Component Composition of Aerosols and their Dynamics in the Atmosphere of the Baikal South-Eastern Coast

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ABSTRACT

This paper presents the results of chemical composition analysis of aerosol samples taken in the summer of 1998–2001 and 2013–2021 at the southeast coast of Lake Baikal. It was revealed that the dominant aerosol ions are $\text{SO}_4^{2-}$, $\text{NO}_3^-$, $\text{Cl}^-$, $\text{Ca}^{2+}$, $\text{Na}^+$. In fire periods, an increase in the proportion of nitrate ions, chloride ions, calcium ions, sulfate ions, bromide ions in suspended particles on average up to 10 times or more compared to background conditions, as well as the proportion of metal ions (calcium, potassium, sodium). The found high correlation between potassium ions and chloride ions ($r = 0.8–0.9$) indicates the predominant proportion of potassium chloride in the composition of atmospheric aerosols at Baikal. In case of smoke emission from the centers of intense wildfires, the proportion of secondary components in the long-range transport of smoke aerosol as a result of its aging was higher than in a regional wildfire (51.6% versus 40.5%).

Keywords: Aerosol, Lake Baikal, Wildfires, Long-range transport, Air pollution

1 INTRODUCTION

Anthropogenic impacts on the ecosystem of Lake Baikal are constantly growing due to the expansion of tourist and recreational infrastructure in the coastal zone, as well as spring-summer wild and peat fires that have become more frequent in recent years, which can lead to irreversible destructive processes (Zhamsueva et al., 2022). In this regard, the study of the spatial and temporal variability of the composition and properties of atmosphere, the assessment and forecast of the transboundary contribution of pollution, as well as a clear definition of their possible consequences for the environment of Lake Baikal is currently an actual problem.

In recent years, due to dry weather conditions, wildfires have occasionally appeared in the boreal forests of Siberia and the Far East: the Republic of Buryatia, the Krasnoyarsk region, the Irkutsk Region and the Republic of Sakha (Yakutia) as a result of thunderstorms and human activity. Thus, since 1996, there has been an increase in the number of wildfires at the territory of Buryatia Republic. The average annual area of wildfires in Buryatia amounted to 100721.7 ha the period from 1996 to 2016 compared to 11984.6 ha during the period of 1966–1995 (Sidorov and Sanzhieva, 2018).

Wildfires that develop in the boreal forests of Siberia in summer adversely affect the quality of atmospheric air in settlements located in the zone of their influence as a result of the transport of air masses (Zhamsueva et al., 2021). With known episodes of wildfires in the northern regions of Eastern Siberia in 2015 and 2019 there was a transport of smoke aerosol over long distances and smoke of atmospheric air in almost all regions of Russia. The potential impact of wildfires on air quality and the negative impact on public health is evidenced by the detected and observed...
elevated concentrations of surface ozone, nitrogen oxides, sulfur dioxide, microdispersed aerosol fraction (Zayakhov et al., 2018) etc. near Baikal (Khodzher et al., 2019; Zhamsueva et al., 2021).

At the Baikal natural territory in the warm season, from April to October, wildfires are major natural sources of atmospheric pollutants emissions.

In addition, a strong influence on the aerosol environment of Lake Baikal is also provided by anthropogenic emissions from industrial enterprises, utilities, and traffic. There are large industrial centers in the region, such as the Slyudyanka, Baikalsk, Babushkin cities, the Kamensk, Selenginsk villages and others. Previously, before its closure in 2013, the Baikal Pulp and Paper Mill (BPPM) was main pollutant of the atmosphere of Lake Baikal, which was a major source of sulfate ions, chloride ions, and sodium ions (Toda et al., 2010). At the plant, soda (sodium carbonate), sulfuric acid, and chlorine compounds were used in the production process (Izrael et al., 1985).

Northwest winds carry pollution from the Irkutsk-Cheremkhovo industrial hub along the valley of the Angara River to the southern water area of the lake. As a result, over the southern part of the lake, including the southeastern coast, the maximum concentrations of suspended matter in the Baikal atmosphere are observed (Potemkin and Makukhin, 2007; Golobokova et al., 2011).

The study of the distribution and transport of aerosol particles in the Baikal region is of great importance for understanding the mechanisms of the atmosphere composition formation and the control of air pollution over Lake Baikal.

The aerosol's soluble fraction chemical composition is one of the indicators of atmospheric pollution. By the component composition of aerosols, one can understand their origin, the role of natural and anthropogenic sources of their formation. The composition of aerosols has a great influence on the chemistry of the environment. Therefore, quantitative information on the chemical composition of smoke emissions from large-scale wildfires is necessary for the creation and verification of models of global and regional climate change. The changes of the aerosol component composition in the southeastern coast atmosphere of Lake Baikal according to summer measurements are analyses in this article.

