

Vertical distribution of nanoparticles in the continental troposphere

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Two typical profiles of nanoparticles were observed over the southern part of Western Siberia. The first type represents the well-known distribution that can be well described by the empirical equation proposed by Jaenicke. The second type of vertical profiles exhibits the so-called z-shaped structure with the secondary maximum in the free troposphere. Analysis of the data obtained in this study enabled us to estimate a new particle production rate in the free troposphere. The maximum production rate was in the 10^{-3} – 10^{-2} $\text{cm}^{-3} \cdot \text{s}^{-1}$ range.

Introduction

Aerosol particles play tremendously important role in the process of formation of the radiation field in the atmosphere, take part in different physical-chemical transformations, including that related to air pollution by the products of industrial activity. Although the importance of aerosol in the climatic system is widely recognized, up to now there are significant gaps in the description and modeling of the aerosol behavior in free troposphere, especially the behavior of nanoparticles, which then grow up to the optically active submicron fraction. The vertical distribution of nanoparticles in the troposphere remains to be poorly studied, as well. Now there are different points of view on the formation of vertical distribution of aerosol particles. One of them is that the larger portion of aerosol particles comes to the free troposphere from lower layers already formed. The smaller portion comes here due to sedimentation of stratospheric aerosol and aerosol of volcanic origin. The latter point of view casts some doubt on the possibility of nucleation in the free troposphere, because the concentration of the aerosol producing substances significantly decreases with height, hence, the rate of formation of aerosol particles is very low.

Some investigations of the vertical distribution of the concentration of nanoparticles during two last decades reveal the presence of aerosol layers in the free troposphere in some episodes. The concentration of nanoparticles in them can be comparable with their content in the boundary layer of the atmosphere. It could be explained by the long-range transport of the aerosol substance, ignoring the fact that the lifetime of ultrafine aerosol particles (of the diameter $d_p < 20$ nm) in the atmosphere is short because of the high rate of the condensation growth. Thus, these particles can be formed only *in situ* during photochemical and catalytic reactions between precursor gases, which can come from remote regions due to the atmospheric transport.

Investigation of the microdisperse aerosol in the free atmosphere by Soviet and Russian scientists was episodic, so only some pilot experiments are known in the literature.^{1,2}

First experiments abroad have been carried out in the middle of the last century and those give only general idea on the vertical distribution of aerosol, including the microdisperse fraction. Weickmann,³ Chagnon and Junge⁴ and other scientists investigated the vertical distribution of Aitken particles in the troposphere in the 1940s–1960s. The profiles obtained showed an exponential drop of the concentration up to a certain height, after which a well pronounced tendency to the constant concentration was observed. These profiles did not reveal any essential difference in the behavior of Aitken particles ($d_p < 200$ nm) and large particles ($d_p > 200$ nm). Based on this fact, Junge⁵ drew the conclusion that sedimentation does not play essential role and other processes almost do not depend on the particle size.

Generalizing all data on the vertical distribution available to that date, Junge proposed the following equation for describing the stable distribution that allows for the vertical transfer, while neglecting the horizontal advection:

$$D \frac{\partial^2 N}{\partial z^2} - aN - bN^2 - V_S \frac{\partial N}{\partial z} = 0, \quad (1)$$

where D is the turbulent diffusion coefficient, N is the concentration of Aitken particles, a is the rate of removal of particles due to scavenging at the mean time of particle residence in the atmosphere $\tau = 1/a$, b is the coagulation coefficient, V_S is the rate of gravitational sedimentation, z is the height.

It is seen from this equation that only first term represents the local increase of concentration due to turbulent diffusion, while other describe the decrease due some or other processes. Hence, according to Eq. (1), only lower layers of the troposphere are the

sources of particles, and the finished particles come from them to the free troposphere due to the turbulent exchange. Based on the generalized data, Junge drew one more important conclusion that the mean concentration of Aitken particles of $200\text{--}300\text{ cm}^{-3}$ makes the equilibrium between the outflow and income of particles and noted that this value is close to the mean concentration of cloud droplets, if taking into account stratus and convective clouds together.

One can find many formulas in the literature, both theoretical and empirical, which describe the vertical distribution of the aerosol number density. The overwhelming majority of them are based on the exponential dependence of the change of the particle number density with height. For example, L.S. Ivlev⁶ has proposed the following dependence based on the analysis of a number of papers, which, in his opinion, is fulfilled in the majority of cases:

$$N_i(h) = N_i(h_0, 0) \exp\left[\frac{-(h_0 - h)}{H_i}\right], \quad (2)$$

where h_0 is the height of formation and accumulation of aerosol, H_i is the half-width of the layer, at which the concentration changes e times. The value of H_i depends on the particles size. For Aitken particles it is some times larger than for large particles.⁷

In many foreign papers published in the last decade, the authors mainly refer to the universal formula for description of the distribution of the aerosol number density proposed by Jaenicke⁸:

$$N(h) = N(0) \left[\exp\left(\frac{-h}{H'_p}\right) + \left(\frac{N_B}{N(0)}\right)^n \right]^n, \quad (3)$$

where

$$n = H'_p / |H'_p|,$$

H'_p is the same that H_i in the formula proposed by L.S. Ivlev⁶; N_B is the equilibrium background aerosol number density in the free troposphere.

One can interpret this formula as universal due to the exponent n , which can conventionally be called the regional index. For example, H'_p in the marine regions⁹ varied in the limits from -290 to 440 m. Negative sign means that the number density increases up to a certain height. Undoubtedly, in the case of $N(0) \ll N_B$ this equation has the limits both at $h \rightarrow \infty$ and $h \rightarrow 0$. The model profiles calculated by this formula using the averaged data on the parameters involved in it are shown in Fig. 1.

It is seen from Fig. 1 that, on the average, the decrease of number density with height is characteristic of continental regions. Both increase and decrease of the number density with height can be observed in marine regions, as well as the equilibrium profile from the ocean surface. Of course, these model profiles are approximate, and Jaenicke notes that significant deviations are observed in anthropogenic plumes, in regions subject to the effect of local sources, and (that is the most important for the

problem considered in this paper) during nucleation events in the free troposphere.

