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**NUCLEATION EVENTS IN THE CONTINENTAL  
PLANETARY BOUNDARY LAYER – PHYSICAL,  
CHEMICAL AND METEOROLOGICAL INFLUENCES**

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Academic dissertation

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Helsinki, August 2003

Michael Boy

## **Nucleation events in the continental planetary boundary layer – physical, chemical and meteorological influences**

Michael Boy

University of Helsinki, 2003

### **Abstract**

The formation of nanometer sized aerosols and their growth in 1-2 days to ~100 nm in the lower atmosphere are important processes involved in climate change and health effects. Aerosols contribute directly to the cooling of the climate by scattering solar radiation back and indirectly by changing the cloud properties.

In this thesis a substantial data base of three years (1999-2001) was investigated to achieve information about meteorological, physical and chemical situations, which favour the formation of new aerosols. Furthermore, results of measurements from four different field campaigns conducted in Hyytiälä within the framework of two EU projects (BIOFOR and OSOA) were included.

The analyses of different parameters measured at the field research station in Hyytiälä showed that some single variables like the solar short wavelength irradiance between 300-330 nm or the concentration of hydroxyl radicals correlate with the number concentration of nucleation mode particles with diameters between 3-6 nm on a daily as well as yearly basis. Other parameters like ozone or particle flux values correlate less during single days, but throughout the year different trends between event and non-event days are clearly visible.

Different aerosol relevant characteristics based on the concentration of precursor gases, especially monoterpenes and sulphur dioxide, were calculated and compared with equivalent values obtained from DMPS-measurements. The results indicated an approximately equal concentration of organic diacid and sulphuric acid molecules. The contribution of the carboxylic diacids to the growth of the nucleation mode particles ranged between 8 and 50 %.

Keywords: particle formation, solar irradiance, condensation sink, monoterpenes, carboxylic diacid molecules, air masses

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## List of publications

This thesis consists of an introductory review section, followed by five research articles. Papers I-V are reproduced with the permission of the journals concerned.

**I** Nilsson, E.D., J. Paatero and M. Boy: Effects of air masses and synoptic weather on aerosol formation in the continental boundary layer, *Tellus*, 53B, 462-478, 2001.

**II** Boy, M. and M. Kulmala: Nucleation events in the continental boundary layer: Influence of physical and meteorological parameters, *Atmos. Chem. Phys.*, 2, 1-16, 2002.

**III** Boy, M. and M. Kulmala: The part of the solar spectrum with the highest influence on the formation of SOA in the continental boundary layer, *Atmos. Chem. Phys.*, 2, 375-386, 2002.

**IV** Boy, M., T. Petäjä, M. Dal Maso, Ü. Rannik, J. Rinne, P. Aalto, M. Kulmala, A. Laaksonen, J. Joutsensaari, T. Hoffmann, J. Warnke, M. Apostolaki, E.G. Stephanou, M. Tsapakis, A. Kouvarakis, C. Pio, A. Carvalho, A. Römpp, G. Moortgat, C. Spirig, A. Guenther and J. Greenberg: Overview of the field measurement campaign in Hyytiälä, August 2001 in the framework of the EU project OSOA, *Atmos. Chem. Phys. Discuss.*, 3, 3769-3831, 2003.

**V** Boy, M., Ü. Rannik, K.E.J. Lehtinen, V. Tarvainen, H. Hakola and M. Kulmala: Nucleation events in the continental PBL – long term statistical analysis of aerosol relevant characteristics, accepted for publication in *J. Geophys. Res.*, August, 2003.

## Review of publications

This thesis consists of establishing a spectral solar radiation monitoring station, intensive data analysis and the investigations on aerosol relevant characteristics. Data used are from three years of continuous measurements (1999-2001) at the field research station SMEAR II in Hyytiälä as well as from four campaigns in Hyytiälä in the framework of two EU projects, BIOFOR and OSOA.

**Paper I** focuses on the effects of synoptic weather systems and air masses on the formation of new aerosols in the continental boundary layer. Weather maps from 143 days were used for the classification of air masses and surface front analyses. Bursts of nanometer sized particles occurred only in arctic and to some extent in polar air masses, but never in sub-tropical air masses. Nucleation was always associated with cold air advection or cold air outbreaks behind cold fronts. Warm air advection, even in arctic or polar air masses, seemed to limit or prevent the formation of new aerosols.

**Paper II** presents a detailed analysis of measurements from 1999 and a first attempt to determine a “nucleation parameter (NP)”, which enables the prediction of situations favouring new particle formation. The equation for the nucleation parameter - UV-A solar radiation divided by the concentration of water vapour and temperature - resulted from the trend of different variables with the number concentration of nucleation mode particles. A high correlation between the NP-values and the concentration of newly formed aerosols was attained, especially in the first half of the year, and non-event days with high NP values were associated with high amounts of pre-existing particles.

**Paper III** describes the establishment and operation of a station for monitoring spectral solar irradiance and the use of the obtained data to investigate which part of the solar spectrum has the greatest influence on new particle formation. The short wavelength interval between 300 and 330 nm showed the highest correlation with particle concentration in the 3-10 nm size range. A potential mechanism explaining the indirect influence of irradiance in this wavelength band is the production of excited oxygen and further the formation of hydroxyl radicals. Although radiation between 300-330 nm is one to two magnitudes smaller than the maximum values of the solar spectrum, it is the main path for the production of OH radicals during daytime in the boundary layer.

**Paper IV** gives an overview of the results obtained during the field measurement campaign in Hyytiälä, August 2001, within the framework of the EU project OSOA. The synoptic weather situation divided the measurement period into two parts: three days with cold air advection and clear particle bursts followed by 13 days with warm air advection and only two weak events. The chemical analyses revealed a clear contribution of organic matter (19 % organic carbon from the particle material), originating from the oxidation of terpenes from the local biosphere.

**Paper V** summarizes the correlation of different variables with the concentration of particles with diameters 3-6 nm and contains calculations of aerosol relevant characteristics. Solar radiation, concentration of OH radicals and condensation sink values showed the highest correlation

or anti-correlation with the concentration of newly formed aerosols. For other parameters (e.g. ozone) there is little or no correlation with the newly formed aerosols during single event days, but clearly different trends for the daily average between the event and non-event days are visible. A comparison of particle growth rates based on precursor measurements to experimental values (based on DMPS measurements) showed that the contribution of carboxylic diacids to particle growth lies between 8 and 50 %.



