Meteorological Effects on the Ionic Composition of Atmospheric Aerosols and Precipitates in West Siberia

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Abstract

Meteorological effects on the ionic composition of atmospheric aerosols and precipitates in West Siberia have been studied. Seasonal variations have been found: decreased mass concentration of aerosol particles, increased contents of water-soluble salts in them, and changes in the proportion of ions originating from the volatile components of the atmosphere or the land or ocean surface (in aerosols and precipitates); these changes were also observed in relation to the periodicity and amount of precipitates. Increased concentrations and fractions of $Ca^{2+} + Mg^{2+}$, Na^+ , and SO_4^{2-} ions in southwestern Siberia correlate with the trajectories of air mass transfer from the territory of Kazakhstan and from the Aral and Caspian Seas. In northwestern Siberia, the effects of remote land sources are weaker, while marine source effects are more pronounced, the major precursors of ions in aerosols being the volatile components of the atmosphere.

INTRODUCTION

Over the last three decades, there has been growth of interest in the chemical composition of atmospheric aerosols (AA) and precipitates (AP) in view of increased air pollution and ensuing problems related to acid deposition and global changes in the climate. The sources of minerals in AA and AP, as well as processes of their transport and transformation in the atmosphere vary significantly; differences are observed not only between regions, but also at the same survey point [1-5]. For West Siberia, these effects are not completely understood. At the same time, Siberia has favorable conditions for these investigations: natural and climatic conditions (long winter, isolating the soil erosion sources of AA with a snow cover; remote position from the ocean) and sources of man-caused air pollution located on the vast territories of this region.

The ion contents of AA and AP reflect the contents of water-soluble salts in aerosol particles and wet precipitations and are part of the total chemical composition of AA and AP. The condition of balance between cations and anions in aqueous solutions will make it possible to calculate the percent of ions whose major precursors are atmospheric gases (NH₄⁺, $SO_4^{2^-}$, and NO_3^- ions), land surface (Ca²⁺, Mg^{2+} , and K^+ ions; partly HCO_3^-), and ocean surface (Na⁺ and Cl⁻ ions). Therefore ion percentage may be directly used for estimating the contributions from the gas-phase, terrigenous, and marine sources to AA and AP. Deriving this information from the element composition of AA involves a number of problems, for example, the necessity of normalization to one of the elements and ambiguous choice of the reference element. Moreover, the composition of AA is generally correlated with the content of solid particles in 1 m³ of air, while the composition of AP is correlated with the solute content in 1 liter of rain or snowmelt water. These difficulties may be alleviated by using ion percentages in different phases. Thus employing data on the ion compositions of AA and AP one can evaluate the contributions from different sources using a unified procedure.

The general tendencies in the seasonal and spatial dynamics of contributions to atmospheric aerosols and precipitates from the gas-phase, terrigenous, and marine precursors were revealed previously for different natural and climatic zones of West Siberia [6-8]. The aim of the present work is to use the same approach to analyze variability of the composition of discrete samples of surface aerosols and precipitates under the influence of meteorological conditions. Meteorological conditions include precipitation and reversal of air mass transfer. The former refers to precipitation after a period of settled dry weather and complements the action of the latter. The precipitates can vary in time and quantity. To take into account these differences we used data for discrete AA and AP samples obtained in series of continuous prolonged observations.

SAMPLING AND ANALYSIS OF AEROSOL AND PRECIPITATE SPECIMENS

Atmospheric aerosol samples were taken from the following localities:

1 – environs of the Tarko-Sale village, 65° N, 78.3° E, forest-tundra zone;

2 – Novosibirsk region, right bank of the Novosibirsk water reservoir, 53.8° N, 82.4° E, forest-steppe zone;

3 – Novosibirsk region, southwest outskirts of Akademgorodok, 90 km to the south of point 2, 54.3° N, 83.6° E, forest-steppe zone;

4 – near the Karasuk city, Novosibirsk region, 53.7° N, 78° E, approximately 500 km southwest of point 3, steppe zone.

