Spatiotemporal distribution of surface aerosol in Baikal region

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The results of chemical analysis of aerosol samples taken in the surface atmospheric layer of Ulan-Ude and towns and villages on the southeastern shore of Lake Baikal in fall of 1998 and spring-summer of 1999 are presented. These results are used to reveal the distribution of aerosol particles depending on the place of generation, season, local time, and meteorological characteristics of the atmosphere. It is shown that generation of secondary aerosols is possible under certain meteorological conditions in the near-shore zone of Lake Baikal.

Introduction

The content of aerosols in the atmosphere is determined by the intensity of their income from sources of different power, the place of generation, and meteorological conditions. The sources of aerosol particles, in their turn, determine the concentration, size spectrum, and chemical composition of aerosols in the atmosphere.

Of particular interest are aerosol particles in the near-ground layer. This layer contains the main fraction of aerosol overburden being in different phase states depending on the surface and meteorological conditions. The statistical regularities of these particles are yet poorly studied, and they call for on-line observations.

The most complicated and important process in the formation of surface aerosol is the transition of some gaseous substances into the disperse phase. This process generates secondary aerosols. The main secondary aerosol products in the atmosphere are nitrogen and sulfur oxides, ammonia, water vapor, as well as oxidized hydrocarbons. Ozone, atomic oxygen, and nitrogen oxides serve as strong basic oxidants.[1]

By now the data are obtained on the disperse and chemical composition of aerosols in the surface atmospheric layer at different sites of the Siberian region.[2] These data indicate that there exist marked differences in the concentration and chemical composition of aerosols sampled in different seasons and at different sites.

In this paper we present some results of analysis of the chemical composition of aerosol samples taken in different seasons of 1998 and 1999 and in different districts of Ulan-Ude and towns and villages of the southeastern shore of Lake Baikal.

Methods of sampling and sample analysis

Suspended particles with the aerodynamic diameter less than or equal to 10 μm were sampled to a Whatman–41 filter with a high-volume PM–10 sampler (made by General Metal Works Inc.) at the volume flow rate of 0.4–1.7 m^3/min and the accuracy of ± 0.03 m^3/min at the temperature ranging from 0 to 45°C.

The ion composition was analyzed at the Limnological Institute SB RAS:

– for anions – by the method of high-performance liquid chromatography (a Millichrom A–02 chromatograph);

– for cations – by the atomic absorption spectrophotometry method (an AAS–30 device).

The accuracy of these methods is not worse than 7% (Ref. 2).

The elemental composition was determined by use of the X-ray-fluorescent method with the use of synchrotron radiation at the Institute of Nuclear Physics SB RAS. This technique as applied to measurement of the elemental composition of atmospheric aerosols was described in Ref. 3.

Air was sampled in different residential areas of Ulan-Ude. A total of 39 sites subject to the effect of technogenic emissions or having the minimum anthropogenic load were selected. The total number of samples was 20 in the fall of 1998 and 40 in spring of 1999.

In summer of 1999 (July, August) suspended particles were sampled in industrial centers of the southeastern shore of Lake Baikal (Babushkin, Baikal'sk, Kamensk) and villages (Boyarsk, Kultushnaya) situated far from sources of industrial emissions. Simultaneously, the

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surface concentrations of minor gases (sulfur dioxide, nitrogen dioxide, carbon monoxide, and ozone) were measured. For these measurements, the following equipment was used: for SO_2 concentration – a Monitor Labs 8850 chemiluminescence gas analyzer, NO_x – an OPTEEK R–310 chemiluminescence gas analyzer, CO – a Palladium–3 electrochemical gas analyzer, O_3 – a Meloy Labs OA–350–2R chemiluminescence gas analyzer.

Discussion

Table 1 gives the results of measurement of fine aerosol in Ulan-Ude. It is seen from Table 1 that the high content of fine particles was observed in air of the areas Novaya Komushka and Vostochnyi. In Zagorsk, the aerosol concentrations in the sum of cations and anions were three times as large as that in the most unpolluted area (BNTs) of the Oktyabrskii District.

