MONITORING OF ATMOSPHERIC AEROSOLS IN SIBERIA

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Results of systematic research into atmospheric aerosols in Siberia are presented. The aerosol size spectrum in Siberia is now known to have a typical three-modal structure adequately described by a model of the continental aerosol of rural territories. The submicron aerosol fraction has well pronounced diurnal and seasonal cycles. A semiempirical model has been developed that adequately describes the experimental data behavior. The data on the ion composition of aerosols and precipitation in their seasonal dynamics have been obtained. Using the roentgenofluorescence method, the data on the multielemental composition of atmospheric aerosols have been obtained. Main components of the coarse fraction that are produced due to soil erosion have been identified. Using the automated electron probe X-ray microanalysis (EPXMA) for individual aerosol particles, nine types of aerosol sources have been identified in the Siberian region. It has been shown that this technique is capable of separating the contribution from an anthropogenic load already in its early stage.

Aerosols play an important role in many atmospheric processes. They determine the quality of atmospheric air and processes of cloud and smog formation and have a significant effect on precipitation and visibility, climate, as well as animal and human health.

Most important classes of atmospheric aerosol are maritime and continental ones. The latter are less understood now. This is connected, in particular, with a wide variety of landscapes. The Siberian region is practically unexplored. It occupies a vast territory of Asia with different soil and climatic zones. The northern boundary of Siberia encloses a large part of the Arctic.

During the last 15 years, the arctic aerosols have been studied in detail within the framework of the International Project "Arctic Haze" (see Refs. 1–4). As a result of these studies, it was revealed that many properties of arctic aerosols are connected with a long-range transport (at distances up to 1000 km and even longer) of gaseous and aerosol pollutants emitted over remote continental territories. In particular, these results suggested that from 20 to 50% of pollution of the Arctic region is due to emissions over the territories of Siberia, Kazakhstan, and Ural.[5,6]

Figure 1 illustrates the above-said. It shows the map of the Northern hemisphere with the estimated distribution of possible anthropogenic SO_2 sources (Fig. 1*a*) as well as the distribution of the largest territories with loess types of soil that may engender severe dust storms (Fig. 1*b*). Thus, it follows from the data shown in Fig. 1*a* that the anthropogenic SO_2 emissions over the territory of Siberia make up about 10% of total SO_2 emissions in the Northern hemisphere. Figure 1*b* indicates that the area of loess soil encompassing Siberia comprises a high percentage of the total territory occupied by easily eroding soil of the Northern hemisphere.

Thus, very strong flows of the atmospheric aerosols may be formed over the territory of Siberia. To support finally the estimates obtained, systematic observations in these regions are needed. This is just the goal of the Project "Aerosols of Siberia." A comprehensive description of objectives and tasks of the Project can be found in Ref. 7. The Project envisages organization of monitoring of atmospheric aerosols over the territory of Siberia.

This paper presents briefly the main results obtained under this Project by the early 1995.

Figure 2 illustrates the state of atmospheric aerosol monitoring in Siberia before implementation of the Project "Aerosols of Siberia" (Fig. 2*a*) and now (Fig. 2*b*).

Figure 2*a* shows the map of a network of stations for background monitoring of the arctic haze developed by the middle 1980s. Among 22 stations located in the Northern hemisphere, no one was in the territory of Siberia.

Figure 2*b* shows a network of aerosol sampling stations in the Siberian region intended for servicing a system of research and stationary stations of the Siberian Branch of the Russian Academy of Sciences.

