

# Correlation between ionic compositions of atmospheric aerosol sampled simultaneously at different sites of Western Siberia

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Received January 23, 2002

Data on ionic composition of atmospheric aerosol sampled simultaneously in different climatic zones in the north and south of Western Siberia in summer and winter periods, 2000, are presented. Mass concentration of aerosol particles was found to increase in summer whereas the concentration and share of water-soluble salts decrease. Seasonal and spatial dynamics of some ion concentrations are connected with variations in action of main sources of atmospheric aerosol formation. Aerosols produced from the gas phase have an excess acidity. The contribution of salts, originated from erosion and sea sources, in neutralization of the acidity was estimated for different nature zones of Siberia.

## Introduction

Water-soluble salts in the composition of atmospheric aerosols (AA) have different sources as precursors: the atmospheric gases, solid substances or water solutions carried away from the ground surface or from the surface of seas and oceans. The portion of salts in the total mass of AA and their chemical composition vary depending on the power and distance from different sources, direction of the processes of transformation of initial substances in the atmosphere, as well as size spectrum and mass concentration of aerosol particles.<sup>1–3</sup> Inasmuch as salts dissociate to ions in water solutions, one can obtain an important information about their sources and the processes of aerosol formation at the global, regional, and local scales when studying seasonal and spatial dynamics of ion composition in water extracts of AA. Another fact that attracts attention to these investigations is the significance of the atmospheric sink for the balance of substances in the ground and water ecosystems, in particular, negative manifestations of acidic precipitation.<sup>4–6</sup>

Regular investigations of the AA ion composition were carried out in Western Siberia since 1997 in the framework of the project "Siberian Aerosols". They allowed us to reveal some peculiarities of AA formation depending on natural and climatic conditions, as well as on the effect of technogenic sources.<sup>7–9</sup> The purpose of this study is to estimate the effect of natural factors on the AA ion composition in different natural-climatic zones of Western Siberia through comparison of results of observations carried out simultaneously at different sites.

## Technique

Synchronic sampling of AA was carried out in January–February and June–July 2000 at 5 observation sites:

Site 1 – near village Samburg, beyond the polar circle, 67°N, 78°E, tundra zone;

Site 2 – near v. Tarko-Sale, 65°N, 78°E, approximately 250 km to the south of site 1, forest-tundra zone;

Site 3 – near v. Krasnoselkup, 66°N, 83°E, forest-tundra zone;

Site 4 – v. Klyuchi, Novosibirsk region, 55°N, 83°E, forest-steppe zone;

Site 5 – near v. Karasuk, Novosibirsk region, 54°N, 78°E, approximately 500 km to a south-westerly direction from site 4, steppe zone.

The period of observations in each winter or summer series was 30 days.

The technique for collecting and analyzing the AA samples is described in Ref. 10. Daily sampling of AA was performed by pumping air through the AFA-KhA filter at the volume rate of 8 m<sup>3</sup>/hour (at sites 1–3) or 13 m<sup>3</sup>/hour (at sites 4 and 5). The filter was weighted before and just after pumping in order to determine the mass concentration  $M$  of aerosol particles. It was moistened by distilled water (10 ml) during a day for chemical analysis. The specific electric conductivity, pH, and concentration of ions NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, F<sup>-</sup> + HCOO<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> were determined in the obtained water extract of AA by the method of liquid chromatography, (Ca<sup>2+</sup> + Mg<sup>2+</sup>), HCO<sub>3</sub><sup>-</sup> – by titration. Concentration of H<sup>+</sup> was determined from the measured values of pH. The obtained values of the ion concentration  $C$  were related to the content of AA in 1 m<sup>3</sup> of air. The sum of the obtained concentrations of individual ions (represented in weight units) is the mass  $W$  of water-soluble salts; its ratio to the total mass of AA is the portion of the water-soluble fraction.

## Results

Mean values of  $M$ , μg/m<sup>3</sup>;  $W$ , μg/m<sup>3</sup>; and  $C$  (numerator is ng-equiv/m<sup>3</sup>, denominator is the portion of equivalents of the given ion relative to the sum of equivalents of cations or anions, %) for each series are shown in Table 1. On the whole, the values of the mass

concentration of aerosol particles increase from north to south. The lowest values of *M* are recorded at site 1 near the Arctic Ocean, and the highest values are observed at site 5 in the south of Western Siberia. This dynamics is better pronounced in summer, when the mass concentration increases in this direction from 22 to 66 μg/m<sup>3</sup>. The values of *M* in winter are lower than in summer at all sites, except for site 3. This is caused by decrease of the quantity of particles carried away from erosion sources. Seasonal difference in *M* is better pronounced in the forest-steppe and steppe zones in the south of Western Siberia, where the role of these sources in formation of AA in summer increases markedly.