The elemental composition of aerosols in different Ulan-Ude districts in fall (November) of 1998 is given in Table 2.

Table 1. Ion composition of atmospheric aerosol in Ulan-Ude

#	Area	Sum	
		cations, μg/m^3	anions, μg/m^3
	Sovetskii District		
1	Levyi bereg	1.98	11.6
2	Steklozavod	7.7	18.7
3	Batareika	5.05	8.01
	Oktyabr'skii District		
4	Mel'kombinat	4.6	11.17
5	Myasokombinat	4.9	13.18
6	47th kvartal	2.3–7.2	5.3–17.1
7	Novaya Komushka	8.35	31.72
8	Gor'kii, Teletsentr	4.42	7.26
9	BNTs	1.98	5.72
10	18th, 19th kvartal	5.95	16.08
11	Energetik	5.81	7.19
	Zheleznodorozhnyi District		
12	Vostochnyi	4.04	25.7
13	Zagorsk	5.69	17.2
14	Arshan	4.71	11.09
15	Shishkovka	5.76	8.9
16	Center	3.57	9.7
17	Kirzavod	8.93	11.99

Table 2. Chemical composition of atmospheric aerosols in Ulan-Ude (November 1998) (in μg/m^3)

Chemical element	Sampling site					
	Gertsen Str., Zagorsk	Chkalov Str., Vostochnyi	Moskovskaya Str.	Mokrov Str., 46th kvartal	Meretskova Str.	Solnechnaya Str.
1	2	3	4	5	6	7
K	0.0	0.0	0.0	0.0	0.0	0.0
Ca	2.32	8.54	1.23	0.53	2.37	0.76
Sc	0.0	0.0	0.0	0.0	0.0	0.0
Ti	0.434	0.931	0.13	0.154	0.512	0.177
V	0.06	0.0	0.0	0.128	0.0	0.0
Cr	0.0	0.126	0.0	0.0	0.025	0.0
Mn	0.0	0.118	0.022	0.0	0.083	0.016
Fe	0.937	4.308	0.803	0.405	1.557	0.326
Ni	0.005	0.0	0.0	0.0	0.0	0.0
Cu	0.021	0.074	0.043	0.016	0.027	0.048
Zn	0.057	0.156	0.076	0.593	0.077	0.041
As	0.0	0.0	0.0	0.0	0.0	0.0
Br	0.02	0.053	0.042	0.016	0.014	0.009
Rb	0.0	0.0	0.0	0.0	0.0	0.0
Sr	0.047	0.117	0.005	0.003	0.078	0.003
Y	0.0	0.0	0.0	0.0	0.0	0.0
Zr	0.003	0.003	0.002	0.002	0.058	0.0
Nb	0.0	0.0	0.0	0.0	0.0	0.0
Mo	0.002	0.004	0.0	0.0	0.0	0.0
Pb	0.036	0.068	0.056	0.018	0.028	0.014
	Cations					
Na^+	1.90	1.69	0.73	0.90	1.04	1.23
K^+	1.52	0.82	0.63	0.34	0.94	0.75
Ca^{2+}	0.84	1.,61	0.15	0.18	1.06	0.11
Mg^{2+}	0.28	0.35	0.08	0.08	0.20	0.09
NH_4^+	5.45	7.45	2.05	1.27	0.94	0.86
Sum of cations	5.69	4.04	3.57	2.30	1.98	1.98
	Anions					
HCO_3^-	3.57	7.06	0.82	2.05	0.20	2.30
Cl^-	1.34	1.58	2.00	0.36	6.33	0.63
NO_3^-	3.56	8.46	0.93	0.79	2.03	0.00
SO_4^{2-}	5.70	7.10	5.07	2,14	3.10	2.45
PO_4^{3-}	3.01	1.53	0.86	0.00	0.00	0.34
Sum of anions	17.17	25.73	9.69	5.34	11.65	5.72

The aerosol is distributed inhomogeneously over Ulan-Ude districts. As to the content of metals (Cu, Ca, Fe, Ti), the most unpolluted area is 46th kvartal, the most polluted one – Vostochnyi, which is in the Zheleznodorozhnyi District, in which main industrial enterprises are concentrated.