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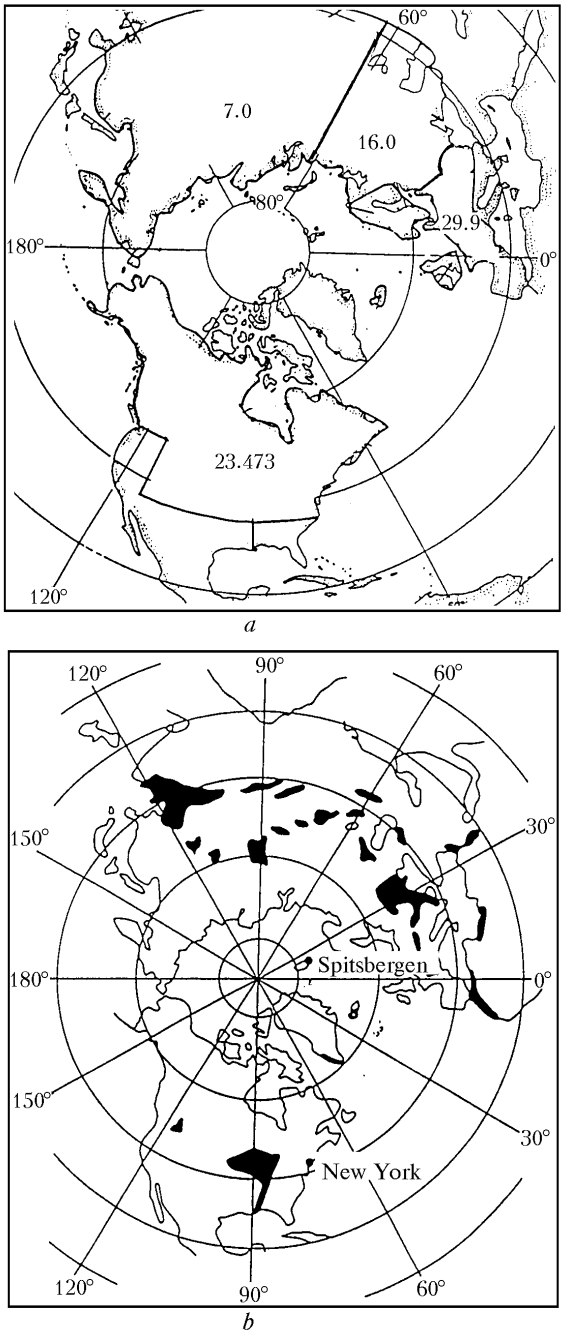

FIG. 1. Sources of gaseous and soil-erosive aerosols in the Northern hemisphere: a) the numbers indicate the mean output of anthropogenic emissions of SO_2 (in Mt*) in the territories enclosed by lines as follows from Ref. 12; b) black areas indicate the territories with loess soil.*

The properties of aerosols are governed by their size spectrum, particle number density, and chemical composition. That is why much attention was given to measurements of these characteristics.

With the use of the complex of methods and instruments including a screen diffusion battery and a condensation nuclei counter and the impactor technique it was shown that the aerosol size spectrum for rural regions of Siberia can be adequately described by the Whitbey three-modal distribution typical of remote continental areas.[8]

