BOREAL ENVIRONMENT RESEARCH 10: 459–477 ISSN 1239-6095
Helsinki 14 December 2005 © 2005

Research Unit of Physics, Chemistry and Biology of Atmospheric Composition and Climate Change: overview of recent results

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Kulmala, M., Hari, P., Laaksonen, A., Vesala, T. & Viisanen, Y. 2005: Research Unit of Physics, Chemistry and Biology of Atmospheric Composition and Climate Change: overview of recent results. *Boreal Env. Res.* 10: 459–477.

In this paper we present research methods and recent results obtained within activities of the Research Unit of Physics Chemistry and Biology of Atmospheric Composition and Climate Change, which is one of the centres of excellence of the Academy of Finland. The centre forms an integrated attempt to understand various, but interlinked, biosphere–atmosphere interactions applying inter- and multidisciplinary approaches in a coherent manner. The main disciplines used cover aerosol and environmental physics, atmospheric chemistry and physics, micrometeorology, forest ecology and ecophysiology. The main objective of the centre is to study the importance of aerosol particles on climate change. Our scientific approach that starts from basic nucleation theories, is followed by detailed aerosol dynamic/atmospheric chemistry models and well-defined laboratory experiments, and ends with wide continuous field measurements in our research stations and 3D modelling. During the last years the joint efforts within our centre of excellence and the Nordic centres of excellence BACCI (devoted to atmospheric physics and chemistry) and NECC (devoted to carbon balance of northern ecosystems) have increased strongly. A thorough understanding of physical, meteorological, chemical and ecophysiological processes obtained by individual research groups lays the foundation of a unique possibility to study biosphere–aerosol–cloud–climate interactions, or the interplay between carbon exchange, BVOC emissions and formation of new aerosol particles. The necessary requirement is jointly working, real inter-, multi- and cross disciplinary teams. The core of activities is in continuous measurements and database of atmospheric and ecological mass fluxes and aerosol precursors and CO_2-aerosol-trace gas interactions in SMEAR field stations. These are supported by models of particle thermodynamics, transport and dynamics, atmospheric chemistry, boundary layer meteorology and forest growth.

Introduction

The Intergovernmental Panel on Climate Change (IPCC) in their 2001 report gave an estimation of the global and annually averaged radiative forcing for direct and indirect contributions from both greenhouse gases and aerosols, along with natural changes associated with the solar energy output. Emphasis was placed on the complexity of the combined direct and indirect forcing from both aerosols and gases. By investigating these components together our understanding of their role in radiative forcing in an integrated system would improve. Such knowledge would reduce the uncertainty in current estimates of radiative forcing and enable a better prediction of the effects of anthropogenic activity on global change. The most important issue to resolve is how the different components affecting radiative forcing interact with one another. Atmospheric aerosol particles influence the Earth's radiation balance directly by scattering and absorbing solar radiation, and indirectly by acting as cloud condensation nuclei (CCN) (e.g. Charlson *et al.* 1992).

IPCC (2001) revised their older prediction of the global average temperature increase during the next century from 1.0–3.5 to 1.4–5.8 K. The increase in the upper limit of the prediction is largely due to the role of aerosols in the climate of the Earth: it is believed that reduction of pollution will result in reduced direct and indirect (via clouds) scattering of sunlight back to space. However, as can be seen from the large uncertainty of the estimated temperature increase, not enough is known about the role of natural and anthropogenic aerosols in climate processes.

Among the key questions in reducing error bars are how aerosol particles are formed, how they will grow from clusters of a few molecules to CCN sizes (> 100 nm) and how they will form cloud droplets. Once formed, clouds have a very extensive influence on the Earth's radiation budget through their albedo and greenhouse effects. With global warming, future cloud properties are likely to change due to the warmer and moister conditions, and possibly due to increased aerosol particle emissions from both primary (e.g. wind generated sea-spray) and secondary aerosols (from biogenically and anthropogenically influenced gas-to-particle conversion processes). Clouds are, however, rather crudely presented in global and regional climate models (GCM, RCM). Processes, such as nucleation, droplet activation during condensation, diffusive growth, droplet evaporation, droplet coalescence and conversion to raindrops, are very crudely taken into account in present-day atmospheric large-scale models. For example, we have recently shown the importance of aerosol formation and growth processes to CCN concentrations (Kulmala *et al.* 2000a, 2004b) as well as the effect of nitric acid and other semivolatile gases in influencing cloud formation processes. In particular, they enhance the cloud droplet population, thereby increasing cloud reflectance (Kulmala *et al.* 1993, Laaksonen *et al.* 1997). The importance of including multi-component aerosol populations, and the dynamic feedback in the cloud forming processes, along with the importance of coupling chemical and physical processes in predicting cloud droplet populations have been illustrated by O'Dowd *et al.* (1999a, 1999b).

Organic compounds represent a significant fraction of atmospheric aerosols resulting from the oxidation process of volatile organic compounds (VOC). VOCs are emitted into the troposphere from anthropogenic and biogenic sources. The forests exchange gases with the atmosphere; they transpire water, photosynthesise carbon dioxide and emit VOCs and act as sources/sinks to nitrogen oxides (NO_x) (e.g. Hari *et al.* 2003) and ozone (O_3). All these fluxes have strong annual cycles reflecting the annual patterns of the activity of trees and the environment. Photosynthesis has a key role in the gas exchange between trees and the atmosphere, it is coupled with transpiration and it evidently provides material for VOC emissions. During the dormant period in winter photosynthesis is inhibited and it recovers slowly in the spring (Pelkonen and Hari 1980). The dependence of photosynthesis on the environment and the stomatal regulation is strong and present models are able to describe it well (Hari *et al.* 1999). The connection between VOC emissions and photosynthesis is weakly known, highlighting the need for more intensive investigations into links between VOC emissions and photosynthesis (*see* e.g. Kulmala *et al.* 2004d).

In urban areas, on the other hand, atmospheric aerosol particles cause a loss of visibility (e.g. Finlayson-Pitts and Pitts 2000) and influence human health (Dockery and Pope 1994). Heavily industrialized areas suffer from pollution fogs (smogs) that are often related to coal burning and nowadays also to traffic. The most well-known example of such a smog is the London "pea-souper" smog, which occurred every once in a while until the 1950s when coal burning was forbidden. Besides visibility degradation, the London smog episodes caused serious health effects and "excess deaths". A significant part of health problems related to atmospheric aerosols and fog droplets is caused by the ability of small particles (< 10 μm) to penetrate deep into the respiratory system (Dockery and Pope 1994). Recently, the effect of ultra-fine particles on urban air quality and human health has been discussed and their local variations have been investigated (e.g. Buzorius *et al*. 1999).