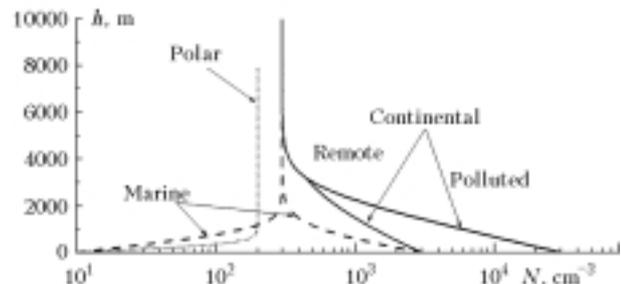


Fig. 1. Characteristic vertical distribution of the aerosol number density.⁸

The characteristic size distribution of aerosol in the free troposphere obtained by Jaenicke on the basis of averaging the experimental data⁸ is shown in Fig. 2.

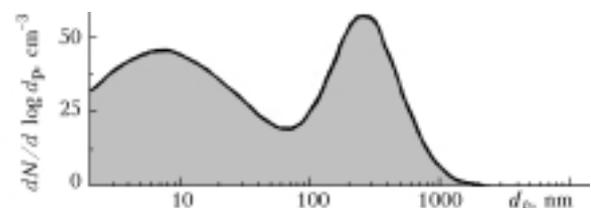


Fig. 2. Characteristic aerosol size distribution in the free troposphere.⁸

In recent years, combined groups of American scientists representing different institutes and universities of the USA joint within different programs and projects^{10–12} have dealt with the study of microdisperse aerosol particles as applied to the problem of cloud formation in the free atmosphere. These groups carry out different airborne investigations of nucleation and vertical distribution of aerosol in the atmosphere of equatorial regions of the Pacific Ocean, which are mainly aimed at studying the processes of cloud formation. Their investigations showed^{11,13,14} that nucleation under favorable conditions can be quite intense, up to the appearance of aerosol layers, in which the concentration of microdisperse particles can exceed that in the boundary layer.

Quite detailed study of nanoparticles in the free troposphere of continental region has been carried out in 1998 in Europe by the Institute for Atmospheric Physics (Germany) in the framework of the Linderberg Aerosol Characterization Experiment LACE-98¹⁵ summer measurement campaign. The profiles obtained showed the presence of maxima of the number density of ultradisperse particles and Aitken nuclei in the free troposphere, which, in opinion of the authors, are the result of *in situ* formation of particles.

1. Experimental data and instrumentation

This paper presents some data on the vertical distribution of microdisperse aerosol obtained during

monthly airborne experiments on the study of gas and aerosol composition of the atmosphere that is being carried out over southern region of Western Siberia. The region under study and the flight routes are shown in Fig. 3. Figure 4 shows the schematic diagram of the measurement system.

Measurements were carried out using Optik-E instrumented AN-30 aircraft.¹⁶ All data are reduced to the nanoparticles number density at the pressure and temperature of the ground level in order to compare the number densities at different heights.

An 8-channel automated diffusion battery (ABD designed by ICKC SB RAS, Novosibirsk)¹⁷ was used for measuring the nanoparticles number density. It is capable of recording the aerosol particles in the diameter range from 2.5 to 200 nm. This particular ABD has been specially designed for use in the airborne measurements, namely: the aspiration block was modified for stabilization of the airflow rate at the change of the flight height (Fig. 4).

Besides, a new software has been developed for controlling the ABD channels and data recording onboard an aircraft. The main reason for modifying the software was the difficulty in obtaining the objective data on aerosol particle number density caused the design peculiarities of the diffusion battery of any type. All diffusion batteries are scanning, i.e., the analyzed air successively passes through each of the eight channels to the condensation growth chamber (CGC) and then comes to the photoelectric counter. In this relation, the

minimum time of one complete scan is about 4 minutes. The AN-30 aircraft covers the distance of 20–30 km during this time that makes the reconstruction of the aerosol number density spatial distribution and size distribution difficult. So only two channels, the zero and the fifth, were used in the airborne version in order to shorten the scanning time. This allowed us to obtain the data on the total number density of aerosol particles as well as on the number densities of particles with $d_p < 70$ nm and $d_p > 70$ nm. Such a choice of the channels was caused by the values of the standard geometric deviation σ_g , which well agrees with the available averaged data on the aerosol number density size distribution in the free troposphere.

2. Vertical distribution over the southern part of Western Siberia

The principal types of the vertical profiles of the nanoparticle number density obtained during monthly airborne sounding over the south of Western Siberia since December 2002 until August 2003 are shown in Fig. 5. One can divide them into two types.

The vertical profile measured on March 5 is related to the first type. Its structure is close to the model distribution described by the Jaenicke formula, namely, the nanoparticles number density takes the background values at the height above 2000 m and undergoes only insignificant variations about the values of 100 cm^{-3} with height.

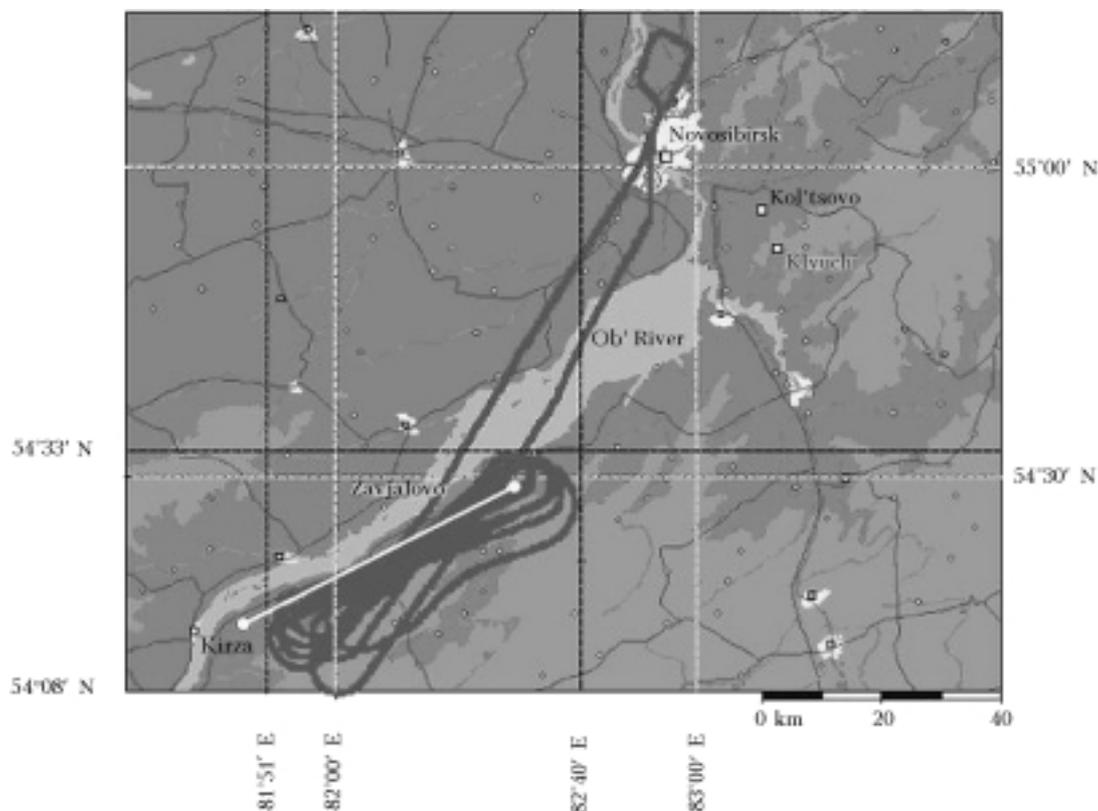


Fig. 3. Region of investigations.