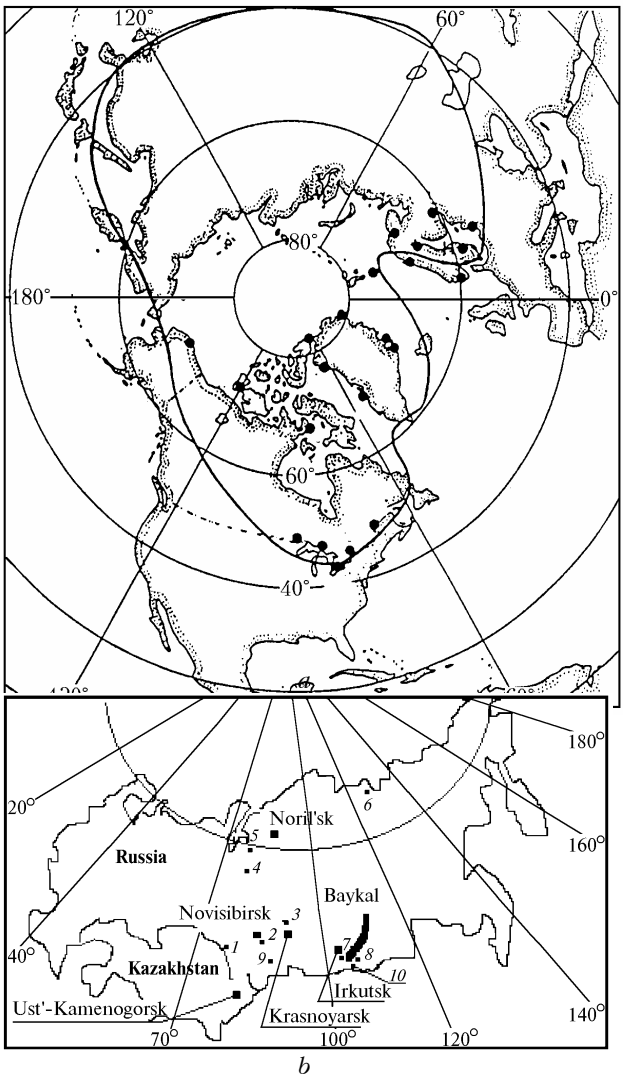

FIG. 2. Networks of stations for monitoring of the arctic haze aerosols[12] (a) and Siberian aerosols (b): large filled squares are for cites of the Siberian region and small filled squares are for sampling sites Karasuk (1), Klyuchi (2), Pogorel'slii Bor (3), Tarko-Sale (4), Samburg (5), Tiksi (6), Listvyanka (7), Tankhoi (8), Ust'-Kan (9), and Mondy (10).

Figure 3 shows the aerosol particle size spectra measured in the Lake Baykal region (vertical bars) and the Novosibirsk region (small squares). The solid line is for the size spectrum of the continental rural aerosol.[8]

It is seen from Fig. 3 that there is no difference between the aerosol size spectra obtained in the Novosibirsk region and the Lake Baykal region. Since these regions are spaced at about 1300 km, one can speak about a single Siberian aerosol. This type of aerosol corresponds closely to the continental aerosol of remote territories.

