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NATURAL AND ANTHROPOGENIC AEROSOLS: A COMPARATIVE ANALYSIS

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Despite an imperfection of the present-day climate theory, the conclusion about an important climate-forming role of the atmospheric aerosol can be considered as quite reliable [1, 5, 24, 34]. The role of aerosol as a climatic system element is at least dual: (i) it directly affects the radiation transfer conditions in the atmosphere, and (ii) it changes the extent, size, distribution and radiative properties of cloudiness.

A purely scattering aerosol raises the albedo of the atmosphere, thereby decreasing the amount of radiation which reaches the Earth's surface. In the presence of aerosol absorption, a direct "energy-feeding" of the atmosphere takes place. Thus the anti-greenhouse effect appears when the atmosphere is excessively heated and the surface is cooled. However, since the absorbing aerosol is, at the same time, a heat source, simultaneously the atmospheric greenhouse effect grows. The total radiative effect of the atmospheric aerosols, which both absorb and scatter radiation, depends on the ratio between the absorption coefficients in the shortwave and IR regions, as well as on the surface albedo, sun elevation and cloud conditions.

The effect of aerosol on cloudiness consists in the following: (i) a certain part of aerosols acts as condensation nuclei, causing an increase in the amount of suspended small droplets, and (ii) aerosol particles, caught by clouds, change the radiative properties of clouds and, consequently, the vertical temperature profile. In its turn, this affects the conditions of the formation of cloudiness and of its subsequent transformation.

Since in real conditions the aerosol gets to the atmosphere through both natural and anthropogenic mechanisms, and a relative contribution of the latter is constantly increasing, keen interest in a search for techniques for adequate evaluation of the disturbing effect of aerosols (anthropogenic, in particular) on climate is justified. Quite recently this interest has grown in connection with a discussion of possible climatic implications of nuclear explosions in the atmosphere, as a manifestation of an extreme anthropogenic impact on the ecological system of the planet [38].

The first stage of the consideration of the effect of aerosol on climate is the modeling of aerosol properties. The models (based on statistically reliable field-measurements data) are to parameterize such characteristics as complex refractive index of particles ($m = n - ki$), their shape and size distribution, vertical profile of aerosol concentrations, as well as variability of these parameters in time and due to humidity.

With regard to the ever-increasing content of anthropogenic aerosols in the atmosphere and to its increasing role as a climate-forming factor, as well as in the light of the above-mentioned discussion, of interest is a comparative analysis of the physico-chemical properties of the natural and anthropogenic aerosols, which together define the term "atmospheric aerosol".

The composition and concentration of the atmospheric aerosol for each localization in space and time can be represented as a superposition of some background and "disturbing" aerosols. The parameters of the latter depend on the character, power, and distance of one source or several sources of "disturbance", and on the effectiveness of the mechanisms of sink. The regions of aerosol-generating mechanisms, both natural and anthropogenic, can serve as sources of disturbance.

Due to the considerably different nature of aerosols and their living conditions in different layers of the atmosphere (which are nearly isolated in the sense of energy- and mass-exchange), the atmospheric aerosol is subdivided into tropospheric, stratospheric, mesospheric, etc., aerosols. Its background and "disturbing" components are, accordingly, differentiated.

The natural mechanisms of atmospheric aerosol generation are as follows: soil-wind erosion, ejections to the atmosphere of salt particles from sea and ocean surfaces, emission of gases and vapors by photosynthesizing plants and by decay products, ejections of the products (soot aerosol, first of all) of natural fires of forests, steppes, peat bogs, and also volcanic eruptions.

The anthropogenic mechanisms are the following: ejections to the atmosphere of solid particles and gases resulting from engine fuel combustion, functioning of industrial enterprises, agriculture (soil plowing, use of chemical fertilizers, herbicides and poisonous fertilizers, planned burning out of forests, prairies, etc.), as well as surface explosions of atomic and thermonuclear systems.

Thus, in general, the anthropogenic aerosol is not only the aerosol, whose chemical composition and other parameters differ from those of natural particles, but also natural particulate matter generated by non-natural mechanisms. For instance, the aerosols, both injected into the atmosphere and formed *in situ* as a result of nuclear explosions in the atmosphere.

There are also "ready" aerosols, which get to the atmosphere in the form of either solid particles (both hygroscopic and hydrophobic) or aqueous droplets, and aerosols formed *in situ*, directly in the atmosphere, as a result of dark and photochemical heterogeneous reactions.

For such a planet as the Earth, whose surface is mostly covered by oceans and seas (70%), the aerosol, genetically determined by water surface — salt and organic (largely bacterial) —, as well as formed *in situ* (due to emission of respective gases and vapors by oceans and seas) should have been considered as a true global background aerosol in the lower troposphere. Of great importance are, however, dust aerosol outbreaks from the continents, which sometimes practically "suppress" the marine aerosol. In the upper troposphere, as a result of the "cloud filter" effect, the true background aerosol should be practically completely void of salt components, and the concentrations of two other components should be considerably lowered. True background aerosols in the stratosphere are exclusively the particles, formed *in situ*. Of course, the above considerations are no more than a rather simplified scheme.

The existence of the continents and of developed meridional and zonal transports of air masses and their intensive vertical eddy mixing necessitates an inclusion of the continent-generated particles into real global background aerosols. Such an enrichment of the background aerosol at all the levels in the lower, and especially in the upper troposphere, as well as in the stratosphere, rather complicates both the general pattern and the notion of the global background aerosol.

Present knowledge of the atmospheric aerosol and the limits of this review do not permit a detailed comparative analysis of the available variety and types of atmospheric particles, whose mechanisms of generation are botb natural and anthropogenic. Therefore, proceeding from comparative data on the power of the sources of different kinds of aerosols and their contribution to the total aerosol optical activity [2, 4, 6, 20, 24], we shall confine ourselves to a discussion of the properties of such aerosols as soil, sea salt, sulfate, formed *in situ*, organic and (as a separate group) soot aerosols.