Contrary to the total mass of aerosol particles, the mass of water-soluble salts is greater in winter than in summer at all observation sites. Maximum seasonal variations of *W* are observed at sites 1 and 2 in the north of Western Siberia. Because seasonal variations of *M* and *W* are of different direction, the portion of water-soluble fraction in the AA composition, reaching 32–34% in winter at sites 1 and 4, in summer decreases to 6%.

These general regularities are violated at site 3. The values of *M* in winter and of *W* in summer sharply contrast with the data taken at sites 1 and 2. High values of *W* at this site in summer are due to anomalously high concentration of ammonium and sulfate ions relative to all other sites. The violation of general regularities in Krasnoselkup is possibly connected with influence of some local source of air pollution.

Analysis of the data on concentration and share distribution of ions of water-soluble fraction of AA (Table 1) shows that there is some well-pronounced spatial and temporal dynamics in operation of different sources producing them: from the gas phase (NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>), from ground sources (Ca<sup>2+</sup> + Mg<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>), and from marine sources (Na<sup>+</sup>, Cl<sup>-</sup>). Ammonium and sulfate ions make a principal contribution into the increase of *W* magnitude in winter. Hence, the increase of *W* results in intensification of action of the gas-phase source on AA formation. Seasonal variations of absolute concentrations of other ions are weakly pronounced, so the action of erosion and marine sources on AA formation is more stable during a year. However, relative contribution of each source changes as it is seen from the comparison of the share distribution of equivalents of different ions.

Sulfate and ammonium are prevalent in the cold season at all sites of observation. The share of sulfate among anions is 82–91%, and the share of ammonium in the cation composition is 42–57%. No spatial dynamics is observed. The total contribution of calcium, magnesium, and sodium in the cation composition is less than the contribution of ammonium that reflects a lesser efficiency of ground erosion and marine sources in formation of AA. The portion of (Ca<sup>2+</sup> + Mg<sup>2+</sup>) increases, and the portion of Na<sup>+</sup> decreases from north to south. The contribution of HCO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> into anion composition changes similarly, though their portion is less against the background of the dominating sulfate.

**Table 1. Ion composition of atmospheric aerosols at sites 1–5**

No. of site	<i>M</i> , μg/m <sup>3</sup>	<i>W</i> , μg/m <sup>3</sup>	Mean concentration of ions, <i>C</i>									
			NH <sub>4</sub> <sup>+</sup>	Ca <sup>2+</sup> + Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	H <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	F <sup>-</sup> +HCOO <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
January–February 2000												
1	10.0	3.40	20.0	9.2	9.7	4.2	4.5	1.6	2.5	2.2	1.0	46.1
			42.0	19.3	20.4	8.8	9.5	3.0	4.7	4.1	1.9	86.3
2	24.0	5.67	42.0	12.5	10.9	7.1	1.2	4.0	3.6	3.5	3.3	73.5
			57.0	17.0	14.8	9.6	1.6	4.6	4.1	4.0	3.8	83.6
3	42.9	5.12	37.7	18.9	7.1	3.5	2.3	3.5	2.5	1.7	1.8	70.5
			54.2	27.2	10.2	5.0	3.3	4.4	3.1	2.1	2.3	88.1
4	15.0	4.87	31.8	21.9	8.0	8.4	0.1	4.2	1.6	1.9	5.0	57.2
			45.3	31.2	11.4	12.0	0.1	6.0	2.3	2.7	7.2	81.8
5	26.4	4.68	38.3	16.4	8.6	4.7	0.6	1.8	0.6	0.7	3.1	62.6
			55.8	23.9	12.5	6.9	0.9	2.6	0.9	1.0	4.5	91.0
June–July 2000												
1	22.0	1.18	4.3	2.0	5.7	1.1	7.1	2.2	1.0	1.9	0.5	13.7
			21.3	10.0	28.3	5.5	35.0	11.4	5.2	9.8	2.6	71.0
2	24.7	2.61	8.5	14.2	9.0	1.5	1.3	13.7	1.9	2.1	1.2	19.3
			24.6	41.2	26.1	4.3	3.8	35.9	5.0	5.5	3.1	50.5
3	20.4	5.06	40.9	11.6	10.0	3.8	7.0	6.5	1.7	2.1	0.7	64.0
			55.8	15.8	13.6	5.2	9.5	8.7	2.3	2.8	0.9	85.3
4	51.0	3.08	7.6	26.8	5.0	2.4	0.3	17.4	2.1	1.7	2.6	19.8
			18.1	63.7	11.9	5.7	0.7	39.9	4.8	3.9	6.0	45.4
5	66.0	3.37	11.7	24.0	7.3	3.0	0.2	14.6	1.2	2.0	3.3	26.8
			25.3	51.9	15.8	6.5	0.4	30.5	2.5	4.2	6.9	55.9

