The evolution of nucleation- and Aitken-mode particle compositions in a boreal forest environment during clean and pollution-affected new-particle formation events

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We applied two tandem differential mobility analyzer methods to shed light on the evolution of the nucleation- and Aitken-mode-particle compositions at a virgin boreal-forest site during nucleation events in varying conditions. The overall results show a clear anthropogenic influence on the nucleation- and Aitken-mode-particle compositions during the events. The SO₂/MTOP and NOₓ/MTOP (monoterpene oxidation products) ratios best explain the variation in the nucleation mode composition during clean and pollution-affected events, suggesting also the importance of organic sulfur compounds, in addition to other sulfur, nitrogen and organic compounds, in particle formation, composition and properties. During the cleanest events, MTOP explain well the time behaviour of the 10-nm particle composition with an estimated organic fraction of over 95%.

Introduction

The geographical extent of the tropical, temperate and boreal forests is about 30% of the Earth’s land surface (e.g. Bonan 2008). Those forests are located around the world in different climate zones affecting widely atmospheric composition via new particle formation at least in European coniferous forests (e.g. Mäkelä et al. 1997, Kavouras et al 1999, Held et al. 2004, Vehkamäki et al. 2004), in European mixed coniferous and deciduous forest (Tunved et al. 2003), in European deciduous forest (Tunved et al. 2003), in European eucalypt forest (Kavouras et al. 1998), in European arctic hill region forest (Lihavainen et al. 2003), in European wetland forest (Svenningsson et al. 2008), in North-American coniferous forests (Marti et al. 1997,
Leaitch et al. 1999), in South-American rain forest (Rissler et al. 2006), in Australian Eucalypt forest (Suni et al. 2008), and in Asian mixed coniferous and deciduous forests (Dal Maso et al. 2008). Additionally, European aquatic kelp forests are known to produce a high amount of new nanometer-sized particles (e.g. O'Connor et al. 2008) and Asian aquatic mangrove forests (Chatterjee et al. 2006) and African savanna forests (Laakso et al. 2008) have a high potential to contribute to new particle formation.

The boreal forests solely cover one third of the forests extent and are one of the largest vegetation environments, forming a circumpolar band throughout the northern hemisphere continents, with a high potential to affect climate processes (e.g. Tunved et al. 2006, Spracklen et al. 2008, Bonan 2008). New particles are frequently formed in virgin boreal forests (e.g. Mäkelä et al. 1997, Kulmala et al. 2004, Dal Maso et al. 2008), and this provides an opportunity to study the properties of biogenic secondary organic aerosols (SOA) during individual nucleation events in situ. Boreal forests are known to emit numerous volatile and semivolatile organic gases such as various monoterpenes (e.g. Jansson et al. 2001, Tarvainen et al. 2005, Sellegri et al. 2006), which are oxidized in the air and form secondary organic compounds (e.g. Sellegri et al. 2006) which can take part in aerosol formation (e.g. O’Dowd et al. 2002, Laaksonen et al. 2008a) and growth processes in different particle sizes (e.g. Allen et al. 2006, Cavalli et al. 2006, Laaksonen et al. 2008a). However, in order to more fully understand the possible climatic effects of the forests, the properties of secondary organic aerosols in varying conditions (e.g. a change in meteorological parameters or in the concentrations of biogenic and anthropogenic trace gases) need to be better known.

Increasing our understanding of these properties in varying conditions requires instrumental methods with high sensitivity and near-online time resolution which are suitable for the small size (diameter < 20 nm) and low mass of nucleation mode particles, the brevity of nucleation events and the rapid changes that may occur in particle composition. In this study, we applied two tandem differential mobility analyzer (TDMA) systems in parallel, namely the UFO-TDMA (ultrafine organic TDMA: Joutsensaari et al. 2001, Vaattovaara et al. 2005) and the UFH-TDMA (ultrafine hygroscopicity TDMA; Hämmeri and Väkevä 2000, Petäjä et al. 2005) to indirectly (via physico-chemical properties) study the composition behaviour of nucleation mode particles as a function of time during boreal forest nucleation events in clean and pollution-affected conditions. The measurements were conducted at a virgin boreal forest research site, Hyytiälä, Finland, during spring 2003, which was characterized by frequent nucleation events.

Additionally, we performed simple linear regression analyses in order to investigate how the particle hygroscopic (HGF) and ethanol (EGF) growth factors, which are indirectly connected with the composition of the particles, were influenced by meteorological parameters and by gas-phase species during the nucleation events. Overall, the focus was on the reasons behind the time behaviour of newly-formed 10 nm particle compositions in varying conditions, but the links between the compositions of the different sized particles from 6 to 50 nm in diameter were also studied.

Methods

Tandem differential mobility analyzers

A tandem differential mobility analyzer (TDMA) method (Liu et al. 1978) provides an insight into interaction between aerosol particles and their surroundings. Briefly, the method utilizes two differential mobility analyzers (DMAs) in series. The first DMA selects a monodisperse sample from a polydisperse aerosol particle population. Then these particles are brought to a different thermodynamic environment in a controlled manner, where they can grow or shrink to a different equilibrium size in accordance with their new environment. This alteration in size is subsequently monitored with the second DMA. The ratio between the measured size in the second DMA and the size selected with the first DMA is called a growth factor (GF).

In this study, two different kinds of TDMAs were used. In a hygroscopicity TDMA (e.g.
McMurry and Stolzenburg 1989, Hämeri and Väkevä 2000) the growth of the selected particles in elevated relative humidities was monitored. On the other hand, the organic TDMA (Joutsensaari et al. 2001, Vaattovaara et al. 2005) relied on ethanol uptake by the particles. Depending on the chemical composition of the particles, different amounts of water and ethanol are consumed at a given saturation ratio by the particles. We applied the ultrafine specific versions of the TDMA, namely the UFO-TDMA (ultrafine organic TDMA; Vaattovaara et al. 2005, see also Joutsensaari et al. 2001) and the UFH-TDMA (ultrafine hygroscopicity TDMA; Hämeri and Väkevä 2000) to monitor the evolution of the nucleation mode and the lower end of Aitken mode sized particles’ compositions as a function of time and size in varying conditions. The dry diameters used were 6, 8, 10, 20, 30, and 50 nm for the UFO-TDMA and 8, 10, 20, 30, and 50 nm for the UFH-TDMA. The error estimate of the GF values of the consecutive UFO-TDMA measurements is smaller than 0.01 for 10–50 nm particles, 0.13 for 8 nm particles, and 0.017 for 6 nm particles (for 6 and 8 nm particles the estimation was carried out based on the 0.1 uncertainty in the particle diameter measurements, i.e. 0.1/6 and 0.1/8; Vaattovaara et al. 2005). For UFH-TDMA, Hämeri et al. (2000) estimated that the overall accuracy in determining the relative size changes with DMA is better than 1%. The saturation ratios (S, unit%) were 82%–83% for the UFO-TDMA and 90% for the UFH-TDMA.