# 1 Introduction

Aerosols play an important role in many physical and chemical processes in the atmosphere; they act as substrates for heterogeneous reactions and affect tropospheric chemistry (Dentener and Crutzen, 1993; Ravishankara, 1997). They also contribute to the climate forcing directly by scattering and absorbing solar irradiance (Jacobson, 2001; Adams et al., 2001; Chung and Seinfeld, 2002) and indirectly by the formation of clouds (Han et al., 1998; Nakajima et al., 2001; Kristjansson, 2002). Furthermore, research about the influence of aerosols on human health, especially the contribution of submicron particles, has recently received increasing attention (Jones, 1999; Harrison and Yin, 2000). Resulting from these issues atmospheric aerosol research has in the last decades developed to an independent field of science.

The emission of primary particles and the precursors of secondary aerosols into the atmosphere are much more difficult to define than the concentration of most of the atmospheric gases. This is because of the short atmospheric lifetime of the particles (days to weeks) and the local or regional emission of aerosols and precursor gases. Estimations of the global primary and secondary aerosol sources are summarised in Table 1.

<b>SECONDARY</b>	<b>Low</b>	<b>High</b>	<b>PRIMARY*</b>	<b>Low</b>	<b>High</b>
<b>Natural</b>			<b>Natural</b>		
Sulphate	28	118	Mineral dust	1000	3000
Sulphate (volcanic)	9	48	Sea salt	1000	6000
Nitrate	1,9	7,6	Biogenic	0	90
Biogenic VOC	8	40			
<b>Anthropogenic</b>			<b>Anthropogenic</b>		
Sulphate	69	214	Biomass burning	50	89
Nitrate	9,6	19,2	Fossil fuel	16	38
Organic compounds	0,3	1,8	Industrial dust	40	130
<b>Total</b>	<b>125,8</b>	<b>448,6</b>	<b>Total</b>	<b>2106</b>	<b>9347</b>

\* Estimations for the year 2000

Table 1: Estimates for secondary aerosol sources and primary particle emission ( $\text{Tg yr}^{-1}$ ) (IPCC, 2001).

Comparing the amount of secondary aerosols with the direct emission of primary particles (latter by a factor of 20 higher) it seems that secondary particles only play a minor role in the global aerosol budget. However, there are several reasons why considering only aerosol mass is inadequate. First, there is a strong correlation between the particle size and their atmospheric lifetime. Mineral dust and sea salt particles are in the upper size range of atmospheric aerosols (coarse mode with diameters  $D_p > 1 \mu\text{m}$ ). The lifetime of these particles is mainly limited by gravita-

tional settling and is very short. In contrast, aerosols formed by gas-to-particle conversion are much smaller. Their sizes range from the nucleation mode (particles with  $D_p = 1-25$  nm), over the Aitken mode (particles with  $D_p = 25-100$  nm) to the accumulation mode (particles with  $D_p = 0.1-1$   $\mu\text{m}$ , Mäkelä et al., 2000a). In this size range the deposition velocity features a minimum at around 100 nm (Rannik et al., 2000; Gallagher et al., 1997), which leads to much longer atmospheric lifetimes of secondary aerosols.

Another aspect which is neglected by only viewing particle masses is the number concentration. At Hyytiälä field research station of the University of Helsinki (61°51' N, 24°17' E, 181 m asl) 50 to 80 particle formation event days per year (Mäkelä et al., 2000b and **Paper III**) with high amount of newly formed aerosols were monitored in the last seven years. The formation of nanometer sized aerosols have also been observed at other sites, like suburban Helsinki (Väkevä et al., 2000), urban Atlanta, Pittsburgh and St. Louis (Woo et al., 2001; Stanier et al., 2002; Shi, 2003), industrialized agricultural regions in Germany (Birmili and Wiedensohler, 2000; Birmili et al., 2003), mountain regions (Birmili et al., 2000), marine environment (Raes et al., 1997), coastal area (O'Dowd et al., 1998) and free troposphere (Weber et al., 2001; Clarke, 1993). For the summary see recent overview (Kulmala et al., 2003).

During the particle bursts the ratio between the number concentration of newly formed particles ( $D_p < 50$  nm) and the existing larger aerosols reached values up to 10 in Hyytiälä. The high concentrations and dominance of nucleation and Aitken mode particles during nucleation events are important in many climatologically relevant processes, e.g. cloud formation. Although larger particles ( $D_p > 1$   $\mu\text{m}$ ) already grow to cloud droplets at low supersaturation of water vapour, their number concentration is too small for a sufficient amount of cloud condensation nuclei (CCN) and for cloud formation. Apart from primarily emitted small particles (e.g. from fossil fuel burning), especially secondary aerosols, interfere here with the climate system. Furthermore, the aerosols with diameters between 0.1 and 1  $\mu\text{m}$  are significantly involved in the direct radiation forcing. Based on the mass of the particles the scattering cross-section of the aerosols reaches a maximum in this size range (Schwartz, 1996).

Secondary aerosols are produced in the atmosphere by transformation of semi- and/or non-volatile molecules from the gas to the particle phase. The condensable vapours are formed through oxidation of precursors, like e.g. sulphur dioxide or nitrogen oxides. These molecules contribute to the inorganic aerosol fraction in the atmosphere. Organic gases, primarily the reaction products of mono- and sesquiterpenes with hydroxyl radicals and ozone, reflect the secondary organic aerosol (SOA) proportion. Table 1 gives a maximum input from SOA into the atmosphere as 40 Tg yr<sup>-1</sup>, which results in a percentage of SOA to the total amount of secondary aerosols of 10 %. Quite recently, Derwent et al. (2003) estimated a higher global SOA production of 63 Tg yr<sup>-1</sup>; Griffin et al. (1999) and Kanakidou et al. (2000) calculated values of 13-24 and 61-79 Tg yr<sup>-1</sup>, respectively. Andreae and Crutzen (1997) suggested that the production of SOA might range from 30 to 270 Tg yr<sup>-1</sup> and thus can be comparable in magnitude to the production of biogenic and anthropogenic sulphate aerosols.

## 2 Aims of the study

The different mechanisms behind the formation of particles are still not completely understood. Condensation of inorganic vapours on existing particles and coagulation of aerosols have been quite well explored. However, the condensation of organic vapours, nucleation process, identification of participating organic species, thermodynamics and coupling of aerosol dynamics with micrometeorology still include many uncertainties. A number of groups in several countries work on developing theories which enable the prediction of newly formed aerosols in the atmosphere. The objectives of the present work were

- to establish a solar irradiance monitoring station at the forest research station SMEAR II in Hyytiälä, Finland, and to discover which part of the solar spectrum has the highest influence on the formation of secondary aerosols in the Boreal Forest (**Paper III**)
- to investigate meteorological, physical and chemical situations, which favour the formation and growth of secondary organic aerosols by analysing measurements of the years 1999 to 2001 (**Papers I, II and V**)
- to explore the availability of precursor gases and the concentration of organic species which are under consideration to participate in the particle formation processes (**Papers IV and V**)
- to determine the quantitative contribution of monoterpene reaction products on the formation and growth of new particles (**Paper V**)

### 3 Setup of a spectral solar irradiance monitoring station

A station designed to monitor spectral solar radiation at the SMEAR II (Station for Measuring Forest Ecosystem-Atmosphere Relations) was set up in Hyytiälä. Hyytiälä is surrounded by extended areas of coniferous forest and the measurement site is located on a moderately sloping terrain in a 41-year old Scots pine (*Pinus sylvestris* L.) forest with the dominant tree height of about 13 m. A detailed description of the SMEAR II can be found in Kulmala et al. (2001a) and in the SMEAR homepage [www.honeybee.helsinki.fi/smeat/](http://www.honeybee.helsinki.fi/smeat/).

