
HYDROCHEMISTRY, HYDROBIOLOGY:
ENVIRONMENTAL ASPECTS

Elemental Composition of the Algae *Spirogyra* (Zygnematophyceae, Charophyta) from the Littoral Zone of Lake Baikal¹

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Abstract—ICP-MS method was used to study the elemental composition of benthic Baikal algae and algae of the genus *Spirogyra*, excessive growth of which was registered within the last decade in the littoral zone of Lake Baikal. The distribution of chemical elements in *Spirogyra* algae (*Spirogyra* “morphotype 1”) dominating stony littoral locations is as follows: $\text{Na} \sim \text{K} \sim \text{Ca} \sim \text{S} \sim \text{Ba} > \text{Mg} \geq \text{P} > \text{Mn} \geq \text{Cl}$) and *Spirogyra* spp. from tributary streams, shallow coves and bays with soft bottom grounds — $\text{Na} > \text{K} \geq \text{Ca} \sim \text{S} \sim \text{P} \sim \text{Ba} \geq \text{Mg}$, $\text{Cl} > \text{Mn}$. *Spirogyra* algae were characterized by higher content of Li, Na, Mn, Ba and atypical ratio of element concentrations: $\text{Na} > \text{P}$, $\text{Na} \geq \text{K}$ and Ca , $\text{Mn} > \text{Fe}$, $\text{Ba} \sim \text{Ca}$ and S , $\text{Ba} > \text{Sr}$ compared to benthic Baikal algae. Maximum total content (ΣC) of all detectable elements, $\Sigma C \text{ Na Mg P S Cl Ca Li Al Si Mn Zn Ba}$, $\Sigma C \text{ Na Cl P Mn}$ are typical *Spirogyra* “morphotype 1”, dominant on littoral areas located in the vicinity to sources of heaviest wastewater emissions. Overgrowths of other *Spirogyra* species, capable of accumulating larger amounts of Li, Na, Cl, Br than *Spirogyra* “morphotype 1” are also confined to such pollution sources.

Keywords: Lake Baikal, domestic wastewaters, *Spirogyra* “morphotype 1”, *Spirogyra* spp., benthic Baikal algae, elemental composition

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Filamentous algae of the genus *Spirogyra* Link., 1820 are common in all climatic zones; they grow in rivers and river oxbows, reservoirs, lakes, ponds, ditches, swamps, fresh and brackish waters [26].

During different years of the last century, in Lake Baikal *Spirogyra* algae were generally encountered in thickets of higher aquatic plants in the nearshore-shallow zone (in Istok Sor, Anga Bay, Zagli and Khorin-Irgi bays, Posolsky Sor, Angara-Kichera shallows and sor, in the Selenga River delta, Dagarskaya and Senogda bays, near Listvennichny Island, in the mouth zones of Tyya, Kurly and Toshka rivers [8, 12, 13, 22, 24, 33]. *Spirogyra* algae are typical constituents of algal flora of cold and thermal mineral springs in Pribaikalye, their mineralization being 0.12–0.27, 2.7–3.4 g/L [28]. Small amounts of *Spirogyra* were constantly encountered in the mouth of the Angara River since 2008. In 2009, some *Spirogyra* filaments were found in tributaries streaming into Bolshye Koty Bay [30]. Negligible portions of this algae were registered in the littoral waters of open Baikal shores in 1976 and 1982 in locations of industrial sewage discharge from Baikalsk Pulp and Paper Plant (BPPP) [11].

Blooms of *Spirogyra*, unusual for Baikal (later designated *Spirogyra* “morphotype 1” [43]), were reported since 2011–2012 in the shallow-water zone of Listvennichny and Bolshye Koty bays [14, 30]. It is this benthic morphotype of *Spirogyra* dominated large areas of shallow lake zones [42, 43]. Maximal masses of this algal genus was confined to the littoral parts neighbouring settlements and recreation centers [36, 42, 44]. Such territories pressed by growing tourist activities (over 3 million people per year taking into account only registered individuals) [9] became sources of pollution for the nearshore waters. Municipal and domestic wastewaters discharged from sewage treatment plants of towns and settlements located in the lake watershed are enriched by pollutants (petroleum products, sulfates, chlorides, nitrates, ammoniacal nitrogen, phosphates, etc.; ~400–500 tons per year) [9]. Besides, biological and chemical contamination of the coastal zone occurs as a result of untended surface runoff of melt, rain, river and flood waters, as well as because of their infiltration through the soil and ground cover of populated areas and recreational areas into the ground waters in Pribaikalye hydraulically connected with the Lake. Complex surveys on the territory of Listvyanka Settlement and in Listvennichny Bay showed that surface and ground waters entering the bay are contaminated with fecal

¹ The contribution of Drs. Kulikova N.N. and Chebykin E.P. into this study is equal.

microorganisms and enriched in soluble Na, Cl, P, Zn, Ba, Pb compounds [18, 27].

The content of elements present in the water of shallow Baikal zone contaminated by industrial and household sewage varies significantly due to active hydrodynamic processes [4], and it does not reflect the actual intake of pollutants in the nearshore zone. Reliable information on the anthropogenic load of the aquatic environments can be provided by elemental composition analysis of benthic algae accumulating certain chemical elements during their growth and regeneration. The data obtained showed that all the algae studied – *Chara* spp., *Hydrodictyon* spp., *Lyngbya* spp., *Nitella* spp., *Pithophora* spp. and *Spirogyra* spp., are biological accumulators of P, S, K, Rb, Mg, Ca, Sr, Ba, Al, As, Se, Cr, Mn, Fe, Co, Cu, Zn, Mo and Pb [40]. Distribution of *Cladophora* sp., *Spirogyra* sp., *Oedogonium* sp. correlated with the eutrophication index, content of chlorides with anthropogenic origin and water mineralization [38]. *Spirogyra* sp. is capable of effective extraction and accumulation of more Na, K, Mg ions than freshwater animals [21]. After a 30-minute immersion in water enriched by Mn, Cu, Zn, Cd, the concentration of metals in *Spirogyra* sp. thallomes increased proportionally to their content in the solution [39]. Some research works [35] confirmed the efficiency of *Spirogyra* spp. in biological monitoring of water bodies receiving wastewater discharge contaminated by Zn, Cu, Pb, Cd.

The aim of this study was to determine the elemental composition of *Spirogyra* algae prominence given to benthic morphotype and to estimate coefficients of biological accumulation of chemical elements by *Spirogyra* in aquatic environments. Based on the data obtained, identify areas of the littoral zone with the maximum, minimum and average content of chemical elements in *Spirogyra* “morphotype 1”.

MATERIAL AND METHODS

Water and benthic algae samples were collected in June – September 2018–2020 in a shallow-water zone of Baikal (Fig. 1). Water was sampled by plastic syringes: 1 m from the water edge; at the depth of 5–7 m (bottom layer); 1 m above the water's edge (interstitial water from holes made on the beaches of the splash zone). Water samples were filtered through membrane filters (pore diameter 0.2 μ m) into sterile polypropylene test tubes. HNO₃ 70% double purified by sub-boiling distillation was used for sample preservation. Algal samples were washed in nearshore and filtered Baikal water immediately after collection. To remove remains of dirt, cleaned algae were examined under a MBC-10 binocular at $\times 30$ –100 magnification, washed by distilled water, dried until air dry state in a desiccator at 60°C, and until constant weight at 105°C. Algae samples with a very large portion of settled suspension that was removed only partially were analyzed as samples with an admixture of fine-dis-

persed mineral particles. Algae samples were prepared for analysis by acid mineralization: dry sample was placed in a polypropylene tube, added HNO₃ 70% purified by sub-boiling distillation, stored in a drying chamber at 80°C for 8 hours, adding extra pure H₂O₂ 30% after cooling. For genus and species-level identification we used microphotographs made by light microscopes Olympus CX-21 and Meiji Techno at $\times 40$ to $\times 400$ magnification, cameras Olympus C-3040 with a NY20005 011705 photo nozzle and Sony Cyber-shot.

Generally, species identification of the genus *Spirogyra* is possible only in terms of available conjugation and mature zygospores which are rather rarely found during sampling in situ [26]. The authors found out that benthic *Spirogyra* samples collected from stony littoral locations allocated with the populated areas and recreational zones in all three lake basins had similar morphological features and was attributed to one species identified as *Spirogyra* “morphotype 1” [42]. The other group of algal samples morphologically different from “morphotype 1” is represented by free-floating *Spirogyra* spp. species from tributary streams, shallow creeks and bays with soft-bottom substrates.

ICP-MS method was used to determine the chemical composition of all samples and the analyses were performed by a mass spectrometer Agilent 7500ce (Agilent Technologies) with a quadrupole mass analyzer at the Center of Shared Use “Ultramicroanalysis” in the Limnological Institute SB RAS. The validity of identifications was assessed using certified standard samples of *Elodea canadensis* (ESEC-1) (Vinogradov Institute of Geochemistry SB RAS), a standard sample of deep Baikal water [41]. Standard errors of measurement (coefficient of variation (*CV*), depending on the concentration of chemical elements, fell in the following range: $< 0.001 - CV > 25$; $0.001 - 0.1 - CV 25 - 10$; $0.1 - 1 - CV 10 - 5$; $> 1 \mu\text{g/L} - CV 5\%$. The concentration function of algae was estimated referring to the elemental water composition: $BAC = C_1/C_2$, where BAC – biological accumulation coefficient, C_1 – element concentration in wet algal biomass; C_2 – the same in deep Baikal water. Content of water and ash in alga thallomes was assessed by thermo-gravimetric analysis.