The usefulness of the UFO-TDMA in the atmospheric background conditions has been demonstrated in laboratory measurements for 6–50 nm nanoparticles (Vaattovaara et al. 2005). It is due to the fact that atmospherically important ultrafine (i.e. diameter < 100 nm) inorganic particles, sodium chloride and ammonium sulfate, do not grow (i.e. EGF is 1) in the sub-saturated (S = 82%–84%) ethanol vapour. On the other hand, particles composed of biogenic organic compounds (e.g. citric acid or tartaric acid) do grow (i.e. EGF is clearly over 1) at sizes between 8–50 nm. Importantly, these measurements are consistent with the bulk ethanol solubility of inorganic and organic compounds given in the literature (e.g. Lide and Frederikse 1996). For 10 nm nucleation-mode particles, EGF values are 1.12 for citric acid and 1.05 for tartaric acid at about 83% ethanol subsaturation. Furthermore, the laboratory measurements show that neither particles of pure ammonium bisulfate nor particles containing ammonium bisulfate and sulfuric acid with sulfuric acid mass fraction up to 33% grow in subsaturated ethanol vapour when the dry particle diameter is 10 nm or smaller and S < 84% (Vaattovaara et al. 2005). Hence, the nucleation mode particles should contain some oxidized organic material, if they grow in about 83% ethanol saturation ratio, which was also used in this study.

In the UFH-TDMA on the other hand, particles composed of inorganic salts grow typically very well. For example, at 90% relative humidity (RH) 10 nm ammonium sulfate particles exhibit hygroscopic growth factors (HGF) of 1.38 (Väkevä et al. 2002), whereas α-pinene and limone oxidation products, as examples of boreal forest relevant compounds, grow significantly less in chamber conditions. For example, Virkkula et al. (1999) measured HGFs of 1.1 for 50 nm particles at 84% RH in α-pinene and limonene oxidation experiment, Saathoff et al. (2003) measured HGFs of 1.10–1.11 for 100 nm and 200 nm particles at 85% RH in α-pinene oxidation experiment and Varutbangkul et al. (2006) measured HGFs of 1.06–1.1 for 80–100 nm particles at 85% RH in terpene photooxidation experiment. The corresponding HGF range according to Wise et al. (2003) is quite larger for single organic acids, varying from 1.00 (succinic and oxalic acid) to 1.51 (1-maleic acid) at 90% RH estimated from bulk properties of organic solutions.

Thus, the UFO-TDMA and the UFH-TDMA provide complementary information about the solubility of the particles to ethanol and water, which can be used to indirectly probe the composition behaviour of the particle phase. The UFH-TDMA also provides important data on the hygroscopicity of atmospheric particles (e.g. CCN, cloud condensation nuclei).

The field site and supporting field data

The nucleation event-related field measurements were carried out as a part of the EU-funded
Quantification of Aerosol Nucleation in the European Boundary Layer (QUEST) intensive field campaign at the SMEAR II (the Station for Measuring Forest Ecosystem–Atmosphere Relations) forest (61°51’N, 24°17’E, 170 m a.s.l.; for details see Hari and Kulmala 2005), located in Hyytiälä, upper Pirkanmaa (the province of Western Finland). The measurements were conducted during a three-week spring period (18 March 2003–8 April 2003), when the forest floor was still covered by snow. The SMEAR II is currently located in a rather homogenous over 40-year-old Scots pine (Pinus sylvestris) stand in which the first newly-formed ultrafine particles were observed experimentally over 10 years ago (Mäkelä et al. 1997). The most intensive event periods occurs during spring (Dal Maso et al. 2005). This campaign was characterized by frequent nucleation events (i.e. fresh 3–10 nm aerosol particles were simultaneously clearly present), accumulating a total of 15 events during the 21-day campaign.

During the QUEST field campaign in Hyytiälä, the UFO-TDMA and the UFH-TDMA systems were set up in a container situated in the central area of the SMEAR II. Inlet drew air from a height of about 4 m through 10 mm (in diameter) steel tube inside the forest canopy. A part of the UFO-TDMA and UFH-TDMA measurements of this campaign has been presented in Petäjä et al. (2005) and in Laaksonen et al. (2008a).

The facilities of SMEAR II enabled us to follow accurately the parameters describing local conditions, including trace gas concentrations (CO, NOx, SO2, O3, H2O), meteorological conditions (temperature, relative humidity, wind speed and direction) and submicron aerosol particle number size distribution starting from 3 nm in mobility diameter. Additional information about the station and its instrumentation can be found in Aalto et al. (2001) and in Hari and Kulmala (2005).

In addition, in this study temperature- and light-dependent emissions of monoterpenes (Tarrainen et al. 2005), measured concentrations of monoterpene oxidation products (MTOP; Sellegrí et al. 2005), concentration of gaseous phase sulfuric acid (Boy et al. 2005) and particulate phase nitrate data (Allan et al. 2006) were utilized in the interpretation of the TDMA data. All the data were measured during the same Hyytiälä QUEST campaign. Furthermore, additional 10 nm and 50 nm UFO-TDMA measurements were conducted during spring 2007 in four different ethanol saturation ratios (i.e. 20%, 60%, 70%, 80%) at the same Hyytiälä site. These aid our discussion on the nature of nucleation-mode and lower end of Aitken-mode sized particles at this boreal forest environment.

Various gas phase concentrations, wind direction (WD), temperature (T) and the measured growth factors in the ethanol (EGF) and water (HGF) vapours during the Hyytiälä QUEST nucleation events were used for calculating linear correlations between one-hour averaged datasets in order to explain the composition behaviour of the particles during nucleation events in varying conditions. The linear correlations provide information on the relations between the meteorological parameters, the gas phase compounds and particulate-phase data.

Supporting chamber measurements

In order to obtain reference data and aid the organic TDMA data analysis of the boreal forest field measurements, we also carried out a smog-chamber and a plant-chamber measurements. Our smog-chamber measurements in EUPHORE (European Photoreactor; Becker 1996) chamber, Valencia, Spain, with the O-TDMA (organic tandem differential mobility analyzer; Joutsensaaari et al. 2001; the syringe pump version) demonstrated that boreal forest relevant α-pinene oxidation products clearly grow in 20 nm size at about 84% ethanol vapour subsaturation (EGF over 1.20). A description of the experimental process of the α-pinene ozonolysis has been presented in Bonn et al. (2007).

The plant chamber (KCAR, Kuopio Center of Aerosol Research, laboratory, Kuopio, Finland) ozonolysis (ozone ca. 200 ppb) experiments with emissions of 2-year-old pines (Pinus sylvestris) in low NOx (< 1 ppb) conditions were carried out in June 2007. The EGFs of the UFO-TDMA ranged from 1.13 up to 1.17 in the 10 nm size at 82%–83% saturation ratio. Note that this ratio is comparable with the UFO-TDMA
saturation ratio used in the measurements of this Hyytiälä campaign.

For the plant chamber experiments, two-year-old Scots pine (*Pinus sylvestris*) seedlings were obtained from the Suonenjoki Research Nursery of the Finnish Forest Research Institute (62°38´N, 27°04´E), Suonenjoki, Finland. The seedlings were individually planted in 0.5 liter plastic pots in 2:1 (vol/vol) quartz sand (diameter 0.5–1.2 mm, SP Minerals Partek, Finland) and fertilized sphagnum peat (Kekkilä PP6, Finland). The seedlings were fertilized once a week with 0.1% superex five fertilizer (Kekkilä, Finland). Before the experiments, the seedlings were grown in controlled conditions in the University of Kuopio Botanical Garden.

