1. INTRODUCTION

It is widely recognised that the increasing atmospheric concentrations of greenhouse gases such as carbon dioxide and methane can potentially drive a significant warming process of the earth’s climate. However, a topic of more recent attention is the possibility that increased atmospheric concentrations of aerosol particles might drive a significant radiative forcing process of the planet (see, for example, Charlson et al., 1992; and Charlson and Wigley, 1994). The increased aerosol concentrations are largely due to secondary particle production i.e. homogeneous nucleation from vapour precursors. The secondary aerosols have both natural and anthropogenic origin. Aerosol particles influence the climate by two distinct mechanisms: the direct reflection of solar radiation by aerosol particles, and the indirect increase in cloud reflectivity caused by enhanced number of cloud condensation nuclei. IPCC (1996) has reported that uncertainties in the estimation of direct and indirect aerosol effects on global climate are big (see Fig. 1.). These uncertainties arise largely from the limited information on the spatial and temporal distribution of aerosols and clouds. However, recently some progress has been made in evaluating the radiative effects of various aerosol components such as sulfate, organics, black carbon, sea-salt, and crustal species (Chuang et al., 1997; Haywood and Ramaswamy, 1998; Kaufman and Fraser, 1997; Winter and Chylek, 1997; Sokolik and Toon, 1996).

Despite these efforts, substantial uncertainties still remain in quantifying the contribution from each source, particularly, for biogenic and natural emissions, including organic vapours. Without understanding the contribution of natural emissions of aerosols and particles to radiative forcing, we can never hope to accurately predict or understand the true effect of anthropogenic emissions.

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., 2000) as well as the effect of nitric acid and other semivolatile gases in influencing cloud formation processes, in particular, in enhancing 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).

Particle formation and growth in the atmosphere have recently received growing experimental and theoretical interest. Therefore, instrumental techniques for measuring concentrations of freshly formed particle have been developed, and particles with diameter of
about 3 nm can be detected. These small particles have been found in large variety of environments: in the free troposphere (Clarke, 1992; Schröder and Ström, 1997; Raes et al., 1997), in the marine boundary layer (Covert et al., 1992; Hoppel et al., 1994; O’Dowd et al., 1998), in the vicinity of evaporating clouds (Hegg et al., 1991), in Arctic and Antarctic areas (Wiedensohler et al., 1996; Pirjola et al., 1998; O’Dowd et al., 1997), in urban areas and in stack plumes (Kerminen and Wexler, 1994; Kerminen and Wexler, 1996; Väkevä et al., 2000).

Starting during the mid-nineties, aerosol formation and growth events have been observed also in forested areas e.g. over boreal forest in Finland (Mäkelä et al., 1997, 2000; Kulmala et al., 1998), and in other type of forests in Portugal (Kavouras et al., 1998), Greece (Kavouras et al., 1999), Canada (Leaitch et al., 1999), and in USA (Marti et al., 1997). In all these cases particle formation and growth events took place in remote forested areas, where the release of highly reactive volatile organic carbons (VOCs) from trees followed by a rapid oxidation to low volatile products, has to be considered as a potential source for nucleating vapours.

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Figure 1: Estimates of globally and annually averaged anthropogenic radiative forcing (in Wm\(^{-2}\)) due to the changes in concentrations of greenhouse gases and aerosols from pre-industrial times to present day and to natural changes in solar output from 1850 to present day (IPCC, 1996).

Atmospheric aerosol particles in urban areas, on the other hand, cause the loss of visibility (e.g. Finlayson-Pitts and Pitts, 2000) and health effects (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 smogs is the London "pea-souper" smog, which occurred every once in a while until the 50’s, when coal burning was forbidden. Besides visibility degradation, the London smog episodes caused serious health effects and "excess deaths". One significant part of health problems related to atmospheric aerosols and fog droplets, since particles having diameters less than 10 μm can penetrate deep into the respiratory system (Dockery and Pope, 1994). Recently, the effect of ultra-fine particles have been discussed and their local variations have been investigated (e.g. Buzorius et al., 1999).
2. AEROSOL DYNAMICS

During the processes of formation and growth of atmospheric aerosols the aerosol dynamics, atmospheric chemistry and meteorology form a coupled system. The importance of atmospheric chemistry (e.g. Pirjola and Kulmala, 1998; Pirjola 1999) as well as meteorological conditions (Nilsson and Kulmala, 1998; Nilsson et al., 2000; Väkevä et al., 2000) on particle formation and growth have been demonstrated under tropospheric conditions. Although ternary nucleation of water-ammonia-sulphuric acid vapours (Korhonen et al., 1999) has shown to be able to explain atmospheric nucleation – i.e. formation of ~1 nm particles - in many cases (Kulmala et al., 2000), the exact routes for formation of 3 nm particles are still unclear, because besides nucleation, also the growth from 1 nm size to 3 nm size is needed.

