

**Galina L. Shinkareva<sup>1\*</sup>, Mikhail Yu. Lychagin<sup>1</sup>, Mikhail K. Tarasov<sup>1</sup>, Jan Pietroń<sup>2</sup>, Marina A. Chichaeva<sup>3</sup>, Sergey R.Chalov<sup>1</sup>**

<sup>1</sup> Lomonosov Moscow State University, Leninskie Gory, Moscow, Russia

<sup>2</sup> WSP Sverige AB, Ullevigatan 19, Gothenburg, 411 40, Sweden

<sup>3</sup> Peoples Friendship University of Russia (RUDN University), 6 Miklukho-Maklaya St., Moscow, Russia

\* **Corresponding author:** galina.shinkareva@gmail.com

## BIOGEOCHEMICAL SPECIALIZATION OF MACROPHYTES AND THEIR ROLE AS A BIOFILTER IN THE SELENGA DELTA

**ABSTRACT.** This study aims to evaluate the biofiltration ability of higher aquatic vegetation of the Selenga delta as a barrier for heavy metals and metalloids (HMM) flows into the Lake Baikal. Main aquatic vegetation species have been collected from deltaic channels and inner lakes: *Nuphar pumila*, *Potamogeton perfoliatus*, *P. pectinatus*, *P. natans*, *P. friesii*, *Butomus umbellatus*, *Myriophyllum spicatum*, *Ceratophyllum demersum*, *Phragmites australis*. Analysis of the obtained data showed that regardless of the place of growth hydrotrophs spiked water-milfoil (*M. spicatum*) and the fennel-leaved pondweed (*P. pectinatus*) most actively accumulate metals. Opposite tendencies were found for helophytes reed (*Ph. australis*) and flowering rush (*B. umbellatus*), which concentrate the least amount of elements. This supports previous findings that the ability to concentrate HMM increases in the series of surface – floating – submerged plants. Regarding river water, the studied macrophyte species are enriched with Mn and Co, regarding suspended matter – Mo, Mn and B, regarding bottom sediments – Mn, Mo and As. We identified two associations of chemical elements: S-association with the predominant suspended form of migration (Be, V, Co, Ni, W, Pb, Bi, Mn, Fe and Al) and D-association with the predominant dissolved form of migration (B, U, Mo, Cr, Cu, Zn, As, Cd, Sn and Sb). Due to these associations three groups of macrophytes were distinguished – flowering rush and reed with a low HMM content; small yellow pond-lily and common floating pondweed with a moderate accumulation of S-association and weak accumulation of D-association elements; and clasping-leaved pondweed, fennel-leaved pondweed, and pondweed Friesii accumulating elements of both S and D groups. The results suggest that macrophytes retain more than 60% of the total Mn flux that came into the delta, more than 10% – W, As, and from 3 to 10% B, Fe, Co, Mo, Cd, V, Ni, Bi, Be, Cu, Zn, Cr, U, Al. The largest contribution is made by the group of hydrotrophs (spiked water-milfoil and pondweed), which account for 74 to 96% of the total mass of substances accumulated by aquatic plants.

**KEY WORDS:** biogeochemistry, deltaic environment, heavy metals and metalloids in aquatic systems, macrophytes, hyperspectral images.

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## INTRODUCTION

In recent years, the growing attention has been paid to ecology and geochemistry of river deltas and their wetland systems (Cui et al. 2009; Iqbal 2010; Thorslund et al. 2017; Wang et al. 2014). Due to increasing anthropogenic pressure on the catchments, the role of deltas as natural filters on the path of substance flows of natural and anthropogenic origin is becoming increasingly important (Thorslund et al. 2017). Aquatic vegetation significantly influences turbulent flow field (Nepf 2012) and thus became an important driver of wetlands hydrological impacts. Through various processes, the aquatic plants provide important environmental services, such as storage of pollutants. Hence, they are often utilized in constructed wetlands to reduce contaminant loads in rivers (Rai 2009; Patel and Kanungo 2010; Leto et al. 2013; Sun et al. 2013; Guittonny-Philippe et al. 2014). Higher aquatic plants, or macrophytes, play an important role in the processes of deposition of substances in river deltas (The Selenga River Delta... 2008; Carbiener et al. 1990; Underwood et al. 2006; Coops et al. 1999; Khedr and El-Demerdash 1997; Kröger et al. 2009; Chaplin and Valentine 2009). For instance, studies in the Volga River delta showed that the accumulation of chemical elements by aquatic plants depends on their ecological and morphological characteristics, biogeochemical specialization, the content of chemical elements in the components of aquatic systems, and migration conditions, determined primarily by the flow characteristics of water streams and bodies (Lychagina et al. 1998; Lychagin et al. 2015).

This study considers Selenga River delta which is the largest freshwater delta in the World and which plays protective role for the Lake Baikal which is the oldest and deepest lake of the planet and a UNESCO World Heritage Site (2019). Selenga accounts for 60% of the total river water flow and 82% of sediment load to Lake Baikal (Pietroń 2017). The

anthropogenic impact on ecosystems in the Selenga River basin has increased in the recent decades, e.g., by the extraction of minerals, primarily gold, urbanization, and agricultural development, especially in the upper, Mongolian, part of the basin (Pietroń et al. 2017; Jarsjö et al. 2017; Malsy et al. 2013). In addition, changing climatic conditions in the basin, such as increasing air temperatures (0.022°C/year, nearly two times faster than the global average; Törnqvist et al. 2014) can also significantly affect the regional ecosystems.

The Selenga River delta acts as a “geochemical filter” by dispersion and storage of metal. According to the previous studies suspended sediment particles are important in heavy metals and metalloids in the Selenga River basin transport (Thorslund et al. 2012; Chalov et al. 2015; Chalov et al. 2017). These particulate matter fluxes can be significantly altered by macrophytes in the Selenga River delta. It was observed that the most effective removal of contaminants occurs along relatively narrow distributary channels adjacent to vast wetland areas (Chalov et al. 2017). In the submerged parts of the delta, affected by the backwater from the Lake Baikal, the sediment can be transported outside the deltaic channels to the nearest water bodies in conditions with water discharge from moderate to high (Pietroń et al. 2018). However, the detailed quantitative characteristics of flows of potentially toxic elements and their amounts deposited in the Selenga River delta are still poorly understood. Moreover, despite the observed hydrological and geochemical patterns little is known about the role of aquatic vegetation in the metal storage function of the Selenga River delta. Hydrofauna and hydroflora of Selenga basin related to algae, fish, plankton, benthos, amphibian fauna species, microbial communities along rivers have been investigated since the end of 19th century within its Mongolian part (Dgebuadze et al. 2010). In the Russian part of Selenga basin a lot of work in aquatic vegetation studies was done by V.V. Chepinoga and co-authors (Chepinoga 2012; Chepinoga

and Rosbach 2012; Lane et al. 2015). However, there is a lack of knowledge regarding the accumulation of chemical elements by different species of aquatic plants due to environmental conditions. This paper considered aquatic vegetation of Selenga River delta to study its ability and effectiveness in filtering of riverborn metals and metalloids. Hence, the working hypothesis is that the storage processes of macrophytes play an important role in the accumulation of the contaminant loads along the deltaic channels.

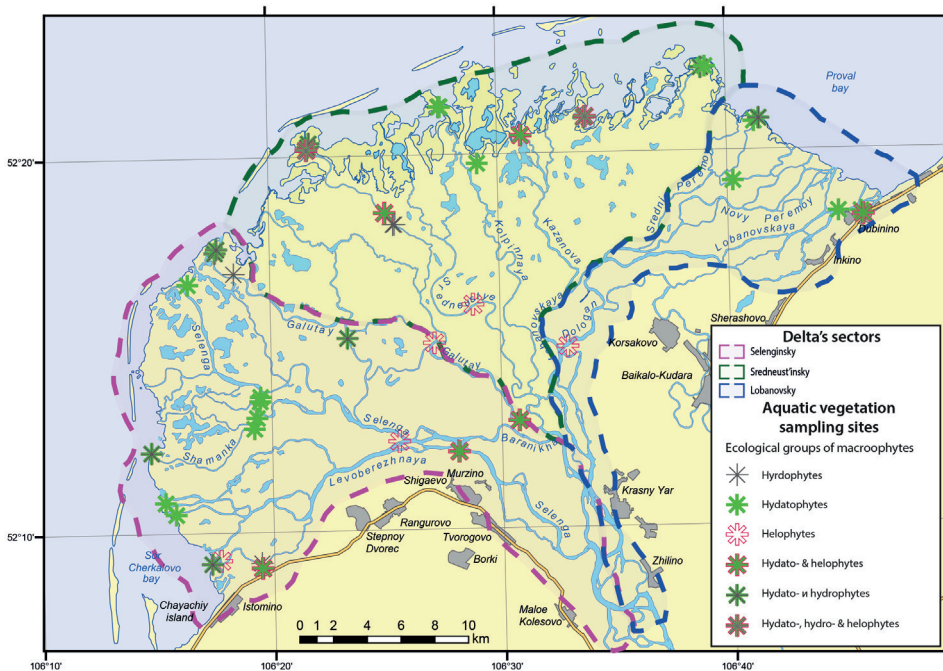
**STUDY AREA**

The Selenga river carries out 2.5 million tons per year of suspended matter to the Lake Baikal, forming a delta with an area of about 540 km<sup>2</sup>. Thickness of sediment layer in the Selenga delta is up to 5000–5500 meters. It was formed by the river sediment flow towards the steep slope of the Baikal rift over 500 thousand years. Such a large amount of sediment inflow of the Selenga allows the delta to protrude into the Lake Baikal (Rogozin 1981): the delta and its underwater continuation divide the Lake into the Southern and

Central basins with average depths about 1100-1500 m (Tulokhonov 2001). Selenga delta is undergoing an active phase of regression (Dong et al. 2013), the closest coastal distance of the Lake (26 km) is still registered across from the Selenga estuary.

