

Diurnal behavior of the concentration of fine and ultrafine aerosol

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Monitoring of the fine and ultrafine aerosol at the TOR station of Institute of Atmospheric Optics SB RAS allowed us to reveal some peculiarities in the diurnal behavior of aerosol with particle size $d < 0.2 \mu\text{m}$. Estimates of the generation rate of aerosols due to gas-to-particle conversion are presented.

Introduction

The study of the aerosol time variation is important for better understanding the mechanisms of aerosol formation and transformation in the atmosphere. In this paper, we present data on the diurnal behavior of the concentration of fine and ultrafine aerosol, formed in the atmosphere. The diurnal behavior itself does not explain the nature of formation and transformation of these particles. However, having understood its peculiarities, one can get better grounds for studying, based on theoretical results available, the processes that govern the behavior of aerosol in the atmosphere.

The aerosol particles with $d < 0.2 \mu\text{m}$ are formed directly in the atmosphere (*in situ*) in the process of gas-to-particle conversion. These particles can be formed in the following processes¹: homogenous condensation of molecules of the same gas (vapor), homogenous heteromolecular condensation of molecules of several gases, adsorption of molecules of a gas (vapor) on the aerosol particles catalysts, and heterogeneous condensation (on nuclei). The first two processes are most efficient under conditions of a slightly dusty atmosphere.

Although many aspects of the physics of the fine and ultrafine aerosol fraction are well studied, the information on its dynamics in the atmosphere is still insufficient. This significantly complicates the interpretation of many atmospheric processes with the participation of aerosol, for example, estimation of aerosol extinction in the case of solar radiation transfer through the atmosphere. The estimates available now are too contradictory because of the lack of data on the size spectra of aerosol, especially, of the fine and ultrafine fraction. It is just for this reason that we have decided to present in this paper a description of the diurnal dynamics of this aerosol fraction.

1. Terminology

The current scientific literature uses a wide variety of terms to describe the aerosol fraction of fine and ultrafine particles. Therefore, let us first pay some attention to terminology that will be used below. The

fraction of fine and ultrafine aerosol particles can be divided into three subfractions: the nucleation mode, the Aitken mode, and the subfraction of the transient particle size (Fig. 1). Such a division is proposed, first, because the particles comprising these subfractions are being formed and transformed in different processes, and not because they contribute to different parts of the size spectrum. Thus, the aerosol of the nucleation mode is formed in the homogeneous processes of gas-to-particle conversion. Thus formed particles then grow due to heterogeneous condensation on them of vapor of the aerosol-forming substances and form the Aitken mode that has the longest lifetime. The existence of the transient-size subfraction reflects the process of particles growth from the size characteristic of the Aitken mode to that characteristic of the so-called accumulation one due to coagulation and condensation that are more efficient with particles from this size range. At the same time, these processes have no significant effect on the formation of the nucleation and Aitken mode. Thus, we can conclude that each aerosol subfraction (mode) reflects certain mechanisms of the aerosol formation and transformation. Thus, the nucleation mode shows the yield of the homogeneous nucleation process, the Aitken mode presents that of the heterogeneous condensation, and the transient mode demonstrate the coagulation and condensation activity.

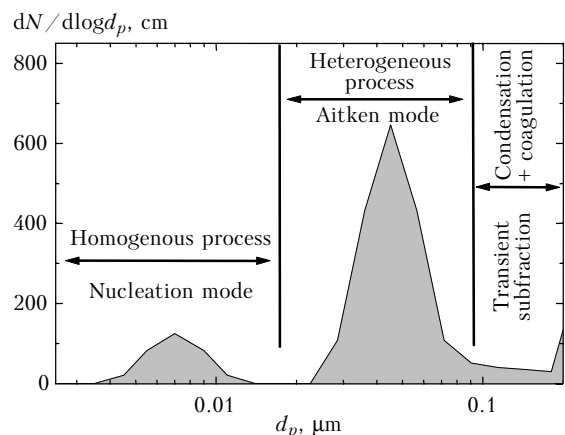


Fig. 1. Typical size distribution of the fine and ultrafine aerosol particles for a remote continental region.

2. Instrumentation and the initial data

To measure the size spectra of the fine and ultrafine aerosol particles, we used a diffusion spectrometer of the aerosol particles (DSA, $0.003 \mu\text{m} \leq d \leq 0.200 \mu\text{m}$) designed at the Institute of Chemical Kinetics and Combustion, SB RAS (Novosibirsk). This device is an analog of the diffusional particle sizer (DPS) manufactured by the TSI Company. In 1991, these devices were intercalibrated and showed close correspondence between the results.²

Episodically the measurements with the use of a DSA started in 1991. Although we have a laboratory version of the device, in 1996 we have managed to organize at the TOR station of the Institute of Atmospheric Optics SB RAS annual hourly monitoring of the disperse composition of aerosol in the size range from 3 to 200 nm. The data acquired at this monitoring formed the basis for the results we present in this paper. Overall, 4600 hourly readouts were obtained for the period of monitoring. The monitoring included simultaneous measurements of the main meteorological quantities and some atmospheric gases.

