

Long-term investigations of atmospheric aerosol and gaseous impurities in Southern Pribaikalye, East Siberia (Russia)



Liudmila P Golobokova*, Tamara V Khodzher, Vladimir A Obolkin, Vladimir L Potyomkin, and Olga I Khuriganowa

Limnological Institute SB RAS, Russia

Submission: April 11, 2018; Published: April 24, 2018

*Corresponding author: Limnological Institute SB RAS, 664033. 3, Ulan-Batorskaya St., Irkutsk, Russia Tel. +7 9149126865; E-mail: lg@lin.irk.ru; lg1912@mail.ru

Abstract

Long-term investigations (2000-2015) of chemical composition of aerosol and its gaseous precursors were performed at three atmospheric monitoring sites in Southern Pribaikalye (Irkutsk, Listvyanka and Mondy) within the International EANET Program. For this period, concentrations of gases NH_3 and SO_2 increased in the atmosphere of Irkutsk and Listvyanka. In comparison with the earlier period of measurements (1993-1999), in 2011-2015 we recorded the decrease of concentrations of major ions (NH_4^+ , SO_4^{2-} , NO_3^- and Ca^{2+}) in aerosol by 14-55% at site Irkutsk, by 56-77% at site Listvyanka and by 46-84% at site Mondy. Concentrations of Na^+ and Cl^- increased in two times at site Mondy. Changes of the quantitative composition of aerosol caused changes in ratio of ion concentrations in aerosol.

As a result, in comparison with 1993-1999, SO_4^{2-} , NO_3^- and NH_4^+ dominated in aerosol at site Listvyanka and SO_4^{2-} , NO_3^- , Cl^- , K^+ and Na^+ at site Mondy. Statistical analysis of the great amount of the material allowed us to distinguish clouds of data for each of these three sites for cold (October-March) and warm (April-September) seasons. Ion composition of aerosol in the warm period was mainly affected by a soil-erosion source, whereas in the cold period it depended on emissions from heat-and-power engineering enterprises. In winter, due to high temperature gradient between water surface of the lake and the land, the winds transported impurities emitted by industrial enterprises located on the lake coast towards Lake Baikal.

Keywords: Aerosol; Atmospheric monitoring sites; Baikal; Chemical composition

Introduction

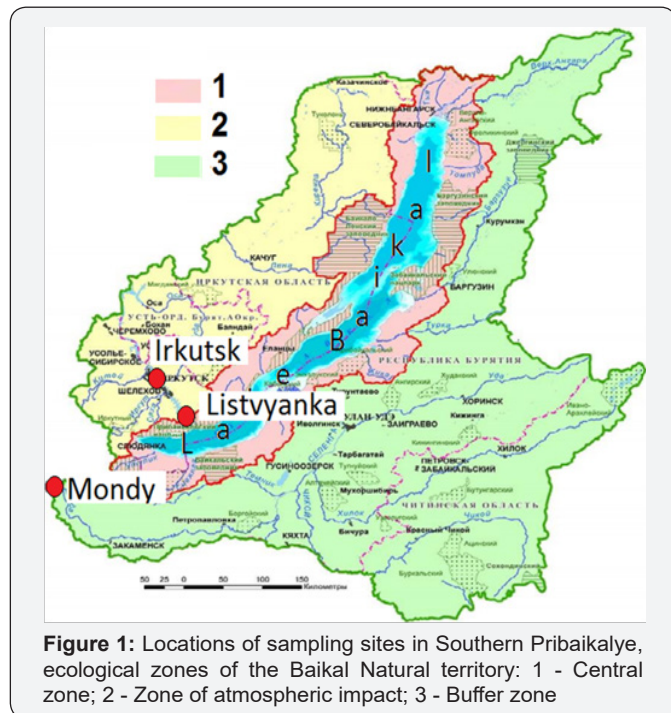
Studies of the air basin in Pribaikalye performed in the 1970-1980s were mainly devoted to the chemical analysis of atmospheric precipitation. The researchers assessed the transport of pollutants with atmospheric precipitation to the southern area of Lake Baikal, which was more subject to pollution, and the entire lake [1-4]. The results obtained in this period presented the first estimates of accumulation of some components on the underlying surface and determined the role of precipitation in the chemical balance of Lake Baikal [3,5]. At that time, operation of the Baikalsk Pulp and Paper Plant (BPPP), the largest local source of pollution, caused another problem – damage of fir and cedar forests on the northern slope of the Khamar-Daban Ridge [6]. By the beginning of the 1990s, the increase of emissions into the atmosphere by industrial centers in the south of East Siberia caused the appearance of environmentally unfavorable territories around the cities. Coniferous forests growing near the cities of Priangarye were significantly affected by atmospheric emissions [7,8]. The studies

performed earlier showed a significant role of atmosphere in the input of substances onto the underlying surface and its effect on the environment in the Baikal region [1-4,9].

However, these studies focused on the analysis of atmospheric precipitation, whereas aerosol studies were singular [10-11]. The first regular observations of chemical and physical characteristics of aerosol in the Baikal region started in 1993. The sites for investigations were chosen according to the level of anthropogenic impact. The studies of chemical composition of surface aerosol in 1993-1996 showed preliminary estimates of accumulation of some components on the underlying surface at dry deposition [12-13]. In 1998, three sites of continuous atmosphere monitoring were set for studying gaseous impurities and chemistry of aerosol and precipitation [14]. In 2001, these sites were included in the Acid Deposition Monitoring Network in East Asia [15]. The aims of this work were to analyze long-term dynamics of the dissolved fraction of aerosol and gaseous impurities in 2000-2015 in connection with climate changes in

this region and to compare the data obtained with the previous data (1993-1999). These studies are of practical value as the impact of atmosphere on chemistry and quality of the water of Lake Baikal and its tributaries has been increased recently.

Sites and Methods



The Baikal Natural Territory (BNT) includes Lake Baikal, its catchment area and the zone of atmospheric impact about 200km wide (Figure 1). The latter is located to the west and north-west from the lake [16]. In the zone of atmospheric impact, possible transport of industrial emissions negatively affects the Baikal ecosystem and its surrounding areas. Ecological zoning is based on identification of ecological territories with their equal level of economic activity. The probability of atmospheric deposition onto the water area from pollution sources on the territory of Southern Pribaikalye directly adjacent to Lake Baikal with a width of 60 km is likely 10 to 100%. This territory is the first protected zone. The boundary of the second protected zone is at a distance of 70 km from the boundary of the first zone. Emissions into the atmosphere basin of Lake Baikal from the sources in this zone are an order less than in the first zone. The contribution of sources of the third zone with a length of about 70 km from the boundary of the second zone is less than 0.1% [17].

In Southern Pribaikalye, there are three monitoring sites characterizing different conditions of atmosphere pollution: Irkutsk (52.30N, 104.40 E) is a site with urban conditions; Listvyanka (51.90N, 104.70E) with rural conditions (760 m a.s.l.) and Mondy (51.60N, 101.00E) with background conditions (2,000 m a.s.l.).