Three sectors are commonly distinguished in the delta (Korytny et al. 2012; Il'icheva 2015; Chalov et al. 2017): the Western – Selenginsky, the Central – Sredneustevsky, and the Eastern – Lobanovsky (Fig. 1). The distribution of runoff across the sectors is uneven: an average of 45% passes through the Lobanovsky sector, 20% along the Sredneustevsky and 35% along the Selenginsky (Korytny et al. 2012).

The Selenginsky sector includes the main channel of the Selenga River, the Levoberezhnaya, Glubokaya, Shumikhka, Shamanka, and Galutai channels. These channels (Fig. 2a) are characterized by a large water discharges (32–157 m<sup>3</sup>/s). The growth of the delta in this sector reaches 2 km per 100 years (Korytny et al. 2012). Bottom sediments in large channels are often sandy or sandy-pebble, whereas



**Fig. 1. Sampling sites of macrophytes in the Selenga delta**

silt dominates (~52%) in floodplain lakes and permanently submerged marshlands (~64%). The submerged channel bank areas of the channels in this part of the delta are characterized by similar content of silt (~57%; Pietron et al. 2018).

The Sredneustievsky sector includes the small channels Krivaya, Kolpinnaya, Sredneustye, Casanova, Severnaya (Fig. 1) with low water discharge (up to 35 m<sup>3</sup>/s). In this parts, content of silt in sediment deposited on banks increases up to 26% (Pietron et al. 2018) and it has been observed that some of the channels dry out in rainless periods. In most recent years, this sector is experiencing flooding along the outer edge, which causes an increase in the area of intra-delta lakes with abundant aquatic vegetation (Chalov et al. 2017).

The Lobanovsky sector consists of the Lobanovskaya channel and its branches Novy Peremoy and Sredniy Peremoy. This part of the delta experiences progradation towards Lake Baikal at a speed of 30–40 m per year (Korytny et al. 2012). The channels are characterized by the moderate water discharge (30–50 m<sup>3</sup>/year) and a small amount of aquatic plants. Sand fractions prevail in bottom sediments (about 47%). At the mouth area of the Lobanovskaya channel bottom sediments are finer, with the silt content exceeding 50% (Kasimov et al. 2019).

## MATERIALS AND METHODS

This work is based on the data collected on field during summer growing period of: (1) 8<sup>th</sup>–14<sup>th</sup> of August 2011, (2) 30<sup>th</sup> of June to 2<sup>nd</sup> of July 2012 and (3) 13<sup>th</sup>–26<sup>th</sup> of July 2013. Areas with the most typical geochemical conditions within the Selenga delta channels were chosen as the sampling locations. At every sampling station field measurements of the physicochemical parameters of river waters and bottom sediments were measured on site by Hanna field instruments (e.g. pH, mineralization, redox potential). In addition, dissolved oxygen content using the Winkler method was

determined. At some locations Van Veen grab was used to take samples of bottom sediments.

Water samples were taken in 2 and 5 liter bottles, after which they were filtered on a Millipore vacuum station with a Millivac Mini Vacuum Pump (230v 50Hz) through pre-weighed membrane filters with a diameter of 47 mm and a pore size of 0.45 µm. To preserve river water samples for further HMM determination 0.1 ml of HNO<sub>3</sub> (concentrated) was added to new 15 ml Saerstedt tubes and filled up to the mark with filtered water. All tubes were carefully closed. The filters and bottom sediments were dried at room temperature (~21°C). Filters were afterwards weighed again to determine the mass of the suspended sediments.

In the coastal part of inner lakes and water channels the sampling of prevailing macrophyte species was carried out: small yellow pond-lily (*Nuphar pumila*), pondweeds (*Potamogeton perfoliatus*, *P. pectinatus*, *P. natans*, *P. friesii*), flowering rush (*Butomus umbellatus*), spiked water-milfoil (*Myriophyllum spicatum*), hornwort (*Ceratophyllum demersum*), reed (*Phragmites australis*). Those samples have been dried in the oven at a temperature of 60°C. Collection of aquatic vegetation samples from premeasured sites (usually 0.25 x 0.25 m) within typical areas where one dominant plant species grow was done separately. Macrophytes collected from those sampling locations were weighed in the laboratory, after which a smaller amount have been taken for further HMM concentrations determination. Each of these smaller samples have been weighed, dried in an oven, and weighed again after drying.

In estuarine vegetation and other components of aquatic systems the content of 21 chemical elements (Table 1) was analyzed using the ICP-MS (ICP-AES) methods. Those elements are Be, B, V, Cr, Co, Ni, Cu, Zn, As, Mo, Cd, W, Pb, Bi, U, Sn, Sb, Mn, Fe and Al.



A total amount of 144 river water, 146 suspended sediments, 118 bottom sediments and 143 macrophytes samples have been analyzed.

To characterize the relationship of the content of elements in aquatic plants and other components of aquatic systems coefficients  $K_w$ ,  $K_s$  and  $K_b$  were used:  $K_w = C_n / (1000 \times C_w / a)$ ,  $K_s = C_n / C_s$ ,  $K_b = C_n / C_b$ , where,  $C_n$  – metal concentration in the aquatic plant (mg/kg of dry matter),  $C_w$  – metal concentration in the river water ( $\mu\text{g/L}$ ),  $a$  – mineralization of water (mg/kg),  $C_s$  – metal content in suspended matter (mg/kg),  $C_b$  – metal concentration in bottom sediments (mg/kg).

Due to a possible high variability of the HMM content in components of aquatic systems, to fully reflect the relationship of the contents of elements in the plant-habitat system we propose to use a multiplicative accumulation coefficient

$$K_{wsb} = \sqrt[3]{K_w \times K_s \times K_b}$$

Furthermore, to assess the evaluation of the total accumulation of chemical elements by macrophytes we also suggest the coefficient

$$Z_{veg} = \sum K_{wsb} \text{ at } K_w > 1.5; K_s > 1.5; K_b > 1.5$$

In addition, remote sensing data obtained during 28/07/2014 – 16/08/2014 when shooting the delta from ultralight aviation (ULM) with sensing platform ULM/Headwall mounted on it was used to compile distribution maps of the main groups of macrophytes. Two main groups of aquatic plants were distinguished: 1) plants with floating leaves with predominance of small yellow pond lily (*N. pumila*) and 2) submerged plants with predominance of pondweeds (*Potamogeton perfoliatus*, *P. pectinatus*, *P. natans*, *P. friesii*) and spiked water-milfoil (*Myriophyllum spicatum*).

Sensing platform ULM/Headwall is a hyperspectral pushbroom sensor. Its original data contains 250 spectral channels with 0.7 m spatial resolution. In our case total amount of bands was reduced to 151 (509.74 nm to 778.74 nm)

and spatial resolution to 5 m to increase processing speed. After geometric, radiometric and atmospheric correction (Cubero-Castan et al. 2015) remote sensed images were processed with Spectral Angle Mapper (SAM) algorithm in ENVI GIS. From total amount of 143 field vegetation sites 90 was used for supervised classification and 53 for its verification. Total accuracy of classification was 79% for classified sites and 64% for verification sites. Based on image classification area of aquatic vegetation distribution was estimated. Water plants with a predominance of small yellow pond-lily (group 1) occupy about 41 sq km of delta, and pondweeds and spiked water-milfoil (group 2) occupy about 11 sq km. The elements accumulation in the  $N$  group (group 1 or group 2) of aquatic vegetation ( $HM_N$ , kg) from the beginning of growing season till the sampling date was determined as follows:

$$HM_N = C_N^{HM} \times B_N \times P_N \times 10^{-6}$$

where  $C_N^{HM}$  is the average concentration of an element in the  $N$  group of aquatic vegetation at the sampling date (mg/kg, wet weight),  $B_N$  is the average phytomass of plants of the  $N$  group at the sampling date,  $\text{kg/m}^2$ ;  $P_N$  is the distribution area of group  $N$  in the delta,  $\text{m}^2$ ,  $10^{-6}$  is the conversion factor from mg to kg.

