DIURNAL AND SEASONAL VARIABILITY OF THE ATMOSPHERIC AEROSOL ION COMPOSITION IN THE SOUTH OF EAST SIBERIA

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In this paper we consider the ion composition of aerosols based on the experimental data from the environmental monitoring stations of Baykal region. The observational results demonstrate that the sites chosen for aerosol sampling characterize the regional aerosol background depending on season. In particular, at the station "Mondy" (the mountain range Khamar-Daban, 2000 m *above the sea level) one observes "background continental aerosol" which is free of the influence of regional and local anthropogenic sources.*

INTRODUCTION

In recent years, a lot of new data on chemical composition of aerosols in the Baykal region have been obtained.[1–4] However almost all information relates to warm seasons. At the same time, considerable seasonal variations in composition and concentration of aerosols may occur due to significant variations in the aerosol source intensity and/or meteorological conditions of the aerosol dispersal.

Under the financial support of INTAS foundation, regular seasonal monitoring of the aerosol chemical composition in the Asian part of the former USSR has been started in 1994-1995. In particular, the aerosol sampling is conducted at some sites of the Baykal Lake region. The geographical positions of these stations have been chosen to provide the representativity of the observational conditions: for example, the global and regional background, an anthropogenic influence on aerosols, etc.

Analysis of aerosol samples is performed by different methods in the Russian and foreign scientific institutions, in order to obtain the most complete and representative data on the aerosol composition. This paper summarizes the results of measurements of soluble aerosol fraction – principal ions analyzed at the Limnological Institute of SB RAS.

THE INVESTIGATION TECHNIQUE

The map of the aerosol monitoring stations in the Baykal region is shown in Fig. 1.

"Mondy" is the astrophysical observatory of the Institute for Studying Solar-Terrestrial Physics of SB RAS, situated on a plane top (2000 m above sea level) of the mountain range Khamar-Daban. The observatory is supplied with electricity from the industrial electric line and, therefore, has no local sources of the atmospheric pollution. There are no settlements in the range of several dozens kilometers around the station. The distance from "Mondy" to important industrial centers (Irkutsk, Baykal'sk) is more than 200 km.

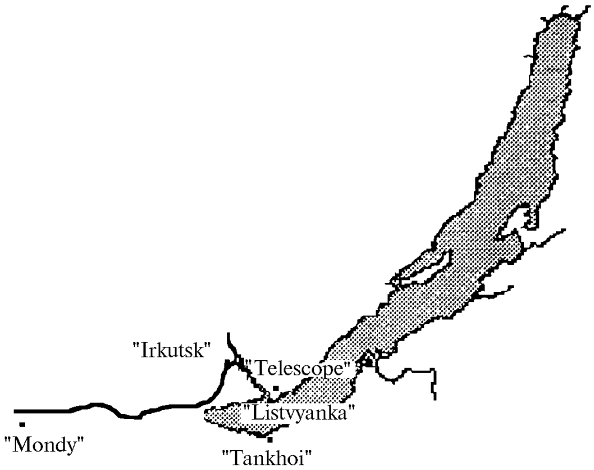

FIG. 1. The map of stations for aerosol sampling in the Baykal Lake region.

In "Listvyanka" there is another one observatory of the same institute. The aerosol sampling was performed on the top of a coastal hill (300 m above the Baykal Lake level), situated several kilometers north-east of the village of Listvyanka (west shore of the lake).

The meteostation "Source of the Angara river" is situated in the Listvyanka village. It was used to compare the measurement results with those obtained at "Listvyanka" observatory and to estimate a settlement influence on the results of observations.

Station "Tankhoi" is situated on the east shore of Baykal, opposite the village Listvyanka. The aerosol sampling was conducted at the territory of Baykal State National Park situated out of the village.

The station "Irkutsk" is in Akademgorodok on the left bank of the Angara river (i.e. in the city of

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Irkutsk). The sampling was performed at the territory of the Limnological Institute, SB RAS.

To analyze the ion composition of the aerosol, it was sampled on "Wathman-41" filters using the air pumping with the vacuum pumps at a rate of 40–50 liter/minute (exposure time is 24 h or 48 h). The anion chemical composition of the aerosol soluble fraction after extractions from the filters with doubly distilled water was determined by methods of highly efficient liquid chromatography (a "MILICHROME" chromatograph), the cation chemical composition was determined by the atomic absorption method (an ASS-30 device). The maximum error of both methods does not exceed 10%.

DISCUSSION OF THE RESULTS

Table I lists the average concentrations of the principal ions. The total concentration of all atmospheric aerosol ions, obtained at the above mentioned stations in the warm and cold seasons in 1995–1996, is shown in Fig. 2.

These data prove that at the station "Mondy," situated far from the industrial centers, one observes minimum concentrations of ions both in summer and winter. This may be caused not only by the large distance to anthropogenic pollution sources, but also by its highland location (influence of vertical gradients of aerosols).