Monitoring Sites

Site Irkutsk: The city of Irkutsk, a large industrial center in the south of East Siberia with the population of about 600,000 people, is located on the western border of the first protected zone. In the city, there is a large heating plant and heat networks, including boilers. Moreover, an airport, railroad and motor traffic are also sources of pollution. The monitoring was performed within the city and in its southern suburbs. Chipanina-Molozhnikova et al. [18] noted that the north-western quarter of air mass transport prevails at site Irkutsk (approximately 47%). Moreover, passing above the Irkutsk-Cheremkhovo industrial region and Krasnoyarsk Krai, the composition of air masses is enriched with impurities. Another prevailing direction of air masses is south-western (up to 28%). Large anthropogenic sources in this direction are located at significant distances from the object of investigations.

Site Listvyanka: Site Listvyanka is located in the first BNT protected zone. The observations were performed at the Solar Observatory of the Institute of Solar Terrestrial Physics SB RAS in the settlement of Listvyanka (760m a.s.l.). This settlement is situated on the south-western coast of Lake Baikal 70 km from Irkutsk. The atmosphere in Listvyanka is affected by the large water body (Lake Baikal), point sources of atmosphere pollution (small boilers and stove heating) and intense pollution from vehicle emissions whose number has increased recently as more and more tourists visit this place every year. Like Irkutsk, the prevailing directions of air masses are north-western and south-western. Polluted air masses from industrial enterprises of Pribaikalye are transported to the western coast and water area of Southern Baikal. For the period of observations, the air masses were also transported from the south-eastern and eastern directions, whose frequency was approximately 4%. To the south-west from Listvyanka, on the opposite coast there is Baikalsk Pulp and Paper Plant that was shut down in December 2013. The southern part of Lake Baikal is surrounded by mountains (height of over 2,000 m) and the wind direction either helps scattering of impurities or promotes their accumulation.

Site Mondy: The background site Mondy is situated on the territory of the Astronomic Laboratory of the Institute of Solar-Terrestrial Physics SB RAS on Mount Chasovye Sopki (the plateau between the East Sayan and Khamar-Daban Ridges) at an altitude of 2,005 m a.s.l. There are no local sources of atmosphere pollution here, the site is over 300 km away from industrial centers and surrounded by mountains. The data obtained at this site reflect the background state of the atmosphere in Southern Pribaikalye and global transport of atmospheric impurities.

Methods of Sampling and Analysis

Aerosol and gaseous impurities were sampled according to the methods applied in the international monitoring nets of EANET (Acid Deposition Monitoring Network in East Asia)

and EMEP (European Monitoring and Evaluation Program). According to the EANET manual [19], four types of filters were used for sampling. The first Teflon filter was installed on the way of air flow for aerosol trapping. The second polyamide ULTIPOR filter adsorbed nitric acid, hydrochloric acid, ammonia and partially sulfur dioxide. The next cellulose filter (ADVANTEC 51A) impregnated with potassium carbonate was used for neutralization of sulfur dioxide and hydrochloric acid. The fourth cellulose filter impregnated with phosphoric acid neutralized ammonia. Pump of membrane type was used to collect samples. Samples were collected weekly and biweekly (Table 1).

Table 1: Duration of sampling and a number of samples.

Site	Site classification	Duration	Number of samples (2000-2015)
Irkutsk	urban	weekly	751
Listvyanka	rural	weekly	700
Mondy	remote	biweekly	298

Water soluble ions were extracted in deionised water using ultrasonic water bath and then the sample was filtered. Filtrate was used to estimate the concentration of ions Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NH_4^+ , NO_3^- , Cl^- and SO_4^{2-} in aqueous extracts of the first filter. Gaseous impurities NH_3 , HNO_3 and SO_2 were estimated from the corresponding ions determined in the extracts of the 2-4 filters. To compare our data with the data from other regions of the world, we analyzed ions using sophisticated analytical methods used by other researchers and the monitoring nets: atomic absorption, high performance liquid and ionic chromatography [19-21]. Taking into consideration that small amount of the substance and low concentrations of dissolved components specify strict requirements to the analysis precision, we used a method for anion measurements in different environmental objects developed by Baram et al. [22] based on high-performance liquid chromatography (Milichrom A-02, Russia) with UV-detection.

This method has an advantage in comparison with other methods: potassium biphthalate as an eluent allows the determination of anions SO_4^{2-} , Cl^- , NO_3^- , NO_2^- and Br^- together with an ion HCO_3^- . In 2011, additional equipment was used. Thorough testing of comparable samples of the analysis showed that the discrepancy in values of recurrence and precision was within the uncertainty of measurements. Measurements were carried out on an atomic absorption spectrometer (Carl Zeiss Jena, Germany), high-performance liquid chromatographer "Milichrom A-02" (Russia) and ionic system ICS-3000 (Dionex, USA). The quality of the analyses has been approved by inter-laboratory comparative experiments performed within the framework of international programs Global Atmosphere Watch (GAW) under the aegis of the World Meteorological Organization (WMO) and Acid Deposition Monitoring Network in East Asia (EANET). The results of these analyses were included in the reports of GAW (QA/SAC) and EANET [23].

To interpret the data of 2000-2015, we used a mean monthly value of ion concentrations for each year of studies, which then was averaged for 2000-2005, 2006-2010 and 2011-2015. Five-year cycles were chosen for more precise identification of changes in the dynamics of ion concentrations in aerosol in the long-term aspect. We compared ion composition of aerosol samples in 1993-1999 and 2011-2015. Samples in 1993-1999 were collected every day for 2-3 months in different seasons. During this period, we collected and analyzed 985 aerosol samples. The same methods were used for studying ions in atmospheric aerosol in 1993-1999 [24] and 2000-2011. To compare the data, we determined a mean monthly value for each year of studies, which was averaged for 1993-1999.

Sources Potentially Affecting Gas and Aerosol Chemistry

The main sources of the atmospheric pollution in Southern Pribaikalye are stationary sources, including enterprises of fuel and energy sector, chemistry and oil chemistry, metallurgic production, carpentry and pulp-and-paper production [25]. Motor transport also contributes significantly to the atmospheric pollution. The number of vehicles in Irkutsk increased by over 80% from 2000 to 2014; annually it increases by over 10,000 vehicles [26]. Their contribution to atmosphere pollution is about 53% of total input of impurity emissions, the contribution of private vehicles being 38%. Carbon oxide (70%), hydrocarbon (up to 19%) and nitrogen oxide (9%) are the main contributors to the total pollution from motor transport [27] State Reports, 2008-2016). Karagulian et al. [28] in their recent review of environment pollution in different regions of the world mentioned motor transport as the main source of pollution, e.g. in India, Southeast Asia, Southeast Europe, South Asia, Brazil and South America.

Forest and peat fires also contribute significantly to atmosphere pollution discharging ammonium and potassium compounds, chloride, organic components and others [29,30]. The greatest forest fires happened in 2003, 2006, 2010-2011 and 2014-2015 [25]. The first peat fires took place in Southern Pribaikalye in the 1980s. The most intense peat combustion was in 2003. This problem arose again in September 2013 [25]. In recent years, changes of climate index have been observed in Southern Pribaikalye. This is attributed to changes of thermal regime, increase of amount of atmospheric precipitation, humidity and wind velocity in this region [31]. Changes of annual air temperature in Pribaikalye were two times faster than in the world: in winter and spring (by 2.0°C and 1.4°C, respectively) than in summer and autumn (by 0.8°C and 0.5°C) [31]. Annual amount of atmospheric precipitation increased by 80mm.