Atmospheric aerosol formation consists of a complicated set of processes that include the production on nanometer-size clusters from gaseous vapours, the growth of these clusters to detectable sizes, and their simultaneous removal by coagulation with the pre-existing aerosol particle population. Once formed, aerosol particles need to grow further to sizes > 50–100 nm in diameter until they are able to influence atmospheric chemistry and physics. Aerosol formation followed by growth has been observed to take place almost everywhere in the atmosphere (Kulmala *et al*. 2004b), yet serious gaps in our knowledge regarding this phenomenon exist. These gaps range from the basic process-level understanding of atmospheric aerosol formation to its various impacts on atmospheric chemistry, climate and human health. In order to be able to understand this phenomenon we need to perform studies on formation and growth of biogenic aerosols, including (a) formation of their precursors by biological activities, (b) related micrometeorology, (c) atmospheric chemistry, and (d) atmospheric phase transitions (Kulmala 2003). The other important issue is the ecosystem–atmosphere interactions. Without understanding the natural background and changes in it, it is impossible to understand the anthropogenic effects on climate generally and particularly on aerosol load.

In this paper we present recent results obtained within activities of the Research Unit of Physics Chemistry and Biology of Atmospheric Composition and Climate Change, which is one of the centres of excellence of the Academy of Finland. The main objective of the Centre is to study the importance of aerosol particles on climate change.

Material and methods

Generals

Our research methods cover both experimental (laboratory and field experiments including development of novel instrumental techniques) and theoretical (basic theories, simulations, model development) approaches. Our research chain starts from detailed nucleation theories, followed by aerosol dynamic/atmospheric chemistry models and well-defined laboratory experiments, and ends with versatile continuous field measurements in the research stations SMEAR II (Station for Measuring Forest Ecosystem–Atmosphere Relations, Hyytiälä, Finland), SMEAR I (Värriö, Finland) and Pallas-Sodankylä GAW (Global Atmospheric Watch) station. The research questions require real cross, inter- and multidisciplinary studies.

The hierarchical method based on a concept of the research chain means that studies are carried out all the way from molecular scale to global scale. In practice we start from molecular properties, which are then used in molecular simulations (Monte Carlo and Molecular Dynamics) aiming to understanding of nucleation processes. Also in thermodynamics the molecular properties are very important. Thermodynamics is needed in the classical nucleation theory. Nucleation together with condensation/evaporation, coagulation and deposition are part of aerosol dynamics. Aerosols influence cloud microphysics together with meteorology, and also boundary layer (BL) meteorology is needed in understanding atmospheric aerosol processes. BL studies form a link to regional-scale processes and further to global-scale phenomena. In order to be able to understand global climate, all these processes should be understood.

Gases and aerosol particles originating from natural and anthropogenic emissions are transported and transformed over geographically large areas. Understanding the spatial distribution of atmospheric pollutants and quantifying their climatic and air quality effects requires therefore mathematical models covering regional and global scales. Comparisons of large-scale model simulations with existing field measurements enhance the possibility to extrapolate results from *in situ* measurements to regional and global scales. On the other hand, the computational intensiveness of large-scale models stresses the importance of developing reliable and efficient parameterizations for emissions, aerosol size and composition distributions, particle formation and growth processes, as well as model sub-grid-scale processes.

In practise our work is divided into ten interlinked work packages that are all operated in a well-defined manner to meet our objectives:

1. Formation of biogenic compounds.
2. Micrometeorology and atmospheric fluxes.
3. Atmospheric chemistry.
4. Thermodynamics.
5. Nucleation, Theories.
6. Nucleation, Experiments.
7. Formation and growth of atmospheric aerosols, Modelling.
8. Formation and growth of atmospheric aerosols, Laboratory experiments.
9. Formation and growth of atmospheric aerosols, Field experiments.
10. Atmospheric gas–aerosol–cloud interactions.

In the following the main methods used in the present investigations are described.

Experimental methods

Laboratory experiments

Experimental laboratory studies are performed in order to obtain data on (a) thermodynamic properties of condensing species, (b) homogeneous nucleation rates, (c) nucleation probabilities of different vapours and vapour mixtures on aerosol particles, (d) growth rates of organic vapours in atmospheric conditions, and (e) mass accommodation coefficients for condensing vapours. In order to obtain thermodynamically consistent vapour pressures, chemical activities, surface tensions and densities for organic compounds and their water solutions as a function of temperature and composition, thermodynamic measurements and modelling have been performed (e.g. Korhonen *et al.* 1999). Also the determination of mass and heat accommodation coefficients has its significance in atmospheric chemistry. Well-defined thermodynamic parameters are needed in studying aerosol dynamics, cloud microphysics and the formation of new atmospheric aerosols, since without these parameters even the basic understanding on atmospheric aerosols remains limited.

As an example, comparison of the time evolution of experimentally-measured condensation/evaporation times (at different conditions) with those obtained from a detailed multi-component condensation model (Vesala *et al.* 1997) allows us to extract information on vapour pressures and activity coefficients. At present there are two techniques available for these investigations. The first technique is based on Size Analysing Nucleus Counter (SANC) located in the University of Vienna. The other technique is based on utilizing the Tandem Differential Mobility Analyzer (TDMA) technique at a controlled RH in a laminar flow reactor setup (Riipinen *et al.* 2005). The basic idea of the experiment is to allow material to evaporate from monodisperse aerosol particles during a well-defined time period and under controlled conditions (temperature, relative humidity, and low concentrations of the organic compound in the gas phase), and to detect the decrease in particle size. These studies have been performed in close co-operation with the University of Vienna and the University of Copenhagen.

As another example the determination of water accommodation coefficients is achieved by observing liquid droplets, nucleated on Ag particles, growing due to condensation of supersaturated water vapor using the experimental system described in e.g. Wagner *et al.* (2003) and Winkler *et al.* (2004). The apparatus includes a source of monodispersed particles and a vapor saturation unit. The vapor supersaturation is achieved by adiabatic expansion in a computer-controlled, thermostated expansion chamber, and the droplet growth is observed using a constant-angle Mie scattering (CAMS) detection method. In order to obtain the values of accommodation coefficients (thermal or mass accommodation coefficient), experimental droplet growth data were compared with theoretical droplet growth curves, in which the starting time of the droplet growth as well as the accommodation coefficients were varied in a two-parameter fitting procedure accounting for the uncertainties of the CAMS data. With the SANC/CAMS method also activation and/or heterogeneous nucleation of different vapours on pre-existing aerosols can be investigated (Petersen *et al.* 2001). All these studies have been performed in close co-operation with the University of Vienna. Other examples on our laboratory experiments include homogenous nucleation measurements of n-alcohols by laminar flow diffusion chamber (Hyvärinen *et al.* 2004) and observations of neutral clusters using condensation particle counters (Kulmala *et al.* 2005).

