sub>10</sub>	27 <sub>9</sub>	12 <sub>5</sub>
6	<i>M. spicat.</i>	519 <sub>52</sub>	6 <sub>3</sub>	370 <sub>26</sub>	4790 <sub>335</sub>	6 <sub>3</sub>	27 <sub>11</sub>	26 <sub>9</sub>	8 <sub>4</sub>
6	<i>P. pect.</i>	299 <sub>30</sub>	8 <sub>3</sub>	523 <sub>37</sub>	3740 <sub>270</sub>	8 <sub>3</sub>	28 <sub>11</sub>	27 <sub>9</sub>	8 <sub>4</sub>
6	<i>E. canad.</i>	773 <sub>77</sub>	8 <sub>3</sub>	281 <sub>23</sub>	6890 <sub>480</sub>	6 <sub>3</sub>	56 <sub>13</sub>	33 <sub>10</sub>	8 <sub>4</sub>
6	<i>C. glomer.</i>	590 <sub>59</sub>	8 <sub>3</sub>	637 <sub>45</sub>	1944 <sub>160</sub>	6 <sub>3</sub>	72 <sub>16</sub>	34 <sub>10</sub>	10 <sub>4</sub>
7	<i>M. spicat.</i>	361 <sub>36</sub>	6 <sub>3</sub>	490 <sub>34</sub>	3830 <sub>270</sub>	7 <sub>3</sub>	35 <sub>12</sub>	29 <sub>9</sub>	5 <sub>2</sub>
7	<i>P. pect.</i>	386 <sub>39</sub>	7 <sub>3</sub>	614 <sub>44</sub>	4870 <sub>340</sub>	6 <sub>3</sub>	44 <sub>11</sub>	31 <sub>9</sub>	7 <sub>3</sub>
7	<i>E. canad.</i>	82 <sub>8</sub>	3 <sub>2</sub>	350 <sub>25</sub>	960 <sub>90</sub>	6 <sub>3</sub>	35 <sub>12</sub>	32 <sub>10</sub>	4 <sub>2</sub>
7	<i>C. glomer.</i>	236 <sub>24</sub>	5 <sub>2</sub>	282 <sub>23</sub>	5560 <sub>390</sub>	5 <sub>2</sub>	47 <sub>11</sub>	28 <sub>9</sub>	8 <sub>4</sub>
8	<i>M. spicat.</i>	222 <sub>22</sub>	4 <sub>2</sub>	450 <sub>31</sub>	2590 <sub>190</sub>	5 <sub>2</sub>	27 <sub>11</sub>	18 <sub>7</sub>	5 <sub>2</sub>
8	<i>P. pect.</i>	320 <sub>32</sub>	5 <sub>2</sub>	211 <sub>18</sub>	3432 <sub>240</sub>	4 <sub>2</sub>	70 <sub>15</sub>	32 <sub>10</sub>	6 <sub>3</sub>
8	<i>C. glomer.</i>	450 <sub>45</sub>	6 <sub>3</sub>	410 <sub>29</sub>	5190 <sub>350</sub>	5 <sub>2</sub>	62 <sub>12</sub>	34 <sub>10</sub>	6 <sub>3</sub>
9	<i>M. spicat.</i>	452 <sub>45</sub>	9 <sub>3</sub>	640 <sub>45</sub>	4970 <sub>348</sub>	6 <sub>3</sub>	40 <sub>13</sub>	37 <sub>10</sub>	6 <sub>2</sub>
9	<i>P. pect.</i>	778 <sub>78</sub>	8 <sub>3</sub>	464 <sub>33</sub>	5670 <sub>400</sub>	5 <sub>2</sub>	35 <sub>12</sub>	26 <sub>9</sub>	8 <sub>4</sub>
