Aerosol and climate studies: current state and prospects
1. Aerosol formation, its properties, and their transformations

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Review of the recent studies of the aerosol and climate problem is presented. It is primarily aimed at demonstrating an exceptional difficulty and intrinsically high uncertainty of considering the climate-forcing role of the interactive aerosol–clouds–trace gases subsystem, which is a part of the climate system.

Introduction

Perhaps there is no other problem like global warming that, on the one hand, has recently become a subject of discussion at the top level of international policy (let me just remind the Summit of coalition of industrialized nations (G8) on July 7–8, 2005 in Perthshire, Scotland), while, on the other hand, being full of so much controversy and doubtless falsification of scientific truth. For instance, A. Kerr, a reporter of a prestigious and popular Science journal, begins his brief summary-article[38] on climate issues with the claim that the scientists know that the world has warmed during recent years, and they suppose the mankind to be responsible for the most of this warming. The article is illustrated with a photo of a storehouse of coffins, fabricated in the period of record-high heat wave in the Western Europe occurred in 2003. Even more grave opinions and bleak prospects can be found in various mass media. Even such a well known scientist as J. Hansen, the director of NASA Goddard Institute for Space Studies (GISS), New York (to be considered the main, though inconsistent, proponent of global warming), has proclaimed that there must be no more any doubts that the anthropogenic emission gases are a dominating cause of the warming.

Unfortunately, J. Houghton,[33] many-year (1988–2002) co-chair of the Intergovernmental Panel on Climate Change (IPCC) and chair of the IPCC Working Group 1 (WG1), responsible for preparation of materials concerning the scientific foundations of the discussed problems also didn't avoid "apocalyptic" estimates. In his opinion, the basic principles of science on climate change had been validated.

Against the background of frequently apocalyptic declarations of policy-makers, U.S. president George W. Bush has advanced quite a weighed opinion yet in year 2001: "We don't know in what degree the naturally caused climate changes may influence the warming. We don't know how strongly our climate would and will change in the future. We don't know how fast can be the changes or, also, in which way our influences may affect the climate. We can say nothing about what level of warming may be dangerous."

The controversial assessments of the climate change are paradoxical in that in debating on climate, some basic and quite obvious circumstances were ignored, while, at the same time, those had been extensively discussed in many publications.[1–72]

1. The first point to be noted is that no agreed definition of climate has been received for common practice so far. According to the classical definition, climate is characterized by a set of meteorological parameters averaged over 30 years. If accepted, this definition makes it irrational the discussion of the problem of global warming because, in fact, of concern is the globally mean increase of surface air temperature (SAT) over a few past decades is being debated. The problem, however arises because some meteorological phenomena as, e.g., heat waves are frequently considered as indicators of climate change. It is also important to note that the focus of climate debate has been on the increase of globally mean SAT. Meanwhile, Essex and McKitrick[20] have convincingly explained the arbitrariness of this quantity.

2. For climate definition, there must be an associated awareness of the fact that the climate changes are determined by complex interplay of interactive components of the atmosphere – hydrosphere – lithosphere – cryosphere – biosphere climate system, with special role of the dynamics of the biosphere (responsible for biotic regulation of the environment[3a]), as well as of the atmosphere–ocean interaction. Of particular importance are such atmospheric components, contributing to climate

forcing, as cloud cover and aerosol.[39c] It is quite evident that complex (and nonlinear) interactivity of the climate system practically excludes the possibility of reliably estimating the influence of an isolated factor (such as the greenhouse effect of the atmosphere) on climate. This situation is further complicated by climate forcing effects of cosmic factors (primarily solar activity[39b]).

The situation becomes even more complicated in the context of long-term (up to the end of twenty first century or longer) climate prediction that has been paid much attention in recent years. In this connection the account of anthropogenic factors calls for necessity of considering the dynamics of the nature–society (NSS) system,[41] which is extremely complicated task. So far, the long-term climate prediction disregards not only the NSS dynamics, but also even critically important interaction among the components of the climate system itself. For instance, it is set in such treatments that CO_2 concentration in the atmosphere increases by 1% per year instead of interactively reproducing the dynamics of the global carbon cycle.

3. Climate had always changed in the past (and, as is well known, much more dramatically than presently, with the evidences from paleoclimatic data suggesting that the variations of surface air temperature and carbon dioxide concentration in the atmosphere were not only positively but also negatively correlated). It should, however, be kept in mind that the data of climate observations (even over twentieth century) are not always quite reliable and complete. This is critically important when reliability of numerical results of climate modeling is to be checked. However strange it may seem, comparisons of a variety of different climate models published can largely be reduced to the statement of satisfactory, on the whole, agreement between numerically simulated results and observations. It is quite obvious that a far more creative way could be quantitative analysis of the discrepancies enabling one to substantiate the quality demands to observations in order to acquire an array of more adequate observation data.

4. Despite the active discussion and gradual development of global observation programs such as Global Climate Observing System (GCOS), Global Ocean Observing System (GOOS), Integrated Global Observing Strategy (IGOS), the problem of obtaining uniform long-term series of integrated observation data on different climate system parameters still remains far from being solved. Even in the case of SAT time series over the preceding one and half century, the observation data can justifiably be considered incompletely correct (primarily because it is impossible to determine quite correctly the SAT corrections for urban heat islands). Recently an intense debating has occurred concerning the data of satellite observations using ultrahigh frequency remote sensing of the troposphere (see, e.g., Refs. 3 and 4); these data suggest that no considerable increase of temperature in the free atmosphere occurred in recent decades, though it might have been even more intense than the SAT increase.

Vigorous debate occurred on paleoclimatic data on SAT variations during the past two millennia, presented as the appearance of a "hockey stick," that is anomalously intense increase of SAT in the past decades as compared with slow variations in the preceding two thousand years.[51] McIntyre and McKitrick[54,55] have shown that this conclusion has been drawn using a statistically incorrect method of processing the paleoclimatic data (moreover, it is not quite clear how adequate are such data, retrieved from different indirect climate indicators). In this regard, Von Storch[65] reasonably noted that IPCC has made the "hockey stick"-shaped reconstructions of the northern hemisphere temperature an icon in climate science. However, the technical part of the IPCC Third Assessment Report (TAR) on Climate Change published in 2001, presented the results on temperature reconstruction over the past millennium with certain reservations that those are insufficiently reliable and that the corresponding uncertainties exist. At the same time, those sections of TAR, which attract much of the public attention, these warnings become less accented. As a result, many people consider the hockey stick as an undoubted indication of the anthropogenic effect on the climate change.

The impact of aerosol on climate is a key item among the sources of uncertainties in assessing the causes of climate changes nowadays and possible causes in the future. This problem has been widely discussed earlier (see, e.g., Refs. 6 and 39c, including a series of overviews summarized in Ref. 5a. However, intense development of the corresponding activities makes us to turn to analysis of most recent studies in this field, primarily of the studies of aerosol properties and their spatiotemporal variability. In this connection, the Siberian Aerosols Program should be mentioned in the first place. The research results obtained under this Program have been extensively discussed, in particular, in the topical issue of the journal *Atmospheric and Oceanic Optics* (2005, V. 18, Nos. 5–6).

Aerosol microphysical and optical properties and processes of aerosol formation

Main difficulties of the studies of aerosol effects on climate lie in the complexity and interactive dynamics of the multi-component aerosol, strong spatiotemporal variability of the microstructure and other properties of aerosols of different types, as well as in the diversity of the processes forming the aerosol properties. Naturally, the needs of numerical simulation of aerosol effect on climate first dictate validation of aerosol models to be used in numerical climate models. Although these activities are still at the initial stage of development, it is important that they attract quite serious attention.

Because of the growing recognition of the role of aerosol as a climate forcing agent, Herzog et al.[31] have developed a dynamic aerosol model taking into account the binary nucleation of sulfate gas and its condensation followed by the formation of aerosol particles. They have also considered the coagulation among sulfate particles themselves and with other particles. This aerosol model is formalized in the form of module, which can be used as a component of global model of a long-range aerosol transport taking into account aerosol conversions; the parameterization of all the processes considered is applicable to modeling both under conditions in the troposphere and stratosphere. At each time step, interaction of processes of aerosol formation and conversion takes place.

