

Some Results of an Experimental Study of the Atmospheric Aerosol in Tomsk: A Combined Approach

V. V. Zuev

*Institute of Atmospheric Optics
Siberian Branch of the Russian Academy of Sciences
Tomsk, Russia*

As widely accepted, the atmospheric aerosol strongly contributes to the formation of the earth's radiation balance through the absorption and scattering of solar radiation. In addition to this direct influence on the radiation balance, aerosols, being active condensation nuclei, also have a role in the cloud formation processes. Consequently, we pay special attention to the block of aerosol studies in our Tomsk Radiation Experiment in Siberia (TRES) Project, proposed for the Atmospheric Radiation Measurement (ARM) Program.

Despite a strong spatio-temporal variability of the aerosol physicochemical parameters, their mean values could be quite characteristic of any specific region.

In this paper we present some results of aerosol studies undertaken on our own initiative at the field measurement sites of the Institute of Atmospheric Optics in Tomsk and the Tomsk region. To a certain extent these results reveal some regional features of the atmospheric aerosol formed over the central part of the Eurasian subcontinent, with its typically midlatitude climate characterized by a long, snowy winter and short, hot, and dry summer.

To keep our discussion within the scope of a single paper, we present here only our studies of aerosol in the near ground atmospheric layer. No results of lidar studies of aerosol in the boundary layer and in the free atmosphere are discussed here, though some of them are mentioned in our proposal on the TRES Project to the ARM Program.

Figure 1 presents the data on annual behavior of the aerosol number density (particles with the diameter $d > 0.4\mu$) recorded in the ground atmospheric layer over Tomsk Akademgorodok in 1993, together with data on the annual behavior of the aerosol column density averaged over many years of airborne observations over West Siberia. As seen in Figure 1, the aerosol number density reaches its maximum during the cold season, while its minimum value is observed during warm periods. Two secondary maxima in July and November are obviously due to regional peculiarities in air mass circulation

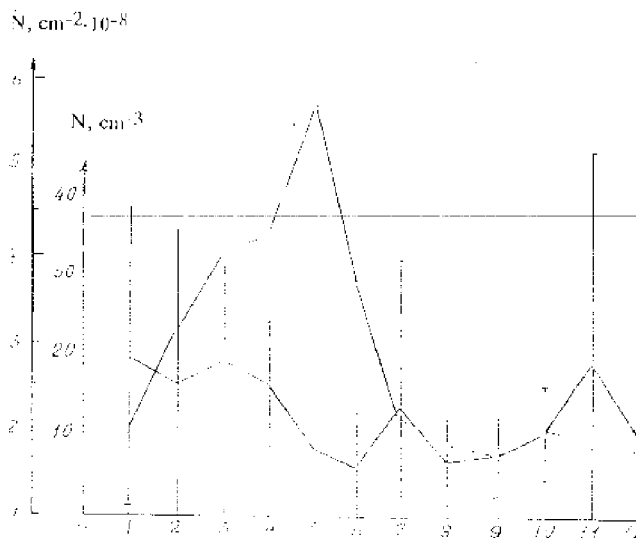


Figure 1. Annual behavior of the aerosol number density in the ground atmospheric layer (—) and of its column density (through the mixing layer) (o—o); vertical bars show rms deviations.

normally observed in these periods. Such a behavior of the aerosol number density in the ground atmospheric layer is mainly determined by the mixing layer height, provided that aerosol sources are constant. The mixing layer height, in turn, reaches its maximum in July, while its minimum occurs in December-January. Seasonal behavior of the aerosol column density is, on the other hand, governed by joint action of several processes. Among these, the photochemical processes play the key role in the *in situ* aerosol particles formation during spring time when forests coming to life start to emit a lot of terpenic phytoncides into the atmosphere.

The intensity of various sources contributing to the formation of the aerosol field in the atmosphere varies during the year. The variability of the aerosol sources can result in changes of the particle size distribution and in different

chemical composition of the particulate matter. The trends in the annual behavior of different size fractions of aerosol can be seen in Figure 2.

As shown in Figure 2a, the annual behavior of the submicron fraction is very similar to that of the aerosol column density presented in Figure 1.

