

Comparison of the Presence of Chemical and Biomarkers in the Surface Microlayer in Water Areas of Health Resort Zones of Lake Baikal and in Atmospheric Aerosol of This Region

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Abstract—The search for the chemical and biomarkers of aerosol originating from the surface microlayer (SML) of water areas of health resort zones at Lake Baikal was performed. The concentrations of Ca, Mg, Na, K, Cu, Zn, Fe, Mn, Al, Ba, Pb, Cd, As, naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, perilene, benz (b) fluoranthene, benz(a)pyrene, 1,2,5,6-dibenz anthracene, benz(ghi)perilene, and total protein in aerosols and water samples collected from the region were experimentally studied. A direct close interrelation was revealed between the concentrations of all chemical elements in aerosol and water samples. The highest concentrations were recorded for Ca, Mg, Na, and K. A polymerase chain reaction method was employed to determine the similar interrelation between the genetic materials of microorganisms (bacterioplankton) found in water and aerosol. A completely adequate marker reflecting the presence of aerosol generated by SML of Lake Baikal water was not found.

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INTRODUCTION

The quality of atmospheric air is determined by the presence of dangerous gas and aerosol pollutants. The methods for air quality estimation based on sanitary criteria are sufficiently developed, while the situation for aerosol pollution is less determined. The point is that, first, there are different natural and anthropogenic sources of aerosols, and, hence, they have different components and chemical compositions. Aerosols from different sources are present in the atmosphere simultaneously. Second, atmospheric aerosols are unstable formations. Various physical and chemical processes run in aerosols under the action of temperature, humidity, and radiation, which result in the formation of new components, chemical compounds, a change in the disperse composition, and particle concentration. Third, aerosols, even produced by one source, are often multicomponent systems, and each of them carries various toxic substances differing in bioaccessibility for the human body.

The same concentrations of toxic substances in aerosol can produce different organism reactions. The degree and character of the human response to toxic substance impact essentially diminish after a decrease in the emissions from the sources mainly contributing to regional aerosol pollution. To estimate the contri-

bution of aerosol from a specific source to the observed concentrations of toxic substances, it is necessary to have the possibility to assess an aerosol fraction just from this source in the total aerosol composition by some markers.

Aerosol sources are local and distant for the Baikal region, as for any other object. The element composition of atmospheric aerosol, originating from different natural sources, reflects their element compositions (the Earth's crust, soil, sea and fresh water, vegetation, and anthropogenic pollutions). Thus, atmospheric aerosols near a powerful source carry a clearly pronounced "imprint" of the chemical composition of the source [1–3]. There are elements in these aerosols which are present in the chemical composition of a powerful source in the largest amounts [4–7]; therefore, a comparison of pollutants in atmospheric aerosol with those in different sources allows for the recognition of these sources.

In this work, we focus on water sources; the most powerful among them is a lake surface.

The most informative methods for recognizing the source of "clear" atmospheric aerosol and, hence, revealing its pollutants, is the analysis of its element composition [8]. The most frequent elements are

Table 1. Periods and routes of atmospheric aerosol sampling over the region and water area of Lake Baikal