3. Diurnal dynamics of the fine and ultrafine aerosol

Let us analyze the results obtained on the fine and ultrafine aerosol as a whole ($d = 3\text{--}200 \text{ nm}$) and each of its subfractions (modes) separately, because the mechanisms of generation and transformation of

particles in the atmosphere are significantly different for these subfractions. To avoid presenting too vast illustrative material, we present here only the data for the central months of a year. Those months are chosen because the aerosol exhibits quite typical diurnal behavior in these periods. To plot one figure, no less than 200 particle size spectra were used.

3.1. Behavior of total number density of the aerosol nanoparticles

Figure 2 shows the monthly mean diurnal behavior of the total number density of the fine and ultrafine aerosol for four months of a year. It is seen from the figure that the diurnal behavior of the particle number density of the fine and ultrafine aerosol is characterized by the presence of a pronounced nighttime minimum. At the same time, a daytime maximum is diffuse, possibly, due to intensification of vertical mixing of air in daytime or because of equal intensities of the processes of aerosol generation and sink for this fraction.

It is worth emphasizing here that at night the concentration of fine and ultrafine aerosol particles does not drop down to zero (is consumed), but keeps at relatively high values. This is indicative of rather a long lifetime of the fine and ultrafine aerosol in the atmosphere. Besides, this fact supports the estimates from Ref. 3, where it was shown that the lifetime of aerosol particles with the size less than $0.01 \mu\text{m}$ does not exceed 24 hour. At the same time, particles with the diameter $0.01 < d < 0.2$ can reside in the atmosphere up to 80 days as long.

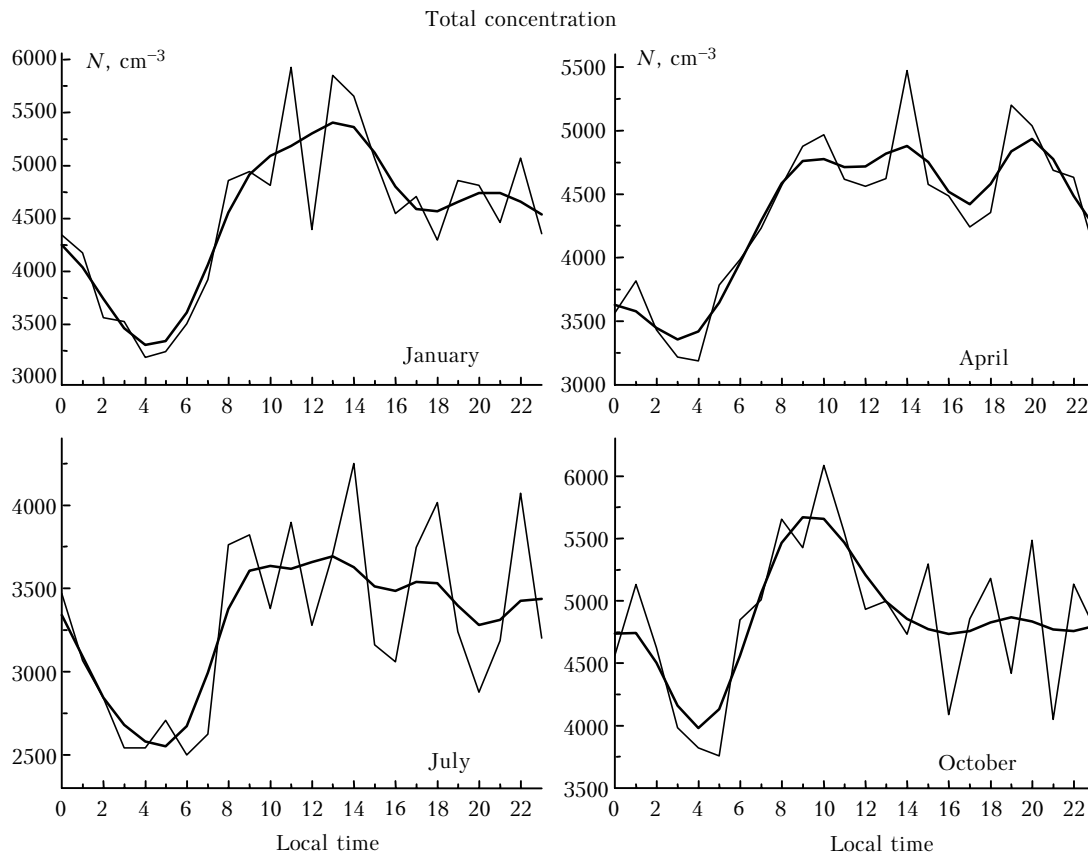


Fig. 2. Monthly mean diurnal behavior of the total number density of fine aerosol.

