Monitoring of ion composition of atmospheric aerosols in the Western Siberia

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We present some results on the ion composition of atmospheric aerosol as observed at four sites in the Western Siberia in 1997–2000. Regularities in the seasonal and spatial behavior of the effect of various sources (gas-phase, erosion, marine) on the formation of aerosol particles are discussed. It is found that natural factors favor higher acidity of aerosol in the north of the Western Siberia.

Introduction

Regular observations of the chemical composition of atmospheric aerosols on the global, regional, and local scales provide important information on the dynamics of aerosol generation and transformation in the atmosphere and on the aerosol effect on land and water ecosystems.[1] The ion composition of atmospheric aerosol characterizes the content of the main cations and anions in the water-soluble fraction of aerosol; therefore, it is a component of the chemical composition that includes the data on the element composition and content of organic carbon and individual organic compounds in the total mass of atmospheric aerosol. Some circumstances favor the high information content of data on a limited set of characteristics of the water-soluble fraction of atmospheric aerosol.

First, the balance between the sums of equivalents of cations Σ_{cat} and anions Σ_{an} necessarily follows from the condition of electric neutrality of a solution. This allows estimation of the contribution of every ion to be done without introducing additional internal standards. These aerosol characteristics can be compared with similar data concerning the atmospheric precipitation and surface water to reveal the effect of various processes of aerosol generation.

Second, among the main cations (NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, K^+, H^+) and anions (HCO_3^-, SO_4^{2-}, Cl^-, NO_3^-, F^-, $HCOO^-$) we can separate out the groups of ions having different sources of aerosol generation.[1] Among cations, only NH_4^+ and H^+ are generated from the gas phase, whereas precursors of Ca^{2+}, Mg^{2+}, Na^+, and K^+ are nonvolatile substances carried out to the atmosphere due to erosion or from the surface of seas and oceans. Almost all anions, on the contrary, have gaseous precursors. It follows therefrom that based on the contribution of ions of different origin we can judge on the contribution of different sources to aerosol generation with a fair degree of confidence.

Finally, the data on the ion composition of atmospheric aerosol are especially important for diagnostics of the problem of acid precipitation. If atmospheric precursors of NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, and K^+ neutralizing the sum of anions in atmospheric aerosol are deficient, their excess is compensated for by H^+. Wet precipitations formed under such conditions have enhanced acidity, and this is the basic precondition for distortion of the activity of land and water ecosystems.

Taking these circumstances into account, the networks of stations for monitoring the ion composition of atmospheric aerosol were organized in some regions of the world. However, such a network is absent on the vast expanses of the Western Siberia. At the same time, the diversity of natural and climatic zones, degree of urbanization, level of development of industry, farming, transport, and power production in the Western Siberia differ significantly from the regions, in which the regularities of aerosol generation are studied sufficiently well. Therefore, systematic studies of the ion composition of atmospheric aerosol and wet precipitation have been arranged at some sites of the Western Siberia within the framework of the Complex Project “Siberian Aerosols.”

At the initial stage, these studies were performed in the south of the Western Siberia[2–5]; the observations of 1994–1997 are generalized in Ref. 5. Then the region of systematic observations was expanded to the north of the Western Siberia up to the forest-tundra zone of Yamalo-Nenetskii Autonomous Region (YaNAR). The effect of such natural and technogenic factors as fires[6] and plumes of oil and gas fields[7] on aerosol generation was established, and the correlation between variation of the ion composition of atmospheric aerosol and directions of air mass transport was revealed.[8] Based on the results on the ion composition obtained from analysis of snow cover and surface water, as well as simulation of the state of metals in water bodies of the

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Western Siberia, the conclusion was drawn on the existence of the problem of acid precipitation in the Western Siberia.[9]

This paper generalizes the results of monitoring ion composition of atmospheric aerosol over the territory of the Western Siberia obtained in 1997–2000. The emphasis is made on the spatial and temporal behavior of natural factors of aerosol generation in different natural and climatic zones.