Date	Time (GMT)	Sample	Height, m (above s.l.)	Route
July 25, 2008	1:26–2:20	Bxa 1–2	4500	Bratsk—source of the Lena River
	2:26–2:36	Bxa 3–4	600	Cape Rytyi—Cape Elokhin
	2:38–2:50	Bxa 5–6	600	Cape Bolshoi Cheremshannyi—Cape Kotel'nikovskii
	2:52–3:09	Bxa 7–8	600	Cape Kotel'nikovskii—Nizhneangarsk—Yarki Island
	3:10–3:15	Bxa 9–10	600	Entry of Upper Angara—Khanusy
	3:16–3:26	Bxa 11–12	800	Khanusy—Cape Pogoni
	3:32–3:47	Bxa 13–14	950	Traverses at a distance of 100 km to the south from Nizhneangarsk
	3:53–4:06	Bxa 15–16	950	Traverses at a distance of 150 km to the south from Nizhneangarsk
	4:08–4:18	Bxa 17–18	1200	Traverses near the Svyatoi Nos Peninsula
	4:25–4:39	Bxa 19–20	1200	Traverses opposite to Ol'khon Island
July 28, 2008	4:41–4:53	Bxa 21–22	1200	Along the Ol'khon Island to the north to Cape Rytyi
	5:11–5:46	Bxa 23–24	4800	Source of the Lena River—Bratsk
	0:44–1:18	Bxa 25–26	4500	Bratsk—Verkholsk
	1:20–1:35	Bxa 27–28	4500	Verkholsk—source of the Lena River
	1:43–2:06	Bxa 29–30	600	To the south from Cape Rytyi to Cape Krestovskii
	2:08–2:25	Bxa 31–32	600	Cape Krestovskii—Bol'shoe Goloustnoe
	2:31–2:49	Bxa 33–34	600	Traverse to Boyarskii Peninsula, traverse pass of the entry of the Selenga River to the Novyi Enkheluk and Sukhaya villages
	2:51–3:04	Bxa 35–36	800	Traverses the Cykhaya village—Ol'khonskie Vorota Strait—Cape Tonkii
	3:08–3:26	Bxa 41–42	800	Traverses Cape Tonky—Cape Ukhan—Gremyachinsk—Cape Izhimey
	3:28–3:39	Bxa 43–44	800	Along the Ol'khon Island to Cape Rytyni
	3:52–4:14	Bxa 45–46	4800	Source of the Lena River—Verkholsk
	4:16–5:03	Bxa 47–48	5400	Verkholsk—Bratsk

present in both aerosol and its source in virtually invariable ratios, but other elements essentially vary [8].

A wide spectrum of organic compounds and various microorganisms, including bacterioplankton, are present in water, along with inorganic compounds. The presence of genetic materials of microorganisms in aerosol can serve as a biocenosis marker characteristic for a place. However, the most characteristic marker of any biological presence is the presence of protein. This allows for the use of the total protein concentration in a sample as an integral marker of microorganisms.

This work is devoted to revealing and comparing the chemical and biomarkers in the SML of water areas of health resort Baikal zones and in atmospheric aerosol of this region, which could serve as a marker of aerosol of water origin.

MATERIALS AND METHODS

Sampling was carried out on the territory of three health resort Baikal zones: near the Listvyanka village, Sakhurta village, and Peschanaya bay. The layout was the same for all experiments. Three sampling points were located on the shore near the water edge at a dis-

tance of about 100 m from each other. The fourth point was windward located onboard the research ship *German Titov* [ital] at a distance of not less than 700 m from the central shore point. The coordinates of the central points were determined using a GPS navigator: 51°50' 31.2"N, 104°52' 42.6"E for Listvyanka village; 53°01' 03.7"N, 106°53' 14.9"E for Sakhurta village; and 52°15' 41.8"N, 105°42' 23.7"E for Peschanaya bay. In addition, air sampling was carried out from onboard an AN 30D aircraft (aircraft laboratory Optik-E [9–11]). The parameters of the flight routes (altitudes, time, and time intervals) are given in Table 1.

The following equipment was mounted in the central shore point:

—Solair 3100+ photoelectric counter of aerosol particles to determine the concentrations and disperse composition of atmospheric aerosol larger than 0.3–25 μm ;

—BP-35/25-4 (Kirishi) 5-step impactor to determine the mass distribution of aerosol particles over size within the 0.5- to 100- μm range and recognize the presence of toxic substances in different size fractions (sampling was carried out on F-Kh-20 filters provid-

ing for sedimentation of more than 99.99% of particles of 10 nm to 100 μm in size);

—three self-contained PVR-50 (vacuum pump) samplers with a volume flow of 50 l/min (sampling was carried out on F-Kh -20 filters) to analyze the concentrations of total protein and multiring benzene hydrocarbons (MBH), the element composition, and the presence of DNA of bacterioplankton genetic materials;

—IVA-6A thermohygrometer to measure air temperature and relative humidity;

—TKA-PKM/50 heat-loss anemometer to measure windspeed.

Similar PVR-50 self-contained samplers were mounted on the ship. In addition, water sampling from SML of up to 200 and 1000 μm in depth was carried out from onboard the ship using bathometers. The basis of the bathometer was brass gauze strained onto a metal chromium frame. The gauze was made of wire 0.2 mm in diameter. The sampling technique is described in [12, 13] in detail. We sampled 30 ml of water film for every layer and used them for biological and element analysis and the determination of concentrations of total protein and MBH.