MS Excel 2007 and Statistica 8 software packages were used for the statistical processing. A homogeneous group of values was drawn from a sampling frame of the data obtained. Variation coefficient [29] was selected for validating this group homogeneity. A sampling frame is considered homogeneous when $CV \leq 33\%$ [2]. Minimal and maximal values were distinguished as separate groups. The results are given as average values, standard deviations and median or (in case of a small data set) as intervals (max–min), or single values. K-means algorithm was used to cluster data from sampling sites of *Spirogyra* (morphotype 1) using three variables: total amount of Na, Mg, P, S,

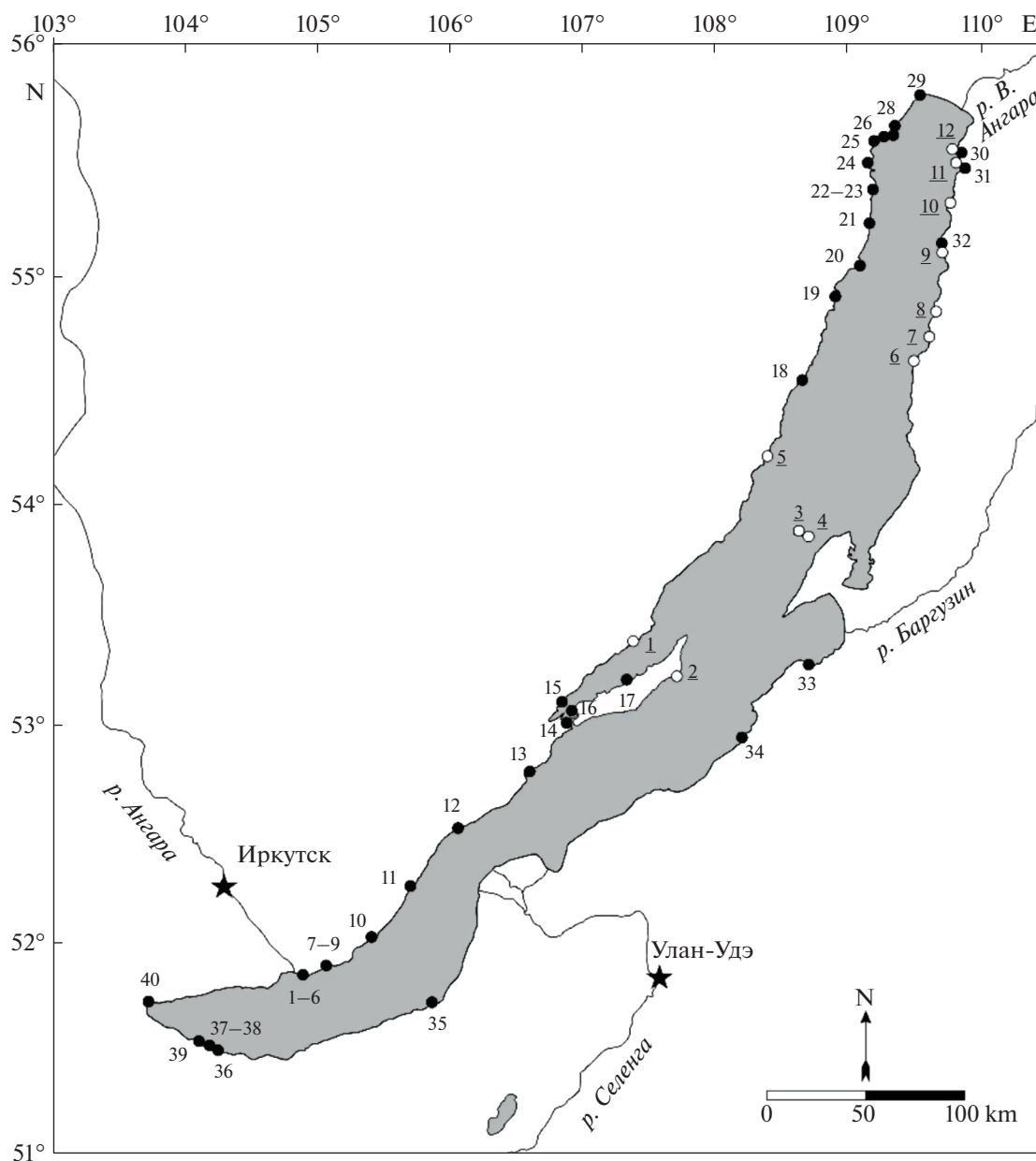


Fig. 1. Schematic map of *Spirogyra* “morphotype 1” and benthic Baikal algae sampling sites in the littoral of Lake Baikal. Black circles [●] – sampling sites of *Spirogyra* “morphotype 1” and benthic Baikal algae: 1. Listvennichny Bay, Listvyanka Settlement, café “Alaniya”; 2. Listvyanka Settlement, 40 m north of the Sennushka river mouth; 3. Listvyanka Settlement, hotel “Mayak”; 4. Listvyanka Settlement, sealarium; 5. Listvyanka Settlement, café “Podkova”; 6. Cape Berezovy; 7. Bolshye Koty Settlement, 300 m north of the Chernay river mouth; 8. Bolshye Koty Settlement, Field Station of LIN; 9. Bolshye Koty Settlement, Field Station of ISU; 10. Bolshoe Goloustnoe Settlement; 11. Peschanaya Bay; 12. Buguldeyka Settlement (opposite Buguldeyka river mouth); 13. Aya Bay; 14. Sakhayurta Settlement; 15. Sarma River; 16. Cape Khorin-Irgi; 17. Khuzhir Settlement, Cape Shamanka; 18. Cape Elokhin; 19. Cape Kovrizhka; 20. Cape Kotelnikovskiy; 21. Cape Krasny Yar; 22. Baikalskoe Village; 23. Cape Ludar; 24. Slyudyanskaya Guba; 25. Senogda Bay; 26. Opposite Zarechny Settlement; 27. Tyva River (channel, mouth); 28. Severobaikalsk Town; 29. Nizhneangarsk Settlement; 30. Frolikha Bay; 31. Ayaya Bay; 32. Tompuda Bay, Hydrometeorological Station; 33. Maximikha Settlement; 34. Turka Settlement; 35. Babushkin Town; 36. Opposite BPPP, section, settling pond; 37. opposite BPPP, section no. 1, depth 1–3 m; 38. Opposite BPPP, section no. 1, depth 3–7 m; 39. Opposite mouth of the Babkha river, depth 4 m; 40. Kultuk Settlement. Open circles [○] – sites the littoral zone of which is free of *Spirogyra* algae: 1. Kargante Bay; 2. Cape Izhimey; 3. B. Ushkany Island; 4. Tonkiy Island; 5. Cape Maly Solontsovy; 6. Cape Kabaniy; 7. Cape Birokan; 8. Guba Irinda; 9. Cape Omagachan; 10. Guba Bolshaya Samdaki; 11. Guba Lakanda; 12. Cape Nemnyanka.

Cl, Ca, Li, Al, Si, Mn, Zn, Ba, their concentrations, except Li, being $> 10 \mu\text{g/g}$ of dry weight; $\sum C_{\text{Na Cl P Mn}}$, the concentrations of which were highly variable; $\sum C$ of all elements under study. To determine the number of clusters, we gradually ascertained the quality of arranging the datasets into 2, 3, 4 and 5 clusters. Raising the number of clusters to 5 showed negligible divergence of sampling site locations in various clusters. Locations of sampling sites were maximally different grouped in 3 clusters. Mann Whitney U test was used to rank the difference between elements in *Spirogyra* spp. and *Spirogyra* “morphotype 1”.

RESULTS AND DISCUSSION

Distribution of Spirogyra spp. in Shallow Zone

Among Baikal green algae (Chlorophyta), *Spirogyra*, the most diverse macrophytobenthos group, attributed to the family Zygnemataceae (Charophyta) by modern systematics, dominated during the last decade [45]. Thickets of *Spirogyra* attached to the stony bottom in the nearshore area at the depths from 0.5 to 6 m are exceptionally formed by *Spirogyra* “morphotype 1” [42]. Blooms of this algae morphotype occurs from late August until November and is territorially bound with the coastal settlements and seasonal centers of recreation.

Large accumulations of silt on the bottom or in the water column in many lake tributary streams and shallow bays, generally soft-bottom, are formed by other *Spirogyra* species. The results of field survey in September 2020 showed that nearshore localities still free of *Spirogyra* were in the close vicinity with natural reserves and unpopulated areas (see Fig. 1). In these places, green algae in most part of stony water shallow habitats preserved the zonation pattern known since investigations of K.I. Meyer [23]: at the depth of 0–1.5 m (I vegetation belt)—*Ulothrix zonata* (Web. et Mohr.) Kütz., depth from 1.5 to 2.5 m (II—*Tetraspora cylindrica* (Wahl.) Ag., *Didymosphenia* M. Schmidt, depth from 2.5 to 10 m (III) — endemic species of the genus *Draparnaldioides* Meyer et Skabitsch. Perennial *Cladophora* Kütz., 1843 species are often abundant on bottom ground in vegetation belts, especially in II and III and deeper [10].

Elemental Composition

Analysis of the chemical composition of *Spirogyra* algae accumulating many elements in proportion to their concentration in water [21, 38–40, 46], will provide reliable information on anthropogenic contamination of the shallow lake zone.

