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Ion and elemental composition of the atmospheric aerosol over West Siberia in 1997-2001

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ABSTRACT

Some results of analysis of more than 400 aerosol samples made over West Siberia regions during last almost five-year studies onboard airborne laboratory are presented. Analysis of samples enabled us to reconstruct differential distributions of ions and elements. The chemical matrix for Si, Al, Fe, Mg, Ca, Ti, Cu, Mn, Cr, Ag, Pb, Ni, Ba, Sn, V, Mo, Co, B, K^+ , Na^+ , Cl^- , SO_4^{2-} , NO_3^- , Br^- , F^- , NH_4^+ and their vertical profiles were computed.

Also analysis of differences in the chemical composition of near-ground aerosol is conducted based on the measurements at two points (Tomsk city and Kireevsk village) located at a 60-km distance from each other in summers 1997-1998. Significant differences caused by the impact of local sources and by the differences in the air masses are found for some chemical elements and ions.

Keywords: airborne sounding of atmosphere; atmospheric aerosol, background, natural, anthropogenic; chemical (ionic and elemental) composition of aerosol.

1. INTRODUCTION

Data on chemical composition of atmospheric aerosol is very important for the understanding a wide range of problems in atmospheric physics and optics. Chemical composition of aerosol particles determines their refraction index and, consequently, regularities of dissipation and absorption of solar radiation in the atmosphere. Aerosol particles can contain heavy metals with carcinogenic properties. Therefore some investigations are of an ecological importance. Also a dissolution of sulphate aerosol particles in cloud drops results in formation of acid rainfalls. Thus, the study of chemical composition of aerosol is an important part of atmospheric studies. Therefore, in recent two decades intense investigations of the aerosol chemical composition are being carried out round the world.

The investigations show that, in spite of the great variability of the aerosol chemical composition at its transfer and transformation in the atmosphere, this characteristic has some conservatism and can provide for the data on the origin of air mass coming to the observation site¹⁻³. At the same time, only macroscale¹⁻³ or microscale^{4,5} variation of the aerosol chemical composition are now well studied because of the difficulties to organize such observations. The data on how stable are the mesoscale parameters of the aerosol chemical composition, are insufficient.

Some results of analysis of more than 400 aerosol samples made over this region during last almost five-year studies onboard airborne laboratory as well as about 65 pairs of near-ground aerosol samples are presented in this paper.

2. SITES AND METHODS

2.1 Airborne measurements

Institute of Atmospheric Optics has been carrying out regular (1 flight per month) airborne sounding over southern regions of West Siberia since July 1997. Airborne surveys have been performed onboard "Antonov-30" aircraft laboratory in the 500 to 7000 m atmospheric layer mainly over forest zone on the right bank of southern part of Novosibirsk impoundment (so called "Ob' Sea") near boundary of Novosibirsk and Altai regions, and, on several occasions, over forest marshland of Tomsk region (near Plotnikovo village) not far from Novosibirsk region boundary.

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In our studies we try to perform flights under clear sky weather conditions. Aerosols are sampled onto Petryanov filters (AFA-type) during 10-15 min time period at each level. The volume of air pumped through each filter is from 1 to 4 m³. Then aerosol samples are analyzed in the Analytic Chemistry Laboratory of Environmental Monitoring at the Tomsk State University. Physico-chemical techniques of quantitative analysis of the chemical composition of aerosol matter are given in table 1.

Table 1. Detectability threshold and accuracy of techniques used in analysis of atmospheric aerosol samples collected on Petryanov filters.

Chemical component	Technique	Threshold, µg/filter	Accuracy, %
Br ⁻ , NO ₃ ⁻ , SO ₄ ²⁻	Ion chromatography	0.6	8
Cl ⁻	Ion chromatography	0.1	12
F ⁻ , NH ₄ ⁺ , NO ₃ ⁻	Ionometry	0.2	10
Na ⁺ , K ⁺	Atomic absorption	0.2	10
Ag, Ba, Cu, Mg, Mn, Pb, Sn, V	Atomic-emission spectroscopy	0.01	20
Al, B, Co, Cr, Mo, Ni, Si, Ti, Zn	Atomic-emission spectroscopy	0.02	20
Fe, Ga, W	Atomic-emission spectroscopy	0.1	20
Ca, Cd	Atomic-emission spectroscopy	0.2	20

2.2 Ground-based measurements

Investigations of the aerosol chemical composition are being carried out at the Institute of Atmospheric Optics at two sites, the background one in the rural area of Tomsk region, and an urban one near the city of Tomsk. An attempt is undertaken in this paper to estimate the differences in the aerosol chemical composition at these two sites that are located at a 60-km distance from each other. For that we use the measurements data obtained in summer 1997 and 1998.