Air sampling on F-Kh -20 filters was carried out from onboard the AN 30D aircraft [9–11] for biological and element analysis and the determination of total protein and MBH with the purpose of accounting for the mass transfer of pollutants from the lake water and arriving at the territory of a health resort zone from other regions.

Concentrations of chemical elements (Ca, Mg, Na, K, Cu, Zn, Fe, Mn, Al, Ba, Pb, Cd, and As) in samples were determined by the atomic absorptive technique using an AA-6300 spectrometer (Shimadzu corporation) with plasma and thermal-electric sprayers.

The total protein in samples was determined by fluorescence analysis using a reagent according to the technique in [14] and a Shimadzu RF-520 spectrofluorimeter. The technique sensitivity was 0.01 $\mu\text{g}/\text{ml}$ with a relative error of less than 20%. The fluorescence of total protein and some MBH is in the same wavelength range. To take into account the system measurement error, we subtracted the independently determined value referring to MBH from the total fluorescence [15].

The concentration of multiring benzene hydrocarbons (MBH) in samples of atmospheric air and water SML was determined by the high-performance liquid chromatography technique [15] using a Spectra Physics SP8800 liquid chromatograph with Shimadzu RF-530 fluorescence and Spectra 100 spectrophotometric detectors.

The genetic materials of heterotrophic bacterioplankton in samples were found with the help of polymerase chain reaction (PCR). The nucleotide sequence of the gene coding for the 16S RNA was used as a target for primers selection in PCR. The use of unique specific

primers consisting of 22–25 nucleotides provided for the high specificity and sensitivity of the technique (less than 10 microorganisms by their RNA or DNA fragments) [16]. For this, we analyzed nucleotide sequences of this gene in different cultures of α , β , and γ proteobacteria present in the GenBank database.

The primers described in [17] in detail were used to reveal conserved regions in the gene coding for the 16S RNA. Finally, nucleotide sequences of primers were chosen using the OLIGO software with accounting for recent data on proteobacteria sequences. F27 and R1387 primers were synthesized at the Natural Compounds Chemistry Department of the Vector State Research Center of Virology and Biotechnology. A band in agarose gel, fluorescent in the presence of ethidium bromide and corresponding to an amplifier length in 1360 pairs of nucleotides, proved the presence of genetic materials of proteobacteria in the samples under study. This pair of primers was then used for further identification of a revealed microorganism by sequence analysis of amplifier fragments.

Water samples 10 ml in volume were filtered through nitrocellulose filters with pores 22 μm in diameter (Millipore, USA). Again, the filters were crumbled up and placed into test tubes with a lysing buffer based on 6 M guanidinisothiocyanate. The lysing solution contained 18 g of guanidinisothiocyanate (6 M), 95 mg of dithiothreitol (0.2 M), and 1 ml of EDTA (0.5 M), pH 8.0. Filters with aerosol samples were processed similarly. The contents of the test tubes were carefully shaken during 30 min at regular intervals. The total nucleotide material, including genomic DNA and RNA, was evolved from the lysing buffer with the Litek kit (Russia) according to the enclosed instruction. Then, either Rt-PCR or PCR was carried out with the use of ribosomal RNA or genomic DNA, respectively, as a matrix. The PCR was carried out in a buffer with components produced by SibEnsim (Russia) excluding primers. The reaction program was the following:

94°C, 4 min, one cycle;

94°C, 60 s; 50°C, 40 s; 72°C, 40 s; 30 cycles; and

72°C, 7 min, one cycle.

Products of Rt-PCR or PCR were analyzed in 1% agarose gel.

Nucleotide sequences of distinguished genome fragments of bacteria “pure lines” were determined by the modified technique described in [18] with a Hitachi Applied Biosystems 3130xl autosequencer using an AB1 Prism Big Dye Terminator V3.1 Cycle kit. Purified amplifiers corresponding to individual organisms were used as a matrix in the sequencing. The AS program was used for alignment [19].

Phylogenetic analysis was carried out with the help of the MEGA3 software (by the NJ Neighbor-Joining method) [20].

