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The Current Ecological State of Water and Bottom Sediments in Lakes Krugloye and Maltsevo in the Tomsk Region

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Abstract. The state of freshwater ecosystems has been studied for several decades and extensively reported in the scientific literature. Programs aimed at water protection and water quality management should include geochemical monitoring of the pollutants and evaluation of the physical-chemical and biochemical processes in natural water ecosystems (both surface water and bottom sediment). The purpose of the present study was to assess the initial state of the surface water and bottom sediments (BS) of Lakes Krugloye and Maltsevo as the basis for further environmental monitoring and evaluation of the anthropogenic impact on them. The methods used to achieve this aim included extraction and determination of organic and inorganic compounds using high-performance chromatography, capillary electrophoresis, electron spectrophotometry, and X-ray fluorescence analysis. The study shows that bottom sediments of these lakes can be classified as moderately polluted, with the total content of hydrocarbons in them varying from 58.14 to 82.20 ng/g. The content of polycyclic aromatic hydrocarbons (PAHs) in the surface water samples varies from 0.01 to 0.13 μ g/L for different compounds and in the bottom sediments – from 0.11 to 14.44 ng/g. The mixture of PAHs in the water samples contains increased amounts of such compounds as naphthalene, fluorene, phenanthrene, and benza[a]nthracene. The lighter bi- or tricyclic polyarenes, which have higher solubility, predominate in water, in contrast to bottom sediments. The contents of ions (Ca²⁺, Mg²⁺, Ma⁺, K⁺, NH₄⁺, Cl⁻, NO²⁻, SO₄²⁻, NO₃⁻, PO₄³⁻, and F⁻) and heavy metals do not exceed their maximum permissible concentration (MPC) values. The natural pigments identified in the BS suggest the satisfactory hydrobiological status of the lakes and indicate normal function of algal communities. The study demonstrates that Lakes Maltsevo and Krugloye can be regarded as reference water bodies, and the proposed integrated approach is an efficient tool for

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assessing the ecological status of the lakes, which can be used as the basis for further lake monitoring.

Keywords: surface waters, bottom sediments, polyaromatic hydrocarbons, heavy metals, natural pigments, anthropogenic impact.

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Первичная оценка экологического состояния вод и донных отложений озер Круглое и Мальцево Томской области

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Аннотация. Состояние пресноводных экосистем изучается уже на протяжении многих десятилетий, и результаты этих исследований широко освещаются в научной литературе. Разработка программ, направленных на охрану и контроль качества вод, должна включать геохимический мониторинг загрязняющих веществ, оценку физико-химических и биохимических процессов в природных водных экосистемах (как поверхностных водах, так и в донных отложениях). Целью работы было определение исходного состояния поверхностных вод и донных отложений (ДО) озер Круглое и Мальцево для дальнейшего экологического мониторинга и оценки влияния на них антропогенной нагрузки. Комплексный подход для решения этой задачи включал в себя такие методы, как экстракция, определение органических и неорганических соединений с применением высокоэффективной хроматографии, капиллярного электрофореза, электронной спектрофотометрии, рентгенофлуоресцентного анализа. Показано, что донные отложения этих озер могут быть отнесены к умеренно загрязненным, суммарное содержание углеводородов изменяется от 58,14 до 82,2 нг/г. Содержание полиароматических соединений (ПАУ) в изученных пробах поверхностных вод изменяется от 0,01 до 0,13 нг/л для различных соединений, а в донных отложениях от 0,11 до 14,44 нг/г. В смеси ПАУ в водных образцах отмечается повышенное содержание таких соединений, как нафталин, флуорен и фенантрен, а также бенз[а]антрацен. В целом в воде, по сравнению с донными отложениями, преобладают более легкие 2-3-ядерные полиарены, обладающие лучшей растворимостью. Содержание ионов (Ca²⁺, Mg²⁺, Na⁺, K⁺, NH⁴⁺, Cl⁻, NO²⁻, SO₄²⁻, NO³⁻, PO₄³⁻, F⁻), а также тяжелых металлов не превышает предельно допустимых концентраций (ПДК). Природные пигменты, определенные в ДО, позволяют охарактеризовать гидробиологическое состояние озер как удовлетворительное и указывают на нормальное функционирование водорослевых сообществ. Исследования показали, что озера Мальцево и Круглое могут рассматриваться как фоновые объекты, а предложенный комплексный подход эффективен для оценки экологического состояния озер и может использоваться как основа для дальнейших мониторинговых исследований.

