CHEMICAL COMPOSITION OF AEROSOL AND TRACE GASES IN THE ATMOSPHERE OVER LAKE BAYKAL

T.V. Khodzher, V.L. Potemkin, and V.A. Obolkin

Limnological Institute,
Siberian Branch of the Russian Academy of Sciences, Irkutsk
Received March 23, 1994

The paper presents the results of investigations on chemical composition of soluble fraction of aerosols (anions and cations) and trace gases (SO_2 and NO_2) over the water area of Lake Baykal in summer. The results demonstrated that, on the whole, the mass concentrations of ions in aerosol and trace gases in the atmosphere over the major part of Lake Baykal are low and comparable with the background values of these components in other uncontaminated regions of the world. However, in the south part of the lake, near large populated areas, an essential excess of concentrations against the background values has been detected. We have also studied the dependence of ion composition of aerosols on the particle size and determined the salt composition of the aerosol over Lake Baykal.

Chemical composition and particle size are the most important parameters of atmospheric aerosol determining the degree of its influence on the environment. The study of these characteristics for the Baykal aerosol is of practical importance because the atmospheric aerosol is one of the factors involved in forming chemical composition and quality of the Baykal water, its basic natural resource. In recent years the research programme into the Baykal aerosol is among various international scientific programmes. The results described in this paper are the part of these investigations. They are devoted to the study of ion fraction of aerosol and trace gases, which can be the source of this aerosol formation.

Up to now, the Baykal aerosol chemical composition, in contrast to its physical characteristics (a great body of data has been accumulated[1–3]), has been poorly investigated. In particular, such data on ion composition are presented either by the estimate of contribution of separate ions (sulfates, more commonly)[4–5] or by more total set of data but at separate point of observations.[6] This paper first presents the results of large–scale aerosol survey over the whole of water area of the lake.

METHODS OF SAMPLING AND SAMPLE ANALYSIS

Aerosol sampling was performed on board a research ship, as a rule, during its motion in order to exclude entrapment of engine exhaust on the receiving devices. In aerosol sampling to determine the ion composition two setups were used: a five–step cascade impactor designed by Institute for Chemical Kinetics and Combustion, SB RAS, with the step average median diameters of particles (30, 19, 7, 3, and less than 3 μm) and a high–volume air intake. For the both setups the aerosol was sampled on WATMAN–41 filters using the air pumping with centrifugal pumps at the rate from 100 to 400 liter/min. The anion chemical composition of the aerosol soluble fraction after extraction from filters with doubly distilled water was determined by the methods of highly efficient liquid chromatography (a MILIKHROM chromatograph) with the error of 4–7 %, the cation chemical composition was determined by the atomic absorption method (an AAS–30 device) with the error of 4–6%.

The concentrations of sulfur and nitrogen dioxides in atmospheric layer adjacent to water were measured with a correlation mass spectrometer designed in the Central Aerological Observatory (Moscow). The operation of the device is built upon measuring the relative difference of the optical radiation intensity for two sets of narrow spectral ranges corresponding to maximum and minimum absorption of a gas under study.[7–9]

The calibration of the device was performed by means of an optical quartz cell containing known quantity of gas, that was regularly set up in the path of received radiation (scattered solar one). The device was certified with an error of 10% for SO_2 in the range of integral gas content along the path from 5 to 500 ppm·m and 15% for NO_2 in the range from 5 to 150 ppm·m. The sensitivity of the device is 0.2 ppb for SO_2 and 0.5 ppb for NO_2 (Ref. 9). Under normal conditions after putting in an efficient path length 1 ppb = 2.8 $\mu g/m^3$ for SO_2 and 2.0 $\mu g/m^3$ for NO_2.

The observations were carried out with simultaneous recording of meteorological data and visibility.

