

# Mesoscale differences in chemical composition of atmospheric aerosol

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Analysis of differences in the chemical composition of aerosol is conducted based on the measurements at two points (Akademgorodok and Kireevsk village) located at a 60-km distance from each other. 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.

The data on chemical composition of atmospheric aerosol are necessary for solving a wide scope of problems in atmospheric physics and optics. The refractive index of particles, and, hence the peculiarities of scattering and absorption of solar radiation in the atmosphere depend on the aerosol chemical composition. Aerosol can include heavy metals, which have carcinogenic properties and thus determine the ecological significance of the study of its chemical composition. Solution of particles containing sulfates in cloud droplets leads to formation of acid rains. 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 site.<sup>1-3</sup> At the same time, only macroscale<sup>1-3</sup> or microscale<sup>4,5</sup> 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.

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, and the other one at the field site near Kireevsk village of Tomsk region. Aerosol samples were collected synchronously during a day at two sites on the filters UFA-HP-20 and UFA-VP-20. Air volume from 200 to 600 m<sup>3</sup> was pumped through the filters during a day depending on the wind velocity. Then the

aerosol samples were processed at the Department of Analytical Chemistry of Tomsk State University headed by Z.I. Otmakhova. The methods used in analysis, detection thresholds, and errors in determining chemical elements are presented in Table 1.

**Table 1. Detection thresholds of the methods used for analysis of the atmospheric aerosol samples**

Components	Method for determination	DTh, $\mu\text{g}/\text{filter}$	Error, %
SO <sub>4</sub> <sup>2-</sup>	Ion chromatography	0.6	4.8
NO <sub>3</sub> <sup>-</sup>	Ion chromatography	0.6	4.1
Cl <sup>-</sup>	Ion chromatography	0.1	11.9
F <sup>-</sup> , NH <sub>4</sub> <sup>+</sup> , NO <sub>3</sub> <sup>-</sup>	Ionometry	0.2	10
Na <sup>+</sup> , K <sup>+</sup>	Atomic absorption	0.2	4.8
Al, Co, Cr, Mo, Ni, Ti, Zn, B, Si	Atomic emission spectroscopy (AES)	0.02	20
Ag, Ba, Cu, Pb, Sn, V, Mg, Mn	AES	0.01	20
Fe, Ga, W	AES	0.1	20
Ca, Cd	AES	0.2	20

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. First, the filters were exposed to atmosphere air during a day before arriving at the laboratory for analysis. 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.

The fractional diagram of the chemical composition of atmospheric aerosol including the principal components in Tomsk and Kireevsk is shown in Fig. 1. 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 regions.<sup>7</sup>

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 2.

The description of the meteorological parameters during the experiment is presented in Ref. 8. 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).

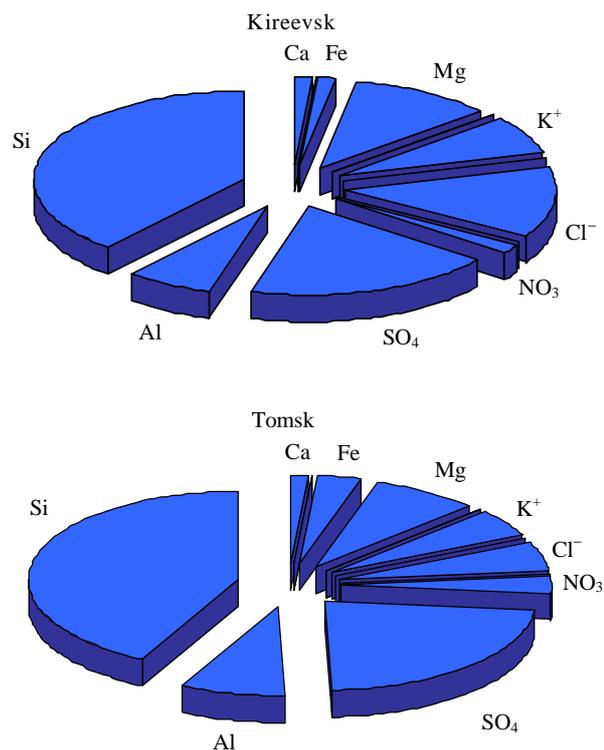


Fig. 1. Relative chemical composition of atmospheric aerosol in Kireevsk village and Akademgorodok in the principal components.

