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Biogenic aerosol formation in the boreal forest

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Aerosol formation and subsequent particle growth in the ambient air have been frequently observed at the boreal forest site (SMEAR II station), southern Finland. The EU funded project BIOFOR (Biogenic aerosol formation in the boreal forest) has focused on a) the determination of formation mechanisms of aerosol particles in the boreal forest site, and b) the verification of emissions of secondary organic aerosols from the boreal forest site, including the quantification of the amount of condensable vapours produced in photochemical reactions of biogenic volatile organic compounds (BVOC) leading to aerosol formation. Although the exact formation route for 3 nm particles is still unclear, the project results can be summarised as follows: (i) The most probable formation mechanism is ternary nucleation (water-sulphuric acid-ammonia) and the growth to observable sizes is mainly due to condensation of organic vapours. However, we do not have a direct proof of these phenomena, since it is impossible to determine the composition of 1 to 5-nm-size particles using the present state-of-art instrumentation; (ii) If nucleation takes place, it always occurs in cold-air advection in polar and Arctic air masses at low cloudiness, and the nucleation is closely connected to the onset of strong turbulence, convection, and entrainment in the morning-noon transition from a stable to an unstable stratified boundary layer; (iii) The emissions rates for several gaseous compounds have been verified. The model calculations showed that the amount of the condensable vapour needed for observed growth of aerosol particles is in the range $1–5 \times 10^7$ cm^{-3}. The estimations for the vapour source rate are in the range $3–8 \times 10^4$ cm^{-3}s^{-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, Charlson and Wigley 1994). The increased aerosol concentrations in remote areas are largely due to secondary particle production, i.e. homogeneous nucleation from vapour precursors. 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 the enhanced number of cloud condensation nuclei. IPCC (1996) has reported that uncertainties in the estimation of direct and indirect aerosol effects on the global climate are big. These uncertainties arise largely from the limited information on the spatial and temporal distribution of aerosols and clouds.

For the reasons mentioned above, particle formation and growth in the atmosphere have recently received growing experimental and theoretical interest. Therefore, instrumental techniques for measuring concentrations of freshly-formed particles have been developed, such that particles with a diameter of about 3 nm can be detected. These small particles have been observed 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 areas (Wiedensohler *et al.* 1996, Pirjola *et al.* 1998), in urban areas and in stack plumes (Kerminen and Wexler 1994, Kerminen and Wexler 1996, Väkevä *et al.* 2000), and recently also in a boreal forest (Mäkelä *et al.* 1997, 2000a, 2000b, Kulmala *et al.* 1998b).

The importance of atmospheric chemistry (Pirjola and Kulmala 1998) and meteorological conditions (Nilsson and Kulmala 1998, Nilsson *et al.* 2000, Väkevä *et al.* 2000) on particle formation has been demonstrated. Although the ternary nucleation between water, sulphuric acid and ammonia vapours is able to explain atmospheric nucleation in many cases (Korhonen *et al.* 1999, Kulmala *et al.* 2000), the exact routes for the formation of 3 nm particles are still unclear.

Compounds participating in the formation and growth of aerosol particles and cloud droplets originate from anthropogenic and natural sources. The coupling between the biosphere and the atmosphere forms a complex interactive and nonlinear system, in which the biosphere affects biogeochemical cycles in several ways.

In this paper, we give an overview of the BIOFOR project (Biogenic aerosol formation in the boreal forest) by summarising the methods used and the main results obtained during the project.

The BIOFOR project

In order to estimate the biogenic aerosol formation and growth, continuous measurements of atmospheric aerosols started in Hyytiälä, southern Finland, in January 1996 (Mäkelä *et al* 1997). Since then, a number of formation and growth events have been observed. The EU-funded BIOFOR (Biogenic aerosol formation in the boreal forest) project started in October 1997, and continued until the end of October 1999. The strategy of the BIOFOR project was to perform intensive measurement campaigns and do intensive modelling together with continuous measurements in order to understand the basic processes leading to the aerosol formation, and to quantify this process.

The general objectives of the BIOFOR project were:

- to determine the formation mechanisms of aerosol particles in the boreal forest site;
- to verify the emissions of secondary organic aerosols from the boreal forest site, and to quantify the amount of condensable vapours produced in photochemical reactions of biogenic volatile organic compounds (BVOC) leading to aerosol formation.

In this paper, we summarise the used methods and the main results obtained during the BIOFOR project.

Description of the experiment

The SMEAR II station

The SMEAR II field measurement station (**S**tation for **M**easuring **F**orest **E**cosystem-**A**tmosphere **R**elations), which is located in Hyytiälä, southern Finland (61°51´N, 24°17´E, 181 m a.s.l.) (*see* Fig. 1) and is a representative of the boreal coniferous forest, was chosen as the experiment site for the BIOFOR project. Boreal forests cover 8% of the Earth's surface and store about 10% of the total carbon in terrestrial ecosystems. The 34-year-old Scots pine (*Pinus sylvestris* L.) dominated stand is homogeneous for about 200 m in all directions from the measurement site, extending to the north for about 1.2 km (60° sector). Under unstable atmospheric conditions the fetch is adequate in all directions (the upwind distance contributing 80% to the flux in the very unstable case is about 100 m, the Monin-Obukhov length being –10 m). The terrain is subject to a modest height variation. The height of the dominant trees in the stand is 13 m, its zero plane displacement is about 9 m, and the roughness length is equal to 1.2 m. The mean diameter of the trees at the breast height is 13 cm, and the total (all-sided) needle area index is 9. The wood biomass is equal to 47 t ha^{-1} and the tree density is 2500 per ha. The nitrogen content per the total needle area varies from 0.67 to 1.2 g m^{-2} increasing with the height, and the nitrogen (mass) concentration is between 1.0 and 1.4%. The dominant stand contains only 1% of

Fig. 1. Map showing the location of the SMEAR II measurement station. Some of the major cities are also indicated.

species other than Scots pine, including downy birch (*Betula pubescens*), grey alder (*Alnus incana*) and aspen (*Populus tremula*). The ground vegetation consists of heather (*Calluna vulgaris*), lingonberry (*Vaccinium vitis-idaea*), and blueberry (*V. myrtillus*). The dominating moss species is *Dicranum undulatum*. The annual mean temperature is 3 °C and precipitation is 700 mm. The parent material of the soil is coarse, silty, glacial till and the soil is a haplic podzol.

