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The influence of a big enough city on the chemical and disperse composition of atmospheric aerosols

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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 (urban and rural). It is shown that the determining factors in formation of aerosol field over a big enough city are the prehistory of air masses and the activity of erosion processes in summer.

1. Introduction

The problem of identification of aerosol anthropogenic fraction is an unconventional and is regarded as a fundamental problem of physics and chemistry of the atmosphere. One of average evaluations of anthropogenic contribution into atmospheric aerosol is 11.5% (Kondratyev K.Ya., ed., 1991). Note that artificial aerosol is emitted from 3% of urbanized areas of the Earth, where more than a half of the population lives. Therefore, investigation of composition and structure of aerosol fields over such regions is of particular interest. We try to estimate anthropogenic influence on atmospheric aerosol composition for the particular big enough city, in terms of physiographic peculiarities of the region and air mass transport regularities on example of Tomsk. Population of Tomsk is about 500,000 people. Significant part of the population is engaged in education and science. There are no very big enterprises. Annual mean emission of pollutants to the atmosphere is about 20-30 kT/year. Mainly they consist of solid matter (31%), nitrogen oxides (23%), carbon oxides (23%), sulfurous anhydride (12%), and 10% of hydrocarbons and other volatile organic compounds. The main pollution sources are power plants and transportation (information of the Regional Ecology Committee).

2. Data and Methodology

To estimate mesoscale variability of surface aerosol composition 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. The field investigations has been performed in July-August 1997-1998, 2000, 2002, October-November 1999 and March-April 2001: during six years four campaigns were carried out in summer, one in fall, and one in spring. The

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each run was from 20 to 50 days in duration. 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.

The table 1 reflects 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-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. The westerlies were observed in 90% of cases in the spring campaign of 2001 as well. Therefore, absolute dominance of the westerly component was observed in mid-seasons. The results of first two summer runs (most representative in the number of samples and transfer cases) have been disscused by Belan B.D. et al., 2001. In this paper, measurement results for midseasons are considered in detail. In this connection we also 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. 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.

Table 1 Prevailing regional atmospheric transport during the measurements (%) according to the AT-850 synoptic maps

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

3. Results and Discussion

First, consider the general variation (from one to another run) of the mean total concentration of the components under study (Fig. 1) and the ratio of individual components at two sites in each experiment (Table 2).

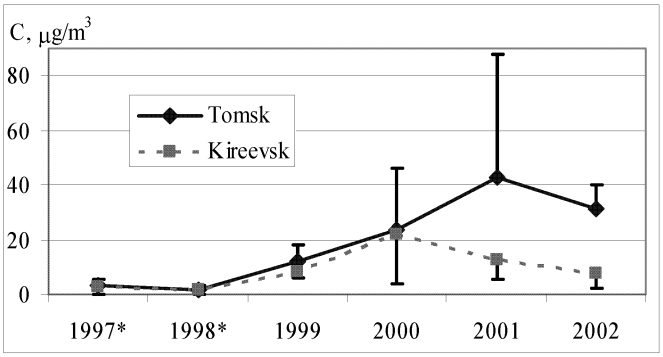

Figure 1. Variations of the mean total concentration of the components under study and rms deviations in Akademgorodok and Kireevsk in different measurement runs (– without silicon and aluminium)*

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.

Table 2 Tomsk/Kireevsk mean concentrations ratios for different measurements runs

	1997	1998	1999	2000	2001	2002		1997	1998	1999	2000	2001	2002
Al	1.5	-	1.2	1.0	1.1	10.0	Mn	1.0	1.2	0.6	1.8	2.4	40.5
Ba	1.1	3.3	4.5	1.2	1.6	-	Na^+	2.0	1.8	1.5	0.1	1.5	2.1
Br^-	0.5	-	0.7	2.2	1.3	7.6	NH_4^+	9.5	-	-	1.9	1.0	0.6
Ca	1.3	0.3	1.2	1.3	1.7	2.9	Ni	1.0	1.7	0.1	1.5	9.1	0.9
Cl^-	0.5	3.5	1.9	3.2	1.6	6.4	NO_3^-	2.2	1.2	1.5	1.2	1.2	4.3
Cr	0.1	3.1	0.5	2.0	0.3	3.5	Pb	1.2	4.8	2.5	4.5	1.6	2.7
Cu	0.7	0.1	0.6	6.3	3.1	0.5	Si	1.3	-	1.2	2.6	5.4	3.1
F^-	2.1	0.8	-	1.0	2.9	17.5	SO_4^{2-}	1.5	0.9	2.0	1.0	0.9	1.0
Fe	2.7	0.1	1.4	0.8	1.7	9.7	Ti	2.1	5.9	1.2	2.2	-	3.0
K^+	0.9	0.5	1.3	2.1	2.5	1.1	V	2.2	1.4	0.4	1.7	0.3	-
Mg	0.9	2.3	1.1	0.9	3.7	3.8	Sum	1.2	0.8	1.5	1.1	3.3	4.2