Synoptic processes occurring above East Siberia also affect the formation and variability of chemical composition of the surface atmospheric aerosol. Statistical methods and analysis of synoptic processes in the atmosphere allowed us to distinguish the contribution of natural and anthropogenic

sources in chemistry of aerosol. [32,33] showed that ion concentrations of alkaline and alkaline-earth metals in Southern Pribaikalye increased because of the transport of continental aerosol with southern and south-eastern air flows. The elevated concentrations of sulfate and nitrate ions are associated with large-scaled transport of air masses from the industrial regions of Siberia.

Results

Atmospheric Aerosol and Gaseous Impurities at Site Irkutsk (2000-2015)

Among gaseous impurities in Irkutsk, we recorded the highest concentrations of SO_2 and NH_3 with their rise in 2011-2015

Table 2: Average long-term concentrations (\bar{x}), mean-square deviations in concentrations (σ) of gaseous impurities in atmosphere, ions and their sum (Σ_{ions}) in aerosol at site Irkutsk, $\mu\text{g m}^{-3}$.

Ions and gaseous impurities	2000-2005		2006-2010		2011-2015	
	\bar{x}	$\pm\sigma$	\bar{x}	$\pm\sigma$	\bar{x}	$\pm\sigma$
SO_4^{2-}	2.83	1.72	2.46	1.00	2.37	1.18
NO_3^-	0.96	0.55	0.80	0.48	0.79	0.53
Cl ⁻	0.25	0.10	0.31	0.19	0.32	0.21
NH_4^+	1.02	0.47	0.62	0.40	0.64	0.45
Na^+	0.15	0.07	0.24	0.10	0.21	0.12
K^+	0.22	0.15	0.14	0.07	0.20	0.08
Mg_2^+	0.09	0.04	0.09	0.02	0.06	0.02
Ca_2^+	0.46	0.15	0.57	0.12	0.42	0.09
HNO_3	0.57	0.53	0.64	0.66	0.26	0.13
NH_3	1.18	0.70	2.28	0.63	1.85	1.16
SO_2	6.40	3.83	10.79	8.37	12.27	9.29

The lowest NH_3 concentrations were recorded in 2000-2005. In the next five-year period, (2006-2010), the NH_3 content increased almost in two times. In 2011-2015, average annual concentrations of NH_3 decreased in 1.2 times compared to the previous period (see Table 2). Concentration levels of NH_3 and NH_4^+ were affected not only by emissions from fuel-energetic enterprises, but also by emissions from vehicles and combustion products from forest and peat fires [35,36,27]. As noted above, for the past 15 years the number of vehicles increased in the Irkutsk region. According to the data of State Reports

Table 3: Potential factors affecting the concentrations of pollutants in atmosphere, site Irkutsk.

Period	Emissions from stationary sources, thousand tons	Mean air temperature (December-February)	Mean air temperature (May-September)	Amount of precipitation, mm (May-September)	Area of forest fires, ha	Number of forest fires
2000-2005	43.76	-16.1 °C	15.5 °C	1739	288,750	7,488
2006-2010	35.06	-16.7 °C	15.1 °C	1837	259,921	6,402
2011-2015	65.01	-16.5 °C	15.5 °C	1739	1245,818	6,930

However, in 2006-2011, the amount of precipitation in warm period (May-September) was higher (Table 3). Besides anthropogenic emissions, at elevated humidity intense decomposition of biomass and its emission from the soil were likely a source of this gas. The dissolved aerosol fraction at site

(Table 2). It is generally accepted that the natural background concentration of SO_2 is $1.28 \mu\text{g m}^{-3}$ in the environmentally favorable areas of the middle latitudes [34]. Recently, we have observed in Irkutsk an excess of the average natural background value of SO_2 in ten times (see Table 2). There is a clear relationship between average SO_2 concentrations and inter-annual dynamics of air temperature in winter months. According to advection in winter, the Asian anticyclone intensifies, especially in combination with the Lena-Kolyma high pressure center (Hazard Phenomena..., 1986). The appearing inversion effects contribute to the pollution of lower atmosphere. The rise of SO_2 in atmosphere was recorded in winter months of 2000-2001, 2005-2006 and 2009-2013 when the winters were the coldest.

(2008-2016), intensity of forest fires increased. As regards a season, the highest concentrations of NH_3 were recorded in summer. However, gaps remain in the scientific understanding of NH_3 emissions. We considered several factors, which could potentially increase ammonium concentrations. In 2006-2010, average number of emissions from stationary sources, average air temperature in warm months, area of burnt woodland and number of forest fires were less than in 2000-2005 and 2011-2015.

Irkutsk was dominated by concentrations of NH_4^+ , Ca^{2+} , SO_4^{2-} , NO_3^- and Cl⁻. Average ion concentrations were the highest during the first five-year period of observations (2000-2005), and by 2011-2015 it reduced. The maximum decrease of concentrations (9-40%) were recorded for NH_4^+ , NO_3^- and SO_4^{2-} (see Table 2),

whereas concentrations of Cl⁻ and Na⁺ in aerosol at this site increased by 30% (see Table 2). Elevated concentrations of Na⁺ and Cl⁻ in the atmosphere were of local origin caused by the use of reagents for road processing in winter against ice.

Atmospheric Aerosol and Gaseous Impurities at Site Listvyanka (2000-2015)

The prevailing ions in Listvyanka aerosol, as in Irkutsk, were NH₄⁺, Ca²⁺, NO₃⁻, SO₄²⁻ and Cl⁻. In 2001-2005, among gaseous impurities we recorded the highest concentrations of HNO₃ and SO₂, and in the next periods those of NH₃ and SO₂ (Table 4). Average ion concentrations in aerosol were the highest in 2005-2006; in

Table 4: Average long-term concentrations (\bar{x}), mean-square deviations in concentrations (σ) of gaseous impurities in atmosphere, ions and their sum (Σ_{ions}) in aerosol at site Listvyanka, $\mu\text{g m}^{-3}$

Ions and gaseous impurities	2000-2005		2006-2010		2011-2015	
	\bar{x}	$\pm\sigma$	\bar{x}	$\pm\sigma$	\bar{x}	$\pm\sigma$
SO ₄ ²⁻	2.35	0.38	1.24	0.29	0.96	0.34
NO ₃ ⁻	0.46	0.13	0.19	0.10	0.20	0.18
Cl ⁻	0.33	0.25	0.11	0.06	0.12	0.08
NH ₄ ⁺	0.91	0.25	0.24	0.09	0.23	0.13
Na ⁺	0.16	0.05	0.10	0.04	0.09	0.06
K ⁺	0.17	0.06	0.08	0.02	0.10	0.06
Mg ₂ ⁺	0.04	0.01	0.02	0.01	0.01	0.01
Ca ₂ ⁺	0.23	0.04	0.16	0.05	0.11	0.05
HNO ₃	1.28	0.50	0.14	0.06	0.23	0.11
NH ₃	0.91	0.32	2.20	0.47	1.10	0.42
SO ₂	3.23	2.49	7.68	4.95	5.39	5.05

Atmospheric Aerosol and Gaseous Impurities at Site Mondy (2000-2015)

In 2000-2005, like in 1993-1999, SO₄²⁻, NO₃⁻, NH₄⁺ and Ca²⁺ dominated among major ions in aerosol at site Mondy. The rise of their concentrations was recorded up to 2005 (Table 3), the highest being in 2003. In this period, intense construction works were performed on the territory of this site. In addition, 2003 was an environmentally unfavorable year because of a high number of forest fires in the south of Pribaikalye with an area of up to 200,000 ha. In comparison with the initial observation period (2000-2005), by 2015 the concentrations of Ca²⁺ decreased in two times, SO₄²⁻ and NO₃⁻ in almost three times and NH₄⁺ in seven times. Semi-desert and desert regions of Mongolia with brown soils and significant distribution of salt marshes and sand could be sources of Cl⁻, K⁺ and Na⁺ [38].