# 2 METHODS AND MATERIALS

## 2.1 Study Location

Scientific station "Boyarsky" (51°50'47"N; 106°04'01"E) is located in the coastal zone of the southeastern coast of Lake Baikal (Buryatia Republic) at a distance of 500 m from the coastline (Fig. 1). Lake Baikal's location, surrounded by mountain ranges on all sides, creates a large temperature difference between the lake and adjacent areas. Due to the indirect influence of several industrial areas, such as Irkutsk-Cheremkhovsky industrial hub, Babushkin, Kamensk, and Selenginsk, the station can hardly be called a background. Nevertheless, it is still possible to consider the observatory as a site of weak anthropogenic influence, given its location in afforested area and considerable distance from the sources of industrial emissions. "Boyarsky" station is 100–130 km away from the nearest large industrial areas.

## 2.2 Sample Collection and Analysis

Aerosol samples were collected on Whatman-41 and AFA-KhP filters using a PM10 high-volume sampler from Andersen Instruments Inc. (USA) during the summer periods 1998–2001, 2013–2021 at the scientific station "Boyarsky". Samples were taken daily for 2–3 weeks. The sample flow rate was maintained at the same level by a volumetric air flow meter in the range of 0.4–1.7 m³ min⁻¹.

The chemical composition of the soluble fraction of aerosol substance was determined using modern analytical methods of atomic adsorption and ion chromatography, recommended to ensure comparability with data from other regions of the world, on atomic absorption spectrometer (Carl Zeiss Jena, Germany), ion chromatograph ICS-3000 (Dionex, USA) (Table 1).

To determine the ionic composition of aerosols, their soluble fraction was used. The filter material was extracted with a known volume of deionized water. In part of the resulting solution, the pH value was measured; the rest of the solution was filtered through a cellulose acetate filter with a pore diameter of 0.2 µm. Ions were determined in the filtrate by atomic absorption for identification of cations (ammonium ions (NH₄⁺), sodium (Na⁺), potassium (K⁺), magnesium (Mg²⁺),
2.3 Methods of the Determination of Aerosol Type

Smoke and anthropogenic aerosols have the main influence on air quality at the Boyarsky station. A special feature of smoke aerosol is its high content of potassium and chloride ions. These ions are contained in plants and enter the aerosol when biomass is burned (Alves et al., 2011). A specific component of anthropogenic aerosols are sulfate ions, products of fuel combustion. Emissions from industrial centers are main source of these aerosols (Fisher et al., 2011). Wildfires are an important source of calcium ions in the atmosphere. Calcium is an element necessary for the functioning of plant cells and is found in plant tissues. During the combustion calcium ions enters the aerosol. Also, rising airflows lift containing calcium soil particles into the atmosphere during a wildfire (Samsonov et al., 2008).

To analyzed the transport of smoke aerosol and its spatial distribution on a regional scale, calculations of air mass transport paths were carried out using the NCEP/NCAR HYSPLIT reanalysis trajectory model (http://www.arl.noaa.gov/ready/hysplit4.html) and archival meteorological data (archive GDAS for 2013–2021 and REANALYSIS for 1998–2001) National Oceanic and Atmospheric Administration (2013).
Administration (USA). The backwards trajectories of air masses movement in the boundary layer of atmosphere were calculated taking into account their vertical movements. To calculate trajectories, the geographical coordinates of the Boyarsky station are set (south-eastern coast of Lake Baikal). The trajectories of air masses were calculated with a duration of 3 days (72 hours) and a step of 6 hours at heights of 100, 500, and 1000 m, reflecting to the greatest extent the transport of impurities on a regional and interregional scale.

The determination of aerosol type was carried out using the measurement data of the space based CALIOP lidar on the CALIPSO satellite (https://www-calipso.larc.nasa.gov) and Terra MODIS (Deep blue aerosol type) satellite image data (https://worldview.earthdata.nasa.gov). Algorithms for processing sensing data from the CALIOP space lidar, in combination with other photo and radiometric measurements from the CALIPSO satellite, allow for conditional classification according to the qualitative type of aerosol.

The study of atmospheric aerosol transport and the distribution of the dominant aerosol components (sulphate aerosol, dust, fumes) was carried out using the global aerosol model NAAPS (Navy Aerosol Analysis and Prediction System, https://www.nrlmry.navy.mil/aerosol), which generates operational six-day forecasts for sulphates, dust, smoke, sea salt and SO2. The model quickly assimilates the filtered and corrected aerosol optical depths of MODIS (Hogan and Rosmond, 1991; Zhang et al., 2008; Dementeva et al., 2022a). Model outputs data are available as a 1 × 1° grid with 6-hour intervals and 24 vertical levels reaching 100 mbar.

