Influence of the Tomsk city on the chemical and disperse composition of the surface aerosol

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The influence of the Tomsk city on the chemical and disperse composition of surface atmospheric aerosols has been estimated by means of carrying out several continuous measurement campaigns at two different sites. One of the sites was located at the rural area (Kireevsk village, 60 km west of Tomsk), and another one – at the eastern suburb of the city. In conditions of predominant zonal westerlies, air masses first passed through the rural site, then Tomsk, and finally reached the suburban measurement site. It is shown that the determining factors in formation of aerosol field over a moderate city are the prehistory of air masses and the activity of erosion processes in summer. The influence of the direct anthropogenic urban emissions on the mesoscale variability of atmospheric aerosol is insignificant. On the whole, dispersion aerosol composition changes slightly except for the increase in the number density in the city. However, a significant transformation occurs in the structure of element and ion distribution over particles of different dispersities: additional concentration peaks for fine ($d < 0.5$ μm) and coarse ($d > 10$ μm) particles of heavy metals were found; peaks in distribution of ions and elements of natural origin tend to the region of coarse particles.

The average anthropogenic contribution into atmospheric aerosol is 11.5%.[1] Note that artificial aerosol is emitted from 3% of urbanized areas of the Earth, where more than a half of population live. Therefore, investigation of composition and structure of aerosol fields over such regions is of particular interest.[2–9]

To estimate mesoscale variability of aerosol and gas components near Tomsk, several runs of synchronous measurements were carried out at two sites. The first site was located near the Kireevsk village, located 60 km to the west from Tomsk, the second – at the eastern suburb of Tomsk, in Akademgorodok. In conditions of predominant westerlies, air masses first pass the Kireevsk (background) site, then Tomsk and Akademgorodok measurement site.

Runs of simultaneous measurements have been performed annually from 1997 to 2002, each run was from 20 to 50 days in duration (Table 1).

Table 1. Periods and numbers of synchronous pairs of aerosol samples

Year	1997	1998	1999	2000	2001	2002
Sampling period	Summer July 31–August 24	Summer July 15–August 25	Fall October 22–November 15	Summer June 29–July 27	Spring March 07–April 26	Summer August 8–27
The number of sample pairs	25	28	7	15	43	6

The sampling was carried out daily or once per 2–3 days (depending on the campaign), beginning in the morning. A mean volume of the filtered air was about 200 m^3. The aerosol number density was measured hourly with a 10-min averaging within particle size range $d = 0.4$–10 μm, using a modernized aerosol counter AZ-5 with 12 channels. As is seen from Table 1, during six years four campaigns were carried out in summer, one in fall, and one in spring.

Consider Table 2, reflecting the statistics of transfer cases during experiments. Daily average rhumbs of atmospheric transfer, predominant along the Kireevsk–Tomsk line, were determined according to the topography maps AT-700 and AT-850 with accounting for the mesoscale character of measurements (70 km between the sites). As is seen, recurrence of westerlies varied from 43% in summer of 1998 to 100% in fall of 1999. Absolute dominance of the westerly component was observed in mid-seasons.

Table 2. Prevailing regional atmospheric transport during the measurements (%) according to the AT-700/AT-850 synoptic maps

Transfer rhumb	Summer 1997	Summer 1998	Fall 1999	Summer 2000	Spring 2001	Summer 2002
0	17	25	–	27	10	–
45	7	14	–	–	–	–
90	3	11	–	–	–	–
135	–	–	–	–	–	–
180	3	7	–	7	–	17
225	28	7	29	13	28	33
270	31	25	57	27	53	33
315	10	11	14	27	10	17

The westerlies were observed in 90% of cases in the spring campaign of 2001 as well. The results of first two summer runs (most representative in the number

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of samples and transfer cases) have been published in Ref. 2. In this work, measurement results for mid-seasons are considered in detail.

First, consider the general variation (from one to another run) of the mean total concentration of the components under study and the ratio of individual components at two sites in each experiment (Fig. 1).

