

MONITORING OF ION COMPOSITION OF ATMOSPHERIC AEROSOLS AND PRECIPITATION IN THE NOVOSIBIRSK REGION IN 1994–1997

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Experimental data on ion composition of atmospheric aerosol (ICAA) and fresh atmospheric precipitation (ICAP) obtained at three observation sites in the Novosibirsk region in winter and summer seasons for the period of 1994–1997 are discussed in the context of stoichiometric composition and statistical factor analysis. A regional peculiarity of ICAA and ICAP is a large contribution of terrigenous sources of their formation. This peculiarity is supposedly caused by the atmospheric transport of terrigenous salts from the Northern Kazakhstan, Aral Sea, and Caspian Sea.

INTRODUCTION

The investigation of spatial and temporal dynamics of chemical composition of atmospheric components is of interest in studying the regional factors of their generation, transformation, transfer, and sink. The data on the ion composition of a water-soluble part of atmospheric aerosols (ICAA) and wet precipitation (ICAP) make it possible to determine the contributions of gas-phase and erosion components in processes of their formation based on taking account of the ratio between ions of atmophile and lithophile elements. These data are of practical use due to the problem of "acid rains" caused by the deficit of cations neutralizing anions generated in the atmosphere from a gas phase or incoming with volatile acids from the ground surface.^{1–3}

Joint study of ICAA and ICAP at the same observation sites extends the capabilities of analysis of the factors of formation, transport, and sink of atmospheric components. Organization of such observations in the Siberian region is one of the problems of the complex project "Siberian Aerosols."⁴ The data obtained in 1994–1996 show that in the south of the Western Siberia ICAA and ICAP are characterized by the increased fraction of lithophile elements that may be a result of the far atmospheric transport of salts of ground origin.^{5–7} In 1997 these observations are being continued and together with the previously obtained data they enable us to generalize the data over a sufficiently long period.

EXPERIMENTAL PROCEDURE

We observed the ICAA and ICAP at the following sites: site 1 is at 30 km to the south-south-east of

Novosibirsk, 57°50'N, 83°10'E, partially-wooded steppe zone; site 2 is at 80 km to the south-south-west of Novosibirsk, 57°30'N, 82°50'E, forest zone; site 3 is close to Karasuk town, 53°45'N, 78°05'E, steppe zone.

In freshly precipitated samples of rain and snow (after thawing), we measured the pH factor and electrical conductivity χ , as well as concentration of NH_4^+ , Na^+ , K^+ , F^- , Cl^- , NO_3^- , SO_4^{2-} ions (by the method of ion chromatography), the sum of $(\text{Ca}^{2+} + \text{Mg}^{2+})$ and HCO_3^- (by the method of conductimetric titration). Taking into account the H^+ concentration calculated from the pH factor, we checked the balance between the sum of cation equivalents ΣCat and that for anions ΣAn and the agreement between the measured and calculated values of χ . These procedures have made it possible to estimate not only the error of separate analytical determinations, but also the completeness of data on the ion composition of samples. As a rule, the discrepancy between compared values did not exceed 10% that sites to the lack of large amounts of other ions in samples.

Freshly precipitated snow was sampled at the site 1, rain was sampled at the site 2; for the site 3 we had only the snow sample sampled later in winter.

Every-day sampling of surface aerosol at sites 1–3 in winter and summer seasons was made onto the filters of AFA–KhA type at air circulation volume rate of $13 \text{ m}^3/\text{h}$. The mass of aerosol particles M was found from the difference in the filter weight before and after exhibition, and it was related to the content in 1 m^3 of air. The part of the exhibited filter was placed in the container with 10 ml of demineralized water for a day, then the filtrate was analyzed by the same methods as wet precipitation.

RESULTS AND DISCUSSION

The averaged data of ICAP observations at the sites 1 to 3 in winter and summer seasons of 1994–1997 are presented in Table I as a contribution of equivalent of a given ion relative to ΣCat and ΣAn , respectively; here the values of pH and general mineralization $\Sigma\Sigma$ are also given. The distribution of the ion equivalent contributions indicates their stoichiometric

ratios in precipitation and does not depend on absolute concentrations. This makes it possible to compare the ion composition of not only wet precipitation under different conditions of their formation, but also to compare ICAA and ICAP, although the initial data on the ion concentrations are normalized to different measurement units (eq/m^3 of air for aerosols and eq/liter for wet precipitation).

TABLE I. Averaged data for ICAP at sites 1–3 in summer and winter seasons.