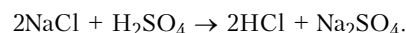
Sulfate is also prevalent in the anion composition of AA in summer all over the territory of Western Siberia, though its contribution noticeably decreases (excepting site 3) due to increase of the portion of chlorides and hydrocarbons. The contribution of  $\text{HCO}_3^-$  increases most significantly and reaches 30–40% of the sum of equivalents of all anions at sites 2, 4, and 5. ( $\text{Ca}^{2+} + \text{Mg}^{2+}$ ) become prevalent in the anion composition at these sites that reflects the increase of the contribution of erosion sources into formation of AA. The contribution of the marine source also increases at all sites: the portion of  $\text{Na}^+$  and  $\text{Cl}^-$  increases relative to winter period. The greatest portion of sodium in the cation composition is observed at sites 1 and 2, where it reaches 26–28%. The portion of ammonium, except for site 3, decreases, that reflects a decrease of the role of gas-phase sources in formation of AA in summer both in the north and in the south of Western Siberia.

Thus, the data of simultaneous observations of AA ion composition above the territory of Western Siberia bear evidence of regular seasonal and spatial variations of the role of principal natural sources in formation of aerosol particles. One of important consequences of this fact can be a change of acid-alkaline balance of water-soluble salts in the composition of AA. As it follows from Table 1, action of the gas-phase source is characterized by significant excess of sulfate concentration over the ammonium concentration, the only cation in the composition of AA being formed from the gas phase. The ratio of equivalents  $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$  is in winter 0.43–0.61 and in summer  $\sim 0.4$ . The deficiency of cations in water solution can be compensated only by  $\text{H}^+$ . Thus, atmospheric aerosols, formed from the gas phase, initially have an enhanced acidity.

It is characteristic that in case of the gas-phase source the anion concentration exceeds the cation concentration in all events and the relation between cations and anions for erosion and marine sources is inverse. This means that surplus acidity in a water extract of AA due to the gas-phase source can be neutralized by cations of salts of marine and erosion origin. Not their total content is therewith important, but the “surplus” relative to the pair anion. Such a “surplus” is different at different sites and in different seasons.

The ratio of equivalents  $[\text{Na}^+]/[\text{Cl}^-]$  is from 3 to 5 in all series of observations, and the surplus of sodium can participate in neutralization of a part of sulfate ions. Different explanations of a steady surplus of sodium relative to chloride in the composition of AA are possible. One of them is based on the fact that only part (from 1/3 to 1/5) of  $\text{Na}^+$  has a marine origin, and another, the greater part, is of a terrigenous origin, for example, in the form of thenardite  $\text{Na}_2\text{SO}_4$  or  $\text{NaHCO}_3$  (as it was mentioned above, sulfate dominates in the composition of anions). However, from the data of Table 1 no seasonal or spatial correlation is observed between concentrations of sodium and sulfate or hydrocarbon. So, without rejection of the possibility of sodium partial income into AA with salts of a

terrestrial origin, one should agree that these sources cannot provide the principal part of the sodium concentration. Besides, as it will be shown below,  $\text{HCO}_3^-$  in the composition of AA is also deficient relative to ( $\text{Ca}^{2+} + \text{Mg}^{2+}$ ), and they could provide the income of the principal part of sodium only in summer at some observation sites. At the same time, significant correlation between  $[\text{Na}^+]$  and  $[\text{Cl}^-]$  evidences that the principal part of sodium comes from marine sources. Essential surplus of sodium in AA can result from displacement of chloride in the form of volatile  $\text{HCl}$  formed at interaction between surplus sulfuric acid and  $\text{NaCl}$ :



Proceeding of this reaction in aerosol particles is possible just due to the differences in volatility of hydrochloric and sulfuric acids, and it results in “depletion” of AA by chlorides and “enrichment” by sodium.

Somewhat other situation is for the erosion source. If in winter the content of calcium in AA 3–5 times exceeds the content of hydrocarbons in the north, and in the south this difference still increases, then in summer the ratio  $[\text{Ca}^{2+} + \text{Mg}^{2+}]/[\text{HCO}_3^-]$  is close to 1 in the north and in the south it increases insignificantly and equals to  $\sim 1.6$ .

Obviously, the surplus of cations in particles coming to AA from ground sources compensates their deficiency in gas phase, that leads to decrease of acidity of natural atmospheric aerosols. However, limited income of the products of erosion processes into the atmosphere in winter, which continues up to 8 months in the northern regions, leads to a deficiency of neutralizing cations, and, hence, to surplus acidity of atmospheric aerosols and precipitation.

