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THE DISTRIBUTION AND ACCUMULATION OF CHEMICAL ELEMENTS IN THE ECOSYSTEM OF LAKE ILMENSKOE

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ABSTRACT: In the present study Mg, Al, Si, P, S, Cl, K, Ca, Mn, Fe, Zn, Ag, Sr contents were determined by X-ray fluorescence analysis in sediments and organisms of *Contectiana listeri* and *Potamogeton lucens L.* of Lake Ilmenskoe located on the territory of the Ilmen State Reserve (South Ural, Russia). It was shown that microelements-rich sapropels are formed in the Lake Ilmenskoe. The Lake Ilmenskoe is free of anthropogenic impact and may be regarded as models while assessing the lakes under anthropogenic impact. The average element composition of macrophytes, gastropod shells and muscles, sapropel and sandy sediment were compared with the clarkes of elements in the continental crust with a preliminary aluminium rating, aluminium being the least fluent and abiogenic element of the system 'sediment – hydrobiont'. Sapropel was particular rich in microelements in comparison with sandy sediments. Study is shown that most elements are accumulated in aquatic organisms. *Contectiana listeri* and *Potamogeton lucens L.* may be considered as geochemical barriers. They can be used as biomonitors. We found out that low-iron, low-calcium, low-ash sapropel was forming in Lake Ilmenskoe.

Keywords: Sediment, Sapropel, Gastropod, Macrophyte, Bioindication

1. INTRODUCTION

Sediments and hydrobionts interact with lake water and soluble constituents in such a manner that they give many unique insights into limnological processes. Sediment information use for understanding water quality into lake monitoring and assessment programmes [1], [2].

Environment comprehensively impacts hydrobionts, gastropods in particular. Each region has its own distinctions caused not only by the factors of nature and geography, climate and meteorology, and other similar factors to which hydrobionts adapt, but also by anthropogenic ones that are closely connected with environmental pollution [3], [4]. Due to the natural and anthropogenic factors complex geo-chemical element associations are forming in gastropod shells and muscles. As a result it may change organism functions, and exhaust adaptive resources [5]–[8].

It is well known that gastropods are long-lived mollusks that are sensitive to water- and bed-sediment quality [9]–[11]. Many laboratory studies have documented freshwater gastropods' sensitivity to water and sediment contaminants that include dissolved metals [12]–[15].

Macrophytes are also important as indicators of water quality, water bodies eutrophication and pollution [16]–[18]. Aquatic macrophytes [19], [20] play an important role in the formation of sediments. The results on macro and microelement composition of water plants can be used to assess xenobiotics presence in waterbodies under anthropogenic impact [21]–[23].

The Ilmen State Reserve is situated in the central part of Chelyabinsk region near the town of Miass. There are 30 lakes in its territory. The lakes of the Reserve that are free of anthropogenic impact may be regarded as models while assessing the lakes under anthropogenic impact. For the study we chose the Lake Ilmenskoe, it is located on the territory of the reserve. It has tectonic origin and a small area, which is typical for lakes of the South Urals.

Previous studies of Lake Ilmenskoe are shown that the dominant species of gastropods and macrophytes are *Contectiana listeri* and *Potamogeton lucens L.*, respectively [24]. We also started to study chemical composition of gastropod shells and muscles [25].

The aim of the research is to study chemical composition of sediments and organisms of *Contectiana listeri* and *Potamogeton lucens L.* of Lake Ilmenskoe and to investigate their potential use in biomonitoring.

2. METHODS

2.1 Study Area

The Ilmen State Reserve is a state nature reserve. In 1920 Ilmen mountains were declared mineralogical reserve. It is one of the first nature reserves created in Russia. Today it is a nature protecting, scientific and researching institution.

Specialists protect animals from extinction.

Total area of Ilmen State Reserve is 303.8 square kilometers. The climate is classified as continental, with warm summers and cold winters. The coldest month of the year is January with an average temperature range of –16 ºC. The warmest month is July with an average monthly temperature of +17 ºC.

There are some rare spices of animals and plants registered in the Red Book.