In order to be able to understand the formation and growth processes of atmospheric aerosols and cloud droplets their thermodynamic properties should be known. For example, in the condensation process, the driving force is the vapour pressure difference between gas phase and surface. However, in the atmosphere where there are multicomponent, multiphase mixtures, their thermodynamic state and phase diagrams are typically very complex. It is very important to obtain thermodynamically consistent vapour pressures, chemical activities, surface tensions and densities for organic and inorganic compounds and their water solutions (for the importance see e.g. Korhonen et al., 1999) as a function of temperature and composition.

In future, development of nucleation theories, modelling and nucleation rate parameterizations are needed. So far, conclusions on whether or not certain substances cause nucleation in the atmosphere conditions are usually based on predictions given by the classical nucleation theory (CNT). CNT treats the nucleating molecular clusters as macroscopic droplets which is a questionable approach since the nucleating clusters often contain less than fifty molecules. Nucleation of various vapors using molecular dynamics (MD) and Monte Carlo (MC) simulation techniques is needed to investigate. So far, some investigations were carried out using ab initio calculations on small sulfuric acid-water clusters (Arstila et al 1998), classical MD (Laasonen et al, 2000) and MC (Vehkamäki and Ford, 1999) simulations of argon nucleation, as well as DFT calculations of nucleation in binary systems imitating water and different organic molecules (Laaksonen et al., 1995, Napari and Laaksonen 2000). Also, a new nucleation mechanism based on stable dimers (Lushnikov and Kulmala, 1998) has been proposed.

In contrast to laboratory conditions, the formation of aerosol in the atmosphere can be kinetically limited by some of the intermediate steps of its formation processes. The equilibrium state is thus not necessarily the aerosol itself but can be, for example, thermodynamically stable clusters (TSC), as we have recently shown (Kulmala et al., 2000). Although there is strong indication that the water-sulphuric acid-ammonia nucleation mechanism (Korhonen et al., 1999) explains the formation of new atmospheric aerosols (diameter < 3 nm) in many circumstances, the condensation of these vapors does not explain the observed growth rates of the particles (Kulmala et al., 2000), and in atmospheric conditions nucleation and growth are decoupled (Kulmala et al., 2000). The other possible relevant nucleation mechanism is ion-induced nucleation.

Aerosol dynamic modelling (nucleation, condensation, coagulation, deposition) with gas phase chemistry to obtain the atmospheric significance of nucleation and condensation of different vapours have been and will be performed. The aerosol dynamics and atmospheric chemistry model used in the present research is based on the model recently developed by our research group (Pirjola and Kulmala, 1998; Pirjola 1999). In these models aerosol formation and growth including aerosol dynamics to evaluate sink terms for condensable molecules and gas phase chemistry to include source terms for these molecules will be used. Process models will be coupled with dispersion models. In the chemistry part of the model the chemistry of O₃, NOₓ, VOC and other relevant species will be related to aerosol formation. The effects of meteorological dynamics on aerosol processes will be studied by applying the aerosol dynamic models in a
Lagrangian approach including wave motions and atmospheric mixing. The results shows that ternary water-ammonia-sulphuric acid system is proper candidate for atmospheric aerosol formation.

3. FORMATION AND GROWTH OF ATMOSPHERIC AEROSOLS, FIELD EXPERIMENTS

Formation and growth of aerosol particles have been observed and will be observed at atmospheric conditions. Our research group has participated in several field campaigns. These includes continuous measurements performed at our field stations and several international intensive campaigns like Aerosol Characterisation Experiment 1 and 2 in 1994 and 1997 (ACE-1 and ACE-2 organised by IGAC), International Arctic Ocean Expeditions 1991 and 1996, Biogenic aerosol formation in the boreal forest (BIOFOR, 1997-1999, SMEAR stations, Finland, Hyytiälä), New particle formation and fate in the coastal environment (PARFORCE, Mace Head, Ireland), and ongoing the OSOA (Origin and Formation of Secondary Organic Aerosol) experiment. As an example we consider here BIOFOR results in more detailed.