The HMM fluxes in dissolved ( $W_c$ ) and suspended ( $W$ ) forms per day have been calculated using the following equations:

$$W_{ci} = Q \times C_{ci} \times 86400 \times 10^{-9},$$

$$W_i = R \times C_i \times 86400 \times 10^{-6}$$

where  $W_{ci}$  is the flux of the  $i$ -element in dissolved form, kg/day;  $W_i$  – flux of the  $i$ -element in suspended form, kg/day;  $Q$  – water discharge,  $\text{m}^3/\text{s}$ ;  $R$  – suspended matter discharge,  $\text{kg/s}$ ;  $C_{ci}$  – concentration of the  $i$ -element in river water,  $\mu\text{g/m}^3$ ;  $C_i$  – concentration of the same  $i$ -element in suspended matter,  $\text{mg/kg}$ ; 86400 – conversion factor seconds to days;  $10^{-9}$  – conversion factor  $\mu\text{g}$  to  $\text{kg}$ .

Taking into account the length of the growing season at the time of sampling, the total flux of elements brought into

the delta in dissolved and suspended forms for this hydrological period the proportion of HMM precipitated in the delta due to the activity of each group of aquatic plants ( $HM_{N\%}$ ) was estimated as follows:

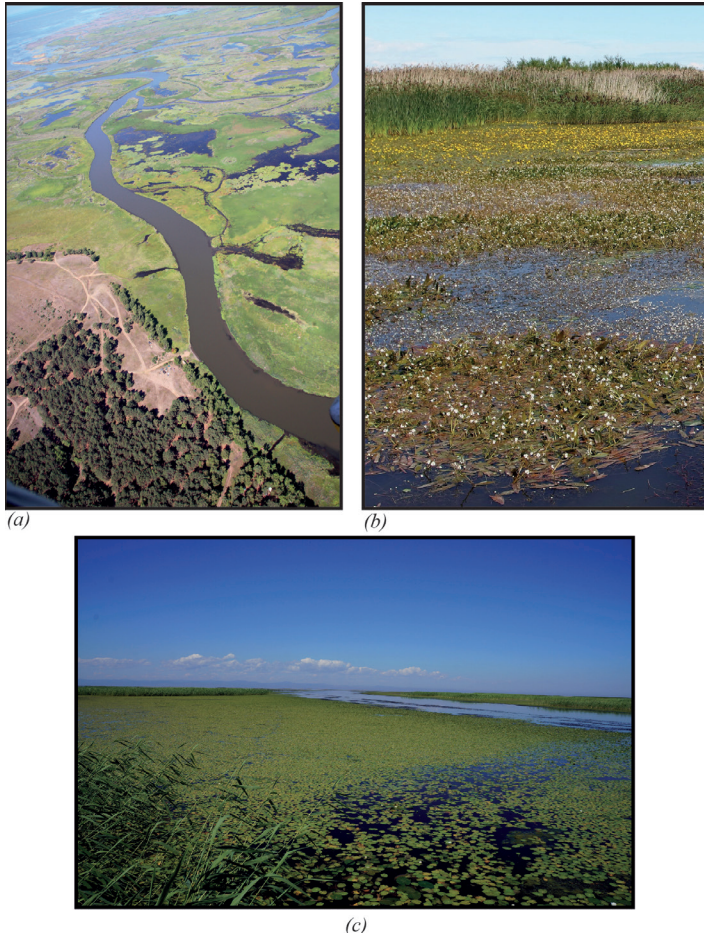
$$HM_{N\%} = \frac{NM_N \times 100}{(W_{Ci} + W_i) \times T},$$

where  $HM_N$  is elements accumulation in the  $N$  group of aquatic vegetation (kg);  $W_{Ci}$  and  $W_i$  are the fluxes of the  $i$ -element in dissolved and suspended form respectively (kg/day);  $T$  – time period from the beginning of the growing season to the time of sampling (days).

## RESULTS AND DISCUSSION

### Spatial distribution of aquatic vegetation

Variation of hydrological conditions of three sectors of the Selenga delta (Fig. 1) has a great influence on the development of aquatic vegetation species. Large water discharges of the Selenginsky sector cause a rare presence of aquatic plants in the channels (mostly reed and small yellow pond-lily) and a large number of macrophytes in the intra-delta lakes Zavernyaekha and Tolstonozhikha (different pondweeds, small yellow pond-lily, spiked water-milfoil, Fig. 2b), and also at the water-stream mouths in the Sor Cherkalov bay (pondweeds, small yellow pond-lily, Fig. 2c). The Sredneustievsky sector with small



**Fig. 2. Aquatic vegetation of the Selenga delta:**  
 (a) – macrophyte-free large channel; (b) – macrophyte communities in delta lakes;  
 (c) – dense fields of macrophytes in the mouth area of the small channel

channels and low water discharges stands out with the greatest distribution of aquatic vegetation. Main species of this sector are small yellow pond-lily, pondweeds and spiked water-milfoil. The Lobanovsky sector with moderate water discharges is characterized with small amount of aquatic plants. The curtains of small yellow pond-lily, clasping-leaved pondweed, spiked water-milfoil were found there.

### Water chemistry of the Selenga delta

Elements migration factors within Selenga delta are weakly variable. Thus, mineralization values ( $M$ ) in the channels is quite stable (110–144 mg/L) and not dependent on the hydrological season. Spatial variability in the delta sectors is also small: about 110–130 mg/L. Differences in mineralization of the waters of the Proval Bay and the Sor Cherkalov Bay are insignificant: 80–104 mg/L. The highest  $M$  values were found at the mouth of the Casanova channel (130 mg/L), which apparently is associated with the supply of mineralized groundwater (Khazheeva and Pronin 2007). Beyond the island bar where river water is diluted by lake waters there is a decrease in mineralization to 77–84 mg/L. Mineralization in Lake Baikal is quite constant and amounts to about 100 mg/L (State Report... 2014). Alkaline conditions are stable too. The average pH value for deltaic river waters is 8.15 with extreme values from 7.0 to 9.91. The lowest pH was noted in the inner delta lakes of the Selenginsky sector and highest in the small channels of the Selenginsky and Sredneustievsky sectors with a lot of aquatic vegetation. Dissolved oxygen is quite evenly distributed over the delta area and varies from 7.7 to 16.2 mg/L. Minimum values were found in the Selenginsky sector of the delta in the Shamanka and Levoberezhnaya channels (7.7–9.8 mg/L), maximal values were found in the Lobanovskaya channel and the Sor Cherkalov Bay (13.2–15.6 mg/L).

### Heavy metals and metalloids in aquatic plants

The data demonstrated high variability of the chemical elements content in plants: the ratio of maximum and minimum contents in various species is up to 70 times for Cu, Zn, Mo, Cd and up to 1000 times or even higher for Co, V, Al, Be, W, Sn, U. Such differences are due to the ecological and morphological features of the species.

According to ecological and biological characteristics developed in the process of adaptation, all macrophytes are divided into three groups (Katanskaya 1981). The first group, hygrophytes (helophytes), is related to coastal-aquatic rooting plants with stems and leaves rising above the surface of the water that can exist and develop both in water and on the wet shores of water bodies. In the Selenga delta this group includes reed (*Phragmites australis*), flowering rush (*Butomus umbellatus*), and bur reed (*Sparganium*). Due to the simultaneously existence of these macrophytes in aqueous and air environments, they do not lack in light nutrition. Hydrophytes are aquatic plants, subdivided into freely floating non-rooting and rooting with freely floating leaves. In the delta, this is a small yellow pond-lily (*Nuphar pumila*), water lily (*Nymphaea tetragona*), limnanth (*Nymphoides peltata*) and Canadian pondweed (*Elodea canadensis*). Hydatophytes are submerged plants; hence, their entire development cycle takes place in water. They are pondweeds (*Potamogeton*), hornwort (*Ceratophyllum demersum*) and spiked water-milfoil (*Myriophyllum spicatum*).

