Original Article

Industrial site of out-of-operation Baikalsk Pulp and Paper Mill as a potential source of pollution in Lake Baikal coastal zone



Zvereva Yu.M.[®]*, Tomberg I.V.[®], Annenkov V.V.[®], Medvezhonkova O.V.[®], Timoshkin O.A.[®]

Limnological Institute, Siberian Branch of the Russian Academy of Sciences, 3 Ulan-Batorskaya Str., Irkutsk, 664033, Russia

ABSTRACT. The Baikalsk Pulp and Paper Mill (BPPM) was functioning on the shore of Lake Baikal for almost 50 years. These years of operation inevitably imposed specific adverse effects on the lake ecosystem. Finally, the BPPM was closed in 2013 but with no measures to mothball the plant. During 2013–2016, we observed a few atypical phenomena through our complex investigations of the coastal zone area next to the BPPM. Water temperature measurements, hydrochemical analysis, and FTIR spectroscopy showed these phenomena as unusual for Lake Baikal's pristine coastal areas. (1) We noted an anomalously high temperature of the interstitial water of the beach next to the BPPM. The water from the hole on the beach reached a temperature of 25 °C in June 2013. (2) The hydrochemical parameters of the water from the beach were analyzed, and the interstitial water there exhibited an appreciably lower concentration of oxygen and higher content of sulfur, sodium, and chlorine comparing the lake's water. (3) We discovered the specific black depositions to cover the stones of the target beach. The IR spectrum of those depositions was found to be identical to the BPPM sludge-lignin. All these observations and results of chemical analyses point out that the industrial site of the nonfunctioning plant is still a substantial source of pollution, which negatively influences the Southern Baikal coastal zone ecosystem.

Keywords: Baikalsk Pulp and Paper Mill, interstitial, Lake Baikal, pollution, sludge-lignin

1. Introduction

Lake Baikal, the oldest and deepest freshwater lake on the Earth, has always been the focal point for scientists and the world community. The uniqueness of the lake is a universally accepted fact, validated by incorporating of this natural object into the UNESCO List of the World's Heritage in 1996. Baikal - the colossal reservoir of freshwater, which contains a tremendous volume (over 23 000 km³; Lake Baikal..., 1998). Facing the global deficit of drinking water, the problems of Lake Baikal protection and its ecosystem monitoring should become a matter of paramount importance (Timoshkin et al., 2019). Considering all these facts, the decision to construct on the lake's shores the pulp and paper mill seems quite paradoxical. Nevertheless, in 1966, one of the most significant sources of local pollution, the Baikalsk Pulp and Paper Mill (BPPM), started its production on the shores of Lake Baikal.

The pulp and paper industry is one of the leading branches of the forestry industrial complex in Russia:

*Corresponding author.

E-mail address: <u>zvereva@lin.irk.ru</u> (Yu.M. Zvereva)

Received: June 23, 2022; Accepted: October 03, 2022; Available online: November 11, 2022

about 20 large pulp and paper mills operating in the country's territory (~150 mills in total; Russian Timber Industry, 2021). This industry is highly resourceintensive and requires much pure water (Fediaeva, 2007). That is why pulp and paper mills are located near big water bodies. For instance, in Russia, the biggest mills are operating on such water bodies as the Northern Dvina River and its tributaries (e.g., Vychegda River), Selenga River, Angara River, Volga River, Lake Onega, and Lake Vygozero (Moiseeva, 2005; Ermolina et al., 2011; Timakova et al., 2014).

The negative impact of the pulp and paper industry on the environment is rather various and complex. This industry is a significant source of pollution of atmospheric air, surface and ground waters, and soil (Fediaeva, 2007; Gavrilescu et al., 2012). A kraft pulping mill contaminates the air by specific sulfur compounds: hydrogen sulfide, methyl sulfate compounds (dimethyl sulfide and methyl mercaptan), and sulfate aerosols (sulfates and sodium sulfides; Obolkin et al., 2010). Mill energy units (e.g., thermal power stations or TPSs)

© Author(s) 2022. This work is distributed under the Creative Commons Attribution-NonCommercial 4.0 International License.



emit sulfates, sulfur, and nitrogen dioxides. All such emissions could be involved in cloud formation that resulted in the acidification of precipitation (Obolkin et al., 2010; 2016).

In the sense of water management and conservation, the pulp and paper industry may be considered one of the most concerning. Pulp and paper manufacture is a large consumer of water and, even worse, it discharges high rates of wastewaters containing ~200 different chemicals (Fediaeva, 2007; Anikanova, 2009). Wastewater is high in chemical oxygen demand, total suspended solids, nitrogen, and phosphorus. In addition, it generates chlorinated organic compounds, including dioxins, furans, and other absorbable organic halides (Gavrilescu et al., 2012). Thorough studies of diverse freshwater ecosystems under the influence of pulp and paper manufacturing have demonstrated structural changes in their biota and water quality deterioration (Productivnost Baikala..., 1974; Moiseeva, 2005; Ermolina et al., 2011; Timakova et al., 2014).

Last but not least, pulp manufacture generates large quantities of solid wastes, which are landfilled (Fediaeva, 2007; Gavrilescu et al., 2012). The main subject of this paper is the impact of untreated wastes of BPPM stored in its landfills. Sludge-lignin, lime mud, fly ash, and solid municipal wastes have been accumulating at the plant's landfills for almost 50 years of its operation. Nowadays, ecology experts call the BPPM an "object of accumulated environmental damage" (Kolotov et al., 2021). World environmentalists include dangerous BPPM's legacy into the list of the immediate threats for the Lake Baikal ecosystem (Simonov et al., 2022).