In Ref. 31, the adequacy of the model was checked by comparing the model results with the numerical simulations using sectional model, which provides reproducing microstructure of aerosol of any form and confident prediction of evolution of the aerosol properties. With four aerosol modes taken into consideration, the new model precalculates number concentration and surface area of particles accurate to a factor of 1.2 with respect to the sectional model (in the case of bimodal parameterization, only insignificant degradation of the results takes place). Within the planetary boundary layer, the calculated number concentrations of particles of the accumulation mode diverge more significantly, agreeing only accurate to a factor of 2.1. Presumably, further model refinement with the purpose of numerical simulation of the width of microstructure for each of the aerosol modes, as well as the number and mass concentration for individual modes will improve the agreement with the sectional model.

The study by Herzog et al.[31] may serve an illustration of the initial approach to how the climate forcing by one of the aerosol types is to be done. Ultimate goal is, however, the justification of incorporation of the entire set of aerosol formation processes and aerosol properties within the corresponding module, being an interactive component of a climate model. Berglen et al.[8] have undertaken such an attempt for the case of sulfate aerosol.

The global sulfate cycle belongs to the group of biological-geophysical cycles, which experience most strong anthropogenic effect. Berglen et al.[8] have developed a new five-component model of sulfur cycle, used as part of the OsloCTM-2 model of long-range transport taking into account the corresponding emissions, as well as the processes of oxidation and sedimentation with special attention paid to such components as DMS, SO_2, MSA, and sulfate. Progress over previous analogous efforts is interactive consideration of the processes of aqueous-phase SO_2 oxidation due to O_3, H_2O_2, and HO_2NO_2 to yield sulfate. Therefore, changes in emission levels of the precursor-oxidants lead to immediate change in the composition of oxidant species. On the other hand, it becomes possible to estimate the influence of the dynamics of sulfur cycle on the content of oxidants.

Calculations were made for meteorological conditions and emission levels occurred in 1996, with the subsequent comparison of numerical simulations of the sulfur cycle against these data. Overall, the comparison appears to be quite encouraging, though there is a tendency in calculations to overestimate SO_2 concentrations and underestimate sulfate concentration in winter in the atmosphere of the Northern hemisphere because of insufficient intensity of the oxidation processes.

According to the calculated data, globally mean lifetimes (global masses) in 1985 were 1.06 days (0.26 TgS) or 3.7 days (0.50 TgS) for SO_2 or sulfates. In 1996, the corresponding values were 0.99 days (0.25 TgS) or 3 days (0.53 TgS). There is a significant difference between Southern hemisphere, with the characteristic dominance of natural SO_2 emissions and losses due to oxidation by O_3 and H_2O_2 and Northern hemisphere characterized by high level of anthropogenic emissions and large losses due to dry deposition. Considerable changes of sulfur emission had taken place during the past decades, when SO_2 emissions decreased in the USA, Western Europe, and former USSR; while in the Southeast Asia, some regions of USA and Western Europe, and in China they increased, with values amounting respectively to –17.6, –47.5, and +95%.

To estimate the influence of emissions on chemical composition of the troposphere, calculations have been performed using data of Global Emission Inventory Activity (GEIA) program performed in 1988. According to the GEIA data, total SO_2 emissions in 1985 were 89.2 TgS/yr for the following values of separate components of SO_2 emissions (given in parentheses, in TgS/yr): anthropogenic emissions (67.1), biomass burning (2.3), volcanoes (8.0), and oxidation (11.8). Total sink has reached 89.2 TgS/yr, while the levels of sink components were characterized by the following values: dry deposition (41.3), moist deposition (1.5), gas-phase oxidation due to OH (7.5), and aqueous-phase oxidation (38.9). In the case of sulfate (for total emissions of 49.9 TgS/yr), the contributions of individual components determine anthropogenic emissions (3.5) and processes of SO_2 oxidation (46.4). Total sinks, equal to 49.9 TgS/yr, are determined by contributions of dry (7.4) and moist (42.5) deposition.

Variations of sulfur emissions have affected significantly the concentrations of sulfur and oxidants in the atmosphere. For instance, increased emissions of nitrogen oxides NO_x and hydrocarbon species in China have resulted in an increase of the tropospheric ozone concentration, though this growth was restrained by the increased SO_2 emissions. Special attention was paid to analysis of SO_2 oxidation by OH, which could have led to formation of new particles of sulfate aerosol. Southward displacement of maximum emissions in the period from 1985 until 1996 favored the growth of the oxidant role of OH, especially in Southeast Asia.

Naturally, reconstruction of the global sulfur cycle is only a part of the problem. Its complete solution must be justification of the aerosol module as a component of a climate model, which could made it possible to take into account the climate forcing effect of the interactive sulfur cycle. The solution of this problem is strongly complicated. We will consider only those difficulties, which are caused by the aerosol of different types.

As known, the process of homogeneous particle nucleation (formation of stable clusters about 1 nm in size) and their subsequent growth to the size of new particles (more than 3 nm) determines the microstructure of aerosol and cloud condensation nuclei. However, no adequate theory of formation of new aerosol particles exists. Kulmala et al.[43] tried to justify such a theory based on explanation of particle formation. They hypothesize that this formation is caused by activation of stable inorganic clusters under influence of vapor of organic species. New theory of nanoparticle formation is analogous to that by Köler describing cloud formation under conditions of water vapor supersaturation, except that it considers activation of inorganic stable nanoclusters up to level of aerosol particles in the presence of supersaturated organic vapor initiating rapid growth of the clusters. Use of the new theory as a component of the models of aerosol formation has led to a conclusion that an increase of the concentration of vapor of inorganic components intensifies the formation of aerosol particles, which influences the aerosol-induced global radiative cooling. Kulmala et al.[43] underscored the need for further improvements of the proposed theory by refining the way of using thermodynamic model in it. An important aspect of this and other efforts is that they illustrate the presence of close interaction between aerosol and atmospheric trace gas constituents (TGCs).

Chemical analysis of snow samples taken in the cap of Mt. Fuji, Antarctica, from deposits formed in summer after snowfall had shown that the snow layer up to 3.4 m in depth was characterized by minimum concentration of non-sea-salt (NSS) sulfates SO_4^{2-} and Na^+ ions, as well as maximum of the ratio of ion concentrations Cl^-/Na^+. This summertime NSS SO_4^{2-} minimum in the snow layer was never recorded earlier nowhere in Antarctica, and despite the existence of well known maximum of NSS SO_4^{2-} concentration in aerosol, it has occurred at the cap of Mt. Fuji during summer.

In order to understand the nature of this phenomenon, laboratory experiments were performed, and their results made it possible to conclude that, in summer, the water vapor sublimates inside the layer of snow cover at day, while at night the water vapor condenses at the snow surface into rime, leading to dissolution and decrease of the NSS SO_4^{2-} concentration. It seems quite likely that this process of sublimation-condensation also takes place in other cold continental regions. Determination of the number of sublayers with low NSS SO_4^{2-} concentration may help in dating the ice cores from the region of Mt. Fuji with high time resolution.

The presence of giant cloud condensation nuclei (GCCN) in stratocumulus clouds favors the occurrence of drizzle. Researchers studied the probability of influence of the film forming compounds (FFC) on droplet surface as a factor alleviating the GCCN effect on the process of drizzle formation. In this connection, Medina и Nenes[56] have analyzed accommodation properties and FFC amount required for significant effect on the size of GCCN particles under conditions typical of stratocumulus clouds. It was shown that, even for small mass fraction (on the order of 0.2%) of FFC and moderate influence on accommodation of water vapor, a considerable decrease of GCCN sizes may occur thus weakening their influence on the drizzle formation. The obtained results apply equally well to both clean atmosphere and the atmosphere polluted by aerosol.

One of the conceptual aspects of the study of aerosol formation processes is associated with the necessity of taking into account the aerosol–cloud interaction.[72] However, because of the substantial complexity and multi-factor character of this problem we will confine ourselves only to consideration of some examples.