According to conventional understanding, size distribution of the atmospheric aerosol has a minimum in the region of 1μ size (that is, between the fine and coarse fractions of aerosol). The annual behavior of the number density of particles of this size is shown in Figure 2b. As shown in Figure 2b, the concentration of this fraction monotonically falls off to the level characteristic of the period from August to December, with the only exception in the May-June period.

The source of a coarse aerosol fraction is, as a rule, the underlying surface and partly the aged aerosol of photochemical origin. From the data presented in Figure 2c, it follows that the main source of coarse aerosol fraction in

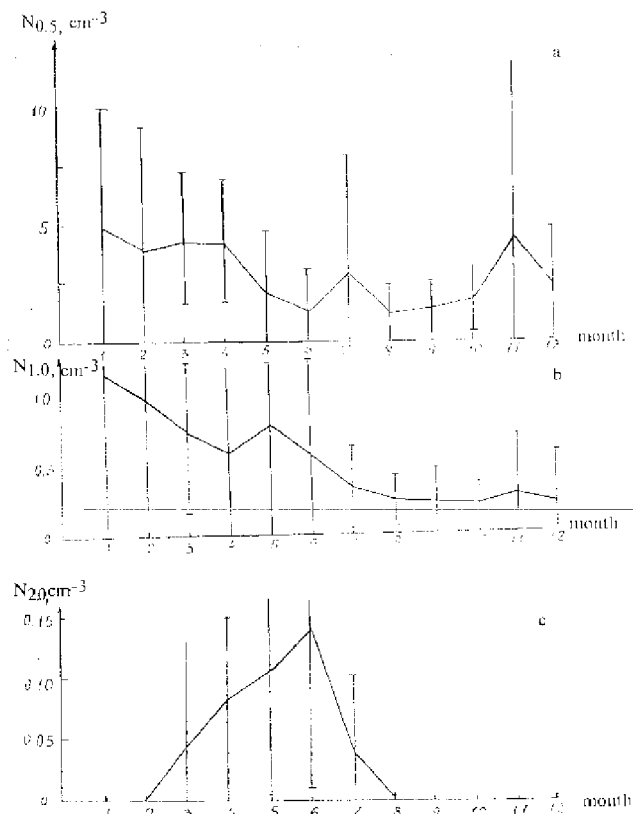


Figure 2. Annual behaviors of the three aerosol fractions.

the measurement site is the underlying surface because the concentration of particles of this size is practically zero in winter. In fact, it is clear because the underlying surface at that time was closed with snow, which could only be a sink for aerosols of coarse fraction and did not produce the aerosol itself. On the contrary, in the summer, stronger winds and dry underlying surface produce more coarse disperse particles which are more easily transported aloft due to stronger turbulence than is seen in the winter. At the same time, it is worth noting the similarity of the curve depicted in Figure 2c to the annual behavior of the aerosol column density shown in Figure 1. This circumstance allows us to assume that in the period of seasonal change from spring to summer the coarse fraction of aerosol is partly composed of particles of photochemical origin that are aging in the upper layers in the course of natural smog formation. Thus, large particles are then descending onto the underlying surface.

Because of regional siberian peculiarities characterized by long winter when snow covers the land from November till April and temperatures vary from 0°C to -30°C , it would be interesting to analyze data on the optical properties of the atmosphere during the winter. In fact, very little experimental data of field measurements of the atmospheric transmission have been available until recently. To fill this gap, a 3-week field measurement campaign was arranged and conducted at the Institute of Atmospheric Optics in the winter of 1992 to study the spectral transmission of the atmosphere in the spectral range from 0.44 to 12μ . These measurements were conducted along a 1-km horizontal path. We recorded about 180 transmission spectra of the atmosphere, of which we have arranged three data sets on the aerosol extinction coefficients $\alpha(\lambda)$ of a winter haze (59 spectra), an ice fog (35 spectra), and a snowfall (75 spectra). We separated the purely aerosol extinction from the total atmospheric extinction using a statistical method.

Mean $\alpha(\lambda)$ spectra for the three optical weather types are shown in Figure 3. Curve 1 in this figure presents the data on winter haze, Curve 2 the ice fog, and Curve 3 the data obtained in snowfalls. Note that ice fogs occur in the atmosphere under anticyclonic conditions and temperatures below 258 K. As shown in this figure, $\alpha(\lambda)$ spectra in winter haze and ice fog are very similar. This clearly demonstrates the fact that particle size spectra of the haze fraction of aerosol are quite stable in winter. So the ice fog only increases the total extinction by approximately 0.2 to 0.25 km^{-1} , this addition being spectrally neutral. This additional extinction is due to ice crystals that do not affect the size spectra of the fine aerosol fraction.