Daily AA samples were taken by pumping $200-300 \text{ m}^3$ of air through AFA-KhA filters. Some of the exposed filters were placed for 1 day in a container with 10 ml of bidistilled water to obtain a water extract. Ion concentrations (NH₄⁺, Na²⁺, K⁺, F⁻ + HCOO⁻, Cl⁻, NO₃⁻, SO₄²⁻) in the extract were determined by ion chromatography. For the rest of the extract, pH and conductivity measurements were carried out. The concentrations of (Ca²⁺ + Mg²⁺) and HCO₃⁻ were determined by titration. The analytical data of the individual ions were used to evaluate balance between the total equivalents of cations and anions and to

calculate the specific conductivity. The difference in balance between the cations and anions and the discrepancy between the experimental and calculated values of conductivity were up to 10-15 %, indicating that we have obtained adequate analytical data on the ionic composition of the aqueous extracts of AA. The data were recalculated based on the ion contents in AA particles in 1 m³ of air.

Discrete (freshly precipitated) AP samples were taken at points 2 (rains) and 3 (snow). The snow samples were melted in a funnel with a paper filter placed under an infrared lamp. For rain and snow samples, ion determination was fulfilled by the same methods. The analytical data were correlated with ion concentration in 1 l of rain or snowmelt water.

PRECIPITATION EFFECTS ON THE ION COMPOSITION OF AA

Changes in the ion composition of the surface aerosols induced by wet precipitates may be observed when a spell of fine weather gives way to nasty weather. Figure 1, a-c shows the dynamics of major ion concentrations and pH values in the water extracts of discrete AA samples taken at point 2 in July 2003. Periods of rainfall are indicated by the hatched segments. In early July, which is usually a period of drought, the surface atmosphere has a high concentration M of aerosol particles (up to 110 μ g/m³). The total content of water-soluble salts W in the particles reached 9.15 μ g/m³; *i. e.*, 8.2 % of M. Hence it follows that water-insoluble products of erosion origin were the bulk of AA during the stated period. As to water-soluble salt cations, Ca^{2+} and Mg^{2+} were dominant $(80 \text{ ng-equiv/m}^3)$, while the concentration of NH_4^+ was much lower (33 ng-equiv/m³) and Na⁺ ions were not found. This distribution of cation equivalents also suggests that the erosion sources of AA dominated over the gas-phase and marine precursors. Among anions the maximal contribution was from SO_4^{2-} (104 ngequiv/m³); the fraction of HCO_3^- was smaller $(23 \text{ ng-equiv/m}^3)$, and other anions contributed up to 2-4 ng-equiv/m³. Despite their high concentration, the sulfates were effectively neutralized with cations (chiefly those of erosion



Fig. 1. Dynamics of the concentrations of the major cations and anions (a, b) and pH values (c) in the water extracts of the daily AA samples taken at point 2 in July 2003: $1 - NH_4^+$, $2 - Ca^{2+} + Mg^{2+}$, $3 - Na^+$, $4 - HCO_3^-$, $5 - Cl^-$, $6 - SO_4^{2-}$. Here and in Fig. 2, rainfall periods are marked with hatched segments.

origin), so that pH of the water extract of AA reached 7.17 (for the sample taken on July 4-5).

The first (relatively weak) rainfall of July 7 (2.3 $1/m^2$) led to a dramatic decrease in the values of *M* and *W* (to 50.5 and 7.0 μ g/m³, respectively); pH of the water extract of AA lowered (to 4.10) and so did the Ca²⁺ + Mg²⁺ concentration; the contents of NH₄⁺ and Na⁺ increased, while the concentration of SO₄²⁻ stayed at the same level. These changes point to differences in the scavenging of aerosol particles by precipitates, which depend on the origin and dimensions of the particles. Variations in the composition of AA were even more conspicuous during the period of prolonged rainfall (July 15–20). Thus the daily AA sample (July 16–17) had *M* dropped to 10.9 μ g/m³,

while the total content of water-soluble salts was $3.11 \,\mu\text{g/m}^3$ (28.5 % of *M*). The content of the ammonium cations $(22.4 \text{ ng-equiv/m}^3)$ became higher than that of $Ca^{2+} + Mg^{2+}$ (13.5 ngequiv/m³); among anions, SO_4^{2-} remained dominant (41.1 ng-equiv/m³), while the contribution of HCO_3^- fell to zero because pH decreased to 4.6. The largest decrease in W (to $1.36 \,\mu g/m^3$) in the water extract of AA was recorded in the samples of July 23-25 when there was heavy rainfall (31.7 l/m^2). The concentrations of all ions except Na⁺ were minimal. Although the content of SO_4^{2-} was low $(11.9 \text{ ng-equiv}/\text{m}^3)$, the acidity of the water extracts of aerosols was high (pH 4.34). Thus acidification of AA was not due to the increased content of the major acid-forming anion (sulfate); rather, it was caused by the defi-