The rise of concentration from the nighttime minimum to the daytime maximum occurs rather fast in the morning, and then the concentration is saturated. This shows that the processes of generation and sink of fine and ultrafine particles in the atmosphere are close to equilibrium in daytime.

Though being only an assumption, to confirm which, the balance of the mass of aerosol matter suspended in the atmosphere should be calculated more correctly, it is the only reasonable explanation for the presence of the diffuse daytime maximum.

3.2. Diurnal behavior of the particle number density of the nucleation mode of aerosol

Let us now consider diurnal behavior of the nucleation mode of aerosol ($d < 0.01 \mu\text{m}$, see Fig. 3). It is characterized by the presence of a pronounced daytime maximum. This fact evidences once more of the photochemical origin of these particles. Most often, this maximum coincides with the maximum intensity of the incoming solar radiation.⁴

According to Ref. 5, aerosol of the nucleation mode is usually an indicator of a homogeneous process of the aerosol formation. Therefore, the variability of

the particle number density (see Fig. 3) can be explained by intensification of the process of homogeneous nucleation in daytime, when photochemical reactions that yield the aerosol-forming substances are most intense.

The diurnal behavior of this aerosol subfraction is well pronounced. Therefore, we can use the increase in the particle number density for estimating the rate of aerosol generation due to gas-to-particle conversion.

In this case, we should keep in mind that it is not quite correct to estimate the generation rate based only on the increase of the number density of particles belonging to the nucleation mode, because their simultaneous sink is thus ignored. The main sink for particles of this subfraction is their conversion into the Aitken mode due to heterogeneous condensation. The condensation growth changes only the size of particles, and not their number. Therefore, the particle number density must be unchanged in the absence of a source of new particles. Consequently, the nucleation rate is equal to the sum increase in the particle number densities of the nucleation and Aitken modes. The above-said is confirmed by the fact that the number density of particles of the Aitken mode starts to grow almost at the same time as that of the nucleation mode does (see Figs. 3 and 4).

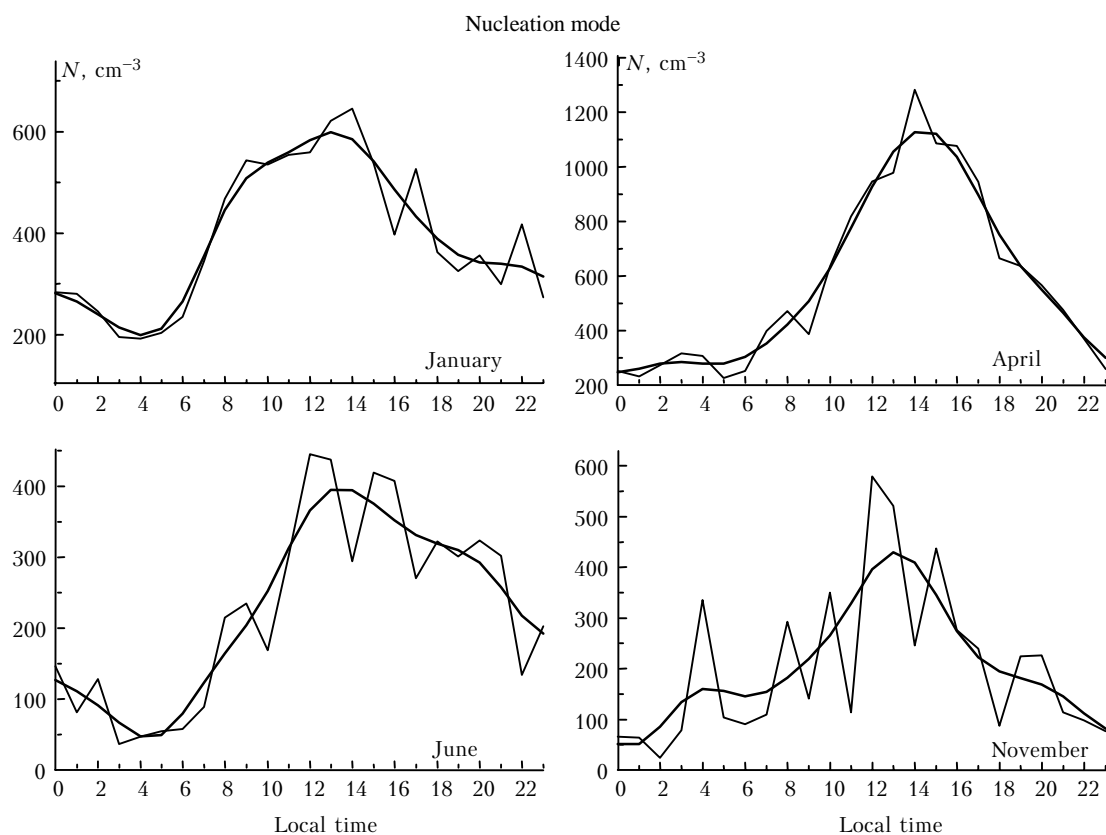


Fig. 3. Monthly mean diurnal behavior of the number density of aerosol particles of the nucleation mode.

