Peculiarities in the chemical composition of atmospheric aerosol against the background of extreme weather conditions in Southern Siberia

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Both the southern and northern synoptic processes affect Lake Baikal, the southern Baikal regions, and highlands of Eastern Sayan, where the climatic changes are the most pronounced. Changes in the chemical composition of the soluble fraction of atmospheric aerosol are shown to be dependent on the extreme weather conditions based on the data of field observations in 2001–2002.

Introduction

In the recently passed decades, high-amplitude anomalies of meteorological parameters have became more frequent all over the world; this is related to the extreme stage of dynamics of synoptic processes.[1]

Behavior of synoptic processes in the northern midlatitudes is determined, in many ways, by frequency, duration, and intensity of continental arctic air flows in cyclone rears developing in the front part of the upper troughs as well as by intensity of warm air advection in the front part of a high-level ridge directed from south.[2]

Chemical reactions in the atmosphere proceed in connection with synoptic processes. A role of chemical processes in the global warming in the 21st century is studied[3] using the photochemical model of the middle atmosphere developed at the Institute for Energy Problems of Chemical Physics RAS. Similar results are also described in Refs. 4 and 5. Noticeably fewer number of papers have been published concerning the effect of climate changes on atmospheric chemistry in different urbanized and background regions of the Earth.

Knowledge of the chemical composition of atmospheric aerosol and its possible influence on climate changes in Siberia has been essentially enriched due to lots of *inset* measurements while monitoring atmospheric aerosol in Western and Eastern Siberia within the framework of "Siberian Aerosols" Project since 1991.[6–9]

The southern regions of Lake Baikal, high-mountain areas of Eastern Sayan and the Khamar-Daban ridge, as well as the Lake Baikal itself are influenced by interaction of different air masses, and so climate changes are the most pronounced there as illustrated by interannual air temperature dynamics in Fig. 1.

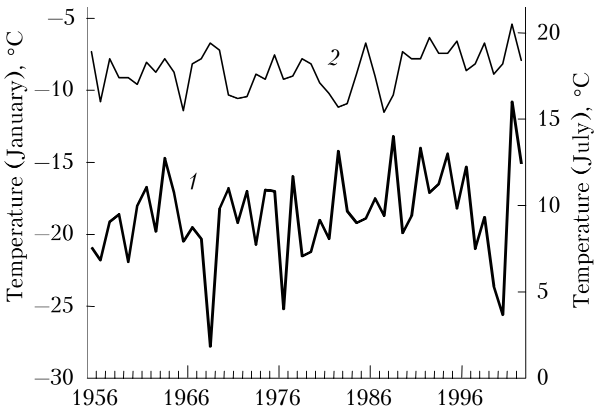

Fig. 1. Many-year variations of average air temperature in Irkutsk in January (*1*) and July (*2*).

The aim of this work is to study conditions of the atmospheric aerosol formation against the background of extreme weather conditions in Southern Siberia in the warm seasons of 2001 and 2002.

Investigation techniques and data

During the period from 2000 to 2004, the chemical composition of soluble fraction of atmospheric aerosol was studied at three monitoring stations (Irkutsk, Listvyanka, and Mondy) in the Baikal region. The following advanced techniques were used: high pressure liquid chromatography, atomic absorption, and spectrophotometry.[10–13] Adequacy of the obtained results was checked through balance of the total content of equivalent anion and cation concentrations having errors less than 5–10% as well as by international intercalibrations of the analysis quality control.[14,15] The synoptic processes over this region were studied

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for a warm season using daily weather charts (surface and altitude); their frequency was calculated for summer months of 2001–2002 because meteorological conditions and the chemical composition of atmospheric contaminants in these months well represent peculiar features of the region.