### 3 RESULTS AND DISCUSSION

#### 3.1 Impact of Industrial Emissions from BPPM. Anthropogenic Aerosol

Comparison of aerosols sampled in different years at Boyarsky station, near of Lake Baikal showed that the concentrations of atmospheric aerosols can reach significant values. The chemical composition of aerosols varies greatly from year to year, depending on the direction of air mass flows, weather conditions, and the transport of smoke emissions. The highest average concentrations of suspended particles were observed under the influence of transport from industrial enterprises or wildfires.

Studies of the component composition and content of atmospheric aerosols at Boyarsky, conducted earlier in 1999, 2001 showed a low concentration of suspended particles. The total content of ions in aerosols in 1999 averaged only 3.06 µg m⁻³ and 3.38 µg m⁻³ in 2001 under conditions of weak anthropogenic load and without smoke emission from wildfires (Figs. S2(b) and S2(c)). The main ions in the composition of aerosol were represented by HCO₃⁻ (0.38–0.75 µg m⁻³, 12.4–22.2% by weight), SO₄²⁻ (1.17–1.34 µg m⁻³, 34.6–43.8% by weight), NO₃⁻ (0.27–0.49 µg m⁻³, 8.8–14.5% by weight), Na⁺ (0.13–0.22 µg m⁻³, 4.2–6.5% by weight), NH₄⁺ (0.43–0.58 µg m⁻³, 13.0–19.3% by weight).

A significant influence on the change in the chemical composition of aerosol in the atmosphere of Baikal coastal zone was provided by the transport of industrial emissions from Baikalsk, a large industrial center on the southern coast of Baikal. The Baikal Pulp and Paper Mill (BPPM) was a major source of pollution until 2013. For example, under-flare sampling of aerosols near the mill at the end of July 1998 revealed high air pollution from emissions of the mill itself. Analysis of aerosol samples showed that the total amount of aerosol ions was 351.92 µg m⁻³, the content of bicarbonate ions was 192.43 µg m⁻³ (54.7%), sodium ions 95.88 µg m⁻³ (27.2%).

Maximum concentrations of atmospheric aerosols were observed July 29, 1998 at Boyarsky station under southwestern and southern transport of air masses from Baikalsk, when a sharp and rapid increase in the content of suspended particles (Fig. S2(a)). The component composition of aerosol particles at Boyarsky station was similar to the component composition of aerosols at Baikalsk station in this period of time and consisted mainly of sodium ions (22% by weight of the total ions) and bicarbonate ions (62% by weight of the total ions). An increase in the content of sulfate ions, calcium, potassium, and magnesium ions in aerosols was also noted.

The total amount of water-soluble ions in Boyarsky increased to 123.71 µg m⁻³, bicarbonate ions concentration was 86.92 µg m⁻³, sodium ions concentration was 27.74 µg m⁻³ on July 29, 1998, compared to the total amount of water-soluble ions 9.18 µg m⁻³, concentration of bicarbonate...
ion concentration 1.01 µg m$^{-3}$ (11%), concentration of sodium ions 1.09 µg m$^{-3}$ (11.9%) during the measurement period, when the sampling point was not affected by BPPM emissions. At the same time, the average content of sulfate ions was 2.23 µg m$^{-3}$, chloride ions 1.25 µg m$^{-3}$, nitrate ions 0.76 µg m$^{-3}$, ammonium ions 1.09 µg m$^{-3}$, calcium 0.27 µg m$^{-3}$ (Fig. 2).

To establish the relationship between the aerosol components, a correlation analysis was carried out (Table 2). Correlation analysis and component composition showed that during periods without transport, ammonium and potassium sulfates prevailed in the aerosol ($r = 0.64–0.78$), but under the influence of transport from BPPM, sodium and ammonium carbonates began to dominate in suspended particles ($r = 0.95–1.0$).

After passing the emission plume from the BPPM, the sum of aerosol ions at Boyarsky decreased to the initial level (7.2 µg m$^{-3}$).

### 3.2 Smoke Aerosol from Wildfires and Ways of its Transport to the Baikal Region

Daily aerosol sampling was carried out at Boyarsky station due to wildfires of varying complexity that have become more frequent in recent years due to dry weather, an increase of the fire-hazardous period duration in several potential smoke emission source regions (the Buryatia Republic, Irkutsk region, Krasnoyarsk region, Yakutia).

Sampling was carried out mainly in July–August 2013–2021 when the largest number of wildfires in the boreal forests of Siberia was observed, as well as the largest area burned each year. During these years, the main influence on the quality of the atmosphere near Lake Baikal in the warm season was rendered by smoke plumes associated with known sources of wildfires in neighboring
regions. Fig. 3 shows the number of wildfires from 2013 to 2021 in the Irkutsk region and Buryatia Republic, the largest number of wildfires was identified in 2014–2015 with further decrease.