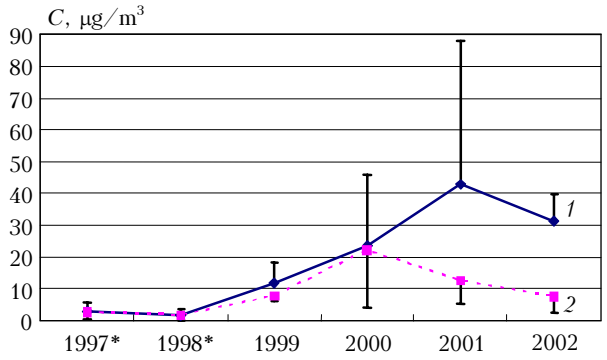

Fig. 1. Variations of the mean total concentration of the components under study and rms deviations in Akademgorodok (*1*) and Kireevsk (*2*) in different measurement runs (* – without silicon and aluminums).

It is seen that interannual and interseasonal variability of the sum of inorganic aerosol matrix attains an order of magnitude, while the difference between concentrations at two sites (background and eastern) reaches several times. This difference in summer has both positive and negative signs and usually is insignificant. The only exception is 2002 because of peat fires between Tom' and Ob' rivers in the immediate proximity to Tomsk. In this case, the combustion products were transported over the city by westerlies, prevailing in all summer runs (83%), which were recorded at the Akademgorodok measurement site. More significant positive difference between aerosol concentrations in Kireevsk and Tomsk in mid-seasonal measurements points to the city influence.

Considering the ratio of concentrations of certain aerosol components in Tomsk and Kireevsk (Table 3), a stable excess of nitrate-anion, lead, and titanium is observed in Tomsk. The first two elements are generally accepted as anthropogenic markers[3]; titanium also can be classed with them. Hence, these elements served markers when analyzing individual runs of measurements.

Let us briefly characterize the synoptic situation and the history of air masses, prevailing during experiments in fall (1999) and spring (2001) runs of synchronous measurements.

Before the beginning of the experiment in 1999, a system of atmospheric fronts have passed on October 20–21, resulted in wide intrusion of a cold arctic mass with snow precipitation. As a consequence, the atmosphere has cleared and the snow cover became stable. A brief intrusion of subtropical air mass occurred at the end of October. The snow cover has partly melted, but recovered again after passing a series of cold arctic fronts at the very end of October.

Table 3. Ratios of mean component concentrations in Tomsk/Kireevsk in different runs of measurements

Component	Summer 1997	Summer 1998	Fall 1999	Summer 2000	Spring 2001	Summer 2002
Al	1.53	–	1.24	1.02	1.09	10.01
Ba	1.07	3.28	4.51	1.18	1.61	–
Br^-	0.45	–	0.65	2.22	1.29	7.63
Ca	1.25	0.27	1.19	1.32	1.66	2.93
Cl^-	0.50	3.49	1.90	3.23	1.55	6.42
Cr	0.13	3.05	0.47	1.99	0.34	3.52
Cu	0.68	0.05	0.63	6.34	3.10	0.49
F^-	2.12	0.77	–	0.96	2.88	17.48
Fe	2.72	0.13	1.37	0.80	1.67	9.65
K^+	0.89	0.46	1.34	2.13	2.51	1.09
Mg	0.93	2.32	1.11	0.90	3.66	3.77
Mn	1.01	1.20	0.57	1.76	2.35	40.47
Mo	0.62	0.31	1.18	0.24	1.04	–
Na^+	2.01	1.83	1.47	0.07	1.50	2.13
NH_4^+	9.51	–	–	1.86	0.98	0.62
Ni	0.97	1.71	0.11	1.46	9.12	0.91
NO_3^-	2.22	1.21	1.47	1.15	1.16	4.34
Pb	1.24	4.78	2.46	4.47	1.64	2.65
Si	1.33	–	1.23	2.57	5.37	3.08
SO_4^{2-}	1.46	0.91	2.01	1.00	0.91	1.02
Ti	2.05	5.91	1.21	2.24	–	2.96
V	2.21	1.43	0.38	1.71	0.33	–
Sum	1.16	0.8	1.51	1.07	3.34	4.19

The wind regime in the period of this experiment was characterized by weak or moderate speeds and west, south- or north-west, then north (along the Ural from the Arctic Ocean) or north-west (from the Atlantic through the European North or the Baltic) directions of back trajectories.