The SMEAR II facility is planned and implemented to determine the material and energy flows in the atmosphere-vegetation-soil continuum at different temporal and spatial scales (Fig. 2). It can be divided into four operational blocks: (I) atmospheric measurements accomplished using a 72-m-high mast, (II) tree measurements performed using a 15-m-high tower, (III) soil measurements carried out on two catchment (watershed with weir) areas, and (IV) aerosol measurements from 2 m above the ground. The station includes set-ups (Vesala *et al.* 1998) for the measurements of aerosol particle size distribution in the size range of 3–500 nm, vertical flux of aerosol particles of diameters down to 10 nm, exchange of trace gases on a shoot-scale and on a soil surface in intervals of 1 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 soil water, dissolved ions, and organic carbon balances. The SMEAR II station is nowadays a platform for a number of international measurement campaigns.

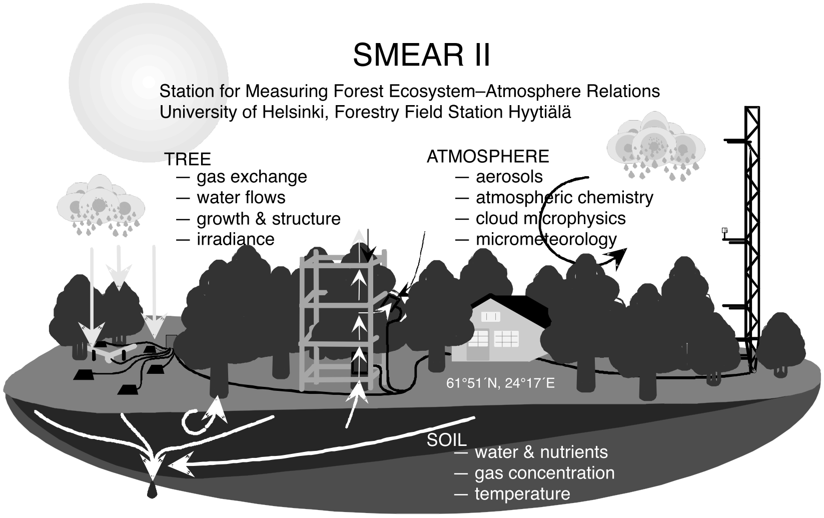

Fig. 2. Overview of the SMEAR II station and the measurements carried out there.

The tasks of the BIOFOR project

The BIOFOR project included the following scientific tasks:

Task 1: Continuous measurements of ultrafine aerosol particle concentrations, their net vertical flux, and the relevant background data (local meteorology, micrometeorology, vertical profiles of inorganic gases) at the SMEAR II station. Task 1 produced the basic long-term data on aerosol size distributions and their vertical fluxes, accompanied by required meteorological data like temperature, relative humidity, solar radiation, and the strength of turbulence. In addition, the state of vegetation (level of photosynthesis) and soil (temperature, water content and bacterial and mycorrhizal activity) was determined. In the SMEAR II station, the formation and growth of natural, biogenic aerosols can be measured and linked to the function of trees and soil. The local formation rate of particles and the fate of nascent particles were identified. Task 1 included also data evaluation and data delivery.

Task 2: Three campaigns on aerosol characteristics (aerosol chemistry and hygroscopic properties) and concentrations of organic gases were performed. The vertical profiles were determined and the meteorological conditions were investigated using radiosoundings, sound detection and ranging (SODAR), surface weather observations, and back trajectories (Pöllänen *et al.* 1997). Also the vertical profiles of aerosol size distributions and nucleation mode concentrations were measured. Task 2 included also the preparation of measurements, calibration of instruments, data evaluation, and data delivery.

Task 3: The data evaluation, model development, and comparison of evaluated data and models were performed. The modeling work was divided into four work packages: (a) atmospheric chemistry models, (b) nucleation models (ternary nucleation, ion-induced nucleation), (c) a Lagrangian model along trajectories with aerosol dynamics and gas phase chemistry, and (d) a boundary layer dynamics model with aerosol dynamics and gas phase chemistry. Also the linkage to the biological activity as a level of organic emissions was formed.

Field campaigns

All data measured during the BIOFOR campaigns

(14 Apr.–22 May 1998, 27 Jul.–21 Aug. 1998 and 15 Mar.–30 Apr. 1999) are available on the BIOFOR web pages at 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 8 subgroups: (1) aerosol total number concentration and size distribution measurements in the size range 3–800 nm, (2) sampling of aerosols, (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) such as terpenes, (7) measurements of the size distribution of wet aerosol from 0.5–32 μm at 18 m height, and (8) solar radiation measurements. The detailed description of the instruments used are given on the web pages.

The intensive field studies consisted of a number of sites where the instruments were installed. The map of each measurement during the BIOFOR campaigns is shown in Fig. 3.

Results and discussion

Long-term measurements

At the SMEAR II Station continuous measurements of the submicron aerosol number size distribution has been performed since January 1996 (every 10 min). The measurements showed approximately 50 days per year with clearly detectable aerosol particle formation events (*see* Mäkelä *et al.* 2000a). The most typical time for these events was March–April. Subsequent to the new particle formation, a significant particle growth was usually observed. Almost 20% of the events continued sufficiently long to produce particles larger than 80 nm in diameter. Particles of this size can be effective cloud condensation nuclei (CCN).

When a particle formation event occurred, a mode of fresh particles appeared into the measurement range. In Fig. 4, a typical spectrum for the aerosol number size distribution during a nucleation event is shown. Here, three log-normal modes were used to explain the structure of the spectrum. The nucleation mode, peaking at about 10 nm, practically dominated the spectrum with its high number concentration The fitting procedure by which the modes have been obtained from the measurement data, has been presented in Mäkelä *et al.* (2000b). As the fitting procedure is fully automatic, it is obvious that some of the fits did not succeed well. However, the general trend was clearly visible, and for this event the particle growth from the nucleation mode up to Aitken mode was clearly observable (Fig. 5). The growth was frequently observed to continue during the following days up to the accumulation mode.