Because of wildfires influence from 2013 to 2021, there was a significant increase in the average ions concentration in the atmosphere of Lake Baikal. The concentrations of potassium ions, chloride ions, and bromide ions increased greatly. Components of anthropogenic origin $\text{HCO}_3^-$, $\text{SO}_4^{2-}$, $\text{NH}_4^+$ predominated in aerosols during period 1998–2001. The industrial emissions transport was the main source of suspended particles at the Boyarsky station in this period. Impact of wildfires was not found (Fig. 4).

The main components of aerosols soluble fraction in the atmosphere of Lake Baikal southeastern coast are $\text{SO}_4^{2-}$ (14–31%), $\text{NO}_3^-$ (7–27%), $\text{Cl}^-$ (16–21%), $\text{Ca}^{2+}$ (10–36%), $\text{Na}^+$ (5–11%) (Fig. S1).

It was revealed that the quantitative and qualitative composition of aerosols during significant wildfires in July–August 2013 and 2015 has a number of distinctive features (Fig. 5). Fig. 5 shows the periods of aerosol sampling when there was strong smoke from intense wild and peat fires with long- and short-range transport to the study region.

The average concentration of suspended particles at Baikal ($8.04 \, \mu g \, m^{-3}$) during smoke emissions from intense wildfires in Yakutia, Krasnoyarsk region and Evenkia of 2013 composed to be 4.5 times lower than aerosol concentration under wildfires in the summer of 2015 ($37.01 \, \mu g \, m^{-3}$) when the
wildfires were located near the Lake Baikal (Fig. S2(d)). The proportion of secondary components, such as sulfates and nitrates, formed as a result of aging of smoke aerosol with long-range transport from wildfires in Yakutia, was higher (51.6% versus 40.5%) than during regional wildfires. Correlation analysis showed that in 2013 there was a high correlation coefficient between sulfates, nitrates and cations ($r = 0.82–0.99$), while in 2015 the correlation between these components was significantly lower ($r = 0.13–0.69$), which shows an increase in the role of secondary components in the formation of atmospheric aerosols during long-range transport. The formation of secondary components during the transport of smoke plumes plays an important role in the formation of the chemical composition of aerosol particles during of wildfires (Diapouli et al., 2014; Pio et al., 2008; Reid et al., 1998).

The content of sulfate ions and nitrate ions reached their maximum—9.06 and 9.45 µg m$^{-3}$, respectively, under of smoke emissions transport influence from August 06 to 07, 2013 compared with 1.37 and 2.81 µg m$^{-3}$, respectively, observed on July 20, 2013, when there was no transport of smoke aerosol to the observation point. Also, under the transport, the concentrations of sodium, ammonium, potassium, magnesium, calcium, chlorine ions increased by an average of 2–3 times, which indicates a strong influence of wildfires on the aerosol component of the Baikal atmosphere.

Under the influence of closely spaced wild and peat fires in 2015, a high daytime air temperature of 30–31°C and low air humidity of 34–42% were observed, the concentration of suspended particles averaged 37 µg m$^{-3}$ with maximum concentrations of 52.5 µg m$^{-3}$. High concentrations of ions characteristic of biomass combustion (bromide ions 6.41 µg m$^{-3}$, sulfate ions 11.54 µg m$^{-3}$, nitrate ions 2.64 µg m$^{-3}$, calcium ions 5.21 µg m$^{-3}$, ammonium ions 6.56 µg m$^{-3}$) indicate that the sources of aerosol particles were wild and peat fires, which is confirmed by MODIS data and NAAPS forecast maps (Fig. 6, Fig. S2(f)).
When burning of biomass in the north of the Irkutsk region in 2016 (Fig. S2(g)), aerosols were similar in content and composition in 2015. The total content of ions was 23.17 µg m⁻³, high concentrations of bromide ions (4.64 µg m⁻³) were noted in the aerosol composition, chloride ions (5.75 µg m⁻³), sodium ions (2.53 µg m⁻³). A distinctive feature of atmospheric aerosols in 2015 was also the high content of bromide ions (6.41 µg m⁻³), although earlier in 2013–2014 their content was insignificant. It is known that some elements (potassium, calcium, manganese, bromine) are necessary for the functioning of plant cells; when plant biomass is burned, they emit in significant quantities into the atmosphere as part of smoke emissions. A large source of Br⁻ are peat fires (Vainikka and Hupa, 2012), the increase in the number of which has been observed in recent years, in particular, in Buryatia (Sidorov and Sanzhieva, 2018), which leads to an increase in the content of bromide ions in atmospheric aerosol. The difference in the chemical composition of sulfate and nitrate ions is possibly due to the influence of anthropogenic factors and the difference in combustion mechanisms.

A more detailed analysis of the aerosol type and its spatial distribution is provided by the results of measurements of the parameters vertical profiles of suspended particles by the space based lidar "CALIOP" on the satellite "CALIPSO". The spatial section of the vertical thickness of the atmosphere in attenuated backscattering by aerosol showed that in July 2016 over the Baikal region, the filling of the atmosphere thickness with smoke aerosol was observed and the transport of smoke aerosol was carried out to a height of 2 to 5 km above sea level (Fig. 7).