Two identical setups were used for sampling the atmospheric aerosol. One of them was deployed in Akademgorodok (suburban zone near Tomsk), and the other one at the field site near Kireevsk village (rural area 60 km westerly Tomsk). Aerosol samples were collected synchronously during a day at two sites on the Petryanov filters. Air volume from 200 to 600 m³ was pumped through the filters during a day. The methods used in this analysis were the same (tabl.1). To plot wind roses of concentrations we used 700-850 hPa absolute topography maps (AT-700, AT-850) or wind velocity readouts from TOR-station¹² monitoring complexes in both sites.

It is important to emphasize that there were other sources of errors in using these methods for investigation of atmospheric aerosol, in addition to those presented in Table 1. The errors in determining the rate of pumping or air volume passing through them could appear during aspiration, i.e., the errors in determining the weight of the aerosol substance collected on the filter. According to data from Ref. 6, the errors occurring at exposition of the filter should not exceed 25% if all necessary requests are met. Hence, the total relative error of a single determination of the aerosol chemical composition does not exceed 45–50%, and decreases by \sqrt{n} times at averaging over n samples.

3. RESULTS AND CONCLUSIONS

3.1 Results of airborne measurements

Analysis of samples enabled us to reconstruct smoothed histograms of ion and element differential distributions of aerosol matter (fig.1). The number of samples in which concentration of element or ion was higher than a detection limit is given in brackets. Ranges of frequency distributions are in accordance with X-scales points ($>1.25E-05 \dots 2.5E-05$; $>2.5E \dots 0.00005$ – the next; etc.).

Average ion and element concentrations for the chemical matrix of aerosol inclusive Si, Al, Fe, Mg, Ca, Ti, Cu, Mn, Cr, Ag, Pb, Ni, Ba, Sn, V, Mo, Co, B, K⁺, Na⁺, Cl⁻, SO₄²⁻, NO₃⁻, Br⁻, F⁻, NH₄⁺ (fig.2) were computed taking into account a differential distribution in order to except abnormally high values (tabl. 2).

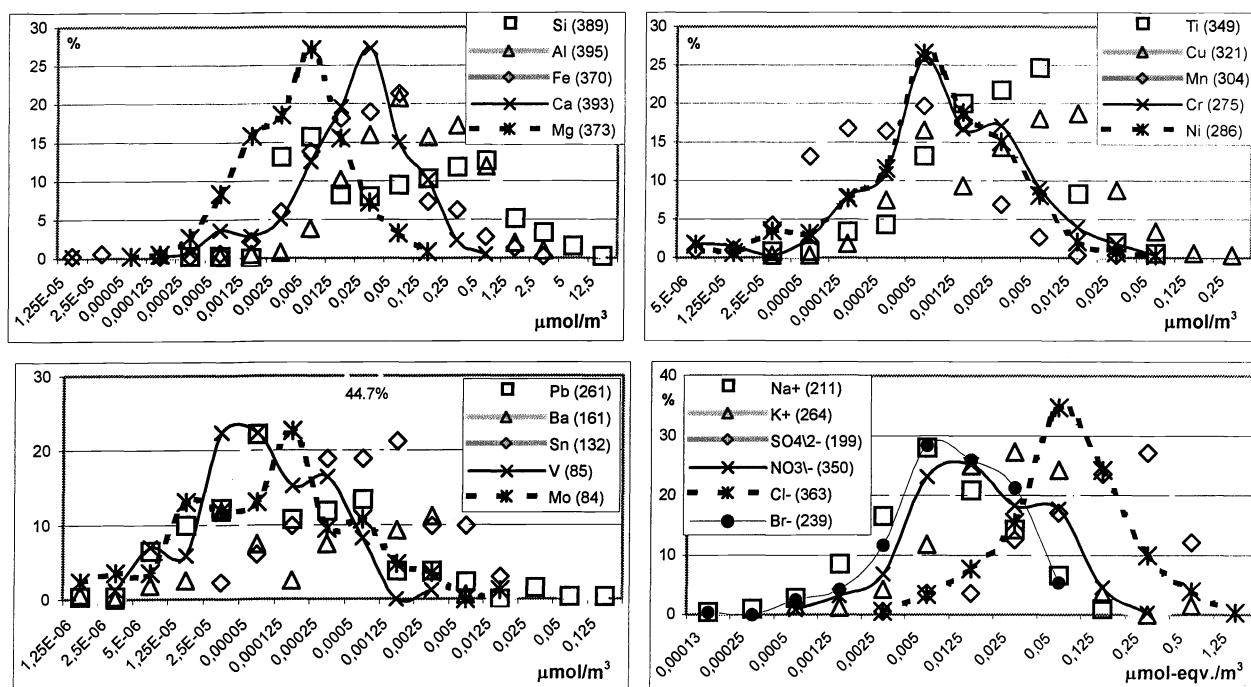


Fig. 1. Differential distributions of ion and element concentrations in the atmospheric aerosol over West Siberia.