In order to examine the details of nucleation and growth from oxidized plant volatiles, we have carried out laboratory experiments involving the ozonolysis of plant chamber air (Joutsensaari *et al.* 2005). Monitoring the temporal evolution of aerosol size distribution using the DMPS (Differential Mobility Particle Sizer) technique provides the nucleation and growth rates of aerosol particles formed during the experiments. The results can be used to infer information related to atmospheric nucleation events, and to close gaps between smog chamber experiments and atmospheric measurements.

The main developments in experimental techniques are ion spectrometers and their use in continuous measurements (Hirsikko *et al.* 2005). Two ion spectrometers, the Air Ion Spectrometer (AIS) and Balanced Scanning Mobility Analyser (BSMA), both manufactured by Airel Ltd., Estonia, and the Differential Mobility Particle Sizer (DMPS) system have measured ion and charged particle mobility distributions, and particle size distributions (Laakso *et al.* 2004a, 2004b). The AIS uses two identical cylindrical aspiration-type differential mobility analyzers to classify and measure all air ions simultaneously in the mobility range 0.0013–2.4 cm^2 V^{-1} s^{-1}. Both mobility analysers, one for positive and the other for negative ions, have 21 insulated collector electrodes. Electric current carried by ions is measured with electrometrical amplifiers connected to these collectors. In AIS mobility distributions are presented at 27 logarithmically uniformly distributed points in the measuring range of the device. The corresponding diameter distributions of single-charged particles are obtained by utilizing the algorithm developed by Tammet (1995). In NTP conditions the size range of the AIS is 0.46–40 nm.

Another recent development concerns Tandem Differential Mobility Analyser (TDMA) techniques. An organic TDMA, using ethanol as working fluid, was developed (Joutsensaari *et al.* 2001) and applied in the laboratory (Joutsensaari *et al.* 2004) and in field measurements (Boy *et al.* 2004). Also ultrafine TDMA techniques (both organic and hygroscopicity), measuring the growth factors of particles larger than about 6 nm in diameter, have been developed and applied in ambient measurements (Petäjä *et al.* 2005).

Continuous and campaign-wise field measurements

The research unit operates three field stations. All of the stations have comprehensive scientific programs to investigate aerosol and trace gas concentrations, aerosol formation and growth processes, and the biogenic background for processes leading to aerosol formation. The stations are the GAW (Global Atmosphere Watch) station in Pallas (FMI, since 1994) and the two SMEAR stations built by the APFE (Aerosol Physics and Forest Ecology) group (SMEAR I in Värriö, since 1991; and SMEAR II in Hyytiälä, since 1994). The APFE group has recorded ultrafine and fine aerosol size distribution at the SMEAR II station since 1996, which is a uniquely-long data set worldwide. The new urban station is under construction and partly built in Helsinki by APFE groups and FMI. In addition to the stations operated by the research unit, continuous particle size distribution measurements have been conducted for three years at the San Pietro Capofiume research station in Po Valley, Italy, within the framework of the EU project "Quantification of Aerosol Nucleation in the European Boundary Layer" (QUEST).

The idea behind continuous measurements is (a) to obtain firm detailed data to verify different models, and (b) to observe trends in concentrations of atmospheric aerosols, ions and trace gases. The continuous measurements as well as the BIOFOR experiments (and also ongoing QUEST experiments) took place at the SMEAR II station (Station for Measuring Forest Ecosystem–Atmosphere Relations) in Hyytiälä, southern Finland (61°51´N, 24°17´E, 181 m above sea level). The station represents boreal coniferous forest which covers 8% of the earth's surface and stores about 10% of the total carbon in the terrestrial ecosystem. The biggest city near the SMEAR II station is Tampere, located about 60 km from the measurement site and with about 200 000 inhabitants.

The SMEAR II facility is planned and implemented to determine material and energy flows in the atmosphere–vegetation–soil continuum at different temporal and spatial scales (*see* e.g. Vesala *et al.* 1998, Kulmala *et al.* 2001). It can be divided into five operational blocks: (1) atmospheric measurements accomplished using a 72-m-high mast, (2) tree measurements performed using a 15-m-high tower, (3) radiation and flux measurements using a 20-m-high tower, (4) soil measurements carried out on two catchment (watershed with weir) areas, and (5) aerosol measurements from 2 m above the ground. The station includes advanced setups for measurements of aerosol particle size distribution in the size range of 3–500 nm, exchange of trace gases on shoot-scale and soil surface in intervals of one minute, spatial distribution of irradiance in the vicinity of a shoot by 800 sensors, spatial distribution of irradiance within the canopy with 200 sensors and two soil catchment areas (890 and 300 m^2) for the soil water, dissolved ions and organic carbon balances. Tree measurements include also sap flow detection with heat pulse techniques and detection of the xylem/stem diameter variations with an accuracy of 1 μm and temporal resolution one minute. The flux measurement instrumentation includes several eddy covariance (EC) setups, Relaxed Eddy Accummulation (REA) setup and facilities for gradient (profile) measurements. EC fluxes are measured for momentum, sensible heat, carbon dioxide and water vapour at four points, two setups are located above the canopy and two at trunk-space. The ozone flux and aerosol particle number flux down to 10 nm are measured above the canopy. By using the REA technique, deposition velocities of sub-100 nm particles are assessed with sharp size discrimination. The SMEAR II station is nowadays a platform for a number of international measurement campaigns. Recently, during the ongoing QUEST campaign (spring 2003 and spring 2005), aimed to investigate the formation and growth of atmospheric aerosols, also an aerosol mass spectrometer, two ion spectrometers, several instruments for organic vapour measurements, gas phase sulphuric acid and ammonia measurements, as well as two aircraft, were involved in the experiments.

The other key station, the Finnish GAW station Pallas-Sodankylä, is located in a remote, subarctic region at the northernmost limit of the boreal forest zone in Europe. The station has been operating since 1994. The tropospheric air composition and related boundary layer meteorological measurements are made at Pallas (67°58´ N, 24°07´E), whereas upper-air soundings, climatological and other meteorological measurements are made at the Sodankylä observatory (67°22´N, 26°39´E) 125 km away from Pallas. One of the main criteria for selecting the Pallas area as the site for tropospheric composition measurements was the absence of large local and regional pollution sources. The distance to the nearest town, Muonio (2500 inhabitants), is 19 km to the west, while the second nearest town, Kittilä (6000 inhabitants), is located 46 km to the south-east of the station.

The stations in the Pallas area are hosted by the Finnish Meteorological Institute (FMI), and maintained together with the Finnish Forest Research Institute. The infrastructure consists of several sites, the most important of which are Sammaltunturi, Matorova, Kenttärova and Laukukero. All the sites are within 12 km of each other. The main site with the largest measurement program is the Sammaltunturi station (67°58´N, 24°07´E, 560 m above sea level). The station lies on a top of a fjeld (an Arctic hill) some 100 above the tree line and 300 m above the surrounding area. The Matorova station (340 m above sea level) is located in a forest clearing and it has been chosen as another aerosol measurement site because the conditions in Sammaltunturi are too harsh for wintertime collection of filter samples. In Kenttärova there is a 20-m-high tower for micrometeorological flux measurements. All the stations, except Matorova, are within the Pallas-Ounastunturi National Park (total area 501 km^2). A more detailed description of the Pallas research station can be found from Hatakka *et al.* (2003).