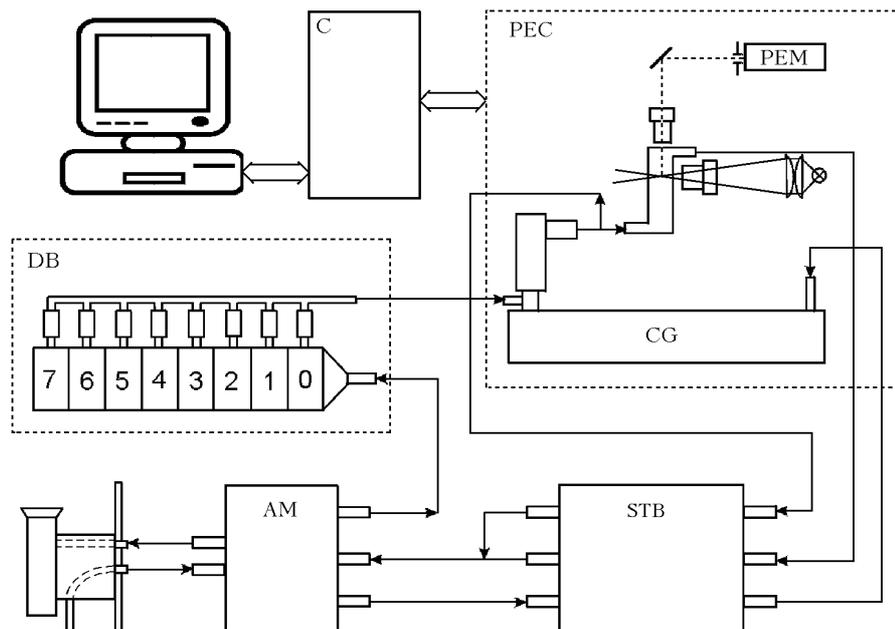


Fig. 4. Schematic diagram of the airborne ADB: DB is module of the diffusion battery, PEC is photoelectric counter, CG is condensation grower, STB is stabilizer of airflow rate, AM is aspiration module, C is controller.

During this flight, the region under study was under the effect of continental Arctic air mass, which explains the relatively low background number density of aerosol particles in the free troposphere according to the averaged data for the Arctic regions (see Fig. 1).

Three other profiles shown in Fig. 5 are related to the second type. It is seen from Fig. 5 that the well-known decrease of the aerosol particle number density with height in the lower troposphere characteristic of continental regions is observed in all the three cases presented. However, the well pronounced secondary maxima of the nanoparticles number density were observed in the middle troposphere. For example, on July 28, 2003 the number density in the layer from 6000 to 7000-m height was practically equal to its near-ground value. In other words, the vertical profiles showed the so-called z-shaped structure similar to that obtained over continental regions of Europe.¹⁵ The profile structure is an evidence of the fact that the upper troposphere is effectively isolated from the surface, because the minimum is observed above the upper boundary of the mixing layer. The exponential decrease of the aerosol number density is observed from the ground surface up to the mixing layer boundary. Formation of the proper nanoparticle aerosol layers occurs in the free troposphere. Obviously, these layers are the result of the processes of formation of new particles in the upper troposphere itself.⁸

The profiles related to the second type differ from each other as well. The first difference lies in the fact that the main secondary maximum of the number density of particles $d_p < 70$ nm is observed at different levels in the free troposphere. For example, on May 31, 2003 it was recorded at the heights below 6000 m, while on July 28 it was above 6000 m.

The second difference is the vertical distribution of nanoparticles observed on August 29, 2003, when two maxima in the free troposphere were well pronounced. The thickness of one of the layers was several kilometers.

Hence, the conclusion follows that the continental mid-latitude air mass passing over the region of observations this day was enriched with aerosol precursors, and intense processes of the formation of new aerosol particles from gaseous phase occurred in the free troposphere. One should note that it cannot be a result of the long-range transport of the aerosol substance, because the number density of older and long-living particles with $d_p > 70$ nm was low and monotonically decreased practically from the ground surface. The number densities of particles with $d_p < 70$ nm and $d_p > 70$ nm would compare if coming due to the long-range transport, because it would be enough time for the formation of large particles.

If considering the behavior of the nanoparticle number density in the lower troposphere, the profile obtained on July 28, 2003 stands out of all the profiles. A monotonic exponential drop of the nanoparticle number density with height was observed in all other profiles starting from the ground to the free troposphere, while this particular profile showed relative constancy of the number density of the aerosol particles with $d_p > 70$ nm from the height of 500 m up to ≈ 1900 m, and for the particles with $d_p < 70$ nm – up to 2300 m. It is the result of the well developed turbulent mixing in the boundary layer of the atmosphere due to strong heating of the underlying surface, which led to the formation of the internal mixing layer (IML) and homogeneous distribution of the aerosol number density over it.