![Fig. 6. MODIS AOD satellite image of (a) wild and peat fires on August 9, 2015, (b) Deep blue aerosol Type (Terra Modis) on August 9, 2015, and (c) NAAPS prognostic map, 08/07/2015.](image)
Fig. 7. Spatial section of the vertical thickness of the atmosphere according to lidar measurements from the CALIPSO satellite by aerosol type.

Under the conditions of weak smoke emission in the Baikal region in 2014, a reduced content of NO$_3^-$, SO$_4^{2-}$ ions characteristic of combustion products was observed in suspended particles. Calcium ions (content of 1.55 $\mu$g m$^{-3}$) was 24.57% by weight of the total ion content of 6.30 $\mu$g m$^{-3}$), chloride ions (25.75% by weight) and potassium ions (10.21% by weight) dominated the aerosols. The low average content of aerosols at Boyarsky in 2017 (12.70 $\mu$g m$^{-3}$) and 2018 (5.33 $\mu$g m$^{-3}$) compared to previous years is undoubtedly associated with precipitation during the measurement period and a weak effect of smoke aerosol transport. During these periods, no significant wildfires were noted, but at the same time, atmospheric air smoke was noted on some days (23, 24, 27–30 July, 17 August 2018 and 08 August 2017). In samples of suspended particles in 2017, potassium ions dominated (31.34%, by mass of the total ions), chloride ions (31.38%), as well as sulfate ions (12.82%), calcium ions (3.51%), sodium (4.86%), ammonium (10.16%) (Fig. 8). Compared to previous years, against the background of a decrease in the proportion of bromide ions, sulfate ions and nitrate ions, an increase in the proportion of chloride ions and potassium ions was observed.

A clear correlation between the variability of the content of sulfate ions and ammonium ions in aerosols (correlation coefficient $r = 0.75$), sodium with magnesium ($r = 0.68$) and calcium ($r = 0.61$), chloride ions and potassium ions ($r = 0.73$) were revealed in aerosol samples in 2017. The noted high correlation coefficients indicate the possibility of the origin of these aerosol components from three different sources. For example, ammonium sulfate is associated with anthropogenic emissions, sodium, magnesium and calcium with dust, earth, potassium chloride with biomass combustion.

Atmospheric aerosols selected in June–August 2018 are also characterized by the predominance of potassium ions (26.67%), chloride ions (35.77%), sulfate ions (12.82%), calcium ions (12.34%), sodium (4.86%), ammonium (5.50%) (Fig. 9). The content of suspended particles in early June, under the conditions of observed smoke from wildfires (on average 8.72 $\mu$g m$^{-3}$), was maximum in the summer expeditionary period of 2018, there was a western air masses transport, with which emissions from wildfires in Southern Siberia were transported to Baikal at that time (Fig. 10(a)).

Also, the transport of smoke aerosol from wildfires in the Irkutsk region and Evenkia was noted in July, when the average sum of suspended particle ions was 5.63 $\mu$g m$^{-3}$ (Fig. 10(b)). The content of atmospheric aerosols decreased and averaged 3.29 $\mu$g m$^{-3}$ in August, due to frequent rains. At the same time, on August 19, in dry weather, during the transport of air masses from the wildfires to the west of Lake Baikal, a high concentration of aerosol particles (13.41 $\mu$g m$^{-3}$) was observed.

In samples of 2018, as well as in 2017, a strong correlation was found between nitrite ions, nitrate ions, chloride ions, magnesium, potassium, calcium ions, and a high correlation between potassium ions and chloride ions ($r = 0.98$) and a large proportion of these components in aerosols indicates the predominance of potassium chloride in aerosols in 2018. In 2017 and 2014,
a high correlation was also found between chloride ions and potassium ions \( (r = 0.73 \text{ and } r = 0.77, \text{ respectively}) \) at a high proportion of these ions. In 2014, however, the main cation was calcium, which also had a high correlation with Cl\(^-\) \( (r = 0.64) \). Calcium is considered to be a typical mineral element (Zhang et al., 2018; Safai et al., 2010), but it is also found in plants; during wildfires, it can get into the aerosol (Samsonov et al., 2008).

It should be noted that even during the rainy periods of 2017 and 2018, with a weak effect of long-range transport, emissions from wildfires had a strong effect on the component composition of atmospheric aerosols. Also, the effect of wildfires on the composition of suspended matter was also observed in 2014 with a weak transport.

Table 3 shows the average content of the main water-soluble ions in atmospheric aerosols at Boyarsky from 1998–2001 and 2013–2021, their range of variability and the total amount of ions \( \pm \) standard deviation. A large number of wildfires in Eastern Siberia in the summer of 2013–2021 led to strong changes in the composition of suspended particles compared to 1999–2001, which undoubtedly indicates a high release of aerosol smoke particles into the atmosphere during wildfires.