In all three sites the aerosol size distributions are measured using the Differential Mobility Particle Sizer (DMPS) system (Aalto *et al.* 2001), which classified particles in diameter range 3–500 nm (SMEAR stations) and 8–500 nm (Pallas). The system consists of two parallel DMPS devices. The devices have a common sample inlet at the 2-m height inside the forest and they both use their own closed loop sheath flow arrangements (Jokinen and Mäkelä 1997). The first device uses a 10.9-cm-long Hauke-type differential mobility analyser (DMA) (Winklmayer *et al.* 1991) and TSI model 3025 condensation particle counter (CPC). This device classifies particles in the size range 3–10 nm. The other device, consisting of a 28-cm-long Hauke-type DMA and TSI model 3010 CPC, classifies particles in diameter range 10–500 nm. The aerosol is neutralized with a 2 mCi Krypton-85 beta source before sizing.

Theoretical work

Detailed theoretical modelling

Basic theories based on molecular level understanding and simulations have been developed. The tools include computational codes for classical and quantum mechanical Molecular Dynamics as well as Monte Carlo and density functional simulations. The development of new hypothesis is based on the understanding of biological, chemical, meteorological and physical processes.

As an example we can take the growth of aerosol particles from 1 nm to 20 nm. The possible steps in the growth process include (a) either heterogeneous nucleation (*see* Petersen *et al.* 2001) of organic insoluble vapours on a ternary (water–sulphuric acid–ammonia) nucleus or activation of the nucleus for condensation of soluble organic vapours i.e. nano-Köhler theory (Kulmala *et al.* 2004a) (a process analogous to activation of cloud droplets, *see* Köhler theory; e.g. Kulmala *et al.* 1997), and (b) the multi-component condensation of organic and inorganic vapours. The activity coefficients and surface tensions obtained in the experimental part of our activities are used. The growth rates are calculated in atmospheric conditions and compared with measured growth rates (Kulmala *et al.* 2001).

Aerosol dynamic modelling

Aerosol dynamics (nucleation, condensation, coagulation, deposition, cloud processes) with gas-phase chemistry and boundary-layer as well as synoptic meteorology are needed to find out the atmospheric significance of the formation and growth of new aerosol particles as well as biosphere–aerosol–cloud–climate interactions. An exact molecular-level aerosol dynamic model has been developed (Lehtinen and Kulmala 2003) and can be used as a reference model.

The recently developed model UHMA (University of Helsinki Multicomponent Aerosol model) (Korhonen *et al.* 2004) is a sectional aerosol dynamics model that offers a flexible tool for a wide range of atmospheric applications. Thus far it has been used to investigate the role of photo-oxidants in new particle formation (Grini *et al.* 2005), transformation of aerosols during atmospheric transport over Scandinavia (Tunved *et al.* 2004), and dynamics of indoor aerosol (Hussein *et al.* 2005). The aerosol dynamics includes currently all the major processes controlling the particle number concentration and size distribution under clear-sky conditions and for non-precipitating clouds (Fig. 1). The chemical compounds simulated include sulphate, ammonium, organic carbon, and insoluble species such as elemental carbon and mineral dust. The model has recently been coupled to a thermodynamic equilibrium model ISORROPIA (Nenes *et al.* 1998), giving also access to nitrate

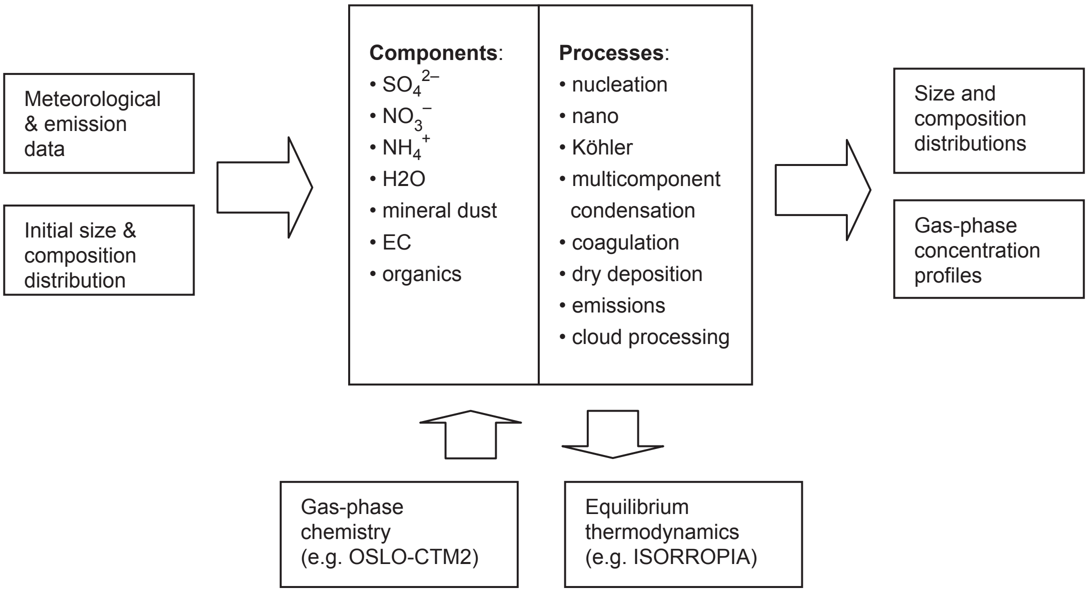

Fig. 1. An aerosol dynamic model UHMA, a schematic picture.

and sea salt. The gas-phase chemistry affecting the aerosol population can currently be simulated with a chemistry scheme extracted from OSLO-CTM2 (Berntsen and Isaksen 1997, Berglen *et al*. 2004).

When simulating atmospheric aerosols with UHMA, the user can choose between several sectional representations of the particle size distribution to best suit the problem at hand. At the moment, the model can simulate the distribution with full moving sections, fixed sections, moving sections that are retracked to a fixed grid, or moving center scheme. Based on our experience with these schemes, we are currently developing a simplified, computationally efficient version of UHMA for 3D modelling applications. Future plans for the development of the box model version include incorporation of precipitation scavenging of the aerosol particles as well as investigation of the role of sesquiterpenes in the new-particle formation with the help of a detailed gas-phase organic scheme.