During this study, we found out that water content in *Spirogyra* thallomes made 82–94% (average— 88.0 ± 6.7); ash— $4.60 \pm 1.03\%$, in samples with admixture of mineral particles—6.0–8.3%. The content of chemical elements in *Spirogyra* “morphotype

1” samples varies significantly depending on sampling location. Concentrations of Fe, Co, Ni, Zn, Ge, Cd, Sn, Sb, Hg, Tl, Pb, Bi, a number of lithophilic elements: Al, P, Ti, V, Br, Zr, Nb, I, Cs, Hf, Ta, Th, rare-earth elements (REE) migrating through the water column mainly as suspensions that partially settle down and are captured in the filamentous algal mats, demonstrated highest variance in *Spirogyra* “morphotype 1” [16, 32]. Maximal content of lithophilic elements: Be, B, Al, Si, Sc, Ti, Zr, Nb, Ag, Cs, Hf, Th, U, REE as well as Pb and Bi was observed in *Spirogyra* samples with admixture of fine mineral particles (Tables 1, 2). The concentrations of Ba, S, Sr, Mg, K, Ca, Mo showed the lowest range of variability (Table 1) ($C_{\text{max}}/C_{\text{min}} - 3-4.0$) in the chemical composition of *Spirogyra* “morphotype 1”. High and low element contents in *Spirogyra* defining inhomogeneity of original data integrity are grouped as minimal and maximal values (Table 1).

Approximately 98–99% of the total element content are $\text{Na} \sim \text{K} \sim \text{Ca} \sim \text{S} \sim \text{Ba} > \text{Mg} \geq \text{P} > \text{Mn} \geq \text{Cl}$ in the dry mass of *Spirogyra* “morphotype 1”; 1–2% — $\text{Fe} > \text{Si} > \text{Zn} > \text{Sr} > \text{Al}$, with 200–30 $\mu\text{g/g}$ in most of the samples; $\text{Br} > \text{Ni} > \text{As} > \text{Cu} > \text{Ti} > \text{Co} > \text{Li}$, I ($10-1.0 \mu\text{g/g}$); $\text{Rb} > \text{B} > \text{Cr} > \text{V} > \text{Mo} > \text{Pb} > \text{U} > \text{Cd} > \text{Y} > \text{Se} > \text{Sc} > \text{Ga}$ ($1.0-0.1 \mu\text{g/g}$); $\text{Zr} > \text{Th} > \text{Sb} > \text{Nb} > \text{W} > \text{Hg} > \text{Sn} > \text{Ge}$ ($0.1-0.01 \mu\text{g/g}$); $\text{Tl} > \text{Ag} > \text{Cs} > \text{Be} > \text{Hf} > \text{Bi} > \text{Ta}$ ($0.005-0.001 \mu\text{g/g}$) (Table 1).

Total concentration of the REE in the dry mass of *Spirogyra* varies widely, from ~ 0.20 in algae collected in the littoral zone of Cape Khorin-Irgi with coarse-grained bottom sediments and rocky shores to 3.0–14.0 $\mu\text{g/g}$ in samples with admixture of mineral particles. This value constitutes 0.38–1.22 $\mu\text{g/g}$ in the majority of samples (average 0.81 ± 0.25), and the concentration variation range of La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu makes $\sim 3.0-4.3$ in averaged values. The content of REE in the algae composition regularly decreases as their atomic numbers grow: light REE ($\sum \text{La Ce Pr Nd Sm Eu}$) exceed heavy REE ($\sum \text{Gd Tb Dy Ho Er Tm Yb Lu}$) approximately by 6–15 times ($U_{\text{REE}} - 0-2$, p (significance level) ≤ 0.01). The studied algae accumulate smallest amounts of heavy Ho, Tb, Tm, Lu (Table 2).

Many other algae morphotypes of the same genus from the rivers Tyra and Sarma are characterized by a similar chemical composition with that of *Spirogyra* “morphotype 1”. *Spirogyra* spp. samples collected in the rivers Chernaya, Verkhnyaya Angara, Listvenichny, Kultuk bays, Senogda, shallows near village Zarechnoe and nearshore lake at the foot of a scarp (Sakhyurta settlement), contain more Na and in many cases, except 2–4 samples, — Li, S, Cl. Some species exceed *Spirogyra* “morphotype 1” by the content of Br. Most part of *Spirogyra* “morphotype 1” and *Spirogyra* spp. samples has identical concentrations of phosphorus (Fig. 2), although maximal phosphorus concentrations were registered in 2 samples of *Spiro-*

Table 1. Elemental composition of the alga *Spirogyra* “morphotype 1”, collected from 30 sampling sites (88 samples) in the shallow zone of Baikal; (Table 1, 2: *n*—number of samples; dash—minimal and maximal concentration of homogeneous datasets obtained at 30 sites)

Element	Concentration, µg/g dry mass								
	minimum		mean				maximum		samples with admixture of mineral particles max–min (<i>n</i> = 6)
	max–min, mean ± standard deviation	number of sites	mean	median	CV, %	number of sites	maximum	number of sites	max–min (<i>n</i> = 6)
Li	0.72	1	2.42 ± 0.75	2.25	31.2	28	5.00	1	4.70–1.10
Be	0.0011 ± 0.0004	8	0.0028 ± 0.0009	0.0028	32.6	21	0.12	1	0.038–0.002
B	0.29	—	0.53 ± 0.15	0.50	28.0	20	3.13 ± 1.35	10	35.0–0.51
Na	1600	1	4500 ± 1400	4500	32.1	27	8200–7350	2	9750–1380
Mg	1600	—	2300 ± 690	2200	29.9	30	4800	—	4900–3000
Al	4.50–4.00	3	27.0 ± 8.5	26.4	31.5	13	72.6 ± 22.5	14	1230–40
Si	15.0	1	82.7 ± 26.7	74.7	32.2	27	160–140	2	800–190
P	810 ± 210	11	1700 ± 560	1550	32.8	17	3300–3200	2	3800–1300
S	2100	—	3150 ± 820	3000	26.2	30	5700	—	7000–4700
Cl	110	1	450 ± 150	490	32.9	26	1800–1000	3	1850–520
K	2800	—	5200 ± 1500	4900	29.8	30	8700	—	10300–2200
Ca	2800	—	3800 ± 1000	3600	26.6	29	9850	1	10300–5100
Sc	0.036	—	0.073 ± 0.019	0.075	25.6	27	0.31–0.23	3	0.78–0.11
Ti	1.06 ± 0.35	9	2.83 ± 0.92	2.86	32.6	12	7.07 ± 1.66	9	62.5–1.72
V	0.16 ± 0.03	5	0.44 ± 0.14	0.44	31.0	22	2.56–1.22	3	6.60–0.26
Cr	0.21	1	0.51 ± 0.16	0.47	31.8	26	1.61–1.22	3	9.40–0.58
Mn	460–230	3	1100 ± 340	990	32.1	27	2000	—	2500–810
Fe	80.0–50.0	4	170 ± 50	170	31.0	23	1300–410	3	2400–280
Co	1.35–0.63	4	2.83 ± 0.92	2.85	32.4	16	7.21 ± 3.66	10	12.8–1.03
Ni	2.33 ± 0.72	6	5.76 ± 1.77	5.37	30.8	13	18.3 ± 5.7	11	24.0–1.39
Cu	2.30	1	4.91 ± 1.62	4.53	32.9	27	11.6–10.1	2	11.8–5.90
Zn	21.6 ± 4.0	9	57.9 ± 18.2	52.5	31.4	17	260–160	4	190–28.0
Ga	0.020	1	0.060 ± 0.019	0.055	31.3	27	0.19–0.12	2	0.75–0.09
Ge	0.0043 ± 0.0013	7	0.010 ± 0.003	0.008	32.2	20	0.19–0.06	3	0.11–0.011
As	2.10–1.88	3	5.74 ± 1.89	5.40	33.0	24	14.3–10.5	3	11.9–5.00
Se	0.029	2	0.085 ± 0.026	0.081	31.1	28	0.14	—	0.31–0.16
Br	2.27 ± 0.42	5	5.68 ± 1.84	5.70	32.4	21	18.7–10.6	4	45.8–1.90
Rb	0.30	—	0.55 ± 0.17	0.50	30.7	28	1.42–1.90	2	4.40–0.97
Sr	21.2	—	32.9 ± 8.2	30.5	25.0	30	59.0	—	71.0–39.0
Y	0.037 ± 0.008	5	0.11 ± 0.036	0.10	32.9	23	0.33–0.18	2	1.49–0.36
Zr	0.018 ± 0.006	7	0.049 ± 0.016	0.044	32.4	16	0.11 ± 0.02	7	0.60–0.15
Nb	0.0052 ± 0.0021	8	0.014 ± 0.005	0.014	32.0	18	0.037–0.027	4	0.38–0.021
Mo	0.21	—	0.40 ± 0.11	0.39	27.0	30	0.75	—	0.99–0.49
Ag	0.0015–0.0013	4	0.0036 ± 0.0012	0.0036	32.8	25	0.0070	1	0.021–0.001
Cd	0.029–0.020	2	0.12 ± 0.04	0.11	32.4	18	0.35 ± 0.08	10	1.03–0.21

Table 1. (Contd.)