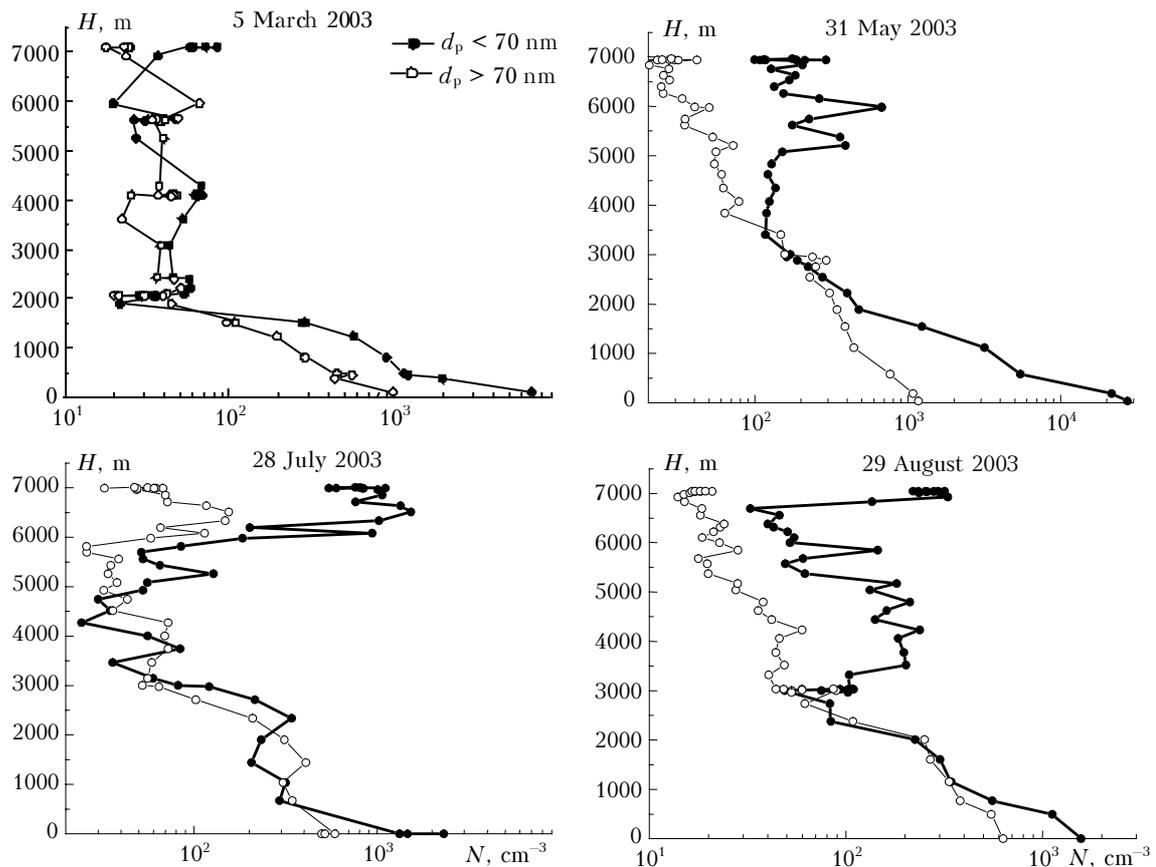


Fig. 5. Principal types of the vertical distribution of the nanoparticle number density in the atmosphere.

All the profiles of nanoparticles considered in this paper are shown in Figs. 6a and b. As seen from Figs. 5 and 6 the number density of particles with $d_p < 70$ nm at the heights above the mixing layer is significantly larger than that of the particles with $d_p > 70$ nm, i.e., small particles make the principal contribution to the total number density of aerosol particles. Hence, finally, the nucleation is the principal source of aerosol, keeping the number density of cloud condensation nuclei in the free troposphere at the necessary level. Since this is closely related to the indirect effect of aerosol on the radiative budget of the atmosphere, one should obviously take into account the processes of formation of new particles in the upper layers of the troposphere when constructing climatic models. Thus, in case of *in situ* formation of aerosol particles, the stable state described by Eq. (1) is broken and this equation can be replaced, in the general form, by the following equation:

$$\frac{\partial N}{\partial t} = D \frac{\partial^2 N}{\partial z^2} - aN - bN^2 - V_s \frac{\partial N}{\partial z} + J, \quad (4)$$

where J is the rate of formation of new particles (nucleation).

This form is identical to the formula proposed in Ref. 18. The difference lies in the fact that the terms describing the vertical and horizontal motion are

absent in the right-hand side of the equation. In the general case, Eq. (4) has no solution. One can calculate four first terms of the right-hand side of the formula in some or other way. However, it seems to be impossible to describe theoretically the height distribution of the nucleation rate, because the processes of gas-to-particle transformation depend on many thermodynamic parameters. In addition, the concentrations of some substances — aerosol precursors are unknown. The reasons for formation of the z-shaped profile of the nanoparticle remain inexplicable, or more precisely, it is still unclear why the process of nucleation in the upper layers of the troposphere has higher rate than at the boundary of the mixing layer. Nevertheless, such a z-shaped structure is also observed in the averaged distribution of the number density of nanoparticles of the size less than 70 nm (Fig. 6c), which means that the process of *in situ* formation of new particles in the upper troposphere is quite a regular phenomenon, and, evidently, it is global.

Analysis of Fig. 6 also allows us to reveal seasonal dynamics of the boundary of the mixing layer (ML). It is seen that the seasonal behavior of the ML height is in a good agreement with the long-term average behavior calculated from the profiles of the number density of large particles ($d_p > 400$ nm) for Western Siberia,¹⁹ i.e., the maximum of the height is observed in summer, and the minimum is in winter.

