Seasonal dynamics of ion composition of atmospheric aerosol and precipitation in Novosibirsk Region

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Data on ion composition of atmospheric aerosol and precipitation (snow and rain) in the Novosibirsk Region in 1996 – 2001 are presented. Seasonal and temporal dynamics of ions' concentration and proportion is associated with a variable contribution of their different sources (gas-phase, terrigenic, sea salt). Acidity of aerosol and precipitation is discussed in a view of their ion balance. Sulfate is the main anion in aerosol particles, and cations from terrigenic sources play an important role in its neutralization, because the ratio of ammonium to sulfate is less than 0.5. The same is true for snow precipitation although a share of sulfate is there substantially reduced. The danger of acidation of the rain precipitation is less, because the ratio of ammonium to sulfate in them is more than 1.

Introduction

Formation of atmospheric aerosols (AA) and precipitation (AP), their transformation, transport in the atmosphere, and sinking to the ground surface play an important role not only in optical characteristics of the atmosphere but also in biogeochemical cycles of elements. In terms of complex characteristic of chemical composition of AA and AP, the study of their ion composition is also important by itself, because it is determined by chemical regularities in water solutions. Besides, data on AA and AP ion composition are of interest due to the well-known problem of acidic precipitation.[1–4]

From this standpoint, systematic investigation of ion composition of AA and AP is carried out in the territory of Western Siberia since 1997 in the framework of the Integration Project of SB RAS. The spatial and seasonal dynamics of the aerosol content has been studied in more detail. It is shown that the contributions of different sources (erosion, marine, gas-phase) into their formation are significantly determined by natural and climatic conditions (period of isolation of erosion sources by snow cover, distance from the ocean, dominating directions of the air mass transport).[5] Against the background of natural factors, the effect of technogenic sources on formation of AA has been distinguished.[6,7]

Seasonal and spatial dynamics of AP in Western Siberia is less studied because of difficulties in organization of fresh-fallen wet precipitation (snow, rain) sampling during the whole season. Joint studies of AA and AP ion composition were carried out based on a limited field material, either with using the data on winter mean composition of snow precipitation or from the data on discrete samples of fresh-fallen snow and rain taken during one season at one observation site.

The peculiarities of seasonal variations of ion composition of aerosol particles and wet precipitation are considered in this paper based on the data of long-term series of observations from 1997 to 2001.

Technique of measurements

Daily sampling of AA was carried out near village Klyuchi of Novosibirsk Region approximately 10 km in a westerly direction from Akademgorodok, in four series of observations (winter, spring, summer, fall). Each series was 30 days long. In summer, the fresh-fallen rain sampling was conducted at site Sinemorjye situated on the coast of Novosibirsk water storage pond, 70 km south-easterly from Akademgorodok. The fresh-fallen snow samples were collected nearby Akademgorodok (0.5 km to south-west).

Sampling of aerosol was performed by pumping air through the AFA-KhA filter at the volume rate of 13 m^3/hour. The filter was weighted before and after pumping, that made it possible to obtain the daily mean mass M of aerosol particles in 1 m^3 of air. To obtain a water extract, part of the filter was placed for a day into the container filled with deionized water. Concentration of ions H^+, Na^+, K^+, NH_4^+, ($Ca^{2+} + Mg^{2+}$), HCO_3^-, ($F^- + HCOO^-$), Cl^-, NO_3^-, and SO_4^{2-} in the water extract was determined by methods of ion chromatography, pH-metry and titrimetry.[8] Measured values were related to the content of ions in aerosol particles per 1 m^3 of air. The sum of the determined concentrations of individual ions characterizes the mass W of water-soluble fraction of AA, and the ratio M/W characterizes its share in the total mass of aerosol particles.

Discrete samples of snow (from November to May) and rain (from June to October) precipitation were collected just after their falling down, then they were filtered (snow was preliminary thawed) through a paper filter, weighted, and then analyzed by the same methods. The ion concentration in precipitation was

related to 1 liter. It is convenient to use relative values for comparison of ion composition of AA and AP – the portion of each ion in the sum of equivalents of cations or anions, respectively. This makes it possible to bring the data related to different measurement units (the content of ion in 1 m^3 of air for AA and the content of precipitation in 1 liter for AP) to one scale of relative units.