The other recently developed model is AEROION, which is a sectional model suitable for studying charged aerosol particle dynamics and ion-induced nucleation (Laakso *et al*. 2002). The model consists of 52 logarithmically divided size classes between approximately 0.3 nm (the radius of one sulphuric acid molecule) and 1000 nm. Each size class is divided to three charge classes (–1, 0 and +1 elementary charge). Two more classes are reserved for ions, because the composition of ions may differ from that of larger particles which are assumed to consist of sulphuric acid and water.

The model takes into account the condensation of organic vapors on aerosol particles. Coagulation follows the Fuchs generalized equation. Ion-aerosol attachment coefficients are calculated based on Fuchs theory. Condensation is considered as coagulation between molecules and particles. We have assumed that the condensation of organic vapors obeys the classical Fuchs-Sutugin formula with enhancement due to mirror Coulomb interactions introduced. In addition, a parameterized version of so-called nano-Köhler theory is applied (Kulmala *et al.* 2004d). The model have been used in studies of ion-induced nucleation (Kulmala *et al.* 2000b, Laakso *et al.* 2002), kinetic nucleation (Laakso *et al*. 2004, Kulmala *et al*. 2005) and condensation (Laakso *et al*. 2003).

Recently, we have also developed a modal regional aerosol transport model for studying the aerosol processes in regional scale. The model has been developed in co-operation with Ford Research Centre Aachen GmbH in Germany and is based on their MADE/EURAD regional transport model system (Asmi *et al*. 2001). The model is especially tuned to investigate different particle formation processes and their effects on the production of cloud condensation nuclei. The modal approach of the model also makes the model much more computationally efficient than most sectional approaches, even though the nucleation processes require some extra consideration. Tests over the Scandinavian domain have shown that the overall aerosol number concentration is very dependent on the formulation of the nucleation process and used aerosol emission function.

Cloud modelling

Indirect aerosol effects caused by aerosol–cloud interactions constitute one of the largest scientific uncertainties in climate modelling. Cloud process models are important tools in advancing our understanding of the indirect aerosol effects (e.g. Charlson *et al*. 2001). We have constructed a cloud box model (Kokkola *et al*. 2003b) capable of simulating several chemical effects that have been identified in recent years as possible influences in cloud drop activation. The model describes an adiabatically lifted air parcel with an aerosol size distribution discretized up to 200 size bins in a moving grid. Condensable gases include water, nitric and hydrochloric acid, ammonia, sulfur dioxide, hydrogen peroxide and ozone. Other condensable species can be defined if needed. The model includes a description of sulfate production due to SO_2 oxidation reactions in cloud droplets and takes into account the surfactant effects on cloud drop activation in a realistic way, allowing for the partitioning of surfactants between the bulk and the surface of a droplet (Sorjamaa *et al*. 2004).

Overview of scientific advances and accomplishments

Aerosol formation and growth

The key hypothesis in our studies is that aerosol particles have a significant effect on climate change and human health. These effects depend mainly on the size and composition distribution of aerosol particles. Over the past decade, the formation and growth of nanometer-size atmospheric aerosol particles have been observed at a number of sites around the world. Measurements of particle formation have been performed on different platforms (ground, ships, aircraft) and over different time periods (campaign or continuous-type measurements). These new discoveries have been made possible by the development of new instruments capable of measuring nanoparticle size distributions and several gases participating in nucleation. Measurements of evolving size distributions down to 3 nm during nucleation episodes can be used to calculate the apparent source rate of 3-nm particles and the particle growth rate. The first and longest continuous data set is from the SMEAR II station (Mäkelä *et al*. 1997, Kulmala *et al*. 2001). Dal Maso *et al*. (2005) found that the number of aerosol formation events has been increasing during the recent years. We have made observations all around the world. Recently we reviewed all existing particle formation data from literature (Kulmala *et al*. 2004b). The main conclusion was that the formation rate of 3-nm particles is often in the range 0.01–10 $cm^{-3} s^{-1}$ in the boundary layer. However, in urban areas the formation rates are often higher (up to 100 $cm^{-3} s^{-1}$) and rates as large as 10^4–10^5 $cm^{-3} s^{-1}$ have been observed in coastal areas and industrial plumes. Typical particle growth rates are in the range 1–20 nm $hour^{-1}$ in mid latitudes depending on the temperature and the availability of condensable vapours. Over polar areas the growth rate can be as low as 0.1 nm $hour^{-1}$. We have recently shown that nucleation can lead to a significant increase in the number concentration of cloud condensation nuclei, even at highly polluted regions such as Po Valley in Italy (Laaksonen *et al*. 2005a) and New Delhi, India (Mönkkönen *et al*. 2005). Therefore, global climate models will require reliable models for aerosol nucleation and growth.

In typical atmospheric conditions the amount of sulphuric acid vapour is not enough to explain the condensation growth (Kulmala *et al*. 2001, Kulmala *et al*. 2004b), and therefore the role of condensable organic vapours is likely to be important. The organic acids concerned include pinonic, pinic, maleic and fumaric acid. Pinonic

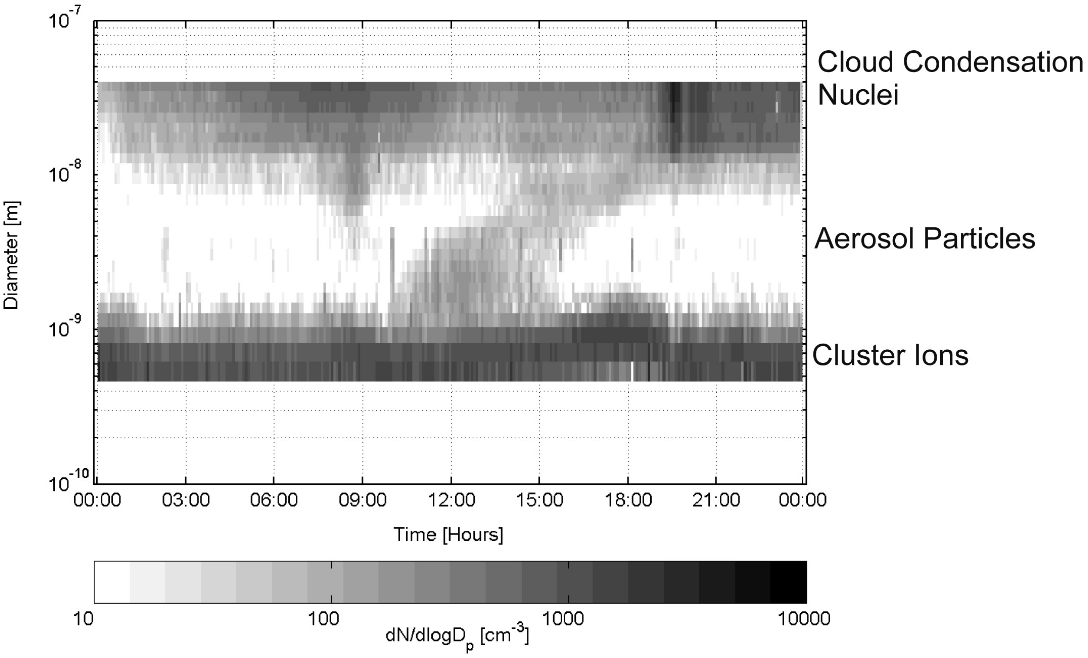

Fig. 2. Daily behaviour of ion clusters and charged aerosol particles measured using AIS in Hyytiälä, Finland, on 16 Feb. 2004.

and pinic acids are oxidation products of terpenes and have been identified in all the chemical analyses of newly formed organic particles in laboratory (Hoffmann *et al.* 1998) as well as in the atmosphere (Kavouras *et al.* 1998). Maleic and fumaric acids are oxidation products of aromatic compounds and are also present in the atmosphere. Beside terpenes, aromatic compounds are another class of organic compound responsible for the formation of organic aerosols in the atmosphere and are of particular importance in urban environments.