9	<i>E. canad.</i>	485 <sub>49</sub>	8 <sub>3</sub>	416 <sub>29</sub>	4650 <sub>325</sub>	5 <sub>2</sub>	32 <sub>11</sub>	31 <sub>10</sub>	5 <sub>2</sub>
9	<i>C. glomer.</i>	273 <sub>27</sub>	10 <sub>4</sub>	230 <sub>20</sub>	5025 <sub>352</sub>	6 <sub>3</sub>	50 <sub>11</sub>	26 <sub>9</sub>	7 <sub>3</sub>
10	<i>M. spicat.</i>	504 <sub>50</sub>	7 <sub>3</sub>	591 <sub>41</sub>	5770 <sub>405</sub>	6 <sub>3</sub>	46 <sub>11</sub>	23 <sub>9</sub>	7 <sub>3</sub>
10	<i>P. pect.</i>	494 <sub>49</sub>	8 <sub>3</sub>	308 <sub>25</sub>	7780 <sub>545</sub>	9 <sub>3</sub>	51 <sub>11</sub>	27 <sub>9</sub>	7 <sub>3</sub>
10	<i>E. canad.</i>	202 <sub>20</sub>	4 <sub>2</sub>	370 <sub>26</sub>	2050 <sub>165</sub>	5 <sub>2</sub>	15 <sub>5</sub>	36 <sub>10</sub>	7 <sub>3</sub>
10	<i>C. glomer.</i>	423 <sub>42</sub>	6 <sub>3</sub>	300 <sub>24</sub>	3910 <sub>310</sub>	5 <sub>2</sub>	48 <sub>10</sub>	25 <sub>9</sub>	10 <sub>4</sub>
11	<i>M. spicat.</i>	632 <sub>63</sub>	6 <sub>3</sub>	424 <sub>30</sub>	5990 <sub>420</sub>	5 <sub>2</sub>	14 <sub>6</sub>	22 <sub>8</sub>	8 <sub>4</sub>
11	<i>P. pect.</i>	788 <sub>79</sub>	11 <sub>4</sub>	344 <sub>25</sub>	9250 <sub>560</sub>	7 <sub>3</sub>	37 <sub>13</sub>	29 <sub>9</sub>	7 <sub>3</sub>
11	<i>C. glomer.</i>	666 <sub>67</sub>	9	590 <sub>40</sub>	4520 <sub>320</sub>	8 <sub>3</sub>	46 <sub>11</sub>	28 <sub>8</sub>	7 <sub>3</sub>
12	<i>M. spicat.</i>	394 <sub>39</sub>	4 <sub>2</sub>	832 <sub>58</sub>	4340 <sub>305</sub>	4 <sub>2</sub>	32 <sub>11</sub>	38 <sub>10</sub>	7 <sub>3</sub>
12	<i>P. pect.</i>	975 <sub>97</sub>	10 <sub>4</sub>	500 <sub>35</sub>	4870 <sub>340</sub>	10 <sub>4</sub>	75 <sub>16</sub>	33 <sub>10</sub>	7 <sub>3</sub>
12	<i>E. canad.</i>	787 <sub>79</sub>	11 <sub>4</sub>	190 <sub>18</sub>	6640 <sub>465</sub>	5 <sub>2</sub>	29 <sub>8</sub>	25 <sub>10</sub>	6 <sub>3</sub>
12	<i>C. glomer.</i>	461 <sub>46</sub>	10 <sub>4</sub>	820 <sub>57</sub>	6340 <sub>444</sub>	6 <sub>3</sub>	48 <sub>12</sub>	31 <sub>9</sub>	8 <sub>4</sub>