The radiospectrometer (Bentham, England) measures spectral solar irradiance between 280 nm and 580 nm with a step width  $\geq 0.05$  nm. Exact monitoring of solar UV-B and UV-A radiation requires instrumentation with a high sensitivity because of the low number of photons in this wavelength band. The well-accepted way of testing the precision is a simultaneous operation of several instruments on cloudless days (Seckmeyer et al., 1994). For this reason the radiospectrometer was moved in spring 1999 to the station of the Finish Meteorological Institute (FMI) at Jokioinen (ca. 100 km North-East of Helsinki). For one week our instrument and three Brewer radiospectrometers were measuring solar radiation continuously.

After the test stage we constructed a small cottage for the instrument and placed it on the top of a building in Hyytiälä above the tree level, which enabled the undisturbed monitoring of spectral solar irradiance throughout the year. Since January 2000 continuous measurements of spectral solar irradiance have been conducted. A detailed description of the instrument can be found in **Paper III**.



Figure 1: “Telephone box” with radiospectrometer on top of the A-house at the SMEAR II in Hyytiälä, Finland. The arrow points to the diffuser.

## 4 Parameters influencing the particle formation process

Particle bursts measured at a detection limit of 3 nm have been observed in Hyytiälä during the last 8 years. The frequency of these so-called event days varied between 50 and 80 yr<sup>-1</sup>. According to their clarity the nucleation event days have been classified into three groups (A-, B- and C-events, Mäkelä et al., 2000b, **Paper II**) and analysed for correlation with many meteorological, physical and chemical parameters measured at the Hyytiälä forest field station. **Papers I, II, III and V** include results concerning these data analyses. The most important parameters concerning the formation of new aerosols will be discussed in the following sub-chapters. In addition, other variables such as the concentration of different vapours (ozone, sulphur dioxide, nitrogen oxides and monoterpenes), horizontal and vertical wind variances, particle flux measurements and temperature were investigated. A detailed discussion of these parameters and their correlation with the number concentration of particles with diameters between 3 and 6 nm on a daily and yearly basis can be found in **Paper V**.

### 4.1 Synoptic weather

In 1998-99 a large research project, BIOFOR (Biogenic Aerosol Formation in the Boreal Forest, see Kulmala et al. 2001a) focused on the observation of the appearance of ultra-fine particles detected at 3 nm, and their subsequent growth to ~100 nm in 1-2 days. BIOFOR took place at the SMEAR II station and included three intensive field campaigns (BIOFOR 1 from 11<sup>th</sup> of April to 22<sup>nd</sup> of May in 1998, BIOFOR 2 from 17<sup>th</sup> of July to 29<sup>th</sup> of August in 1998 and BIOFOR 3 from 11<sup>th</sup> of March to 30<sup>th</sup> of April in 1999). The data obtained during the three campaigns were evaluated with a focus on what context of synoptic circulation the nucleation occurs and what kind of air masses favour nucleation (**Paper I**).

For the experimental time period the air masses were classified and surface front analysis was carried out by using a large number of weather maps from the European Meteorological Bulletin (German Weather Service), Berliner Wetterkarte (Institute for Meteorology, Free University of Berlin) and NOAA-14-satellite images in the visible and infrared channels. Three types of air masses - arctic, polar and sub-tropical - were classified. An air mass is a large body of air with similar temperature and/or humidity, which is formed in a stable "source region". Sub-tropical air masses come from the south and originated over the Mediterranean, North Africa, the Azores or the Caribbean. Arctic air masses have formed over the pole, while polar air masses have formed south of arctic air masses. Table 2 summarizes the results of the entire BIOFOR campaign period.

Clear particle formation events (A- and B-events) occurred in arctic (71 %) or polar (29 %) but never in sub-tropical air masses. Nucleation occurred only with cold air advection or cold air outbreaks behind cold fronts. The results agree with the conclusions from Väkevä et al. (2000) that warm air advection, even in an arctic or polar air mass, appears to be a limiting meteorological condition. The analyses of backward trajectories revealed that arctic and polar air masses

arrived at Hyttiälä from a southwest to northeast direction during periods of cold air advection. These air masses typically originated northwest to northeast (Atlantic or Arctic Ocean) of the experimental site, but occasionally a polar air mass followed a cyclonic flow over Europe to reach Finland from the southwest.

	Event day	Unclear cases	Non-event day
<b>Air mass</b>			
Arctic	71 %	22 %	11 %
Polar	29 %	65 %	81 %
Sub-tropical	0 %	13 %	8 %
<b>Cold air outbreaks</b>	100 %	48 %	20 %
<b>Sector of air flow to Hyttiälä</b>			
Southwest to northeast	16 %	24 %	61 %
South to east	4 %	12 %	85 %
<b>Number of days</b>	14	32	97

Table 2: Statistics of air mass types, frequency of cold air outbreaks and of air flow (revealed by four-day backward trajectories arriving at 925 hPa) for the entire BIOFOR (**Paper I**).

The annual cycle of the nucleation frequency (**Paper III**, minimum of events in summer and winter) might be partly explained by the fact that arctic air masses rarely form in the northern hemisphere during the summer months in Finland. However, 11 % of the days with arctic and 81 % of the days with polar air masses were non-event days. Consequently, there are other limiting factors for the particle formation process.

## 4.2 Solar radiation

The importance of solar irradiance on particle formation has been pointed out in the past by many authors (e.g. Birmilli and Wiedensohler, 2000; Clement et al., 2001). However, it still has been an open question as to what part of the solar spectrum is responsible for these processes. To explore the possible existence of a solar wavelength band which is more correlated with the new particle formation, spectral solar radiation data from two years (2000 and 2001), measured with the radiospectrometer (presented in chapter 3) were investigated.

