

SIBERIAN HAZE. INTEGRATED STUDY OF AEROSOLS IN SIBERIA

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We present here some results of many-year integrated studies of atmospheric aerosols in Novosibirsk region (from 1992 to 1995) along with the first observational data for Krasnoyarsk Territory and the northern part of West Siberia (1995). Data include size spectra, aerosol particle number and mass densities, ion composition, light scattering characteristics and multielement composition of individual particles. Methods and instrumentation used are described. Comparison of spatiotemporal aerosol characteristics is performed. It is concluded that the integrated study of atmospheric aerosols helps to better understand the mechanisms of local-, regional-, and global-scale aerosol formation and estimate the powers of contributing sources.

1. INTRODUCTION

The methods recently used by the authors to study characteristics of Siberian aerosols include measurements of aerosol physical properties such as aerosol light scattering, particle (mass and number) density, ion composition (using ion chromatography), as well as multielement composition of individual particles.

Comparison of the results from the multielement chemical analysis of individual aerosol particles to data from other techniques provides a unique opportunity to better understand the mechanisms of aerosol formation and transformation in the atmosphere.

The analysis in the present paper mainly concentrates on submicron and micron aerosol particles which, being most long living in the atmosphere, can travel long distances from the source, up to 10 000 km or longer.¹ Normally, background aerosol of micron fraction has maximum mass density. This implies that particles of this size range are major long-distance travelers and major contributors to aerosol sedimentation. Even when a local source produces many small particles, smaller than 0.2 μm in diameter, they quite rapidly coagulate with submicron and micron particles, thus forming cumulative fraction of atmospheric aerosols (AA) which, through this process, accumulates the bulk of chemical elements found in aerosol particles of this fraction.

2. PLACES OF AEROSOL SAMPLING

Most of the measurements considered here have been conducted in Novosibirsk region located on the South-West Siberian plain and occupying about 20 000 km². The aerosol study in Novosibirsk region was conducted during 1992 and 1993 expeditions, 1994 summer expedition, as well as long-term observations in Novosibirsk Academician Town in 1993-1994. Academician Town is located 25 km south of Novosibirsk. It is non-industrial district with about 100 000 population.

In Novosibirsk region we chose three points for aerosol sampling as corresponding to remote background territories.

1. First point, 12 km east of Academician Town, and 30 km away from Novosibirsk, near Klyuchi settlement.

2. Second point, near Chany Lake, in the western part of Novosibirsk region.

3. Third point, in the south-western part of Novosibirsk region, 12 km away from Karasuk town.

The distance between Karasuk and Chany sites is about 100 km, and the two are about 500 km away from Academician Town. Thus our experiments in Novosibirsk region had regional-scale coverage.

Special aerosol sampling was undertaken in the north Siberia, for assessing the effect of Siberian haze on the Arctic haze⁶ in the region where the two overlap.

Because of high costs, only several samples from north Siberia are available to us presently. So, aerosols over north Siberia were analyzed using method of determining multielement composition of individual particles, because the apparatus for aerosol sampling in that case was sufficiently simple, compact, and light-weighted.

The aerosol sampling in the north Siberia was made in March of 1995 at two points. First site was near small town Tarko-Sale (65°N, 78°E); it has about 20 000 population, small airport, and local power plants. Aerosol samples were taken between March 16 and 21, 1995, the mean ambient air temperature being around -7°C at the time of sampling.

Second site was 500 m north of small village Samburg (67°N, 78°E), devoid of any industry, located in Tundra, and having about 300 population. Sampling devices were located on a small hill about 10 m in height. The mean ambient air temperature at the time of sampling (March 21 through 27, 1995) was around -5°C .

In addition, in summer of 1995, during the study of aerosols from burning combustible forest materials, we sampled atmospheric aerosols for the period of no-forest fires. Between June 4 and 14, 1995, four samplings have been done. The aerosol samples were taken in the forest of Krasnoyarsk Territory, at the Pogorel'skii Bor permanent facility of the Forest Institute, SB RAS (57°N, 93°E), located 100 km north of Krasnoyarsk.

3. MEASUREMENT TECHNIQUES

Total aerosol light scattering was measured with a commercially available FAN-A nephelometer, whose readings were scaled to the total molecular light scattering by air purified from aerosol particles, the latter value being measured by the same nephelometer.

Considering the detector's sensitivity and assuming realistic size spectrum of atmospheric aerosol, this method was proved² to be capable of monitoring the changes in concentration of particles with diameters from 0.2 to 1 μm , which covers the size range of submicron particles.

Aerosol mass density was determined from daily mass-gain of the filters of AFA-HA type, through which filtered air was pumped at a rate of 120 l/min. Additionally a series of experiments was run in which daily aerosol samples were acquired using Whatman-41 filters blown at a rate of 500 l/min.

