Atmospheric nucleation: from molecular to global scale (ATMNUCLE)

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The extended synopsis of the project

Background and the state-of-the-art

Atmospheric aerosol particles and trace gases affect the quality of our life in many different ways. In polluted urban environments they have adverse effects on human health and deteriorate visibility (e.g. Nel, 2005; Pope and Dockery, 2006), whereas on regional and global scales they have a potential to change climate patterns and affect the hydrological cycle (Lohmann and Feichter, 2005; IPCC, 2007). Aerosol particles also influence the radiation intensity distribution that reaches the earth surface, thus having a direct influence on the terrestrial carbon sink (Gu et al. 2002). Better understanding of the various effects in the atmosphere requires detailed information on how different sources (including those related to the biosphere) and atmospheric transformation processes modify the properties of aerosol particles and the concentrations of trace gases. Trace gases and atmospheric aerosols are tightly connected with each other via physical, chemical, meteorological and biological processes occurring in the atmosphere and at the atmosphere-biosphere interface. Human actions, such as emission policy, forest management and land use change, as well as various natural feedback mechanisms involving the biosphere and atmosphere, have substantial impacts on the complex couplings between atmospheric aerosols, trace gases, air quality and climate (Brasseur and Roeckner, 2005; Dentener et al., 2006).

An important phenomenon associated with the atmospheric aerosol system is the formation of new atmospheric aerosol particles. Atmospheric aerosol formation consists of a complicated set of processes including the production of nanometer-size clusters from gaseous vapours, the growth of these clusters to detectable sizes and the removal of growing clusters by coagulation with the pre-existing aerosol particle population (e.g. McMurry and Friedlander, 1979). Once formed, aerosol particles need to grow further to sizes >50-100 nm in diameter until they are able to influence climate, even though smaller particle may affect human health and atmospheric chemistry. While aerosol formation has been observed to take place almost everywhere in the atmosphere (Kulmala et al., 2004a), several gaps in our knowledge regarding this phenomenon still exist. These gaps range from the basic process-level understanding of atmospheric aerosol formation to its various impacts on atmospheric chemistry, climate, human health and environment. E.g. despite the importance of gas-to-particle nucleation, little is known about the detailed molecular-scale processes behind the observed particle formation events. As a summary, we can state that aerosol particles and their interaction with the climate systems remain the dominant uncertainty in predicting radiative forcing (IPCC 2007, Baker and Peter, 2008), and that the development of better aerosol parameterizations is perhaps the single most important challenge for the next generation of climate models (Ghan and Schwartz, 2007).

Aitken (1897) was the first to report evidence for new particle formation in the atmosphere. However, quantitative measurements of aerosol formation and growth rates have required the recent developments in instrumentation for measuring size distributions down to sizes as small as 3 nm in diameter (McMurry, 2000). On the other hand, these sizes are not small enough to allow nucleation process studies, since the phase change between vapour and liquid will occur
typically at around 1-2 nm in diameter. More recently, Kulmala et al. (2007a) have developed instruments capable of detecting atmospheric nucleation and also methods capable of indirectly measuring the composition of 2-10 nm particles (Kulmala et al., 2007b).

Given the ubiquity of new-particle formation events in the global atmosphere (see Kulmala et al., 2004a), it is likely that different nucleation mechanisms are at work under different environmental conditions. Nevertheless, new-particle formation rates have been observed to correlate with the concentration of sulphuric acid in a surprisingly large variety of conditions (Weber et al., 1996). Based on this and other observations, the main candidates for nucleation in the troposphere have been thought to be binary sulphuric acid–water and ternary sulphuric acid–water–ammonia mixtures (e.g. Kulmala et al., 2004a). Ion-induced or ion-mediated nucleation involving charged clusters may contribute significantly to particle formation in the upper atmosphere, but recent experimental evidence (Kulmala et al., 2007a) indicates that its contribution to boundary layer nucleation is likely to be small. A comparison of field measurements with laboratory experiments on sulphuric acid–ammonia–water mixtures (Ball et al., 1999) reveals some curious discrepancies. For example, the nucleation rate typically depends on the 7th or 8th power of the sulphuric acid concentration in the laboratory experiments, but only on the 1st or 2nd power in the field experiments (e.g. Weber et al., 1996, Kulmala et al., 2006). This indicates that the critical cluster (the smallest cluster for which growth is thermodynamically more favorable than decay) in field conditions contains only 1-2 sulphuric acid molecules, as opposed to 7-8 molecules in laboratory conditions. This, in turn, implies that in addition to the three compounds mentioned above, other substances are likely to participate in atmospheric nucleation. The result also indicates that the critical clusters in atmospheric conditions may be surprisingly small, and thus treatable by advanced quantum chemistry methods. On the other hand, it is very probable that the atmospheric nucleation is a two-step process that proceeds via an intermediate state (atmospheric clusters), as suggested by Kulmala et al. (2000) and verified by Kulmala et al. (2007a). Under typical atmospheric conditions, the amount of sulphuric acid vapour is not enough to explain the observed condensation growth (Kulmala et al., 2001; Kulmala et al., 2004b), and thus also the role of low- and non-volatile organic compounds is crucial.

The main focus of our research team has been in the following topics (for all topics we have published papers either in Nature or in Science): 1) formation and growth mechanisms of atmospheric aerosols, aerosol dynamics and air ion and cluster dynamics: (Kulmala et al., Nature, 2000; Kulmala, Science, 2003; Berndt et al., Science, 2005; Kulmala et al., 2007, Science; Winkler et al., 2008, Science) 2) the effect of secondary biogenic aerosols on global aerosol load: (O’Dowd et al., Nature, 2002a; O’Dowd et al., Nature, 2002b; O’Dowd et al., Nature, 2005; Tunved et al., Science, 2006) 3) aerosol-cloud-climate interaction: (Kulmala et al., Nature, 1997; Charlson et al., Science, 2001) 4) the relationships between the atmosphere and different ecosystems, particularly the boreal forest: (Hari et al., Nature, 2003). Besides that, we have developed and constructed the SMEAR (Station for Measuring Forest Ecosystem-Atmosphere Relations) stations, where we have versatile continuous, long-term measurements of atmospheric and ecological mass fluxes and aerosol and biosphere-atmosphere CO₂/aerosol interactions (Kulmala et al., 2001). We have also developed, constructed and tested novel instruments such as the disjunct eddy covariance technique for flux measurements, twig chambers for simultaneous measurements of CO₂, O₃, NOx and BVOC exchange, xylem/stem diameter monitoring system, continuous in-situ techniques for measuring the hygroscopicity, volatility and composition of nucleation mode particles (diameter < 20 nm) and techniques for measuring charged and neural atmospheric clusters (AIS/NAIS; air ion/neutral cluster and air ion spectrometers).

Aims
The main scientific objectives of this project are 1) to quantify the mechanisms responsible for atmospheric new particle formation and 2) to find out how important this process is for the behaviour of the global aerosol system and, ultimately, for the whole climate system.

