

# Atmospheric aerosol as a climate-forming component of the atmosphere. Part 1. Properties of various-type aerosols

K.Ya. Kondratyev

*Center for Ecological Safety RAS / Nansen Environmental and Remote Sensing Center, St. Petersburg*

Received September 9, 2003

A review is presented of a new research into the physical and chemical properties of various types of atmospheric aerosols (sulfates, dust, organic, marine, biogenic, urban, etc.) as well as of the spatiotemporal variability of aerosol content in the atmosphere. Processes of aerosol formation and its impact on heterogeneous chemical reactions in the atmosphere have been briefly discussed.

## Introduction

The fact that the atmosphere is a colloidal medium, that is, contains suspended aerosol particles, is important, since aerosols significantly affect the air quality, visible range, various heterogeneous chemical reactions occurring on the surface of aerosol particles, and so on. However, the most significant role of aerosol is its impact on climate that has been insufficiently studied as yet. In spite of the obvious exaggeration of conclusions concerning the climate-forming contribution of the man-made greenhouse effect, the need of correctly taking into account the aerosol impact on climate becomes obvious.<sup>4-9</sup>

Analysis of the evolution of numerical simulation of climate from the viewpoint of how to take into account the climate-forming contribution of atmospheric aerosol demonstrates rather a contradictory pattern caused by quite conditional estimates of the global warming (increase in the mean annual global air temperature due to higher concentration of the greenhouse gases in the atmosphere). The initial estimates of the secular increase in the mean temperature gave very encouraging, at first sight, results: if we take into account not only "greenhouse" warming (due to the growing CO<sub>2</sub> concentration), which turns out overstated, but also cooling due to the purely scattering sulfate aerosol, then the calculated temperature trend reproduces observed temperature variations quite satisfactorily. From the very beginning it was clear that this result is no more than fudge. Shortly after that, the same specialists in numerical simulation of climate (Hansen and his co-workers from the Goddard Institute for Space Studies<sup>27,28</sup>) have arrived at a conclusion that the contributions from greenhouse warming and cooling from sulfate aerosols almost compensate for each other. Therefore, the increase of the methane concentration in the atmosphere should be of critical importance as a factor of global warming. It is beyond questions that this conclusion is premature as well.

The complexity of the processes of formation of the aerosol concentration field in the atmosphere, wide diversity of aerosol types, and space and time variability of aerosol concentration, microstructure, and properties dictate the need in complementing the existing numerical models of climate with an aerosol module capable of reproducing actual dynamics of the properties of various aerosols in the interactive mode. Only this approach, within the framework of integral models,<sup>23</sup> can provide for realistic consideration of the aerosol effect on climate.

Spiridonov and Ćuric<sup>60</sup> proposed a model of transport and chemical transformation of atmospheric sulfates, which can be used for interactive solution of the aerosol-climate problem. On the other hand, the need in checking the adequacy of models by comparing the model data with experimental findings requires justification of the optimal global observation system based on the combined use of spaceborne and ground-based remote sensing facilities, as well as direct (*in situ*) ground-based observations of aerosol properties and other atmospheric parameters. For solution of such problems, it is important to analyze, in the first turn, the adequacy of modern concepts of the atmospheric aerosol and its properties. This was partly made in the recent overview.<sup>8</sup> The aim of this paper is to supplement the results considered earlier with the up-to-date information.

## 1. Variety of sources, processes of formation, and types of atmospheric aerosol

Even regional investigations of atmospheric aerosol reveal its wide variety, which is clearly demonstrated, for example, by the results of Siberian Aerosol Program published in the topical issue of *Atmospheric and Oceanic Optics*<sup>10,11</sup> and many other developments.<sup>1-3</sup> The global aerosol is very diverse; it includes such types as sulfate aerosol (especially,

connected with dust storms in deserts and experiencing long-range transport in the atmosphere), organic (in particular, biogenic) aerosol featuring significant absorptance, volcanic aerosol, aerosol generated by biomass burning, etc.

### 1.1. Sulfate aerosol

The sulfate aerosol still attracts the principal attention, especially because in this case it seems possible to interactively take the aerosol into account as a climate-forming factor in numerical simulation of the global climate through consideration of the global biogeochemical sulfur cycle. In this context, Boucher and Pham<sup>15a</sup> discussed the evolution of the global sulfur cycle using the data on SO<sub>2</sub> emissions in 1990 and the earlier published data on the trends of emissions in different countries. The results obtained allowed estimation of the radiative forcing due to sulfate aerosol. This forcing increased gradually (due to the direct and indirect effect of aerosol) for the period of 1850–1990 from close-to-zero values (0 to  $-0.17 \text{ W/m}^2$ ) to  $-0.4$  to  $-1 \text{ W/m}^2$ . The forcing magnitude (defined as the ratio of the radiative forcing to the content of anthropogenic sulfate aerosol) remained nearly constant for this period in the case of the direct effect, being equal to  $-150 \text{ W/g}$  of sulfate, but significantly decreased for the indirect effect even under conditions of the enhanced sulfate content.

The evolution of the sulfate aerosol in the atmosphere and the corresponding trend of radiative forcing for some regions in the USA and Western Europe in the period from 1980 until 1998 were calculated in Ref. 15a using the model of global sulfur cycle developed at the Laboratory of Dynamic Meteorology (France). The results calculated were compared with the observations; they show a relatively constant forcing during the period under study. The need was emphasized quite justly in numerical simulation and observation for other types of atmospheric aerosol.

In their further investigations into the problem of sulfate aerosol, Hicks and his co-workers<sup>36</sup> have analyzed the information about the quality of near-surface air using the data of long-term observations at the NOAA atmospheric integrated research-monitoring network in combination with the data on chemical composition of precipitations obtained within the framework of the National Atmospheric Deposition Program. The main objective of that work based on the data of 7 stations situated to the east from the Mississippi River for the observation period since 1983–1986 until 1997 was justification of the quantitative indicators of chemical processes occurring in the lower atmospheric layers.

The analysis of the results obtained showed that the level of sulfur compounds in the atmosphere peaked in the late 1980s, and after that it decreased gradually at a rate about 2.8% a year, but during some periods of the 1990s it increased at a rate of 5%

a year. The observations revealed no stepwise change, which could be assigned to beginning of emissions market measures, and the related decrease of SO<sub>2</sub> emissions in 1995. According to the observations, this favored only continuation of the long-term trend of air quality improvement started before. The results of observations at some sites indicate that positive effects of the total decrease of emissions not necessarily manifest themselves at all sites, since in some cases local conditions may dominate. However, in general, the data on the air quality well correlate with the data on sulfur emissions obtained by the Environmental Protection Agency (USA). The relative decrease of the sulfur concentration in the planetary boundary layer to the east from the Mississippi River fully corresponds to the relative decrease of emissions from electric power plants. Regional air quality is largely determined by emissions from large sources, rather than by the joint effect of small sources.

Of fundamental importance for understanding the role of aerosol as a component of the troposphere is the information about the phase state of aerosol. The estimates of the NO<sub>x</sub> content in the upper troposphere showed, for example, that from 20 to 60% of the NO<sub>x</sub> loss rate is caused by heterogeneous hydrolysis of N<sub>2</sub>O<sub>5</sub>, and the efficiency of this process depends on the phase state of aerosol. Liquid aerosol gives rise to a more intense hydrolysis than solid aerosol.

The initial phase of the tropospheric aerosol significantly affects the development of the nucleation mechanism of ice particles, which determines the properties of cirrus clouds. Initially, it was assumed that the dominant component of the tropospheric sulfate aerosol is H<sub>2</sub>SO<sub>4</sub>, but observations revealed also a considerable amount of ammonium ions. Thus, it can be concluded that ammonium sulfate and bisulfate, as well as letovicite may be important components of the aerosol. In this connection, Fortin and his co-authors<sup>24</sup> have performed laboratory studies of the phase state of ammonium sulfate (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> at low temperatures using data of Fourier transform spectroscopy.

If deliquescence of water vapor by aerosol from ammonium sulfate at the temperature above the ice eutectic point and anhydride ammonium sulfate at 254 K is studied quite thoroughly, then the phase properties at lower temperatures are investigated much more poorly. Therefore, the experiments discussed were conducted at the temperature from 166 to 235 K. The results obtained at low relative humidity (*RH*) confirm the presence of the ferroelectric phase of ammonium sulfate at temperatures below  $216 \pm 8 \text{ K}$ . The dependence on *RH* indicates that at temperatures below the eutectic point the phase transformation occurs: crystal (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> transforms into the metastable aqueous solution (similar process was called deliquescence). At a temperature above 203 K, deliquescence took place at  $RH = (88 \pm 8)\%$ , which is in a close

agreement with the results of extrapolation of measurements at temperatures above the eutectic point, as well as with the theoretical conclusions.

In the experiments conducted at temperatures from 166 to 203 K, deliquescence was sometimes observed, and in other cases the ice was formed directly from the gas phase, which is possibly indicative of selective heterogeneous nucleation. Formation of ice particles prevents the increase of relative humidity up to the level needed for deliquescence, which explains the variability of the experimental results obtained at low temperatures. Possible consequences of this for the formation of cirrus clouds are discussed in Ref. 24.

The issue of the sulfate aerosol was mostly discussed in the context of its role as a factor of climate cooling. As was noted earlier, it is important to determine radiative forcing taking into account both direct and indirect effects of aerosol on climate. In the latter case, the effect comes about through the change of microphysical and optical properties of clouds due to aerosol particles as the condensation nuclei. This issue incorporates various aspects, one of which is connected with the fact that chemical activity and efficiency of aerosol particles as cloud condensation nuclei depends on their phase state. If the deliquescence (uptake of water at formation of solutions) and efflorescence (loss of water at formation of crystals) in the case of pure ammonium sulfate are known rather well, then for organic components, whose fraction in the aerosol composition may be 50% as high and even higher, is quite different. Organic components, like dicarboxylic acids, are often water-soluble.

The transition of pure ammonium sulfate (AS) from the solid to the liquid state occurs at room temperature and the deliquescence relative humidity (*DRH*) of 80%, and *DRH* in the presence of SA mixture with other electrolyte is always lower than *DRH* for pure AS. This lower *DRH* was called the eutonic *DRH*. Brooks with co-workers<sup>17</sup> discussed the results of laboratory measurements of eutonic *DRH* for the mixture of dicarboxylic acids (from C-2 to C-6) and ammonium sulfate at temperatures from +24 and down to -10°C. These experiments confirmed the earlier conclusion about the decrease of *DRH* for a mixture as compared with the pure ammonium sulfate and revealed the dependence of *DRH* on temperature. Thus, in such a case, aerosol particles can become liquid at lower values of relative humidity.

Volcanic eruptions are another significant source of many minor gaseous constituents (MGCs) of the atmosphere and aerosol,<sup>39</sup> and the mechanisms of formation of aerosol as a secondary product of gas-phase and other reactions are quite various. Sansone and co-workers have carried out observations along the shoreline of the Kilauea volcano (Hawaii)<sup>59</sup> and detected trace elements produced by lava-seawater interactions in the volcanic aerosol plume. Analysis of concentrations measured in the plume normalized

to the Hawaiian basalt composition showed their linear log-log covariation with the emanation coefficient (as an indicator of element volatility).

Normalized aerosol concentrations also consistently varied with the corresponding normalized concentrations in dilute fumarolic gas from Kilauea volcano and fumarolic gas condensates from Kudryavyi and Merapi volcanoes, despite different mechanisms of element volatilization. Conservatively estimated regional ocean deposition rates of Cu, Cd, Ni, Pb, Mn, Zn, Fe, and P were more than 50 times the background rates. Thus, volcanoes may be an important source of both toxic and nutrient elements to the surrounding ocean. However, it is unlikely that this volcanism can exert a significant impact on the global ecosystem, even during massive lava outflow.