Midlatitude clouds typically have mixed-phase composition, characterized by coexistence of supercooled water droplets and ice crystals at temperatures down to –38°C. Since the role of these clouds in climate forcing is still insufficiently studied, *in situ* microphysical measurements of partition of aerosol particles between droplets, cloud crystals, and within-cloud air[29] were undertaken at high-level Alpine station. The obtained results indicate that the activated aerosol fraction F_N with particle diameter $D_F > 100$ nm decreases from ~ 0.54 in summer (under conditions of liquid water clouds) to ~0.08 in winter (mixed-phase clouds). This phenomenon can be explained by the work of Bergeron–Findeisen mechanism, causing crystal growth from water droplets, accompanied by return of the initially activated aerosol particles back into the in-cloud air. This type of aerosol can play a role of cloud condensation nuclei and can undergo multiple activations until being removed due to moist deposition. Thus, the necessity arises of taking into account the indirect aerosol effect on climate, because of the phenomenon discussed here which manifests itself through the aerosol-induced changes of cloud properties.

Yin et al.[72] performed numerical simulation in order to analyze processing of sulfate aerosol by mixed-phase convective clouds and of the aerosol feedback on cloud microphysical properties and precipitation. It was shown that under such conditions aerosol number concentration increases, due to vertical transport, in the upper troposphere by several times causing intensification of aerosol effect on the process of cloud evolution.

At present, it is reliably established that humus-like substances (HULIS) make up an invariable part of fine continental aerosol and account for most fraction of organic species in aqueous solutions of rural and urban aerosols, as well as in aerosol products of biomass burning. Obviously, this secondary aerosol may be formed by gas-phase conversion of different trace-gas constituents, emitted to the atmosphere by natural and anthropogenic sources. Possibility of HULIS formation is not self-evident because the processes of humification in soil proceed slowly (during years) and require the presence of specific microbial environment.

As concerning this problem, different hypotheses of HULIS formation in the atmosphere were proposed. One of them is based on consideration of polymerization of volatile aldehydes arising during photochemical reactions (taking into account the drops of sulfuric acid as catalysts), and formation of chemiacetal/acetal. Another possibility consists in an immediate HULIS formation from isoprenoid or terpenoid hydrocarbon compounds (also in the presence of aromatic hydroxyacids, found in the composition of fine continental aerosol, which may react with participation of hydroxyl radical in cloud water with subsequent formation of colored organic species).

Having these circumstances in mind, Hoffer et al.[32] studied the chemical structure and properties of the products of reactions (called the synthetic HULIS), formed from 3.5-dihydroxy-benzoic acid in synthetic cloud water. It is shown that the characteristic aerosol products of biomass burning of the type of lignin react with OH radicals in the cloud water, leading to formation of colored organic compounds. The obtained results of laboratory studies make it possible to conclude that the process of oligomerization with participation of free radicals in aqueous phase leads to formation of products with larger molecular weight. This process is similar to the naturally observed process of formation of humus-like species making up the aerosol in rural regions, as well as aerosol formed at biomass burning. Since this aerosol can absorb solar radiation, its existence may have certain climatic consequences.

Cirrus clouds in tropics have a considerable influence on the global climate and chemical processes in the atmosphere, producing strong changes of the earth radiation budget, which depend on such physical characteristics of cloud cover as cloud top height, cloud thickness, microstructure, and shapes of water ice crystals. In the context of this problem, Kojima et al.[39a] have undertaken Cirrus Regional Study of Tropical Anvils and Cirrus Layers – Florida Area Cirrus Experiment (CRYSTAL-FACE) to study cirrus clouds and anvils in the area over Florida State (USA). In the framework of this experiment, aerosol samples were collected from aircraft in the upper troposphere (UT) and lower stratosphere (LS) using instrumentation installed on aircraft. For analysis of the samples, the method of transmission electron microscopy (TEM) was used.

Samples collected by Kojima et al.[39a] are classified into three categories: 1) in-cloud samples within UT; 2) outside-cloud samples within UT; and 3) samples collected in the LS. In all of the three cases, the sulfate particles (including the initial H_2SO_4 droplets) dominate. The morphology of H_2SO_4 droplets indicates that a partial "ammonation" of droplet composition took place during drop sampling. This composition was characterized by the presence of internal mixing with organic substance, metal sulfates, and solid particles of different composition.

Typical feature of all the three sample types was the presence of K- and S-containing organic particles and Si- and Al-rich particles. Specific feature of in-cloud samples was considerable content of Zn-rich particles. Origin of these particles remains unclear; however, it is quite probable that they are a pollution product due to the work of aircraft engine. A consequence of "ammonation" and internally mixed H_2SO_4 particles in UT aerosol may be freezing of particles at temperatures higher than in the case of pure H_2SO_4 aerosol. A cause of a relatively high "ammonation" of the in-cloud UT samples may be an intense ammonium transport by convection. It is characteristic of non-sulfate particles that their content decreases with height. These particles are formed in the lower troposphere and then transported to the UT and LS.

Quantitative estimates of radiative forcing by cirrus clouds (CC) are characterized by high level of uncertainty, mostly because the mechanisms of CC formation are insufficiently studied. In this context, cirrus clouds significantly influence the heterogeneous chemical reactions in the upper troposphere. Presumably, CCs are formed due to homogeneous nucleation in the upper troposphere, when temperature decreases and background aerosol particles become supersaturated with respect to ice. When temperature and relative humidity are at the corresponding levels, these particles may cause homogeneous or non-homogeneous nucleation of ice, leading to formation of ice CC particles.

Recent studies have revealed that the tropospheric sulfate aerosol contains about 50% and higher organic components whose influence on the processes in the atmosphere is insufficiently studied. Using flow cell, Wise et al.[70] performed laboratory studies to determine temperature at which ice nucleation occurs in particles consisting of ammonium sulfate and mixtures of ammonium sulfate with different dicarboxylic acids. Analysis of the results obtained has shown that the critical freezing point for ammonium sulfate remains unchanged in the case of mixtures of ammonium sulfate with dicarboxylic acids (for fixed aqueous activity of the solution), despite the fact that the solutions contained different fractions of inorganic and organic components. Similar behavior was observed for particles consisting of only dicarboxylic acids.

However, further studies of water uptake and ice formation are required for other mixed-phase particles consisting of inorganic and organic components at different temperatures and relative humidity values. It is of special concern the fact that (non-water-) soluble organic compounds may form a film on the surface of particles of ammonium sulfate aerosol, thereby preventing the water uptake.

The role of organic compounds in transformation of aerosol particles and their properties is even more significant because, as demonstrated by Lohmann and Leck[48] through analysis of observations over central part of Arctic Ocean with partial ice cover, the composition of high-latitude aerosol is characterized by the presence of considerable fraction of organic compounds, which affects the activity of aerosol particles as cloud condensation nuclei (CCN). They detected significant presence of Aitken nuclei, which influence the indirect aerosol effect on climate, enhancing the cooling effect in comparison with that caused by particles formed due to phytoplankton-derived dimethylsulfide.

Earlier, it was shown that air flows from marine stratus and cumulus clouds give rise to new particles of atmospheric aerosol. Luo et al.[50] have discussed the results of airborne measurements, as a part of CRYSTAL-FACE program, of cirrus cloud characteristics, whose analysis revealed the presence of ultrafine aerosol particles with diameters (D_p) from 4 to 9 nm (N_{4-9}) in the in-cloud aerosol. The observations were performed in July 2002 in Florida State (USA) at altitudes from 7 to 16 km using aerosol spectrometers installed onboard WB-57 research aircraft.

Analysis of the results obtained has shown that about 72% of samples collected in clouds had signs of the events of new particle formation with the mean number concentration $N_{4-9} = 3.0 \cdot 10^3$ cm^{-3}, whereas only 56% of outside-cloud samples showed the formation of new particles with this same number density $N_{4-9} = 3.0 \cdot 10^3$ cm^{-3}. The periods during which high N_{4-9} values were observed coincided with intervals of increase of the cloud ice water content (IWC) and high relative humidity with respect to ice (RHI). However, no quantitative correlation between measured N_{4-9} values and IWC occurred. Scales and repeatability of the events of formation of new particles in cirrus clouds were found to be more substantial than observed earlier in tropical/subtropical upper troposphere in the absence of cirrus clouds. The discussed situation indicates that the presence of CC may create favorable conditions for formation of new aerosol particles because of the low temperature, high RHI, intense formation of hydroxyl OH (because of sufficiently high water vapor content), influence of the electric field in clouds and convection. However, it is still unclear what are the mechanisms of formation of new aerosol particles in clouds.

