COMPARISON OF ION COMPOSITION OF ATMOSPHERIC AEROSOL AND WET DEPOSITIONS IN THE SOUTH OF WEST SIBERIA

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We describe here some experimental results on ion composition of atmospheric aerosol (WSPA) and wet depositions (WD) in different areas of West Siberia. The distribution of ion equivalents of WSPA and WD is not equal, especially for Cl^-, SO_4^{2-} *and* NH_4^+, *and varies in winter and summer. High content of lithophylic cations is observed. These peculiarities of ion composition of WSPA and WD are exhibited at the observation points in the south of the Novosibirsk region. We can conclude that these peculiarities are caused by the atmospheric transport of soil salts from the areas of the Northern Kazakhstan and Aral Sea.*

INTRODUCTION

The characterization of chemical composition of atmospheric components is very important both for the investigations of atmospheric parameters and for the account for the part the atmospheric transport of aerosol particles plays in the atmosphere – surface system.[1,2] The ion composition of wet precipitation (rain, snow) is the main part of their mineral composition. The significance in a global hydrologic cycle for the forming of surface waters and their quality determines a considerable amount of information obtained at regular observations of ion composition of atmospheric precipitation. A lesser amount of information is available relative to the ion composition of solid aerosol particles. It is apparent if we take into account small content of solid aerosol particles in the air and minor amount of water-soluble aerosols of WSPA varying from $n{\cdot}10\%$ in the ocean to n% in continental regions. It should be noted that here we have to do not with the determination of concentration of separate ions but with the total analysis of ion composition. Although the general regularities of ion composition of WSPA were determined depending on the particle size, region and sampling point,[1–5] a series of problems should be solved. In particular, not so much is known about the dynamics of ion composition of WD and WSPA near the Earth's surface as well as about the influence of local factors. Except for a more detailed description of the dependence of atmospheric characteristics (including optical ones) on the chemical composition of atmospheric components, such complex investigations are necessary for better understanding of mechanisms of their formation.

The chemical composition of atmospheric components and the factors determining its dynamics over vast region of the West Siberia remain poorly investigated. Within the framework of the complex project "Aerosols of Siberia"[6] we have previously studied the dependence of anions distribution in WSPA on the aerosol particle size,[7] acidity and ion composition of WD and WSPA in the "background" areas of Novosibirsk region.[8] In these investigations some peculiarities were determined in the distribution of various ions in WD and WSPA in the south of West Siberia. The effect of atmospheric transport of soil salts from other regions is a probable cause of the above-mentioned peculiarities.[8,9]

In this paper much attention is paid to the analysis of dynamics of ion composition of WD and WSPA in the series of simultaneous observations performed in summer and in winter of 1995–1996.

THE OBSERVATION TECHNIQUE

For regular observations two points in Novosibirsk region were chosen: No. 1 in the forest area, 80 km southwest of Novosibirsk, and No. 2 in the partially-wooded steppe, 30 km south-southeast of Novosibirsk (54°N and 84°E), where the observations were made previously.[8,9] For a comparison of the data on ion composition of WSPA some observations were made in Tyumen region at the point No. 3, located near the settlement Isetskoye (56°N, 65°E). Fresh precipitation was collected in a polyethylene container and analyzed at once. The daily sampling of aerosols (an AFA–XA-filter, a volumetric air flow rate of 6 – 13 m^3p^{-1}) at these points was made during several series of measurements of 15 – 30 days. Each filter was weighed before and after sampling and then on the basis of the difference we calculated the total mass of aerosol particles, ΔM, which was assigned to the volume of pumped out air. The part of water-soluble volume, *B*, was found from the ion sum ratio calculated when analyzing the water drawing (1/2 of the filter, 10 ml of deionized water).