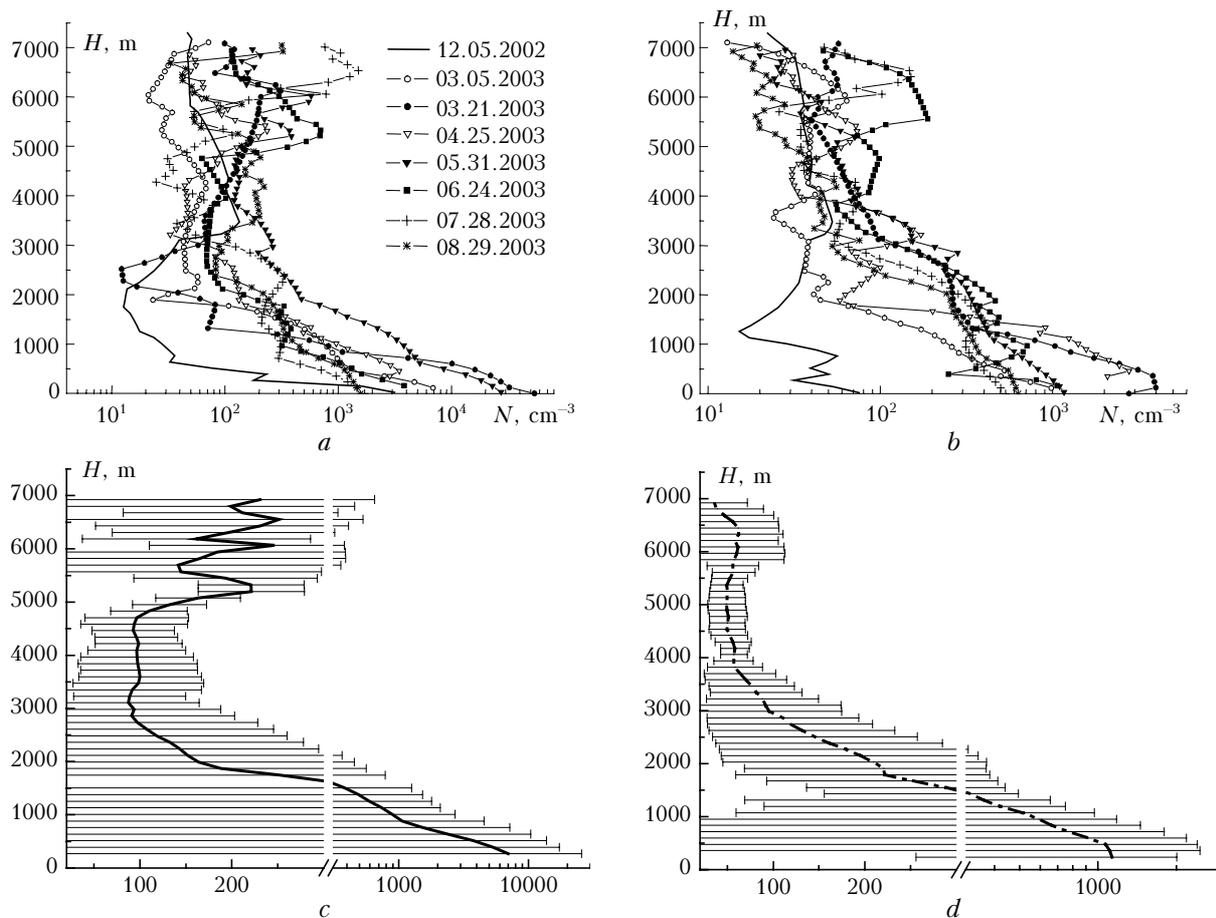


Fig. 6. Vertical profiles of the nanoparticle number density in the atmosphere over the south of Western Siberia: (a) $d_p < 70$ nm, (b) $d_p > 70$ nm, (c) averaged for particles with $d_p < 70$ nm, (d) averaged for particles with $d_p > 70$ nm.

The exception is the profile acquired in June, because the flight has been carried out in the morning and the height of the layer was a little bit lower because of the poorly developed convection in these hours.

3. Discussion

3.1. Vertical profiles of nanoparticles

Vertical profiles of nanoparticles similar to aforementioned ones were also obtained over central regions of Western Europe.¹⁵ Both secondary maximum of the number density of ultradisperse particles and of the Aitken nuclei were observed in the free atmosphere of the continental Europe. Schröder with co-authors¹⁵ relate this maximum to the processes of formation of new particles, or, in other words, nucleation, and prove this point of view as follows. The simplified diagram of the possible aerosol states in the troposphere constructed on the basis of the results of their measurements in Central Europe is shown in Fig. 7. The NS block represents the typical number densities of particles N ($3 < d_p < 100$ nm) ≈ 2500 cm⁻³, formed by nucleation and still non-interacting with larger particles. The low total surface area of aerosol particles existing in the free troposphere provides favorable conditions for

formation of particles from the gas phase. The AS block characterizes the well-developed state of accumulated aerosol $N(d_p > 100$ nm) ≈ 200 cm⁻³, i.e., accumulation of aged aerosol particles resulting from coagulation, convective transfer of particles from the underlying surface, and condensation growth of “new” particles in the way “NS→AS”.

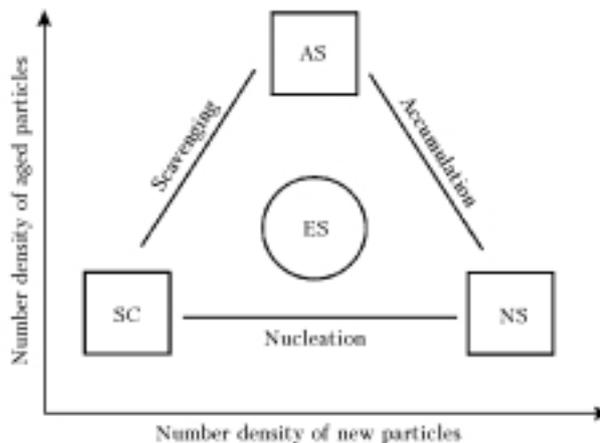


Fig. 7. The diagram of the probable states of aerosol in the upper troposphere: NS is nucleation state, AS is accumulation state, SC is state after the influence of clouds, ES is equilibrium (background) state.¹⁵

After the accumulation of quite high surface concentration, the “aged” particles begin to suppress the processes of formation of new particles. Finally, the third SC block is the state with the number density of particles $N(d_p > 100 \text{ nm}) \approx 20 \text{ cm}^{-3}$, hypothetically decreased due to scavenging by large cloud droplets. The ES block means equilibrium number densities: $N(d_p > 100 \text{ nm}) \approx 60 \text{ cm}^{-3}$ and $N(3 < d_p < 100 \text{ nm}) \approx 300 \text{ cm}^{-3}$. So, it is necessary to clarify that only the data of flights in the cloudless atmosphere and mainly in the daylight time were used in our analysis.

Many experiments on the study of the processes of formation of new particles were carried out by the group of American scientists in remote regions of Pacific Ocean in the frameworks of the international ACE-1¹³ and PEM-T¹² experiments. These studies revealed the presence of powerful nucleation processes occurring in the daylight time in the free atmosphere both in the vicinity of convective clouds and under clear sky conditions. Generalizing the results of these experiments, it was concluded that usually nucleation in the free troposphere is observed in the regions “cleaned” from large aerosol particles (the surface area less than $5 \mu\text{m}^2\text{cm}^{-3}$) by clouds.

It is worth noting here an important fact that the dynamics of the vertical distribution of the nanoparticle number density was revealed when flying over the same region in different time of day. In the morning their concentration practically does not change with height remaining at the level of the background values, which agrees with the vertical distribution satisfactorily described by the Jaenicke formula. The thick layer of nanoparticles was observed near noon in the free troposphere, and their number density was 10 times higher than that in the boundary layer of the atmosphere. It can be an evidence of the photochemical mechanism of nucleation in the free atmosphere.