Lake Ilmenskoe belongs to the Kars hydrographic basin (Ob basin of the Arctic ocean). It has a flow in a system of rivers Miass – Iset – Tobol – Irtish – Ob. Lake Ilmen runs in the foothills of the South taiga landscapes of the gray forest soils which are covered with pine-birch forests with an admixture of small-leaved breeds such as an aspen, an alder, a linden. Lake Ilmenskoe is of tectonic origin (surface area: 4.56 km², water volume: 14.6 km^3, max. depth: 6.1 m, average depth: 3.0), and is located at an altitude of 331.4 m a.s.l.

The sampling was carried out during the vegetation period in June-July 2015 in 7 stations distributed along the entire Lake Ilmenskoe perimeter (Fig.1). The coordinates of the sampling stations are: site 1 – 54°59'40.48" N, 60° 9'44.35" E; site 2 – 54°59'45.33" N, 60° 9'49.57" E; site 3 – 55° 0'3.23" N, 60° 9'47.11" E; site 4 – 55° 0'17.20" N, 60° 9'56.03" E; site 5 – 55° 0'51.95" N, 60° 9'9.17" E; site 6 – 55° 1'2.40"N, 60° 8'53.64" E; site 7 – 55° 1'13.31" N, 60° 8'3.24" E.

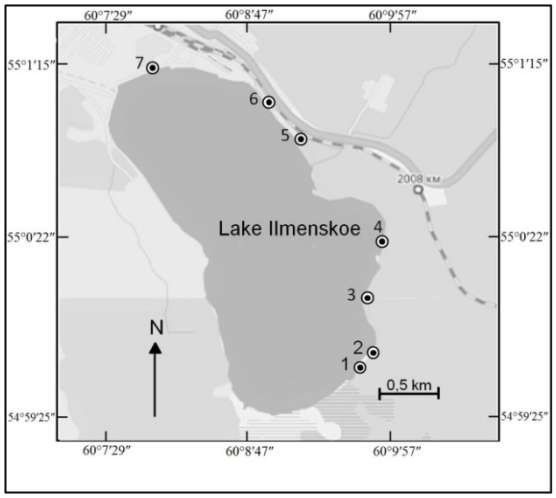

Fig.1 Map of Lake Ilmenskoe and location of the sampling stations

2.2 Sample Collection

In this work, we used the taxonomic system of gastropods developed by Y. I. Starobogatov's school, which is followed by Russian malacologists. *Contectiana listeri* (Forbes et Hanley, 1849) (= *Viviparus contectus auct.*) is a species of a large, freshwater snail with an operculum and a gill, an aquatic gastropod mollusk of *Viviparidae* family. However, it has been found that the waterbodies of South Ural are inhabited by another viviparous species, which has slight, but consistent conchological differences from *Contectiana listeri.* Starobogatov [26]. Vinarski [27] determined it as *Contectiana fennica*, but this suggestion should be confirmed by examining the type material of the species that have been described from Eastern Europe but not accepted by current European malacological taxonomy. So, in this work we determined it as *Contectiana listeri*.

Contectiana listeri was collected using the hydraulic arm. Also manual collection along the lakesides was used. Samples were washed on a 1 mm mesh sieve. Live mature individual gastropods were collected at all sites. Snails ≥20 mm were defined as matures.

Potamogeton lucens L. was hand picked from the freshwater habitat. The plant material was washed thoroughly using water from the sampling sites and was then freed of any adhering material.

Sediment samples were collected from all the sites. Sediment was collected from relatively slow-moving water near physically adequate gastropod habitat consisting of riffle/run complexes with relatively stable gravel sized particles. Each composite sample contained 3 subsamples collected within an approximately 1 m^2 area, from water less than 15 cm deep. Collected subsamples were deposited into a high density polyethylene (HDPE) mixing vessel using a plastic scoop. Approximately 0.5 kg of sediment was collected at each location.

2.3 Sample Analysis

Samples were collected for verification by X-ray fluorescence (XRF) analytical results.

The gastropods were boiled and separated. The muscles (soft tissue) were removed from each gastropod.

Macrophytes, sediment, shells and muscles were washed and dried. Air-dry samples were ashed at 550 °C for five hours. Ashed samples were ground in a mortar. The finely ground rock powder, mixed with a small amount of polyvinyl alcohol dissolved in water, were compressed using a hydraulic press into a pellet.

