

# Bioaccumulation of macro- and microelements by macrophytes in Lake Baikal is one of factors in the dynamics of near-shore food webs and biodiversity

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## Abstract

Chemicals in macrophytes and in suspended matter precipitated on the plants surface represent a part of flows of matter incoming into a food chain and participating in formation of water and bottom sediments elemental composition in the littoral. At this studies stage, to characterize the elements distribution in natural and anthropogenic sites of the littoral, we determined by ICP-MS method the elemental composition in *Potamogeton perfoliatus* L., *Potamogeton filiformis* Pers., *Myriophyllum spicatum* L., *Batrachium trichophyllum* (Chaix) Bosch, *Butomus umbellatus* L., *Sagittaria natans* Pall. In the studied species, such macroelements dominate as K, Ca and Na; dominant microelements are Mn, Fe, Si and Sr. There are some peculiarities in the elemental composition of each species: *P. filiformis* is characterized by elevated content of B, Ge and Sb, *B. trichophyllum* by Mn and Ag, *B. umbellatus* by Ti and Cr. The highest content of U and the lowest one of K, Rb, Tl, Nb, Cs, LREE are characteristic for *M. spicatum*. *S. natans* exceeds other species by content of Br, Zr, REE, Ta, W and Th. Compared to the aquatic environment in the littoral, the macrophytes accumulate 4200–15000 times more P, in 2000–26000 times more Mn, 4000–14000 times more Zn. In *M. spicatum* sampled at the stations adjacent to the territories of settlements and touristic units there are elevated concentrations of Cl, Na, P, K and highest values of summary content of macroelements and of all determinable elements.

## Keywords

Lake Baikal, macrophytes, macro- and microelemental composition, biological accumulation coefficient, bioindication

## Introduction

Macrophytes are widely distributed in freshwater and marine ecosystems, where they contribute to shoreline stabilization, wave attenuation, and near-shore current reduction. They also influence oxygen saturation, nutrient dynamics, and overall productivity of water bodies (Voronikhin 1953; Lukina and Smirnova 1988; Madsen et al. 2001; Riis and Hawes 2002; Baldantoni et al. 2005). Owing to anatomical features such as a weakly developed cuticle, thin lamina, and the presence of aerenchyma, aquatic higher plants can absorb and accumulate substantial amounts of fine-disperse suspension as well as dissolved organic and inorganic compounds from the water column (Kokin 1982; Zaytseva et al. 2004; Yanin 2020). The accumulation capacity of macrophytes for heavy metals has been extensively documented (Mikryakova 2002; Kurilenko and Osmolovskaya 2006; Chukina and Borisova 2010; Oyedeji et al. 2013; Borisova et al. 2017; Farias et al. 2018; Anishchenko et al. 2023).

In Lake Baikal, the greatest diversity and abundance of macrophytes occur in areas sheltered from the main water body (e.g., gulfs, estuaries, bays), where wave exposure is reduced and summer water temperatures are slightly elevated compared to open shores. Along exposed shores characterized by strong wave action, stony substrates, and low summer water temperatures, aquatic plants are found sporadically on sandy, sandysilty, and silty bottoms; common species include *Potamogeton* spp., *Myriophyllum sibiricum*, *M. spicatum*, *Lemna trisulca*, *Batrachium trichophyllum*, *Elodea canadensis*, and *Fontinalis* spp. (Azovsky 2003; Azovsky and Chepinoga 2007).

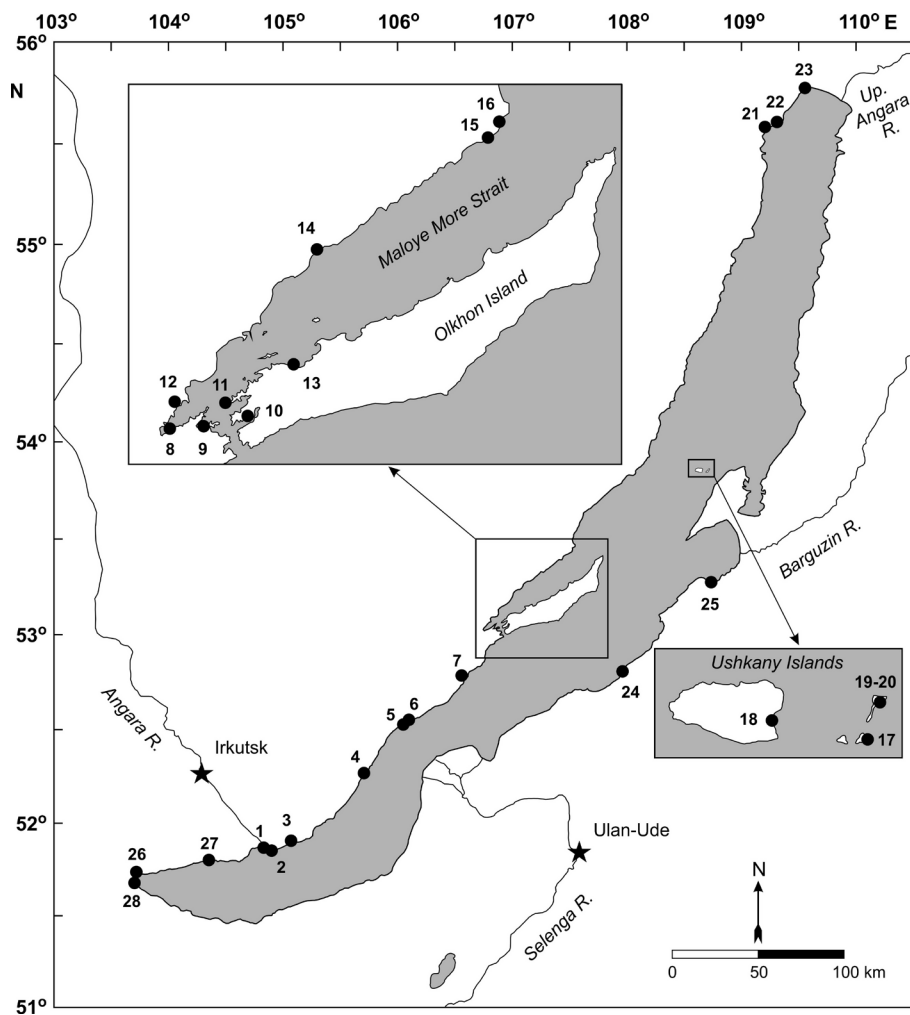
The present study aimed to: (i) determine the elemental composition of *Potamogeton perfoliatus* L., *Potamogeton filiformis* Pers., *Myriophyllum spicatum* L., *Batrachium trichophyllum* (Chaix) Bosch, *Butomus umbellatus* L., and *Sagittaria natans* Pall.; (ii) calculate species-specific bioaccumulation factors relative to ambient water chemistry; (iii) identify macrophyte species most suitable for bioindication of anthropogenic pollution; and (iv) identify sites with the highest elemental concentrations in the selected bioindicator species.

## Materials and methods

### Study Area and Sampling

Sampling was conducted during July–August, 2017–2020 in the littoral zone of Lake Baikal (Fig. 1). Six aquatic higher plant species were collected by scuba divers along transects at varying depths: *Potamogeton perfoliatus* L., *Potamogeton filiformis* Pers., *Myriophyllum spicatum* L., *Batrachium trichophyllum* (Chaix) Bosch, *Butomus umbellatus* L., and *Sagittaria natans* Pall. For each species, separate samples were taken of whole plants, leaves, stalks, roots, and rootstocks where applicable.

Water samples were collected using plastic syringes along transects at distances of 1, 10, 20, 30, and 50 m from the water edge. Interstitial water was also sampled from beach holes approximately 1 m above the water edge.



**Figure 1.** Schematic map of station of sampling of macrophytes and water. 1. Listvyanka settl., southern part. 2. Beryozovy Cape. 3. Bol'shiye Koty Bay, LIN Station. 4. Peschanaya Bay. 5. Bugul'deyka settl. 6. 2.3 km from the Bugul'deyka R. mouth. 7. The Anga R. bed. 8. Mukhor Gulf. 9. Kurkutsкая Bay. 10. Zagli Gulf. 11. Khorin-Irgi Bay. 12. Shida Gulf. 13. Semisosenskaya estuary. 14. Yadyrtuy Gulf. 15. Zama Cape. 16. 300 m southward from Kodovy Gulf. 17. Maly Ushkaniy Island. 18. Bol'shoy Ushkaniy Island. 19. Tonkiy Island. 20. Tonkiy Island, "Seal-Center". 21. Senogda Bay. 22. Zarechny settl. (micro-district of Severobaikalsk town). 23. Nizhneangarsk settl. 24. Gremyachinsk settl. 25. The Maksimikha R. mouth. 26. Kultuk settl. 27. Opposite to the Bol'shaya Polovinnaya R. mouth. 28. Slyudyanka City, opposite to the Pokhabikhа R. mouth (see Suppl. material 1: Table S1).

## Sample Preparation

Collected plants were washed in filtered lake water, then examined under a binocular microscope (MBS-10) to remove remaining debris. Cleaned samples were rinsed with distilled water and dried at 60°C to air-dry state. Dried samples were ground in an agate mortar and further dried to constant mass at 105°C. An additional sample of organic-mineral sediment was collected from *P. perfoliatus* leaves as greenish-grey microscopically thin crusts and processed separately.

Water samples were filtered immediately after collection using sterile single-use syringe filters (Minisart 16555-K, 0.45 µm pore size, cellulose acetate) into pre-weighed polypropylene Eppendorf tubes containing 40 µL of preservative (70% HNO<sub>3</sub>, purified twice by subboiling distillation). Filtration was performed in the laboratory of the R/V Academician V.A. Koptug.

## Elemental Analysis

For plant analysis, 30 mg aliquots of dried material were placed in sterile polypropylene tubes with 0.7 mL of 70% HNO<sub>3</sub> (subboiling distilled) and heated at 80°C for 8 hours. After cooling, 0.2 mL of 30% H<sub>2</sub>O<sub>2</sub> was added, and the volume was brought to 15 mL with distilled water.