Site, season	$\Sigma\Sigma$, mg/l	pm	ΣCat , $\mu\text{mol}/\text{l}$	ΣAn , $\mu\text{mol}/\text{l}$	NH_4^+	m^+	$\text{Ca}^{2+} + \text{Mg}^{2+}$	Na^+	K^+	$\text{m}\text{q}\text{O}_3^-$	F^-	Cl^-	NO_3^-	SO_4^{2-}
	% of equivalents													
Summer														
2, 14.06–25.09.94	7.8	5.58	109	105	33.5	6.1	16.4	31.2	12.8	21.9	2.9	23.6	16.2	35.0
2, 16.06–18.09.95	7.8	5.25	121	108	41.9	6.4	18.1	21.5	12.1	11.7	1.9	22.0	16.0	47.4
2, 24.06–24.09.96	8.3	5.44	119	113	35.0	5.4	38.1	13.2	8.6	29.1	3.4	14.2	17.1	36.2
2, 27.06–19.09.97	16.0	5.79	230	220	37.3	2.0	35.7	15.2	9.8	40.3	3.1	12.4	16.4	27.9
Winter														
1, 21.11.94–15.03.95	11.3	5.76	167	164	43.2	1.1	10.1	43.2	3.4	13.5	4.1	32.6	23.1	26.7
1, 25.10.95–28.04.96	11.9	5.72	181	171	10.5	1.1	55.2	26.6	6.6	18.9	2.7	28.6	16.2	33.8
1, 20.10.96–14.03.97	9.2	5.50	172	159	16.9	3.6	61.6	12.4	5.2	15.4	8.8	18.2	24.4	33.1
3, 20.10.96–15.02.97	7.0	6.03	95	82	22.9	1.0	51.0	16.7	8.3	34.6	4.9	19.8	21.0	19.8

The net mineralization $\Sigma\Sigma$ of rainfall precipitation at the site 2 in 1997 turned out to be about twice as much as in 1994–1996 that evidently is due to small amount of precipitation. In winter precipitation, this amount is higher than in summer, although for the site 3 spaced from sites 1 and 2 by about 500 km the lowest mineralization of wet precipitation was observed in 1996–1997. It is believed that the data on ICAP for the sites 2 and 3 show the regional background level.

The mean acidity of precipitation in winter and summer seasons is close to the calculated one at equilibrium of distilled water with air at the background level of content of gaseous ammonia, carbon and sulfur dioxides ($\text{pH}=5.8$, Ref. 1). This means that the continuous factors of precipitation oxidation and alkalizing of natural and anthropogenic character were lacking in the region of the observation period. However, the neutralizing effect of cations was provided not only by ammonia, but also by the cations of lithophile elements to a great degree. Really, the data of Table I show that the contribution of lithophile elements exceeds the contribution of NH_4^+ , and in winter season even to a larger degree than in summer season. In this case, the sulfates are not dominating in the anion composition and their contribution is approximately the same for rains and snows.

These results differ from the data for the other regions. In Ref. 3, noted is the direct relations between acidity and sulfate concentration in precipitation found by a number of researchers in Eastern Europe, European part of Russia, USA, and Canada, as well as the fact of decrease of this dependence for snow precipitation. It is evident from our data that in the

south of the Western Siberia this relation does not manifest itself. It is apparently the regional characteristic property of the factors of ICAP formation. Another characteristic property is the high content of chlorides in the anion composition, which increases in winter precipitation. It is generally agreed that the chloride component in precipitation is almost totally of marine origin, and its contribution decreases rapidly as moving away from seas and oceans.¹ Consequently, the chloride source in wet precipitation in the Novosibirsk region should be of different origin. Because the chloride contribution remains significant at the observation sites separated by a distance of more than 500 km and manifests itself constantly, anthropogenic activity is unlikely the source of chlorides; the action of a natural ground factor of regional character is most probable.

Thus, the stoichiometric composition of atmospheric precipitation in the Novosibirsk region is determined by approximately equal ratio of hydrocarbonates, chlorides, nitrates and sulfates, significant part of which is neutralized by the cations of lithophile elements of terrigenous origin. In this connection, of interest is the comparison of the stoichiometric composition of atmospheric precipitation and aerosols in observations coinciding in time and place. Table II gives the data on ICAA in the form similar to Table I; in this case, $\Sigma\Sigma$ denotes the net mineralization of water-soluble fraction of aerosol particles, Ug/m^3 ; W denotes its part in the total mass, %; ΣCat and ΣAn are expressed in $\text{ng}\text{-eq}/\text{m}^3$.