1. SOIL-DERIVED AEROSOL (SDA)

Estimates of the power of natural sources of SDA injected in to the atmosphere through wind erosion mechanism vary within (1-5) 10^8 t/year [2, 15, 40]. However, as is noted by Ivlev [4], these figures are probably very much underestimated, and should be considered as the amount of the SDA contribution to the background global concentration of the atmospheric aerosol.

The SDA dispersiveness in the air surface layer is determined by natural dispersiveness of soil as a source of aerosol, and by effectiveness of the sand-jet effect of saltating particles. The formation of the real size distribution of SDA in this atmospheric layer is determined by the processes of sedimentation, impingement, condensation and adsorption of gases and vapors, capture and sedimentation on obstacles and surfaces [6]. Real size distributions of soil-erosion aerosols (SEA) can be described by the power law:

$$\frac{dN}{d \lg r} = \alpha \cdot r^{-\gamma}$$

where $\gamma = 2 \div 3$ [4, 6, 24]. However, in some cases the real number density of SEA is characterized with due regard to several components, for which γ varies from 2 to 4. These cases either refer to the conditions of residence of the aerosols that have not reached a relative equilibrium, or reflect the fact that a given aerosol ensemble is produced by several independent sources. The size distribution of such ensembles of aerosols can be described by the log-normal law. A study of log-normal distributions has revealed two modes in SEA: A-mode ($1\ \mu m < r < 10\ \mu m$) and B-mode ($10\ \mu m < r < 100\ \mu m$). The A-mode is present in the SEA size spectra at any amount of dust-loads in the atmospheric surface layer. These particles are mostly of clay. The B-mode is typical of the conditions of increased dust-loads: these are quartz grains, whose surface is covered with a thin layer of clay dust. Since the B-mode particles have a shorter lifetime as compared to A-particles, the optical properties of remote-area

SEA should be determined, mainly, by the A-mode aerosol. The latter is characterized by substantially constant size distributions: for weak dust loads $r_m < 0.4$ μm, $\sigma = 2.2$; for moderate and heavy dust loads $r_m = 0.45$ μm, $\sigma = 2.1$ (r_m is the mean radius of particles in the number log-normal distribution; σ^2 the dispersion of distribution).

The B-mode characteristics are more variable: r_s and r_v vary from 15-20 to 30-35 μm, and σ from 1.4 to 2.0 (r_v, r_s are mean radii, respectively, by volume and surface distribution). With increasing height over the surface the mean radius of particles, r_m, decreases: it decreases for large particles, and the spectrum of aerosol sizes is formed into a rather narrow distribution, with a maximum for middle troposphere conditions at $r = 0.2\text{-}0.5$ μm.

The concentration field and chemical composition of SEA differ as to considerable space/time variety in the lower atmospheric layers, which is, no doubt, determined by specific features of the SEA-generating mechanism, by non-uniform geographical distribution of aerosol sources, and by complicated atmospheric general circulation. In the regions of dust storms the SEA mass concentration (C_m SEA) may constitute $(10^{-1} - 10^{-2})$ g/m^3. In the region of a powerful advection C_m averages (2-3) 10^{-4} g/m^3. In the areas with a low level of soil erosion C_m SEA varies from 2×10^{-5} to 4×10^{-5} g/m^3. In the off-shore regions of the Northern Hemisphere Atlantic C_m SEA constitutes (0.5-0.1) 10^{-6} g/m^3. In deep regions of the Antarctic C_m SEA appears to be far less.

The SEA number density field (C_N SEA) is also rather variable. From data of complex observational programmes GAAREX and CAENEX [6, 9] C_N SEA in the air surface layer of the Karakum desert (for particles with $r > 0.2$ μm) constitutes 8-270 cm^{-3}. In the air surface layer (0.5-2 *m*) of north-eastern Kazakhstan (for particles with $r > 0.2$ μm) C_N averages 50-80 cm^{-3} [11]. During the Saharan aerosol outbreak across the Atlantic the values of C_N near the sea surface reached 6-40 cm^{-3} (for particles with 0.3 μm $< r <$ 10 μm).

Vertical profiles of C_m and C_N SEA are, as a rule, characterized by an exponential decrease. However, a stratified structure is often observed; it is most characteristic of the summer period and afternoon hours.

In most cases the mineral composition of SEA is represented by quartz, different kinds of clayey soil, carbonates, calcites, and gypsum. For some regions the content of iron oxide (hematite) turns out to be considerable.

An analysis of the mechanisms for SDA generation by nuclear explosions in the atmosphere [38] shows that in such conditions soil particles can get to the atmosphere as a result of soil loosening and blowing away of soil dust from the surface by a shock wave, as well as of the thermal heating of soil in the epicentre of the explosion, with subsequent repeated nucleation of the *in situ* aerosol particles in the form of smallest glass-like spheroids [28]. From the data obtained during nuclear tests, the atmosphere receives (1-6) 10^5 tons of dust per 1 Mt charge equivalent exploded either on the surface or immediately over it [16]. The dust thus generated is preserved in the form of a persistent cloud, confined from above (Z_{top}, km) and from beneath (Z_{bot}, km). The values of the latter are functions of the height of the tropopause (Z_t, km) and of the yield of explosion (ξ, Mt):

$$Z_{top} = (Z_t - 13) + 21\ \xi^{0.2}$$

$$Z_{bot} = (Z_t - 13) + 13\ \xi^{0.2}$$

Inside this cloud the size distribution of particles can be characterized by normal-logarithmic distribution with $r_m = 0.25$ μm, $\sigma = 2.0$ (for particles with $r < 3$ μm) and the power law ($\gamma = 4.0$), to describe the "trail" of distribution in the range of particle sizes 3 – 1,000 μm. C_N values in such clouds are greatest for the submicron fraction. About 8% of the total SDA mass in the cloud are assumed to be particles with $r < 1$ μm. The complex refractive index, *m* of dust particles in clouds is assumed to be 1.5-0.001i [38]. Figure 1 shows model temporal dependences of the vertical optical thickness, τ, of a post-nuclear dust cloud, calculated for the Northern Hemisphere [38]. As is seen, τ values (0.55 μm), immediately upon the formation of the cloud, can vary from ~ 0.25 to ~ 3, depending on the SDA mass concentration in the cloud and on its size distribution.