Ключевые слова: поверхностные воды, донные отложения, полиароматические углеводороды, тяжелые металлы, природные пигменты, антропогенная нагрузка.

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Introduction

The ecological state of natural water bodies has attracted considerable research effort since the second half of the 20th century. In 1972, the National Service for Observation and Monitoring of the State of the Environment (NSOM), based on weather stations, was established in Russia. The major tasks of special observations and research performed in the framework of the NSOM are as follows:

- to identify the common mechanisms of self-purification;

 to determine the impact of the pollutants accumulated in bottom sediments on the water quality;

to analyze balance of pollutants (chemical substances) in the water bodies or water course segments;

- to assess the dispersal of the chemical substances through the river outlet; to assess the transfer of chemical substances with the collector and drainage waters, etc. (Petin et al., 2006).

The assessment of the ecological status of water bodies should be based on an integrated approach. However, the studies dealing with the state of natural objects frequently focus on determining the contents of polyaromatic hydrocarbons and natural pigments in the surface waters and bottom sediments (Belyaeva et al., 2018; Zimnik, Semenov, 2011; Kramer, Tikhonova, 2012; Semenov et al., 2017). Furthermore, the monitoring studies are generally carried out at large lakes of great importance (such as Lake Baikal, Lake Ladoga, etc. (Zimnik, Semenov, 2011; Takhteev et al., 2020; Belkina et al., 2015; Sharipova, 2015)), while small lakes remain overlooked.

In order to understand the reasons for the changes in the ecological and trophic states of the lakes and to get an insight into the mechanisms of these changes, it is necessary to conduct continuous monitoring taking into account a variety of biological, climatic, and anthropogenic factors influencing the water systems. The necessity to conduct long-term monitoring of the hydrologic regimes of the water bodies is caused by water level variations, which frequently result from the improper use of the lakes and adjacent areas. It is known for a fact that water level fluctuations give rise to variations in the chemical and biological characteristics of the water systems (Hydrology, 2010; Savkin et al., 2005).

"Lake System of the Settlement of Samus" is a local-scale nature conservation area, which is located in the vicinity of the settlement of Samus', 21 km north of Tomsk (the Tomsk

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Region), on the right bank of the Tom River arm across from the Kizhirovskii island. The area was given the preferential conservation status in order to preserve a unique water ecosystem of an environmental, scientific, esthetic, recreational, and health-promoting significance for the citizens of the towns of Seversk and Tomsk. This area includes a unique natural site with small forest lakes Maltsevo, Krugloye, and Yakovo. The total area of this ecosystem is 3732 ha.

All of these lakes have sandy bottoms; their water has a deep brown shade, as the lakes are supplied by the streams originating in the peat bogs. Lakes Maltsevo and Krugloye form a single limnetic system connected by a stream; they are associated with the second terrace rising above the floodplain of the Tom River and form a cascade in the local relief.

The status of the nature conservation area does not protect Lakes Maltsevo and Krugloye from the anthropogenic impact. The lakes and the neighboring area are a favorite recreational zone of the local population, with the beach and barbecue sites.

The purpose of the present study was to characterize the current state of the surface waters and bottom sediments (BS) of Lakes Krugloye and Maltsevo in order to provide the basis for their further ecological monitoring and assessment of the anthropogenic impact.

Materials and methods

The small area of the water surface of the Lakes – Krugloye about 0.23 km² and Maltsevo 0.28 km² – makes it possible to sample water from the opposite shores as an essential minimum for a primary assessment of their geochemical and ecological state (Fig.). The lakes have gently sloping bottoms; the maximum depth is 4–5 meters.