Table 2. Mean and rms errors of the concentrations of elements and ions ( $\text{ng}/\text{m}^3$ ), their absolute and relative (%) difference in Tomsk and Kireevsk in 1997 and 1998

Element	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 <sup>+</sup>	256.00±99.28	288.28±124.42	50.20±35.28	110.19±93.54	-32.28	-59.99	-18	-33
Na <sup>+</sup>	19.55±21.76	9.72±23.10	17.79±10.16	9.72±10.66	9.83	8.06	36	7
Cl <sup>-</sup>	265.11±152.39	526.48±933.19	328.93±525.75	94.15±80.86	-261.37	234.78	-120	126
F <sup>-</sup>	15.74±9.82	7.41±5.67	19.80±24.20	25.66±27.11	8.32	-5.87	50	-35
NO <sub>3</sub> <sup>-</sup>	159.37±122.55	71.95±96.63	115.97±62.04	95.58±89.29	87.42	20.39	93	22
SO <sub>4</sub> <sup>2-</sup>	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 <sup>-</sup>	2.28±5.68	5.05±10.19	-	-	-2.77	-	-16	-
NH <sub>4</sub> <sup>+</sup>	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 2 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 2. The concentrations of Pb, Ti, V,  $\text{Na}^+$ ,  $\text{NO}_3^-$ , and Mn are higher in Akademgorodok. The excess in Cu, Mo, and  $\text{K}^+$  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 2) were obtained by means of dividing the

absolute 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 2 that deviations exceeding this level were observed both in 1997 and in 1998. Twelve of 23 elements and compounds included in the Table 2 have significant differences in one of the measurement periods, and some have that in both periods.

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 sites.<sup>1-3</sup> Namely, as the specific circulation<sup>9</sup> appears in the region of large industrial centers, air can come to Akademgorodok along different trajectories.