Results of investigations

The investigation of synoptic processes in the southern Baikal regions during the warm seasons of 2000–2004 showed that constant level surfaces in the layer of 1000–500 hPa height and circumpolar vortex troughs displace polewards in summer due to a high level of solar radiation. Usually the main trough of a high cyclone is oriented to the Central-Siberian Plateau while a second one, more flat, to Chuckchee and the Far Eastern seas (more often, to the Bering Sea). In 55% of cases, a high-level ridge affects the southern Baikal regions (Fig. 2) where warm air masses are transported from south and southwest in the rear part and along the axis of the ridge in 65% of cases. In 31% of cases, the region under study is influenced by high-level troughs oriented from Khatanga regions and Yakutia, where colder air comes to Southern Siberia from the north in the rear part and along the axis of a trough in 74% of cases. At the height of the main airflow, westerly ones prevail (31.4%) while meridional northwest and southwest flows occurred in 29% of cases each.

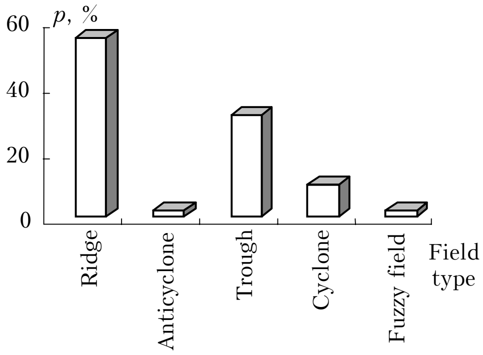

Fig. 2. Frequency of occurrence (%) of baric field types (H_{700}) in the south of Baikal region in the warm seasons of 2000–2004.

Due to frequent influence of the rear part of a high-level ridge, its axis, and axis of a high-level trough (59%) with the dynamic factor of air pressure drop, the low-pressure field prevails (44%) near the Earth surface (Fig. 3); in 32% of cases, it is characterized by passage of katafronts followed by cloud formation and precipitation events. Dynamic factors of air pressure rise, observed in the rear part of high-level troughs and the front part of a high-level ridge, stimulate (in 35% of cases) formation of a high-pressure surface field with characteristic descending flows resulting in dissipation of clouds and precipitation.

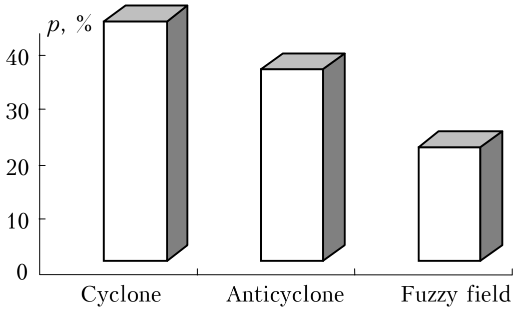

Fig. 3. Frequency of occurrence (%) of surface baric field types in the south of the Baikal region in the warm seasons of 2000–2004.

In 2000–2004 the aerosol chemistry in the industrial center (Irkutsk) was formed, against the background of synoptic processes, under the influence of sources common for all the urbanized areas, i.e., power plants, motor transport, and industrial enterprises. In Irkutsk, a peculiarity of the chemical composition of the soluble aerosol fraction was frequent occurrence of situations that the total mass concentrations of ions were below the average annual value for the period from 2000 to 2004, equal to 7.1 μg/m^3, in 67% of cases. In Listvyanka, where there were no powerful air pollution sources, the average annual total ion content in aerosol was equal to 5.4 μg/m^3, that was less than in Irkutsk; values up to 5.0 μg/m^3 were observed in 59% of cases. The main source of aerosol in Mondy was terrigenous substances. While the average annual total ion concentration was equal to 1.4 μg/m^3, 65% of measured values were below this level. The main ions in the chemical composition of aerosol were SO_4^{2-} and NH_4^+ (Table 1) at all the stations.