Bacteria were isolated and cultured in the following way. After SML sampling, depth inoculation was per-

Table 2. Average values* of hydrometeorological parameters measured while sampling atmospheric air and water SML at Lake Baikal

Sampling site	Relative humidity, %	Air temperature, °C	Average wind velocity	Wind velocity, m/s	Air pressure, mm Hg	Water temperature, °C	Air temperature above the water surface
Listvyanka village	57 ± 4	14.8 ± 0.7	S–W	2.8 ± 1.0	720	15	13
Sakhyurta village	57 ± 3	14.4 ± 1.5	N	1.3 ± 0.4	718	14.5	16
Peschanaya Bay	51 ± 5	14.0 ± 1.7	N–W	4.9 ± 1.1	712	12	11

* ± – rms deviation from mean in the columns where it was calculated.

Table 3. Characteristics of aerosol particles in air of different parts of Lake Baikal

Sampling site and time	D_{50} , μm	σ_g	Aerosol concentration, particles/ m^3	Aerosol concentration, $\mu\text{g}/\text{m}^3$
Listvyanka village, August 22, 2008 16:48–20:00	0.3*	1.3*	8–13	1.5
Sakhyurta village, August 23, 2008 07:55–10:57	0.3*	1.3*	38–67	2.5
Peschanaya Bay, August 24, 2008 06:37–09:39	0.3*	1.3*	32–40	3.2
Height samples (600–1000 m), July 25 and 28, 2008	0.6	2.0–2.9	5–13	0.01–0.12

* Estimates with accounting for particles less than 0.3 μm in diameter.

formed for 1 ml of water in 1 : 10 and 1 : 100 dilutions. Organotrophic bacteria were cultured on 1 : 10 diluted fish-peptone agar (FPA : 10) at room temperature; psychrotolerant ones, at a temperature of 4°C on R₂A medium (Becton Dickinson, USA), g/l: 0.5 g of yeastrel, 0.5 g of peptone, 0.5 g of casamino acids, 0.5 g of dextrose, 0.5 g of soluble starch, 0.3 g of sodium pyruvate, 0.3 g of dipotassium phosphate, 0.05 g of magnesium sulfate, and 15 g of agar. Different bacteria cultures were isolated by the exhaustive inoculation method after calculating all full-grown clumps.

To calculate the total bacterium population, the samples were fixed by glutaraldehyde added to a final concentration of 1%. Microorganisms in a water SML sample (20 ml) were stained with fluorochromic DAPI dye (4,6-diamino-2-phenylindole) to a 0.5 $\mu\text{g}/\text{ml}$ concentration, filtered through a Nuclepore (PC) 0.2 μm in pore diameter, and examined under an Olympus (Japan) epifluorescent microscope. Cells were calculated using the bundled software developed at the Limnological Institute, Siberian Branch, Russia Academy of Sciences (certificate of authorship No. 2005610667).

RESULTS AND DISCUSSION

Hydrometeorological and hydrochemical monitoring data obtained while sampling atmospheric air and water SML at Lake Baikal are given in Table 2.

The aerosol concentration and disperse composition were determined according to the above-described techniques. Data for the aerosol fraction

with particles larger than 0.3 μm in diameter are given in Table 3. It follows from data analysis that particles larger than 10 μm in diameter are virtually absent in the air of the health resort Baikal zones; the main particle mass is concentrated within a range of less than 1 μm ; the integrated particle mass is small. The mass aerosol concentration is about 3 $\mu\text{g}/\text{m}^3$ in Sakhyurta village and Peschanaya Bay and is 1.5 $\mu\text{g}/\text{m}^3$ in Listvyanka village, which is ten times smaller than the usually recorded atmospheric aerosol concentrations [21, 22].

It was impossible to determine quantitatively the mass distribution of aerosol particles over size due to the smallness of mass aerosol concentrations in the air of the health resort zones.

It is shown that the health resort Baikal zones are quite clear. In particular, the aerosol concentration in the air of near-shore zones did not exceed several tens of particles (cm^3) in the period under study (see Table 3). At that, the main number of particles was in the 0.3- to 0.5- μm range of optical diameters; hence, the total aerosol mass did not exceed 3 $\mu\text{g}/\text{m}^3$.

Tables 4–6 present the data on concentrations of various *chemical elements*, determined by the high-performance liquid chromatography technique [15], in the samples collected around the health resort Baikal zones. The last rows of Tables 4 and 5 contain values of 0.1 MCL of the working zone air taken from normative documentation GN 2.2.5.1313-03.