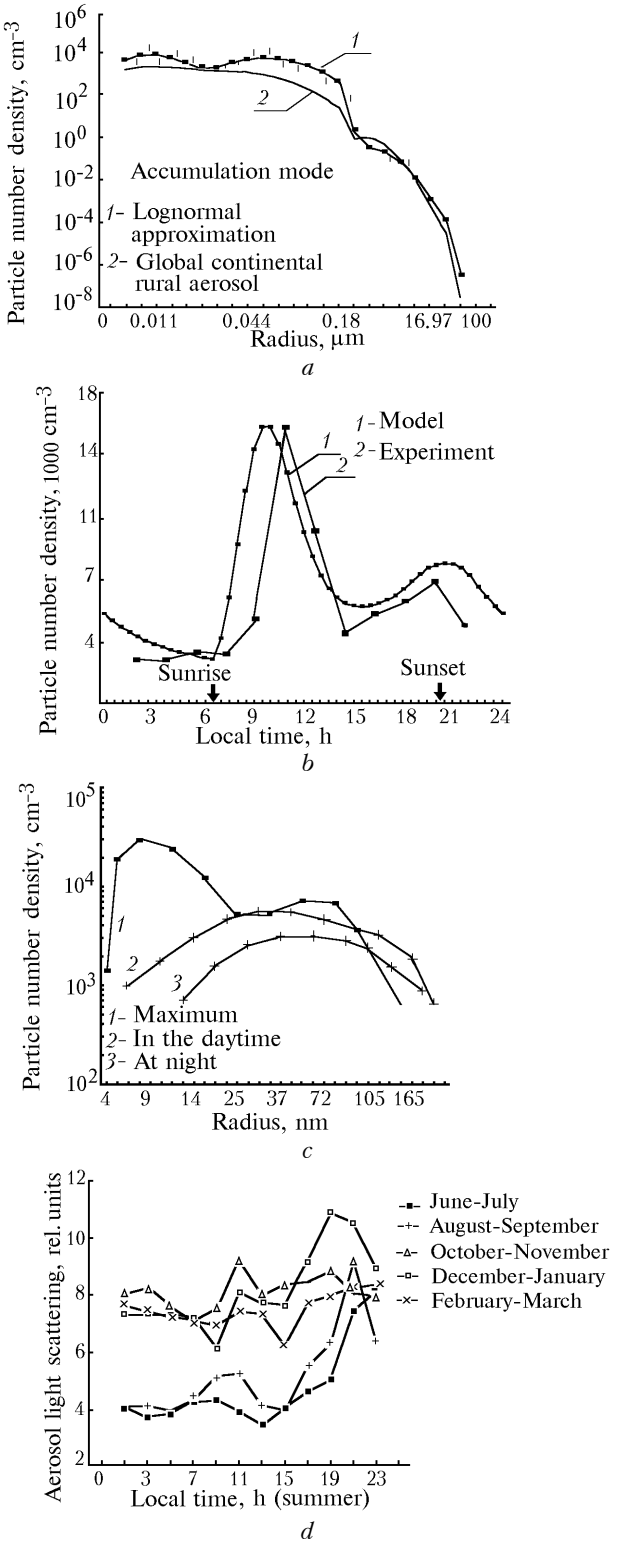

FIG. 3. Size spectrum of aerosols in Siberia (a); dynamics of the diurnal variations of the number density of the submicron fraction of atmospheric aerosol particles in Siberia, experimental and theoretical data (b); dynamics of variations of the size spectrum of the submicron aerosol fraction (c); seasonal variations of the diurnal behavior of light scattering by the submicron fraction (d).

Based on the dynamics of the diurnal variations of the aerosol particle number density and the size spectrum, main regularities of variation of the submicron fraction were revealed. It was shown that these regularities can be described based on concepts of the photochemical conversion of gaseous precursors into aerosol particles with regard for the diurnal variation of the boundary layer height. Figure 3*b* indicates good agreement between the theoretical results and the experimental data. These concepts also provide a qualitative explanation for the dynamics of the diurnal (Fig. 3*c*) and seasonal (Fig. 3*d*) cycles of variation in the particle number density of the accumulation mode ($0.1 < d < 1$ μm). Simultaneous measurements of the ionic composition of aerosols in winter and summer provide the feasibility of identifying the main constituents and the mass concentration of water-soluble components of aerosol particles as well as of estimating their relative contribution to the total aerosol mass.

Figure 4 shows the dynamics of variation of the ionic composition of aerosols in the Novosibirsk region in summer. It is seen from the figure that the average daily concentration of sulfates and nitrates in different regions spaced at 450 km changes symbatically. This indicates that these components are connected with processes of a regional or global scale. The mean concentration of these ions in summer and winter differs by several times. It seems likely that this is primarily connected with variations in the atmospheric boundary layer thickness in different seasons.

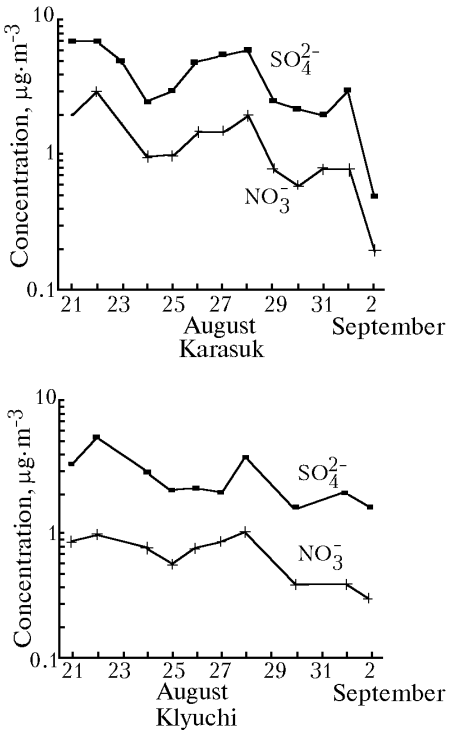

FIG. 4. Dynamics of variation of aerosol ionic composition in the Novosibirsk region (Karasuk and Klyuchi settlements).

Simultaneous observations of the seasonal variations of the ionic composition of atmospheric aerosols and precipitation (Fig. 5) show that the ionic composition of aerosols varies slightly with seasons. Much larger difference was observed in the ionic composition of precipitation. Clearly seen are also the periods during which precipitation is acid or alkaline. At the same time, the mean pH of precipitation (both liquid (rain) and solid (snow)) is close to its equilibrium value. From these data, a conclusion can be drawn that the precipitation composition is governed by not only washing out of aerosol particles, but also the processes of heterogeneous interaction with gaseous impurities. In addition, the ionic composition of precipitation is determined by the prehistory of air mass motion.