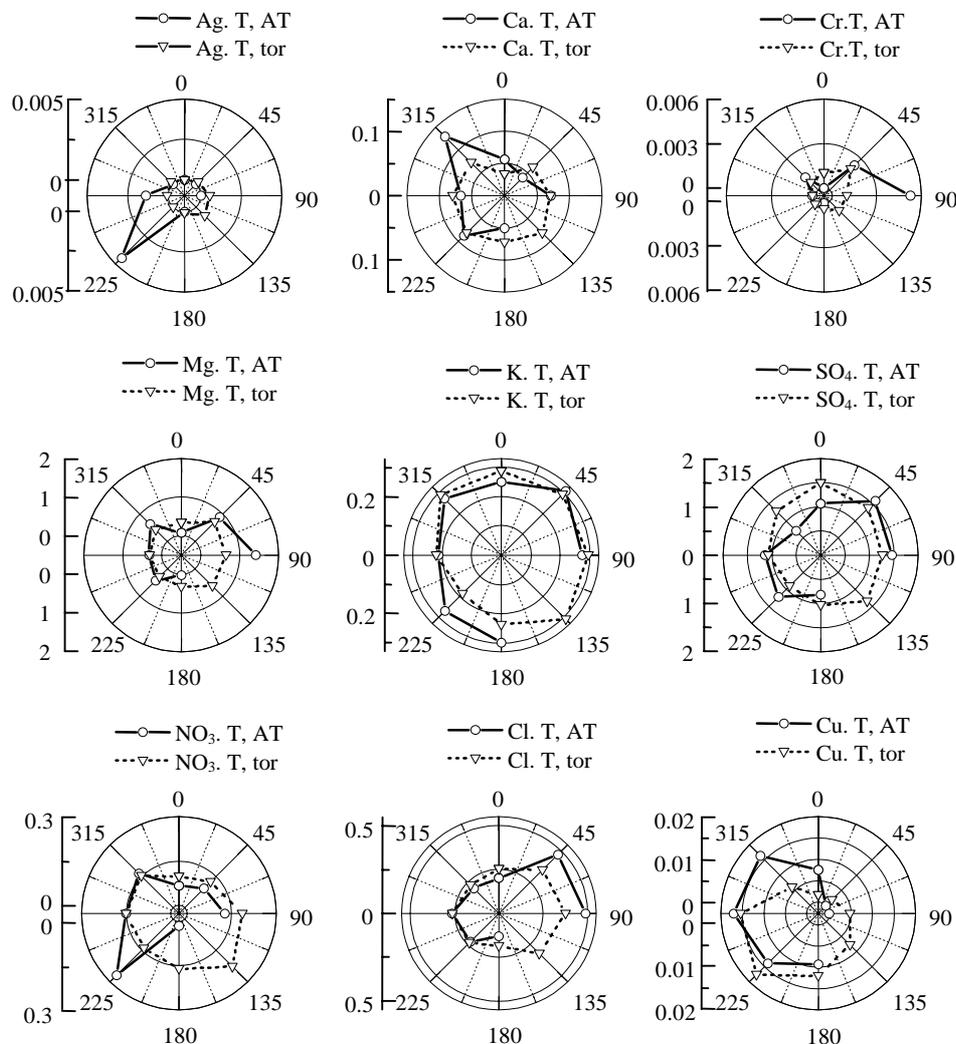
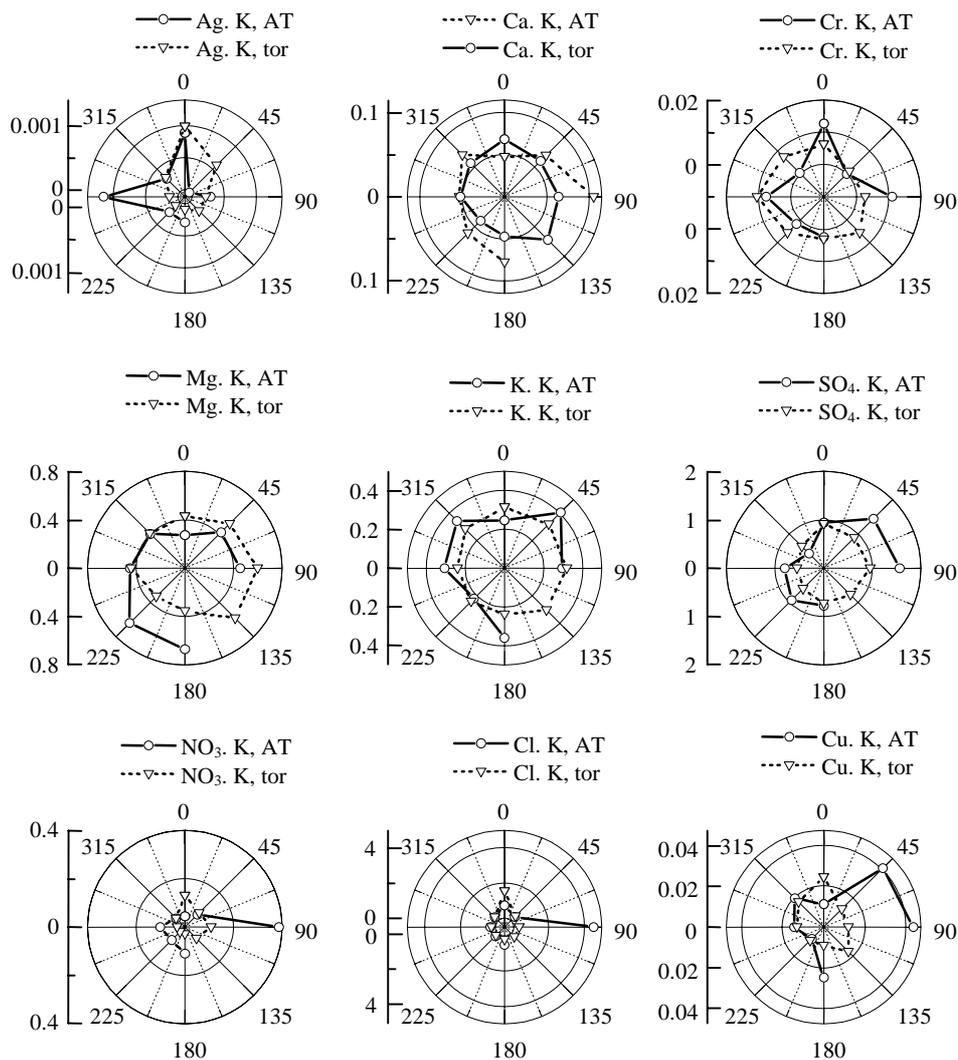


Fig. 2. Mean aerosol chemical composition ( $\mu\text{g}/\text{m}^3$ ) in the region of Tomsk in 1997 for different directions of air transfer determined from the maps (T, AT) and from the wind directions (T, tor).