Element	Concentration, µg/g dry mass								
	minimum		mean				maximum		samples with admixture of mineral particles max–min ($n = 6$)
	max–min, mean \pm standard deviation	number of sites	mean	median	CV, %	number of sites	maximum	number of sites	max–min ($n = 6$)
Sn	0.0050 \pm 0.0017	10	0.012 \pm 0.004	0.011	32.5	16	0.12–0.023	4	0.21–0.015
Sb	0.0060 \pm 0.0020	19	0.016 \pm 0.005	0.016	32.2	7	0.055–0.025	4	0.087–0.016
I	0.39 \pm 0.11	7	0.86 \pm 0.29	0.85	33.0	14	1.96 \pm 0.62	9	6.50–1.38
Cs	0.0020–0.0009	3	0.0035 \pm 0.0012	0.0033	32.9	19	0.0078 \pm 0.0015	8	0.088–0.008
Ba	2150	—	3350 \pm 800	3300	24.0	30	5600	—	6200–3400
Hf	0.0005 \pm 0.0002	7	0.0017 \pm 0.0005	0.0014	31.3	16	0.0043 \pm 0.0022	7	0.021–0.004
Ta	0.0003 \pm 0.0001	8	0.0009 \pm 0.0003	0.0009	32.4	19	0.0071–0.0020	3	0.0065–0.0010
W	0.0080 \pm 0.0006	3	0.015 \pm 0.005	0.014	32.2	25	0.040–0.030	2	0.069–0.021
Hg	<0.009	5	0.013 \pm 0.004	0.014	32.6	21	0.030–0.022	4	0.040–0.005
Tl	0.0017 \pm 0.0005	5	0.0046 \pm 0.0015	0.0043	31.8	18	0.12 \pm 0.004	7	0.028–0.003
Pb	0.13 \pm 0.02	5	0.34 \pm 0.11	0.35	32.0	18	0.81 \pm 0.12	7	9.90–0.81
Bi	0.0005 \pm 0.0001	6	0.0011 \pm 0.0004	0.0011	31.1	17	0.0049 \pm 0.0021	7	0.013–0.0038
Th	0.0061 \pm 0.0026	7	0.029 \pm 0.010	0.027	32.8	18	0.065 \pm 0.023	5	0.74–0.057
U	0.14–0.11	4	0.25 \pm 0.08	0.23	32.1	22	0.67–0.48	4	2.80–0.46

gyra spp. Na dominates the elemental composition of free-floating Spirogyra spp. filaments not attached to the bottom. Unlike many freshwater algae and terrestrial plants of non-saline landscapes [6], the dry mass of Spirogyra spp. contains approximately 2–10 times more Na > Ca ($U_{Na-Ca} = 0$, $p = 0.00001$) and Na > K ($U_{Na-K} = 3$, $p = 0.00001$) in most of the samples (Fig. 3).

The chemical composition of all Spirogyra samples collected from the rivers, a nearshore lake, bays and creek, as well as Spirogyra “morphotype 1” most common at many localities of the stony littoral zone varies significantly from other Baikal algae. Benthic Baikal algae from the vegetation belts due to poorly mineralized hydrocarbonate-calcium water [7] contain identically small amounts of Li, Na, Mn and Ba. The concentration of these elements is much higher in Spirogyra thallomes, although Spirogyra “morphotype 1” shows highly variable concentrations of Li, Na, Mn (variation coefficient: CV—4–44%) (Fig. 4). Among all elements examined, the concentrations of Ba, Mg, S, K, Ca and Sr in Spirogyra exhibit homogeneous values (CV—18–31%) (Figs. 4, 5).

Spirogyra “morphotype 1” uptakes and accumulates Mg, P, S, Cl, K, Ca, dominant in the dry mass of

U. zonata, T. cylindrica var. bullosa, D. geminata, D. compacta, in equal or often less extent (Fig. 5). It contains noticeably less Mg than D. baicalensis, D. arenaria, D. geminata. Spirogyra does not actively accumulate S and is far behind U. zonata, C. floccosa, C. glomerata, C. compacta, D. geminata in this respect. Many algae from littoral vegetative belts contain more K and Cl than Spirogyra “morphotype 1” (Fig. 5). Spirogyra species (Spirogyra spp.) from rivers, a nearshore lake, creek and bays with soft-bottom substrates accumulate Mg, P, S, Cl, K, Ca as intensively as benthic Baikal algae.

Increased content of Na, Ba and Mn in Spirogyra thallomes accounts for an atypical ratio of some element concentrations in the chemical composition of most freshwater algae and terrestrial plants. In most of Spirogyra “morphotype 1” samples—Ca/Na—0.65–1.80; this ratio in T. cylindrica, D. baicalensis, D. arenaria—3–30, in U. zonata, C. floccosa, C. glomerata, C. compacta—30–100, in D. geminata—100–300. In the average concentration of living matter (according to A.P. Vinogradov) [6] Ca/Na = 25. In all of the benthic Baikal algae studied Na/P < 0.5, whereas Spirogyra accumulates much more Na (Na/P—2.30–4.30). In the average composition of living matter Na/P = 0.28. The ratio of Na/Cl in the thallomes of typical

Table 2. Concentrations of rare earth elements in Spirogyra “morphotype 1” collected at 30 sites (88 samples) in a shallow zone of Baikal (nd—no data)

Element	Concentration, µg/g dry mass								
	minimum		mean				maximum		samples with admixture of mineral particles
	max—min, mean ± standard deviation	number of sites	mean	median	CV, %	number of sites	mean, max—min	number of sites	max—min (n = 6)
La	0.080–0.061	2	0.20 ± 0.06	0.19	32.1	22	0.39 ± 0.04	6	2.70–0.63
Ce	0.015/0.071 ± 0.019*	1/6	0.28 ± 0.08	0.31	29.4	18	0.51 ± 0.12	5	5.80–1.08
Pr	0.003/0.010 ± 0.005*	1/5	0.035 ± 0.011	0.038	32.3	18	0.063 ± 0.006	6	0.67–0.13
Nd	0.042 ± 0.023	8	0.17 ± 0.05	0.17	30.6	22	0.25	—	2.70–0.49
Sm	0.019	—	0.046 ± 0.014	0.047	29.9	30	0.071	—	0.54–0.12
Eu**	nd		nd				nd		nd
Gd	0.0080 ± 0.0037	8	0.029 ± 0.009	0.029	30.4	20	0.064–0.058	2	0.58–0.12
Tb	0.0008 ± 0.0004	5	0.0030 ± 0.0010	0.0029	32.2	20	0.0061 ± 0.0020	5	0.050–0.012
Dy	0.0060 ± 0.0026	10	0.019 ± 0.006	0.018	31.6	19	0.059	1	0.31–0.063
Ho	0.0009 ± 0.0004	6	0.0028 ± 0.0009	0.0025	31.2	19	0.0067 ± 0.0035	5	0.058–0.012
Er	0.0042 ± 0.0018	13	0.011 ± 0.004	0.010	32.7	16	0.037	1	0.16–0.035
Tm	0.0006 ± 0.0001	6	0.0015 ± 0.0005	0.0015	32.4	22	0.0060–0.0046	2	0.021–0.004
Yb	0.0031 ± 0.0012	12	0.0084 ± 0.0027	0.0080	32.7	17	0.032	1	0.13–0.028
Lu	0.0004 ± 0.0001	5	0.0011 ± 0.0003	0.0010	31.7	20	0.0027 ± 0.0014	5	0.063–0.004

*—nominator—element concentration in samples collected at a single site, denominator — element concentration in samples from sites 5 and 6.

**—when the concentration of Ba is high, Eu determination by ISP-MS is complicated due to difficulties with accounting BaO interferences.

Baikal algae, except *T. cylindrica*, *D. geminata*, < 1. There is more Na in Spirogyra than Cl—4.0–17.0 times. Most terrestrial plants, freshwater algae in general and Baikal littoral algae in particular, accumulate much more K, than Na. In the average composition of living matter the ratio of K/Na = 15. In Spirogyra “morphotype 1” K > Na in single samples, in most samples K ~ Na (K/Na – 0.90–1.80). Spirogyra contains more Mn compared to Fe (Mn/Fe—1.60–8.50), benthic Baikal algae contain more Fe than Mn. Average content of the living matter includes 10 times more Fe > Mn. A typical feature of Spirogyra genus is a high, very rare for most plants content of Ba, close to Ca (Ca/Ba—0.60–0.90) and S (Ba/S—0.90–1.10). According to [37], Ba accumulates in the Spirogyra cell cytoplasm in the form of = sulfate crystals. In contrast to typical littoral benthic algae accumulating Sr ≥ Ba, Spirogyra accumulates Ba (Ba/Sr—20–100).

Thus, Spirogyra blooms and dominance at the sites bordering settlements and areas of intensive recreational activity entails variations in the composition and ratio of chemical element concentrations within the biogeochemical barrier, the basis of which until recently have been formed by benthic Baikal algae,

active concentrators of the majority of chemical elements entering it with surface and ground effluents.