Figure 2 gives the ratio of solar irradiance for the sum of all clear event days (54) to all non-event days and to all days of the two years, respectively. A significant peak in both curves with maxima of 1.64 and 1.42 appear in the range between 300 and 310 nm followed by a steep decrease to close to 1 at 340 nm. This result as well as more detailed analyses for monthly trends (**Paper III**) indicated that solar short wavelength radiation (SWR, 300-330 nm) is higher on

most of the event days during autumn and winter compared to average reference curves of the corresponding months. During the rest of the year this trend disappears. However, the absolute amount of SWR is still one order of magnitude higher in spring and summer compared to autumn and winter. The calculated correlation coefficients between solar irradiance in 10 nm wavelength bands (from 280-580 nm) and the number concentration of particles ( $D_p = 3-10$  nm) confirmed this statement with the highest correlations in the SWR range.

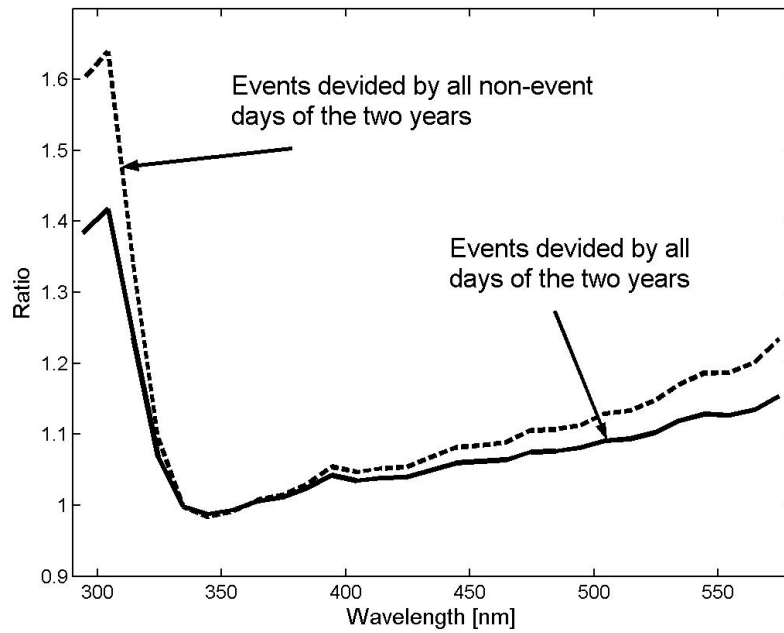


Figure 2: Ratios of spectral solar irradiance per wavelength interval of 10 nm between the sum of all event days and the sum of all non-event days or the sum of all days from the years 2000 and 2001, respectively.

The question how solar short wavelength radiation participates in aerosol formation is believed to be caused by two main mechanisms: First, turbulent kinetic energy on cloudless, calm days and therefore the evolution of the mixed layer are mainly produced through the radiation steered buoyancy forces. In this context Nilsson et al. (2001) suggested that the mixing of different air masses from the residual and the surface layer with different loadings could cause the onset of nucleation. Another possible impact of solar radiation might be photochemistry. In **Paper III** we introduced one possible photochemical reaction path by calculating the production rate of excited oxygen atoms ( $O(^1D)$ ), Seinfeld and Pandis, 1998) with

$$O(^1D) = Pho \cdot Q_{O_3} \cdot ACS_{O_3} \cdot [O_3]. \quad (1)$$

Here Pho is the number of photons,  $Q_{O_3}$  is the quantum yield and  $ACS_{O_3}$  is the absorption cross-section for ozone. The results showed that a maximum concerning the wavelength occurred

around 310 nm with a gradient of one order of magnitude in less than 15 nm in both directions. This is a combination of the decrease in the absorption cross-section and quantum yield of ozone with higher wavelengths on one side and the steep increase of the irradiance with higher wavelength on the other side. According to Seinfeld and Pandis (1998), a hydroxyl radical yield of approximately 0.2 molecules OH per one O<sub>3</sub> molecule from Eq. 1 is achieved via the reaction



Although in terms of absolute values the solar irradiance in the SWR band is one to two orders of magnitudes lower than the maximum values of the solar spectra, it is the only source of excited oxygen atom in the troposphere and the main source of hydroxyl radicals during daytime. OH radicals had the highest correlation coefficients with 3-6 nm particles ( $r^2 = 0.7$  for the clear A-events, **Paper V**) from all parameters mentioned in the beginning of this chapter (ozone, sulphur dioxide, nitrogen oxides, monoterpenes, temperature, horizontal and vertical wind variances, particle flux measurements and number concentration of pre-existing aerosols). Further contributions of the hydroxyl radicals to the formation processes of new particles will be discussed in chapter 5.

### 4.3 Existing particle number concentration

In contrast to solar irradiance the number concentration of existing larger particles with diameters > 20 nm is anti-correlated with the amount of newly formed aerosols. The importance of pre-existing aerosols on the particle formation process is examined in **Paper II**. In this paper we calculated, for one single year (1999), a “nucleation parameter”, described by

$$NP = \frac{UVA}{[H_2O] \cdot T} . \quad (3)$$

UVA is ultraviolet radiation (320-400 nm), H<sub>2</sub>O is the concentration of water vapour and T is the temperature. Throughout the year nearly all days with intense particle formation gave a “nucleation parameter” value of at least  $5.4 \cdot 10^{-25} \text{ W m molecules}^{-1} \text{ K}^{-1}$ . Non-event days with high values ( $> 2.7 \cdot 10^{-25} \text{ W m molecules}^{-1} \text{ K}^{-1}$ ) were mostly accompanied by high concentrations of existing aerosols. Figure 3 gives half-hour-average NP-values and number concentrations of particles in the size ranges 3-10 nm and 10-500 nm (normalised to unity) for the 12<sup>th</sup> of May 2000 (class A-event day).

The amount of newly formed aerosols with  $D_p = 3-10 \text{ nm}$  starts to increase at the time when the number concentration of existing larger particles reached the minimum. This effect correlates with the evolution of the mixed layer and was observed on most of the event days. An air mass with a lower loading of pre-existing aerosols is transported downwards and decreases the total number concentration of particles at the surface. The NP-curve reflects high conformity with the curve of the small particles. However, the number concentration of the small particles starts to decrease already when the number concentration of the aerosols with  $D_p > 10 \text{ nm}$  reached about



30 % of the daily maximum. This fact is due to the coagulation of small particles with larger ones (Kerminen and Kulmala, 2001; Buzorius et al., 2003) and the decreasing concentration of condensable vapours through condensation on the existing aerosols.