Comparison of water-soluble ions concentrations in aerosols sampled during intense wildfires in the region in 2015 with concentrations in the absence of wildfires in 1999 and 2001 shows an
Fig. 10. Backward trajectories of air mass transport at Boyarsky station, the color scale on the right shows the AOD value, (a) June 1, 2018, (b) July 14, 2018.

Table 3. Average content of the main water-soluble ions in atmospheric aerosols at Boyarsky station, µg m⁻³.

<table>
<thead>
<tr>
<th>Year</th>
<th>NH₄⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
<th>HCO₃⁻</th>
<th>Br⁻</th>
<th>Sum of ions</th>
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<td>1998</td>
<td>µg m⁻³</td>
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<tr>
<td>1998</td>
<td>1.16</td>
<td>0.68</td>
<td>0.16</td>
<td>0.07</td>
<td>0.01</td>
<td>0.10</td>
<td>1.04</td>
<td>1.94</td>
<td>1.16</td>
<td>0.00</td>
<td>7.22 ± 2.49</td>
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<td>1999</td>
<td>µg m⁻³</td>
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<td>1999</td>
<td>1.08</td>
<td>30.61</td>
<td>1.99</td>
<td>1.59</td>
<td>0.30</td>
<td>2.81</td>
<td>0.97</td>
<td>8.19</td>
<td>75.39</td>
<td>0.00</td>
<td>99.82 ± 22.86</td>
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<td>2001</td>
<td>µg m⁻³</td>
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<td>2001</td>
<td>0.88</td>
<td>24.90</td>
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<td>0.24</td>
<td>2.29</td>
<td>0.79</td>
<td>6.66</td>
<td>61.33</td>
<td>0.00</td>
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<td>2014</td>
<td>1.98</td>
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<td>0.31</td>
<td>1.88</td>
<td>0.43</td>
<td>2.54</td>
<td>5.00</td>
<td>3.89</td>
<td>0.00</td>
<td>0.00</td>
<td>17.16 ± 8.44</td>
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<td>2017</td>
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<td>2017</td>
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<td>2.54</td>
<td>5.00</td>
<td>3.89</td>
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<td>17.16 ± 8.44</td>
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<td>2018</td>
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<td>2018</td>
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<td>3.89</td>
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<td>17.16 ± 8.44</td>
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<td>2019</td>
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<td>2019</td>
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<td>0.87</td>
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<td>3.89</td>
<td>0.00</td>
<td>0.00</td>
<td>17.16 ± 8.44</td>
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<tr>
<td>2020</td>
<td>µg m⁻³</td>
<td>%</td>
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<td>2020</td>
<td>1.98</td>
<td>0.87</td>
<td>0.31</td>
<td>1.88</td>
<td>0.43</td>
<td>2.54</td>
<td>5.00</td>
<td>3.89</td>
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<td>17.16 ± 8.44</td>
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<td>2021</td>
<td>µg m⁻³</td>
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<td>2021</td>
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<td>17.16 ± 8.44</td>
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1 period without taking into account the influence of pollution transport.
2 period taking into account the influence of pollution transport.
increase in the proportion of nitrate ions, chloride ions, calcium ions, and sulfate ions in suspended particles, on average, up to 10 times or more. The sum of ions in 2015 was 37.0 µg m⁻³ against 3.06 µg m⁻³ (1999) and 3.38 µg m⁻³ (2001) (Table 2). In aerosol samples in 2013–2021 bicarbonate ions were not detected; probably, HCO₃⁻ ions were displaced from suspended particles by stronger anions (Cl⁻, NO₃⁻, SO₄²⁻). The main water-soluble components of atmospheric aerosols in 2015 were 6 ions: Cl⁻, NO₃⁻, SO₄²⁻, NH₄⁺, K⁺, Ca²⁺, formed as a result of wildfires.

The content of sulfate ions in 1999, 2001 averaged 1.17–1.34 µg m⁻³, in 2015 it increased to 11.54 µg m⁻³. The concentration of nitrate ions increased from 0.27–0.49 µg m⁻³ in 1999 and 2001 up to 2.64 µg m⁻³ in 2015; chloride ions from 0.01–0.2 to 1.42 µg m⁻³; sodium ions from 0.13–0.22 µg m⁻³ to 1.65 µg m⁻³; potassium ions from 0.06 to 0.9 µg m⁻³; ammonium ions from 0.44–0.59 to 6.56 µg m⁻³; calcium from 0.07–0.21 to 5.21 µg m⁻³; magnesium from 0.01–0.02 to 0.48 µg m⁻³, respectively.