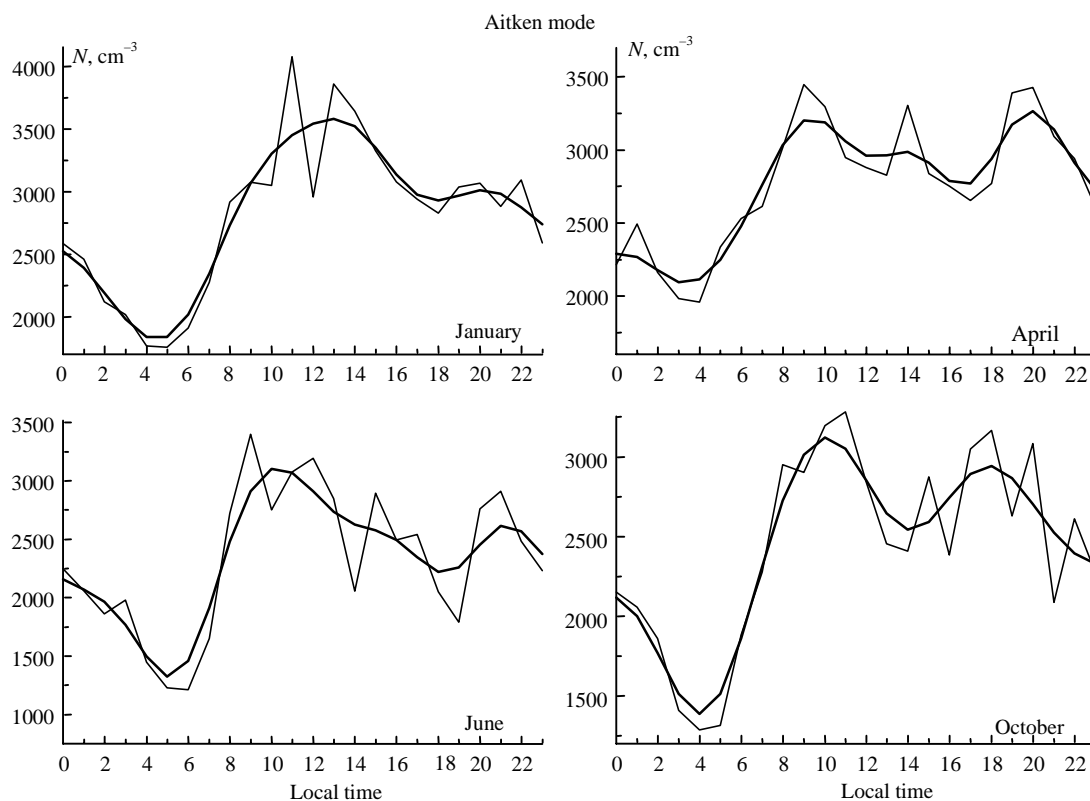


Fig. 4. Monthly mean diurnal behavior of the number density of aerosol particles of the Aitken mode.

The generation rates are estimated by the equations:

$$J_n = (N_{max} - N_{min}) / \Delta t_{max-min}, \tag{1}$$

$$J_A = (N_{max} - N_{min}) / \Delta t_{max-min}, \tag{2}$$

where N_{max} and N_{min} are the maximum and minimum values of the aerosol particle number density for each mode observed during a day. The estimated generation rates are given in Table 1, which includes the calculated results for those months, in which the diurnal behavior was most pronounced.

Table 1. Increase of the number density of aerosol particles of the nucleation mode (J_n), Aitken mode (J_A), and generation rate for the fine and ultrafine aerosol (J_g), in $cm^{-3} \cdot s^{-1}$

Month	J_n	J_A	$J_g = J_n + J_A$
January	$1.3 \cdot 10^{-2}$	$9.2 \cdot 10^{-2}$	$1.1 \cdot 10^{-1}$
February	$1.1 \cdot 10^{-2}$	$7.0 \cdot 10^{-2}$	$8.1 \cdot 10^{-2}$
April	$2.3 \cdot 10^{-2}$	$8.3 \cdot 10^{-2}$	$1.1 \cdot 10^{-1}$
May	$2.0 \cdot 10^{-2}$	$4.5 \cdot 10^{-2}$	$6.5 \cdot 10^{-2}$
June	$1.3 \cdot 10^{-2}$	$1.3 \cdot 10^{-1}$	$1.4 \cdot 10^{-1}$
July	$0.9 \cdot 10^{-2}$	$1.4 \cdot 10^{-1}$	$1.5 \cdot 10^{-1}$

It follows from Table 1 that the generation rate ranges from 6.5 to 15 particles per 100 s in 1 cm^3 for the nucleation aerosol and from 4.5 to 14 particles per 100 s for the Aitken mode.