Reed (*Phragmites australis*) is a typical helophyte and characterized by a wide range of habitat conditions (Ye et al. 1997; Baldantoni et al. 2004; Quan et al. 2007). It forms dense thickets both along the banks of delta channels and intra-delta lakes with water depth of up to 2 m. Contents of the most heavy metals and metalloids (except Mo) in reed are the lowest among macrophytes of the Selenga delta (Table 1).

**Table 1. The average content of chemical elements in macrophytes of the Selenga delta (mg/kg of dry matter)**

Elements	<i>Ph. australis</i> (n=8)	<i>B. umbellatus</i> (n=7)	<i>N. pumila</i> (n=27)	<i>P. natans</i> (n=8)	<i>P. perfoliatus</i> (n=21)	<i>P. friesii</i> (n=6)	<i>P. pectinatus</i> (n=5)	<i>M. spicatum</i> (n=14)	<i>C. demersum</i> (n=8)
Fe	409	379	929	1011	2306	10863	8014	9079	2246
Al	312	304	808	703	2312	5225	5297	5196	1872
Mn	393	760	330	1064	1328	1873	1486	3700	2697
Zn	30	25	17	16	22	33	31	25	17
Cu	4.1	6.1	3.8	4.71	6.7	8.9	11	10	5.6
Pb	0.23	0.29	0.6	0.59	1.2	2.3	2.9	3.0	0.98
Bi	0.001	0.01	0.0	0.02	0.03	0.06	0.07	0.08	0.03
Ni	0.72	1.3	1.7	1.78	5.1	6.5	9.4	8.8	6.3
Co	0.17	0.28	0.9	1.25	2.9	2.8	3.7	5.0	4.7
Sn	0.04	0.06	0.0	0.02	0.07	0.1	0.28	0.1	0.08
Cd	0.01	0.04	0.0	0.05	0.16	0.06	0.13	0.15	0.12
Cr	0.62	0.82	1.7	1.38	3.5	8.4	9.9	8.6	3.0
V	0.99	0.9	2.7	2.7	6.2	16	19	17	5.7
Be	0.01	0.01	0.03	0.03	0.08	0.14	0.19	0.19	0.07
W	0.05	0.08	0.1	0.001	0.06	0.25	0.1	0.12	0.16
B	5	11	16	10	12	9	56	26	25
As	0.17	0.23	0.5	1.11	1.6	8.9	4.3	7.3	4.3
Mo	2.5	1.01	0.9	0.58	1.3	2.0	1.6	1.8	0.87
U	0.04	0.08	0.3	0.35	1.27	1.3	1.5	1.7	0.65
Sb	0.001	0.01	0.001	0.001	0.02	0.03	0.05	0.02	0.02

In the Volga delta, reed was also characterized by the lowest HMM contents (Lychagina et al. 1998; Kazmiruk 2008; Brekhovskikh et al. 2009; Tkachenko 2011). However, the average contents of Mn, Fe, Cu, Zn in reed of the Selenga delta are 7–15 times higher than ones in the Volga delta. These metals are closely related to organic matter, amount of which in water of the Selenga delta is significantly higher. At the same time

in the Selenga delta the contents of Ni, Co, Pb, Cd are 2–59 times lower due to lower content in components of aquatic systems.

*Flowering rush (Butomus umbellatus)* in the Selenga delta was found in the Glubokaya, Severnaya channels and the main Selenga channel. This is a rather large plant with a thick, fleshy rhizome, basal upright leaves, and umbellate inflorescences at the top

of the stem, usually growing in water bodies 0.5–0.7 m deep. A flowering rush is a helophyte, as well as a reed, with a similar low content of HMM (table 1).

*Small yellow pond-lily (Nuphar pumila)* is most often found in the mouth areas of water streams, low-flow sections of the channels, and also along the shores of the intra-delta lakes. Water-lily family consists of perennial aquatic plants with a long rhizome, rounded floating leaves and yellow flowers. The species belongs to large-leaved hydrophytes and is characterized by a higher accumulation of HMM than the helophytes (Table 1).

*Pondweeds (Potamogetons)* are widespread within the Selenga delta. These are floating plants with leaves of various shapes and sizes, inflorescence-spike of grayish-green or brownish-green colour. They belong to the group of hydatophytes and generally accumulate HMM more actively than helophytes and hydrophytes (Table 1). Pondweeds form the following range according to increase of HMM content: common floating pondweed (*P. natans*) – clasping-leaved pondweed (*P. perfoliatus*) – pondweed Friesii (*P. friesii*) – fennel-leaved pondweed (*P. pectinatus*). The difference is significant: average content of Mn, Cu, Pb, Ni, Co in *P. pectinatus* is 2-5 times higher than in *P. natans*, Fe, Al, As, U, Be – 5–7 times. *P. friesii* stands the greatest accumulation W, As, Mo, and Zn.

Common floating pondweed was found mainly in the Selenginsky sector of the delta. Fennel-leaved pondweed is widespread in the Lobanovsky sector. Pondweed Friesii is common for small shallow channels of the Sredneustevsky sector. Clasping-leaved pondweed is the most widespread in the whole delta, grows fairly evenly and is characterized by moderate accumulation of HMM.

*Hornwort (Ceratophyllum demersum)* is a perennial herbaceous aquatic plant with thin branches, a rigid stem with sessile leaves. The plant does not form a

root system and, provided the bottom is close to retain in the bottom sediments, specific rhizoid branches can develop. This is a shade-loving plant, sensitive to light, which, nevertheless, grows to a depth of 9 m. Often, the hornwort forms quite dense clusters, freely drifting in the water column. Since photosynthesis at a depth is difficult, the hornwort is more in need of chemical elements necessary for photosynthesis and respiration (Fe, Mn, Zn, etc.) than other types of macrophytes (Lychagina et al. 1998). It has air cavities (70% of the volume), which creates favorable conditions for the concentration of the elements. In the Selenga delta, the hornwort is often found in the mouths of the channels of the Sredneustevsky sector with low flow rates and hindered water exchange. It is characterized by a high content of B, to a lesser extent Ni and Co (Table 1). Due to the fact that the hornwort does not form the root system, it receives the necessary substances and elements from the surrounding water, actively accumulating Zn, Pb, and Cu (Keskinkan et al. 2004). It should be noted that the hornwort plays an important role as a biofilter precipitating suspended particles. This was previously noted in the Volga delta (Lychagina et al. 1998), where the hornwort is characterized by a high content of Mn, Ni, Co, and Cd.

*Spiked water-milfoil (Myriophyllum spicatum)* is a genus of perennial aquatic plants with ascending shoots rising above the surface, creeping rhizomes. Water-milfoil has long and flexible stems up to 2 m length, pinnate leaves, dissected into very narrow, threadlike lobes, green or brown color. The flowers are small, collected in spike-shaped inflorescences towering above the water. Spiked water-milfoil is widespread throughout the delta. Due to the strongly dissected cirrus leaves, water-milfoil is the best trap of the suspended substances among all considered species. Compared to the other plant species, water-milfoil mostly concentrates B, Cr, Co, Ni, Pb, and U (Table 1). It was reported for



Muraviovka Park located in the southern part of Zeya-Bureya Depression (Amur Region, Russia) that spiked water-milfoil accumulates Cu, Zn and Pb in larger quantities than other submerged and rooted hydrophytes with floating leaves (Pakusina et al. 2018).

These results indicate that regardless of the hydroclimatic conditions and the place of growth, hydrophytes spiked water-milfoil and the fennel-leaved pondweed (*P. pectinatus*) most actively accumulate metals, and opposite tendencies were found for helophytes reed and flowering rush which concentrate the least amount. A similar trend of increasing contents of HMM in the following series: helophytes – hydrophytes – hydrophytes was observed for aquatic plants of the Volga delta, as well as an increase in the contents of HMM from large-leaved species to diverse-leaved (Tkachenko et al. 2016). The average HMM concentrations in macrophytes of the Selenga and Volga deltas are generally close, only the content of Mn, Cu, Ni, and Pb are 1.5–3 times higher in the Volga delta, and Fe and Zn are 1.2 times higher in the Selenga delta.

Content of heavy metals and metalloids in aquatic plants is, in general, different from terrestrial plants (Table 2). The latter ones show wider range of Cu, Zn, Pb, Ni, Co values due to the stronger variability of environmental geochemical conditions in terrestrial ecosystems. However, content of Fe and Mn in aquatic plants in many cases exceeds content in terrestrial species. It is less pronounced for marine and more for freshwater plants. This is clearly seen in the Volga and Selenga deltas. The reason is the widespread development of reducing conditions in bottom sediments and wetlands of river deltas, which are very favorable for the migration of Fe<sup>2+</sup> and Mn<sup>2+</sup> compounds.