TABLE I. Seasonal mean concentrations C (μg/m^3) *of ions and their standard deviations σ in aerosol particles sampled in the Baykal region in* 1995–1996

Ions	Sampling stations									
	"Irkutsk"		Listvyanka (village)		"Listvyanka" (observatory)		"Tankhoi"		"Mondy"	
Winter										
	C	σ	*C*	σ	*C*	σ	*C*	σ	*C*	σ
Na^+	0.12	0.10	0.15	0.17	0.12	0.11	0.18	0.12	–	–
K^+	0.18	0.09	0.11	0.08	0.06	0.03	0.07	0.06	0.02	0.01
Ca^{2+}	0.44	0.31	0.32	0.51	0.08	0.07	0.07	0.16	0.02	0.09
Mg^{2+}	0.13	0.09	0.11	0.09	0.04	0.03	0.03	0.01	0.02	0.02
NH_4^-	1.96	1.84	1.74	1.80	0.78	0.72	0.42	0.11	0.09	0.04
HCO_3^-	–	–	0.15	0.26	0.07	0.07	0.08	0.12	0.05	0.08
Cl^-	0.20	0.18	0.10	0.12	0.02	0.03	–	–	–	–
NO_3^-	1.29	1.32	2.07	1.46	1.14	0.83	0.27	0.25	0.02	0.02
SO_4^{2-}	3.98	5.79	6.76	5.56	2.51	1.69	2.33	1.04	0.28	0.19
Summer										
Na^+	0.04	0.06	0.02	0.03	0.08	0.07	0.05	0.05	0.04	0.08
K^+	0.17	0.06	0.05	0.02	0.11	0.09	0.06	0.03	0.12	0.07
Ca^{2+}	0.71	0.32	0.12	0.09	0.23	0.24	0.02	0.03	0.04	0.04
Mg^{2+}	0.22	0.09	0.07	0.04	0.08	0.04	0.03	0.01	0.04	0.03
NH_4^-	0.73	0.30	0.44	0.15	0.43	0.17	0.34	0.31	0.22	0.13
HCO_3^-	0.10	0.12	0.05	0.13	0.04	0.11	–	–	0.03	0.04
Cl^-	0.04	0.07	–	–	0.02	0.02	0.01	0.04	0.03	0.05
NO_3^-	0.38	0.23	0.20	0.18	0.44	0.24	0.09	0.05	0.10	0.09
SO_4^{2-}	1.28	0.66	0.83	0.46	1.53	1.01	0.45	0.30	0.51	0.44

The summer ion concentration observed at this station is higher than that in winter (see Fig. 2). On the contrary, at other stations, one observes explicitly higher total winter ion concentration than the summer one. The following two factors may result in the above mentioned explicit differences in the seasonal behavior of the aerosol ions concentrations: (i) decrease of the aerosol generation from the soil during the cold season due to a snow cover influence; (ii) unfavorable conditions for dispersal of the impurities from anthropogenic sources (due to domination of the inverse atmospheric stratification in winter). The latter leads to the increase of the pollution concentration near the sources, and, therefore, it decreases their contribution to a global background. Thus, the decrease of the ions concentration observed at the station "Mondy" in winter proves that the polluted air-mass from a regional anthropogenic sources does not reach this site, and one observes a global aerosol background there.

The pattern observed at other stations confirms this assumption. For example, in Irkutsk, the winter ion concentration is 2–3 times higher than the summer one, but the ratio of ions changes slightly (the content of sulfates increases). The main reasons of this phenomenon are evident, it is the increase of the fuel consuming and unfavorable atmospheric conditions for dispersal of impurities.

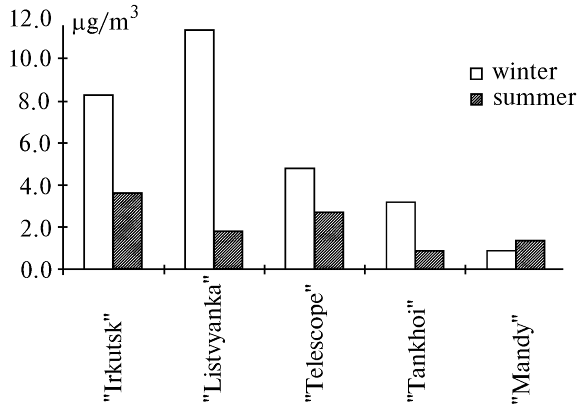

FIG. 2. Seasonal mass concentration of the ion fraction of aerosols sampled in the Baykal region.

In the South Baykal region sites (several tens kilometers from Irkutsk) there is also observed the seasonal from summer to winter growth of ion concentration though 1 to 1.5 times only. In this case, the increase of the ion concentration is mostly due to sulfates (see Table I), because they primarily are in small-size particles, and can be transported to a long distance.