The research questions

In order to meet our objective, we need to answer the following, yet largely open research questions:

- What are the key processes related to new particle formation in the atmosphere?
  - What are the compounds participating? Are other $\text{SO}_2$ oxidation products than $\text{H}_2\text{SO}_4$ participating in atmospheric nucleation, and what are those compounds? Are other nitrogen-containing basic compounds than ammonia participating in atmospheric nucleation, and also how to identify these compounds? Are organosulphates participating atmospheric nucleation? Are terpene oxidation products or other related organic compounds participating in atmospheric nucleation? What is the role of iodide compounds in coastal nucleation?
  - How does the atmospheric nucleation rate depend on nucleating vapour concentration?
  - What is the role of atmospheric ions on atmospheric new particle formation? Is this related to galactic cosmic rays or other ion sources?
  - Is activation of existing clusters a key process like it seems right now?
- What are the processes behind formation and dynamics of atmospheric clusters?
  - What are the sources and sinks of neutral clusters and ion clusters? What is the composition of atmospheric clusters?
  - How are these clusters activated?
- How does atmospheric new particle formation affect the global aerosol load and radiative forcing?
  - What fraction of freshly-formed particles is able to grow to cloud condensation nuclei (CCN) size and to form cloud droplets? How will changing sources (all aerosol sources) and sinks affect cloud droplet populations?
  - What fraction of freshly-formed aerosol particles can be stated to be biogenic and anthropogenic, or can this distinction be made at all? How will these particles influence the human health and air quality?
  - How will the emissions and properties of biogenic aerosol precursors be altered in the changing climate?
- How have the role of biogenic freshly-formed aerosol particles changed from pre-industrial time to the present, and how will it change in the future, e.g. by 2100?
  - How to combine the results obtained during this project to answer the above-mentioned question?

Hypotheses

It is already known that atmospheric aerosol particles significantly influence the climate and human health, and that these effects depend mainly on the size and composition distribution of aerosol particles. A substantial fraction of atmospheric aerosols is formed by nucleation, which is a highly non-linear process. Our main hypothesis is that by solving the problem of atmospheric nucleation, we are able to reduce the present uncertainty in the global radiative balance by a factor of 2-3. The second hypothesis is that cluster formation is related to biospheric processes (e.g. photosynthesis, photorespiration), and that the activation of clusters by sulphuric acid and amines or organosulphates are the key processes behind new-particle formation. In practice, ion clusters will always activate before neutral clusters, if proper activating vapours are present (see Kulmala et al., 2007b).
Methods
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 (Kulmala et al., 2004a). Measurements of particle formation have been performed on different platforms and over different time periods (campaign or continuous-type measurements). The recent development of new instruments to measure nanoparticle size distributions and several gases that participate in nucleation have enabled these new discoveries. Measurements during nucleation episodes of evolving size distributions, earlier down to 3 nm and nowadays down to 1.5 – 2 nm, can be used to calculate the apparent source rate of 3-nm particles, and also the atmospheric nucleation rate at 2 nm. Simultaneously, the particle growth rate as a function of size can be determined. The first and longest continuous data set is from SMEAR II (Stations to Measure the forest Ecosystem – Atmosphere Relationships), which will serve as the scientific backbone of our research. The long continuous data series and the versatile measurement equipment provide continuous information on the long-term trends in the aerosol loading over boreal forests, and on the other hand allow for testing of novel instrumentation and theories in the boreal forest conditions. This provides a unique basis to diversify the aerosol measurements into different environments (see Kulmala and Tammet, 2007) all around the globe to further provide useful information for global models (see e.g. Spracklen, et al., 2006).

In order to be able to meet our objectives, and to answer our research questions, we need to perform inter-, multi and cross-disciplinary research with a high level of technological and scientific innovation. To understand the complex, non-linear system requires a diverse range of scientific and technological expertise in the areas of chemistry, physics, biology, and meteorology, and involves laboratory studies, ground, ship, and airborne field studies, satellite remote-sensing and numerical modelling studies ranging from the molecular ab initio level to the global scale Earth system models. Our research approach covers all those experimental and theoretical aspects. Figure 1 shows the general philosophy for our All-Scales-Modelling and actually the whole approach from nanoclusters to integrated Earth System Models (EMS).

Figure 1. Model and Data Integration Philosophy over spatio-temporal scales. CTM is Chemical Transport Model (see also Kulmala et al., 2007c).

The work is divided to five work packages:

- Atmospheric clusters; instrument development, quantum chemistry models, laboratory experiments
• Formation and growth of atmospheric aerosol particles; atmospheric observations, aerosol dynamic modelling, aerosol chemistry, atmospheric chemistry of precursors
• Aerosol-cloud interactions; atmospheric observations (CCN-counters), cloud microphysics, prediction of CCN concentrations
• Biosphere-atmosphere interactions; BVOC emissions, processes behind BVOC formation
• Synthesis; global aerosol load: past, present and future, global modelling

On expected research results

Due to our long experience and recent outstanding results on aerosol formation and growth studies, we have a unique possibility to find out the mechanisms behind atmospheric new particle formation and the significance of the different formation and growth processes at different atmospheric conditions. The results can be applied in understanding biosphere-aerosol-cloud-climate interactions, and specifically in reducing the uncertainty related to aerosol particles in the global radiative balance.

Section 2: The Research project

i. State-of-the-art and objectives

Atmospheric aerosol particles and trace gases affect the quality of our life in many ways. In polluted urban environments, they influence human health and deteriorate visibility (e.g. Nel, 2005; Pope and Dockery, 2006; Hand and Malm, 2007). On regional and global scales, aerosol particles and trace gases have a potential to change climate patterns and the hydrological cycle (Chung et al., 2005; Lohmann and Feichter, 2005; IPCC, 2007). Aerosol particles also influence the radiation intensity distribution that reaches the Earth's surface, and thus have a direct influence on the terrestrial carbon sink (Gu et al., 2002). Better understanding of the various effects in the atmosphere requires detailed information on how different sources (including biospheric ones) and transformation processes modify the properties of aerosol particles and trace gases. Trace gases and atmospheric aerosols are tightly connected to each other via physical, chemical, meteorological and biological processes occurring in the atmosphere and at the atmosphere-biosphere interface. Atmospheric aerosol formation, for example, is an important phenomenon which involves the production of nanometer-size particles by nucleation, and their growth to detectable sizes (Kulmala, 2003). Human actions, such as emission policy, forest management and land use change, and various natural feedback mechanisms involving the biosphere and atmosphere, have an impact on the coupling between aerosols and trace gases (Brasseur and Roeckner, 2005; Dentener et al., 2006).

The fourth assessment report of the Intergovernmental Panel on Climate Change (IPCC, 2007) concludes that anthropogenic contributions to aerosols together produce a cooling effect. Aerosols remain the dominant uncertainty in predicting radiative forcing (IPCC, 2007; Baker and Peter, 2008), and the development of better aerosol parameterisations is perhaps the single most important challenge for the next generation of climate models (Ghan and Schwartz, 2007). One of the key issues related to aerosol dynamics is the formation and growth of atmospheric aerosol particles. Although aerosol formation has been observed all over the world (Kulmala et al., 2004a), and although it seems to be frequent (see e.g. Dal Maso et al., 2005; 2007), there are still several gaps in our knowledge of this process. The status of current knowledge is that atmospheric aerosol formation is a result of photochemical reactions in the gas phase, in particular the formation of sulphuric acid (Eisele and McMurry 1997; Weber et al. 1995; Weber et al. 1996; Kulmala et al., 2006; Sihto et al., 2006; Riipinen et al., 2007a) and other vapours of very low volatility, such as multifunctional organic compounds and iodine oxides (e.g. Allan et al., 2006; O'Dowd et al., 2002a,b; 2005). Pre-existing aerosol particles act as a sink for these
vapours and nucleated clusters, thus inhibiting atmospheric aerosol formation (e.g. McMurry and Friedlander, 1979; Kerminen and Kulmala, 2002; McMurry et al. 2005). Aerosol formation also seems to be affected by several meteorological parameters and phenomena, including the intensity of solar radiation and atmospheric mixing processes, such as the evolution of a continental boundary layer or the mixing of stratospheric and tropospheric air near the tropopause.