Generally, HMM levels in macrophytes of the Selenga delta are similar to macrophytes of the Volga delta and aquatic plants of unpolluted estuaries (Table 2).

### Biogeochemical specialization of macrophytes

The content of HMM in aquatic plants is largely determined by their physiological characteristics and ecological group to which this plant belongs. Due to the

**Table 2. Heavy metals content in plants, mg/kg of dry weight**

Elements	Terrestrial plants <sup>1</sup>	Marine plants <sup>2</sup>	Aquatic plants of unpolluted estuaries <sup>3</sup>	Macrophytes of the Selenga Delta <sup>4</sup>	Macrophytes of the Volga Delta <sup>5</sup>
Fe	18–100	20–5000	50–40000	67–43000	64–36000
Mn	16–1840	7–1740	70–15000	72–47000	54–13000
Cu	1–150	1.2–86	4.5–8.9	1–20	2–32
Zn	12–300	1.4–165	10–100	4–85	2–72
Ni	0.07–48	1–154	3–40	0.1–20.0	0.8–60
Co	0.01–200	0.1–1090	–	0.01–15.0	0.7–15
Pb	0.1–300	2.6–19	2–49	0.05–7.4	0.5–12
Cr	–	–	0.2–50	0.2–30.0	0.02–318

<sup>1</sup> according to Kabata-Pendias and Pendias (1984); <sup>2</sup>Saenko (1992); <sup>3</sup>Moore and Ramamurthy (1987); <sup>4</sup>authors data; <sup>5</sup>Lychagina et al. (1998)

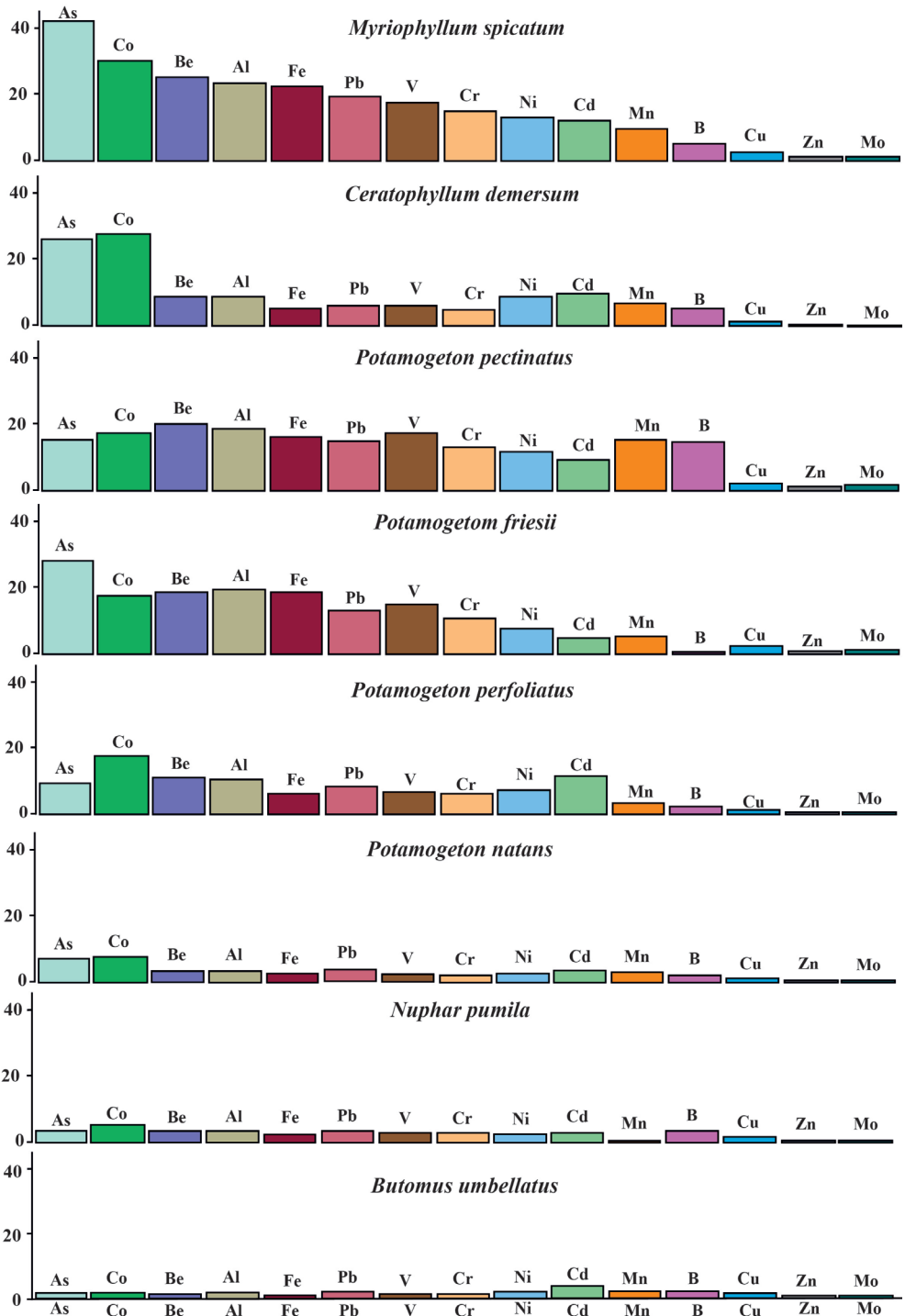


Fig. 3. Enrichment factor  $EF_r$  of chemical elements in various macrophyte species regarding content in reed

high variability of the contents exceeding for the most chemical elements 100%, it is difficult to compare species among themselves. For this, the Enrichment Factor  $EF_r = C_n/C_r$  was calculated (Fig. 3), where  $C_n$  is the content of a chemical element in a particular plant species, and  $C_r$  is the content of this element in a reference species.

Reed has been selected as the latter for several reasons. It has the widest ecological amplitude of growth and participates in a wide variety of plant associations. Reed receives nutrients mainly from bottom sediments through the root system. Content of HMM in reed leaves weakly related to the content in river water. It determines the lowest HMM content in reed among macrophyte species in the Selenga delta. Previously reed was used as a reference species in biogeochemical studies in the Volga delta (Lychagina et al. 1998).

Sviridenko with co-authors (2017) studied ecotopes of aquatic macrophytes of the West Siberian Plain. They reported that some species could be found within areas with high concentrations of dissolved metals. This fact could stand for this species high tolerance to certain element. Thus small yellow pond-lily could withstand rather high concentrations of dissolved Pb, Ni; hornwort – Pb, Ni, Zn, Cu, Mn; pondweeds – Pb, Ni, Mn and to a lesser extent Zn, Cr, Cu; reed – Pb, Ni, Zn, Cd, Cr, Cu, Mn; spiked water-milfoil – Zn; flowering rush – Zn and to a lesser extent Mn. This data confirms previous conclusions about the possibility of using reed as a reference species.

The maximum  $EF_r$  values are common for U. This is due to its very low content in a reference species, as well as high migratory ability in alkaline water and easy accessibility to aquatic plants. Submerged macrophytes fennel-leaved pondweed, clasping-leaved pondweed, pondweed Friesii, spiked water-milfoil, hornwort are characterized with the highest content of U and As, which generally corresponds to the published data (Reay 1972; Outridge and Noller 1991; Favas et al. 2012; Favas et al. 2014).

Analysis of  $EF_r$  values makes it possible to identify the features of biogeochemical specialization of various aquatic plant species (Fig. 3). As clearly seen in Fig. 3, *Myriophyllum spicatum* is characterized by the greatest accumulation ( $EF_r > 10$ ) of a wide group of chemical elements, including both elements that are highly soluble (U, As, B, Cd) and slightly soluble (Fe, Al, Pb, Ni, Co, Be, Cr, V) in the waters of the Selenga delta. Obviously, this plant species has a high ability to accumulate both dissolved and suspended forms of chemical elements. The ability to group concentration of chemical elements is slightly less pronounced for *Ceratophyllum demersum*.  $EF_r$  values for this plant are lower, for most elements are in the range of 5 to 10. As already noted, the high ability to accumulate elements in the Selenga delta is distinguished by pondweeds, among which *Potamogeton pectinatus* and *P. friesii* stand out. For the both species  $EF_r$  values mainly exceed 10.

Weak accumulation of chemical elements is characterized by *Nuphar pumila* and *Butomus umbellatus* species. The average content of Fe, Mn, Pb, Ni, Cr, V, U, As in *Nuphar pumila* is 2–3 times higher than in *Phragmites australis*. For *Butomus umbellatus*, this is noted only for U, Cd and Pb.