XRF patterns were registered in the lab of Center for Nanotechnology at South Ural State University. Rigaku SuperMini200 XRF Spectrometer was used for XRF analysis. The relative standard results deviation was not more than 5 %.

Organic matter content was calculated then as the difference in weight between the sample dried

at 60 ºC and the ash created following ignition at 550 ºC within a high temperature muffle furnace.

The following instream parameters including pH, dissolved oxygen (DO), and water temperature (WT) were measured in situ by a Portable Meter (Multitest IPL-513, Semico Ltd, Russia, Novosibirsk).

Conductivity (COND) and salinity (SALIN) were measured in situ by a Portable Meter (Multitest KSL-111, Semico Ltd, Russia, Novosibirsk) Air temperature was determined mercury thermometer. Oxygen saturation (P, %) was calculated.

At each site, water samples were also collected for further laboratory analysis including redox potential (Eh), nitrate–nitrogen (NO_3^-), nitrite–nitrogen (NO_2^-), ammonium–nitrogen (NH_4^+), orthophosphate-phosphorus (PO_4^{3-}), chlorides (Cl^-), sodium (Na^+), potassium (K^+), carbon dioxide (CO_2), bicarbonates (HCO_3^-), total hardness (H), calcium hardness (Ca^{2+}), permanganate oxidability ([O]), total iron (Fe). All these parameters were measured in the lab of the Department of Chemistry of South Ural State University according to the standard methods [25]. For spectrophotometric analysis the Spectrophotometer KFK-3 was used. Dissolved CO_2 concentrations were determined bycalculation from pH and alkalinity, measured by titration with 0.1 N HCl to an end point pH of 3.5.

3. RESULTS AND DISCUSSION

Lake Ilmenskoe is a freshwater, salinity 114...123 mg/l. The lake belongs to the bicarbonate type, calcium group. Lake's waters are slightly alkaline with pH of 8.16...8.88. Waters have high levels of oxygen saturation from 76.2 to 98.6 % (Table 1).

In two stations there were sandy sediments (organic matter content 5.1 %, SiO_2 58.5–70.1 %, Al_2O_3 9.9–11.4 %). In five stations we found silty sediments (organic matter content – 40.6 %, SiO_2 – 0.4–1.8 %, Al_2O_3 – 0.2–0.6 %). According to Korda, silty sediments may be referred to sapropels [28]. Sapropels are organic rich lake sediments formed from aquatic plants, plankton and benthic organisms and transformed under influence of bacteria.

Table 1 Physico-chemical parameters

Codes of chemical parameters	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7
TW	18	15	17	19	18	22	21
DO	7.2	7.84	7.52	7.68	7.2	8.64	8.32
P,%	76.2	77.8	77.9	82.9	76.2	98.6	93.5
pH	8.16	8.24	8.23	8.46	8.62	8.88	8.85
Eh	271	274	213	249	256.2	248.5	226.7
COND	21.83	21.53	21.72	22.59	23.22	23.22	21.66
SALIN	115	114	115	120	123	123	114
NH_4^+	0.088	0.620	0.900	0.930	0.71	0.74	0.85
NO_3^-	1.24	1.52	1.32	1.49	1.71	1.96	1.96
NO_2^-	0.033	0.046	0.105	0.043	0.066	0.043	0.053
PO_4^{3-}	0.005	0.005	0.050	0.026	0.005	0.005	0.016
DIN	0.350	0.829	1.021	1.062	0.946	1.017	1.106
N/P	214	508	63	125	580	624	212
Cl^-	39.8	38.0	40.8	44	49	44.7	49
Na^+	6.33	6.33	6.05	6.05	6.05	5.52	6.33
K^+	4.09	4.09	4.70	2.36	4.48	1.55	2.7
HCO_3^-	48.80	51.85	54.90	42.70	48.8	51.85	51.85
SO_4^{2-}	31.61	33.15	38.03	25.54	10.87	19.02	11.94
CO_2	4.4	3.5	3.5	3.5	0	0	0
H	2.2	2.2	2.4	2.1	2	2.2	2.1
Ca^{2+}	32	26	26	26	24	26	26
Mg^{2+}	9.6	13.2	15.6	12	9.6	10.8	9.6
Fe	0.29	0.41	0.61	0.41	0.34	0.32	0.38
[O]	18	28	17.6	26.4	20	19.2	22.4
$Ca^{2+}+Mg^{2+}/Na^++K^+$	3.67	3.53	3.64	4.23	3.19	5.21	3.94
$HCO_3^-/SO_4^{2-}+Cl^-$	0.68	0.73	0.70	0.61	0.82	0.81	0.85

Formation of sediments with high organic matter content (over 15 %) is typical of freshwater lakes of South Urals [28].