Aerosol sampling and technique of analysis

The longest observations of ion composition of atmospheric aerosol in 1997–2000 were conducted at four sites:

– site 1, near Samburg village, within the Polar Circle, 67°N, 78°E, tundra zone;

– site 2, near Tarko-Sale village (YaNAR), 65°N, 78°E, roughly 250 km to the south of site 1, forest-tundra zone;

– site 3, Klyuchi village (Novosibirsk Region), 55°N, 83°E, forest-steppe zone;

– site 4, near Karasuk town (Novosibirsk Region), 54°N, 78°E, roughly 500 km to the southwest of site 3, steppe zone.

Some series of observations were conducted at other sites, in particular, Krasnosel'kup village (YaNAR, 66°N, 83°E) and near Zav'yalovo village (Novosibirsk Region, 54°N, 82°E). Since observations at these sites were conducted for a limited time, we do not consider the results in this paper.

At sites 1–4, diurnal samples of surface atmospheric aerosol were taken onto AFA-KhA filters in 30-day-long observation series in different seasons. The volume of air pumped through the filter was 190–310 m^3/day. Every filter was weighed before and after the exposure; the mass concentration Σ of aerosol particles was determined from the weight difference, and then related to the total mass of aerosol particles in one m^3 of air.

A part (1/2) of the filter after exposure was used to obtain aqueous extract; for this purpose, it was placed in a container with 10 ml of demineralized water. In aqueous extracts, the pH-factor, electric conductivity, and concentration of the main cations (Ca^{2+} + Mg^{2+}, Na^+, NH_4^+, K^+, H^+) and anions (HCO_3^-, F^- + $HCOO^-$, Cl^-, NO_3^-, SO_4^{2-}) were determined by the methods of ion chromatography, conductometric titration, and potentiometry.[2] These data were used to calculate the contribution of equivalents of individual ions to the salt composition of the water-soluble fraction of aerosol, its concentration W, and the fraction in the total mass Σ of aerosol particles. The methods of statistical analysis were applied to estimate the coefficients of pair correlation and ion ensembles having the common sources of aerosol generation from the variability of ion concentrations in observation series. These data, along with the average values of ion concentrations (in the form of equivalents, their fractions in Σ_{cat} and Σ_{an}, and mass concentration) were entered into the data bank of characteristics of atmospheric aerosol.

The values of Σ_{cat} and Σ_{an} were balanced, as a rule, accurate to 10%. This is indicative of the sufficient completeness of data on the ion composition of atmospheric aerosol; the latter, in its turn, determines the reliability of estimating the contribution of each ion to Σ_{cat} and Σ_{an}.

Seasonal and spatial dynamics of the ion composition

Table 1 gives the mean values of the parameters of the ion composition from each measurement series at sites 1–4 in 1997–2000, as well as the data from each site averaged over the entire period of observation. The mass concentration of aerosol particles Σ for each site varies widely, peaking in summer. Seasonal variations of the mass W of the water-soluble fraction are far narrower, and its part in the total mass of aerosol Σ in winter reaches 54% and in summer drops down to 4–6%. This fact can be explained by the seasonal character of surface sources of erosion: screening of the land surface by the snow cover in winter decreases the amount of erosion products coming to the atmosphere.

The minimum values of Σ and W are characteristic of the most northern site (Samburg); they are markedly higher in Tarko-Sale – the site situated 250 km to the south, and with the further advance to the south, they grow not so fast. By comparing the mean concentrations of sulfates and nitrates for the entire observational period with the data from Ref. 10, sites 1 and 2 can be classified as geochemically clear regions, and sites 3 and 4 approach the level of industrial regions.