The meteorological data, including radiation, is available for the interpretation of weather conditions typically encountered during particle production events (*see* BIOFOR webpage at http://mist.helsinki.fi/Biofor/index.html). Also the vertical distributions (4–67 m) of inorganic gaseous impurities (SO_2, NO_x and O_3) are available.

Intensive field studies

During the BIOFOR project, three intensive field campaigns were performed. During the campaigns, the hygroscopicity, composition, and vertical profiles of particles were measured. Atmospheric concentrations of organic and inorganic gases were also measured.

Studies on particle composition

The measurements carried out so far have demonstrated the advantages of combining detailed campaign measurements with more continuous measurements. For example, a detailed chemical analysis will provide insight into the composition of newly-formed particles. Nevertheless, the task to analyse the chemical composition of nucleation mode particles is very difficult. Indirect in-

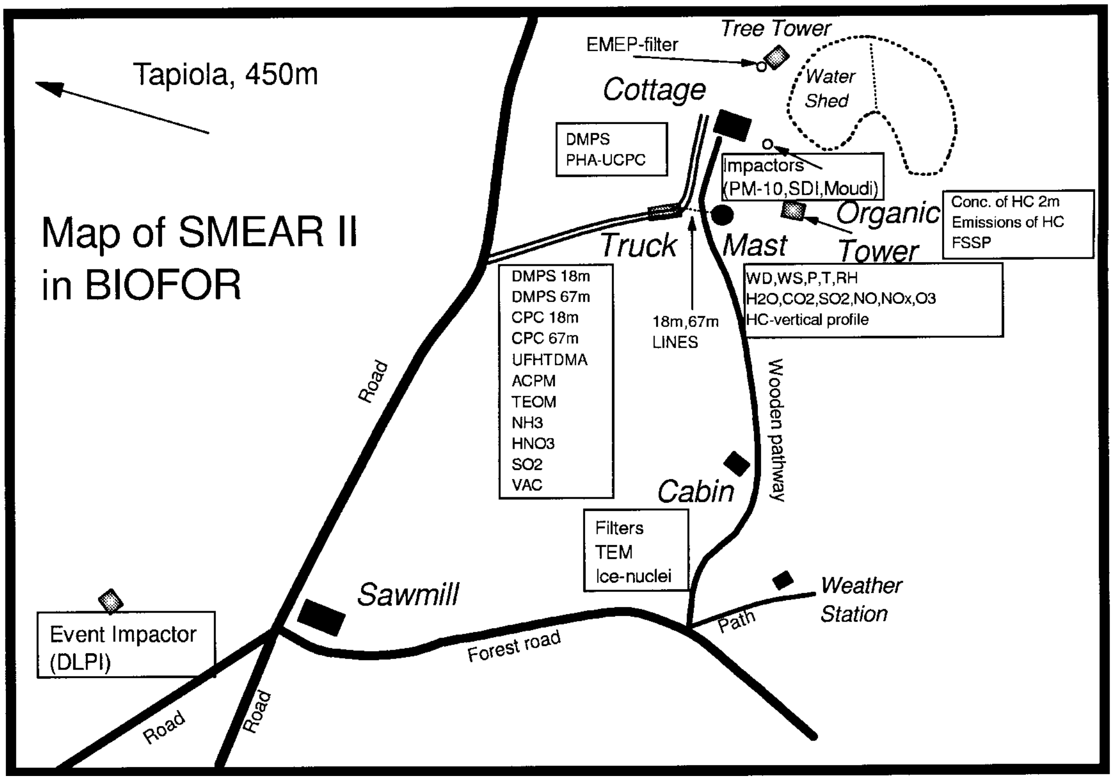

Fig. 3. The map showing the location of various instruments during the BIOFOR campaign.

formation of the particle composition was obtained by determining the hygroscopic properties of individual particles. The hygroscopicity of nucleation mode particles indicates their soluble fraction. Changes in the soluble fraction are indicative of changes in the particle composition *in situ* (Väkevä and Hämeri 1999). The result obtained showed clear changes in the particle composition during the growth process.

In order to obtain more fundamental information on the chemical compounds involved, size-segregated aerosol sampling was performed using multi-stage low-pressure and micro-orifice impactors. The chemical analysis of the impactor stages was carried out afterwards using ion chromatography. The impactor samples were taken selectively using two identical impactors. One impactor sampled during the particle formation period, and the other one sampled during the times when no particle formation was observed. The division into event and non-event cases was done *in situ* in the field, based on the on-line DMPS-data.

The results on the chemical ionic composition of the particles showed only small differences between the event and non-event sample sets for most of the compounds such as sulphate and ammonia. Furthermore, no systematic difference between the particulate carboxylic acid concentrations could be found between the two sample sets. In the event samples some ultra-fine particulate methanesulphonic acid (MSA) was found to be present. This is a consequence of the fact that the events showed preference for polar and Arctic marine air masses. The most significant difference between the two sample sets was found for dimethylamine (DMA) which seemed to be present in the particle phase during the particle