For residual sediment from *M. spicatum* and *B. trichophyllum* leaf samples (2.0 mg), a modified digestion was used: 0.012 mL of 45% HF (subboiling distilled), 0.010 mL of 30% H<sub>2</sub>O<sub>2</sub>, and 0.22 mL of H<sub>3</sub>BO<sub>3</sub> solution (2.2% with 0.165% EDTA) were added, and the final volume was adjusted to 1.0 mL with distilled water. Elemental composition was determined by inductively coupled plasma mass spectrometry (ICP-MS) using an Agilent 7500ce quadrupole mass spectrometer at the Center for Collective Use "Ultramicroanalysis," Limnological Institute, Siberian Branch of the Russian Academy of Sciences. Analytical accuracy was verified using certified reference standard for deep Baikal water composition (Suturin et al. 2003) and certified reference material *Elodea canadensis* (EC-1, A.P. Vinogradov Institute of Geochemistry, SB RAS)

Typical measurement errors (coefficient of variation, CV) depended on element concentration:

< 0.001 µg/L: CV > 25%, 0.001–0.1 µg/L: CV 25–10%, 0.1–1 µg/L: CV 10–5%, 1 µg/L: CV < 5%. Water content and ash content of plant samples were determined by thermogravimetric method.

## Data Analysis

The concentrating function of plants relative to water was assessed using the biological accumulation factor (BAF):  $BAF = C_1 / C_2$ , where  $C_1$  is element concentration in plant fresh mass, and  $C_2$  is element concentration in shallow-zone lake water (the formula of recalculation of chemicals content in dry mass ( $C_{dry\ mass}$ ) for content

in wet (fresh) mass:  $C_{\text{wet (fresh) mass}} = C_{\text{dry mass}} \times (100 - W)/100$ ,  $W$  – water content in macrophytes (median value)).

For each element, data were stratified into minimal, average, and maximal value groups. Group homogeneity was assessed using coefficient of variation (CV), with  $CV \leq 33\%$  considered homogeneous (Teveleva 2021).

Sampling stations for *M. spicatum* were clustered using k-means method based on six standardized variables: Cl, P, Na, and K content in plants, total macroelement content ( $\Sigma C$  macro), and total content of all determinable elements ( $\Sigma C$  total). The number of clusters was selected based on the maximum center separation.

The assessment of statistical importance of differences between elements contents in the plants was performed by U-criterion of Mann-Whitney Statistical significance was set at  $p < 0.05$ . Statistical analyses were performed using MS Excel 2010 and StatSoft Statistica 8.

## Results and discussion

### Chemical elemental composition of macrophytes

Water content in the sampled macrophytes ranged from 90–98% (mean  $94.0 \pm 4.0\%$ , median 94.3%). Ash content (% dry mass) varied by species: *Potamogeton perfoliatus* 5.6–9.8%, *P. filiformis* 9.4–14.5%, *Myriophyllum spicatum* 4.5–11.7%, *Batrachium trichophyllum* 15.6–17.0%, *Butomus umbellatus* 7.4–12.4%, and *Sagittaria natans* 10.7–12.5%.

The highest total concentration of determinable elements ( $60\text{--}75 \text{ mg g}^{-1}$  dry mass) was observed in *S. natans*. Values ranged from  $48\text{--}55 \text{ mg g}^{-1}$  in *B. trichophyllum*, *B. umbellatus*, *P. filiformis*, and *P. perfoliatus*, and  $23\text{--}40 \text{ mg g}^{-1}$  in most *M. spicatum* samples. Macroelements (Na, Mg, P, S, Cl, K, Ca), each present at  $\geq 1000 \mu\text{g g}^{-1}$ , constituted approximately 98–99% of this total. Elements with concentrations between 10 and  $1000 \mu\text{g g}^{-1}$  (B, Al, Si, Mn, Fe, Zn, Br, Sr, Ba) accounted for  $\sim 1\text{--}2\%$ . Elements with concentrations  $\leq 10 \mu\text{g g}^{-1}$  contributed 0.03–0.1% and were categorized as follows:  $1.0\text{--}10 \mu\text{g g}^{-1}$  (Ti, Ni, Cu, Rb, Mo, I);  $0.1\text{--}1.0 \mu\text{g g}^{-1}$  (Li, V, Cr, Co, As, Se, Y, Pb, U);  $0.01\text{--}0.1 \mu\text{g g}^{-1}$  (Sc, Ga, Ge, Zr, Cd, Sb, W, Hg, Tl, Th);  $0.001\text{--}0.01 \mu\text{g g}^{-1}$  (Be, Nb, Ag, Sn, Cs, rare earth elements (REE), Hf, Bi); and  $<0.001 \mu\text{g g}^{-1}$  (Ta, Au).

Potassium dominated the macroelement composition across all species, contributing 60–70% of the total macroelement sum in *S. natans*, *B. trichophyllum*, and *B. umbellatus*; 40–50% in *P. perfoliatus* and *P. filiformis*; and 20–40% in *M. spicatum*. Calcium was the second most abundant element, except in *S. natans*, where the order was  $K > Na > Ca$ . Significant sodium accumulation was also observed in *M. spicatum*, *P. perfoliatus*, and *P. filiformis*, with the general sequence  $K \geq Ca > Na > P \geq S, Mg, Cl$  (Table 1).

**Table 1.** Macroelement concentrations ( $\mu\text{g g}^{-1}$  dry mass) in the studied macrophyte species; sample size (n) is given in parentheses; dash indicates no data available

| Element                              | Macroelements contents, $\mu\text{g g}^{-1}$ dry mass |         |                  |                 |
|--------------------------------------|-------------------------------------------------------|---------|------------------|-----------------|
|                                      | minimal                                               | average |                  | maximal         |
|                                      | min–max                                               | median  | min–max          | min–max         |
| <i>Potamogeton perfoliatus</i> (15)  |                                                       |         |                  |                 |
| Na                                   | 1300–2500 (6)                                         | 3700    | 3200–6100 (9)    | –               |
| Mg                                   | –                                                     | 3400    | 2000–5600 (15)   | –               |
| P                                    | 990–1830 (8)                                          | 3400    | 2800–5700 (7)    | –               |
| S                                    | –                                                     | 2900    | 2000–4400 (15)   | –               |
| Cl                                   | –                                                     | 1465    | 960–2300 (14)    | 4600 (1)        |
| K                                    | 5700–8400 (5)                                         | 20000   | 13400–33000 (10) | –               |
| Ca                                   | –                                                     | 11400   | 6100–18100 (14)  | 42000 (1)       |
| <i>Potamogeton filiformis</i> (10)   |                                                       |         |                  |                 |
| Na                                   | –                                                     | 5600    | 4000–9500 (9)    | 11600 (1)       |
| Mg                                   | –                                                     | 1430    | 1080–2000 (10)   | –               |
| P                                    | –                                                     | 2150    | 1180–3000 (8)    | 4700; 5200 (2)  |
| S                                    | –                                                     | 5350    | 3100–7100 (10)   | –               |
| Cl                                   | –                                                     | 2800    | 1710–3200 (10)   | –               |
| K                                    | –                                                     | 25000   | 14000–37000 (10) | –               |
| Ca                                   | –                                                     | 8850    | 5900–10600 (10)  | –               |
| <i>Myriophyllum spicatum</i> (37)    |                                                       |         |                  |                 |
| Na                                   | –                                                     | 4500    | 2700–9700 (33)   | 10300–15200 (4) |
| Mg                                   | –                                                     | 1810    | 940–3700 (37)    | –               |
| P                                    | –                                                     | 1820    | 750–3300 (33)    | 3500–5100 (4)   |
| S                                    | –                                                     | 2150    | 1260–4500 (36)   | 5500 (1)        |
| Cl                                   | 470–1510 (17)                                         | 2150    | 1560–4200 (20)   | –               |
| K                                    | –                                                     | 10000   | 5600–17400 (37)  | –               |
| Ca                                   | –                                                     | 7200    | 4000–14700 (37)  | –               |
| <i>Batrachium trichophyllum</i> (10) |                                                       |         |                  |                 |
| Na                                   | –                                                     | 2900    | 2100–5400 (10)   | –               |
| Mg                                   | –                                                     | 2400    | 1820–3000 (10)   | –               |
| P                                    | 1460–3300 (5)                                         | 4500    | 4000–6000 (5)    | –               |
| S                                    | –                                                     | 2600    | 1620–4100 (10)   | –               |
| Cl                                   | –                                                     | 2090    | 1520–3400 (8)    | 5600; 7200 (2)  |
| K                                    | –                                                     | 28000   | 23000–59000 (9)  | 61000 (1)       |
| Ca                                   | –                                                     | 5900    | 4200–7900 (10)   | –               |
| <i>Butomus umbellatus</i> (11)       |                                                       |         |                  |                 |
| Na                                   | –                                                     | 2700    | 1670–3900 (11)   | –               |

| Element                      | Macroelements contents, $\mu\text{g g}^{-1}$ dry mass |         |                 |                |
|------------------------------|-------------------------------------------------------|---------|-----------------|----------------|
|                              | minimal                                               | average |                 | maximal        |
|                              | min-max                                               | median  | min-max         | min-max        |
| Mg                           | –                                                     | 2700    | 1720–5100 (11)  | –              |
| P                            | –                                                     | 2900    | 2000–5600 (11)  | –              |
| S                            | –                                                     | 2200    | 2000–3800 (11)  | –              |
| Cl                           | –                                                     | 2500    | 1850–4100 (9)   | 5200; 5400 (2) |
| K                            | 8500 (1)                                              | 29000   | 14700–43000 (9) | 60000 (1)      |
| Ca                           | –                                                     | 8500    | 5500–12300 (11) | –              |
| <i>Sagittaria natans</i> (3) |                                                       |         |                 |                |
| Na                           | –                                                     | 5600    | 5500–7000       | –              |
| Mg                           | –                                                     | 1380    | 1090–1520       | –              |
| P                            | –                                                     | 3600    | 1900–4300       | –              |
| S                            | –                                                     | 1600    | 1350–1760       | –              |
| Cl                           | –                                                     | 3700    | 3500–4100       | –              |
| K                            | –                                                     | 49000   | 39000–54000     | –              |
| Ca                           | –                                                     | 3900    | 3100–3900       | –              |

Note: in Tables 1, 2, 3 – differences among the ranges of element content (minimal, average, maximal) are significant according to the Mann-Whitney test ( $p < 0.05$ ) (Suppl. material 2: Table 2).

