

Dynamics of the ion composition of atmospheric aerosols of Western Siberia in 1996–2004

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We present data on dynamics of the ion composition of atmospheric aerosols during the period from 1996 until 2004 for four observation sites in the Western Siberia differing in natural climatic conditions and in industrial load. Two groups of ions formed from volatile and nonvolatile precursors are distinguished in the aerosol composition. Factors determining the seasonal and spatial concentration variability of the first group of ions are common for all sites and have a regional nature. For the second group of ions, their action depends on local conditions. The ratio between the contributions of ions from both of these groups determines also the level of the aerosol acidity. Influence of industrial sources of the big center (Novosibirsk) on the ion composition of aerosols is discussed in this paper.

Introduction

Processes of generation, transformation, transfer, and sink of atmospheric aerosols (AA), playing an important role in the Earth's radiation balance, climate, and in the material exchange in the atmosphere–surface system, are subjected to essential variations in time and space.^{1–4} This is caused by the variability of the action of AA volatile and nonvolatile precursors of natural and technogenic origin, and by the conditions of various reactions of their transformations in the atmosphere. In recent years, numerous researches have been devoted to studying chemical composition of the near ground aerosol in various regions of the world and to analysis of tendencies in its time behavior. Some of them are generalized in Ref. 5. To a considerable extent, such researches are stimulated by the well-known problem of acid precipitation that has determined the increased attention to the studies of AA ion composition in different regions of the world.

Action of natural and technogenic factors on the formation of AA ion composition in Siberia remains yet poorly investigated. In recent years, only few studies of the ion composition of atmospheric precipitation have been conducted, limited by terms and sites of the observations^{6–9} in this region. This makes difficult to isolate the AA formation factors from different sources and long-term tendencies of their modification in Siberia. The aim of this study was to analyze the dynamics of the ion composition and the AA acidity in the Western Siberia for quite a long period (since 1996 until 2004).

Sampling and analysis of atmospheric aerosols

The AA samples were taken in different seasons (winter – spring – summer – fall) in the following sites in the north and in the south of the Western Siberia:

1 – not far from the village of Tarko-Sale (64°56'N, 77°26'E), approximately 170 km to the south of the North polar circle, Yamal-Nenets Autonomous Region, a tundra forest belt;

2 – Klyuchi (55°10'N, 83°30'E), a village approximately 30 km to the southeast from Novosibirsk, a forest-steppe zone;

3 – not far from the town of Karasuk (53°50'N, 78°00'E), approximately 500 km to the southwest from Novosibirsk, a steppe zone;

4 – Novosibirsk (55°10'N, 82°49'E), a big industrial center.

The most complete data for the period since June of 1996 until February of 2004 were obtained at the observation sites 1–3, but at the site 4, they were limited by the period since April of 2000 until February of 2004. Unfortunately, in different sites, we did not succeed in sampling the AA in some seasons and there are no data for these periods in the results presented below. Nevertheless, the total variability of the AA ion composition was shown clearly enough.

Daily AA samples were obtained by pumping of 200–300 m³ of air through the AFA-KHA filters. Each filter was dried in the exicator before and after the air pumping, weighed and aerosol mass M in 1 m³ of the air was estimated by the mass difference. For obtaining the AA aqueous extract, a part of the exposed filter (¼ or ½) was put into the container filled with 10 ml of twice-distilled water for 24 hours, then the filter was pulled out, and the solution was used for analysis of the ion composition by the technique described in Ref. 8.

Results and Discussion

Mass concentration of AA and contribution of water-soluble salts

Ion concentration in the daily AA samples varied over a wide range that was caused by the dynamism