Bioaccumulation

Bioaccumulation alongside other factors decreases migration and concentration of chemical elements in aquatic environments [25]. The concentration of examined elements in benthic Baikal algae beds: *U. zonata*, *T. cylindrica*, *D. geminata*, *D. baicalensis*, *D. arenaria*, *C. floccosa*, *C. glomerata*, *C. compacta* significantly exceeds the content of chemical elements in Baikal water, excluding Na. The uptake of this element by benthic algae of the vegetative belts from the water medium is exceptionally low. Index of BAC_{Na} , that is responsible for the element concentration degree in a living organism relative to its habitat [5], makes ≤ 1 or 1.5–6.1, maximum 10–30 in benthic Baikal algae. This index of Baikal Spirogyra species is much higher: for instance, BAC_{Na} of Spirogyra “morphotype 1”—100–300; Spirogyra spp.—300–1250. The uptake of Li, Mn, Ba by Spirogyra is more intense compared to other algae studied, and alongside with a diatom *D. geminata*, it extracts and captures Co, Cd,

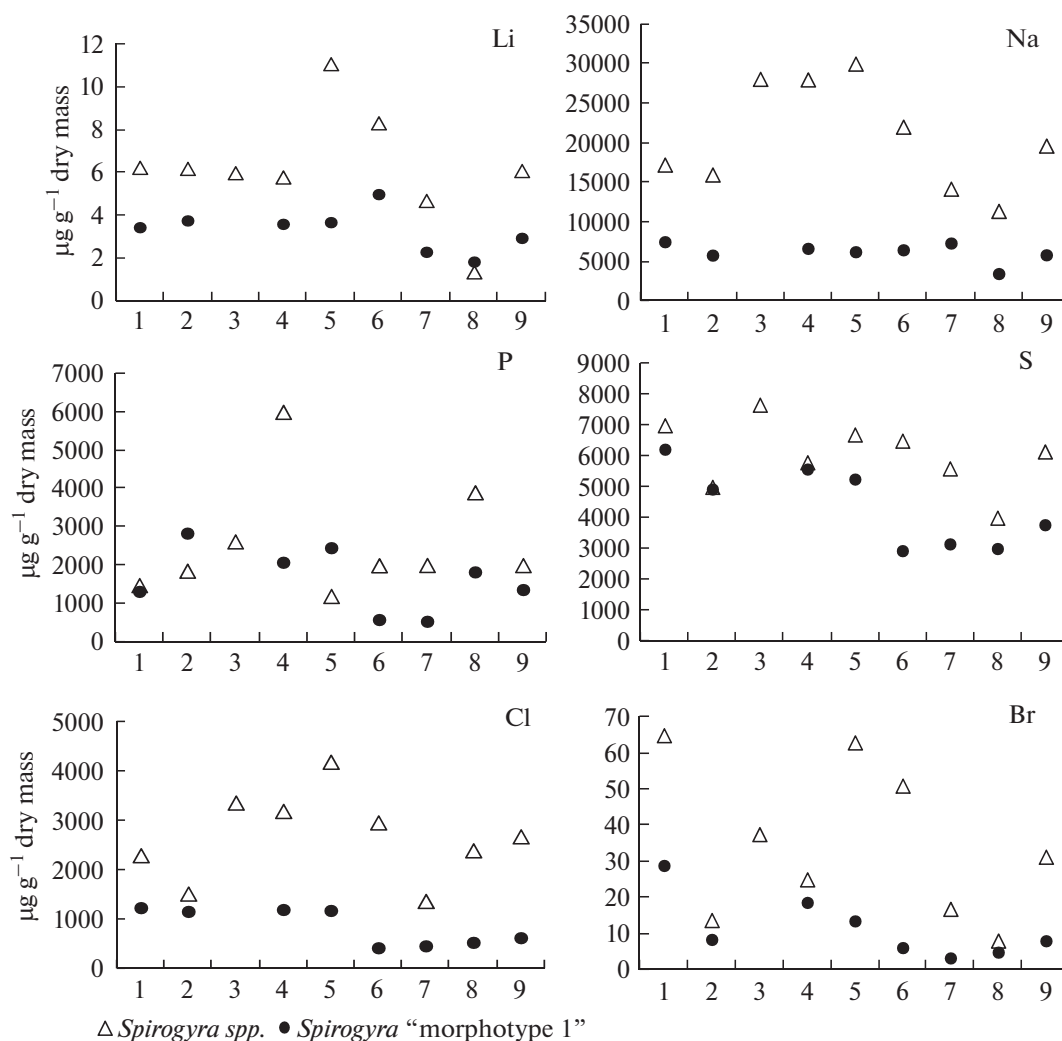


Fig. 2. Concentration of Li, Na, P*, S, Cl, Br in *Spirogyra* spp., *Spirogyra* "morphotype 1", dry mass. (P* – statistically insignificant differences, $U = 19, p = 0.3$); for Na, Cl – $U = 0, p = 0.001$; Li – $U = 8, p = 0.02$; S, Br – $U = 9, p = 0.03$). 1–8, sampling sites: 1, 28.07.16, 23.07.17., Listvennichny Bay; 2, 27.09.20, Berezovy Cape; 3, *Spirogyra* spp., 15.09.18, mouth of the Chernay river; 4, 13.09.19, 28.09.20, Kultuk Bay; 5, 10.08.19, 22.09.19, Senogda Bay; 6, 12.06.18, 10.08.19, shallows near Zarechnoe settlement; 7, *Spirogyra* spp., 23.07.20, riverbed of the Verkhnyaya Angara; *Spirogyra* "morphotype 1", 23.07.20, area near Nizhneangarsk settlement; 8, *Spirogyra* spp., 18.09.19, nearshore lake at the foot of a scarp (Sakhyurta settlement); *Spirogyra* "morphotype 1", 18.09.19, Khuzhir Village, Shamanka Cape; 9, median values.

Zn, Ni maximally from the ambient water. The concentration degree of these elements in the benthic algae of the vegetative belts is approximately 2–5, 10–40 times less. Judging by the uptake intensity of other elements, *Spirogyra* is less active in concentrating them or does not differ from benthic Baikal algae (Fig. 6).

The data presented shows ten- and hundred-fold growth of uptake intensity and accumulation of Mn, Ba, Na, Li, and several times increase of Co, Cd, Zn and Ni by *Spirogyra* mass dominating the littoral localities marginal to settlements and areas of recreational activities compared to benthic Baikal algae (Fig. 6).

On the contrary, mineralization of organic residues enhances migration activity of elements enriching the surface waters by these nutrients [25]. As the algae die off and are decomposed, the main portion of accumulated chemical elements are released back into the littoral water. Chemical composition of water collected from beach holes (in the region of Zarechny settlement) underneath thick long standing rotting *Spirogyra* mass is essentially different from that of deep Baikal water, bottom and interstitial water from the near-shore. The concentration of Mn in the water sampled under the rotten algal mass is thousand times more than that in deep Baikal water, Fe—approximately 500 times, Co, La, Ce—100–70 times, Cl, Ba, Ni, As, I, Br—40–10 times, 10–5 times higher is the con-

centration of Na, K, Ca, Mg, Al, Sr, ~4 – P and consequently, we observed higher water mineralization. Among all elements examined, the concentration of S, V, Cu, Mo, U in the water sampled from these beach holes does not exceed either that of deep Baikal water or nearshore waters (Fig. 7, Table 3). Huge long-standing rotting mass of *Spirogyra* is a complementary supplier of nutrient effluent into the shallow zone, including dissolved compounds of Na, Cl, Mn, Fe, Co, Ni, Ba, the concentration of which being constantly low in the unpolluted littoral Baikal waters [19]. In the splash zone dead and washed up benthic Baikal algae from the vegetative belts disintegrate much more rapidly without forming long-standing heaps, enriching the water with Mn, Fe, Co, Ba, Cl, Ni, As compounds to a much lesser extent and, in contrast to rotten *Spirogyra*, release none of Na, Ca, Mg, Sr, I in the water (Table 3).

Clustering of Sampling Sites

K-mean clustering of *Spirogyra* “morphotype 1” sampling sites with three variables: (Var1) total content (ΣC) Na, Mg, P, S, Cl, Ca, Li, Al, Si, Mn, Zn, Ba in *Spirogyra*, their concentration, except Li, being > 10 $\mu\text{g/g}$ of dry mass; (Var 2) ΣC Na Cl P Mn the concentrations of which are highly variable; (Var 3) ΣC of all measured elements showed significant differences between average variable values in the clusters. It is evidenced by low values of intragroup (Within SS), higher values of intergroup (Between SS) dispersion of features, higher F-criterion values (F) and significance level (signif. p) < 1% (Table 4). Plotting cluster centers (Fig. 8) shows that all coordinates of cluster centers are different, especially the third and second clusters.

Cluster 2— six sites in the shallow zone of Southern Baikal under high anthropogenic load: (1) Listvennichny Bay, Listvyanka Village, opposite “Podkova” café; (2) Listvyanka Village, opposite “Alanya” café; (3) Listvyanka Village (depth 1–1.5 m); (4) Berezovy Cape (depth 3 m); (5) Berezovy Cape (depth 1 m); (6) Bolshoe Goloustnoe Village, 2020. The highest values of total concentration of the elements in *Spirogyra* “morphotype 1” measured were: ΣC of all elements under study—49600–41600, ΣC Na Mg P S Cl Ca Li Al Si Mn Zn Ba—47000–41300 ΣC Na Cl P Mn—15500–10000 $\mu\text{g/g}$ of dry matter. The lowest variable value was estimated in cluster 3 at 13 sampling sites in the shallow zone: (1) Bolshye Koty Bay, ISU Field station; (2) Bolshoe Goloustnoe village, 2019; (3) Peschanaya Bay; (4) Kharin-Irgi Cape; (5) BPPP, opposite shop floor no. 1, depth 1–3 m, 2019; (6) BPPP, opposite shop floor no. 1, depth 2–3 m, 2020; (7) Babushkin and Maksimikha settlements; (8) Ayaya Bay; (9) Tyva river channel; (10) Zarechny settlement, 2020; (11) Baikalskoe Village (pier), Ludar Cape; (12) Kotelnikovsky Cape, Krasny Yar Cape, Kovrizhka Cape; (13) Elokhin Cape. The values of