3.2. Nucleation processes in the free troposphere

In some cases, one can use the data on the ozone concentration as an indicator of photochemical processes occurring in the atmosphere. For example, it was revealed when analyzing the data of monitoring the microdisperse aerosol fraction and ozone in the near-ground layer that the processes of ozone and ultradisperse particles ($d_p < 12 \text{ nm}$) generation occur synchronously.²⁰ The profiles of the ozone concentration and the nanoparticle number density obtained during airborne sounding on May 31, 2003 are shown in Fig. 8.

It is seen from Fig. 8 that the maxima of concentrations of these two components in the upper troposphere practically coincide. Hence the conclusion follows that favorable conditions are formed in the upper troposphere for photochemical formation of new particles.

Let us address the question on which thermodynamic parameters of the atmosphere and

processes can favor the *in situ* formation of particles in the free troposphere.

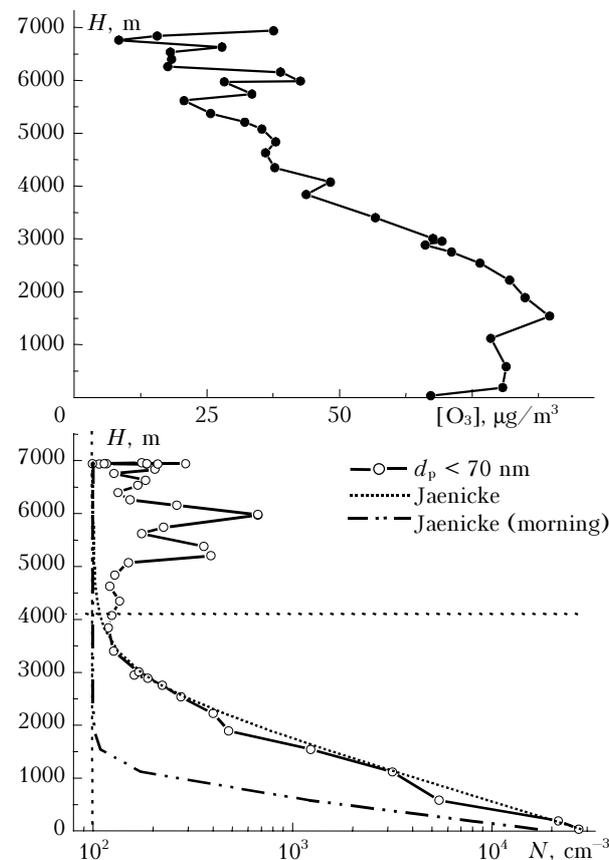


Fig. 8. Vertical distributions of the ozone and nanoparticles on May 31, 2003.

According to the data available^{21–24} from measurements of the nanoparticle number density and sulfuric acid concentration, the mechanism of binary nucleation of the system $\text{H}_2\text{SO}_4\text{--H}_2\text{O}$ is prevalent in the free atmosphere. Doyle²¹ was the first who theoretically described and calculated the rates of nucleation of such a system, yet in 1961, laying a foundation for the so-called classic theory of binary nucleation of sulfuric acid and water. Experimental data on the rate of nucleation differed from the theoretically calculated values several orders of magnitude. Later on the modifications have been introduced to the theory taking into account the effect of formation of hydrates in the system $\text{H}_2\text{SO}_4\text{--H}_2\text{O}$,²² developed in the last decade by Jaeker-Voirol and Mirabel,²³ Kulmala and Laaksonen.²⁴ According to the revised theory, the presence of hydrates decreases the rate of binary homogeneous nucleation $\text{H}_2\text{SO}_4\text{--H}_2\text{O}$ as compared with the rate calculated neglecting hydrates (old theory) 5–6 orders of magnitude.

3.3. Possible reasons for formation of the z-shaped vertical distribution of the nanoparticle number density

As applied to the atmospheric conditions, the formula for calculation of the critical concentration

of sulfur acid ($\mu\text{g}/\text{m}^3$) necessary for the rate of nucleation $J = 1 \text{ cm}^{-3} \cdot \text{s}^{-1}$ is widely used for estimating of the possibility of occurrence of essential processes of the binary nucleation in the system $\text{H}_2\text{SO}_4\text{--H}_2\text{O}$ (Ref. 25):

$$[\text{H}_2\text{SO}_4]_{\text{cr}} = \text{const} \exp(0.1T - 3.5RH - 27.7), \quad (5)$$

where T is the air temperature, K; RH is the relative humidity in fractions of unity.

It follows from this formula that favorable conditions for nucleation are formed at quite low air temperature and high relative humidity. In this case nucleation is also possible at low critical values of the concentration of sulfur acid. When the critical value of the sulfur acid H_2SO_4 concentration in the atmosphere is exceeded, one can expect the beginning of the process of generation of particles, because the rate of nucleation strongly changes even at not very large changes in the concentration of H_2SO_4 .

Generalizing all the above-said, we can conclude that the most favorable conditions for binary nucleation of sulfur acid and water are the following: the daylight time, because photochemical processes lead to formation of H_2SO_4 vapor; low total surface of aerosol particles existing in the unit volume in the atmosphere (minimization of heterogeneous condensation); and quite high relative humidity and low air temperature.

The vertical profiles of the critical concentration of H_2SO_4 calculated using the parameters involved in Eq. (5) are shown in Fig. 9.

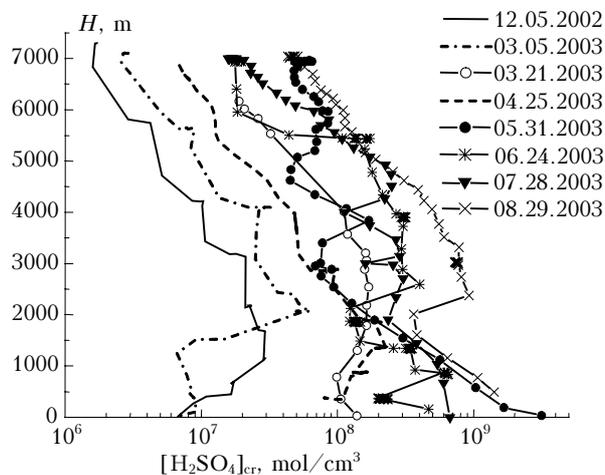


Fig. 9. Model profiles of the critical concentration of sulfur acid calculated by Eq. (5) using the data of airborne sounding over the south of Western Siberia.