of atmospheric processes, including the variations of meteorological situations (transfer directions of air masses, periodic precipitation). Influence of these factors is considered separately in Ref. 10. In this paper, we have used the mean daily values of M , W , and concentrations of individual ions for each observation series, represented by the arithmetic mean values for 30 discrete daily samples. Dynamics of the mean values of M and the fraction W/M of water-soluble salts in the AA total mass for the sites 1–3 during the period of 1996–2004, presented in Fig. 1, has a cyclic seasonal behavior. The maximum values of the AA mass concentration typical of summer, reach 50 to 70, and in some periods up to $150 \mu\text{g}\cdot\text{m}^{-3}$. In winter, the values of M were reduced up to $20\text{--}30 \mu\text{g}\cdot\text{m}^{-3}$; in Karasuk and Klyuchi, they appeared to be minimum for the whole observation period in October of 2000 (7.7 and $9.4 \mu\text{g}\cdot\text{m}^{-3}$, respectively), and in Tarko-Sale – in February of 2003 ($9.9 \mu\text{g}\cdot\text{m}^{-3}$). Mean long-term values of M at these sites appeared to be close (34.3 , 40.1 , and $33.1 \mu\text{g}\cdot\text{m}^{-3}$ in Tarko-Sale, Klyuchi, and Karasuk, respectively). The values obtained in Novosibirsk were higher ($56.3 \mu\text{g}\cdot\text{m}^{-3}$).

It is interesting to compare these values with the data obtained in different regions around the globe, generalized in Ref. 5. The minimum values of M ($3.4 \mu\text{g}\cdot\text{m}^{-3}$) were recorded in Antarctica; and can be considered as the global background values. The higher annual mean values of M ($40\text{--}83 \mu\text{g}\cdot\text{m}^{-3}$) are typical of the territories in the USA and Central Europe. Thus, we can conclude that the AA mass concentration in the sites 1–3 reduces, from time to time, down to the level of the global background, and in summer raised up to the values typical of the continental and urban territories. In all observation

sites, the total concentration of water-soluble salts W is much less than the AA mass concentration: in winter, it reached 6 to 11 and reduced down to $2\text{--}5 \mu\text{g}\cdot\text{m}^{-3}$ in the summer–fall period. According to data on the concentration of individual ions in the AA composition, the value of W in Antarctica makes 1.43 and for the continental urban territories it increases up to $20\text{--}30 \mu\text{g}\cdot\text{m}^{-3}$ (see Ref. 5). Hence, the amount of water-soluble salts in the AA composition in the Western Siberia during the summer–fall period approaches the global background level, and in winter exceeds it by 5 to 8 times, while remaining 2 to 3 times lower, than in the territories with concentrated industrial activity. In summer, a fraction of W in M reduces to 4 to 6%, whereas in winter it reaches 20–30% and more (61% in February of 1999, in Karasuk). This means that in summer, the water-insoluble compounds make more than 90% of the total mass of the near-ground aerosol.

That well expressed mass concentration variations of aerosol particles and contribution of soluble and insoluble compounds can be connected with a seasonal nature of different sources contributing to formation of the AA matter. In forming the aerosol particles from atmospheric gases and marine sources, the water-soluble salts are formed (sulfate and ammonium nitrate, sodium, magnesium, and calcium chlorides). The water-insoluble and slightly soluble compounds (aluminosilicates, silicates, carbonates) in the AA matter are typical of the substances coming into the atmosphere from the ground surface due to erosion. Duration of winter period in the observation sites makes 6 to 8 months; the ground surface is covered by snow that reduces the contribution of local erosion to minimum.