With the total increase of Σ along the direction from north to south, the concentrations of individual ions change in different ways. Among cations, the mean concentration of ammonium, calcium, magnesium, and potassium increases, whereas the concentration of sodium drops down to the minimum value at site 3 (Klyuchi) and increases a little bit at site 4. As to anions, the concentration of chlorides decreases analogously (with a minimum at site 3), while the concentration of HCO_3^-, NO_3^-, SO_4^{2-} increases. Such a difference in the spatial behavior of the concentration of Na^+ and Cl^- can be explained by the fact that the effect of marine source of aerosol generation weakens farther and farther away from the ocean and the region of the Aral Sea. This confirms our early assumption on the remote atmospheric transport of sea salts from the region of the Aral Sea to the south of the Western Siberia.[2]

As to the ions – products of gas-phase reactions in the atmosphere, it is worthy to note the increase of the mean concentration of NO_3^- in the south of the Western

Siberia and the combination of NH_4^+, NO_3^-, SO_4^{2-} ions at the most southern site (Karasuk). The effect of seasonal variability with the maximum in winter manifests itself for these ions at sites 3 and 4. Another seasonal dependence is observed for the concentration of (Ca^{2+} + Mg^{2+}): minimum values are observed in winter and maximum ones – in the season of farm works. This confirms the fact that the main precursors of these ions at sites 3 and 4 are the products of erosion of the land surface, rather than power production plants, whose emissions to the atmosphere are minimum in summer.

Besides analysis of the dynamics of absolute ion concentrations in the water-soluble fraction of atmospheric aerosol, it is interesting to estimate the fractions of individual ions. These data calculated from the mean values of the concentrations for the period of observations in 1997–2000 are given in Table 2. The contribution of ammonium and sulfates is almost the same at all the observation sites, but the contribution of SO_4^{2-} proves to dominate among anions. The fraction of Na^+ in cations is comparable with the fraction of (Ca^{2+} + Mg^{2+}) in the north, and this ratio changes sharply in the atmospheric aerosol in the south of the Western Siberia. The maximum fraction of the latter is (51%) in Klyuchi. At this site, the fraction of HCO_3^- reaches its maximum too. This combination points to the important role of erosion sources of aerosol generation.

Table 1. Mean concentrations of ions, ng-equ/m^3, mass concentration of aerosol particles Σ, and water-soluble fraction *W*, μg/m^3

