From nano- to global scales: properties, processes of formation, and aftereffects of atmospheric aerosol impacts. 3. Processes of aerosol formation (nucleation)

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The processes of aerosol formation (nucleation) are overviewed.

Introduction

The observations discussed in my earlier papers[3–10] illustrate the considerable efforts made in recent years to obtain more complete information on the spatiotemporal variability of aerosol properties on a global scale. One of the striking examples is the Asian Particle Environmental Change Studies (APEX) observational experiment that has been conducted since 1999 being aimed at the study of the aerosol impact on climate.[43] This program is carried out under the leadership of Prof. T. Nakajima from the Center for Climate System Research, University of Tokyo, Tokyo, Japan. The intense development of aerosol studies makes it necessary to mention briefly the results of the latest studies before addressing the main subject of this paper.

Streets et al.[49] compiled a detailed summary of atmospheric emissions of trace gases and aerosol in Asia using the data of observations in 2000. Emissions were estimated for all major anthropogenic sources, including biomass burning, in 64 regions of Asia. Total Asian emissions were estimated as follows: 34.3 Tg SO_2, 26.8 Tg NO_x, 9870 Tg CO_2, 279 Tg CO, 107 Tg CH_4, 52.2 Tg NMVOC, 2.54 Tg black carbon (BC), 10.4 Tg organic carbon (OC), and 27.5 Tg NH_3. In addition, non-methane volatile organic compounds (NMVOC) were classified into 19 subcategories according to functional groups and reactivity. This allowed identifying the major source regions and types for many of the significant gaseous and particle emissions that influence pollutant concentrations in the regions of the TRACE-P and ACE-Asia field measurements.

Emissions in China dominated the signature of pollutant concentrations in the region under study, which is characterized by the following yearly emission levels: 20.4 Tg SO_2, 11.4 Tg NO_x, 3820 Tg CO_2, 116 Tg CO, 38.4 Tg CH_4, 17.4 Tg NMVOC, 1.05 Tg BC, 3.4 Tg OC, and 13.6 Tg NH_3. Emissions were mapped at a variety of spatial resolutions from $1° \times 1°$ and higher.[49] The data tabulated below characterize the levels of emissions of different compounds.

The comparison of the data of this summary and observations in the period of TRACE-P (February–April 2001) revealed quite close agreement between the average values. Uncertainties in the emission estimates (at 95% confidence level) range from of $\pm 16\%$ as low for SO_2 to about $\pm 450\%$ for OC.

Alfaro et al.[11] discussed the results of observations of the chemical composition and optical properties of aerosol at Zhenbeitai (ZBT) near the city of Yulin (38°17′N, 109°43′E, Shaanxi province, China) in April 2002. One year earlier, ZBT had been one of the continental supersites of the ACE-Asia international experiment. In spring, this site, located on the southwestern edge of the Mu Us desert, becomes a crossroad of the pathways along which dust originating from the main Chinese dust sources moves in the atmosphere.

Levels of emissions of various trace gases and aerosol (PM-10, PM-2.5, and sea-salt aerosol)

Component	Natural sources	Internal combustions	Open combustion	All sources
SO_2	2.0	5.6	0.2	7.8
NO_x	0.005	4.0	1.1	5.1
CO_2	–	1453.0	459.6	1912.6
CO	–	34.7	27.8	62.5
CH_4	–	16.5	1.3	17.8
NMVOC	18.3	6.7	5.0	30.0
BC	–	0.3	0.2	0.5
OC	–	1.2	1.4	2.6
NH_3	–	4.7	0.4	5.1
PM-10	107.7	–	–	116.0
PM-2.5	26.2	–	–	31.2
Sea-salt aerosol	41.6	–	–	41.6

The instrumentation, employed to measure the aerosol size distribution, provided for the measurement of the mass concentrations, number concentrations, size distributions, elemental composition, and scattering properties of the PM-9 aerosol (particles smaller than 9 μm in diameter). A Sun-tracking photometer served to measure the aerosol optical thickness (AOT) and the single scattering albedo. During the measurement period, several dust events, one of them a major dust storm when PM-9 mass concentrations reached the values of $4650\ \mu g/m^3$ as high. At this time the aerosol scattering coefficient reached 2800 $M(10^{-6})m^{-1}$. These dust events were separated by periods when optical properties were altered, or even dominated, by anthropogenic aerosol of local origin. For these periods, the content of PM-9 was significantly lower (always below $100\ \mu g/m^3$) than during dust events, mass concentration of the black carbon (BC) was between 0.9 and $6.7\ \mu g/m^3$, and the aerosol scattering coefficient between 7 and 800 Mm^{-1}.

No difference in elemental composition was detected between the various dust episodes. Measured Fe/Al (0.63 ± 0.04) and Mg/Al (0.32 ± 0.03) ratios are consistent with an aerosol source located in the "northwestern high desert sources." This result is also supported by the air mass back-trajectories analysis. The transported dust had already incorporated an anthropogenic carbonaceous component upon reaching the measurement site. The size distribution of this transported mixture was relatively constant and characterized by the presence of a particle population with the mean diameter between 1 and 2 μm. The mass scattering efficiency of this aerosol was $1.05 \pm 0.13\ m^2/g$, and the Angström exponent was close to 0.19. The single scattering albedo was found to increase from 0.89 at 441 nm to 0.95 at 873 nm. These relatively large values of the single scattering albedo indicate that, though mixing of mineral dust and anthropogenic aerosols is the rule rather than the exception at ZBT, the aerosol is still not very strongly absorbing during intense dust events.

Iwasaka with co-authors[28,29] analyzed the results of lidar sensing of the vertical profile of aerosol concentration in the troposphere at Dunhuang (China, 40°00′N, 94°30′E) over the Taklamakan Desert in summer 2002. The data on the vertical profile of the backscattering ratio $(BSC_1 + BSC_2)/BSC_1$, where $BSC_{1,2}$ are the molecular and aerosol backscattering coefficients at the wavelength of 532 nm, indicate that the aerosol was concentrated in the lower 6-km atmospheric layer, and rapidly decreased from 2.5 down to about 1 above 6 km. The depolarization ratio $P_1/(P_1 + P_2)$ varied in the same manner ($P_{1,2}$ are the orthogonal components of the degree of polarization) with a sharp change near 6-km height. Electron-microscopic analysis of aerosol sampled with a balloon-borne particle impactor suggested that the large depolarization ratio was certainly due to irregularly shaped dust particles. Such irregularly shaped nonspherical dust particles float from near the surface to about 6 km in the presence of the dominant easterly transport.

Jordan et al.[31] analyzed the chemical composition and physical properties of atmospheric aerosol collected in the lower troposphere onboard a DC-8 instrumented aircraft during TRACE-P experiment in spring of 2001. Depending on the type of the back trajectories of air masses calculated (that is, directions of long-range transport), the observations were grouped into four categories, corresponding to the long-range transport from the west (WSW), regional circulation over the western Pacific and Southeast Asia (SE Asia), polluted transport from northern Asia with substantial sea salt at low altitudes (NNW), and a substantial amount of dust (Channel).

The WSW was generally characterized by low mixing ratios at both middle and high altitudes, with the bulk of the aerosol mass due to non-sea-salt water-soluble inorganic species. Low altitude SE Asia also had, in general, low mean mixing ratios with the majority of the aerosol mass comprised of non-sea-salts, however, soot was also relatively important in this region. The NNW had the highest mean sea salt mixing ratios, with the aerosol mass at low altitudes (< 2 km) evenly divided between sea salts, non-sea-salts, and dust. The highest mean mixing ratios of water-soluble ions and soot were observed at the lowest altitudes (< 2 km) in the Channel sector. The bulk of the aerosol mass exported from Asia concentrates in this sector in both low and middle latitudes, due to the prevalence of dust (compared with other sectors).

Number densities for Channel and NNW showed enhanced content of fine particles, while their volume distributions were enhanced due to sea salt and dust. Low-altitude Channel exhibited the highest condensation nuclei (CN) number densities along with enhanced scattering coefficients, compared to those in the other sectors. In the midlatitudes (at heights of 2 to 7 km), low mean CN number densities coupled with a high proportion of nonvolatile particles ($\geq 65\%$) observed in the polluted sectors (Channel and NNW) were attributed to wet scavenging, which removes hygroscopic CN particles. Low single scattering albedo in the SE Asia reflected the enhanced soot content.

As a result of progressing desiccation of internal regions of the Asian continent under the effect of the stepwise rise of the Tibet Plateau in the late Cenozoic epoch, the income of dust from sand deserts into the atmosphere increased significantly. Then this dust experienced a long-range transport, and the Loess Plateau served the main center of the dust accumulation. Stratigraphic investigations showed that this accumulation of dust aerosol started no less than 7 to 8 thousand years ago in the main part of the Loess Plateau and as far back as 22 thousand years ago in its western region. According to the available paleoclimatic data, the process of dust

accumulation, occurring for the past 2500 years, was characterized by the intervals of intense dust deposition and weak chemical weathering (pedogenesis) during glacial periods, which were alternated with moderate dust deposition and intense pedogenesis during interglacial periods. The dependence of the dust deposition process on the dynamics of paleomonsoons determines the possibility of the corresponding retrievals from the stratigraphic data.

Sun with the co-workers[50] analyzed samples of dust aerosol collected at six sites on the Chinese Loess Plateau during 1995–1996 and 2000. The dusts were mainly composed of mineral grains in addition to a considerable amount of organic material, especially in the case of the dusts deposited in summer. The magnetic susceptibility of these modern dusts was generally higher than that of glacial loess, and, in addition, they showed clear seasonal variations with maximum values in summer dust and minimum values in the winter dust. Assuming that the effects of pollution on the modern dust can be excluded, implies that high susceptibility values of Quaternary paleosols may arise either from the direct effect of climate or from further enhancement due to post-depositional pedogenesis. The pattern of seasonal dust flux shows that most of the total annual dust deposition is generated by continuous deposition throughout the year rather than by dust storms in specific seasons; however, the flux does exhibit seasonal variability with the highest values occurring in spring or early summer, especially in the northern Loess Plateau.

