ANALYSIS OF INDIVIDUAL AEROSOL PARTICLES IN SIBERIAN REGION. PROVISIONAL RESULTS

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We present provisional results of analysis of qualitative and quantitative composition of the atmospheric aerosol in some areas of Siberia, in particular, in Novosibirsk region and over Lake Baykal.

1. INTRODUCTION

Siberia is of great scientific interest from the standpoint of such aspects as environmental chemistry, air pollution, and atmospheric aerosols. First and foremost there are some thinly populated and far removed from industrial centers areas, where the aerosols are assigned by definition to global background type. Currently the investigations into such a type of aerosol have attracted widespread attention in the context of the global climate change. The rise in interest in the background atmospheric aerosols is connected with opinions of some specialists that the green–house effect can be counterbalanced by these aerosols. This known effect leads to the climate getting warmer due to increase in concentration of a number of gaseous atmospheric components such as CO_2 or CH_4.

Scientific estimates show that exposure of the climate to the atmospheric aerosols makes itself evident in two ways. Firstly, it is a direct influence of aerosol particles on scattering and absorption of the solar radiation. Secondly, it is an involvement of aerosols in the processes of cloud formation, since the aerosols are the active condensation nuclei. The role of the atmospheric aerosols is bound to be most pronounced in the polar regions. At the same time, investigations into characteristics of the atmospheric aerosols in Arctic region of Norway and Alaska, which have been performed in recent years, have shown that the long–distance transport from West and Central Siberia can be essential contributor of pollution in the Arctic. Such a pollution determines the composition of its air basin in many respects (the Arctic haze, as it is called). At present, there are no systematic insights into characteristics of Siberian atmospheric aerosols as well as estimates of their influence on the climate.

It is well known that there are powerful industrial centers whose atmosphere is extremely contaminated by base metals in Siberia. This contamination presents a severe hazard to human health. The majority of these cases is giant local sources of anthropogenic nature, it essentially simplifies studying their influence on environment and people's health from the standpoint of problems of atmospheric and environmental chemistry. Nevertheless, quantitative data on the flows of base metals are yet entirely absent.

It seems likely that an atmospheric precipitation plays an important role in base–metal contamination of Lake Baykal. Environment of the northern part of the lake retains its natural state, whereas the southern part is under anthropogenic impact. Analysis of aerosols over different parts of the lake makes it possible to describe quantitatively the atmospheric flow of the base–metal sediment and to compare this flow with level of contamination due to industrial emissions and river effluents.

Microscopic analysis of individual aerosol particles performed by techniques developed in Center of Micro– and Trace Analysis at the University of Antwerpen allows us to assign majority of aerosols to soil–erosive or maritime types. These techniques make it possible to obtain more comprehensive data on the spread sources of aerosol as against the ordinary techniques of analysis. Other aerosol particles sources of natural or anthropogenic nature do not play an essential part, as a rule. As for Central and South Siberia, it should be noted that these regions are well off the powerful sources of soil–erosive dust and salt particles formed over water surface. Besides, in winter the earth's surface are covered with snow, and lakes and seas are frozen. It takes place not only at center of Siberia, but also in territories remote from the center. Under these conditions the measured characteristics of aerosols are connected with most interesting part of atmospheric aerosols, namely, with particles which can be transported to long distances and determine the background pollution of the atmosphere.

Hence, the long–term goal of these studies is the elucidation of the processes of formation and transport of the aerosols in Siberian region (at local, regional, and

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global levels) both from natural and anthropogenic sources, in order to estimate the exposure to the base metals sediments in contaminated regions and over Lake Baykal. Besides, it is of great importance to determine the extent to which the Arctic region and global climate are affected by the aerosols of Siberia.

2. EXPERIMENT

2.1. Technique and sites of aerosol sampling

At Lake Baykal sampling was performed during two expeditions, in June 1992 and September 1993.

For analysis of individual particles more than 60 aerosol samples were collected over the whole of water area of Lake Baykal, both in northern "unperturbed" part of the lake and in southern more contaminated one. Sampling was performed on board the research ships *Balkhash* and *Titov*.

At a period from February 5 till March 4, 1992 the aerosol samples were taken three times per day at Karasuk. (It is the point relatively remote from industrial centers and typical for West Siberia. It is situated 400 km west from Novosibirsk.) Then from August 20 till September 3, 1992 the samples were taken at this point once again, in order to compare the seasonal variations in composition of atmospheric aerosols. At the same time the samples were taken at another point of Novosibirsk region, namely, on the outskirts of Novosibirsk in geophysical station at Klyuchi. This point is situated 40 km from Novosibirsk. Additionally, in winter 1993/1994 the fourth set of samples was taken at Klyuchi to compare the seasonal dynamics. During each company all aerosol particles were sampled on polycarbonate diaphragm filters of NUCLEPORE type 47 mm in diameter with pores diameter of 0.4 μm. The filters were placed in filter holders made of organic glass and completed with capshaped cover that protected filter from rain. The filter holder was connected with a vacuum pump via a hose. Aerosols were pumped through the filter with rate from 20 to 50 liter/min. Period of sampling was controlled by timer, and volume filtered out was controlled by meter of gas flow.