Mass concentration of aerosol particles and the water-soluble fraction in summer is lower than in

winter that accounts for higher snow mineralization with respect to rains. The lowest values of $\Sigma\Sigma$ (2.00–2.21) recorded at site 2 are comparable with the value $1.13 \text{ } \mu\text{g}/\text{m}^3$ from the data of Ref. 8 obtained during summer period for the high-mountain station Mondy in

the south of the Eastern Siberia. This value reflects, on the authors opinion, the global aerosol background. It is believed that the data on ICAA for the site 2 represent the regional aerosol background for the south of the Western Siberia.

TABLE II. Averaged data for ICAA at sites 1–3 in summer and winter seasons.

Site, season	$\Sigma\Sigma$	W	ΣCat	ΣAn	NH_4^+	m^+	$\text{Ca}^{2+} + \text{Mg}^{2+}$	Na^+	K^+	mq O_3^-	F^-	Cl^-	NO_3^-	SO_4^{2-}
Summer														
1, 18.08–02.09.95	4.09	9.1	65	60	21.0	0	47.7	24.3	7.0	0	1.7	12.2	6.6	79.6
2, 21.08–07.09.95	3.51	9.1	58	54	12.0	0	35.7	48.9	3.3	–	3.0	4.7	16.2	76.2
1, 05–30.06.96	2.53	3.4	42	36	16.2	0	61.4	12.3	10.0	–	6.0	12.6	13.8	67.7
2, 07–28.07.96	2.00	6.9	32	29	43.3	2.0	36.2	11.4	7.1	0	5.6	8.0	4.7	81.8
1, 14.06–14.07.97	4.14	7.3	49	44	14.2	1	69.0	8.8	7.0	31.7	2.8	4.4	11.6	49.5
2, 14–31.07.97	2.21	6.0	35	33	31.6	2.9	44.8	14.8	5.8	5.4	10.0	4.7	10.6	69.3
3, 20.06–19.07.97	4.28	7.1	59	55	30.0	9.8	42.1	9.4	8.7	10.2	4.2	4.7	10.0	70.9
Winter														
1, 29.11–28.12.95	5.80	18.7	83	82	11.8	0	36.7	46.3	5.2	–	1.8	4.2	14.6	78.5
1, 22.10–26.11.96	5.65	–	78	85	37.3	0.6	45.2	11.9	4.8	1	4.4	3.0	15.7	75.9
1, 11.02–12.03.97	7.05	22.2	105	129	48.7	8.5	30.4	8.5	4.2	2.1	2.2	1.0	12.8	81.9
3, 19.02–20.03.97	8.00	31.6	110	119	63.7	3.8	21.7	6.5	4.3	1.8	0.7	0.9	16.0	80.6

The maximum values of $\Sigma\Sigma$ and W were recorded at site 3 in winter of 1997. This is not consistent with the low level of snow mineralization at the same site (see Table I) and can be explained only as the effect of a local source of aerosol particles.

As in wet precipitation, lithophile elements contribute considerably to the cation composition of ICAA, especially in summer. Deeper differences can be seen when comparing the data shown in Tables I and II: the share of chlorides in ICAA decreases sharply (especially in winter) and the share of sulfates increases. If the shares of sulfates, chlorides and hydrocarbonates are approximately equal in ICAP, sulfates dominate in ICAA. It should be particularly emphasized that a considerable fraction of sulfates is connected not with atmophile ammonia that is characteristic of typical continental regions,^{1–3} but with lithophile calcium, magnesium, and sodium.

Supplementary information on the factors of ICAA and ICAP formation can be obtained from the data of the statistical factor analysis of variability of ion concentrations in discrete samples in every series of observations. Some of these data are given in Table III as the values of the factor load of every ion (the values greater than 0.69 are denoted by boldface type) and the fraction of each factor in the common variability of parameters. Here, N is the number of discrete samples, for which the statistical analysis was made. High correlation of concentration variability of one or other type of ions in one factor (cluster) indicates that their source in ICAA or ICAP is common. The "acid" factor (association of high values of load for H^+ , SO_4^{2-} , NO_3^- in the common cluster) and the "marine" factor (combination of Na^+ , Mg^{2+} , and Cl^- ions), and the "soil-erosion" factor (combination of ions of lithophile elements) are distinguished; the association of SO_4^{2-} ,

NO_3^- , and NH_4^+ at low correlation with H^+ variability are assigned to the effect of the "well-aged aerosol."⁹