The total concentrations of ions in the aerosol varied from 1.1 µg m⁻³ to 16.4 µg m⁻³ (the average value for the entire period was 3.14 µg m⁻³) in 2019 and 1.5–14.9 µg m⁻³, with an average content of 8.6 µg m⁻³ in 2020. The chemical composition of the aerosol in 2020 is actually comparable to the aerosol of 2019. The aerosol was dominated by Cl⁻, SO₄²⁻, Ca²⁺, Na⁺ ions, the correlation analysis showed that these ions have a good relationship with K⁺ (r = 0.6–0.8), which is a smoke aerosol tracer and a key indicator of biomass combustion emissions. On some days, the transport of smoke aerosol from the centers of wildfires in the Irkutsk region was noted. In 2020, the concentration of SO₄²⁻ was 3.3 times higher, other ions—2 times higher than in 2019, which is caused by more intense smoke.

In 2021, atmospheric smoke was observed at the Boyarsky station due to the transport of smoke aerosol from Yakutia and the north of the Irkutsk region, where wildfires were going on (Dementeva et al., 2022b). The total number of ions varied greatly from 1.34 µg m⁻³ to 44.2 µg m⁻³ (mean 8.3 µg m⁻³). The main ions are SO₄²⁻ (28%), NH₄⁺ (22.6%), Cl⁻ (21%), NO₃⁻ (12.5%). The high correlation of sulfate ions and nitrate ions with potassium (r = 0.84–0.88) points to wildfires as the main source of aerosols at Boyarsky.

A relatively low correlation of potassium ions with chloride ions (r = 0.49) and nitrate ions (r = 0.46) is associated with the aging of aerosols in the process of long-range transport. An increase in the correlation coefficient between K⁺ and SO₄²⁻ in 2019–2021 (r = 0.6–0.8) was noted in 2019–2021 under the conditions of a decrease in the sum of water-soluble ions in samples compared to previous years. This indicates that the decrease in the aerosols content in these years occurred, primally, due to a reduction in the influence of industrial emissions on the formation of suspended particles at Boyarsky.

A similar comparison of the results of aerosol samples analysis in 2020–2021 with 1999 and 2001 aerosol samples shows that, despite the low level of smoke emission in the surface layer of the atmosphere, the content of ions sum was on average 2.5 times higher than in previous years without wildfires and amounted to 8.3–8.6 µg m⁻³ against 3.06 and 3.38 µg m⁻³. When transport of air masses from the centers of wildfires, a sharp increase in the content of calcium, potassium, sodium, magnesium, chloride ions was observed, as well as during intense wildfires in 2013 and 2015.

Starting from 2018 the number of rainy days at the Boyarsky station has increased. Rainy days accounted for 76 and 66.67% of the measurement period of 2020 and 2021 (Table 4). This led to a decrease in the concentration of suspended particles in the air from 2018 to 2021, up to 3.4–9.6 µg m⁻³ on average per year. The component composition of aerosols during the period from 2018 to 2021 not much different from the composition for the period 2013–2017. Biomass combustion is still the main source of aerosol during period of 2018–2021.

To identify aerosol sources, a correlation analysis between potassium and chloride ions, which are products of vegetation combustion, and between ammonia and sulfate ions, predominantly of industrial origin was conducted (Fig. 11). High correlation coefficient (r) was observed between potassium and chloride ions, it is average 0.81 (2013–2021). At the same time, the correlation between ammonium and sulfate ions, mainly of industrial origin, is average 0.47. Opposite values were observed in 1998–2001 under the influence of anthropogenic emissions. The highest r was between ammonium and sulfate ions—from 0.61–0.78, with an average of 0.73. At the same time, r between potassium and chloride ions was low.
Table 4. Number of days with precipitation.

<table>
<thead>
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</tr>
<tr>
<td>2021</td>
<td>10</td>
<td>15</td>
<td>66.67</td>
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</tbody>
</table>

Fig. 11. Correlation coefficients between K⁺ and Cl⁻ (red) and between NH₄⁺ and SO₄²⁻ (blue) at Boyarsky station, 1998–2021.

Differences were found in the component composition of aerosols between the period 1998 and 2001 and the period 2013–2021 (Fig. 12). The average annual K⁺ content in aerosols ranged from 0.198 to 3.480 µg m⁻³ or from 1.85 to 31.34% by weight, 1.07 µg m⁻³ or 8.8% by weight on average during the period 2013–2021 due to smoke aerosol transport from wildfires. The observed low potassium content in 2013, 2015, and 2016 was associated with the predominance of smoldering processes during the combustion of wood and peat fires. This significantly exceeded the K⁺ content in aerosols for the period 1998–2001 (potassium ranged from 0.056 to 0.163 µg m⁻³ and 1.66–2.26% by weight, 0.09 µg m⁻³ and 2% by weight on average) when anthropogenic components predominated.