### Environmental impacts on metal accumulation in macrophytes

Aquatic plants can receive nutrients mainly in two ways: via the root system from bottom sediments and through the stem and leaf surface from the river water (Sawidis et al. 2001). The wider root system development contributes to the absorption of chemical elements from a larger area, enhancing their accumulation by macrophytes (Wang et al. 1997). The presence of underwater and floating leaves provides a large area for capturing solid suspended particles from the water flow, as well as sorption of the dissolved HMM (Bonnano and Giudice 2010). Macrophytes of wetlands are known to have a greater or comparable ability to accumulate metals compared to other

plant species and biota (Jana 1988). Moreover, the ability to concentrate HMM increases in the series of surface – floating – submerged plants.

The relationship of the contents of elements in aquatic plants and other components of aquatic systems can be characterized using the coefficients  $K_w$ ,  $K_s$  and  $K_b$ . Mean values of HMM are given in the Table 3.

Regarding river water, the studied macrophyte species are enriched with Mn ( $K_w$  up to 26.3) and Co (2.7), regarding suspended matter – Mo ( $K_s$  up to 2.9), Mn (2.8) and B (1.4), regarding bottom sediments – Mn ( $K_b$  up to 9.9), Mo (4.2) and As (1.5).

According to  $K_{wsb}$  values (Table 4) all plant species accumulate mainly Mn and Mo. The widest range of accumulating elements is characteristic for spiked water-

**Table 3. Average content of HMM in components of aquatic systems of the Selenga Delta**

Elements	Suspended sediment, mg/kg (n=83)	Bottom sediment, mg/kg (n=70)	River water, µg/L (n=83)
Be	1.6	2.1	0.03
B	51	–	7.28
V	109	95	1.58
Cr	54	39	3.37
Co	20	11	0.23
Ni	38	23	1.11
Cu	43	18	1.69
Zn	116	63	8.33
As	20	4.8	0.96
Mo	1.67	1.2	1.17
Cd	0.50	0.28	0.02
W	0.90	2.3	0.03
Pb	33	19	1.15
Bi	0.66	0.26	0.00
U	2.8	2.9	0.97
Sn	2.4	2.8	0.06
Sb	0.30	0.85	0.07
Mn	2077	585	25.9
Fe	41125	26365	408
Al	38207	74571	275

**Table 4. Series of HMM accumulation factor by macrophytes according to the values of the coefficient  $K_{wsb}$** 

Species	$K_{wsb}$ value				
	> 10	10–1.0	1.0–0.5	0.5–0.1	< 0.1
<i>M. spicatum</i>	Mn	As, Co, Mo, Fe, Cd	Bi, Cu, Ni, U, V, Zn, Al	Cr, Be, Pb, W, Sn	Sb
<i>C. demersum</i>	–	Mn, Co	As, Cd, Mo, Ni, Cu	Zn, W, U, Fe, Bi, V, Al, Cr, Be, Sn, Pb	Sb
<i>P. friesii</i>	–	Mn, Mo, As	Zn, Cu, Fe, Co, U, Bi, V, Ni	Al, Cd, W, Cr, Be, Pb, Sn	Sb
<i>P. perfoliatus</i>	–	Mn, Cd	Mo, Co, U, Cu, Zn, Ni	Bi, As, Fe, Al, V, Be, Cr, Pb, W	Sn, Sb
<i>P. pectinatus</i>	Mn	Mo	Cu, Zn, Fe, Co, Cd, Ni, U, V, As, Bi	Al, Cr, Be, Sn, Pb, W, Sb	–
<i>P. natans</i>	–	Mn	–	Mo, Cu, Zn, Co, Cd, As, Ni, U, Bi, Fe, V	Al, Cr, Pb, Be, Sn, Sb, W
<i>N. pumila</i>	–	Mn	Mo	Zn, Cu, Cd, Co, Ni, U, Bi, Fe, As, W, V	Al, Cr, Be, Pb, Sn, Sb
<i>B. umbellatus</i>	–	Mn, Mo	Zn, Cu	Cd, W, Ni	Co, Sn, Bi, Fe, U, V, As, Al, Cr, Pb, Sb, Be
<i>Ph. australis</i>	–	Mo, Mn	Zn	Cu, W	Cd, Ni, Sn, Fe, Co, Bi, V, As, Al, Cr, Pb, U, Be, Sb

milfoil:  $Mn_{11.5}, As_{1.6}, Co_{1.4}, Mo_{1.3}, Fe_{1.2}, Cd_{1.1}$ . The shorter series found for the pondweed Friesii  $Mn_{6.4}, Mo_{3.3}, As_{1.1}$ , clasping-leaved pondweed ( $Mn_{4.2}, Cd_{1.1}$ ), fennel-leaved pondweed ( $Mn_{18.4}, Mo_{3.7}$ ) and hornwort ( $Mn_{8.5}, Co_{1.3}$ ). Reed and flowering rush are characterized by the lowest  $K_{wsb}$  values (1.2–2.3), which confirms the relatively weak relationship of these plant species with the habitat.

The highest  $Z_{veg}$  values are common for the fennel-leaved pondweed (22.1) and spiked water-milfoil (13.1), followed by the pondweed Friesii (9.7), hornwort (8.5), clasping-leaved pondweed (4.2), and flowering rush (4.1), common floating pondweed (3.4) and reed (1.9).

To identify the peculiarities of accumulation of suspended and dissolved forms of HMMs

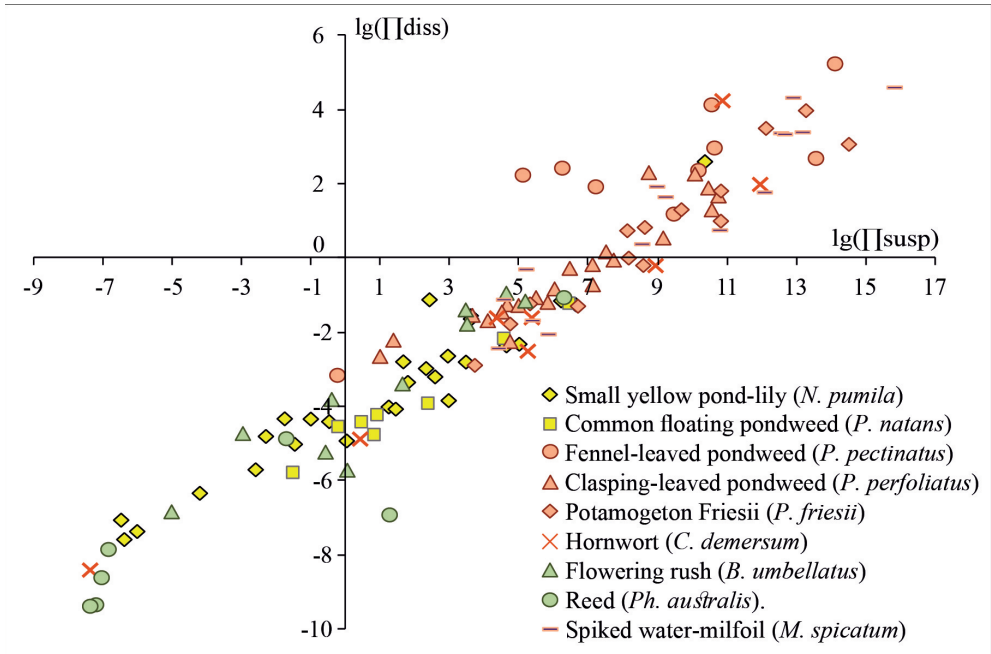
by aquatic plants, we examined the ratio of decimal logarithms of the products of the concentrations of chemical elements migrating in aquatic systems of the Selenga delta mainly in suspended or dissolved forms. Two associations of chemical elements were identified:

- 1) S-association with the predominant suspended form of migration – Be, V, Co, Ni, W, Pb, Bi, Mn, Fe and Al;
- 2) D-association with the predominant dissolved form of migration – B, U, Mo, Cr, Cu, Zn, As, Cd, Sn and Sb.

Due to these associations three groups of macrophytes were distinguished (Fig. 4):

- 1) helophytes flowering rush and reed with a low HMM content (green zone in the figure);





**Fig. 4. Accumulation of suspended and dissolved forms of HMM by macrophyte species**

2) hydrophyte small yellow pond-lily and hydathophyte common floating pondweed with a moderate accumulation of S-association elements and weak accumulation of D-association elements (yellow zone);

3) hydathophytes submerged with a large leaf area, accumulating both elements of group S and D – claspingleaved pondweed, fennel-leaved pondweed, and pondweed Friesii (orange zone).