Organic matter content of *Contectiana listeri* shells and muscles was 6.3 % and 89.8 %, respectively. Potamogeton lucens contained 0.5 % of organic matter.

The average element composition of macrophytes, gastropod shells and muscles, sapropel and sandy sediment were compared with the clarkes of elements in the continental crust [29] with a preliminary aluminium rating, aluminium being the least fluent and abiogenic element of the system "sediment – hydrobiont", according to Eq. (1) [30]:

$$EF = \frac{(x_i / x_{Al})_{Sample}}{(x_i / x_{Al})_{ACC}}, \quad (1)$$

$x_{iSample}$ is the abundance of i-element in the researched object; $x_{AlSample}$ – the abundance of aluminium; x_{iACC} – the abundance of i-element in the continental crust; x_{AlACC} sample – the abundance of aluminium in the continental crust.

Figure 2 illustrates the chemical element abundance coefficients of different researched objects.

Sapropel was particular rich in microelements in comparison with sandy sediments, the abundance coefficient of which is close to 1.

Magnesium is found in gastropod muscles (it is not accumulated in shells) and macrophytes, as it is a part of chlorophyll pigment. Unlike in sandy sediments magnesium abundance in hydrobionts was much higher. There was no magnesium in sapropels. It should be noted that small Mg abundance in sandy sediments may be partly explained by carbonates as they have magnesium (magnesian calcite – $MgCaCO_3$) in their composition.

Cuprum, zink and argentum were found to be extremely abundant in sapropels and gastropods. It is associated with high cuprum and zink concentration in the water. We didn't study the presence of argentum in the lake, but there is a 80-meter-deep well of artesian water rich in Ag.

So we may assume that Ag gets into the lake from underground. Hydrobionts are the geochemical reservoirs of these elements. Gastropods actively accumulate Ag, Cu, Zn and it may be connected with their feeding habits. Gastropods are detritophages whose food is primarily silty mass.

The largest cuprum concentration was in sapropels and muscles of *Contectiana listeri*, as Cuprum is a part of respiratory pigments of gastropods. Zink activates ferments in hydrobionts. Cuprum and zink accumulation is associated with physiological processes in living organisms.

Sulfur, phosphorus and chlorine prevailed in gastropod muscles and in sapropels where they have an autochtonous origin, i.e. they are accumulated by plants and with plants withered away they get into the silt.

Mangan abundance coefficient was high, with its most concentration in plants. There is a lode amazonite pegmatite mine on the lakeside. Its distinguishing feature is a great amount of helvine with Mangan concentration of 35 % [31].

Due to this the water of Lake Ilmenskoe is getting enriched with Mn accumulated by hydrobionts. In addition, there are literature data on the increased content of Mn in the lakes of the South Urals [32].