The plant chamber experiments were carried out in a continuous and constant flow-through chamber (see VanReken et al. 2006) made of Neflon™ FEP film type NF-0050 (Daikin Industries, Ltd., Japan). The chamber volume was about 2 m³ (1.2 m × 1.2 m × 1.4 m) and it was held up with an aluminium frame. Plants emitting volatile organic compounds (VOC) were placed into a separate chamber from which the air was directed into a transparent reaction chamber, admitting a part of solar radiation (e.g. UV-A radiation) coming through room windows in order to participate in particle formation related processes. Air with the VOC was mixed with an airflow enriched with ozone at the inlet of the reactor. At the beginning of the trials, the VOC from the trees were introduced into the chamber about one hour before the ozone addition. Submicron aerosol particle number size distributions were measured using two instruments, a scanning and a fast mobility particle sizers (SMPS and FMPS) in order to follow the formation and growth of the particles. The number concentration during nucleation reached a maximum near 10⁵ cm⁻³. The total flow of air was 36 liters per minute (lpm) leading to a residence time of about one hour in the reactor chamber.

**Results and discussion**

In order to survey the evolution of newly-formed nucleation-mode particles as a function of time in varying conditions in a virgin boreal forest environment during new-particle formation events (when the simultaneous presence of both 3 nm and 10 nm newly-formed particles was clearly observable in the same mode), the growth factors of nucleation-mode particles were measured in ethanol and water vapours in subsaturated conditions at Hyytiälä during the QUEST-2003 spring campaign. A total of 15 nucleation events occurred during the three-week (18 Mar. 2003–8 Apr. 2003) campaign. Based on the SO₂ (> 0.5 ppb) and/or NOₓ (> 1.5 ppb) concentrations (Table 1), 9 of the 15 events were classified as pollution-affected (21, 26 and 29 March; 1, 2, 3, 4, 7 and 8 April) and six as clean (18, 20, 23, 24, 25 and 28 March) events (see Table 1). This classification is in a good agreement (7 April is the only difference) with the air mass based categorization in Boy et al. (2005).

**Effect of local conditions on the composition of nucleation-mode particles on a single event basis**

The growth factors in the ethanol and water vapours were examined in different concentrations of SO₂, NOₓ, sulfuric acid, and monoterpenes oxidation products. The similarities and differences in wind direction and temperature during the observed new-particle formation events were also analyzed.

Generally, the highest EGFs of the 10 nm particles were observed during the clean events whereas these events revealed the lowest HGFs (Fig. 1). During the pollution-affected events the nucleation mode EGFs were the lowest and at the same time the HGFs were the highest. The data clearly show that northern wind directions are associated with the low SO₂ and NOₓ concentration levels (see Fig. 2 and Table 1).

Time evolution of the measured EGFs revealed that generally the 10 nm particles were more and more soluble in ethanol as the event progressed (Fig. 1). During three events the EGFs decreased whereas during one event the EGF remained at 1.08 throughout the event. One potential reason for the decrease in the EGFs of the 25.3 nucleation event was a very sudden wind direction change from a clean to a more polluted origin during the event. It is worth
Table 1. Minimum and maximum values measured for relevant gas phase compounds, meteorological parameters and 10 nm growth factors during 15 new-particle formation events from 18 March to 8 April 2003. Also estimated average sulfuric acid fraction in the newly formed particles (Boy et al. 2005) are shown. * = pollution-affected events. # = MTOP values based on the SO$_2$ concentrations, the 10 nm EGFs shown in this table, and on the regression equation shown of EGF 10 nm vs. SO$_2$/MTOP in Fig. 5a.

<table>
<thead>
<tr>
<th>Nucleation event day and time</th>
<th>T (K)</th>
<th>WD</th>
<th>RH (%)</th>
<th>NO$_x$ (ppb)</th>
<th>SO$_2$ (ppb)</th>
<th>H$_2$SO$_4$ (10$^{-6}$cm$^{-3}$)</th>
<th>Estimated H$_2$SO$_4$ fraction (%)</th>
<th>MTOP (ppt)</th>
<th>O$_3$ (ppb)</th>
<th>CO (ppb)</th>
<th>NO (ppb)</th>
<th>EGF 10 nm</th>
<th>HGF 10 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>18 Mar. 2003 max 279.6 301 65.8 1.20 0.28 1.5 – 470 43.3 154.7 0.03</td>
<td>1.12 –</td>
<td>14:00–17:00 min 279.2 287 64.3 1.11 0.05 0.3 – 380 41.9 153.3 0.00</td>
<td>1.12 –</td>
<td>20 Mar. 2003 max 268.2 353 65.8 0.67 0.32 2.6 12.6 200 42.5 152.9 0.03</td>
<td>1.11 –</td>
<td>13:00–20:00 min 265.0 13 46.4 0.58 0.17 0.2 10.2 100 41.8 149.9 0.00</td>
<td>1.05 –</td>
<td>21 Mar. 2003* max 271.9 225 45.6 3.14 0.86 5.2 9.1 360 42.3 167.5 0.37</td>
<td>1.08 1.37</td>
<td>13:00–17:00 min 271.2 218 36.5 2.20 0.43 1.4 8.5 200 40.5 155.3 0.08</td>
<td>1.08 1.31</td>
<td>23 Mar. 2003 max 280.8 259 64.1 1.36 0.24 2.5 – 800 44.1 156.5 0.03</td>
<td>– 1.34</td>
</tr>
</tbody>
</table>
noting that the clear presence of both 3 nm and 10 nm newly-formed particles was required in the nucleation mode at the same time, thus minimizing a time history effect on the 10 nm particles measured during the event.

During this campaign, gaseous phase sulfuric acid, an SO$_2$ oxidation product, had a strong diurnal cycle peaking at noon in Hyytiälä (Boy et al. 2005) decreasing towards the evening following the diel cycle of photochemically produced hydroxyl radical. A similar sulfuric acid cycle was also observed during spring 2007 campaign in Hyytiälä (Petäjä et al. 2008). During the events of the 2003 campaign (Boy et al. 2005), the H$_2$SO$_4$ concentrations (sulfuric acid, H$_2$SO$_4$, maximum and minimum values during individual events; see also Table 1) tended to decrease as the event progressed, indicating that sulfuric acid contributed less to the particle growth at later times. This suggests an explanation for the increasing trends observed in the EGFs. Even though the event of 20 March was quite clean according to the wind direction and pollution data (NO$_x$ and SO$_2$ low), the measured EGFs had one of the lowest values. This could be due to differences in the monoterpene emission rates, which are temperature dependent in a boreal forest (Tarvainen et al. 2005). The temperatures during this event were below zero and on averaged several degrees lower than during other events. Based on this argument, during the events the ambient concentrations of monoterpenes would have been lower than during the other events. This would also lead to a low concentrations of monoterpene oxidation products during this event as observed by Sellegri et al. (2005; see Table 1). Related to that, SO$_2$/MTOP and NO$_x$/MTOP ratios (see Fig. 3; data of MTOP, monoterpene oxidation products, for days 18–28 March 2003) increased and the EGFs were low during the 20 March event. The higher SO$_2$/MTOP ratios suggest the presence of a relatively high content of sulfur containing compounds in the nucleation mode particles during this clean event. On the other hand, the higher NO$_x$/MTOP ratios suggest changed relative roles in monoterpene and MTOP alkyl peroxy radicals reaction pathways (i.e. there would be fewer alkyl peroxy radical self- (Eq. 1) and cross-reactions (Eq. 2) and reactions with hydroperoxy radicals (Eq. 3),
producing organic peroxides, and more reactions between alkyl peroxy radicals and NO (Eqs. 4a and 4b), producing alkoxy radicals and organic nitrates, than in the lower NOx/MTOP ratio conditions.

\[
\begin{align*}
RO_2 + RO_2 & \rightarrow ROOR + O_2 \\
RO_2 + R'O_2 & \rightarrow ROOR' + O_2 \\
RO_2 + HO_2 & \rightarrow ROOH + O_2 \\
RO_2 + NO & \rightarrow RO + NO_2 \\
RO_2 + NO [+M] & \rightarrow RONO_2 [+M]
\end{align*}
\]

Reaction in Eq. 3 may lead to formation of peroxyhemiacetals in the presence of an acid catalyst, when the peroxides react with aldehydes in the particles phase (Tobias and Ziemann 2000). Alkyl peroxy radicals may also react with NO₂ in order to produce peroxy nitrates (ROONO₂).