Among anions, the main, by the equivalent ratio, in the chemical aerosol composition in Irkutsk was sulphate-ion concentration with the average content of 25%-eq/m^3. In absolute values, SO_4^{2-}-ion concentration varied from analytic zero to 21.0 μg/m^3. Its highest values were recorded in cold

Table 1. Average ion concentrations in atmospheric aerosol at monitoring stations in the Baikal region in 2000–2004, μg/m^3

Station	HCO_3^-	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Sum of ions
Irkutsk	1.02	2.83	0.99	0.27	1.04	0.14	0.21	0.09	0.46	7.1
Listvyanka	0.69	2.35	0.46	0.33	0.88	0.20	0.24	0.05	0.22	5.4
Mondy	0.19	0.64	0.09	0.06	0.21	0.04	0.07	0.01	0.08	1.4

seasons. Contribution of HCO_3^--ions in the ion composition of aerosol was also considerable; their average relative concentration was equal to 11%-eq/m^3 and maximum content was observed in 2000 and 2004. NO_3^--ions with the average relative concentration of 7%-eq/m^3 were important as well; their contribution in the total ion concentration was the most significant in the period from July to December of 2002. Among the cations, ammonium (27%-eq/m^3) and calcium (12%-eq/m^3) ions were of highest priority.

In comparison with Irkutsk, the content of SO_4^{2-} and NH_4^+ ions (33 and 31%-eq/m^3, respectively) in the chemical atmospheric aerosol composition is higher in the region near Listvyanka; the latter, if presented in relative units, is more stable that can point out constant factors taking part in air chemistry formation on the south-west coast of Lake Baikal.

Aerosol chemistry in high-mountain areas of Eastern Sayan formed from natural sources mainly of land-erosion and biological origin. At Mondy station, significant concentrations of HCO_3^- and Ca^{2+} ions were recorded (9%-eq/m^3 of each) along with high content of SO_4^{2-} (32%-eq/m^3) and NH_4^+ (29%-eq/m^3) ions in the total aerosol ion concentration.

Relative concentration of NH_4^+-ions decreased while that of Ca^{2+}, Mg^{2+}, Na^+, and K^+ ions of terrigenous origin increased in warm seasons. At all the stations, three peaks were observed in time behavior of the total ion concentration. The first peak was observed in January–March, when impurities accumulated in the atmosphere at low air temperature and weak winds. The second peak in Mondy and Irkutsk was observed in the period from April to the beginning of June, when turbulent heat exchange and atmospheric convection intensified under high-level solar radiation, and in Mondy it was usually higher than in the cold season. In Listvyanka, the second peak was noted in July due to certain weakening of wind from Baikal under local anticyclogenesis. The third peak in distribution of the total ion concentration was observed in the fall (September–November) at all the stations. In this period the cyclogenesis becomes more intense again at transformation of the baric field near the Earth from summer to winter type.

On the whole, the spatial inhomogeneity, seasonal variability, and chemical composition of the soluble aerosol fraction obtained at the Baikal monitoring stations well agreed with the data of long-term observations. However, essential distinctions were revealed in the interannual dynamics of these parameters. The most significant deviations in quantitative and qualitative compositions of the soluble fraction of atmospheric aerosol were observed in the summer periods of 2001 and 2002. In this work, we do not examine the chemical aerosol composition in 2003, anomalous with respect to the ecological situation due to wast forest fires affecting air chemistry.

In comparison with long-term records (1993–2000), total ion concentrations were elevated in 2001 at lower air temperature, especially in the beginning of summer (Fig. 4). In some periods under study significant amounts of hydrogen carbonate ion (up to 36%-eq/m^3), chloride (up to 25%-eq/m^3), and calcium (up to 35%-eq/m^3) ion concentrations were observed. If comparing whole years, the air temperature in 2002 was higher than in 2001, and the total mass concentration of ions in atmospheric aerosol in Irkutsk and Listvyanka was lower than the annual mean values. Since April and until October it was close to values at the background station in Mondy. The most frequent values during the year were the following: 1.0–2.5 μg/m^3 in Irkutsk (up to 75% of the measured values), 1.0–4.0 in Listvyanka (up to 50%), and 0.1–1.4 μg/m^3 in Mondy (up to 80%). In addition, a significant buildup of nitrate ions (up to 16%-eq/m^3) was revealed, especially in the summer.

As part of the study, the observation periods were isolated, when distinctions in the chemical composition of aerosol in 2001 and 2002 were extreme and differed from the average data of long-term observations (Table 2).