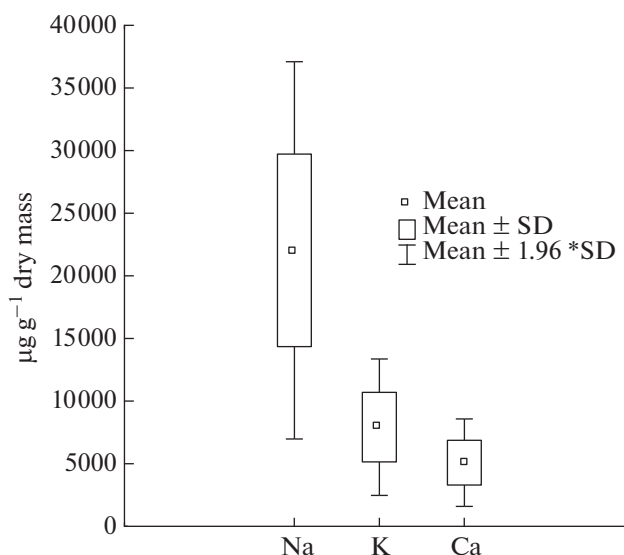


Fig. 3. Average content of Na, Ca and K in *Spirogyra* spp. *Spirogyra* spp. samples collected: 15.09.18, mouth of the Chernaya river; 28.07.16, Listvennichny Bay; 27.09.20, Berezovy Cape; 13.09.19, Kultuk Bay; 10.08.19, Senogda Bay; 12.06.18, in the vicinity of Zarechnoe settlement; 10.08.19, in the vicinity of Zarechnoe Settlement; 23.07.20, channel of the Verkhnyaya Angara river, 18.09.19, nearshore lake at the foot of a scarp (Sakhyurta settlement).

variables for this cluster are ~2 times less: 24200–19500, 24000–19300, 7600–4800 $\mu\text{g/g}$ of dry matter respectively. Cluster 1—17 sites: (1) Listvyanka Village, ~40 m north of the Sennushka river mouth; (2) Listvyanka Village, opposite sealarium, depth 7 m; (3) Aya Bay; (4) Buguldeika Village; (5) Khuzhir Village, Shamanka Cape; (6) Kultuk Village; (7) opposite the Babkha river mouth, depth 4 m; (8) BPPP, opposite settling pond; (9) opposite production site of BPPP, depth 3–7 m, 2019, 2020; (10) Turka Village; (11) Tompuda Guba (hydrometeorostation); (12) Frolikha Bay, 2019, 2020; (13) Nizhneangarsk (urban-type locality); (14) Severobaikalsk town, town beach; (15) Zarechny Village, 2019; (16) Senogda Bay, 2018, 2019, 2020, (17) Slyudyanskaya Guba 2019, 2020. Total amount of all elements measured in *Spirogyra* “morphotype 1” ΣC —35400–23400, ΣC Na Mg P S Cl Ca Li Al Si Mn Zn Ba—35000–23200 and ΣC Na Cl P Mn—11000–5300 $\mu\text{g/g}$ of dry matter.

Most sites where we collected *Spirogyra* “morphotype 1” were characterized by one common feature—surface and underground sewage effluent from municipal and industrial sources, located on the territory of nearshore towns, settlements and recreational areas, into the shallow zone of the lake. Dissolved and suspended particles of these effluents are transported into and enrich the nearshore waters of the neighbouring littoral areas owing to cyclonic circulation of Baikal waters and diffusion processes along the shoreline. For

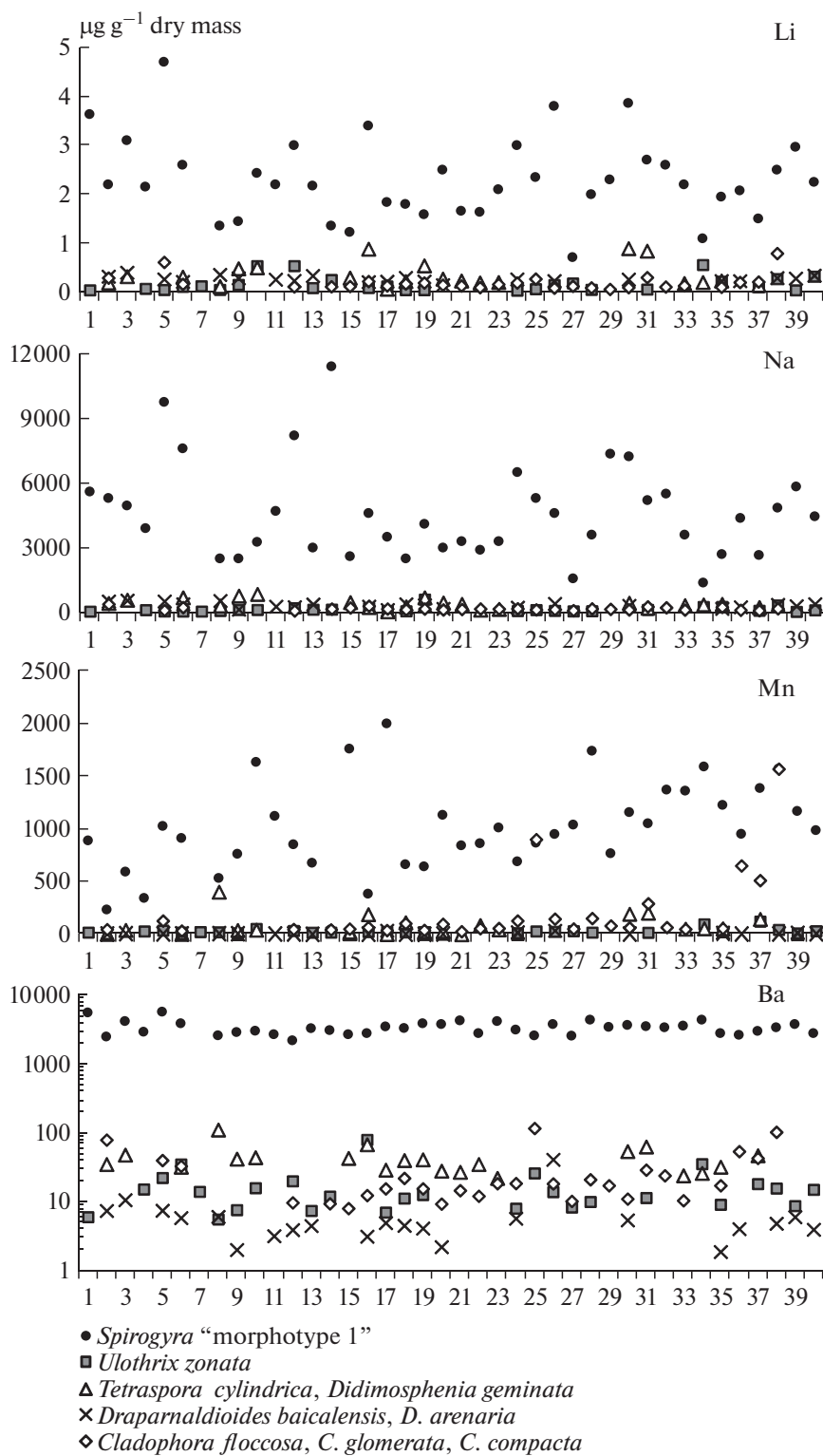


Fig. 4. Concentration of Li, Na, Mn, Ba in *Spirogyra* "morphotype 1" and typical benthic Baikal algae (1–40 – sampling sites (Fig. 1)).

instance, water contaminated by municipal waste flows from Nizhneangarsk (urban-type settlement), Severobaikalsk town, Baikalskoe village are trans-

ferred by currents along the north-west shore southwards [3, 15], polluting the waters of Senogda Bay, Slyudyanskaya Guba, nearby Ludar, Kotelnikovsky,