It can be shown, based on the size spectrum of Siberian aerosols determined earlier,³ that the main bulk of deposited matter on the filters is made up of particles with the diameters from 0.2 to 10 μm .

Concentration of sulfates, nitrates, and chlorides in samples, intercepted by Whatman-41 or AFA-HA filter, was determined by ion chromatography. To measure multielement composition of individual particles, aerosol samples were acquired using nucleus-

pore filters with the pore diameter of 0.4 μm . The resulting samples were then analyzed by the electron probe X-ray micro-analysis (EPXMA) technique.⁴

4. RESULTS OF ANALYSIS AND DISCUSSION

The study has shown that in summer the aerosol characteristics well agree at all sites except for Academician Town. For instance, total aerosol light scattering, diurnal behavior of light scattering characteristics, ion composition of aerosols as measured in Klyuchi, near Chany lake, and in Karasuk town agreed within the measurement accuracy.^{2,5} At the same time, simultaneous measurements in Klyuchi and Academician Town showed considerable disagreement despite only the 12-km separation. Comparison of the results of these simultaneous measurements from 1994 expedition, when such measurements were taken in Academician Town, Klyuchi, and near Lake Chany has shown that the measurement results practically coincide for the latter two despite of their almost 500-km separation.

In this connection, we have divided all the measurements into two groups: those of aerosol affected by urban conditions (in Academician Town), and those of Siberian background aerosol (other observations from within the Novosibirsk region).

In winter, however, such a subdivision is impossible. This means that in winter the areas subject to the impact of local sources of air pollution increase to hundreds kilometers. Thus in winter season the impact of most powerful point sources is unavoidable within a radius of several hundred kilometers from a source, so that background aerosol measurements are only possible to perform when an observational point is removed by hundreds kilometers from a local source.

Mean light scattering is several times larger in winter than in summer. This is because in winter the weather conditions favor accumulation of aerosol near the earth's surface. Table I presents data on the content of basic ions in aerosol particles. From these we can conclude that the major contribution from anions comes from sulfates, whose fractional mass density, however, is not so large. These data, as the following demonstrates, qualitatively agree with the results on chemical composition of aerosol particles. For instance, from analysis of chemical composition of the aerosol particles, sulfur-containing particles percentage 5-10% of the total number of particles sampled. From analysis of ion composition, sulfates percentage 2-10% of the total mass density of aerosol.

From analysis of cation composition,⁷ significant contributor to neutralization of aerosol particles are their Ca-containing ingredients. This finding is further supported by the analysis of composition of individual particles, in which sulfur is detected either together with the biogenic components, or in combination with Ca.

In winter total aerosol mass density is less, while the percentage of soluble fluids (anions) is greater than in summer, due to decelerated formation of

biogenic, organic and insoluble aerosol particles. In winter, considerable (by mass) portion of aerosol particles are insoluble components of inorganic matter, presumably of condensation origin. Of course, the presence of soot is most likely, however experimental support is needed. Summer samples are mostly composed of insoluble aerosol fraction. We think that these particles have organic, biogenic, and soil-erosion origin.

In Table II we present averaged results of determining the multielement composition of individual particles. Entries are both previous results⁴⁻⁸ and more recent ones.

Data from Table II are the results from hierarchical cluster analysis (HCA) of multielement composition of individual aerosol particles. Several major particle populations portray background aerosols of Siberia. The first group are aluminosilicates, primarily fly ash particles from combustion of mineral fuel which is the main energy source in the power-station system of Siberia. Among the other group are Si-containing or quartz particles which most likely are arid aerosols. This assumption is supported in particular, by the fact that in snow-covered regions the fraction of such particles is the same as in snow-free ones.

Certain methodological features inherent in the hierarchical cluster analysis limit its ability to separate

Si-containing particles from aluminosilicates (Al, Si group). Together, the two groups contribute no less than 50% to the total aerosol content of the Central Siberia thus dominating it.

One more group common to all the summer samples comprises biogenic particles composed simultaneously of such elements as K, Cl, P, and S. In summer samples such particles make up 10-30%.

Particles participating in background scattering of electrons, but producing no Roentgen spectra, are identified as particles of inorganic matter composed mostly of C, O, and N species. All these species can be detected by the techniques discussed here. These particles contribute about 10% to the total sampled population. We put submicron and micron particles, coagulating with S- and Pb-containing particles, into a separate category (S- and Pb-containing population).

The last broad group includes Fe-containing aerosols, which also contain species, typical of soil and earth's crust, such as Ti, Si, and S among others. This group can be thought of as being formed by soil and earth's crust erosion, and it contributes about 10% to the total population sampled. The presence of trace constituents in aerosols is identified from the analysis of multielement composition of individual particles in Table III. Such an approach was taken because HCA technique inherently emphasizes dominant, high-content groups, while masking lower content ones.

TABLE I. Mean aerosol characteristics in Novosibirsk region.