Some chemical elements were detected in aerosol particles; these elements are the most significant for referencing the aerosol particles containing them to one or another type of sources [1–3]. Analyzing the

Table 4. Concentrations of some chemical elements in air samples above Lake Baikal (sample number corresponds to Table 1)

No. of sample (filter)	Element concentration in air, $\mu\text{g}/\text{m}^3$												
	Ca	Mg	Na	K	Cu	Zn	Fe	Mn	Al	Ba	Pb	Cd	As
2	0.26	0.09	0.07	0.02	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
4	0.23	0.08	0.10	0.04	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
6	0.41	0.12	0.10	0.04	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
8	0.29	0.11	0.09	0.03	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
10	0.45	0.13	0.12	0.04	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
12	0.41	0.12	0.10	0.03	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
14	0.37	0.12	0.09	0.03	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
16	0.36	0.11	0.10	0.03	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
18	0.40	0.08	0.10	0.03	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
20	0.43	0.10	0.03	0.04	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
22	0.05	0.03	0.04	0.04	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
24	0.09	0.04	0.05	0.03	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
26	0.01	0.03	0.05	0.04	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
28	0.10	0.01	0.04	0.04	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
30	0.07	0.03	0.08	0.03	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
32	0.05	0.02	0.04	0.03	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
34	0.03	0.03	0.04	0.03	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
36	0.33	0.05	0.06	0.03	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
42	0.21	0.04	0.05	0.03	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
44	0.45	0.03	0.03	0.03	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
46	0.15	0.02	0.03	0.02	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
48	0.65	0.01	0.01	0.01	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
0.01 MCL	10	100	2*	10	10	1*	100	10	20	15*	0.5	0.5	0.4
According to data [46]	0.55	0.35	0.4	0.2	0.25	0.15	0.55	0.8	1.1	<0.1	<0.1	n/a	n/a

* The value is given for the most toxic compounds of the metal.

Note: n/a, not available.

data from Tables 4–6, we can see that Ca, Mg, Na, and K are present in SML in water areas of the health resort Baikal zones in the highest quantities as compared with other chemical elements under control, which are in much lower quantities. Ca, Mg, Na, and K are present in the highest concentrations in atmospheric aerosol samples collected several meters from the lakeside, as well as at heights of 600–900 m above the lake surface. The elements, the concentrations of which in SML of water areas of the health resort Baikal zones are lower, have aerosol concentrations lower than the limit of their detection. Thus, the atmospheric aerosol of these zones and the SML of their water areas have similar element compositions.

The SML of water areas is the water–atmosphere interface. Aerosol is formed here due to the breakup of air bubbles at the interface [23–27]. The physico-chemical parameters of a liquid sharply change in SML [28]. Here, the concentration of different admixtures present in water (molecular hydrosols)

occurs due to mass exchange with air. It is different for different components and can reach tens and thousands of times [7, 29–34]. This layer is also enriched with biological matter and microorganisms due to oxygen transfer from the atmosphere [24, 35–37].

According to recent data [38], SML is $(50 \times 10) \mu\text{m}$ from the water–atmosphere interface, below the change in the physico-chemical liquid parameters is more smooth, and gradients of these parameters become small at a depth of about 0.5 m (if there is no stratification caused by factors unconnected with the interface). Ascending air bubbles enrich the surface with pollutants from the surface layers and water SML; therefore, aerosol formed after their breakup is also enriched with pollutants of the surface water layers [24, 31, 32, 36, 39].

Atmospheric aerosol of a region is not formed by one, even powerful, source. It usually consists of particles of different origin: from the Earth's crust, soil, sea and fresh water, biogenic, and anthropogenic

Table 5. Concentrations of some chemical elements in air samples collected in different health resort Baikal zones

Sampling point	Element concentration, $\mu\text{g}/\text{m}^3$												
	Ca	Mg	Na	K	Cu	Zn	Fe	Mn	Al	Ba	Pb	Cd	As
Listvyanka village	0.23	0.07	0.16	0.17	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
	0	0.06	0.13	0.12	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
	0.22	0.06	0.14	0.12	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
Sakhyurta village	0.65	0.07	0.27	0.21	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
	0.24	0.08	0.17	0.15	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
	0.19	0.07	0.12	0.10	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
Peschanaya Bay	0.24	0.06	0.12	0.13	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
	0.41	0.05	0.21	0.15	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
	0.07	0.04	0.13	0.13	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
0.01 MCL	0.21	0.05	0.18	0.23	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
	0.21	0.04	0.44	0.45	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
	1.02	0.11	0.20	0.40	<0.01	<0.01	<0.02	<0.01	<0.05	<0.05	<0.01	<0.005	<0.05
Data [46]	10	100	2*	10	10	100	10	20	15*	0.5	0.5	0.4	
	0.55	0.35	0.4	0.2	0.25	0.15	0.55	0.8	1.1	<0.1	<0.1	n/a	n/a

* The value is given for the most toxic compounds of the metal.
 Note: n/a – not available.