The mass concentrations of Fe, Mn, Mg, Ti, and Sr have a specific and local character depending on the closeness to a source of pollution. The concentrations of these elements in Vostochnyi and other areas are markedly different. Such a distribution assumes the presence of large particles emitted by plants of the aircraft industrial association. It is well-known[4] that the lifetime of such particles in the atmosphere is short – about several minutes.

Analysis of the chemical composition of suspended particles in Ulan-Ude districts showed that the content of NO_3^-, NH_4^+, and SO_4^{2-} ions is distributed inhomogeneously too. High concentrations of NO_3^-, SO_4^{2-}, PO_4^{3-}, and NH_4^+ were observed in Vostochnyi and Zagorsk. The concentrations of SO_4^{2-} and NH_4^+ ions in these areas are almost equal. This is explained by the fact that these ions exist in the atmosphere only in the form of ammonium sulfate $(NH_4)_2SO_4$ (Ref. 2). They are emitted from furnaces of the aircraft plant. Thus, for example, smelting furnaces emit, along with dust and iron oxides, large amounts of SO_2 and ammonia NH_3 (Ref. 5). Then, oxidation of SO_2 in water droplets in the presence of ammonia yields ammonium sulfate.[6] When sampling in the fall season, fog of an advective origin was often observed. High atmospheric humidity favored formation of the high concentrations of SO_4^{2-} and NH_4^+ ions.

High concentration of NO_3^- ions at these sites is explained by superposition of emissions from the heat power plant TETs–1, industrial enterprises, and boiler-houses of Zagorsk and Vostochnyi at the southwestern transport of air masses, in which liquid-phase oxidation of nitrogen oxides and generation of nitrates probably occur. The concentrations of NO_3^- in other areas were almost an order of magnitude lower.

Table 3 gives the mean characteristics of the ion composition of aerosols and their variability in Ulan-Ude in the cold season. For a comparison, Table 3 shows also the characteristics of the ion composition of aerosols for other meteorological stations situated in the same region (Irkutsk, Mondy).[8] It was found that the distribution of the concentrations of SO_4^{2-} and NH_4^+ ions in Ulan-Ude and at the station Irkutsk in the cold season is almost the same. Some excess of sulfate ions over ammonium ions (2.3 times in Ulan-Ude, 3.2 times at the station Irkutsk) is indicative of the presence of H_2SO_4, besides ammonium sulfate, near the source of emission.[7,8]

The relatively high concentration of NO_3^- ions is indicative of the presence of nitrogen oxides, which are emitted to the atmosphere from chimneys and motor transport. At the station Mondy, which falls in the category of background stations, the concentration of NO_3^- ions is low.

Table 4 gives the results of analysis of aerosol samples taken in towns and villages on the southern shore of Lake Baikal. The distribution of the soluble aerosol fraction is very irregular and inhomogeneous. The total concentration of ions in Baikal'sk far exceeds that in other sites: 60 times as large as the sum of cations in Ulan-Ude and 17 times as large as the sum of anions. That high concentrations of ions in Baikal'sk are connected with the effect of a large source of emissions – Baikal Pulp and Paper Mill. The concentration of ions in aerosols of other sites of the southern shore of Lake Baikal is far lower than that in Ulan-Ude and Baikal'sk.

Of special interest is the content of NO_3^-, SO_4^{2-}, and Na^+ ions in aerosols in Boyarsk village situated in the relatively unpolluted region of the southern Baikal shore. The elevated concentrations of sodium ions and sulfates in Boyarsk are likely connected with the processes of remote transport of pollutants, whose source is the Pulp and Paper Mill, which uses such substances as NAOH and H_2SO_4 for pulp production.