Based on the data presented in Table III, in the region of our observations the effect of these factors manifests itself in different combinations. In separate series of observations, the effect of "acid" factor stands out. It is demonstrated by the correlation, in $F1$, of the variability of H^+ , SO_4^{2-} , NH_4^+ at the site 1 for the period from October 22 to November 26, 1996, and the variability of H^+ , SO_4^{2-} , HCO_3^- , and Cl^- at the same site from February 11 to March 12, 1997. Nonacid factor of gas-phase formation of aerosol particles (correlation of SO_4^{2-} , NO_3^- , and NH_4^+) such as $F2$ is noticeable for the sites 1 and 3 in February–March, 1997. Terrigenous sources (correlation of concentration variability of Ca^{2+} , Mg^{2+} , Na^+ with HCO_3^- and Cl^-) turned out to be most significant in summer observations of ICAA and ICAP at the site 2 in 1996. The "marine" factor (high correlation between Na^+ and Cl^-) stands out as an independent cluster in some situations in both winter and summer seasons (ICAA, site 1, June 14–July 14, 1997; October 22–November 26, 1997).

In some series of observations (especially for ICAP), the joint action of gas-phase and terrigenous sources takes place. This results in the formation of a common cluster $F1$ for ammonium and lithophile cations in combination with nitrate and sulfate (ICAP at the site 2 in summer of 1997, at the site 1 in winter of 1996–1997, ICAA at the site 3 in summer of 1997). It is believed that such a superposition of different sources of matter in symbiotic variability of ICAA and ICAP reflects the effect of rapid neutralization of gas-phase components of the atmosphere by salts carried off the ground surface. The presence of the "marine" factor has engaged our

TABLE III. Data of statistical factor analysis of ICAA and ICAP at the sites 1–3.

Ion composition	ICAP						ICAA									
	Site 2, 24.06–24.09.96 N = 34				Site 2, 27.06– 19.09.97 N = 23		Site 2, 07–28.07.96 N = 21			Site 1, 14.06–14.07.97 N = 27			Site 3, 21.06–19.07.97 N = 24			
	F1	F2	F3	F4	F1	F2	F1	F2	F3	F1	F2	F3	F1	F2	F3	
	Summer															
NH ₄ ⁺	0.471	0.389	0.130	0.715	0.853	0.172	-0.151	-0.896	-0.120	0.801	-0.439	-0.020	0.904	0.035	-0.021	
Ca ²⁺ +Mg ²⁺	0.898	0.305	0.149	0.113	0.188	0.952	0.723	0.474	0.318	0.509	0.205	0.775	0.792	-0.305	0.412	
Na ⁺	0.590	0.025	0.095	0.678	0.916	0.253	0.847	-0.324	-0.171	-0.203	0.920	-0.110	0.055	0.002	0.845	
K ⁺	0.031	0.196	0.169	0.898	0.829	0.463	-0.104	-0.235	0.846	0.831	0.118	0.168	0.551	0.140	0.726	
H ⁺	-0.478	-0.198	-0.583	-0.137	-0.136	-0.409		-			-		-0.133	0.891	0.145	
mCO ₃ ⁻	0.932	0.058	0.162	0.079	-0.016	0.896		-		0.043	-0.053	0.949		-		
F ⁻	-0.020	-0.030	0.927	0.134	0.832	-0.097	0.893	0.160	0.095		-		0.201	-0.208	0.614	
Cl ⁻	0.781	-0.010	-0.102	0.434	0.910	0.217	0.861	0.350	0.009	0.258	0.772	0.266	-0.030	-0.834	0.336	
NO ₃ ⁻	0.350	0.767	0.429	0.037	0.668	0.600	0.292	0.422	0.586	0.600	0.252	0.495	0.609	-0.158	0.603	
SO ₄ ²⁻	0.000	0.911	-0.153	0.322	0.634	0.598	-0.053	-0.916	0.252	0.937	0.008	0.271	0.916	-0.045	0.334	
True share	0.253	0.183	0.225	0.138	0.468	0.296	0.286	0.282	0.173	0.367	0.220	0.241	0.335	0.186	0.266	
	ICAP						ICAA									
Ion composition	Site 1, 25.10.95– 28.04.96 N=22		Site 1, 20.10.96– 14.03.97 N=34		Site 1, 29.11– 28.12.95 N=22		Site 1, 22.10–26.11.96 N = 32			Site 1, 11.02–12.03.97 N = 30				Site 3, 19.02–20.03.97 N = 30		
	F1	F2	F1	F2	F1	F2	F1	F2	F3	F1	F2	F3	F4	F1	F2	F3
	Winter															
NH ₄ ⁺	0.228	-0.885	0.786	0.365	0.904	-0.087	0.909	0.146	-0.170	-0.630	0.718	-0.140	0.101	0.200	0.949	-0.081
Ca ²⁺ +Mg ²⁺	0.928	0.265	0.775	-0.099	0.173	0.737	0.122	0.818	0.048	0.186	0.084	0.166	0.918	0.829	0.108	0.372
Na ⁺	0.363	0.766	0.537	0.296	-0.310	0.599	-0.286	0.278	0.855	0.335	0.248	0.662	0.132	0.311	0.093	0.662
K ⁺	0.721	-0.017	0.777	0.266	0.169	0.792	-0.142	0.847	0.64	0.115	0.631	0.502	0.075	0.538	0.690	0.109
H ⁺		-	0.279	-0.749		-	0.903	0.042	-0.011	-0.773	-0.265	0.361	-0.264	-0.719	0.561	-0.158
mCO ₃ ⁻	0.714	0.257	0.254	0.779		-	-0.536	0.080	0.009	0.835	0.047	0.142	0.110		-	
F ⁻	0.709	0.097	0.344	0.562	0.724	0.322	0.256	0.692	0.115	-0.085	0.013	0.762	0.298	-0.006	-0.100	0.714
Cl ⁻	0.395	0.691	0.823	0.318	0.867	-0.311	0.014	0.022	0.962	0.849	0.131	0.166	0.132	0.161	0.063	0.775
NO ₃ ⁻	0.846	0.061	0.773	-0.492	0.838	0.360	0.045	0.874	0.092	0.216	0.904	0.128	0.061	0.896	0.261	0.074
SO ₄ ²⁻	0.885	0.200	0.768	-0.073	0.019	0.824	0.866	0.288	-0.136	-0.769	0.168	-0.103	0.504	-0.082	0.936	0.079
True share	0.465	0.226	0.423	0.213	0.369	0.318	0.286	0.282	0.173	0.322	0.192	0.152	0.133	0.274	0.297	0.194