Table 2. Database structure of the chemical composition of atmospheric aerosol sampled over West Siberia during 1997-2001 and results of statistical processing at significance level $P = 0.1\%$ * (values of concentration are given in $\mu\text{g}/\text{m}^3$)

	N	$N_{>\text{threshold}}$	Max. val.	N*	Max. val.*	Means*	Std. dev.*
Cu	370	321	30.864	299	2.124	0.5069	0.5410
Ag	332	35	0.100	26	0.003	0.0014	0.0004
Ti	400	349	3.505	328	0.769	0.2026	0.1858
Sn	400	132	2.038	115	0.477	0.1335	0.1228
Ca	400	393	27.985	319	3.333	1.0208	0.7645
V	400	85	0.193	84	0.037	0.0088	0.0096
Al	400	395	94.637	349	16.400	4.0863	4.0382
Fe	400	370	161.856	306	7.035	1.9126	1.6960
Si	400	389	658.242	311	16.000	3.1177	4.1971
Pb	400	261	27.054	225	0.199	0.0419	0.0516
Cr	400	275	3.230	246	0.332	0.0837	0.0819
Mg	400	373	5.892	332	0.612	0.1625	0.1471
Mn	400	304	2.323	275	0.149	0.0367	0.0372
Ni	400	286	3.665	261	0.320	0.0804	0.0794
Ba	400	161	1.271	156	0.460	0.1199	0.1143
Mo	352	84	2.333	73	0.067	0.0150	0.0171
B	183	31	2.680	30	0.474	0.1745	0.1508
Co	104	8	0.003	8	0.003	0.0023	0.0006
Na ⁺	402	211	5.750	192	1.003	0.2763	0.2420
K ⁺	402	264	31.700	250	4.240	1.3575	0.9771
SO ₄ ²⁻	402	199	52.740	194	36.585	10.9093	8.6683
NO ₃ ⁻	402	350	16.402	326	6.389	1.6761	1.5470
Cl ⁻	402	363	64.032	335	12.627	3.8568	2.9379
Br ⁻	334	239	8.901	234	4.562	1.3580	1.0724
NH ₄ ⁺	48	22	2.577	22	2.577	0.7106	0.8697
F ⁻	96	56	1.314	56	1.314	0.3614	0.3494

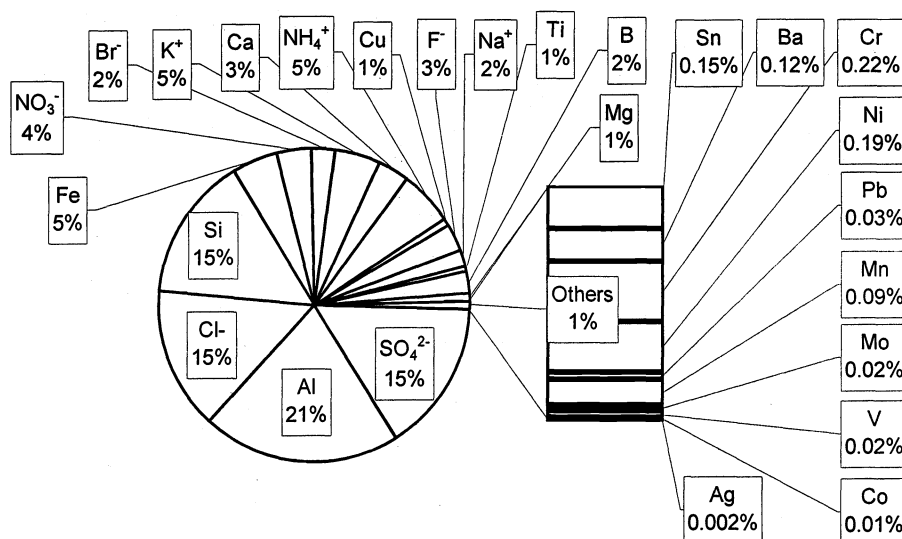


Fig. 2. Relative chemical composition (mol.%) of aerosol matter in the atmospheric layer from 500 to 7000 m over West Siberia based on the results of airborne sounding (1997-2001)

Data obtained during this study showed that at all altitudes there is a seasonal behavior of the concentrations of some elements and ions. Amplitude of the seasonal behavior is higher in the boundary layer. Concentration peaks at higher altitudes in the vertical distribution were observed during springtime that, most likely, can be a result of trans-boundary transport (fig.3).