During the last years we have focused on the formation and growth of nanometer size (diameter 1–3 nm) atmospheric particles/clusters. This task is challenging, since the present methods are not able to detect those particles directly. However, Kulmala *et al.* (2000a) proposed a theory to explain the existence of inorganic atmospheric clusters. Investigations on the initial steps of growth of thermodynamically stable clusters are in progress, showing strong evidence that the effect of organic vapours on growth processes is probable (O'Dowd *et al.* 2002, Kulmala *et al.* 2004a, Hirsikko *et al.* 2005).

On the other hand, the existence of ion clusters of similar size has been observed for decades, and the main existing question is the existence of neutral atmospheric clusters. Actually, based on measurements of air ion size distributions (Fig. 2), we can state that below the nucleation mode there is a cluster mode which is always — at least if we are not inside a cloud — present. Figure 2 also demonstrates the growth of clusters to the nucleation mode and further to size typical for cloud condensation nuclei.

Our recent laboratory experiments on nucleation induced by ozonolysis of plant chamber air (Joutsensaari *et al.* 2005) support the picture that the role of organic species formed by the oxidation of plant volatiles is to speed up the growth of freshly-nucleated particles. Specifically, the observed nucleation rates were similar to those in the atmosphere, whereas the particle growth rates were 2–3 times faster than the maximum growth rates observed during ambient nucleation events. This indicates that in order to nucleate homogeneously (or around ions), the concentration of oxidized organics needs to be 2–3 times higher than what their atmospheric concentrations are at maximum. At usual atmospheric concentration levels, however, the oxidized organ-

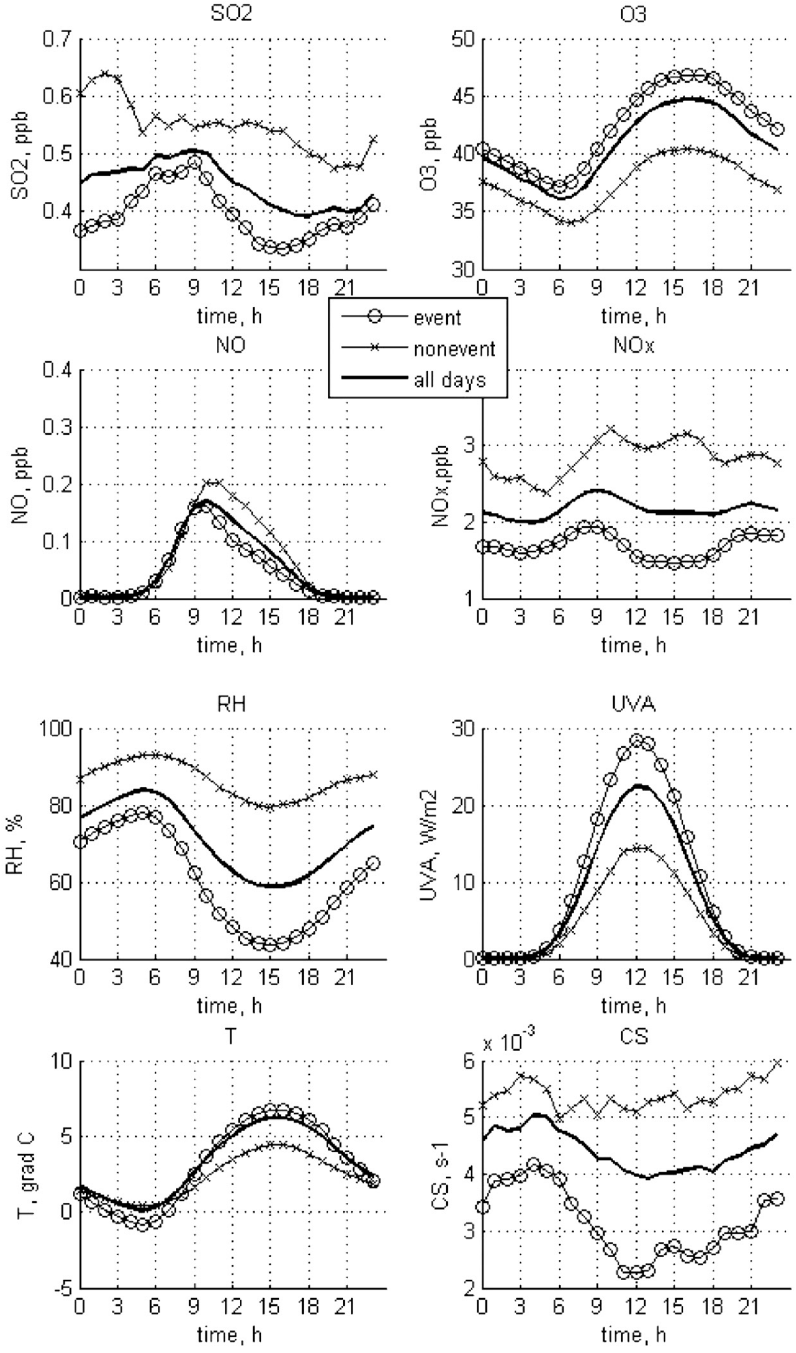

Fig. 3. Mean diurnal behavior of SO_2, O_3, NO and NO_x concentrations, temperature (*T*), relative humidity (RH), UV-A radiation intensity and condensation sink (CS) for all days as well as for event and non-event days during the springs (March–May) of 1998–2003 at the SMEAR II station.

ics will very likely nucleate on 2–3 nm sulfate clusters and participate in their condensational growth (which may involve chemical reactions in the growing particles).