Compared to reference plant values (Na 150, Mg 2000, P 2000, S 3000, Cl 2000, K 19000, Ca 10000  $\mu\text{g g}^{-1}$ ; Markert 1992; Markert et al. 2015), all studied species showed 20–40 times higher Na concentrations, while levels of Mg, P, S, Cl, K, and Ca were comparable. Statistically significant differences (Mann-Whitney test,  $p < 0.05$ . Suppl. material 3: Table S3) yielded the following macroelement series:

- *P. perfoliatus*:  $\text{K} \sim \text{Ca} > \text{Na} \sim \text{Mg} > \text{P} \sim \text{S} > \text{Cl}$ ;
- *P. filiformis*:  $\text{K} > \text{Ca} > \text{Na} > \text{S} > \text{Cl} \sim \text{P} > \text{Mg}$ ;
- *M. spicatum*:  $\text{K} > \text{Ca} > \text{Na} > \text{S} > \text{P} \sim \text{Cl} \sim \text{Mg}$  (samples from Bol'shiye Koty Bay, 1986–1988:  $\text{K } 14300 > \text{Na } 6350 \geq \text{Cl } 6550 \geq \text{Ca } 3000 \mu\text{g g}^{-1}$ ; Kozhova et al. 1993);
- *B. trichophyllum*:  $\text{K} > \text{Ca} > \text{P} \sim \text{Na} \sim \text{S} \sim \text{Cl} \sim \text{Mg}$ ;
- *B. umbellatus*:  $\text{K} > \text{Ca} > \text{P} \sim \text{Mg} \sim \text{Na} \sim \text{Cl} \sim \text{S}$ ;
- *S. natans*:  $\text{K} > \text{Na} > \text{Ca} \sim \text{Cl} \sim \text{P} > \text{S} \sim \text{Mg}$ .

The highest combined concentration of B, Al, Si, Mn, Fe, Zn, Br, Sr, Ba (1300–800  $\mu\text{g g}^{-1}$ ) was found in *B. trichophyllum*, *S. natans*, and *P. perfoliatus*. In *M. spicatum*, *P. filiformis*, and *B. umbellatus*, this total ranged from 560–700  $\mu\text{g g}^{-1}$ . Boron accumulation was weakest across most species, except in *P. filiformis*, where B content was 20–26 times higher. *S. natans* exhibited 2–10 times higher Br concentrations (Suppl. material 4: Table S4). Manganese exceeded iron only in *B. trichophyllum*; approximately equal amounts were found in *B. umbellatus* and *S. natans*. In *Potamogeton*

and *M. spicatum*, Fe > Mn, with Fe/Mn ratios of ~2.5 in *M. spicatum* and *P. perfoliatus*, and ~6.0 in *P. filiformis*. Elevated Zn (40–70 µg g<sup>-1</sup>) was observed in *P. filiformis*, *M. spicatum*, and *B. trichophyllum*. All species accumulated more Sr than Ba, with Mn, Fe, Si, and Sr being the dominant elements in this group (Table 2).

**Table 2.** Content of B, Al, Si, Mn, Fe, Zn, Br, Sr, Ba in the studied macrophyte species

| Element                             | Elements contents, µg g <sup>-1</sup> dry mass |         |                |                            |
|-------------------------------------|------------------------------------------------|---------|----------------|----------------------------|
|                                     | minimal                                        | average |                | maximal                    |
|                                     | min–max                                        | median  | min–max        | min–max                    |
| <i>Potamogeton perfoliatus</i> (15) |                                                |         |                |                            |
| B                                   | –                                              | 12.6    | 7.10–18.2 (14) | 23.0 (1)                   |
| Al                                  | 10.2–31.0 (5)                                  | 81.5    | 56.0–112 (6)   | 180–280 (4)                |
| Si                                  | –                                              | 87.0    | 45.0–153 (15)  | –                          |
| Mn                                  | 14.5–18.7 (3)                                  | 160     | 94.0–240 (8)   | 360–830; 1800 (3; 1)       |
| Fe                                  | 65.0; 80.0 (2)                                 | 390     | 135–510 (9)    | 750; 2100; 5600; 6800 (4)  |
| Zn                                  | –                                              | 23.0    | 16.3–32.0 (12) | 50.0–71.0 (3)              |
| Br                                  | –                                              | 26.5    | 14.4–40.3 (14) | 120 (1)                    |
| Sr                                  | –                                              | 86.5    | 58.0–129 (14)  | 180 (1)                    |
| Ba                                  | –                                              | 26.0    | 13.0–39.0 (11) | 50.0–110 (4)               |
| <i>Potamogeton filiformis</i> (10)  |                                                |         |                |                            |
| B                                   | –                                              | 250     | 130–310 (8)    | 420; 440 (2)               |
| Al                                  | 9.55 (2)                                       | 32.5    | 19.0–47.0 (6)  | 110 (2)                    |
| Si                                  | –                                              | 67.5    | 50.0–98.0 (10) | –                          |
| Mn                                  | –                                              | 18.7    | 12.6–21.0 (5)  | 38.0–56.0; 1210 (4; 1)     |
| Fe                                  | –                                              | 120     | 59.0–140 (7)   | 290–440 (3)                |
| Zn                                  | 11.4–26.0 (4)                                  | 68.0    | 55.0–98.0 (5)  | 130 (1)                    |
| Br                                  | –                                              | 47.5    | 25.0–76.0 (10) | –                          |
| Sr                                  | –                                              | 68.5    | 42.0–80.0 (10) | –                          |
| Ba                                  | –                                              | 13.1    | 8.70–17.1 (8)  | 26.0; 36.0 (2)             |
| <i>Myriophyllum spicatum</i> (37)   |                                                |         |                |                            |
| B                                   | –                                              | 15.5    | 8.30–27.0 (31) | 31.0–65.0 (6)              |
| Al                                  | 4.30; 6.30 (2)                                 | 17.7    | 10.8–28.0 (15) | 32.0–74.0; 90–270 (11; 9)  |
| Si                                  | –                                              | 85.0    | 57.0–120 (37)  | –                          |
| Mn                                  | –                                              | 44.0    | 24.0–63.0 (19) | 70–220; 2200; 3800 (16; 2) |
| Fe                                  | –                                              | 110     | 57.0–200 (25)  | 230–500; 540–1700 (8; 4)   |
| Zn                                  | 8.00–34.0 (15)                                 | 48.0    | 40.0–110 (22)  | –                          |
| Br                                  | –                                              | 31.0    | 17.6–57.0 (33) | 60–110 (4)                 |
| Sr                                  | –                                              | 65.5    | 37.0–128 (36)  | 130 (1)                    |
| Ba                                  | –                                              | 13.0    | 7.80–25.0 (29) | 26.0–48.0; 190 (7; 1)      |

| Element                              | Elements contents, $\mu\text{g g}^{-1}$ dry mass |         |                |                     |
|--------------------------------------|--------------------------------------------------|---------|----------------|---------------------|
|                                      | minimal                                          | average |                | maximal             |
|                                      | min-max                                          | median  | min-max        | min-max             |
| <i>Batrachium trichophyllum</i> (10) |                                                  |         |                |                     |
| B                                    | 5.60–10.0 (5)                                    | 14.9    | 13.1–18.5 (5)  | –                   |
| Al                                   | 18.4; 35.0–54.0 (1; 3)                           | 89.0    | 77.0–113 (5)   | 190 (1)             |
| Si                                   | –                                                | 120     | 100–150 (10)   | –                   |
| Mn                                   | 120; 200 (2)                                     | 840     | 480–1070 (5)   | 1250–3200 (3)       |
| Fe                                   | –                                                | 200     | 120–360 (8)    | 370; 800 (2)        |
| Zn                                   | 15.6–35.0 (5)                                    | 47.0    | 43.0–53.0 (5)  | –                   |
| Br                                   | –                                                | 47.0    | 31.0–56.0 (6)  | 111–210 (4)         |
| Sr                                   | –                                                | 52.0    | 44.0–76.0 (10) | –                   |
| Ba                                   | –                                                | 21.0    | 11.5–31.0 (9)  | 52.0 (1)            |
| <i>Butomus umbellatus</i> (11)       |                                                  |         |                |                     |
| B                                    | –                                                | 15.1    | 7.40–22.0 (11) | –                   |
| Al                                   | 12.0–47.0 (5)                                    | 91.0    | 75.0–95.0 (3)  | 200–670 (3)         |
| Si                                   | –                                                | 110     | 74.0–180 (11)  | –                   |
| Mn                                   | –                                                | 83.0    | 45.0–100 (8)   | 160–370 (3)         |
| Fe                                   | –                                                | 93.0    | 53.0–130 (5)   | 190–360; 940 (5; 1) |
| Zn                                   | –                                                | 19.0    | 11.8–26.0 (7)  | 35.0–46.0 (4)       |
| Br                                   | –                                                | 58.0    | 26.0–66.0 (8)  | 87.0–120 (3)        |
| Sr                                   | –                                                | 67.0    | 41.0–91.0 (11) | –                   |
| Ba                                   | –                                                | 21.0    | 13.9–34.0 (11) | –                   |
| <i>Sagittaria natans</i> (3)         |                                                  |         |                |                     |
| B                                    | –                                                | 9.70    | 7.90–10.0      | –                   |
| Al                                   | –                                                | 130     | 120–150        | –                   |
| Si                                   | –                                                | 140     | 130–160        | –                   |
| Mn                                   | –                                                | 160     | 150–240        | –                   |
| Fe                                   | –                                                | 270     | 220–330        | –                   |
| Zn                                   | –                                                | 19.0    | 15.5–20.0      | –                   |
| Br                                   | –                                                | 140     | 130–160        | –                   |
| Sr                                   | –                                                | 34.0    | 27.0–36.0      | –                   |
| Ba                                   | –                                                | 11.1    | 10.4–11.2      | –                   |