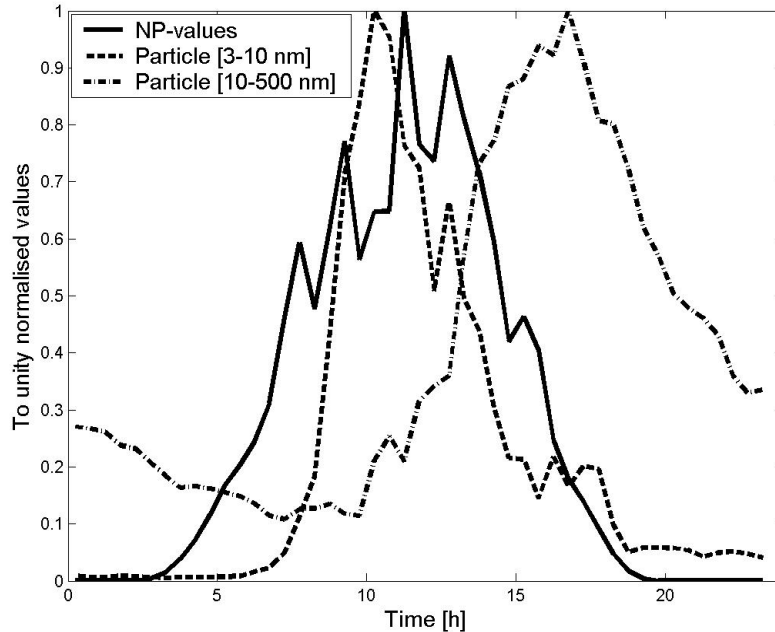


Figure 3: NP-values and number concentration of particles (normalised to unity) in two size ranges for the 12<sup>th</sup> of May 2000.

The condensation sink (CS) determines how rapidly molecules will condense onto pre-existing aerosols (Kulmala et al, 2001b, **Paper IV and V**). In **Paper V** the correlation of condensation sink values with the number concentration of particles in the range  $D_p = 3-6$  nm was presented. These two parameters were anti-correlated on a daily as well as on a yearly basis. High numbers of CS values ( $> 0.002$  molecules  $\text{cm}^{-3} \text{s}^{-1}$ ), especially during the summer months might be a limiting factor for the formation of new particles. In these cases the scavenging of condensable vapours by larger aerosols decreases the concentration of the condensing species to such an extent, that the formation and growth of new particles might be prevented.

#### 4.4 Water vapour content

Data analysis from the years 1999 to 2001 revealed a clear trend of low amounts of water vapour concentration on event days compared to non-event days (**Paper II and V**). Especially during the summer months, with  $\text{H}_2\text{O}$  values  $> 2 \cdot 10^{17}$  molecules  $\text{cm}^{-3}$ , only a few days with particle formation were observed. On some event days the detection of newly formed aerosols occurred

when the concentration of water vapour decreased under the mentioned value. This effect is demonstrated in a H<sub>2</sub>O-time-day plot for the month May 1999 in Fig. 6 in **Paper II**.

It is still unclear how the water vapour content limits the particle formation process. However, there are two hypotheses: The first one is based on the fact that the particle number concentration is measured with a Differential Mobility Particle Sizer (DMPS) system, which measures particles at dry conditions. The real diameter of the existing particles and further the volume and surface will increase depending on the amount of water vapour in the air (average hygroscopic growth factors for Hyytiälä, GF = 1.1-1.6, Hämeri et al, 2001). Consequently the values of the condensation sink, which are proportional to the particle diameters, will increase and the concentration of the condensing species will decrease, hence limiting the particle formation process. The second theory is based on chamber experiments from Bonn et al. (2002a and 2002b). They found that aerosols formed during the ozonolysis of exocyclic monoterpenes (e.g.  $\beta$ -pinene) are negatively affected by the concentration of water vapour.

Until now only hypothesis exist concerning the effects of water vapour and other parameters on the processes involved in the formation of secondary aerosols. Although long-term data analyses have given strong indications which variables play important roles, it will still take time until we are able to develop a complete understanding.

## 5 Aerosol relevant characteristics

In the previous chapter the meteorological, physical and chemical conditions during times of particle formation were discussed. This chapter focuses on the formation process itself and especially reflects the contribution of biogenic volatile organic compounds (VOC).

Nucleation, or gas-to-particle conversion, occurs when similar (homomolecular) or different (heteromolecular) molecules with low saturation vapour pressures ( $E_s$ ) collide and the thermodynamic properties enable the formation of stable clusters. The most common proposed mechanisms for atmospheric nucleation are: binary nucleation of H<sub>2</sub>O and H<sub>2</sub>SO<sub>4</sub> (Vehkamäki et al., 2002), ternary nucleation of H<sub>2</sub>O, NH<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> (Coffman and Hegg, 1995; Korhonen et al., 1999) and ion induced nucleation (Yu and Turco, 2000; Arnold 1982). The contribution of organic species in the nucleation process is still an open question. According to Kulmala et al. (1998, necessary saturation vapour pressure for atmospheric nucleation to occur:  $E_s < 10^6$  molecules cm<sup>-3</sup>) homogeneous nucleation of carboxylic diacids (monoterpene reaction products with the lowest saturation vapour pressures, e.g. pinic acid:  $E_s \approx 3.4 \cdot 10^9$ - $3.4 \cdot 10^{10}$  molecules cm<sup>-3</sup>, Jang and Kamens 1999) will not occur in the real atmosphere. However, heteromolecular homogeneous nucleation of different diacid molecules like e.g. cis-pinic and norpinic acid might be possible (Hoffman et al., 1998).

Another question concerning the appearance of particle bursts is what are the limitations for the aerosol formation process? Is it the amount of clusters, which are stable enough to grow to the detectable size of 3 nm or the concentration of the condensing vapour(s) along with pre-existing particles? Kulmala et al. (2000) suggest that nucleation occurs almost everywhere in the atmos-

where, at least during the daytime and leads to a reservoir of thermodynamically stable clusters (TSC - with diameter < 3 nm), which under certain conditions grow to detectable sizes. In the next sub-chapter biogenic VOCs (especially monoterpenes), which are considered as precursors, will be discussed and thereafter the focus is on the influence of the reaction products from these vapours on the formation and growth of particles.

## 5.1 Precursor gases and condensable vapours

Formation of secondary organic aerosols in rural areas like the boreal forest in Finland was one topic of the EU project OSOA (Origin and Formation of Secondary Organic Aerosols). Within the framework of OSOA, one intensive field campaign was conducted in Hyytiälä (1.-16. of August 2001, **Paper IV**). Altogether eight institutes from six countries participated the project with some newly developed analytical instrumentations and methodologies.