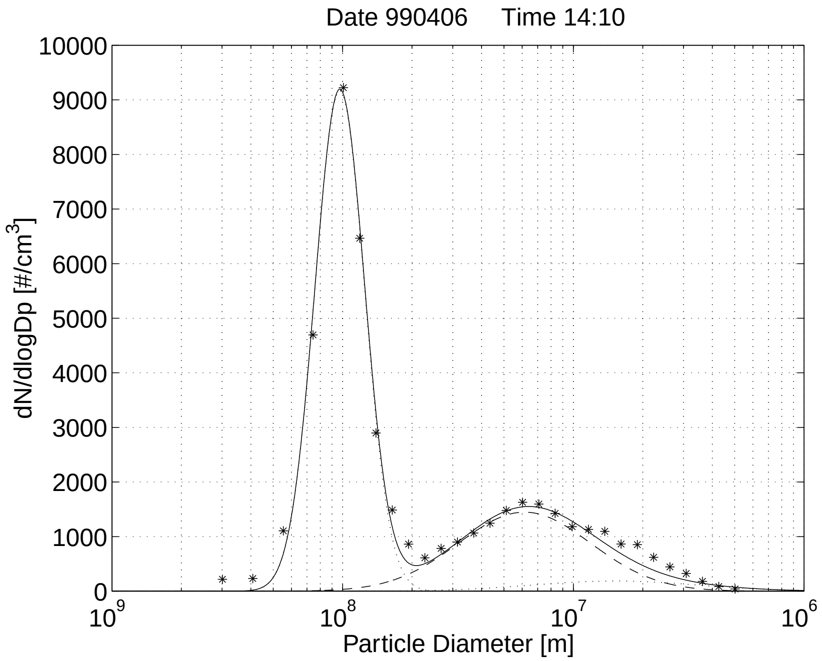

Fig. 4. An aerosol number size distribution measured using a DMPS (**D**ifferential **M**obility **P**article **S**izer) system during a nucleation event. The measured data (*) are shown together with three log-normal functions that have been used to explain the structure of the spectrum. The log-normal size distributions have been numerically fitted into the measured spectrum. Also shown is the sum of the three log-normal functions.

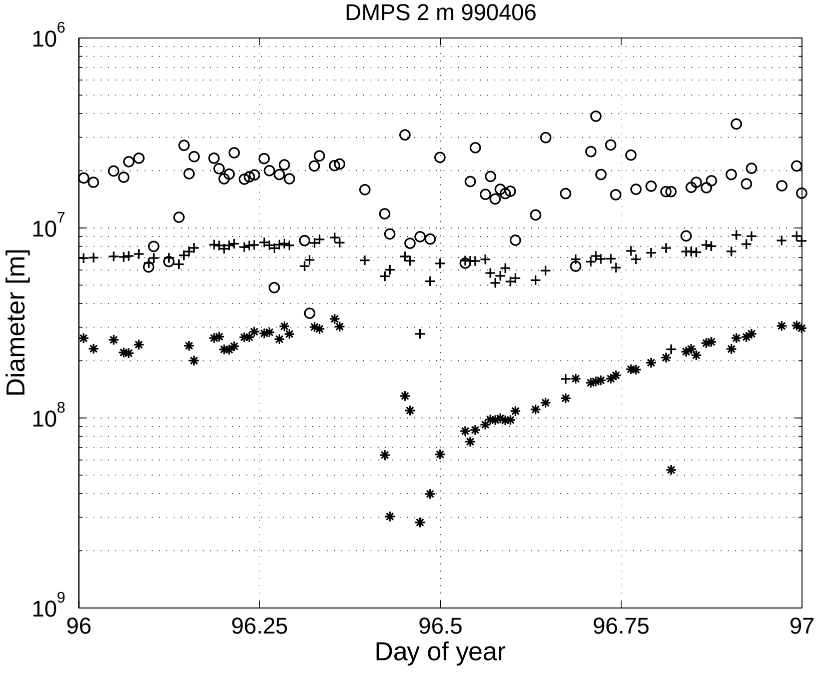

Fig. 5. The evolution of the modal mean diameters of nucleation (*), Aitken (+) and accumulation (o) mode particles during a nucleation day (6 April 1999, same as Fig. 4).

formation periods and/or during the subsequent particle growth. An example of the particle chemical spectrum is shown in Fig. 6. The particles were sampled during a number of event periods in order to gain sufficient mass for the chemical analysis of the ultrafine fraction of the particle spectra.

During the particle formation periods, an average total concentration of 20–40 ng m^{-3} of particulate DMA was found, whereas during the non-formation periods particlulate DMA concentrations did not exceed 2–3 ng m^{-3}.

Dimethylamine is a volatile organic base which behaves quite like atmospheric ammonia. Ambient DMA has been observed in several locations (e.g. Mosier *et al.* 1973, Tuazon *et al.* 1978), but its gas/particle partitioning has been investigated mostly in marine air (Gibb *et al.* 1999). Regarding to the various sources, DMA may be assumed to be abundant during most of the time in Hyytiälä, since the amines, as well as NH_3, are known to be end products of the microbial turnover of labile organic matter. Also anthropogenic sources such as industrial activities, feedlot operations, waste incineration, and sewage treatment are known to exist.

The relevant question is, why DMA was so systematically transformed into the particulate phase only during particle formation periods.

Vertical flux and vertical profile of the particles

Using the eddy covariance method (Buzorius *et al.* 1998), usually a small overall downward flux of particles was observed. The downward flux clearly increased during the nucleation events, with the exception being the cases when the surface wind was from the direction of 220–250° (the direction of the Tampere city and the Hyytiälä institute buildings). In these cases a strong upward particle flux was observed.

The vertical profiles of particle size spectra were obtained by sampling the air from two elevated levels: 18 m and 67 m above ground. The sampling was done using a high flow rate to minimise particle losses. The particle size spectra (corrected for the diffusion losses) from the 67-m level for one nucleation event are shown in Fig. 7 (*see* also Fig. 5). In this plot, the contour plots of the measured size distributions are shown. The comparison with spectra measured at a 2-m height showed practically no differences. The event could be seen at different levels almost simultaneously, and it was hard to determine any significant gradient from the particle spectra. This is what is expected in this type of well-mixed boundary layer. The convective time scale was usually around 10 minutes, so any compound with a lifetime larger than 10 minutes would be homogeneously mixed through the mixed layer.

The difficulties in the absolute calibration of the DMPS set ups and the loss of particles in the sampling lines suggested that the gradient of particles could be determined best by placing two identical CPC pairs on the mast (18 m and 67 m height). The CPC pairs consisted of an ultrafine CPC (TSI inc. 3025) for the determination of particles larger than 3 nm in diameter, and a CPC (TSI Inc. 3010) for the determination of particles larger than 10 nm in diameter. The difference between the readings of the two CPC's gives an approximate value for the nucleation mode particle concentration in the beginning of the burst. The data from the CPC pairs is shown for one event day (Fig. 8). The difference between the CPC readings from the two levels showed that the ultrafine particles had higher concentrations at the higher level during the nucleation burst (midday). This result supports the particle flux data, indicating that the particle source was located at higher altitudes.

Concentrations and vertical profiles of gaseous species

The diurnal variation of the concentration of several BVOCs was measured on selected days during the BIOFOR campaigns at three different heights (17.8, 38.4, and 64.6 m; the canopy height was about 14 m). Based on these data, the fluxes of terpenes, the main BVOCs in this region, were estimated using the gradient approach.