Consequently, the higher NOx/MTOP ratios make possible higher portions of organic nitrates. A recent review of the organic peroxy radical (RO₂) and alkoxy radical (RO), which can also produce variety of low-volatility compounds, chemistry with varying NOx concentration is available in Kroll and Seinfeld (2008). Alkoxy radical path (Eq. 4a) is the major channel under conditions in which NOx is present.

Furthermore, for alkyl peroxy radicals, reaction in Eq. 4a can form the corresponding alkoxy (RO) radical together with NO₂, or the corresponding alkyl nitrate, reaction in Eq. 4b, with the yield of the alkyl nitrate increasing with decreasing temperature (e.g. Seinfeld and Pandis 2006).

The event of 26 March is also interesting from the viewpoint of monoterpenes, because the temperature was relatively high as compared with that for low temperature events and thus the emission rates of monoterpenes and the concentrations of monoterpenic oxidation products were at least comparable to those of the other events. However, the EGFs of this pollution-affected event were lower than the EGFs during the cleanest events (see Table 1 and Fig. 1). That is reasonable, because the SO₂/MTOP and NOx/MTOP ratios were higher during this pollution-affected event than during
the cleanest events. On the other hand, the HGFs of the 26 March pollution-affected event were lower than those of the 21 March pollution-affected event. The behaviour of the HGFs can be again explained by the higher SO$_2$/MTOP and NO$_x$/MTOP ratios during the 21 March event compared to those during the 26 March event (see Fig. 4).

A series of four pollution-affected events from 1 to 4 April showed quite low EGFs (see Fig. 1). Unfortunately, MTOP concentrations were not available. Thus, we had to rely on monoterpane emission rates, temperature and NO$_x$ concentrations for explaining the behaviour of measured growth factors. The temperature was below 0 °C during the midday 3 April event (see Fig. 1). According to Tarvainen et al. (2005) the emission rates at noon on 1 and 2 April were much lower than during the cleaner and warmer March events. On 3 April, the emission rates increased slightly but were still lower than those during March. SO$_2$ concentrations were low during 1 and 4 April and higher on 2 and 3 April. Consequently, sulfuric acid concentrations were also on average higher during the 2 and 3 April events than during the 1 and 4 April events. Generally, higher sulfuric acid concentrations were measured during those four pollution-affected events than during the cleanest events. This was clearly affecting the relatively high HGFs observed during this period.

To discuss further the behaviour of the EGFs of the 1, 2, 3 and 4 April pollution-affected events, let us also take a closer look at NO$_x$ concentrations. They were similar during all of those four events and were higher than during the cleaner events. A high NO$_x$ level chemistry produces a higher amount of relatively volatile organic nitrates and a lower amount of oxidized condensing organic compounds in $\alpha$-pinene ozonolysis than a low NO$_x$ level chemistry (see Presto et al. 2005). Because temperatures were below or close to 0 °C during the 1, 2, 3 and 4 April events, organic nitrates were most likely in particle phase during these low temperature and high NO$_x$ level events (see Table 1). The NO$_x$/MTOP values are expected to be high due to the low temperature. The event of 21 March was a case with high NO$_x$/MTOP ratios and low temperature. Low temperatures make the less
oxidized relatively volatile organic compounds, as well as organic nitrates, condensable onto nucleation mode particles. Potential candidates for the formation of condensing organic nitrates are the oxidation products of sesquiterpenes (see Ng et al. 2007), and the oxidation products of monoterpenes (e.g. α-pinene). Previously, Allan et al. (2006) discussed the presence of organic nitrates in the accumulation mode during this same boreal forest campaign.

During the 7 and 8 April events, the temperatures were close to 0 °C and the sulfuric acid concentrations were high. Also the SO$_2$ and NO$_x$ levels were above the cleanest cases. These conditions consequently lead to the low EGFs and to the high HGFs (see Fig. 1). The EGFs and HGFs of the 7 and 8 April events are explained similarly as the other pollution-affected events with low temperature, consequently leading to a higher SO$_2$/MTOP and NO$_x$/MTOP ratios than during the clean events.

In summary, wind direction (associated to pollution levels) and temperature are important factors to regulate the quality of air mass (biogenic vs. anthropogenic) which strongly affects the composition of the atmospheric newly-formed nucleation mode particles.

Relations among multiple events

In order to further study the reasons behind the composition behaviour of the boreal forest particles during the new particle formation events, we carried out a simple linear regression analyses for the EGFs and HGFs of the newly-formed 10 nm particles, with trace gas concentrations and meteorological parameters. In the following analysis, the correlation is considered very strong if $r > 0.8$, strong if $0.6 < r < 0.8$, and moderate if $0.3 < r < 0.6$. In the following, usually $r^2$ are shown instead of $r$.

Relation between the 10 nm EGFs and HGFs

The 10 nm EGF and HGF values were anticorrelated for events between 18 March and 8 April 2003 ($r^2 = 0.55, p = 4.2 \times 10^{-5}, n = 12$), and for events between 18 and 28 March 2003 ($r^2 = 0.65, p = 3.02 \times 10^{-8}, n = 44$). The anticorrelation is in agreement with the reasoning for the behaviour of the EGFs and the HGFs in varying conditions. As indicated in the earlier sections, the pollution associated with SO$_2$ and NO$_x$ is an important reason for the behaviour. This is partly due to sulfur dioxide which is a precursor for sulfur-containing compounds, such as ammonium sulfate, in the particle phase. The particles of ammonium sulfate do not grow in subsaturated ethanol vapour (Vaattovaara et al. 2005), but are hygroscopic in the 10 nm size with the HGF of 1.38 at 90% saturation ratio (Väkevä 2002).

The effect of pine emissions on the composition of the 10 nm particles

The 10 nm particles grow, as ethanol-soluble or very-ethanol-soluble organic particles do, with the EGF values up to 1.16 at 83% saturation ratio (note that neither particles of pure ammonium bisulfate nor particles containing ammonium bisulfate and sulfuric acid with sulfuric acid mass fraction up to 33% grow in 10 nm sizes at that saturation ratio; Vaattovaara et al. 2005) during one of the cleanest events (28 March 2003) (Fig. 1). Importantly, the EGF of 1.16 for the newly-formed 10 nm particles during the clean event corresponds to the EGFs ranging from 1.13 up to 1.17 at 82%–83% ethanol saturation ratio observed during clean environment pine chamber ozonolysis experiment. The spring 2007 UFO-TDMA measurements with varying ethanol saturation ratios (i.e. 20%, 60%, 70%, 80%) for 10 nm particles typically showed a growth already in the lowest 20% saturation ratio and no-deliquesence type behaviour when the higher saturation ratios were applied, indicating high ethanol solubilities for nucleation mode particles, and thus a high organic content in the particles.