Samples were collected from two sites in each lake (Fig.; Site 1 - N 56°45'00,8" E 84°44'33,8"; Site 2 - N 56°45'02,1" E 84°44'14,1"; Site 3 - N 56°45'08,6" E 84°42'22,1"; Site 4 - N 56°45'13,6" E 84°42'44,9") in August 2021. The water samples were collected from a depth of 0.4–0.6 m from the surface, followed by their n-hexane preservation. The BS samples were taken from a depth of 0–10 cm using a PDO-500 sampler; they consisted of fine-grained sand with single inclusions of plant debris.

In the water and BS samples, we determined the total content of hydrocarbons (HCs) using the Russian Federation environmental protection regulation documents PND F 14.1:2.116–97 and RD 52.18.647–2003. Extraction of organic



Fig. Sampling sites in Lakes Maltsevo and Krugloye

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hydrocarbons from the water and soil was performed using a triple chloroform extraction followed by a cleanup of the extract by the method of chromatography in a column packed with alumina (Al_2O_3) of level II activity ratio.

The content of polycyclic aromatic hydrocarbons (PAHs) in the water sample was determined in accordance with the current governmental environmental control procedure PND F 14.1:2:4.70-96. The PAHs were extracted using n-hexane (Ecos, Russia; 99.9 %). The resulting extract was boiled down to a trace concentration of hexane and the sample volume was made up to 1 ml using acetonitrile. The PAHs from the bottom sediments were extracted according to the RD 52.24.537-2019 procedure. A weighted (10 g) sample was triple-extracted by a mixture of hexane and acetonitrile in the ratio of 10:1. The extracts were filtered through a paper filter into a test vial and vacuum concentrated to a volume of 0.5 ml. The resulting extract was cleaned up by the method of thinlayer alumina chromatography and the sample volume was made up to 1 ml using acetonitrile for the subsequent analysis. The content of PAHs in water and BS was determined by the method of high-performance liquid chromatography (HPLC) in a Shimadzu LC-20 (Shimadzu, Japan) with simultaneous diode array and fluorescence detection chromatograph, using a SupelcoSil LC-PAH reversed-phase column 150*4.6, C 18 phase, and 5 µm particle size. The eluent was a mixture of acetonitrile (Grade 1) and double-distilled water. The chromatography was run in a gradient mode: acetonitrile/water = (50:50) - (100:0) first 20 min, 100 % acetonitrile from the 20th to the 40th minutes of the analysis. The solvent flow rate was 1 ml/min, the sample volume - 20 µl, the column operating temperature - 40 °C. The time of analysis under selected conditions was 32 min. The spectra were recorded in the 190-500 nm range, followed by recording of the signal

at a wavelength of 254 nm for the quantitative determination of the components.

The concentration of photosynthetic pigments in bottom sediments was determined by the procedure proposed by (Sigareva, 2012) in a Cary 50 spectrophotometer (Varian, U.S.A.). The pigments were extracted from the BS using a 90 % aqueous acetone solution. The extracts were kept in a dark place for a few hours to prevent disintegration of the pigments and then centrifuged. Their absorbance was measured in the 350–800-nm range.

The content of heavy metals (HMs) was measured using an ARL PERFORM'X 4200 O spectrometer (Thermo Fisher Scientific, Switzerland) for sequential analysis of solid and liquid samples, which is equipped with an FRCSC detector, at an X-ray tube voltage of 30 kV, 80 mA, using LiF200, Ge111, and AX09 crystals. The bottom sediments were ground in a Pulverisette 6 (Fritsch, Germany) planetary mill to a grain size of 200 mesh, sieved, and dried at 105 °C for one hour and then compacted to form tablets/pellets 29 mm in diameter in a Fluxana Vaneox 40t automatic press (FLUXANA GmbH & Co. KG, Germany) on an H₃BO₃ substrate. Their X-ray fluorescence (XRF) analysis was performed in vacuum. The results were calculated using the Thermo OXSAS 2.1.54 UniQuant program (Thermo Fisher Scientific, Switzerland). We used standard Lake Baikal BS samples (BIL-2, type registration number SS No. 7176-95) for constructing a calibration curve (Revenko, 1994).