Fig. 2. Dynamics of the concentrations of the major cations (a, b) and pH values (c, d) in the water extracts of the daily aerosol samples taken at point 3 in January – February 2002 (a, c) and in 2003 (b, d): $1 - NH_4^+$, $2 - Ca^{2+} + Mg^{2+}$, $3 - Na^+$.

ciency of neutralizing cations due to the scavenging of aerosols of erosion origin by precipitates.

Weather reversal effects on the ionic composition of AA were also observed during the winter period. Figure 2, a-d shows the dynamics of the major cation concentrations and pH values in the water extracts of aerosols at point 3 during the snowfalls of January - February 2002 and 2003. In the first series of observations (a, c), snowfalls were heavier and occurred more frequently. Thus the amount of snowfall was 28.7 kg/m² from January 19 to 27, 2002, and only 10.8 kg/m^2 from January 20 to February 20, 2003. During the winter period the values of M were appreciably lower, while the percent of water-soluble salts was higher. At the end of the long dry period (January 30) the total mass of AA in the surface atmosphere was $35.9 \,\mu\text{g/m}^3$, and the total content of water-soluble salts was $8.63 \,\mu g/m^3$,

or 24 %. At the end of the long period of snowfall (January 27, 2002) the respective characteristics were 19.0 μ g/m³ and 4.10 μ g/m³, or 21.6 %. Consequently, in winter the content of the insoluble products of surface origin in AA is lower than in summer. The differences in the occurrence and amount of snowfalls between 2002 and 2003 led to differences between the levels and proportions of the $(Ca^{2+} +$ Mg^{2^+}) and NH^+_4 concentrations. As can be seen from the data shown in Fig. 2, the situation with increased frequency of snowfalls is characterized by the lower fraction of $(Ca^{2+} + Mg^{2+})$ and higher fraction of NH_4^+ . After a prolonged period of snowfall in January 19-27, 2002, the $(Ca^{2+} + Mg^{2+})$ content in AA decreased from 16.8 to 9.5 ng-equiv/ m^3 . At the same time, the NH_4^+ content increased from 11.5 to 27.0 ngequiv/m³, which was probably due to the reversal of air mass transfer. As in the summer period, precipitation led to more effective

scavenging of aerosol particles of erosion origin. Accumulation of these particles in the atmosphere during dry weather periods is accompanied by growth of pH for the water extract of AA. In contrast, after a period of frequent snowfalls in the first series of observations, both the mean pH values and their fluctuation amplitude were lower than in the second series.

IONIC COMPOSITIONS OF RAINFALL AND SNOWFALL

In wet precipitates, some of the ions having no volatile precursors are formed by solution of the salts of the captured AA particles during vapor condensation processes or by adsorption during in- and below-cloud scavenging processes. These are primarily Ca²⁺, Mg²⁺, and Na^+ cations. Other cations (NH_4^+ and H^+) and all anions appear in atmospheric precipitates either by solution of AA particles or by absorption of volatile acids and ammonia from the gas phase. That is why the AA and AP samples taken at the same time and at the same point of observation differ in the ionic composition [7]. It is interesting to trace how the meteorological situation affects these differences. Table 1 compares the contributions of the equivalents (in percent of the sum of equivalents of the cations or anions) of various ions for the summer and winter periods. Data are given for three situations: (1) start and (2)end of the prolonged precipitation period and (3) single heavy precipitate. For the summer period, we used data for AA and AP samples taken on July 16, 17, and 24, 2003 (situations 1, 2, and 3, respectively). From July 16 to 17 the total content of salts in AP decreased from 10.1 to 2.1 mg/l, and in the July 24 sample it was 1.36 mg/l. In the snow samples, the salt contents were as follows: 16.3 mg/l for situation 1 (January 20, 2002), 9.1 mg/l for situation 2 (January 27, 2002), and 8.9 mg/l for situation 3 (February 6-8, 2002).