About 200 samples were taken at Karasuk, Klyuchi, and near Lake Baykal. Composition, size and shape of typical particles were determined in the University of Antwerpen. We have analyzed about 400 individual particles for each sample.

2.2. *X*–ray microanalysis with electron microsonde (XRMEM)

XRMEM is the fast and reliable method which allows one to determine the chemical composition and morphology features of micron particles. We used a setup where XRMEM was fully automated. This made it possible to analyze several hundreds of individual particles over 2 hours.

Analysis of about 80 000 particles transported from Siberia (about 400 particles per sample) was performed with a device of 733 SUPERPROBE (JEOL, Japan) type equipped with energy–dispersive Si(Li) detector 10 mm^2 in area, secondary–electron detectors, transillumination–electron detectors for observation of sample, and backscattering–electron detectors for automatic determination of particle location. This equipment was connected up to a TN–2000 (Tracor Northern, USA) system performing automatic processing of aerosol samples. Typical operating parameters of XRMEM were: acceleration voltage of 25 kV, beam current of 1 nA, magnification of 1 200 X. For each particle *X*–ray spectrum was collected during 20 s. Minimum content of element in detecting with XRMEM was approximately equal to 1 000 ppm (0.12%). For automatic analyzing of individual particles we used version of the software "particle revealing and classification" (PRC, Tractor Northern) of our own elaboration. This code performed localization of particle by consecutive horizontal scanning with electron beam. Wherever signal of backscattering intensity being higher than beforehand given level was fixed, contour pixel of particle was recorded in the system storage. Perimeter and diameter of particle were calculated over all recorded contour pixels. Then *X*–ray spectrum was collected and all information was stored on a disk.

2.3. Compression of data on aerosol characteristics

As a result of experiments, a great body of data was accumulated, hence there was a need for compression of information obtained. Multivariational techniques such as analysis of primary factors and hierarchical and unhierarchical cluster methods can provide clearer notion of collected information. Thus, combination of automatized XRMEM and multivariational techniques is an effective and useful instrument of analysis of aerosols. In this paper we present the results of analysis of data set using multivariational techniques. Objective recognition of particle type in a sample and then description of its behavior and relatively rate over the period of all observational time during some weeks are not universally correct. Each sample was taken under different conditions not only temporal, but also at different wind speed and direction, relative humidity, and so on. Hence, the global interpretation of data collected over the whole of sampling period is a very complicated problem, that can be solved via correlation of results obtained by different multivariational techniques.

3. FIRST RESULTS

3.1. Company at Lake Baykal in 1992

Obtained during this expedition 37 samples were partitioned into three groups in accordance with point of sampling: upper, middle, and lower parts (zones or regions) of Lake Baykal, from north to south. We do not consider here samples taken in September 1993. We performed hierarchical cluster analysis of every individual sample in oder to gain the average composition of each sample. Then the data were averaged over three basic regions to obtain average value typical for each selected region of Lake Baykal. Then the data were analyzed by cluster technique a second time to obtain average composition of aerosols of given region. We used this average composition as a centroid in performing three unhierarchical analysis for separate regions. After complete analysis we performed ZAF–correction for transition from the intensity of *X*–ray peaks to the relative mass concentration of elements. Results of such processing are given in Tables I–III.

In all tables aluminosilicates constitute one of the largest particle fractions (45, 61, and 33% in different zones, respectively). It is seen from the tables that such a type of particles is more frequent in the middle zone of Lake Baykal. A major portion of the atmospheric aerosols in the northern zone of Lake Baykal (25% in the upper zone) refers to the particles of organic nature. This type of particles is also observed in middle and lower zones, but it is less common there. Partly, such particles put on a mask of other groups (clusters) of particles. Thus, fraction of organic matter in group No. 3 (middle zone) and group No. 6 (southern zone) is sufficiently large (12 and 33%, respectively). At the same time, fraction of organic particles clearly decreases from north to south (these particles content is 25, 11, and 6% for upper, middle, and lower zones, respectively). Contribution of gypsum particles is high and constant for upper and middle zones of the lake (13 and 14%, respectively), but this contribution is sufficiently less in southern zone (only 4.7%). It is in contrast with particles enriched with sulfur (more than 80% of total *X*–ray intensity for these particles are caused by presence of sulfur). Sulfur–enriched particle group is the most representative in lower zone of the lake (6.4%) in contrast with middle and upper zones (3.9 and 3.7%, respectively). Such a profile of sulfur–enriched particle concentration, likely, is connected with sulfur–containing emissions from Baykal pulp and paper mill located in southern part of the lake. Picture is the same for Al–containing particles (more than 60% of radiation correspond to *X*–ray peak from Al).