Given the ubiquity of new-particle formation events, it is likely that different nucleation mechanisms are at work in different conditions. Nevertheless, particle formation rates have been observed to correlate with the concentration of sulphuric acid in a surprisingly large variety of conditions (Weber et al., 1995; Sihto et al., 2006; Kuang et al., 2008). Based on this and other observations, the main candidates for nucleation in the troposphere have been thought to be binary sulphuric acid – water and ternary sulphuric acid – water – ammonia mixtures (e.g. Kulmala et al., 2004a). Ion-induced or ion-mediated nucleation (Yu and Turco, 2000; Yu, 2006) involving charged clusters may contribute significantly to particle formation in the upper atmosphere, but recent experimental evidence (Iida et al., 2006; Kulmala et al., 2007a) indicates that its contribution to boundary layer nucleation is small. A comparison of field measurements with laboratory experiments on sulphuric acid - ammonia - water mixtures (Ball et al., 1999) reveals some curious discrepancies. For example, the nucleation rate typically depends on the 7th or 8th power of the sulphuric acid concentration in the laboratory experiments, but only on the 1st or 2nd power in the field experiments (e.g. Weber et al., 1996; Riipinen et al., 2007; Kuang et al., 2008). This indicates that the critical cluster (the smallest cluster for which growth is thermodynamically more favourable than decay) in field conditions contains only 1-2 sulphuric acid molecules, as opposed to 7-8 in laboratory conditions. This, in turn, implies that in addition to the three compounds mentioned above, other substances are likely to participate in atmospheric nucleation. The result also indicates that the critical clusters in atmospheric conditions may be surprisingly small, and thus treatable by advanced quantum chemistry methods. On the other hand, it is very probable that the atmospheric nucleation is a two-step process which proceeds via an intermediate state (atmospheric clusters) as suggested by Kulmala et al. (2000) and verified by Kulmala et al. (2007a).

The new aerosol particles formed by atmospheric nucleation events (see e.g. Kulmala et al., 2004a) become climatically important only if they grow to sizes larger than about 50-100 nm in diameter. Particles of this size and larger can scatter sunlight back to space, and can also act as nuclei for cloud drop formation, thus having an indirect effect on the albedo of the Earth. Furthermore, the health effects of airborne particles are related not only to the toxicity of the particle material, but also to the particle size, since size determines whether or not the particles are able to penetrate to the lungs and further to the blood circulation. According to our studies on the growth of freshly formed particles, both in pristine (Pallas, Finland; Lihavainen et al., 2003; Kerminen et al., 2005) and highly polluted (Po Valley, Italy; Laaksonen et al., 2005) environments, nucleation can produce a significant fraction of the cloud condensation nuclei, regardless of the regional emission strength of primary particulate matter (see also Spracklen et al., 2006, 2008).

The amount and representativeness of field data collected within the recent efforts of our Nordic Center of Excellence (BACCI, Biosphere-Aerosol-Cloud-Climate-Interactions) have allowed us to test the overall performance of new-particle formation parameterizations in a global chemical transport model (Spracklen et al., 2006). This study has demonstrated that new-particles formation is likely to contribute significantly (about 30 %) to the total particle number concentration in the global troposphere. Our most recent studies also indicate that the global budget of cloud condensation nuclei, a quantity relevant to the climatic effects of aero-sols, may be significantly affected by atmospheric aerosol formation (Spracklen et al., 2008).
We have recently proposed a mechanism that couples the climatic effects of CO₂ and aerosol particles (Kulmala et al 2004b). This suggestion is based on connections between photosynthesis, emissions of non-methane biogenic volatile organic compounds (BVOCs), and their ability to form aerosol particles. Photosynthesis drives plant gross primary production (GPP), which is the difference between net ecosystem exchange of CO₂ (NEE) and total ecosystem respiration (TER) (see e.g. Valentini et al., 2000). Forest ecosystems are usually sinks of CO₂, and a direct negative feedback exists between increasing atmospheric CO₂ concentrations and photosynthesis, whereas a positive feedback couples ecosystem respiration and temperature (Piao et al., 2008). With higher temperatures, water becomes a more important factor, influencing both GPP and TER. On the other hand, forest ecosystems also act as significant sources of atmospheric aerosols. Terrestrial vegetation is the major source of a variety of VOCs into the atmosphere (Guenther et al., 1995) via processes closely linked with photosynthesis (e.g. Grote and Niinemets, 2008), and newly formed particles in forested areas have been found to contain large amounts of organic material (O'Dowd et al., 2002a; Allan et al., 2006; Tunved et al., 2006). The carbon lost as BVOC emissions related to assimilation is generally a few percent (Grace and Rayment, 2000), but due to the significant process couplings, climate change may increase the formation and emissions of several BVOCs, and possibly modify the aerosol particle formation routes.

Since the time of Aitken (1897), atmospheric observations have been an essential tool in investigating new-particle formation and related processes. However, quantitative measurements of aerosol formation and growth rates have not been possible until the recent developments in instrumentation for measuring size distributions down to sizes as small as 3 nm in diameter (McMurry, 2000). Even these instruments do not allow direct nucleation process studies, since the phase change between vapour and liquid typically occurs at around 1-2 nm in diameter. Ion spectrometers can measure the charged fraction of atmospheric aerosol down to approximately 0.4 nm, and are thus able to reveal part of the evolution and dynamics of small atmospheric ion clusters. Using ion spectrometers recently developed by us (e.g. Mirme et al., 2007), we are able to observe the initial steps of particle formation and growth (e.g. Kulmala et al., 2004c). We have seen that molecular ion clusters are present almost all the time, in all environments where measurements have been performed (e.g. Kulmala and Tammet, 2007). Model calculations predicted the existence of neutral clusters, similar to those already observed with the ion instruments, already in 2000 (Kulmala et al., 2000), and several efforts toward detecting them have been undertaken in recent years. Kulmala et al. (2005) found evidence on the existence of neutral clusters in vivo several years ago (see also Weber et al., 1995). Since then, we have developed new instruments capable of both detecting neutral clusters and estimating their number concentrations in different atmospheric environments (Kulmala et al., 2007a). Using these new instruments, atmospheric nucleation can be observed to start from around 1.5 -2.0 nm. Very recently, neutral clusters have also been detected using condensation particle counter techniques (Sipilä et al., 2008). The composition of 2-10 nm particles can be measured indirectly using the CPCB (condensation particle counter battery) technique (Kulmala et al., 2007b), and new diethylene glycol CPCs (Iida 2007) will further provide useful data on cluster concentrations.