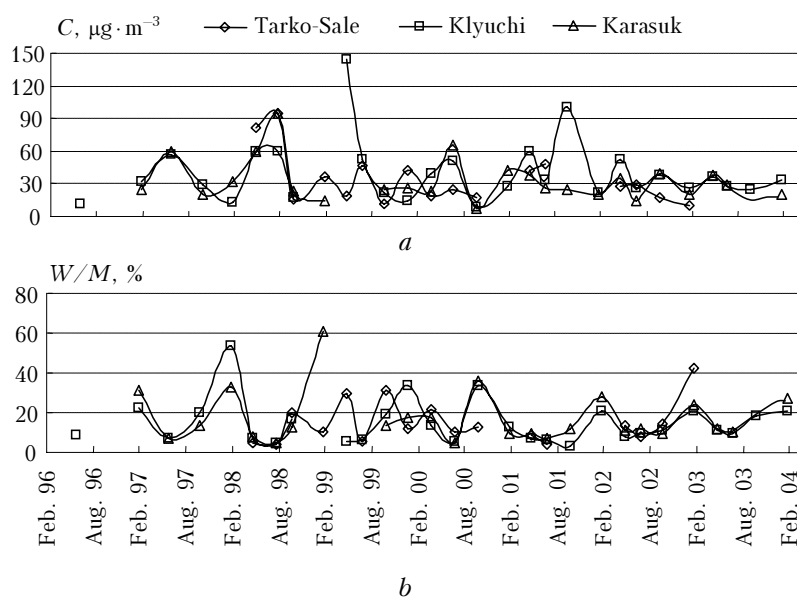


Fig. 1. Dynamics of mass concentration M , $\mu\text{g}\cdot\text{m}^{-3}$ (a), and a fraction of water-soluble salts W/M , % (b), at the sites 1–3 during the period from 1996 until 2004.

Their contribution becomes considerable in summer, especially in dry weather that is shown by the growth of M and contribution of insoluble substances. Thus, dynamics of M and W observed on the territory of the Western Siberia reflects a seasonal behavior of the ratio between contributions of different sources of aerosol forming substances.

Ion composition of AA

The annual mean concentration of individual ions and their fraction in cationic (Cat) or anionic (An) sums, during the period from 1996 until 2004, are summarized in the table. The data from Antarctica (Hut Point, McMurdo Research Station) that we have recalculated from Ref. 11 are presented here.

In analyzing these data, we can conclude that, on the whole, content of water-soluble salts (Cat + An) was sufficiently close to that in AA in the north and in the south of the Western Siberia and was approximately by 3 times higher, than the global background level (Antarctica).

The total cationic contribution to AA from the volatile and nonvolatile precursors, removed from the ground surface ($\text{Ca}^{2+} + \text{Mg}^{2+} + \text{NH}_4^+ + \text{K}^+$), makes 85–90% of the equivalents of all cations in the Western Siberia, whereas in Antarctica it is only 47.4%. These differences are caused by the higher contribution of marine salts in the Antarctic AA, for this reason the fraction of Na^+ in them reaches 52.6%. Notice that the fraction of another marker of the marine aerosol (Cl^-) in the north of the Western Siberia (Tarko-Sale) makes 7.2%, in the south of Siberia (Klyuchi, Karasuk, Novosibirsk) it is only 3% in the sum of An against 39% in Antarctica. For other regions, with an appreciably high fraction of Na^+ and Cl^- , usually the contribution of marine sources to the concentration of such ions as SO_4^{2-} , Ca^{2+} , and K^+ , based on the ratio of their equivalents to Na^+ in marine water is taken

into account (0.12 for $\text{SO}_4^{2-}/\text{Na}^+$, 0.043 for $\text{Ca}^{2+}/\text{Na}^+$, and 0.021 for K^+/Na^+) (see Ref. 12). In this approximation, we shall find that the contents of Ca^{2+} – 7%, SO_4^{2-} – 13%, and K^+ – 51% in the AA composition in Antarctica, can have a marine origin, in the south of the Western Siberia, those are respectively 1, 2, and 4%, and in the north of the Western Siberia (Tarko-Sale) – 2.5, 4, and 8%. Hence, the AA formation in Siberia conforms to the typical continental conditions and takes place, basically, due to the volatile and nonvolatile precursors of a ground origin out of natural and technogenic sources at a low contribution (especially in the south) from marine sources.

The main role in forming the anion composition of the AA water-soluble salts, both in Siberia and in Antarctica, belongs to SO_4^{2-} , a fraction of which reaches 77% of the sum of all anions in Karasuk. Though, the concentration of SO_4^{2-} in aerosols of Novosibirsk is close to that in other observation sites in Siberia, its fraction appeared lower due to the higher contribution of HCO_3^- . These and other differences of the AA ion composition in the industrial center will be considered below. Atmospheric gases are also the precursors of nitrate, the fraction of which is by 6 to 10 times lower. The total contribution of the rest anions to compound of the AA water-soluble salts in the Western Siberia makes 6 to 10%. For Antarctica, Cl^- makes the weighty contribution to the anion composition which, however, is neutralized by the Na^+ cation.