It is seen from Fig. 9 that favorable conditions for binary nucleation are formed in the upper troposphere where the values $[\text{H}_2\text{SO}_4]_{\text{cr}}$ are the lowest. It should be emphasized that the low values of the nanoparticles number density and the critical concentration of sulfur acid in the lower layers of the troposphere during cold season and, in contrast, high in summer contradict to the classical theory of binary nucleation. This is caused by the fact that this theory

is poorly applicable within the mixing layer, because of superposition of other nucleation mechanisms, for example, triple nucleation with participation of ammonia, whose principal source is soil. Measurements of the concentration of gaseous sulfur acid were not carried out in this study; however, analysis of critical (threshold) values of the H_2SO_4 concentration calculated using Eq. (5) shows that they begin to significantly decrease at the heights above 4000 m.

Apart from the considered factors favoring the formation of aerosol particles from the gas phase, a number of investigations that have been carried out in recent time²⁶ point out the essential effect of the so-called ion-induced nucleation (IIN) on these processes in the lower stratosphere and the upper troposphere. The role of IIN consists in increasing the stability of electrically charged clusters. Carlslaw with co-authors²⁷ assume that the presence of a charge decreases the nucleation threshold thus stabilizing the aerosol particle nuclei ($\sim 1\text{--}2 \text{ nm}$). Therefore, binary nucleation can start at lower concentrations of $\text{H}_2\text{SO}_4\text{--H}_2\text{O}$ than in the unionized atmosphere. The charge on stable nuclei, in its turn, increases the rate of heterogeneous growth due to electrostatic forces. Airborne investigations by means of the mass-spectrometer have revealed high concentrations of clusters with positive ions in the upper troposphere²⁸ and plenty of negative ions with bisulfate nucleus in the stratosphere and troposphere.^{29,30} The source of ions in the upper layers of the atmosphere can be cosmic rays.³¹

3.4. Estimated rate of formation of new particles in the free troposphere

Since the concentration of vapors – aerosol precursors was not measured in our experiments, estimation of the rate of formation of new particles in the free troposphere was performed using the increase in the content of nanoparticles during the time corresponding to the measurement period. To do this, one can use the diagram of aerosol states in the free troposphere¹⁵ (see Fig. 7) and the Jaenicke formula for calculation of the vertical distribution of the aerosol number density. Let us suppose that the aerosol state in the free troposphere in the morning under clear sky weather and in the absence of nucleation corresponds to equilibrium or to the state after the influence of clouds, according to the diagram shown in Fig. 7. Then, Eq. (3) can be used to calculate the probable profile. Let us assume that the equilibrium background aerosol number density in the free troposphere N_B is equal to the minimum values of the nanoparticle number density in the z-shaped profile measured in daytime. Calculate the total content of the upper part of the profile, where the nanoparticle number density does not vary with height. The vertical distribution of nanoparticles on May 31, 2003 and two model distributions (Jaenicke) of particles are shown in Fig. 8b. One of them has been obtained based on the above considerations, the

another being calculated using the measured profile assuming the absence of nucleation processes in the upper troposphere.

To calculate the increase of the nanoparticle number density, use the following simple approach. Having known the particle number density in the layer from the height h_{ML} up to the maximum height h_{max} , where airborne sounding has been carried out, calculate the total number of particles contained in this vertical column of air in the morning and near noon by integrating over height within these limits. The difference between these integrals gives the increase of particles due to nucleation. Dividing this value by Δt , we obtain the number of particles formed in the air column of a unit cross section 1 cm^2 for 1 s.

$$\frac{\Delta n}{\Delta t} = \Delta S \left(\int_{h_{ML}}^{h_{max}} N(h)dh \Big|_d - \int_{h_{ML}}^{h_{max}} N(h)dh \Big|_m \right) / \Delta t \text{ \#}/s, \quad (6)$$

where the indices “m” and “d” mean morning and daytime, respectively, n is the number of particles, $\#$ /s is the number of particles per 1 second.

Assuming the horizontal distribution of aerosol over a certain area to be homogeneous and normalizing the values obtained by Eq. (6) to the volume of the column of the 1 cm^2 cross section, we obtain the mean rate of formation of particles in the generally accepted units: $\text{cm}^{-3} \cdot \text{s}^{-1}$. The data of these calculations are given in Table 1.

Table 1. Estimate of the mean rate of formation of particles in the free troposphere

Date	H_{ML} , m	h_{max} , m	Δn , particles	J^* , $\#$ /s	J , $\text{cm}^{-3} \cdot \text{s}^{-1}$
12.05.2002	1690	7300	$2.9 \cdot 10^7$	$1.6 \cdot 10^3$	$2.9 \cdot 10^{-3}$
03.05.2003	1890	7100	$1.2 \cdot 10^7$	$4.1 \cdot 10^2$	$7.8 \cdot 10^{-4}$
03.21.2003	2180	7080	$5.1 \cdot 10^7$	$1.8 \cdot 10^3$	$3.9 \cdot 10^{-3}$
04.25.2003	3180	6860	$1.9 \cdot 10^7$	$4.7 \cdot 10^2$	$1.2 \cdot 10^{-3}$
05.31.2003	3840	6940	$3.2 \cdot 10^7$	$8.9 \cdot 10^2$	$2.9 \cdot 10^{-3}$
06.24.2003	2590	6930	$2.6 \cdot 10^7$	$2.4 \cdot 10^3$	$5.5 \cdot 10^{-3}$
07.28.2003	3460	7000	$1.0 \cdot 10^8$	$2.8 \cdot 10^3$	$8.0 \cdot 10^{-3}$
08.29.2003	3000	7040	$4.1 \cdot 10^7$	$1.3 \cdot 10^3$	$3.1 \cdot 10^{-3}$

Besides, we can estimate the maximum rate of formation of nanoparticles in the free troposphere using the increase of the number density at the height where the maximum is observed in the z-shaped profile. The results of this estimation are given in Table 2.

Table 2. Estimate of the maximum rate of formation of particles in the free troposphere

Date	H , m	J_{max} , $\text{cm}^{-3} \cdot \text{s}^{-1}$
12.05.2002	3430	$6.9 \cdot 10^{-3}$
03.05.2003	7100	$2.2 \cdot 10^{-3}$
03.21.2003	6170	$1.2 \cdot 10^{-2}$
04.25.2003	5390	$5.8 \cdot 10^{-3}$
05.31.2003	5970	$1.4 \cdot 10^{-2}$
06.24.2003	5440	$2.8 \cdot 10^{-2}$
07.28.2003	6510	$4.2 \cdot 10^{-2}$
08.29.2003	6930	$9.3 \cdot 10^{-3}$

As is seen from Tables 1 and 2, the rate of formation of nanoparticles in the free troposphere is low and lies in the range from 0.001 to $0.04 \text{ cm}^{-3} \cdot \text{s}^{-1}$. The maximum rate of formation was observed on July 28, 2003 at the height of ~ 6500 m. If we compare the results of these estimates with those obtained earlier in the near-ground layer,³² we can see that they are comparable in some cases.