The ensembles of ions in AA and AP composition correlating in the dynamics of their concentrations were estimated by the methods of statistical analysis for each series of observations. On this basis, using the combination of certain ions in one ensemble, one can distinguish the effect of erosion ($Ca^{2+} + Mg^{2+}$, HCO_3^-), marine (Na^+, Cl^-), and gas-phase (NH_4^+, SO_4^{2-}) sources during the period of observations. The presence of H^+ in the latter ensemble characterizes the effect of "acid" factor. The data on AA and AP ion composition averaged over each series reflect the stoichiometric ratios of ions and so they make it possible to estimate the contribution of different sources into formation of aerosols and precipitation.

Results

Ion composition of aerosols

The data on AA ion composition averaged over each series of observation (ng-equiv/m^3) are summarized in Table 1, where the values of the mass concentration M and its water-soluble fraction W are also presented. The long-term average data of observations for 1997–2000 are shown in the last row. The denominator shows the portion (%) of equivalents of each ion in the sum of equivalents of cations or anions, respectively. Comparing the values of the parameters for individual series of observations with them, one can notice some seasonal cyclicity both in the aerosol mass concentration and in the concentration of individual ions.

So, the total concentration M of aerosol particles increases in summer and decreases in winter. One can

relate this fact to the increasing contribution of erosion sources in summer, when the ground surface is free of snow cover. Variations of W in water-soluble salts are significantly less. Obviously, a significant part of the AA substance, emitted into the atmosphere from local erosion sources, is represented by water-insoluble compounds.

Concentrations of ammonium and sulfate, the precursors of which in the aerosol composition are volatile compounds, increase in winter and decrease to minimum in July and August. Sulfate remains to be dominating in the anion composition almost in all series of observations (except for May 1999), while the contribution of ammonium into the cation composition is prevalent only in winter. Seasonal dynamics of calcium, magnesium, and hydrocarbons, i.e., the ions, the precursors of which are non-volatile products of the ground surface erosion, is the reverse. Their contribution is minimal in winter and reaches maximum in summer. Concentrations of Na^+ and Cl^- ("marine" factor in formation of AA), as well as K^+, ($F^- + HCOO^-$) and NO_3^- have not so well pronounced seasonal dynamics.

The dynamics of H^+ concentration, which reflects the level of AA acidity, is noteworthy. The sum of equivalents of cations NH_4^+, ($Ca^{2+} + Mg^{2+}$), Na^+, and K^+ in two series of measurements (February–March 1997 and January–February 1998) is insufficient for neutralization of the sum of anions. As the result, the surplus acidity of AA was observed in these periods. There was no deficiency of the ions in summer 1997 and 1998, and their concentration was sufficient for practically full neutralization of the acid-forming ions. In succeeding years, such a situation was not repeated neither in winter no in summer.

Intra-serial variability of action of different factors on formation of the AA ion composition can be found based on statistical (factor) analysis, the results of which are presented in Table 2. Combinations, characterizing the gas-phase ($\underline{NH_4^+}$, $\underline{SO_4^{2-}}$), erosion ($Ca^{2+} + Mg^{2+}$, HCO_3^-), and marine (**Na$^+$**, **Cl$^-$**) sources,