Now the management of these accumulated wastes is the most acute problem facing ecologists since the BPPM production abandonment. The allocation of vast amounts of such wastes in a seismically active zone accompanied by a mudflow danger (Laperdin et al., 2016) might lead to a large-scale ecological disaster in the future (Suturin et al., 2021). A sudden discharge of all accumulated hazardous wastes of the plant into Lake Baikal will equal the volume of the BPPM effluents during 700 years of its operation (Kolotov et al., 2021). Moreover, the overfilled plant waste pits near the lake present another ecological risk - contamination of the lake's coastal zone. At first, we faced the threatening effects of the BPPM in 2013, when we observed warm dark-colored water flowing on the shore next to the mill's territory. Later, we detected the thermal and chemical contamination of the coastal zone there that is the focal point of this work.

2. Materials and methods 2.1. Study site

Lake Baikal is located on the border of Eastern Siberia and Central Asia (Fig. 1). Its maximum depth is 1 637 m and estimated age is over 25 million years (Lake Baikal..., 1998). Since the late 20th century, the opinion of experts on the state of Lake Baikal ecosystem was based on its high self-purification ability,



Fig.1. Schematic map of Lake Baikal (on the left) and the map of its Southern basin (on the right). Hollow circles mark large settlements. A black circle marks the location of reference site for the FTIR analyses of interstitial water. A black triangle marks the location of the BPPM.

sustainability, and a huge body of water regarded as the protection against the pervasive global changes even under the growing load of economic activities on its shores (Grachev, 2002). However, the first decades of the 21st century showed that, notwithstanding its enormous volume, the lake could not evade the imminent large-scale ecological crisis.

According to (Kravtsova et al., 2014; Timoshkin et al., 2014), the earliest negative changes in the lake coastal zone became clear during 2010-2011. Currently, the lake-wide problems include changes in zonation and the species composition of the benthic algae and macrophytes, growth of their biomass (filamentous algal blooms), and the large coastal accumulations of the detritus formed by these rotting algae (up to 90 kg m⁻²), active proliferation of the benthic cyanobacteria, including toxin-producing species, mass sickness and mortality of endemic Lubomirskiidae sponges (Timoshkin et al., 2019). One of the most evident reasons for these changes is nutrient pollution in groundwater (Timoshkin et al., 2018), but complex changes in climate (Potemkina et al., 2018), nutrient transport, lake hydrodynamics, and food web structure may also facilitate these emerging threats (Vadeboncoeur et al., 2021).

Above-mentioned ecological problems have been observed in almost the entire lake area, including certain remote localities, but the primary focus of this paper is the local source of pollution, the Baikalsk Pulp and Paper Mill (Fig. 2). The mill is situated in Baikalsk town, on the eastern shore of Southern Baikal (Fig. 1). The BPPM started production in 1966. Almost 50 years of the plant operation included the periodical slowdowns and even an attempt to transfer the mill to a closed cycle in 2008. After lengthy proceedings, the BPPM was finally closed in 2013, though it has stopped only the malodorous emissions and the direct discharge of industrial wastewaters into the lake.

The main reason for concern – no measures were taken to mothball the plant (Kolotov et al., 2021). The overfilled BPPM waste pits were just abandoned with no recycling procedures. At present, the wastes from sulfate pulp production (sludge-lignin, wastes from the chemicals' recovery process, ash from the TPS, and solid municipal wastes) occupy \sim 350 ha, including Babkhinsky and Solzansky landfills, and the BPPM industrial site (Fig. 3).

For the sampling and measurements, we chose the beach next to the BPPM industrial site (Fig. 2B, Fig. 3). The initial reason for choosing exactly this beach area was detecting a dark-colored warm water flow, which was seeping through the beach pebbles. Further, this water flow is referred to as a "warm brook" for the sake of convenience. We should note that the "warm brook" we found was an irregular phenomenon, and the intensity of its seeping was variable. Theoretically, it could depend on the amount of atmospheric precipitation that feeds groundwaters and also on the seismic activity. For instance, we observed a small but visible trickling brook in 2013, whereas there were only a few small puddles on the beach during 2014–2015.

2.2. Sampling and measurements

This study is based on the complex interdisciplinary investigations of the Limnological Institute staff aboard the research vessel "V.A. Koptyug". The bulk of the data was collected during the expeditions in June and September 2013–2016.

2.2.1. The water temperature and hydrochemical characteristics

The temperature was measured for the water's edge and interstitial water using the Checktemp thermometer. We considered water's edge samples to be water from a depth of 10-20 cm, and interstitial samples to be water from holes on the beach. On the target beach, we usually dug holes 0.5–1 m above the water's edge. These holes were about 20-50 cm deep and about 50-60 cm wide. As soon as water filled the dug holes, we started sampling and measuring, so that the interstitial water parameters did not change under the influence of various factors (e.g., solar activity, precipitation, and atmospheric oxygen). During 2013-2014, the measurements were taken according to the following schemes (Fig. 4, Fig. 5). As the central point, we chose one where the outlet of the "warm brook" was visible. Other temperature measurements were taken both eastward and westward from the central hole with an interval of ~ 5 m along the water's edge.

During 2013–2015, the hydrochemical characteristics were estimated for the following samples: (1) water of "warm brook", (2) the interstitial water from the hole, (3) the edge's water, (4) pelagic lake's water. The SCUBA divers collected the last type of samples at the depth of \sim 7 m. Before the analysis, we used the acetate cellulose membrane filters (0.45 µm pore size) to remove the suspended particulate matter from the samples. The dissolved oxygen (DO), electrical conductivity (EC₂₅), pH, and the chemical oxygen demand (COD) were measured in the unfiltered water.