Based on Lagrangian microphysical model of aerosol–cloud interaction, Haag and Kärcher[25] have analyzed regularities of the dynamics of cirrus clouds under conditions of Northern hemisphere midlatitudes. Numerical simulation was performed taking into account the available empirical *a priori* information characterizing aerosol microstructure, cooling rate, relative air humidity at which droplets freeze, and sedimentation rate of CC particles. The results obtained by Haag and Kärcher[25] indicate that among most significant processes determining the CC dynamics are: "competition" between insoluble and volatile aerosol particles, as well as perturbing effects of high-frequency gravity waves on the temperature field. Conclusions on leading role of these factors follow from the data observation available.

Normally, CCs form in the regions of cold air, and their microphysical properties are determined by mesoscale variability of the vertical wind velocity. Substantial transformation of CC properties may be caused by heterogeneous nucleation nuclei, known as ice nuclei (IN), at their number concentration in the range from below 0.01 to 0.03 cm^{-3} typical for middle latitudes. However, INs are unable to control the cirrus cloud formation. The key IN effect on CC is the reduction of ice crystal concentration, giving rise to indirect aerosol effect on clouds, manifested in a decrease of the cloud albedo due to the increase of effective particle radius and decrease of CC liquid water content. In addition, there also occur nonlinear changes of the frequency of CC formation, optical extinction, and the fraction of invisible (below detection limit) clouds. The nonlinear dependences of these three quantities manifest themselves after IN concentration increases above the threshold level of 0.01 cm^{-3} (exact value of this threshold depends on the temperature at which cloud formation takes place, cooling rate, and relative humidity at which IN freezing occurs). Under these conditions, IN become a control factor of the CC formation, making the role of homogeneous freezing less important.

Ice nuclei, whose freezing threshold is close to the saturation level over ice, can cause strong changes of cloud properties even if their concentration is low. Optically thin CC, near the detection threshold, are most sensitive to IN effect. Even low (as low as 0.001 cm^{-3}) concentrations of IN may favor considerable growth of the frequency of CC formation. If these clouds predominately form on IN, they may be subject to anthropogenic effects. Possible future changes of cooling rates in the upper troposphere, responsible for formation of ice aerosol particles, may lead to changes of the frequency of cirrus cloud formation, comparable with observed ten-year tendencies of cirrus clouds on global scales.

Development of studies of indirect aerosol effect on cloud cover (and, hence, the indirect aerosol effect on climate) has made it possible to obtain various information on dynamics of cloud systems and the corresponding feedbacks. In particular, such aspects of the problem as aerosol-induced changes of cloud albedo, modification of ice and water clouds, precipitation formation, and atmospheric composition have also been analyzed. In recent years, it also has become clear that, aside from the effect of aerosol microstructure and chemical composition on microphysical processes in clouds, some "chemical factors" also may give rise to additional climate cooling. These chemical factors are determined by the presence of trace gas constituents (TGCs) readily soluble in water, slightly soluble fluids, and decrease of surface tension, caused by organic TGCs. As a rule, these chemical factors favor an increase of the droplet number concentration (other conditions being the same) and, thereby, climate cooling. A factor, which may cause a decrease of the droplet number concentration (and, hence, warming effect) is deceleration of the growth of certain droplets due to formation of films of organic species on their surface.

From the viewpoint of indirect effect of aerosol in the case of warm clouds it is of special interest the role of gas-phase HNO_3, which is highly soluble trace gas constituent. It was just this circumstance that motivated the study of the influence of HNO_3 on cloud radiative forcing. The theoretical estimates have shown that at the mixing ratio of gas-phase HNO_3 of 5 ppb in the presence of ascending airflow in clouds with the speed of 0.1 m/s the number concentration of cloud droplets may increase (in comparison with that under conditions when HNO_3 is absent) by 60%. This increase is comparable with the growth of droplet number concentration due to doubling of the number concentration of aerosol particles.

Xue and Feingold[71] obtained new estimates of HNO_3 influence on microphysical and radiative cloud properties using adiabatic model of cloud particle for a given aerosol microstructure and different values of water vapor mass accommodation coefficient and HNO_3 concentration. The calculations showed that the presence of HNO_3 leads not only to an increase of the number concentration of cloud droplets N_d but also to considerable broadening of the particle size spectrum both toward small and large particle sizes. This broadening causes the "competition" between H_2O and HNO_3 with respect to particles of different size. Broadening to the large-size part of the particle spectrum is associated with intensification of the factors of droplet growth. In the case of small droplets, the growth factors become weaker in the presence of HNO_3. Though N_d grows with the increase of HNO_3 concentration, the accompanying increase of cloud optical depth and albedo is difficult to estimate with the help of the existing methods of calculating cloud optical properties. In particular, dependence of cloud optical depth on N_d taking into account one-third power law appears to be overestimated because of a considerable broadening of particle size spectrum due to HNO_3 effect. This result indicates the importance of taking into account the effect of nitric acid on cloud optical properties and, correspondingly, climate.

Iron is a critically important biogenic matter regulating the rate of development of microorganisms in seawater. It is conjectured, in particular, that it limits the formation of phytoplankton in such regions of the World Ocean, for which high concentration of nitrates and low level of chlorophyll is typical situation. The concentration of chlorophyll in such regions appears to be lower than expected because the low iron concentration limits phytoplankton growth and initial production. These regions include subarctic and equatorial Pacific and oceans of the Southern Hemisphere where the level of deposition of dust aerosol on ocean surface is low. In these regions the iron supplied via upwelling may be insufficient; some external source of iron is needed for more effective use of biogenic matter. In addition, iron deposition significantly influences CO_2 budget because higher income of iron to the ocean favors a decrease of CO_2 concentration in the atmosphere (on the timescales of periods of Ice Age).

It is also supposed that the presence of iron in marine aerosol may influence the sulfur cycle through participation in oxidation reactions including the oxidation of dimethylsulfide and formation of cloud condensation nuclei. The development of biogeochemical processes in the ocean with the participation of iron is determined by iron solubility, which strongly depends on iron mineralogy and degree of oxidation. On average relative iron content in the earth crust is about 3.5% with domination of insoluble iron (FeIII) in the form of aluminosilicate. The solubility of iron contained in soils is generally less than 0.1% that indicates possible important role of processing of mineral aerosol in the atmosphere to increase the accessibility of iron as biogenic matter. In this connection, the studies of processes in the atmosphere, which favor the transformation of insoluble iron into more soluble species, become quite urgent. These processes are especially important in remote regions of the World Ocean where iron may play a role of biogenic matter limiting the biological productivity.

Hand et al.[27] discussed the results of shipborne measurements of solubility of aerosol-derived iron during three missions in 2001 to the regions of Atlantic and Pacific oceans. According to results obtained, the concentration of soluble iron varied in the range 0–45% [average being $(4 \pm 9)\%$] in fine aerosol (with particle diameter less than 2.5 μm) and 0–87% [$(2 \pm 10)\%$] in coarse aerosol. Taking these results into account, Hand et al.[27] have analyzed reliability of two hypotheses on the effect of soluble iron on ecodynamics using global models of mineral aerosol. One of these hypotheses assumes that the solubility of iron increases when exposed to solar radiation (we mean the photoreduction reactions which serve a mechanism of growth of soluble iron in the presence of acidic solutions). The second hypothesis takes into account iron processing by clouds and growth of concentration of soluble iron during interaction of mineral aerosol with clouds. In both of these cases, estimates of the average fraction of soluble iron compared with real one have been close, while being incapable to reproduce the observed variations. It is quite possible that the cause of this situation could be the neglect of interaction with the components other than mineral aerosol, which could be significant factors of the increase in concentration of soluble iron.