Compared to reference values (B 40, Al 80, Si 1000, Mn 200, Fe 150, Zn 50, Br 4, Sr 50, Ba 40  $\mu\text{g g}^{-1}$ ; Markert 1992; Markert et al. 2015), the macrophytes showed higher Br levels, and *P. filiformis* had 3–7 times higher B. Lower Si concentrations were attributed to the acid ( $\text{HNO}_3$ ) digestion method, which incompletely solubilizes Si compounds. In leaf samples of *M. spicatum* and *B. umbellatus*, a residue (6–8%

of aliquot mass) consisting of ~20% biogenic and particulate Si remained; total Si in these samples, including the residue, was 1.5–2.0%. For most samples, the residue mass was insufficient for analysis, indicating significantly lower Si concentrations. The concentration series for this group (including acid-soluble Si) were ( $p < 0.05$ , Suppl. material 3: Table S3):

- *P. perfoliatus*: Fe > Mn ~ Sr ~ Si ~ Al > Ba ~ Br ~ Zn > B;
- *P. filiformis*: B ~ Fe > Si ~ Sr ~ Zn ~ Br ~ Mn ~ Al > Ba;
- *M. spicatum*: Fe > Si ~ Mn > Sr > Zn ~ Al ~ Br > B ~ Ba (samples from 1986–1988: Fe 3000 ≥ Mn 200 > Zn 36 μg g<sup>-1</sup>; Kozhova et al. 1993);
- *B. trichophyllum*: Mn > Fe > Si > Sr ~ Br ~ Al > Zn ~ Ba > B;
- *B. umbellatus*: Fe ~ Si ~ Mn ~ Al ~ Sr ~ Br > Ba ~ Zn > B;
- *S. natans*: Fe ~ Mn ~ Br ~ Si ~ Al > Sr > Zn > Ba > B.

Total concentration of Ti, Ni, Cu, Rb, Mo, I ranged from 10–15 μg g<sup>-1</sup> in *M. spicatum*, *P. perfoliatus*, and *P. filiformis*, to 20–30 μg g<sup>-1</sup> in *B. umbellatus*, *S. natans*, and *B. trichophyllum*. Titanium showed the highest variability (CV 80–130%), particularly in *B. umbellatus* and *S. natans*, likely due to sorption of fine mineral suspensions. Rubidium (≤1.0 μg g<sup>-1</sup>), closely associated with K, was lowest in *M. spicatum*. Iodine was higher in *M. spicatum*, *S. natans*, and *B. trichophyllum* compared to *Potamogeton* and *B. umbellatus*. No significant differences in Ni, Cu, or Mo accumulation were observed, except for lower Ni in *S. natans* (Table 3, Suppl. material 4: Table S4).

**Table 3.** Content of Ti, Ni, Cu, Rb, Mo, I in the studied macrophyte species

| Element                             | Elements contents, μg g <sup>-1</sup> dry mass |         |                |                             |
|-------------------------------------|------------------------------------------------|---------|----------------|-----------------------------|
|                                     | minimal                                        | average |                | maximal                     |
|                                     | min–max                                        | median  | min–max        | min–max                     |
| <i>Potamogeton perfoliatus</i> (15) |                                                |         |                |                             |
| Ti                                  | 0.42–1.44 (5)                                  | 3.00    | 2.70–4.10 (4)  | 6.60–10.9; 18.7;21.0 (4; 2) |
| Ni                                  | –                                              | 1.73    | 1.05–3.10 (14) | 5.30 (1)                    |
| Cu                                  | –                                              | 2.70    | 1.58–4.50 (15) | –                           |
| Rb                                  | –                                              | 4.00    | 2.40–5.60 (12) | 7.80–18.7 (3)               |
| Mo                                  | –                                              | 1.28    | 0.80–2.00 (15) | –                           |
| I                                   | 0.42–0.72 (3)                                  | 1.31    | 0.93–2.10 (8)  | 2.30–2.70 (4)               |
| <i>Potamogeton filiformis</i> (10)  |                                                |         |                |                             |
| Ti                                  | 0.47 (2)                                       | 1.45    | 1.11–2.10 (4)  | 3.60–6.60 (4)               |
| Ni                                  | –                                              | 1.95    | 1.06–3.00 (8)  | 3.70; 6.20 (2)              |
| Cu                                  | –                                              | 2.65    | 1.86–4.70 (10) | –                           |
| Rb                                  | –                                              | 4.70    | 4.56–7.50 (9)  | 7.70 (1)                    |
| Mo                                  | –                                              | 1.72    | 1.31–2.60 (10) | –                           |
| I                                   | –                                              | 2.35    | 1.15–3.70 (8)  | 4.20; 6.10 (2)              |

| Element                              | Elements contents, $\mu\text{g g}^{-1}$ dry mass |         |                |                               |
|--------------------------------------|--------------------------------------------------|---------|----------------|-------------------------------|
|                                      | minimal                                          | average |                | maximal                       |
|                                      | min-max                                          | median  | min-max        | min-max                       |
| <i>Myriophyllum spicatum</i> (37)    |                                                  |         |                |                               |
| Ti                                   | 0.12–0.89 (13)                                   | 1.21    | 0.99–2.20 (12) | 3.60–9.90; 11.4; 12.5 (10; 2) |
| Ni                                   | –                                                | 2.00    | 1.13–3.80 (32) | 4.20–7.10 (5)                 |
| Cu                                   | –                                                | 2.30    | 1.20–4.30 (33) | 4.40–5.00 (4)                 |
| Rb                                   | –                                                | 0.24    | 0.11–0.40 (28) | 0.49–0.73; 1.38 (8; 1)        |
| Mo                                   | –                                                | 0.80    | 0.52–1.57 (34) | 1.58–3.90 (3)                 |
| I                                    | –                                                | 4.10    | 1.82–7.00 (29) | 7.60–15.3 (8)                 |
| <i>Batrachium trichophyllum</i> (10) |                                                  |         |                |                               |
| Ti                                   | 0.28 (1)                                         | 1.31    | 0.64–1.48 (5)  | 2.10–3.60; 12.5 (3; 1)        |
| Ni                                   | 0.65–1.12 (4)                                    | 3.15    | 2.30–3.90 (6)  | –                             |
| Cu                                   | 1.90–3.60 (4)                                    | 6.20    | 4.80–6.80 (6)  | –                             |
| Rb                                   | –                                                | 15.2    | 11.6–28.0 (8)  | 32; 40.0 (2)                  |
| Mo                                   | –                                                | 1.32    | 0.73–2.00 (7)  | 2.60–2.70 (3)                 |
| I                                    | –                                                | 3.80    | 2.60–5.10 (7)  | 7.80–9.30 (3)                 |
| <i>Butomus umbellatus</i> (11)       |                                                  |         |                |                               |
| Ti                                   | 0.55–2.50 (4)                                    | 5.90    | 2.90–8.80 (4)  | 12.1–26.0 (3)                 |
| Ni                                   | 0.74–1.30 (3)                                    | 2.20    | 1.52–3.80 (8)  | –                             |
| Cu                                   | –                                                | 2.60    | 1.60–3.40 (7)  | 4.50–6.10 (4)                 |
| Rb                                   | –                                                | 7.30    | 3.30–11.4 (11) | –                             |
| Mo                                   | –                                                | 1.17    | 0.35–1.56 (10) | 1.80 (1)                      |
| I                                    | –                                                | 1.56    | 0.86–2.10 (9)  | 3.30 (2)                      |
| <i>Sagittaria natans</i> (3)         |                                                  |         |                |                               |
| Ti                                   | –                                                | 8.50    | 8.30–10.0      | –                             |
| Ni                                   | –                                                | 0.75    | 0.64–0.78      | –                             |
| Cu                                   | –                                                | 2.40    | 1.85–3.20      | –                             |
| Rb                                   | –                                                | 5.30    | 3.40–8.80      | –                             |
| Mo                                   | –                                                | 1.07    | 0.86–1.24      | –                             |
| I                                    | –                                                | 5.50    | 3.29–5.70      | –                             |

Compared to reference values (Ti 5, Ni 1.5, Cu 10, Rb 50, Mo 0.5, I 3  $\mu\text{g g}^{-1}$ ; Markert 1992; Markert et al. 2015), Rb and Cu were lower. The concentration series for these elements (1–10  $\mu\text{g g}^{-1}$ ) were ( $p < 0.05$ , Suppl. material 3: Table S3):

- *P. perfoliatus*: Rb ~ Ti ~ Cu > Ni ~ I ~ Mo;
- *P. filiformis*: Rb > Cu ~ I > Mo ~ Ni ~ Ti;
- *M. spicatum*: I > Cu ~ Ni > Ti > Mo > Rb;
- *B. trichophyllum*: Rb > Cu ~ I > Ni ~ Mo ~ Ti;

- *B. umbellatus*: Rb ~ Ti ~ Cu > Ni ~ I > Mo;
- *S. natans*: Ti ~ Rb ~ I ~ Cu > Mo > Ni.

By summary content of Li, V, Cr, Co, As, Se, Y, Pb, U (concentration in the plants is  $\leq 1.0 - \geq 0.1 \mu\text{g g}^{-1}$  d. m.) *M. spicatum*, *B. trichophyllum* and *P. perfoliatus* are particular, in them this value is  $4.9-3.5 \mu\text{g g}^{-1}$  d. m. Among the elements in *S. natans*, *B. umbellatus* and *P. filiformis*, summary content of Li, V, Cr, Co, As, Se, Y, Pb, U is  $3.0-2.8 \mu\text{g g}^{-1}$ . *M. spicatum* and *P. perfoliatus*, compared to other species, concentrate more of V. *M. spicatum* is characterized by a high content of U. *B. trichophyllum*, *B. umbellatus* and *P. perfoliatus* accumulate Co more than other studied plants. Elemental composition of *B. umbellatus* is characterized by elevated concentration of Cr (Suppl. material 4: Table S4). The worst studied plants concentrate Li, Se and Y (Fig. 2A). Baikalian macrophytes differ from elemental composition of the reference plant (Li – 0.2, V – 0.5, Cr – 1.5, Co – 0.2, As – 0.1, Se – 0.02, Y – 0.2, Pb – 1, U –  $0.01 \mu\text{g g}^{-1}$  of d. m.) (Markert 1992; Markert et al. 2015) by higher content of U and Co and by lower one of Cr and Pb. By content level in the studied macrophytes species, the elements are listed as follows ( $p < 0.05$ . Suppl. material 3: Table S3):

- *P. perfoliatus* – V ~ Co ~ U ~ Cr > Li ~ As ~ Pb > Y ~ Se;
- *P. filiformis* – V ~ U > Pb ~ Cr ~ As ~ Co > Se ~ Li ~ Y;
- *M. spicatum* – U > V ~ As ~ Co ~ Cr > Pb > Y ~ Se > Li (in dry mass of *M. spicatum* of 1986–1988 (Kozhova et al. 1993) –  $\text{Se}0.63 \sim \text{Co}0.42 \sim \text{Gr}0.30 \mu\text{g g}^{-1}$ );
- *B. trichophyllum* – Co > U ~ V ~ As > Pb ~ Cr > Li ~ Y > Se;
- *B. umbellatus* – Co ~ Cr ~ U ~ V > Pb ~ As ~ Li > Y ~ Se;
- *S. natans* – Co ~ V ~ Cr > Li ~ As ~ U ~ Y ~ Pb > Se.