Sea salt emissions from the ocean surface to the atmosphere contribute significantly to formation of the global aerosol. According to the up-to-date estimates, these global emissions exceed all other natural and anthropogenic emissions altogether, being as high as 3.300 Tg/yr in 2000, which determines the significant role of the sea salt aerosol as an optically active component of the atmosphere that affects climate formation. Approximate calculations suggested that by 2100 the global sea salt emissions may achieve 5.880 Tg/yr and their contribution to radiative forcing may be -0.8 W/m<sup>2</sup>. One of the still unclear aspects of the studies of the sea salt aerosol is the formation of organic films (consisting likely of biogenic fat acids) on the particle surface. The presence of these films can alter chemical, physical, and optical properties of the sea salt aerosol.

Tervahattu and co-workers<sup>64</sup> have conducted mass-spectrometric (by the TOF-SIMS technique) studies of marine aerosol particles, whose results indicate that the dominating component of the organic coatings is the palmitine acid, while other fat acids play only insignificant role. Analysis of TOF-SIMS images obtained under the laboratory conditions showed that surface coating by the palmitine acid is typical for small particles similar to sea salt particles. Thus, the results discussed confirm the presence of biogenic fat acids as an important ingredient of the surface organic coating on marine sea salt aerosol particles. This aerosol significantly affects the chemical composition of the near-surface atmospheric layer.

Gaseous HCl existing in the marine air plays an important role in the chemical reactions occurring in the marine atmospheric boundary layer (MABL), as follows from direct measurements of the concentration of such elements as molecular chlorine and hypochlorous acid (Cl<sub>2</sub>, HOCl) in MABL. Such components are photolabile, and in the presence of insolation they produce free chlorine (Cl), which quickly reacts with any available volatile organic compound (VOC). Marine aerosol may also be the source of chemically active chlorine.

As was shown in laboratory studies, the data on uptake of gaseous hypoiodine acid (HOI) on the surface of NaCl and NaBr particles and sea salts can be used for estimation of the anticipated chlorine release from marine aerosol particles produced in MABL due to reactions with iodine compounds.

McFiggans and co-workers<sup>47</sup> have justified the theoretical model of the corresponding processes with regard for the reactions involving chemically active chlorine and two activation mechanisms. To analyze the significance of the mechanisms of reactions regulated by chlorine and nitrogen, the results of field measurements of the IO and NO<sub>3</sub> radicals were used as restrictors of the results of numerical simulation.

The calculations showed that the HOI and N<sub>2</sub>O<sub>5</sub> uptake in the MABL may result in a significant release of Cl atoms from marine salt aerosol particles. Proofs of functioning of this iodine-controlled mechanism are "bursts" of chlorine formation at the Cl atom concentration about several thousands per cubic centimeter that occurred after sunrise. Numerical simulation predicts a stable Cl production in daytime at the concentration from hundreds to thousands per cubic centimeter over vast ocean territories. Under certain conditions, chemical reactions with the participation of bromine emitted from fresh sea salts may play a dominating role in the formation of free chlorine.

In aerosol particles consisting largely of concentrated (in aqueous solution) mixtures of H<sub>2</sub>SO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, and NH<sub>4</sub>HSO<sub>4</sub>, homogeneous nucleation of ice may occur, if liquid particles include no insoluble substance, or heterogeneous nucleation may occur on the surface of insoluble nuclei inside aerosol particles or in crystal salt nuclei. Using the technique of optical microscopy, Zuberi and co-workers<sup>66</sup> have performed a laboratory investigation of heterogeneous nucleation of ice on liquid (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O particles with mineral dust immersions of two types: kaolin and montmorillonite, who have close ice nucleation efficiency. The measurement results show that the freezing point differs by 8–20 K from that under conditions of homogeneous nucleation, and the difference increases in the case of particles with the weight concentration of intrusions higher than 27%. At the temperatures ranging from 198 to 239 K heterogeneous nucleation occurs in (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> particles with mineral dust intrusions only at the supersaturation level (with respect to ice) from 1.35 to 1.51. The results from Ref. 66 suggest that mineral dust particles serve efficient nuclei for ice nucleation in (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O aerosol and thus favor the formation of ice clouds in the upper troposphere at a higher temperature and lower supersaturation level than under conditions of homogeneous nucleation.

Volcanic eruptions are powerful sources of sulfate aerosol. Thus, for example, the explosive eruption of Mt. Pinatubo (Philippines, 15.1°N, 120.4°E), the most powerful eruption of the 20th

century, that occurred on June 14–16 of 1991 emitted 14–26 Mt of SO<sub>2</sub> into the stratosphere (up to 30 km). At the time constant of about 35 days, SO<sub>2</sub> quickly transformed into the sulfuric acid aerosol H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O with the mass as high as about 30 Mt. The main part of the volcanic cloud rapidly moved to the west, and in three weeks after the eruption it encircled the globe. For about two weeks a significant part of the cloud crossed the equator and reached ~10°S.

For the first two months, the main part of the cloud was concentrated in the latitude belt between 20°S and 30°N, and thus it formed the tropical reservoir of aerosol matter that was under the strong effect of quasi-biannual oscillation (QBO). This reservoir is stable or unstable depending on the QBO phase (east or west) (the eruption occurred during the east QBO phase, and therefore the tropical maximum of the eruptive aerosol layer was stable; only in three to four months the aerosol began to spread to mid-latitudes of the Southern Hemisphere). At the altitudes lower than 20 km, the aerosol moved relatively rapidly into the middle and high latitudes of the Northern Hemisphere. Stratospheric aerosol entered the troposphere through breaks in the tropopause and due to gravitational sedimentation. The global mass of the sulfate volcanic aerosol reached its maximum in October 1991 and then decreased by roughly *e* times for a year.

Liu and Penner<sup>43</sup> have performed numerical simulation of eruptive aerosol transformation on the global scale using the LLNL/IMPACT model developed at the Livermore National Laboratory (USA). This model takes into account both chemical processes and aerosol transport with regard for the actual weather conditions with the use of a 46-level global atmospheric circulation model (spatial resolution of 2° latitude × 2.5° longitude) developed in the Goddard Space Flight Center, NASA (USA).

Analysis of the results of numerical simulation showed that they reliably reconstruct formation of the tropical reservoir of aerosol in the 20°S–30°N latitude belt in a few months after the eruption and agree with the aerosol spread characteristics obtained from the SAGE-II satellite data. The data on the global distribution of the eruptive sulfate aerosol were used to calculate the rate of homogeneous nucleation of ice particles from H<sub>2</sub>O/H<sub>2</sub>O [number of frozen aerosol particles/(cm<sup>3</sup>·s)] in the lower stratosphere and upper troposphere. The results obtained were compared with similar data on the near-surface emissions of natural and anthropogenic sulfate aerosol.

The high values of the nucleation rate are characteristic (in the case of volcanic aerosol) of the layer near the equatorial tropopause (at the bottom of the main volcanic aerosol layer) for the first year after eruption. In the case of the eruptive aerosol, the nucleation rate is much higher than that for the sulfate aerosol from ground-based sources, but in the second year after the eruption the nucleation rates

become comparable. From the results discussed it follows that the volcanic aerosol can significantly affect (through homogeneous nucleation) the conditions of formation of cirrus clouds and their global evolution. However, to obtain reliable estimates, it is necessary to perform numerical simulation with regard for microphysics and dynamics of cirrus clouds.

## 1.2. Dust aerosol

As was already mentioned, mineral particles coming into the atmosphere over deserts in the saltation process form the most significant component of the dust aerosol.<sup>4</sup> The saltation process (at its initial stage), which is believed responsible for the income of mineral dust aerosol into the atmosphere, is connected with sandblasting producing aerosol particles. The intensity of this process is largely determined by the surface wind shear, and earlier this process was believed oscillating. Grini and co-workers<sup>32</sup> proposed a new theoretical model of saltation, which demonstrated that actual aerosol emissions are characterized by a monotonic dependence on the wind shear. Although oscillations of aerosol emissions are still observed, they are connected with the specific microstructure of soil particles.

An important feature of the dust aerosol is its very long-range transport. It is for this reason that the dust aerosol turns out a significant component of the tropospheric aerosol over oceans during the events of dust storms in deserts.

Based on the combined use of the factor analysis model called Positive Matrix Factorization (PMF) and cluster analysis of back trajectories of the long-range aerosol transport in the days of intense or weak transport, the group headed by Lee<sup>41</sup> have identified the types of aerosol observed at Brigantine National Wildlife Refuge, NJ, USA, which is a good location to study Mid-Atlantic regional aerosol.

Sulfate (expressed as ammonium sulfate) was the most abundant species, accounting for 49% of annual mean fine aerosol mass ( $PM_{2.5}$ ). Organic compounds (22%; expressed as 1.4 x organic carbon) and ammonium nitrate (10%) were the next abundant species. Herein some evidence has been suggested that the secondary organic aerosol formation makes an important contribution to the summertime aerosol on regional scale.

The results obtained in Ref. 41 show that nine factors contributed to the  $PM_{2.5}$  mass concentrations: coal combustion factors (66%, summer and winter), sea salt factors (9%, fresh and aged), motor vehicle/mixed combustion (8%), diesel/Zn-Pb (6%), incinerator/industrial (5%), oil combustion (4%), and soil (2%). The aged sea salt concentrations were the highest in springtime, when the land breeze-sea breeze cycle is most strong. Comparison of backward air trajectories of high- and low-concentration days suggested that Brigantine is surrounded by sources of

oil combustion, motor vehicle/mixed combustion, and waste incinerator/industrial emissions that together amount to 17% of  $PM_{2.5}$  mass. In addition to  $SO_2^{2-}$  (43–49%), the contribution of organic carbon was 22–33%, and that of  $NO_3^-$  was 10%.

Deserts of northwestern China cover the territory of  $1.3 \cdot 10^6$  km<sup>2</sup>, which is the threefold area of the loess plateau ( $0.4 \cdot 10^6$  km<sup>2</sup>) and lies at high latitudes in the zone of west-to-east transport. This desert region is characterized by dry climate and favorable conditions for the formation of the soil (dust) aerosol (SA) especially at a rather high occurrence of the dust storms. The studies carried out during recent decades identified this region as the main source of SA to the North Pacific in spring and early summer. It was just in the period of 1995–1996 when Liu and co-workers<sup>45</sup> collected about 180–190 aerosol samples from three observatories at Northwest China desert region (Minqin), coastal suburb area (Qingdao), and an island in the Yellow Sea (Qianliyan).

Analysis of the samples for the concentrations of trace metals (Al, Fe, Mn, Na, Cr, Zn, Cu, Co, Ni, Pb, V, Sr, and Cd) has revealed a wide spatial and temporal variability and the pronounced annual trend (Qingdao and Qianliyan) of the trace metal levels with the concentrations generally 2 to 3 times higher in spring than in summer. However, daily variations of trace metal concentrations at Minqin are more significant than those in Qingdao and Qianliyan. Enrichment factors for the crustal source  $EF_{crust}$  at Minqin are relatively low compared with those at Qingdao and Qianliyan.

Some of the trace species like Pb, Zn, and Cd have relatively high contributions from the anthropogenic source ( $R_p$ ), and > 98% are found at Qingdao and Qianliyan, with  $EF_{crust}$  values 1 to 2 orders of magnitude higher than those at Minqin. Manganese is mainly from low-temperature weathering products and the contribution from the crustal source ( $R_c$ ) is > 70% at Qingdao and Qianliyan. The coastal atmosphere responds to the episodic dust storms in the desert region (Minqin) by an increase in the level of aerosol content and in higher concentration of the crust-dominated materials. The percentage contributions from the crustal source ( $R_c$ ) of trace metals, such as Pb, Cd, and Zn, could be increased considerably by 5 to 10 times during the passage of cold fronts than during calm weather periods over the Yellow Sea.