In general, the rates of generation of nanoparticles obtained both in the near-ground layer of the atmosphere in the region of Tomsk³² and in the free troposphere over the south of Western Siberia are within the limits of the rate values observed in the background regions. The following typical values of the rate of formation in the near-ground layer are presented in the review by Prof. Kulmala³³ on the rates of formation and growth of microdisperse particles based on the data of observations in the atmosphere:

- Background regions – $0.01\text{--}10 \text{ cm}^{-3} \cdot \text{s}^{-1}$;
- Urban areas – up to $100 \text{ cm}^{-3} \cdot \text{s}^{-1}$;
- Coastal zone, SO_2 plumes from enterprises – up to $10^4\text{--}10^5 \text{ cm}^{-3} \cdot \text{s}^{-1}$.

The data from Ref. 33 indicate that the values of the rate of formation of nanoparticles in the near-ground layer of the atmosphere can be lower. For example, the values of the rate in the background regions of the zone of boreal forests of Finland range from 0.001 to 1 (see Ref. 34) and from 0.002 to $0.6 \text{ cm}^{-3} \cdot \text{s}^{-1}$ (see Ref. 35). On the one hand, the values of the rate of formation of nanoparticles in the free atmosphere over the south of Western Siberia are less than $1 \text{ cm}^{-3} \cdot \text{s}^{-1}$, i.e., lower than the threshold value, which is usually considered significant for the nucleation process.²⁵ On the other hand, analysis of the profiles shows that in some cases the number density and the rate of nanoparticle formation in the upper layer of the troposphere are comparable with the values observed in the near-ground layer of the atmosphere. This may be caused by the fact that the detection limit of ADB is $2.5\text{--}3$ nm and, hence, the number density of particles of smaller diameter and clusters ($d_p \sim 1$ nm) remains unknown. According to the theory of homogeneous nucleation, a cluster is a stable i -mer that reached some critical size and can grow further only after exceeding this critical size. For the nucleation to continue, the number density of clusters should exceed the number density of the aerosol particles formed.⁹ Since the thermodynamically stable clusters of the size ~ 1 nm, being yet not an aerosol particle, is formed due to nucleation, O’Dowd defines the formation of new particles as the instant when the cluster has reached the size ~ 3 nm or greater due to condensation.³⁶ If the nucleus does not grow sufficiently quickly, it will be absorbed by existing particles due to coagulation. Therefore, the nucleation process cannot be completely identified as the process of new particles formation. For these reasons, the obtained estimates of the rate of formation of new particles in the free troposphere can be considered significant, because this means that the

rate of nucleation should be greater to compensate for the sink of clusters on the existing particles and to provide for their condensation growth for reaching the size on the order ~ 3 nm.

3.5. Size distribution of nanoparticles in the free troposphere

Since it is impossible to precisely reconstruct the size distribution of nanoparticles having available only the data on the total number density of particles with $3 \text{ nm} < d_p < 70 \text{ nm}$ and $d_p > 70 \text{ nm}$, in this section we consider their probable lognormal distribution. The well-known formula⁹ was used for its reconstruction:

$$\frac{dN}{d \log d_p} = \sum_i^k \frac{N_i}{\sqrt{2\pi} \log \sigma_i} \exp\left(-\frac{(\log d_p - \log \bar{d}_{pi})^2}{2 \log^2 \sigma_i}\right), \quad (7)$$

where N_i is the number density, \bar{d}_{pi} is the mean diameter, σ_i is the standard deviation of the i th lognormal mode, k is the number of modes.

In our case $i = 2$, the standard deviation σ_i and the mean diameter of the i th mode were taken from literature data on the aerosol particle size distribution in the free troposphere, both model⁹ and experimental.¹⁵ The probable size distributions of nanoparticles at the heights, where the maximum of the number density of particles $d_p < 70 \text{ nm}$ occurs, are shown in Fig. 10 (see Table 2).

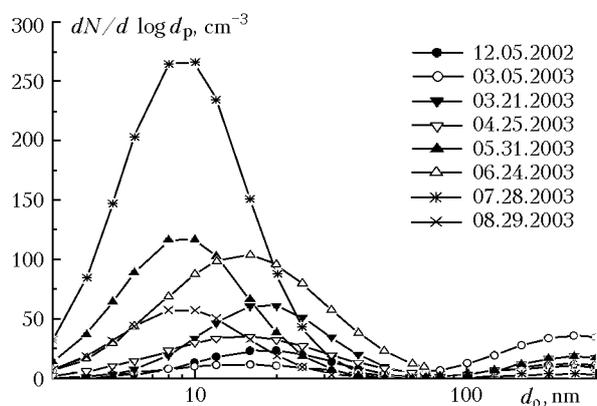


Fig. 10. Probable size distribution of nanoparticles in the free troposphere over the south of Western Siberia.

It is seen in Fig. 10 that the size distribution of nanoparticles for the case of profiles of the first type corresponds to the averaged distribution⁸ shown in Fig. 2. Intensification of the first mode of lognormal particle size distribution is characteristic of the cases when intense nucleation has been observed in the free troposphere (profiles of the second type).

Conclusions

1. Vertical profiles of two types have been revealed during investigation of nanoparticles in the troposphere over the south of Western Siberia. The first type is satisfactorily described by the Jaenicke

empirical formula. The second type of profiles shows the presence of the z-shaped height profile of the number density of nanometer-size particles.

2. Favorable conditions for nucleation processes leading to formation of the z-shaped profiles of the nanoparticles number density are formed in the free troposphere. Thermodynamic parameters of the upper troposphere can be among the factors causing the formation of such conditions, which lead to the decrease of the threshold values of the concentration of vapor of aerosol-producing substances necessary for starting the processes of formation of new particles. The presence of ions in the upper troposphere can be the second cause, which stabilizes the critical nuclei, preventing their disintegration and simplifying their condensation growth. This increases the probability that they reach the size of ~ 3 nm.

3. Analysis of the data on nanoparticles vertical distribution allowed us to estimate the rate of *in situ* formation of aerosol particles in the free troposphere. The maximum rate of formation of new particles ranges from 10^{-3} to $10^{-2} \text{ cm}^{-3} \cdot \text{s}^{-1}$.

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