Table 1. Ion composition of atmospheric aerosols, ng-equiv/m^3

Period	NH_4^+	$(Ca + Mg)$	Na^+	K^+	H^+	HCO_3^-	$(F^- + HCOO^-)$	Cl^-	NO_3^-	SO_4^{2-}	W, μg/m^3	M, μg/m^3
2–3/97	51.1	31.8	8.9	4.4	8.9	2.5	2.8	1.2	16.4	106	7.1	31.8
6–7/97	6.9	33.6	4.3	3.4	0.5	13.8	1.2	1.9	5.1	21.6	4.1	56.6
10/97	19.7	40.0	5.5	6.8	3.3	25.8	4.8	3.7	23.3	28.0	5.9	29.2
1–2/98	43.2	25.1	4.5	6.4	19.1	1.9	1.7	0.5	16.1	88.4	7.0	13.0
4–5/98	22.2	29.1	7.6	2.8	0.6	13.6	0.6	0.9	3.7	51.2	4.7	60.3
7–8/98	3.9	31.7	4.5	1.9	0.3	19.2	3.1	1.5	3.5	17.7	3.1	59.5
10/98	10.0	19.5	4.8	3.3	1.6	7.1	1.3	1.5	5.0	27.4	2.9	17.3
05/99	13.5	78.8	10.7	6.2	0.1	48.5	3.6	3.1	11.3	40.9	7.9	144
9–10/99	16.8	33.3	6.1	3.4	0.1	12.1	2.2	1.9	7.7	40.2	4.4	22.4
1–2/00	31.8	21.9	8.0	8.4	0.1	4.2	1.6	1.9	5.0	57.2	4.9	14.5
4–5/00	14.5	35.9	7.2	4.6	0.2	25.8	2.5	1.9	9.6	34.1	5.1	38.7
10/00	16.0	14.3	8.7	3.1	0.4	8.5	1.4	2.3	1.7	32.5	3.2	9.4
Long-term mean	$\underline{20.8}$ / 30.6	$\underline{32.9}$ / 48.5	$\underline{6.7}$ / 9.9	$\underline{4.6}$ / 6.8	$\underline{2.9}$ / 4.3	$\underline{15.3}$ / 20.7	$\underline{2.2}$ / 3.0	$\underline{1.9}$ / 2.6	$\underline{9.0}$ / 12.2	$\underline{45.4}$ / 61.5	5.0	41.4

were set off among the ion ensembles with mutually correlating dynamics of concentration, the "acid" factor (NH_4^+, SO_4^{2-}, H^+) was isolated individually. The first of them occurred most frequently (8 of 12 series), the second was observed in 6 series, and the third one – in 4 summer–fall series of observations. The acid factor was observed in one series. In addition to these factors, a correlation between H^+ и HCO_3^- concentration variations was observed in 6 series of 12. This points to the significant role of carbonates in neutralization of AA acidity.

Ion combinations characteristics of individual sources are not observed in some series, and they occur in different ensembles. This demonstrates a weak correlation in variability of their concentrations during the period of observations. It may be supposed that such situations appear either because of additional arrival of ions from some other source (for example, sodium from the erosion source) or due to chemical interaction in AA of substances from different sources.

Ion composition in snow and rain precipitation

Seasonal mean values for ion composition of snow and rain precipitation are shown in Table 3 together with the data on the number of samples N and total mineralization of precipitation Σ (mg/liter).

Table 2. Ensembles (1–4) of ions in the composition of AA with mutual dynamics of concentrations

Series	1	2	3	4
2–3/97	$\underline{NH_4^+}$, $\underline{SO_4^{2-}}$	Na^+, NO_3^-, K^+	H^+	Ca + Mg
07/97	$\underline{NH_4^+}$, $\underline{SO_4^{2-}}$, K^+, NO_3^-	Na^+, Cl^-	H^+, HCO_3^-	–
10/97	Ca + Mg, K^+, NO_3^-, F^- + HCOO$^-$	H^+, HCO$_3^-$	Na^+, Cl^-	–
1–2/98	$\underline{NH_4^+}$, $\underline{H^+}$, $\underline{SO_4^{2-}}$	NO_3^-, Cl^-, F^- + HCOO$^-$	Na^+, K^+	Ca + Mg
4–5/98	$Ca + Mg$, HCO_3^-, H^+, Na^+, NO_3^-	K^+, Cl^-	$\underline{NH_4^+}$, $\underline{SO_4^{2-}}$	–
7–8/98	SO_4^{2-}, NO_3^-, Cl^-, F^- + HCOO$^-$, K^+	NH_4^+	$Ca + Mg$, HCO_3^-	–
10/98	Ca + Mg, NO_3^-, K^+, Cl^-	H^+, HCO_3^-	$\underline{NH_4^+}$, $\underline{SO_4^{2-}}$	–
05/99	$\underline{NH_4^+}$, $\underline{SO_4^{2-}}$, Na^+	$Ca + Mg$, HCO_3^-, H^+, Cl^-	NO_3^-, F^- + HCOO$^-$	–
9–10/99	Ca + Mg, SO_4^{2-}	Na^+, Cl^-, HCO_3^-, H^+	K^+	–
1–2/00	$Ca + Mg$, HCO_3^-, Na^+, NO_3^-, K^+	$\underline{NH_4^+}$, $\underline{SO_4^{2-}}$		–
4–5/00	$Ca + Mg$, HCO_3^-, NO_3^-, K^+	$\underline{NH_4^+}$, $\underline{SO_4^{2-}}$	H^+, Na^+	–
10/00	$\underline{NH_4^+}$, $\underline{SO_4^{2-}}$, K^+, H^+	$Ca + Mg$, HCO_3^-	Na^+, Cl^-	F^-, NO_3^-