attention in the complex clusters with symbiotic variability of atmophile and terrigenous sources in both winter and summer periods (ICAP at the site 1 in winter, 1995–1996, and the site 2 in summer, 1997).

Thus, the data on the statistical factor analysis also point to a considerable contribution of terrigenous sources to the formation of chemical composition of atmospheric components in the Novosibirsk region. Peculiarity of these sources lies in the fact that they appear not only in summer period, but in winter, as well as in their chemical composition. Large portion of sodium and chloride in stoichiometric composition of ICAP and manifestation of the "marine" factor in variability of ICAA and ICAP point to the specific character of terrigenous sources being not characteristic of typical continental zones of other regions. Previously^{5–7} we made a proposal about the influence of atmospheric transfer of salts of surface origin from regions of the Northern Kazakhstan, the Aral and Caspian Seas in the aerosol sink in the south of the Western Siberia. Generalization of the material of the field observations made in 1994–1997 with the use of the statistical analysis of experimental data supports this proposal.

CONCLUSION

Organization of systematic observations of ion composition of atmospheric precipitation and aerosols in the vast area of Siberia makes it possible to compensate for a deficiency of the data on matter exchange in the "atmosphere – surface" system, as well as on the factors of generation and transformation, transfer and sink of atmospheric components. The complex studies of ICAA and ICAP were made in 1994–1997 at several sites of the Novosibirsk region located at a considerable distance from local technogenic sources and from each other. A comparison of mass aerosol concentration and the overall mineralization of wet precipitation with the data for the other regions enable us to assume that the selected sites represent the regional aerosol background for the south of the Western Siberia.

Stoichiometric ratios of molar concentrations of ions and the data of statistical factor analysis indicate the existence of regional peculiarities in ICAA and ICAP manifesting themselves in a large contribution of terrigenous sources not only in summer, but also in winter periods, when the local ground-based sources are isolated by snow cover. The gas phase processes of ICAA generation are supplemented by reactions of neutralization with the salt cations from the ground-based sources that results in the absence of oxidation of wet precipitation. We noted the difference in ion composition of aerosol particles and wet precipitation, which is most pronounced in the chloride-to-sulfate ratio. These regional peculiarities of ICAA and ICAP may be the result of atmospheric transfer of terrigenous salts from regions located to the south-west of the Novosibirsk region. For further testing of this conclusion, it would be useful to combine the observations of chemical composition of atmospheric components with study of the dynamics of the air mass transfer.

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