The organic species which are mostly suggested to be involved in the formation of new particles are the reaction products of mono- and sesquiterpenes (Koch et al., 2000; Gao et al., 2001; Hopfel et al., 2001; Larsen et al., 2001). Although nucleation of biogenic compounds is still questionable, the condensational growth of clusters in the size range around 1 nm should be encouraged by vapour(s) with very low saturation vapour pressure(s) (Kulmala et al., 1998; Kerminen et al., 2000; Anttila and Kerminen, 2003). In Hyytiälä  $\alpha$ -pinene is the dominating monoterpene with around 45 vol. % (Lindfors and Laurila, 2000 and **Paper V**). The reaction mechanisms of this precursor gas with ozone, hydroxyl radical and nitrate are shown schematically in Figure 4.

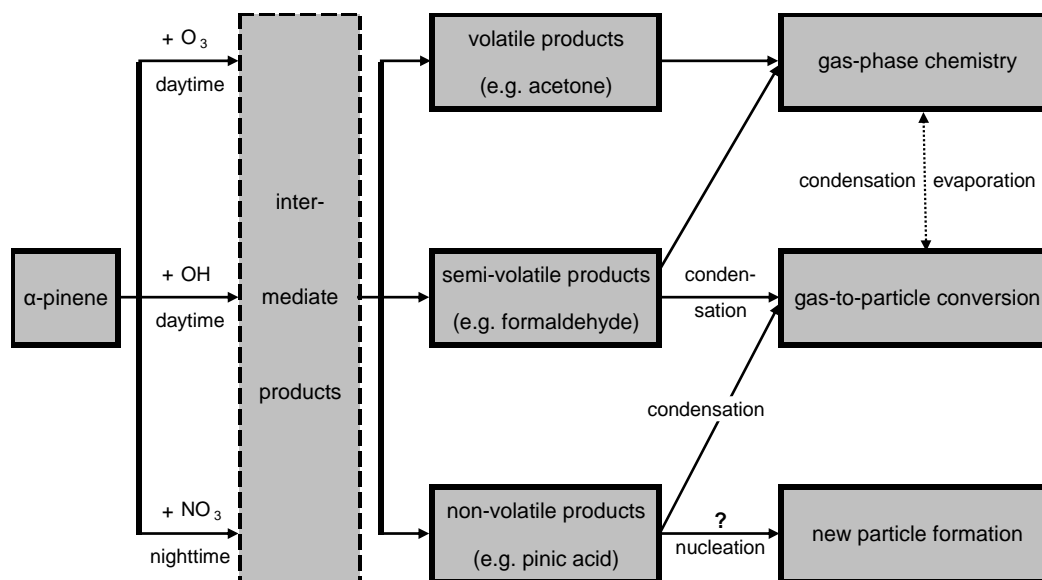


Figure 4: Generalized scheme of atmospheric VOC-oxidation for  $\alpha$ -pinene, quantitatively the most important monoterpene (Hoffmann, 1999).

During the summer months sesquiterpenes show emission rates comparable to those of the monoterpenes (Hakola et al., 2003). A fractional aerosol yield (fraction of a hydrocarbon that is converted to aerosol) of close to 1.0 was found in outdoor smog chamber experiments for some single naturally emitted sesquiterpenes (Hoffmann et al., 1997). However, their atmospheric lifetime is so short (some minutes or less - Shu and Atkinson, 1995), that their concentrations in the atmosphere are difficult to measure and until now no sesquiterpenes concentration data from Hyytiälä are available.

Gas/particle partitioning of photo-oxidation products was also measured during the OSOA campaign in Hyytiälä (**Paper IV**). The result of this analysis showed that pinonaldehyde (semi-volatile) is distributed roughly equally between the particle and gas phase. Pinic acid (non-volatile), in contrast, was only detectable in the particle-phase with average concentrations of around  $5.6 \text{ ng m}^{-3}$  ( $\sim 1.8 \cdot 10^7$  molecules  $\text{cm}^{-3}$ ). In addition to pinic acid, other carboxylic diacids (pinonic, norpinic, sabinic, limonic and caric acid) were detected in the particle phase during the experiments with concentrations up to  $62 \text{ ng m}^{-3}$  ( $\sim 2 \cdot 10^8$  molecules  $\text{cm}^{-3}$ ). The sampling of these particles ( $\text{PM}_2$ ,  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  - PM applies to particles with aerodynamic diameters smaller than 2, 2.5 and 10 micrometers, respectively) was carried out for 12-hour periods on quartz filters.

Measurements of terpenes and some other reaction products during the campaign did not show any evidence of higher concentrations on event days compared to non-event days. However, the experimental period of 16 days is too short for any conclusions to be drawn about the limiting influence of these vapours on the particle formation process over the year. In the previous chapter the temporal variability of several parameters was already highlighted.

In **Paper V**, measured and calculated data sets from two years (2000 and 2001) were used to estimate the source rates and concentrations of carboxylic diacids and sulphuric acid on nucleation event days. Carboxylic diacid molecules show the lowest saturation vapour pressure(s) from all oxidation products of the monoterpenes (Jang and Kamens, 1999). For this reason we used the carboxylic diacids along with sulphuric acid as the responsible species in the particle formation process. The production yield of these molecules ( $P_{\text{CD}}$ ), which reflects the fraction of carboxylic diacid molecules formed per one monoterpene molecule reacting with OH or ozone, was assumed to be 0.05 in these calculations. A detailed description of calculating the source rates of carboxylic diacids and sulphuric acid is given in **Paper V**. With the vapour source rates and condensation sink values the concentration of the condensing species can be determined by

$$\frac{dC_{v,\infty}}{dt} = Q_v - CS_v (C_{v,\infty} - C_{v,R_p}), \quad (4)$$

where  $Q_v$  is the source rate,  $CS_v$  is the condensation sink,  $C_{v,\infty}$  and  $C_{v,R_p}$  are the vapour concentrations far from the particles and at the particle surface, respectively. Assuming steady-state conditions for the time dependence of the vapours enables the calculation of the concentrations. Since the identities of the condensing vapours (and thus their saturation vapour pressures) are not known,  $C_{v,R_p} = 0$  was assumed for simplicity.

Figure 5 shows calculated vapour concentrations for sulphuric acid and the carboxylic diacids by using two different condensation sink values (CS was calculated using molecular properties of sulphuric acid or pinic acid, see chapter 4.3) for organic compounds.