Hara et al.[28] have performed regular measurements of the composition of atmospheric aerosol in 1997 and 1998 at Syowa and Dome Fuji Japanese Antarctic stations. According to data from Syowa station, the annual behavior of mass background concentration of the sea-salt aerosol particles is characterized by average Na^+ content equal to 2.7 nmoles/m^3 in summer and by the increase of the concentration in winter due to long-range transport from the region of Indian Ocean and local emissions caused by strong winds. Though analogous annual behavior was also observed at inland station of Dome Fuji, the concentration of sea-salt aerosol in this case was found to be lower (in comparison with the data for station Syowa), i.e., from 10% up to a few tens of percent. The sea-salt aerosol observed at the Dome Fuji station was brought there by the long-range transport from the boundary layer and lower troposphere of the Antarctic sectors of Indian, Atlantic, and Pacific Oceans. From this, it follows in particular that the data acquired from ice core samples must bear information on the evolution of long-range transport, as well as on the sources and sinks (or accumulation) of aerosol on the surface of snow cover.

The release of Cl^- and Br^- ions from the sea-salt aerosol occurred at the Syowa station primarily in summer. At the same time, the molar ratios Cl^-/Na^+ and Br^-/Na^+ were, respectively, about 0.5 and 0. In the process of long-range transport, the aerosol properties might be modified due to heterogeneous chemical reactions with the participation of SO_4^{2-}, $CH_3SO_3^-$, NO_3^-, and their precursors. The dominating release of Cl^- (contained primarily in HCl) in summer was also observed at the station of Dome Fuji; but the Cl^-/Na^+ values were lower throughout the year. For the station of Dome Fuji the researchers found positive correlation between Na^+ and NO_3^-, as well as the presence of such chemically active trace gas constituents as HNO_3, N_2O_5, and NO_3. Therefore, in the process of transport toward this station there might occur significant release of Cl^- (seemingly, sea-salt particles in Antarctic serve an important NO_3^- transport agent). The concentration of Cl and Br (in gas phase) at the Syowa station varied, respectively, from below detection limit (BDL) to 5.3 nmoles/m^3 (average being 1.2 nmole/m^3) and from BDL to 1.4 nmole/m^3.

From the data on the annual behavior of Cl concentration it follows that under conditions of dominating release of Cl^- from sea-salt particles in summer, there might occur accumulation of Cl^- in winter. This suggests that lifetime of Cl^- has to have annual behavior associated with the variations of the extents of the ice cover of the sea. The concentration of Br^- markedly decreased at low content of near-ground aerosol. At both of the stations considered, decrease of concentration took place due to formation of mirabilite. Decrease of sulfate concentration, recorded at the Dome Fuji station, might be due to sublimation at the snow surface. In the presence of strong wind at the Syowa station, a fractioning of Mg^{2+}, K^+, and Ca^{2+} in the sea-salt aerosol was observed.

To determine the characteristics of mobilization and concentration of dust aerosol varying in time in the source regions, Luo et al.[50] have performed numerical simulation making it possible to analyze the processes yielding the aerosol emissions into the atmosphere. To perform this numerical simulation, they used the data of two series of reanalysis of meteorological information and two variants of parameterization of aerosol sources; the calculations were performed for six aerosol-source regions.

Analysis of the results obtained by numerical simulation showed that 35 to 70% of variations of the aerosol mobilization is associated with the diurnal behavior of mobilization of dust aerosol in the considered source regions, irrespective of specified meteorological conditions and parameterization of the sources. Synoptic-scale variations account for 6 to 50% of variations of the aerosol mobilization and even higher differences depending on the meteorological conditions and on the source parameterization scheme chosen. The variations of aerosol concentration in the source region are very sensitive to specific meteorological conditions and to parameterization when synoptic scale variations contribute to within 30 to 50% of the total variations under certain conditions or to 6 to 40% under some other conditions. Variations determined by diurnal behavior lie in the range from 20 to 50 or 25 to 80% depending on the specific model.

The results obtained by Lubin et al.[49] indicate that mobilization of dust aerosol and its concentration is determined to a higher degree by synoptic variations in source regions located in Australia and East Asia than those in North America and Arabia, what agrees with the data of observations of cold fronts and motions of cyclonic systems causing mobilization and long-range transport. Contrasts of variations for different types of *a priori* information on the meteorological conditions and source parameterization reflect the possibility that feedbacks influencing aerosol cycles may be sensitive to source parameterization and specific model features.

Treatment of the atmospheric aerosol as a climate-forcing agent having great importance in numerical climate modeling is seriously limited by low spatial resolution of the model. In this connection Cakmur et al.[10] have suggested a parameterization of the emissions of dust aerosol to the atmosphere, caused by small-scale atmospheric circulation. This was done by specifying probability distribution function of wind velocity within an elementary cell of the spatial resolution. This function depends on the velocity directly calculated using the general circulation model (GCM), as well as the amplitude of fluctuations relative to this velocity. At the same time, the considered GCM ensures adequate parameterization of the planetary boundary layer taking into account the processes of dry and moist convection.

Aerosol emissions depend on the fraction of wind speed values exceeding the threshold speed that determines the occurrence of the emissions. Therefore, the emissions turn out to be possible at the GCM-calculated wind speed, if sufficiently high wind-speed variations above this threshold occur on the sub-grid resolution scale. Since in the considered GCM a dominating influence on the aerosol emissions is exerted by wind fluctuations of the sub-grid resolution scale determined by the process of dry convection, this favors the emissions in arid zones where an intensive mixing in the boundary layer occurs due to strong heating of the underlying surface. Particles emitted in deserts appear to be farther from the zones of precipitation and experience mixing (by the process of dry convection) within larger atmospheric depth which favors the increase of the characteristic time of dry and moist aerosol deposition and, hence, leads to the growth of aerosol abundance in the atmosphere at a given emission levels. Treatment of wind speed variations of the sub-grid resolution scales gives more reliable values of the total aerosol content in the atmosphere in the regions of Sahara and Taklamahan deserts than those obtained from satellite data on the aerosol optical depth.

Results of recent observations favor the hypothesis, according to which formation of ions (ionization) plays an important role in the formation of ultrafine atmospheric aerosol, as ions become the nucleation centers. This hypothesis is very interesting in the context of the assumption that the observed positive correlation between globally mean cloud amount and intensity of Galactic cosmic rays (GCR), varying in the course of 11-year solar cycle, can be explained to be due to ions participating in the aerosol formation and originating due to the effect of GCR (in turn, aerosol particles, formed in such a way, act as cloud condensation nuclei).

Using the theoretical model of ion-induced aerosol formation, taking into account experimental data on thermodynamics of cluster ions, Kazil and Lovejoy[39] have analyzed formation of ultrafine aerosol in the troposphere for different levels of background ionization and concentration of vapor of sulfuric acid. The numerically obtained results demonstrate the possibility that ultrafine aerosol particles can be formed due to ion-induced nucleation. Both the number concentration and surface area of these particles depend significantly on the ionization level varying, in particular, under the influence of 11-year GCR cycle. However, depending on the environmental conditions, this dependence may be both positive and negative. Taking into account the possibility, revealed in numerical experiments, of forming large particles too it can be concluded that ion-caused nucleation is an important process in the atmosphere, which can favor the manifestation of the solar activity impact on the troposphere.

Vana et al.[68] compared quantitative characteristics of the processes of formation and growth of nucleation-mode aerosol particles according to data of observations at the three sites: Hyytiälä and Värriö in Finland and Tahkuse in Estonia. The observation program at all the three sites included measurements of aerosol microstructure, as well as mobility of ions (in Tahkuse). According to observations conducted during 157 days (during three periods: March 28 – May 2, 2000, March 20 – May 16 and September 18 – November 19, 2001), the nucleation events were observed on 62nd, 50th, and 45th days in Hyytiälä, Värriö, and Tahkuse, respectively. Overall, 18 simultaneous nucleation events were recorded at all the three sites.