Fig.2. Industrial site of BPPM. (A) View from the water (May 31, 2013). (B) Coastal area near the target beach where the smoke-stacks of the mill's thermal power station are clearly visible (June 11, 2014).



Fig.3. Location of the BPPM industrial site and its two landfills (Babkhinsky and Solzansky), storing different types of industrial and municipal wastes. The BPPM's area is shaded, and 14 plant's waste pits are marked with their numbers. A black cross sign marks the target beach.

Concentration of sodium (Na⁺) was determined by the flame emission method on an Atomic Absorption Spectrophotometer 30 (AAS-30; Carl Zeiss Jena, Germany) with 5–7% error (Fomin, 2000). Anion concentrations (chloride (Cl⁻), sulfate (SO₄⁻²), nitrate (NO₃⁻)) were measured by high-performance liquid chromatography on a chromatograph Milichrom A-02 (EcoNova, Russia) with 7–10% error (Khodzher et al., 2016). Dissolved oxygen concentration was measured *in situ* by the Winkler test with 3% error. Nutrient analyses (phosphate (PO₄⁻³), ammonium (NH₄⁺), nitrite (NO_2)) were performed with a spectrophotometer KFK-3 (Zagorsky Optical-Mechanical Plant, Russia) with 10–20% error. Mineral phosphorus concentrations (soluble reactive phosphate) were estimated with ammonium molybdate, ammonium nitrogen concentrations were measured with indofenol, and nitrite concentrations were estimated with the Griess reagent (Boeva, 2009).

We measured the electrical conductivity at the sampling sites with the portable conductometer (Horiba, Japan) and the pH with the use of the pH meter (Hanna, Germany). Chemical oxygen demand was quantified by permanganate index (estimation error up to 40%).

2.2.2 Fourier-transform infrared (FTIR) spectroscopy

We analyzed two types of samples from the target beach with FTIR spectroscopy: (1) interstitial water samples and (2) the samples of solid black depositions from the stones. These measurements were performed with an Infralum FT-801 spectrometer (SIMEX, Russia) using KBr pellets. In the case of the interstitial water samples, we chose the beach of Berezovy Cape as a reference site (Fig. 1).

To analyze the solid black depositions from the beach stones, the samples were extracted with 0.1 M NaOH, precipitated with $2 \text{ M H}_2\text{SO}_4$ at pH 3, centrifuged, washed with water, and dried in a vacuum. Mechanical scraping may lead to contamination by the inorganic components of a stone, so extraction was indispensable. The procedure of extraction we used was described in (Tiranov, 1997).

2.2.3 Earthworms sampling

In June 2013–2016, we quantified the number of earthworms (Annelida, Oligochaeta, Lumbricidae) in the splash zone of the target beach (Table 1). The earthworms were sampled from squares with a side of 1 m. The results were performed as a mean number of individuals with a standard error of mean per square meter of the beach (ind. m⁻²). For comparison, we used data obtained in the splash zone of Bolshie Koty Bay (Fig. 1). In general, the ecology of the splash zone as a part of the coastal zone of Lake Baikal has been little known (Timoshkin et al., 2012). Concerning earthworms as inhabitants of the lake splash zone, to date, there are only sparse observations on their number got by our research group for Bolshie Koty Bay in 2010-2013 (Timoshkin et al., 2012; Zvereva et al., 2012). Environmental conditions of the target beach and the beach of Bolshie Koty Bay differ, but the absence of data makes us to compare these sites for Lumbricidae abundances.



Fig.4. The temperature of the interstitial water of the beach next to the BPPM industrial site (May 31, 2013).



Fig.5. The temperature of the interstitial water of the beach next to the BPPM industrial site (June 11, 2014).

3. Results and discussion

3.1. Temperature deviations of the interstitial water

During routine sampling on the beach and in shallow parts, the limnologists registered a few phenomena unusual for the lake's pristine coastal areas. A thermal anomaly was one of the atypical cases observed. We registered a temperature of 25 °C in a hole dug above the water's edge on the shore. The temperature measurement with 5 m intervals in both directions from the central hole showed a downward gradient (Fig. 4). The interstitial water temperature gradually decreased from 25 °C to 18.6 °C westward and up to 12.1 °C eastward. Concurrently, the lake water temperature did not rise above 6.5–7.5 °C at the water's edge.

Long-term observations of Baikal near-shore water temperature dynamics, with Bolshie Koty Bay selected as the reference lakeshore site (Fig. 1), revealed that the interstitial water temperature in the holes varied within 9–13 °C from late May to early June and was only a couple of degrees warmer than the

 Table 1. Earthworms (Annelida, Oligochaeta, Lumbricidae) sampling data for the splash zone of the beach next to the BPPM site (2013–2016).

Sampling date	May 31, 2013	June 11, 2014	June 13, 2015	June 12, 2016
N samples	4	4	16	8

temperature near the water's edge (Timoshkin et al., 2017). According to the same data, water temperature in the holes may reach 15–17 °C only on the hottest summer days. Consequently, the temperature of the interstitial water of the target beach was 2–3 times higher compared to the normal situation, and this phenomenon was registered at \sim 200 m along the shoreline in 2013 (Fig. 4).