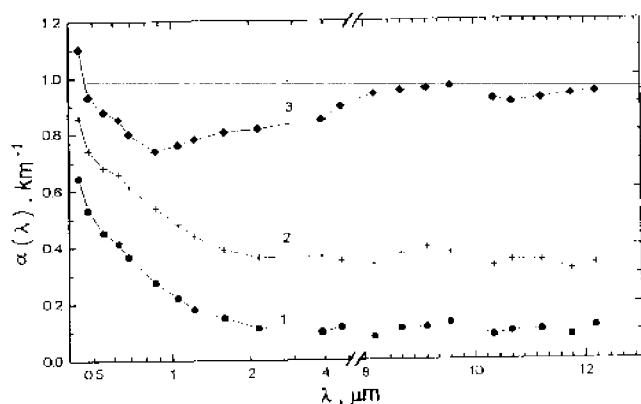


Figure 3. Spectral behavior of the aerosol extinction coefficient measured in a winter haze (1), an ice fog (2), and a snowfall (3).

This conclusion is well confirmed by the data presented in Figure 4. This figure shows the spectra of the parameter $\Delta\alpha(\lambda) = \alpha(\lambda) - \alpha(3.9)$ which characterizes only the contribution from fine aerosol fraction into the total extinction of radiation by atmospheric aerosol. Curves 1 and 2 of Figure 4 are practically coincident.

In contrast to the ice fog, snowfalls essentially modify the $\alpha(\lambda)$ behavior in winter haze and create a significant increase of the extinction over the entire spectral range. This takes place because of washing out of fine aerosol fraction (see Curve 3 in Figure 4). Once $\alpha(\lambda)$ spectra are measured, the distribution of a particle's geometric cross sections over the particle's radii can be reconstructed by solving the system of equations of the form

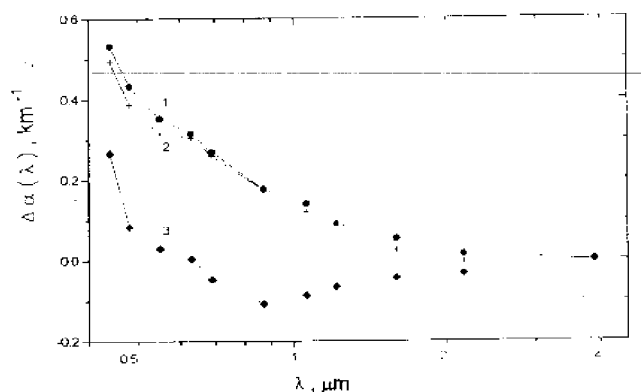


Figure 4. Spectral behavior of the parameter $\Delta\alpha(\lambda) = \alpha(\lambda) - \alpha(3.9)$ for a winter haze (1), an ice fog (2), and a snowfall (3).

$$\int_{R_1}^{R_2} K(r, \lambda_i) s(r) dr = \alpha(\lambda_i)$$

where r is the particle radius and $K(r, \lambda_i)$ is the extinction efficiency factor of a particle for radiation at the wavelength λ_i . The extinction efficiency factor also depends on the refractive index of particulate matter.

Figure 5 presents mean spectra $\alpha(\lambda)$ measured under different visibility conditions in winter hazes ($S_m > 20$ km in Curve 1 and $S_m < 5$ km in Curve 2) at ten wavelengths within the spectral region from 0.44 to 3.9 μ . The results obtained by inverting these data using Tikhonov regularization method are presented in Figure 6. The complex index of refraction was taken in this case according to a model which assumes it to be equal to $m = (1.36 - 10.00i)$ in the visible spectral region. When solving the inverse problem, we also considered the fact that in most situations the relative humidity of the air exceeded 90%. The $s(r)$ distributions reconstructed clearly reveal the cumulative fraction of aerosol in the submicron size range and the coarse fraction of aerosol with the maximum in the size range 2.6 to 2.9 μ .