Coming back to the soil-erosion type of SDA, note that a review of the estimates of *m*-values for SEA has been given in [6, 24]. The value of the refractive index, *n*, for a dry SEA sample varies within relatively narrow limits 1.50 – 1.558. In the near UV region a trend to an increase of *n* is observed (at $\lambda = 400$ nm $n \cong 1.59$). The values of the imaginary part, *k*, of the complex refractive index are greatly variable. In the visible the value of *k* varies from 0.007 to 0.0163, which, no doubt, reflects an increased sensitivity of *k* to the SEA chemical composition variability. In the near UV region the *k*-value can reach 0.025. In the near IR region a minimum of absorption by the SEA substance at $\lambda = 1$ μm and a

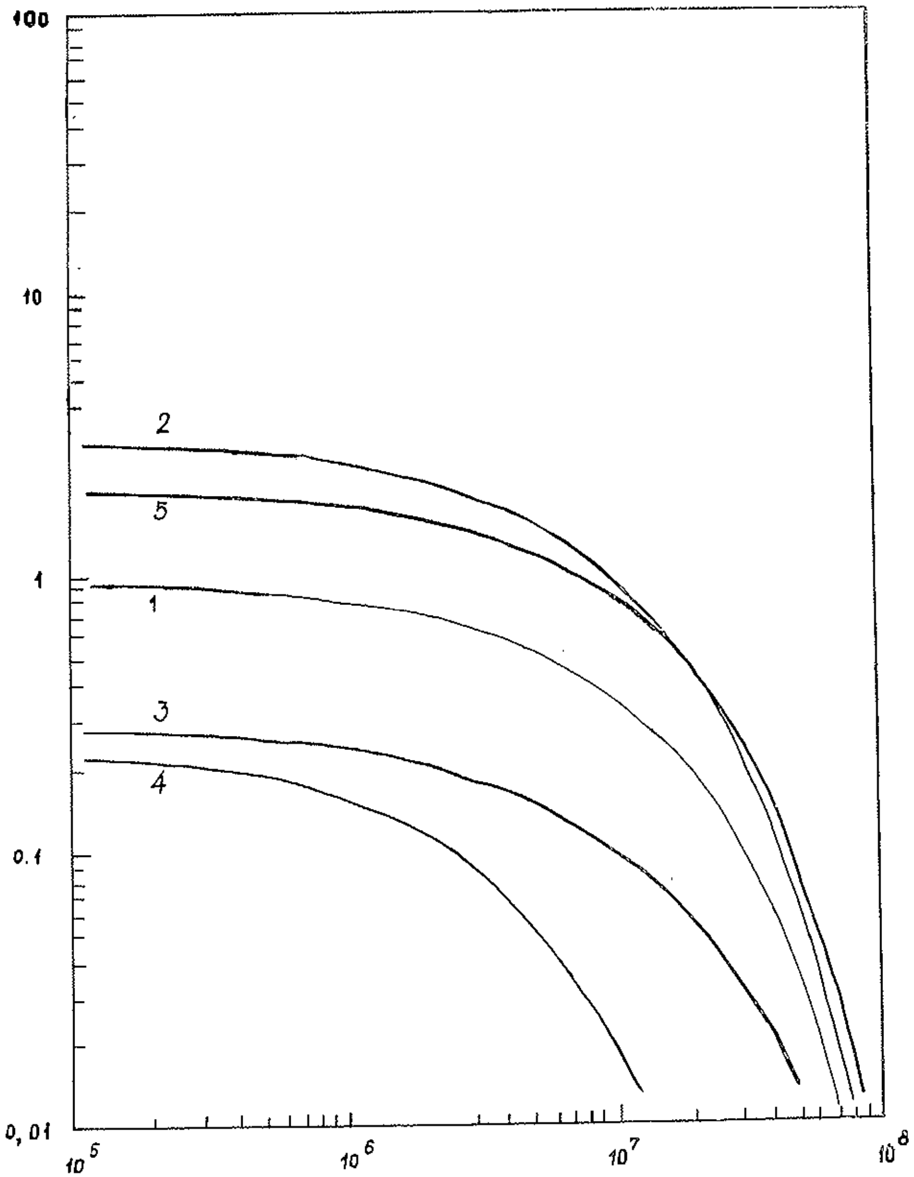

FIG. 1. Model calculations of the temporal dependence of the vertical optical thickness of a "nuclear" dust cloud, averaged over the Northern Hemisphere ($\lambda = 550$ nm). The mass concentration of dust particles in the cloud corresponds to the injection to the atmosphere of 3.3×10^5 (1), 1×10^6 (2), and 1×10^5 (3) tons of particulate matter per Mt of an equivalent charge. Particles' size distribution is log-normal and parameterized by the power law (see the text); 4,5 — calculations on the assumption of the prevailing content in the cloud of large ($r_m = 1.0$ µm) and small ($r_m = 0.1$ µm) particles.

maximum at $\lambda = 10$ μm are observed (the latter is determined by the effect of the SiO_2 absorption band). The presence in SEA of considerable amounts of aluminum and/or iron oxides intensifies the above spectral dependence of *k*. Note that in the visible the *k*-value for hematite is rather high: 0.0165 ($\lambda = 0.5$ μm), 0.154 ($\lambda = 0.55$ μm) and 0.135 ($\lambda = 0.6$ μm).

2. MARINE SALT AEROSOL (MSA)

Estimates of the annual amounts of MSA injected to the atmosphere vary within (1-2) 10^9 ton. Sea-surface generated salt particles, due to specific character of the bubble mechanism, should be characterized by two considerably overlapping ranges of dispersion [6]. The smallest particles lie within $r \geqslant 0.1$ μm. The upper limit depends considerably on the speed of surface winds and on air humidity: in corresponding conditions, particles with $r > 100$ μm can be detected in the lower 10-*m* layer of the maritime air [21].