Table 6. Concentrations of some chemical elements in water SML (down to 1000 μm) of water areas of different health resort Baikal zones (the samples were collected at a distance of more than 700 m from the shore)

Sampling site	Element concentration, mg/l												
	Ca	Mg	Na	K	Cu	Zn	Fe	Mn	Al	Ba	Pb	Cd	As
Listvyanka village	16.74	3.02	3.49	1.14	0.51	0.184	0.053	0.0002	0.02	0.017	0.29	0.0001	0.00004
Sakhyurta village	16.17	3.26	3.04	1.07	0.47	0.167	0.051	0.0001	0.02	0.018	0.26	0.0001	0.00004
Peschanaya Bay	15.43	3.10	3.12	1.05	0.41	0.155	0.045	0.0001	0.01	0.015	0.25	0.0002	0.00004
Data [44, 45]	16	3.0	3.6	0.9	0.001	0.009	0.030–0.045	n/a	0.08	0.010	0.0005	0.0001	n/a*
MCL from GN 2.1.5.689–98	–	–	200	–	1.0	1.0	0.3	0.1	0.5	0.1	0.03	0.001	0.05

* Not available.

sources. The maximum concentrations of Al and Fe, as compared with other monitored chemical elements, are characteristic for the first two sources, of Na and Mg for sea water, and increased concentrations of K, Zn, and Sr for biogenic sources [1–4, 40–43].

Ca, Mg, Na, and K predominate in water and aerosol of the health resort Baikal zones (Tables 4–6). These data are in good agreement with [44–46] for both Baikal water and the atmospheric aerosol of the region. A significantly lower concentration of Al and increased concentrations of Zn, Cu, and Pb is a characteristic feature of lake water. The increased concentrations of Zn and Cu can be explained by their presence in the bathometer brass gauze, while a significantly increased concentration of Pb in water SML is explained by its presence in spelter, used to attach gauze to a carcass.

The bathometer is used for sampling to analyze MBH and total protein and to determine the presence of genetic materials of heterotrophic bacterioplankton; hence, increased concentrations of the above elements can be ignored. Slightly lower concentrations of monitored elements were recorded in both height and surface samples in comparison with those presented in [33–46].

Generalized analysis of the obtained samples allows the conclusion about the prevalence of the same chemical elements in atmospheric aerosol and lake water while monitoring; hence, atmospheric aerosol and water SML are closely interrelated. On one hand, atmospheric aerosol from soil and other sources precipitates into the water SML; dissolving and redistributing throughout the whole depth there, it forms the observed element composition of the layer. On the other hand, this water layer, being the source of water aerosol, “delivers” particles with a similar element composition into atmospheric aerosol, thus closing the cycle.

As was mentioned above, the same elements prevail in water and aerosol of the health resort Baikal zones; therefore, it is impossible to determine the sole source of atmospheric aerosol in the Lake Baikal region. A

terrestrial aerosol source is evidently significantly more powerful than even such large water source as Lake Baikal; hence, aerosol of water origin, being a component of atmospheric aerosol in the lake region, forms its small part identifiable with the use of *specific biomarkers*.

Before analyzing the presence of such markers as *total protein* in the aerosol under study, we emphasize that MBH and heavy metals are virtually undetectable in the water of the health resort Baikal areas, as well as in the studied aerosol (Tables 4–7).

We noted in the Introduction that protein is the marker of any living material on the Earth. Data on the total protein content in samples from the health resort Baikal zones are given in Tables 8–10.