As can be concluded from the data of Table 1, the relative fraction of $Ca^{2+} + Mg^{2+}$ in AA is close to that in AP and is therefore independent of the character of precipitate. The same is typical of the Na⁺ content during the summer period, except situation 3 (short heavy rain), when AA had an increased fraction of sodium. For snowfall, however, the fraction of that cation was higher in all situations than in aerosol particles. The case is different for ammonium. Its fraction in AA is high during both summer and winter periods; in rainfall,

TABLE 1

Ion composition of AA and AP in relation to meteorological conditions, equivalent %

| Ions | Summer | | | | | | Winter | | | | | |
|-----------------------|--------|------|------|------|-------|-------|--------|------|------|------|------|-------|
| | 1 | | 2 | | 3 | | 1 | | 2 | | 3 | |
| | AA | AP | AA | AP | AA | AP | AA | AP | AA | AP | AA | AP |
| NH_4^+ | 44.0 | 47.1 | 45.3 | 30.9 | 18.0 | 35.6 | 35.6 | 26.7 | 41.4 | н.о. | 50.0 | 7.5 |
| Ca^{2+} + Mg^{2+} | 31.8 | 30.3 | 27.3 | 32.6 | 25.3 | 21.9 | 33.4 | 19.3 | 23.9 | 47.8 | 38.3 | 31.9 |
| Na ⁺ | 8.7 | 12.7 | 11.1 | 12.7 | 31.4 | 10.0 | 21.5 | 43.0 | 21.0 | 38.2 | 8.2 | 40.0 |
| K^+ | 11.3 | 7.8 | 11.3 | 5.5 | 6.9 | b. l. | 9.5 | 11.1 | 9.2 | 13.2 | 3.4 | 18.0 |
| H^+ | 4.2 | 2.1 | 4.9 | 18.4 | 18.4 | 12.2 | 0 | 0 | 4.5 | 0.8 | 0 | 2.4 |
| HCO_3^- | 0 | 2.2 | 0 | 0 | 0 | 0 | 22.7 | 18.5 | 0.3 | 14.2 | 10.2 | 27.9 |
| F^- + $HCOO^-$ | 5.0 | 4.5 | 4.6 | 6.9 | b. l. | 14.2 | 2.7 | 3.7 | 1.5 | 3.1 | 0.5 | b. l. |
| C1 ⁻ | 3.9 | 14.8 | 3.7 | 13.1 | 12.5 | 16.9 | 2.7 | 44.8 | 1.8 | 29.8 | 0.9 | 30.3 |
| NO_3^- | 2.0 | 23.6 | 2.0 | 23.4 | 4.9 | 32.9 | 2.3 | 5.0 | 2.0 | 8.2 | 0.7 | 13.1 |
| SO_4^{2-} | 89.1 | 54.9 | 89.7 | 56.5 | 82.6 | 35.4 | 72.6 | 28.1 | 94.4 | 44.7 | 87.7 | 28.7 |

Note. b. l. - below the detection limit.

it stays at the same high level, but decreases abruptly in snowfall. The latter circumstance is probably caused by decreased absorption of ammonia by snowflakes compared to absorption by raindrops. It is interesting to note that in AA the ratio of the equivalents of $\rm NH_4^+$ and $\rm SO_4^{2-}$ is close to 0.5, while in AP it approximates 1 in all situations. The minor fraction of chlorides in AA changes to a drastically increased fraction in AP, especially during the winter period; for nitrates, this increase occurs in summer.

In situations of prolonged or heavy precipitates, the contributions from different ions generally change insignificantly, although the total content of salts decreases dramatically. More pronounced changes in the ion ratio were reported for discrete AP samples taken after prolonged periods of dry weather. The same was also noted above for discrete AA samples. It seems reasonable to assume that the wide variations of the ionic composition of AA and AP are caused by the action of another meteorological factor, namely, by the reversal of air mass transfer.