The grain-size distribution of modern dust shows an asymmetrical pattern that is analogous to Quaternary loess. Seasonal variations in dust grain size are characterized by coarsening in spring and summer and by fining in fall and winter. In a specific site, the dust grain-size strongly depended on height above the local ground surface and decreased nonlinearly with increasing height. Vertical profiles of dust concentration, spatial trends, and the seasonal variability of dust flux and grain size evidence that modern dust, and thus Quaternary loess, is mostly transported at a low level of the atmosphere throughout the year with intensified dust deposition in spring and early summer. Nowadays signatures of the anthropogenic component can be found in the atmospheric dust.

The tropical Indian Ocean is likely the unique region on the globe, where the highly polluted air masses from the Northern Hemisphere contact clear air of the Southern Hemisphere as the monsoon flow crosses the equator. That is why the water area of the Indian Ocean, situated west and south of the Indian Subcontinent (10°N–11°S, 55°E–75°E), was selected as the main region for the Indian Ocean Experiment (INDOEX), whose main objective was to study the annual (November–April) spread of the Indo-Asian haze. During the Intense Field Phase-99 (IFP) in January–March 1999, various satellite, airborne,

shipborne, and ground-based observation facilities were used.

In this connection, Franke with co-authors[25] discussed the results of aerosol sensing of the atmosphere with a unique aerosol Raman lidar at Hulhule (4°N, 73°E), Maldives, as a part of the Indian Ocean Experiment (INDOEX) between February 1999 and March 2000. The obtained vertical profiles of the aerosol extinction coefficient at the wavelengths of 355 and 532 nm corresponded to conditions of heavily polluted atmosphere. The mean 532-nm aerosol optical depth was about 0.3; maximum values of 0.7 were measured. Above the polluted marine boundary layer, lofted plumes were found at up to 4-km heights. On the average, the free-tropospheric aerosol layers contributed 30 to 60% to the aerosol optical depth. The aerosol extinction coefficient at 532 nm typically ranged from 25 to 175 Mm^{-1} in the elevated layers.

The pollution plumes j were characterized in Ref. 25 separately for the air masses from Southeast Asia, North India, and South India. The extinction-to-backscatter ratio (lidar ratio) at 532 nm was mostly between 30 and 100 sr, and about 50 to 80 sr for highly absorbing particles from the northern India. The shift of the lidar-ratio distribution for northern Indian aerosols by about 20 sr toward larger values compared to European values is consistent with an aerosol black-carbon content of up to 20%. The Angström exponent (for short wavelengths 355/400/532 nm) ranged mostly from 1 to 1.6 for Southeast Asian particles, from 0.8 to 1.4 for North Indian pollution, and from 0.6 to 1 for South Indian air masses. The comparably low Indian Angström exponents are possibly caused by the high contribution of biomass combustion to the aerosol formation in India. Correlation analysis of the lidar ratio, extinction coefficient, Angström exponents, and relative humidity showed that in the most cases this correlation was weak or absent at all.

During the ACE-Asia intensive observation period (IOP), aimed at the study of aerosol characteristics, on April 23 of 2001 near Tokyo, Murayama with co-workers[42] conducted ground-based lidar sensing of the atmosphere, whose results were compared with the data of airborne measurements. Four ground-based lidars were simultaneously operated in Tokyo region, while the aircraft flew a stepped-ascent profile between the surface and 6 km over Sagami Bay southwest of Tokyo. The airborne observation package included a tracking Sun photometer and *in situ* packages measuring aerosol optical properties, aerosol size distribution, aerosol ion composition, and SO_2 concentration.

The three polarization lidars suggested that the observed modest concentrations of Asian dust in the free troposphere extended up to an altitude of 8 km. A good agreement was found in the backscattering coefficient at 532 nm among lidar and nephelometer observations. The intercomparison indicated that the aerosol layer between 1.6 and 3.5 km was a

remarkably stable and homogenous in mesoscale. A reasonable agreement was also observed between the aerosol extinction coefficients ($\sigma_a \sim 0.03$ km^{-1}) derived from the airborne tracking Sun photometer and those estimated from the lidars above the planetary boundary layer (PBL). Considerable vertical variation of the aerosol depolarization ratio (δ_a) and a negative correlation between δ_a and the backscattering coefficient (σ_{bsp}) below 3.5 km were found.

Airborne measurements of size-dependent optical parameters (e.g., the scattering by fine-mode fraction) and of aerosol ion compositions suggests that the mixing ratio of the accumulation-mode and coarse-mode (dust) aerosols was primarily responsible for the observed variation of δ_a. Aerosol observations during the intercomparison period have revealed the following three types of layers in the atmosphere: 1) a PBL (from surface to 1.2−1.5 km) where fine (mainly sulfate) particles with a low δ_a (< 10%) dominated; 2) an intermediate layer (between the top of the PBL and 3.5 km) where fine particles and dust particles were moderately externally mixed, giving moderate δ_a; 3) and an upper layer (above 3.5 km) where dust dominated, giving a high δ_a (30%). A substantial dust layer between 4.5 and 6.5 km was observed west of Japan by the airborne instruments and was found to have a lidar ratio of 50.4 ± 9.4 sr. This agrees well with nighttime Raman lidar measurements made later in this same dust layer as it passed over Tokyo, which found a lidar ratio of 46.5 ± 10.5 sr.

Fast industrial development and population growth in Eastern Asia have resulted in a considerable increase of the anthropogenic pollution of the atmosphere due to industrial and farming sources, which is also complemented with powerful atmospheric emissions of dust aerosol during dust storms in Northwestern China, especially, in spring. Tropospheric pollutions by various trace gases, as well as anthropogenic, dust, volcanic, and marine aerosol experience transformation and long-range transport to the western sector of the Pacific Ocean. Carrico et al.[18] analyzed the results of observation of the trace gases and aerosol concentration in the troposphere over the Pacific Ocean carried out during the *Ron Brown* cruise as a part of ACE-Asia (March 15−April 20 of 2001).

The use of nephelometer measurements allowed the determination of scattering (σ_{sp}) and backscattering (σ_{bsp}) coefficients at different wavelengths depending on the relative humidity *RH* for particles with the aerodynamic diameter d_p from 1 to 10 μm. During the first ten days of the cruise, which started near Hawaii under conditions of unpolluted air masses, the backscattering coefficient at 550 nm was $\sigma_{sp} = (23 \pm 13) \cdot 10^{-6}$ Mm^{-1}, the absorption coefficient was $\sigma_{ap} = (0.5 \pm 0.3)$ Mm^{-1} (relative humidity of, respectively, 19 and 55%, $d_p < 10$ μm). The marine aerosol was highly hygroscopic and showed quite distinct signs of

deliquescence and hysteresis. As approaching the East-Asian coast, the air masses became more polluted, which was represented by the following values: $\sigma_{sp} = (64 \pm 30)$ Mm^{-1}, $\sigma_{ap} = (6.6 \pm 4.4)$ Mm^{-1} and the large contribution of submicron aerosol to the formation of σ_{sp}. Aerosol in these cases was less hygroscopic and characterized by a wide range of vegetation variability.

Strong scattering was typical of the volcanic aerosol as well:

$$\sigma_{sp} = (114 \pm 66) \text{ Mm}^{-1} \text{ and } \sigma_{ap} = (11.7 \pm 5.6) \text{ Mm}^{-1},$$

as well as significant role of the submicron aerosol fraction. This aerosol was highly hygroscopic. The most intense scattering is typical of the dust aerosol: $\sigma_{sp} = (181 \pm 82)$ Mm^{-1}; $\sigma_{ap} = (12.1 \pm 6.4)$ Mm^{-1} with a significant contribution from both super- and submicron particles to the formation of optical properties.

The most important features of the aerosol observed over the Pacific Ocean in the Northern Hemisphere consisted in the domination of scattering caused by such aerosol properties as deliquescence, hysteresis, and existence of metastable droplets. The average *RH* values, at which deliquescence and crystallization occurred were 77 ± 2% and 42 ± 3%, respectively. The mean value of the ratio $R = \sigma_{sp}$(*RH* corresponding to the conditions of the ambient atmosphere)/σ_{sp}(at *RH* = 19%) ranged from 1.25 (dust) to 2.88 (volcanic). The hemispheric backscatter fraction at ambient *RH* ranged from 0.077 (marine) to 0.111 (dust), while single scattering albedo at ambient *RH* ranged from 0.94 (dust and polluted) to 0.99 (marine). The Angström coefficient was characterized by a weak dependence on *RH*, but differed widely for aerosol of different types, varying from 0.16 ± 0.60 (marine aerosol) to 1.49 ± 0.29 (volcanic aerosol).

The dependence of the single scattering albedo on the content of the aerosol components absorbing the short-wave radiation (first of all, the soot component) is the dominant factor of the sensitivity of aerosol radiative forcing to the chemical composition of aerosol. In this connection, Höller et al.,[27] studied the dependence of the aerosol optical properties on the size and composition of aerosol particles within the framework of the Asian Pacific Regional Aerosol Characterization Experiment (ACE-Asia) campaign for three weeks in March−April 2001 at Yasaka (Japan: 35.37°N; 135.81°E) on the coast of the Sea of Japan. On the other hand, the optical properties of aerosol were calculated using preset chemical composition and size distribution of the aerosol particles, including absorbing material, for the following comparison with the experimental findings. Continuous, size-resolved measurements of aerosol scattering and backscattering coefficients were made at the wavelengths of 450, 550, and 700 nm. Aerosol size distribution measurements were taken three times during the campaign for a period of

3−4 days each, using cascade impactors. One of the measurement periods was influenced by an intense yellow dust event originating on the Asian continent (20−25 March 2001), while the other two data sets were only weakly influenced by the dust particles.