The measurements of the interstitial water temperature were made likewise at the same beach in early June 2014 (Fig. 5). In that case, we did not register such noticeable upsurge in the temperature. Only the central hole showed a relatively higher temperature for this period (18.3 °C). The temperature gradually reached typical values with distance at different sides from the central hole: 14.6 °C westward and 11.8 °C eastward (Fig. 5).

The mill with two big landfills and 14 waste pits occupied a vast territory (Fig. 3). The groundwater layer is found between 4–5 m to 20–25 m depths on the territory of the BPPM. At the shoreline of Lake Baikal, the groundwater level is located close to the Earth's surface (Anikanova, 2009). Since 2000, the source of wastewater contamination at the BPPM's site has been localized by a protective groundwater dam. However, a special plant's service had registered an increase in the chemical concentration in the groundwater in 2007 (Anikanova, 2009). This fact reasonably indicates the depreciation of the protective constructions, the state of which is now not monitored. According (Kolotov et al., 2021) waste pits No. 1 and 8 of Solzansky landfill showed a high level of groundwater pollution.

Due to the above circumstances, we tend to associate increased temperatures of interstitial water in 2013–2014 with polluted groundwater infiltration. Several publications (Anikanova, 2009; O probleme..., 2009; Suturin et al., 2015; 2021) clearly indicate that there is an industrially polluted groundwater ridge under the BPPM's site. Anikanova (2009) reported that the intensity of the underground flow is irregular and could be related to the seismic events that induced the discharge of the industrial groundwater. The case of the record-breaking high temperatures in 2013 could point out not only the mixing of industrial and natural groundwater but to an emergency release of warmed-up technical waters into the coastal zone.

The water temperature is one of the universal ecological factors for the dwellers of the shallow and interstitial zones as well as for the rest of the poikilothermic hydrobionts. It is well-known that the temperature of the environment is an important driver that affects the rate of biochemical reactions (Konstantinov, 1986). Water is a relatively stable medium, and its temperature changes gradually owing to its thermal properties (Bezmaternykh, 2009). Such stability allows the hydrobionts to adapt to a specific temperature range. For instance, the Baikal amphipods common for the lake coastal zone, Eulimnogammarus verrucosus (Gerstfeldt, 1858) and E. vittatus (Dybowsky, 1874), prefer a water temperature of 5–6 °C (Timofeyev and Shatilina, 2007). Therefore, a dramatic temperature rise can negatively affect the Baikal hydrobionts. Moreover, the majority of Baikal organisms are oxyphilous, and a temperature increase can exacerbate their breathing conditions.

3.2. Hydrochemical parameters of the interstitial water

Hydrochemical parameters of different water samples were analyzed: (1) water collected from the "warm brook", (2) interstitial water from a hole on the target beach, (3) the water from the lake's edge, (4) the lake's pelagic water (Fig. 6). In our case, the



Fig.6. Results of hydrochemical analyses for (1) water of the "warm brook", (2) the interstitial water from the hole, (3) the edge's water, (4) pelagic water of Lake Baikal. Samples were collected in the coastal area adjacent to the BPPM site during 2013–2015. The less intensive color of a bar depicts a higher value of a parameter.

oxygen concentration in the water was one of the most indicative characteristics. It is quite clear that the oxygen content was significantly lower in the hole and "warm brook" comparing the lake's water. We noted the oxygen concentration was close to zero in the water from the "warm brook" in 2014. As for the pH, its measurements displayed stable low alkalinity in the water edge's and pelagic samples (~8), whereas the "warm brook" and the hole values were closer to neutral. The electrical conductivity in the "warm brook" during 2014–2015 testified to a moderately increased water mineralization there (up to 250 μ S cm⁻¹).

In the context of our study, the sulfate content could be the most useful hydrochemical indicator for monitoring. Air emissions and wastewaters produced during sulfate pulping include large amounts of various sulfur compounds that entail contamination of rather spacious areas in the BPPM vicinity. While the mill was functioning, sulfates and other sulfur compounds were registered in the atmosphere (Obolkin et al., 2010; 2016) as well as in the water (Anikanova, 2009). The "warm brook" water showed the highest concentrations of SO₄⁻² (28–44 mg L⁻¹), which could signify the influence of the BPPM site on the chemical composition of the groundwater.

FTIR analysis also showed the presence of sulfur compounds in interstitial water samples from the target beach (Fig. 7). The spectra of solid residues obtained after the evaporation of water from the reference site (Berezovy Cape) presented the following absorption bands associated with organic matter: 870 cm⁻¹, 1410–1530 cm⁻¹, and 1645 cm⁻¹ (Fig. 7A). The band at 1130 cm⁻¹ is associated both with fluctuations of an ether group (C-O-C) and inorganic compounds containing oxygen (Si-O-Si, Al-O-Si, Al-O-Al groups). Examination of the interstitial water samples from the beach next to the BPPM exhibited characteristic IR spectral deviations (Fig. 7B). The bands at 640 cm⁻¹ and 1140 cm⁻¹ allowed us to suggest the presence of sulfonate compounds.

Sodium and chlorine could be the other possible pollution tracers, as it was used in pulp production in the BPPM. Concentration of Na⁺ showed a quite clear pattern (Fig. 6): there were high concentrations in the "brook" and interstitial, but low ones in the waters of Lake Baikal. The Cl⁻ concentration followed this pattern. Drawing a conclusion about high concentrations of these tracers, we keep in mind that normal mean concentration for the water of Southern Baikal is ~3.3 for sodium and ~0.4 for chlorine (Khodzher et al., 2017). Other chemicals as nitrogen compounds, phosphates and organic matter concentration did not demonstrate any obvious patterns in the distribution (Fig. 6).