In samplings of WD and WSPA we measured pH and specific electrical conductivity χ. The concentrations of F^-, Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+ were determined by the method of ion chromatography (conductometric detector, sorbent KhIKS and carbonate-bicarbonate eluant for analyzing among, sorbent Katieks and nitric acid for analyzing cations). The sum of ions $Ca^{2+} + Mg^{2+}$ was determined by trilonometric titration, in samples of WSPA, which were prediluted by a factor of 5. In samples of WD we determined additionally the alkalinity (HCO_3^- concentration) by HCl titration. The concentration of H^+-ions was determined from the pH data when analyzing WSPA we took into account the H^+ concentration in deionized water used for obtaining the water drawing of aerosol particles.

The data of analysis of ion composition (taking into account an idle sampling) were expressed in units of concentration of equivalents of every ion per one liter for checking the balance between the sum of cations, Σ_{cat}, and the sum of anions, Σ_{an}, and the calculation of χ. Check of the balance of Σ_{cat} and Σ_{an}, as well as the comparison of experimental and calculated values of χ enables one to estimate the completeness of analysis of ion composition. Unfortunately, in a series of papers such a check was not conducted and the data presented for the ions determined do not give general picture of ion composition of samples as a whole as well as of the contribution of individual ions to the sum ion composition. Since for our purposes the partial distribution of ion equivalents is important, the results of analysis will be represented in this form of the expression for concentrations (mg-eq/l for WD, ng-eq/m^3 for WSPA) that makes it possible to estimate the balance of Σ_{cat} and Σ_{an}. If necessary, these data can easily be calculated in the form of mass concentrations – mg/l for WD, $\mu g/m^3$ for WSPA, more frequently used in the literature. Note that it is that the partial distribution of ion equivalents enables us to compare the composition of different atmospheric components, i.e., solid aerosol particles and water solutions (wet precipitation).

RESULTS AND DISCUSSION

Ion composition of wet precipitation

Ion composition of WD as well as of some other characteristics of atmospheric components, is very dynamic as is evidenced by the data on the values of pH and specific electrical conductivity χ of discrete snow samples (Fig. 1*a*, point 2) and rain samples (Fig. 1*b*, point 1).

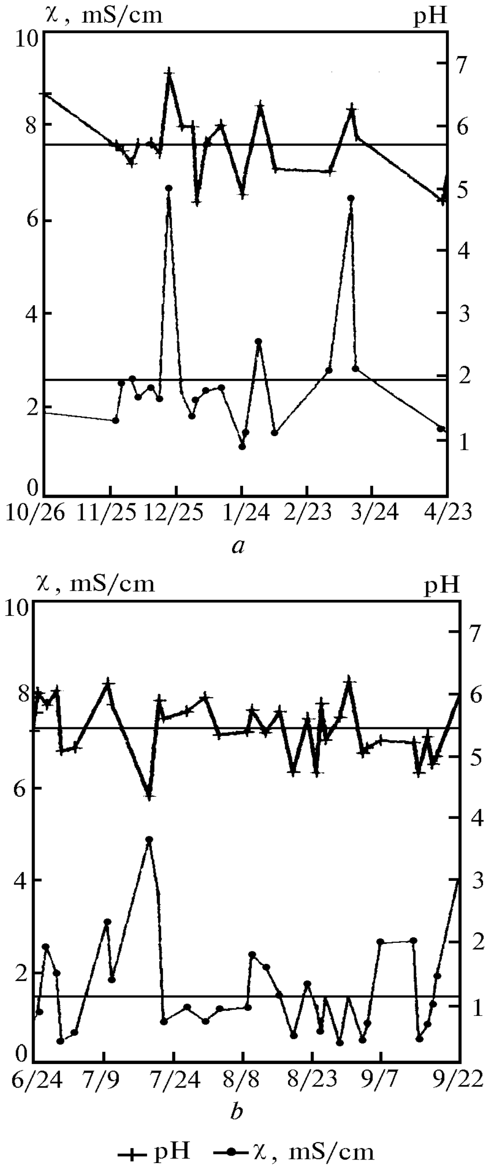

FIG. 1. Dynamics of pH *and* χ *in discrete snow samples (a) and rain samples (b).*