In 2001, the synoptic conditions during spring experiments were more complicated and uncertain as compared to fall ones. Frequent intrusions of warm air were observed in March, accompanied by precipitations (even rain) on March 10 and 16 and the last five days of the month. Nevertheless, stable snow cover in the background region held till the middle of April, when frequent intrusions of cold air with snow were observed. Most back trajectories during the spring experiment coincided with fall ones at micro- and mesoscale distances. However, they drastically differed at the macroscale level, being of south-west origin: from Mediterranean, Middle East, or southern part of Western Europe through Central Asia and Kazakhstan.

Figure 2 shows mean concentrations of inorganic aerosol components with rms deviations for the fall run of synchronous measurements in 1999.

The mean 1.5-fold increase in macroelements and ions, which form the basis of inorganic aerosol matrix, is evident at the Akademgorodok measurement site. The largest increase is observed for two microelements: lead (2.5-fold) and barium (4.5-fold). However, some decrease in concentration of other elements, most of which are also of anthropogenic origin, is observed in the urban aerosol. This fact in the spring run of measurements can be explained by the snow cover of soil or its neutralization due to overmoisturing, as

well as by prevailing western transport with southern carrying over.

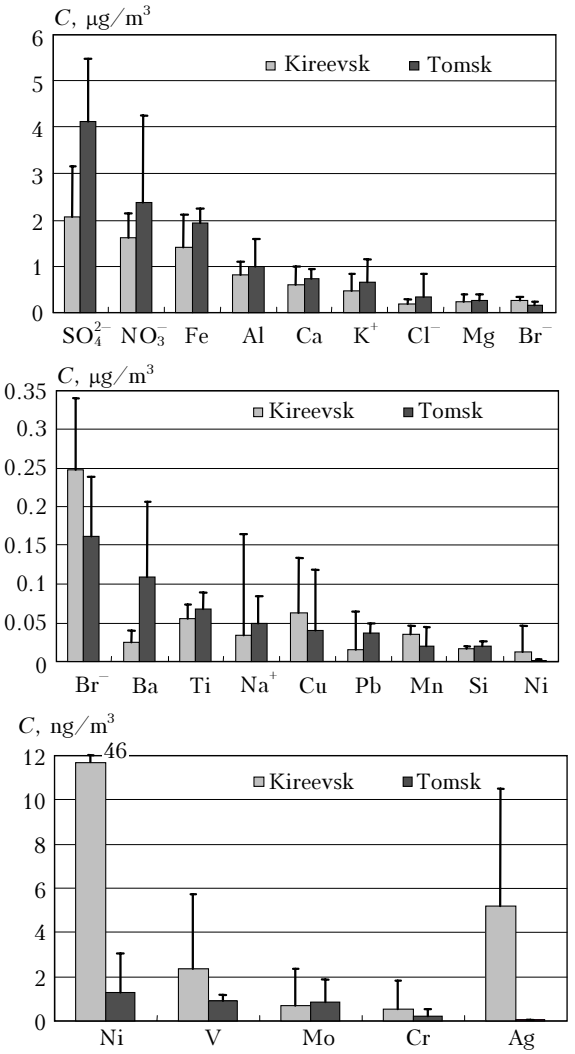

Fig. 2. Mean concentrations of inorganic aerosol components and rms deviations in the fall run of measurements in 1999.

The general time variability of total concentration of ions and elements throughout the measurement period from March 7 to April 27 is shown in Fig. 3.