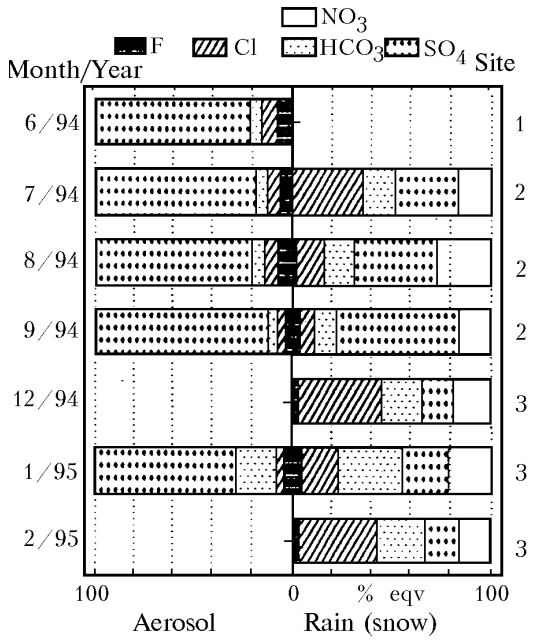

FIG. 5. Seasonal variation of the ionic composition of aerosols and precipitation in the Novosibirsk region.

The impactor technique (IT) combined with the roentgenofluorescent analysis with the use of the synchrotron radiation (RA–SR) allowed some regularities in the behavior of the aerosol multielemental composition to be revealed.[9] Table I lists the results of analysis of the aerosol muiltielemental composition in one of the rural areas of the Novosibirsk region (Klyuchi settlement).

Based on the relative elemental content of aerosol particles of different size, all elements can be grouped into three classes. Elements mainly contained in the coarsely dispersed aerosol fraction ($d > 1$ μm) belong to the first class. The second class is for the elements for which 60% of their total mass is contained in the submicron fraction ($d < 1$ μm). And the third class occupies intermediate position. If we normalize the concentration of elements to the Fe concentration and compare this ratio with that for the Earth's crust, the difference between types of particles belonging to different classes will be clearly seen. The first class is for the particles of soil-erosive origin, the second class is for the particles of anthropogenic origin, and the third class is for the particles of mixed origin.

TABLE I. Multielemental composition of aerosols obtained by IT in combination with RA-SR in Klyuchi in 1993 and the enrichment coefficient.

Serial number of group	d50, μm	Ca, Ti, Fe, Ni, Rb, Sr, Y, Zr	Sc, V, Cu, Br, Nb, Mo, Ba	Mn, Zn, As, Pb
	Elemental composition of aerosol particles (relative contribution of the given group, %)			
1	>6.6	26.1	11.5	11.3
2	6.6–3.8	44.2	12.7	21.1
3	3.8–1	26.1	10.8	30.1
Filter	<1	2.4	63.8	36.4
	Enrichment coefficient			
1	>6.6	1.4	18.2	24.9
2	6.6–3.8	1.3	11.5	24.5
3	3.8–1	1.4	21.4	61.6
Filter	<1	0.4	150.2	162.7

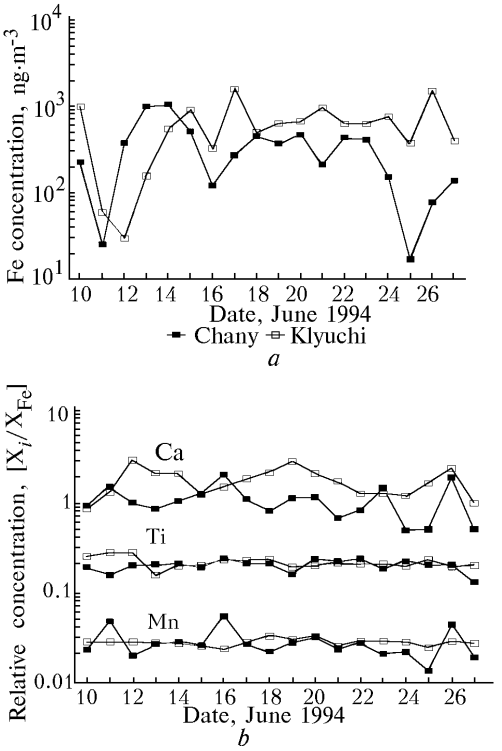

FIG. 6. Dynamics of the Fe *concentration variation in Klyuchi and Chany (a) and X_i/X_{Fe} variation for* Ca, Ti, *and* Mn *(b). Here, X_i is the concentration of the ith element and X_{Fe} is the Fe concentration.*