Continued Table 3. XRF results of aquatic plants, collected in the Bratsk reservoir

Site	Plant species	Metal concentration, µg/g dry weight							
		Ti	Cr	Mn	Fe	Ni	Cu	Zn	Pb
13	<i>M. spicat.</i>	501 <sub>50</sub>	7 <sub>3</sub>	1255 <sub>63</sub>	14020 <sub>560</sub>	14 <sub>5</sub>	58 <sub>13</sub>	64 <sub>16</sub>	12 <sub>6</sub>
13	<i>E. canad.</i>	541 <sub>54</sub>	8 <sub>3</sub>	1220 <sub>61</sub>	15711 <sub>630</sub>	6 <sub>3</sub>	39 <sub>10</sub>	53 <sub>14</sub>	11 <sub>5</sub>
13	<i>C. glomer.</i>	617 <sub>62</sub>	8 <sub>3</sub>	919 <sub>55</sub>	17881 <sub>715</sub>	5 <sub>2</sub>	86 <sub>18</sub>	29 <sub>9</sub>	11 <sub>5</sub>
14	<i>M. spicat.</i>	440 <sub>44</sub>	5 <sub>2</sub>	494 <sub>34</sub>	4280 <sub>300</sub>	5 <sub>2</sub>	31 <sub>11</sub>	35 <sub>10</sub>	8 <sub>4</sub>
14	<i>E. canad.</i>	125 <sub>13</sub>	3 <sub>2</sub>	1798 <sub>90</sub>	6245 <sub>437</sub>	6 <sub>3</sub>	21 <sub>9</sub>	24 <sub>8</sub>	6 <sub>3</sub>
14	<i>C. glomer.</i>	458 <sub>46</sub>	9 <sub>3</sub>	395 <sub>28</sub>	7304 <sub>512</sub>	6 <sub>3</sub>	89 <sub>19</sub>	26 <sub>9</sub>	9 <sub>4</sub>
15	<i>M. spicat.</i>	545 <sub>55</sub>	9 <sub>3</sub>	590 <sub>40</sub>	4070 <sub>285</sub>	5 <sub>2</sub>	20 <sub>8</sub>	26 <sub>9</sub>	8 <sub>4</sub>
15	<i>C. glomer.</i>	322 <sub>32</sub>	5 <sub>2</sub>	443 <sub>31</sub>	7290 <sub>510</sub>	4 <sub>2</sub>	75 <sub>17</sub>	24 <sub>9</sub>	8 <sub>4</sub>
	CRM EK-1	77	5.1	520	2600	3.7	11.2	20.6	1.1
	<i>E. canad.</i> *	-	3.8	290	1200	-	-	36	-
	<i>M. spicat.</i> *	-	1.3	135	300	-	-	30	-
	<i>C. glomer.</i> *	-	5.1	77.5	1630	-	-	< 2	-
	<i>E. canad.</i> **	-	2.8	356.8	2041	5.5	16.3	22.1	3.3
	<i>M. spicat.</i> **	-	1.6-3.5	174-471	230-2482	2.1-5	5.3-17.7	15.4-22.8	1.8-3.5
	<i>P. pect.</i> **	-	1.5-1.8	46-390	120-630	3.4-3.8	5-8.7	13.5-23.7	1.4-1.8

\* Data from (Kozhova et al. 1994); \*\* - (Zhigzhitzhapova et al. 2019)

Analysis error is presented as the subscript

the reduction of the average content in the samples is presented as: Fe > Mn > Ti > Cu > Zn > Pb > Cr > Ni. Also considerable content variations are noted in *C. glomerata*: from 2.5 (Ni and Zn) to 9-17 (Fe and Pb). The element line is presented as: Fe > Ti > Mn > Cu > Zn > Pb > Cr > Ni. To a lesser extent, the element contents varied in *P. pectinatus* and *M. spicatum*: within the limits of 2 (Zn) -6 (Cr and Cu) times for the first plant and 2.4-2.8 (Pb and Ni) -5.5 (Fe and Cu) for the second one. The metal line was in *P. pect.*: Fe > Ti > Mn > Cu > Zn > Cr > Pb > Ni. The element line was Fe > Mn > Ti > Cu > Zn > Cr > Pb > Ni for *M. spicat.*

The accumulation capacity of the species was assessed using Bioaccumulation Factor (*BF*), (Ahmad et al., 2016). Table 4 presents minimum and maximum values of calculated *BF*.