The main focus of our research team has been in the following topics (for all topics we have published papers either in Nature or in Science): 1) formation and growth mechanisms of atmospheric aerosols, aerosol dynamics and air ion and cluster dynamics: (Kulmala et al., Nature, 2000; Kulmala, Science, 2003; Berndt et al., Science, 2005; Kulmala et al., 2007, Science; Winkler et al., 2008, Science)) 2) the effect of secondary biogenic aerosols on the global aerosol load: (O’Dowd et al., Nature, 2002a; O’Dowd et al., Nature, 2002b; O’Dowd et al., Nature, 2005; Tunved et al., Science, 2006) 3) aerosol-cloud-climate interaction: (Kulmala et al., Nature, 1997; Charlson et al., Science, 2001) 4) the relationships between the atmosphere and different ecosystems, particularly the boreal forest: (Hari et al., Nature, 2003). Besides that, we have developed and constructed the SMEAR (Station for Measuring Forest Ecosystem-Atmosphere Relations) stations.
**Objectives:** The main scientific objectives of this project are 1) to quantify the mechanisms responsible for atmospheric new particle formation and 2) to find out how important this process is for the behaviour of the global aerosol system and, ultimately, for the whole climate system.

In order to meet our objective, we need to answer the following, at present largely open, research questions given in section 1b.

**Hypotheses:** It is already known that atmospheric aerosol particles significantly influence the climate and human health, and that these effects depend mainly on the size and composition distribution of aerosol particles. A substantial fraction of atmospheric aerosols is formed by nucleation, which is a highly non-linear process. Our main hypothesis is that by solving the problem of atmospheric nucleation, we are able to reduce the present uncertainty in the global radiative balance by a factor of 2-3. The second hypothesis is that cluster formation is related to biospheric processes (e.g. photosynthesis, photorespiration), and that the activation of clusters by sulphuric acid and amines or organosulphates are the key processes behind new-particle formation. In practice, ion clusters will always activate before neutral clusters, if proper activating vapours are present (see Kulmala et al., 2007b).

**ii. Methodology**

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 (Kulmala et al., 2004a) These new discoveries have been enabled by the recent development of new instruments to measure nanoparticle size distributions and several gases that participate in nucleation. Measurements of particle formation have been performed on different platforms and over different time periods (campaign or continuous-type measurements). Measurements during nucleation episodes of evolving size distributions, earlier down to 3 nm and currently down to 1.5 – 2 nm, can be used to calculate the apparent source rate of 3-nm particles, the nucleation rate at 2 nm, and also the particle growth rate as a function of size. The first and longest continuous data set is from SMEAR II stations (Kulmala et al., 2001), which will serve as the scientific backbone of our research. The long continuous data series and the versatile measurement equipment provide information on the long-term trends in the aerosol loading over boreal forests, and also allow the testing of novel instrumentation and theories in boreal forest conditions. Our instrumentation and knowledge provide a unique basis to diversify aerosol and cluster measurements into different environments all around the globe (see Figure 2). Thus, we can provide useful information for global models (see e.g. Spracklen, et al., 2006, 2008).
In order to meet our objectives, and to answer our research questions, we need to perform inter-, multi and cross-disciplinary research with a high level of technological and scientific innovation. To understand the complex, non-linear system requires a diverse range of scientific and technological expertise in the areas of chemistry, physics, biology, and meteorology, and involves laboratory studies, ground, ship, and airborne field studies, satellite remote-sensing and numerical modelling studies, ranging from the molecular \textit{ab initio} level to the global scale Earth System Models. Therefore, our scientific approach starts from basic nucleation theories, followed by models of detailed aerosol dynamic/atmospheric chemistry and vegetation – atmosphere exchange, well-defined laboratory experiments and versatile continuous field measurements at our research stations, and extends to global-scale modelling. Our approach thus covers both experimental (laboratory and field experiments) and theoretical (basic theories, simulations, model development, parameterizations) points of view. The general philosophy for our All-Scales-Modelling and the whole approach from nanoclusters to integrated Earth System Models (EMS) is shown in section 1b (Figure 1, section 1b).

The work is divided into five inter-linked work packages (WP) that support each other. From each WP we are expecting at least one scientific breakthrough.

1. Atmospheric clusters; instrument development, quantum chemistry models, laboratory experiments
2. Formation and growth of atmospheric aerosol particles; atmospheric observations, aerosol dynamic modelling, aerosol chemistry, atmospheric chemistry of precursors
3. Aerosol-cloud interactions; atmospheric observations (CCN-counters), cloud microphysics, prediction of CCN concentrations
4. Biosphere-atmosphere interactions; BVOC emissions, processes behind BVOC formation
5. Synthesis; global aerosol load: past, present and future, global modelling

WP 1. Atmospheric clusters

This WP gives insight on cluster dynamics and the existence of neutral clusters. The existence of atmospheric neutral clusters has been suggested some years ago by Kulmala et al. (2000). Kulmala et al. (2007a) observed that the formation of new aerosol particles is connected with the existence of atmospheric clusters. The existence of small ion clusters in the atmosphere has been known already for several decades (see e.g. Laakso et al., 2004), but the existence of neutral atmospheric clusters has been remained an open question (Kulmala et al., 2005) until recently (Kulmala et al., 2007a). In this WP, we will answer the following questions:

- What are the processes behind the formation and dynamics of atmospheric clusters?
- What are the sources and sinks of neutral clusters and ion clusters? What is the composition of the atmospheric clusters?
- How are these clusters activated?

Instrument development

Critical clusters – if electrically neutral – formed by atmospheric nucleation events cannot yet be measured quantitatively due to instrumental limitations. More work on the distribution and composition of such clusters is needed to refine our understanding of atmospheric nucleation. However, ion clusters can be and have been measured during nucleation events (e.g. Hörrak, 2001; Laakso et al., 2004). Recent developments enable us to measure sub - 2 nm clusters using instruments like Pulse Height Condensation Particle Counters (PH-CPC), Expansion CPCs or neutral cluster and Air Ion Spectrometers (NAIS) (see Kulmala et al., 2007a; Sipilä et al., 2008). Also, condensation particle counters with different condensing liquids and temperature differences between saturator and condenser will be further developed, tested and used to indirectly investigate the composition of clusters smaller than 3 nm (see Kulmala et al., 2007b). The efficiency of different working fluids was also studied recently (Iida 2007). However, all these instruments need to be further developed and tested before they can be continuously used in atmospheric studies.

In practice, we will use different working fluids and different temperature differences in CPCs, and also use different mobility standards, in order to find the proper mass, mobility and size connections. In the case of NAIS, further studies on charging probability, and also on the effect of charger ions on the observed signal, will be performed.

Molecular - scale simulations

We have previously used quantum chemical methods to quantitatively replicate experimental results on the hydration of sulphuric acid (Kurtén et al., 2007a) and to explain the role of ammonia in neutral (Kurtén et al., 2007b; Torpo et al., 2007) and ion-induced (Ortega et al., 2008) sulphuric acid - water nucleation. The starting point for the simulations planned in the present proposal is that the picture of atmospheric nucleation as a process involving sulphuric acid, water and ammonia needs to be complemented in three ways. First, as indicated by the experiments of Berndt et al. (2005), some other sulphur - containing compounds than sulphuric acid may participate. Second, some other basic nitrogen-containing compounds than ammonia (namely, various amines) may participate. Third, some organic compounds originating from terpene oxidation may also participate. As all three nucleation pathways may contain contributions from both neutral and ion-induced mechanisms, both neutral and charged clusters will be studied in each case. Additionally, the activation of clusters via heterogeneous nucleation of the above-mentioned compounds will also be investigated.
Based on earlier work by the group (Kurtén et al., 2007a,b; Ortega et al., 2008), some cost-effective combinations of computational approaches for atmospheric molecular cluster studies have been developed. For each of the three objectives, we will first carry out high-level (MP2 and coupled-cluster) simulations on small (up to 4-5 molecules) clusters. The results of these simulations will already yield valuable information on the fundamental chemical behaviour of the systems under study, and help to constrain further research with respect to e.g. the precise selection of chemical compounds. The high-level computational results will then be used to validate the more computationally affordable combination methods being developed, for example via the computation of force field parameters for molecular dynamics simulations. The most promising nucleation candidates from each of the three systems under study will finally be combined in simulations intended to describe nucleation processes in the real atmosphere, where all three types of compounds are likely to be present at the same time.