Table 2 presents the data on the rate of coagulation of aerosol particles.⁶ Comparing the calculated results for the generation rate and coagulation coefficients (see Tables 1 and 2) we can see that the process of coagulation has no significant effect on the aerosol of these subfractions, because the values of the coagulation coefficients for the smallest particles are of much lower magnitude.

Table 2. Coagulation coefficients for aerosol particles of different size, in $cm^{-3} \cdot s^{-1}$

$d_{p2}, \mu m$	$d_{p1}, \mu m$					
	0.002	0.01	0.1	1	10	20
0.002	$8.9 \cdot 10^{-10}$	$5.7 \cdot 10^{-9}$	$3.4 \cdot 10^{-7}$	$7.7 \cdot 10^{-6}$	$8.3 \cdot 10^{-5}$	$1.7 \cdot 10^{-4}$
0.01		$1.9 \cdot 10^{-9}$	$2.4 \cdot 10^{-8}$	$3.3 \cdot 10^{-7}$	$3.4 \cdot 10^{-6}$	$6.8 \cdot 10^{-6}$
0.1			$1.4 \cdot 10^{-9}$	$4.7 \cdot 10^{-9}$	$4.2 \cdot 10^{-8}$	$8.4 \cdot 10^{-8}$
1				$6.6 \cdot 10^{-10}$	$2 \cdot 10^{-9}$	$3.7 \cdot 10^{-9}$
10					$6 \cdot 10^{-10}$	$6.8 \cdot 10^{-10}$
20						$6 \cdot 10^{-10}$

Consequently, at sufficiently intense generation of particles of the nucleation and Aitken mode, that is, those that primarily determine the total concentration of the fine and ultrafine aerosol, the diffuse daytime maximum in the time behavior of the total number density is most likely due to the withdrawal of the formed particles from the near-ground atmospheric layer due to turbulent mixing.

In conclusion, one more fact should be mentioned. As a rule, the number of nucleation particles begins to increase several hours before the sunrise, i.e., before possible beginning of photochemical processes in the air. Sometimes, even secondary nighttime maxima are observed. This indicates that homogeneous nucleation can proceed at night as well, most likely, in the chemical reactions of atmospheric gases and water vapor. Since this process not always manifests itself in the diurnal behavior, it will be analyzed later on with the allowance for its specific character.

3.3. Diurnal behavior of the Aitken mode and the transient subfraction

The monthly mean diurnal behavior of the particle number density of the Aitken mode is shown in Fig. 4. It is seen from the figure that this diurnal behavior is similar to that of the total number density of the fine and ultrafine aerosol. This is natural, because particles of the Aitken mode make up the major portion of the aerosol particles with the size ranging from 3 to 200 nm. That is why in this section we consider the reasons for the long lifetime of Aitken particles and the behavior of the total size spectrum of the fine and ultrafine aerosol.

The main source of Aitken particles is the rapid growth of nucleation particles mostly due to heterogeneous condensation. At the same time, the sink of Aitken particles due to coagulation is insignificant, as was mentioned above. So, this mode is most stable in the fraction of nanoparticles.

The maximum in the diurnal behavior of the aerosol particle number density for the transient subfraction falls on the nighttime (Fig. 5). The increase in the number of particles of this subfraction and, consequently, the decrease in the number of Aitken particles is about $5.5 \cdot 10^{-3} \text{ cm}^{-3} \cdot \text{s}^{-1}$ (as estimated by the method described in the previous section). Consequently, the rate of generation for particles of this mode is two orders of magnitude lower than that for the Aitken mode. Obviously, this is mainly caused by slow coagulation processes, rather than by faster nucleation and condensation ones.

Thus, from analysis of the diurnal behavior of different subfractions and estimation of the sink and generation rates of the fine and ultrafine aerosol, it follows that the generation rate for the primary particles is high enough, as compared with the sink rate; and permanent presence of the well-developed Aitken mode is the result of competition between the process of formation and transformation of the fine and ultrafine aerosol.