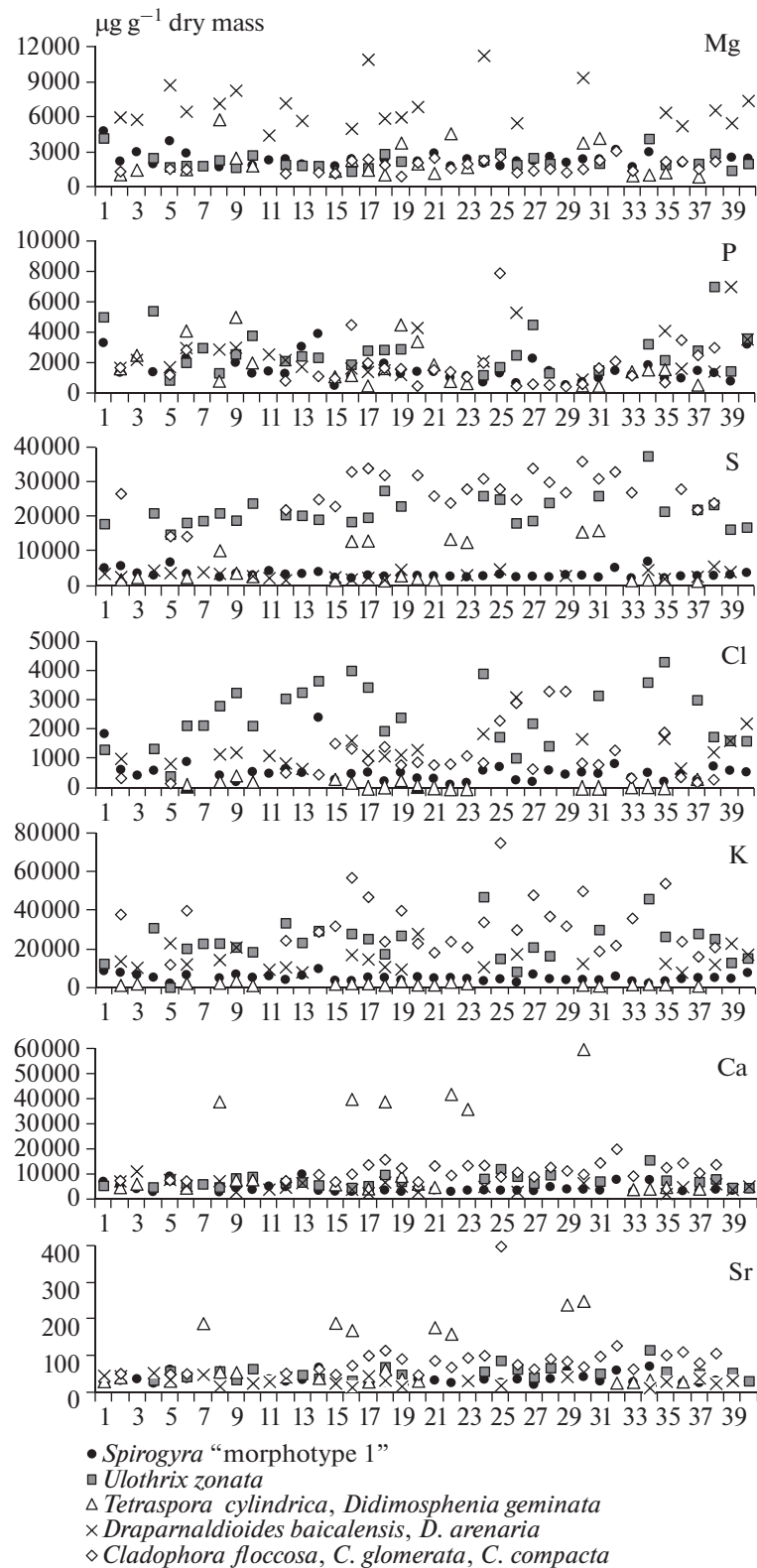


Fig. 5. Concentration of Mg, P, S, Cl, K, Ca and Sr in *Spirogyra* "morphotype 1" and typical benthic Baikal algae (1–40 — sampling sites (Fig. 1)).

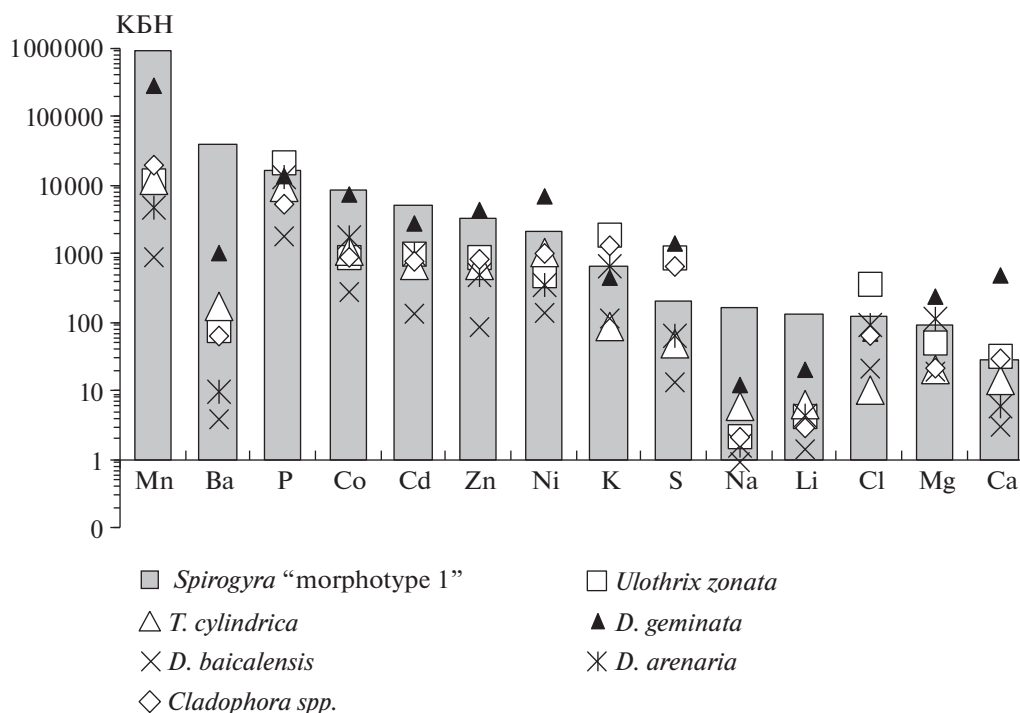


Fig. 6. Coefficients of biological accumulation (median values of elemental composition in *Spirogyra* "morphotype 1" and benthic algae from the littoral zone of Lake Baikal.

Krasny Yar, Kovrizhka, Elokhin capes This list should be complemented by a beach area stretching from the mouth of the Tyra river to Senogda Bay, that accumulates thick long-standing crops of decomposing algae. Each cluster included sites with maximal $\sum C$ Na Cl P Mn in the composition of the algae studied. Cluster 1 showed highest values of this variable—9500–11000 $\mu\text{g/g}$ of dry matter (mean—8400 \pm 1300, median 8400) determined in *Spirogyra* "morphotype 1" samples collected from the littoral zone nearby Kultuk, Buguldeika settlements in Frolikha (Frolikhinsky Sanctuary cordon, camping sites) and Senogda bays (~8 km south of Zarechny village). Cluster 2 showed maximal values of $\sum C$ Na Cl P Mn—15500–13900 (mean—12000 \pm 2300, median—11 200) $\mu\text{g/g}$ of dry matter determined in algae samples from Bolshoe Goloustnoe sites in 2020 and in Listvennichny Bay, "Podkova" café; cluster 3 – *Spirogyra* "morphotype 1" samples with highest values of $\sum C$ Na Cl P Mn—7600–7200 $\mu\text{g/g}$ of dry matter (mean—6000 \pm 900, median – 5600) collected at the sites: BPPP, opposite shop floor no. 1, 2020, Ayaya Bay (Frolikhinsky Sanctuary condon, camping sites). Elevated accumulation of these chemicals in *Spirogyra* "morphotype 1" samples may be related to direct effluent of domestic wastewaters containing large portion of fecal sludge and drained into the nearshore zone. Such waste discharges are most strongly enriched by Na, Cl, P compounds [1, 20, 31].

It has been found out that *Spirogyra* algae take up and accumulate many elements (Na, Mg, P, Cl, K, Ca, Mn, Co, Cu, Zn, Cd, Pb) in proportion to their concentration in water [21, 38–40). The concentration of dissolved and suspended matter in the waters of Baikal littoral is notably variable in time and space that imparts elucidating the correlation between the elemental composition of algae and water. Transfer of suspended and dissolved constituents of wastewaters through the lake has on obvious effect on its hydrodynamic processes. Their intensity is strongly dependent on wind and water level fluctuations, geological structure and the profile of the shoreline, underwater and above-water slope dips, amount of debris material on the shores, bottom relief, etc. Continuous regeneration occurs as a result of alongshore water migration and transverse circulation within the alongshore flow, turbulent mixing, local circulations, storm currents, surge events, etc. [3]. Thus, chemical composition of water and algae are under the cumulative effect of various factors that may combine in different ways in each individual case. On the whole, it should be noted that *Spirogyra* "morphotype 1" samples collected at localities adjacent to largest industrial and household wastewater sources (Listvyanka Village, Bolshoe Goloustnoe, Kultuk, settling pond and production site of BPPP, Buguldeika village, Nizhneangarsk, Severobaikalsk and its microdistrict Zarechny) are characterized by higher total concentrations of all elements measured; $\sum C$ Na Mg P S Cl Ca Li Al Si Mn Zn

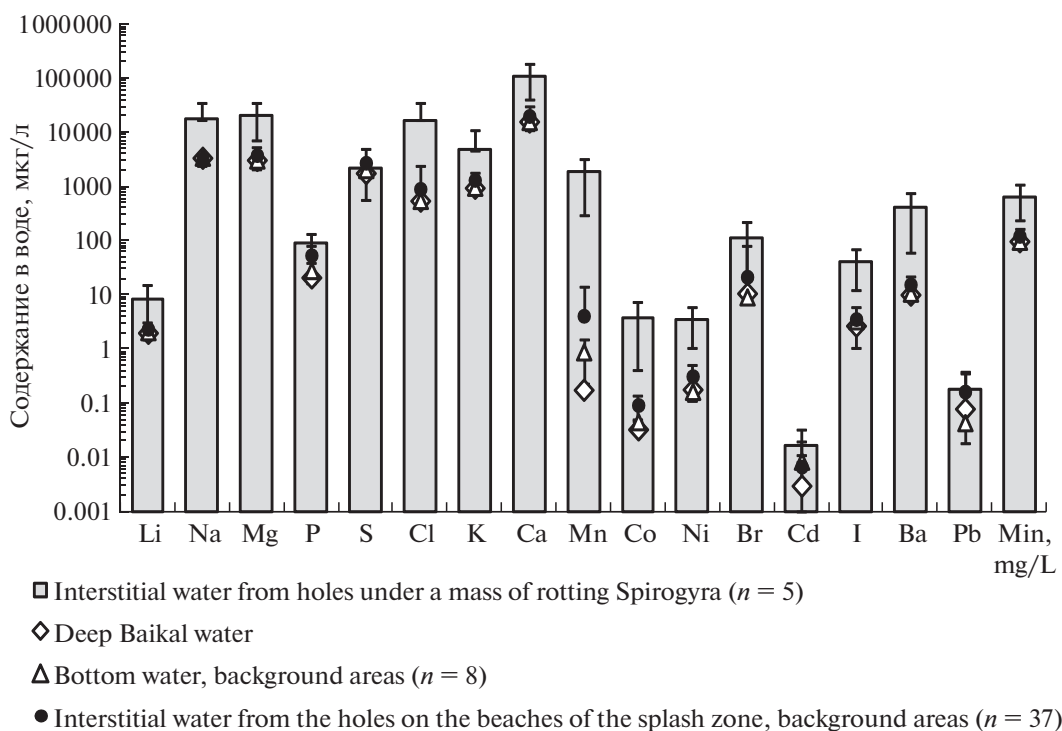


Fig. 7. Chemical element concentration in Baikal and interstitial water sampled from beach holes underneath rotting *Spirogyra* mass (\pm standard deviation) (Min, mg/L—water mineralization).