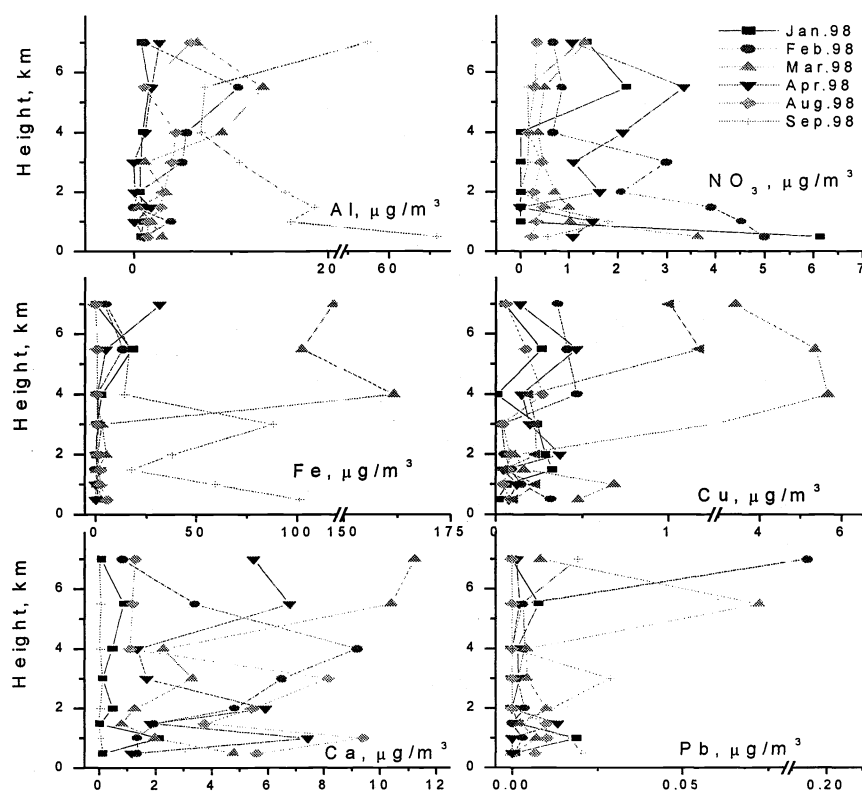


Fig. 3. Vertical profiles of a number of aerosol chemical components for different months 1998.

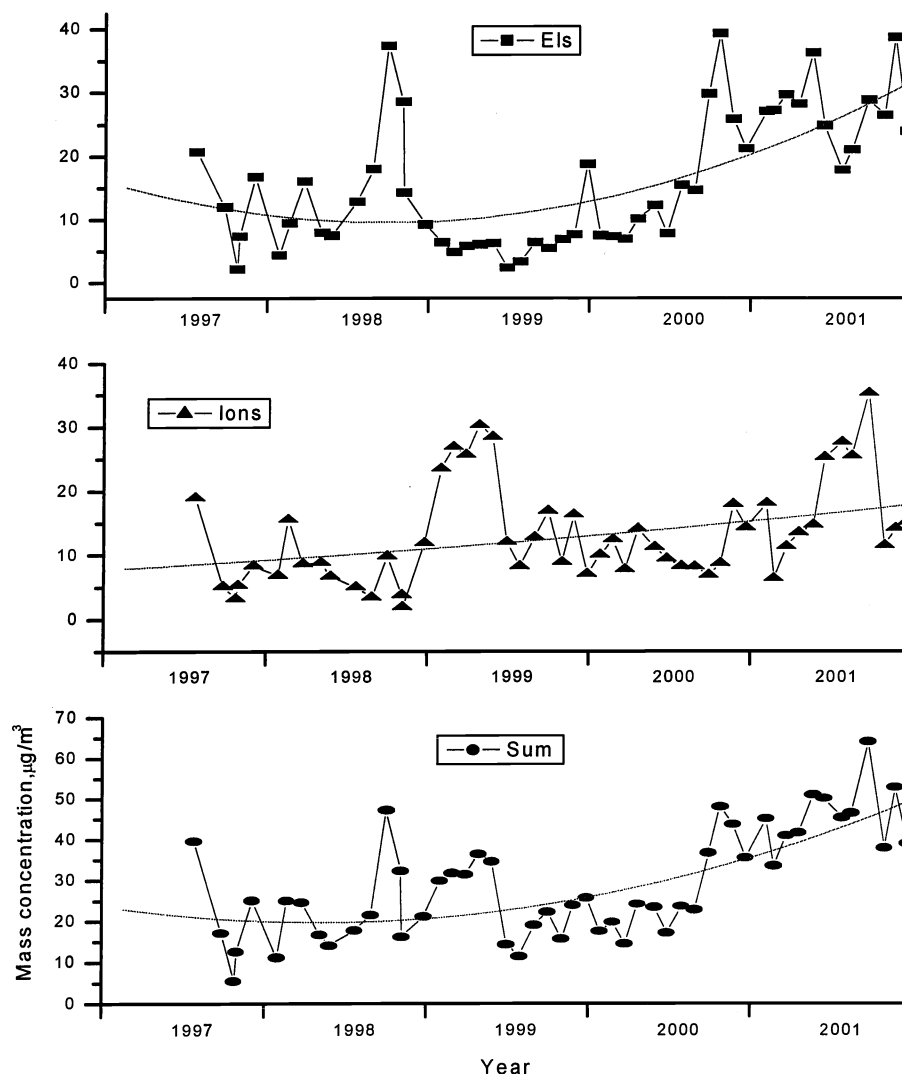


Fig. 4. Long-term behavior of total ion (Ions) and element (Els) concentrations, and their total sum (Sum) in aerosol matter; solid line - 4 order polynomial fittings.