Date	NH_4^+	Ca^{2+} + Mg^{2+}	Na^+	K^+	H^+	HCO_3^-	F^-+$HCOO^-$	Cl^-	NO_3^-	SO_4^{2-}	*W*	Σ
						Samburg						
Oct–Nov 97	15.4	9.1	13.9	2.0	8.7	3.0	1.1	5.2	3.6	34.7	3.1	6.6
Apr–May 98	14.1	11.9	12.1	3.6	8.1	6.4	4.3	2.3	1.4	39.9	3.5	77
July 98	18.0	10.2	7.3	3.9	7.9	3.5	2.5	2.0	0.8	49.0	3.6	96
Sep–Oct 98	5.1	8.3	11.6	1.2	9.6	4.6	3.1	4.3	1.2	25.1	2.3	11.5
July 99	6.0	6.8	5.9	1.7	0.1	7.6	2.4	2.2	0.8	9.5	1.5	26.8
Oct 99	6.9	10.2	13.8	1.2	0.1	6.7	1.7	6.3	1.6	17.3	2.3	6.7
Jan 2000	20.0	9.2	9.7	4.2	4.5	1.6	2.5	2.2	1.0	46.1	3.4	10.0
Average	12.2	9.4	10.6	2.5	5.6	4.8	2.5	3.5	1.5	31.7	2.8	25.4
						Tarko-Sale						
Dec 97	14.8	11.8	7.5	3.3	13.3	0	1.1	0.8	4.2	37.2	2.9	8.3
May–June 98	16.8	25.5	8.4	2.3	0.1	18.2	1.6	2.5	1.8	30.3	3.8	81
July–Aug 98	9.0	24.7	6.0	2.4	0.1	19.7	2.4	2.4	2.0	25.3	3.5	95
Sep–Oct 9	12.6	11.3	12.5	2.1	2.7	10.1	3.5	3.5	2.1	28.8	3.1	15.5
Jan 99	24.1	12.5	7.6	4.1	0.1	10.4	2.9	3.3	1.9	46.2	3.8	36.6
Apr 99	27.6	15.4	16.1	4.8	0.1	13.2	1.6	3.6	5.0	60	5.5	18.3
July 99	7.8	17.1	7.7	1.6	0.1	19.2	1.2	1.9	1.3	15.1	2.7	46.4
Nov 99	20.0	13.2	16.5	2.6	0.7	7.8	1.9	3.8	4.8	37.6	3.8	12.2
Jan 2000	42.4	12.5	10.9	7.1	1.2	4.0	3.7	3.5	3.3	73.5	5.7	24.0
Average	19.5	16.0	10.4	3.4	2.0	11.4	2.2	2.8	2.9	39.3	3.9	41.1
						Klyuchi						
Feb–Mar 97	51.1	31.8	8.9	4.4	8.9	2.5	2.8	1.2	16.4	106	7.1	31.8
June–July 97	6.9	33.6	4.3	3.4	0.5	13.8	1.2	1.9	5.1	21.6	4.1	56.6
Oct 97	19.7	40.0	5.5	6.8	3.3	25.8	4.8	3.7	23.3	28.0	5.9	29.2
Jan–Feb 98	43.2	25.1	4.5	6.4	19.1	1.9	1.7	0.5	16.1	88.4	7.0	13.0
Apr–May 98	22.2	29.1	7.6	2.8	0.6	13.6	0.6	0.9	3.7	51.2	4.7	60.3
July–Aug 98	3.9	31.7	4.5	1.9	0.3	19.2	3.1	1.5	3.5	17.7	3.1	59.5
Oct 98	10.0	19.5	4.8	3.3	1.6	7.1	1.3	1.5	5.0	27.4	2.9	17.3
May 99	13.5	78.8	10.7	6.2	0.1	48.5	3.6	3.1	11.3	40.9	7.9	144
Sep–Oct 99	16.8	33.3	6.1	3.4	0.1	12.1	2.2	1.9	7.7	40.2	4.4	22.4
Apr–May 2000	14.5	35.9	7.2	4.6	0.2	25.8	2.5	1.9	9.6	34.1	5.1	38.7
Average	20.2	35.9	6.4	4.3	3.5	17.0	2.4	1.8	10.2	45.6	5.2	47.3
						Karasuk						
Feb–Mar 97	63.7	21.7	6.5	4.3	3.8	1.8	0.7	0.9	16.0	80.6	8.0	25.3
May 97	17.5	24.7	5.5	5.1	5.8	5.6	2.3	2.6	0.5	39.0	4.3	60.4
Oct–Nov 97	22.2	40.3	12.7	12.7	9.0	5.7	4.6	6.5	31	42.3	6.5	48.7
Jan–Feb 98	75.8	22.0	9.7	18.5	6.1	4.7	3.0	1.2	24.8	119	10.3	31.4
May 98	27.4	18.5	9.2	4.5	0.3	10.0	2.2	1.0	5.8	57,1	5.0	60.3
Aug 98	16.8	34.4	8.3	5.2	1.3	17.1	3.6	2.5	4.3	38.3	4.6	94.8
Oct 98	11.1	16.9	7.1	4.5	1.0	4.0	0.8	1.1	5.6	53.3	3.1	23.6
Feb 99	45.4	69.1	6.7	5.3	0.2	10.0	1.8	1.7	20.3	97.6	9.0	14.7
Average	35.0	31.0	8.2	7.5	3.4	7.4	2.4	2.2	13.5	65.9	6.4	44.9

Table 2. Fractional distribution, in % equ., of cations and anions in aerosol at different observation sites