Table 3. Ion composition of snow and rain depositions in 1996–2001

Year	N	Σ	pH	NH_4^+	Ca + Mg	Na^+	K^+	H^+	HCO_3^-	F^- + HOOC$^-$	Cl^-	NO_3^-	SO_4^{2-}
							Snow deposition						
1996–1997	40	10.9	5.50	$\frac{29}{16.9}$	$\frac{106}{61.6}$	$\frac{21.5}{12.5}$	$\frac{9.1}{5.3}$	$\frac{6.1}{3.6}$	$\frac{24}{15.4}$	$\frac{14}{8.8}$	$\frac{29}{18.2}$	$\frac{39}{24.4}$	$\frac{53}{33.1}$
1997–1998	37	9.0	5.26	$\frac{17}{12.8}$	$\frac{50}{37.3}$	$\frac{43}{31.9}$	$\frac{17}{12.6}$	$\frac{7.2}{5.3}$	$\frac{19}{14.2}$	$\frac{11}{8.5}$	$\frac{40}{30.6}$	$\frac{27}{20.4}$	$\frac{34.5}{26.2}$
1998–1999	39	10.7	5.73	$\frac{14}{6.9}$	$\frac{84}{44.8}$	$\frac{69}{36.3}$	$\frac{20}{10.3}$	$\frac{3.1}{1.6}$	$\frac{29}{15}$	$\frac{17}{8.7}$	$\frac{61}{31.1}$	$\frac{38}{19.3}$	$\frac{51}{26.2}$
1999–2000	36	14.2	6.19	$\frac{26}{13.1}$	$\frac{100}{49.8}$	$\frac{53}{26.6}$	$\frac{21}{10.3}$	$\frac{1.0}{0.5}$	$\frac{64}{30.4}$	$\frac{28}{13.3}$	$\frac{50}{23.5}$	$\frac{31}{14.9}$	$\frac{38}{17.8}$
2000–2001	40	10.4	5.77	$\frac{8.4}{4.9}$	$\frac{63}{40.7}$	$\frac{65}{41.3}$	$\frac{17}{11.1}$	$\frac{3.1}{2.0}$	$\frac{28}{17.9}$	$\frac{11}{7.1}$	$\frac{57}{37.0}$	$\frac{27}{17.2}$	$\frac{32}{20.9}$
Long-term mean	**38**	**11.0**	**5.69**	$\mathbf{\frac{19.0}{10.9}}$	$\mathbf{\frac{80.6}{46.8}}$	$\mathbf{\frac{50}{29.7}}$	$\mathbf{\frac{17}{9.9}}$	$\mathbf{\frac{4.7}{2.6}}$	$\mathbf{\frac{33}{18.6}}$	$\mathbf{\frac{14}{9.3}}$	$\mathbf{\frac{47}{28.1}}$	$\mathbf{\frac{32}{19.2}}$	$\mathbf{\frac{42}{24.8}}$
							Rain deposition						
1996	34	7.8	5.44	$\frac{42}{35.7}$	$\frac{46}{39.1}$	$\frac{16}{13.6}$	$\frac{11}{9.4}$	$\frac{3.6}{3.1}$	$\frac{32}{28.3}$	$\frac{4}{14.5}$	$\frac{16}{14.2}$	$\frac{18}{15.9}$	$\frac{43}{38.1}$
1997	39	16.8	5.79	$\frac{83}{37.6}$	$\frac{80}{36.3}$	$\frac{34}{15.4}$	$\frac{22}{10}$	$\frac{1.6}{0.7}$	$\frac{88}{40.2}$	$\frac{6.8}{3.1}$	$\frac{27}{12.3}$	$\frac{36}{16.5}$	$\frac{61}{27.9}$
1998	23	12.3	5.83	$\frac{38}{24.7}$	$\frac{87}{56.5}$	$\frac{18}{11.7}$	$\frac{9.6}{6.2}$	$\frac{1.4}{0.9}$	$\frac{72}{51.3}$	$\frac{0.7}{0.5}$	$\frac{12.6}{9.0}$	$\frac{24}{17.1}$	$\frac{31}{22.1}$
1999	20	11.9	6.04	$\frac{47}{30.3}$	$\frac{72}{46.5}$	$\frac{23}{14.8}$	$\frac{12}{7.7}$	$\frac{0.9}{0.6}$	$\frac{58}{35.8}$	$\frac{6.2}{3.8}$	$\frac{22}{13.6}$	$\frac{31}{19.1}$	$\frac{45}{27.7}$
2000	23	5.1	5.74	$\frac{19}{27.1}$	$\frac{34}{48.6}$	$\frac{10}{14.3}$	$\frac{5.2}{7.4}$	$\frac{1.8}{2.6}$	$\frac{29}{39.7}$	$\frac{3.1}{4.2}$	$\frac{18}{24.7}$	$\frac{10.5}{14.4}$	$\frac{12.4}{17.0}$
2001	37	6.5	5.59	$\frac{37}{40.5}$	$\frac{29}{31.7}$	$\frac{12}{12.9}$	$\frac{9.6}{10.6}$	$\frac{3.8}{4.3}$	$\frac{26}{29.2}$	$\frac{1.5}{1.7}$	$\frac{12}{13.8}$	$\frac{24}{27.8}$	$\frac{24}{27.5}$
Long-term mean	**30**	**10.1**	**5.74**	$\mathbf{\frac{45}{32.7}}$	$\mathbf{\frac{58}{43.1}}$	$\mathbf{\frac{19}{13.8}}$	$\mathbf{\frac{11.6}{8.5}}$	$\mathbf{\frac{2.2}{2.1}}$	$\mathbf{\frac{38}{31.7}}$	$\mathbf{\frac{3.8}{3.2}}$	$\mathbf{\frac{18}{15.0}}$	$\mathbf{\frac{24}{20.0}}$	$\mathbf{\frac{36}{30.1}}$