Measured size distributions of salt particles are monomodal and can by parameterized by the power law, with the index varying within 0.97-4.2 (average 2.3-2.6). The density of MSA particles is close to 2.35 – 2.40 g/m^3. The spatial distribution of C_N MSA ($r > 1$ μm) for different regions of the world ocean can be illustrated by the following values: in the Pacific Ocean C_N = (1.2-1.5) cm^{-3}; in the Indian Ocean (0.9-1.0) cm^{-3}; near the Australian coastline 0.4 cm^{-3}; near the boundaries of the Antarctic ice sheet (1.8-2.1) cm^{-3}, and near the Black Sea coastline (0.32-1.93) cm^{-3} [8]. The vertical distribution of C_N MSA has some specific features. A maximum of C_N distribution is often observed at altitudes of several hundred meters (apparently, because of a decrease in the C_N MSA near the water surface, resulting from the capture of salt particles by sea waves). At altitudes 2-3 km the value of C_N MSA constitutes $\leq 1\%$ of the total C_N value, which is explained by the "cloud filter". However, over land, near the coastline, at an altitude of 3 km, C_N MSA is somewhat higher than at the same level over the sea surface. This is connected with a more intensive turbulence over land. In general, sea-salt aerosol particles have to be chemically composed of dried sea water: 88.7% chlorides, 70.8% sulfates, 0.3% carbonates, and 0.2% other salts.

In fact, *in situ* measurements revealed deviations in the chemical composition of MSA, manifested in a relative enrichment of MSA (by a factor of 1.5-2.5) with some microelements (for instance, K, Ca, Mg, I, Sr, Ba, F), as compared to the composition of sea water.

Observational data suggest an explanation to this fact: there is a surface layer $\leq$ 150 μm thick, enriched with the above-mentioned elements, as compared to the layers beneath. The enrichment is most manifested in MSA particles with $r \leq 0.5$ μm and $r \geqslant 10$ μm. The hypotheses explaining this fact have been discussed in detail in [6].

Studies of MSA in the Atlantic [32] have shown that values of n of the refractive index at $\lambda = 550$ nm and 589 nm constitute, respectively, 1.548 ± 0.002 and 1.544 ± 0.002. The imaginary part, k, of the complex refractive index ($\lambda = 480$-520 nm) is estimated at 10^{-3}, and in the region $\lambda = 550$-670 nm it is almost half an order of magnitude as much. Data on n and k for H_2O and NaCl [37, 39] give an idea about the chemical properties of MSA in the IR spectral region. Note that in the region $\lambda \geqslant 1.5$ μm the role of the contribution of H_2O in the absorption of MSA increases. In this connection, of great importance is the problem of the effect of humidity on the values of n and k. So, for instance, at a relative humidity of $f = 0.2$ $n = 1.546$ ($\lambda = 0.5$ μm), and at $n = 0.9$ $f = 1.345$ (which is very close to n_{H_2O}). The imaginary part of the complex refractive index varies in this case from 0.054 to 0.003-0.001.

Summing up the discussion of the properties of this kind of aerosol, note that, to our knowledge, there is no quantitative evaluation in literature of salt aerosols in the upper troposphere and lower stratosphere, resulting from near-water nuclear explosions. Nevertheless, there are estimates [38], according to which an explosion of the 1 Mt yield immediately over the sea surface, should lift up about 1.0×10^6 tons of water. Thus, for the case of multiple nuclear explosions over (or beneath) the surface of oceans and seas, the problem of mass injection of salt aerosols to the upper troposphere and lower stratosphere requires thorough investigation.

3. Soot aerosol (StA)

Forest, steppe and peat bog fires are one of the sources of StA. The extrapolation of data on the global-scale contribution of the atmospheric aerosol of solid products of forest fires in the USA has given a value of (0.3-3.6) 10^8 ton/year [2,7]. A substantial amount of soot particles comes from anthropogenic sources: the amount of solid-phase anthropogenic aerosol, containing elemental carbon (EC), is estimated at (0.3-1.3) 10^8 ton/year. The EC percentage in this aerosol varies, according to different data, from 27 to 48% (by weight). The StA number density in natural conditions varies from several particles/cm^3 to, probably, $10^6/\text{cm}^3$ (on the output of the source).

In case of multiple nuclear explosions in the atmosphere about 1.8×10^8 t of aerosols are supposed to be injected into the atmosphere, with 7.6×10^7 t StA, resulting from burning of industrial enterprises, wooden constructions, oil supplies, asphalt, and polymers. The supposed scale of forest fires (over an area of about 10^6 km^2) should lead to the 1.6×10^8 t load of the atmosphere, with about 1.3×10^7 t StA [12]. Thus, on the whole, the atmosphere should be loaded with about 8.9×10^7 t of the pure soot (EC) aerosol. The mean bulk density of StA in these conditions is supposed to be 2×10^4 cm^{-3}. The StA estimates substantially depend on data on EC percentage in the fuel-combustion derived aerosol. From laboratory data [12], the EC percentage from burning of wooden constructions varies from 8 to 50% (20% on the average); oil products from 2 to 90% (25% on the average); polymers from 12 to 50% (25% on the average); forest fires give from 3 to 27% (8% on the average).

The major mechanism of generation of both the natural and anthropogenic StA is a pyrolysis in the gas- or condensed-phase of the carbon-containing material. The microphysical characteristics of the resulting StA depend on the specific nature of the source: so, for instance, the particles produced by oil combustion have a coral-like structure and an effective spherical shape; the pyrolysis of coal gives particles in the form of spheres, with a great amount of smaller, randomly oriented spheroids inside them [11].