The data on observed aerosol microstructure were used to estimate the concentrations of condensed water, intensity of water vapor sources, particle growth rate, total condensational sink, rate of formation of particles with 3-nm size, and the rate of formation and number concentration of 1-nm size particles. Estimates of particle growth rate gave values in the range 2 to 9 nm/h. The growth rates obtained from measurement data on the distribution of ion mobility have led to nearly the same results. The concentration of water vapor being condensed in Hyytiälä varied in the range from 1 to 12 by 10^7 cm^{-3}, what was less than in Tahkuse and Värriö. The rate of increase of intensity of sources was found to be (6 to 55)$\cdot 10^4$ cm$^{-3}\cdot$s^{-1} (Tahkuse) and (2–14)$\cdot 10^4$ cm$^{-3}\cdot$s^{-1} (Hyytiälä and Värriö). The condensational sink was generally more significant in Tahkuse than in the other two sites.

Analysis of data on aerosol microstructure in Tahkuse has led us to a conclusion that the neglect of particles with the diameters in excess of 500 nm produces underestimation of the intensity of total condensational sink. The fraction of charged nucleation-mode particles in Tahkuse was found to be much higher than the probability of charging a single particle. Consideration of the air mass trajectory and data of meteorological observations has demonstrated that nucleation events are synoptic-scale phenomena with the horizontal scale exceeding 1000 km.

Such of the reduced sulfur compounds (RSC) as H_2S, COS, CH_3SH, CH_3SCH_3, and CS_2 are emitted into the atmosphere both by biogenic sources (formed by assimilation and non-assimilation reduction of sulfate due to volcanic activity) and by anthropogenic sources (natural gas production, oil refining and paper production enterprises, biomass burning, etc.), ultimately acting on the local and global climate. Dimethylsulfide (DMS), formed due to phytoplankton-derived biogenic products, is the only gas-phase sulfur compound having natural origin. It influences the global climate through a multistage and complex mechanism feedbacks, which includes the formation of cloud nuclei in the atmosphere over oceans. This process influences the albedo of the marine stratus clouds.

Generally, RSCs suffer photooxidation and long-range transport in other regions. Most abundant in the remote troposphere is COS (formed by photooxidation of CS_2), whose average concentration is about 500 pptv. Because of low chemical activity and, hence, long lifetime in the atmosphere (on the order of 1 year), COS is the only sulfur species (set aside volcanically emitted SO_2), that can reach the stratosphere. The inflow of COS to the atmosphere can be an important source of sustaining the layer of stratospheric sulfate aerosol in volcanically quiet periods because of its effective photolysis and transformation into the sulfuric acid. Most of the RSCs are toxic and so can be hazardous to the environment and human beings.

Because of the scarcity of information on reduced sulfur compounds in South America, Nunes et al.[57] performed air sampling at a few sites in two regions of Brasilia (All Saints Bay and Reconcavo Baiano) using cryogenic devices for subsequent analysis for the presence of RSCs using the methods of gas chromatography and flame photometry. At the sites where biogenic sources dominated, the COS concentration varied in the range from 0.5 to 1.0 pptv. Regions unaffected by industrial emissions were characterized by low concentration of all volatile sulfur species (≤ 0.25 pptv). The RSC concentration increased, however, near oil production plant (Camaçari): COS (8 pptv), CH_3SH (1.50 pptv), H_2S (1.35 pptv), and CS_2 (0.3 pptv). In the region of oil production plant in Landulfo Alves the concentrations of COS, DMS, and CS_2 were respectively 2.0, 0.55, and 0.2 pptv.

One of the most important consequences of the aerosol pollutions of the atmosphere is degradation of the visibility. This situation frequently occurs in the USA where reduction of the visibility range is caused primarily by fine aerosol including such its types as carbonate (elemental and organic), sulfate, nitrate, and dust (soil) aerosols. Using global three-dimensional interactive model of aerosol and trace gas constituents-oxidants (GEOS-CHEM), Park et al.[58] estimated the influence of natural factors and transboundary transport on the formation of sulfate-nitrate–ammonium aerosol under conditions in the USA. The corresponding calculations have been made in order to reproduce the evolution of content and chemical composition of aerosol during one year (results for 1998 and 2001 are considered). The numerical simulation for 2001 has led to values of annually mean mass concentration for ammonium sulfate and nitrate of 1.52 and 1.53 $\mu g/m^3$ respectively, in the west region of the USA and 4.11 and 3.26 $\mu g/m^3$ in the east region. Estimates of the levels of natural concentration gave values of 0.11 and 0.03 $\mu m/m^3$. Results of numerical simulation are compared with the data of observations at the networks of different federal departments of the USA. Exclusion of the contribution of anthropogenic emissions on the territory of the USA has made it possible to analyze the influence of natural factors and long-range transport.

Park et al.[58] have shown that for sulfate and nitrate aerosol components the contribution of transboundary transport from Canada, Mexico, and Asia to aerosol composition dominates over natural factors. For the background and sulfate components for both west and east regions of the USA the contribution of trans-Pacific transport of Asian pollutants is about 30%. Results of most reliable calculations of naturally occurring concentrations of ammonium sulfate and ammonium nitrate either agree with or are below the estimates made by USA Environmental Protection Agency (EPA) for variations of the visibility under the impact of natural factors aimed at determination of the threshold levels of the admissible pollutions. However, the presence of large contribution of the transboundary pollutions, demonstrated by the discussed calculations, indicates that the attainment of these levels is impossible without taking measures toward international control over the emissions.

Though global models of aerosol distribution can adequately reproduce many observed features of the mass concentration and aerosol optical depth, the calculations seem to be less reliable of the aerosol microstructure characterized by underestimation of the concentration of large particles after long-range transport. Formation of the dust aerosol (DA) is caused primarily by two interrelated processes – saltation and sandblasting. Saltation is the process of horizontal transport of large particles in the turbulent atmosphere. Sandblasting means emission of dust and larger particles due to impact on the underlying surface of different external factors ("saltators").

Grini and Zender[24] analyzed these discrepancies in estimates of large-particle DA concentration arising because of insufficiently adequate treatment of the four factors responsible for the DA formation. These factors are as follows: 1) DA microstructure at location of the source (considered as variable or constant on account of the saltation and sandblasting processes); 2) distribution of wind velocity (specified as average or as probability distribution function PDF); 3) structure (granularity) of the soil assumed to be the aerosol source; and 4) discretization level of aerosol microstructure. To reproduce the results of 2000 Puerto Rican Dust Experiment (PRIDE), aimed at obtaining data on dust aerosol, global model of involvement, long-range transport, and DA deposition is used.

The results obtained showed that the joint treatment of saltation-sandblasting leads to higher values of the large-particle concentration than schemes neglecting the sandblasting. An important factor influencing the microstructure of aerosol coming to the atmosphere is the structure of soil as the source of aerosol. Transition from large-grain structure of soil and soil with smaller-sized grains entails 50% increase of the fraction of large aerosol particles (with the diameter $D > 5$ μm). Best agreement with PRIDE data was achieved by setting an intermediate soil structure, which is typical for West Africa, being at the same time the main DA component in all regions sources of aerosol.

Henze et al.[30] have proposed a generalized approach based on the use of formalism of adjoint equations; this approach is used in analysis of data on atmospheric aerosol in models of its long-range transport and chemical transformation taking into account the microstructure and chemical composition of multi-component aerosol. They discussed the results of testing the adequacy of this technique when the initial distribution of the chemical composition of particles is specified according to particle sizes and water vapor concentration being set with complete or partial incorporation of measurement results on all components of the aerosol composition. It was shown that the use of the method of adjoint equations allows the reconstruction of the initial aerosol microstructure and water vapor concentration to be performed even if input information is used only partially. However, in the latter case the success depends on specific features of observations, characteristics of estimates of the initial state and duration of the assimilation period. This method is promising from the viewpoint of its use in three-dimensional transport models taking into account chemical transformations.

Convective cloud systems have a diverse influence on the atmosphere and climate. Chemically active trace gas constituents are washed out and so they contribute to formation of acid precipitation and transboundary pollution of the atmosphere. Convective clouds cause long-range transport and mixing of trace gas constituents between the planetary boundary layer and the upper troposphere and, thus, they influence the spread of urban pollutants and trace gas constituents in the upper troposphere which, in turn, influences the radiative transfer. Because of lightning discharges the convective clouds become important source of nitrogen oxides NO_x, the key component of global nitrogen cycle and an important factor governing ozone concentration field in the troposphere. The convective clouds are a significant factor of the processes of formation of odd hydrogen, associated with the transport of such precursors of OH hydroxyl as hydrogen peroxide, acetone, formaldehyde, and other peroxides. On the other hand, as the main oxidizing component of the troposphere, OH regulates destruction of almost all trace gases in the atmosphere.