In accordance with the procedures specified by PND F 16.1:2:2.2:2.3.74–2012, PND F 14.1:2:4.167–2000, PND F 14.1:2:3:4.282–18, and PND F 16.1:2:2.3:2.2.69–10, we determined the weight concentrations of the ionic composition of water and water extracts from the BS. For capillary electrophoresis, water samples were prepared according to the requirements of operation of the Kapel-205 device and filtered on a membrane cellulose acetate filter with a porosity of 0.40 μ m (Vladipor, Russia). The tests were carried out using a Kapel – 205 (Lumex, Russia) droplet electrophoresis system. The lower detection limit was 0.004 mg/L.

All analytical tests were carried out in triplicate for each sample, and results are presented as means \pm SE. All values obtained for bottom sediments are expressed on a dry weight basis.

Results and discussion

The study of the water and BS samples from Lakes Krugloye and Maltsevo provided the basis for assessing the current state of these lakes and estimating the contribution of anthropogenic impact to the environmental situation. According to the Russian Federation Sanitary standards and requirements 1.2.3685-21 "Hygienic standards and requirements for ensuring the safety and (or) harmlessness of environmental factors for humans" (hereinafter SanPiN), the total content of oil products should not exceed 0.1 mg/L. The total content of HCs in the water samples from Sites 1, 3, and 4 ranged between 1.3 and 1.5 μ g/L, while the maximum content observed at sampling point 2 in Lake Maltsevo was 20.8 µg/L. The HC content in BS varied from 58.14 to 82.2 ng/g.

PAHs are a group of chemicals of various origins (both natural and anthropogenic); most of them are toxic and (or) carcinogenic. According to the available literature data, 5–6 cyclic aromatic compounds are generally classified as industrially produced ones and the lighter polyarenes – as originating from humic substances and terrestrial higher plants (Opekunov et al., 2015; Khalikov, Lukyanova, 2020). As stated in SanPiN 1.2.3685–21, the content of naphthalene in water should not exceed 10 μ g/L and benz[a]pyrene – 0.01 μ g/L. In soils, the maximum permissible concentration (MPC) for naphthalene is not standardized, and for benz[a]pyrene it is 20 ng/g.

In the current study, the following PAHs were quantified based on their chromatographic yields in the water and BS samples from Lakes Maltsevo and Krugloye: naphthalene, 2- methylnaphthalene, fluorene, phenanthrene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benz[b]fluoranthene, benz[k] fluoranthene, benz[a]pyrene, and dibenz[a, h] anthracene (Table 1).

The PAH contents in the surface water samples ranged from 0.01 to 0.13 μ g/L for different compounds. The mixture of PAHs found in the water samples contained increased levels of such compounds as naphthalene, fluorene, phenanthrene, and benz[a]anthracene. In contrast to BS, the water samples contained predominantly the lighter 2–3 cyclic polyarenes, exhibiting better solubility.

To assess the degree of pollution, the results obtained in this study were compared with the data on PAH contents in other lakes, including Lake Baikal. The results obtained for Lakes Maltsevo and Krugloye were comparable with the PAH concentrations in surface waters and bottom sediments of Lake Baikal. In Lake Baikal, the total PAH content varies from 0.03 to 0.13 μ g/L in the water (Gorshkov et al., 2010) and from 24 to 245 ng/g in bottom sediments (Khalikov, Lukyanova, 2020). Lakes located in areas of increased anthropogenic impact are characterized by higher values of PAH content in water and bottom sediments. Studies show that PAH concentrations in bottom sediments can reach 1207-4754 ng/g (Taihu Lake in East China) (Qiao et al., 2006) and 101.3-322.8 ng/g (Bayangdian Lake in North China) (Hu et al., 2010).