The horizontal line in the figure denotes the mean value of these quantities obtained during the observation periods (22 snow samples taken over the period from October 25, 1995 to April 28, 1996; 34 rain samples taken from 24 June to 24 September 1996). The mean values of pH (5.72 in winter, 5.44 in summer) slightly differ from the calculated value 5.8[1] for water balance with CO_2, SO_2 and NH_3 at their simultaneous presence in air at the level of "background" concentrations. This points to the lack of the effect of constant factors of overacidity and alkaline washing of precipitation as it was noted before.[8,9] No correlation was observed in the pH dynamics and general mineralization of WD, whose characteristic is the quantity χ in the first approximation. Larger mean values of χ in winter (2.58 m/cm, Fig. 1*a*) than in summer (1.79, Fig. 1*b*) agree with higher snow mineralization (11.9 mg/l) relative to rains (8.25 mg/l). It should be noted here that sometimes there occur situations of sharp increase in χ in some snowfalls (Fig. 1*a*) coinciding in time with incidental effects of "dusty storms." In these samples the increase in mineralization was mainly connected with the rise of concentrations of calcium, magnesium, and sulfates.

Table I gives the mean observed concentrations of some ions together with the values of their partial contribution to the sum of equivalents of cations and anions, respectively.

A good agreement between Σ_{cat} and Σ_{an} is observed based on the data presented in Table I. The values of χ calculated for concentrations of some ions (2.27 and 1.61 mg/cm for snow and rainfalls, respectively) are also in good agreement with the experimental values. These calculations confirm the conclusion about the lack in WD of large amounts of other ions except for those presented in Table I. In the composition of winter WD cations the part of lithophylic elements is almost 90% of equivalents. In this case the main part accounts for (Ca^{2+} + Mg^{2+}). In summer the part of NH_4^+ grows essentially, whose contribution reaches 35.3%. At the same time, the absolute concentration of NH_4^+ increases and that of (Ca^{2+} + Mg^{2+}) decreases more than twice; the concentration of Na^+ decreases by a factor of three. The increase of NH_4^+ concentration in summer can be due to the growth of its emission in summer from an open ground surface. It is evident that the absence of snow cover must assist the transport of lithophylic elements with the soil erosion products to the atmosphere. The observed decrease of their concentration shows that in summer the activity of sources of lithophylic cations is less than in winter. Previously[8,9] this effect was due to the atmospheric transport of soil salts to the south of West Siberia from the regions of Kulunda plain and Northern Kazakhstan, where the annual salt transport to the atmosphere is about 4 – 7 thousand tons from 1 km^2 of the earth's surface.[10] These regions are located southwest of the areas of our observations in Novosibirsk region, where the southwest winds are typical for annual observations except for summer.[11]

TABLE I. Ion composition of wet precipitation in winter and summer seasons (numerator – μg–eq/l, denominator – % eq.).

χ	pH	NH_4^+	Ca^{2+} + Mg^{2+}	Na^+	K^+	H^+	Σ_{cat}	HCO_3^-	F^-	Cl^-	NO_3^-	SO_4^{2-}	Σ_{an}
Point 2, snowfalls, October 25, 1995 – April 28, 1996, *n* = 22													
2.58	5.72	19	100	48	12	1.9	181	32.5	4.6	49	27.7	59	173
		10.5	55.2	26.6	6.6	1.1	100	18.9	2.7	28.6	16.2	33.8	100
Point 1, rainfalls, June 24 – September 24, 1996, *n* = 34													
1.79	5.44	42	46	16	11	3.7	119	32	4.0	16	18	43	113
		35.3	38.7	13.4	9.2	3.1	100	28.3	3.5	14.2	15.9	38.1	100

In the WD anion composition the essential seasonal variations appear as a summer decrease in Cl^- and NH_3^- concentration (by a factor of 3 and 1.5, respectively). In the fraction distribution the HCO_3^- contribution increases and the chlorides contribution decreases. The presence of chlorides is usually due[1] to the effect of an oceanic (or sea) source. The nearest source, the Aral Sea, is located southwest of the area of our observations. From analysis of the dynamics of the cation composition we draw the conclusion that in winter the effect of atmospheric transport of soil salts is observed from the source located southwest of Novosibirsk region.