Monoterpene oxidation products (MTOP, data available for 18–28 March 2003, see Sellergren et al. 2005) are the natural explanation for the relatively high EGFs of nucleation mode particles in the boreal forest environment. In the previous analysis (Laaksonen et al. 2008a), MTOP strongly correlated with 10 nm EGFs ($r^2 = 0.64$) during this same campaign nuclea-
tion events (the presence of newly-formed 10 nm particles were required). In this study, $r^2 = 0.51$ ($p < 0.001$) (Table 2; the simultaneous presence of newly-formed 3 nm and 10 nm particles were required during the nucleation events), thus explaining approximately one half of the behaviour of the EGFs. When the pollution-affected events were neglected, $r^2$ increased to 0.84 ($p < 0.001$), thus evidently explaining composition behaviour of 10-nm particles during the clean events. The MTOP concentration was strongly correlated with temperature ($r^2 = 0.63$, $p < 0.001$) during the events. This is in agreement with the previous study by Tarvainen et al. (2005) who observed the relation between monoterpene emissions and temperature during this same campaign [more generally, vegetation emitted VOC are known to be dependent on the temperature and/or light (Guenther et al. 2006)]. However, the MTOP was not correlated with the HGFs of 10 nm event particles, but its strong correlation for the clean events was found ($r^2 = 0.44$; see Table 2; $r^2 = 0.00$ if two earlier mentioned points are ignored). These suggest also an additional contribution to the particle composition.

The role and formation of organic sulfur compounds

The commonly accepted reaction pathway for sulfuric acid ($\text{H}_2\text{SO}_4$) is as follows (e.g. Seinfeld and Pandis 2006):

\[
\begin{align*}
\text{OH} + \text{SO}_2 & \rightarrow \text{HOSO}_2 \\
\text{HOSO}_2 + \text{O}_2 & \rightarrow \text{SO}_3 + \text{HO}_2 \\
\text{SO}_3 + 2\text{H}_2\text{O} & \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2\text{O}
\end{align*}
\]

During the same QUEST measurement campaign at Hyytiälä, Boy et al. (2005) estimated that sulfuric acid contribution to nucleation mode particle growth is on average about 9%, ranging from 3% during a clean event to 17% during a pollution-affected event (see Table 1). Previously, Boy et al. (2003) estimated the sulfuric acid contribution to be 4%–31% during autumn at the same site. During the spring 2005 cam-

<table>
<thead>
<tr>
<th>$y$</th>
<th>CO</th>
<th>NO$_x$</th>
<th>MTOP</th>
<th>SO$_2$</th>
<th>WD</th>
<th>T</th>
<th>RH</th>
<th>H$_2$O</th>
<th>H$_2$SO$_4$</th>
<th>T/SO$_2$</th>
<th>O$_3$</th>
<th>SO$_2$/MTOP</th>
<th>NO$_x$/MTOP</th>
<th>H$_2$SO$_4$/MTOP</th>
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<td>15 events</td>
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<td>-0.11*</td>
<td>-0.16**</td>
<td>+0.44***</td>
<td>+0.52***</td>
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<td>-0.23***</td>
<td>+0.38***</td>
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<td>–</td>
</tr>
<tr>
<td>8 events</td>
<td>-0.69***</td>
<td>-0.14 (NS)</td>
<td>-0.47***</td>
<td>+0.49***</td>
<td>+0.59***</td>
<td>0.00 (NS)</td>
<td>-0.47***</td>
<td>-0.27***</td>
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<td>+0.18*</td>
<td>-0.31**</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>clean</td>
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<td>+0.27*</td>
<td>-0.42**</td>
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<td>+0.72***</td>
<td>-0.02 (NS)</td>
<td>+0.56***</td>
<td>-0.37**</td>
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<td>+0.11 (NS)</td>
<td>+0.11 (NS)</td>
<td>–</td>
<td>–</td>
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<td>+0.28*** (+0.29)</td>
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<td>-0.32** (-0.37)</td>
<td>-0.23** (-0.30)</td>
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<td>+0.38*** (+0.43)</td>
<td>+0.35*** (+0.40)</td>
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<tr>
<td>8 events</td>
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<tr>
<td>clean</td>
<td>+0.56*** (0.00)</td>
<td>+0.35** (0.00)</td>
<td>+0.11 NS (+0.05)</td>
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<td>+0.27* (+0.15)</td>
<td>+0.44*** (0.00)</td>
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<td>+0.01 (NS) (0.00)</td>
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<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 2. Correlation coefficients ($r^2$) of linear correlations between EGF 10 nm and $y$, and between HGF 10 nm and $y$. Numbers of observation pairs ($n$) are also shown. $y$ = variables during 15, 8, and clean new-particle formation events when 3–10 nm newly-formed particles were clearly observable. MTOP data obtained from Sellegri et al. (2005; 8 events) and sulfuric acid data from Boy et al. (2005; 15 events). + = an increasing trend; – = a decreasing trend. $r^2$ in parenthesis indicate correlations or anticorrelations if two measurement points are ignored in UFH-TDMA data due to the possible effect of pre-existing nucleation mode sized particles (significance not calculated). Significance levels: * = $p < 0.05$, ** = $p < 0.01$, *** = $p < 0.001$, NS = not significant.

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<tr>
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another mode corresponds with the hygroscopicity typically detected during the clean events of this campaign. Additionally, the event was not very intensive as compared with the other events. In the middle of the event, the more hygroscopic mode disappeared for a while, but appeared again in the end of the event. However, NOx, SO2 or H2SO4 measurements, which were carried out about 50 m from the TDMA container, did not detect any signs which would support the variation of the nucleation mode composition.

Overall, SO2 concentrations (via reaction products) clearly affect the composition formation of those nucleation mode particles during the events. The fact that nucleation events seem to stop if gas phase sulfuric acid concentration drops to 105 cm–3 also supports the importance of sulfur compounds. Interestingly, the anticorrelation between H2SO4/MTOP and 10 nm EGF (r2 = 0.86, p < 0.001) and the correlation between H2SO4/MTOP and 10 nm HGF (r2 = 0.41, p < 0.001) were weaker than those between SO2/MTOP and 10 nm EGF (r2 = 0.86, p < 0.001) or between SO2/MTOP and 10 nm HGF (r2 = 0.63, p < 0.001) (Table 2). The difference can be explained using the additional HOSO2 oxidation pathway

\[
\text{HOSO}_2 + \text{O}_2 + \text{M} \rightarrow \text{HOSO}_2\text{O}_2 + \text{M} \quad (8)
\]

(i.e. Eq. 8 in addition to Eq. 6) forming peroxy type sulfur compound radicals (see Berndt et al. 2007, 2008, Laaksonen et al. 2008b), which make possible the direct formation of sulfur compounds other than sulfuric acid. The formation of organosulfates from monoterpene oxidation products has been detected earlier in laboratory conditions (e.g. Liggio and Li 2006, Ng et al. 2007, Surratt et al. 2007). They proposed that organosulfates (sulfate esters) were formed from reactions of MTOP (e.g. pinonaldehyde, which belongs to MTOP) and sulfuric acid. This would explain why anticorrelations between 10 nm EGFs and H2SO4/MTOP have higher r2 values (0.64, p < 0.001) than between MTOP and EGF (r2 = 0.51, p < 0.001) during the events from 18 to 28 March 2003 (Table 2). The correlation between 10 nm HGFs and H2SO4/MTOP was also strong (r2 = 0.41, p < 0.001) but HGFs and MTOP were not correlated (r2 = 0.00, NS).
However, the additional SO$_2$ reaction pathway (Eq. 8) including peroxy type sulfur compounds (Berndt et al. 2007, Berndt et al. 2008, Laaksonen et al. 2008b) would explain why the correlation between 10 nm GF and SO$_2$/MTOP is higher than that between 10 nm GF and H$_2$SO$_4$/MTOP during the events. Berndt et al. (2008) proposed that up to 30% of HOSO$_2$ can be converted into HOSO$_2$O$_2$. Because it is a peroxy-type radical and, analogous to organic peroxy radicals (RO$_2$), it can react with HO$_2$, other peroxy radicals or with NO and NO$_2$ (see e.g. Finlayson-Pitts and Pitts 2000).