An example of the measured vertical concentration gradients is shown in Fig. 9. Since the turbulent diffusivities $K(z)$ were known from the simultaneous momentum and heat flux measure-

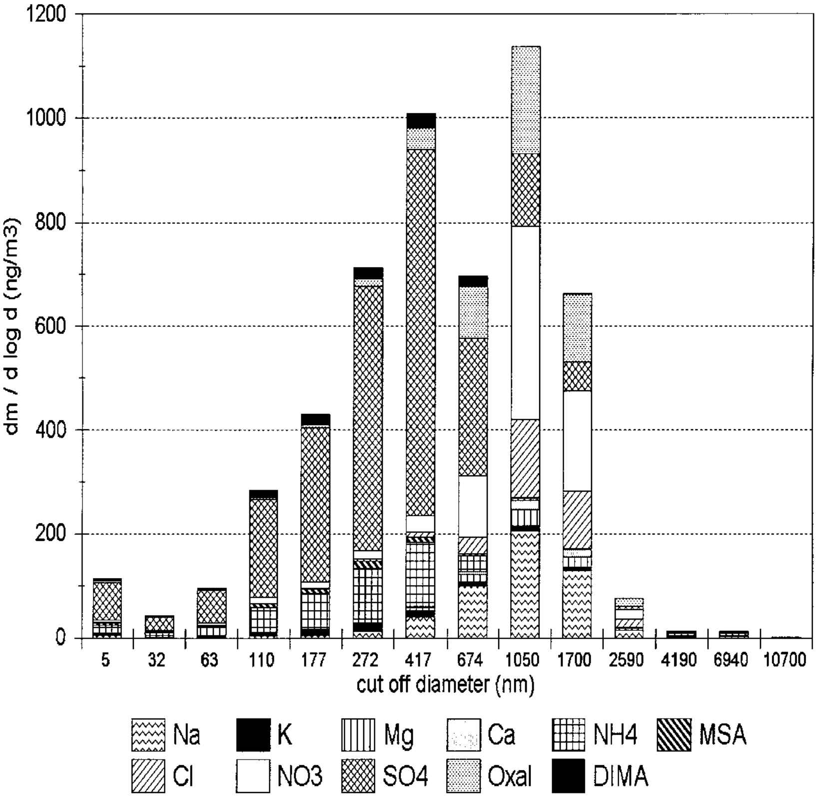

Fig. 6. An example of the particle chemical composition as function of particle size. Here the particles were collected during several particle events using a low pressure impactor. The days when the samples were taken are 2, 4, 5, 6, 8 and 10 April.

ments, the flux of long-living natural VOCs from the forest could be estimated.

Based on the measured vertical VOC concentration gradients, fluxes were calculated using the assumption that the chemical degradation takes place on a longer timescale than the turbulent vertical mixing i.e., the chemical reaction term was neglected in the flux calculations. The fluxes with uncertainty interval were estimated from the concentration measurements at three levels by making a least square fitting to the profiles predicted by the atmospheric surface layer similarity theory (Rannik 1998).

The non-reactive volatile hydrocarbons, such as tricyclene, had almost the same concentration at all levels, and no clear gradient could be determined. The flux of α-pinene depends on the temperature and radiation during daytime. The concentration ratio of reactive and non-reactive VOCs was then used as a measure of the significance of chemical degradation reactions in determining the mixing ratios of the biogenics above the forest. Thereby, the concentration ratio provided an indirect approach to predict the formation of non-volatile oxidation products that finally can undergo gas-to-particle conversion.

In contrast, the flux of very reactive biogenics, such as polyunsaturated VOCs which have tropospheric lifetimes of the same order of magnitude as the turbulent transfer times in the considered layer, cannot be quantified using the traditional gradient approach for conservative quantities. In order to identify a link between biogenic VOCs and particle formation it is more interesting to estimate the importance of chemical reactions of the biogenics in or above the forest canopy.

The atmospheric concentration of nopinone, the main oxidation product of β-pinene, was mostly below the detection limit during the third measurement campaign, enhanced during BIOFOR 1, and showed the highest values during BIOFOR 2. Most probably, this is due to the higher