Site	NH_4^+	$(Ca^{2+} + Mg^{2+})$	Na^+	K^+	H^+	HCO_3^-	$F^- + HCOO^-$	Cl^-	NO_3^-	SO_4^{2-}
Samburg	30.3	23.3	26.3	6.2	13.9	10.9	5.7	8.0	3.4	72.0
Tarko-Sale	38.0	31.2	20.3	6.6	3.9	19.5	3.8	4.8	4.9	67.1
Klyuchi	28.7	51.1	9.1	6.1	5.0	22.1	3.1	2.3	13.2	59.2
Karasuk	41.1	36.4	9.6	8.8	4.0	8.1	2.6	2.4	14.8	72.1

High fraction of H^+ in the composition of cations at the most northern observation site (Samburg) deserves special attention. This means that there, in spite of the "unpolluted" atmosphere (minimum values of Σ and W, see Table 1), the excess of anions or, more precisely, deficit of cations neutralizing the excess of anions in atmospheric aerosol is observed. As a result, at this site there exist conditions for the excess acidity of atmospheric components (aerosol particles, wet precipitation). The fraction of H^+ at other observation sites is markedly lower. It should be emphasized that the above-said concerns with the mean values of the parameters of the ion composition for a relatively long period; at the same, short-term situations of acidification of atmospheric components may occur at different sites.

Since sulfate is the major anion in the composition of atmospheric aerosol at all the above sites, it is interesting to estimate the contribution of different cations to neutralization of SO_4^{2-}. These data are presented in Table 3 as the ratio of the equivalents of the main cations to the equivalent of sulfate calculated from the data on the mean ion composition of atmospheric aerosol in each site.

Table 3. Equivalent ratio of cations and sulfate at different observation sites

Site	$[NH_4^+]/[SO_4^{2-}]$	$[Ca^{2+} + Mg^{2+}]/[SO_4^{2-}]$	$[Na^+]/[SO_4^{2-}]$
Samburg	0.38	0.30	0.33
Tarko-Sale	0.50	0.41	0.26
Klyuchi	0.44	0.79	0.14
Karasuk	0.53	0.47	0.12

The contributions of cations of gas-phase (NH_4^+), erosion ($Ca^{2+} + Mg^{2+}$), and marine (Na^+) origin to sulfate neutralization are roughly the same in Samburg; at other sites, the fraction of the two first classes increases while the fraction of sodium decreases. None of them can completely neutralize the concentration of sulfate in aerosol, which makes up to 59–72% of the sum of equivalent anions (see Table 2). The contribution of the marine source decreases, as expected, and that of the erosion source increases in the direction from north to south of the Western Siberia; the ratio $[Ca^{2+} + Mg^{2+}]/[SO_4^{2-}]$ is highest in Klyuchi. The resources of gas-phase sources in neutralization of sulfates ($[NH_4^+]/[SO_4^{2-}]$ ratio) vary not that significantly in different natural and climatic zones of Siberia. From this it follows that only joint action of aerosol from various sources can lead to efficient neutralization of the acidic anions.

Factors of formation of the ion composition of atmospheric aerosol

As was shown above, the variability of stoichiometric relationships of ions in atmospheric aerosol is caused by the spatial and seasonal behavior of different sources. How their variations manifest themselves in time can be judged on from the data of statistical (factor) analysis of the results of determination of the ion composition in each observation series at a specific site. These data are given in Table 4 as combinations of ions, whose concentrations correlated for the period of observations (usually 30-day long). If atmospheric aerosol would be generated due to only one common source, then the variations of the concentrations are determined only by the intensity of this source and all ions form a single group. In the presence of different sources, this result can be observed only if they have a synchronous dynamics.

It should be noted that high correlation or the absence of correlation between the concentration variations of some ions is not connected with the part of these ions in the stoichiometric composition of atmospheric aerosol. Actually, the ions comprising a small fraction of the total ion composition can have a common source. Variations of the source intensity manifest themselves similarly in the dynamics of the concentration of such ions, and this leads to high correlation. On the contrary, ions, whose fraction in the atmospheric aerosol is large, that come from different sources (for example, gas-phase and erosion ones) have different dynamics, and may prove to be in different factors. Consequently, the information on the effect of different sources of aerosol generation that is obtainable from statistical analysis of the data of daily samples is based on the regularities different from those in the stoichiometric composition of atmospheric aerosol.