Evidently, the considered water plants of the Bratsk reservoir exhibit a good accumulative ability  $BF > 10^3$  (Ahmad et al., 2016). These species primarily accumulate Fe and Ti (*BF* is above  $10^6$ ) and, least of all, they do Ni and Zn (above  $10^4$ ). Chromium, manganese, copper and lead are captured by plants to the middle degree (above  $10^5$ ). The species differ a little among themselves in the terms of accumulation; each of them could be considered as the element bioconcentrator. However, small discrepancies distinguish the species. For instance, maximum iron was found in the filamentous alga *Cladophora* at 1.8 %. This plant also provides high consumption of Cr, Cu and Pb to 26, 129 and 104 µg/g, respectively. The significant contents of Ti (1050 µg/g), Cr (33 µg/g) and Cu (177 µg/g) in addition to iron (1.3 %) were fixed in pondweed. Water milfoil and Canadian waterweed show high manganese (1200-1950 µg/g), titanium (1030 µg/g) and iron (1.40-1.58 %). At the same time, in all plants, maximum contents of nickel and zinc slightly differ from each other and change in the range of 10-14 (Ni) and 55-64 µg/g (Zn). Some authors already reported the specific metal accumulation by some mentioned plants. For instance, *E. canadensis* accumulates Cu and Zn (Ceglowska et al., 2016), *P. pectinatus* accumulates Cu (Costa et al., 2018), *P. pectinatus* shoots keep Cr, Cd, V, Cu, Ni, Zn and Pb (Baldantoni & Alfani, 2018) and *M. spicatum* - Pb, Fe, Cu, Ni, and Zn (Wang et al., 2014). In the ongoing research, *M. spicatum* and *C. glomerata* are suitable for the BR environment monitoring, and they, as opposed to *P. pectinatus* and *E. canadensis*, were found at all sampling points.

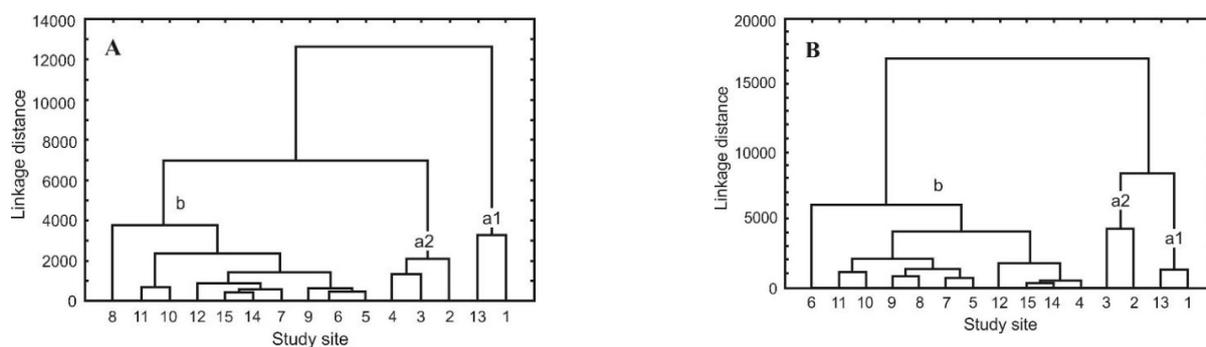
**Table 4.** Bioaccumulation factors (BF) for the studied species