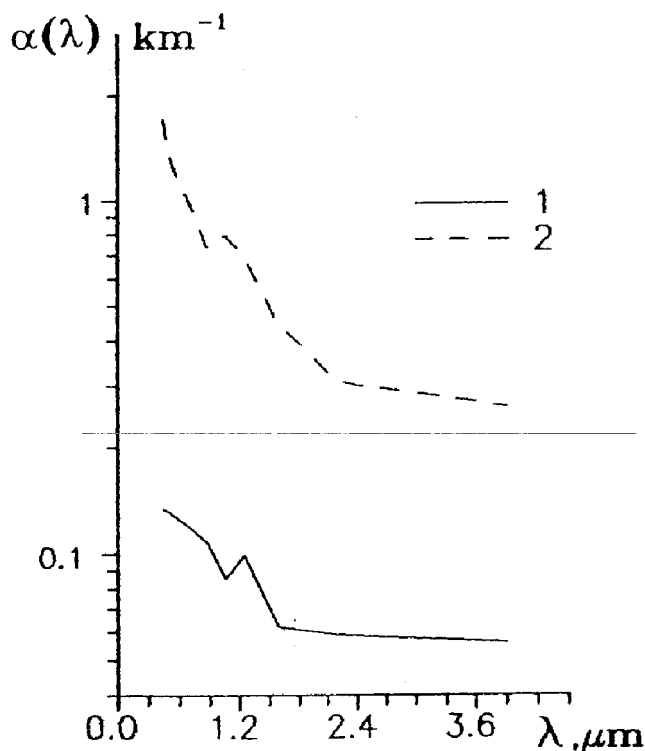


Figure 5. Spectral behaviors of the aerosol extinction coefficient (monthly mean measurement data for December 1992) obtained at meteorological visual ranges $S_m > 20$ km (1) and $S_m < 5$ km (2).

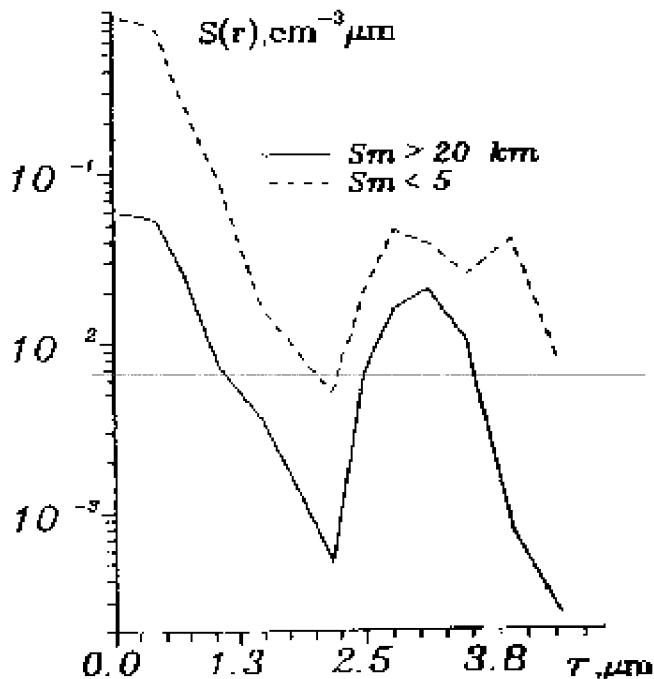


Figure 6. Size spectra of aerosol particles cross sections as reconstructed by inverting the extraction coefficients spectra presented in Figure 5.

The size distributions $s(r)$ and the value of the total geometric cross section corresponding to it are convenient for use in studies of the influence of particle size spectra on the optical properties of the atmosphere. However, in some applied studies like, for instance, studies of aerosol pollutions of air, it is more convenient to use the size distribution functions for a particle's volume [$v(r) = (4/3) \pi r^3 n(r)$] and the total volume of particles contained in 1 cm^3 . These quantities enable one to estimate mass concentration of aerosol per an interval of a size spectrum.