As is seen from the data of factor analysis (see Table 4), in the series of observation of the ion composition of atmospheric aerosol in the Western Siberia there are three (more rarely two or four) ensembles of ions with correlation between the concentrations, and their composition varies. In these groups, we have separated the combinations (factors) characteristic of different precursors of ions in atmospheric aerosol: gas-phase reactions can yield combination of NH_4^+, H^+, and SO_4^{2-} ("acid factor") or NH_4^+ and SO_4^{2-} (well aged aerosol),[11] erosion sources can contribute to the combination of ($Ca^{2+} + Mg^{2+}$) and HCO_3^-, and the marine source manifests itself in the combination of Na^+ and Cl^-. All these ensembles were observed at different sites, and in some series – as independent factors. Most often (in six of eight series) the acid factor shows itself in the most northern site (Samburg), and in five series – in the first ensemble, which is the heaviest in the common dynamics of ion concentrations. At this site, as well as in Tarko-Sale, the marine factor most often manifests itself (in four of eight and in five of nine series, respectively). In the south of the Western Siberia, the repetition rate for these factors is lower, but that for the erosion factor is higher (in four of ten series in Klyuchi and in three of eight series in Karasuk). The gas-phase mechanisms of aerosol generation in Klyuchi and Karasuk most often manifest themselves in the combination of NH_4^+ with SO_4^{2-}, rather than the acid factor. This can be explained by the sufficient amount of substances carried out from the land surface in aerosol particle; these substances react with excess sulfuric acid – product of gas-phase reactions.

Table 4. Ion ensembles in the composition of aerosol with the common dynamics of the concentration