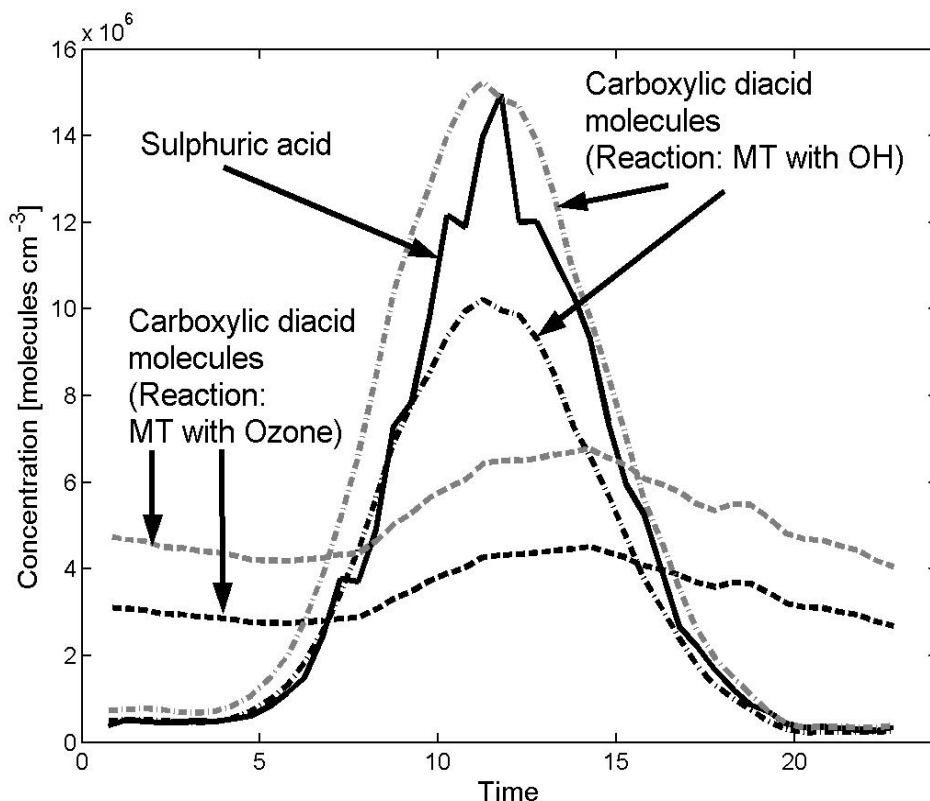


Figure 5: Estimated mean diurnal concentrations of three different vapours for 32 event days in 2000 and 2001. Black curves from the diacids use CS-values calculated with the molecular properties of sulphuric acid and grey curves use molecular properties of pinic acid.

The effect of the molecular properties is significant and affecting the estimated concentrations of the carboxylic diacid molecules by 50 %. There are many uncertainties concerning the condensing vapour(s) in the first stage when the thermodynamically stable clusters start to grow. However, the results of **Paper IV and V** indicate that carboxylic diacid molecules like pinic or cis-pinonic acid are available in sufficient concentration to participate significant in new particle formation process. In this context O'Dowd et al. (2002) have suggested that molecules with properties like pinic and cis-pinonic acid are partly responsible for the growth of newly formed particles in the  $D_p = 3-5$  nm size range in Hyytiälä.

## 5.2 Particle formation and growth rates

Aerosol relevant characteristics were calculated with size distributions obtained using the DMPS system in Hyytiälä. During the years 1996-98, the growth rates ( $dD_p/dt$ ) of the nucleation mode particles varied between 2 and 15 nm h<sup>-1</sup> (average = 5.4 nm h<sup>-1</sup>) and the formation rates ( $J_3$  = number of particles formed at 3 nm) between 0.01 and 0.42 particles cm<sup>-3</sup> s<sup>-1</sup> (average = 0.17 particles cm<sup>-3</sup> s<sup>-1</sup>) (Mäkelä et al., 2000b). The equivalent values for the five event days observed during the OSOA field campaign in Hyytiälä were rather high (especially the growth rate) but comparable with earlier summertime observations ( $dD_p/dt$  = 6.24-10.74. nm h<sup>-1</sup>,  $J_3$  = 0.17-0.38 particles cm<sup>-3</sup> s<sup>-1</sup>, **Paper IV**).

**Paper V** presents another way to obtain these characteristics. First we calculated the growth rates by using the vapour concentrations obtained using the method outlined in the previous sub-chapter with (Kulmala et al., 2001b; Dal Maso et al., 2002)

$$\frac{dD_p}{dt} = \frac{4 \cdot m_v \cdot \beta_m \cdot D_v \cdot C_v}{D_p \cdot \rho_p}. \quad (5)$$

Here  $m_v$  is the molecular mass,  $\beta_m$  is the transitional correction factor for the mass flux (Fuchs and Sutugin, 1971),  $D_v$  is the diffusion coefficient and  $\rho_p$  is the liquid density. Next we used the general dynamic equation

$$\frac{\partial n(D_p, t)}{\partial t} + \frac{\partial}{\partial D_p} \left( \frac{dD_p}{dt} n(D_p, t) \right) = -CoagS(D_p) \cdot n(D_p, t) - \frac{v_{dep}(D_p)}{h_{bl}} n(D_p, t), \quad (6)$$

in which CoagS is the coagulation sink (Kulmala et al., 2001b), describing the scavenging rate of particles of diameter  $D_p$  onto all other particles,  $v_{dep}$  is the particle dry deposition velocity and  $h_{bl}$  the atmospheric boundary layer height. Integrating equation (6) from 3 to 6 nm and including measured and calculated values of  $v_{dep}$ ,  $h_{bl}$ , CoagS and  $N_{3-6}$  enabled us to estimate the formation rate of particles at  $D_p = 3$  nm,  $J_3$ -values. A detailed description and the necessary assumptions are presented in **Paper V**. Also for these two parameters ( $dD_p/dt$ ,  $J_3$ ) we used for sensitivity studies the molecular properties of sulphuric and pinic acid with a constant production yield for the carboxylic diacids of 0.05.

The results in Figure 6 demonstrate that the formation rates using both calculation mechanisms and both molecular properties are in acceptable ranges. However, the growth rates achieved through equation 5 are by a factor of 4.6 (sulphuric acid molecular properties) and 1.5 (pinic and sulphuric acid molecular properties) too low compared to the growth rates obtained from the DMPS measurements. This indicates that the total concentrations of both vapours combined (carboxylic diacid plus sulphuric acid) are high enough to explain the amount of newly formed aerosols at 3 nm, but are too low to account for the experimentally determined growth rates in the nucleation mode. By comparing the growth rates from the DMPS system and the growth

rates obtained only from the carboxylic diacids gives a contribution of between 8 and 50 % of the latter ones depending on  $P_{CD}$  and the molecular properties.