Though the aerosol sampling stations are out of settlements, it was important to observe here regional background aerosol (created by remote industrial sources, e.g. Irkutsk) and that from small local sources, in these settlements. To estimate the reliability of such "aerosol classification" observed in these sites, we have conducted parallel observations at the stations in "Listvyanka" (observatory), the village of Listvyanka, and in Irkutsk.

In the village Listvyanka, the influence of many small sources (stoves of private houses) was found to be considerable in winter. In particular, the winter concentration of ions under consideration here is 5–10 times greater than that observed in the summer, whereas its concentration increased 1.5 times in "Listvyanka" observatory (i.e. out of the village territory) (see Fig. 2.). However, in "Listvyanka" observatory the ratio of contributions of local and remote sources to aerosols remains unknown.

Unfortunately, the attempts to find correlation between the aerosol content variations and wind directions (taking into account the position of potential aerosol sources) as well as with the meteorological situation failed. This may be caused by the duration of the aerosol sampling process (24 or 48 h), since, as a rule, the weather changes several times during such period of time. The authors did not find any influence of the remote transfer (using the inverse trajectories of the air masses moving) on the concentration and distribution of ions at the sampling sites. Most likely the data on aerosol ion composition can not be used for investigations with tracers (it is much better to use the data on the element composition for this purpose). The variability of the daily mean ion concentration is most likely caused by the general state of the boundary atmospheric layer (e.g., its stability or the dissipation ability at the observation site) than by a concrete direction of the air mass transfer.

In this connection we have tried to statistically assess the contributions from different localities into the ion concentration measured in Listvyanka (observatory) in order to reveal possible sources of ions.

According to the correlation analysis, the ion composition of aerosols in winter in "Listvyanka" (observatory) is determined mainly by the anthropogenic sources of the village Listvyanka: the correlation coefficient for the ion ratio was found to be 0.8 (with respect to village Listvyanka), and 0.0 (Irkutsk). In summer, the correlation coefficient for the ion ratio is 0.6 (correlation with respect to Irkutsk), and 0.0 (Listvyanka). Thus, the aerosol sampling stations situated near even small settlements (e.g., Listvyanka, Tankhoi) can characterize only a summer aerosol background, since in winter, it is strongly affected by local anthropogenic sources (stoves of houses).

TABLE II. Most probable chemical compounds forming the ion aerosol fraction at the Baykal region sites.

Season	Listvyanka (village)	"Listvyanka" (observatory)	"Tankhoi"	"Mondy"
Winter	$(NH_4)_2SO_4$ Na_2SO_4	$(NH_4)_2SO_4$ $MgSO_4$	$(NH_4)_2SO_4$ Na_2SO_4 NH_4NO_3	$(NH_4)_2SO_4$ NH_4HCO_3
Summer	$Ca(NO_3)_2$ KNO_3 $(NH_4)_2SO_4$ K_2SO_4 $MgSO_4$	$Ca(HCO_3)_2$ NH_4NO_3 $(NH_4)_2SO_4$	$Mg(NO_3)_2$ KCl	$(NH_4)_2SO_4$ $MgSO_4$

It is the magnitude of correlation between cations and anions that was used as a criterion for the estimation of the most probable chemical compounds in the ion aerosol fraction observed at the settlements of interest. Table II gives the list of chemical compounds with the anion-cation correlation exceeding 0.5 (listed in order of the correlation coefficient decrease). The obtained data show that at all sites, the ammonium sulfate dominates in aerosol composition in winter whereas it dominates only at the background station "Mondy" in summer period (this is typical for background regions[5]). As to other stations, one observes the domination of other chemical substances that may come from soil. In the South Baykal region sites ("Listvyanka" and "Tankhoi"), the probability of the Na_2SO_4 presence in aerosols is relatively high (see Table II) that can be explained by the influence of the Baykal pulp and paper mill. Note, that the hydrogen ions were not analyzed in the course of our experiments. That is why H_2SO_4 and HNO_3 acids may dominate in the list from Table II. This assumption is proved by the fact of a frequent absence of the hydrocarbonate ion in the water extractions from the aerosol samples, since it annihilates in the course of the acid neutralization reactions if a solution PH factor is less than 5.2–5.4.[6] The observed frequency of occurrence of such cases (in %) according to our experiments is listed in the following table:

	"Irkutsk"	"Listvyanka" (observatory)	"Tankhoi	"Mondy"
Winter	87	53	25	47
Summer	40	75	93	36

Diurnal variability of the aerosol ion concentrations has often an explicitly positive asymmetrical distribution (from 0.3 to 2 and more). That is why, the geometrical mean values of concentrations are considered to be more representative characteristics of the average concentrations than the mathematical expectation.

CONCLUSION

The sites for aerosol sampling chosen characterize a regional aerosol background depending on season. The station "Mondy" is a typical example of the "background continental aerosol" which is free from the regional and local sources influence during the whole year. The sites "Listvyanka" and "Tankhoi" can be used for the regional aerosol background investigations only in summer since during winter the aerosols observed at these stations may strongly be affected by local anthropogenic sources.

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