Concentrations of individual ions are presented in nominators, and the portion (%) of their equivalents in the sum of equivalents of cations or anions, respectively, is in the denominator. The long-term mean values during the period of observations (1996−2001) are bolded. Deviations of the values in some seasons are, obviously, related not only to the total number and quantity of precipitation but also to other meteorological peculiarities. This is better seen in the data on rain deposition. Thirty nine rain samples were collected during summer 1997, and their mean mineralization was the highest of the whole period of observations (16.8 mg/liter), while only 23 samples were collected in drought summer 2000, but their mineralization was three times less (5.1 mg/liter). To reveal the role in such situations of different sources of AP formation, it is expedient to deal with relative portions of individual ions in the sum of equivalents rather than with their absolute concentrations. Indeed, there is more than four-fold difference between ammonium mean concentrations in rains of 1997 and 2000, but its shares in the sum of cations differ essentially less (37.6 and 27.1%, respectively).

The long-term mean values of the total mineralization of snow are somewhat higher and the values of pH are somewhat lower than these of rain precipitation. On the whole, the values of pH are close to the calculated ones (5.8) for condensation of water vapor in the atmosphere with the background content of CO_2, SO_2, and NH_3.[1] This is the evidence of the fact that there are no perpetually acting factors of AP acidation in the atmosphere over the observation site. However, some individual precipitation have an enhanced acidity. The maximal acidity of rain (pH = 4.18) was observed in September 5−6, 1999, that of snow (pH = 4.33) − in February 23, 1997.

When comparing the share distribution of different ions in the composition of snow and rain precipitation, three groups of ions can be distinguished. The first group includes (Ca^{2+} + Mg^{2+}), K^+ and NO_3^-, the concentrations of which in snow and rain practically coincide. The share of the second group

(NH_4^+ and HCO_3^-) is essentially lower in snow precipitation than in rain. The third group comprises Na^+, Cl^-, and (F^- + $HCOO^-$), the portion of which in snow is essentially greater than in rain. Sulfate can be also included in this group, though its concentration increases weaker.