Element	<i>M. spicat.</i>	<i>E. canad.</i>	<i>P. pect.</i>	<i>C. glomer.</i>
Ti	0.7-4.0*10 <sup>6</sup>	0.2-2.7*10 <sup>6</sup>	0.7-4.8*10 <sup>6</sup>	0.2-4.0*10 <sup>6</sup>
Cr	0.4-2.0*10 <sup>5</sup>	0.2-1.1*10 <sup>5</sup>	0.5-2.2*10 <sup>5</sup>	0.4-1.7*10 <sup>5</sup>
Mn	0.5-4.6*10 <sup>5</sup>	0.3-4.3*10 <sup>5</sup>	0.4-2.0*10 <sup>5</sup>	0.4-4.6*10 <sup>5</sup>
Fe	0.3-1.7*10 <sup>6</sup>	0.2-1.8*10 <sup>6</sup>	0.3-1.8*10 <sup>6</sup>	0.4-1.7*10 <sup>6</sup>
Ni	1.3-3.7*10 <sup>4</sup>	1.2-3.8*10 <sup>4</sup>	1.7-3.9*10 <sup>4</sup>	1.0-3.8*10 <sup>4</sup>
Cu	0.3-1.6*10 <sup>5</sup>	0.3-1.6*10 <sup>5</sup>	0.4-1.5*10 <sup>5</sup>	0.5-1.7*10 <sup>5</sup>
Zn	1.1-3.0*10 <sup>4</sup>	1.4-3.9*10 <sup>4</sup>	1.4-2.8*10 <sup>4</sup>	0.5-3.9*10 <sup>4</sup>
Pb	0.2-1.6*10 <sup>5</sup>	0.15-1.3*10 <sup>5</sup>	0.2-1.5*10 <sup>5</sup>	0.2-1.4*10 <sup>5</sup>

The dissimilarity between different plants species was defined using Kruskal–Wallis ANOVA,  $p < 0.05$ . The four plant species are not statistically different in the contents of all elements, except for Cu. In most metals, the calculated  $H$ -criteria values changed from 1.75 to 7.19,  $p$  0.06-0.62. In case of copper, the  $H$ -criteria value was 14.0,  $p = 0.0029$ . Additional statistical evaluations using the Mann Whitney test between the two data series revealed no differences in the copper content in some plant pairs: *M. spicatum* and *P. pectinatus*, *M. spicatum* and *E. canadensis*, as well as between *E. canadensis* and *P. pectinatus* and *P. pectinatus* and *C. glomerata* ( $p > 0.05$ ). Conversely, Cu in *M. spicatum* and *C. glomerata* as well as in *E. canadensis* and *C. glomerata* significantly differs ( $p$  equals 0.0037 and 0.0175, respectively). That means that one plant species is not enough for biomonitoring assessments for all elements under study.

The two lines of the Table 3 give the threshold contents of metals in some macrophytes from Lake Baikal (Kozhova et al., 1994) and Gusinoye Lake (Zhigzhitzhapova et al., 2019), which is located about 600 km to south of BR. Comparison between the average concentrations in *E. canadensis* from the Bratsk reservoir and in the CRM EK-1 (Lake Baikal) revealed, that the values for the first plant are several-fold higher, e.g. Ti – 6; Cr – 2-2.6; Ni – 1.9; Fe – 3-6.7; Mn – 1.5-2.6; Cu – 4 Zn – 1.2-2; and Pb – 7.3. The metal levels in *M. spicatum* and *P. pectinatus* from the BR exceed significantly those in the plants of the Baikal and Gusinoye lakes, pointing to dirtier ecosystem of the Bratsk body relative to the other Siberian lakes. The purest water in Lake Baikal is the result of its purification by unique biological organisms not available in the Bratsk reservoir. In this context, the metal contents in the aquatic plants of this water body correspond to the natural background or threshold values.