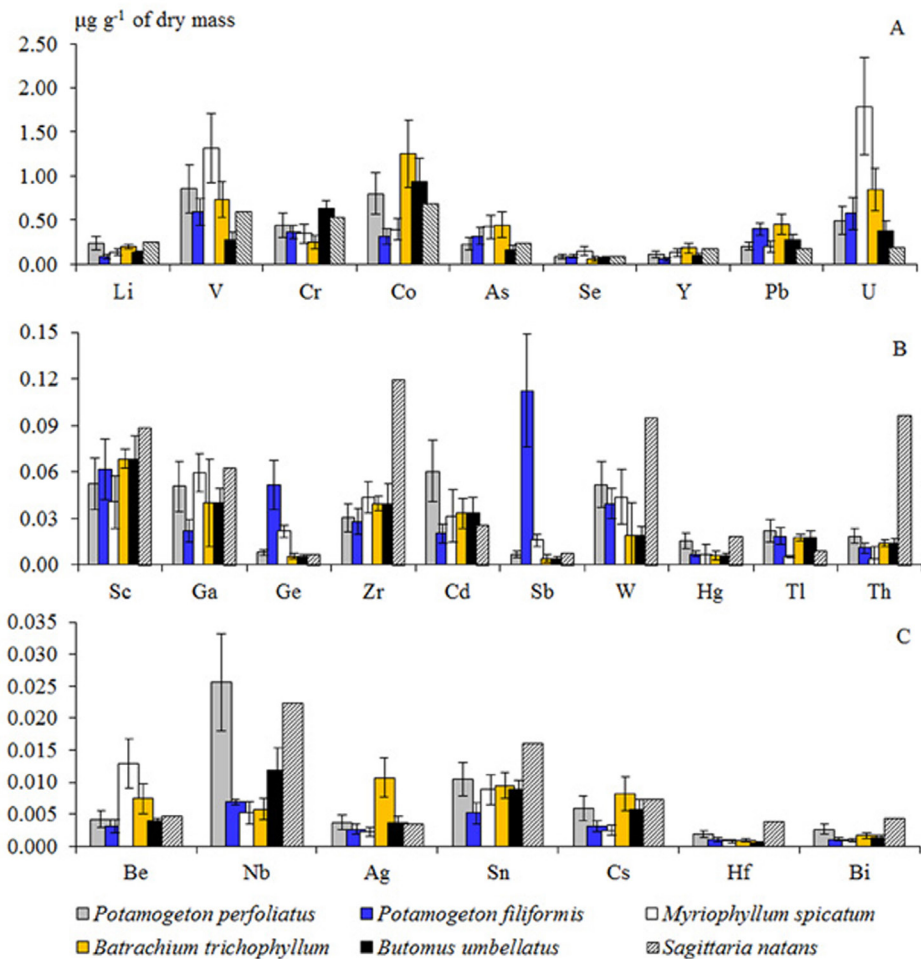
Total concentration of Sc, Ga, Ge, Zr, Cd, Sb, W, Hg, Tl, Th ( $\leq 0.1 \mu\text{g g}^{-1}$ ) was  $0.25-0.37 \mu\text{g g}^{-1}$  in most species and  $0.50-0.60 \mu\text{g g}^{-1}$  in *S. natans*, which also showed the highest levels of Zr, W, and Th. *P. filiformis* exhibited maximal Ge and Sb accumulation (Fig. 2B, Suppl. material 4: Table S4). Compared to reference values (Sc 0.02, Ga 0.1, Ge 0.01, Zr 0.1, Cd 0.05, Sb 0.1, W 0.2, Hg 0.1, Tl 0.05, Th 0.005  $\mu\text{g g}^{-1}$ ; Markert 1992; Markert et al. 2015), the species accumulated less Zr (except *S. natans*), 6–20 times less Sb (except *P. filiformis*), and more Th. The concentration series were ( $p < 0.05$ . Suppl. material 3: Table S3):

- *P. perfoliatus*: Cd ~ Sc ~ W ~ Ga ~ Zr ~ Tl ~ Th ~ Hg > Ge ~ Sb;
- *P. filiformis*: Sb > Sc ~ Ge ~ W ~ Zr ~ Ga ~ Cd ~ Tl ~ Th ~ Hg;
- *M. spicatum*: Sc ~ W ~ Cd > Ga ~ Zr > Ge ~ Sb > Hg ~ Th > Tl (samples 1986–1988: Sc 0.086, Sb 0.07, Th  $0.10 \mu\text{g g}^{-1}$ ; Kozhova et al. 1993);
- *B. trichophyllum*: Ga > W ~ Cd ~ Sc ~ Zr > Hg ~ Sb ~ Tl ~ Ge ~ Th;
- *B. umbellatus*: Sc ~ Ga ~ Zr ~ Cd > W > Tl ~ Th ~ Hg ~ Ge ~ Sb;
- *S. natans*: Zr ~ Th ~ W ~ Sc ~ Ga > Cd > Hg > Tl ~ Sb ~ Ge.

Total concentration of Be, Nb, Ag, Sn, Cs, Hf, Bi ranged from  $0.023-0.036 \mu\text{g g}^{-1}$  in *M. spicatum*, *P. filiformis*, and *B. umbellatus* to  $0.044-0.062 \mu\text{g g}^{-1}$  in *B. trichophyllum*, *P. perfoliatus*, and *S. natans*. *M. spicatum* showed higher Be and lower Cs and

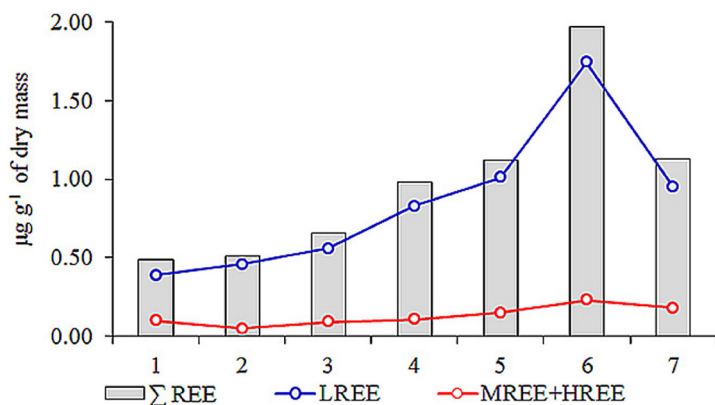
Nb. *B. trichophyllum* had elevated Ag (Fig. 2C). Compared to reference values (Be 0.001, Nb 0.05, Ag 0.2, Sn 0.2, Cs 0.2, Hf 0.05, Bi 0.05  $\mu\text{g g}^{-1}$ ; Markert 1992; Markert et al. 2015), Be was higher, while Ag, Sn, Cs, Hf, and Bi were considerably lower. The concentration series were ( $p < 0.05$ , Suppl. material 3: Table S3):

- *P. perfoliatus*, *P. filiformis*: Nb  $\sim$  Sn  $\sim$  Cs  $\sim$  Be  $\sim$  Ag  $>$  Bi  $\sim$  Hf;
- *M. spicatum*: Be  $>$  Sn  $\sim$  Nb  $>$  Cs  $\sim$  Ag  $>$  Bi  $\sim$  Hf;
- *B. trichophyllum*: Ag  $\sim$  Sn  $\sim$  Cs  $>$  Be  $\sim$  Nb  $>$  Bi  $\sim$  Hf;
- *B. umbellatus*: Nb  $\sim$  Sn  $\sim$  Cs  $\sim$  Be  $\sim$  Ag  $>$  Bi  $\sim$  Hf;
- *S. natans*: Nb  $>$  Sn  $>$  Cs  $\sim$  Be  $\sim$  Bi  $\sim$  Hf  $\sim$  Ag.



**Figure 2.** Mean concentrations ( $\pm$  standard deviation) of microelements in the studied macrophyte species, grouped by concentration range in dry mass: (A)  $\leq 1.0 \mu\text{g g}^{-1}$ , (B)  $\leq 0.1 \mu\text{g g}^{-1}$ , (C)  $\leq 0.01 \mu\text{g g}^{-1}$ .

Among rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), light REE (LREE: La, Ce, Pr, Nd) dominated, with middle and heavy REE (MREE, HREE) present at 4–8 times lower concentrations. High variability (CV 60–100%) in REE content was attributed to sorption of fine mineral particles, the primary transport phase for REE in surface waters. The lowest total REE concentrations ( $0.50\text{--}0.70\ \mu\text{g g}^{-1}$ ) were found in *M. spicatum*, *P. filiformis*, and *B. umbellatus*, while higher values ( $0.98\text{--}1.97\ \mu\text{g g}^{-1}$ ) were observed in *B. trichophyllum*, *P. perfoliatus*, and *S. natans*. Differences were most pronounced for LREE. *M. spicatum*, *P. filiformis*, and *B. umbellatus* had 3–7 times lower La, Ce, Pr, and Nd compared to the other three species, in which concentrations were La  $0.21\text{--}0.41$ , Ce  $0.44\text{--}0.89$ , Pr  $0.039\text{--}0.092$ , and Nd  $0.15\text{--}0.35\ \mu\text{g g}^{-1}$ . The highest total REE content was observed in *S. natans* (Fig. 3).