This indicates tentatively an important atmospheric pathway which is also able to produce organic sulfur compounds directly without a sulfuric acid reaction. Potential products from the Eq. 6 pathway (Berndt et al. 2008, Laaksonen et al. 2008b) in NO$_x$ free conditions include peroxy sulfuric acid (Eq. 9), organic peroxy sulfates (Eq. 10) and HOSO$_2$OSO$_3$ (Eq. 11).

$$\text{HOSO}_2\text{O}_2 + \text{HO}_2 \rightarrow \text{HOSO}_2\text{OH} + \text{O}_2 \quad (9)$$
$$\text{HOSO}_2\text{O}_2 + \text{RO}_2 \rightarrow \text{HOSO}_2\text{OR} \quad (10)$$
$$\text{HOSO}_2\text{O}_2 + \text{SO}_2 \rightarrow \text{HOSO}_2\text{OSO}_3 \quad (11)$$

As HOSO$_2$ radical is analogous to organic peroxy radicals (RO$_2$), also self-reactions could be possible.

$$\text{HOSO}_2\text{O}_2 + \text{HOSO}_2\text{O}_2 \rightarrow \text{HOSO}_2\text{OsO}_3\text{OH} \quad (12)$$

The presence of NO$_x$ could also make sulfur nitrates possible, analogically to reactions of organic peroxy radicals. Like RO$_2$, HOSO$_2$O$_2$ would react with NO producing also organic alkoxy radical (RO) type sulfur radical

$$\text{HOSO}_2\text{O}_2 + \text{NO} \rightarrow \text{HOSO}_2\text{O} + \text{NO}_2 \quad (13)$$

or a sulfur nitrate

$$\text{HOSO}_2\text{O}_2 + \text{NO} [\text{+M}] \rightarrow \text{HOSO}_2\text{ONO}_2 [\text{+ M}] \quad (14)$$

Note that alkoxy radical (RO) formation is the major channel for organic peroxy radicals (RO$_2$) when NO$_x$ is present. Reactions of the alkoxy-type sulfur radical, including an acidic part, could play an important role in the Eq. 6 reaction pathway chemistry.

Interestingly, the additional reaction channel in Eq. 8 makes the sulfur chemistry more complicated connecting organic chemistry, sulfur chemistry and nitrogen chemistry. Naturally, the reaction channel occurred is highly dependent on the relative amount of reactants available. For example, the correlation between 10 nm EGF and MTOP was very strong ($r^2 = 0.84$, $p < 0.001$; Table 2) during the clean events, suggesting less organosulfur compound formation during the clean (a low SO$_2$ gas concentration) than the pollution-affected (a higher SO$_2$ gas concentration) events.

Overall, based on the analysis, organic sulfur compounds seem to play an important role in the composition behaviour of the newly-formed nucleation mode particles in this boreal forest environment. Importantly, Berndt et al. (2008) and Laaksonen et al. (2008b) proposed that SO$_2$ oxidation products other than H$_2$SO$_4$ would be a trigger of new particle formation in atmospheric conditions.

The fraction of organic oxidation products during the clean events

The very strong correlation between MTOP and 10 nm EGF ($r^2 = 0.84$) explains well 10 nm EGFs during the clean events (Table 2). The anticorrelations between the EGFs and SO$_2$/MTOP or NO$_x$/MTOP were also very strong ($r^2 = 0.85$, $p < 0.001$ for both; Table 2), showing the importance of organic, sulfur and nitrogen chemistry during the clean events too. The highest EGFs (i.e. 1.12–1.16) of the clean Hyytiälä events (maximum particle concentration between $10^4–10^5$ cm$^{-3}$) correspond to very-ethanol-soluble oxidation products originating from pine emission oxidation in clean plant chamber conditions (i.e. EGFs 1.13–1.17 at 82%–83% saturation ratio; maximum particle concentration slightly below $10^5$ cm$^{-3}$). Furthermore, $r^2 = 0.64$ ($p < 0.01$) for the correlation between 10 nm EGF and O$_3$ (increasing trend), and $r^2 = 0.62$ ($p < 0.001$) for the correlation between 10 nm EGF and CO (decreasing trend; CO is a remarkable OH radical sink) suggest the importance of both oxidants (O$_3$ and OH) in the organic fraction formation during the clean events.
From the viewpoint of inorganic compounds, those EGFs are clearly higher than the EGFs observed for nucleation mode particles (with EGFs up to 1.08 for 10 nm at saturation ratio of 86%) which are known to include a high fraction of inorganic iodine oxides, in addition to a high organic fraction at the sea coast (Vaattovaara et al. 2006). For the Hyytiälä forest, Laaksonen et al. (2008a) found $r^2$ value of 0.965 for the correlation between particle diameter growth rates (GR, nm h$^{-1}$) and gas-phase MTOP concentration (ppt) during ten different nucleation events of this same spring 2003 campaign, supporting a high organic contribution to the particles. On the other hand, Boy et al. (2005) estimated sulfuric acid fraction in new particle formation and growth to be between 3% to 17% during the event days (Table 1). Actually, the percentage was mostly below 10%. Furthermore, Fiedler et al. (2005) estimated the sulfuric acid fraction to be below 10% in condensing vapours during the same campaign. Their lowest values were close to 5%. In our study, $r^2$ values for the correlation between GFs and H$_2$SO$_4$ were low both for 10 nm EGF (0.13, NS) and for HGF (0.03, NS) during the clean events (Table 2). Even though sulfuric acid concentrations decreased from the maximum value to the minimum value (see Table 1) during the event, owing to its diurnal cycle, the EGFs did not change much, which was supported by the calculated $r^2$ values. Overall, the organic fraction increased close to 100% at the end of the cleanest events. However, some sulfur containing acids seemed to be always present at least in small amounts [the lowest estimate (3%–4%) of Boy et al. (2003, 2005) may be close for sulfur compounds], the acids working also as a catalyst and pH regulator. However, the exact organic/inorganic fraction estimation is difficult, especially in the pollution-affected events, owing to HOSO$_2$O$_2$ radicals, sulfuric acid and their inorganic derivates which can react with different organics both in gaseous and particle phase, forming organic sulfur compounds.

According to the correlations (Table 2) and the EGFs and HGFs observed, the overall particle-phase solubility estimate of organic sulfur compounds is ethanol-insoluble or slightly-soluble and at the least slightly-water-soluble. In the cleanest events, the HGFs were still about 1.2 for 10 nm particles at 90% RH, indicating the presence of slightly-water-soluble content. Ehn et al. (2007a) also observed the HGFs of 1.2 at 90% RH at the same site, when the gaseous phase sulfuric acid concentration was the lowest.