EFFECTS OF DIRECTIONS OF AIR MASS TRANSFER ON THE IONIC COMPOSITION OF $\mathbf{A}\mathbf{A}$

Dry weather spells were chosen to exclude the effects of precipitates on the ionic composition of AA in series of observations. Moreover, from the time dynamics data for the major ion contents in AA we chose dates at which the ion ratio characteristic for terrigenous, gas-phase, and marine sources (Ca^{2+} + Mg^{2+} , NH_4^+ , and Na^+ , respectively) changed. Thus for composition dynamics of discrete AA samples taken at point 3 (see Fig. 2, a), these conditions were realized on February 1 and 4. Compared to the February 1 sample, in the February 4 sample the content of equivalents in water extracts increased from 35.8 to 58.2~%for NH_4^+ and from 12 to 17.5 % for Na^+ ; for $Ca^{2+} + Mg^{2+}$, it decreased from 48.3 to 17.5 %. For these dates, trajectories of air mass transfer were plotted using the HYSPLIT program of the Transport and Dispersion Model and meteorological data of the National Oceanic and Atmospheric Administration (USA) [9]. Using the reverse trajectories method for identification of sources of atmospheric aerosols is described in [10]. Figures 3, a (01.02.2002) and b (04.02.2002) show the trajectories of an aerosol particle calculated for a period of three days preceding the moment when air mass had arrived at point 3. A comparison with the above data on the fractional contents of different ions indicates that the higher content of ions from the gas-phase and marine sources is due to the northwestern direction of air mass transfer, while the increased role of terrigenous sources agrees with the change of the transfer to southwestern direction.

The ionic compositions of AA were similarly correlated with the air mass transfer trajectories at point 3 throughout other periods of observations. It appeared that the given example reflects the typical situation of the winter period when the vast territory of Siberia is covered with snow that isolates the local erosion sources. For summer, no correlation has been established between the changes in the ionic composition of AA and the directions of air flows. After the snow cover has vanished, the local sources surrounding the sampling site in different directions start to act in addition to remote sources.

Similar results were obtained by analyzing data for point 4 which is ~500 km southwest of point 3. For illustration Fig. 4, a compares the contributions of ions to AA samples taken on February 19 and 21, 2002; the reverse trajectories of air mass transfer are shown in Fig. 4, b. For southwestern air mass transfer, aerosols have increased concentrations and fractions of sulfates and of $Ca^{2+} + Mg^{2+}$ and Na^+ cations. These ions dominate in the dust flows on the territory adjacent to the former coastline of the Aral Sea [1]. This region lying on the way of the air flows that hit the survey point in Karasuk on February 19, 2002, it may be safely suggested that the long-range atmospheric transfer of salts from land sources was the reason for the growing concentration of the stated ions. The reversal of air flows to the north on February 21 resulted in the concentrations of these ions decreased by a factor of two; the concentration of NH_4^+ increased, and its fractional contribution to the sum of the cation equivalents increased more than two-



Fig. 3. Reverse trajectories of air mass transfer at a height of 500 m for point 3 (Klyuchi): a, b – end time is midnight on 01.02.2002 and 04.02.2002, respectively.

fold. The hypothesis about the effect of the long-range atmospheric transfer of salts to southwestern Siberia due to their aeolian withdrawal from the territories of Kazakhstan and from the Aral and Caspian Seas was formulated previously based on the analytical data about the average stoichiometric composition of AA [11]. It can be seen that this is confirmed for discrete AA samples taken for different directions of air mass transfer.

The action of other remote sources contributing to AA may be revealed by correlating the dynamics of the ionic composition of aerosols with air flows in northwestern Siberia. Figure 5, a presents the ion composition of three discrete AA samples taken at the Tarko-Sale village (point 1) in winter (January 16 and 25) and summer (June 30) 2000; Fig. 5, b-d shows the reverse trajectories of air mass transfer for the same dates. Compared to southwestern Siberia, the total concentration of aerosol particles and water-soluble salts in them is lower at point 1 and higher for south wind. The fraction of cations from marine sources is higher, especially for north wind in summer. In winter, the major contribution is from the ammonium cation, whose precursor is the gas

phase. In summer, the fraction of this cation decreases, while that of $Ca^{2+} + Mg^{2+}$ increases. Therefore, it is concluded that in winter remote erosion sources play a less significant role in northwestern Siberia.