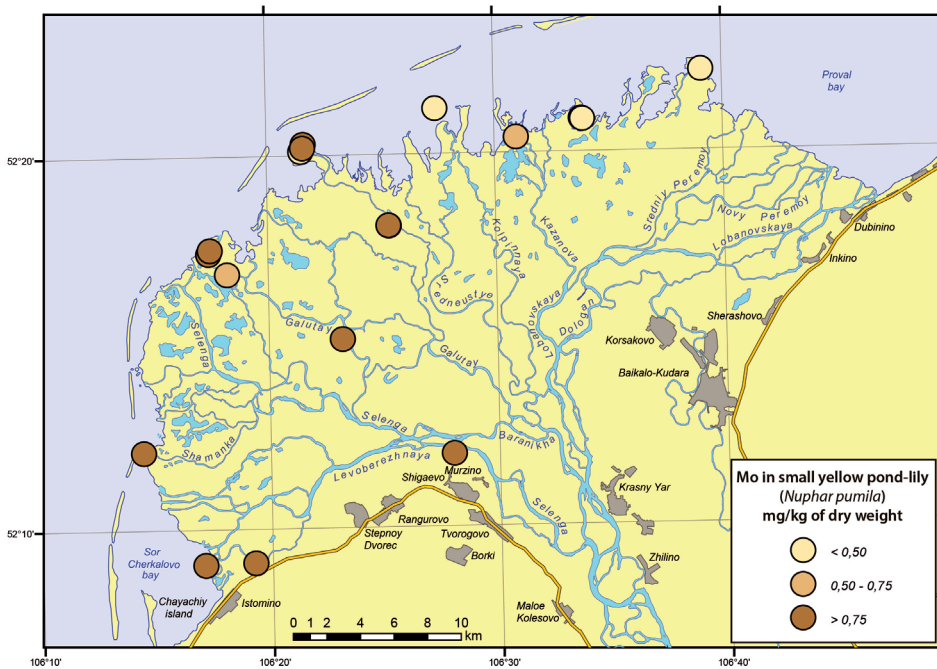
In the I quarter of the field in Figure 4 (orange zone) with active accumulation of both dissolved and suspended forms of elements, with the predominance of the latter, there are spiked water-milfoil, hornwort and pondweeds. Flowering rush and reed are located in IV и III quarters. They are characterized by weak accumulation of both dissolved and suspended forms of elements, which is caused by the prevailing root nutrition from the bottom sediments. Common floating pondweed and small yellow pond-lily (yellow zone) are mainly located in the IV quarter. They show relatively weak accumulation of suspended forms of elements because they do not have

such dissected leaves as spiked water-milfoil and hornwort, and cannot precipitate the suspended matter with the same intensity.

Mn, which actively accumulates in macrophytes of the Selenga delta, migrates mainly in suspended form. This element is necessary for plants to build large molecules (proteins), and is also involved in the photosynthesis of oxygen in chloroplasts (Kabata-Pendias and Pendias 1984). The highest concentrations of Mn were found in spiked water-milfoil (3700  $\mu\text{g/g}$ ) and hornwort (2697), and the smallest – in the small yellow pond-lily (330) and reed (393).

#### Spatial features of HMM distribution

The main spatial features of the spatial distribution of HMM can be shown by example of Mo. This is one of the main elements concentrating in aquatic plants to a greater extent than in other components of aquatic landscapes, presented in the Selenga water mainly in dissolved form. It is accumulated by macrophytes 70 times more intensively than Co and As. The great demand of macrophytes in Mo is associated with its functions in their body: it is a part



**Fig. 5. Mo content in the small yellow pond-lily (*Nuphar pumila*)**

of proteins and enzymes, participates in nitrogen fixation and redox reactions (Kabata-Pendias and Pendias 1984). Most of all Mo was found in reed (2.5  $\mu\text{g/g}$ ) and spiked water-milfoil (1.8), and least of all in common floating pondweed (0.6) and small yellow pond-lily (0.9).

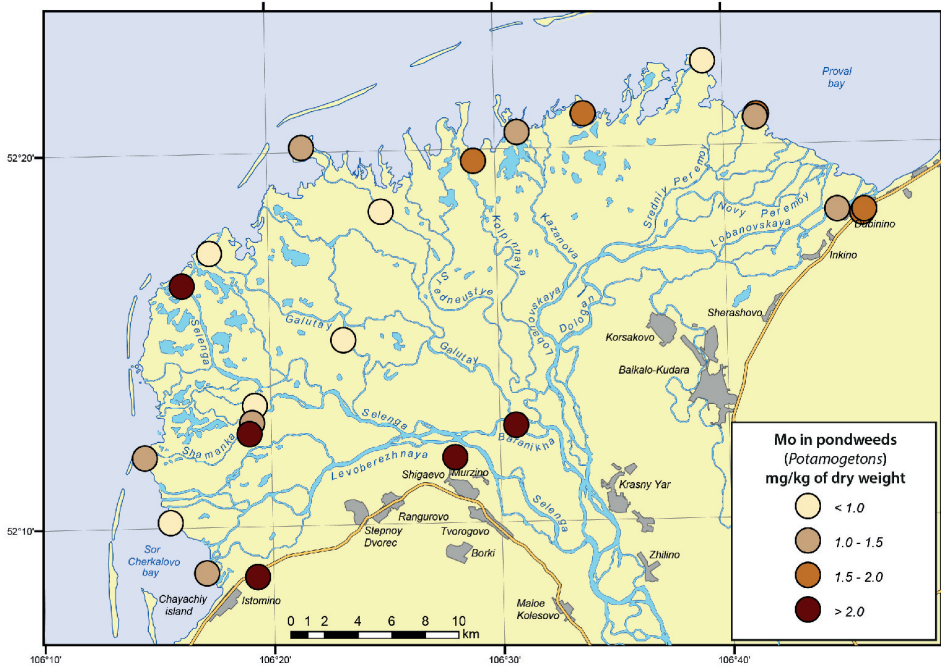
*Nuphar pumila*. Relatively high concentrations of HMM in *Nuphar pumila* were observed in the Selenginskiy sector of the delta (Fig. 5) during the summer low water season, when fine particles sedimentation processes occur in the mouths of large channels. Reduced contents were noted in the Lobanovskaya channel during the flood period.

*Potamogetons*. On the whole, they more actively accumulate HMM than water lilies, reeds, and flowering rush (Table 1), but each species has its own peculiarities. Common floating pondweed was found mainly in the Selenginskiy sector of the delta and in small quantities in the Sredneustevsky sector (Fig. 6a). It accumulates only small amounts of suspended matter. Fennel-leaved pondweed, widespread in the Lobanovsky sector, is characterized by the highest content of a number of metals. Pondweed

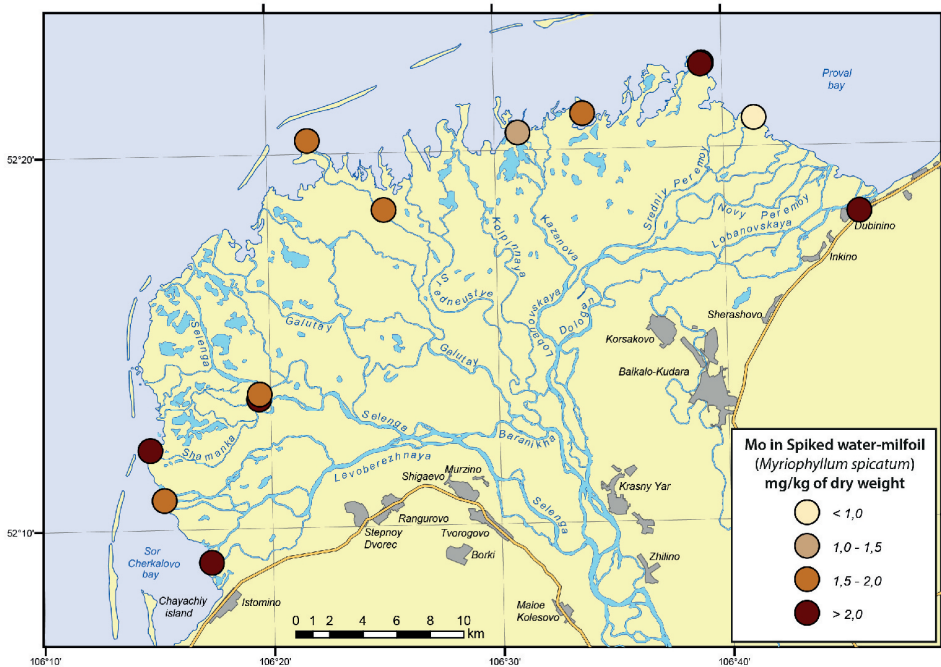
*Friesii*, common in small shallow channels of the Sredneustevsky sector, accumulates mainly Cu and Zn, which are necessary for the synthesis of chlorophyll.