The role of NO$_x$ in the 10 nm particle composition

As introduced in earlier chapters, NO$_x$ chemistry seems to play less important role in 10 nm particle composition in the cleanest events (i.e. a low NO$_x$ level) than in the pollution-affected events (i.e. a higher NO$_x$ level; see Fig. 4b). Consequently, various reactions of organic compounds with organic peroxy radicals, hydroperoxy radicals and each other play more dominating role in the composition formation of the 10 nm particles during the clean nucleation events than during the polluted events. Thus, the organic composition of the clean events was different than that of the pollution-affected events, because of a higher NO$_x$ level in the pollution-affected events as compared with that in the clean events.

Linear correlation shown in Fig. 4b is in agreement with this kind of chemistry. In addition to organic chemistry, NO$_x$ may also play an important role in the sulfur chemistry (i.e. HOSO$_2$O$_2$ radical pathway, see Eqs. 13 and 14). Berndt et al. (2008) noticed that with increasing amounts of NO$_x$ being present, new particle formation is inhibited. We suggest that this observation can be related to reactions given in Eqs. 13 and 14. This is because NO (nitric oxide) can react with HOSO$_2$O$_2$ radicals producing alkoxy radicals and nitrates, therefore decreasing the amount of HOSO$_2$O$_2$ reactions with HO$_2$, RO$_2$, SO$_2$ and itself (see Eqs. 9, 10, 11, and 12) and consequently decreasing also the amount of species capable of nucleating or condensing in the smallest sizes.

Similarity in the composition of 6–50 nm particles

In order to indirectly probe similarities between the nucleation-mode and the lower end of the Aitken-mode-sized particles (see Table 3 for
GFs), and especially the temporal evolution of their chemical compositions, we examined the correlations between the EGFs of 6–50 nm and the HGFs of 8–50 nm particles, and SO$_2$/MTOP and NO$_x$/MTOP (see Table 4). These linear anti-correlations with the EGFs have $r^2$ values of 0.30–0.86 and 0.44–0.68, respectively (see Table 4), and linear correlations with the HGFs have $r^2$ values of 0.30–0.86 and 0.44–0.68, respectively (see Table 4).

Table 3. Minimum and maximum HGFs and EGFs for 6, 8, 10, 20, 30, and 50 nm particles during 15 new-particle formation events from 18 March 2003 to 8 April 2003. * = pollution-affected events.

<table>
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<tr>
<th>Nucleation event day and time</th>
<th>HGF</th>
<th>EGF</th>
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<td>8 nm</td>
<td>10 nm</td>
<td>20 nm</td>
</tr>
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<td>–</td>
</tr>
<tr>
<td>14:00–17:00</td>
<td>min</td>
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<td>–</td>
</tr>
<tr>
<td>21 Mar. 2003*</td>
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</tr>
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<td>13:00–17:00</td>
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<tr>
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</tr>
<tr>
<td>13:00–16:00</td>
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<td>1.19</td>
</tr>
<tr>
<td>1 Apr. 2003*</td>
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</tr>
<tr>
<td>11:00–18:00</td>
<td>min</td>
<td>1.19</td>
</tr>
<tr>
<td>2 Apr. 2003*</td>
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</tr>
<tr>
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<td>1.28</td>
</tr>
<tr>
<td>3 Apr. 2003*</td>
<td>max</td>
<td>1.40</td>
</tr>
<tr>
<td>9:00–15:00</td>
<td>min</td>
<td>1.23</td>
</tr>
<tr>
<td>4 Apr. 2003*</td>
<td>max</td>
<td>1.24</td>
</tr>
<tr>
<td>10:00–14:00</td>
<td>min</td>
<td>1.19</td>
</tr>
<tr>
<td>7 Apr. 2003*</td>
<td>max</td>
<td>1.35</td>
</tr>
<tr>
<td>12:00–17:00</td>
<td>min</td>
<td>1.22</td>
</tr>
<tr>
<td>8 Apr. 2003*</td>
<td>max</td>
<td>1.24</td>
</tr>
<tr>
<td>12:00–14:00</td>
<td>min</td>
<td>1.23</td>
</tr>
</tbody>
</table>

Table 4. Correlation coefficients ($r^2$) of linear regressions between GFs of 6–50 nm particles and SO$_2$/MTOP and NO$_x$/MTOP ratios during the new-particle formation events from 18 to 28 March 2003. + = an increasing trend; – = a decreasing trend. Significance levels: * = $p < 0.05$, ** = $p < 0.01$, *** = $p < 0.001$.

<table>
<thead>
<tr>
<th>GF vs. SO$_2$/MTOP</th>
<th>$r^2$: EGF (8 events; $n = 17–27$)</th>
<th>$r^2$: HGF (6 events; $n = 33–34$)</th>
<th>GF vs. NO$_x$/MTOP</th>
<th>$r^2$: EGF (8 events; $n = 17–27$)</th>
<th>$r^2$: for HGF (6 events; $n = 33–34$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 nm</td>
<td>$-0.30^*$</td>
<td>–</td>
<td>6 nm</td>
<td>$-0.51^{**}$</td>
<td></td>
</tr>
<tr>
<td>8 nm</td>
<td>$-0.42^{***}$</td>
<td>$+0.40^{***}$</td>
<td>8 nm</td>
<td>$-0.44^{***}$</td>
<td>$+0.36^{***}$</td>
</tr>
<tr>
<td>10 nm</td>
<td>$-0.86^{***}$</td>
<td>$+0.64^{***}$</td>
<td>10 nm</td>
<td>$-0.59^{***}$</td>
<td>$+0.83^{***}$</td>
</tr>
<tr>
<td>20 nm</td>
<td>$-0.52^{***}$</td>
<td>$+0.54^{***}$</td>
<td>20 nm</td>
<td>$-0.66^{***}$</td>
<td>$+0.48^{***}$</td>
</tr>
<tr>
<td>30 nm</td>
<td>$-0.59^{***}$</td>
<td>–</td>
<td>30 nm</td>
<td>$-0.68^{***}$</td>
<td></td>
</tr>
<tr>
<td>50 nm</td>
<td>$-0.63^{***}$</td>
<td>$+0.68^{***}$</td>
<td>50 nm</td>
<td>$-0.44^{***}$</td>
<td>$+0.56^{***}$</td>
</tr>
</tbody>
</table>
values of 0.40–0.68 and 0.36–0.63, respectively (see Table 4). This suggests that the nucleation and the lower end of Aitken-mode-sized particles have clear similarities in the composition change during the nucleation events. Laaksonen et al. (2008a) made a similar conclusion. In some instances, there are 10 nm particles present at the onset of nucleation which clearly belong to the old Aitken mode (see e.g. Petäjä et al. 2005: fig. 2). Thus it is possible that sometimes when the nucleation mode merges together with the old Aitken mode, 10 nm particles form an external mixture. However, in our case the events were intensive enough so that the concentrations of fresh 10 nm particles certainly overwhelmed the concentrations of aged 10 nm particles, and any influences from the old Aitken modes to the measured GFs must have been minuscule.

We also examined the relations between the EGFs and HGFs of 6–50 nm particles to study the similarity in the composition of particles during the nucleation events (Table 5). We found that the correlations between 8 nm and 10 nm, 10 nm and 20 nm (Fig. 5a), 30 nm and 50 nm, 10 nm and 30 nm, 10 nm and 50 nm (Fig. 5b), 6 nm and 10 nm (Fig. 5c), 6 nm and 8 nm, and 20 nm and 50 nm are very strong or strong ($r^2 = 0.44–0.81$) for the EGFs when the events from 18 March to 8 April are included in the analysis. The correlations are even stronger ($r^2 = 0.54–0.89$) when the analysis is restricted to the events from 18 to 28 March. For the HGFs (see Table 5), the correlations between 8 nm and 10 nm, 10 nm and 20 nm (Fig. 5a), 10 nm and 50 nm (Fig. 5b), and 20 nm and 50 nm are very strong or at least strong ($r^2 = 0.46–0.76$) when the events from 18 March to 28 March or the events from 18 March to 8 April are included in the analysis (Table 5).