For further analysis of the factors determining the AA ion composition in the Western Siberia, it is advisable to distinguish between two groups of ions formed from volatile and nonvolatile precursors. The concentration dynamics of most considerable ions of the first group (SO_4^{2-} , NO_3^- , and NH_4^+) appeared to be very similar for the whole observation period in the sites 1–3 (Fig. 2).

Mean values of concentration C_i (ng-eqv · m⁻³) and the fraction (%) of the equivalents, of ions in AA in the Western Siberia and in Antarctica

Parameter	Western Siberia								Antarctica	
	Village of Tarko-Sale		Village of Klyuchi		Karasuk		Novosibirsk		Hut Point (Ref. 11)	
	C_i	%	C_i	%	C_i	%	C_i	%	C_i	%
NH_4^+	16.1	30.4	16.0	25.8	25.4	39.5	9.1	9.9	2.66	13.4
$\text{Ca}^{2+} + \text{Mg}^{2+}$	20.3	38.4	31.8	51.3	23.8	37.0	70.6	76.5	6.24*	31.5
Na^+	11.9	22.5	8.2	13.2	7.8	12.1	8.4	9.1	10.4	52.6
K^+	3.1	5.9	4.6	7.4	5.1	7.9	4.0	4.3	0.49	2.5
H^+	1.5	2.8	1.4	2.3	2.2	3.4	0.2	0.2	–	–
Cat	52.9	100	62.0	100	64.3	100	92.3	100	19.8	100
HCO_3^-	9.8	17.2	13.7	20.6	5.3	7.8	39.3	42.9	–	–
$\text{F}^- + \text{HCOO}^-$	2.1	3.7	2.2	3.3	1.9	2.8	2.4	2.6	–	–
Cl^-	4.1	7.2	2.2	3.3	1.8	2.7	2.7	2.9	6.77	39.0
NO_3^-	2.9	5.1	7.0	10.5	6.1	9.0	4.7	5.1	0.95	5.5
SO_4^{2-}	38.0	66.7	41.5	62.3	52.9	77.3	42.5	46.4	9.63	55.5
An	57.0	100	66.6	100	67.9	100	91.6	100	17.4	100

* In Ref. 11, there are no data for Mg^{2+} , here there are values only for Ca^{2+} . The cross out section means the absence of data.