Zhang and co-workers<sup>65a</sup> have collected aerosol samples from Zhenbeitai (38°17' N, 109°42' E) in order to determine the aerosol mass concentration during nine dust storm events in spring of 2001, lasting a combined total of twenty six days. Peak mass loadings greatly exceeded the average ( $260 \mu\text{g}/\text{m}^3$ ), and ~82% mass of the total aerosol particles was ascribed to Asian dust, of which Al, Ca, Fe, K, Mn, Si, and Ti amounted to 7%, 6%, 4%, 2%, 0.1%, 32%, and 1% by weight, respectively. The estimated dry deposition of Asian dust for the spring

of 2001 was  $189 \text{ g/m}^2$ , of which 85% was due to dust storms. Factor analysis indicated that ~89% of the dust load during this period was due to remote or regional transport, and only ~11% was due to local or background dust.

Having carried out the scanning electron microscopy of aerosol samples collected in the Negev desert in Israel during a summer and winter campaign in 1996–1997, Sobanska and co-workers<sup>62a</sup> found (through hierarchical cluster analysis) the presence of 11 classes (groups) of particles. If the summer samples were enriched in sulfates and mineral dusts, then the winter samples contained more sea salts, aged sea salts, and industrial particles. The fine aerosol fraction, with diameters below  $1 \mu\text{m}$ , was enriched in secondary particles, which (in the case of sulfate particles) were mainly attributed to long-range transport.

Colarco and co-workers<sup>21</sup> have developed a three-dimensional numerical model for simulating Saharan dust emissions and transport over the tropical North Atlantic Ocean. The computed dust fields were constrained by data from ACE-2. The imaginary part of the complex refractive index of the aerosol substance ( $k$ ) was retrieved from the data of the Total Ozone Mapping Spectrometer on the Earth Probe satellite (EP-TOMS) using the observed ratio between the aerosol index (AI) and the aerosol optical depth (AOD).

In Ref. 21, this problem has been solved for three sites: Dakar, Sal, and Tenerife. At Sal and Tenerife the dust imaginary refractive index  $k = 0.0048$  (0.0024–0.0060) at 331 nm and  $k = 0.004$  (0.002–0.005) at 360 nm. At Dakar the dust imaginary refractive index  $k$  was approximately 0.006 (0.024–0.0207) and 0.005 (0.0020–0.0175) at 331 and 360 nm, respectively. These values are considerably lower than the refractive index currently used in TOMS retrievals of dust optical depth and single scattering albedo. With regard for the retrieved refractive index values, the single scattering albedo (SSA) was determined by integrating over the particle size distribution. The SSA values at 331 nm at Dakar, Sal, and Tenerife turned out to be 0.81 (0.65–0.90), 0.84 (0.82–0.91), and 0.86 (0.83–0.89), respectively.

The presence of dust aerosol in the atmosphere significantly affects various processes occurring in the atmosphere and even in the ocean. An example of the effect on the ocean is variation of the marine phytoplankton concentration due to the dust aerosol.

The biomass of marine phytoplankton is characterized by a very intense variability: it is replaced, on the average, every 1 or 2 weeks. Carbon compounds produced in the process of photosynthesis, including particulate organic carbon (POC) and particulate inorganic carbon (PIC), as well as dissolved organic carbon are exported below 100 m (on the global scale) at the rate of  $10 \text{ Pg C/yr}$ . This process called the biological pump plays an important role in the formation of the global carbon cycle.

The biological pump is still poorly studied, and this causes the need in obtaining a comprehensive information about the phytoplankton dynamics. For this purpose two autonomous robotic profiling floats were deployed in the subarctic North Pacific (near  $50^\circ\text{N}$ ,  $145^\circ\text{E}$ ) on 10 April 2001 that provided direct records of carbon biomass variability from surface to 1000 meters below the surface at daily and diurnal time scales. Analysis carried out by Bishop with co-workers<sup>14</sup> of the measurement data acquired during the first eight months allowed studying the effect of such phenomena as hydrographic changes, multiple storms, and the April 2001 dust event on the phytoplankton dynamics. High-frequency observations of the upper ocean particulate organic carbon variability showed nearly doubling of the biomass in the mixed layer over a 2-week period after the passage of a dust cloud from Gobi desert. The evolution of particulate organic carbon enhancement and an increase in the chlorophyll use efficiency after the dust storm suggest a biotic response to natural iron fertilization by the dust.

### 1.3. Carbonaceous aerosol

The public concern with the anthropogenic changes in the gas and aerosol composition of the atmosphere and their climate impact is caused, in particular, by the atmospheric emissions of carbonaceous aerosol (CA) due to fossil fuel burning. This aerosol consists of two fractions: organic carbon (OC) and chemically inactive black carbon (BC) with quite different optical properties. Organic carbon is characterized by the prevalence of scattering in the visible spectrum, while BC has strong absorption in the short-wave range of sunlight, and it is the only one absorbing aerosol occurring everywhere. Depending on the type of fuel and burning processes, the BC/OC ratio can vary widely, and such an important characteristic as radiative forcing strongly depends on this ratio.

Using the Geophysical Fluid Dynamics Laboratory SKYHI general circulation model (GCM) (latitude-longitude resolution of  $\sim 3^\circ \times 3.6^\circ$ ), Cooke and co-workers<sup>22</sup> have conducted numerical simulation of the global atmospheric distribution of carbonaceous aerosols in order to investigate the seasonal and interannual variability of the concentrations at specific locations and to investigate the sensitivity of the distributions to various physical parameters. Comparisons were made with several sets of observational data obtained at four specific sites (Mace Head, Mauna Loa, Sable Island, and Bondville).

The measurements of monthly mean surface concentrations of black carbon made over several years revealed that the model simulation records the successes as well as the failures. Comparisons were also made with averages of measurement data made over different time periods, segregated by geography and rural/remote locations. Generally, the measured mean

surface concentrations in remote regions exceeded those obtained by simulation. Notwithstanding the large variability in measurements and model simulations, the simulations of both black and organic carbon tend to be within about a factor of 2 in the majority of sites. There are major challenges in conducting comparisons with measurements due to inadequate sampling at some sites, the generally short length of an observational record, and different methods used for estimating the black and organic carbon amounts. The interannual variability in the model and in a few such measurements available pointed to the necessity of comparing with long-term measurements. Notwithstanding there were very few altitude profile measurements with large uncertainties, the comparisons suggested an overestimation by the model in the free troposphere.

The global column burden of the black and organic carbon in the present standard model integration were lower than in previous studies and thus could be regarded as approximately a lower value bracketing the simulated anthropogenic burden due to these classes of aerosols, based on the modern understanding of the carbonaceous aerosol cycle. Of the physical factors examined, the intensity and frequency of precipitation events are critical in governing the column burden values. The wet deposition, transformation from hydrophobic to hydrophilic state, and the partitioning of the emitted aerosol between the hydrophobic and hydrophilic varieties also play a significant role. The column burden over remote regions appeared to be most sensitive to changes in each of the parameter, thus confirming once more the importance of measurements in those locations for a proper evaluation of model simulation of these aerosols. So, the most important tasks for future investigations could be: 1) modernization of the observation system to obtain a more complete and representative data sets; 2) study of physical characteristics and transformation processes of aerosol, in particular, secondary OC; 3) more comprehensive observations of the intensity and frequency of the precipitation events; 4) adequate numerical simulation of the tropospheric meteorology, including the wind and precipitation fields.

Organic carbon makes up a significant part of atmospheric aerosol, and so it can play an important role as a climate-forming factor. The primary carbonaceous aerosol is emitted into the atmosphere mostly from internal combustion engines and due to biomass incineration, while the secondary carbonaceous aerosol is the product of gas-phase reactions with the participation of gaseous organic compounds of both anthropogenic and natural origin. In the latter case, such compounds are mainly isoprene and terpenes, the products of whose oxidation in the atmosphere (with the participation of ozone  $O_3$  and hydroxyl radical OH in daytime and nitrate radical  $NO_3$  at night) are among such functional groups as COOH, COH, C–O,  $CONO_2$ ,

and others. The specific feature of these oxidation products is that they have the saturating vapor pressure much lower than that of the initial compounds, which favors condensation and growth of aerosol particles.

An important feature of the organic aerosol is its hygroscopic properties: about 20–70% of organic substance of this aerosol is water-soluble and can absorb water until equilibrium with the atmospheric water vapor pressure. Pirjola and co-workers<sup>53</sup> have studied the condensation growth of atmospheric particles from insoluble organic vapors using a monodisperse aerosol dynamics model NONO32 including atmospheric chemistry mechanism. The source rate of the vapor and its saturation vapor density on a particle surface have been varied. The initial particle size distribution was assumed to be bimodal, and aerosol was initially an internal mixture of particles consisting of soluble sulphuric acid and insoluble organic material in a 1 : 1 ratio.

Model simulations predicted that if the ratio of the vapor source rate and the condensation sink of particles,  $Q/CS$ , exceeds  $10^8 \text{ cm}^{-3}$  and the vapor was nonvolatile or low volatile, the 10 nm nuclei grew with the growth rates of  $2.5$  to  $3 \text{ nm} \cdot \text{h}^{-1}$  and could act as cloud condensation nuclei at a supersaturation of 1.6% or lower after 24 h simulation. However, the higher the ratio of  $Q/CS$ , the higher the saturation vapor pressure could be. When the vapor was taken highly volatile, i.e., the saturation vapor density was high enough, the nucleation mode particles were not able to grow, but coagulated with larger particles without causing any significant impact on the climate.

#### 1.4. Urban aerosol

This type of aerosol occupies a particular place because of a high complexity of its formation processes under conditions of a polluted atmosphere. The urban and regional scale gas-phase chemical mechanisms in the atmosphere describe the formation of oxidants such as ozone ( $O_3$ ), the hydroxyl radical (OH), and the nitrate radical ( $NO_3$ ), the consumption of reactive organics, and reactions of the resulting organic peroxy radicals with the species such as the nitrogen oxides ( $NO_x = NO + NO_2$ ).

An important product of the reactions discussed is the secondary organic aerosol (SOA), which is formed in two steps. First, a sufficiently large parent organic is oxidized, resulting in products that have vapor pressures sufficient that these products can partition to the aerosol phase via condensation (adsorptive or absorptive) or homogeneous nucleation. Because the low-vapor pressure products are needed to form the SOA, in general, only those parent organics with that have six or more carbon atoms are capable of producing oxidized products that form the SOA.

The existing gas-phase atmospheric chemical mechanisms do not include the detailed organic chemistry necessary for prediction of the SOA formation. One reason for this is that mostly the chemistry of the larger organics that leads to semivolatile products is unknown. In this connection, Griffin and co-workers<sup>29</sup> proposed a new chemical mechanism, called the Caltech Atmospheric Chemistry Mechanism (CACM; developed at the California Institute of Technology), which has two goals: (1) to include state-of-the-art treatment of the ozone formation chemistry; and (2) to explicitly predict the concentrations of secondary and tertiary semivolatile oxidation products that have to act as constituents of the SOA.

The mechanism proposed in Ref. 29 contains a significant expansion of the organic product chemistry in order to predict the formation of multifunctional, low-pressure vapor products, which act as parents of organic aerosol in the atmosphere. The CACM model includes about 191 species: (1) 120 fully integrated species (fully integrated species have concentrations that are solved for numerically based on kinetics, emission, and deposition) (15 inorganic, 71 reactive organic, and 34 unreactive organic); (2) 67 pseudo-steady-state species (2 organic and 65 inorganic); and (3) 4 species that have fixed concentrations.