Clasping-leaved pondweed is most widespread in the whole delta, grows fairly evenly and is characterized by moderate accumulation of HMM. Local maximum of the elemental abundances in pondweeds (Fig. 6a) were noted in the Severnaya (common floating pondweed), Sredny Peremoy (fennel-leaved pondweed), Lobanovskaya (clasping-leaved pondweed) and Galutay (pondweed *Friesii*) channels.

*Myriophyllum spicatum*. Spiked water-milfoil (with a stem up to 2 m long) was found throughout the Selenga delta; its largest accumulations are characteristic for the western end of the delta (Fig. 6b). The highest metal content in spiked water-milfoil was found at the mouths of the Severnaya and Srednyaya channels of the Sredneustevsky sector. Due to the strongly dissected cirrus leaves, water-milfoil is the best trap of river suspended sediments among all considered species.



(a)



(b)

Fig. 6. Mo content in (a) pondweeds (*Potamogetons*) and (b) spiked water-milfoil (*Myriophyllum spicatum*)

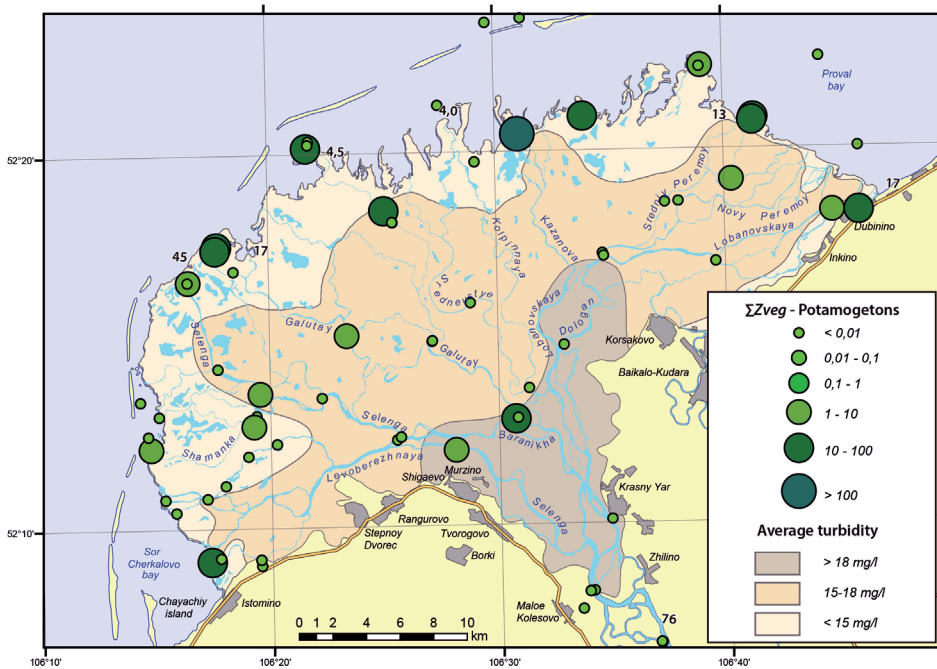


Fig. 7. Spatial distribution of the additive coefficient  $\Sigma Z_{veg}$  in hydatophytes by the example of pondweeds

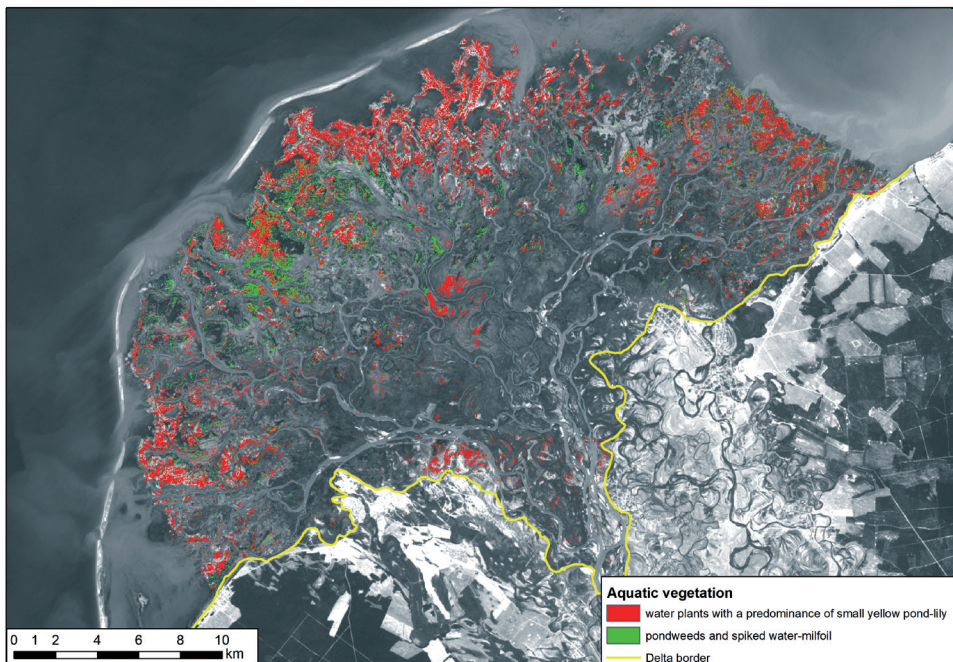


Fig. 8. Distribution scheme of the main groups of macrophytes: red shows the distribution of associations of water plants with a predominance of small yellow pond-lily, green shows the distribution of pondweeds and spiked water-milfoil



Total accumulation coefficient  $Z_{veg}$  (Fig. 7) increases at the delta-lake edge where the accumulation of HMM by macrophytes is significant. Small backwaters of large channels and intra-delta lakes where under low flow conditions both with shallow depths and highwater temperature rapid development of aquatic plants occurs, especially of hydato- and hydrophytes. These plants as a biofilter in a large extent participate in the deposition of suspended matter. Hydatophytes are characterized by higher  $Z_{veg}$  values than hydrophytes. This is caused by the active accumulation of suspended particles on the leaf surface. The result of the remote sensing data can be seen in Fig. 8. The analysis made it possible to compile a series of HMMs on the intensity of biofiltration by macrophytes: they retain more than 60% of the total Mn flux that came into the delta, more than 10% – W, As, and from 3 to 10% B, Fe, Co, Mo, Cd, V, Ni, Bi, Be, Cu, Zn, Cr, U, Al. The largest contribution is made by the group of hydatophytes (spiked water-milfoil and pondweed), which account for 74 to 96% of the total mass of substances accumulated by aquatic plants.

## CONCLUSIONS

The study reveals the biogeochemical specialization of higher aquatic vegetation which is dominated by accumulation of Mn and Mo. These elements are part of proteins and are necessary for the reaction of photosynthesis and redox reactions.

Macrophyte accumulation levels of HMM are determined by plant species. The reed with low  $Z_{veg}$  coefficients (1.2–2.3) was used as a reference plant. HMM accumulation in macrophytes in relation to reed was revealed for U, As, Cd and B. These elements dominated in dissolved form in the Selenga delta regardless of hydroclimatic conditions.

Species with a very weak accumulation of elements were distinguished (reed and flowering rush) from well-accumulating species (a group of pondweeds, small yellow pond lily, hornwort and spiked water-milfoil). Spiked water-milfoil accumulates the maximum number of elements in relation to

other components of aquatic systems. The accumulation series according to  $Z_{veg}$  for it are as follows:  $Mn_{11.5}, As_{1.6}, Co_{1.4}, Mo_{1.3}, Fe_{1.2}, Cd_{1.1}$ . Among pondweeds the group concentration of HMMs is common for the pondweed *Friesii* ( $Mn_{6.4}, Mo_{3.3}, As_{1.1}$ ). Claspingleaved pondweed ( $Mn_{4.2}, Cd_{1.1}$ ), fennel-leaved pondweed ( $Mn_{18.4}, Mo_{3.7}$ ) and hornwort ( $Mn_{8.5}, Co_{1.3}$ ) accumulate only 2 elements each. The active concentration of elements by well-accumulating species is explained by the physiological characteristics of these plants: they have very dissected leaves, a large area of which allows them to retain a significant amount of suspended matter. Moreover, immersed species are more in need of trace elements due to lack of light.

Delta macrophytes precipitate more than 60% of Mn, more than 10% of W, As, and from 3 to 10% of B, Fe, Co, Mo, Cd, V, Ni, Bi, Be, Cu, Zn, Cr, U, Al from the total flux of the element that came into the epic part of the delta. The largest role in the accumulation of suspended matter enriched with HMMs is played by hydatophytes, which capture a large amount of suspended matter and act as biological "traps".

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