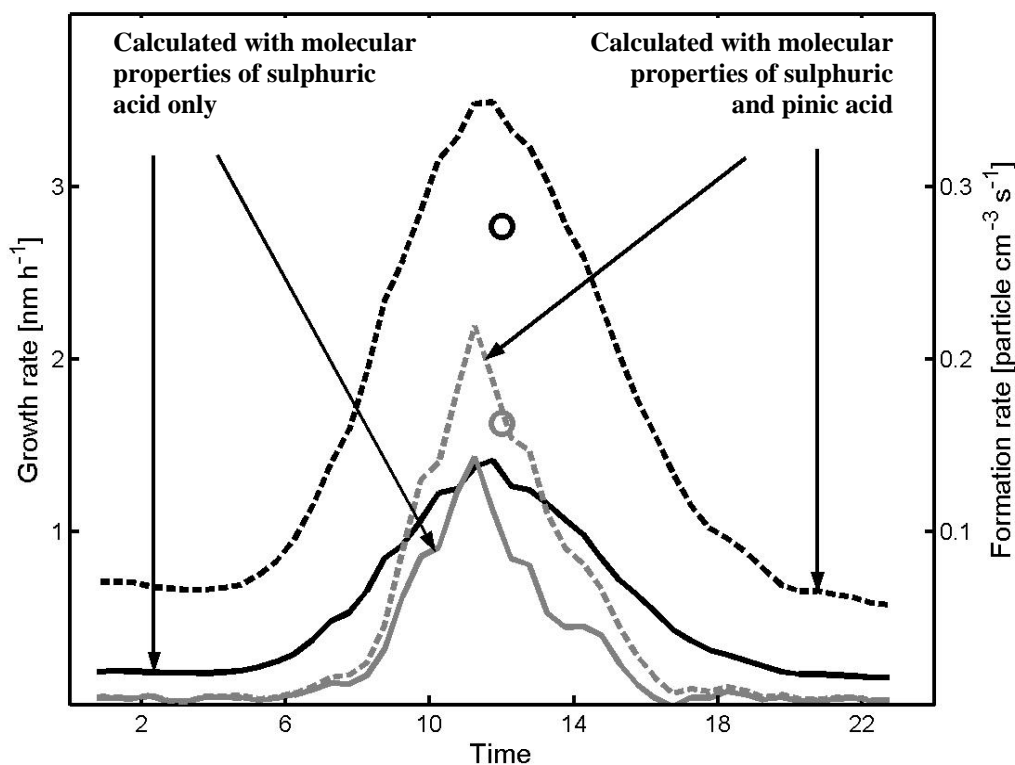


Figure 6: Mean diurnal growth (black) and formation (grey) rates for 32 event days in 2000 and 2001. Circles represent equivalent results calculated from DMPS measurements; the growth rate (black circle) was divided by 2 for clarity.

## 6 Conclusions

This thesis presents studies on the influence of different meteorological, physical and chemical parameters on the formation of secondary organic aerosols (SOA) at the field research station of the University of Helsinki in Hyytiälä, Finland. A substantial data base of three years (1999-2001) was investigated to obtain information about the situations which favour particle formation processes. Furthermore, results of measurements of four different field campaigns conducted in Hyytiälä within the framework of two EU projects (BIOFOR and OSOA) were included.

Analyses of weather maps of 143 days during the BIOFOR field campaigns indicated that newly formed particles occurred only in arctic and to some extent in polar air masses, but never in subtropical air masses. During these time periods nucleation was always connected with cold air

advection or cold air out breaks behind cold fronts. Warm air advection seems to be a limiting factor for the particle formation process. The air masses which arrived at Hyytiälä on event-days originated mostly from north of the station over the Atlantic or Arctic Ocean.

A monitoring station for spectral solar irradiance was constructed and measurements started in January 2000. The data obtained enabled the determination of which part of the solar spectrum has the greatest influence on the formation of SOA. The results showed that short wavelength radiation between 300 and 330 nm gives the highest correlation of the investigated wavelength range (280-580 nm) with newly formed particles of diameters 3-10 nm. Accordingly, photochemical reactions, especially the production of hydroxyl radicals seems to be one important parameter.

Another important variable concerning the formation of new particles is the number concentration of the existing aerosols. A clear anti-correlation between the occurrence of nucleation mode particles and concentration of pre-existing particles on daily and yearly basis were observed. The investigation of a "nucleation parameter", calculated by dividing solar UV-A radiation by the concentration of water vapour and temperature, indicated that non-event days with high values of this parameter are associated with large numbers of pre-existing aerosols.

One phenomenon still not completely understood is the anti-correlation of water vapour concentration with the occurrence of nucleation mode particles. A possible explanation for it is the effect on the ozonolysis of monoterpenes. Bonn et al. (2002a and 2002b) found that the nucleation rate of new particles during the reaction of exocyclic monoterpenes (e.g.  $\beta$ -pinene) with ozone is negatively affected by high concentrations of water vapour.

The obtained results reflect the situations under which the formation of new particles can be expected in a forest area like Hyytiälä. The question remains as to what the nucleating and condensing species are? Gas- and particle-phase measurements from carboxylic diacid molecules (reaction products from the oxidation of monoterpenes with the lowest saturation vapour pressures) gave a preference of these vapours to the particle-phase. It is still unclear whether nucleation of organic species occurs in the atmosphere or if organic gases only contribute to the growth process of thermodynamically stable clusters. However, a clear contribution of organic matter, originating from the oxidation of terpenes from the local biosphere was found during the OSOA field campaign in the particle phase (19 % organic carbon).

Calculations of source rates and concentrations of carboxylic diacids (a selected representative oxidation product for the monoterpenes = pinic acid) estimated for 32 event days from 2000 and 2001 showed that they are in the same range as equivalent values of sulphuric acid. These concentrations enabled the calculation of growth and nucleation rates. A comparison of these aerosol characteristics with equivalent values obtained from DMPS measurements indicated that the concentrations of carboxylic diacid and sulphuric acid molecules are by a factor of 1.5-4.6 too low to explain the observed growth rates in Hyytiälä (corresponding to a contribution to the growth of the nucleation mode particles between 20 and 66 %). If only organic species are considered, a contribution of these vapours between 8 and 50 % to the experimental observed



growth rates were estimated. The particle formation rates calculated by using the precursor measurements and the DMPS data at a size of 3 nm are approximately in the same range.

The current thesis reveals that the knowledge of the formation processes for secondary organic aerosols in rural areas has increased during the last years; however there is still an urgent need for more research work in this scientific area. Future instruments might detect particles below 3 nm in diameter, and sampling techniques will hopefully be able to gain enough mass from nucleation mode particles such that the composition of these very small particles can be investigated. This information could help to disclose the secrets on aerosol formation. In addition to the advances in measurement techniques, theoretical knowledge has also to be improved. Some single processes like e.g. the nucleation or the condensation of organic species are still unclear and interdisciplinary models including meteorology, physics and chemistry have to be developed and improved.

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