Many-year behavior of total mass concentration of definable ions and elements, especially that of elemental part of aerosols, is in a good agreement with many-year behavior of the number concentration of atmospheric aerosol over West Siberia⁷.

3.2 Results of measurements in the surface atmospheric layer

The fractional diagram of the chemical composition of atmospheric aerosol including the principal components in Tomsk and Kireevsk is shown in fig. 5. The components, whose contribution exceeds 1% of the total aerosol mass, are included. It is seen from this figure that the principal components of the aerosol chemical composition at two sites are the same, although the relative contribution of some components is not the same. In principle, taking into account the nearness of two sites, one could expect this result in absence of the local sources of some compounds.

The elements and ions characteristic of terrigenous and sulfate aerosol prevail in the aerosol chemical composition, i.e., in the aerosol observed over continental regions⁸.

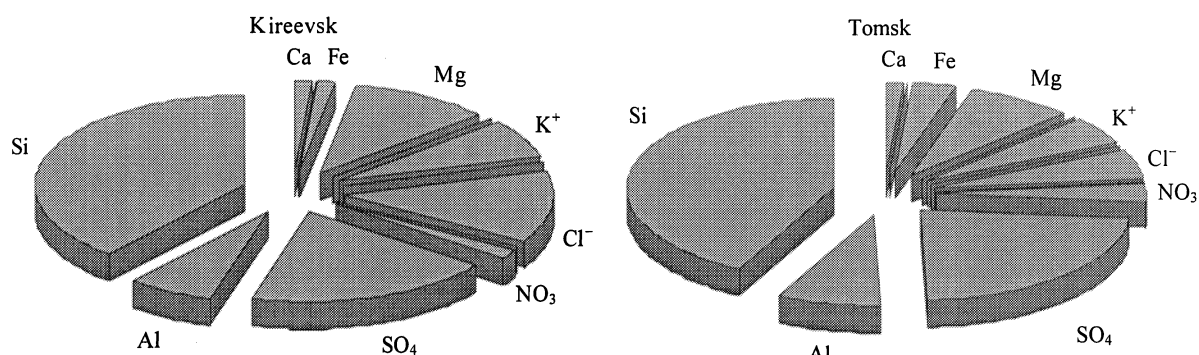


Fig. 5. Relative chemical composition of atmospheric aerosol in Kireevsk village and Akademgorodok (Tomsk) in the principal components.

The absolute and relative differences in the aerosol chemical composition averaged over 54 samples (25 in Tomsk and 29 in Kireevsk) in 1997 and over 75 samples (40 in Tomsk and 35 in Kireevsk) in 1998 are shown in Table 3.

The description of the meteorological parameters during the experiment is presented in Ref. 9. In addition to the meteorological conditions, precipitations also affect the aerosol composition. In 1997, 15 of 25 samples in Tomsk were collected on days with precipitation (18 of 29 in Kireevsk). The number of rainy days in 1998 was lower. Eleven samples of 40 in Tomsk were collected on days with precipitation (7 of 35 in Kireevsk).

Table 3. Mean and rms errors of the concentrations of elements and ions (ng/m^3), their absolute and relative (%) difference in Tomsk and Kireevsk in 1997 and 1998