In 2008, according to the government document (O probleme..., 2009), monitoring of the groundwater at Solzansky landfill revealed a stable high concentration of toxic elements exceeding maximum permissible concentrations (MPC) accepted for fishery water bodies of the premium category: iron (up to 4 MPC), manganese (up to 13 MPC), copper (up to 22 MPC), zinc and aluminum (up to 3 MPC), methanol (4 MPC), and formaldehyde (30 MPC). Higher concentrations of



Fig.7. FTIR spectroscopy measurements of solid residues after evaporation of interstitial water. (A) The beach of the Berezovy Cape (reference site). (B) The beach next to the BPPM site.

petroleum products and lignin were constantly reported in the groundwater, and higher amounts of organic matter were observed periodically. Chromaticity and concentrations of sulfate ions were also high. The study (Kolotov et al., 2021) revealed an increase in the content of heavy metals in the splash zone of this area.

Data obtained in our work also demonstrate that the groundwater flow contains high concentrations of pollutants (Fig. 6) that were going on entering the lake. For instance, in 2013, the sulfates in the water at the shoreline next to the BPPM site were three times as high as the typical Baikal water values: 14.4 mg L⁻¹ vs. \sim 5.5 mg L⁻¹ (Khodzher et al., 2017). The influence of this runoff on the interstitial waters of the beach was quite remarkable: the hydrochemical parameters in the interstitial rarely differed from the "warm brook". Particularly, the changes in the oxygen concentration were obvious, while it is vital for oxyphilous Baikal dwellers. The crucial role of the dissolved oxygen concentration for abundant endemic species of the upper littoral zone of the lake has been already established by several studies (Zaitseva et al., 2008; Timofeyev and Shatilina, 2010).

Needless to say, the effects on the shallow-water hydrobionts are far from extreme as the water of the "warm brook" entering the littoral zone is strongly diluted by the lake waters. However, we have solid grounds for suspecting local negative effects on the beach interstitial. A low concentration of oxygen from the "warm brook" water accompanied by an increase in organic matter content can lead to a drop of the oxygen concentration to zero, as registered in 2014 (Fig. 6). Though some inhabitants of the splash zone may be tolerant to hypoxia (Zvereva et al., 2015), the nearcomplete absence of dissolved oxygen is highly stressful for its biota (Medvezhonkova et al., 2018).

3.3. Depositions on the stones forming the target beach

Besides the other phenomena that are abnormal for the pristine shores of Lake Baikal, we discovered specific depositions covering the beach boulders and pebbles. In 2013, we localized a relatively large zone of the beach (Fig. 4), where each stone had a black slimy ring-like stripe (Fig. 8). This substance from the stones was collected to be analyzed by FTIR spectroscopy. We compared the obtained results to the spectra of the pulp production wastes as untreated sludge-lignin and a dry solid residue of the plant wastewaters (Fig. 9). It was revealed that the IR spectrum of the black depositions and the spectra of the BPPM sludge-lignin were identical (Fig. 9), which enabled us to ascertain the origin of the substance from the beach stones. Finding lignin on the beach suggests the contamination of the lake, but we can only speculate about the source of the pollution. Theoretically, the surface runoff formed by the atmospheric precipitations may carry out solid residues from the BPPM's waste pits to the shore.

Lignin is a high-molecular aromatic compound, decomposition of which produces toxic the low-molecular substances: phenols, methanol, and carbon acids. Lignin produced through a sulfate pulping (sulfate lignin) harms hydrobionts when its concentration in water is higher than 100 mg L⁻¹ (Kalinkina, 1993). Moreover, lignin is highly resistant to degradation, which leads to its accumulation in water in a concentration that becomes hazardous to aquatic organisms (Kalinkina, 1993). For instance, the structural changes in the lake's macrozoobenthic communities were most evident on the sediments with a layer of black pulp flakes and slime residues (Productivnost Baikala..., 1974). Long-term studies of Chironomidae taxocenosis in the Utulik-Murino region revealed a biodiversity decline on such highly polluted sediments and the appearance of eutrophication indicating species (Erbaeva and Safronov, 2010).

Concerning the lignin input, the authors of this paper came across an interesting phenomenon in this coastal area – a high population density of earthworms (Annelida, Oligochaeta, Lumbricidae) in the splash zone of the target beach (Table 2). Earthworms are typical inhabitants of soil and forest litter, with an extraordinary contribution to soil formation and functioning. It is noteworthy that the number of these oligochaetes is rarely above 1 ind. m⁻² in the splash zone of Bolshie Koty Bay (Zvereva et al., 2012), whereas we observed up to 15 ind. m⁻² in the splash zone of the beach next to the BPPM in 2013 (Table 2).

Lignin contamination of this area appears to be one of the possible reasons for the observed abundance of earthworms on this beach. The earthworms alone are not able to decompose either lignin or pulp (Marhan and Scheu, 2006). Fungi and bacteria are the primary lignin destructors (Buswell et al., 1987). There is evidence that soil communities of microorganisms change their structure under the lignin contamination: yeast and micromycetes begin to dominate (Zyrianova, 2003). Apparently, lignin affects the number of Lumbricidae indirectly: changes in the community composition of microorganisms and fungi may attract earthworms there.



Fig.8. Boulders and pebbles with abnormal black depositions. The beach next to the BPPM site (May 31, 2013).