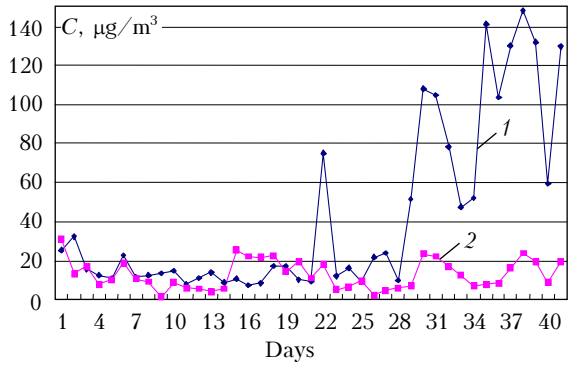

Fig. 3. Time variations of daily mean concentrations of sums of ions and elements of aerosol, collected synchronously at Tomsk (*1*) and Kireevsk (*2*) sites, for the entire measurement period in spring of 2001.

First points of time abscissa till 25 belong to March and the rest of points – to April (with rejection of some days). It is evident that this run of measurements is clearly divided into two periods with about week transition period: March with comparable concentrations and April with the sharp manifold (even by orders of magnitude) increase of total mass in Akademgorodok as compared to the background site.

It is hardly probable that the reason of this difference is in increase of the urban pollution emission: the both curves run quite synchronously, the correlation factor between series is 0.314, which corresponds to 0.95-level significance for this number of measurements ($n = 41$). Sooner the reason is in general dynamics of surface aerosol in this region, which at the mesoscale level was determined by global sources in the period under study.

However, the city essentially changes the composition of the passing aerosol. In winter period, this proceeds due to direct effect of heat-and-power enterprises, vehicles, etc. In spring, first of all, the objective irregularity in development of atmospheric processes, connected with the increasing inhomogeneity of the underlying surface (difference in albedo) plays its part. Second, the part of factors, contributing to both destruction of arriving aerosol and generation of new aerosol particles, becomes ambiguous.

To estimate the influence of these factors on aerosol composition at two sites, we have artificially divided the sample to March and April; mean values for these two periods are given in Fig. 4.

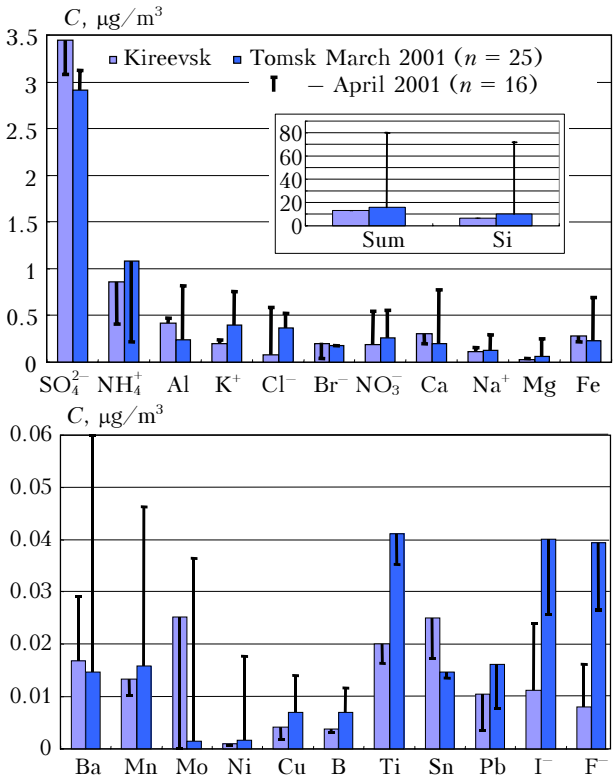

Fig. 4. Mean concentrations of components of the inorganic aerosol fraction for two sub-periods of the spring run of measurements in 2001.