The way of burning governs the character of resulting StA. A smouldering source gives large flakes of soot (since in this case the coagulative growth of small, embryo particles is quite possible). In case of fast burning, small particles with $r \leq 0.1$ μm are mostly formed. Also, the environment characteristics strongly affect the StA size distribution [27]. Initially-formed particles have a radius of 0.01-0.1 μm. As a result of coagulation, these "embryo" particles rapidly recombine. Therefore, the atmosphere residence-time of the embryo particles should be rather short (less than several days). Particles with $r > 3$ μm, formed both in most favourable conditions for coagulation, and due to eddy "mechanical" lifting of large particles (from the sites of burnt houses, coal working, weathered carbon-containing rocks, etc.) are rapidly removed from the atmosphere by gravitational sedimentation. Particles with r = 0.1-3 μm (particles of accumulative mode) in the atmosphere can be rather long-lived, being limited from above with effective sink mechanisms. Globally-averaged estimates [30] have led to the following residence times of particles: 1 week in the lower troposphere (up to 1.5 km), 1 month in the upper troposphere, and more than a year in the stratosphere. In estimation of the life-time of the accumulative mode StA particles of great importance is the external and internal mixing of aerosol particles. The external mixing gives larger particles due to recombination of EC homogeneous particles ("young" StA); in case of internal mixing, EC is in physical contact with aerosol particles of different chemical composition ("old" StA). The external mixing generates hydrophobic aerosols, while the internal mixing leads, as a rule, to the formation of hygroscopic particles. As a result, the mechanisms for washing out of these two types of merged aerosols are quite different. Electronmicroscope studies of EC particles have shown that "embryo" particles are, as a rule, spheroids; often these are aglomerates in the form of chains and clusters. Their specific surface is about 1,000 m^2/g [30].

Depending on the character of the inflaming material, the conditions of the pyrolysis process and the properties of the EC- residence medium, their surface can be covered with adsorbed substances. Often these are hydrophobic, incompletely burnt, hydrocarbons. However, the cover may happen to be hydroscopic (due to adsorption of atmospheric gases), ready to form hydrogen and coordinate bonds. Pure EC is absolutely inert at usual temperatures. This is an hydrophobic, insoluble substance (it may be oxidized at about 600 °C or in the atmosphere of F_2, but such conditions do not occur in the real atmosphere). EC is capable of reacting with radicals, which may be essential from the viewpoint of the chemical reactions taking place in the atmosphere. The EC catalytic activity in reactions of atmospheric SO_2 oxidation has been reported in [29]. These reactions can he driven by two mechanisms: "dry" (in the presence of water) and "moist", when an EC particle is filmed with water. The "moist" mechanism is more effective [10].

As has been mentioned above, the StA size distribution depends both on specific inflaming material and on the way of its pyrolysis, and on the properties of the environment, into which the StA particles are injected [42]. The size distribution of StA from urban and forest fires has been suggested to be parameterized by log-normal distribution [38] (in the first case $r_m = 0.1$ μm, $\sigma = 2.0$; in the second case $r_m = 0.05$ μm, $\sigma = 2.0$). A study of the laboratory-generated StA size distribution (propane pyrolysis, undertaken by E. Hindman *et al.* [24]) has shown that the size distribution is a 3-mode one (Fig. 2): $r^{I}_{m} = 5 \times 10^{-3}$ μm, $r^{II}_{m} = 5 \times 10^{-2}$ μm, $r^{III}_{m} = 0.3$-0.4 μm. For the accumulative mode, as a most long-lived one in the atmosphere, a representation of the size distribution by the power law can be characterised, after A. Boden [24],

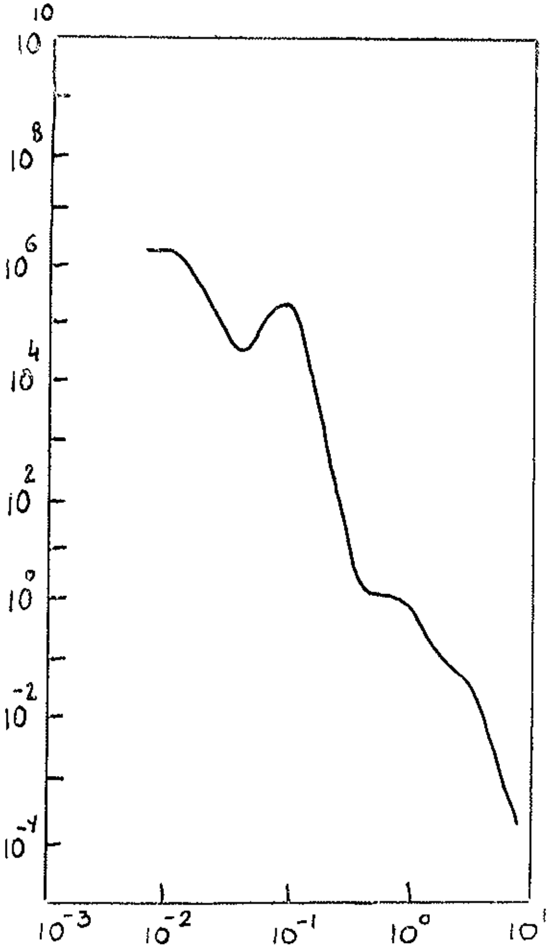

FIG. 2. Size distributions of laboratory-produced soot particles (propane soot). d_g — mean geometrical diameter.

in the following way: $\gamma = 4.9$ ($r < 0.25$ μm); $\gamma = 4.6$ ($r \leq 0.35$ μm); $\gamma = 5.1\text{-}5.2$ ($r > 0.4$ μm).

The specific weight of StA is estimated at 1.9-2.0 g/cm^3 [24, 38], depending on porosity of the particles (the density of graphite is 2.21-2.25 g/cm^3).

Rather meagre and contradictory are data on vertical profiles of the StA distribution in the atmosphere. This problem requires thorough investigation. The following heights have been proposed [28] for the top (Z_{top}) and bottom (Z_{bot}) levels of smoke clouds: urban fires $Z_{bot} = 1$ km, $Z_{top} = 7$ km; accidental forest fires $Z_{bot} = 1$ km, $Z_{top} = 5$ km; vast post-nuclear fires (a 10% contribution from urban fires):

$$Z_{top} = 1.5 \ (4A_f/\pi)^{3/2}$$

$$Z_{bot} = 1/3 \ Z_t$$

where Z_t is the height of the tropopause, A_f the area under fire.