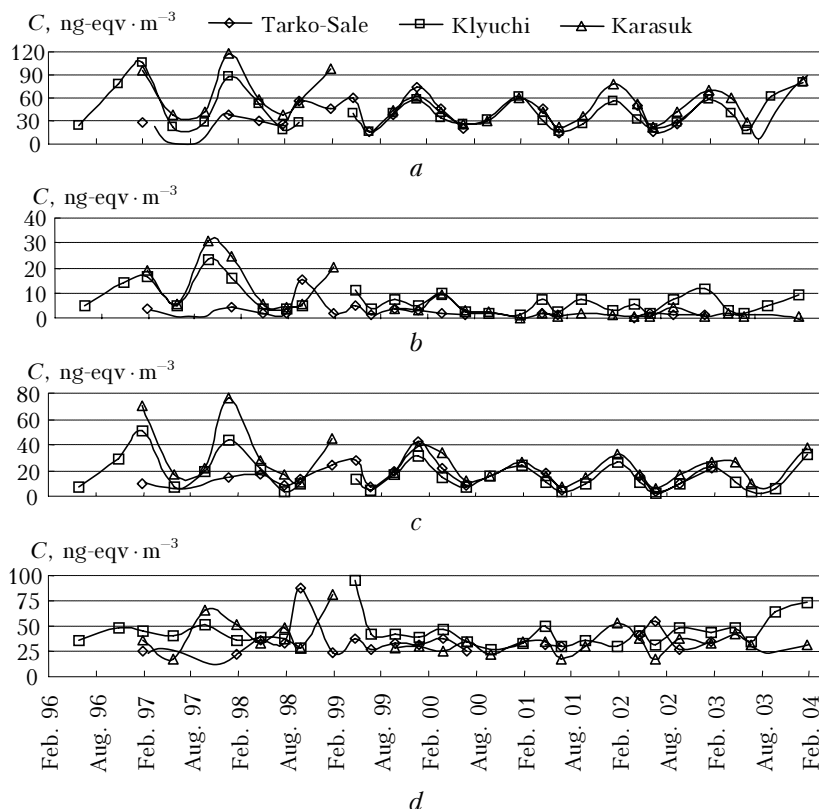


Fig. 2. Dynamics of the ion concentration in AA at the sites 1–3 during the period from 1996 until 2004, $\text{ng-equiv}\cdot\text{m}^{-3}$: SO_4^{2-} (a); NO_3^- (b); NH_4^+ (c); $\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+$ (d).

For SO_4^{2-} and NH_4^+ , the seasonal cyclicality with the maxima in winter is distinctly shown at high correlation of their co-variability at each observation site (r^2 equal 0.959 in Klyuchi, 0.921 in Karasuk, and 0.872 in Tarko-Sale). It should be noted that such a high correlation is not connected with a seasonal concentration dynamics of their volatile precursors (SO_2 and NH_3) in the free air. The concentration of NH_3 in the air is maximum in summer, when the concentration of NH_4^+ in AA, is, on the contrary, minimum.

Distinctions in the seasonal variability of NH_4^+ concentration in AA and of the NH_3 concentration in the air have also been marked in other regions, in particular in Japan.¹³ At the same time, the maximum of the SO_4^{2-} concentration in AA in winter correlates with the concentration maximum of SO_2 in the air above the Northern hemisphere. It is possible to assume that the NH_4^+ concentration in AA is limited by the processes of the SO_4^{2-} formation in aerosol particles, instead of the NH_3 concentration in the air.

A seasonal dynamics of the NO_3^- concentration appeared to be a little bit different, with no distinct maximum in winter. Maybe, the reason for the displacement of the NO_3^- maximum concentration toward fall or spring, in some years, is burning of plant remains since, under such conditions, the concentration of these ions in AA increases.¹⁴ The less expressed correlation between variability of the NO_3^- and NH_4^+ concentrations in AA (r^2 equal 0.565 in

Klyuchi, 0.615 in Karasuk, and 0.109 in Tarko-Sale), than between variability of SO_4^{2-} and NH_4^+ marked above, can be caused by this circumstance. Besides, the NO_3^- concentration in AA was well below, than the SO_4^{2-} concentration (see Fig. 2). Thus, the sulfate aerosol formation was a primary factor, determining the ammonium concentration in AA in the Western Siberia during the period from 1996 until 2004.

Dynamics of the total concentration of ions of another group ($\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+$) in AA, the precursors of which are the nonvolatile salts, as can be seen from data presented in Fig. 2, has no any expressed seasonal prevalence and is individual for each of the observation sites. This fact can be explained by imposing of the action of various sources of these ions, both local, and distant. The soil-erosion sources are to be related to the local sources, their action is enhanced during the spring-to-fall period and is weakened in winter because of long insulation of the earth's surface by snow cover, and the technogenic effluents into the atmosphere, mainly, produced by the heat and power plants.

Action of distant sources can manifest itself at a transport of salts of soil or marine origin from other regions. In particular, in the south of the Western Siberia, at winds from south-west, the concentration of Ca^{2+} in AA, increases, and in the north of the Western Siberia, at winds from the north, the Na^+ concentration increases.¹⁰ It is worthy to note the difference between seasonal variability of cations of

this group and ammonium – the only cation in the AA matter, its precursor is a volatile compound detected at all the observation sites.

The data presented in Fig. 2 show that the formation of ions from volatile precursors in the AA composition during the observation period in the north of the Western Siberia remained more stable than in the south. Winter maxima of the SO_4^{2-} , NO_3^- , and NH_4^+ concentrations in AA in Klyuchi and Karasuk decreased during the period from 2000 until 2004 in comparison with the period from 1996 until 1999, while keeping unchanged the level of their content in AA in summer. Owing to this fact, the annual mean concentrations of the indicated ions decreased, to a smaller degree this relates to the sulfates and ammonium, with the decrease of the nitrate concentration being the most considerable (by two times in Klyuchi and by more than six times in Karasuk). The cause of such a decrease is not clear;

probably, it was connected with the volume decrease of technogenic effluents of sulfur and nitrogen oxides during the period from 2000 until 2004 in this region.