Date	Ensemble 1	Ensemble 2	Ensemble 3	Ensemble 4
		Samburg		
Nov 97	NH_4^+, H^+, SO_4^{2-}, F^-	$Ca^{2+} + Mg^{2+}$, Na^+, Cl^-, NO_3^-	K^+	–
Apr–May 98	$Ca^{2+} + Mg^{2+}$, Na^+, NO_3^-	NH_4^+, H^+, SO_4^{2-}	K^+, Cl^-, F^-	–
July 98	NH_4^+, H^+, SO_4^{2-}, $Ca^{2+} + Mg^{2+}$, HCO_3^-, Na^+	K^+, NO_3^-, F^-	–	–
Sep 98	H^+, HCO_3^-, F^-	Na^+, Cl^-, NO_3^-	$Ca^{2+} + Mg^{2+}$	NH_4^+, SO_4^{2-}
Oct 98	H^+, HCO_3^-, SO_4^{2-}	$Ca^{2+} + Mg^{2+}$, Na^+, Cl^-	NH_4^+, F^-	–
July 99	NH_4^+, H^+, SO_4^{2-}, $Ca^{2+} + Mg^{2+}$, HCO_3^-	K^+, Cl^-, NO_3^-	F^-	–
Oct 99	NH_4^+, H^+, SO_4^{2-}, HCO_3^-	Na^+, Cl^-	K^+	–
Jan–Feb 2000	NH_4^+, H^+, SO_4^{2-}, HCO_3^-	Cl^-, F^-	Na^+, K^+	–
		Tarko-Sale		
Dec 97	Na^+, NO_3^-, F^-	NH_4^+, SO_4^{2-}, K^+	H^+, Cl^-	–
May–June 98	$Ca^{2+} + Mg^{2+}$, HCO_3^-, H^+	NH_4^+, SO_4^{2-}	Na^+, Cl^-	–
July–Aug 98	NH_4^+, SO_4^{2-}, K^+	Na^+, HCO_3^-	F^-, Cl^-	–
Oct 98	Na^+, Cl^-, NO_3^-	NH_4^+, H^+, SO_4^{2-}	$Ca^{2+} + Mg^{2+}$, HCO_3^-	–
Jan 99	NH_4^+, SO_4^{2-}, $Ca^{2+} + Mg^{2+}$, HCO_3^-, NO_3^-	H^+, K^+	Na^+, Cl^-	–
Apr 99	Na^+, Cl^-, HCO_3^-, H^+	NH_4^+, SO_4^{2-}, K^+	NO_3^-, F^-	–
July 99	NH_4^+, SO_4^{2-}	$Ca^{2+} + Mg^{2+}$, NO_3^-, K^+	H^+, HCO_3^-, F^-	Na^+, Cl^-
Nov 99	NH_4^+, H^+, SO_4^{2-}, K^+, HCO_3^-	$Ca^{2+} + Mg^{2+}$, NO_3^-, Cl^-	F^-	–
Jan–Feb 2000	NH_4^+, $Ca^{2+} + Mg^{2+}$, Na^+, K^+, NO_3^-	H^+, HCO_3^-, SO_4^{2-}	Cl^-	–
		Klyuchi		
Mar 97	NH_4^+, SO_4^{2-}	Na^+, NO_3^-, K^+	H^+	$Ca^{2+} + Mg^{2+}$
July 97	NH_4^+, SO_4^{2-}, K^+, NO_3^-	Na^+, Cl^-	H^+, HCO_3^-	–
Oct 97	$Ca^{2+} + Mg^{2+}$, K^+, NO_3^-, F^-	H^+, HCO_3^-	Na^+, Cl^-	–
Jan–Feb 98	NH_4^+, H^+, SO_4^{2-}	NO_3^-, Cl^-, F^-	Na^+, K^+	$Ca^{2+} + Mg^{2+}$
Apr–May 98	$Ca^{2+} + Mg^{2+}$, H^+, HCO_3^-, Na^+, NO_3^-	K^+, Cl^-	NH_4^+, SO_4^{2-}	–
July–Aug 98	SO_4^{2-}, NO_3^-, Cl^-, F^-, K^+	NH_4^+	$Ca^{2+} + Mg^{2+}$, HCO_3^-	–
Oct 98	$Ca^{2+} + Mg^{2+}$, NO_3^-, K^+, Cl^-	H^+, HCO_3^-	NH_4^+, SO_4^{2-}	–
May 99	NH_4^+, SO_4^{2-}, Na^+	$Ca^{2+} + Mg^{2+}$, HCO_3^-, H^+, Cl^-	NO_3^-, F^-	–
Sep–Oct 99	$Ca^{2+} + Mg^{2+}$, SO_4^{2-}	Na^+, HCO_3^-, H^+, Cl^-	K^+	–
Apr–May 2000	$Ca^{2+} + Mg^{2+}$, HCO_3^-, NO_3^-, K^+	NH_4^+, SO_4^{2-}	H^+, Na^+	–
		Karasuk		
Mar 97	$Ca^{2+} + Mg^{2+}$, NO_3^-	NH_4^+, H^+, SO_4^{2-}	Na^+, Cl^-, F^-	–
July 97	SO_4^{2-}, $Ca^{2+} + Mg^{2+}$, NO_3^-, K^+, F^-	H^+, HCO_3^-, Cl^-	Na^+	–
Oct 97	NH_4^+, SO_4^{2-}, F^-	$Ca^{2+} + Mg^{2+}$, HCO_3^-, Na^+	NO_3^-	–
Jan–Feb 98	NH_4^+, SO_4^{2-}, K^+	$Ca^{2+} + Mg^{2+}$, F^-	NO_3^-	–
Apr–May 98	$Ca^{2+} + Mg^{2+}$, HCO_3^-, Na^+, NO_3^-	K^+	NH_4^+, SO_4^{2-}	–
Aug 98	NH_4^+, SO_4^{2-}, $Ca^{2+} + Mg^{2+}$, Na^+, K^+, NO_3^-	Cl^-, F^-	H^+, HCO_3^-	–
Oct 98	SO_4^{2-}, $Ca^{2+} + Mg^{2+}$, Na^+, K^+, F^-	H^+, HCO_3^-	NH_4^+, Cl^-	–
Feb 99	NH_4^+, H^+, SO_4^{2-}, NO_3^-, K^+	Na^+, Cl^-, F^-	$Ca^{2+} + Mg^{2+}$, HCO_3^-	–