To determine the dynamics of ion composition of WD discrete samples a statistical analysis was conducted of the data for 22 snow samples and 34 rainfall samples. The sampling results are given in Table II as the coefficients of pair correlations of the corresponding ions.

TABLE II. Results of statistical analysis of seasonal variations of ion concentration in the snow and rain.

	Snow, October 25, 1995 – April 28, 1996, *n* = 22				Rain, June 24 – September 24, 1996, *n* = 34			
Ions	Ca^{2+} + Mg^{2+}	NH_4^+	Na^+	K^+	Ca^{2+} + Mg^{2+}	NH_4^+	Na^+	K^+
HCO_3^-	0.71	–0.05	0.50	0.44	0.72	0.53	0.63	0.29
F^-	0.60	0.04	0.47	0.34	0.47	0.28	0.20	0.19
Cl^-	0.50	–0.47	0.51	0.37	0.62	0.74	0.69	0.33
NO_3^-	0.80	0.05	0.48	0.60	0.50	0.53	0.41	0.28
SO_4^{2-}	0.92	–0.08	0.49	0.51	0.52	0.42	0.15	0.22

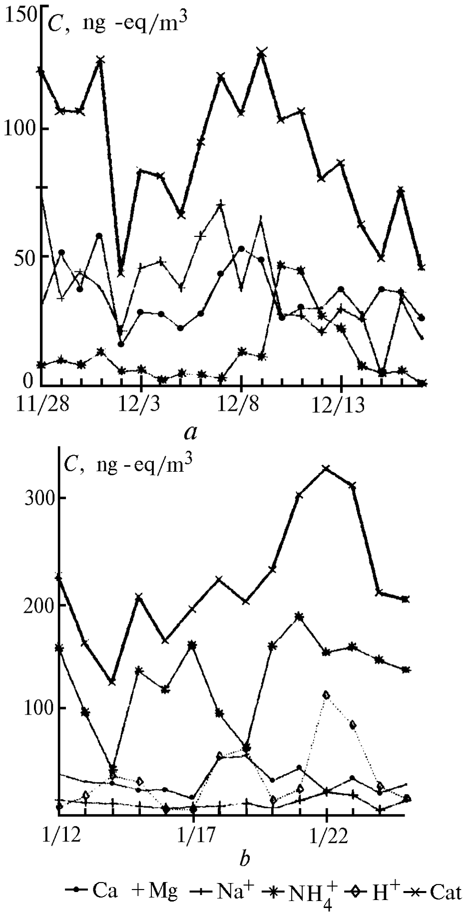

FIG. 2. Dynamics of $\Sigma_{\rm cat}$ *and concentrations of some cations in discrete samples of WSPA at points 3 (a) and 2 (b) during winter.‘*

From Table II we notice that in winter the dynamics of $(Ca^{2+} + Mg^{2+})$ concentration correlates with the SO_4^{2-} NH^+ concentration variations, to a lesser degree – with HCO_3^- and F^-; Na^+ concentration correlates equally with all anions; no correlation is observed between NH_4^+ concentration and anions. Another picture is typical for summer period when the correlation grows in the variations of cation concentration (except for K^+) with Cl^-; the correlation decreases (except for NH_4^+) – with SO_4^{2-}. For different seasons the most strong are the interconnections between NH_4^+ and anions.

Ion composition of water-soluble part of aerosols

As in the case with WD, the surface aerosol is characterized by a high variability of chemical composition, including the WSPA ion composition.

One can judge about this from the data of analysis of WSPA cations shown in Fig. 2 for two series of observations, at the point 2 (Fig. 2*a*) and point 3 (Fig. 2*b*) during winter period. Noteworthy is an essential difference in the contribution from the NH_4^+, dominating in the cation composition at the point 3, and lithophylic cations, first $(Ca^{2+} + Mg^{2+})$, dominating in WSPA at the point 2. It is evident, as in the case of WD, that an increased quantity of lithophylic cations is typical for WSPA in the south of the Novosibirsk region.