In the bottom sediments of Lakes Maltsevo and Krugloe, the total PAH content was higher than in water samples, which was associated with the accumulation of PAHs. The contents of fluorene, phenanthrene, fluoranthene, chrysene,

PAHs*		M	altsevo			K	rugloye	
	Wa	iter, µg/L	B	S, ng/g	Wa	ter, µg/L	B	S, ng/g
	1	2		2	3	4	m	4
Naph	0.02 ± 0.003	0.12 ± 0.019	1.06 ± 0.169	0.11 ± 0.018	0.01 ± 0.002	0.05 ± 0.008	1.59 ± 0.254	0.21 ± 0.034
2- Naph	< 0.003	0.10 ± 0.016	1.62 ± 0.259	0.32 ± 0.051	$0.01 {\pm} 0.002$	$0.03 {\pm} 0.005$	1.18 ± 0.189	0.70 ± 0.112
Fl	< 0.003	0.08 ± 0.014	6.65±1.197	4.85 ± 0.873	0.07 ± 0.013	0.07 ± 0.013	9.83±1.769	6.31 ± 1.136
Phe	0.09 ± 0.018	0.08 ± 0.016	11.77 ± 2.350	8.56±1.712	0.06 ± 0.012	0.08 ± 0.016	13.19 ± 2.640	11.13 ± 2.230
Flu	$0.04 {\pm} 0.007$	0.05 ± 0.001	13.54 ± 2.437	9.74±1.753	$0.04{\pm}0.007$	0.07 ± 0.013	14.44±2.599	12.66±2.279
Py	0.01 ± 0.002	0.02 ± 0.004	$3.32 {\pm} 0.598$	1.76 ± 0.317	$0.01 {\pm} 0.002$	$0.03 {\pm} 0.005$	3.27 ± 0.589	2.76 ± 0.497
B[a]A	0.01 ± 0.002	0.04 ± 0.007	1.83 ± 0.329	0.45 ± 0.081	$0.04{\pm}0.007$	0.13 ± 0.023	0.83 ± 0.149	0.68 ± 0.122
Chry	0.01 ± 0.002	$0.03 {\pm} 0.007$	8.83 ± 1.943	$3.38{\pm}0.744$	0.02 ± 0.004	$0.04{\pm}0.009$	6.21±1.366	5.21 ± 1.146
B[b]F	< 0.003	0.01 ± 0.002	4.79 ± 1.054	< 0.003	< 0.003	0.02 ± 0.004	0.98 ± 0.216	0.47 ± 0.103
$\mathbf{B}[\mathbf{k}]\mathbf{F}$	< 0.003	< 0.003	1.38 ± 0.248	< 0.003	< 0.003	0.01 ± 0.002	$0.40 {\pm} 0.072$	< 0.003
B[a]P	< 0.003	$0.01 {\pm} 0.002$	2.870 ± 0.570	< 0.003	< 0.003	0.02 ± 0.004	< 0.003	< 0.003
D[a, h]A	$0.01 {\pm} 0.002$	$0.03 {\pm} 0.006$	10.03 ± 2.006	1.24 ± 0.248	0.02 ± 0.004	0.06 ± 0.012	3.83 ± 0.766	1.06 ± 0.212
S PAHs	0.20	0.59	67.70	30.40	0.28	0.62	55.76	41.18

Table 1. Contents of polycyclic aromatic hydrocarbons (PAHs) (mean±SE, n=3) in water and bottom sediments (BS) of Lakes Maltsevo and Krugloye of the Tomsk Region

I z[b] 5 2 ז[מ]מ [n]r P.1 5 fluoranthene, B[k]F – benz[k]fluoranthene, B[a]P – benz[a]pyrene, D[a, h]A – dibenz[a, h]anthracene and dibenz[a, h]anthracene were the highest. However, at two sampling sites (1 and 3), BS samples contained higher levels of the identified compounds. The reason for that was that those two sites were located at the shoreline, which, in summer, is densely populated by vacationers burning log-fires. The indicators of fire-induced pollution were the high contents of such compounds as benz[a]pyrene, pyrene, and benz[a] anthracene. The present study demonstrates that the PAH contents in Lakes Maltsevo and Krugloye do not exceed the MPCs for controlled compounds and are similar to their levels in Lake Baikal.