Note. NH_4^+, H^+, SO_4^{2-} – acid factor, NH_4^+, SO_4^{2-} – aged aerosol, $Ca^{2+} + Mg^{2+}$, HCO_3^- – erosion factor, Na^+, Cl^- – marine factor.

Combinations of ions in ensembles separated based on the correlation between variations of their concentrations likely reflect the superposition of the effects of different aerosol sources at a given point for a certain period of observations. In such situations, additional information can be obtained from the values of the correlation coefficients between ion pairs. Thus, in the series of observation in Tarko-Sale in October 1998, the marine, acid, and erosion factors are clearly separated. Correspondingly, the cations Na^+, NH_4^+, and $(Ca^{2+} + Mg^{2+})$ proved to be in different ensembles as it can be drawn from the results of factor analysis (see Table 4). The correlation coefficients in the pairs $Na^+ - NH_4^+$, $Na^+ - (Ca^{2+} + Mg^{2+})$, $NH_4^+ - (Ca^{2+} + Mg^{2+})$ did not exceed 0.15. For the same site in December 1999, the gas-phase and erosion factors proved to be in the same ensemble, whereas the marine factor found itself in another ensemble. This corresponded to high correlation (0.779) of the variability of NH_4^+ and $(Ca^{2+} + Mg^{2+})$ concentrations, whereas the correlation coefficients of these ions with Na^+ were, respectively, − 0.28 and − 0.29.

We can suppose that differences in the dynamics of different aerosol sources for a given site are determined by variations of not only source intensity (for example, seasonal variations), but also by air mass transport. In this connection, it is interesting to compare the data on the dynamics of ion composition of atmospheric aerosol with the trajectories of atmospheric transport estimated from meteorological data. The possibility of this comparison for revealing possible effect of a technogenic source that is far from an observation site is illustrated in Refs. 8 and 12. It is proposed to use similar approach for localization of natural sources determining the ion composition of atmospheric aerosol.

Conclusion

Information on the ion composition of atmospheric aerosol collected in various natural and climatic zones of Siberia enables one to reveal certain peculiarities in the aerosol formation. Seasonal dynamics of land erosion sources plays a significant part in this region. This manifests itself in the seasonal dynamics of the mass concentration, in the role of soluble fraction, in the stoichiometric composition, and in the ratios among ions, whose precursors are gaseous atmospheric constituents and substances carried out from the land surface. The contributions of gas-phase, erosion, and marine sources to the composition of cations in atmospheric aerosol are roughly equal at the most northern observation site, but the sum of their equivalents is insufficient for neutralization of acidic anions. As a consequence, the conditions at this site favor acidification of atmospheric components, though at a minimum concentration of atmospheric aerosol. Farther to the south, toward the observation site Klyuchi in the Novosibirsk Region, the contribution of the marine source decreases, but then the tendency of its growth arises likely due to the air transport of salts from the Aral Sea region. In the ion composition of atmospheric aerosol in the south of the Western Siberia, the contribution of erosion processes increases markedly, and this favors the decrease of the acidity level of atmospheric components.

Application of statistical analysis to the data on the ion composition of atmospheric aerosol for the series of long-term observations at each site allows separating out the situations of individual and joint effects of the gas-phase, erosion, and marine sources. It is supposed that the more detailed information on the location of these sources can be obtained by combining these data with the data on the transport of air masses.

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