The complete set of data for ion composition of WSPA at different points of observations and for different seasons may be seen in Table III, where the mean data are presented for mass aerosol particle concentration ΔM, μg/m^3, as well as for water-soluble part, *B*, %.

TABLE III. Mean ion composition (numerator – ng-eq/m^3*, denominator – % equivalents) WSPA at points 1 – 3 during winter and summer.*

NH_4^+	$Ca^{2+} + Mg^{2+}$	Na^+	K^+	H^+	$\Sigma_{\rm cat}$	F^-	Cl^-	NO_3^-	SO_4^{2-}	$\Sigma_{\rm an}$	ΔM	*B*
Series 1. Point 2, August 18 – September 03, 1995, *n* = 15												
15	31	16.4	4.4	–	65	1.1	7	4.3	47.3	60	4.09	9.1
21.0	47.7	24.3	7		100	1.7	12.2	6.6	79.6	100		
Series 2. Point 2, November 29 – December 28, 1995, *n* = 30												
9.9	31	39	4.4	–	83	1.5	3.5	12.1	65.1	82	5.80	18.7
11.8	36.7	46.3	5.2		100	1.8	4.2	14.6	78.5	100		
Series 3. Point 3, January 12 – 26, 1996, *n* = 14												
130	33	11	11	36	221	3.7	4.5	32	201	241	15.5	37.1
58.8	15	5	5	16.3	100	1.5	1.9	13.3	83.4	100		
Series 4. Point 2, June 5 – 30, 1996, *n* = 25												
6.8	26	5.2	4.2	–	42	2.2	4.5	5.0	24.3	36	2.53	3.4
16.2	61.4	12.3	10		100	6	12.6	13.8	67.7	100		
Series 5. Point 1, July 7 – 28, 1996, *n* = 21												
14	12	3.7	2.6	4.3	36	1.6	2.3	1.4	23.9	29	2.00	6.9
38.7	32.6	10.1	7.1	11.9	100	5.6	8	4.7	81.8	100		
Series 6. Point 1, 29.August 29 – September 10, 1996, *n* = 13												
8.8	3.3	3.9	1.5	3.1	20.6	1	0.84	1.4	12.3	15.5	1.1	9.0
42.7	15.9	18.7	7.5	15	100	6.3	5.3	8.6	76.9	100		

In contrast to WD in the aerosol anion composition the sulfate dominates independent of season and observation site. The part of the sum of other anions is much less, although the relative contribution from each of them varies markedly. In the cation composition the contribution of ammonium and lithophylic cations of calcium, magnesium and sodium can vary within wide limits. The correlation analysis, the results of which are given in Table IV, enables one to determine the interconnections in the dynamics of ion concentrations in WSPA.

The consideration of the data presented in Tables III and IV, shows that the variability of WSPA ion composition reflects the joint action of different factors of their formation. When the sulfates dominate in the anion composition in all series of observations it is expected that it is precisely with this anion we shall observe the largest correlation of those cations, which have high content of equivalents. Actually, in the series 4 the part of (Ca^{2+} + Mg^{2+}) is 61.4% of equivalents of all cations or it is close to the SO_4^{2-} content (67.7%) is in the anion content (Table III) and their correlation coefficient is large (0.67, Table IV). However, for the series 3 at large sampling fraction of NH_4^+ (58.8%) the correlation coefficient with SO_4^{2-} is small (0.19), although in the other series it can be 0.98 (series 6). It is evident that the complex nature of mechanisms of aerosol particles transformation in the atmosphere, especially taking into account such variable processes as aerosol particle transport by air, inner and undercloud wash out by wet precipitation is well presented by the WSPA ion composition.

TABLE IV. Coefficients of pair ion correlation in the dynamics of WSPA composition.