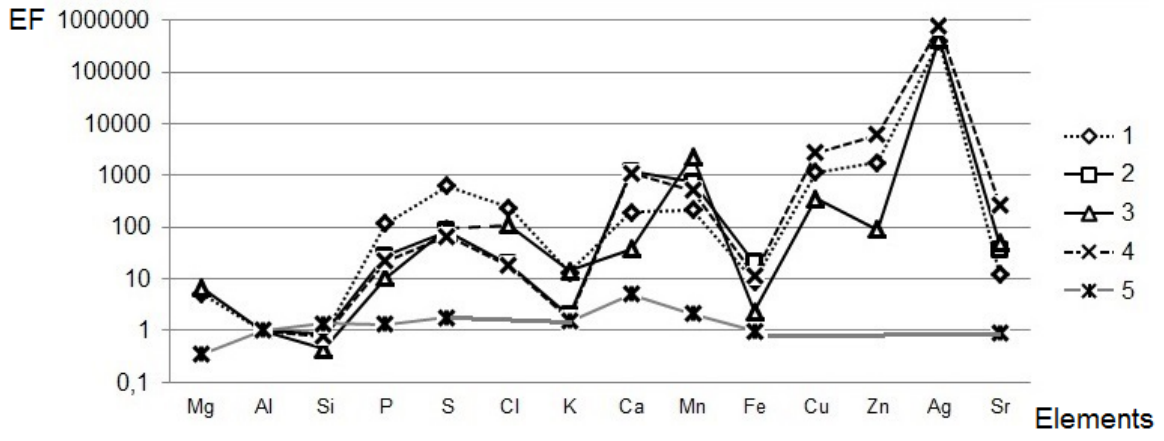

Fig.2 The abundance coefficients (EF): 1 – gastropod muscles; 2 – gastropod shells; 3 – macrophytes; 4 – sapropels; 5 – sandy sediments of Lake Ilmenskoe. The rating was done with Al and clarkes of the continental crust

Table 2 Oxides in sandy sediments, sapropels, macrophytes, gastropod shells and muscles of Lake Ilmenskoe (average data in all the points, in % in ash)

Oxide	Sandy sediments	Sapropels	Gastropod muscles	Gastropod shells	Macrophytes
MgO	0.58	–	0.87	–	2.59
Al_2O_3	10.68	0.30	1.09	0.29	2.20
SiO_2	64.30	1.0	3.83	1.129	3.73
P_2O_5	1.48	0.70	13.29	0.83	1.95
SO_3	0.32	0.33	11.15	0.40	2.54
Cl	–	0.02	1.13	0.02	1.99
K_2O	3.75	0.12	3.44	0.13	11.79
CaO	15.49	95.56	59.77	94.03	33.19
MnO	0.11	0.72	1.10	0.98	36.55
Fe_2O_3	3.15	1.05	2.90	1.80	2.07
CuO	–	0.12	0.18	–	0.14
ZnO	–	0.82	0.85	0.01	0.13
Ag_2O	–	0.09	0.17	–	0.68
SrO	0.26	0.18	0.27	0.26	0.45

Calcium was accumulated by gastropod shells, plants and sapropels. Gastropods were rich in Ferrum, when they wither away, Fe is accumulated in sapropels. Kalium was mainly accumulated in plants and gastropod muscles.

Silicon abundance coefficient of all the samples was close to 1. This fact allows us to compare the abundance of different elements not only against Alluminium but also against Silicon as we have done in our previous research [25].

Strontium was particularly worth mentioning, it was accumulated in sapropels, gastropod shells and shining pondweed. Stable strontium is known for its insignificant value for animals and plants but it is always present in them as a constant companion of calcium partially replacing the latter.

The Strontium enrichment of the sediment is explained by the fact that this element is included in the composition of carbonates, in particular calcite and aragonite. Strontium is likely to accumulate in hydrobionts of the Ilmen State Reserve from water and silt where its concentration is the highest.

In sandy sediments silicon oxide prevailed – 64.3 %, calcium oxide content was slightly higher than 15 % (see Table 2). The chemical composition of sapropels (Table 2) was dominated by calcium oxide. Its content was to 95.5 % in the organic part of sediment. The content of silicon oxide (terrigenous component) was much lower, around 1%. Thus, sapropels were highly calcareous. It is associated with high phytoplankton production.

Two biological types of sapropels are now known to be forming in small lakes of Ural region. They are plankton-genetic with plankton being the main producer of organic substance; and macrophyte-genetic with macrophytes as the main producer of organic substance of sapropel. Thus, we can assume that sapropel of Lake Ilmenskoe is primarily plankton-genetic, but we can't exclude the sapropel dual character because of the element accumulation both in macrophytes and sapropels.

4. CONCLUSION

The results of the analysis carried out in this research show that sapropels are formed in Lake Ilmenskoe. The distinguishing geochemical characteristic of the sapropel in the lake is high carbonate content.

It should be conclusions that hydrobionts are natural geochemical reservoirs of metals and may be considered as geochemical barriers. The given research is of an exceptional importance as baseline. The elemental composition data received may be further used in bio-indication study of South Ural lakes.

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