3900 3700 3500 3300 3100 2900 2700 2500 2300 2100 1900 1700 1500 1300 1100 900 700 500 **v, cm**⁻¹

Fig.9. FTIR spectroscopy analysis of the depositions on the stones from the beach next to the BPPM site compared to the data on pulp production wastes. (A) Acid-precipitated alkaline washout from a stone. (B), (D) Untreated sludge-lignin. (C) Dry residue of the BPPM wastewaters.

4. Conclusions

The results of our research during 2013–2016 revealed a few facts that allowed us to conclude that even after its closure, the BPPM was threatening Lake Baikal. We hypothesized this influence includes the pollution of the groundwater via drainage flows and surface runoff with precipitation. As a result, we observed the rise of the interstitial water temperature, oxygen deficit, high concentration of pollution tracers compounds (sulfur, sodium, chlorine), and the presence of lignin on the beach adjacent to the plant – all these factors can cause alterations in the thermal and chemical regime of the coastal zone. These drastic fluctuations of

Table 2. The number of earthworms (Annelida, Oligochaeta, Lumbricidae) in the splash zone of the beach next to the BPPM site (2013–2016).

Sampling date	May 31, 2013	June 11, 2014	June 13, 2015	June 12, 2016
Number, ind. m ⁻²	15 ± 2	6 ± 2	4 ± 1	2 ± 1

environmental factors could affect the biota inhabiting the beach and shallow-water parts of the lake. The present investigation is one more argument in favor of the urgent need for adequate management and recycling of the BPPM wastes, the intrusion of which into the lake might lead to a massive ecological disaster in the future. The authors believe the findings will serve not only as a baseline for the risk assessment but an impetus for the regional and federal government of the Russian Federation to determine emergency actions for the BPPM wastes elimination and its site active remediation.

Acknowledgements

We gratefully thank Lukhnev A., Potapskaya N., and Dambinov Yu. (Laboratory of Aquatic Invertebrate Biology and Laboratory of Biogeochemistry of Limnological Institute SB RAS) for the fieldwork assistance; Sakirko M. and other members of Laboratory of Hydrochemistry and Atmosphere Chemistry (Limnological Institute SB RAS) for the sampling and chemical analyses; and the members of the Laboratory of Biomolecular Systems (Limnological Institute SB RAS) for the FTIR spectroscopy analyses. This study was supported by the Siberian Branch of the Russian Academy of Sciences (State Project No. 0279-2021-0007, supervised by Prof. Timoshkin O.).

Conflict of interest

The authors declare no conflict of interest.

References

Anikanova M.N. 2009. Soedineniya sery stochnykh vod Baikalskogo tsellyulozno-bumazhnogo kombinata (sostav, metody, analizy, monitoring) [Sulfur compounds of waste waters of the Baikal Pulp and Paper Mill (composition, methods, analyzes, monitoring)]. Moscow: Nauchniy mir. (in Russian) URL: <u>https://www.rfbr.ru/rffi/portal/ books/o 26044</u>

Bezmaternykh D.M. 2009. Vodnyie ekosistemy: sostav, struktura, funktsionirovanie i ispolzovanie [Aquatic ecosystems: composition, structure, functioning, and use]. Barnaul: Altai State University. (in Russian)

Boeva L.V. 2009. Rukovodstvo po khimicheskomu analizu poverkhnostnykh vod sushi [Manual for the chemical analysis of surface waters]. Rostov-na-Donu: NOK. (in Russian)

Buswell J.A., Odier E., Kirk T.K. 1987. Lignin biodegradation. Critical Reviews in Biotechnology 6: 1-60. DOI: 10.3109/07388558709086984

Erbaeva E.A., Safronov G.P. 2010. Chironomides of soft sediments of Utulik–Murino site (Southern Baikal) influenced of Baikalsk Pulp and Paper Combine (BPPC). Long-term analysis (1975–2004). Izvestiya Irkutskogo Gosudarstvennogo Universiteta. Seriya: Biologiya, Ecologiya [Bulletin of Irkutsk State University. Series: Biology, Ecology] 3: 12-22. (in Russian) URL: <u>https://elibrary.ru/item.asp?id = 15131401</u>

Ermolina T.V., Aizenshtadt A.M., Bogdanov M.V. et al. 2011. Integral indices of surface water quality in operating zone of pulp-and-paper mill based on example of the Northern Dvina (in Russian). Lesnoy Zhurnal [Russian Forestry Journal] 5: 83-88. (in Russian) URL: <u>http://lesnoizhurnal.ru/</u>

apxiv/2011/%E2%84%965-2011.pdf

Fediaeva O.A. 2007. Promyshlennaya ecologiya: konspekt lektsiy [Industrial ecology: the lectures notes]. Omsk: Omsk State Technical University. (in Russian)

Fomin G.S. 2000. Water. Kontrol khimicheskoy, bakterialnoyiradiatsionnoybezopasnostipomezhdunarodnym standartam [Inspection of chemical, bacteriological, and radiation safety according to international standards: an encyclopedic reference book]. Moscow: Protektor. (in Russian)

Gavrilescu D., Puitel A.C., Dutuc G. et al. 2012. Environmental impact of pulp and paper mills. Environmental Engineering and Management Journal 11: 81-85. DOI: <u>10.30638/eemj.2012.012</u>

Grachev M.A. 2002. O sovremennom sostoyanii ekologicheskoy sistemy ozera Baikal [On the current state of Lake Baikal ecosystem]. Novosibirsk: SB RAS. (in Russian)