Ions	Series 1				Series 2				Series 3			
	(Ca + Mg)	NH_4^+	Na^+	K^+	(Ca + Mg)	NH_4^+	Na^+	K^+	(Ca + Mg)	NH_4^+	Na^+	K^+
F^-	0.24	−0.28	−0.26	−0.39	0.39	0.49	−0.15	0.23	0.43	0.16	0.49	0.19
Cl^-	0.11	−0.45	−0.42	0.06	−0.13	0.86	−0.25	−0.12	0.43	0.14	0.57	0.39
NO_3^-	0.42	0.39	−0.09	−0.20	0.36	0.69	−0.06	0.56	−0.01	0.41	0.29	0.20
SO_4^{2-}	0.45	0.71	0.56	−0.24	0.51	0.05	0.53	0.44	0.39	0.19	0.76	0.45
		Series 4				Series 5				Series 6		
F^-	0.47	0.08	0.09	0.18	−0.03	−0.32	0.09	−0.38	0.47	0.58	0.43	062
Cl^-	0.24	0.12	0.16	0.22	0.49	−0.36	0.36	0.21	0.58	0.52	0.20	0.54
NO_3^-	0.60	0.39	0.32	0.23	0.76	−0.09	0.25	0.13	0.74	0.69	0.62	0.65
SO_4^{2-}	0.67	0.45	0.31	0.64	0.27	0.79	0.20	0.36	0.67	0.98	0.83	0.94

TABLE V. Values of the relation X_{WSPA}/X_{WP} in winter and summer.

Period	NH_4^+	(Ca^{2+} + Mg^{2+})	Na^+	K^+	F^-	Cl^-	NO_3^-	SO_4^{2-}
Summer, 1994	–	–	–	–	1.50	0.18	0.28	1.84
Winter, 1994–1995	–	–	–	–	0.88	0.05	0.59	3.24
Summer, 1995	0.27	1.85	2.17	0.54	1.58	0.20	0.90	1.39
Winter, 1995	1.97	0.67	1.37	0.95	0.75	0.14	1.07	2.23
Summer, 1996	0.92	0.95	1.02	0.89	1.71	0.61	0.57	1.98

Comparison of ion composition of WD and WSPA.

Although the direct comparison of concentrations of individual ions in the solution (WD) and solid particles (WSPA), expressed in different units, is incorrect, we can compare the fractional ion distribution in WD and WSPA. Such a comparison is given in Table V as the relation of a fraction of a given ion equivalent in aerosols, X_{WSPA}, to its fraction in wet precipitation, X_{WD}, with the use of our previous observations at the same points.[8,9]

As is seen from these data, aerosol particles, as compared with wet precipitations, are enriched with sulfates and are depleted in chlorides to a greater extent in winter. The content of ammonium and fluorides in winter aerosols is larger than in precipitation. For the remaining ions the seasonal periodicity of their fractional distribution in WD and WSPA does not manifests itself markedly. It is believed that these regularities are connected with seasonal difference in the aerosol particle size spectrum since it is known that sulfates and ammonium are concentrated in small particles while chlorides and nitrates are concentrated in larger particles.[2] However, the causes may be different (for example, seasonal differences in the composition of substances transported to the atmosphere from local or removed ground sources). Their refinement needs further studies.

CONCLUSION

Determination of ion composition of atmospheric components makes it possible to obtain the information on the conditions of their formation and transformation due to interactions between them. Simultaneous observations of ion composition of surface aerosol and wet precipitation in winter and summer of 1995–1996 in the south of West Siberia show that their formation differ as demonstrated by the distinctions in fractional distribution of ion equivalents of WD and WSPA. Not only the large fraction of lithophylic elements (sodium, calcium, magnesium) is unusual but also its increase during winter period when snow cover isolates the local ground sources of the elements transport to the atmosphere. The fraction of chlorides increases in WD composition in winter. Taking these facts into account as well as the prevailing southwest winds it is believed that the atmospheric transport of the soil salts from the regions of the Northern Kazakhstan and the Aral Sea affects the ion composition of atmospheric components in the Novosibirsk region.

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