That study had two goals: (1) to describe the inorganic and organic chemistry in the mechanism and (2) to evaluate the performance of the mechanism in simulating the gas-phase chemistry during a well-studied episode in the South Coast Air Basin (SOCAB) of California, 27–29 August 1987. Total predicted concentrations of the gas-phase SOA compounds are compared with the levels of SOA that have been inferred on the basis of ambient organic aerosol measurements during this period. Thus predicted concentrations indicate that the total gas-phase potential of SOA-forming compounds can account for the observed aerosol concentrations. The main sources of uncertainties in the results of numerical simulation lie in the incompleteness of data on the emissions of numerous gaseous constituents and such their properties as reaction rates and product dynamics. Uncertainties in the chemical mechanism determining the direct conversion of aldehydes to acid groups in certain reactive products are important as well.

Pun and co-workers<sup>54</sup> have developed a model that predicts secondary organic aerosol (SOA) formation based on the thermodynamic equilibrium partitioning of secondary organic oxidation products. Hydrophobic secondary products were assumed to partition to an absorbing organic aerosol consisting of primary organic aerosol (POA) and other secondary hydrophobic organics according to an equilibrium partitioning coefficient calculated iteratively for each the secondary compound present. The hydrophobic module was evaluated by studying the partitioning of octadecanoic acid to surrogate the POA species.

As expected, the amount of octadecanoic acid predicted to be present in the aerosol phase increases as the total amount of absorbing material increases or as the total amount of acid present increases. The hydrophilic secondary compounds partition to an aqueous phase via Henry's law; the fraction of each compound's mass that partitions is determined by its Henry's law constant and its acid dissociation constant(s). The available liquid water content (LWC) of the aerosol is determined iteratively between an inorganic aerosol module and the hydrophilic module, which is evaluated by studying the partitioning of glyoxalic and malic acids. While glyoxalic acid tends to remain in the gas phase, the malic acid partitions strongly to the aqueous phase, with ions being the dominant form in the aqueous phase.

As expected, an increase in the relative humidity increases the amount of water associated with the organics ( $\Delta$ LWC), and a lower aerosol pH favors molecular solutes over ionized forms. Increasing the pH results in higher effective Henry's law constants for the acids, yielding higher organic aerosol concentrations. The results also indicate that increasing  $\Delta$ LWC induces additional partitioning of inorganics to the aqueous phase.

Using the California Institute of Technology (CIT) three-dimensional urban/regional atmospheric model allowing comprehensive gas- and aerosol-phase simulations, Griffin with co-workers<sup>30</sup> considered the 8 September 1993 smog episode in the South Coast Air Basin of California (SoCAB). That work focused primarily on simulations of secondary organic aerosol (SOA) and determination of the species and processes that lead to this SOA. The predictions indicated that SOA formation in the SOCAB was dominated by partitioning of hydrophobic secondary products of the oxidation of anthropogenic organics. The biogenic contribution to the total SOA increased in the eastern parts of the rural areas of the region, as did the fraction of hydrophilic SOA, the latter reflecting the increasing degree of oxidation of SOA species with the increasing atmospheric residence time. For future works, it was planned to carry out the detailed comparison of numerical simulations with observations.

In the framework of the Trans-Siberian Observations into the Chemistry of the Atmosphere (TROICA) project in June–July 1999, Oberlander with co-workers<sup>52</sup> have carried out measurements of  $O_3$ , NO,  $NO_2$ , CO,  $CO_2$ ,  $CH_4$ ,  $^{222}Rn$ ,  $J(NO_2)$  ( $NO_2$  photodissociation rate), and black carbonaceous aerosol on the Trans-Siberian railroad more than 16 000 km long, from Kirov (~58°N, 49°E; 972 km east of Moscow) to Khabarovsk (~48°N, 135°E) and back to Moscow. The diurnal variations of these gases and of  $CH_4$  due to micrometeorological conditions, as well as their dependence on various soil sources and vegetation types, were used to estimate ecosystem fluxes of  $CO_2$  and  $CH_4$ .

The highest outflow of CH<sub>4</sub> from soil was  $70 \pm 35 \mu\text{mol}/(\text{m}^2 \cdot \text{h})$  for the wet habitats of the West Siberia, and the lowest CH<sub>4</sub> flux was  $3.2 \pm 1.6 \mu\text{mol}/(\text{m}^2 \cdot \text{h})$  for drier habitats of the eastern Siberia. Although the wet tundra emissions found between 67° and 77°N are higher than in comparable environments at much lower latitudes, the boreal wetlands in Siberia at 50°–60°N represent a very important player in the global methane budget. The CO<sub>2</sub> density fluxes exhibited the opposite to CH<sub>4</sub> fluxes tendency. The ozone mixing ratios varied from a few nmol/mol during nighttime inversions to more than 60 nmol/mol during daytime. These values were generally higher than those during the 1996 summer campaign (TROICA 2). The CH<sub>4</sub> and CO levels followed the pattern observed during TROICA 2; elevated levels of CH<sub>4</sub> with the mean mixing ratio of  $1.97 \pm 0.009 \mu\text{mol}/\text{mol}$  were found over the West Siberian lowlands, decreasing to  $1.88 \pm 0.13 \mu\text{mol}/\text{mol}$  toward East Siberia. In contrast, while the background CO level of the West Siberian wetlands was generally below 140 nmol/mol, high CO concentrations, once even exceeding 2  $\mu\text{mol}/\text{mol}$ , were recorded east of Chita (~52°N, 113°E), as a consequence of forest and other vegetation fires, which significantly affect the chemical composition of the air over some parts of Russia.

### 1.5. Biogenic aerosol

As was already mentioned, recent numerical simulations have indicated a insignificant direct and indirect effect of the non-sea-salt sulfate aerosol (nssSO<sub>4</sub><sup>2-</sup>) on climate because of its specific microstructure leading to an intense scattering of short-wave sunlight. On the other hand, sulfate aerosol (SA) particles, acting as the cloud condensation nuclei, change the cloud microstructure and optical properties (albedo, on the first place). The estimates made have shown that the joint direct and indirect effect of sulfate aerosol could reduce the net radiation by 1 to 2 W/m<sup>2</sup> and more, which is comparable with the greenhouse effect, that is, SA contributes significantly to compensation of greenhouse climate warming.

The formation of nssSO<sub>4</sub><sup>2-</sup> aerosol over ocean is determined by the contributions from two sources: 1) biogenic sources of gaseous sulfur compounds (mostly dimethyl sulfide DMS); 2) anthropogenic sources (mostly SO<sub>2</sub>). Both of these sources are characterized by a wide spatiotemporal variability.

The biogenic contribution is usually estimated by the concentration of methanesulfonate (MSA), which is one of the stable products of DMS oxidation by hydroxyl radical OH. The process of this oxidation remains, however, poorly studied, what complicates estimating the SO<sub>4</sub><sup>2-</sup>/MSA concentration ratio. In order to obtain data about the biogenic and anthropogenic SA sources, as a part of the

Atmosphere/Ocean Chemistry Experiment (AEROCE) Savoie and co-workers<sup>59a</sup> have collected daily aerosol samples in marine boundary layer at Barbados, West Indies (13.17°N, 59.43°W), Bermuda (32.27°N, 64.87°W), and Mace Head, Ireland (53.32°N, 9.85°W), and in the free troposphere over Izaca, Tenerife, Canary Islands (28.30°N, 16.48°W; 2360 m asl).

Multiple variable regression analyses with methanesulfonate (MSA) and Sb and/or NO<sub>3</sub> as independent variables were performed to assess the relative contributions of the marine biogenic and anthropogenic sources to the total non-sea-salt (nss) SO<sub>4</sub><sup>2-</sup> concentrations at the AEROCE sites. On the basis of 2-year set of data at Bermuda and Barbados, the marine nssSO<sub>4</sub><sup>2-</sup>/MSA mass ratios ( $19.6 \pm 2.1$  and  $18.8 \pm 2.2$ ) were consistent throughout the year and comparable with those at American Samoa in the tropical South Pacific ( $18.1 \pm 0.9$ ). At Mace Head (based on 1-year data array), this ratio was about ( $3.01 \pm 0.53$ ). Analysis of residuals and an assessment of the root mean square deviations indicated that the ratio at Mace Head could also be reasonably applied throughout the year. However, there was quite high uncertainty during the winter so that it was impossible to rule out a significant increase. The results of 4-year observations indicate that the marine contribution is too low to permit a reasonable assessment of the biogenic nssSO<sub>4</sub><sup>2-</sup>/MSA ratio at Izaca. The continental nssSO<sub>4</sub><sup>2-</sup>/Sb mass ratio varies significantly from one location to another. At Bermuda, where North American sources are expected to dominate, the ratio is about 29,000, about a factor of 2 higher than the average of 13,500 at Mace Head where European sources dominate. Intermediate values occurred at Barbados (18,000) and Izaca (24,000) where both European and North African sources are significant. Estimates based on these ratios indicate that, on an annual basis, the contributions from anthropogenic sources account for about 50% of the total nssSO<sub>4</sub><sup>2-</sup> in aerosols over Barbados, 70% over Bermuda, 85–90% over Mace Head, and about 90% at Izaca. If the same biogenic nssSO<sub>4</sub><sup>2-</sup>/MSA ratios are applicable to rainwater, then the relative contributions in precipitation in Barbados and Bermuda are comparable with those in aerosols.

Organic substances are permanent components of the atmospheric aerosol, which comes to the atmosphere from the surface, being produced during combustion, or is produced in the atmosphere as a result of the gas-phase reactions of oxidation of volatile organic compounds (VOC). Formation of the organic aerosol (OA) in gas-phase reactions occurs because the vapor pressure decreases and/or solubility increases as compared with those of parent compounds.

Significant contribution of the secondary organic aerosol to the OA concentration stimulated development of techniques for assessing the

partitioning of organic compounds between the aerosol and gas phases. In this connection, surrogate organic oxidation products have been separated into two groups, hydrophobic and hydrophilic, depending on whether the product is more likely to dissolve into an organic or an aqueous phase. The surrogates are then allowed to partition only via the dominant mechanism, governed by molecular properties of the surrogate molecules. The distinction between hydrophobic and hydrophilic is based on structure and physical characteristics of the compound. In general, the secondary oxidation products, because of low vapor pressures and high polarities, express affinity for both the organic and aqueous aerosol phases.

Griffin and co-workers<sup>29</sup> have developed a fully consistent hydrophobic-hydrophilic organic gas-particle partitioning model, which concurrently achieves mass conservation, equilibrium between the gas phase and the organic aerosol phase, equilibrium between the gas phase and the aqueous aerosol phase, and equilibrium between the molecular and ion forms of the partitioning species in the aqueous phase. Simulations have been performed using both a zero-dimensional model and the California Institute of Technology three-dimensional atmospheric chemical transport model. Simultaneous partitioning of species by both mechanisms typically leads to a shift in the distribution of products to the organic aerosol phase and an increase in the total amount of SOA predicted as compared to previous work in which partitioning was assumed to occur independently of the organic and aqueous phases.

## 2. Combined investigations of aerosol

Certainly, the combined investigations of a real system of different types of aerosols are of greatest interest. Such investigations are now numerous and various.

Quinn and co-workers<sup>55</sup> have discussed a unique 3-year record of simultaneously measured aerosol chemical and optical (absorption and scattering) properties at Barrow, Alaska. All the results were reported to be obtained at the relative humidity  $\leq 40\%$ ; they allowed detailed analysis of the annual cycles of the concentration of aerosol mass, sea salt, non-sea-salt (nss) sulfate, methanesulfonate or  $\text{MSA}^-$ ,  $\text{NH}_4^+$  and  $\text{nssK}^+$ ,  $\text{Mg}^{+2}$  and  $\text{Ca}^{+2}$  for the submicron and supermicron size ranges.