The experimental findings showed that the dust was accompanied by fine accumulation-mode particles during the dust event. The effects of the mineral dust particles on the optical and chemical properties of the aerosol were discussed, and data sets with and without desert dust influence were compared. Before the optical closure calculation, a mass closure of the aerosol was performed for each aerosol component, and the influence of the nonanalyzed fraction (mostly, the volatile and absorbing components) on the calculated optical properties of the aerosol was investigated. In general, good agreement between measured and modeled aerosol optical properties was found for the aerosol scattering and absorption coefficients, while the agreement was found for the backscattering coefficients, especially for the coarse mode of the aerosol was worse. A distinct difference between the dust and dust-free periods was found for the wavelength-dependent single-scattering albedo. In the former case, when the mass concentration of aerosol was maximum, the single scattering albedo increased with the increasing wavelength, whereas in the third observation period (minimum aerosol content) the albedo decreased with the wavelength.

Bahreini with co-authors[14] considered the results of observation of the size distribution and chemical composition of the atmospheric aerosol conducted during ACE-Asia using an Aerodyne aerosol mass spectrometer (AMS) set onboard the Twin Otter aircraft. Research flights were carried out from 31 March to 1 May 2001 over the area that covered 127°E−135°E and 32°N−38°N region, and valid data were obtained during 15 out of a total of 19 research flights. The AMS measured distinct layers (from the boundary layer to about 3.7 km) of submicron aerosols composed of sulfate, ammonium, and organics, separated by layers with much lower aerosol concentrations. Sulfate and organics mass concentrations of up to 10 $\mu g/m^3$ and 13 $\mu g/m^3$, respectively, were measured in some aerosol layers.

Back-trajectory analysis showed that the polluted aerosol layers originated in urban and industrial areas of China and Korea. The mass-weighed size distribution of the submicron sulfate was relatively constant from day to day and layer to layer, with an aerodynamic diameter mode of 0.4−0.5 μm and a width (full width at half maximum) of about 0.45 μm in most of the layers. On the days with low influence of dust in the aerosol outflow, the total mass of nonrefractory aerosols correlated well with the total volume of aerosols.

Airborne (C-130 aircraft) measurements of aerosol light scattering (using nephelometers) and absorption (using particle/soot absorption photometers; PSAPs) in the period from March 28 to May 6 of 2001 yielded rich information about the optical properties of the atmospheric aerosol. The analysis of these observations[13] revealed the presence of the dominant components: fine-mode pollution and coarse-mode mineral dust. Fine-mode pollution was found to be moderately absorbing (single scattering albedo at 550 nm under conditions of low RH is $\omega = 0.88 \pm 0.03$; within 95% confidence interval) and moderately hygroscopic (relative increase in scattering with the increasing RH, from 40% to 85%), while coarse-mode dust was found to have very low absorption ($\omega = 0.96 \pm 0.01$) and to be almost nonhygroscopic. These results can be used as constraints on optical models of the Asian aerosol in calculations of the direct radiative effects.

Zhang et al.[57] analyzed the aerosol samples collected at Kumamoto (32°48′N, 130°45′E), a coastal city in southwestern Japan, during three dust storm events in spring of 2000. The elemental composition and size of individual dust particles and the state of their mixing with sea salt, sulfate, and nitrate were analyzed using electron microscopes and an energy disperse X-ray spectrometer. About 60−85% of all dust particles were internally mixed with sea salt. Weather records indicated that these particles were most probably formed by the collisions and coagulations of dust particles and sea-salt particles.

The relative weight ratios of mineral components to sea salt in individual particles showed that the mixtures of particles were dominated by mineral, by sea salt, or by both. Size distributions of the particles in the three dust storm events were similar, and all distributions showed a diameter range of 1−8 μm with maximum mode around 3 μm. Out of 1−8 μm size range, dust particles were rarely detected. The combination of dust particles with sea salt caused an increase in size of the dust particles. The decrease of particle concentrations in the range of diameters > 3 μm suggests that a dust particle might be removed rapidly if it became larger than this scale in the marine atmosphere.

Detection of sulfate and nitrate revealed that 91% of dust particles or even more contained sulfate and 27% or less contained nitrate. The comparisons of the relative weight ratios of sodium, sulfur, and chlorine in mixture particles and in sea-salt particles confirmed previous results that mineral materials could enhance particulate sulfate and nitrate formation and restrain chlorine depletion from the sea-salt components in mixture particles. It was emphasized that these results were obtained in the absence of aerosol "processing" by clouds, which significantly change the aerosol properties.

As a part of the APEX-E2 and ACE-Asia field campaigns, Sano et al.[48a] investigated the optical properties of the atmospheric aerosol using multispectral Sun photometers (CE-318-1 and -2) and a polarimeter (PSR-1000) over Amami-Oshima (28.37°N; 128.50°E), Noto (37.33°N; 137,13°E), and Shirahama (33.68°N; 135.35°E).

The radiometer data were used to retrieve the optical thickness of aerosols and the Angström

exponent, while other aerosol characteristics, e.g., size distribution, refractive index, etc., were retrieved using the entire set of the measurement data. The HYSPLIT-4 back trajectory analysis was performed to determine the origin of aerosols. The results obtained showed that aerosol optical thickness, Angström exponent, and refractive index can be classified into two categories: 1) a background type detected in winter and 2) a soil dust type appeared in Chinese dust events in spring. The obtained size distribution of Asian dust indicated the dominance of large particles.

The fourth field campaign of PEM-Tropics B was carried out in March—April 1999 as a part of the Global Tropospheric Experiment (GTE) and involved the study of the gas and aerosol composition of the troposphere using the instrumentation installed onboard a DC-8 and P-3 instrumented aircrafts. Aerosol sampling onto filters from the NASA Wallops Island P-3 aircraft and a tower on Christmas Island provided an opportunity to study the aerosol-associated final products of the sulfur cycle: non-sea-salt sulfates nss-SO_4^{2-} and methane sulfates MS^-, in order to check the adequacy of the model of sulfur cycle in the marine boundary layer.

The analysis of the observations carried out by Dibb with co-workers[22,23] showed that the concentration of the most aerosol-associated ions decreases strongly with height above the sea surface, making direct comparisons between mixing ratios at 30 m on the tower and the lowest flight level of the P-3 (150 m) open to interpretation. Theoretical considerations suggest that vertical gradients of sea-salt aerosol particles should show exponential decreases with height. Observed gradients of Na^+ and Mg^{2+}, combining the tower observations with P-3 samples collected below 1 km, are well described by exponential decreases, though the curve fit underestimates average mixing ratios at the surface by 25%.

Cascade impactor samples collected on the tower show that >99% of the Na^+ and Mg^{2+} mass is on supermicron particles, 65% on the particles of 1—6 micron size range, and just 20% on the particles with diameters larger than 9 microns. These results indicate that the airborne aerosol sampling probes must efficiently catch particles up to at least 6 microns size. The observations also showed that nss-SO_4^{2-} and NH_4^+, which are dominantly on accumulation mode particles, tended to decrease at heights between 150 and 1000 m, but they were often considerably higher at the lowest P-3 sampling altitudes than at the tower. This finding is presently not well understood. It is possibly a consequence of a decrease in the concentration of nss-SO_4^{2-} and NH_4^+ near the sea surface due to their condensation on the surface of large particles, which are then involved quickly in the process of dry sedimentation.

Using the data of sampling on 414 filters collected in spring 2001 from onboard the DC-8

aircraft, Dibb et al.[22,23] analyzed the concentration of aerosol-associated soluble ions and the radionuclide tracers ^7Be and ^{210}Pb. The comparison of the results corresponding to the coastal Pacific (flights from Hong Kong and Japan) and remote Pacific revealed large enhancements of NO_3^-, SO_4^{2-}, $C_2O_4^{2-}$, NH_4^+, K^+, Mg^{2+}, and Ca^{2+} in the coastal zone. There the boundary layer and the lower troposphere were most strongly influenced by the continental outflow, and the largest enhancement was seen in Ca^{2+} (a dust tracer) and NO_3^- (reflecting uptake of HNO_3 onto the dust). Comparing the TRACE-P data with earlier results from the same region during PEM-West B (in 1994) showed at least twofold enhancement during TRACE-P in most of the ions listed above. The concentrations of Ca^{2+} and NO_3^- were most enhanced according to this comparison as well (more than sevenfold higher in the boundary layer and threefold higher in the lower troposphere). Most probably, the enhancements largely reflect the fact that TRACE-P focused on characterizing the Asian outflow, and thus the DC-8 was more frequently flown into regions that were influenced by well-organized flow off the continent. Thus, there are no grounds to believe that the atmosphere became much more polluted for the period of 1994—2001.

Mass-independent (MI) sulfur isotopic anomalies recently observed in Precambrian rock samples have been attributed to photochemistry and used to establish oxygen levels in Earth's early atmosphere. In this connection, Romero and Thiemens[48] considered the first data on the MI sulfur isotopic composition in the present atmosphere, obtained from samples of Northern Hemispheric aerosol sulfate. The analysis of the paleo- and current data revealed no correlation between MI sulfur isotopic compositions and MI oxygen signatures previously observed in the same samples. Antarctic dry valley soil sulfate, which is atmospheric in origin and has an MI oxygen signature, appeared to be mass-dependent (MD) with respect to sulfur. Therefore, a different process than that proposed is required to explain the MI oxygen signature in sulfate. Possible sources of the anomaly were discussed, as well as potential applications to global climate and implications for Archean geology and the Earth's early atmosphere.[48]

Existing studies of the composition of volcanic plumes generally interpret the presence of sulfate aerosol as the result of comparatively slow oxidation of gaseous SO_2. Allen et al.[12] reported new observations from Masaya Volcano, Nicaragua, which demonstrate that sulfate aerosol may also be emitted directly from volcanoes. Simultaneous aerosol and gaseous SO_4^{2-}, Cl, and F compounds were collected at the rim of the passively degassing crater in May 2001. Mean concentrations of SO_4^{2-}, Cl^-, and F^- within the plume were 83, 1.2, and 0.37 µg/m^3, respectively (fine aerosol fraction < 2.5 µm) and 16, 2.5, and 0.56 µg/m^3, respectively (coarse aerosol fraction > 2.5 µm).