The frequency of dust storms increased on the territory of Mongolia [39-40]. The decrease of amount of precipitation and soil humidity and, as a result, degradation of vegetation and intense cattle grazing caused desertification of the territory [40]. The highest concentrations of NH₃ and SO₂ were in 2000-2005. Average concentrations of these gases, as those of ions, decreased by 2011-2015. In general, concentrations of gaseous impurities and major ions in aerosol were low at site Mondy and

2006-2010, they reduced. No similar tendency was observed in the concentrations of gaseous impurities. Concentrations of NH₃ and SO₂ were minimal in the first five years and maximal in the second five years. Concentrations of HNO₃, on the contrary, were maximal in 2001-2005 with the decrease in the following years (see Table 4). If in 1993-1999 sulfate, and ammonium and calcium ions prevailed in Listvyanka aerosol at the end of the previous century, 10-15 years later sulfate and nitrate remained dominant among anions and ammonium among cations, i.e. the role of alkaline components decreased. Obolkin et al. [37] noted that this was likely one of the reasons of acidification of atmospheric precipitation in Southern Baikal.

comparable with reference values for the purest regions of the world [41-43].

Discussion

Despite the anthropogenic impact on climate change on a global scale, which is expressed in changes of the gaseous composition of atmosphere, decrease of biodiversity and deterioration of ecosystem functioning and increase of concentrations of greenhouse gases and aerosol in atmosphere [35,28,44,45] in Southern Pribaikalye we observe reduction of ion concentrations in aerosol (Figure 2). For example, at site Irkutsk the decrease of Na⁺ was about 14%, SO₄²⁻ 23%, Cl⁻ and NO₃⁻ over 30% and NH₄⁺ and Ca₂⁺ about 55% (Figure 2). At site Listvyanka, by 2011-2015 ion concentrations decreased by 72-77%, except Cl⁻ (56%) (Figure 2). At the background site Mondy, concentrations of NO₃⁻ (82%) and NH₄⁺ (84%) reduced, while those of Cl⁻ and Na⁺ increased in two times (Figure 2). On the one hand, the reduction of ion concentrations in aerosol at the beginning of a new millennium was attributed to the integration of several heat and power stations into one heat center and treatment improvement from ash components. On the other hand, frequency of cyclones from the Atlantic and Mongolia has significantly increased [46,47], thus purifying the atmosphere. Intensification of wind velocity and increase of precipitation

amount observed in the region [31] affected the decrease of pollution level in the atmosphere.

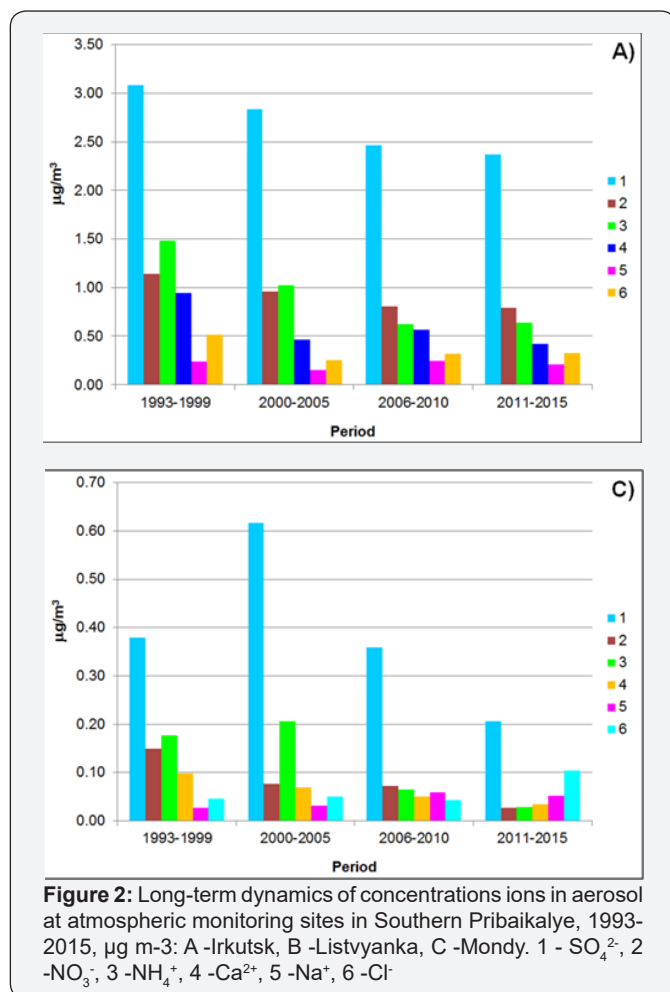


Figure 2: Long-term dynamics of concentrations ions in aerosol at atmospheric monitoring sites in Southern Pribaikalye, 1993-2015, $\mu\text{g m}^{-3}$: A -Irkutsk, B -Listvyanka, C -Mondy. 1 - SO_4^{2-} , 2 - NO_3^- , 3 - NH_4^+ , 4 - Ca^{2+} , 5 - Na^+ , 6 - Cl^-

In the atmosphere at site Mondy, the rise of chloride and sodium was attributed to prevailing wind direction and intensifying cyclone processes, which were accompanied by wind

of the south direction from Mongolia and zonal and northwestern winds blowing from the bald mountains of the Central Sayan. During zonal anticyclonic processes, concentrations of Na^+ and Cl^- in aerosol increased [33]. Synchronous inter-annual dynamics of average monthly concentrations of SO_2 and SO_4^{2-} , NO_3^- , NH_4^+ and Ca^{2+} was recorded in Irkutsk aerosol, attesting to the identity of their sources. Their seasonal concentration fluctuations increased in cold periods because of the operation of fuel and energy enterprises and decreased in warm periods (Figure 3). Unlike the industrial center, in Listvyanka, there is no significant seasonal trend of major ions in aerosol. This is due to the absence of large sources of atmosphere pollution and constant purification of the atmosphere from impurities by precipitation, fogs and dry deposition in the vicinity of such a large water body.