For the background site, the beginning of spring is characterized by some decrease in concentration of the mineral aerosol component. This is seemingly due to deposition of large particles in soil, over-wet because of the melting snow and unable to produce erosion aerosol. In contrast, the water-soluble fraction (majority of halogenide-ions, nitrates) with enhancement of solar activity is involved into evaporation and aerosol-forming processes *in situ*. Among ions, only ammonium cation concentration decreases both under natural (by 2-fold) and urban (by 3-fold) conditions. Such seasonal behavior of ammonium has been noted by many researchers.[4–6] They explain this phenomenon by similar seasonal decrease of the contractor – sulphate-anion. However, in our case, the concentration of the latter in the background region decreased insignificantly and even increased in the city. The mechanism of the phenomenon is probably more complicated. Possibly, ammonium salts have a tendency to hydrolytic destruction to ammonia under the considered conditions, especially in the city. Nevertheless, all these processes result in generally neutral trend of the total inorganic component.

Urban aerosol is characterized by an opposite tendency: negative or neutral trend of the ion component and sharp increase of the mineral fraction of aerosol at the cost of silicon and other elements. The increase in their concentrations in aerosol is seemingly connected with atmospheric destratification of air mass, passing over the city, due to the turbulence intensification in spring.

A combination of different aerosol sources in the urban medium in spring along with development of other processes and the presence of spring haze give the base for supposition that the aerosol field is the most complicated in composition over urbanized area in this period.

This difference also manifests itself in the dispersion aerosol composition (Fig. 5). The aerosol number density can increase 2–3-fold in April at the city as compared to March and can exceed by an order of magnitude as compared to the background site. At the same time, key factors, determining the medium dispersity in the background region, are both natural and regional processes.

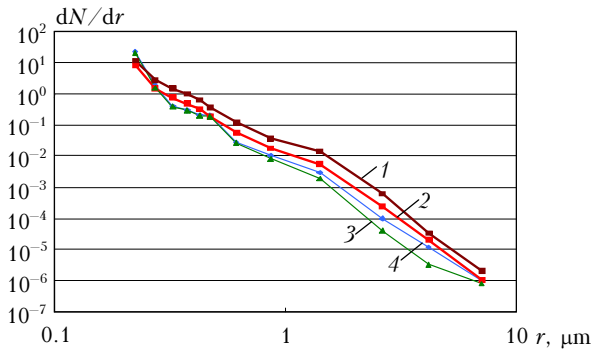

Fig. 5. Mean differential curves of disperse aerosol composition at different sites and different periods of the fall–spring run of synchronous measurements in 2001: Tomsk, April (*1*) and March (*2*); Kireevsk, April (*3*) and March (*4*).

The fall measurements are similar to early spring (March) ones in the character of occurring processes. Another history of air masses in this case gives an inverse ratio city/background, especially with respect to microelements, the concentration of which in the background arctic air mass can be quite significant.[10] This can be due to accumulation of some of them in the gas–vapor phase.[11] Probably, in urban medium, they actively precipitate, condensing on large particles. This is reflected in differential curves of disperse composition (Fig. 6): a small peak in a 0.4–0.5 μm range (typical for "immature" aerosol) is characteristic for Kireevsk. Such a peak is absent in the aerosol mass having passed above the city.

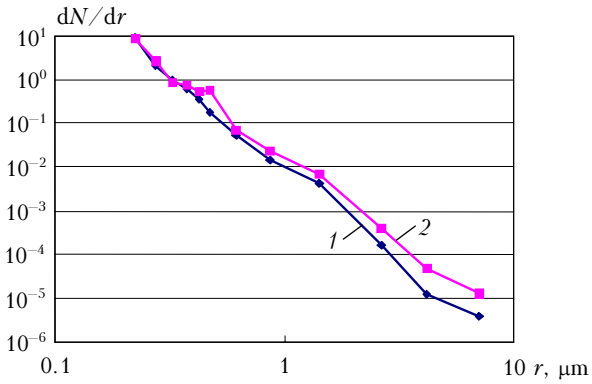

Fig. 6. Composite differential curves of disperse aerosol composition at different sites in the fall run of synchronous measurements in 1999: Tomsk (*1*) and Kireevsk (*2*).