Component	1997		1998		1997	1998	1997	1998
	Tomsk	Kireevsk	Tomsk	Kireevsk	Difference Tomsk-Kireevsk			
					absolute		relative	
Ca	73.15±34.28	58.66±34.39	39.29±23.23	148.18±241.03	14.49	-108.88	17	-124
Cr	0.62±1.23	4.92±10.75	1.22±1.23	0.40±0.52	-4.30	0.82	-127	24
Cu	10.20±10.18	15.04±14.02	0.81±0.66	17.83±32.72	-4.85	-17.03	-56	-196
Fe	163.88±111.63	60.33±49.43	47.06±18.72	352.33±421.53	103.55	-305.27	60	-177
Mg	423.08±362.50	452.97±290.67	50.49±15.19	21.72±16.20	-29.89	28.78	-15	15
Mn	12.60±11.12	12.48±12.21	7.52±12.23	6.25±12.30	0.12	1.27	1	9
Mo	0.34±0.35	0.55±0.63	0.04±0.17	0.13±0.29	-0.21	-0.08	-92	-36
Ni	0.66±0.96	0.68±1.81	0.12±0.16	0.07±0.29	-0.02	0.06	-3	7
Pb	4.19±3.94	3.39±5.58	1.72±0.85	0.36±0.60	0.81	1.36	42	71
Sn	1.62±2.31	6.99±14.89	0.08±0.02	0.07±0.07	-5.36	0.01	-320	1
Ti	20.40±14.07	9.93±5.40	21.04±11.08	3.56±6.71	10.46	17.48	43	72
V	1.04±0.71	0.47±0.43	0.20±0.09	0.14±0.22	0.57	0.07	168	20
K ⁺	256.00±99.28	288.28±124.42	50.20±35.28	110.19±93.54	-32.28	-59.99	-18	-33
Na ⁺	19.55±21.76	9.72±23.10	17.79±10.16	9.72±10.66	9.83	8.06	36	7
Cl ⁻	265.11±152.39	526.48±933.19	328.93±525.75	94.15±80.86	-261.37	234.78	-120	126
F ⁻	15.74±9.82	7.41±5.67	19.80±24.20	25.66±27.11	8.32	-5.87	50	-35
NO ₃ ⁻	159.37±122.55	71.95±96.63	115.97±62.04	95.58±89.29	87.42	20.39	93	22
SO ₄ ²⁻	1156.2±449.95	791.00±534.20	805.65±443.58	883.60±414.55	365.32	-77.94	23	-5
Al	417.48±251.37	272.83±218.28	-	106.36±132.17	144.65	-	67	-
Si*	2.14±1.49	1.61±1.14	-	-	532.60	-	44	-
B	4.31±2.00	3.08±2.79	-	-	1.22	-	33	-
Br ⁻	2.28±5.68	5.05±10.19	-	-	-2.77	-	-16	-
NH ₄ ⁺	8.56±14.39	0.90±1.86	-	-	7.66	-	18	-
Total*	3.02±1.26	2.60±1.59	1.51±0.67	1.88±0.79	414.00	-373.00	14	-13

* – mean and rms errors are in $\mu\text{g}/\text{m}^3$

It follows from Table 3 that in 1997 the total aerosol concentration in Tomsk was higher than that in Kireevsk. On the contrary, in 1998 it was higher in Kireevsk than in Tomsk. But one of the principal elements, Si, was not determined in the aerosol composition in 1998 due to technical reasons. Taking into account small difference in concentrations of some elements and compounds, there are few stable differences in Table 3. The concentrations of Pb, Ti, V, Na^+ , NO_3^- , and Mn are higher in Akademgorodok. The excess in Cu, Mo, and K^+ is observed in Kireevsk in both measurement seasons. Obviously, two factors are active here. The first is the proximity of Akademgorodok to Tomsk, hence, to the anthropogenic sources. The second is the difference in the chemical composition of soil and, hence, in terrigenous fraction of particles.

Relative deviations (the right-hand part of Table 3) were obtained by means of dividing the solute differences by the mean (for the specific region) values. Taking into account the number of the processed aerosol samples as well as the measurement errors, one can suppose that the deviations exceeding 55% are significant at the level of 99%. It follows from Table 3 that deviations exceeding this level were observed both in 1997 and in 1998. Twelve of 23 elements and compounds included in the Table 3 have significant differences in one of the measurement periods, and some have that in both periods.