The study of the cation-anion composition of natural waters and bottom sediments is necessary for assessing the ecological state of water bodies, including a possible determination of their anthropogenic pollution (Sagdeev et al., 2017). Using the method of capillary electrophoresis, we determined the ionic composition including major cations – Ca^{2+} , Mg^{2+} , Na^+ , K^+ , and NH_4^+ and anions – Cl^- , NO_2^- , SO_4^{2-} , NO_3^- , PO_4^{3-} , and F^- .

The increased contents of nitrogen and phosphorus in water bodies indicate pollution by industrial and domestic wastewater (Neverova-Dziopak, Tsvetkova, 2020). In areas subject to high economic activity, the contents of NH₄⁺ and PO₄³⁻ often exceed their MPC values. The water of small lakes located in oil-producing regions was found to contain increased concentrations of NH₄⁺, up to 1.432 mg/L, and PO₄³⁻, up to 0.417 mg/L (Agbalyan, Shinkaruk, 2019). The concentrations of NH_4^+ and PO_4^{3-} in Lakes Krugloye and Maltsevo did not exceed their maximum permissible concentrations (Table 2), suggesting the absence of any polluting runoffs. The contents of all cations and anions detected in water samples did not exceed their MPCs (SanPin 1.2.3685-21). The results of testing indicated a satisfactory quality of natural waters, and all parameters were within the normal limits.

Bottom sediments are the most conservative components of natural water bodies; they contain information on pollution of the watershed and its distinctive characteristics. They can therefore serve as indicators for identifying the composition, rate, and scale of the anthropogenic pollution.

Table 3 presents the data on the contents of heavy metals in the samples. Most researchers studying HMs in natural water bodies (Sharipova, 2015; Strakhovenko et al., 2014) primarily focus on such elements as V, Ni, Cr, Mn, Cu, Zn, Cd, Sn, and Pb because these metals can accumulate in the environment and exhibit their toxic properties (Papina, 2001). The study by Papina (2001) demonstrated a relationship between the change in pH and the possibility of the transition of dissolved heavy metals to the adsorbed form. The pH value in the samples of surface waters of Lakes Maltsevo and Krugloye varied between 6.8 and 7.2.

The total content of all heavy metals detected in the samples did not exceed the MPCs stated in SanPin 1.2.3685–21 (Table 3).

To assess the degree of pollution, we compared lakes of Russia and the world with different contents of HMs. The clean lakes included the shallow lake Raduzhnoye (Ergaki Nature Park) with the following HM contents: Ni - 20.8 mg/kg, Zn - 104.4 mg/kg, and Mn -160 mg/kg (Anishchenko et al., 2015). In lakes located in the immediate vicinity of industrial production, the HM content reached high values: Cd – 4.2 mg/kg (Lake Yakovo, Tomsk Region), Pb - 3345 mg/kg (Lake Bolshie Rakity, Altai Territory) (Strakhovenko, 2011). The study by Akono et al. (2022) reported the contents of HMs in lakes located in Cameroon, Turkey, Tanzania, and China. The samples collected from those lakes contained various concentrations of HMs, depending on the sedimentation conditions (pH, amount of suspended solids, anthropogenic