It is important to note that even though the correlations suggest similarities in the composition change for the nucleation- and Aitken-mode-sized particles during the nucleation events, their overall composition is not necessarily the same because of different history of different-sized particles. The overall similarities in the particle composition can be checked comparing the absolute GFs of different-sized particles with each other during individual clean events. We notice that the values of GFs are often close to each other for different-sized particles in an oxidative environment. If the composition was the same, this should not be a case because of the Kelvin effect (see Vaattovaara et al. (2005) for the 6–50 nm particle EGF values). For example, if the 50 nm particles are very-ethanol-soluble, they should show the EGFs of about 1.45 (Vaattovaara et al. 2005) instead of 1.15–1.20 observed during pine chamber ozonolysis experiments and the cleanest nucleation events in the Hyytiälä forest. For 10 nm particles, the EGFs of pine chamber ozonolysis experiments, and boreal forest field measurements and very-etha-

Table 5. Correlation coefficients ($r^2$) of linear regressions between the GFs of 6–50 nm particles during the new-particle formation events from 18 March to 8 April 2003 (15 events) and from 18 to 28 March 2003 (eight events). The plus (+) sign indicates an increasing trend.

<table>
<thead>
<tr>
<th></th>
<th>EGF</th>
<th>HGF</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15 events</td>
<td>8 events</td>
</tr>
<tr>
<td></td>
<td>($n = 34–49$)</td>
<td>($n = 13–20$)</td>
</tr>
<tr>
<td>8 vs. 10 nm</td>
<td>+0.81***</td>
<td>+0.81***</td>
</tr>
<tr>
<td>10 vs. 20 nm</td>
<td>+0.68***</td>
<td>+0.77***</td>
</tr>
<tr>
<td>20 vs. 30 nm</td>
<td>+0.80***</td>
<td>+0.89***</td>
</tr>
<tr>
<td>30 vs. 50 nm</td>
<td>+0.73***</td>
<td>+0.80***</td>
</tr>
<tr>
<td>10 vs. 30 nm</td>
<td>+0.67***</td>
<td>+0.88***</td>
</tr>
<tr>
<td>10 vs. 50 nm</td>
<td>+0.44***</td>
<td>+0.68***</td>
</tr>
<tr>
<td>6 vs. 10 nm</td>
<td>+0.46**</td>
<td>+0.60**</td>
</tr>
<tr>
<td>6 vs. 8 nm</td>
<td>+0.45***</td>
<td>+0.54**</td>
</tr>
<tr>
<td>20 vs. 50 nm</td>
<td>+0.44***</td>
<td>+0.59***</td>
</tr>
</tbody>
</table>
nol-soluble organic compounds laboratory measurements, are all in good agreement with each other (i.e. EGFs around 1.13–1.16). These indicate that the overall composition of the nucleation and Aitken-mode-sized particles is not very similar in the boreal forest environment.

The dissimilarity in the composition between nucleation-mode and the Aitken-mode-sized particles may be mainly due to acid-catalyzed particle phase aging processes during the particles growth to bigger sizes, including peroxymelacetal formation (Tobias and Ziemann 2000), polymerization (Jang and Kamens 2001, Kalberer et al. 2004), hemiacetal and acetal formation, hydration and aldol condensation (Jang et al. 2002) and esterification (Joutsensaari et al. 2004).
and partly because different kinds of compounds can condense onto different sized particles depending on conditions.

In the pollution-affected cases, possible differences in the origin of different sized particles play a role too. As regards the aging process, Ehn et al. (2007b) observed during the Hyytiälä 2005 spring campaign that non-volatile cores of nucleation mode particles grew at an average rate of $0.6 \pm 0.3$ nm h$^{-1}$ which was about a fourth of the growth rate of the particles. We suggest that the non-volatile core, observed by Ehn et al. (2007b), can also be related to the acid-catalyzed (e.g. sulfuric acid) aging processes listed above and the formation of organic sulfur compounds.

Conclusions

In this study, we applied the UFO-TDMA and the UFH-TDMA methods to shed light on the composition behaviour of the newly-formed nucleation (6–10 nm) and Aitken-mode (20–50 nm) sized particles within the accuracy of the methods as a function of time and size at a virgin boreal forest site, Hyytiälä, Finland, during nucleation events in varying spring conditions. Additionally, we calculated linear correlations in order to explain the variability in the growth factors observed in water and ethanol and thus the reasons behind the composition behaviour of the particles during multiple nucleation events. To aid the interpretation of the results, we utilized laboratory and plant chamber measurements, as well as the available literature.

The results show a clear anthropogenic influence on the newly-formed nucleation- and Aitken-mode sized particles composition during the events, making the particles more hygroscopic and thus increasing the capacity of Aitken-mode particles to act as cloud condensation nuclei, affecting that way the radiative balance of boreal forests. Because the emission rate of volatile organic compounds (VOCs, such as monoterpenes, for example) is temperature dependent, producing higher rates at higher temperatures, ambient temperature can regulate the atmospheric VOC concentrations in a certain temperature range. Subsequently, these have important effects on the composition and the properties of nucleation- and Aitken-mode sized particles in different vegetation zones, especially in pollution-affected cold environments such as boreal and polar regions or mountainous areas, and thus to important issues from the viewpoint of climate change.

The linear correlation analysis showed that $\text{SO}_2$/MTOP and $\text{NO}_x$/MTOP ratios well explain the event-to-event variation in the nucleation mode EGF and HGF values, and thus in the nucleation mode particles composition behaviour. The linear regression equation for the 10 nm EGF vs. $\text{SO}_2$/MTOP was also applied to estimate the concentrations of monoterpene oxidation products during the nucleation events in which MTOP were not measured. For the clean events, MTOP well explain the 10 nm particle composition behaviour with an estimate of over 95% organic fraction for the cleanest events. The difference in the particle composition and properties during the pollution-affected events compared with the clean events is a result of the different reaction pathways preferred during the varying event conditions. The results suggest that the difference is also partly due to the presence of organic sulfur and organic nitrogen compounds and a sulfate fraction, in addition to a major fraction of pure organics.

Furthermore, comparison of correlations and anticorrelations for multiple events suggest that the $\text{HOSO}_2\text{O}_2$ radical (see Berndt et al. 2007, Berndt et al. 2008, Laaksonen et al. 2008b) formation occurs in the boreal forest environment. The analysis supports the formation of organic sulfur compounds both via sulfuric acid (products such as sulfate esters) and via $\text{HOSO}_2\text{O}_2$ radical reactions (products such as organic peroxy sulfates), suggesting the importance of organic sulfur compounds, in addition to other sulfur and organic compounds, in nucleation mode particle formation, composition and properties. Importantly, $\text{NO}_x$ play an important role both in organic and sulfur chemistry.

Even though the change in the composition is similar for 6–50 nm particles during the nucleation events, the overall composition of those particles is quite dissimilar. In unpolluted cases, this seems to be mainly due to the acid-catalyzed organic particle phase aging processes (probably including also some organic sulfur compounds),
occurring during the growth of particles in the nucleation mode and in the lower end of Aitken mode sizes. More generally, the aging processes can be expected to occur as a function of time in the particle phase.

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References


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