**Laboratory experiments**

Nucleation experiments for the sulphuric acid–ammonia/amine–water and various organic acid–water–ammonia/amine systems, as well as activation experiments for both neutral and ion clusters, will be carried out in order to produce data for reliable nucleation rate parametrizations. Particle formation experiments will also be performed in the O₃/alkene/SO₂/H₂O system under experimental conditions, including reactant concentrations, close to those present in the troposphere. These experiments will be performed both with and without contributions from alkene ozonolysis, and the influence of NH₃ and different amines will be investigated. Observed nucleation rates from both experimental approaches, with and without added NH₃, will be compared. Nucleation rate measurements in various organic acid-water systems with and without added ammonia/amine will be performed in a laminar flow chamber with a turbulent vapour mixing unit. Formic acid–water and acetic acid–water. mixtures will be studied first, followed by, acids of higher molecular weight. The effect of added NH₃ will also be studied. Nucleation probability studies (heterogeneous nucleation, activation) of different types of neutral and ion clusters will be performed in the presence of several organic compounds. The first experiments will include neutral and charged metal clusters, iodide clusters, organic clusters and inorganic salt clusters in the presence of organic and water vapours. The newly developed instruments will be used in these experiments, together with the size analyzing nucleus counter (SANC; e.g. Winkler et al., 2008), in co-operation with the University of Vienna. H₂SO₄ and OH concentrations will be measured using a CIMS apparatus, which is now being constructed in co-operation with NCAR, Boulder. PTR-MS is used for organic gases, and also SO₂, O₃, CO and NOₓ are monitored.

**WP 2. Formation and growth of atmospheric aerosol particles**

This WP gives insight on atmospheric nucleation and subsequent growth. Sulphuric acid, which is known to be one of key components in new particle formation and growth, cannot alone account for the observed particle growth (Kulmala et al., 2004a, Stolzenburg et al., 2005), and organic vapours are typically needed to explain it. In particular, mono- and sesquiterpenes are known to have a high potential to participate in secondary organic aerosol formation (Hoffmann et al., 1997; Bonn and Mørtgat, 2003; Jaoui et al., 2003). Recently, also polymers of isoprene have been detected in organic aerosols (Claeys et al., 2004).

In this WP, we will answer the following questions:

- What are the key processes related to new particle formation in the atmosphere?
  - Which compounds participate? Are other SO₂ oxidation products than H₂SO₄ participating in atmospheric nucleation, and what are those compounds? Are other nitrogen-containing basic compounds than NH₃ participating in atmospheric nucleation, and how can they be identified? Are organosulphates participating in atmospheric nucleation? What is the role of terpene oxidation products or other
related organic compounds in atmospheric nucleation? What is the role of iodide compounds in coastal nucleation?
- How does the atmospheric nucleation rate depend on the concentrations of the nucleating vapours?
  - What is the role of atmospheric ions on atmospheric new particle formation? Is this related to galactic cosmic rays or other ion sources?
  - Is the activation of existing clusters a key process like it seems right now?

Future work includes continuous observations of aerosol particle size distributions in diverse locations, measurements of gaseous compounds participating in aerosol formation, and determination of the chemical composition and other properties of nucleated particles. These measurements would significantly improve our understanding of the formation process itself. On the other hand, also new aerosol dynamic models will be developed in order to test different hypotheses related to aerosol formation and growth.

**Atmospheric observations**

Field measurements are our core activity. They include continuous measurements at the SMEAR stations (see Hari and Kulmala, 2005), intensive measurement periods and separate measurement campaigns. Continuous measurements will be conducted at all our stations (SMEAR I-III) and a number of other stations worldwide. The continuous measurements include aerosol particle and air ion number size distribution, trace gas and basic meteorological measurements. Intensive measurements will be conducted roughly once a year at each station. During the intensive periods, very detailed measurements of trace gases, aerosol chemistry and various boundary layer parameters will be conducted. Separate field campaigns will be carried out in different locations all over the world, either as part of the international projects, or on a co-operative basis.

The atmospheric observations at different conditions will improve our understanding of the effect of atmospheric conditions on new particle formation. Therefore, the measurements will be performed at different conditions such as boreal forest, coastal environment, marine boundary layer, rain forest, temporal forest and urban areas. From the observations, the formation rates of 2 nm particles can be calculated (see Kulmala et al. 2007a). The formation and growth rates can be compared with trace gas concentrations in order to find out which vapours participate in the formation and growth processes of the clusters. The functional dependence of these rates on the vapour concentrations will also be investigated.

**Aerosol dynamic modelling**

Aerosol models are used here for two purposes: to interpret and understand field observations, and to develop new parameterizations for large-scale atmospheric models. The employed models will be either box models or one-dimensional chemical transport models. The box models like UHMA (see Korhonen et al., 2004) and Ion-UHMA (Leppä et al., 2008, manuscript in preparation) will contain a very detailed description of aerosol dynamical processes and various degrees of complexity in simulating gas/aerosol chemistry. The one-dimensional models will be somewhat simpler in terms of aerosol dynamics and chemistry, but allow a more detailed description of various boundary layer processes, including transportation and surface-atmosphere interactions. The new hypotheses and theories for aerosol dynamical processes can be first studied and tested in box models, and then parameterized for one-dimensional models and, further, local and global models. Through collaboration with the University of Leeds, we will test these new mechanisms in a global aerosol microphysics model (GLOMAP: http://researchpages.net/glomap), an approach that has already proved successful (Spracklen et al., 2006, 2008). Development of such global aerosol-chemistry-transport models and testing them against extensive observations is an essential step towards the development of complete
Aerosol Chemistry

Studying the composition of freshly-nucleated particles is currently impossible with commercially-available instrumentation. Several in situ systems have been developed for on-line measurements, including aerosol mass spectrometers (AMS) for the particle phase (Sullivan and Prather, 2005) and proton-transfer ion-trap mass spectrometry for the gas phase (Warneke et al, 2005). For nanoparticles, the thermal desorption chemical ionization mass spectrometer (TDCIMS), which can measure composition to sizes as small as 7-8 nm (Smith et al. 2005; Voisin et al. 2003), is a very promising instrument. The in situ measurements are a requisite for obtaining highly time-resolved analyses that are capable of measuring changes in aerosol chemistry. Indirect information of particle composition can be obtained from measurements of hygroscopic and ethanol uptake properties of aerosol particles and their volatility (e.g. Vaattovaara et al., 2005, Wehner et al., 2005). These results give an in situ indication of changes in particles composition as a function of time and size.