Kalinkina N.M. 1993. Ecologo-toxikologicheskaya otsenka opasnosti sulfatnogo lignina dlya gidrobiontov [Ecological and toxicological assessment of the hazard of sulfate lignin for the aquatic organisms]. Cand. Sc. Dissertation, Institute of Inland Waters RAS, St. Petersburg, Russia. (in Russian) URL: http://elibrary.krc.karelia.ru/218/

Khodzher T.V., Domysheva V.M., Sorokovikova L.M. et al. 2016. Methods for monitoring the chemical composition of Lake Baikal Water. In: Mueller L., Sheudshen A.K., Eulenstein F. (Eds.), Novel methods for monitoring and managing land and water resources in Siberia. Springer Water, pp. 113-132. DOI: <u>10.1007/978-3-319-24409-9 3</u>

Khodzher T.V., Domysheva V.M., Sorokovikova L.M. et al. 2017. Current chemical composition of Lake Baikal water. Inland Waters 7: 250-258. DOI: 10.1080/20442041.2017.1329982

Kolotov A.A., Rikhvanova M.P., Simonov E.A. et al. 2021. Ob'ekt nakoplennogo ekologicheskogo vreda (Baikalskiy TsBK) [The object of accumulated environmental damage (Baikal PPM)]. (in Russian) URL: <u>https://bellona.ru/</u> <u>publication/2021-bcbk/</u> (accessed on Oct 26, 2021)

Konstantinov A.S. 1986. Obschaya gidrobiologiya [General hydrobiology]. Moscow: Vysshaya shkola. (in Russian)

Kravtsova L.S., Izhboldina L.A., Khanaev I.V. et al. 2014. Nearshore benthic blooms of filamentous green algae in Lake Baikal. Journal of Great Lakes Research 40: 441-448. DOI: 10.1016/j.jglr.2014.02.019

Lake Baikal – evolution and biodiversity. 1998. In: Kozhova O.M., Izmest'eva L.R. (Eds.). Leiden: Backhuys Publishers.

Laperdin V.K., Levi K.G., Imaev V.S. et al. 2016. Geological hazards of the southwestern Baikal region. Irkutsk: Institute of the Earth's Crust SB RAS. (in Russian) URL: <u>https://www.elibrary.ru/item.asp?id = 27234805</u>

Marhan S., Scheu S. 2006. Mixing of different mineral soil layers by endogeic earthworms affects carbon and nitrogen mineralization. Biology and Fertility of Soils 42: 308-314. DOI: 10.1007/s00374-005-0028-7

Medvezhonkova O.V., Zvereva Yu.M., Poberezhnaya A.E. et al. 2018. Impact of beached algae on psammon development in the North basin of Lake Baikal. In: International Conference "Freshwater Ecosystems – Key Problems", p. 237.

Moiseeva E.A. 2005. Ekologo-toxikologicheskaya otsenka vliyaniya stochnykh vod tsellyulozno-bumazhnogo proizvodstva na vodnyie organismy (po analizu raboty Segezhskogo TsBK) [Ecological and toxicological assessment of the impact of pulp and paper production wastewater on aquatic organisms (based on the analysis of the Segezha PPM)]. Cand. Sc. Dissertation, Petrozavodsk State University, Petrozavodsk, Russia. (in Russian) URL: <u>https://static.</u> <u>freereferats.ru/ avtoreferats/01002853758.pdf</u> O probleme likvidatsii nakoplennykh otkhodov v resultate deiatelnosti Baikalskogo TsBK [On the problem of elimination of the wastes accumulated during the operation of the Baikalsk PPM]. 2009. In: Interdepartmental Commission for the Protection of Lake Baikal, Information and analytical materials. Moscow-Irkutsk: Russian Federal Geological Foundation, Siberian Branch of "Rosgeolfond". (in Russian) URL: <u>http://geol.irk.ru/baikal/law/mlawmcom/deyatelnostkomissii/informatsionno-analiticheskie-materialy-27052009</u> (accessed on Jan 20, 2021)

Obolkin V., Khodzher T., Sorokovikova L. et al. 2016. Effect of long-range transport of sulphur and nitrogen oxides from large coal power plants on acidification of river waters in the Baikal region, East Siberia. International Journal of Environmental Studies 73: 452-461. DOI: 10.1080/00207233.2016.1165481

Obolkin V.A., Potemkin V.L., Khodzher T.V. et al. 2010. Dynamics of sulfur-containing admixtures in the atmosphere around the point source – the Baikal Pulp and Paper Plant (south-east of Baikal Lake). Atmospheric and Oceanic Optics 23: 32-38. URL: <u>https://www.elibrary.ru/item.</u> <u>asp?id = 26953792</u>

Potemkina T.G., Potemkin V.L., Kotsar O.V. et al. 2018. Climate factors as a possible trigger of modern ecological changes in shallow zone of Lake Baikal. International Journal of Environmental Studies 75: 86-98. DOI: 10.1080/00207233.2017.1406727

Produktivnost Baikala i antropogennye izmeneniya ego prirody [Productivity of Lake Baikal and its anthropogenic changes]. 1974. In: Kozhova O.M. (Ed.). Irkutsk: Irkutsk State University. (in Russian)

Russian Timber Industry. 2021. URL: <u>https://</u> programlesprom.ru/en/ (accessed on Oct 26, 2021)

Simonov E., Kreyndlin M., Ivanov A. et al. 2022. Lake Baikal in crisis. In: DellaSala D.A., Goldstein M.I. (Eds.), Imperiled: the encyclopedia of conservation. Oxford, pp. 389-408. DOI: <u>10.1016/B978-0-12-821139-7.00055-6</u>