The samples were fluorescence analyzed [14] (see above). Protein is identified in all samples of atmo-

Table 7. Concentrations of various multiring benzene hydrocarbons in atmospheric air collected around the health resort Baikal zones and in water SML of these zones

Chemical compound	MBH concentration	
	in air, $\mu\text{g}/\text{m}^3$	in water, $\mu\text{g}/\text{l}$
Naphthalene	<0.0022	<0.248
Acenaphthene	<0.0016	<0.179
Acenaphthylene	<0.0026	<0.294
Fluorene	<0.0023	<0.262
Phenanthrene	<0.0004	<0.045
Anthracene	<0.0023	<0.261
Fluoranthene	<0.0010	<0.118
Pyrene	<0.0010	<0.114
Benz(a)anthracene	<0.0005	<0.053
Perilene	<0.0021	<0.239
Benz(b)fluoranthene	<0.0012	<0.131
Benz(a)pyrene	<0.0013	<0.142
1,2,5,6-Dibenzanthracene	<0.0006	<0.065
Benz(ghi)perilene	<0.0006	<0.063

Table 8. Total protein concentrations in air samples above Lake Baikal (sample number corresponds to Table 1)

No. of sample (filter)	Protein concentration, $\mu\text{g}/\text{m}^3$
1	0.129
3	2.125
5	1.076
7	0.468
9	2.653
11	1.108
13	0.534
15	0.097
17	0.380
19	0.984
21	0.990
23	0.241
25	0.243
27	0.252
29	0.706
31	0.399
33	0.912
35	0.531
41	1.054
43	1.610
45	0.447
47	0.165
Background	0

spheric air in concentrations from 0.1 to 2.65 $\mu\text{g}/\text{m}^3$; in height samples, from 0.15 to 0.5 $\mu\text{g}/\text{m}^3$; and in SML of water areas of Baikal zones under study, in concentrations of 2–3 mg/l. A comparison of the obtained data shows that the observed concentrations of total protein in atmospheric aerosol of the health resort Baikal zones can be caused by water aerosol. Long-term monitoring of atmospheric bioaerosols in the south of Western Siberia shows that the mean over-year level of total protein in the atmosphere is about 2 $\mu\text{g}/\text{m}^3$ [47, 48]. There are no powerful water bio-aerosol sources in the south of Western Siberia comparable with Lake Baikal, but the total protein concentrations here are similar to those observed in the Baikal region; hence, the latter can well be produced by other nonwater sources, as in the case of Western Siberia.

Analyzing concentrations of different *MBH* in the samples collected around the health resort Baikal zones given in Table 7, we can see that the concentrations do not exceed the threshold concentration obtained by the above-described method of analysis [15]. Therefore, only the threshold concentrations for water SML and air samples are given in Table 7, while the concentrations have smaller values.

Table 9. Total protein concentrations in air samples collected around the health resort Baikal zones

Sampling site		Protein concentration, $\mu\text{g}/\text{m}^3$
Listvyanka village	Ship	0.463
	Shore:	
	right point	
Sakhyurta village	center	0.441
	left point	0.473
	Ship	0.398
Peschanaya Bay	Shore:	0.497
	right point	0.154
	center	0.309
Peschanaya Bay	left point	0.232
	Ship	0.497
	Shore:	0.154
Peschanaya Bay	right point	0.309
	center	0.309
	left point	0.232

Table 10. Total protein concentrations in water SML (down to 1000 μm) of water areas of different health resort Baikal zones (the samples were collected at a distance of more than 700 m from the shore)

Sampling site	Protein concentration, mg/l
Listvyanka village	2.985
Sakhyurta village	2.093
Peschanaya Bay	2.487

Table 11. The total amount (TAB) and the number of cultured bacteria in the SML of Lake Baikal water

Sampling site	The number of cultured bacteria, 10^3 CFC/ml		TAB, 10^6 cell/ml
	R2A medium	FPA/10 medium	
Listvyanka village	3.30	0.98	1.34
Sakhyurta village	1.92	0.20	0.36
Peschanaya Bay	0.23	0.22	1.07

Another one of the most adequate markers for aerosol from SML of water areas of the health resort Baikal zones is the present *genetic materials* of the same bacteria (bacterioplankton) which live in lake water. Many various microorganisms live in lake water, including proteobacteria [22, 49–57], which account for about 50% of the total bacteria amount. The results of PCR according to the above-described technique show (Figs. 1–3) that this genetic marker is absent