Measured quantities	Summer		Winter	
	Background aerosol of Siberia	Academician Town	Background aerosol of Siberia	Academician Town
$S - 1$	3.4	5.5	9	8
m , mass density	55	170	39	105
Number density ($r > 1 \mu\text{m}$)	0.13	0.17	0.06	0.06
$m \text{SO}_4^{2-}$	2.3	2.9	8.4	10.5
$m \text{NO}_3^-$	0.6	1.0	3.3	3.8
$m \text{Cl}^-$	0.2	0.2	0.4	0.31
Ion concentration, %	2-14	2	21-61	14

Note. $S - 1$ is the aerosol light scattering (in part of molecular light scattering); m_i is the total mass and ion density (in $\mu\text{g}/\text{m}^3$); $N(r > 1 \mu\text{m})$ is the number density of particles with radii larger than $1 \mu\text{m}$ (cm^{-3}).

TABLE II. Main element groups as a result of hierarchical cluster analysis of the multielement composition of individual aerosol particles by EPXMA technique.

Identification of the group	Observation site and season					
	Karasuk, winter, %	Klyuchi, winter, %	Samburg, winter, %	Karasuk, summer, %	Klyuchi, summer, %	Krasnoyarsk, summer, %
Al, Si	57	57	50	64	54	18
Quartz	12	24	12	—	—	9
Ca, S	11	5	6	10	20	18
Fe, Ti	10	3	9	10	16	2
S	4	—	13	—	4	—
Organic	—	10	9	—	—	13
Biogenic	—	—	—	7	6	33
Unidentifiable	6	1	1	9	—	7

TABLE III. Average percentage of aerosol particles containing different elements, out of the total number measured.

Element	Winter		Summer		
	Karasuk	Samburg	Karasuk	Klyuchi	Krasnoyarsk*
Na	0.79	0.6	2.5	1.8	1.4
Al	63	55	60	56	25
Si	86	70	83	78	46
P	1.6	0.5	5.3	5.7	37
S	53	60	30	39	42
Cl	3.4	0.7	17	4.6	17
K	38	26	47	45	55
Ca	27	21	31	37	25
Ti	8.4	6.4	6.4	8.2	22
Fe	56	46	62	58	25
Ni	0	0.3	0.14	0.14	0.5
Zn	2.5	2.0	0.7	0.23	0.3
Pb	1.9	2.9	0.55	0.33	0

* one sample from the forest zone

From Table III we see no any -significant difference in chemical composition of atmospheric aerosol samples taken in the same season but different regions in the west, central, and north Siberia. This observation supports our conclusion that aerosols are well mixed over the entire Siberia to form the global "Siberian haze". Save for a few, very localized point sources, very seldom in Siberia, Siberian haze has the following features.

1) Major contributor to the micron and submicron fractions is burning coal, also contributing are mineral particles from local sources or transported from south, as well as biogenic type particles.

2) Fly ash particles and particles of natural origin serve as sinks for small particles of anthropogenic type and for particles formed by the process of chemical conversion of gas to disperse phase. However, the two processes are only minor contributors to aerosol mass density. This conclusion is supported by the results of determining mass fraction of insoluble part of ion concentration in aerosol composition. As indicated above, it is a minor constituent of the atmospheric aerosol. Pb-containing particles are mostly found in the west Siberia as small-sized particles, which may be indicative of their possible converging from nearby territories. Other elements, also associated with activities in non-ferrous metallurgy, such as Zn and Ti, are generally present simultaneously with elements originating from soil and mountain erosion (Fe or Al and S). So, we assume these elements to be of natural origin.

Recently considerable interest appeared in the mechanism of sulfur conversion to assess the effect of sulfur-containing particles on atmospheric radiation balance and greenhouse effect. Some conclusions about Siberian region can also be drawn from our research. First, SO_4 -containing particles formed via gas-particle conversion are insufficiently large to scatter much solar radiation and, thereby, affect significantly the radiation effects.

Such particles should, by coagulation process, most rapidly grow to the optically active size in the submicron region. However, it is shown by the analysis that in this region either aerosol particles of natural origin, or fly ash particles dominate. Sulfur-containing particles, when coagulating with such particles, make little addition to the mass density. Quite possibly, only sulfur-containing particles are sulfate-containing aerosols, made originally of inorganic impurities and, hence, giving no signal other than that of S-presence.

In the majority of practical cases, S is sampled simultaneously with Ca. Therefore, if sulfates were primarily formed by gas-particle conversion to yield small, S-containing particles subsequently coagulating with larger ones, then the presence of S would be common to all particles. However, the fact of frequent coupling of S with Ca, the latter primarily originating from erosion, indicates that the general distributors of S over aerosol particles are heterogeneous reactions of gaseous SO_2 with Ca-containing particles yielding $CaSO_4$ present in aerosols.

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