Since interaction between TGCs and water ice-phase clouds is still poorly understood, Stuart and Jacobson[66] have undertaken a study of the relationship between mixed-phase components during freezing of liquid hydrometeors in the process of “dry” growth due to riming, defined as collisions of supercooled droplets with ice crystals followed by freezing and formation of hail particles. This process is characterized by full freezing of the colliding droplets at surface temperature of riming particles below 0°C. In contrast, the “moist” growth due to riming is characterized by partial freezing of hydrometeors at surface temperature of 0°C. Different chemical components initially dissolved in supercooled water droplets can either be captured by droplets or released as they freeze. The degree of retention influences the availability of different components for liquid- and gas-phase chemical reactions and their travel inside the cloud that may produce a considerable effect on the distribution of different TGCs over the troposphere and deposition onto the underlying surface.

Because of the importance of reliable determination of the above-said retention, Stuart and Jacobson[66] discussed the possibility of retention calculation for conditions of “dry” growth by riming. They calculated the dimensionless indicators of retention λ, which are then compared with measured values of the fraction of retained component, Γ. This comparison showed good agreement. Rather adequate is the parameterization: $\Gamma = 1 - \exp(-0.002\lambda)$, which applies to many chemical compounds.

Chemically reactive oxygen species (ROSs), including such oxygen-containing species with strong oxidizing capability as H_2O_2 molecules, ions of the type of hypochlorite ion (OCl^-), radicals of the type of hydroxyl OH, and superoxide anion O_2^-, are formed by the photochemical reactions in the polluted atmosphere. At the same time, it is observed that two most important ROS precursors are volatile organic compounds (VOCs) and nitrogen oxides (NO_x). It is also observed that ROS is endogenously formed by biological systems as a protection against aggressive organisms and other adverse environmental factors (such as engine exhausts). The ROSs can also be a product of burning the organic substances (such as wood and cigarettes). They have different lifetimes in the atmosphere, depending on their specific sources, and exist in both gas and aerosol phases.

It was found that ROS content in aerosol particles is determined, in particular, by particle age. For instance, silicon dust is characterized by high concentration of free radicals, exponentially decreasing with half-period of about 30 h. The ROS concentration in plumes, arising in smoke during welding, also decreases exponentially with time, but with half-period of about 10 days. It was found that “fresh” ROSs have stronger toxic effect than the “old” ROSs. The ROS presence is associated with pathogenesis of many pulmonary diseases including asthma, as well as plays certain role in the development of oncological diseases.

According to observations in Rubidoux, California, Venkatachari, et al.[69] studied the diurnal behavior of ROS content in different aerosol fractions sampled every 3 h using impactors. They analyzed the factors causing the variations of ROS content with special attention paid to the relation between ROS concentration and intensity of photochemical reactions; the indicator of the intensity was chosen to be the concentration of near-surface ozone. It was shown that the role of photochemical reactions, as a factor determining ROS concentration during day, is only minor. The observations demonstrated that the ROS concentration is larger in small aerosol particles, especially those in the size range from 10 to 56 nm.

Liu et al.[46] have substantiated an algorithm for processing data of two-channel lidar, installed onboard CALIPSO satellite for discriminating between clouds and aerosol. They discuss two versions of the algorithm, the one that uses one-dimensional (1D) and the other multidimensional probability distribution function (PDF). Both of these versions make up the basis for development of an efficient algorithm. The latter uses three-dimensional (3D) approach taking into account layer-average backscattering at 532 nm wavelength, backscattering ratio at the wavelengths of 1064 and 532 nm, and average height of the layer. Data obtained with the cloud probing lidar (CPL) were used for testing the algorithm.

Liu et al.[46] performed comparisons between results obtained using 3D CALIPSO algorithm and currently used 2D algorithm, and found quite good agreement between these methods of data processing. However, after processing data for 228 264 layers, in 5.7% of all cases the results of classification had been different, primarily because of the misidentification of optically thin clouds as aerosol by the 2D algorithm. The level of this misidentification substantially decreases in the case of three-dimensional PDF (CALIPSO algorithm). Special conditions of identification appear in the presence of dust aerosol, primarily because light scattering by dust layers is similar to scattering by clouds. In this connection, an additional algorithm was developed allowing identification of optically thick dust aerosol layers such as those formed due to dust storms in Sahara. An exception, however, are dust layers of very large optical depth.

Measurements of temperature at which aerosol becomes volatile contain information on components present in aerosol and having low volatility. By measuring the characteristics of hygroscopic aerosol behavior, it is possible to determine the solubility of such low volatile components. To perform these measurements, volatilization and humidification tandem differential mobility analyzer (VH-TDMA) technique was developed. It was first used by Johnson et al.[37] for measuring volatile fractions and hygroscopic growth of aerosol particles in application to coastal aerosol in Brisbane, Australia. The coastal observation site was located on sandy tidal strip 10 km away from the nearest road and was surrounded by mangrove forest and sandy surface uncovered during low tides.

The results of considered field measurements were compared with those using laboratory-generated aerosol of known composition. According to the results obtained, Aitken-mode particles are characterized by the dynamics of volatility similar to that observed in laboratory aerosol consisting of methane-sulfonic acid and ammonium sulfate. Measurements with particles of 60 nm size, arising during nucleation events, contained larger fraction of substance with volatility close to that corresponding to ammonium sulfate. However, these particles were less hygroscopic than particles from pure sulfate ammonium. Observations at the center of Brisbane under conditions of sea breeze gave practically the same results as for the coastal aerosol, but revealed the presence of additional low volatility aerosol components. This aerosol might arise due to urban sources or marine particles, which acquired additional secondary components in the course of long-range transport.

As part of mineral dust aerosol and tropospheric chemistry (MINATROC) studies of dust aerosol and tropospheric chemistry, Bauer et al.[7] discussed the experience of using the interactive global model of atmospheric general circulation taking into account heterogeneous chemical reactions taking place on the surface of mineral aerosol particles. The goal was to analyze the effect of these reactions on the concentration field of tropospheric ozone (TO). Overall, this model provides adequate reproduction of Saharan dust aerosol (DA), but seems to underestimate DA content over East Asia and northern Pacific Ocean. Therefore, the obtained estimates are considered to characterize the lower limit of losses of TO precursors, caused by heterogeneous reactions.

The calculations showed that globally mean annually average decrease of TO concentration due to heterogeneous chemical reactions is about 5%, reaching maximum (20%) over equatorial Atlantic and Africa. Most significant TO loss was found to be due to uptake of gaseous nitrogen acid on DA particles. The heterogeneous chemical reactions cause removal from the troposphere of about 35% of nitric acid, leading to substantial depletion of nitrogen reservoir in the background troposphere and, hence, to reduction of the level of TO formation in clean atmosphere.

Estimates of the influence of the process of uptake of different trace gas constituents on global TO budget have led to a conclusion that the most significant component is HNO_3. Much less contributions come from uptake of N_2O_5 or NO_3, causing destruction of only 1% of TO due to uptake of these trace gases by aerosol particles. Insignificant contribution also comes from direct O_3 uptake by aerosol, becoming marked only under conditions of dust thunderstorms, and so being negligible on a global scale. Most significant uncertainties of the discussed estimates are associated with insufficient reliability of uptake coefficients (UCs). In the cases of HNO_3, N_2O_5, and O_3 these uncertainties have weak effect on globally mean estimates of TO concentration, except under such conditions when UC for HNO_3 varies by two orders of magnitude (this is the real level of discrepancy for two groups of the data).

The results of numerical simulation of TO concentration field depend significantly on reliability of calculations of HNO_3 concentration (generally having been overestimated). Because of high solubility and uptake probability of HNO_3, the calculated HNO_3 concentration is strongly related to specific chemical reactions with participation of aerosol. Therefore, models taking into account only gas-phase chemical processes can be considered inadequate. Since the discussed model does not take into consideration all possible mechanisms of formation of nitrate aerosol, it can overestimate HNO_3 concentration. Nevertheless, in Central Africa, where DA effect must be considerable, comparison of observed and calculated values of HNO_3 concentration has demonstrated unexpectedly good agreement provided heterogeneous reactions are taken into consideration.