		MPC*, mg/L			2.0		200.0	50	180		350.0	3.0	500.0	45.0	1.5	3.5
		gloye	4		0.33±0.05	3.51±0.56	9.83±1.57	2.56±0.41	10.55±1.69		1.98 ± 0.4	0.45±0.10	1.4 ± 0.30	0.47±0.07	<0.1	0.14
•	sediments	Kru	m	Cations, mg/kg	0.47 ± 0.08	3.00±0.48	15.07±2.4	5.14±0.82	12.86±2.06	s, mg/kg	1.63 ± 0.4	0.37±0.07	2.35±0.60	$0.54{\pm}0.08$	<0.1	0.16
)	Bottom s	Maltsevo	2		0.97± 0.16	3.02± 0.48	5.27± 0.84	2.18± 0.35	9.52± 1.52	Anion	0.86 ± 0.20	0.26± 0.07	1.35 ± 0.30	<0.1	<0.1	0.18
			1		2.41 ± 0.39	4.15±0.66	4.96± 0.79	1.35 ± 0.22	7.02± 1.12		1.3 ± 0.31	0.30 ± 0.07	2.49 ± 0.60	<0.1	<0.1	0.12
		ugloye	4		0.15 ± 0.04	2.06±0.29	2.34 ± 0.33	0.94 ± 0.13	3.50±0.49		2.65±0.64	<0.2	2.94±0.69	<0.2	<0.1	<0.2
	/ater	Kn	3	ns, mg/L	0.15 ± 0.04	1.81±0.36	2.47±0.35	1.02 ± 0.14	3.43 ± 0.48	ns, mg/L	2.67±0.64	<0.2	2.67±0.62	<0.2	<0.1	<0.2
	Μ	ltsevo	2	Catio	0.21±0.05	2.27±0.32	2.67±0.37	0.96 ± 0.19	2.99 ± 0.42	Anior	1.97±0.47	<0.2	3.63±0.74	<0.2	<0.1	<0.2
		Ma	1		0.05 ± 0.02	2.23±0.31	0.99 ± 0.20	0.96 ± 0.19	2.66± 0.37		0.74 ± 0.18	<0.2	1.6 ± 0.32	<0.2	<0.1	<0.2
		Tota C	1011		$\mathrm{NH_4^+}$	\mathbf{K}^+	Na^+	Mg^{2+}	Ca ²⁺		CI-	NO ²⁻	SO4 ²⁻	NO ₃ -	Ŀ	PO_4^{3-}

Table 2. Cation-anion composition (mean±SE, n=3) of surface water and bottom sediments of Lakes Maltsevo and Krugloye

*- maximum permissible concentrations, guideline values refer to the content in water samples

HMs	М	altsevo	K	Krugloye			
	1	2	3	4			
V	102.1±10.2	74.9±7.5	92.3±9.2	81.2±8.1	150		
Ni	31.6±4.7	27.7±4.2	79.1±11.9	65.8±9.9	80		
Cr	376.6±18.8	300.2±15.0	139.2±6.9	234.1±11.7	ND		
Mn	1270.4 ± 63.5	704.4±35.2	715.2±35.8	744.2±37.2	1500		
Cu	31.5±1.6	13.4±0.7	11.7±0.6	24.3±1.2	132		
Zn	82.6±12.4	96.5±14.5	169.9 ± 25.4	122.2±18.3	220		
Cd	$0.4{\pm}0.1$	$0.8{\pm}0.1$	0.5 ± 0.1	0.7±0.1	2		
Pb	26.2±2.6	31.1±3.1	17.7±1.8	15.2±1.5	32		
Sn	< 0.001	< 0.001	39.1	34.4	ND		
Total ΣHMs	1921.4	1249.0	1264.7	1322.1			

Table 3. Contents (mean±SE, n=3) of heavy metals (HMs, mg/kg) in bottom sediments of Lakes Maltsevo and Krugloye

MPC - maximum permissible concentrations, ND - not determined

impact, etc.): Pb - 5.83-91.3 mg/kg, Zn - 53.24-123.0 mg/kg, Cd - 0.08-3.53 mg/kg.

Results obtained in the current study can be compared with the data on the contents of these metals in Lake Baikal (Yanchuk, 2021) and various other ecosystems (Anishchenko et al., 2015). The results obtained indicate that the contents of Cu, Zn, Cd, and Pb are at the background level and suggest moderate pollution (Anishchenko et al., 2015), which does not significantly affect the biota. At sampling point 1, the total HM content was higher than at other sampling points. Currently, there is no adequate explanation for this result. An increased content of Cr was revealed, but no reason for that can be suggested at this stage of the study.

Natural water bodies are complex ecosystems; therefore, the assessment of their state should be based on determination of both chemical parameters (contents of ions, HMs, PAHs, etc.) and biological characteristics.

Monitoring of the surface water quality using hydrobiological parameters should include a study of phytoplankton photosynthesis and organic matter decomposition, determination of the ratio of photosynthesis intensity to organic matter decomposition, and measurement of the content of chlorophyll (Sidelev, Babanazarova, 2008).