The distribution of elements and ions over particles of different sizes is of interest. Correlation curves (Figs. 7 and 8), qualitatively characterizing the component distribution over particles of different sizes, have been built from comparison of integral concentration of chemical components and aerosol number concentrations for $d = 0.4 \div 10$ μm during the most representative spring run and averaged over the sampling period.

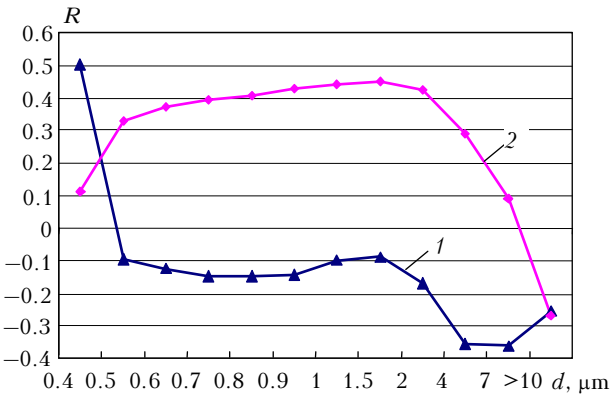

Fig. 7. Correlation curves of lead distribution over aerosol particles in Tomsk (*1*) and Kireevsk (*2*), built by the results of the spring run of measurements, 2001.

It is seen in Fig. 7 that the multimodal distribution is characteristic for lead in the urban aerosol; the tendency to its concentration in the vapor–gas phase

is evident. Along with the lead, similar distributions are characteristic for some other heavy metals, i.e., vanadium, nickel, and copper. Curves for components of primarily natural origin behave similarly for both sites, though some peak shift (Fig. 8) in the distribution is observed in this case.

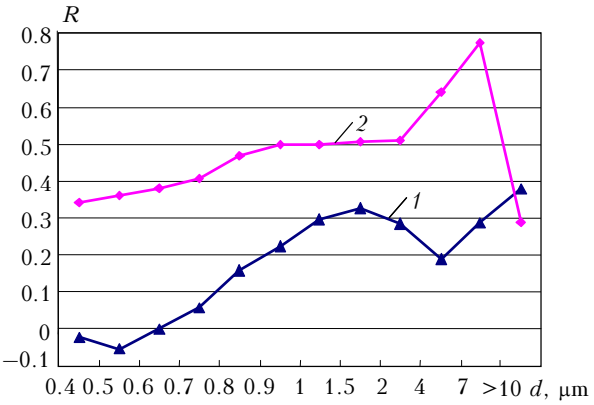

Fig. 8. Correlation curves of sodium ion distribution over aerosol particles in Tomsk (*1*) and Kireevsk (*2*), built by the results of the spring run of measurements, 2001.

Thus, the following conclusion can be drawn.

Key factors in formation of aerosol filed over a moderate city are the air mass prehistory and the soil erosion activity in summer. The influence of urban anthropogenic emission on mesoscale variability of atmospheric aerosol is insignificant. The composition of the basis of inorganic aerosol matrix changes slightly. However, destabilizing effect of the urban heat island and developed turbulence in the boundary layer of urban atmosphere results in aerosol precipitation on the surface layer, which is especially pronounced in spring, when the total mass of inorganic component manifold increases at the city measurement site.

In addition to the increase in the aerosol number concentration in the city, the disperse composition in general varies insignificantly. However, probably, essential transformation of structure distribution of elements and ions over particles of different dispersities occurs: additional peaks are noticeable in the ranges of fine ($d < 0.5$ μm) and coarse ($d > 10$ μm) particles of heavy metals, as well as the shift of peaks in the distribution of ions and elements of natural origin toward the region of coarse particles.

Acknowledgement

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