CONCLUSIONS

Thus it has been shown that data on the ionic composition of discrete samples of atmospheric aerosols and precipitates are quite informative for revealing the effects of meteorological changes on substance exchange processes between the atmosphere and the earth surface. After prolonged spells of dry weather, precipitations lead to decreased mass concentration of AA, primarily, due to the scavenging of particles of erosion origin. As a result, the aerosol particles remaining in the atmosphere have increased fractions of watersoluble salts with lower contents of Ca^{2+} + Mg^{2+} cations and higher contents of NH_4^+ and Na⁺ cations. These effects show themselves after the first precipitates and become stronger after prolonged and heavy falls. The lower the content (in aerosols) of the products of ero-



Fig. 4. Fractional distribution of some ion equivalents in the daily AA samples taken at point 4 (Karasuk city) on February 19 and 21, 2002 (a) and reverse trajectories of air mass transfer on the same dates (b and c, respectively).

sion origin washed out by precipitates, the higher the acidity of the water extract of AA. This means that for Siberia, the increased acidity of AA and AP is explained by the deficiency of the neutralizing cations coming mostly from erosion sources, rather than by the excess of acid-forming substances inherent in the atmosphere of industrialized regions.

In AP and AA samples taken simultaneously during periods of precipitation, the proportion of anions is less uniform than that of cations. This may be explained by additional absorption of the volatile components of the atmosphere by precipitates during in- and below-cloud scavenging processes. In AP samples, the fraction of sulfates is much lower, while the fractions of chlorides and nitrates are higher than those in AA samples. In southwestern Siberia, the fraction of chlorides and nitrates depends on the season: more chlorides are observed in winter, and more nitrates in summer. The case is different for ammonium. In atmospheric aerosols, the fraction of these cations is always high irrespective of the season and weather. In precipitates, however, it remains high in summer, but decreases appreciably in winter, the decrease being more pronounced after periods of frequent and heavy



Fig. 5. Fractional distribution of some ion equivalents in the daily AA samples taken at point 1 (Tarko-Sale village) on January 16 and 25 and June 30, 2000 (a) and reverse trajectories of air mass transfer on the same dates (b-d, respectively).

snowfalls. While the decreased fraction of ammonium in snow agrees with less intense emission of ammonia from the snow-covered land surface, the difference between the contributions of NH_4^+ to AP and AA demands more detailed studies.

Thus data on the ion composition of discrete, simultaneously taken AA and AP samples permit one to assess the role of precipitates (their periodicity and quantity) in the flow of the components of the atmosphere on the surface. Observations accomplished in Siberia make it possible to assess the effects of the state of the land surface, which supplies volatile and non-volatile components to the atmosphere in summer and is isolated by snow preventing this supply in winter.

The effects of remote sources of substances in atmospheric air can also be traced by using data on the ionic composition of discrete AA samples given the trajectories of air mass transfer at the sampling point. To exclude the effects of scavenging by precipitates, in series of continuous observations we employed situations with increased ion contents in AA. It appeared that in winter, situations with increased contents of $Ca^{2+} + Mg^{2+}$, Na^+ , and SO_4^{2-} ions in southwestern Siberia correlate with air mass transfer from Kazakhstan and from the Aral and Caspian Seas. The reversal of air mass transfer to northwest leads to decreased fractions of these ions and increased fraction of the ammonium ions. Thus it is concluded that during their aeolian travel from the stated regions the salts hit southwestern Siberia, where they fall on the land surface with dust or precipitates.

In northwestern Siberia, atmospheric transfer of terrigenous products from remote territories is much weaker, volatile substances being the major source of AA in winter. When air mass transfer is directed northward, the concentrations of all ions are lower than those for southward transfer. The Na⁺ and Cl⁻ ions typically occurring in marine sources make pronounced contributions even in winter and increase further in summer.

Variability of the ion composition of the solid and liquid components of the atmosphere over Siberia is useful for evaluating regional peculiarities of the atmospheric transfer of substances and may be employed for identification of sources and exchange of substances between the atmosphere and the land surface.

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