DISCUSSION OF THE RESULTS

Aerosol survey was conducted in June and July, 1992 practically over the whole of water area of the lake. All in all, 227 aerosol samples were selected and analyzed and 64 sets of measurement of trace gases (SO_2 and NO_2) (10–15 counts along different directions in each set) were conducted. Since the samples of aerosol and trace gases were taken at different places and different time, it is difficult basing on selected samples to assess the association of spatiotemporal variability of aerosol characteristics and the meteorological data or local conditions. Therefore, we consider below only the average characteristics of ion composition and trace gases in three parts of the lake, namely, north, middle, and south basins as well as at the part of water area near Baykal'sk, being together with the Baykal pulp and paper mill (BPPM) the largest anthropogenic source of aerosol at the lake coast.

0235-6880/94/08 566-04 $02.00

Figure 1 presents the mean values and variation levels of mass concentration of basic ions at the considered parts of water area. It is evident that among anions sulfates, hydrocarbonates, and chlorides are predominant ones. However, their mutual relation in different basins is different. Thus, in the south basin the content of sulfates is essentially increased as compared to the other anions, and in the middle basin the largest values are determined for hydrocarbonates. In the north basin the limits of variations of mass concentration of these anions are closely allied although the average values of sulfates are larger than those of remaining ions.

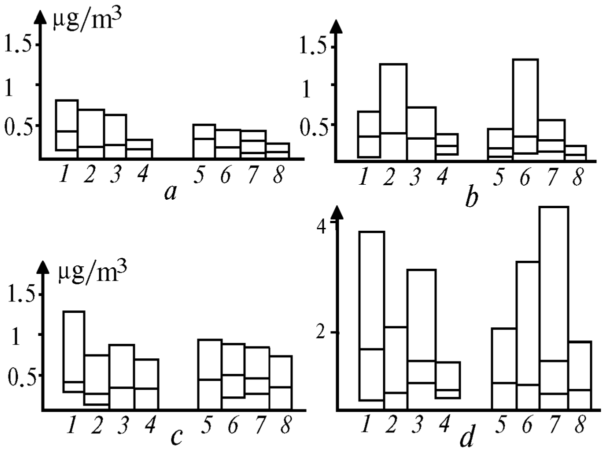

Fig. 1. Average values and levels of variations of the ion mass concentration of the Baykal aerosol (μg/m³): SO_4^{2-} *(1),* HCO_3^- *(2),* CL^- *(3),* NO_3^- *(4),* NH_4^+ *(5),* Ca^{2+} *(6),* Na^+ *(7), and* K^+ *(8); the north Baykal (a), the middle Baykal (b), the south Baykal (c), and near Baykal'sk (d).*

There are some differences between the cation mass concentrations in different basins. The ions of calcium, ammonium, and sodium are primary ones in this context. As for the anions, the differences between their concentrations in the north basin are insignificant, since in the middle basin the number of calcium ions is significantly in excess of the number of other ions, and in the south basin the ammonium ions are predominant. It is evident that these differences between the relations of ions in basins are connected, first of all, with the differences between natural conditions of coasts. The middle basin are characterized by dry climate, and significant part of its coasts is represented by steppe and semi–desert landscapes (especially the region of Maloye More), which are the source of high content of such salts as carbonates and sulfates of calcium in aerosol particles. Besides, there are brine lakes with high concentrations of the above–mentioned salts in water.[10]

The coasts of north and south basins are covered with forests, which can be the sources of ammonium ions in summer. Apart from this reason, the increased mean background of all ions is typical for south basin as compared with the other ones, and higher variations of sulfates are related to an additional contribution of anthropogenic sources concentrated mainly in the south part of the lake. As the survey performed above the water area near the city of Baykal'sk has shown (Fig. 1), there is a considerable excess of ion concentrations under study as compared with the mean background of the south basin. In this region the ratio between ions in aerosol is different, thus sulfates and chlorides are in excess of other anions. Among cations sodium occupies the first place. Such ion composition in the vicinity of the BPPM is connected with the use of such substances as NaOH, Cl_2, ClO_2, and H_2SO_4 in the technology of pulp production. It should be noted that on the average for the south part of the lake the ions of sodium and chloride–ions do not essentially differ in mass concentration as compared to the other ions. By this is meant that the main contribution to atmospheric industrial emissions is conditioned by large aerosol fractions which are deposited near the source.