All data measured during the BIOFOR campaigns are available on the Biofor web pages http://mist.helsinki.fi/Biofor/index.html (ask for usercode and password from the corresponding author). In addition to the numerical data there are also a number of plots produced as a result of the analysis of the data. The data are classified into 9 subgroups: 1) aerosol total number concentration and size distribution measurements in the size range 3-800 nm, 2) aerosol chemistry, 3) aerosol and gas fluxes by eddy covariance and gradient methods, 4) measurements of meteorological parameters and gas concentrations at six different levels from the mast, 5) meteorology of boundary layer and trajectories, 6) concentrations and emissions of BVOC (biological volatile organic compounds), 7) ground level concentrations of inorganic gases, 8) measurements of the size distribution of wet (ambient) aerosol from 0.5-32 μm at 18 m height, and 9) solar radiation measurements. The detailed descriptions of the instruments used are given on the web pages.

When the particle formation event occurs, the mode of the fresh particles appears into the measurement range. In Figure 2, aerosol number size distributions measured using Differential Mobility Particle Sizer (DMPS) during a typical nucleation event day are shown. The nucleation mode practically dominates the spectrum with its high number concentration during the nucleation burst. For this event, particle growth from nucleation mode up to accumulation mode is clearly observable. The growth is frequently seen to continue during the following days up to accumulation mode (see also Kulmala et al., 2001).

![Figure 2: Aerosol size distributions measured by DMPS from 2m height inside the forest (6.4. 1999).](image-url)
During the events, aerosol fluxes determined using an eddy covariance technique are observed to be downwards. Also the measurements made by Condensation Particle Counters (CPC) and DMPS at different heights support this finding. From particle flux data, using the eddy covariance method (Buzorius et al., 1998), usually a small overall downward flux is observed. The downward flux clearly increases during nucleation events, with an exception of the cases when the surface wind was from direction of 220-250° (direction of the Tampere city and the Hyytiälä institute buildings). Then a strong upward particle flux is observed due to local surface-level pollution.

The difficulties in absolute calibration of the DMPS set ups as well as sampling losses in the lines suggested that the gradient of particles will be best determined placing two identical CPC pairs in the mast (18 m and 67 m height). The CPC pairs consisted of the ultrafine CPC (TSI Inc 3025) for determination of the particles larger than 3 nm in diameter and conventional CPC (TSI Inc. 3010) for particles larger than 10 nm in diameter. The difference of the reading of the CPC’s gives an approximate value for the ultrafine mode particle concentrations in the beginning of the burst. The data from the CPC pairs is shown for the event day of 6 April 1999 in Figure 3. The difference between the CPC readings from the two levels shows that the ultrafine particles have higher concentrations in higher level during the nucleation burst. This result will support the particle flux data that illustrate a net loss of particles to the canopy; however, it does not necessarily indicate a particle source at the top of the boundary layer or higher altitudes, even though nucleation is more probable in these regions.

4. CONCLUSIONS

According to recent results on atmospheric aerosol formation some preliminary conclusions can be made on atmosphere aerosol formation. (see Kulmala et al., 2001)

The most probable formation mechanism is ternary nucleation (water – sulphuric acid – ammonia) and the growth to observable sizes takes place mainly owing to condensation of organic vapours. Nevertheless, there is no direct proof of this phenomenon because the composition of 1–5 nm size particles is very difficult to determine using present state-of-art instrumentation. The other possible nucleation mechanism is ion induced nucleation with sulphuric acid and water vapours.
Nucleation takes place typically in very specific weather conditions: e.g. in Hyytiälä in cold air advection in Polar and Arctic air masses, at low cloudiness, and no precipitation. Furthermore, the nucleation was closely connected to the onset of strong turbulence in the morning-noon transition from stable to unstable stratification, which should also correspond to the onset of convection and entrainment from aloft.

The emission rates for several gaseous compounds have been determined (Kulmala et al., 2001). Using four independent ways the amount of the condensable vapour needed for observed growth of aerosol particles was estimated to $2-10 \times 10^7$ vapour molecules cm$^{-3}$. The estimations for source rate gives $7.5-11 \times 10^4$ cm$^{-3}$ s$^{-1}$.

REFERENCES