The frequency of new aerosol production events in Finland is highest during spring months (March–May) (Dal Maso *et al.* 2005). This seems to be connected with a low condensation sink, high solar radiation intensity, low sulphur dioxide concentration, high ozone concentration and low relative humidity (Fig. 3). The details of the connections between chemistry and aerosol

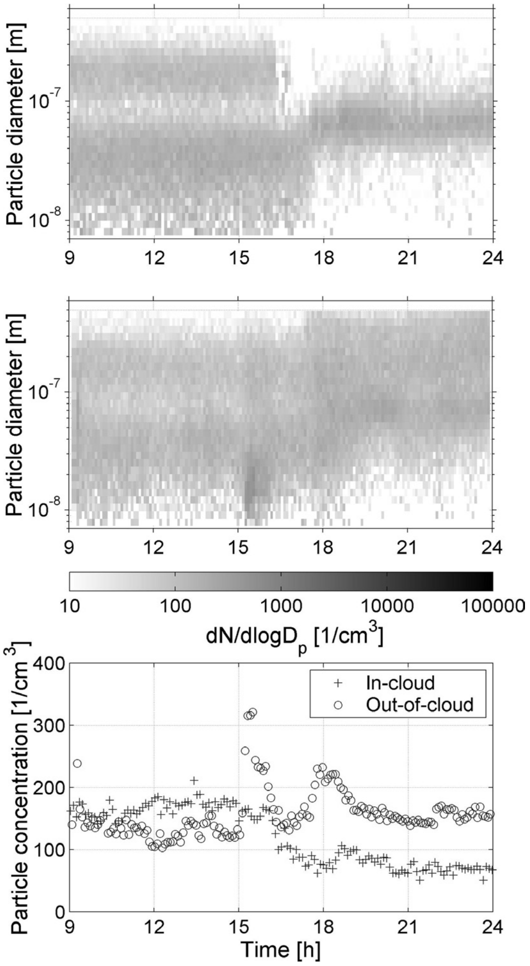

Fig. 4. Aerosol-cloud interactions measured at two sites at the Pallas station on 13 Dec. 2000. The two pictures on the top show the daily behaviour of aerosol number size distributions measured with a DMPS. The aerosol system is inside a cloud after about 16:00 at one site (top panel) and outside the cloud at the other site (middle panel). The bottom panels shows the total particle number concentration.

formation are presented by Lyubotseva *et al.* (2005).

The clear connections between new particle formation and their subsequent growth to CCN sizes and their participation in cloud droplet formation can clearly be seen in Fig. 4 (*see* also Lihavainen *et al.* 2003, Kerminen *et al.* 2005, Komppula *et al.* 2005). The observations have been made in Pallas and are based on direct measurements of aerosol size distributions inside and out-of cloud using DMPS systems.

Other highlights of scientific progress during 2002–2004

A collection of other highlights are listed below.

Experimental works and their results

- Continuous measurements of atmospheric and ecological mass fluxes and aerosol precursors and CO_2/aerosol/trace gas interactions in SMEAR stations (e.g. Kulmala *et al.* 2001, Hari *et al.* 2003).
- Connection between aerosol formation, nucleation mode growth rate, carbon sink and oxidation products of terpenes has been shown to occur using six years' data observed at the SMEAR II station (Kulmala *et al.* 2004d).
- TDMA investigations of the diurnal behavior of aerosol growth factors in water and ethanol vapors (Boy *et al.* 2004) and of the growth factors of aerosols in air masses exposed to different levels of anthropogenic sulphur pollution (Petäjä *et al.* 2005).
- Phase transitions in aerosols, heterogeneous nucleation theories and experiments (Bogdan *et al.* 1998, Petersen *et al.* 2001).
- A mass accommodation coefficient of unity was observed for water vapour with well-defined experiments using a SANC/CAMS technique (Winkler *et al.* 2004).
- Construction of a new condensation particle counter (Mordas *et al.* 2005).
- UV-radiation generates NO_x flux from Scots pine needles (Hari *et al.* 2003).
- Determination of properties of organic vapors by comparing flow reactor experiments with multi-component evaporation modelling (Svenningsson *et al.* 2004).
- Formation and growth dynamics, characteristics of the aerosol number size distribution and seasonal and diurnal concentrations and variations of atmospheric aerosols were investigated in a highly-polluted Asian mega city, New Delhi. The experimental results showed that the formation and growth of atmospheric aerosols is possible in this kind of environment even though the smallest growing particles face effective scaveng-

ing by the pre-existing aerosol population (Mönkkönen *et al*. 2005).

- Especially the micrometeorological techniques for measurements of small particles (smaller than 100 nm) have been further developed (Rannik *et al*. 2003) and the approach based on Relaxed Eddy Accumulation (REA) is unique (Gaman *et al*. 2004). The flux measurements of sub-100 nm aerosol particles is very challenging and the field data on fluxes and deposition velocities over rough surfaces (like forests or urban areas) is scarce. The present deposition models are not in overall agreement with the measurements and the general aim is to improve understanding on deposition processes.
- First monitoring of VOC emissions with an advanced PTR-MS instrument (Ruuskanen *et al*. 2005).
- There is a debate on best methods to measure soil gas exchange and hence we tested several chamber types showing that various methods are in fact in quite close agreement (Pumpanen *et al*. 2004). The measurements covered only carbon dioxide and a limited number of different soil textures. However, the obtained results gave promise for more quantitative monitoring of soil efflux in the field.
- We have shown that the effect of forest thinning may be marginal for exchange of biological controlled compounds like water vapor, carbon dioxide and ozone while deposition velocity of particles is decreased due to lower foliage area (Vesala *et al*. 2005). The results for gases are somewhat surprising but the study showed that they are due to redistribution of sources and sinks between canopy and ground vegetation and, for carbon dioxide, due to interplay of the effects of thinning to autotrophic and heterotrophic processes. The current models of biogeochemical cycles are not able to predict all observations and the study brought valuable information for further model developments.

Modeling and its results

- Development of a detailed gas-phase chemistry-aerosol box model as a first step towards a combined global chemistry transport and size resolved aerosol dynamics model (Grini *et al*. 2005).
- Development of a new parameterization for aerosol formation suitable for large-scale models (Kerminen *et al*. 2004).
- Semi Lagrangian method was used to evaluate nucleation, condensation, coagulation and dry deposition in clean and polluted air masses during clear sky conditions by use of long term measurements at Swedish-Finnish sites. Measurements and models showed very good agreement (Tunved *et al*. 2004, 2005).
- Gibbsian surface thermodynamics was used to find out how the partitioning of surfactants between droplet surface and the bulk of the droplet affects the surface tension and the surfactant bulk concentration in droplets large enough to act as cloud condensation nuclei (Sorjamaa *et al*. 2004). It was found that surfactant partitioning may significantly alter the critical supersaturation required for particle activation predicted by not accounting for partitioning. Model results were supported by experimental data on SDS.
- The Köhler theory accounting for condensable trace gas effects was extended to polydisperse aerosol populations. It was shown that at low cooling rates of air, the condensation of the trace gas may lead to splitting of the aerosol populations at relative humidities below 100%, with possible consequences to polar stratospheric cloud formation during seasonal cooling (Kokkola *et al*. 2003a).
- It was shown that nitric acid pollution may explain observations of increased haze mode particle concentrations at relative humidities above 50% in the upper troposphere (Romakkaniemi *et al*. 2004).
- A parametrization of the effect of nitric acid on cloud drop activation was derived (Romakkaniemi *et al*. 2005).
- It was shown that the droplet growth rates calculated in cloud model studies are consistent with experimental results obtained so far only if a water mass accommodation coefficient of unity is applied (Laaksonen *et al*. 2005b).