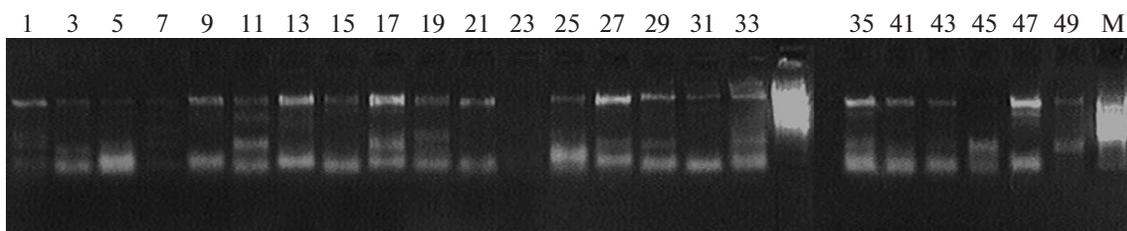


Fig. 1. Electrophoresis of amplification products: 1–35 and 41–49 tracks are the samples under study; the M track is the marker of fragment length (Medigen, Novosibirsk).



Fig. 2. Electrophoresis of amplification products: M track is the marker of fragment length (Medigen, Novosibirsk); other tracks correspond to the Listvyanka region (1), the Sakhyurta region (2), and Peschanaya Bay (3). The indices M and K relate to the SML of up to 200 and up to 1000 μm in depth, respectively.

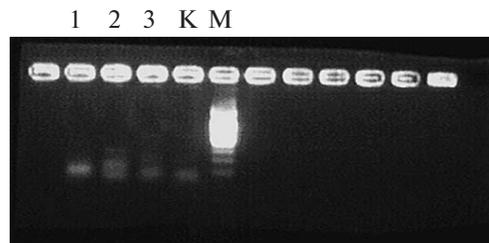


Fig. 3. Electrophoresis of amplification products of surface air samples: track 1 corresponds to Peschanaya Bay; 2, to the Listvyanka village; and 3, to the Sakhyurta village; K means negative control, M is the marker of fragment length (Medigen, Novosibirsk).

only in 3 of 23 height air samples collected above the lake water area (Fig. 1).

However, as follows from Fig. 2, the specific band pointing out the positive PCR result has been revealed only in two samples, and the length of the amplification product corresponds to the designed one (1360 nucleotides). In addition, genetic materials of detectable bacteria are present in only one of the surface samples of atmospheric air (Listvyanka village) collected on the territory of the health resort Baikal zones (Fig. 3).

PCR analysis of pure bacteria lines obtained from the same samples with random primers and further sequencing of the obtained fragments and their identification in the GeneBank has shown the presence of other bacteria species among the identified ones, in addition to those which have been detected with the use of synthesized primers. The absence of genetic materials of proteobacteria in some samples of atmospheric air and SML of water areas of the health resort Baikal zones is evidence of the fact that the performed analysis of genetic material is not exhaustive. It is necessary to work out a method allowing for the revelation of genetic materials of the majority of microorganisms present in the samples.

Data on the total amount of bacteria and the number of cultured microorganisms revealed in the sampling are given in Table 11.

As follows from Table 11, viable microorganisms have been found in all of the studied samples. The

technique for revealing microorganisms with the use of lipotropic fluorophor DAPI, detecting both viable and nonviable microorganisms, allows one to reveal by three orders of magnitude more particles as compared with the method of submerged bacteria cultivation on nutrient agar. The concentration of viable bacteria in the Baikal water varies from several hundreds to several thousands of CFC/ml when culturing in R_2A and FPA/10 media.

CONCLUSIONS

In this work, the summer data (July–August 2008) are presented. Therefore, our conclusions are valid only for the specific experimental conditions.

The analysis of the obtained results shows that the same chemical elements are present in maximum concentrations in virtually all of the aerosol and SML water samples. This allows for the conclusion of a close interrelation between atmospheric aerosol and water SML, which is confirmed by the revealed genetic materials of microorganisms and cultured bacteria living in water and in the majority of aerosol samples from the health resort Baikal zones, including the height samples collected above the lake water area.

Viable bacteria were revealed in some aerosol and water samples. None of the samples contain MBH pollutants within the limit of test sensitivity. The fractional lacustrine aerosol in the Baikal region is significantly less than the aerosol of another origin; there-

fore, the most informative marker of water aerosol is the genetic materials of bacteria living in water, i.e., the feature of the intrinsic substantially of the lake water. However, even this marker is not fully informative, reflecting the presence of aerosol of water origin in all of the aerosol of the Baikal region.

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