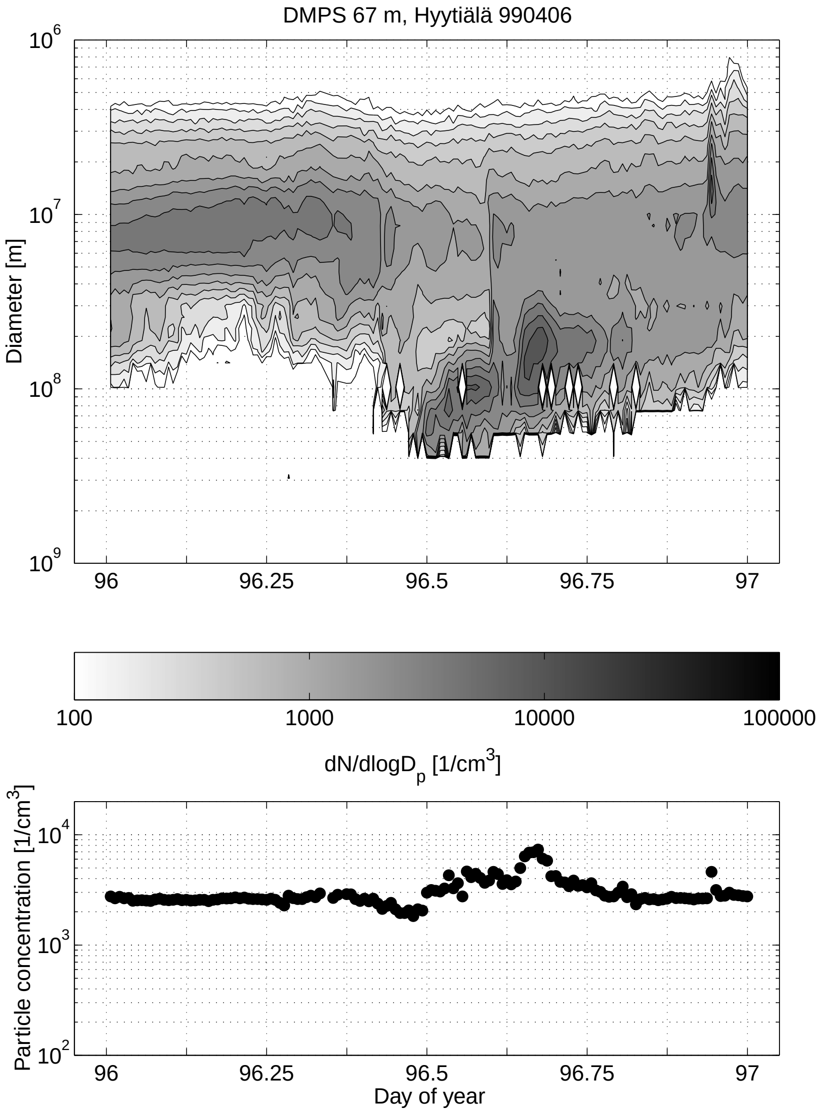

Fig. 7. The particle number size distributions from the 67-m level during 6 April 1999.

temperature during summertime, accompanied with higher natural emissions and higher photolysis rates that yield higher OH-radical concentrations. Therefore, a rapid degradation of the more reactive BVOCs could be observed during the summertime campaign, which explains the high values of the biogenic oxidation product. The dominant influence of chemistry on educt and product concentrations during the August campaign can be demonstrated plotting the concentration ratios of oxidation product and the parent hydrocarbon (Fig. 10). As can be seen from the figure, the maximum values were observed around noon, strongly indicating the influence of the OH-chemistry.

Occurrence of the nucleation events

The main focus of the BIOFOR activities may be formulated in the following way: Why the particle formation events are observed on certain days

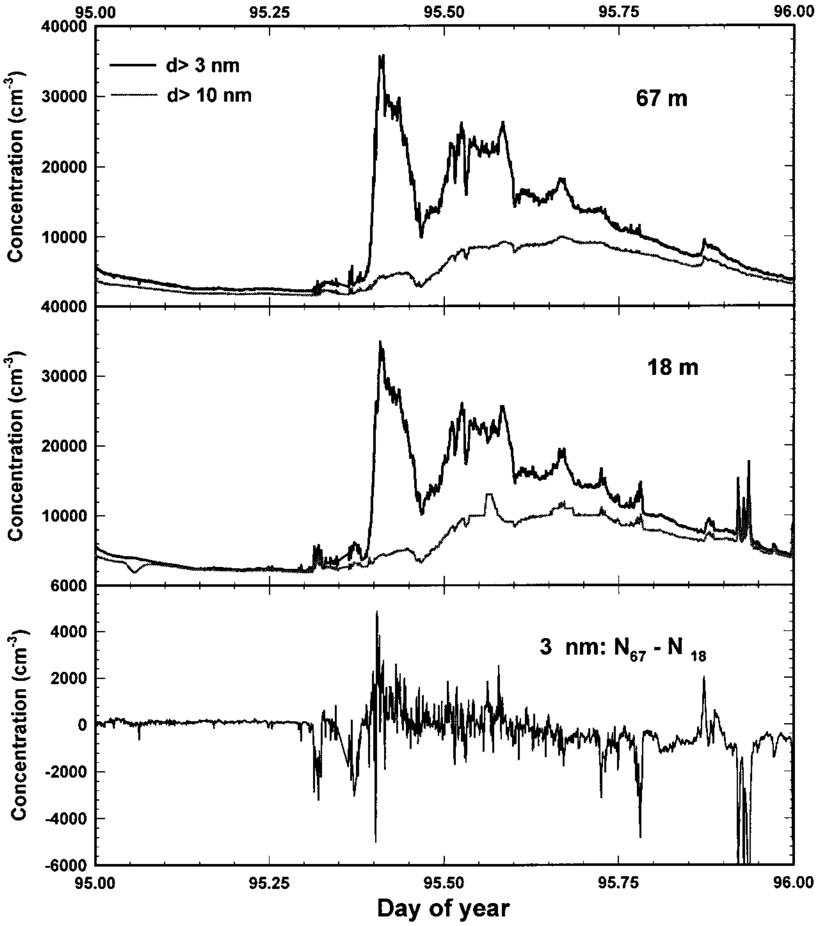

Fig. 8. Total aerosol particle number concentration during 5 April 1999. The concentration of particles larger than 3 nm and larger than 10 nm are shown for the 67-m (top) and the 18-m (middle) sampling levels. The data is plotted as 1-min averages. The difference in the concentration of particles larger than 3 nm between the two levels is shown in the bottom subplot.

and not on other days with rather similar conditions? As a summary two different cases — one with nucleation and another when conditions were largely similar but nucleation was not observed — can be compared (for more details *see* BIOFOR webpages at http://mist.helsinki.fi/Biofor/index.html):

Nucleation day in spring, when 5 000–10 000 new particles cm^{-3} were usually formed coinciding with moderate hydrocarbon emissions from the forest. General meteorological conditions comprised polar or Arctic marine air masses in transition, clear skies, no precipitation, and large diurnal amplitudes in the boundary layer structure, turbulence and convection.

Typical clear sunny summer day, with no nucleation observed, however, high hydrocarbon emissions from the forest were encountered. Ambient temperatures were typically high, the temperature difference between the day and night being relatively low.