3.3 Discussions

Comparison of water-soluble ions concentrations in aerosols sampled during period of intense wildfires in the region during 2013–2021 with concentrations in the absence of wildfires in 1998 and 2001 are showed that in aerosol samples bicarbonate ions were not detected during 2013–2021. Probably, HCO₃⁻ ions were displaced from suspended particles by stronger anions (Cl⁻, NO₃⁻, SO₄²⁻) (Song and Carmichael, 1999). It is revealed increase in the proportion of nitrate ions, chloride ions, calcium ions, and sulfate ions in suspended particles, on average, up to 10 times or more, formed as a result of wildfires.
Fig. 12. Potassium content in aerosol at Boyarsky station, 1998–2021.

A large source of potassium chloride is the combustion of plant biomass, because potassium is a characteristic element of plant tissues and a tracer of biomass combustion. Potassium chloride is an important component of atmospheric aerosols formed during the combustion of biomass (Cao et al., 2016; Yang et al., 2018). Therefore, one can reasonably assume that the aerosol originated in smoke during this period. Under wildfires the concentration of secondary aerosols increases (Reid et al., 1998), the mass concentrations of typical types of inorganic secondary aerosols (sulfate ions, nitrate ions, ammonium ions) reach their highest values (Pio et al., 2008) during the process of long-distance transport due to aging of smoke aerosol.

Besides in (Balin et al., 2016, 2020) based on the results of remote sensing aerosol fields using the LOSA-M2 lidar at Boyarsky station in 2013–2019 a homogeneous filling of the atmospheric boundary layer up to 3.5 km with smoke aerosol showed. The content of which exceeded the background values. A high correlation was revealed between the spectral characteristics of the aerosol optical depth (AOD) and the mass concentration of PM$_{2.5}$ and PM$_{10}$ during the period of high aerosol turbidity of the atmosphere by smoke plumes from wildfires. In the summer of 2020, when the atmosphere was densely filled with smoke aerosol, a sharp increase of AOD ($\tau_{0.5} > 0.47$) was noted at Boyarsky station and at the same time an increase of mass concentrations of PM$_{2.5}$ (19–24 µg m$^{-3}$) and PM$_{10}$ (42–59 µg m$^{-3}$) was recorded. The cross-correlation coefficient between the mass concentration of PM$_{10}$ (PM$_{2.5}$) and AOD was 0.87 (0.86) (Dementeva et al., 2022a).

During measurements in 2014 and 2018, a high calcium content was revealed. Calcium is considered to be a typical mineral element (Zhang et al., 2018; Safai et al., 2010), but it is also found in plants; during wildfires, it can get into the aerosol (Samsonov et al., 2008). In addition, mineral dust is carried out from the territories of Mongolia and Buryatia, which are subject to soil erosion, which leads to an increase in the content of ions of soil origin (calcium, magnesium, sodium) (Golobokova et al., 2022).

4 CONCLUSIONS

Studies of aerosols chemical composition taken in different years (1998–2001 and 2013–2021) near the water area of Lake Baikal showed that the ion sum of atmospheric aerosols can reach significant values. The chemical composition of aerosols varies greatly from year to year, depending on the direction of air mass flows, weather conditions, and the transport of smoke emissions. An analysis of the concentrations of aerosol components, their correlation coefficients, and modeling of meteorological conditions show that in recent years (2013–2021), the main factor influencing the formation of aerosol composition is smoke emission from intense wild and peat fires over the vast territory of Siberia. The main water-soluble components of atmospheric aerosols during fire periods were 6 ions: Cl$^-$, NO$^-$, SO$_4^{2-}$, NH$_4^+$, K$^+$, Ca$^{2+}$, formed during wildfires.

The found high correlation between potassium ions and chloride ions ($r = 0.8–0.9$) indicates
the predominant proportion of potassium chloride in the composition of atmospheric aerosols at Baikal.

A difference in the composition of aerosols when transport of pollutants from wildfires, located both near and at a considerable distance, was revealed. Thus, during smoke emission from intense wildfires located at a considerable distance from the sampling point (in Yakutia), the average concentration of suspended particles in Baikal (8.04 µg m⁻³) turned out to be 4.5 times lower than the average concentration of aerosol (37.01 µg m⁻³) recorded during wildfires near Lake Baikal. But the proportion of secondary components in the long-range transport of smoke aerosol as a result of its aging was higher than in a regional wildfire (51.6% versus 40.5%).

In 1998–2001 on average the concentrations of aerosol particles were low, however, there were episodes of emissions transport from the BPPM, which led to a sharp increase in the content of aerosols with a predominance of carbonate ions and calcium ions.

The study of the formation and transport of aerosol particles in the Baikal region is very important for understanding the mechanisms of atmosphere composition formation and the control of air pollution over Lake Baikal.

**ACKNOWLEDGMENTS**

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**SUPPLEMENTARY MATERIAL**

Supplementary material for this article can be found in the online version at https://doi.org/10.4209/aaqr.230161

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