Comparison of the concentrations of NO_3^- ions in Boyarsk, Baikal'sk, and Babushkin showed that they are close and equal, respectively, to 0.73, 0.85, and 0.74 $\mu g/m^3$. Since the effect of anthropogenic sources is improbable because of remoteness from the industrial centers, the peculiarities of chemical and photochemical reactions in the slightly polluted atmosphere of the near-shore zone of Lake Baikal are likely determined to a high degree by the radiation conditions and air humidity. The presence of shortwave radiation leads to formation of oxidants, which give rise to the main processes of generation of secondary aerosols.[10] Nitrogen compounds play a significant role in generation of secondary aerosols. This transformation of aerosols from the gas phase of nitrogen oxides can be represented as the following sequential reactions:

$$1)\ NO + O_3 \rightarrow NO_2 + O_2,$$

$$2)\ 2NO_2 + H_2O \rightarrow 2H^+ + NO_3^- + NO_2^-.$$

The first reaction proceeds rather fast with the participation of ozone being a strong oxidant and yields easily condensable gas NO_2. Then, liquid-phase oxidation of NO_2 and formation of nitrates occur at heterogeneous processes. Catalytic liquid-phase oxidation with the participation of calcium and magnesium ions, which accelerate the process of generation of NO_3^- ion, is also quite possible. It is well known that heterogeneous processes play supreme role in transformation of aerosols. This is evidenced by experimental data on the correlation between the number of solid aerosol particles in the atmosphere and the rate of transformation of nitrogen oxides into nitrates.[7]

Table 3. Mean characteristics of ion composition of aerosols in different areas of the Baikal region

Characteristic	Ion composition of aerosols, in μg/m^3										
	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	H^+	HCO_3^-	Cl^-	NO_3^-	SO_4^{2-}	PO_4^{3-}
Ulan-Ude (November 1998)											
Mean	1.25	0.83	0.66	0.18	3.0	0.15	2.67	2.04	2.63	4.26	0.96
Max	1.9	1.52	1.61	0.35	7.45	0.21	7.06	6.33	8.46	7.1	3.01
Min	0.73	0.34	0.11	0.08	0.86	0.09	0.2	0.36	0	2.14	0
Ulan-Ude (March 1999)											
Mean	1.73	0.57	1.4	0.22	2.11	0.18	2.42	2.32	2.71	6.41	–
Max	2.58	1.09	2.13	0.52	2.97	0.27	3.49	3.72	8.04	17.24	–
Min	1.26	0.25	0.77	0.12	1.01	0.03	1.4	1.5	0.73	2.38	–
station Irkutsk (winter)											
Mean	0.12	0.18	0.44	0.13	2.17	–	0.0	0.2	1.29	3.98	–
Max	0.31	0.36	1.24	0.42	7.0	–	0.0	0.58	5.33	22.46	–
Min	0.0	0.07	0.05	0.04	0.41	–	0.0	0.0	0.23	0.31	–
station Mondy (winter)											
Mean	0.0	0.02	0.02	0.02	0.09	–	0.05	0.0	0.02	0.28	–
Max	0.06	0.03	0.38	0.09	0.18	–	0.29	0.02	0.07	0.71	–
Min	0.0	0.01	0.0	0.0	0.01	–	0.0	0.0	0.0	0.0	–

Table 4. Ion composition of aerosols at different sites of the southeastern shore of Lake Baikal

Sampling site	Babushkin	Boyarsk	Kultushnaya	Kamensk	Baikal'sk	Ulan-Ude
Cations						
Na^+	0.55	8.0	0.74	0.47	202.46	1.56
K^+	0.36	0.0	0.96	0.02	8.98	0.6
Ca^{2+}	0.25	0.0	0.0	2.77	22.53	1.3
Mg^{2+}	0.11	0.03	0.08	0.58	2.5	0.22
H^+	0.02	0.116	0.038	0.107	0.0004	0.2
Sum of cations	1.29	8.15	1.82	3.95	236.47	3.88
Anions						
HCO_3^-	1.45	0.87	0.62	3.62	152.74	2.25
Cl^-	0.77	0.0	0.0	0.0	11.34	2.4
NO_3^-	0.74	0.73	0.62	1.23	0.85	1.94
SO_4^{2-}	2.49	2.66	1.34	2.52	27.97	4.75
Sum of anions	5.45	4.26	2.58	7.37	192.9	11.34