In microstructure studies of the atmospheric aerosol, the data of direct sizing measurements are very often approximated using a combination of lognormal distribution functions according to the following:

$$n(r) = \frac{1}{\sigma r \sqrt{2\pi}} \exp \left[- \left(\ln \frac{r}{r_m} \right)^2 / 2\sigma^2 \right]$$

where r_m is the median radius and σ is the standard deviation. It would be interesting to analyze the applicability of this formula to the description of results obtained by solving an inverse problem. Approximations of the size distributions $v(r)$ reconstructed by solving the inverse problem with a combination of two lognormal distribution

functions are shown in Figure 7 by solid curves. For the distributions $v(r)$ reconstructed from data averaged over the entire data set, we have found that the parameter is $r_{m1} = 0.32 \mu$ and $\sigma = 2.27$ for the cumulative fraction and $r_{m2} = 2.74 \mu$ and $\sigma = 1.19$ for the coarse aerosol fraction. As shown in Figure 7, the main contribution to the atmospheric turbidity in winter haze comes from a submicron aerosol fraction. It is also clear that in winter the coarse fraction of aerosol is mainly localized in a narrow size interval.

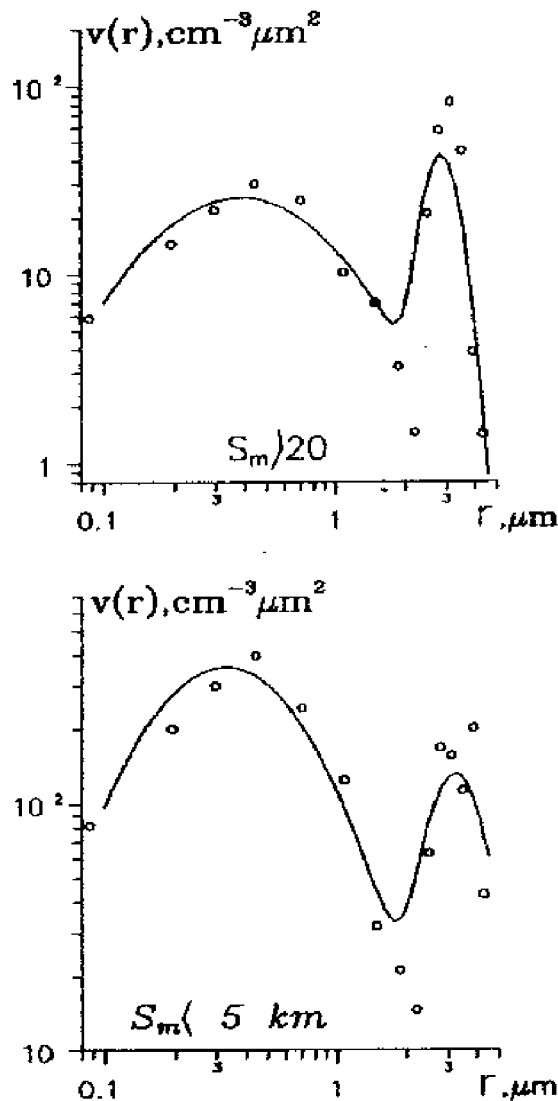


Figure 7. Size spectra of aerosol particles volume reconstructed by solving an inverse problem (circles) and their analytical approximations with superpositions of lognormal size-distributions (solid curves).

In 1994, we conducted a 3-week cycle of field measurements of the atmospheric spectral transmission in summer hazes. These measurements were carried out from June 16 till July 9 under low relative humidity conditions and low turbidity.

The mean spectrum of the aerosol extinction, $\alpha(\lambda)$, measured in a summer haze is shown in Figure 8 (Curve 1). The view of the spectrum presented here is indicative of the fact that the atmospheric turbidity at that time was mostly caused by background factors, which reveals a lack of fine aerosol fraction (the mean meteorological visual range, S_m , was about 23 km). In comparison, the mean spectrum $\alpha(\lambda)$ measured in 1992 in winter hazes is also shown in Figure 8 (Curve 2). These two curves quite clearly demonstrate the difference between the optical properties of the atmosphere observed in winter and in summer. The main difference is due to essentially different fine aerosol fractions in these seasons. This is in good agreement with the data presented in Figure 2.