At site Mondy, seasonal dynamics of ions in aerosol was weak, although an insignificant increase of ion concentrations should be noted in warm period, especially in spring, the driest season of the year, when aerosol components emitted into atmosphere from the underlying surface. It is known atmospheric pollutants can be transported in layers of the stratosphere for tens of thousands of kilometers [45,48,49]. In winter, due to high temperature gradient between water surface of the lake and the land, the winds transported impurities emitted by industrial enterprises located on the lake coast towards Lake Baikal [50]. We performed correlation analysis of concentrations of major ions in aerosol and gaseous impurities at sites Irkutsk and Listvyanka. This analysis showed that in 2011-2015 the correlation increased in 40% of ion pairs and gaseous impurities, in 16% of which the correlation being high ($r > 0.70$). The maximal correlation ($r = 0.84$) was recorded in concentrations of $\text{SO}_4^{2-}(\text{Irk})$ - $\text{SO}_4^{2-}(\text{Listv})$ (Table 5). It is likely attributed to the increase of the recurrence of transport directions of air masses from Irkutsk to Listvyanka in this period.

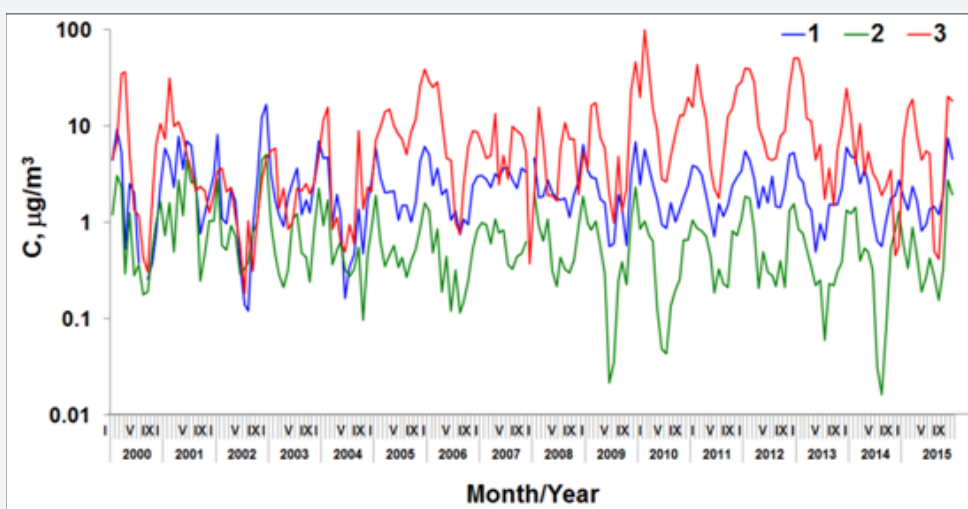


Figure 3: Inter-annual dynamics of average monthly concentration of SO_2 , ions SO_4^{2-} and NH_4^+ in aerosol at site Irkutsk, $\mu\text{g m}^{-3}$: 1 - SO_4^{2-} , 2 - NH_4^+ , 3 - SO_2 .

Table 5: Average long-term concentrations (\bar{x}), mean-square deviations in concentrations (σ) of gaseous impurities in atmosphere, ions and their sum (Σ_{ions}) in aerosol at site Mondy, $\mu\text{g m}^{-3}$.

Ions and gaseous impurities	2001-2005		2006-2010		2011-2015	
	\bar{x}	$\pm\sigma$	\bar{x}	$\pm\sigma$	\bar{x}	$\pm\sigma$
SO ₄ ²⁻	0.62	0.29	0.36	0.14	0.21	0.12
NO ₃ ⁻	0.08	0.05	0.07	0.08	0.03	0.03
Cl ⁻	0.05	0.03	0.04	0.10	0.10	0.07
NH ₄ ⁺	0.21	0.08	0.06	0.04	0.03	0.02
Na ⁺	0.03	0.01	0.06	0.08	0.05	0.05
K ⁺	0.05	0.04	0.03	0.01	0.05	0.03
Mg ²⁺	0.01	0.01	0.01	0.00	0.01	0.01
Ca ²⁺	0.07	0.03	0.05	0.02	0.03	0.02
HNO ₃	0.19	0.14	0.10	0.11	0.10	0.16
NH ₃	0.46	0.20	0.71	0.33	0.34	0.22
SO ₂	0.88	0.19	1.09	0.63	0.59	0.65

Table 6: Correlation coefficients of major ions in aerosol and gaseous impurities at sites Irkutsk and Listvyanka.

	SO ₄ ²⁻ Listv	NO ₃ ⁻ Listv	Cl ⁻ Listv	NH ₄ ⁺ Listv	Ca ²⁺ Listv	HNO ₃ Listv	NH ₃ Listv	SO ₂ Listv
2000-2005								
SO ₄ ²⁻ _{Irk}	0.43	0.37	0.24	0.34	0.48	0.26	0.09	0.34
NO ₃ ⁻ _{Irk}	0.40	0.39	0.47	0.46	0.42	0.25	0.13	0.21
Cl ⁻ _{Irk}	0.38	0.30	0.30	0.32	0.41	0.17	0.05	0.16
NH ₄ ⁺ _{Irk}	0.43	0.36	0.36	0.37	0.48	0.24	0.14	0.21
Ca ²⁺ _{Irk}	0.62	0.53	0.23	0.51	0.58	0.43	0.27	0.34
HNO ₃ _{3Irk}	0.12	0.09	0.08	0.13	0.14	0.06	0.03	0.11
NH ₃ _{3Irk}	0.34	0.39	0.19	0.42	0.25	0.32	0.43	0.09
SO ₂ _{2Irk}	0.33	0.23	0.16	0.27	0.33	0.26	0.13	0.50
2006-2011								
SO ₄ ²⁻ _{Irk}	0.62	0.53	0.43	0.52	0.63	0.36	0.45	0.61
NO ₃ ⁻ _{Irk}	0.55	0.50	0.37	0.49	0.53	0.39	0.38	0.65
Cl ⁻ _{Irk}	0.45	0.47	0.29	0.42	0.41	0.23	0.25	0.55
NH ₄ ⁺ _{Irk}	0.53	0.49	0.39	0.44	0.52	0.32	0.33	0.59
Ca ²⁺ _{Irk}	0.70	0.64	0.37	0.66	0.73	0.49	0.58	0.48
HNO ₃ _{3Irk}	0.18	0.09	-0.02	0.12	0.26	0.12	0.19	-0.03
NH ₃ _{3Irk}	0.65	0.51	0.26	0.65	0.62	0.47	0.73	0.46
SO ₂ _{2Irk}	0.28	0.27	0.32	0.24	0.28	0.22	0.30	0.75
2011-2015								
SO ₄ ²⁻ _{Irk}	0.84	0.37	0.21	0.61	0.77	0.38	0.28	0.53
NO ₃ ⁻ _{Irk}	0.79	0.42	0.20	0.57	0.72	0.45	0.25	0.55
Cl ⁻ _{Irk}	0.76	0.36	0.24	0.50	0.58	0.46	0.17	0.47
NH ₄ ⁺ _{Irk}	0.77	0.38	0.22	0.60	0.76	0.32	0.27	0.52
Ca ₂ ⁺ _{Irk}	0.71	0.22	0.17	0.48	0.70	0.44	0.30	0.36
HNO ₃ _{3Irk}	0.58	0.40	0.30	0.38	0.50	0.66	0.32	0.32
NH ₃ _{3Irk}	0.70	0.24	0.17	0.53	0.50	0.40	0.70	0.35
SO ₂ _{2Irk}	0.66	0.35	0.19	0.33	0.59	0.31	0.06	0.58