Obviously, so noticeable differences in the AP ion composition of the second and third groups are caused by seasonal variations of the power of different sources. Isolation of the ground surface by snow cover and decrease of intensity of biological processes in winter result in the decrease of emission of ammonia and emission of carbonate products from erosion sources.

The inverse seasonal dynamics of ions of the third group, probably, has some other reason. The increase of the concentration of ions Na^+ and Cl^-, characteristic of marine sources, in snow deposition can be attributed to the effect of some remote source (saline-land regions of North Kazakhstan, Aral and Caspian seas) situated south-westerly from our observation sites. Earlier we made such a proposal[9] based on the fact that winds of a south-westerly direction are prevalent in Novosibirsk region in winter.[10] This fact can also explain the increase in concentration of sulfates, because thenardite Na_2SO_4 constituents a significant portion in carrying away aeolian from the ground surface in saline lands of North Kazakhstan.[11]

The data of statistical (factor) analysis of variability of the ion concentrations in some samples of AP shown in Table 4 favor the version of the increase of the role of remote marine sources in winter. Combination of Na^+ and Cl^- is observed in every winter period and only in a half of summer series. The effect of the erosion factor (joint dynamics of calcium, magnesium, and hydrocarbon concentrations) has been observed during three summer seasons and only one winter season. Variations of ($F^- + HCOO^-$) concentration, as a rule, do not correlate with other ions. Based on this fact, we can suppose that these ions originate from a source of some other nature, different from that of other ions.

Table 4. Ensembles (1−4) in the composition of snow and rain precipitation

Period	1	2	3	4
		Snow deposition		
1996−1997	**Na$^+$**, **Cl$^-$**, K$^+$	H$^+$, HCO$_3^-$	Ca+Mg, SO$_4^{2-}$, NO$_3^-$	
1997−1998	$\underline{NH_4^+}$, $\underline{SO_4^{2-}}$, Ca + Mg, NO$_3^-$	**Na$^+$**, **Cl$^-$**, K$^+$, F$^-$ + HCOO$^-$	H$^+$, HCO$_3^-$	F$^-$ + HCOO$^-$
1998−1999	**Na$^+$**, **Cl$^-$**, H$^+$	$\underline{NH_4^+}$, $\underline{SO_4^{2-}}$, NO$_3^-$	F$^-$ + HCOO$^-$	
1999−2000	Ca+Mg, HCO$_3^-$, **Na$^+$**, **Cl$^-$**, K$^+$, NO$_3^-$	H$^+$	NH$_4^+$	
2000−2001	**Na$^+$**, **Cl$^-$**, K$^+$	Ca+Mg, SO$_4^{2-}$, NO$_3^-$	H$^+$, HCO$_3^-$	F$^-$ + HCOO$^-$
		Rain deposition		
1996	Ca+Mg, HCO$_3^-$, Cl$^-$	SO$_4^{2-}$, NO$_3^-$	F$^-$ + HCOO$^-$	NH$_4^+$, K$^+$
1997	**Na$^+$**, **Cl$^-$**, K$^+$, NO$_3^-$, NH$_4^+$	Ca+Mg, HCO$_3^-$		
1998	$\underline{NH_4^+}$, $\underline{SO_4^{2-}}$, NO$_3^-$	Ca+Mg, HCO$_3^-$, H$^+$	**Na$^+$**, **Cl$^-$**, K$^+$	
1999	Ca+Mg, NH$_4^+$, NO$_3^-$	Ca+Mg, SO$_4^{2-}$	F$^-$ + HCOO$^-$	
2000	NH$_4^+$, K$^+$, HCO$_3^-$	Ca+Mg, SO$_4^{2-}$, NO$_3^-$	F$^-$ + HCOO$^-$	
2001	$\underline{NH_4^+}$, $\underline{SO_4^{2-}}$, **Na$^+$**, **Cl$^-$**, Ca+Mg K$^+$, NO$_3^-$	HCO$_3^-$, H$^+$		

Comparison of ion compositions in aerosols, snow and rain precipitation

The ion composition of atmospheric aerosols, snow and rain precipitation can be compared based on the share distribution of the equivalents of individual ions in the sum of equivalents of cations and anions, respectively. Such distribution of ions in samples of aerosols and snow precipitation related to the same days in January–February 2001, i.e., at the same state of the atmosphere, are shown in the Figure.