Submicron  $\text{nssSO}_4^{2-}$ ,  $\text{NH}_4^+$ ,  $\text{nssK}^+$ ,  $\text{Mg}^{+2}$ , and  $\text{Ca}^{+2}$  peak in winter and early spring corresponding to the arrival and persistence of Arctic Haze. Submicron sea salt displays similar annual cycle presumably due to long-range transport from the northern part of the Pacific Ocean. Supermicron sea salt peaks in summer corresponding to a decrease in the sea ice extent. Submicron and supermicron  $\text{MSA}^-$  peak in summer due to a seasonal increase in the flux of dimethylsulfide from the ocean to the atmosphere.

Analysis of concentrations of the aerosol mass and chemical species showed that for the submicron size range the ion mass and associated water make up from 80 to 90% of the aerosol mass from November to May. In this ion mass, the sea salt and  $\text{nssSO}_4^{2-}$  are the dominant species. The residual mass fraction is equivalent to the ion mass fraction in June through October. For the supermicron size range the ion mass and the associated water make up from 60 to 80% of the aerosol mass throughout the year with the sea salt being the dominant species.

Also reported for the submicron size range were the annual cycles of aerosol light scattering and absorption at 550 nm, Angström exponent for the 450 and 700 nm wavelength pair, and single scattering albedo at 550 nm. On the basis of linear regressions between the concentrations of sea salt and  $\text{nssSO}_4^{2-}$  and the light scattering coefficient, the sea salt has a dominant role in controlling light scattering during winter,  $\text{nssSO}_4^{2-}$  is dominant in spring, and both components contribute to scattering in summer. Submicron mass scattering efficiencies of the dominant aerosol chemical components ( $\text{nssSO}_4^{2-}$ , sea salt, and residual mass) were calculated from a multiple linear regression of the measured light scattering versus the component concentrations. Submicron  $\text{nssSO}_4^{2-}$  mass scattering efficiencies were relatively constant throughout the year with the seasonal means ranging from  $4.1 \pm 2.9$  to  $5.8 \pm 1.0 \text{ m}^2 \cdot \text{g}^{-1}$ . Seasonal means for the submicron sea salt ranged from  $1.8 \pm 0.37$  to  $5.1 \pm 0.97 \text{ m}^2 \cdot \text{g}^{-1}$  and for the residual mass from  $0.21 \pm 0.31$  to  $1.5 \pm 1.0 \text{ m}^2 \cdot \text{g}^{-1}$ .

Concentrations of  $\text{nssSO}_4^{2-}$  measured at Barrow were compared with those measured at Poker Flat (Rocket Range), Denali National Park, and Homer for the 1997/1998 and 1998/1999 Arctic Haze seasons. Concentrations were the highest at Barrow and decreased with latitude from Poker Flat to Denali to Homer revealing a north to south gradient in the extent of the haze.

One of the most difficult aspects in accounting for the variety of aerosol optical properties is the problem of considering the properties of aerosol having a mixed composition. With the serial combination of a differential mobility analyzer (DMA) and an optical particle counter (OPC), Heintzenberg and co-workers<sup>35</sup> have studied optical state of mixture in the suburban aerosol at Tsukuba, Japan. On the average  $\sim 50\%$  of the analyzed particles were classified as optically external mixtures. The average of the measured distribution of optical signals was combined with the average size distribution to calculate an estimate of the integral scattering properties of the submicrometer aerosol for the measured state of optical mixture. This estimate yields 71% of the scattering coefficient of a size distribution in which all particles of a given size have the optical properties of ammonium sulfate. However, for extended periods this percentage was as

low as 41%. Accounting for nonspherical particles model, whose number fraction is sometimes about 50%, was shown to be important.

In spite of the urgency in obtaining information on the optical properties of aerosol, the data available are quite fragmentary. This is especially true for the complex refractive index (CRI) of the particulate matter and its wavelength dependence. For example, CRI data for sulfuric acid, nitric acid trihydrate, aluminum oxide, potassium chloride, ammonium sulfate aerosol particles, as well as various types of dust aerosol are almost lacking. Using high-resolution Fourier-transform infrared absorbance and transmittance spectral data for ammonium sulfate (AMS), calcium carbonate (CAC:  $\text{CaCO}_3$ ), and ammonium nitrate (AMN:  $\text{NH}_4\text{NO}_3$ ), Jarzembki and co-workers<sup>37</sup> have studied the data on refractive index for AMS and CAC to determine the imaginary part of the refractive index for AMN in the infrared wavelength range from 2 to 20  $\mu\text{m}$ . The backscatter calculations were performed using a log-normal size distribution for AMS, AMN, and CAC aerosols to show differences in their backscattered spectra, keeping in mind the future improvement of aerosol lidar sensing techniques.

The impact of the atmospheric aerosol as a polluting and climate-forming component significantly depends on the phase state of particles (solid or liquid), water content, and aerosol/gas partitioning of volatile components. Therefore, aerosol models are needed for predicting the aerosol state and composition in a wide range of air temperature and humidity. Although the assumption of thermodynamic equilibrium is quite acceptable, even in this case the phase state of aerosol particles may be rather complex, because (1) there are different ways for formation of the solid phase; (2) the behavior of the liquid phase of aerosol is, likely, strongly nonideal at a high concentration of solution under low-temperature conditions. In many cases, a significant part of the aerosol mass consists of inorganic electrolyte compounds subjected to dissociation in water leading to ion production.

Using mole fraction based equations for aqueous phase activities, together with equilibrium constants for the formation of gases and solids, combined with a Gibbs free energy minimization algorithm Wexler and Clegg<sup>65</sup> have created equilibrium phase partitioning models of inorganic atmospheric aerosols. This model predicts the water content, phase state (solid or liquid), and gas/aerosol partitioning for known ion composition, relative humidity, and temperature. The models are valid from < 200 to 328 K for the subsystems ( $\text{H}^+ - \text{SO}_4^{2-} - \text{NH}_3 - \text{Cl}^- - \text{Br}^- - \text{H}_2\text{O}$ ) and ( $\text{H}^+ - \text{NH}_4^+ - \text{SO}_4^{2-} - \text{NH}_3 - \text{H}_2\text{O}$ ), and 298.15 K only for ( $\text{H}^+ - \text{NH}_4^+ - \text{Na}^+ - \text{SO}_4^{2-} - \text{NH}_3 - \text{Cl}^- - \text{H}_2\text{O}$ ). The models involve no simplifying assumptions and include all solid phases identified in bulk experiments, including hydrated and double salt forms not treated in most other studies. The Henry's law constant of  $\text{H}_2\text{SO}_4$  was derived as a function of

temperature, based upon available data, and the model treatment of solubility of HBr in aqueous  $\text{H}_2\text{SO}_4$  was revised. Phase diagrams were calculated for the  $(\text{NH}_4)_2\text{SO}_4/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  system at low temperatures (down to 210 K). The models were also used to explore the importance of the double salts in urban inorganic aerosols. Double potassium sulfate salts were shown to be likely most important.

The field work for the AEROSOL Intercomparison 2000 took place from 4 to 14 April 2000 at Melpitz, Germany. One of the objectives of this experiment conducted by Maenhaut and co-workers<sup>46</sup> was to assess the extent of aerosol chemical mass closure could which be reached at the site. For this purpose, four filter samplers were operated in parallel: two Gent PM10 stacked filter unit (SFU) samplers (one with coarse and fine Nuclepore polycarbonate filters, the other with a Gelman Teflo filter as fine filter) and two single filter holders (one with PM2.5 inlet, the other with PM10 inlet) with Whatman QM-A quartz fiber filters.

All samples were analyzed for the particulate mass (PM) by weighing; the samples from the first SFU were analyzed for 42 elements by a combination of particle-induced X-ray emission spectroscopy and instrumental neutron activation analysis, those from the other SFU for major anions and cations by ion chromatography. All quartz filters were analyzed for organic carbon and elemental carbon by a thermal-optical transmission technique. Aerosol chemical mass closure calculations were done for separate fine (PM<sub>2.5</sub>, < 2  $\mu\text{m}$ ) and coarse (2–10  $\mu\text{m}$ ) aerosol fractions; nine aerosol types (or components) were considered. Crustal matter, organic aerosol, and nitrate were the major aerosol types in the coarse fraction; the dominant aerosol types in the fine fraction were the organic aerosol, nitrates, and sulfates. The components included explained 116% and 86% of the gravimetric PM in the coarse and fine fractions, respectively. The data tabulated below characterize the mass distribution of various aerosol components.

**Mean relative mass fraction (%) and mass variance for different aerosol components (fine and coarse fractions)**

Type of aerosol	Mass fraction	
	< 2 $\mu\text{m}$	2–10 $\mu\text{m}$
Organic aerosol	26 ± 7	32 ± 11
Elemental carbon	3.2 ± 1.2	3.5 ± 1.7
Sulfates	17 ± 4	10 ± 7
Ammonium	10 ± 2	5.7 ± 3.8
Nitrates	25 ± 6	18 ± 9
Sea salt	1.5 ± 1.3	11 ± 11
Soil component	3.2 ± 1.8	36 ± 12
Trace elements	0.3 ± 0.1	0.3 ± 0.1
Smoke	0.4 ± 0.2	0.1 ± 0.3
Total	86 ± 4	116 ± 19

The studies dealing with the aircraft exhaust plumes occupy an important place in combined atmospheric aerosol investigations.

A series of SULFUR 1–7 experiments was conducted in 1994–1999 to determine the aerosol particle and contrail formation properties of aircraft exhaust plumes for different fuel sulfur contents (FSC, from 2 to 5500  $\mu\text{g/g}$ ), flight conditions, and aircraft (ATTAS, A310, A340, B707, B747, B737, DC8, DC10). Schumann and co-authors<sup>59b</sup> discussed the results obtained, including new data from SULFUR 7.

The conversion fraction  $\epsilon$  of fuel sulfur to sulfuric acid was measured in the range 0.34 to 4.5% for an older (MK501) and  $3.3 \pm 1.8\%$  for a modern engine (CFM56-3B1). For low FSC,  $\epsilon$  is considerably smaller than implied by the volume of volatile particles in the exhaust. For FSC  $\geq 100 \mu\text{g/g}$  and  $\epsilon$  measured, sulfuric acid is the most important precursor of volatile aerosols formed in aircraft exhaust plumes of modern engines.

The aerosol measured in the plumes of various aircraft and models suggests  $\epsilon$  to vary between 0.5 and 10% depending on the engine and the state of its operation. The number of particles emitted from various subsonic aircraft engines or formed in the exhaust plume per unit mass of burned fuel varies from  $2 \cdot 10^{14}$  to  $3 \cdot 10^{15} \text{ kg}^{-1}$  for nonvolatile particles (mainly black carbon or soot) and is of order  $2 \cdot 10^{17} \text{ kg}^{-1}$  for volatile particles  $> 1.5 \text{ nm}$  for plumes of a few seconds age. Chemions (CIs) formed in kerosene combustion were found to be quite abundant. The CIs contain sulfur-bearing molecules and organic matter. The concentration of CIs at the engine nozzle is nearly  $10^9 \text{ cm}^{-3}$ .

Positive and negative CIs were found with masses partially exceeding 8500 atomic mass units. The measured number of volatile particles cannot be explained with binary homogeneous nucleation theory but is strongly related to the number of CIs. The number of ice particles in new contrails is close to the number of soot particles at low FSC and increases with the increasing FSC. Changes in soot particles and FSC have little impact on the threshold temperature for contrail formation (less than 0.4 K). Although the effect of soot and condensed matter on the contrail formation is studied quite well, the effect of contrail particles on clouds and chemical processes in the atmosphere is still far from being well understood. It is just this topic that should become a subject for further investigations. The EU Inter-Hemisphere Comparison of Aircraft-induced Cirrus Clouds (IHCAA) project serves just these purposes.