Both aerosol time-of-flight mass spectrometers (AMS) with unique size selective sampling valves and portable comprehensive two-dimensional gas chromatographs (GCxGC) with on-line sampling, will be developed and utilized. The main emphasis is on the identification of oxidation and oligomerisation/polymerisation products of terpenes. Standards necessary for quantitative analysis of the oxidation products will be produced by the neoteric liquid phase reaction method. By simultaneous measurements with the novel AMS and GCxGC instruments, detailed qualitative and quantitative information of the organic composition of aerosols will be produced within fast analysis cycles (10-30 min). For indirect composition determination, we will further develop different hygroscopic, organic and volatility differential mobility analysers (HTDMA, OTDMA and VTDMAs) and also CPC Batteries.

Atmospheric Chemistry of Precursors

The most important precursors are sulphuric acid and different BVOCs (e.g. terpenes, isoprene). Their atmospheric chemistry will be studied using atmospheric measurements and models. Models describing atmospheric chemistry, such as MALTE (Boy et al., 2006), will be constrained by continuous on-line measurements conducted by chemical ionization mass spectroscopic (CIMS) methods, such as proton transfer reaction – mass spectrometry (PTR-MS). The chemical schemes will also be further developed and implemented in our models. In atmospheric conditions, boundary layer meteorology is strongly coupled with atmospheric chemistry and aerosol formation. The MALTE model includes all these couplings.

WP 3. Aerosol-cloud interactions

This WP gives insight on how newly formed particles will form cloud condensation nuclei (CCN). The freshly formed particles can, depending on the location, increase the concentrations of CCN by a factor of more than two over the course of one day (e.g. Laaksonen et al., 2005), and ultimately lead to significant enhancements in cloud droplet concentrations (Kerminen et al., 2005). We conclude, therefore, that atmospheric new-particle production is an important process that must be understood and included in global climate models. In this WP, we will answer the following questions:

- What fraction of freshly-formed particles is able to grow to cloud condensation nuclei (CCN) size and form cloud droplets?
How will changing sources (all aerosol sources) and sinks affect cloud droplet populations?

**Atmospheric observations**

In order to quantify CCN formation from atmospheric aerosol formation, influenced by biogenic and anthropogenic organic emissions, we will perform long-term and intensive campaign measurements using CCN counters at five different stations. Each of these stations has different characteristics with respect to natural and anthropogenic influences. The Pallas station has very clean air quality most of the time, while Värrö is almost similar, but with occasional strong influences from industrial activities on the Kola Peninsula (smelter emissions), and more influences from biogenic forest emissions. Hyytiälä represents relatively clean environments, in which the anthropogenic influence depends on the air mass origin. Helsinki is a moderately polluted area and, finally, San Pietro Capofiume represents a heavily polluted environment. This host of stations thus offers us an opportunity to study the biogenic vs. anthropogenic influence on CCN formation from atmospheric nucleation events in different environments, and to quantify the importance of the events to the local CCN budgets in such a way that larger scale (regional/global) assessments become possible.

**Cloud microphysics**

The influence of different chemical factors (water solubility of aerosols, their surfactant properties, effects from condensable gases, see Charlson et al. 2001, McFiggans et al., 2006) have received considerable attention in recent years. It is now becoming clear that some of these effects are relatively minor (Kokkola et al., 2006). Also, a recent study by Dusek et al. (2006) demonstrated that the aerosol size distribution has a much stronger influence on cloud activation than the chemical composition of the particles. However, there are chemistry-related issues influencing cloud activation that need to be studied further. Thus, we will develop a theoretical formulation for the activation of wettable, insoluble organic particles, which have in the laboratory been found to activate as easily as water-soluble organics (Raymond and Pandis, 2002), whereas nonwettable particles need much higher supersaturations for activation. Another issue that remains worth pursuing is the influence of soluble gases on activation. We are especially interested in clarifying the influence of HNO₃ under a future scenario in which the atmosphere has been cleared of particulate pollution, but NOₓ emissions remain at a present-day levels and also the atmospheric nucleation due to biogenic processes is producing new particles. We also aim to extend our studies to include the effect of ammonia, although we now know that this is a difficult task, due to the fact that ammonia may partition to the aqueous phase already considerably below 100% relative humidity, depending on the acidity of the droplets (Romakkaniemi et al, 2005).

**Prediction of CCN concentrations**

It has recently been shown that atmospheric nucleation and growth of secondary particles can contribute significantly to regional CCN budgets both in clean (Lihavainen et al, 2003) and polluted (Laaksonen et al., 2005) environments. The local CCN concentrations (particles of sizes bigger than 50 nm) can be predicted using aerosol dynamic models like UHMA (Korhonen et al., 2004), and global CCN concentration can be predicted using GLOMAP (Spracklen et al., 2008). Analytically, the predicted CCN concentration depends on the growth rate of the freshly formed particles and on their coagulation sink to pre-existing particles (Kerminen and Kulmala, 2002).

**WP 4. Biosphere-atmosphere interactions**
This WP studies the coupling of the biosphere to physical and chemical processes of the atmosphere. Biogenic volatile organic compounds (VOCs) have a central role in tropospheric chemistry. Many VOCs participate in aerosol growth and formation processes (Went, 1960; Claeyss et al., 2004; Tunved et al., 2006). The products formed in the reactions of VOCs with ozone, or OH and NO3 radicals, may have lower volatility, and thus condense into aerosol particles. VOCs also affect the production and destruction of tropospheric ozone (Atkinson and Arey, 2003). As they compete for OH with methane, they may have an influence on the atmospheric lifetime and concentration of this powerful greenhouse gas (Kaplan et al., 2006). VOCs may also affect the optical properties of aerosol particles (Nozière and Esteve, 2005). Even though the anthropogenic VOC emissions generally surpass the biogenic emissions in most of Europe, in Northern Europe the biogenic emissions dominate (Simpson et al., 1999). Also, on the global scale, the biogenic VOC emissions clearly dominate over the anthropogenic ones (Guenther et al., 1995).

Different BVOCs participate in different stages of aerosol formation and growth. Sesquiterpene oxidation products may take part in aerosol formation itself (Bonn and Moortgat, 2003), while isoprene and monoterpene oxidation products are mainly connected to aerosol growth (Claeyss et al., 2004; Tunved et al., 2006). Oxygenated VOCs (OVOC) such as carbonyls can also affect the light absorption properties of sulfate aerosols (Nozière and Esteve, 2005). In order to understand the role of the terrestrial vegetation on atmospheric aerosol formation, growth and properties, we need to investigate especially the poorly known emissions of sesquiterpenes and OVOCs (alcohols and carbonyls), and in particular the regulating factors underlying temporal and spatial variations in emissions from different plant species. In this WP, we will answer the following question:

- How will the emissions and properties of biogenic aerosol precursors be altered in the changing climate?

**BVOC emissions**

We will monitor the fluxes between the biosphere and the atmosphere. Emissions will be measured at various temporal and spatial scales utilizing e.g. enclosure techniques (Bäck et al., 2005; Ruuskanen et al., 2005) and micrometeorological disjunct eddy covariance techniques (Rinne et al., 2007). The aerosol fluxes can also be determined either with eddy covariance (Buzorius et al., 2000) or relaxed eddy accumulation techniques (Gaman et al., 2004). The micrometeorological disjunct eddy covariance measurements will utilize fast-response proton transfer reaction mass spectrometers (PTR-MS, Lindinger et al., 1998) and gas chromatographic mass spectrometry techniques for closer compound identification. In order to interpret the measured above-canopy fluxes of the gas-phase precursors, interaction between within- and above-canopy chemistry and turbulent transport will be studied using a stochastic Lagrangian transport model with a chemistry module (Rinne et al., 2007).