As is seen from these data, ions of calcium and magnesium dominate in the composition of cations of snow precipitation in this period. As a rule, their fraction in aerosols is less as compared to ammonium and potassium. The anion composition differs to a greater degree. Dominating role of sulfates in AA disappears in snow, where contributions of all other ions increase. The same pattern is observed in other series of observations as well.

The differences in the ion composition of AA and AP can be analyzed through correlation of stoichiometric relationships between ions, characteristic of the gas-phase, erosion and marine sources, using their long-term mean concentration values (see Tables 1 and 3). These data are shown in Table 5.

In snow and aerosols ammonium neutralizes only a half of sulfates, and their significant portion is neutralized by cations which are absent in the composition of volatile compounds, i.e., Ca^{2+}, Mg^{2+} and Na^+, the concentrations of which are "surplus" relative to HCO_3^- and Cl^-, respectively. From the data of Table 1, the difference $(SO_4^{2-} - NH_4^+)$ is 24.6, $(Ca^{2+} + Mg^{2+} - HCO_3^-)$ – 17.6, and $(Na^+ - Cl^-)$ – 4.8 ng-equiv/m^3. It follows herefrom that the contribution of erosion sources into neutralization of sulfate (71.5%) significantly exceeds the contribution of marine sources (19.5%).

This fact is of especial significance for acidity of aerosols in winter, when the content of SO_4^{2-} in their composition increases. The deficiency of NH_4^+ for complete neutralization of sulfates, dominating in their composition, must be compensated by the products of the erosion origin, but their arrival into the atmosphere from local sources is limited by snow cover. Therefore, the important role is played by far atmospheric transport of nonvolatile salts of the ground origin to Novosibirsk Region, as noted above.
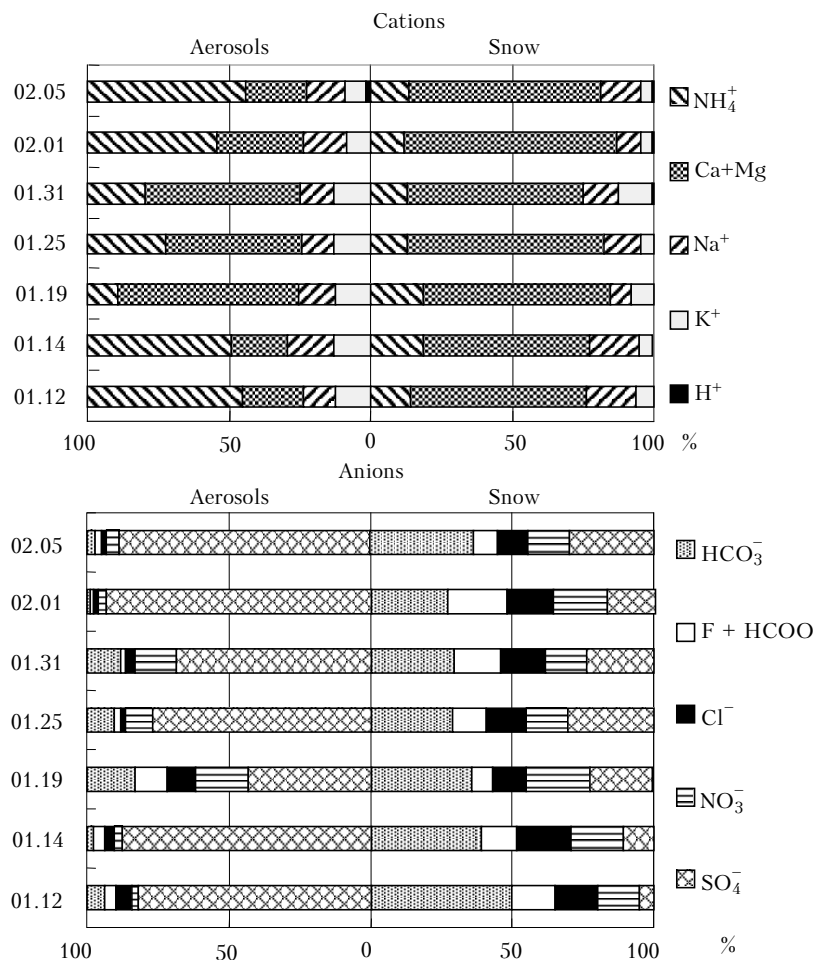

Fig. 1. Share distribution (%) of the equivalents of cations and anions in discrete samples of aerosols and snow in January–February 2001.