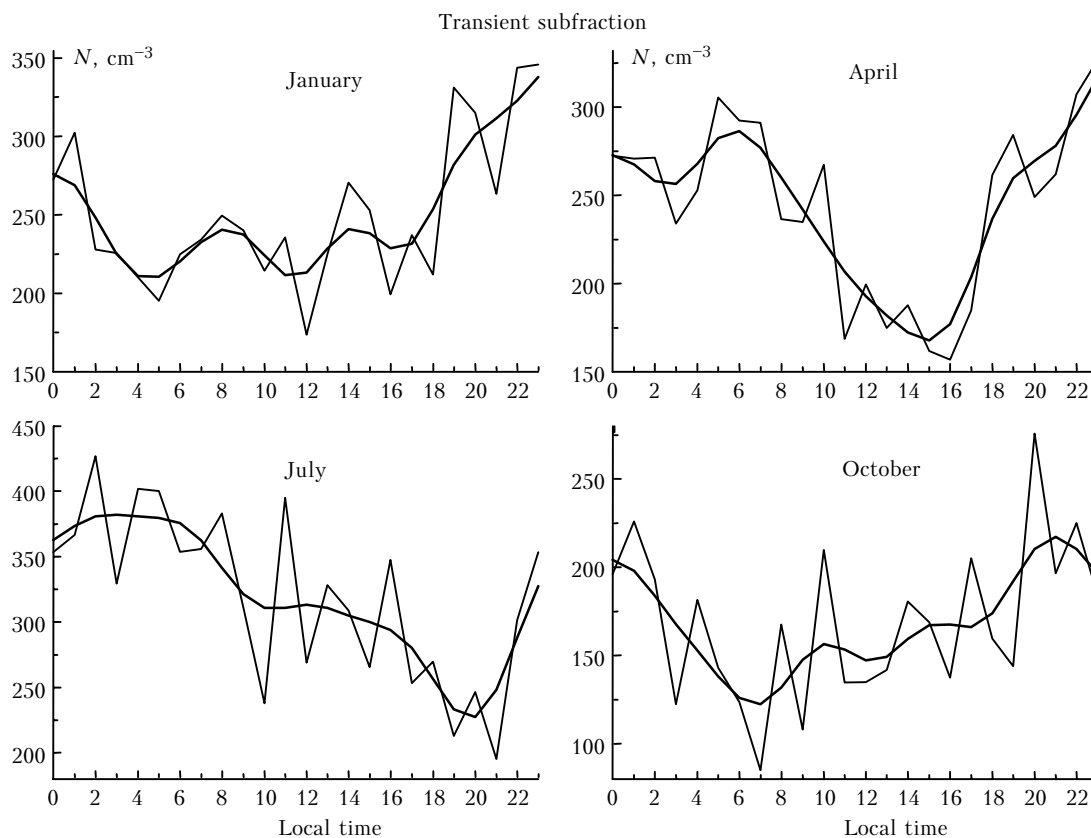


Fig. 5. Monthly mean diurnal behavior of the number density of aerosol particles of the transient subfraction.

We can outline the following qualitative mechanism of the diurnal behavior of the fine and ultrafine aerosol. In the morning, intense nucleation due to gas-to-particle conversion starts. This gives rise to a great number of new aerosol particles with $d < 0.01 \mu\text{m}$. The particles begin to grow fast due to condensation of vapor of aerosol-forming substances on them. Thus, the Aitken mode is formed. Near the upper limit of the size range of the Aitken mode, the intensity of condensation growth decreases, because the major portion of vapor is consumed for more mobile particles of the nucleation mode or particles with the diameter above $0.1 \mu\text{m}$ that have large total surface. The intensity of coagulation for particles of this size range is even lower, thus providing the possibility of accumulation of Aitken particles in the atmosphere.

At night, nucleation of particles sharply decreases, and the particles that have passed to the Aitken mode begin to coagulate, thus forming the transient subfraction.

3.4. Diurnal dynamics of the size spectrum of the fine and ultrafine aerosol

Let us consider now the diurnal dynamics of the whole size spectrum of the fine and ultrafine particles. Figure 6 shows the monthly mean size spectra for January and June obtained at different time. To check

the general regularity, this figure also shows the size spectra for some particular days in these months.

It is seen from Fig. 6 that the Aitken mode is permanently present in the size spectrum for 24 hours. However, its behavior in different seasons is different. Considering the variability of the spectrum in January (Fig. 6a), we can see that only the amplitude varies, while the position of the center of the mode is almost constant during a day. In June, (Fig. 6b) the modal diameter shifts markedly during a day. It shifts toward smaller size in daytime and toward larger size at night.

Such a behavior of the size spectra of the fine and ultrafine particles likely results from the change of the relative air humidity during a day, because condensation plays a significant role in the life of the aerosol nanoparticles. The relatively stable position of the mode during a day in January can be explained in the same manner. For explanation, turn our attention to Fig. 7. It is seen from this figure that the monthly mean diurnal variability of the relative humidity at the place of our observation is significantly different in January and June. The relative humidity in June varied from 63 to 97%. Therefore, the intensity of condensation growth decreased in daytime (the minimum fell on 15:00 L.T.) with the decrease in the humidity, and the modal radius shifted toward smaller size. In January the amplitude of variability of the relative humidity was less than 10%, and therefore the position of the mode did not change markedly.