Influence of the industrial center (Novosibirsk) on the AA ion composition

The comparison of data on the composition of the AA samples, collected simultaneously in Novosibirsk and in two other sites, removed from it at a distance of 30 km (Klyuchi) and 500 km (Karasuk), allows one to reveal the role of technogenic sources of the aerosol forming substances. Consider now the data presented in Fig. 3, during the period from 2000 until 2004, the values of M in Novosibirsk were, as a rule, higher, but the values of W/M lower than in Klyuchi and Karasuk.

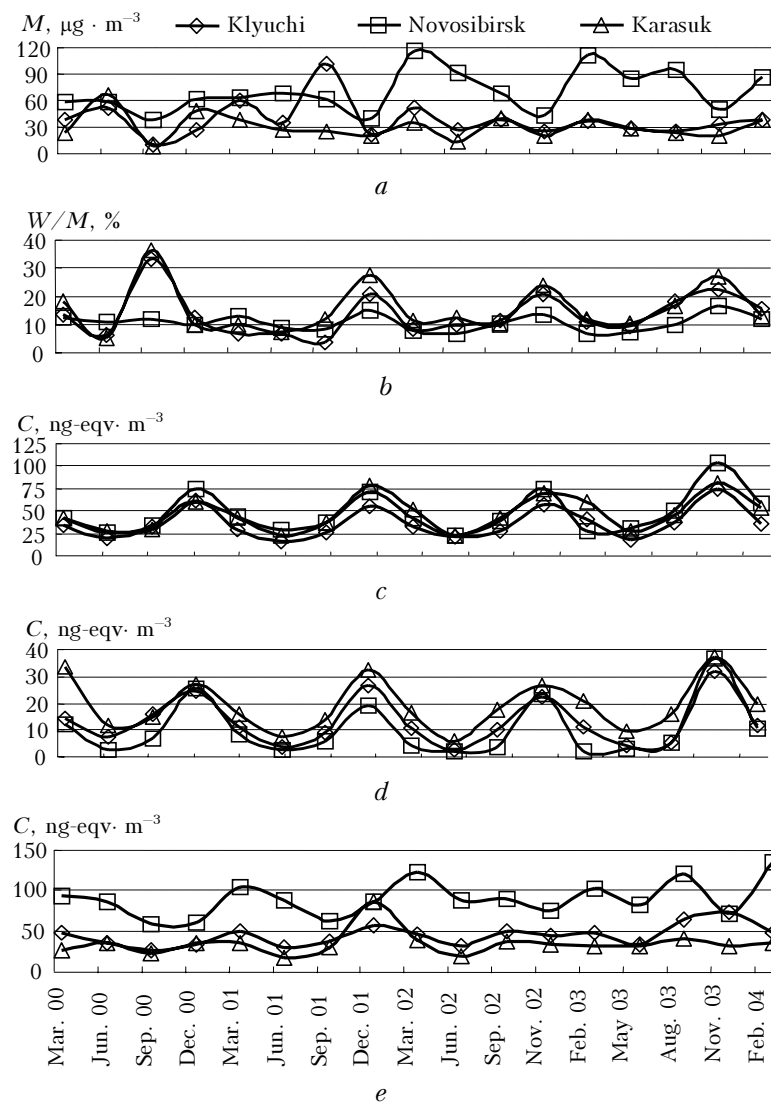


Fig. 3. Comparison of the AA parametric variability in Klyuchi, Novosibirsk, and Karasuk during the period from 2000 until 2004: the mass concentration M , $\mu\text{g} \cdot \text{m}^{-3}$ (a); the fraction of water-soluble salts W/M , % (b); the concentration of SO_4^{2-} (c); NH_4^+ (d); ($\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+$), $\text{ng-eqv} \cdot \text{m}^{-3}$ (e).