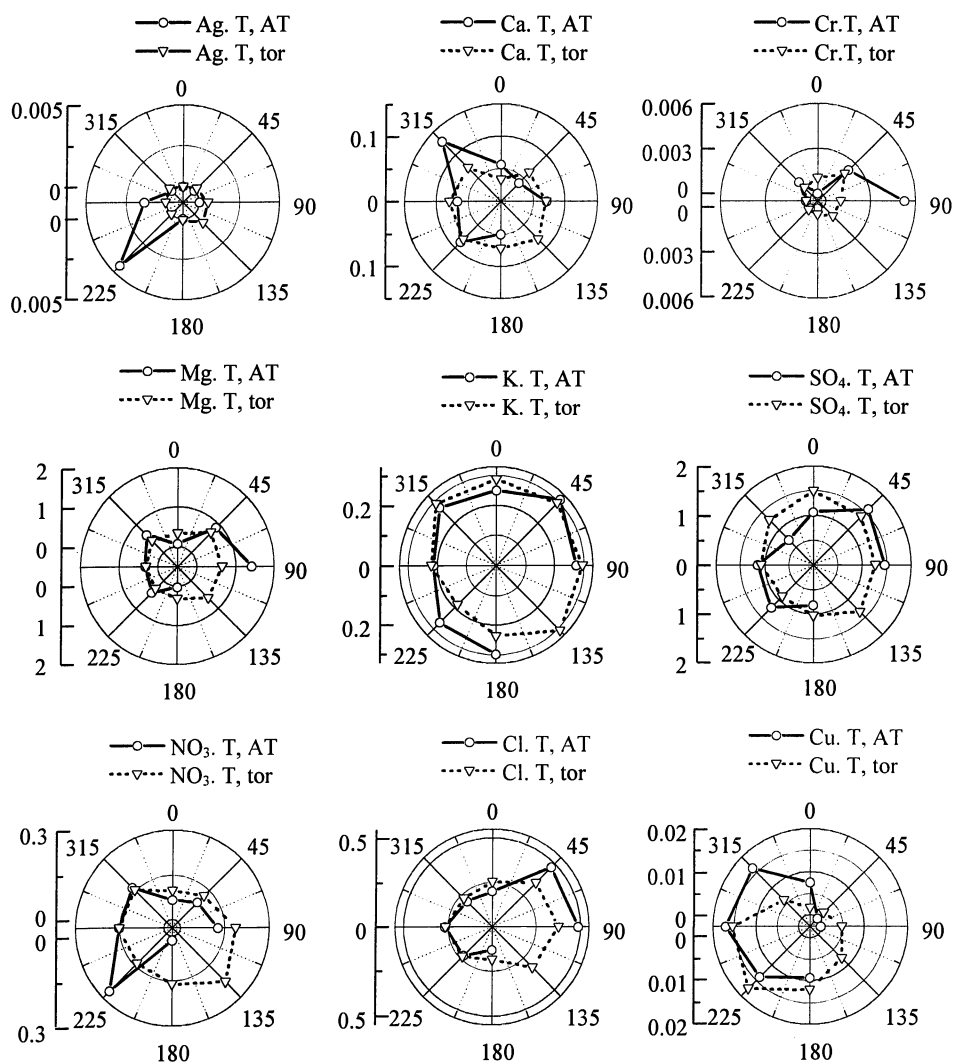


Fig. 6. Mean aerosol chemical composition ($\mu\text{g}/\text{m}^3$) in the region of Tomsk in 1997 for different directions of air transfer determined from the 700-850 hPa absolute topography maps (T, AT) and from the surface wind directions (T, tor).

Three reasons are possible that lead to the differences in the aerosol chemical composition. Two of them are characteristic of the aforementioned macro- and microscale levels. Third, at the mesoscale level, lies in the prehistory of air masses coming to the observation sites¹⁻³. Namely, as the specific circulation¹⁰ appears in the region of large industrial centers, air can come to Akademgorodok along different trajectories.

One can easily estimate two first factors by the permanently existing difference between the data obtained in Tomsk in Kireevsk on one or another compound (see Table 3). One can estimate the third factor by the wind direction at the site of measurements, or calculate the back trajectories along the governing flux using the pressure maps.¹⁻³ The first approach is justified in some cases. On the contrary, calculation of the back trajectories provides for better results in other cases when there are no local sources.