The aerosols were highly acidic, with estimated pH of < 1.0 in the fine aerosols. Sulfate was present mainly in smaller particles, with the fine fraction accounting for about 80% of the mass. The bulk of the sulfate was emitted into the atmosphere directly through the magmatic vents. Acidity in the aerosols derived from the presence of sulfuric acid and, to a lesser extent, hydrofluoric acid, with $[H^+]/[SO_4^{2-}]$ equivalent values of 0.5–0.8 and 0.3–3 for fine and coarse aerosols, respectively. Gas phase/aerosol phase mass ratios were, on average, 458 (S), 330 (F), and 186 (Cl), with ranges of 95–1178, 37–659, and 43–259, respectively.

On the basis of observations with a cascade impactor at the research station Halley, situated near the coast in the Weddell Sea region of Antarctica, Rankin and Wolff[47] analyzed the dependence of aerosol composition on the particle size. According to the results obtained during 2 week intervals throughout a year, sea salt is a major component of aerosol, and at least 60% of the total sea salt arriving at Halley is from brine and frost flowers on the sea ice surface rather than open water. Chloride in sea-salt particles is depleted relative to sodium in summer, consistent with the loss of HCl as sea-salt particles react with gaseous acidic species, but is enhanced in large particles in winter because of fractionation occurring during the production of new sea ice.

Non-sea-salt sulfate (nss-SO_4^{2-}) peaks in the summer, with the majority being in small particles indicative of a gas phase origin. The distribution of methane sulfonic acids (MSA) closely follows that of non-sea-salt sulfate. The peak of the MSA content is observed in summer mostly being caused by the submicron aerosol. Gas-phase oxidation of dimethylsulfide is likely the main source of both nss-SO_4^{2-} and MSA. The mass concentration ratio of MSA to nss-SO_4^{2-} increases with the increasing particle size.

In winter, nss-SO_4^{2-} is frequently negative, especially in the case with large particles, what is consistent with that the source of sea salt in winter is predominantly the sea ice surface rather than open water. Aerosol nitrates peak in spring and summer and show some association with sea-salt particles. The size distribution of nitrates is similar to that of sodium, and they are probably determined by the reaction of the nitric acid vapor with particles of sea-salt aerosol (this process is likely the main contributor to the decrease of the chloride content).

The wide spatiotemporal variability of the aerosol properties naturally dictates the need in using not only ordinary, but also spaceborne observational facilities. This explains the long history of the development of remote sensing of aerosol from satellites.[1–3,32]

One of the successful examples of satellite aerosol monitoring is the observation of the evolution of biomass burning on regional and global scales.

Depending on such factors as precipitation amount and deforestation decisions, the biomass burning due to both natural (forest fires) and anthropogenic causes varied very widely. Dramatic events included, in particular, forest fires in Indonesia (1997–1998) and Mexico (1998), associated with El Niño/South Oscillation (ENSO) phenomenon, leading to droughts. Although such events mostly occur in tropics, large forest fires took place in middle and high latitudes of the Northern Hemisphere as well (for example, forest fires in Western Europe in summer of 2003).

Duncan et al.[24] proposed a methodology for estimating the seasonal and interannual variation of biomass burning designed for use in global chemical transport models. The average seasonal variation was estimated from 4 years of fire-count data from the Along Track Scanning Radiometer (ATSR) and 1–2 years of similar data from the Advanced Very High Resolution Radiometer (AVHRR) World Fire Atlases. The Total Ozone Mapping Spectrometer (TOMS) Aerosol Index (AI) data product was used as a surrogate to estimate interannual variability in biomass burning for six regions: Southeast Asia, Indonesia and Malaysia, Brazil, Central America and Mexico, Canada and Alaska, and Asian Russia.

This methodology was applied to estimate mean seasonal and interannual variations for emissions of carbon monoxide from biomass burning, and it was found that no trend is apparent in these emissions over the past two decades (1979–2000), but that there is significant interannual variability. The annual emissions of CO in the studied regions varies from 20 (Asian Russia and China) to 170 Tg/year (Indonesia and Malaysia in 1997–1998) with the mean total global emissions equal to 437 Tg/year (annual values varying from 429 to 565 Tg/year).

Wang et al.[53] analyzed the matched (in space and time) results of retrieval of the aerosol optical thickness (AOT) at 670 nm, using the following sources of information: 1) ground-based observations with Sun photometers at 12-site AERONET network; 2) AATS-6 6-channel Sun photometer onboard a C-130 instrumented aircraft; 3) AATS-14 14-channel airborne (Twin Otter) Sun photometer; 4) shipborne (RV *Ronald H. Brown*) Sun photometer; 5) Visible Infrared Spin-Scan Radiometer (VISSR) onboard a GMS-5 geostationary satellite. In addition, the data of ground-based observations of the aerosol size distribution at the Gosan station (Cheju Island, South Korea) were used. Particular attention was paid to analysis of the GMS-5 data for 30 days (April 2001) with the half-hour interval and the comparison of observations with AOT calculated based on the DISORT technique.

The results discussed were obtained during ACE-Asia and correspond to the Western Pacific (20°–45°N; 110°–150°E). The comparison of satellite and ground-based (AERONET) data on AOT revealed a good agreement with the linear correlation coefficient *R* for four ground sites equal to 0.86,

0.85, 0.86, and 0.87. The satellite-derived AOTs were also in good agreement with the airborne ($R = 0.87$) and shipborne measurements ($R = 0.98$). The average uncertainty in AOT retrievals was about 0.08 with a maximum value of 0.15 mainly due uncertainties in calibration (± 0.05), surface reflectance ($\pm 0.01 - \pm 0.03$), and imaginary part of the refractive index (± 0.05). The monthly mean AOT spatial distribution from GMS-5 retrievals in April 2001 clearly showed the transport pattern of aerosols with high AOT near the coast of east Asia and low AOT over the open ocean. An important advantage of the data of geostationary satellites is that they provide the information about the diurnal behavior of AOT.

The use of the Moderate Resolution Imaging Spectroradiometer (MODIS) (7 channels: 470–2100 nm, 250–500 m resolutions) as a part of the research instrumentation installed onboard the Terra and Aqua satellites has opened new possibilities in studying the atmospheric aerosol. MODIS retrieves not only aerosol loading but also the fine aerosol fraction. MODIS can be used in monitoring of global, regional, and local air pollution. Its capabilities were demonstrated[19] by the results of processing the data on Italy, Los Angeles, and Beijing in order to retrieve the aerosol optical depth τ_a for the analysis of regional and local air pollution in terms of accuracy $\Delta\tau_a = \pm(0.05 \pm 0.2)\tau_a$.

Under stagnant conditions, accumulated aerosol abundance can reach $\tau_a > 1$ (at 550 nm) before being removed by wind or precipitation. The correlation found between Aerosol Robotic Network (AERONET) daily averaged τ_a and 24-hour PM-10 (particulate matter with the diameter < 10 μm) concentration (μg/m^3) in northern Italy was encouraging with the correlation coefficient of 0.82. The derivation of PM concentration from satellite measurements can be possible once the detailed aerosol vertical distribution is known. The promises of obtaining such information (and, consequently, the data on the aerosol concentration near the surface) are connected with the use of results of satellite lidar sensing (Geoscience Laser Altimeter System (GLAS) launched in 2003 and Cloud-Aerosol Lidar CALIPSO to be launched in 2004).

To compare aerosol loading in different regions of the globe, Chu with co-workers[19] chose two most populated regions (eastern China and India) and two most industrialized regions (the eastern United States/Canada and western Europe). The time series of MODIS monthly mean τ_a from July 2000 to May 2001 showed a strong seasonal variation with maxima in spring/summer and minima in the winter. Clear separation between (1) the eastern United States/Canada and western Europe and (2) eastern China and India is determined by the fact that the values τ_a in (2) are 50% to 2–3 times higher than those in (1). The observed enhancements of aerosol loading were due to smoke originated from Montana/Idaho forest fires transported to the eastern United States in late August 2000 and dust outbreaks

from Taklamakan and Gobi Deserts to eastern China as well as smoke from Southeast Asia to southern China in February–April 2001.

Summarizing the results of the analysis of observed properties of atmospheric aerosol, the well-known fact should be emphasized that further developments and realization of the global observation system involving both ordinary and satellite observational facilities, as well as regular conduction of coordinated problem-oriented combined field campaigns are needed.

Processes of aerosol formation (nucleation)

Because of the wide variety of aerosol formation processes, the analysis of these processes has to be restricted to consideration of most significant and well-studied processes.[3,35,36,39,41,46] The central problem in this context is the problem of nucleation of aerosol particles. Külmälä[36] fairly noted that many aspects in nucleation processes remain unclear from the viewpoint of justification of the priorities, but the indisputable progress has been achieved in recent years in the development of measurement techniques, which allowed the processes of particle nucleation and growth to be monitored in all ranges of the particle size, starting from nanoparticles, and not only near the Earth's surface, but also in the free atmosphere, including the lower stratosphere. New important data about the surprisingly high concentration of ultrafine particles in the upper troposphere were obtained by Lee with co-workers.[39] They discovered the particular role of ion-induced nucleation as a globally important mechanism of formation of aerosol particles. In recent years, the particular attention was paid to the study of nucleation in coastal zones.