An important part of the atmospheric aerosol studies concerns the study of its chemical composition. This information is useful both for identifying the sources of aerosol and for the determination of optical constants of the particulate matter necessary for making various calculations for the radiation models. Monthly mean characteristics of the aerosol chemical composition are shown in Figure 9, where all

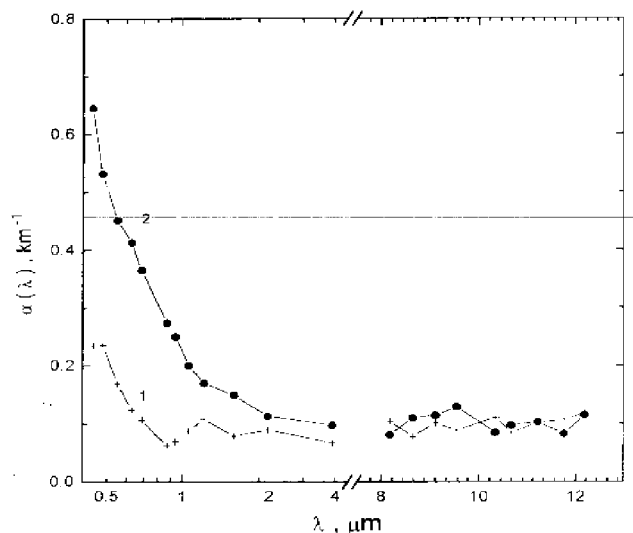


Figure 8. Spectral behavior of the mean aerosol extinction coefficients, measured in summer 1994 (1) and in winter 1992 (2).

the ions and elements identified are conditionally divided into three groups. The upper histogram shows those which are met in particles of natural origin. These components are usually called terragenic ones. The middle histogram presents the elements of anthropogenic and photochemical origin. The bottom histogram presents the microelements of both terragenic and anthropogenic origin. Normally the ratio of the total concentrations of the first group to that of the second one is practically constant over the whole Siberian region, and the total contribution coming from microelements to the chemical composition of aerosol makes only a few percent.

As shown in Figure 9, some changes in composition are observed during the change from spring to summer. Thus the concentration of Na^+ increased twice that which is indicative of more frequent arrival of marine air masses at the measurement site. Figure 9 also shows that the concentration of Al decreased by a factor of three, and the decrease of Ca concentration was even larger (about 40 times). At the same time, the concentration of Si and Mg increased almost ten times that which is indicative of difference in air masses coming there in July and April. In July an essential fall off of the anthropogenic components Cl^- , Br^- , NO^+ , and F^- was observed (if such components as Zn^{2+} , As^{5+} , Cd^{2+} , and Hg^{2+} , whose concentrations in our region are 10 to 100 times lower than the concentrations of other elements, are ignored). This situation may be explained by better dispersal of anthropogenic emissions in the summer compared to the winter. Concentration of microelements also decreased from April till July, except for Cr, B, and Mo.

The above results have been obtained in the ground atmospheric layer over Tomsk Akademgorodok and therefore possible contributions to the atmospheric aerosol from industrial emissions of Tomsk city must be remembered. This possibility is the subject of the next section.

In order to provide for separation of the above mentioned contribution from city of Tomsk, in 1993 we arranged simultaneous measurements at the Institute measurement site in a rural area (Kireevsk village) and in Akademgorodok, Tomsk. In this intercomparison experiment, we measured the same aerosol characteristics as our previous study. We also performed aerosol sampling in equal periods to provide a control of chemical composition of aerosol substance. Note that Kireevsk is 60 km to the West from Tomsk at the bank of the river Ob'. Since there are no big industrial centers near Kireevsk, it is quite reasonable to assume that changes in the physicochemical properties of the air mass coming from Kireevsk to Tomsk