Emissions determined at different spatial scales will be linked by up-scaling, using vegetation inventories including the dominant tree species and minor species and ground vegetation. Currently, measured concentration ratios of isoprene and monoterpenes (Hakola et al., 2003) do not agree with the modeled emissions (Simpson et al., 1999; Tarvainen et al., 2007). This may be due to the omission of minor species with high isoprene emission, such as willows and mosses (Haapanala et al., 2006) in the emission models, or due to incomplete model parameterizations, which do not fully account for e.g. seasonal variations in specific emission factors. The regional scale emissions will first be modeled using parameterized light and temperature responses, but the aim is to develop at more mechanistic emission model, which can be linked to global climate models. The experimental results will be used for improving emission parameterizations and for adjusting mechanistic models to different forest tree species, which can later be used as input in the regional and larger scale vegetation modelling.
Processes behind BVOC formation

Laboratory experiments with controlled environmental conditions will be used to study the mechanisms of VOC synthesis and emission by plants, and will be linked with the VOC and carbon metabolism studies in the field. Inhibitors and inducers of biosynthesis, isotopic fractionation and stable isotope labeling will also be used. Studies on gene expression (using DNA microarrays) as well as on the seasonal changes in substrate (DMAPP) concentrations and isoprene and monoterpane synthase activities will be performed. The combined effects of the external (temperature, light) and inherently determined (stage of development, level of gene expression) factors affecting biosynthesis, both in the deciduous, isoprene-emitting aspen and willow, and in the evergreen, monoterpane-emitting pine, will be embedded into a mechanistic, physiologically sound model structure describing VOC biosynthesis and emissions (Bäck et al 2005).

WP5. Synthesis

This WP integrates the whole research from nano and local scales up to regional and global scales. A major enterprise conducted at the international level is the development of complex Earth System Models (ESM). Such models integrate our knowledge regarding the atmosphere, ocean, cryosphere and biosphere, accounting for the couplings between physical and biogeochemical processes in these components of the Earth System. We can provide unique data and detailed information especially from boreal regions to ESMs. However, ESMs are numerically highly demanding, and the modelling of aerosol processes must be simplified before they can be included. An important part of our strategy is therefore to explore the impact of new emissions and processes in a sophisticated offline global aerosol model (GLOMAP) in collaboration with Leeds. In the other WPs, we concentrate on obtaining results from processes that are not yet fully understood, and have therefore not been implemented in integrated models. We are a part of COSMOS, a new project for community ESM, led by the Max Planck Institute in Hamburg. The activities are strongly linked to those in the Integrated EU Project EUCAARI (co-ordinated by M. Kulmala). The most novel (beyond EUCAARI) aspect of this project is to couple the biogenic aerosol production with a global aerosol dynamics model for the first time, in the context of global Earth System Modelling. In this WP, we will answer the following questions:

- How does atmospheric new particle formation affect the global aerosol load and radiative forcing?
- What fractions of freshly-formed aerosol particles can be stated to be biogenic and anthropogenic, or can this distinction be made at all? How will these particles influence human health and air quality?
- How has the role of biogenic freshly-formed aerosol particles changed from pre-industrial time to the present, and how will it change in the future, e.g. by 2100?
  - How to combine the results obtained during this project to find out the past, present and future role of biogenic freshly-formed aerosol particles?

Global aerosol load

As mentioned above, nucleation can contribute significantly to regional CCN budgets both in clean and polluted environments. Similar result have been observed for global CN (Spracklen et al., 2006) and CCN (Spracklen et al., 2008) concentrations. Less attention has been given to the possibility that atmospheric nucleation may have been a very important source of CCN in the pre-industrial world. In this context, it should be noted that atmospheric aerosol formation is a source of CCN that is currently missing from climate models; even though nucleation of sulfate particles is described in some climate models, no models treat the nucleation of sulfate particles and their
subsequent growth to sizes above 50 nm due to biogenic (or anthropogenic) secondary organics. Understanding natural ecosystem – atmosphere relationships helps to re-cognize the anthropogenic effects on climate in general, and on the aerosol load in particular.

After verification and quantification of the atmospheric nucleation mechanisms and their effects on CCN production, and also after verification and quantification of the future changes of biogenic precursor production due to climate change, the past, present and future global aerosol load can be calculated. To achieve this, we use three different tools: a) an analytical approach, aided by box-model simulations, which are able to calculate order-of-magnitude estimates of the effects and relative importance of different processes, b) GLOMAP chemical transport model simulations, which give more quantitative information on the behavior of the system at different spatial and temporal scales, and c) COSMOS Earth System Model simulations, which are needed to discover and quantify the effects of various feedbacks between the biosphere, atmosphere and climate.

Biogenic aerosol forcing

In this task, we intend to narrow the uncertainty range for estimates of aerosol radiative forcing. Aerosol properties (composition, size, shape) vary strongly in time and space. Thus, despite computational constraints, new aerosol modules in global modelling now distinguish between different aerosol components (e.g. sulfate, organic carbon, black carbon, mineral dust and sea-salt). Advanced modules further discriminate aerosol size (e.g. size-bins or size-modes) and permit mixtures among components (e.g. Kinne et al., 2006; Textor et al., 2006; Pierce et al., 2007). A realistic representation of the aerosol properties is a key to improvements regarding aerosol processing and interactions with the climate system (Ghan and Schwartz, 2007). By using the appropriate parameterizations obtained from the other WPs, computationally effective aerosol models will be developed and tested against observations, and finally implemented into the COSMOS ESM.

Biogenic VOC are thought to be a major, and probably dominant, source of organic aerosol, at least in Northern Europe. Emissions of natural precursors to secondary organic aerosols (such as monoterpenes) from vegetation have been observed to depend strongly on temperature, at least on weekly to seasonal timescales. If the same temperature dependence holds on longer timescales, the concentration of secondary organic aerosols is expected to increase in a warmer climate, thus increasing the cooling effect of aerosols. This negative feedback may be modulated by shifts in plant functional types and/or decreases in plant productivity because of various environmental stresses. The ESM will be used to investigate the strength of the feedback and the role of modulating processes. Updated current emission databases, making use of improved databases on European forest cover, and recent work on improved European and global databases, are utilized.

Current large-scale models are, to some extent, capable of predicting responses related to e.g. temperature changes and resulting feedbacks. However, the general significance of recently verified links and feedbacks between the temperature, photosynthesis, VOC emissions and particle formation (Kulmala et al., 2004b), or between particle load, diffuse radiation and photosynthesis (Gu et al., 2002), are not presently known. As a result of the present project, the effect of biogenic aerosol formation on global aerosol load is therefore verified, and also the radiative effects are estimated.

International co-operation: Our research group has direct working connections to more than 60 international laboratories and has participated in more than 30 EU-projects. We also have working connections to IPCC, IGAC and ILEAPS. We are participating e.g. in the global
Fluxnet (flux tower network) and international field campaigns to investigate atmospheric aerosols and tropospheric chemistry, as well as the Earth System Model consortium (COSMOS). In this project, we will co-operate closely with the University of Leeds. Dr. Spracklen has been appointed to the team. The co-operation with Leeds has enabled the mechanisms developed in Helsinki to be extended to the global scale for the first time.