Suturin A.N., Goncharova A.I., Dambinov Yu.A. 2015. Rekultivatsiya kart-shlamonakopiteley Baikalskogo TsBK [Remediation of waste pits of the Baikal Pulp and Paper Mill]. Tsellyuloza Bumaga Karton [Pulp Paper Board] 6: 2-4. (in Russian)

Suturin A., Goncharov A., Dambinov Yu. et al. 2021. Remediation of the Solzan industrial waste landfill at the Baikal Pulp and Paper Mill (BPPM). Ecologiya i Promyshlennost' Rossii [Ecology and Industry of Russia] 25: 41-47. (in Russian) DOI: <u>10.18412/1816-0395-2021-2-41-47</u>

Timakova T.M., Kulikova T.P., Litvinova I.A. et al. 2014. Changes in biocenoses of Kondopoga Bay, Lake Onego, under the effect of effluents from a pulp and paper mill. Water Resources 41: 78-86. DOI: <u>10.1134/S0097807814010126</u>

Timofeyev M., Shatilina Z. 2007. Different preference reactions of three Lake Baikal endemic amphipods to temperature and oxygen are correlated with symbiotic life. Crustaceana 80: 129-138. URL: <u>https://www.jstor.org/stable/20107791</u>

Timofeyev M.A., Shatilina Zh.M. 2010. Detection of oxygen- and pH-preferences in some endemic and Palearctic species of Baikalian amphipods. Amurskiy zoologicheskiy zhurnal [Amurian Zoological Journal] 2: 3-8. (in Russian) URL: <u>https://azjournal.ru/index.php/azjournal/article/view/103</u>

Timoshkin O.A., Bondarenko N.A., Kulikova N.N. et al. 2019. Protection of Lake Baikal requires more stringent, not more lenient, environmental regulation. Journal of Great Lakes Research 45: 401-402. DOI: 10.1016/j.jglr.2019.04.002

Timoshkin O.A., Malnik V.V., Sakirko M.V. et al. 2014. Ecological crisis on Lake Baikal: diagnosed by scientists. Science First Hand 5: 75-91. URL: <u>http://lin.irk.ru/pdf/12841.pdf</u>

Timoshkin O.A., Medvezhonkova O.V., Troitskaya E.S. et al. 2017. Water temperature dynamics in the coastal zone of Lake Baikal (western side of the southern basin). URL: <u>http://lin.irk.ru/temperature/web/index.</u> php?r=site%2Findex&lang=en (accessed on Mar 15, 2022)

Timoshkin O.A., Moore M.V., Kulikova N.N. et al. 2018. Groundwater contamination by sewage causes benthic algal outbreaks in the littoral zone of Lake Baikal (East Siberia). Journal of Great Lakes Research 44(2): 230-244. DOI: 10.1016/j.jglr.2018.01.008

Timoshkin O.A., Suturin A.N., Bondarenko N.A. et al. 2012. Introduction into biology of the coastal zone of Lake Baikal. 1. Splash zone: first results of interdisciplinary investigations and its role for the lake ecosystem monitoring. Izvestiya Irkutskogo Gosudarstvennogo Universiteta. Seriya: Biologiya, Ecologiya [Bulletin of Irkutsk State University. Series: Biology, Ecology] 5: 33-46. URL: <u>https://izvestiabio. isu.ru/ru/article/file?id = 260</u>

Tiranov P.P. 1997. Method for production of alkali lignine (patent No. RU19930052838 19931122). URL: https://worldwide.espacenet.com/publicationDetails/ biblio?FT = D&date = 19970227&DB = &locale = en EP&CC = RU&NR = 2074189C1&KC = C1&ND = 4 (accessed on Dec 3, 2020) URL: https://www.elibrary.ru/item. asp?id = 11032386

Vadeboncoeur Y., Moore M.V., Stewart S.D. et al. 2021. Blue waters, green bottoms: benthic filamentous algal blooms are an emerging threat to clear lakes worldwide. BioScience 71: 1011-1027. DOI: <u>10.1093/biosci/biab049</u>

Zaitseva E.P., Mizandrontsev I.B., Yuma M. et al. 2008. The first data on respiration of mass shallow-water triclad species (*Turbellaria*) from Lake Baikal and water bodies of its basin. Russian Journal of Zoology 87: 771-778. (in Russian)

Zvereva Yu.M., Mizandrontsev I.B., Zaytseva Ye.P., Timoshkin O.A. 2015. Respiration of aquatic oligochaetes (Annelida, Oligochaeta) and peculiarities of oxygen uptake by endemic Enchytraeidae of Lake Baikal. Hydrobiological Journal 51: 14-24. DOI: <u>10.1615/HydrobJ.v51.i5.20</u>

Zvereva Yu.M., Timoshkin O.A., Zaitseva E.P. et al. 2012. Ecological characteristics of *Mesenchytraeus bungei* (Annelida, Oligochaeta) – dominant oligochaete species from the splash zone of Lake Baikal (in Russian). Izvestiya Irkutskogo Gosudarstvennogo Universiteta. Seriya: Biologiya, Ecologiya [Bulletin of Irkutsk State University. Series: Biology, Ecology] 5: 123-135. (in Russian) URL: <u>https://izvestiabio.isu.ru/ru/ article?id=258</u>

Zyrianova N.V. 2003. Soil microbial associations and their interaction with lignin substances from the pulp and paper industry wastewaters. Cand. Sc. Dissertation, Irkutsk State University, Irkutsk, Russia. (in Russian) URL: <u>https://static.freereferats.ru/_avtoreferats/01002616566.pdf</u>