To identify similarities and differences between the studied sites in respect to the metal contents in aquatic plants the dendrograms were created for *M. spicatum* and *C. glomerata* (Fig. 2a and 2b). Main clusters have been identified. Two subgroups “a1” and “a2” include the locations near the industrial areas (points 1 and 13 as well as P. 2, 3 and 4 in Fig. 2a and P. 1 and 13 as well as P. 2 and 3 in Fig. 2b). Even if the sampling sites 1 and 13 are located too far from each other, however, they both are under the harmful impact of similar industries. Hence, they appeared side by side on the tree scheme, showing similar patterns of metal contents. The plant samples from these points are featured by high Ti content (600-1040  $\mu\text{g/g}$ ), Mn (900-1250), Fe (11400-18000), Cu (60-130) and Zn (50-64) due to industrial emissions (Tabl. 1). Other sources of Ti, Mn and Fe are the ore deposits occurring near the studied sites. The samples of points 2 and 3 demonstrate the high contents ( $\mu\text{g/g}$ ) of Cr (17-26), Fe (7000-14400), Ni (9-13) and Cu (68-130) (subgroup “a2”). These metals come into the aquatic environment from metallurgical and chemical enterprises, as well as of agriculture runoffs. Among the other components of the emission, the Pb content was recorded as highest near Svirsk town, P. 3 (reaching 104  $\mu\text{g/g}$  in the algae), as the component of the waste from the lead battery plant. This subgroup on the Fig. 2a also includes the point 4, as the pattern of metal distribution in *M. spicatum* from this area is similar to the patterns for neighboring points.



**Fig. 2a and 2b.** Diagrams for 15 sampling points based on the concentrations of 8 elements in *M. spicatum* and *C. glomerata* with complete-linkage clustering algorithm and the Manhattan distance method

Cluster “b” is represented by the sites located in bays and settlements with forest and recreational surroundings (P. 5-12 and 14 and 15). It is divided into more small subgroups. Some sites with adjacent sequence numbers are combined, for example, points 8 and 9 or 10 and 11 as well as 14 and 15 in Fig. 2b, also some numbers in Fig. 2a. This feature is associated with close spatial locations of these points and with similar geochemical, climatic and topographic characteristics. The points 12, 14 and 15 showed similar trends in the metal contents of Mn (to 820  $\mu\text{g/g}$ ), Fe (to 7300  $\mu\text{g/g}$ ) and Cu (to 89  $\mu\text{g/g}$ ) in *C. glomerata*. The contents,  $\mu\text{g/g}$ , of Mn (832) and Zn (38) in *M. spicatum* are enough high. The probable resource of these metals is iron and copper ore occurrences (Boyarkin VM & Boyarkin IV, 2011). For the same reason, the points 10 and 11 fell into other subgroup. Despite the fact that the points 5, 6 and 9 (Fig. 2a), or 5, 7, 8 and 9 (Fig. 2b) are located at considerable distances from each other, the metal distribution patterns are similar; they characterize the sites with low emission load. Eventually, the average contents of elements in *M. spicatum* in the natural environment (group “b”) are: Ti (420), Cr (6), Mn (540), Fe (4530), Ni (6), Cu (30), Zn (28) and Pb (7)  $\mu\text{g/g}$ . The average contents in *C. glomerata* are: Ti (490), Cr (8), Mn (450), Fe (5480), Ni (6), Cu (60), Zn (28) and Pb (10)  $\mu\text{g/g}$ . However, one point in each figure is located separately: the point 8 in the diagram A and the point 6 in the diagram B. Isolation of first point is based on the lowest concentrations ( $\mu\text{g/g}$ ) of Ti (220), Cr (4), Fe (2590) and Zn (18) in *M. spicatum* due to distance from any human activity (Fig. 2a). Also, the microelement composition of *C. glomerata* (point 6, Fig. 2b) is specified to compare with the other points: the lowest content of Fe (1940  $\mu\text{g/g}$ ), however high concentrations of Mn (637  $\mu\text{g/g}$ ) and Cu (72  $\mu\text{g/g}$ ) take place. The last two elements can be supplied as fertilizer ingredients and as waste from human activity (Polechonska & Klink, 2021).