The earlier investigations revealed the presence of biogenic sources of aerosol formation in the boundary layer in different regions of the globe (this especially applies to boreal forests and coastal tidal zones). Likely, nucleation events regularly appear in the sea coastal zones. This is true at least for Western Europe, where the formation of nucleation aerosol (NA) was often observed on Scotland, Ireland, England, and French coasts. The formation of NA was also recorded in the Southern Hemisphere near the shoreline in Antarctic and in Tasmania.

The observations of the increased concentration of aerosol particles in the coastal boundary layer are dated back to the 1880s, when Aitken found the considerable increase in the aerosol number concentration near the western coast of Scotland from 200–300 cm^{-3} to more than 10^4 cm^{-3}. Modern studies detected the regularity in the events of the enhanced NA concentration, which achieved sometimes 10^6 cm^{-3} and higher with the dominant particle size ranging from 0.003 to 0.01 μm. A dedicated study into the formation of new particles, New Particle Formation and Fate in the Coastal

Environment (PARFORCE), was conducted over a period from 1998 to 1999 at the Mace Head Atmospheric Research Station on the western coast of Ireland. Continuous measurements of new particle formation were taken over a 2-year period while two intensive field campaigns were also conducted, one in September 1998 and the other in June 1999.

The analysis carried out by O'Dowd et al.[44] of the results obtained showed that new particle events were observed on ~ 90% of days and occurred throughout the year and in all types of air mass. These events lasted for, typically, a few hours, with some events lasting more than 8 hours, and occurred during daylight hours coinciding with the occurrence of low tide and exposed shorelines. During these events, peak aerosol concentrations often exceeded 10^6 cm^{-3} under clean air conditions, while measured formation rates of detectable particle sizes (i.e., $d > 0.003$ μm) were of the order of $10^4 – 10^5$ cm$^{-3} \cdot$ s^{-1}. Nucleation rates of new particles were estimated to be, at least, of the order of $10^5 – 10^6$ cm$^{-3} \cdot$ s^{-1} and occurred for sulfuric acid concentrations above $2 \cdot 10^6$ molecules $\cdot$ cm^{-3}. However, no correlation existed between peak sulfuric acid H_2SO_4 concentrations, low tide occurrence, or nucleation events.

Ternary nucleation theory of the $H_2SO_4 – H_2O – NH_3$ system predicts that nucleation rates far in excess of 10^6 cm$^{-3} \cdot$ s^{-1} can readily occur for the given sulfuric acid concentrations. However, modeling studies of the aerosol growth predict that there is insufficient sulfuric acid to grow new particles (of 0.001 μm in size) into detectable sizes of 0.003 μm. Hygroscopic growth factor analysis of recently formed 0.008-μm particles illustrates that these particles must comprise some species significantly less soluble than sulfate aerosol.

The nucleation-mode hygroscopic data, combined with the lack of detectable VOC emissions from coastal biota, the strong emission of biogenic halocarbon species, and the fingerprinting of iodine in recently formed (0.007 μm) particles suggest that the most likely species resulting in the growth of new particles to detectable sizes is an iodine oxide as suggested by previous laboratory experiments. However, it remains an open question on whether the nucleation is driven by self-nucleation of iodine species, a halocarbon derivative, or first, stable clusters are formed through ternary nucleation in the $H_2SO_4 – H_2O – NH_3$ system, followed by condensation growth into detectable sizes by condensation of iodine species.

Airborne measurements confirm that nucleation occurs all along the coastline and that the coastal biogenic aerosol plume can extend many hundreds of kilometers away from the source. During the evolution of the coastal plume, particle growth is observed up to optically active sizes of 0.1 μm. Modeling studies of the yield of cloud-condensation nuclei suggest that the cloud condensation nuclei population can increase by 100%. Given that the production of new particles from coastal biogenic sources occurs at least all along the western coast of Europe, and possibly many other coastlines, it was suggested that coastal aerosols contribute significantly to the natural background aerosol population. Although the results obtained during PARFORCE are very important, they still do not allow opening the real mechanisms of nucleation and growth of aerosol particles in coastal zones.

Condensation particle counters (CPCs), having different detection limits, are among the most efficient tools for studying the formation of new aerosol particles in the atmosphere. Thus, for example, the TST-3025 instrument measures the total number concentration of particles larger than 0.003 μm in diameter (at the relative humidity of 50%), whereas the detection limit of TST-3010 is 0.01 μm (number concentration N_{10}). The difference $N_3 – N_{10}$ determines the number concentration of particles having the diameter from 0.003 to 0.01 μm. The short lag of the instruments (about 1 Hz) provides for the possibility to track fast changes in the aerosol properties, as well as to distinguish among the accumulation mode, Aitken mode, and other particles.

Hämeri et al.[26] discussed the results of observations with four counters for measurement of N_3, arranged in a spatial array comprising a triangular distribution with nodes approximately 100 m apart (two at 3 m height, and two others at 10 m and 20 m). The counters at 10-m and 20-m heights had the detection limits of 0.005 and 0.01 μm. During the nucleation events it was found that peak particle concentrations of the order of $1.8 \cdot 10^5$ cm^{-3} were encountered. From the field calibration, it was found that, at concentrations over 10^5 cm^{-3}, the CPCs significantly underestimated the true concentrations by a factor of 5–6. Total particle concentrations measured with CPC were compared with the integrated concentration derived from the ultrafine Differential Mobility Particle Sizer (DMPS). This comparison confirmed that peak particle concentrations during coastal nucleation bursts result in new particle concentrations as high as $1.2 \cdot 10^6$ cm^{-3}. The rates of formation of N_3 particles were estimated to be higher than 10^5 cm$^{-3} \cdot$ s^{-1}. The analysis of spatial homogeneity in the distribution of concentration revealed that within the general coastal nucleation plume, there are numerous microplumes with spatial scales of the order of 10–100 m when sampling is conducted near the source region. Farther from the source region, these microplumes merge into the general coastal plume.

The direct effect of atmospheric aerosol on the radiative transfer through the atmosphere and the indirect effect through the change of microphysical and radiative properties of clouds as a result of their mixing with aerosol are among the important climate-forming factors. In the context of the indirect effect of aerosol on radiative forcing, of critical significance is the adequate understanding of such processes of

aerosol–cloud interaction, which are connected with coagulation, condensation, chemical reactions in the aqueous phase, and deposition, which change the size distribution of both aerosols and clouds. In this connection, it is very important to study the formation of new aerosol particles under the conditions of unpolluted atmosphere. In this context, O'Dowd et al.[45] discussed the results of observation of coastal nucleation events at Mace Head (Ireland) during intensive New Particle Formation and Fate in the Coastal Environment (PARFORCE) field campaigns in September 1998 and June 1999.

Nucleation events were observed almost on a daily basis during the occurrence of low tide and solar irradiation. In September 1998, average nucleation mode particle concentrations were 8600 cm^{-3} during clean air events and 2200 cm^{-3} during polluted events. By comparison, during June 1999, mean nucleation mode concentrations were 27000 cm^{-3} during clean events and 3350 cm^{-3} during polluted conditions. Peak concentrations often reached $5 \cdot 10^5 - 1 \cdot 10^6 \text{ cm}^{-3}$ during the most intense events and the duration of the events ranged from 2 to 8 hours with the mean of 4.5 hours. Source rates for detectable particle sizes ($d > 3 \text{ nm}$) were estimated to be between 10^4 and $10^6 \text{ cm}^{-3} \cdot \text{s}^{-1}$ and the initial growth rates of new particles were as high as $10^{-4} - 3.5 \cdot 10^{-4} \text{ μm} \cdot \text{s}^{-1}$ at the tidal source region. Recently formed 8-nm size particles were subjected to hygroscopic growth and were found to have a growth factor of $1.0 - 1.1$ for humidification at 90% relative humidity. The low growth factors implicate a condensable gas with very low solubility. However, it remains unclear if this condensable gas also leads to homogeneous nucleation.

Measured sulfuric acid and ammonia concentrations suggest that ternary nucleation of thermodynamically stable sulfate clusters is still likely to occur. In clear air, significant particle production ($> 10^5 \text{ cm}^{-3}$) was observed with sulfuric acid gas-phase concentration as low as $2 \cdot 10^6$ molecules cm^{-3} and under polluted conditions as high as $1.2 \cdot 10^8$ molecules $\cdot \text{cm}^{-3}$. The observed concentration of sulfuric acid vapor was sufficient for formation of nucleation-mode particles, but too low for production of new particles with detectable size. For formation of detectable-size particles, an additional biogenic source of a low-solubility gas is needed. The most probable gas of this kind is iodine oxide, produced at photodissociation of CH_2I_2 molecule.

Further investigations are needed in order to reveal whether the observed concentration of H_2SO_4 vapor is sufficient for formation of the necessary amount of stable clusters. Otherwise, the observations of particles formation at Mace Head can be interpreted only as a consequence of nucleation and condensation growth of iodine oxide.

According to theory of nucleation, gaseous sulfuric acid is an immediate precursor and the main source of submicron particles of atmospheric sulfate aerosol. Such particles, $0.1 - 1 \text{ μm}$ in diameter,

contribute considerably to the extinction of solar radiation reaching the Earth's surface both directly and indirectly — through the aerosol-induced increase of the cloud albedo. Since many problems concerning *in situ* formation of new aerosol particles through gas-phase transformation of H_2SO_4 are still unsolved and the estimates of the aerosol-induced radiative forcing are insufficiently reliable, Berresheim et al.[15] measured atmospheric concentrations of gaseous sulfuric acid (H_2SO_4), methane sulfonic acid (MSA), and hydroxyl radicals (OH) by chemical ionization mass spectrometry (CIMS).