We performed a factor analysis of variability of ion composition in aerosol at these three sites (Table 6) [51]. To interpret the results of ion composition of aerosol at site Irkutsk, we chose three factors, whose total contribution was approximately 80% of total dispersion of initial data. Factor I represents relationship between Na⁺ and Cl⁻ and gaseous

impurity SO_2 . We suppose that the elevated values of Factor I are associated with the local urban pollution caused by the processing of roads with salt in the cold period. Factor II combines salts of soil origin and effect of heat and power engineering and motor transport. Factor III shows additional contribution of the city industry and remote transport of impurities in atmospheric chemistry (see Table 7). Two significant factors (total dispersion

of about 72%) were distinguished for Listvyanka aerosol. Factor I showed high positive factor loads on almost all parameters of analyzed aerosol samples and the effect of the regional transport of pollution from the Irkutsk-Cheremkhovo industrial complex. Factor II included ion K^+ and partially HNO_3 , NH_3^+ and Cl^- and resulted from the effect of forest fires whose frequency had increased for the recent years [25].

Table 7: Factor loads of ions in aerosol.

Ions and gaseous impurities	Irkutsk			Listvyanka		Mondy		
	Factor I	Factor II	Factor III	Factor I	Factor II	Factor I	Factor II	Factor III
SO_4^{2-}	0.58	0.39	0.65	0.94	0.16	0.98	-0.05	-0.01
NO_3^-	0.55	0.38	0.68	0.92	0.03	0.38	0.65	0.50
Cl^-	0.87	0.01	0.27	0.69	0.35	-0.06	0.77	-0.06
NH_4^+	0.46	0.26	0.79	0.86	0.38	0.88	-0.18	0.07
Na^+	0.94	0.14	0.03	0.62	0.35	-0.01	0.91	0.04
K^+	-0.02	-0.05	0.75	0.44	0.65	0.53	0.50	-0.31
Mg_2^+	0.31	0.78	0.30	0.90	0.13	0.69	0.32	-0.32
Ca_2^+	0.21	0.91	-0.04	0.91	-0.05	0.88	0.17	0.07
HNO_3	-0.30	0.75	-0.23	0.76	0.48	0.47	0.38	-0.46
NH_3	-0.08	0.25	-0.69	-0.28	-0.60	0.20	0.10	0.72
SO_2	0.88	0.00	0.12	0.22	0.00	0.29	0.05	-0.47
Variance,%	47.6	18.9	12.8	59.1	13.3	38	18.5	12.6

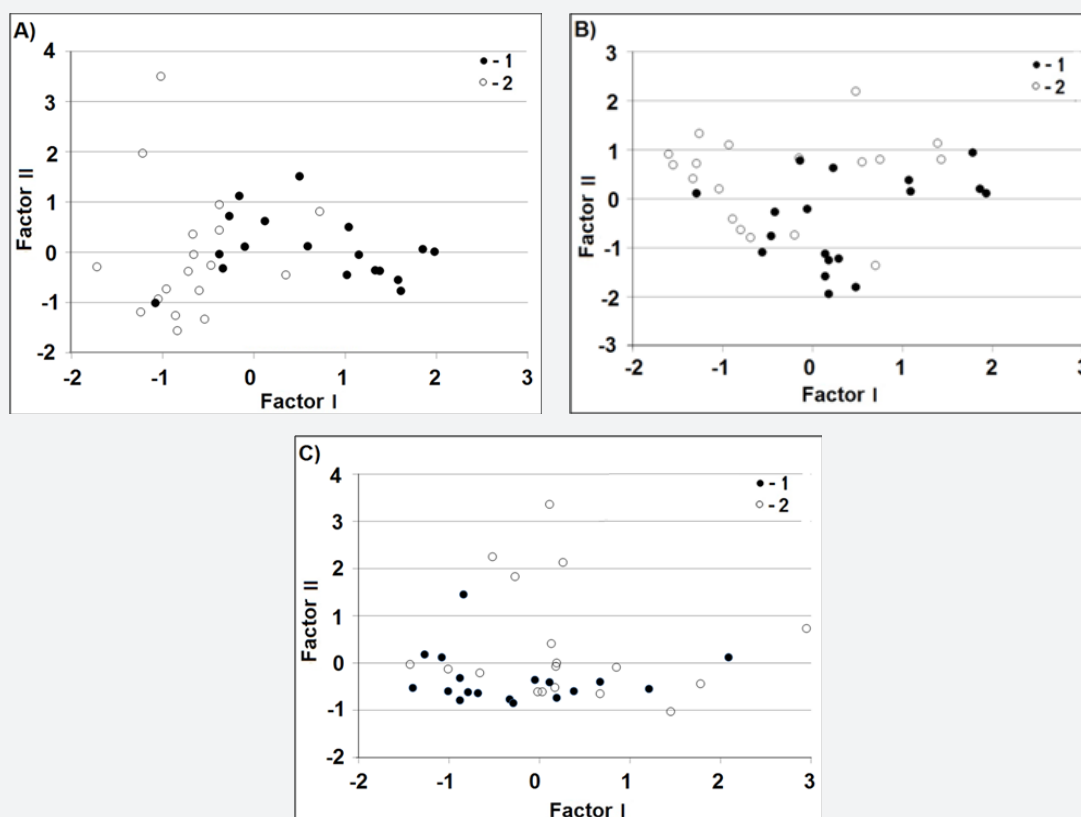


Figure 4: Distribution of aerosol samples within the plain of the first two factors: a) Irkutsk, b) Listvyanka, c) Mondy, 1 -cold period, 2 -warm period.

Three factors (dispersion of about 70%) were identified for Mondy aerosol. Factor I united ions that pointed to the soil heterogeneity of the underlying surface. Factor II combined components of the remote transport of frequent dust storms with southern cyclones. Factor III was likely resulted from forest fires (see Table 7). The factor analysis of the great amount of data allowed us to distinguish statistically significant differences in ion composition of aerosol for cold (October-March) and warm (April-September) seasons at all three sites (Figure 4). Figure 4 (A) shows distribution of aerosol samples at site Irkutsk within the plain of the first two factors. As seen, the data cloud of ion composition of the samples collected in the cold season (October-March) and the cloud of samples of the warm season (April-September) were shifted relative to each other. Similar distribution was recorded in aerosol from Listvyanka and Mondy sites (Figure 4). Calculated Student's criteria were 4.02 for Irkutsk, 3.40 for Listvyanka and 2.65 for Mondy and exceeded the critical t-Student threshold (2.03) [52-53].