Table 5. Ratios of the equivalents of ions characteristic of different sources in aerosols and precipitation

Deposition	$[NH_4^+]/[SO_4^{2-}]$	$\dfrac{[Ca^{2+} + Mg^{2+}]}{[HCO_3^-]}$	$[Na^+]/[Cl^-]$
Aerosols	0.46	2.15	3.53
Snow	0.45	2.44	1.06
Rain	1.25	1.53	1.06

The situation is less dramatic for acidity of snow precipitation, because sulfates do not play dominating role in its composition. However, the portion of nitrates in snow increases. They can be neutralized by potassium only by half. Calcium and magnesium should play the principal role in neutralization of SO_4^{2-} and NO_3^-, the surplus of which relative to HCO_3^- is higher in snow than in aerosols. The situation in rain precipitation is different, because the share of ammonium in them significantly increases, but the surplus of $(Ca^{2+} + Mg^+)$ decreases. Obviously, violation of proportion between these cations and anions in discrete samples can result in the surplus acidity of AA and AP.

Changes in proportion between different cations and anions in the composition of aerosol and wet precipitation can be attributed to several factors. As it is shown in Ref. 12, the ratio of cations (without H^+) to anions varies for aerosol particles of different sizes and for AA collected in different zones (background, urban, industrial). It reaches minimum for the background regions and becomes less than 1 for the accumulation mode (0.2–0.8 μm of aerodynamic diameter of particles), that determines their enhanced acidity. Such ratio of cations to anions at the presence of significant quantity of sulfates can be observed for large-size particles because of displacing of volatile chlorides from the particles of marine origin as the result of the following reaction:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$
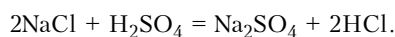
Similar reactions with other salts in the AA composition can lead to "enrichment" of aerosol particles by sulfates and their "depletion by other anions.

The ratio of cations to anions is also minimal for particles of accumulation mode in industrial and urban regions, but this minimum is close to 1. This value significantly exceeds 1 for large-size particles, what is mainly related to the presence in their composition of carbonates from ground sources.

Thus, temporal heterogeneity of the action of different sources (moreover, in different seasons) of AA formation can determine variations of their dispersity and, hence, their ion composition. Different hygroscopicity of particles of different sizes should be considered in subsequent transformation of their ion composition together with their different ability to initiate condensation of water vapor and to be washed out by wet precipitation. So it is evident that ion compositions of AA and AP are different.

Conclusion

Accumulation of field data on ion composition of atmospheric aerosols and precipitation in Novosibirsk Region in the framework of the project "Siberian Aerosols" made it possible to analyze the dynamics of seasonal factors of their formation. It occurred that the ion compositions of snow and rain precipitation are significantly different; in its turn, the composition of water-soluble aerosol fraction differs from the composition of wet deposition. Seasonal variations of the compositions of AA and AP are caused by a change in proportion between contributions from gas-phase, erosion and marine sources. The effect of gas-phase sources on formation of AA both in winter and in summer is characterized by exceeding of the sulfate concentration over the ammonium one. This leads to the deficiency of cations, and, hence, to a surplus acidity. The effect of local erosion sources capable to compensate the deficiency of cations and neutralize the surplus acidity of aerosols noticeably increases in summer. Significant increase of the water-soluble fraction evidences this fact. Weakening their activity in winter is compensated by remote transport of salts of ground origin and the salts characteristic of marine sources. These natural factors favor the decrease of the danger of acidic precipitation in Novosibirsk Region, though the discrete snow and rain precipitation can be of enhanced acidity.

Acknowledgments

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