The measurements were conducted during the second New Particle Formation and Fate in the Coastal Environment (PARFORCE) campaign in June 1999 at Mace Head, Ireland. Overall median concentrations in marine background air were 1.5, 1.2, and $0.12 \cdot 10^6 \text{ cm}^{-3}$, respectively. H_2SO_4 was also present in the marine boundary layer at night indicating significant contributions from nonphotochemical sources. A strong correlation was found between daytime OH and H_2SO_4 levels in clean marine air suggesting a fast local production of H_2SO_4 from sulfur precursor gases. Steady state balance calculations of ambient H_2SO_4 levels agreed with measured concentrations if either very low H_2SO_4 sticking coefficients ($0.02 - 0.03$) or sources in addition to the $SO_2 + OH$ reaction were assumed.

Overall, variations in ambient H_2SO_4 levels showed no correlation with either the tidal cycle or ultrafine particle (UFP) concentrations. However, on particular days an anticorrelation between H_2SO_4 and UFP levels was occasionally observed providing evidence for the contribution of H_2SO_4 to new particle formation and/or particle growth. Gaseous MSA concentrations were inversely correlated with dew point temperature reflecting a highly sensitive gas-particle partitioning equilibrium of this compound.

Analysis of these observations gives rise to serious doubts in the possibility of using the MSA as a conservative tracer to infer the relative production yield of H_2SO_4 from dimethylsulfide (DMS) oxidation. MSA/H_2SO_4 concentration ratios typically ranged between 0.06 and 1.0 in marine air at the ground level. Measured vertical OH profiles showed a significant deviation from concurrent variations of the ozone photolysis frequency. They also showed up to an order of magnitude lower values compared with the OH concentrations calculated using a simple photochemical box model. These differences were most pronounced during particle nucleation events occurring on sunny days around noon and at low tide. The results obtained suggest that both the oxidation capacity and the particle formation potential in the coastal boundary layer were significantly affected by reactions of unknown compounds prevailing in this type of environment.

Development of new types of high-sensitivity and fast-response instrumentation for investigation of

the properties of nucleation-mode aerosol opened new capabilities of studying the detailed dynamics of properties of this aerosol. Väkevä with co-authors[52] discussed the results of measurement of nucleation aerosol characteristics, which were carried out using an Ultrafine Tandem Differential Mobility Analyzer (UF-TDMA) and a CCN counter as a part of PARFORCE program. These measurements gave indirect *in situ* information on the composition and state of mixing of the aerosol particles. The UF-TDMA was used for monitoring of hygroscopic diameter growth factors of aerosol particles with dry mobility diameters 0.008–0.02 μm, when taken from dry state, to a controlled humid environment (*RH* 90%)). The CCN counter was used to study the activation of aerosol particles when exposed to supersaturated conditions (dry diameters of 0.015–0.15 μm).

The analysis of observations showed that in clean marine air masses during the observed particle formation events, the newly formed nucleation-mode particles ((0.008–0.01 μm) most often had low growth factors (between 1.0 and 1.1) resulting from low solubility. This indicates that the nucleation-mode particles consist of insoluble or weakly soluble species, possibly accompanied by a small soluble part. However, when nucleation-mode particles were observed outside the event periods, the growth factors were higher (about 1.3–1.4). In contrast, the 0.02 μm particles usually belonged to the Aitken mode and had hygroscopic properties similar to some common salts (growth factors 1.4–1.5). For all particles measured with UF-TDMA (0.008, 0.01, and 0.02 μm), the growth factor under clear air conditions was close to that for $(NH_4)_2SO_4$. According to the results obtained, there was no correlation between the Aitken-mode and the nucleation-mode particles, which is indicative of different origin of these particles.

Determination of the rate of hygroscopic growth of aerosol particles due to condensation of water vapor is of great importance for a number of reasons, in particular, from the viewpoint of the effect of cloud condensation nuclei on the formation of cloud droplets. It has been hypothesized that the presence of organic films on the surface of aerosols can strongly inhibit condensational growth. In this connection, Chuang[20] reviewed the literature on the effects of films on the mass transfer of water and conducted an experiment for the measurement of the timescale for condensational growth (τ_g) for ambient aerosols. Measurements were taken during the wet season (25–27 September 2000) and dry season (16–17 November 2000) in Mexico City for particles with diameters of 0.05 and 0.1 μm. The results showed that most of the particles exhibit τ_g < 2 to 3 s. However, only small number (between 0 and 2.0% depending on the particle size and season) of particles exhibits τ_g values larger than this. The accommodation coefficient of this minority of particles is estimated to be approximately in the

range of 1 to $4 \cdot 10^{-5}$, which is in the lowest range of the observed values for laboratory aerosols. The observations showed a strong dependence of the occurrence of such particles on season and time of day. It was hypothesized that an even larger concentration of such particles may exist. The existence of such particles would be important to the indirect effect of aerosols on climate.

In recent years, particular attention has been paid to investigations of the processes of nucleation, i.e., formation of new aerosol nanoparticles with the size larger than 0.003 μm and their following growth up to the size of 0.1 μm for 1–2 days in the atmospheric boundary layer. As was already mentioned, the most probable mechanisms of nucleation are ternary nucleation with participation of H_2O, NH_3, and H_2SO_4, and ion-induced nucleation. Nucleation occurs in the atmosphere almost everywhere (at least in daytime) and leads to formation of a reservoir of thermodynamically stable molecular clusters (TSC) with diameter larger than 0.003 μm. Under certain conditions, they grow up to the detectable size. However, it is still unclear which of the minor gaseous component of the atmosphere is responsible for the growth of TSC. Earlier high correlation was found between the intensity of the shortwave solar radiation in the wavelength range of 300–340 nm and the number concentration of nucleation-mode particles with the size from 0.003 to 0.01 μm. The radiation at the wavelengths shorter than 330 nm lead to formation of hydroxyl radical OH through the production of excited oxygen atoms and the accompanying formation of condensable vapor. Just in this context, the need in taking the account of reactions of monoterpenes with O_3, OH, and NO_3 as mechanisms of particle growth was demonstrated.

Boy et al.[16] analyzed the observations from the Station for Measuring Forest Ecosystem–Atmosphere Relations (SMEAR II) field measurement station in Hyytiälä, Finland, for the years 2000 and 2001. The results can be divided into two main parts: first, a study of common trends and correlation between concentration of particles with d_p = 0.003–0.006 μm and different parameters; and second, the calculation of different aerosol related characteristics. It was found, in particular, that solar radiation and the reciprocal condensation sink values correlate in their daily profiles with the number concentrations of the nucleation mode particles. Also, the daytime mean values (09:00 to 15:00 LT) of these parameters correlate during the 2 years with the small particles. Particle flux, vertical wind variance, or ozone are weakly correlated with the particle concentrations during some days. However, they show the same yearly behavior as solar radiation or the reciprocal condensation sink values. The condensing vapor source rates and concentrations and the growth and the nucleation rates were calculated on the basis of measured monoterpenes and sulfur dioxide concentrations. Afterward, these values were

compared with the results obtained using measured particle number concentrations. The estimated oxidation products of monoterpenes (carboxyl diacids, including, in particular, pinic acid) were found to be able to explain 8–50% from observed growth rates. The estimates of the number concentration of particle with the diameter $d_p = 0.001–0.003$ μm suggested that the real concentration of such particles can be 2 to 3 times higher than the observed concentration of particles with $d_p = 0.003–0.006$ μm.

The complexity of gas-phase processes of aerosol formation and imperfection of measurement techniques are the main reasons for inadequacy of the current understanding of these processes. For example, well-founded theory is still absent and there is no needed thermodynamic information for explanation of the process of multicomponent nucleation. As to measurements, the problem is that nucleation yields particles with the diameter about 0.001 μm, whereas the up-to-date instrumentation is capable of detecting only particles with the diameter of about 0.003 μm and larger. Therefore, nucleation events can be detected only some time after the formation of particles. The correlation between the concentrations of gaseous sulfuric acid and nanoparticles 0.003–0.004 μm in diameter allowed a binary homogeneous $H_2SO_4–H_2O$ nucleation to be assumed as a possible mechanism of aerosol particle formation. However, classical theory of nucleation failed to reproduce the observed formation of particles, due to which the hypothesis of ternary nucleation was proposed. Laboratory experiments showed that addition of NH_3 to the $H_2SO_4–H_2O$ system enhances the nucleation rate.

As one of possible versions, Weber with co-workers[54] proposed the mechanism of ion-mediated nucleation. Investigations of nucleation in the urban environment were of great significance for this study. One of the important objectives of the TRACE-P experiment conducted in spring 2001 was to study the formation of new particles in the pollution plume spreading from the Asian continent to the Northwestern Pacific using the data of airborne observations. The measurements carried out at latitudes ranging from 20 to 45°N revealed the high concentrations of 0.003–0.004 μm diameter particles in the most polluted part of the plume both inside it and near its top boundary. Analysis of the results of observation during two flights indicated that the number concentration of 0.003–0.004 μm diameter particles usually correlated with the concentration of gaseous sulfuric acid. Sulfuric acid H_2SO_4 and surface area concentrations reached $7 \cdot 10^6$ cm^{-3} and 750 μm^2/cm^{-3}, respectively, in regions of particle formation. In contrast to these anthropogenic plumes, few 0.003–0.004-μm diameter particles were observed in the clean background. Similar situation was observed even in volcanic plumes where the highest H_2SO_4 concentrations ($> 10^8$ cm^{-3}) were recorded. Enhanced SO_2 concentrations in the range of

approximately 2 to 7 ppb, in conjunction with other unidentified, possibly co-emitted species, appeared to be the driving factor for nucleation.