Inside carbonaceous-smoke clouds, the C_N value is considered as unvariable, which is too rough an approximation. The problem of the optical characteristics of StA, with due regard to its porosity, has been considered in [11]. If ϕ is the solid-phase part (EC) of the particle's volume, and m_1 and m_2 complex refractive indices for EC and air, then the complex refractive index for a soot particle, m_p is expressed by the formula:

$$m_p = n_p - k_p{}^i = [\phi\, n_1 + (1 - \phi)\, k_1] - [\phi\, k_1 + (1 - \phi)\, k_2]\, i =$$
$$= 1 + \phi\,(n_1 - 1) - \phi\, k_1\, i$$

and, thus, is a function of the ϕ-parameter.

The problem of the optical characteristics of the aerosols, soot particles included, was discussed at the First International Workshop on Light Absorption by Aerosol Particles (IWLAAP) [24]. The real part, n, of the StA complex refractive index in the visible (0.3-0.7 μm), according to V. Egan [24], varies from 1.665 to 1.775 ($m_{EC} = 2.0\text{-}1i$, for the visible).

An estimate of the imaginary part, k, (for the same spectral region) from data of the IWLAAP participants, varies from 0.4 to 1.04. In model calculations [38], m was taken to be 1.75-0.38i. In the IR spectral region (from 2 to 40 μm), from data of F. Voltz [24], the k-value increases with increased wavelength: at $\lambda = 3$ μm $k = 0.35$; at $\lambda = 40$ μm $k = 1$ (a technique of embedding in KBr pills was used).

The scattering index of StA, σ_s, was estimated by the IWLAAP participants at (1-3.5) 10^{-4} m^{-1} (average $\sigma_s = 2.41 \times 10^{-4}$ m^{-1}), and the StA absorption index, σ_a, at (3.8) 10^{-4} m^{-1}. The specific index of scattering for soot particles, B_s, is assumed in [12] to be 4 m^2/gC, and the specific absorption index, B_a, 6 m^2/gC. B_s estimates by the IWLAAP participants were within 4-11 m^2/gC (on the average, x7.14 m^2/gC). The single scattering albedo, $\tilde{\omega}$, from the same estimates, varied within 0.090-0.292 (StA average 0.171).

The IWLAAP participants have also undertaken a study of the dependence of the optical properties of StA on the percentage of ammonium sulfate in the particles, as a model of interior mixing of aerosols (Table 1).

These data, apart from being of purely practical interest, are also important from the viewpoint of understanding the laws of formation of the optical properties of the internally mixed atmospheric aerosol.

And finally, studies of the phase function, P (Θ), of StA, undertaken by G. Grams within the framework of IWLAAP [24], have made it possible to estimate the asymmetry coefficient $g = \langle \cos \Theta \rangle = 1/2 \int_{-1}^{+1} \cos \Theta \, P(\Theta) \, d \cos \Theta$, of the phase function of soot particles. It turned out to be 0.48. For the particles with equal amount of EC and ammonium sulfate, $g = 0.58$.

Summing up the discussion of the optical properties of StA, an importance should be emphasized of consideration of not only the inner structure but also the shape of soot particles. Model calculations made in

TABLE 1 - *The Dependence of Averaged Optical Characteristics of the Soot Aerosol on the Percentage of Ammonium Sulfate in It* [24].

Parameter	EC percentage in aerosols		
	100	50	4
B_a	7.14	2.20 -2.38	0.394-0.761
$\tilde{\omega}$	0.171	0.549-0.618	0.761-0.939
k	0.581	0.132-0.179	0.027-0.0541

[33] for an ensemble of randomly oriented particles, have shown that in the "Rayleigh" region of aerosol sizes the substitution of spheroids by ellipsoids (with the axis lengths ratio 3:1) leads to a 40% increase of the specific absorption by such an ensemble. For large soot particles with $r \gg \lambda$ (λ is the length of the incident wave) the ratio of the specific light extinction by an ellipsoidal particle to that by a spheroid depends on the factor $Z = a/b$, where a and b are the lengths of ellipsoid's axes; in case of a flattened StA particle this ratio is $Z^{1/3}/4$, and in case of an extended one $Z^{2/3}/2$.

There is no doubt that in view of high optical activity of StA, further specification is needed of its microphysical properties, optical constants and of the distribution of concentrations in space and time.

4. SULFATE AEROSOL, FORMED "IN SITU"

From the estimates available, the annual amount of particles formed in the atmosphere as a result of chemical heterogeneous reactions constitutes 840-1,400 Mt, 20-30% falling on anthropogenic particles.

The tropospheric air always contains a considerable amount of small submicron particles, the so-called Aitken particles (AP), which are widely spread. Experimental data show that, on the average, not less than 50-75% of the total mass concentration of AP fall on sulfates [43]. The average percentage of the mass concentration of organic and nitrate components in the aerosol of the sub-micron range is estimated at 20-25% [2, 22]. Undoubtedly, nuclear explosions (with a yield of about 10^{32} NO molecules per 1 Mt of trinitrotoluene equivalent [12] should generate great amounts of nitrate and sulfate aerosols, but there are no estimates so far.

Natural and anthropogenic emissions of H_2S, SO_2, CH_3SH, $(CH_3)_2S$, CS_2, $CH_2(CH_2)_2SH$, and some other compounds are sources of sulfate aerosols [6]. In the rich-in-oxygen atmosphere of the earth and in the presence of such strong oxidizers as O_3, OH, O, NO, NO_2, the oxidation reactions take place, giving first SO and then SO_2. The latter, through the mechanism of homogeneous gas-phase reactions (apparently, with participation of OH and HO_2 radicals), is oxidized into SO_3, after which the last, very fast stage of the oxidation process starts — the formation of H_2SO_4. H_2SO_4 is rapidly hydrated in the moist atmosphere and reacts with NH_3, giving ammonium sulfate and such semi-neutralized compounds as NH_4HSO_4 and $(NH_4)_3H(SO_4)_2$.

The concentration field of sulfate aerosols is characterized by changes in C_N from several particles to hundreds of thousands of particles per cm^3. Relatively low mean values of C_N are observed over the oceans, and high values over the continents (except for high latitudes). In the northern Pacific and Atlantic Oceans the value of C_N AP often decreases to 5 cm^{-1} [21]; over the ice sheet of Greenland it constitutes 150-950 cm^{-3}; in the tropics and at midlatitudes over the oceans C_N AP averages about 300 cm^{-3}; over the continents by an order of magnitude higher. In the air over large industrial centers C_N AP can reach 10^5 cm^{-3} near the surface and 10^3-10^{-1} at an altitude of 3,000 m [26].