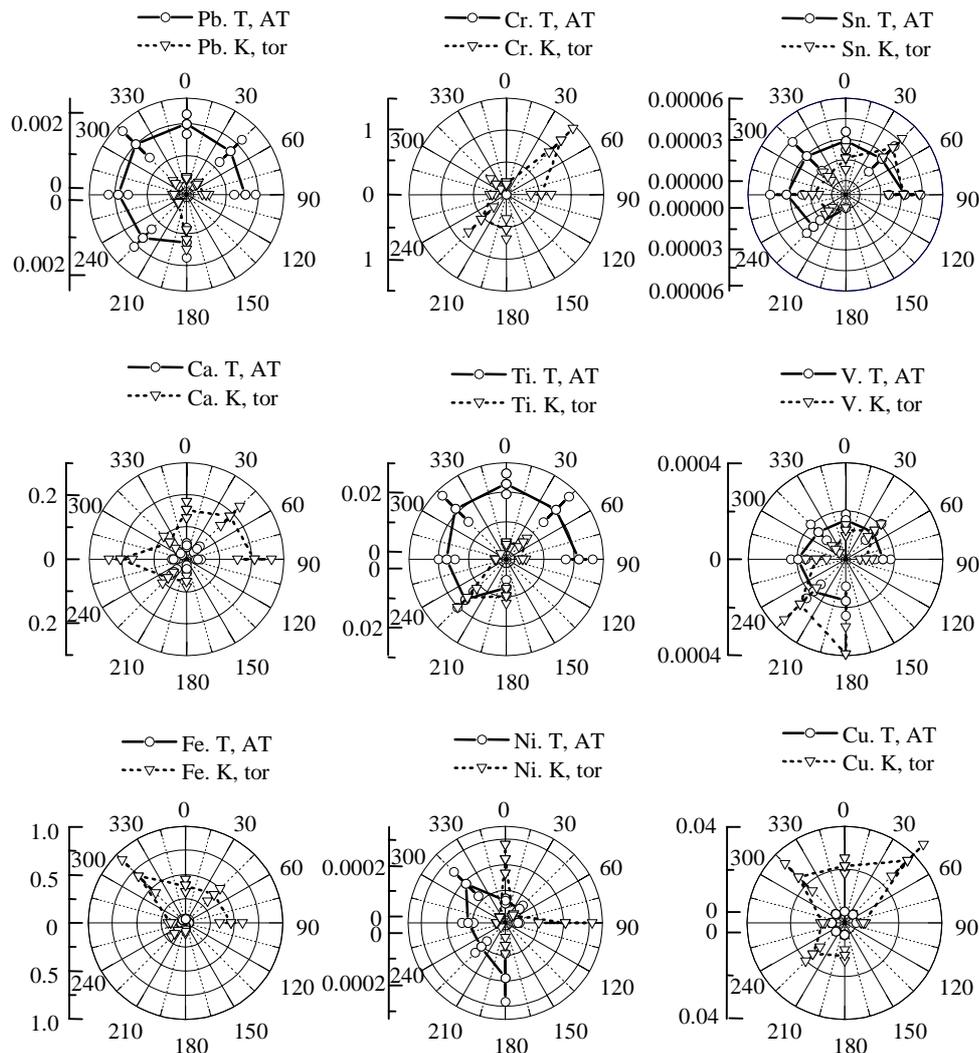
**Fig. 3.** Mean aerosol chemical composition ( $\mu\text{g}/\text{m}^3$ ) in Kireevsk in 1997 for different directions of air transfer determined from the maps (K, AT) and from the wind directions (K, tor)

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 2). 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.<sup>1-3</sup> 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.

We have examined both approaches (Figs. 2 and 3). 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.

Let us analyze the differences in chemical composition of particles at both sites taking into account the prehistory of air masses determined from the pressure maps shown in Fig. 4. Let us suppose, when considering Fig. 4, that if the curves have been similar in directions, but different in values, that means that the local sources work. If the curves have been different in different directions, the difference in transfer from other regions may have affected.



**Fig. 4.** Mean aerosol chemical composition ( $\mu\text{g}/\text{m}^3$ ) in Tomsk and Kireevsk in 1998 for different directions of air transfer determined from synoptic maps taking into account the standard error.

It is seen from Fig. 4 that the local differences are characteristic of the majority of the considered elements and ions. Mn, Ba,  $\text{Na}^+$ ,  $\text{Cl}^-$ , Pb, Cr, Mg, and Sn prevail in Tomsk, i.e., the elements and compounds characteristic of terrigenous processes or anthropogenic. The content of  $\text{K}^+$ , Fe, and Ca is higher in Kireevsk. Comparable values have been fixed in 1998 for  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and V. Wind roses for microelements and ions Ni, Mo,  $\text{Na}^+$ , Cu, Ti do not coincide. 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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