Atmospheric formation of new aerosol particles is a subject of particular concern in modern atmospheric sciences. Related processes cause the increase in the number concentration of submicron aerosol particles, which is important from the viewpoint of the effect on climate and human health. That is why Komppula with co-authors[33] discussed the results of two years of continuous aerosol particle number size distribution measurements carried out in the Pallas-Ounastunturi National Park in northern Finland, where there are no significant pollution sources, from June 2000 to August 2002. The measurements have been conducted at two different heights (340 and 560 m above sea level) and surroundings (inside a forest and at the top of a hill). Measured aerosol particle size range was 0.007–0.5 μm. Average total number concentration in the year 2001 was 700 cm^{-3} at the high and 870 cm^{-3} at the low site. Daily averages varied between 40 and 3500 cm^{-3}.

Seasonal variations of total concentration were observed to be similar at both stations, high values in spring and summer and low values in winter. Diurnal variation of the total particle concentration was similar at both sites as well. Analysis of the data on concentration of individual modes of aerosol suggested that 65 new particle formation events were recorded during the entire measurement period. The largest number of events occurred in April and May. Particle formation events started between 08:25 and 15:50 (UTC plus 2 hours), and the calculated start times of 0.001 μm particle formation (nucleation) varied between 04:50 and 14:20. The particle growth rate was found to be 0.0014–0.0082 μm/h, and the formation rate of 0.007 μm particles varied from 0.06 to 0.40 particles·cm^{-3}·s^{-1}. Start times of the formation events at the two stations had maximum difference of 30 min, and it could not be explained by wind direction and speed. One possible explanation for the time difference is vertical motion of air masses caused by turbulence. Wind direction was mostly between west and north on the days the formation occurred what is indicative of polar or arctic air masses.

Since the beginning of industrial revolution, the atmospheric concentrations of different-type anthropogenic aerosols, including, first of all, submicron aerosol particles consisting of sulfates, nitrates, and secondary organic compounds, increased substantially. This anthropogenic aerosol exerts a significant effect on climate formation, acid precipitation, air quality, and human health. In recent years, particular attention has been paid to the processes of formation of sulfate aerosol, especially, its submicron fraction. Though the events of *in situ* new particle formation are observed quite frequently in the atmosphere, microphysical mechanisms of nucleation remain poorly studied. As was already

mentioned, most often it was assumed that the main mechanism is binary nucleation of sulfuric acid and water vapor molecules. However, the data of field observations indicate that the nucleation rate often exceeds that calculated by use of this hypothesis, as well as those that, additionally, account for the data of laboratory measurements. This discrepancy may be caused by participation of one more element (most probably, ammonia) in the nucleation process.

To check this hypothesis, nucleation was modeled using recently developed parameterizations for binary nucleation of water and sulfuric acid and ternary nucleation of water, sulfuric acid, and ammonia. A comparison with older nucleation parameterizations, combined with full aerosol dynamics, demonstrated that the difference in nucleation rate (1−2 orders of magnitude) is clearly reflected in the resulting total concentration of particles. A comparison of binary and ternary nucleation schemes showed that above 240 K the ternary nucleation rate exceeds the binary by over 10 orders of magnitude, indicating that in the most cases, under low troposphere conditions, the ternary nucleation dominates.

Korhonen et al.[34] analyzed the performance of aerosol dynamics models applying a multimode monodisperse, or a fixed sectional representation of the size distribution with respect to a molecular resolution model, which, molecule by molecule, follows the changes in the nucleation mode size distribution. This analysis suggested that, regarding the total number concentration, the sectional method converged to the molecular resolution approach when increasing the number of size sections. In the presence of a strong condensational growth, however, the "numerical diffusion" problems arise. Overall, the performance of the sectional method with low number of sections was not satisfactory. The monodisperse method gave very good results, at least in terms of total number, when the background modes were set to match the condensation sinks of the respective lognormal modes. Based on this study, the multimode monodisperse model seems to be a possible candidate in selecting the size distribution approach for large-scale atmospheric models.

Despite the intense investigations of the initial processes of aerosol formation, performed in the last decades, the mechanism of formation of ultrafine aerosol particles, manifesting itself everywhere, is still poorly understood. It was usually believed that the major role is played by the binary homogeneous nucleation (BHN) of H_2SO_4 and H_2O. However, this assumption proved to be inadequate, which stimulated the consideration of ternary homogeneous nucleation (THN) in the $H_2SO_4-H_2O-NH_3$ system, as well as ion-mediated nucleation (IMN) in the $H_2SO_4-H_2O-$ions system. According to THN theory, the fast increase of the nucleation rate is attributed to ammonia that stabilizes the aerosol embryos by decreasing their size. It follows from IMN theory that charged molecular clusters are formed around

ions in the atmosphere. These clusters are much more stable and can grow much more quickly than neutral clusters and, thus, can achieve stable detectable sizes. One of the main differences between the IMN and classical nucleation theory is that, at a given concentration of H_2SO_4, IMN theory allows the kinetics of the cluster evolution to be reconstructed, starting from the stage of monomers, whereas classical theory assumes the presence of instantaneous pseudo-steady-state concentration of the aerosol embryos (though some doubts are cast upon this assumption). Although the mentioned theories (THN and IMN) are based on the account for new components, the key role in the process of nucleation (of NH_3 and ions) is still given to H_2SO_4.

Using a kinetic model, Yu[55] estimated the time t_0 needed to establish a pseudo-steady-state nucleation when sulfuric acid concentration suddenly increases to a certain fixed level. It was found that t_0 is roughly inversely proportional to H_2SO_4 content. The assumption on instantaneously achieved pseudo-steady-state concentration of critical clusters, on which the classical nucleation theories are based, is no longer valid when t_0 is longer than the time, after which the H_2SO_4 content can be treated as constant. Under conditions of low marine atmosphere considered, the nucleation rate predicted by ion-mediated nucleation theory is very sensitive to H_2SO_4 when H_2SO_4 is low ($\lesssim 7 \cdot 10^6/cm^3$) but such sensitivity reduces significantly as H_2SO_4 increases. This result is quite different from that predicted with classical binary and ternary homogeneous nucleation theories.

It is well known that homogeneous nucleation is one of the mechanisms of new particle formation in the atmosphere. Sometimes particles are generated as products of binary nucleation of sulfuric acid and water, but there are also other mechanisms (for example, ternary homogeneous nucleation of sulfuric acid, ammonia, and water). Photolysis of CH_2I_2 in the presence of O_3 has been proposed as one of the possible mechanisms leading to intense formation of new particles in coastal areas. In this connection, Jimenez et al.[30] discussed the results of the laboratory chamber study of this system. Rapid homogeneous nucleation was observed at CH_2I_2 mixing ratio varying over three orders of magnitude, down to a level of 15 ppt ($\sim 4 \cdot 10^8$ molecule/cm^3) comparable to the directly measured total gas-phase iodine species concentrations in coastal areas.

After the nucleation burst, the observed aerosol dynamics in the chamber was dominated by condensation of additional vapors onto existing particles and particle coagulation. Particles formed under dry conditions are fractal agglomerates with mass fractal dimension, $D_f \sim 1.8-2.5$. Higher relative humidity (65%) does not change the nucleation or growth behavior from that under dry conditions, but results in more compact and dense particles ($D_f \sim 2.7$).

Based on the known gas-phase chemistry, OIO is the most likely gas-phase species to produce the observed nucleation and aerosol growth; however, the current understanding of this chemistry is very quite incomplete. Chemical analysis of the aerosol using an aerosol mass spectrometer revealed that the particles are composed mainly of iodine oxides but also contain water and/or iodine oxyacids. The system studied could produce nucleation events as intense as those observed in coastal areas. From a comparison between the particle characteristics in coastal nucleation and in the experiments reported in Ref. 30, it follows that photooxidation of CH_2I_2, probably aided by other organic iodine compounds, is the mechanism leading to the observed new particle formation in the west coast of Ireland.

Sea-salt aerosol (SSA), generated at rough sea and as a result of air bubble explosion, plays an important role in atmospheric chemistry and in the formation of climate. After long-range transport, sea-salt aerosol reaches the land, where it can interact with urban atmospheric pollutants. There is also reverse process of pollution coming from coastal cities to the water areas. It is just for this reason that the problem of interaction between the sea-salt aerosol and pollutant of the continental atmosphere attracts a considerable attention. In this connection, Cai and Griffin[17] described the current models of formation of the secondary organic aerosol (SOA) through absorption of semivolatile oxidation products (SVOP) by an organic aerosol mixture and/or dissolution into an aerosol aqueous phase.

In coastal areas, freshly formed sea-salt aerosol absorbs secondary semivolatile organic oxidation products onto its surface organic layer, which consequently allows for the partitioning of the secondary organics to the sea-salt aerosol brine core. Numerical simulation of this process has demonstrated the establishment of the equilibrium between the gas phase and a continental primary organic aerosol phase, a sea-salt organic layer, and a continental aqueous aerosol, as well as the equilibrium between the organic layer and the brine core.

In Ref. 17, dissociation of acidic species and processes determining pH were considered. Six semivolatile organic oxidation products that have been observed as secondary organic aerosol constituents, eight primary organic aerosol constituents representative of urban aerosols, five sea-salt organic layer species, and four organic components of the brine core were described molecularly. Numerical iteration techniques were used to solve the relevant nonlinear governing equations for the concentrations of each product in each aerosol phase and the gas phase, as well as for the pH of the relevant aqueous phases.

The results obtained indicated that the aqueous aerosols and the sea-salt aerosol brine core are the most efficient media for absorption, under the conditions described, the organic layers enhance the partitioning to the brine core, and that secondary organic acids contribute to the acidification of the sea-salt aerosol brine core.

According to a number of investigations mentioned above, nucleation of atmospheric aerosol particles in the ternary system "sulfuric acid—ammonia—water vapor" serves an efficient mechanism of new particle formation under conditions of forest, marine boundary layer, coastal environment, remote (background) troposphere, and in emissions from internal-combustion engines.