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

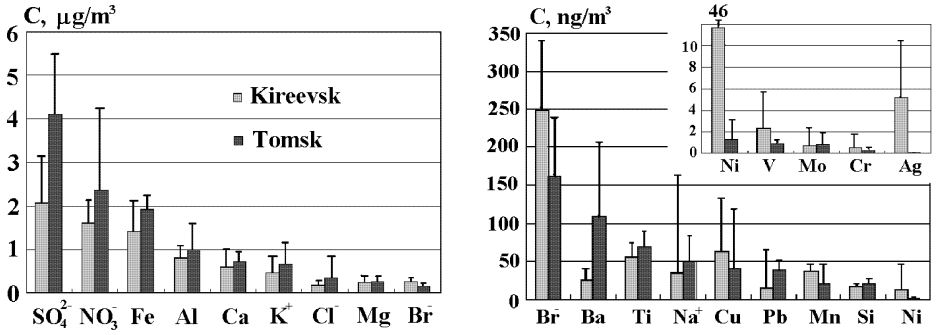

Figure 2. Mean concentrations of inorganic aerosol components and rms deviations in the fall run of measurements in 1999 (n = 7 sample pairs).

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.

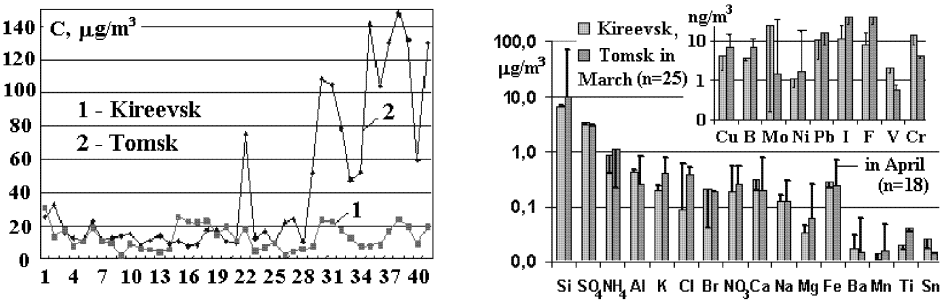

Figure 3. Time variations of daily aerosol sums at Tomsk and Kireevsk sites in spring of 2001, and the means of components for two sub-periods (March and April) in the run.

The general time variability of total concentration of ions and elements throughout the measurement period from March 7 to April 27 is shown in upper part of Fig. 3. 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 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 also given in Fig.3. 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 Smolyakov et al., 2006, and Yamamoto et al., 1995. 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 (curve 1 on Fig.3). 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 destroy of stable stratification 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.

The distribution of elements and ions over particles of different sizes is of interest. Correlation curves (Fig. 4), 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÷10 μm during the most representative spring run and averaged over the sampling period. 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 in the distribution is observed in this case.

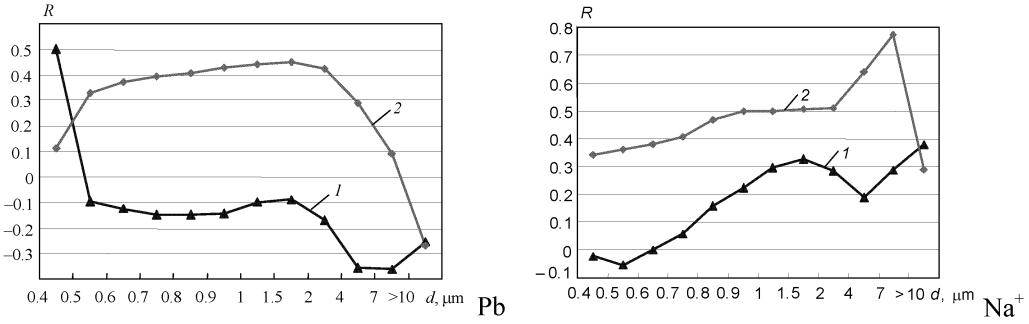

Figure 4. Correlation curves of two component distribution onto aerosol particles in Tomsk (1) and Kireevsk (2), built by the results of the spring run of measurements,2001.

Thus, although the size distribution in general varies insignificantly (certainly, the increase in the aerosol number concentration take place in the city in comparison with rural site), it is obvious that essential transformation of structure distribution of elements and ions in particulate matter of different sizes 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.

4. Acknowledgments

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