**On expected research results:** Due to our long experience and recent outstanding results in aerosol formation and growth studies, we have a unique possibility to find out the mechanisms behind atmospheric new particle formation and the significance of the different formation and growth processes at different atmospheric conditions. The results can be applied in understanding biosphere-aerosol-cloud-climate interactions, and specifically in reducing the uncertainty related to aerosol particles in the global radiative balance.

**Publications and dissemination of information:** The results of the investigation will be published in international journals, e.g., *Nature, Science, Physical Review Letters, Atmospheric Chemistry and Physics, Journal of Geophysical Research, Geophysical Research Letters, Journal of Aerosol Science*, etc. The results will also be presented in international and national conferences and workshops.

**Section 3: The Research Environment**

i. PI's Host institution

**University of Helsinki:** The Department of Physics at the University of Helsinki has over 25 years of experience in atmospheric and urban air pollution research. 80 scientists and doctoral students are currently engaged in this area. The main research subjects are aerosol dynamics (nucleation, condensation, coagulation, deposition), formation and growth of atmospheric aerosol particles and cloud droplets, atmospheric chemistry, urban aerosols, air quality, forest-atmosphere interactions (fluxes, photosynthesis, water transport), and aerosol-cloud-climate interactions. The basic theoretical resources consist of detailed computer codes describing basic phenomena such as multicomponent nucleation and condensation, photosynthesis, and of extensive models for aerosol dynamics, atmospheric chemistry, cloud microphysics as well as regional and climate models. The basic experimental resources consist of three field stations (SMEAR I and SMEAR II and Urban SMEAR) and a state-of-the-art aerosol laboratory. In the field stations parameters related to e.g. aerosol dynamics, atmospheric chemistry, micrometeorology and urban particulate matter are measured continuously.

The activities presented in the present proposal are supported by the University of Helsinki. The scientific approach starts from basic nucleation theories followed by detailed aerosol dynamic / atmospheric chemistry models and well defined laboratory experiments, and ends in very versatile continuous field measurements at our research stations and 3D modelling. We are currently using the COSMOS earth System Model (Max Planck Institute, Hamburg) and it can readily be modified and run in this project. We also have a Global Chemical Transport model (Global Model of Aerosol Processes, GLOMAP; University of Leeds, UK), which has already been successfully used. Satellite data is also used together with point measurements and 3D-models. Several scientists from the University of Helsinki are involved in international scientific organisations and networks such as IPCC, IGAC/IGBP and iLEAPS/IGBP. The latter has its international project office in Helsinki, hosted by Markku Kulmala.

The core facilities related to proposed research are the SMEAR II field station (Hari and Kulmala, Boreal Environment Research, 10:315-322, 2005), extended instrumentation for aerosol particle and atmospheric ion measurements and iLEAPS (integrated Land Ecosystem Atmosphere Processes Study) ([http://www.atm.helsinki.fi/ILEAPS](http://www.atm.helsinki.fi/ILEAPS)).
SMEAR II

The SMEAR II (Station for Measuring Forest Ecosystem--Atmosphere Relations) station is located in a rather homogenous Scots pine (Pinus sylvestris L.) stand on a flat terrain at the Hyytiälä Forestry Field Station of the University of Helsinki (61°51’N, 24°17’E, 181 m above sea level) 220 km NW from Helsinki. The managed stand was established 1962 by sowing after the area had been treated with prescribed burning and light soil preparation. The station represents boreal coniferous forests, which cover 8% of the earth’s surface and store about 10% of the total carbon in the terrestrial ecosystem. The biggest city near the SMEAR II station is Tampere, which is about 60 km from the measurement site with about 200 000 inhabitants. Another long-term field site for carbon (carbon dioxide, methane and VOC) and energy exchange studies and soil (peat) processes is located close to the SMEAR II station at the Siikaneva wetland (fen) area.

At SMEAR II, measurements are carried out at a number of storage pools and interfaces involving three different layers, extending from the soil to the atmosphere. Several different methods, operating simultaneously but at different spatio-temporal scales, are applied to monitor the material and energy fluxes between the different pools, and to understand the processes responsible for these fluxes. For example, the surface between a tree and the atmosphere, or between the soil and the atmosphere, can be enclosed in a chamber, and the corresponding flux of interest can then be determined from the mass balance of the chamber. Turbulent fluxes can be measured by micrometeorological techniques. Concentration gradients in the air and soil can also be used for making flux estimates by applying available transport coefficients. Electric sensors are available to measure radiation fluxes. For further details see Hari and Kulmala (2005).

The main components of SMEAR II are i) an instrumented, 73-m-tall mast, ii) systems for monitoring aerosols and air ions, iii) instrumentation for monitoring tree functions and radiation (by two 25 m towers) and iv) two instrumented mini catchments. The mast monitors CO₂, H₂O, CO, O₃, SO₂, NO, NO₂, temperature and wind speed profiles, properties of solar and thermal radiation of the stand and fluxes of CO₂, H₂O, O₃ aerosols and several volatile organic compounds between the canopy and atmosphere. The mast measurements are usually reported as half-hour means. Aerosol and ion size distributions are measured in order to be able to study ion, cluster and aerosol dynamics. Chamber techniques are used to monitor tree processes generating the fluxes between trees or soil and the atmosphere. The most relevant processes are: photosynthesis, respiration, transpiration, NOₓ emission and deposition, O₃ deposition and emission of volatile organic compounds. The fluxes between the soil and the atmosphere, as well as between the soil and the canopy, are also important. The catchments are closed with a dam, and the run-off from the area is monitored. The leakage of substances with the run-off is monitored by taking samples for chemical analysis. The water content and tension, CO₂ and temperature profiles are monitored. Solar radiation is the source of energy for several processes in the trees and the atmosphere. Therefore, irradiance, diffuse irradiance, photosynthetically active radiation and radiation balance are monitored above the canopy. Stem diameter changes are monitored both above and under bark continuously with a precision of less than 1 μm. This allows us to indirectly estimate the water tension in xylem and phloem, which is an ecophysiology important parameter, but very difficult to determine.

One of the basic principles of our research team is the utilization of continuous, long-term field measurements. Therefore, the system operates the year around, and only those rare instruments, which may be damaged by freezing water, are turned off during winter. In addition, the growth of the trees around the measuring station has been measured retrospectively to the age of three years. All data are available for the research community in the database of SMEAR II, and much of the data are also available at various databases of international projects (like CarboEurope) and
programmes (like Fluxnet). It should finally be noted that the description given above only provides a general methodological framework and the most important measurement set-ups. The SMEAR II station is actually under continuous development due to the construction and installation of new set-ups or modifications of existing ones.

iLEAPS

iLEAPS (integrated Land Ecosystem Atmosphere Processes Study) is the land-atmosphere project within the framework of the second phase of IGBP. It aims to improve the understanding of processes, linkages and feedbacks, and changes due to human activities, in the land-atmosphere interface affecting the Earth System. The research ranges from the cellular level to the global scale, diurnal to centennial and past to future. It encourages international and cross- and multi-disciplinary collaboration. The main themes are land-atmosphere exchange, feedbacks between land biota, aerosols and atmospheric composition, teleconnections in the land surface-atmosphere-water-system and transfer of material and energy in the soil/canopy/boundary-layer system. Both measurements and modelling of interaction processes are applied.

iLEAPS provides the forum and facility which directly support the themes and work packages. It is especially important regarding the linkages of different tasks and the merging of results by means of Earth System Modelling.

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