Below, we analyze synoptic conditions for periods of elevated and reduced total concentrations of ions in the atmospheric aerosol. The behavior of synoptic processes in summer months of 2001 differed markedly from those in the same period of 2002.

In summer 2001, the south of Baikal region was frequently affected by rear, axis, and south periphery of a high-level trough (39%). At the same time dynamic factors favored trapping of the high-pressure field (52%) near the Earth surface for a long time as well as active heating of the ground layer of the atmosphere (monthly mean temperatures occurred to be 3.7°C higher than normal ones).[17]

Under conditions of domination of the northwest and west airflows (80%) aloft (Fig. 5), air masses moving over industrial areas of Krasnoyarsk and Irkutsk regions, entrained particles of anthropogenic origin what, together with anticyclone ascending airflows, caused an increase in the total ion content in atmospheric aerosol observed at the Baikal monitoring stations. The relative concentrations of ammonium, potassium, sodium, sulphate, nitrate, and chloride ions increased in the chemical composition of aerosol. A common source of atmospheric aerosol in this period is indicated by high correlation coefficient, r, between concentrations of ammonium and nitrate ions ($r = 0.78$), sulphate-ion ($r = 0.74$), and weaker correlation with chloride ion concentration ($r = 0.59$). In the beginning of July, abundant rainfall resulted in quick scavenging of these ions from the atmosphere. As a result, the total mass concentration of ions decreased from 31.8 to 1.8 μg/m^3 in Irkutsk, from 21.7 to 1.7 in Listvyanka, and from 3.2 to 1.6 μg/m^3 in Mondy.