Conclusion

Aerosol and minor gaseous impurities are the most dynamic components of atmosphere, which determine its physicochemical characteristics. In this study, we have analyzed dynamics of ion composition of aerosol and gaseous impurities for the recent long-term period of observations (2000-2015) at three atmospheric monitoring sites in Southern Pribaikalye – Irkutsk, Listvyanka and Mondy. In comparison with the early period (1993-1999), in 2011-2015 we recorded the reduction of major ions (NH_4^+ , SO_4^{2-} , NO_3^- and Ca_2^+) in aerosol at all three sites. We suggest that the reduction of concentrations of dissolved substances in Irkutsk aerosol was attributed to the integration of several heat and power stations into one heat center in 2005, treatment improvement from ash components, rise of precipitation amount and intensification of wind velocity at the background of climate changes. The maximal reduction of ion concentrations in aerosol was recorded at sites Listvyanka and Mondy, thus causing changes in their ratios. Compared to 1993-1999, SO_4^{2-} , NO_3^- and NH_4^+ dominated in Listvyanka aerosol.

The reduction of Ca_2^+ in Listvyanka aerosol and the prevalence of acid-forming ions were one of the reasons of acidity increase of atmospheric precipitation. Changes of climatic and synoptic processes in the region caused the rise of Na^+ and Cl^- in aerosol at site Mondy, which came with air flows from the desert areas of Mongolia. Therefore, the Mondy aerosol was dominated by SO_4^{2-} , NO_3^- , Cl^- , K^+ and Na^+ . Concentrations of gaseous impurities NH_3 and SO_2 increased in Irkutsk and Listvyanka, whereas in Mondy they decreased. In 2011-2015, the role of substance transport from Irkutsk onto the southern water area of Lake Baikal increased. Correlation between variability of concentrations of gaseous impurities and aerosol ions in Irkutsk and Listvyanka increased, reaching >0.70 for some impurities. Despite physico-geographic differences in location of the sites and degree of

anthropogenic impact, the chemical composition of aerosol in Irkutsk and Listvyanka is dependent mainly on the same sources: in the warm period soil-erosion aerosol and frequent forest fires, and in the cold period additional sources of heat and power engineering and motor transport. The main source of ions in aerosol at site Mondy is soil-erosion processes occurring in the steppe and desert areas of Mongolia.

Acknowledgements

This study was supported by State Project 00345-2016-0008 "Assessment and Forecast of Ecological State of Lake Baikal and Adjacent Territories under Conditions of Anthropogenic Impact and Climate Change" and RFBR project 17-29-05044 "Monitoring and Assessment of Effect of Dangerous Natural Phenomena (Forest and Peat Fires) and Anthropogenic Sources on Quality of the Baikal Region Atmosphere based on Comprehensive Remote and On-Line Local Measurements and Mathematical Modelling". The investigations were carried out using Shared Research Facilities for Physical and Chemical Ultramicroanalysis LIN SB RAS.

References

1. Khodzher TV (1983) Chemical composition of atmospheric precipitation Ecology of Southern Baikal, East-Siberian. Book Publishing House, Irkutsk, Russia, p. 44-50.
2. Vetrov VA, Klimashevskaya ZA (1985) Monitoring of pollution of the land surface and Lake Baikal with inorganic components of emissions from Baikalsk Pulp and Paper Plant. Improv of regional monitoring of Lake Baikal state, Hydrometeoizdat, Leningrad, pp. 136-158.
3. Obolkin VA, Khodzher TV (1990) Annual input of sulfate and mineral nitrogen from atmosphere in the area of Lake Baikal. Rus Meteorol Hydrol 7: 71-76.
4. Anokhin Yu A, Kokorin AO, Prokhorova TA, Anisimov MP (1991) Aerosol pollution of atmosphere above Lake Baikal and effect of industrial sources. Monitoring of Lake Baikal state. Hydrometeoizdat, Leningrad, p. 44-50.
5. Ryaboshapko AG, Gallardo L, Kjellstrom E, Sergey G, Sergey p, et al. (1998) Balances of oxidized sulfur and nitrogen over the former Soviet Union territory. Atmosph Environ 32(4): 647-658.
6. Morozova TI (1991) Phytopathological situation in coniferous forests of the Khamar-Daban Ridge. Forestry 4: 15.
7. Mikhailova TA (2000) The physiological condition of pine trees in the Prebaikalia (East Siberia) Forest Pathology 30: 1-17.
8. Mikhailova TA (2003) Impact of industrial emissions on forests of Baikal Natural Territory. Geography and Natural Res 1: 51-58.
9. Mattias Maser S, Obolkin V, Khodzher T, Janiekie R (2000) Seasonal variation of primary biological aerosol particles in the remote continental region of Lake Baikal/Siberia. Atmos Environ 34(22): 3805-3811.
10. Koutsenogii PK, Bufetov NS, Drosdova VI, Golobokova LP, Khodger TV, et al. (1993) Ion composition of atmospheric aerosol near Lake Baikal. Atmos Environ 27A(11): 1629-1633.
11. Van Malderen H, Van Grieken R, Khodzher TV, Obolkin VL, Potemkin VL (1996) Composition of individual aerosol particles above Lake Baikal, Siberia. Atmos Environ 30(9): 1453-1465.