The anthropogenically-induced AP can be transported to other regions. The insolation regime markedly influences the content of these aerosol particles, and therefore both seasonal and diurnal changes are observed [25].

The values 4×10^{-6} g/m^3 (the lower troposphere over the continents) and 0.1×10^{-6} g/m^3 (the middle and upper troposphere) are proposed as an averaged characteristic of the mass concentration of sulfate aerosols [40]. The *in situ* produced aerosol has a characteristic bimodal distribution dS/dlgr. The first mode is determined by Aitken particles themselves ($r \leq 0.1$ μm). The second, coagulative mode (0.1 μm $< r <$ 1 μm) is constantly supplied with heterogeneously coagulating Aitken particles and, for these particles, it is the last form of existence before the aerosol particles in question leave the atmosphere. The parameters of the coagulative mode are: d_g (mean geometrical diameter) = 0.37 μm, $\sigma = 2.00$ [41]. The relative air humidity, f, substantially affects the size distribution of particles: with it increasing, the maximum of the spectrum is shifted to the region of large radii.

The hygroscopic properties of sulfate aerosols largely determine their specific weight. Depending on size, it varies from 1 to 2 g/cm^3. So, for instance, the mean bulk density of submicron particles substance is estimated in [41] at 1.37 g/cm^3 and in [17] at (1.82-1.93) g/cm^3.

The optical constants of sulfate aerosols greatly depend on the value of f. Since at 525 nm the refractive index, n, for water, H_2SO_4 ($f = 0.5$), and $(NH_4)_2SO_4$ ($f < 0.8$) are, respectively, 1.33, 1.4, and 1.52, one may believe that in the visible the refractive index, n, of real sulfate aerosols varies within 1.4-1.52 at $f < 80\%$, and at $f > 80\%$ $n \rightarrow 1.33$.

The imaginary part, k, of the complex refractive index for sulfate aerosols in the visible, from the estimates of the IWLAAP participants [24], varies within 8.1×10^{-6} -- 5×10^{-3}. These estimates (the upper limit, in particular) are overestimated by several orders of magnitude, since in this spectral interval tbe *k*-value for ammonium sulfate does not reach even 10^{-7}. The specific absorption index averages 0.139 m^2/g [24]. The single scattering albedo for this kind of particles is 0.971.

5. ORGANIC AEROSOL (OA) *

5.1 *Organic aerosols, formed* in situ

There is an opinion about the global spreading and substantial role of organic aerosol in the formation of the properties of the atmospberic aerosol. However, information about this component is very meagre and fragmentary. From the estimates available, the atmosphere obtains annually from 90 to 600 million tons of organic vapors, then formed *in situ* into organic aerosol. Of this amount, 15-20% fall on anthropogenic aerosols [2, 4].

At the initial stage of the *in situ* formation of organic aerosol, an aqua-chemical interaction of hydrocarbon molecules is supposed to take place with such atmospheric oxidizers as O_3, OH, NO_x [31].

It has been stated in [2] that the OA content over western Europe at an altitude of 3-4 km constitutes 1×10^{-6} g/m^3. This, apparently, means that up to the mid-troposphere, OA is well mixed. This is confirmed by chemical analysis data. OA in the lower and middle troposphere has the following characteristics: the concentration of neutral aliphatic, aromatic, and polar hydrocarbons varies, respectively, within: (6.2-0.8) 10^{-6}, (0.12-0.52) 10^{-6}, and (0.1-0.35) 10^{-6} g/m^3. The concentrations of organic acids constitute, respectively, (0.15-0.70) 10^{-6} and (0.03-0.2) 10^{-6} g/m^3. As has been mentioned above, the average percentage (by mass) of the organic component in the submicron range is estimated at 20-25%. The specific weight of this aerosol (based on the above-given data on the chemical composition, on the whole) constitutes about 1 g/m^3.

5.2 *Rough-disperse OA*

Organic particles are also observed in the rough-disperse fraction of

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* The notion does not include soot particles.

the atmospheric aerosol. Studies of the chemical composition of SEA testify to the presence in it of 1-2% of rough-disperse organic particles [6]. Besides, organic matter is present in SEA in the form of "cementing" agents, considerably governing the size distribution of the SEA itself. In soils the organic component is a mass with a very complicated composition, containing living organisms, fragments of dead organisms, biologically synthesized compounds, as well as decay products and their derivatives. In the aerosol samples taken over Repetek and Ankata (the Kara-Kum desert) [9], the mass concentration of the organic component in the SEA rough-disperse fraction constituted about 2 mg/m^3 [4].

The organic component is also present in marine aerosol. It is also characterized by a complicated chemical composition. Over remote oceanic regions the concentration of organic matter in the rough-disperse aerosol fraction can reach 2-4 mg/m^3 [41], but in other cases it does not exceed 0.15-0.47 mg/m^3 [18].

Most characteristic sizes of organic particles of marine aerosols do not exceed 10 μm. Data on organic aerosol are rather inadequate and do not even permit one to draw, in general terms, a reliable pattern of its optical properties. No doubt much effort is required before real possibilities appear to consider this component in a general model of aerosol.

6. GLOBAL BACKGROUND AEROSOL (GBA) IN THE LOWER TROPOSPHERE

The problem of the global background aerosol has been briefly discussed above. The sophisticated nature and substantial uncertainty of this notion have been mentioned. Apparently, of all the global regions most favourable for studies of GBA the Antarctic continent is the best.

Systematic studies of the atmospheric aerosol in the Antarctic revealed a strong annual change in Mirny and at the South Pole, with summer-season values of aerosol concentrations exceeding tenfold those in winter, which points to a substantial effect of meteorological conditions on the values of C_{GBA}.