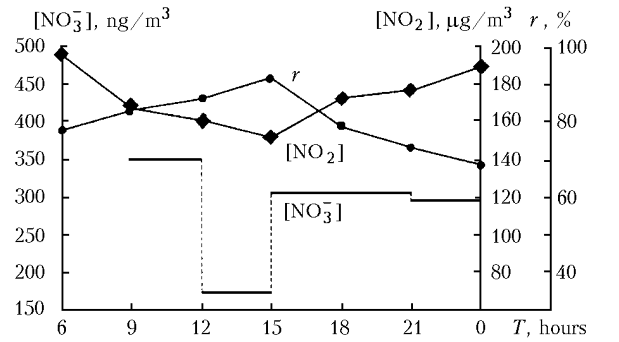

Fig. 1. Diurnal variations of the surface concentrations of NO_2 and NO_3^- and the relative humidity *r*, in %, Boyarsk, August 1999.

Figure 1 shows the diurnal variations of [NO_2] and [NO_3^-], as well as the values of the relative humidity averaged for every 3 hours of the observational period. The increased levels of [NO_3^-] correspond to the high values of the relative humidity; this can be interpreted as the growth of [NO_3^-] due to water vapor adsorption by nitrogen dioxide and its further solution, for example, with the participation of ions of calcium or other metals. For nitrates (NO_3^-) there exists some correlation with NO_2 in the morning (08:00 – 10:00 L.T.). No pronounced correlation of nitrates with the ozone content is observed.

Thus, nitrates are likely generated by two sources: from NO_2 in the morning at high relative air humidity and on particles due to heterogeneous reactions in the evening.

In conclusion, it should be noted that the chemical composition of aerosols in different districts of Ulan-Ude and villages and towns of the southeastern shore of Lake Baikal is extremely inhomogeneous. The concentration of the main ions in the close proximity of industrial enterprises far exceeds the background levels.

In the slightly polluted near-shore zone of Lake Baikal at high intensity of the solar radiation and high relative humidity of the air, photochemical processes of generation of secondary aerosols are possible.

For detailed study of the spatiotemporal dynamics of the chemical composition of aerosols on the southeastern shore of Lake Baikal, continuous measurements of the concentrations of both gaseous and aerosol atmospheric constituents are needed. The data obtained in this way would allow evaluation of the correlation between aerosol and gaseous constituents and estimation of their contributions to the formation of the composition of the regional atmosphere.

References

1. M.V. Kabanov, *Regional Monitoring of the Atmosphere.* Part 1. *Scientific and Methodical Principles*, ed. by V.E. Zuev (SB RAS Publishing House, Tomsk, 1997), 211 pp.
2. T.V. Khodzher, V.L. Potemkin, L.P. Golobokov, V.A. Obolkin, and O.G. Netsvetaeva, Atmos. Oceanic Opt. **11**, No. 6, 550–552 (1998).
3. K.P. Koutsenogii, G.A. Koval'skaya, A.N. Smirnova, A.S. Bufetov, and V.B. Baryshev, Atmos. Oceanic Opt. **10**, No. 7, 512–517 (1997).
4. Ts.Ts. Dambiev, S.M. Legostaev, et al., *Protection of the Environment in Power Production of the Baikal Lake Region* (Buryatiya Publishing House, Ulan-Ude, 1997), 125 pp.
5. C.E. Junge, *Air Chemistry and Radioactivity* (Academic Press, New York – London, 1963).
6. C.E. Junge and T.G. Ryan, Quart. J. Roy. Meteorol. Soc. **84**, No. 359, 46–55 (1958).
7. L.S. Ivlev, *Chemical Composition and Structure of Atmospheric Aerosols* (Leningrad State University, Leningrad, 1982), 368 pp.
8. T.V. Khodzher, V.L. Potemkin, and V.A. Obolkin, Atmos. Oceanic Opt. **7**, No. 8, 566–569 (1994).
9. Yu.A. Dovgalyuk and L.S. Ivlev, *Physics of Water and Other Atmospheric Aerosols* (St. Petersburg State University, St. Petersburg, 1998), 321 pp.