As was already noted, the atmospheric aerosol is a mixture of many components, in particular, inorganic acids (for example,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ), their salts (such as  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$ ), and water. Since most aerosol components are highly hygroscopic, the mass of water contained in aerosol particles often exceeds their dry mass, especially, under conditions of a humid air of the low troposphere. The multicomponent composition of the atmospheric aerosol is still ignored by global models

of atmospheric chemistry and climate models, because this requires very time-consuming computations.

Metzger and co-workers<sup>48</sup> have proposed a computationally efficient model to calculate gas/aerosol partitioning of semivolatile inorganic aerosol components for use in global atmospheric chemistry and climate models, which can be used as a module describing chemical processes in the global atmosphere in climate models. The main distinction of the new aerosol model is the technique of considering the equilibrium gas/aerosol partitioning within the equilibrium simplified aerosol model (EQSAM).

Having coupled a computationally efficient gas-aerosol scheme (EQSAM) to a global atmospheric chemistry-transport model (TM3), Metzger and co-workers<sup>48</sup> have performed a numerical simulation of gas/aerosol partitioning of multicomponent aerosols and aerosol associated water on a global scale. The results obtained have shown that gas/aerosol partitioning strongly affects the gas-phase concentrations at relatively low temperatures. During winter and at night during all seasons the calculated aerosol load, including water, is considerably higher than that without the account for gas/aerosol partitioning. The reason is that gaseous nitric acid near the surface is often neutralized by ammonia and therefore partitions almost completely into the aerosol phase to yield ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ). The aerosol  $\text{NH}_4\text{NO}_3$  has a longer atmospheric residence time compared to the corresponding precursor gases ( $\text{NH}_3$  and  $\text{HNO}_3$ ) and can therefore be transported over longer distances, for instance from India to Africa and Europe.

These modeling results are intriguing; however, their verification requires *in situ* measurements. A comparison with a limited set of ground-based measurements indicated that the model yields realistic results for the ammonium-sulfate-nitrate-water aerosol system in relatively polluted locations where ammonium nitrate is important. For remote locations for which we underestimate the total aerosol load, however, it will also be necessary to account for other aerosol species such as sea salt, mineral dust, and organic compounds. In Ref. 48 it was shown that assumptions on turbulent mixing and model resolution have a much stronger effect on aerosol calculations than the uncertainties resulting from the simplifications made in EQSAM.

One of the most stable sources of aerosol formation in the atmosphere is the mechanism of gas-phase transformation of trace gases into particles with participation of sulfuric acid vapor (there are many evidences of high correlation between  $\text{H}_2\text{SO}_4$  and new-born particles). Ammonia is also a possible key participant of such a transformation. Hanson and Eisele<sup>34</sup> have conducted flow-through laboratory measurements of the concentration of molecular cluster ions  $\text{HSO}_4^-(\text{H}_2\text{SO}_4)_{n-1}(\text{NH}_3)_m$  corresponding to the neutral species  $(\text{H}_2\text{SO}_4)_n(\text{NH}_3)_m$  for  $n = 2$  to 6 and  $m = 0$  to  $(n - 1)$  at temperatures up to  $\sim 285 \text{ K}$ .

A transverse chemical ionization apparatus was located inside a cooled flow tube where water, sulfuric acid, and ammonia vapors were mixed and formed clusters (without ammonia no clusters were observed). Typical  $\text{NH}_3$  and  $\text{H}_2\text{SO}_4$  concentrations were  $2 \cdot 10^6 \text{ cm}^{-3}$ , i.e.,  $\sim 100$  pptv at atmospheric pressure. Under these conditions, cluster concentrations were estimated to be multiple of  $10^6 \text{ cm}^{-3}$  and the critical, particle-forming cluster likely contained two  $\text{H}_2\text{SO}_4$  molecules at 275 K. The results are consistent with the species  $(\text{H}_2\text{SO}_4)_2\text{NH}_3$  playing an important role in the formation of new particles in the atmosphere.

In recent years, the interest to atmospheric nanoparticles has been growing for two main reasons. First, nanoparticles are important precursors of the formation of larger particles, which are known to strongly influence the global climate; second, atmospheric nanoparticles may play critical role in the deleterious human health effects associated with air pollution. In addition to these well-recognized facts, nanoparticles may also significantly influence the chemistry of the atmosphere. In chemistry, physics, and science of materials, nanoparticles are defined as particles of such a size that their properties differ from the properties of particulate matter. However, in atmospheric aerosol studies nanoparticles are defined as particles with diameters less than 50 nm. Larger aerosol particles can often have a nanostructure that manifests itself as mineral grain agglomerates, soot spherules, or layer coatings and influencing various aerosol properties. Thus, for example, nanostructures probably affect water uptake via capillary condensation, and nanoscale aqueous surface films may provide a medium for heterogeneous chemistry. Anastasio and Martin<sup>12</sup> have made a detailed review of the available information about nanoparticles in the atmosphere, especially, from the viewpoint of their formation and growth, chemical, physical, and mechanical properties.

In the context of assessment of the aerosol impact on climate, a particular attention is paid to the study of the aerosol effect on the cloud formation processes.

Leck and co-workers<sup>40</sup> have studied the chemical composition, sources, and methods of production of cloud condensation nuclei (CCN) over the Arctic Ocean covered with pack-ice in summer (July 15 – August 24 1996) (The observations were conducted aboard the Oden icebreaker mostly to the north from 85°N). After  $\sim 2$  days' trip of air over the pack-ice, two local CCN sources were identified: particles derived from the bursting bubbles on open water between ice floes (film and jet drops) and particles reaching CCN size by acquisition of oxidation products of dimethyl sulfide (DMS).

According to a number of studies, the most significant source of sulfur compound in the remote marine atmosphere is DMS produced in the ocean under the effect of biological processes and then emitted into the atmosphere, where its gas-phase

transformation into CCN occurs. The surprisingly high stability of the CCN number concentration in remote marine regions determines, however, the need of searching another source maintaining this high stability, because to function as CCN, particles should have the diameter no less than 60 nm, but, likely, only a small amount of particles of gas-phase origin can reach such a size for the time of their residence in the atmospheric boundary layer.

Therefore, it should be believed that the significant part of aerosol is formed bursting air bubbles containing sea salts of soluble organic surfactants and other admixtures. Two mechanisms determine formation of aerosol particles from bursting bubbles: (1) formation of particles as fragment of the film covering bubbles (film drops); (2) formation of particles at evaporation of drops in the atmosphere (jet drops).

The bubble-derived particle modes were found to have an exponential dependence on prevailing wind speed. The film drop generation depended less on wind speed and jet drop production depended more on wind speed than particles over open water did. However, the enhanced presence of film drop particles at wind speeds  $< 5 \text{ m}\cdot\text{s}^{-1}$  suggested a source of bubbles, other than wind, that is most active during clear sky days and ice melting.

The film drop particles were mainly organic in nature, but their sea-salt component increased at high wind speeds  $> 12 \text{ m/s}$  to dominate both mass and number. The jet drop mode was composed largely of sea salt, making a significant mass contribution already for wind speeds  $> 5 \text{ m/s}$ . However, the smaller-sized jet drops were not pure sodium chloride but contained a varied and appreciable organic component. The sulfur-containing particles dominated the CCN population and mass for the most common wind speeds of 5–12 m/s.

Measured CCN concentrations were on average less than would have been expected from either a sulfate or a sea-salt composition and the observed particle-size distribution. It was concluded that other components, probably organic, depressed the nucleating ability of the particles. However, on clear sky days, there were a majority of occasions on which CCN concentrations were more than predicted from a sulfate composition and the measured size distribution. An important task for the future should be evaluation of the role of the organic aerosol component and study of its interaction with the inorganic component.

An important aspect of the multicomponent composition of aerosol is connected with its role in heterogeneous chemical reactions on the particle surface, which significantly affect the concentration of various trace gases in the atmosphere.

Events of low ozone mixing ratios have frequently been observed in the arctic marine boundary layer (MBL) during polar sunrise. The ozone loss has been hypothesized to be caused by the gas-phase chain reactions involving Br atom. Gaseous

Br<sub>2</sub> and BrCl are produced by the reaction of HOBr with sea salt or ice particles and then photolyzed to result in halogen atom. Heterogeneous reactions involved with halogen chemistry on sea salt particle or ice are now recognized as an important mechanism for the destruction of ozone in the arctic marine boundary layer in spring. Organic compounds in the atmosphere also participate in the surface ozone depletion together with halogen compounds. It was noticed that during low ozone periods in the arctic spring the concentrations of non-methane hydrocarbons decrease and their compositions change.

The studies on the arctic aerosols showed that short chain (C<sub>2</sub>–C<sub>6</sub>) dicarboxylic acids became 5–20 times more abundant in March to April than in the preceding dark winter months. These results imply that low molecular weight dicarboxylic acids are produced by an enhanced photochemical oxidation of volatile organic compounds, which were transported and accumulated in the arctic atmosphere during the dark winter. A strong positive correlation was also found between the concentrations of small dicarboxylic acids and particulate Br in the arctic aerosols. This means that the production of diacids is linked with halogen chemistry. This conclusion is supported by the fact that bromine and chlorine containing succinic acids have been identified for the first time in the marine aerosols from the North Pacific.

To better understand the linkage between dicarboxylic acids and halogen chemistry, Narukawa and co-workers<sup>50</sup> have carried out the chemical analysis of aerosol samples collected during dark winter and light spring seasons as part of polar sunrise experiment ALERT2000. The concentrations of such halogenated dicarboxylic acids as bromomalonic (Br–C<sub>3</sub>), chlorosuccinic (Cl–C<sub>4</sub>), and bromosuccinic (Br–C<sub>4</sub>) in the dark winter (14 to 22 February 2000) and light spring (17 April to 6 May 2000) at Alert, Nunavut, Canada (82°27'N, 62°32'W) were determined for the first time.

The observed concentrations of the acids in spring were (in ng/m<sup>3</sup>): 0.11–0.68 (Br–C<sub>3</sub>), 0.04–0.10 (Cl–C<sub>4</sub>), 0.12–0.20 (Br–C<sub>4</sub>). The concentration of Br–C<sub>3</sub> increased from late April to early May, whereas the concentration of Cl–C<sub>4</sub> decreased. The concentration of Br–C<sub>4</sub> peaked in the middle of the experiment. A strong negative correlation ( $R = -0.98$ ) was found between the concentrations of Br–C<sub>3</sub> and Cl–C<sub>4</sub>. Concentrations of methanesulfonic acid (MSA) increased during the period of observations, whereas those of Cl<sup>–</sup> ion decreased. The strong positive correlation was observed between the concentrations of Cl–C<sub>4</sub> and Cl<sup>–</sup> ( $R = 0.99$ ), as well as Br–C<sub>3</sub> and MSA ( $R = 0.96$ ). These results suggest that Br–C<sub>3</sub> diacid is primarily derived from marine biogenic source, whereas Cl–C<sub>4</sub> diacid is secondarily formed by heterogeneous reaction involving halogen chemistry on sea salt. Satellite images of the sea ice concentrations and backward air mass trajectories suggest that the aerosols containing halogenated

diacids were transported over the sampling sites from the Arctic Ocean covered with sea ice.

The chemical composition and the physical state (for example, liquid or crystal) of atmospheric aerosol particles affect significantly their optical properties, chemical activity, and the atmospheric residence time. Therefore, consideration of the phase state of particles is very important for numerical simulation of the aerosol impact on atmospheric processes. Though various thermodynamic models have been developed for solution of the corresponding problems, their use is seriously complicated at the low relative humidity, when it is difficult to simulate the phase dynamics because of the prevalence of phase state metastability caused by the slow nucleation kinetics.