It is well known (Koreneva, Sigareva, 2022; Belyaeva et al., 2018) that the distribution of pigments is heterogeneous and depends not only on the quality of water, but also on the properties of bottom sediments. For marine coastal zones with a high sand content, the total content of pigments is insignificant, reaching 4.9 µg/g, while for silts the content of Cchl a + Ph is 9.1–19.5 μ g/g (where Ph is pheophytin). For sandy bottom sediments of fresh-water environments, the total content of Cchl a + Ph varies between 0.1 and 5.5 μ g/g (Belyaeva et al., 2018). In the present study, we measured the contents of natural pigments – chlorophylls a, b, c and carotenoids – in bottom sediments (Table 4). The total content of chlorophylls varied from 0.5 to 1.14 μ g/g, and the content of carotenoid pigments did not exceed $0.9 \ \mu g/g$.

Such low concentrations of pigments can be associated with the grain-size composition of BS, represented by sandstone with a fraction size of

		Maltsevo		Krugloye			
Phytopigments	1	2	3	4			
Cchl a	$0.871 {\pm} 0.07$	0.247±0.02	0.277 ± 0.02	$0.454{\pm}0.04$			
Cchl b	$0.148 {\pm} 0.02$	$0.100 {\pm} 0.01$	$0.091 {\pm} 0.01$	$0.154{\pm}0.01$			
Cchl c	$0.125 {\pm} 0.02$	$0.153 {\pm} 0.02$	$0.100{\pm}0.01$	$0.184{\pm}0.02$			
Ccarot	$0.915 {\pm} 0.07$	$0.490 {\pm} 0.04$	0.445 ± 0.04	$0.710 {\pm} 0.06$			
PR*	1.050	1.980	1.610	1.570			
% Cchl <i>a</i> of \sum chl	76.197	49.443	59.147	57.295			

Table 4. The contents of phytopigments (μ g/g, mean \pm SE, n=3) in the bottom sediments of Lakes Maltsevo and Krugloye in the Tomsk Region

*- pigment ratio: PR= Ccarot/ Cchl a

0.5–0.25 mm, and the hydrodynamic parameters of the coastal zone. The content of chlorophylls in bottom sediments is not uniform. The lakes examined in the present study can be defined as mesotrophic (Mineeva, 2004).

The content of chlorophyll *a* can characterize the state of the autochthonous organic matter. This pigment is the first to undergo microbiological and physical-chemical degradation, which results in the accumulation of more stable carotenoids (Smolskaya et al., 2018; Fisher et al., 2019).

The level of the functional activity of a plant community is assessed using the pigment ratio (PR): a ratio of the concentration of total carotenoids to the concentration of chlorophyll *a* (Smolskaya et al., 2018). The optimal state of the algal system is generally characterized by the PR value between 2 and 5 (Fisher et al., 2019). In addition, seasonality affects the value of PR as well (Mineeva, 2004). Mesotrophic water bodies are characterized by the predominance of carotenoids over green pigments. For the lakes studied in this work, this condition is fulfilled, which indicates the normal functioning of algal communities.

Conclusion

The present study showed that the surface waters of the lakes contain insignificant amounts

of PAHs, mostly represented by bi- and tricyclic compounds. The surface layer of BS, consisting of fine-grained sandstone, contains a low total amount of PAHs, 30–68 ng/g, consisting of 5- and 6-cyclic structures; their supply is due to the human activity, and they are of pyrogenic origin. In accordance with the currently accepted gradation levels for the HC content, the lakes were classified as weakly polluted.

The data on the cation-anion composition and HM content in these water bodies conform to the standard and do not exceed the MPC values.

The natural pigments identified in the BS suggest the satisfactory state of the lakes and indicate normal functioning of the algal communities.

The present study demonstrated that the anthropogenic impact did not significantly affect the current ecological state of Lakes Maltsevo and Krugloye. The results obtained in this study make it possible to consider these ecosystems as reference ones, which can be used for comparison purposes in studies of other aquatic ecosystems of the Tomsk Region.

The integrated approach proposed in this study is effective for assessing the ecological state of lakes and can be employed in further monitoring research.

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