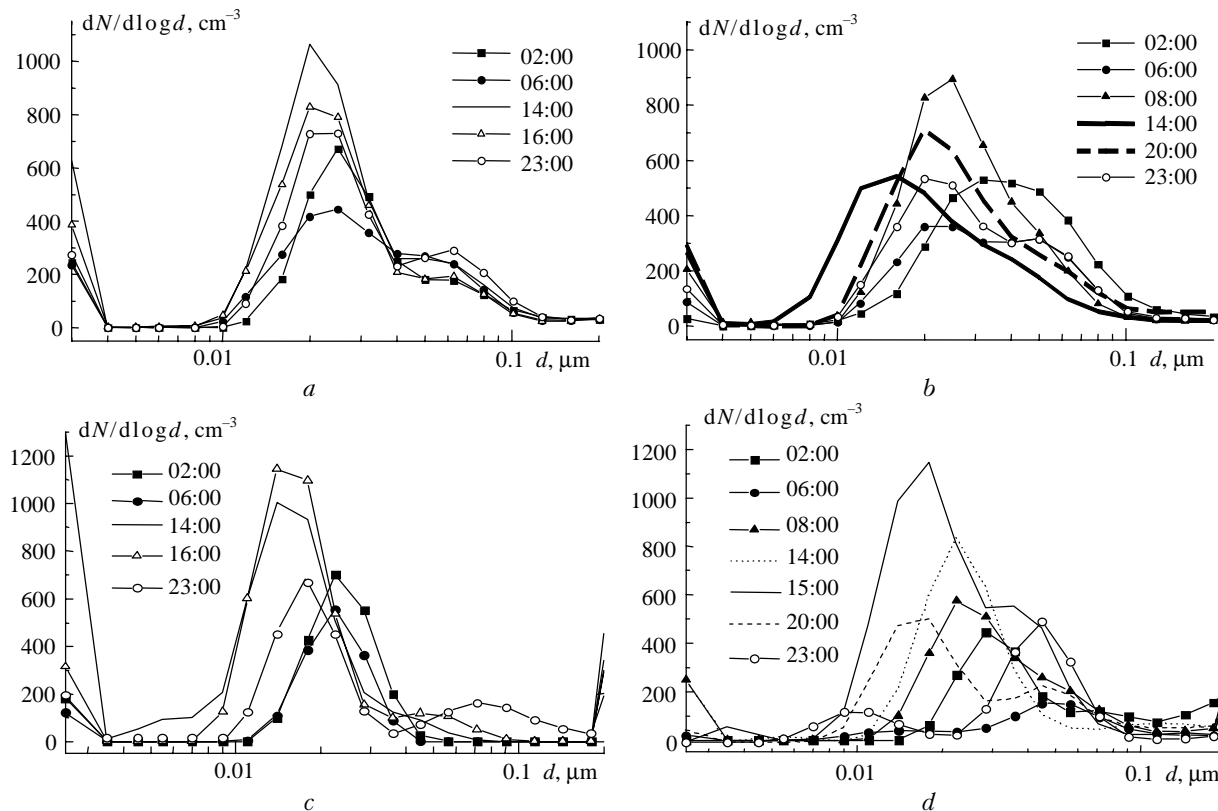


Fig. 6. Diurnal behavior of size-distribution of the fine and ultrafine aerosol: monthly mean for January 1996 (a), monthly mean for June 1996 (b), for January 24, 1996 (c), and for June 18, 1996 (d).

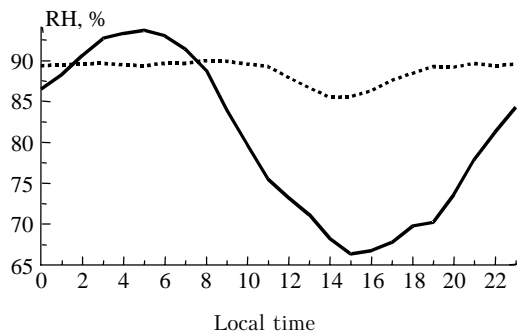


Fig. 7. Monthly mean diurnal behavior of the relative humidity: January 1996 (---) and June 1996 (—).

4. Nucleation

The fine and ultrafine aerosol is formed mostly in photochemical and catalytic reactions involving some atmospheric gases directly in the atmosphere. Nitrogen dioxide is one of such gases – precursors of aerosol. In December 1998 three-week monitoring of the fine and ultrafine aerosol and nitrogen dioxide was performed at the TOR station of the Institute of Atmospheric Optics SB RAS. The analysis of data obtained in this experiment allowed us to find a well-pronounced synchronism in the diurnal behavior of these atmospheric constituents with a positive feedback.⁷ This fact supposes that nitrate compounds can form a significant part in the composition of newly formed particles.

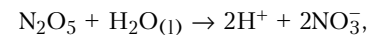
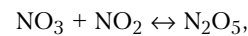
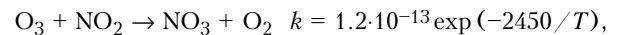
Consider now correlation between the diurnal dynamics of aerosols close to clusters in size ($d = 0.003 - 0.008 \mu\text{m}$), solar radiation intensity, and concentration of nitrogen dioxide and ozone using as an

example the day of December 17, 1998 (Fig. 8). It is seen from the figure that new aerosol particles are mostly formed in the photochemical reactions in the atmosphere. The similarity and synchronism in the behavior of the intensity of the net solar radiation, number density of particles of the nucleation mode, and concentration of nitrogen dioxide also evidence this.