The results of studies of individual aerosol particles (especially, using mass-spectrometry) revealed the complex composition of particles. Particles of one characteristic type are insoluble components of the earth's crust covered by soluble electrolytes. Examples of insoluble components are mineral dust particles from Gobi and Sahara deserts. These circumstances stimulated laboratory studies of the effect of mineral dust inclusion on the particle phase (for example, through heterogeneous nucleation). In particular, a series of works devoted to the processes of formation of aerosol particles as insoluble mineral dust inclusions covered by liquid ammonium sulfate have been carried out. It was shown, in particular, that the presence of an insoluble component provides for the presence of a surface, which leads to a significant decrease of critical oversaturation needed for crystallization of ammonium sulfate.

Han and co-workers<sup>33</sup> have discussed further results on the formation of particles from mineral dust covered by ammonium nitrate, which is a typical component of atmospheric aerosol particles and has mostly anthropogenic origin. For this purpose, the influence of relative humidity ( $RH$ ) and mineral dust inclusions on the physical state of NH<sub>4</sub>NO<sub>3</sub>/H<sub>2</sub>O particles was investigated through aerosol flow tube experiments. It was shown that neat submicron aqueous particles do not effloresce, while those bearing mineral inclusions ranging from 150 to 400 nm in diameter effloresce between 3 and 10%  $RH$  at 298 K. NH<sub>4</sub>NO<sub>3</sub>/H<sub>2</sub>O coatings were achieved on hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), corundum ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>), mullite (Al<sub>6</sub>Si<sub>2</sub>O<sub>13</sub>), and amorphous silica (am-SiO<sub>2</sub>) through an HNO<sub>3</sub> vaporization–condensation technique followed by neutralization with NH<sub>3</sub>. The extent of internal mixing in the aerosol ranges from 7 to 27% depending on the diameter of a mineral dust particle.

Evidences have been presented of a mechanism of heterogeneous nucleation that proceeded by chemisorption of nitrate on the surface of the oxide minerals followed by epitaxial germ formation of crystalline NH<sub>4</sub>NO<sub>3</sub>. Under actual atmospheric conditions, nitrate-containing particles can be divided into two subgroups according to their hygroscopic

properties. Since heterogeneous chemistry and radiative properties of complex particles strongly depend on their physical state, the properties of air masses containing nitrate particles change considerably in the presence of mineral dust.

Ricard and co-authors<sup>56</sup> have discussed the results of observation of the size-resolved aerosol components (major ions, selected organic acids, and crustal elements) made with 12-stage impactors during the summers of 1997 and 1998 and winter 1997–1998 at Sevettijarvi in Finnish Lapland (69°35' N, 28°50' E, 130 m asl). The samples were classified depending on their degree of marine and continental origin. Modal parameters (aerodynamic diameters and dispersion) were identified from the size distribution of each species. In general, the aerosol comprises two submicron modes (condensation mode at  $0.30 \pm 0.05 \mu\text{m}$  and the droplet mode at  $0.65 \pm 0.15 \mu\text{m}$ ) and one or two supermicron modes (the first one between 3.5 and 4.5  $\mu\text{m}$  associated with marine species and the second one between 5 and 6  $\mu\text{m}$  associated with crustal species). The results suggest internal mixing of nss (non-sea-salt) sulfate, ammonium, and organic acids in the submicron modes. The results on the supermicron modes indicate interactions of nss sulfate, ammonium, nitrate, and organic acids with the marine and crustal particles. During summer and winter the supermicron mass fraction largely decreases from the marine air masses to the continental ones.

Global distributions of aerosol optical depth (AOD) derived from satellite observations of backscattered radiation indicate persistent seasonal aerosol plumes downwind of many continental regions. In March through May a plume extends from Asia eastward across the North Pacific Ocean. During the winter monsoon period (December through April), a plume is located off the southwest coast of India over the Indian Ocean. In the summer months of June through August an aerosol plume originates from the mid-Atlantic states of the United States and extends across the North Atlantic Ocean. Likewise, in the spring and summer months a plume is transported from Europe to the North Atlantic Ocean.

Since satellite observations are not able to provide information about aerosol chemical composition, size distributions, optical properties, or mass loading in the boundary layer, it is needed to conduct direct *in situ* measurements of the corresponding characteristics, which was partly realized in recent observation campaigns within the framework of the Aerosol Characterization Experiments ACE-1 and 2 (European plume), Indian Ocean Experiment INDOEX (the plume coming from the Indian subcontinent), ACE-Asia (Asian plume), Tropospheric Aerosol Radiative Forcing Observational Experiment TARFOX, and New England Air Quality Study NEAQS (the eastern U.S. plume).

Quinn and Bates<sup>57</sup> have analyzed some of the results obtained with their classification into "Marine" referring to sampled air masses that had not been in contact with land for 5 or more days, "Continental," "Polluted," and "Polluted with Dust" referring to sampled air masses that had recent (< 3 days) contact with continental regions with known sources of pollution and/or dust aerosol. The results obtained evidence that sea salt dominates sub- and supermicron aerosol mass and light extinction in the remote marine atmosphere. It turned out that non-sea-salt (nss)  $\text{SO}_4^{2-}$  derived from oceanic dimethyl sulfide (DMS) did not make a significant contribution to aerosol mass or light extinction nor did it play any role in new particle production in the marine boundary layer, but contribute to the growth of existing particles and nucleation of new particles in the free troposphere.

The results discussed reflect a wide diversity of aerosol types. A large and variable fraction of submicron aerosol is not sulfate, including a significant amount of  $\text{nssSO}_4^{2-} + \text{NH}_4^+$ , as well as elemental carbon and organic carbon (OC), which is important for correct determination of the optical properties of aerosol. The largest submicron concentrations and mass fractions of EC were observed in air masses from the Indian subcontinent, and the highest concentration of submicron aerosol and mass fraction were characteristic of EC that absorbs in the visible spectral region. EC causes reduction in solar radiation reaching the surface, but, on the other hand, it may result in cloud evaporation in the MBL, which complicates estimation of the EC impact on radiative forcing.

The eastern U.S. plume is comparable with the Indian and Asian plumes in terms of aerosol mass, surface extinction, and aerosol optical depth. According to TARFOX and NEAQS data, the OC concentration in the eastern U.S. plume appeared higher than that in the Asian plume, while the AOD values for these plumes are comparable. The Asian plume aerosol was (in contrast to expectations) only weakly absorbing. The mean single scattering albedo was  $0.94 \pm 0.03$ .

## Conclusion

It is beyond question that the major task of further investigations is to conduct *in situ* observations in order to adequately understand the properties of different types of aerosol and their contributions to various atmospheric properties (formation of the chemical composition, climate impact, and others). In the context of climate studies, it is of great importance to development techniques for interactive parameterization of the global aerosol dynamics in climate models. However, it is obvious that this task will not be accomplished in the nearest future.

## References

1. A.I. Borodulin, A.S. Safatov, V.V. Marchenko, A.N. Shabanov, B.D. Belan, and M.V. Panchenko, *Atmos. Oceanic Opt.* **16**, Nos. 5–6, 387–390 (2003).
2. A.I. Borodulin, A.S. Safatov, B.D. Belan, and M.V. Panchenko, *Atmos. Oceanic Opt.* **16**, Nos. 5–6, 479–482 (2003).
3. G.I. Gorchakov and K.A. Shukhurov, *Izv. Ros. Akad. Nauk, Fiz. Atmos. Okeana* **39**, No. 1, 85–97 (2003).
4. K.Ya. Kondratyev, ed., *Aerosol and Climate* (Gidrometeoizdat, Leningrad, 1991), 542 pp.
5. K.Ya. Kondratyev, *Izv. Rus. Geogr. Ob.* **134**, No. 5, 1–10 (2002).
6. K.Ya. Kondratyev, *Izv. Rus. Geogr. Ob.* **135**, No. 6 (2002).
7. K.Ya. Kondratyev, *Atmos. Oceanic Opt.* **14**, No. 3, 153–160 (2001).
8. K.Ya. Kondratyev, *Atmos. Oceanic Opt.* **15**, No. 2, 105–124 (2002).
9. V.F. Krapivin and K.Ya. Kondratyev, *Global Changes in the Environment: Ecoinformatics* (NIKHI SPbGU, St. Petersburg, 2002), 721 pp.
10. A.S. Safatov, I.S. Andreeva, A.N. Ankilov, A.M. Baklanov, B.D. Belan, A.I. Borodulin, G.A. Buryak, N.A. Ivanova, K.P. Kutsenogii, V.I. Makarov, V.V. Marchenko, Yu.V. Marchenko, S.E. Ol'khin, M.V. Panchenko, V.A. Petrotsenko, O.V. P'yankov, I.K. Reznikova, and A.N. Sergeev, *Atmos. Oceanic Opt.* **16**, Nos. 5–6, 491–495 (2003).
11. M.V. Panchenko, ed., *Atmos. Oceanic Opt., Topical issue "Siberian Aerosols"* **16**, Nos. 5–6, 371–520 (2003).
12. C. Anastasio and S.T. Martin, *Rev. Miner. and Geochem.* **44**, 293–349 (2001).
13. A. Ansmann, F. Wagner, D. Müller, D. Althausen, A. Herber, W. von Hoyningen-Huene, and U. Wandinger, *J. Geophys. Res. D* **107**, No. 15, AAC8/1–AAC8/14 (2002).
14. J.K.B. Bishop, R.E. Davis, and J.T. Sherman, *Science* **298**, No. 5594, 817–821 (2002).
15. A.I. Bokoye, A. Royer, N.T. O'Neill, and L.J.B. McArthur, *Arctic* **55**, No. 3, 215–228 (2002).
- 15a. O. Boucher and M. Pham, *Geophys. Res. Lett.* **29**, No. 9, 2211–2214 (2002).
16. H.M. Ten Brink, H. Puxbaum, W. Maenhaut, J.-P. Putaud, U. Baltensperger, and K. Maller, *Eurotrac Newsletter. Winter 2002/2003*, No. 24, pp. 26–30.
17. S.D. Brooks, M.E. Wise, M. Cushing, and M.A. Talbart, *Geophys. Res. Lett.* **29**, No. 19, 23/5–23/4 (2002).
18. W.L. Chameides, C. Luo, R. Saylor, D. Streets, Y. Huang, M. Bergin, and F. Giorgi, *J. Geophys. Res. D* **107**, No. 10, AAC2/1–AAC2/17 (2002).
19. W.L. Chameides and M. Bergin, *Science* **297**, 2214–2215 (2002).
20. J.T. Houghton, Y. Ding, D.J. Griggs, M. Noguera, P.J. van der Uuden, X. Dai, K. Maskell, and C.A. Johnson, eds., *Climate Change 2001: The Scientific Basis. Contribution of WG 1 to the Third Assessment Report of the IPCC* (Cambridge University Press, 2001), 892 pp.
21. P.R. Colarco, O.B. Toon, O. Torres, and P.J. Rasch, *J. Geophys. Res. D* **107**, No. 16, AAC4/1–AAC4/18 (2002).
22. W.F. Cooke, V. Ramaswamy, and P. Kasibhatla, *J. Geophys. Res. D* **107**, No. 16, ACH2/1–ACH2/32 (2002).
- 22a. J.E. Dibb, R.W. Talbot, G. Seid, C. Jordan, E. Scheuer, E. Atlas, N.J. Blake, and D.R. Blake, *J. Geophys. Res. D* **108**, No. 2, PEM2/1–PEM2/17 (2003).
23. O. Dubovik, B.N. Holben, T. Lapyonok, A. Sinyuk, M.I. Mishcherko, P. Yang, and I. Slutsker, *Geophys. Res. Lett.* **29**, No. 10, 54/1–54/4 (2002).
24. T.J. Fortin, J.E. Shilling, and M.A. Tolbert, *J. Geophys. Res. D* **107**, No. 10, AAC4/1–AAC4/10 (2002).
- 24a. K. Franke, A. Ansmann, D. Müller, D. Althausen, C. Ventkataraman, M.S. Reddy, F. Wagner, and R. Scheele, *J. Geophys. Res. D* **108**, No. 2, AAC6/1–AAC6/17 (2003).
- 24b. P. Ginoux, *J. Geophys. Res. D* **108**, No. 2, AAC3/1–AAC3/10 (2003).
25. P. Glantz, K.J. Noone, and S.R. Osborne, *Quart. J. Roy. Meteorol. Soc.* **129**, Part A, No. 590, 1329–1350 (2003).
26. P. Ginoux, M. Chin, I. Tegen, J.M. Prospero, B. Holben, O. Dubovik, and S.-J. Lin, *J. Geophys. Res. D* **106**, No. 17, 20255–20274 (2001).
27. J. Hansen, R. Ruedy, M. Sato, M. Imhoff, W. Lawrence, D. Easterling, T. Peterson, and T. Karl, *J. Geophys. Res. D* **106**, No. 20, 23947–34961 (2001).
28. J. Hansen, M. Sato, L. Nazarenko, et al., *J. Geophys. Res. D* **107**, No. 18, Acl 2–1–2–37 (2002).
29. R.J. Griffin, D. Dabdub, and J.H. Seinfeld, *J. Geophys. Res. D* **107**, No. 17, AAC3/1–AAC3/26 (2002).
30. R.J. Griffin, K. Nguyen, D. Dabdub, and J.H. Seinfeld, *J. Atmos. Chem.* **44**, No. 2, 171–190 (2003).
31. R.J. Griffin, D. Dabdub, M.J. Kleeman, M.P. Fraser, G.R. Cass, and J.H. Seinfeld, *J. Geophys. Res. D* **107**, No. 17, AAC5/1–AAC5/14 (2002).
32. A. Grini, C.S. Zender, and P.R. Colarco, *Geophys. Res. Lett.* **29**, No. 18, 15/1–15/4 (2002).
33. J.-H. Han, H.-M. Hung, and S.T. Martin, *J. Geophys. Res. D* **107**, Nos. 9–10, AAC3/1–AAC3/10 (2002).
34. D.R. Hanson and F.L. Eisele, *J. Geophys. Res. D* **107**, No. 12, AAC10/1–AAC10/18 (2002).
35. J. Heintzenberg, K. Okada, and B.P. Luo, *J. Geophys. Res. D* **107**, No. 11, AAC2/1–AAC2/10 (2002).
36. B.B. Hicks, R.S. Artz, T.P. Meyers, R.P. Hosker, Jr., *J. Geophys. Res. D* **107**, No. 12, ACH6/1–ACH6/12 (2002).
- 36a. B.N. Holben, D. Tanré, A. Smirnov, T.F. Eck, I. Slutsker, N. Abuhassan, W.W. Newcomb, J.S. Schafer, B. Chatenet, F. Lavenu, Y.J. Kaufman, J. Vande Castle, A. Setzer, B. Markham, D. Clark, R. Frouin, R. Halthore, A. Karneli, N.T. O'Neill, C. Pietrac, R.T. Pinker, K. Voss, and G. Zibordi, *J. Geophys. Res. D* **106**, No. 11, 12067–12097 (2001).
37. M.A. Jarzembski, M.L. Norman, K.A. Fuller, V. Srivastava, and D.R. Cutten, *Appl. Opt.* **42**, No. 6, 922–930 (2003).
38. A. Kerkweg, S. Wurzel, T. Reisin, and A. Bott, *Quart. J. Roy. Meteorol. Soc.* **129** (in print) (2003).
39. K.Ya. Kondratyev and I. Galindo, *Volcanic Activity and Climate* (A. Deepak Publ. Co., Hampton, VA, 1997), 382 pp.
- 39a. A. Laskin, D.J. Caspar, W. Wang, S.W. Hunt, J.P. Cowin, S.D. Colson, and B.J. Finlayson-Pitts, *Science* **301**, No. 5631, 340–344 (2003).
40. C. Leck, M. Norman, E.K. Bigg, and R. Hillamo, *J. Geophys. Res. D* **107**, No. 12, AAC1/1–AAC1/17 (2002).
41. J.H. Lee, Y. Yoshida, B.J. Turpin, P.K. Hopke, R.L. Poirot, P.J. Liyo, and J.C. Oxley, *J. Air and Waste Manag. Assoc.* **52**, 1186–1205 (2002).
42. G. Lesins, P. Chylek, and U. Lohmann, *J. Geophys. Res. D* **107**, Nos. 9–10, AAC5/1–AAC5/14 (2002).
43. X. Liu and J.E. Penner, *J. Geophys. Res. D* **107**, No. 12, AAC2/1–AAC2/18 (2002).
44. F. Li and V. Ramanathan, *J. Geophys. Res. D* **107**, No. 16, AAC2/1–AAC2/13 (2002).

