INTRODUCTION

Atmospheric new particle formation is proposed to happen via activation of nanometer-sized condensation nuclei (nano-CN), which can be neutral or charged clusters and/or large molecules. These nano-CN seem to be always present in the boreal forest boundary layer, even when no secondary particle formation is detected with traditional instrumentation (Kulmala et al. 2007, Lehtipalo et al. 2009). Daytime new particle formation is a widely observed and frequent phenomenon, but also nocturnal particle formation can be a significant source of particles in some environments (e.g. Lee et al., 2008).

In Hyytiälä, southern Finland, night-time events have been observed in the ion spectrometer data (Junninen et al. 2008), but the ions rarely grew to sizes larger than a few nanometers. Developments in measurement techniques have recently made it possible to detect also electrically neutral nano-CN (e.g. Sipilä et al. 2008). We believe that studying nocturnal events and nano-CN can give us insight to the critical steps of the new particle formation process.

METHODS

We analyzed the particle size distributions measured with several independent methods at Hyytiälä SMEAR II-station, during intensive campaigns in March-June 2007, May 2008 and May 2009. The size distribution of neutral particles ~1.3-5 nm was derived by applying pulse-height-analysis method to a modified CPC (PH-CPC; Sipilä et al. 2009). The particle size distribution 3-1000 nm was measured with a twin-DMPS, and the ion mobility distribution (0.8-7.5 nm) with a Balanced Scanning Mobility Analyzer (BSMA, Tammet 2006). Additionally, in May 2009 the composition of natural ions was measured with an API-TOF mass spectrometer (Junninen et al. 2010).

RESULTS & CONCLUSIONS

<table>
<thead>
<tr>
<th>Year</th>
<th>Neutral</th>
<th>Ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>2007</td>
<td>17/26 = 65%</td>
<td>18/31 = 58%</td>
</tr>
<tr>
<td>2008</td>
<td>20/30 = 67%</td>
<td>17/26 = 65%</td>
</tr>
<tr>
<td>2009</td>
<td>10/19 = 53%</td>
<td>15/23 = 65%</td>
</tr>
<tr>
<td>Tot</td>
<td>47/75 = 63%</td>
<td>50/80 = 63%</td>
</tr>
</tbody>
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Table 1. Frequency of night-time events (events/all measurement days in May of each year) observed with the PH-CPC (neutral) and the BSMA (ions).
The total concentration of ~1.3-3 nm particles in Hyytiälä ranged from $10^3$ to $10^5$ cm$^{-3}$, the highest values being regularly detected at night-time. A distinct rise in the nano-CN concentration, a ‘night-time event’, was observed on more than 60% of nights in May within a few hours from sunset (Table 1). The elevated concentrations lasted for several hours, occasionally longer. On most nights, the particles did not grow further, but at times the particles reached sizes a bit above 3 nm and became visible in the lowest channels of the DMPS. One of such cases is presented in Figure 1 as an example of a night-time event.

Usually the concentration small ions increased almost simultaneously as the neutral nano-CN, and the mean mobility of the ions decreased, indicating larger size. However, generally only about 1% of the observed particles in the size range of 1.3-3 nm were charged, and the charged fraction dropped as the night-time event started. The API-TOF detected in the night-time a lot of larger ($m/Q > 300$) probably organic peaks in the negative mass spectrum, which were either not present or much lower in the daytime.

**Figure 1.** An example of a night-time event. Particle size distributions measured with the a) PH-CPC (1.3-5 nm, neutral), b) DMPS (3-1000 nm, total), c) BSMA (0.8-7.5 nm, neg. ions), and d) BSMA (0.8-7.5 nm, pos. ions) in Hyytiälä 3 May 2008.

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REFERENCES