However, particular attention is attracted to the presence of two secondary maxima in the aerosol number density at night and in the evening and to the fact that the aerosol number density begins to increase several hours before the sunrise. To understand the mechanism of these processes, we should consider the dynamics of the NO_2 concentration, because the sharp increase of the NO_2 concentration occurs just in the same hours.

Physical and chemical processes that take part in the nitrate cycle of aerosol formation are diverse, because nitrogen dioxide can oxidize by several mechanisms, especially, during daytime. These mechanisms are described in Ref. 8 in sufficient detail. In this paper, we concentrate just on the mechanism of aerosol formation from the gas phase during nighttime.

The measurements show that under certain conditions it can be rather efficient. One of such mechanisms is presented in Ref. 8. According to Ref. 8, nitrates can be formed at night in water droplets via the following sequence of reactions:



where (l) denotes the liquid phase.

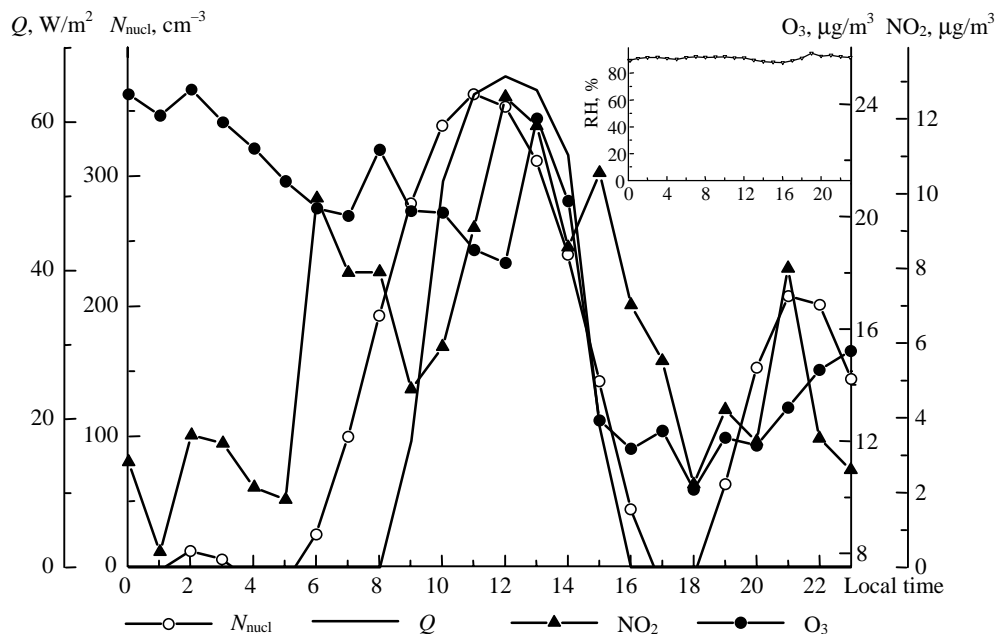


Fig. 8. Diurnal behavior of the number density of aerosol particles with $d = 0.003 - 0.008 \mu\text{m}$ (N), concentration of ozone (O_3) and nitrogen dioxide (NO_2), solar radiation intensity (Q), and relative humidity (RH); December 17, 1998.

Based on the data of our observations, we can conclude that this mechanism is active in nighttime at high humidity. Thus, the fine and ultrafine aerosol can be generated both in the presence and in the absence of solar radiation.

Conclusion

The analysis of the observed diurnal behavior of the fine and ultrafine aerosol allows the following conclusions to be drawn:

1. The fine and ultrafine aerosol can be divided into three subfractions in accordance with the mechanisms of their formation, namely, aerosol of the nucleation mode, aerosol of the Aitken mode, and the transient subfraction.

2. It can be assumed that the aerosol formed from the gas phase (nucleation mode) very rapidly begins to grow due to heterogeneous condensation of vapor of aerosol-forming substances and water vapor on them, and thus it grows up into the Aitken mode. In its turn, the main sink for particles of the Aitken mode is coagulation with aerosol of the accumulative fraction. At low concentrations of the accumulative aerosol, this process of sink has no significant effect on removal of the Aitken particles and, consequently, on their lifetime. Therefore, in the presence of a sufficiently stable source of generation of the nucleation mode, the loss of particles from the Aitken mode due to coagulation with large particles can be fully compensated for by the income of particles from the nucleation size range.

3. The Aitken mode is most pronounced and long-lived among the three subfractions considered. It is permanently present during 24 hours. The estimates of

the generation and sink rates indicate that the processes of removal of these particles are not sufficiently intense to suppress this mode at no (or weak) process of aerosol generation during nighttime.

4. Nitrogen dioxide plays a significant role in the formation of aerosol nanoparticles. Aerosol generation with participation of nitrogen dioxide can take place during both day- and night-time.

Acknowledgments

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