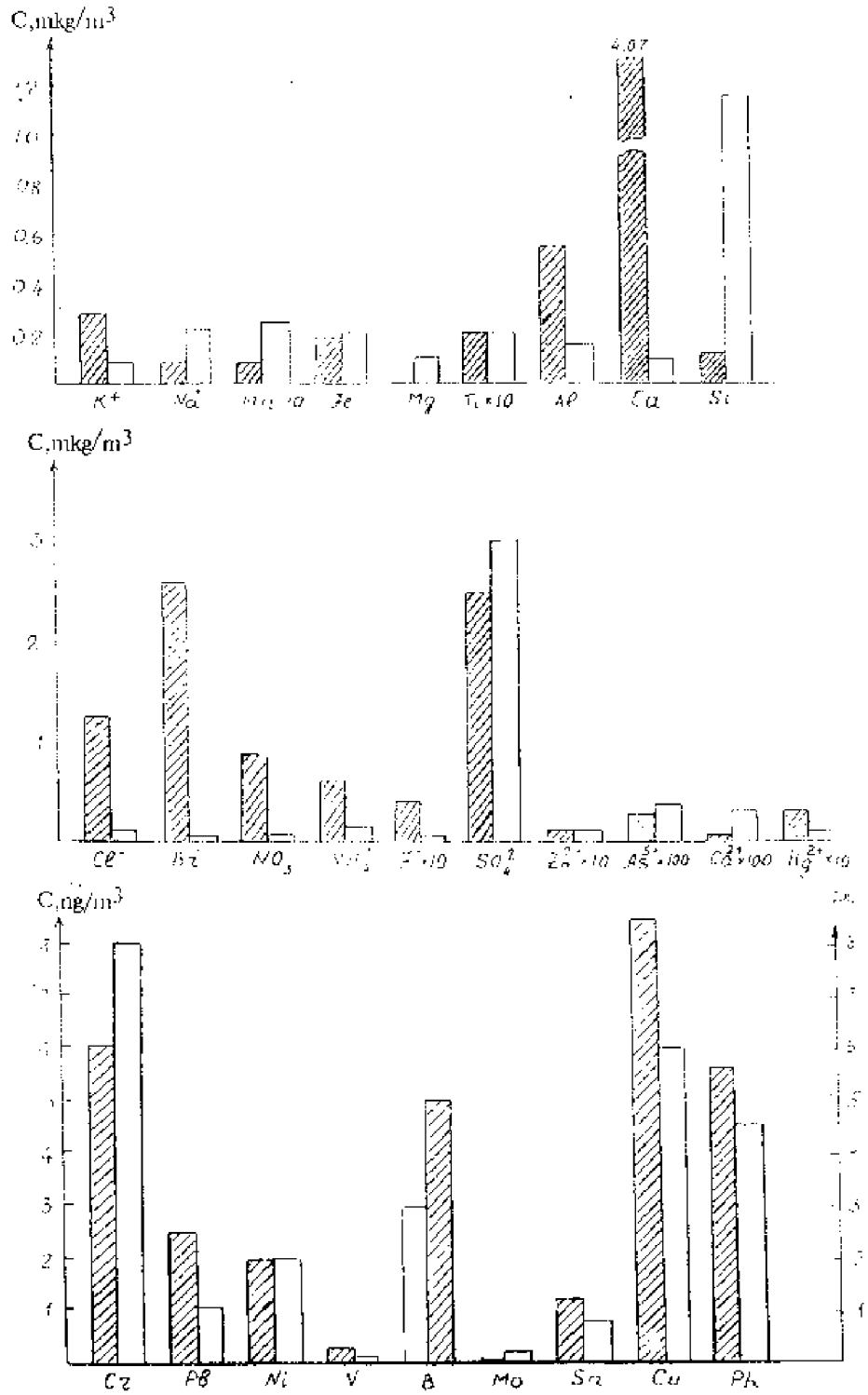


Figure 9. Monthly mean characteristics of the particulate matter chemical composition (shaded columns for April, clear columns for July).

as detected in Tomsk could bear information on the contribution from city aerosol sources. The variations of the aerosol number density and of the coefficient of directed scattering $\mu_0(45^\circ)$ observed in Tomsk Akademgorodok and Kireevsk took place synchronously at both sites and had approximately the same amplitudes. It is important to note that measurements of $\mu_0(45^\circ)$ were performed with a nephelometer for dry air. The air coming to the nephelometric measurement cell was dried by heating in the pipe leading to the cell. Time behavior of the daily mean values of $\mu_0(45^\circ)$ measured in Tomsk and Kireevsk are plotted in Figure 10. Good agreement between the curves is indicative of the general character of the processes governing the aerosol variability at both points. These data also confirm the regional nature of the processes of formation and evolution of the main mass of the submicron aerosol in the ground atmospheric layer.