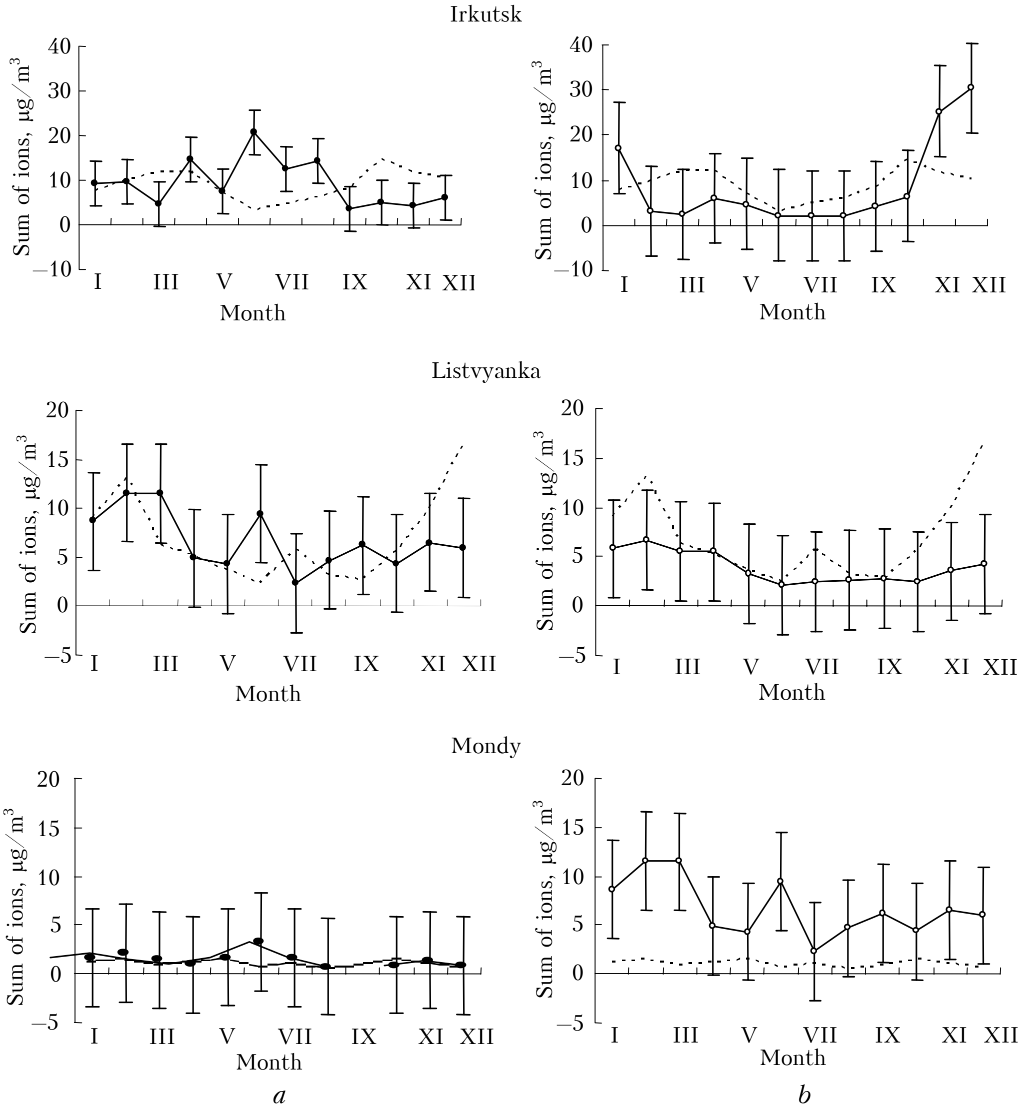

Fig. 4. Annual variation of total ion content in the atmospheric aerosol at monitoring stations in Baikal region, μg/m^3: 2001 (*a*), 2002 (*b*), annual mean over the period from 1993 to 2000 (- - -).

Table 2. Extreme values of the total mass concentration of ions in the aerosol in summer periods of 2001 and 2002 at the Baikal monitoring stations, μg/m^3

Station	Sampling period	Sum of ions, μg/m^3	Average annual sum of ions (summer period), μg/m^3
Irkutsk	06.28.01–07.09.01	31.6	6.2
	06.24.02–07.01.02	1.5	
Listvyanka	06.20.01–07.02.01	21.3	4.8
	06.20.02–06.30.02	1.1	
Mondy	06.24.01–07.03.01	3.3	1.2
	06.15.02–07.01.02	1.0	

Table 3. Frequency of occurrence (%) of baric surface field types in the south of Baikal region 06.20–07.10.2001 and 06.20–07.10.2002

Year	Type of baric field		
	cyclonic	anticyclonic	fuzzy field
2001	39	52	9
2002	31	26	43

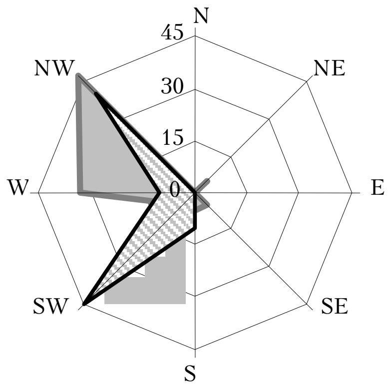

Fig. 5. Frequency of occurrence (%) of the main directions of airflow at the altitude of 3–5 km in the south of the Baikal region 06.20–07.10.2001 (gray area) and 06.20–07.10.2002 (dashed area).

As was shown in previous investigations of contributions coming from large-scale factors to changes of chemical composition of the water-soluble aerosol fraction, based on longer records, ion concentrations of alkali and alkaline-earth metals increase in Mondy under south and southeast flows from Mongolia. Increased content of sulphate and nitrate ions is related to zonal and meridional air mass transport when anticyclones and cyclones coming to the territory of Eastern Sayan along the polar and ultrapolar trajectories. In industrial areas of the south of Eastern Siberia and on the west coast of Lake Baikal, increased content of ammonium, sulphate, and nitrate ions is due to large-scale meridional air mass transport. Note that in moving (during about several days) over industrial Siberian regions to the territory of the Baikal region and Eastern Sayan, particles capture nitric and sulfur oxides.

Among all the periods under study, the warm season of 2002 was the most close to normal climate indices, when south Baikal regions were frequently influenced by rear and axis of a high-level ridge oriented from Mongolia and high-mountain areas of Eastern Sayan and dynamic factors favored low pressure periods (74%) near the Earth surface (see Table 3).