Ba; $\sum C$ Na Cl P Mn. Overgrowths of other *Spirogyra* species accumulating by far more Li, Na, S, Cl, Br than *Spirogyra* “morphotype 1” (see Fig. 2) are also

confined to areas coastal water of which are contaminated by industrial and household sewage effluents (Listvyanka Village, Kultuk, Zarechny, Senogda Bay, settlements and recreational areas in the valleys of the Verkhnyaya Angara and Chernaya rivers. Apparently, high concentrations of Li, Na, P, Cl, Mn, Zn, Ba in *Spirogyra* algae are substantially induced by an effluent of inadequately treated or untreated household waste waters.

CONCLUSIONS

During our studies, we observed algal blooms of *Spirogyra* “morphotype 1” and *Spirogyra* spp. with atypical chemical composition compared to benthic Baikal algae in the littoral zones neighbouring populated areas and recreation localities.

The thallomes of *Spirogyra* “morphotype 1” and *Spirogyra* spp. collected in the littoral zone, tributary streams and a lake located in the surf zone, accumulated larger amounts of Na, K, Ca, S, Ba, Mg, P, Mn, Cl. *Spirogyra* algae, irrespective of the species, have one peculiarity — equally high content of Ba close to that of Ca and S, a rare case for most plants.

Benthic filamentous *Spirogyra* “morphotype 1” sampled in the littoral zone with neighbouring villages and recreational areas demonstrated an alternative pattern of macro- and microelement accumulation in contrast to *Spirogyra* spp. species not attached to the

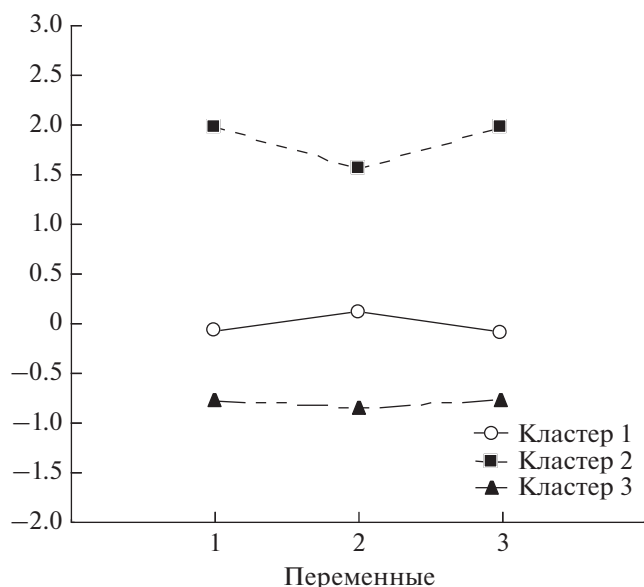


Fig. 8. Line graph of cluster centers. Variables: Var 1— $\sum C$ of Na Mg P S Cl P Mn in *Spirogyra* composition; Var 2— $\sum C$ Na Cl P Mn; Var 3— $\sum C$ of all elements analyzed.

Table 3. Ratios of the chemical element concentration (C_i) in the interstitial water from beach holes underneath decomposing benthic algal mass and in deep Baikal water (C_{BW}). Dash—element concentration in water from holes below detection limit

Element	C_{BW}	C_i in water under decomposing Spirogyra mass, ($n = 4$)	C_i under decomposing algal mass/ C_{BW}			
	$\mu\text{g/L}$		Spirogyra spp.	U. zonata*	T. cylindrica*	D. baicalensis*
Mn	0.18	1800	10000	620	30	60
Fe	3.00	1670	560	80	60	40
Ce	0.0025	0.39	150	10	20	50
Co	0.033	3.80	120	—	3.3	6.1
La	0.0037	0.24	65	60	10	20
Ba	10.1	420	40	4.4	2	0.81
Th	0.0006	0.024	40	—	1.7	20
Cl	550	16400	30	2.3	0.95	4.0
Ni	0.18	3.40	20	6.4	6.7	10
As	0.37	6.70	18	2.1	1.8	3.5
I	2.70	40.1	15	1.9	0.48	0.85
Br	10.7	110	10	2.7	—	1.7
Al	1.40	13.3	9.5	7.2	3.1	7.9
Ca	15900	110000	6.9	1.2	1.0	0.63
Mg	3100	20700	6.7	0.97	0.94	0.94
Sr	107	671	6.3	1.4	1.1	0.56
Ti	0.14	0.78	5.6	5.9	4.3	2.1
Cd	0.0030	0.017	5.7	18	2.0	20
Na	3400	16920	5.0	0.76	0.85	0.91
K	950	4700	5.0	3.2	3.1	2.5
Cr	0.11	0.48	4.4	2.0	1.3	5.7
P	21.0	91.0	4.3	40	3.8	3.3
Si	770	2210	2.9	0.86	0.71	0.73
Zn	2.00	4.47	2.2	2.7	0.65	3.3
Pb	0.079	0.18	2.3	4.8	1.9	20
Rb	0.59	1.15	1.9	1.9	0.48	0.85
V	0.38	0.55	1.4	1.0	1.1	0.95
U	0.58	0.76	1.3	0.29	0.26	0.19
S	1780	2100	1.2	0.56	0.73	0.22
Cu	1.48	0.83	0.56	40	0.81	0.68
Mo	1.33	0.64	0.48	0.67	0.83	0.47

*—element composition of interstitial water from holes underneath decomposing algal mass [16].

bottom. Spirogyra spp. includes $\text{Na} > \text{K} \geq \text{Ca} \sim \text{S} \sim \text{P} \sim \text{Ba} \geq \text{Mg}$, $\text{Cl} > \text{Mn}$ and Spirogyra “morphotype 1”— $\text{Na} \sim \text{K} \sim \text{Ca} \sim \text{S} \sim \text{Ba} > \text{Mg} \geq \text{P} > \text{Mn} \geq \text{Cl}$, the concentration of Li, Na, S, Cl, Br being often less than that in Spirogyra spp.

The chemical composition of Spirogyra spp. and Spirogyra “morphotype 1” differs from benthic Baikal algae from vegetative belts by higher concentration of

Li, Na, Mn, Ba and atypical for freshwater algae element concentration ratio. In the genus Spirogyra $\text{Na} > \text{P}$, $\text{Na} \geq \text{K}$ и Ca , $\text{Mn} > \text{Fe}$, $\text{Ba} \sim \text{Ca}$ and S , $\text{Ba} > \text{Sr}$. Such elements as Mg, P, S, Cl, K, Ca, dominating benthic algae from the littoral vegetative belts are accumulated by free-floating Spirogyra as intensively, whereas Spirogyra “morphotype 1” accumulates them to about an equal extent or often lesser amounts.

Table 4. Dispersion analysis data

Variable	Between SS	df	Within SS	df	F	signif. <i>p</i>
Var1	31.50545	2	3.49455	33	148.7572	0.000000
Var2	24.58784	2	10.41216	33	38.9640	0.000000
Var3	31.36036	2	3.63964	33	142.1694	0.000000

As Spirogyra algae bloom and dominate the littoral zones nearby populated or recreational areas, the composition and ratio of elements in the biochemical barrier varies. Spirogyra, compared to benthic Baikal algae, exhibits ten-, hundred-fold intensity increase of accumulating of Mn, Ba, Na, Li from the water and several times increase of Co, Cd, Zn and Ni.

Thick long-lasting wash-ups of decomposing Spirogyra algae that have been regularly registered on beaches of Northern Baikal, opposite Maksimikha village and other lake regions since almost 2010, became an additional effluent of dissolved Na, Cl, Mn, Fe, Co, Ni, Ba compounds discharged into nearshore waters.

Maximal values of total content of all elements accessed; ΣC Na Mg P S Cl Ca Li Al Si Mn Zn Ba; ΣC Na Cl P Mn are typical for Spirogyra “morphotype 1” dominating the littoral parts located in the close vicinity of most heavy contamination sources of industrial and household sewage (Listvyanka Village, Bolshoe Goloustnoe, settling pond and production site of BPPP, Buguldeika village, Nizhneangarsk town, Severobaikalsk town and its microdistrict Zarechny).

The data obtained from this study attest to significant theoretical and applied role of biochemical research into aquatic vegetation. Regular observations of the variations in the chemical composition of the coastal zone as well as elements in dominant algae and macrophytes of Baikal will allow to predict areas under heaviest anthropogenic loads in future. In our opinion, biochemical monitoring of aquatic plant life as the most sensitive instrument of finding anthropogenic contamination spots in limnetic ecosystems should be considered an indispensable constituent of global monitoring networks. As for monitoring Baikal ecosystem, it is strongly suggested to include this unit into Federal ecosystem monitoring of nearshore lake zones.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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