Some other factors contribute to the metal concentrations of plants in the Bratsk reservoir, regardless of the sample location. Among them are the exogenous processes (abrasions and landslides) and tectonic faults (Kuskovskii et al., 1999). These natural sources supply some chemical elements and their compounds to the reservoir ecosystem, thus increasing the available element levels in it. It should be noted that the intensive erosion of the coastline as a result of strong wave processes is inherent in this man-made water body. The coastal zone, where aquatic plants inhabit, is a dynamic area of entry, accumulation and movement of sedimentary material (Karnaukhova, 1999). This natural factor, specific to environment of the Bratsk reservoir, provides higher metal contents in its aquatic plants, compared with the plants from the background water bodies, exactly Lake Baikal and Gusinoe Lake (Table 3). The next supplier of some metals in the reservoir environment is rotting of bottom-lying vegetation stuff (Poletaeva et al., 2018). Massive areas of forests have not been cleaned from the woods and million cubic meters of trees were under the water after the power plant was launched 50 years ago. As a result, enormous amounts of metals and non-metals are released into the aquatic

**Table 5.** Pollution indices (*CF*, *PLI* and *NPI*) for the water samples and aquatic plants of the Bratsk reservoir

Sample group	Sample	<i>CF</i>								<i>PLI</i>	<i>NPI</i>
		Ti	Cr	Mn*	Fe	Ni	Cu	Zn	Pb*		
a	<i>M. spicat.</i>	9.2	3.0	2.9	3.7	2.8	5.5	1.7	3.0	3.0	7.1
b		5.7	1.3	1.5	1.7	1.6	2.7	1.4	2.1	1.8	4.3
a	<i>C. glomer.</i>	7.4	3.4	1.7	5.3	2.1	9.6	2.2	12.1	3.5	11
b		5.5	1.4	1.3	2.0	1.5	5.1	1.4	2.6	2.0	4.7
a	water	2.2	2.6	6.1	1.4	2.4	3.1	4.5	5.8	2.6	5.6
b		1.2	1.6	2.5	0.5	2.1	1.6	2.1	4.0	1.5	3.5

\* Threshold concentrations (Zhigzhitzhapova et al. 2019)

surroundings. Thus, the combined impact of industrial and natural factors is responsible for raising the element contents in the water and plants in the Bratsk reservoir.

To assess the environment quality, individual polluting factors (*CF*) and the total pollution load indexes *PLI* and the integration Nemerov indexes *NPI*, specified in the section “Data analysis” were calculated. Table 5 gives their values for eight metals in *M. spicatum* and *C. glomerata* for the sampling groups distinguished by numerical classification. The calculated *CF* values allowed the contribution of each metal to the total pollution of each site under study. The *PLI* pollution index (Tomlinson et al., 1980) ranks the places by the level of their pollution, informing about the simultaneous contamination with several pollutants. To strengthen the assessment, the *NPI* indices were applied. They were initially used in some publications to assess the state of the water (Poletaeva et al., 2021) and bottom sediments (Benhaddya et al., 2019). However, these indices have been recently applied to aquatic plants (Balatony et al., 2018; Polechonska et al., 2018; Polechonska & Klink, 2021).

In *NPI* calculations, the authors employed the geochemical background concentrations of metals in the Polish waters (Polechonska & Klink, 2021) and the concentrations for terrestrial plants (Markert, 1992) as threshold values. In this work, these indices were evaluated relative to the reference water of Lake Baikal. For the plants they were obtained by normalizing the contents in the samples from BR to metal contents in *Elodea canadensis* collected in the uncontaminated environment of Lake Baikal and Gusinoye Lake (Catalogue, 2013; Zhigzhitzhapova et al., 2019).