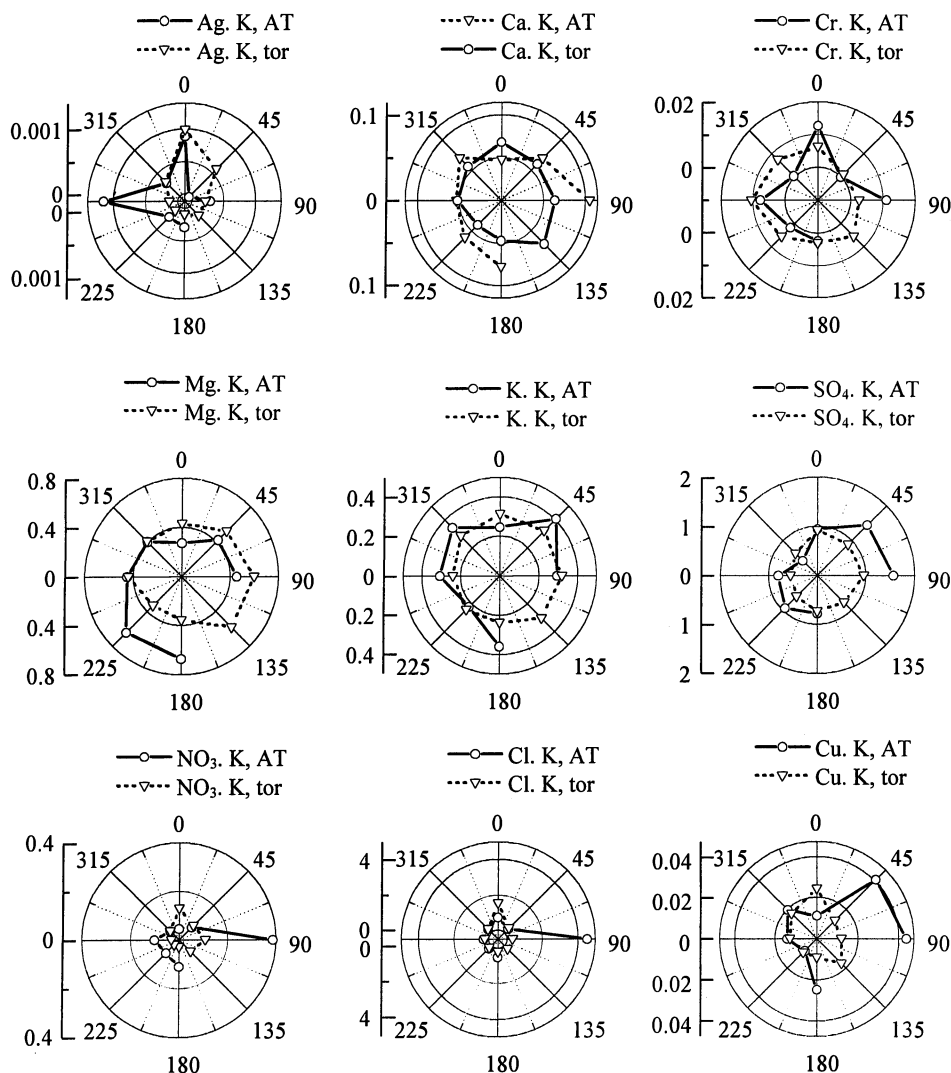


Fig. 7. Mean aerosol chemical composition ($\mu\text{g}/\text{m}^3$) in Kireevsk in 1997 for different directions of air transfer determined from the 700-850 hPa absolute topography maps (K, AT) and from the surface wind directions (K, tor).

We have examined both approaches (Figs. 6 and 7). It is seen in these figures that there are no big difference for Tomsk, which method was applied to determination of the prehistory of air mass. The exception is the Ag and Cr elements, the concentration of which in aerosol is small. As their content in particles is comparable with the detection threshold, the decrease of the number of the observed cases impoverishes statistics and increases the scatter of the

mean values. The difference in the chemical composition of air masses coming to Kireevsk along different direction is larger. This is possibly caused by the fact that breeze effect is observed near Ob' River in summer, which hides the principal transfer. Hence, it is better to use the method of trajectories in both cases. Although, identification of air masses coming to the observation sites by wind is possible for prompt estimates.

In summer 1998 aerosol chemical components Mn, Ba, Na⁺, Cl⁻, Pb, Cr, Mg, and Sn prevail in Tomsk, i.e., the elements and compounds characteristic of terrigenous processes or anthropogenic. The content of K⁺, Fe, and Ca is higher in Kireevsk. Comparable values have been fixed in 1998 for SO₄²⁻, NO₃⁻ and V. Wind roses on AT-maps for microelements and ions Ni, Mo, Na⁺, Cu, Ti do not coincide¹¹. Obviously, the latter is caused both by the remote transfer and by the presence of local sources.

Thus, there are significant differences in the aerosol chemical composition at the mesoscale level, which show the effect of local sources, as well as the role of differences due to the prehistory of air masses coming to the observation sites.

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REFERENCES

1. A.A. Vinogradova, *Izv. Ros. Akad. Nauk, Ser. Fizika Atmos. Okeana* **32**, No. 4, 479-486 (1996).
2. A.A. Vinogradova and V.A. Egorov, *Izv. Ros. Akad. Nauk, Ser. Fizika Atmos. Okeana* **33**, No. 6, 70-757 (1997).
3. A.A. Vinogradova and T.Ya. Ponomareva, *Izv. Ros. Akad. Nauk, Ser. Fizika Atmos. Okeana* **35**, No. 5, 558-595 (1999).
4. B.D. Belan, V.I. Vaver, V.K. Kovalevskii, et al., *Atmos. Oceanic Opt.* **6**, No. 5, 332-339 (1993).
5. B.D. Belan, V.I. Vaver, O.Yu. Luk'yanov, et al., *Atmos. Oceanic Opt.* **6**, No. 5, 340-348 (1993).
6. *Guidance on the Control of Atmospheric Pollution*. RD 52.04.186-89 (Gidrometeoizdat, Moscow, 1991), 694pp.
7. M.Yu. Arshinov, B.D. Belan, V.K. Kovalevskii, et al., *Atmos. Oceanic Opt.* **13**, No. 6-7, 580-583 (2000).
8. L.S. Ivlev and Yu.A. Dovgalyk, *Physics of Atmospheric Aerosol Systems* (Scientific-Research Chemical Institute, St. Petersburg, 1999), 258 pp.
9. B.D. Belan and T.M. Rasskazchikova, *Atmos. Oceanic Opt.* **14**, No. 4, 267-270 (2001).
10. V.V. Penenko and M.G. Korotkov, *Atmos. Oceanic Opt.* **11**, No. 6, 567-572 (1998).
11. B.D. Belan, T.M. Rasskazchikova, D.V. Simonenkov, et al., *Atmos. Oceanic Opt.* **14**, No. 4, 295-299 (2001).
12. M.Yu. Arshinov, B.D. Belan, D.K. Davydov, et al., *Meteorol. Gidrol.*, No. 3, 110-118 (1999).