Figure 6*a* demonstrates the dynamic of variations of the Fe concentration in two sites of the Novosibirsk region spaced at about 450 km. As is seen from the figure, the amplitude of ferrum concentration variations

in each site reaches two orders of magnitude. The time behavior in both sites is very similar. A conclusion can be drawn therefrom that in summer the soil-erosive component of aerosols in Siberia is regional or, possibly, global in character. The data shown in Fig. 6*b* support this conclusion. Shown in Fig. 6*b* is the variation of the relative concentration of some elements. Ferrum is chosen as a reference element. The relative content of Ca, Ti, and Mn in the coarsely dispersed aerosol fraction is seen to be practically constant. This is indicative of the constant elemental composition of the soil-erosive component throughout the Novosibirsk region. We succeeded in obtaining more comprehensive information about the composition of atmospheric aerosols in Siberia using the electron probe *X*-ray microanalysis (EPXMA) of the multielemental composition of individual aerosol particles. The statistical analysis of these data allowed us to identify up to nine different sources of aerosol.[10,11] Table II exemplifies this analysis.

TABLE II. Analysis of the multielemental composition of atmospheric aerosols in the Novosibirsk region with the use of the EPXMA method.

Karasuk, winter		Karasuk, summer		Klyuchi, summer	
Type of particles	Relative contribution, %	Type of particles	Relative contribution, %	Type of particles	Relative contribution, %
Si, Al, Fe	57.4	Si, Al, Fe	64.0	Si, Al, Fe	53.5
Ca, S	11.4	Ca, S	10.4	Ca, S	19.6
Si, S, Fe	11.4	Fe, Si	10.4	Fe, Zn, Ti	8.5
Fe	9.1	Cl, K, P, S	7.1	Fe	8.0
Pb	5.2	Ca, Si	6.8	P, S, K	3.9
S	3.5	Pb	1.3	S	3.5
Zn	1.2			K, Cl	2.1
Ti	0.7			Pb	0.9

Thus, the results obtained show that the developed system for monitoring of atmospheric aerosols in Siberia provides an integrated idea of the characteristics of aerosol particles and their structure and composition as well as identification of the main sources of aerosols in the Siberian region and evaluation of scales of spatiotemporal variability of aerosol parameters.

REFERENCES

1. Atmos. Envir. Special Issue on Arctic Air Chemistry **15**, 1345–1516 (1981).
2. Atmos. Envir. Special Issue on Arctic Air Chemistry **19**, 1987–2208 (1985).
3. Atmos. Envir. Special Issue on Arctic Air Chemistry **23**, 2345–2638 (1989).
4. Atmos. Envir. Special Issue on Arctic Air, Snow and Ice Chemistry **27A**, Nos. 17/18, 2695–3038 (1993).
5. K.A. Rahn, Atmos. Envir. **19**, No. 12, 1987–1994 (1985).
6. F.A. Akeredoln, L.A. Barrie, M.P. Olson, et al, Atmos. Envir. No. 8, 1555–1572 (1994).
7. K.P. Koutzenogii, Atmos. Oceanic Opt. **7**, No. 8, 542–545 (1994).
8. P. Koutsenogii, *"Measurements of remote continental aerosol in Siberia,"* Ph. D. Thesis, Johannes-Gutenberg University, Mainz (1992), 106 pp.
9. V.B Baryshev, N.S. Bufetov, K.P. Koutzenogii, et al., Nucl. Inst. Meth. Phys. Res. **A359**, 297–301 (1995).
10. H. Van Malderen, R. Van Grieken, T.V. Khodzer, et al., Atmos. Oceanic Opt. **7**, No. 8, 622–627 (1994).
11. H. Van Malderen, R. Van Grieken, N.S. Bufetov, and K.P. Koutzenogii, Envir. Sci. Tech. **30**, No. 1, 312–321 (1990).
12. L.A. Barry, Atmos. Envir. **20**, 643–663 (1986).