Modelling

Aerosol dynamics

The modeling activities in BIOFOR (e.g. Pirjola 1999) are concurrently being carried out in close

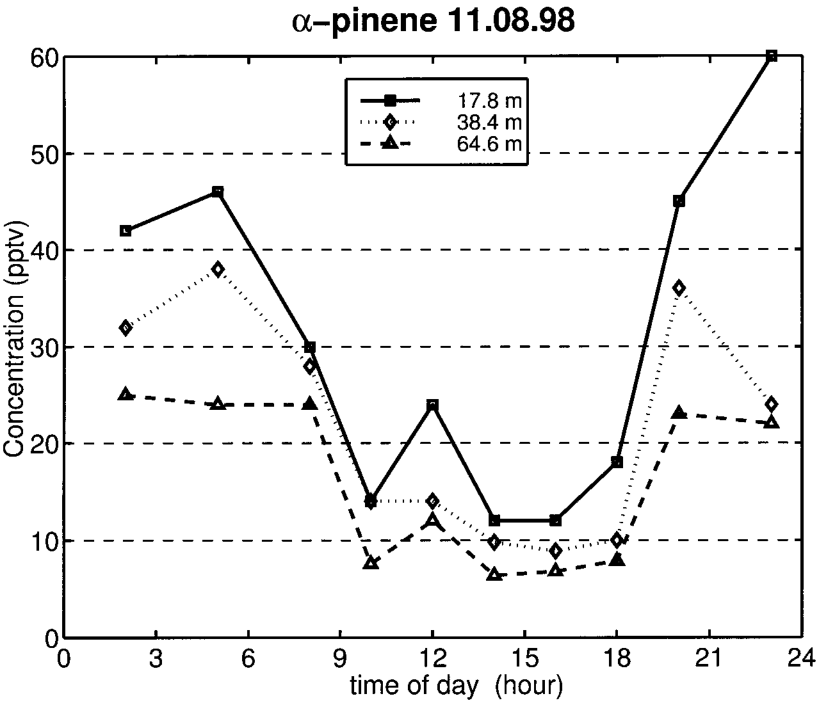

Fig. 9. α-Pinene concentration gradient measured on 11 August 1998. The lines connecting the data points are for guiding the eye.

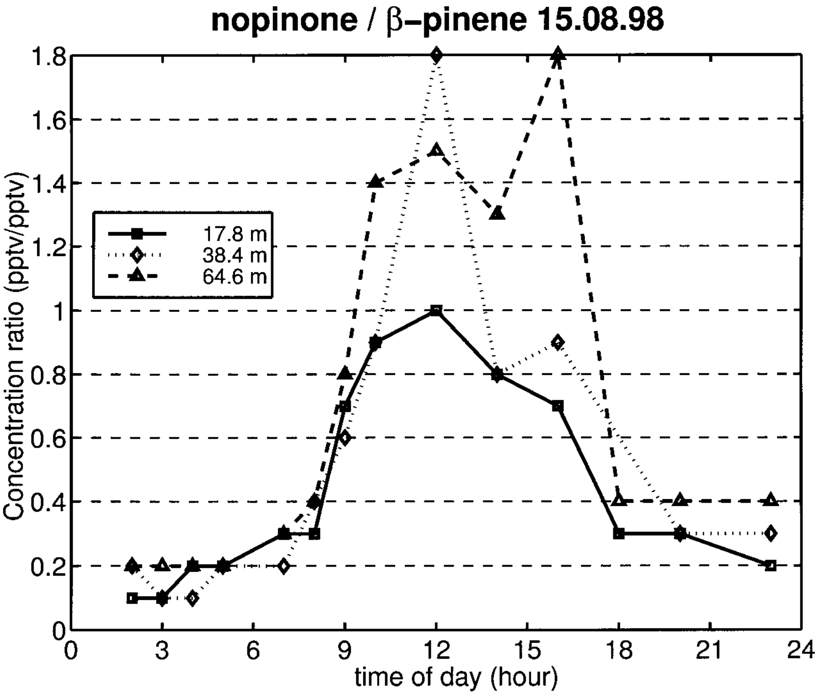

Fig. 10. Nopinone/β-pinene ratio measured on 15 August 1998. The lines connecting the data points are for guiding the eye.

conjunction with the interpretation of the field data. The investigation of aerosol formation, atmospheric chemistry, aerosol processes, and meteorology has been combined in the present project. Preliminary modeling of nucleation and growth events has shown a good agreement with the experimental data (see e.g. Kulmala *et al.* 2000). Although the exact particle production mechanism remains still unclear, the best guess so far is that the ternary nucleation between water, ammonia and sulphuric acid is responsible for nucleation, and that the particles grow to detectable sizes mainly by the condensation of organic vapours. However, the results are still preliminary and more detailed data analysis and modeling activities are needed in order to elucidate the primary formation and growth processes.

BVOC concentrations and fluxes

Another modeling activity has been the investigation of BVOC fluxes and emissions using a one-dimensional multilayer canopy-chemistry model CACHE (Canopy Atmospheric CHemistry Emission Model, Forkel *et al.* 1999). CACHE predicts the diurnal courses of temperature and the concentrations of water vapor and chemical constituents by solving the prognostic equations for heat and mass within and above the forest canopy. The model accounts for vertical turbulent transport of heat, water vapor, and chemical compounds, the heat and water transport within the soil, the radiation transfer, the heat and water vapor exchange between leaves/needles and the ambient air, the emission of monoterpenes and isoprene by trees and of NO from the soil, the deposition of trace species, and the chemical transformations which are described with the RACM mechanism (Stockwell *et al.* 1997).

Summary of the main results

The experimental results, observations, and model calculations are summarised below (for more details *see* BIOFOR webpages at http://mist.helsinki.fi/Biofor/index.html, Kulmala and Hämeri 2000, Mäkelä *et al.* 1997, Kulmala *et al.* 1998a, Kulmala *et al.* 1998b, Becker *et al.* 1999, Korhonen *et al.* 1999, Vesala *et al.* 1998, Kulmala *et al.* 2000, Mäkelä *et al.* 2000, Nilsson *et al.* 2001).

— Particle production occurred in arctic, and to some extent, in polar air masses, with a preference for air in transition from marine to continental air masses, but never in sub-tropical air. These air masses had an origin north of the measurement site and reached the site through flows from the south-west to the north-east.

— Nucleation was always associated with cold-air advection, cold-air outbreaks behind cold fronts, but never with warm-air advection. Nucleation was related typically to a low cloudiness and large diurnal amplitudes in the continental boundary layer associated with clear skies. However, Arctic and Polar air together with cold-air advection did not always lead to nucleation. The limiting factors were found to be a high cloudiness and precipitation due to cold front passages, a large pre-existing aerosol condensational sink, or limited sources of precursor gases.

— As a result of the weather conditions, nucleation was always associated with the boundary layer evolution during the late morning, when the boundary layer transitioned from stable, nocturnal conditions to a deep and convective well-mixed boundary layer. The onset of nucleation coincided with the onset of strong turbulence so well that it strongly suggests that nucleation was associated with turbulence, convection, or entrainment.