Content of such particles is sharply elevated (7%) in lower zone of the lake in contrast with that for upper and middle zones (0.4 and 0.6%, respectively). Iron–containing particle group (more than 80% of Fe intensity) is uniformly distributed over territory of Baykal (about 5% of total content). Pronounced group of quartz particles (96% of *X*–ray intensity correspond to Si) is observed only for lower zone. However, this group is one of the most representative here (25% of total content). There is no a group of K–containing particles (65% of K intensity) in the southern zone. In upper and middle zones K–enriched particle group (1.9 and 1.2%, respectively) has sometimes high level (up to 50% of characteristic *X*–rays) in contrast with P–containing particles (3 and 1.2%, respectively).

Surprisingly, particles of anthropogenic nature are observed in every zone. While still these particles constitute very small fraction of total content. Net content of such particles exceed 2% of total mass in no case. So, there are Ti– and Pb–enriched particle groups (0.4 and 0.2%, respectively) in lower zone. Zn–enriched aerosols occur both in upper and middle zones (1.2 and 1.1%, respectively). Ti–containing particles are observed in the middle zone (1.0% of total content) as well as in the southern part of the lake.

Besides, it should be noted that from obtained data one can clearly see the difference between composition of aerosol particles in each separated out zone, although aerosol compositions of upper and middle zones are very close. For the most part the group compositions differ by several percent. This fact can be easily explained by daily variations in aerosol content, essential difference between vegetable cover (woodlands and mountains), as well as closeness of shore in sampling. These conditions do not essentially influence on nature and source of particles in upper and middle zones, but it is not valid in analyzing of aerosol composition for lower zone of Baykal. Predominant group (aluminosilicates) is common for every zone, and content of Fe–enriched particles is the same for every zone too, but other groups observed in upper and middle zones either are absent in southern part or their content essentially differ from that observed in lower zone. Quartz– S– and Al–enriched particles as well as Ca–enriched aluminosilicates are contained in aerosols of southern part of the lake in noticeable elevated concentrations in contrast with other zones. At the same time, K–enriched and gypsum particles are few and far between. Aerosol particles containing base metals are observed in each site of sampling, but, as a rule, their concentration do not exceed 3% of total content.

3.2. Company at Karasuk and Klyuchi in 1992

Primarily we have analyzed 118 samples taken at Karasuk in February (63 samples) and August (27 samples) 1992 as well as 28 samples taken at Klyuchi in August 1992. The fourth set of samples was taken in winter 1993/1994 at Klyuchi to obtain complete picture of seasonal variations in composition of atmospheric aerosols at observational sites.

To obtain comprehensive notion of the incidence of different particle types in every sample taken over all observational period, each set of experimental data was analyzed by unhierarchical cluster method. These results are presented for every sample in form of percent contribution of each particle group to their total content. Average percent contribution for three sets of samples is given in Table IV.

It is seen from this table, that one can separate out 6 ... 8 groups of basic particle types. In all cases aluminosilicates are the most impressive group.

It is easily understood for summer sampling, since the production of great quantity of particles formed with soil erosion is to be expected. But it is unexpected for samples taken at Karasuk in winter, at a glance. Predominance of aluminosilicates in winter samples can be explained by essential contribution of aerosols of volatile ashes. Contribution of gypsum particles ($CaSO_4$ $*2H_2O$) in samples taken at Klyuchi (19.6%) is higher than that for Karasuk (about 10%). Group of Ca–enriched particles absent in winter samples from Karasuk is connected, likely, with dust–erosive sources. Iron–enriched particles contribution is almost constant in every sample (about 9%). In summer P– S– and K–enriched

TABLE I. Results of unhierarchical cluster analysis of data obtained by XRMEM for upper zone of Lake Baykal.

No. of group	Contribution of given group, %	Particle diameter, μm	Chemical elements															
			Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Zn	Pb	Org
1	45.0	1.8	0.4	1.2	17	58	0	2.0	0.2	3.8	3.0	0.4	0	0	14	0	0	0
2	25.2	1.2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	100
3	13.0	1.6	0	2.7	2.4	4.8	0.9	19	3.0	0.6	58	0.3	0	0.3	6.9	0.6	0	0.3
4	4.4	1.6	0	0.7	2.1	6.1	0	0.9	0.1	0.1	0.9	0.3	0.1	0.4	87	0.7	0	0.1
5	3.9	1.5	1.4	0	0	5.7	0	86	0	0	1.4	0	0	0	1.4	0	0	4.3
6	3.0	2.6	0	0	0	0	55	8.2	9.6	26	0	0	0	0	0	0	0	1.4
7	1.9	2.0	0	0	0	0	0.9	9.1	4.5	82	1.8	0	0	0	0	0	0	1.8
8	1.9	1.6	5.2	0	0	0	0	1.9	84	5.8	0	0	0	0	1.3	0	0.6	0.6
9	1.2	1.3	0	0	1.2	4.3	0	2.2	1.0	0.4	2.7	18	18	0	4.5	35	12	0
10	0.4	1.0	10	0	70	2.0	0	1.3	0	1.3	1.3	0	1.0	0	3.3	0	9.3	0.3

Note: Concentration of element in sample is expressed in weight percent and mormalized to total content of element taken as 100%.