Under conditions of prevailing winds from the southern quarter (see Fig. 5) aloft, remoteness of the above territories from industrial areas caused low total ion content in atmospheric aerosol, which had mainly regional origin.

Development of ascending flows in the low could make for the flux of nitrate ions. The main sources of these in summer are top-soil (Mondy) and land transport emission (Irkutsk, Listvyanka). This condition can explain increased relative concentrations of these ions against the background of low sulphate-ion content at low total ion concentration in atmospheric aerosol in the described period.

Thus, our research has shown that the chemical composition of atmospheric aerosol depends essentially on the behavior of synoptic processes, which show strongest differences in anomalously warm and cold years. Increasing of the total mass ion concentration in the atmospheric aerosol is probably caused by the development of movable pressure fields in addition to industrial particles captured in moving over Siberian industrial centers. Low content of the atmospheric aerosol in Southern Siberia is caused by a long residence of a homogeneous air mass under blocking conditions over Europe, Atlantic, and Mongolia.

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References

1. B.I. Sazonov, *Severe Winters and Droughts* (Gidrometeoizdat, Leningrad, 1991), 240 pp.
2. G.P. Kurbatkin, A.I. Degtyarev, and E.A. Korotkova, Izv. Ros. Akad. Nauk, Ser. Fiz. Atmos. Okeana **40**, No. 5, 586–592 (2004).
3. I.K. Larin and A.A. Ugarov, Khimich. Fizika **22**, No. 4, 21–28 (2003).
4. J.H. Seinfeld, G.R. Carmichael, R. Arimoto, et al., Bull. Am. Meteorol. Soc. **85**, No. 3, 367 (2004).
5. C. Wang, R.G. Prinn, and A.A. Sokolov, J. Geophys. Res.-Atmosph. D **103**, No. 3, 3399–3417 (1998).
6. K.P. Kutsenogii and P.K. Kutsenogii, Sib. Ekol. Zh. **VII**, No. 1, 11–20 (2000).
7. T.V. Khodzher, L.P. Golobokova, V.A. Obolkin, V.L. Potemkin, and O.G. Netsvetaeva, Atmos. Oceanic Opt. **10**, No. 6, 403–406 (1997).
8. T.V. Khodzher, V.L. Potemkin, L.P. Golobokova, V.A. Obolkin, and O.G. Netsvetaeva, Atmos. Oceanic Opt. **11**, No. 6, 550–552 (1998).
9. B.D. Belan, T.M. Rasskazchikova, D.V. Simonenkov, and G.N. Tolmachev, Atmos. Oceanic Opt. **14**, No. 4, 295–299 (2001).
10. *RD 52. 24. 383-95. Methodological Instructions. Technique for Measuring Mass Concentrations of Ammonia and Ammonia Ions in Waters by Photometric Method Using Nessler's Reagent* (Rostov-on-Don, 1995), 18 pp.
11. *ISO 7890-86 Water Quality. Calcium and Magnesium Detection. Atomic Absorption Spectrometric Method* (Moscow, 1997), 6 pp.
12. *ISO 9964-3-93 Water Quality. Natrium and Potassium Detection with Spectrometric Method of Flame Emission* (Moscow, 1993), 12 pp.
13. G.I. Baram, A.L. Vereshchagin, and L.P. Golobokova, Zh. Analit. Khim. **54**, No. 9, 962–965 (1999).
14. *Manual for Sampling and Chemical Analysis*, EMEP/CCC – Report 1/95/ 0– 7726/ June 1995, 176 pp.
15. T.V. Khodzher, L.P. Golobokova, and O.G. Netsvetaeva, Atmos. Oceanic Opt. **17**, Nos. 5–6, 425–428 (2004).
16. L.P. Golobokova, "*Development and realization of techniques for study the chemical composition of trace gases and atmospheric aerosol (by an example of the Baikal territory)*," Author's Abstr. Cand. Tech. Sci. Dissert., Barnaul (2004), 19 pp.
17. *Climate of Irkutsk* // http://www.icc.ru/wx/climat.htm.