Based on the average values of the *CF* index (Table 5), metals Mn, Cu, Zn and Pb are abundant in the BR water. *CF* values for Mn and Pb are  $\geq 6$  (Hakanson, 1980). Therefore, very high contamination of the water with these metals takes place in the locations of groups “a1” and “a2” (sampling sites with industrial load). The water pollution with Cu and Zn is significant ( $3 < CF < 6$ ). The rest metals provide the average level of contamination (Hakanson, 1980). The water samples in group “b” are corresponded mainly to the average level of pollution, except for Pb (high contamination) and Fe (low contamination). The synthetic assessments indicated that the BR water is referred to the category “severely polluted” by *NPI* values in the locations of both clusters and “polluted” by *PLI* classification. High levels of metals deteriorate the water quality.

The analysis of *CF* indices in the plants showed that the samples under industrial load (cluster “a”) are significantly contaminated in Ti, Cr, Fe, Cu and Pb. Of particular concern are the levels of Ti, Cu and Pb that exceed the threshold values in the plants maximum 9-12 times. High plant contamination by Ti and Cu was also observed in the cluster “b”. According to the total pollution index *PLI* (Tomilson, 1980), the plants from all sites in the BR differently undergo metal pollution. The status of “polluted areas” refers even to the locations that are far from the centers of metal emission, cluster “b”, ( $PLI > 1$ ). For the cluster “a”, the *PLI* values in the industrial points (1-4 and 13) are higher or equal to 3. With respect to the *NPI* parameters, they provided the same pollution trends as for the reservoir water. The variations of the *NPI* values for polluted

sites (cluster “a”) were estimated as 5.4-10.1 for *M. spicatum* and 5.5-23.2 for *C. glomerata*. In the cluster “b”, the *NPI* values varied from 2.3 to 6 for *M. spicatum*, and 3.1 to 6 for algae. The highest *NPI* values were acquired in the points of the first group: 10.4 near Angarsk (P. 1) for *M. spicatum* and 23.2 near Svirsk towns (P. 3) for *C. glomerata*. At the sampling points 1 and 3, metals Ti, Cu and Pb were dominant. The sampling points 6 and 11 (residential areas) and 12, 14 and 15 (near ore deposits) showed high enough pollution indices due to the Ti and Cu contributions to the total parameters. That is, the selected plant species can equally be used to assess the state of the aquatic environment in the BR.

## CONCLUSIONS

The indicator abilities of three macrophytes *Myriophyllum spicatum*, *Elodea canadensis*, *Potamogeton pectinatus* and algae *Cladophora glomerata* were tested to use them for assessment of the Bratsk reservoir environment, Russia, the huge man-made water body of the world. It was found that these species have high indexes of metal accumulation caused by both natural and man-made sources: their bioaccumulation factors *BF* are  $10^4$ - $10^6$ . However, only *M. spicatum* and *C. glomerata* were chosen as bioindicators because of their habitat in all sampling sites. The study showed that for an objective assessment of the environmental pollution, it is preferable to use two or more bioindicator species. The dendrograms constructed for these plants provided similarities and differences in the metal accumulation patterns depending on the locations. The sites located near industrial enterprises are characterized by high metal contents in the water and plants. Metals Ti, Cr, Mn, Fe, Cu and Zn near Angarsk city are due to the industrial emissions and titanium deposits. The machine-building and ferroalloy industries in Bratsk town release Mn, Fe, Cu, Zn and Pb. High Pb in the samples near Svirsk town comes from waste of lead battery plant. The sources of Mn, Fe, Cu and Pb close to Usolye-Sibirskoye town are metallurgic and chemical enterprises and agricultural use. The metal contents in the water and plants sampled relatively far from the metal emission centers were significantly lower. At the same time, they exceeded the threshold values in the samples taken in Lake Baikal with the clean environment due to the sedimentation processes, coastal erosion, as well as rotting of bottom-lying wood and ore deposits. The assessments of pollution through the total pollution load index (*PLI*) and the integration Nemerov index (*NPI*) provided the classification of the locations mainly as medium and highly polluted ones. As a result, the metal pollution of the Bratsk reservoir environment was identified using the bioindicator plant species.

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## CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct,

data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

## LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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