Aerosol samples collected in this study enable us to estimate in which elements the aerosol could be enriched on its way from Kireevsk to Tomsk Akademgorodok. Table 1 shows that the monthly mean number density of aerosol over Akademgorodok is a little bit (1.18 times) higher than in Kireevsk. For the majority of the elements identified, a certain, not random, enrichment can be seen. At the same time, some decrease in the concentrations can be seen for such elements as K^+ , As^{5+} , Si , Mo , and Cu . The concentration of Cl^- , Br^- , SO_4^{2-} , Zn^{2+} , Hg^{2+} , Ti , V , and Ca was constant or almost constant, which is indicative of the absence of sources of these elements on the way from Kireevsk to Tomsk. The marked increase of concentrations

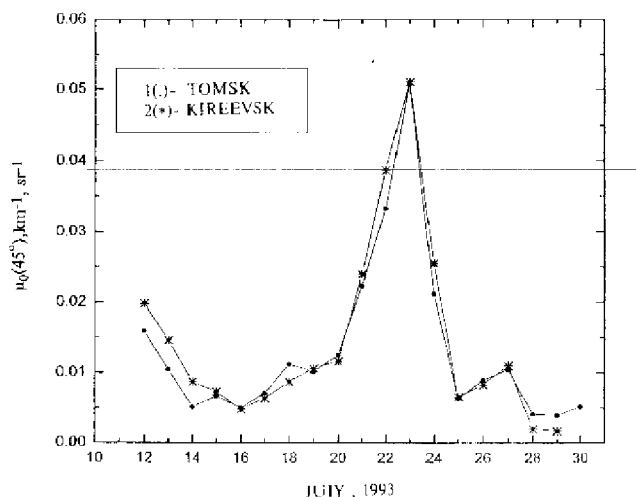


Figure 10. Time behavior of the daily mean values of $\mu_0(45^\circ)$ measured in Tomsk (Curve 1) and in Kireevsk (Curve 2).

Table 1. Chemical composition of aerosol (mkg/m³) in Kireevsk and Tomsk in July 1993.

Element	Tomsk	Kireevsk	Relationship
pH	4.64+0.63	4.89+0.59	0.95
K^+	0.08+0.05	0.24+0.07	0.33
Cl^-	0.01+0.003	0.01+0.01	1.00
Br^-	0.03+0.01	0.03+0.02	1.00
NO_3^-	0.005+0.03	0.02+0.01	2.50
NH_4^+	0.13+0.12	0.03	-
F	0.004	-	-
SO_4^{2-}	2.90+1.19	2.58+1.92	1.12
Zn^{2+}	0.01+0.006	0.009+0.006	1.11
Hg^{2+}	0.001+0.001	0.0008+0.0006	1.25
As^{5+}	0.003+0.003	0.008+0.007	0.38
Mn	0.025+0.01	0.015+0.010	1.67
Fe	0.2+0.14	0.13+0.08	1.54
Cr	0.008+0.001	0.005+0.001	1.60
Pb	0.001+0.001	0.0006+0.0003	1.67
Mg	0.11+0.03	0.08+0.04	1.34
Ni	0.002+0.001	0.001+0.0004	2.00
Ti	0.04+0.02	0.05+0.02	0.80
V	0.0001+0.0001	0.0001+0.0001	1.00
Al	0.15+0.06	0.10+0.03	1.50
B	0.005+0.004	0.0025+0.0020	2.00
Ca	0.09+0.03	0.10+0.06	0.90
Si	0.14+0.5	0.48+0.40	0.29
Mo	0.0001+0.0001	0.0002+0.0001	0.50
Sn	0.0008+0.0001	0.0005+0.0002	1.60
Cu	0.0006+0.0005	0.004+0.002	0.15
Σ	5.5926	3.9477	1.42

of NO_3^- , Ni, and B are evidently due to the influence of the city, though their contribution into the total aerosol mass is inessential.

Simultaneous measurements of the meteorological parameters of the atmosphere in Tomsk and Kireevsk showed their complete coincidence. The time behaviors of temperature and moisture recorded at both these measurement sites confirm the validity of the assumption that the same air mass travels across both sites.

The decrease in concentrations of K^+ , As^{5+} , Si, Mo, and Cu that occurred in the air mass on its way from Kireevsk to Tomsk could be connected with the varying underlying surface. Thus, near Kireevsk, river sand can be a source of Si. Since Si particles mainly contribute to the coarse fraction of aerosol, they rapidly descend to the surface and are therefore being removed from the air.

In summary, at least in July 1993, the city of Tomsk did not essentially contribute to the changes in the atmospheric aerosol composition. At the same time, simultaneous measurements of the meteorological quantities performed in Kireevsk and Akademgorodok showed, especially by their synchronous variations, that mainly the general circulation processes in the atmosphere were important at that time at both measurement sites.