- 44a. Z. Li, R. Fraser, J. Jin, A.A. Abuelgasim, I. Criszar, P. Gong, R. Pu, and W. Hao, *J. Geophys. Res. D* **108**, No. 2, ACL20/1–ACL20/14 (2003).
45. C.L. Liu, J. Zhang, and Z.B. Shen, *J. Geophys. Res. D* **107**, No. 14, ACH17/1–ACH17/17 (2002).
- 45a. R. Lu, R.P. Turko, K. Stolzenbach, S.K. Friedlander, C. Xiong, K. Schiff, L. Tiefenhalter, and G. Wang, *J. Geophys. Res. D* **108**, No. 2, AAC11/1–AAC11/24 (2003).
46. W. Maenhaut, J. Schwarz, J. Cafmeyer, and X. Chi, *Nucl. Instrum. and Meth. Phys. Res. B* **189**, 233–237 (2002).
47. G. McFiggans, R.A. Cox, J.C. Mössinger, B.J. Allan, and J.M.C. Plane, *J. Geophys. Res. D* **107**, No. 15, ACH10/1–ACH10/13 (2002).
48. S. Metzger, F. Dentener, S. Pardis, and J. Lelieveld, *J. Geophys. Res. D* **107**, No. 16, ACH16/1–ACH16/24 (2002).
49. S. Metzger, F. Dentener, M. Krol, A. Jenken, and J. Lelieveld, *J. Geophys. Res. D* **107**, No. 16, ACH17/1–ACH17/23 (2002).
- 49a. P. Midgley, P. Builtjes, D. Fowler, R. Harrison, N. Hewitt, N. Moussiopoulos, K. Noone, K. Tørseth, A. Vulz-Thomas, eds., *Towards Cleaner Air for Europe-Science, Tools and Applications. Part 1. Results from the EUROTRAC-2 Synthesis and Integration Project* (Margaret Publ., Germany, 2003), 246 pp.
- 49b. P. Midgley and M. Reuther, *Towards Cleaner Air for Europe-Science, Tools, and Applications. Part 2. Overviews from the Final Reports of the EUROTRAC-2 Subprojects* (Margaret Publ., Germany, 2003), 321 pp.
- 49c. K.G. Moore II, A.D. Clarke, and V.N. Kapustin, *J. Geophys. Res. D* **108**, No. 2, PEM8/1–PEM8/27 (2003).
50. M. Narukawa, K. Kawamura, H. Hatsushika, K. Yamazaki, S.-M. Li, J.W. Bottenheim, and K.G. Anlauf, *J. Atmos. Chem.* **44**, 323–335 (2003).
51. T. Novakov, V. Ramanathan, J.E. Hansen, T.W. Kirchstetter, M. Sato, J.E. Sinton, and J.A. Sathaye, *Geophys. Res. Lett.* **30**, No. 6, 1324–1328 (2003).
52. E.A. Oberlander, C.A.M. Brenninkmeijer, P.J. Crutzen, N.F. Elansky, G.S. Golitsyn, I.G. Granberg, D.H. Scharffe, R. Hofmann, I.B. Belikov, H.G. Paretzke, P.F.J. van Velthoven, *J. Geophys. Res. D* **107**, No. 14, ACH13/1–ACH13/15 (2002).
53. L. Pirjola, H. Korhonen, and M. Kulmala, *J. Geophys. Res. D* **107**, No. 11, ACH1/1–ACH1/10 (2002).
54. B.K. Pun, R.J. Griffin, C. Seigneur, and H. Seinfeld, *J. Geophys. Res. D* **107**, No. 17, AAC4/1–AAC4/15 (2002).
55. P.K. Quinn, T.L. Miller, T.S. Botes, J.A. Ogren, E. Andrews, and G.E. Shaw, *J. Geophys. Res. D* **107**, No. 11, AAC8/1–AAC8/15 (2002).
56. V. Ricard, J.-L. Jaffrezo, V.-M. Kerminen, R.E. Hillamo, K. Teinilä, W. Maenhaut, *J. Geophys. Res. D* **107**, No. 14, AAC4/1–AAC4/18 (2002).
57. P. Quinn and T. Bates, *IGACTiv Newsletter*, No. 28, 24–30 (2003).
- 57a. G.C. Roberts, A. Nenes, J.H. Seinfeld, and M.O. Andreae, *J. Geophys. Res. D* **108**, No. 2, AAC9/1–AAC9/19 (2003).
58. H. Rodhe, G. Ayers, L.C. Peng, and M.R. Bala, *IGACTiv Newsletter*, No. 28, 12–13 (2003).
59. F.J. Sansone, C.R. Benitez-Nelson, J.A. Resing, E.H. De Carlo, S.M. Vink, J.A. Heath, and B.J. Huebert, *Geophys. Res. Lett.* **29**, No. 9, 49/1–49/4 (2002).
- 59a. D.L. Savoie, R. Arimoto, W.C. Keene, J.M. Prospero, R.A. Duce, and J.N. Galloway, *J. Geophys. Res. D* **107**, No. 18, 3/1–3/21 (2002).
- 59b. U. Schumann, F. Arnold, R. Busen, J. Curtius, B. Kärcher, A. Kiendler, A. Petzold, A. Schlager, F. Schröder, and K.-H. Wohlfrom, *J. Geophys. Res. D* **107**, No. 15, AAC2/1–AAC2/27 (2002).
60. A. Shimota, H. Kobayashi, and K. Wada, *J. Geophys. Res. D* **107**, No. 14, AAC6/1–AAC6/10 (2002).
61. V. Spiridonov and Čurić, *Időjárás* **107**, No. 2, 1–84 (2003).
62. U. Schumann, F. Arnold, R. Busen, J. Curtius, B. Kärcher, A. Kiendler, A. Petzold, H. Schlager, F. Schröder, and K.-H. Wohlfrom, *J. Geophys. Res. D* **107**, No. 15, AAC2/1–AAC2/27 (2002).
- 62a. S. Sobanska, C. Coeur, W. Maenhaut, and F. Adams, *J. Atmos. Chem.* **44**, 299–322 (2003).
63. T. Takemura, I. Uno, T. Nakajima, A. Higurashi, I. Sano, *Geophys. Res. Lett.* **29**, No. 24, 11/1–11/4 (2002).
64. H. Tervahattu, J. Juhanoja, and K. Kupiainen, *J. Geophys. Res. D* **107**, No. 16, ACH18/1–ACH18/7 (2002).
65. A.S. Wexler and S.L. Clegg, *J. Geophys. Res. D* **107**, No. 14, ACH14/1–ACH14/14 (2002).
- 65a. X.Y. Zhang, S.L. Gong, R. Arimoto, Z.X. Shen, F.M. Mei, D. Wang, and Y. Cheng, *J. Atmos. Chem.* **44**, 241–257 (2003).
66. B. Zuberi, A.K. Bertram, C.A. Cassa, L.T. Molina, and R.J. Molina, *Geophys. Res. Lett.* **29**, No. 10, 142/1–142/4 (2002).