The distinct seasonal variability of SO_4^{2-} and NH_4^+ , two basic ions formed from volatile precursors, is identical for all observation sites. Obviously, it is caused by the natural factors. Close level of the SO_4^{2-} concentrations points to the minor contribution of its technogenic sources in Novosibirsk. The ammonium concentration in the AA composition of this industrial center is lower than in distant sites. This means that the NH_4^+ precursor in AA (gaseous NH_3) has a biogenic origin instead of technogenic one. The sum concentration of ($\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+$) ions in AA, that have no volatile precursors, is much higher in Novosibirsk than in Klyuchi and Karasuk, both in winter and in summer. Since its value is higher in summer, but not in the beginning of heating season, we assume that the technogenic source of these ions are not power production plants, but road dust. The fact that the influence of the technogenic sources of aerosol forming substances in the atmosphere of Novosibirsk is most considerable in the increase of concentration of not acid-forming anions, but of cations neutralizing them, also manifests itself in the aerosol acidity.

Acidity of AA in Western Siberia

The long-term mean pH values of the AA aqueous extract during the observation period made 5.66, 5.79, 5.24, and 6.55 for the observation sites 1–4, respectively, that is at the sites 1 and 2, they were close to the “standard” characteristic of the clean air (pH equal 5.8, see Ref. 3); at the site 3 it is lower, and at the site 4 it is higher. From the first sight, it seems logical to connect pH with the SO_4^{2-} concentration, the basic acid-forming anion in the AA composition. However, such an interconnection is not confirmed by a comparison of the mean pH values and the SO_4^{2-} concentration at the sites 1–4. Actually, according to data from the Table, at the sites 1 and 2, the SO_4^{2-} concentration was lower, than at the site 4 that should be accompanied by a higher value of pH at these observation sites. The data presented above show quite the opposite. Besides, variability of the SO_4^{2-} concentration in various sites (see Fig. 1) differently correlates with the variability of the pH values (r^2 equals to -0.676 in Klyuchi, -0.612 in Novosibirsk, -0.226 in Tarko-Sale, and -0.192 in Karasuk). This calls for estimating the action of factors determining the AA acidity level in a more detail.

As follows from data on the AA ion composition in the Western Siberia, (see the Table), we can conclude that SO_4^{2-} and NO_3^- are the basic acid-forming anions generated from the volatile precursors. Concentration of the only NH_4^+ cation, the precursors of which are the atmospheric gases, makes no more than a half of the sum of the equivalents of SO_4^{2-} and NO_3^- . In view of the above-mentioned high correlation among the SO_4^{2-} , NO_3^- , and NH_4^+ concentrations, aerosol particles formed

from volatile precursors constantly have the excess acidity. It is expedient to present it as the acidity potential of aerosol particles A ($A = [\text{SO}_4^{2-}] + [\text{NO}_3^-] - [\text{NH}_4^+]$). For the effective neutralization of the A potential, the cations formed from other nonvolatile precursors are necessary. Such cations are Ca^{2+} , Mg^{2+} , Na^+ , and K^+ , since in the Western Siberia, their total concentration in AA is much higher than concentration of other anions, except for SO_4^{2-} and NO_3^- (see the Table). As a first approximation, it allows one to present the sum of these cations as a neutralization potential B ($B = \text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+$). At the excess of A relative B in the AA aqueous extract, there is an excess of the acid-forming anions that leads to the reduced pH values.

It is necessary to note that concepts of the acidity and neutralization potentials are frequently used in revealing the factors determining the acidity level of atmospheric precipitation. It is a logical consequence of the cationic and anionic balance condition in a water solution. Depending on the relative contribution of different ions, the choice of those ions, which appear considerable for estimation of the A and B potentials, basically, can be different. So, for estimation of the A value in atmospheric precipitation in Japan, the sum of $\text{SO}_4^{2-} + \text{NO}_3^-$ is chosen, and for estimation of the B value – the sum of $\text{Ca}^{2+} + \text{NH}_4^+$ (see Ref. 15). The same approach can also be used for the aqueous extract of solid aerosols. However, in our case, the choice of other ions for estimation of the A and B values reflects a different role, which is played by the volatile and nonvolatile precursors of the AA substance for the aerosol acidity.