The earlier works showed that though the concentration of gaseous sulfuric acid can be sufficient for new particle formation, it is too low to provide for the particle growth up to the detectable size or for the fast growth of nuclei with their following scavenging from the atmosphere yet at the stage, when they do not achieve the detectable size (≤ 0.003 μm). Therefore, there must be the components of atmospheric chemistry (in addition to sulfuric acid), which favor the increase of nuclei up to the observed sizes. Zhang and Wexler[56] noted that pairs of organic compounds can be among these components.

Heterogeneous chemical reactions can serve, in this case, the mechanism of the particle growth, and the performance of this process depends on three characteristic timescales: 1) τ_{heter} for heterogeneous reactions between sulfuric acid and organic compounds; 2) τ_{coag} for coagulation of new nuclei; 3) $\tau_{alkenes}$ for alkenes taking into account their major sink in the atmosphere through the reaction with participation of hydroxyl radical and near-surface ozone. The condition for efficient growth of particles is $\tau_{heter} < \tau_{coag}$ and τ_{sink} (characteristic time of alkenes sink). Otherwise, the concentration of alkenes or new nuclei will decrease until the heterogeneous reactions will be capable of contributing to the increase of the particle size. Some examples illustrating these reasons were presented.

In recent years, the atmospheric formation (sometimes in the form of bursts) of nucleation aerosol has been discovered with the particle size about 0.003 μm. However, the mechanisms of this process remain unclear. Ternary nucleation is one of the possible mechanisms, but simultaneous functioning of several mechanisms is also possible.

Laakso et al.[37] performed the theoretical analysis of the possible role of ion-induced nucleation and dynamics of the charged aerosol particles. The results of this analysis suggested that this nucleation is able to produce a considerable amount of new particles if the preexisting particle concentration is sufficiently low. One more condition for this to happen is that only positive or negative ions favored nucleation of a large amount of particles of the observable sizes. It was also found that there can be continuous nucleation in particle sizes below the detection limit of the most commonly used aerosol instruments at low temperatures and high preexisting particle concentrations. Under some simulated conditions, fair agreement with observed particle formation events in

boreal forest environment was achieved. According to the results obtained, in certain situations ion-induced nucleation changes the charge distribution of the particles, which may allow the observation of ion-induced nucleation in the atmosphere.

Although episodes of "explosive" nucleation in the atmosphere have been discovered in some recent works, the mechanism of this process is mysterious. The already mentioned mechanism of ternary nucleation with participation of water vapor, sulfuric acid, and ammonia was proposed as one of the possible ways. However, this assumption resulted in significantly overestimated calculated nucleation rates as compared to the observed ones. In this connection, it was noted that this mechanism is able of providing the formation and following growth of thermodynamically stable molecular clusters up to the detectable size only with the "explosive" enhancement of the concentration of some organic vapor, which, however, does not occur. On the other hand, if ion-induced (or ion-mediated) nucleation (i.e., nucleation occurs only on ions, and the fast growth of particles is determined by the electrostatic interaction between charged particles and condensing molecules, which are characterized by dipole electrostatic nature) is proposed as this mechanism, this yields quite realistic results.

In this context, Laakso with co-authors[38] analyzed the effect of condensation enhancement due to Coulomb forces, and the main aim was to find out the upper limit of the effect and its significance for the dynamics of the nucleation mode particle growth. The enhancement factor seems to be below 5 for charged particle radius growth from 0.0015 to 0.01 μm. However, only a limited amount of particle population is charged, and the overall maximum effect was less than 2. This, combining with a vapor concentration of 10^7 molecules/cm^3, is enough for explaining nucleation mode growth of 0.001 μm/h. The effect of enhanced condensation on the total observed aerosol concentration was simulated using an aerosol dynamic model. The calculations showed that in the case of neutral nucleation, the effect is negligible for small enhancement factor (EF). With higher EF, the final concentration was found to decrease. In the case of ion-induced nucleation, the effect varied with preexisting particle concentration and enhancement factor. Under such conditions, the total aerosol concentration can increase three times.

In a wide range of geographic localities, from subarctic Lapland to industrialized farming regions of Germany, as well as in vast coastal regions, "bursts" in the formation of nucleation-mode aerosol particles with the size of 0.003−0.005 μm in the boundary layer and the following growth of particles up to about 0.1 μm for 1−2 days were observed. Dal Maso et al.[21] carried out a numerical simulation of the formation and growth of new nucleation-mode particles taking into account the condensation of vapor and coagulation sink of particles determined using the measured formation rate of 0.003 μm particles.

Condensation and coagulation sinks were estimated from the observation of the ambient aerosol size distribution and its variations. These estimates were used to analyze the particle formation and growth rates observed during coastal and boreal forest nucleation events. The calculations showed that the condensation sinks were typically $(4-7) \cdot 10^{-3} \cdot s^{-1}$ in the forest and $2 \cdot 10^{-3} \ s^{-1}$ under coastal conditions, while the coagulation sinks for 0.001, 0.002, and 0.003 μm particles were typically smaller by factors 1.5−2, 5−7, and 11−15, respectively. The measured growth rates were 0.002−0.010 μm/h for the boreal forest and ranged from 0.015−0.180 μm/h at the coast, corresponding to a vapor concentration of $(2-13) \cdot 10^7$ and $10^8 \ cm^{-3}$ to $10^9 \ cm^{-3}$, respectively. The vapor source rate was $(1-2) \cdot 10^5 \ cm^{-3} \cdot s^{-1}$ in the boreal forest and $(2-5) \cdot 10^6 \ cm^{-3} \cdot s^{-1}$ in the coastal environment. The estimated formation rate of 0.001 μm particles in the forest environment was 8−20 $cm^{-3} \cdot s^{-1}$ and 300−10000 $cm^{-3} \cdot s^{-1}$ at the coast.

Under conditions of the coastal environment, the coarse aerosol affected considerably the level of the condensation sink, but over the forest the significant effect was exerted only by the Aitken and accumulation mode particles. The calculated nucleation rate and number concentration of 0.001 μm particles proved to be much higher at the coast than in the boreal forest. The high particle growth rate in the coastal air reflects the higher concentration of condensable vapor under these conditions than in the forests, as well as more intense emissions of vapor into the atmosphere.

Although there are hundreds of organic compounds composing the atmospheric aerosol, their total mass fraction in the urban and rural aerosol is less than 10%. The major components of the continental organic aerosol are humic-like substances (HULIS), whose contribution to the formation of water-soluble organic aerosol under urban and rural conditions varies from 20 to 50%. This means that HULIS have a pronounced impact, affecting the hygroscopic properties of aerosol, the formation of cloud condensation nuclei, and, thus, the climate. Spectroscopic IR fingerprints of this aerosol indicate that the production of the corresponding macromolecular components can be attributed to processes of "agricultural biomass burning."

However, as was noted by Limbeck with co-authors,[40] the high concentration of HULIS, observed under Hungarian rural conditions in aerosol samples with low content of black carbon, evidences of that the HULIS in this case cannot be explained by biomass burning. Thus, the interesting fact is that the most significant sources of chemically active organic compounds at land are isoprene and terpene emissions. If photooxidation of isoprene does not contribute significantly to aerosol formation, then for terpenes the situation is quite different. This makes them a possible significant source of secondary aerosol.

It was shown that secondary aerosol formation occurs by heterogeneous reaction of isoprenoid or terpenoid emissions in the presence of a sulfuric acid aerosol catalyst. Competing oxidants such as ozone or the presence of humidity decreases the reaction yield, but the formation of humic-like substances is not disabled. Calculations in Ref. 40 indicated that the presented reaction pathway could be an additional source for HULIS in the continental aerosol.

Formation of new aerosol particles can occur through a homogeneous bimolecular nucleation in the course of gas-phase reactions with the participation of gaseous sulfuric acid and water. This mechanism is favored by the high concentrations of sulfur dioxide and hydroxyl radical (which react yielding the formation of gaseous sulfuric acid), the high concentration of water vapor, and the low temperature. In addition, it is assumed that new particles are formed more frequently in clear air with gaseous sulfuric acid easily condensable on the existing particles. Although the conditions for homogeneous nucleation actually exist in the atmosphere, observations indicate that in some cases the formation of new particles occurs more frequently than predicted by homogeneous nucleation models with participation of only gaseous sulfuric acid and water. This means that other components, including ammonia and organic vapor, can also play role in new particle formation.

In this connection, Twohy et al.[51] studied the process of new particle formation in the region downwind of a mesoscale convective system (MCS) stretching across much of the central United States. For this purpose, airborne measurements were conducted of the condensation nuclei (CN), cloud particle surface area, water vapor, and other gases. The analysis of the results revealed that CN concentrations were greatly enhanced above and downwind of the cirrus anvil, with maximum concentrations of 45000 cm^{-3}. Volatility and electron microscope measurements showed that most of the particles were likely small sulfate particles. The enhancement extended over the region of at least 600-km size.

Multivariate statistical analysis revealed that high CN concentrations were associated with the surface tracers, as well as the convective elements. Convection apparently brings gas-phase particle precursors from the surface to the storm outflow region, where particle nucleation is favored by the extremely low temperatures. Simple calculations showed that deep convective systems may contribute to a substantial (up to 20%) portion of the background aerosol in the upper troposphere at midlatitudes.

Conclusions

The main conclusion, which should be drawn based on the analysis of the current ideas about the mechanisms of formation and properties of atmospheric aerosol, is that these ideas are still far from being adequate. This is especially significant in the context of aerosol as one of the most important climate-forming factors. On the one hand, it is obvious that the interactive consideration of aerosol as a climate-forming component of the atmosphere is necessary. On the other hand, it is beyond question that the high degree of uncertainty in the data on the global spatiotemporal variability of aerosol properties and mechanisms of its formation fails to provide for the adequate parameterization of aerosol dynamics in climate models. More detailed consideration of this problem will be presented in the following parts of this review.

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