The previous investigations of chemical composition of atmospheric precipitation have shown that the rainfall in this region became sulfate–sodium in contrast to hydrocarbonate–calcium one typical for the remaining part of Lake Baykal.[11]

Figures 2 and 3 present the data on mass ion concentrations in different size fractions of aerosol (based on the impactor steps). The coincidence of maxima of the anion and cation mass concentrations within one of the size ranges is the indicative of their water–soluble compound in particles of this size. From the analysis of Fig. 2 one can conclude that in the north basin in small particles (less than 3 μm) the water–soluble salt, ammonium sulfate $(NH_4)_2SO_4$, predominates. The particles 3 μm in size and larger are mainly presented by the water–soluble salt calcium hydrocarbonate, $Ca(HCO_3)_2$.

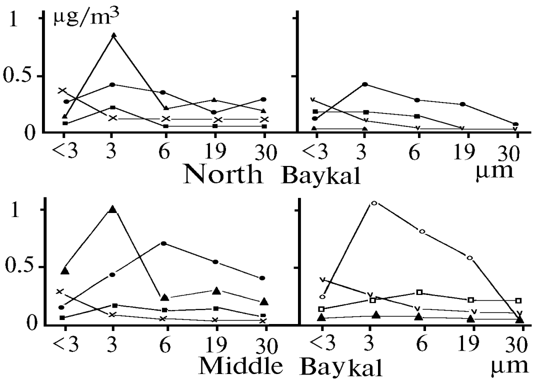

FIG. 2. Distribution of ion mass concentration in the Baykal aerosol based on the measurements of the cascade impactor (μg/m³). The middle and the north Baykal: Na^+ (●), Ca^{2+} (▲), NH_4^+ (×), K^+ (■), HCO_3^- (○), NO_3^- (△), SO_4^{2-} (v), Cl^- (п).

In the middle Baykal, as expected, $Ca(HCO_3)_2$ prevails in aerosol particles but the $NaHCO_3$ content is large too. Small particles are presented by ammonium sulfate.

TABLE I. Mass concentrations of SO_2 *and* NO_2 *in separate regions of Lake Baykal over the period from June 6 to July 12, 1992.*

Date	Region	Visibility, km	Time, h, min	Concentration, μg/m^3		Wind, m/s
				SO_2	NO_2	
June 6	Baykal'sk	25	mean (9.00–12.00)	24.1–57.5	11.8–17.0	calm
June 7	South Baykal	25	<	7.5–15.3	2.3–5.2	calm
June 10	Severobaykal'sk	30	<	19.1–22.4	8.7–10.2	calm
June 12	North Baykal	40	9.00	2.4	–	calm
			12.00	9.4	2.0	calm
			14.00	10.9	2.1	calm
June 15	Delta of the Selenga	10	8.00	17.9	7.4	N, 1
			10.00	43.5	7.3	NE, 3
			12.00	49.7	6.9	NE, 6
			14.00	29.5	11.7	NE, 4.8
			16.00	35.2	13.3	NE, 4
June 17	Baykal'sk	50	mean	32.8–62.5	5.4–10.7	calm
June 19	Over the water area	50	mean	9.6–12.1	2.1–2.7	E, 4
June 25	Baykal'sk	40	9.40–10.30	47.8–51.4	2.2	calm
			11.40–13.10		1.5–6.0	calm
	Over the water area	40	13.15–18.00	5.7–26.3	1.0–4.0	NW, 2
			mean	20.4	1.2	NW, 2
June 26	Baykal'sk	35	14.45	34.5–41.3	1.7	NW, 1...3
	Over the water area	35	13.00–17.00	12.6	1.4	NW, 1...3
June 27–29	Middle Baykal	40 – 45	mean	3.5–8.2	n/d*	NE, 1...2
June 30–July 2	North Baykal	40	mean	2.0–3.4	1.5–2.4	calm, low wind
July 3	Barguzin Gulf	40	14.50–15.15	5.7–10.2	n/d	SW, 5
	Ust'–Barguzin, 2 km from the shore	40	16.30–18.30	14.2–34.6	0.3–10.8	SW, 5
July 4–5	Chivyrkujskii Gulf	45	mean	9.1–18.5	n/d	S, 2...4
July 6	Chivyrkujskii Gulf	45	11.00–12.00	17.6–24.6	n/d	S, 5
	Bol'shoi Ushkanii Island	50	13.00–17.00	9.1–13.3	n/d	S, 5
		50	18.00	4.3	n/d	S, 6...8
July 7	Bol'shoi Ushkanii Island	45	7.30–8.00	5.1	n/d	low wind
			8.30	6.8	n/d	
			9.00–11.00	8.8	n/d	
	Middle Baykal	50	16.30	3.0	n/d	N, 1...3
			17.30	n/d	n/d	
			18.00–19.40	2.9–8.2	n/d	
July 8	Bol'shaya Peschanaya	35	8.00–11.00	2.1–11.1	n/d	NE, 4...6
	near the Selenga	30	11.00–19.00	12.5–14.8	4.3	
July 9	Posol'sk	35	13.00–17.30	6.4–22.1	5.2	N, 3...5
July 10	Kultuk	35	14.00–18.00	4.9–16.0	n/d	N, 3...5
July 11	Utulik	30	10.50–11.55	12.7–15.0	n/d	W, 5
	Baykal'sk	30	12.10	17.3	3.5	E, 1...3
	Over the water area	30	12.15	131.2	n/d	E, 3...5
	Smoke plume**	30	12.15–16.50	12.4–14.9	n/d	E, 3...5
	Over the water area	30	15.25	57.3	n/d	E, 3...5
	Baykal'sk	30	17.10	77.3	1.8–2.1	E, 3...5
July 12	Baykal'sk	30	9.05–11.20	36.7–68.2	2.5–3.7	E, 2...3
	Smoke plume	30	12.30–13.00	62.7–104.9	4.9	
	Over the water area	30	13.15–14.00	6.3–13.6	n/d	
	Cross section		14.30	14.0	n/d	E, 1...3
	Baykal'sk–	30	15.00	2.9	n/d	
	Tankhoi***	45	15.30	1.6	n/d	
			17.10	n/o	n/d	