**Figure 3.** Summary content of rare-earth elements in plants: 1 – *Myriophyllum spicatum*, 2 – *Potamogeton filiformis*, 3 – *Butomus umbellatus*, 4 – *Potamogeton perfoliatus*, 5 – *Batrachium trichophyllum*, 6 – *Sagittaria natans*, 7 – reference plant (Markert 1992; Markert et al. 2015).

Among 64 determinable elements, minimal content in the studied plants is found out for Ta and Au. In dry mass of *P. perfoliatus* and *S. natans* Ta content is  $0.0008\text{--}0.0010$ , in *B. trichophyllum*, *P. filiformis*, *M. spicatum* and *B. umbellatus* –  $0.0003\text{--}0.0005\ \mu\text{g g}^{-1}$ . Au in the sampled macrophytes counts –  $0.0004\text{--}0.0006\ \mu\text{g g}^{-1}$ . In the reference plant Ta and Au count  $0.001\ \mu\text{g g}^{-1}$  of d. m. (Markert 1992; Markert et al. 2015).

### Elemental composition in vegetative organs in the studied macrophyte species

Substantial differences in elemental composition were observed not only among macrophyte species but also between different vegetative organs (leaves, stalks,

roots) (Suppl. material 5: Table S5) and between plant tissues and the fine-disperse organic-mineral suspension deposited on leaf surfaces (collected under a binocular microscope from *P. perfoliatus* leaves).

Compared to the plant itself, the suspension contained 10–20 times higher concentrations of Ca, Ti, Zr, Cs, and Th; 7–9 times higher Al, Cr, Y, Pr, Nd, MREE, and HREE; and 3–6 times higher Li, Be, Sc, V, Ga, Sr, Nb, Ba, La, Ce, Hf, and Bi. The majority of these elements are characterized by weak migration with organic complexes and are predominantly transported in suspended form. The wide variability in their concentrations in plant samples is largely attributable to variable amounts of such adsorbed mineral and organic-mineral particles.

Calcium accounted for approximately 96% of the total determinable elements in the leaf surface suspension, reflecting the presence of biomineral crusts (<1 mm thick) composed primarily of calcite ( $\text{CaCO}_3$ ) microcrystals (Katkova et al. 2019). Precipitation of  $\text{CaCO}_3$  is favored by fluctuations in  $\text{CO}_2$  and bicarbonate concentrations within macrophyte stands during photosynthesis (Lukina and Smirnova 1988). Such carbonate encrustations are known for numerous aquatic plants, including *Potamogeton*, *Myriophyllum*, *Ceratophyllum*, and *Elodea canadensis* (Voronikhin 1953).

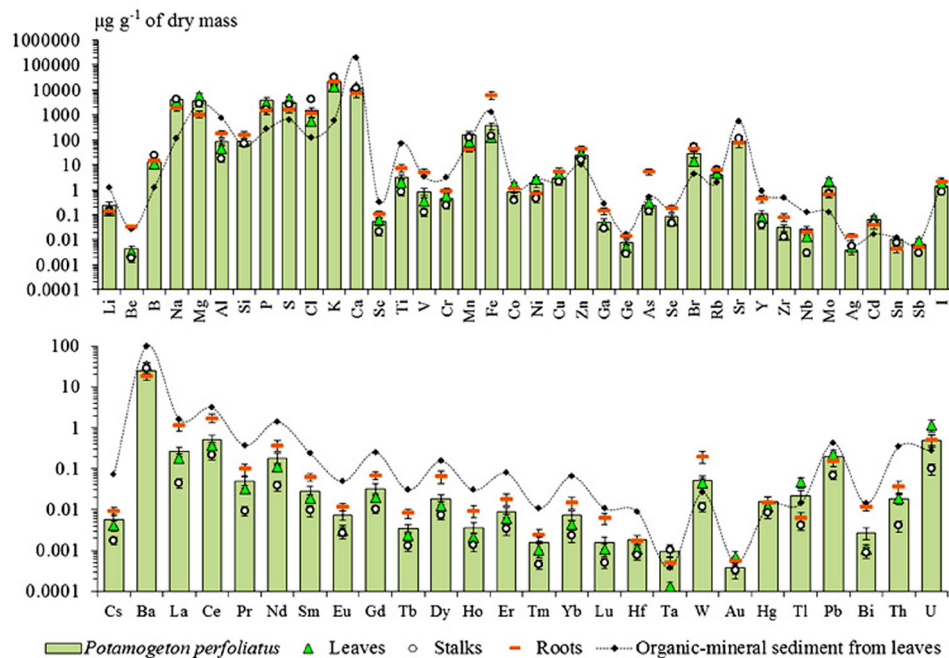
In contrast to the deposited suspension and carbonate crusts, *P. perfoliatus* tissues (leaves, stalks, roots) were markedly enriched in B, Na, P, S, Cl, K, Br, Mo, and Cd. Additionally, roots showed higher W content, while leaves exhibited elevated Tl and U (Fig. 4).

The roots of *Potamogeton perfoliatus*, which are in direct contact with bottom sediments and pore waters, showed elevated concentrations of weakly and low-mobile elements (Be, V, Ga, Y, La, Ce, Dy, Lu, W) compared to leaves and stalks. Iron was particularly enriched in roots (20–50 times higher than in whole plants, leaves, or stalks), along with As (>20–40 times higher). This enrichment is attributed to radial oxygen loss from roots, which oxidizes mobile  $\text{Fe}^{2+}$  in pore waters and precipitates iron (oxyhydr)oxides on the root surface (Taylor et al. 1984; Valitutto et al. 2006); these Fe hydroxides effectively adsorb As, regulating its mobility (Putilina et al. 2011). Stalks contained higher Cl than whole plants, leaves, or roots, and higher Br and Ta than leaves, but lower Sc, V, Co, Ni, Sb, La, Pr, Nd, Pb, Th, and U. Whole-plant *P. perfoliatus* had 3–7 times higher Cl, Fe, and Ta than leaves, whereas leaves showed slightly higher U. Leaves differed from roots by elevated Mg, Ni, Mo, and Tl (Fig. 4, Suppl. material 6: Table S6).

### *Potamogeton filiformis*

In *P. filiformis*, leaves, stalks, and roots showed broadly similar concentrations of many elements (Li, Be, Na, Mg, Si, P, S, Cl, K, Ca). However, leaves were enriched in B, Ge, Nb, Mo, Sb, and Tl (5–10 times higher than in roots or stalks). Manganese in leaves exceeded wholeplant levels by ~30fold, and stalk/root levels by 20–30fold. Stalks contained higher Ni, As, Ag, and Hg. Roots were characterized by elevated

Al, Sc, and Cs. Iron was concentrated mainly in roots and stalks (5–7 times higher than in leaves). Light and middle REE were evenly distributed among organs, while heavy REE were lowest in stalks (Suppl. material 6: Table S7).



**Figure 4.** Mean concentrations ( $\mu\text{g g}^{-1}$  dry mass) of chemical elements in *Potamogeton perfoliatus* whole plants ( $n = 15$ ), leaves ( $n = 14$ ), stalks ( $n = 11$ ), roots ( $n = 16$ ), and in organic-mineral sediment collected from leaf surfaces ( $n = 1$ ). Error bars represent standard deviation.

### *Myriophyllum spicatum*

No statistically significant differences in elemental composition were found between whole *M. spicatum* and its leaves, except for Li (threefold lower in leaves). Stalks showed 3–4 times lower Be, Cl, V, Mn, Fe, Zr, and Nb. Roots accumulated 5–7 times more Sb, Nb, Ce, and W; 3–4 times more V, Fe, Co, Ge, Y, Pr, Nd, Sm, Gd, Er, Yb, Hf, Pb, and Th; but 3–5 times less Mn than whole plants, and lower Na than stalks (Suppl. material 6: Table S8).

### *Batrachium trichophyllum*

Elemental composition of whole *B. trichophyllum* did not differ significantly from that of leaves and stalks for most elements. Leaves contained 3–6 times higher Cr, Mn, Zr, Tl, and Bi; stalks had 3–8 times higher Br, LREE, Au, and Th, but ~3 times

lower Ni, U, and Pb. Roots were strongly enriched in Fe (>30–60 times), As (>7–20 times), and Be, Al, Ti, V, Cr, Y, Zr, Nb, Sn, Sb, REE (except Eu), Hf, Au, Hg, and Th (>3–9 times) relative to leaves, stalks, and whole plants (Suppl. material 6: Table S9).

### *Butomus umbellatus*

Only the submerged form of *B. umbellatus* was collected, characterized by linear green leaves emerging from a short rhizome with roots. Submerged leaves absorb nutrients directly from the water column (Lukina and Smirnova 1988). Differences between whole plants and leaves were primarily in elements associated with fine-disperse suspension. Accumulated suspension on leaf surfaces, subject to daily pH and oxygen fluctuations driven by photosynthesis and respiration (Votintsev and Samarina, 1957), gradually releases low-mobility elements that may be adsorbed by leaves. Accordingly, leaves accumulated more Al, Ti, Nb, Cs, LREE, MREE, Hf, Ta, Th, Li, V, Fe, and Hg than whole plants. Compared to roots, leaves showed higher Cl, Al, Ni, Zr, Sn, Br, and Pb, but 3–4 times lower Fe and As (Suppl. material 6: Table S10).

### *Sagittaria natans*

The collected *S. natans* represented the aquatic form with submerged linear leaves and a short rhizome. Leaves contained 7–8 times less Fe and As, and 3–4 times less Be, S, V, Co, Nb, Mo, Cd, Cs, and REE than the rhizome. No other significant differences in elemental composition were observed between leaves and rhizomes (Suppl. material 6: Table S11).

## Concentration function of macrophytes

All studied macrophyte species adsorbed and accumulated chemical elements from their habitat to varying degrees. Concentrations of both macro- and microelements in plant fresh mass consistently exceeded those in littoral waters. The highest bioaccumulation factors (BAF; concentration in plant fresh mass divided by concentration in water) were observed for P, Mn, and Zn, reaching several thousand.

- Phosphorus: BAF  $\geq 10\,000$  in *B. trichophyllum*, *B. umbellatus*, and *S. natans*.
- Manganese: BAF 6500–26 500 in *B. trichophyllum* and *S. natans*.
- Zinc: BAF 9000–14 000 in *M. spicatum*, *P. filiformis*, and *B. trichophyllum*.