12. Khodzher TV, Potemkin VL, Obolkin VA (1994) Chemical composition of aerosol and trace gases in the atmosphere over Lake Baikal. *Atmos and Oceanic Optics* 7(8): 566-569.
13. Arguchintsev VK, Kutsenogii KP, Makukhin VL, Obolkin VA, Potemkin VL, et al. (1997) Experimental study and numerical simulation of aerosols and gaseous pollution in the atmosphere over Southern Baikal. *Atmos and Oceanic Optics* 10(6): 370-373.
14. Khodzher TV, Golobokova LP, Obolkin VA, Potemkin VL, Netsvetaeva, OG (1997) Diurnal and seasonal variability of the atmospheric aerosol ion composition in the south of East Siberia. *Atmos and Oceanic Optics* 10(6): 403-406.
15. (2006) EANET (Acid Deposition Monitoring Network in East Asia) Periodic Report on the State of Acid Deposition in East Asia (Part I) (Regional Assessment).
16. (1999) Federal Law of May 1 No 94-FL "On Protection of Lake Baikal" (1999).
17. (1990) Territorial complex scheme of nature protection of the Lake Baikal basin: fundamentals. Part II Giprogor, Moscow, Russia, p. 403.
18. Chipanina Molozhnikova EV, Golobokova LP, Kuchmenko EV, Netsvetaeva OG, Khodzher TV (2007) Conditions for formation of chemical composition of atmospheric aerosol and precipitation over the Baikal Natural Territory. *Atmos and Oceanic Optics* 20(10): 822-826.
19. EANET (Acid Deposition Monitoring Network in East Asia) (2003) Technical Document for Filter Pack Method in East Asia.
20. Ren L, Zhang R, Bai Z, Chen J, Liu H, et al. (2012) Aircraft Measurements of Ionic and Elemental Components in PM_{2.5} over Eastern Coastal Area of China. *Aerosol and Air Qual Res* 12: 1237-1246.
21. Habeebullah TMA (2016) Chemical Composition of Particulate Matters in Makkah-Focusing on Cations, Anions and Heavy Metals. *Aerosol and Air Qual Res* 16: 336-347.
22. Baram GI, Vereshchagin AL, Golobokova LP (1999) Microcolumn High-Performance Liquid Chromatography with UV Detection for the Determination of Anions in Environmental Materials. *J of Anal Chem* 54(9): 854-857.
23. (2017) EANET (Acid Deposition Monitoring Network in East Asia) (1998-2015) Report of the Inter-Laboratory Comparison Project.
24. Golobokova LP (2004) Development and application of techniques for studies of chemical composition of gaseous impurities and atmospheric aerosol (exemplified by Baikal Natural Territory). Thesis for a doctoral degree of Engineering Sciences. Barnaul p 19.
25. (2008-2016) State Reports "On State and Protection of the Irkutsk Region Environment".
26. (2016) BSM (Brief Statistical Manual). Irkutsk Region. Brief Statistical Manual.
27. Sahu SK, Beig G, Parkhi N (2014) Critical Emissions from the Largest On-Road Transport Network in South Asia. *Aerosol and Air Qual. Res.* 14: 135-144.
28. Karagulian F, Belis CA, Dora CFC, Prüss-Ustün AM, Bonjour S, Adair-Rohani H, Amann M (2015) Contributions to cities' ambient particulate matter (PM): A systematic review of local source contributions at global level. *Atmos. Environ* 120: 475-483.
29. (2015) Recommendation on peat fire extinguishing on dried bogs. Experience of volunteer forest firemen. Cityprint, Moscow p 110.
30. Baylon P, Jaffe DA, de Gouw J, Warneke C (2017) Influence of Long-Range Transport of Siberian Biomass Burning at the Mt. Bachelor Observatory during the Spring of 2015. *Aerosol and Air Qual Res* 17: 2751-2761.
31. Shimaraev MN, Starygina LN (2010) Zonal circulation of atmosphere, climate and hydrological processes at Lake Baikal (1968-2007) *Geography and Natural Resour* 3: 62-68.
32. Golobokova LP, Latysheva IV, Mordvinov VI, Khodzher TV, Obolkin VA, et al. (2005) Peculiarities in the chemical composition of atmospheric aerosol against the background of extreme weather conditions in Southern Siberia. *Atmos and Oceanic Optics* 18(8): 616-620.
33. Golobokova LP, Latysheva IV, Ivanova AS, Mordvinov VI, Potemkin VL, et al. (2006) Mesoclimatic and aerosynoptic conditions of ionic composition formation of atmospheric aerosol in high-mountain regions of Eastern Sayans. *Geography and Natural Res* 2: 83-88.
34. Stozharow AN (2008) *Medicine ecology; tutorial aid.* Vyshaya Shkola, Minsk p. 368.
35. Kelly FJ, Fussell JC (2012) Size source and chemical composition as determinants of toxicity attributable to ambient particulate matter. *Atmos. Environ* 60: 504-526.
36. Behera SN, Sharma M, Aneja VP, Balasubramanian R (2013) Ammonia in the atmosphere: a review on emission sources, atmospheric chemistry and deposition on terrestrial bodies. *Environ Scie and Pollut Res* 20 (11): 8092-8131.
37. Obolkin V, Khodzher T, Sorokovikova L, Tomberg I, Netsvetaeva O, 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. *Int J Environ Stud* 73(3): 452-461.
38. Lopatovskaya OG, Sugachenko AA (2010) Soil melioration. Saline soils (tutorial aid) Irkutsk State University, Irkutsk, p. 101.
39. Jugder D, Shinoda M, Sugimoto N, Matsui I, Nishikawa M, et al. (2011) Spatial and temporal variations of dust concentrations in the Gobi Desert of Mongolia. *Global and Planetary Change* 78: 14-22.
40. Lee EH, Sohn BJ (2011) Recent increasing trend in dust frequency over Mongolia and Inner Mongolia regions and its association with climate and surface condition change. *Atmos. Environ* 45: 4611-4616.
41. Zappoli S, Andracchio A, Fuzzi S, Facchini MC, Gelencse A, et al. (1999) Inorganic, organic and macromolecular components of fine aerosol in different areas of Europe in relation to their water solubility. *Atmos Environ* 33(17): 2733-2743.
42. Osada K, Kido M, Nishita C, Matsunaga K, Iwasaka Y, et al. (2002) Changes in ionic constituents of free tropospheric aerosol particles obtained at Mt. Norikura (2770 m a.s.l.), central Japan, during the Shurin period in 2000. *Atmos Environ* 36 (35): 5469-5477.
43. Preunkert S, Wagenbach D, Legran M (2002) Improvement and characterization of an automatic aerosolsampler for remote (glacier) sites. *Atmos. Environ* 36 (8): 1221-1232.
44. Vu TV, Delgado Saborit JM, Harrison RM (2015) Review: Particle number size distributions from seven major sources and implications for source apportionment studies. *Atmos Environ* 122: 114-132.
45. Argyropoulos G, Samara C, Diapouli E, Eleftheriadis K, Papaioannidou K, et al. (2017) Source apportionment of PM₁₀ and PM_{2.5} in major urban Greek agglomerations using a hybrid source-receptor modeling process. *Sci Total Environ* 601-602: 906-917.
46. Dementieva AL, Zhamsueva GS, Zayakhanov AS, Tsydyrov VV (2012) Study of meteorological parameters of atmosphere in the Gobi Desert. *Natural and Technic Scie* 3: 507-509.
47. Loshchenko KA, Latysheva IV (2015) Regional Characteristics of Synoptic Processes in the Territory of Irkutsk Region in 2000-2013. *The Bull of Irkutsk State University* 11: 38-54 (in Russia)
48. Fiedler V, Nau R, Ludmann S, Arnold F, Schlager H, et al. (2009) East Asian SO₂ pollution plume over Europe-Part 1: Airborne trace gas

- measurements and source identification by particle dispersion model simulations. *Atmos Chem Phys* 9: 4717-4728.
49. Li Y, Wang Y, Ding A, Liu X, Guo J, et al. (2011) Impact of long-range transport and under-cloud scavenging on precipitation chemistry in East China *Environ. Sci Pollut Res* 18: 1544.
50. Obolkin VA, Potemkin VL, Makukhin VL, Khodzher TV, Chipanina EV (2017) Far transfer of trails ejected by regional electric power stations to the South Baikal water area. *Atmos and Oceanic Optics* 30(1): 60-65.
51. Mulaik S (2009) *Foundations of Factor Analysis, Second Edition*. New York: Chapman and Hall CRC, Pp 548.
52. (2017) GAW (Global Atmosphere Watch) The Quality Science Activity Centre Americas. <http://qasac-americas.org>.
53. (1968) Hazard phenomena on the territory of Siberia and Ural, Part II. Irkutsk Region, southwestern part of Buryat ASSR. Leningrad, Hydrometeoizdat pp. 244.



This work is licensed under Creative Commons Attribution 4.0 License
DOI: [10.19080/IJESNR.2018.10.555786](https://doi.org/10.19080/IJESNR.2018.10.555786)

Your next submission with Juniper Publishers will reach you the below assets

- Quality Editorial service
- Swift Peer Review
- Reprints availability
- E-prints Service
- Manuscript Podcast for convenient understanding
- Global attainment for your research
- Manuscript accessibility in different formats
(Pdf, E-pub, Full Text, Audio)
- Unceasing customer service

Track the below URL for one-step submission
<https://juniperpublishers.com/online-submission.php>