In comparing dynamics of the pH values and the B/A relation during the period from 1996 until 2004, it turned out that both values in all observation sites vary in a rather wide range and quite well correlate among themselves (r^2 equals 0.534 in Tarko-Sale, 0.595 in Karasuk, 0.763 in Klyuchi, and 0.619 in Novosibirsk). It should be noted that correlation between the pH variability and values of the A acid potential is either missing (r^2 equal to -0.017 in Tarko-Sale, -0.250 in Klyuchi), or is expressed more weakly (-0.652 in Karasuk, and -0.380 in Novosibirsk). Hence, the neutralizing action of cations formed from volatile precursors appeared most considerable for acidity of the AA aqueous extract in Tarko-Sale and Karasuk. However, in the last point, it is poor, and the long-term mean value of pH in Karasuk (5.24) is much lower, than in Tarko-Sale (5.66), in Klyuchi (5.79), and in Novosibirsk (6.55). These pH values are in a good agreement with the values of B/A for the same sites (1.06 in Karasuk, 1.39 in Klyuchi, 1.65 in Tarko-Sale, and 2.26 in Novosibirsk).

Thus, estimation of the acidity and neutralization potentials in that form, as we have made, allows one to better understand, what factors determine the AA acidity level at different observation sites.

Conclusion

Observations of the ion composition of the near ground AA conducted during the period from 1996 until 2004 in the north and in the south of the Western Siberia, allows us to reveal the basic factors of the AA formation and tendency of their variation in this region. It is possible to distinguish among certain features of the AA composition compared with other regions of the globe, not so far from the ocean, with milder climate and undergone the more intense technogenic load. One of them consists in considerable seasonal variations of the AA mass concentration and a fraction of water-soluble salts in it. Such variations occur because the major factors of the AA formation are the formation of aerosol particles from volatile precursors and the uplift of terrigenous products into the atmosphere at minor contribution of salts of a marine origin. Role of the first one considerably increases in winter when the ground surface is isolated from air by snow cover. During this period, a fraction of water-soluble salts in the AA total mass reaches 20 to 30%, and in some situations up to 60%. Salts formed from the volatile precursors, like sulfur and nitrogen oxides and ammonia make up their basic part. It reduces to 4–6% in summer when the AA mass concentration sharply increases due to the increase in contribution of slightly soluble products of an erosive origin.

The long-term synchronous observations carried out at the sites removed at considerable distances from each other with a technogenic load different by intensity, have revealed common features in the processes and in the AA formation sources from volatile precursors of a regional origin. High correlation among the time behaviors of SO_4^{2-} , NO_3^- , and NH_4^+ concentrations, points to it in all sites. Concentrations of these ions in AA are maximum in winter when the concentration of sulfur and nitrogen oxides is maximum in the atmosphere, while being minimum for ammonia, the volatile precursor of NH_4^+ . Since the SO_4^{2-} concentration in AA is much higher than NO_3^- concentration, it is possible to assume that formation of sulfate aerosol is controlled by the volatile precursors of sulfur instead of ammonia.

Formation of AA from nonvolatile precursors in the Western Siberia is caused to a greater degree by the action of local sources. The most typical ions in the AA composition, characterizing these sources, are Ca^{2+} , Mg^{2+} , and K^+ . Dynamics of their concentration observed at different observation sites is poorly correlated and shows no clear seasonal variation. Probably, apart from the local erosive sources, the action of which is considerably limited in winter, they can come to the atmosphere from technogenic (local and distant) sources, the action of which

increases in winter. Their action is clearly shown in analysis of the AA ion composition in Novosibirsk. Comparison of the ion composition of the AA samples synchronously collected in the industrial center and in the sites far from it, allows one to distinguish among the influences of technogenic factors on the atmospheric pollution against the background of natural processes.

Summing up the study, one can note that data of monitoring of the AA ion composition in the south of the Western Siberia allowed us to reveal the features of the exchange by substances in the atmosphere–surface system of this region.

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