High accumulation was also found for elements present at  $<1.0\ \mu\text{g L}^{-1}$  in littoral water (except Al, K, Fe), including Zr, Nb, K, Cd, Tl, Co, Ni, Fe, Ti, Th, Al, and Rb. Among the species, *M. spicatum* showed comparatively lower accumulation of Fe, K and its geochemical analogs Rb and Tl.

Elements with BAF ranging from 10 to  $<1000$  included Cs, Ag, Sn, Pb, Hf, Br, Cl, B, Be, Ba, Ta, V, Cu, Ge, Cr, S, Na, Mg, Mo, U, Sr, Ca, As, Se, and Sc. *P. filiformis* exhibited notably higher B for B (BAF  $> 1000$ ). BAF values for Li and Sb were  $<10$  in all species except *P. filiformis*, which accumulated Sb at 50 times the water concentration.

All species were effective concentrators of rare earth elements (REE), particularly Ce, Gd, and Dy (Table 4). Based on overall elemental accumulation, the species ranked as follows: *B. trichophyllum* > *S. natans* > *P. perfoliatus* > *P. filiformis* > *M. spicatum* > *B. umbellatus*. For REE accumulation specifically, the order was *S. natans* > *B. trichophyllum* > *P. perfoliatus* > *B. umbellatus* > *M. spicatum* > *P. filiformis*.

**Table 4.** Element concentrations ( $\mu\text{g L}^{-1}$ , mean  $\pm$  standard deviation) in littoral water (CW) and bioaccumulation factors (BAF) for the studied macrophyte species. BAF values are provided for: 1 – *Potamogeton perfoliatus*, 2 – *P. filiformis*, 3 – *Myriophyllum spicatum*, 4 – *Butomus trichophyllum*, 5 – *Butomus umbellatus*, 6 – *Sagittaria natans*

| Element | CW (30)             | 1    | 2     | 3     | 4     | 5    | 6     |
|---------|---------------------|------|-------|-------|-------|------|-------|
| Mn      | 1.70 $\pm$ 0.49     | 5630 | 1730  | 3990  | 26540 | 2750 | 6500  |
| Zn      | 0.31 $\pm$ 0.10     | 4580 | 13800 | 10620 | 9200  | 3780 | 3510  |
| P       | 19.4 $\pm$ 6.3      | 4190 | 6760  | 5930  | 15160 | 9230 | 10110 |
| Nb      | 0.0007 $\pm$ 0.0002 | 2280 | 610   | 470   | 510   | 1060 | 1990  |
| Zr      | 0.0012 $\pm$ 0.0004 | 1490 | 1380  | 2140  | 920   | 1940 | 5870  |
| K       | 900 $\pm$ 260       | 1440 | 1590  | 710   | 2190  | 1990 | 3170  |
| Cd      | 0.0031 $\pm$ 0.0008 | 1160 | 390   | 610   | 740   | 640  | 490   |
| Tl      | 0.0012 $\pm$ 0.0003 | 1120 | 960   | 260   | 330   | 920  | 470   |
| Co      | 0.048 $\pm$ 0.014   | 990  | 390   | 490   | 1560  | 1170 | 860   |
| Ni      | 0.16 $\pm$ 0.05     | 700  | 730   | 810   | 1220  | 940  | 280   |
| Fe      | 36.1 $\pm$ 11.9     | 610  | 180   | 50    | 370   | 160  | 450   |
| Ti      | 0.34 $\pm$ 0.11     | 560  | 270   | 100   | 210   | 850  | 1560  |
| Th      | 0.0023 $\pm$ 0.0007 | 490  | 280   | 100   | 240   | 370  | 2540  |
| Al      | 11.3 $\pm$ 2.9      | 450  | 170   | 100   | 230   | 460  | 700   |
| Rb      | 0.59 $\pm$ 0.10     | 400  | 460   | 30    | 1700  | 710  | 590   |
| Cs      | 0.0014 $\pm$ 0.0004 | 250  | 130   | 100   | 350   | 240  | 310   |
| Ag      | 0.0011 $\pm$ 0.0003 | 210  | 150   | 120   | 600   | 200  | 190   |
| Sn      | 0.0031 $\pm$ 0.0010 | 210  | 100   | 170   | 190   | 170  | 310   |
| Pb      | 0.063 $\pm$ 0.018   | 190  | 380   | 190   | 430   | 270  | 170   |
| Hf      | 0.0006 $\pm$ 0.0003 | 170  | 91    | 70    | 80    | 50   | 350   |
| Br      | 10.3 $\pm$ 2.7      | 160  | 290   | 190   | 260   | 300  | 840   |
| Cl      | 600 $\pm$ 200       | 150  | 270   | 240   | 240   | 260  | 380   |
| B       | 5.04 $\pm$ 1.51     | 150  | 2750  | 180   | 190   | 170  | 110   |
| Be      | 0.0018 $\pm$ 0.0004 | 140  | 100   | 420   | 240   | 130  | 150   |
| Ba      | 11.7 $\pm$ 3.7      | 130  | 65    | 70    | 110   | 110  | 56    |
| Ta      | 0.0005 $\pm$ 0.0001 | 120  | 50    | 40    | 60    | 35   | 130   |

| Element             | CW (30)       | 1    | 2    | 3    | 4    | 5    | 6     |
|---------------------|---------------|------|------|------|------|------|-------|
| V                   | 0.45±0.11     | 120  | 80   | 180  | 100  | 37   | 81    |
| Cu                  | 1.46±0.37     | 110  | 120  | 100  | 250  | 100  | 100   |
| Ge                  | 0.0044±0.0014 | 110  | 710  | 300  | 100  | 76   | 92    |
| Cr                  | 0.26±0.08     | 100  | 80   | 80   | 60   | 140  | 120   |
| S                   | 2240±730      | 80   | 140  | 60   | 70   | 70   | 40    |
| Na                  | 3280±1050     | 80   | 110  | 90   | 60   | 50   | 110   |
| Mg                  | 3120±910      | 70   | 30   | 40   | 40   | 60   | 30    |
| Mo                  | 1.29±.35      | 60   | 90   | 40   | 60   | 50   | 50    |
| U                   | 0.51±0.17     | 60   | 70   | 210  | 100  | 40   | 20    |
| Sr                  | 110±30        | 50   | 40   | 40   | 30   | 40   | 20    |
| Ca                  | 15800±2800    | 45   | 30   | 30   | 20   | 30   | 14    |
| I                   | 2.08±0.65     | 40   | 70   | 130  | 110  | 40   | 140   |
| As                  | 0.35±0.10     | 40   | 50   | 70   | 75   | 30   | 40    |
| Se                  | 0.16±0.05     | 30   | 30   | 55   | 20   | 30   | 40    |
| Sc                  | 0.10±0.03     | 30   | 40   | 20   | 15   | 40   | 50    |
| Li                  | 2.02±0.40     | 7.2  | 2.6  | 4.1  | 5.8  | 4.0  | 7.7   |
| Sb                  | 0.13±0.03     | 3.0  | 52   | 7.3  | 5.4  | 1.9  | 3.4   |
| Rare-earth elements |               |      |      |      |      |      |       |
| La                  | 0.013±0.004   | 1170 | 440  | 520  | 930  | 240  | 1840  |
| Ce                  | 0.0052±0.0013 | 5950 | 2890 | 2040 | 5000 | 3360 | 10170 |
| Pr                  | 0.0030±0.0009 | 960  | 410  | 390  | 770  | 620  | 1830  |
| Nd                  | 0.012±0.004   | 890  | 450  | 410  | 760  | 410  | 1730  |
| Sm                  | 0.0037±0.0012 | 460  | 200  | 270  | 450  | 400  | 1110  |
| Eu                  | 0.0014±0.0004 | 310  | 150  | 370  | 390  | 210  | 440   |
| Gd                  | 0.0008±0.0003 | 2390 | 1330 | 1540 | 2690 | 1820 | 5180  |
| Tb                  | 0.0002±0.0001 | 860  | 420  | 730  | 1240 | 790  | 1980  |
| Dy                  | 0.0007±0.0002 | 1550 | 200  | 1690 | 2390 | 1360 | 3150  |
| Ho                  | 0.0003±0.0001 | 770  | 510  | 960  | 1240 | 690  | 1420  |
| Er                  | 0.0006±0.0002 | 910  | 560  | 1200 | 1690 | 870  | 1713  |
| Tm                  | 0.0006±0.0002 | 160  | 58   | 250  | 240  | 120  | 210   |
| Yb                  | 0.0006±0.0002 | 730  | 460  | 1050 | 1510 | 710  | 1300  |
| Lu                  | 0.0006±0.0002 | 160  | 90   | 190  | 260  | 120  | 180   |

## Usage of macrophytes for indication of aquatic environment anthropogenic pollution

Aquatic macrophytes act as dynamic mediators at the sediment–water interface and within the food web, and their elemental composition reflects an interplay of biological affinity and environmental forcing. This study revealed significant interspecific and intraspecific variability in the elemental composition of Lake Baikal macrophytes, with concentration ranges for individual elements varying by an order of magnitude within the same species.

Although the elemental composition of open littoral water closely resembles that of deep Baikal waters (Oganesyants et al. 2021), shallowwater and interstitial environments are enriched – particularly in Mn and Fe (10 fold) and in nutrients (P, Si) and REE (3–7 fold). While these gradients arise from internal sedimentation and biogeochemical processes and are relatively subtle in the water column, macrophytes integrate and amplify them over time, with tissue concentrations substantially exceeding ambient water levels. This amplification makes macrophytes effective sensors of terrestrial runoff, especially given elevated Na, K, P, and Cl observed near anthropogenic sites.

### Bioindicator potential of *Myriophyllum spicatum*

Among the species surveyed, *Myriophyllum spicatum* proved the most suitable bioindicator for the lake's nearshore zone, due to its widespread distribution across all three basins (southern, central, northern). Importantly, *M. spicatum* exhibited stable homeostatic baselines for a suite of elements (B, Mg, Si, S, K, Ca, Se, Br, Sr, Mo, Tl, U), with coefficients of variation below 33%. This low intrinsic variability enables highconfidence detection of deviations driven by external factors.