TABLE II. Results of unhierarchical cluster analysis of data obtained by XRMEM for middle zone of Lake Baykal.

No. of group	Contribution of given group, %	Particle diameter, μm	Chemical elements															
			Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Zn	Pb	Org
1	61.1	1.9	0.4	1.3	19	56	0	1.1	0.1	4.4	3.4	0.3	0	0	14	0	0	0.4
2	14.3	1.6	0	2.8	2.4	7.9	1.0	11	1.2	0.6	67	0	0	0.6	5.9	0	0	0.2
3	10.6	1.1	0	12	12	18	0	12	0	0	18	0	0	0	18	0	0	12
4	5.3	1.5	0	0.4	2.6	6.8	0	1.3	0.5	0.5	1.3	0	0.2	0.6	84	1.3	0.2	0.1
5	3.7	1.1	9.8	0	0	2.4	0	79	0.8	1.6	4.1	0	0	0	0.8	1.6	0	0
6	1.2	1.5	0.8	2.0	0.8	0	4.8	19	3.9	66	2.0	0	0	0	0	0.4	0	1.2
7	1.2	1.9	0	0	0	0	56	10	13	18	2.2	0	0	0	0	0	0	1.2
8	1.1	1.3	0	0	0	0	0	2.1	22	5.3	0	0	0	0	0	46	24	1.0
9	1.0	1.5	0	0	3.1	11	0.1	0.9	0	0.5	3.5	68	0	0.3	12	0.2	0	0.2
10	0.6	1.4	26	0	61	1.8	0	1.7	0.3	1.5	0.5	0.3	0.5	0	4.6	1.5	0	0.6

TABLE III. Results of unhierarchical cluster analysis of data obtained by XRMEM for lower zone of Lake Baykal.

No. of group°	Contribution of given group, %	Particle diameter, μm°	Chemical elements															
			Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Zn	Pb	Org
1	33.4	1.3	0	0	35	47	0	1.0	0	1.9	2.8	0.1	0	0	11	0	0	0.3
2	24.5	1.1	0	0	0.5	96	0	0.9	0	0	0.2	0	0	0	1.4	0	0	0.7
3	11.6	1.4	0.2	1.2	20	35	0	6.0	1.1	0.8	13	1.4	0.3	0.3	20	0.3	0	0.2
4	7.1	0.8	21	0	70	0.6	0	5.3	0.3	1.3	0	0	0	0	1.6	0	0	0
5	6.4	1.0	23	0	1.5	0	0	71	0	2.3	0	0	0	0	0.8	0	0	1.6
6	6.0	1.2	0	0	0	0	11	0	33	22	0	0	0	0	0	0	0	33
7	5.7	1.2	0.4	0.1	2.0	6.6	0	2.0	0.4	0	0.5	0.2	0	2.9	87	0.9	0	0
8	4.7	1.4	0.4	1.1	4.8	6.3	0.4	27	1.3	0.2	45	2.0	0.2	0.4	11	0	0	0
9	0.4	1.2	0	0	4.2	6.4	0	1.3	3.6	0	2.1	71	0	0	12	0	0	0
10	0.2	0.8	0	0	0	0	0	0	0	0	0	0	0	0	0	0	100	0

TABLE IV. Relative contribution of particles of different types in aerosol samples taken at Klyuchi and Karasuk at different periods.

Karasuk, winter		Karasuk, summer		Klyuchi, summer	
Particle type	Contribution, %	Particle type	Contribution, %	Particle type	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

groups are observed in aerosol samples both from Karasuk and Klyuchi. It is evident, that these particles are of vegetable origin. Anthropogenic contaminators are often observed in all samples, but their content is higher in winter instead of summer. For instance, Pb–enriched particles are found in winter samples (5.2%) more often than in summer ones (1.3%) by a factor of 4. Small quantity of aerosols of other types, which contain Zn, Ti, and S, are observed only in winter. It is possible that such particles occur in summer samples too, but they are masked by large content of soil–erosive particles.

In the immediate future we plan to analyze the forth set of samples taken at Klyuchi. We also shall try to link the particle type with such meteorological data as the wind direction. We hope that it will give an elucidating glimpse into sources of every type of aerosol.

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