- A model for VOC emissions linked to photosynthesis dynamics was developed (Bäck *et al*. 2005).
- A comprehensive review on aerosol formation and growth events in the global atmosphere was constructed (Kulmala *et al*. 2004b).
- The contribution of sulfuric acid and organic vapors to aerosol growth in the SMEAR II station in Hyytiälä was estimated (Boy *et al*. 2005).
- The so-called nano-Köhler theory describing the activation of inorganic clusters by water-soluble organic vapors was developed (Anttila *et al*. 2004, Kulmala *et al*. 2004a).
- A theoretical analysis concerning the initial steps of aerosol formation was made (Kulmala *et al*. 2004c).
- Preliminary estimates were made on the influence of aerosol formation in regional cloud condensation production and indirect climatic forcing (Kurten *et al*. 2003, Kerminen *et al*. 2005).
- A model simulating cluster formation and growth in the presence of ions was developed (Laakso *et al*. 2004b).
- A new aerosol dynamics model, designed specifically for simulations on atmospheric aerosol formation and growth, was developed (Korhonen *et al*. 2004).
- A theory/analysis of ammonium sulphate cluster formation (Vehkamäki *et al*. 2004) was developed. It was discovered that the previous treatments of water-sulphuric acid-ammonia nucleation are internally inconsistent. In fact all sulphuric acid in the atmosphere seems to be bound to tiny ammonium bisulfate clusters which are the basic building blocks in the nucleation process.
- The temperature and supersaturation dependence of experimental water nucleation rates was reproduced by classical Monte Carlo simulations. A wrong temperature dependence in nucleation theories has been puzzling the nucleation community for decades (Merikanto *et al*. 2004).
- Molecular dynamic simulations of monomer-cluster collision processes were performed. It was discovered that although dimer formation requires the presence of a carrier gas molecule, larger clusters are long-lived enough to allow subsequent growth even without the involment of carrier gas (Napari *et al*. 2004).
- Methods for estimating flux footprints have been developed toward a more realistic direction by the taking into account of homogeneities and varying topography (*see* Vesala *et al*. 2004). We have used two approaches, another based on Lagrangian trajectory calculations (Markkanen *et al*. 2003) and the other on Boundary Layer closure model (Sogachev *et al*. 2004). For homogeneous surfaces with long fetches the question of footprints (source areas) is not important but very few flux sites are in that sense ideal. The assessment of footprint over rough surfaces with non-neutral stratifications is still a challenging task and no universal model, fully validated in the field, is available.

Conclusions

During the last years the joint efforts within our centre of excellence and the Nordic centres of excellence BACCI and NECC have strongly increased. As an example, we have a unique possibility to study biosphere–aerosol–cloud–climate interactions like energy and mass fluxes within canopy environment or the effect of photosynthesis and photorespiration on BVOC and aerosol formation. This is mainly due to the fact that we have a real inter-, multi- and cross disciplinary team. To fully understand particle formation processes would require new insight on physical, chemical, meteorological and biological processes, feasible by joint efforts of several research groups.

The atmosphere of inter- and multidisciplinary together with international environment affect also the educational experience of students working in the Centre. Our research unit has been very effective in doctoral education. Challenging problems, a combination of theoretical and modelling approaches with laboratory experiments and field measurements, and topics having both fundamental scientific relevance and socio-economic values (climate change, health effects, carbon sinks, forest growth) can make students uniformly enthusiastic (P. H. McMurry, pers. comm.).

Our scientific approach starts from basic nucleation theories and molecular level simulations followed by detailed aerosol dynamic/atmospheric chemistry models and well-defined laboratory experiments and ends with versatile continuous field measurements in our research stations and 3D modelling. A real interdisciplinary team facilitates a unique possibility to study biosphere–aerosol–cloud–climate interactions. In future also satellite data will be used together with point measurements and 3D-models.

One of the best examples so far is our recent study on the possible connections between carbon balance and aerosol–cloud–climate interactions, which are significant in studies of global climate. Kulmala *et al.* (2004d) investigated, based on long-term continuous data, the coupling between atmospheric carbon exchange and aerosol formation and growth in a continental boundary layer. They compared a six-year data set of aerosol formation and growth rates and of carbon dioxide fluxes with a two-year data set of monoterpene concentrations. The measurements were performed between April 1996 and December 2001 by measuring aerosol size distributions and using the eddy covariance technique over a Scots pine forest in the SMEAR II station. Two important connections in terms of the seasonal variability were revealed: (1) one between the growth rate of nucleation-mode aerosol particles and ecosystem gross primary production (photosynthetic sink), and (2) the other between the formation rate of nucleation-mode particles and ozonolysis of monoterpenes. In addition, the seasonal pattern of particle growth rates was similar to that of the oxidation products of monoterpenes with OH radicals. An interesting link and a potentially important feedback among forest ecosystems, greenhouse gases, aerosols and climate exists through increased photosynthesis and forest growth due to increasing temperatures and CO_2 fertilization. An increase in the forest biomass would increase non-methane biogenic volatile organic compound emissions and thereby even organic aerosol production. This couples the climate effect of CO_2 with that of aerosols in a novel way, and shows the strength of our scientific approach.

In aerosol formation point of view, the formation of new particles and their subsequent growth seem to occur almost everywhere (Kulmala *et al.* 2004b). These new particles can, depending on the location, increase the concentration of cloud condensation nuclei by a factor more than two over the course of one day. We can therefore conclude that atmospheric new-particle production is an important process that must be understood and include when developing global climate models. Future work should include continuous observations of aerosol particle size distributions in diverse locations, measurements of gaseous compounds participating in nucleation and growth, and determination of the chemical composition and other properties of nucleated particles. Measurements concerning the distribution and composition of nucleating clusters would significantly improve our understanding of the nucleation process itself. Future work should also include measurements of ion mobility distributions and ion compositions.

From the perspective of global biosphere–atmosphere interactions research, future works should aim at constructions of comprehensive stations similar to SMEAR II, investigating soil-land ecosystem–atmosphere continuum (*see* also Hari and Kulmala 2005). The importance of inter-, multi- and cross disciplinary in environmental and atmospheric research has been fully proved in the work of our Centre of Excellence.

Acknowledgements: The Centre of Excellence team acknowledges the financial support from the Academy of Finland.

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Received 29 April 2005, accepted 20 September 2005