Elevated concentration of elements migrating in Lake Baikal near-shore zone in dissolved compounds (Cl, Na), mobile and weakly mobile elements (P, K) in some *M. spicatum* samples is found out in samples collected at the stations adjacent to the territories of settlements and tourist sites. According to data from (Suturin et al. 2016; Kulikova et al. 2021; Chebykin et al. 2024; Chebykin et al. 2025a; Chebykin et al. 2025b), polluted surface and ground water with high content of Na, K, P, Cl income often from such territories into the lake littoral. By content level of Na, Cl, P, K in *M. spicatum* dry mass, summary content of macroelements and of all determined elements by k-average method, three clusters were revealed; they include station of sampling of *M. spicatum* with maximal (cluster 1), minimal (cluster 2) and average (cluster 3) values of listed variables. Lower values of intragroup (Within SS) and higher ones (except P content) intergroup (Between SS) dispersions of features, values of F-criterion (F) exceeding ones in the Tables and significance level (signif. p) < 1% suggest statistically valuable differences between average variables values for the revealed clusters (Table 5).

**Table 5.** Results of dispersion analysis

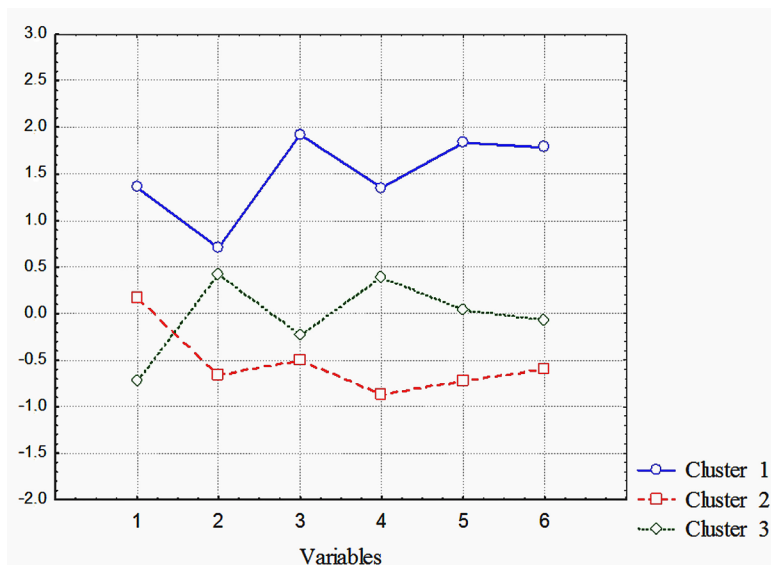
| Variables | Between SS | df | Within SS | df | F        | signif. p |
|-----------|------------|----|-----------|----|----------|-----------|
| 1         | 19.41412   | 2  | 16.58588  | 34 | 19.89886 | 0.000002  |
| 2         | 12.44295   | 2  | 23.55705  | 34 | 8.97948  | 0.000739  |
| 3         | 27.08383   | 2  | 8.91617   | 34 | 51.63932 | 0.000000  |
| 4         | 25.16590   | 2  | 10.83410  | 34 | 39.48833 | 0.000000  |
| 5         | 28.50014   | 2  | 7.49986   | 34 | 64.60158 | 0.000000  |
| 6         | 25.00146   | 2  | 10.99854  | 34 | 38.64373 | 0.000000  |

*M. spicatum* sampled at the cluster 1 station was characterized by elevated concentration of Cl (2000–4200), P (1200–5100), Na (8300–15200), K (12300–17400), by maximal values of summary content of macroelements (28100–39300) and of all determinable elements (41000–65000  $\mu\text{g g}^{-1}$  d. m.). In *M. spicatum* sampled at cluster 3 stations with average variables values, content of Cl and Na is 2–4 times less, one of P, K, as well as summary concentration of macroelements and of all determinable elements is  $\sim 1.5$  time less. The lowest level of accumulation of listed elements, except Cl, is found out in samples from cluster 2 stations (Fig. 5).

Maximal level of chemical elements accumulation (cluster 1) is characteristic for samples of *M. spicatum* collected in shallow water near Zarechny settl. (wastewaters sewage from Severobaikalsk town into the Tuya R.), in Bol'shiye Koty Bay opposite to perennial drainage of surface and ground waters from territory with buildings (LIN of RAS SB station), in the Anga R. bed (on the shores there are Kuret' and Khuray-Nur villages, Yalga-Uzur squatting and province center – Yelantsy village) and the Maksimikha R. mouth (along the mouth shores there are Maksimikha village and tourist sites). The same cluster includes stations with a high tourist charge, Zagly Gulf (1.5 km from ferry service) and Tonkiy Island (tourist site “Seal-Center”). Cluster 3 unites mainly stations situated some distance from settlements. If there is no sewage network, in major part of them liquid and solid household wastes are accumulated in ditches, waste deposits, toilet pits with incomplete hydroisolation or without it. Such territories, especially in summer when tourists amount increases abruptly, are also a source of surface and underground waters pollution incoming to the lake's coastal zone. Minimal level of accumulation of chemical elements (P, Na, K, macroelements and all determinable elements) (cluster 2) is characteristic for samples of *M. spicatum* collected mainly outside the zone of intense anthropogenic impact on bays and gulfs of Maloye Morye strait, Ol'khon Island, in Bol'shoy Ushkaniy Island water area, 29.07.2018 and Tonkiy Island, at the depth of 3.5 m, 29.07.2018 (Fig. 5).

These findings align with hydrological studies documenting the input of polluted surface water enriched with Na, K, P, and Cl from developed coastal areas (Suturin et al. 2016; Kulikova et al. 2021; Chebykin et al. 2024, 2025a, 2025b). The

data suggest that *M. spicatum* not only passively reflects this pollution but actively accumulates it, potentially serving as a vector for introducing these elements into the littoral food web.



**Figure 5.** Graph of coordinates of clusters centers. Variables – content in *Myriophyllum spicatum*: 1 – Cl, 2 – P, 3 – Na, 4 – K, 5 –  $\Sigma$ C macro, 6 –  $\Sigma$ C total. Clusters: 1 – Zagli Gulf, depth – 3.9 m; Zarechny settl.; Tonkiy Island (“Seal-Center”), 3.2 m; Bol’shiye Koty settl., LIN of RAS SB station; the Anga R. bed; the Maksimikha R. mouth; 2 – Bol’shoi Ushkaniy Island, 1.8 m (29.07.2018.); Tonkiy Island, 3.5 m (29.07.2018 r.); 300 m southward from Kodovy Gulf, 1.3 m; Yadyrtuy Gulf; Mukhor Gulf, tourist hostel “Togot”; Shida Gulf; Khorin-Irgi Bay; 2.3 km eastward from the Buguldeyka R. mouth, 3.6 m; Semisosenskaya estuary; 3 – Beryozovy Cape; Kultuk settl.; Listvyanka settl., southern part; Bugul’deyka settl., Zama settl.; Bol’shiye Koty settl., 300 m southward from Kodovy, 1.5 m; 2.3 km eastward from the Bugul’deyka R. mouth, 3.0 m; Bol’shoi Ushkaniy Island, 1.7 m, 1.8 m (21.07.20.), Maly Ushkaniy Island, 2.3 m (see Suppl. material 1: Table 1).

## Conclusion

The elemental composition of macrophytes in Lake Baikal exhibits pronounced interspecific and intraspecific variability, reflecting differential uptake and accumulation patterns. Species such as *Batrachium trichophyllum* and *Sagittaria natans* show the highest overall elemental enrichment, whereas *Myriophyllum spicatum* displays a stable homeostatic baseline for several key elements. The integration of environmental signals over time, combined with the strong concentration gradients between plants and ambient water, underscores the utility of macrophytes as sensitive

bioindicators. Among the studied species, *M. spicatum* is particularly well-suited for monitoring nearshore zones owing to its broad distribution and low intrinsic elemental variability, allowing effective detection of anthropogenic influences and terrestrial runoff.

## Acknowledgements

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## Supplementary material 1

### Table S1. Description and coordinates of water and macrophytes sampling

Authors: Natalia N. Kulikova, Evgeny P. Chebykin, Alexander N. Suturin

Data type: table

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Link: <https://journal.asu.ru/biol/article/view/19399/16719>

## Supplementary material 2

### Table S2. The significance of the differences between the minimal (1), average (2) and maximal (3) ranges of the elements in macrophytes

Authors: Natalia N. Kulikova, Evgeny P. Chebykin, Alexander N. Suturin

Data type: table

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### Supplementary material 3

#### **Table S3. Ranked series of elements in macrophytes, (Mann-Whitney test). Statistically significant differences between the content of chemical elements in macrophytes**

Authors: Natalia N. Kulikova, Evgeny P. Chebykin, Alexander N. Suturin

Data type: table

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### Supplementary material 4

#### **Table S4. Statistically significant differences in the content of elements in plants**

Authors: Natalia N. Kulikova, Evgeny P. Chebykin, Alexander N. Suturin

Data type: table

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### Supplementary material 5

#### **Table S5. Statistically significant differences in the content of elements in plants, stalks, leaves and roots**

Authors: Natalia N. Kulikova, Evgeny P. Chebykin, Alexander N. Suturin

Data type: table

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## Supplementary material 6

**Table S6. Average content of chemical elements (SD – standard deviation) in dry mass of *Potamogeton perfoliatus*, its leaves, sediment from leaves, stalks and roots**

**Table S7. Average content of chemical elements (SD – standard deviation) in dry mass of *Potamogeton filiformis*, its leaves, stalks and roots**

**Table S8. Average content of chemical elements (SD – standard deviation) in dry mass of *Myriophyllum spicatum*, its leaves, stalks and roots**

**Table S9. Average content of chemical elements (SD – standard deviation) in dry mass of *Batrachium trichophyllum*, its leaves, stalks and roots**

**Table S10. Average content of chemical elements (SD – standard deviation) in dry mass of *Butomus umbellatus*, its leaves, stalks and roots**

**Table S11. Average content of chemical elements in dry mass of *Sagittaria natans*, its leaves and rootstocks**

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Data type: tables

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