* n/d – is not detected. ** Plume over the water area. *** Shore – middle of the like.

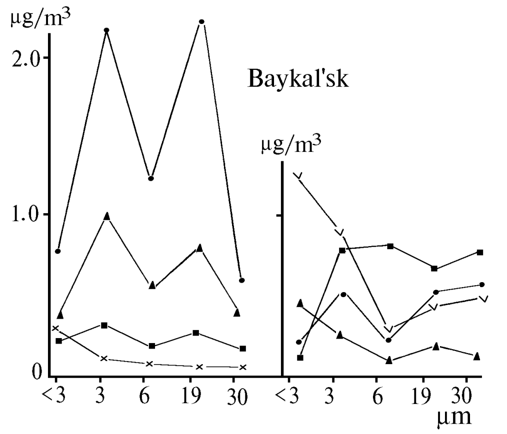

FIG. 3. Distribution of ion mass concentration in the Baykal aerosol by the steps of cascade impactor ($\mu g/m^3$*) in the vicinity of Baykal'sk:* Na^+ (●), Ca^{2+} (▲), NH_4^+ (×), K^+ (■), HCO_3^- (○), NO_3^- (△), SO_4^{2-} (v), Cl^- (п).

In the vicinity of Baykal'sk the distribution of mass concentrations over particle size for the majority of ions is of bimodal form with maxima about 3 and 19–30 μm. The second maximum occuring in range of large particles is connected with the nearness of a high–power anthropogenic source. As can be seen from Fig. 3, this large fraction of aerosol contains mainly salts NaCl and $NaHCO_3$. In small fractions such salts as $(Na)_2SO_4$, $NaHCO_3$, and $(NH_4)_2SO_4$ are additionally observed. A considerable increase of sulfates as compared to the ions of ammonium in the particle size range less than 3 μm indicates that in this range one more cation is not probably taken into account, for example, the hydrogen ion. This assumption is confirmed by the investigations of the other authors.[12] Then in this particle size range in the vicinity of the BPPM the atmosphere may contain sulfuric acid in addition to ammonium sulfate.