— During the events, aerosol fluxes determined using eddy covariance technique were observed to be downwards. Also the measurements made by CPC-pairs and DMPS at different heights support this finding.

— The formation rate of 3-nm particles was observed to vary in the range 0.01–5 cm^{-3} s^{-1}.

— The growth rate (in particle diameter) can be obtained from the DMPS data, after which the mean source rate for the condensable vapour can be obtained using the condensational sink data. The growth rate of the nucleation mode during the spring campaigns was observed to be in the range 2–5 nm h^{-1}, which corresponds to a vapour concentration of $2–5 \times 10^7$ cm^{-3}. The source rate for this vapour was calculated to be approximately 5×10^4 cm^{-3} s^{-1}.

- A diurnal pattern for the hygroscopic growth factors of nucleation mode particles between 10 and 20 nm were observed during the nucleation days. The lowest values were detected during the late evening and early morning, whereas the highest growth factors were observed during the midday. The large growth factors during the nucleation events indicates that the condensing compounds during the early growth were water soluble. Nevertheless, the ultrafine particles transformed to become relatively insoluble later in the evening.
- As a general result, we can see that the mass flux of insoluble vapours to the particle phase was of similar magnitude as the respective flux of soluble vapours. The model studies performed during the project by aerosol dynamical model AEROFOR2 (Pirjola and Kulmala 2000) show that the sulphuric acid concentration was much less than what is needed to explain the particle growth. This indicates that a significant fraction of soluble mass can not be explained by sulphuric acid, but a soluble organic compound is more likely.
- There was a clear gradient in emitted BVOCs during all the days. Not only the emission rate, but also the chemical reactions and the turbulent mixing played significant roles in the development of the gradients. During the night the concentrations of emitted BVOCs were significantly higher than during the daytime.
- Ternary (water-sulphuric acid-ammonia) nucleation mechanism was seen to be able to predict the aerosol nucleation process. At measured temperatures (typically below 5 °C) and ammonia concentrations (always over 10 ppt, often over 50 ppt), and at estimated daytime sulphuric acid concentrations (10^6–10^7 cm^{-3}), the nucleation rates calculated using the recently developed ternary nucleation code were high enough (more than 100 cm^{-3} s^{-1}). The other possible nucleation mechanism is related to the biological activity. The ion-induced nucleation mechanism was not strong enough to explain the observed aerosol formation.
- There are several possible ways to explain the linkage between the boundary layer dynamics and the aerosol formation: (a) A particle source aloft, such that small aerosol particles or clusters may have been entrained from aloft i.e. the ternary nucleation may have produced small clusters aloft which were entrained into the free troposphere such that condensable gases in the mixed layer could contribute to the aerosol growth; (b) two or more precursor gases may have been mixed with each other by the entrainment, one having a high concentration in the mixed layer and the other at higher altitudes; (c) the adiabatic cooling in convective plumes and the turbulent fluctuation in temperature and vapours generated by the entrainment fluxes may have enhanced the aerosol formation as much as 10 orders of magnitude.

Conclusions

The IPCC (1996) report highlights the fact that the current estimates of the global mean radiative forcing due to anthropogenic aerosols is highly variable (from –0.3 to 3.5 W m^{-2}) and of comparable magnitude but opposite in sign to the radiative forcing due to anthropogenic greenhouse gases. To estimate the radiative forcing due to anthropogenic aerosols, the formation and growth mechanisms of natural aerosols and their importance in climate processes needs to be known. As a result, predictions of climate change due to anthropogenic influences are inaccurate and it appears difficult for the EU to make decisions about strategic policy changes related to the climate change. A better understanding of natural biogenic aerosols, which is obtained from BIOFOR measurements and process model studies, will enable more reliable climate model predictions. This in turn will help the decision making.

The data collected during three intensive BIOFOR campaigns and during continuous measurements are available in the BIOFOR data archive, and the access to this archive is freely available to all BIOFOR investigators and other scientists who are interested. Further processing and interpretation of the data are in progress.

During the project, new measurement techniques were developed and tested. These include e.g. a continuous eddy covariance technique for aerosol particles. These techniques are now available for scientists and can be used in future studies. A new code and parameterisation for binary nucleation between water and sulphuric acid was developed and tested (Kulmala *et al.* 1998a), as well as a new code for ternary nucleation between water, sulphuric acid and ammonia (Korhonen *et al.* 1999). Also, a new multicomponent aerosol dynamical code AEROFOR2 was developed and tested (Pirjola and Kulmala 2000).

The major scientific impact of the project is to provide quantitative estimation of aerosol and cloud condensation nuclei (CCN) formation at a boreal forest site. The results will also be applied in aerosol packages in regional and global-scale numerical models.

As scientific conclusions, we are able to give preliminary answers to our objectives

The most probable particle formation mechanism was ternary nucleation (water-sulphuric acid-ammonia), and the growth of particles to observable sizes took place mainly due to condensation of organic vapours. Nevertheless, we do not have a direct proof of this phenomenon, since it is impossible to determine the composition of 1–5 nm size particles using the present state-of-art instrumentation.

If the nucleation took place, it always occurred in very specific weather conditions: cold-air advection in polar and Arctic air masses at a low cloudiness and no precipitation. Furthermore, the nucleation was closely connected to the onset of strong turbulence in the morning-none transition from stable to unstable stratification, which should also correspond to the onset of convection and entrainment from aloft.

The emissions rates of several gaseous compounds were investigated. The amount of the condensable vapour needed for the observed particle growth was $1–5 \times 10^7$ cm^{-3}. Estimations for the respective source rate gave values in the range $3–8 \times 10^4$ cm^{-3} s^{-1}.

The close connection of the physics and chemistry of the particle formation with meteorology and partly also with biological activity was shown. Although the nucleation burst were observed simultaneously around Finland (e.g. Mäkelä *et al.* 1998, Väkevä *et al.* 2000) more experiments are needed to verify the actual geographical scale of this phenomena. In addition, more accurate measurements of condensable organic compounds are necessary in order to identify the condensable vapours needed for the aerosol growth.

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