From data of measurements at the South Polar Plateau the mean bulk aerosol density varies from 15 particles/cm^3 (in winter) to 100-150 particles/cm^3 (in summer). A prevailing size of particles lies within 0.02-0.2 μm. In summer, at the expense of downward air fluxes, the values $C_N = 500\text{-}1{,}500\ cm^{-3}$ were registered. This jump attributed to the appearance in the Antarctic air of considerable concentrations of particles with $r \leq 0.01$ μm (and in some cases $r \leq 0.005$ μm). With moist air advection from the Wedell Sea toward the South Polar Plateau, and in strong surface winds, the number density of aerosol reached 250-600 particles/cm^3 [19].

The size distribution of the Antarctic aerosol is described in [35] by a two-mode model (Fig. 3, Table 2).

As for submicron particles (AP) consisting, as has been mentioned above, of transformed minor gaseous components nucleation products, it is assumed that their lifetime does not exceed 2-3 days and they are locally formed over ice caps at a rate of about 4×10^{-21} g/cm^3 s.

The concentration of rough-disperse particles with $r \geq 0.14$ μm constituted about 0.5 cm^{-3}. These particles contribute most to the aerosol mass. Undoubtedly, they are driven from remote regions. Covering the surface, these particles form aerosol insertions into polar ice. Their long-term concentration variations can serve as indicators of paleoclimate changes.

A major chemical component of this mode during the Antarctic summer was sulfate (80-90% by mass), which probably appeared due to

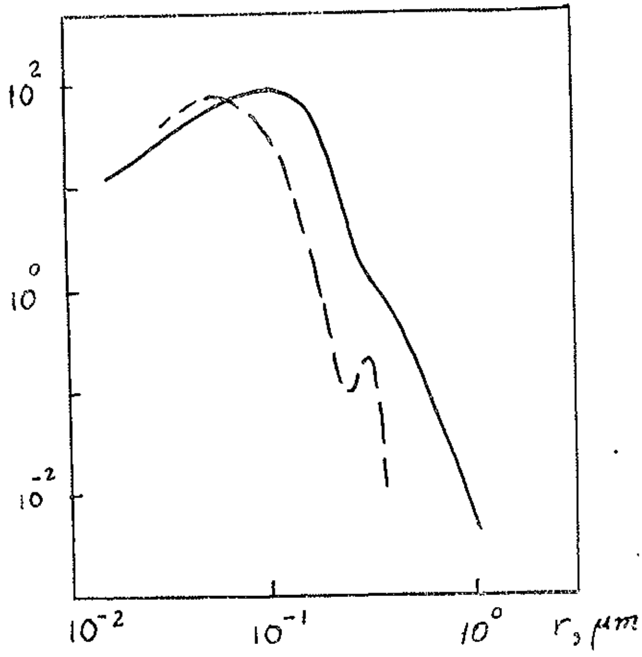

FIG. 3. Number density of polar aerosol. a) South Pole; b) Barrow, Alaska.

Table 2 - *Characteristic Values of the Parameters of a Two-Mode Arctic Aerosol Model.*

Parameters	Rough disperse mode	Aitken mode
Average radius, μm	0.4	0.005
Number density, cm^{-3}	0.5	1000
Particles density, g/cm^3	2.16 (NaCl)	1.0
Mass of particles, g	5.78×10^{-13}	5.23×10^{-19}
Mean mass concentration, ng/m^3	288	0.78
Mixing ratio (with respect to air), $mlrd^{-1}$	0.37	0.001
Thickness of layer, km	10	10
Total content in the atmosphere, g/cm^2	2.88×10^{-7}	7.84×10^{-10}
Optical thickness (at $\lambda = 500$ nm)	0.010	4.01×10^{-9}
Stox rate of sedimentation, cm/s	4.7×10^{-3}	3.4×10^{-7}
Coefficient of diffusion, cm^2/s	8×10^{-7}	2×10^{-3}

transport in the lower stratosphere or in the upper troposphere. In winter, the portion of sulfates drops to about 60%. In summer, the contribution of dust from the Southern Hemisphere arid zones (Australia, Kalahari and Atacama deserts), as well as of sea salts does not exceed several per cent. In winter the portion of dust decreases, and that of particles grows to 30-40% (by mass).

In summer, surface inversions over the ice cap are weaker, which stimulates aerosol mixing in the troposphere and its motion to the surface. A relative spreading of the tropopause favours the air transport from the lower stratosphere to the upper one. The transport takes place, apparently, near the boundaries of the continent, but it may also take place over its interiors. As a result, rather a homogeneous distribution of aerosol concentrations and composition over the Antarctic continent is observed [36].

In winter the surface inversion layer is almost isolated from the above atmosphere and only a small part of dust and, largely, salt particles, reaches the South Pole. It is this that determines an increase in the winter-season concentrations of sodium but a decrease in the content of other components (Table 3) [13].

Estimations of the aerosol optical thickness in the Antarctic [36] gave values (for $\lambda = 500$ nm), ranging from (0.012 ± 0.005) to (0.025 ±

TABLE 3 - *Mean Concentrations* (ng/m^3) *of Various Elements in the Antarctic Aerosol in the Summer and Winter Seasons.*

Element	Concentration, ng/m^3	
	summer	winter
S	76 ± 24	29 ± 10
Na	5.1 ± 1.17	40 ± 31
Al	0.83 ± 0.41	0.30
Fe	0.63 ± 0.25	0.25 ± 0.12

0.010). Note that, so far, no anthropogenic impact on the composition of the Antarctic aerosol has been detected.

CONCLUSION

Summing up the discussion of the microphysical and optical properties of the atmospheric natural and anthropogenic aerosols, again it is important to emphasize the fact that to construct adequate optical atmospheric models, reliable, well-substantiated models of aerosol properties are needed. Unfortunately, present knowledge in this field is quite inadequate. It concerns all the types of aerosols, but, first of all, those formed *in situ* (here organic aerosol is studied least of all), soot aerosol, and solid-phase industrial aerosol. Of great importance are representative sets of parameters obtained from synchronous complex observations, needed for numerical simulation of the atmospheric processes, which characterize each of the main types of the atmospheric aerosol. Along with substantiation of parameterization of the properties of cloudiness as a stochastic system, the above-mentioned problem has been and still is one of the most urgent problems in the physics and chemistry of the atmosphere.

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