Though the model considered does not take into account the reactions with the participation of non-methane hydrocarbon compounds (NMHCs), what didn't provide adequate reproduction of the entire complexity of chemical processes under conditions of polluted atmosphere, the results obtained by numerical simulations have been quite realistic. The calculations showed that about 80% of the TO concentration fall off takes place in periods of dust-loaded events in the atmosphere and can be explained by arrival of unpolluted air masses to the observation site, and that about 20% of the decrease is due to heterogeneous chemical reactions with the participation of DA. In the case of Mount Cimone (North Italy) August 2000 episode of strong pollution of the atmosphere due to Saharan DA, the corresponding levels of the decrease were 60 and 40%.

Rodriguez and Dabdub[60] have analyzed the dependence of chemical composition of aerosol particles on their sizes; this dependence was obtained through calculations using IMAGES model of global evolution of the atmospheric chemical composition in the process of long-range transport in combination with SCAPE-2 model of formation of chemical composition of the aerosol particles. Main attention in this analysis was paid to numerical simulation of the equilibrium values of concentration of ammonium, nitrate, sulfate, and water taking into account the interaction with ions of sea salts and dust. For the calculation of long-range transport of the aerosol and trace gas constituents, a semi-Lagrangian scheme is used in specifying the fields of monthly mean values of meteorological parameters according to data of objective analysis performed in the European Center for Medium-Range Weather Forecast (ECMWF).

They have considered the calculated annually mean size distributions of dry mass of aerosol particles for different observation sites in North America and Western Europe, and performed comparison of numerical results, based on the interactive IMAGES-SCAPE2 model and IMAGES model for different key components of the atmospheric aerosol. In the case of nitrate, the values of concentration, calculated with the use of interactive model, agree better with observation data than IMAGES-based calculations.

In accordance with the obtained results, the aerosol microstructure is generally bimodal. The presence of sea-salt and dust aerosol in the regions of the polluted atmosphere over continents leads to intensification of sulfate formation by 20 to 80% (in the atmosphere over oceans of the Southern Hemisphere the influence of the salt aerosol dominates). Under these conditions, the nitrate formation is intensified by about 14 to 60%, whereas the processes of ammonium formation become weaker by 20 to 60%. Many European observation sites are characterized by a significant role of nitrate as a factor influencing aerosol microstructure, but the regions of maximum nitrate concentration at the surface level coincide with the sources of intense emissions of dust aerosol in North Africa, Saudi Arabia, and Central Asia. The nitrate lifetime in the atmosphere is 7.69 days. The presence of water favors the change of the microstructure by its deformation toward larger particles.

In August 2000, Fire Locating and Monitoring of Burning Emissions (FLAMBE) program was initiated with the purpose of global monitoring and numerical simulation of the processes of biomass burning. The main goal of the program was to provide 5-day forecasts of the development and consequences of substantial episodes of long-range transport of smokes from biomass burning. It is based on the US Navy Aerosol Analysis and Prediction System (NAAPS) model of smoke analysis and prediction of smoke transport. The USA National Oceanic and Atmospheric Administration (NOAA) WA_ABBA algorithm ensured processing of data of satellite observations (geostationary satellites GOES) of fires every 0.5 h.

Reid et al.[59] discussed the experience of tracking the spread of smoke aerosol (SA) and estimates of SA fluxes into the atmosphere according to observations in 2001 and 2002. In agreement with earlier estimates, the SA emissions to the atmosphere were found to be 10 to 25 Tg/yr. Good agreement with data of satellite (MODIS instrumentation) and network of ground-based (AERONET) observations was also obtained from comparison of aerosol optical depths. A characteristic feature of SA (in comparison with other aerosol types) is its strong spatiotemporal variations, which complicates the parameterization of the long-range transport and transformation of aerosol properties. Timely prediction of the dynamics of SA concentration field can only be made if SA flux is specified not later than 6 hr after SA emissions. Therefore, it is natural that the only adequate source of information is the data of remote sensing from satellites.

In recent years, substantially higher concentrations of ultrafine aerosol (with particle radii on the order of a few nanometers) have been observed in different regions of the globe. Though there is no doubt that the formation of such particles is associated with the process of nucleation, the reasons for nucleation events have remained unclear. For this reason, there was an active debate in scientific literature about specific meteorological conditions, which would prevent the formation of new particles and growth of their measurable sizes. In particular, some researchers studied the influence of the development of planetary boundary layer (PBL) and turbulent mixing on the microphysical processes.

In this connection, Sieber et al.[63] discussed the results of the first observations of ultrafine aerosol, performed in 2002 in the framework of field observation experiment SATURN at heights up to 1200 m using instrumentation installed on a tethered balloon. Main components of the measurement system were condensational counters of aerosol particles and ACTOS sensors for measurements of turbulence characteristics, as well as sensors of temperature and air humidity. Analysis of the observed vertical profiles of aerosol number concentration (ANC) has revealed the presence of the layer with increased ANC near the inversion, representing a part of PBL. The ANC values reached 600 cm^{-3} for particles with the size in the range from 5 to 10 nm. At the same time there was a high correlation between increased ANC and strong fluctuations of temperature and humidity caused by invasion of plumes penetrating the inversion layer. The latter caused intense mixing, which favored considerable increase of nucleation rate. ANC observed near inversion layer substantially exceeded those recorded within near-surface layer at the underlying surface level. This fact favors the hypothesis that ultrafine particles formed near inversion, and then descended lower thus causing ANC increase at the level of underlying surface.

Studies of different aerosol effects (influence on climate, heterogeneous chemical reactions, variations of visibility range) must be preceded by analysis of their phase state and hygroscopic properties. At present, it is found that aerosol particles consist both of inorganic and organic components. For instance, according to observations at a number of sites, the mean chemical composition of fine urban aerosol, in relative weights, is characterized as follows: 37% (sulfate), 24% (organic carbon), 11% (ammonium), 5% (elemental carbon), and 4% (nitrate). The phase and hygroscopic properties of such an aerosol component as ammonium were studied in detail; whereas particles of organic and mixed composition are very poorly understood.

In this connection, Pant et al.[57a] performed laboratory measurements of deliquescence and crystallization of particles of ammonium sulfate-glutaric acid and sodium chloride-glutaric acid, keeping in mind that glutaric acid, constituting dicarboxylic acid, was detected as a component of atmospheric aerosol particles, while ammonium sulfate and sodium chloride are among two main inorganic aerosol components. The main purpose of measurements was determination of the levels of relative humidity (RH), at which deliquescence (DRH) and crystallization (CRH) of particles of the above-mentioned composition occur. Information on DRH and CRH for mixed-composition particles is of key importance for assessment of the role of aerosol in different processes in the atmosphere.

The DRH measurements are in a good agreement with the earlier results, whereas CRH values appear to be substantially underestimated as compared with the results available from literature. The discussed measurement results indicate that both in the case of DRH and CRH for ammonium sulfate and sodium chloride, these values are underestimated only insignificantly if the molar fraction of acid did not exceed 0.4. At the same time, if the behavior of other organic compounds present in the atmosphere turns out to be analogous, then the DRH and CRH values for mixed-composition (organic-inorganic) particles is only somewhat less than for purely inorganic particles in those cases when molar fraction of organic matter is less than 0.4. Therefore, it can be concluded that if particles contain considerable amount of organic compounds (molar fraction is larger than 0.5), the level of relative humidity at which crystallization occurs decreases considerably, suggesting higher probability for particles to stay in liquid phase.

Conclusion

The results discussed above are no more than illustration of the general conclusion that the modern level of knowledge on atmospheric aerosol is very far from being quite adequate. Undoubtedly, it is required to develop long-term international program of comprehensive laboratory and field studies into the interactive aerosol – clouds – trace gas constituents processes performed in close collaboration with the efforts in the field of numerical simulation of the corresponding processes.

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