Using the data on concentration of some ions presented in Table 1, one can estimate the contribution of salts from different sources into neutralization of the surplus sulfate. For example, the difference in concentrations of equivalents  $[\text{SO}_4^{2-}] - [\text{NH}_4^+]$  in winter at site 1 is 20.1,  $[\text{Ca}^{2+} + \text{Mg}^{2+}] - [\text{HCO}_3^-] = 7.6$ ,  $[\text{Na}^+] - [\text{Cl}^-] = 7.5$  ng-equiv/ $\text{m}^3$ . The contribution of salts from the erosion sources into neutralization of the surplus sulfate is 29.1%, and that of salts from the marine sources is 28.7%. The concentration of cations of salts from these sources is insufficient for complete neutralization of sulfates, and this results in a surplus of cation  $\text{H}^+$  in a water extract. A similar estimate for site 5 points to significant increase of contribution of salts from the erosion source (up to 60.1%) as compared to the marine one (up to 32.5%). This results in practically complete compensation of excess of the sulfate concentration over the ammonium concentration, therefore the surplus acidity in a water extract of AA in the south is not observed.

The contribution from erosion and marine sources into neutralization of the surplus acidity of AA at sites 1–5 in summer and winter is presented in Table 2.

Contribution of the marine source in winter is practically the same all over the territory of Western

Siberia and makes 20–30% of the surplus of sulfates. Contribution of the erosion source regularly increases from the north (30%) to the south (70%).

**Table 2. Contribution of principal sources into neutralization of surplus acidity of gas-phase part of AA, %**

No. of site	Winter		Summer	
	Marine	Erosion	Marine	Erosion
1	28.7	29.1	40.4	0
2	23.5	27.0	63.9	4.6
3	16.5	47.0	34.2	3.5
4	24.0	69.7	27.0	77.0
5	32.5	60.1	35.1	62.2

Total influence of the both sources is sufficient for almost complete neutralization of the surplus acidity of AA only in the south of Western Siberia due to more intense action of the erosion source. Contribution of the erosion source in summer remains dominating in the south of Western Siberia and sharply decreases in the north. The role of the marine source in formation of AA in such a situation is determining for compensation of the surplus of sulfates. Its contribution at the most northern site of observation (site 1) was about 40% at zero contribution of the erosion source, and the aerosol acidity was enhanced (the portion of  $H^+$  was 30% of the sum of equivalents of all cations in a water extract, see Table 1).

Contribution of the marine source at site 2, more distant from the Arctic coast, increased up to 64%, and, together with the erosion source, the neutralization of the sulfate surplus was almost 70%. It has led to a sharp decrease of the degree of AA acidity (the portion of  $H^+$  decreased to 3.8%). It should be noted that aerosol samples at site 1 were collected in June and at site 2 in July 2000. Possibly, the intensification of action of the marine source in formation of aerosols occurred in that period due to thawing of Arctic ice that determined the increase of its contribution at site 2.

Thus, the surplus acidity of water-soluble fraction of AA in Western Siberia is determined by the balance in relation between concentrations of acid-forming anions and neutralizing cations rather than by their absolute concentrations. The greatest danger of AA acidification appears near the coast of Arctic, where the total concentration of water-soluble salts is minimal as compared to all other sites of observation. This is due to decrease of the role of local erosion sources in formation of aerosol particles. It should be noted that the total concentration of water-soluble salts in composition of AA, including salts from erosion and marine sources, is greater in winter than in June–July, when the ground surface is free of snow cover, and marine surface is free of ice. Besides, the contribution of the gas-phase source, the primary cause of the surplus acidity of AA, is more powerful all over the territory of Western Siberia in winter. Complex combination of these factors leads to the necessity of taking into account the balance of cations and anions of individual salts characteristic of different sources of aerosol particles.

## Conclusion

The obtained data of simultaneous observations of atmospheric aerosol ion composition at different sites of Western Siberia in different seasons show the presence of regional peculiarities of their sources and of the processes of their formation. The contributions of gas-phase, marine, and erosion sources into formation of ion composition of AA undergo seasonal and spatial variations caused by natural and climatic conditions (long winter period of isolation of erosion sources by snow cover, long distance from the ocean). Concentration and portion of water-soluble salts decrease in summer at increase of total mass of AA. Aerosols produced from the gas phase have a surplus acidity due to deficiency of cations of the gas-phase origin (ammonium) relative to sulfates. Surplus of sulfates can be neutralized by cations of salts from ground and marine origins. Efficiency of the neutralization depends on the balance between cations and anions of salts characteristic of different sources rather than on their absolute concentrations. No enhanced acidity of AA is observed in the south of Western Siberia due to significant contribution of salts of the erosion origin, while salts from the marine source play the principal role in the north, because their deficiency can cause an enhanced acidity of a water extract of aerosols.

## Acknowledgments

This work was supported in part by the Presidium of SB RAS in the framework of Integration Projects 64–00 and 69–00.

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