Being the precursor of sulfate and nitrate aerosols, the gases SO_2 and NO_2 in their spatial distribution indicate the regions of anthropogenic contamination (see Table I), where we can observe large values of ion SO_4^{2-} and NO_3^- in aerosol.

The background content of analyzed gases in the atmosphere over the water area of Lake Baykal in summer is, on the average, 1 ... 7 $\mu g/m^3$ for sulfur dioxide and 0.5 ... 2.5 $\mu g/m^3$ for nitrogen peroxide. The increased values of concentrations of sulfur dioxide and nitrogen peroxide are observed in the vicinity of industrial and agricultural sources (Baykal'sk, Severobaykal'sk, and Ust'–Barguzin). In the smoke plume and emission tonques of Baykal'sk we observed high gas content fastly decreasing towards the lake. This decreasing was caused by wind directed along the coast.

The increased values of nitrogen peroxide were observed in the region of the Selenga and the Barguzin gulf (up to 10 $\mu g/m^3$). Along the Angara from Baykal to Irkutsk the NO_2 concentration increases being lower than the maximum permissible values taken for populated areas. In the middle part of the lake the nitrogen peroxide was not often recorded.

The daily variation of trace gases concentrations was observed during sunny days with maximum at 1.00–6.00 p.m.. In conclusion it should be noted, that, as a whole, the concentrations of basic ions in aerosol and trace gases for major part of water area of Lake Baykal are very low and comparable with the background ones for the most ecologically uncontaminated regions of the world.[13–16] Essential excesses of background levels are observed only in the immediate vicinity of large populated areas. The data obtained will make it possible to assess in future contribution of dry sedimentation of water–soluble salts from the atmosphere into the Baykal water area and to calculate more precisely the atmospheric component of geochemical balance.

REFERENCES

1. M.P. Anisimov, A.A. Aksenov, S.N. Vershinin, et al., in: *Regional Monitoring of the Lake Baykal Condition* (Gidrometeoizdat, Leningrad, 1987), pp. 105–110.
2. V.A. Zagainov, A.A. Lushnikov, O.N. Nikitin, et al., Dokl. Akad. Nauk SSSR **308**, No. 5, 1087–1090 (1989).
3. V. Bashurova, V. Dreiling, T.V. Hodger, et al., J. Aeros. Sci. **23**, No. 2, 191–199 (1992).
4. I.M. Bruskina, A.A. Ignat'ev, A.N. Krasa, et al., in: *Regional Monitoring of the Lake Baykal Condition* (Gidrometeoizdat, Leningrad, 1987), pp. 79–88.
5. *Monitoring of the Lake Baykal Condition* (Gidrometeoizdat, Leningrad, 1991), 294 pp.
6. K. P. Koutsenogii, N.S. Bufetov, V.I. Drozdova, et al., Atmos. Environ. **27A**, No. 11, 1629–1633 (1993).
7. V. Bonafe, G. Cesari, G. Giovenelli, T. Tirabassi, and O. Vittori, Atmos. Environ. **12**, 469–474 (1976).
8. É.A. Chayanova and M.K. Shaikov, Tr. Tsentr. Aerol. Obs., No. 161, 43–48 (1986).
9. M.K. Shaikov, É.A. Chayanova, and E.V. Ivanov, Atm. Opt. **3**, No. 3, 320–324 (1990).
10. *Mineral Waters of the Southern Part of the East Siberia* (Nauka, Moscow, 1962), 198 pp.
11. K.K. Votintsev and T.V. Khodzher, Geography and Natural Resources, No. 4, 28–36, (1981).
12. P. Janike, Uspekhi Khimii **59**, No. 10, 1654–1675 (1990).
13. L.A. Barrie, Atmos. Environ. **20**, No. 4, 643–663 (1986).
14. S. Eggleston, M.P. Hackman, C.A. Heyes, et al., Atmos. Environ. **26B**, No. 2, 227–239 (1992).
15. A.–M. Kitto, Atmos. Environ. **26A**, No. 13, 2389–2399 (1992).
16. J.N. Galloway, D.L. Savoie, W.C. Keene, et al., Atmos. Environ. **27A**, No. 2, 235–250 (1993).