Observations on nocturnal growth of atmospheric clusters

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ABSTRACT
In this paper, we summarize recent observations of nighttime nucleation events observed during 4 yr, from 2003 to 2006, at the SMEAR II station in Hyytiälä, southern Finland. Formation of new atmospheric aerosol particles has been frequently observed all around the world in daytime, but similar observations in nighttime are rare. The recently developed ion spectrometers enabled us to measure charged aerosol particles and ion clusters to diameters < 1 nm and are efficient tools for evaluating cluster dynamics during nighttime. We observed clear growth of cluster ions during approximately 60 nights per yr. The newly formed intermediate ions usually persisted for several hours with typical concentrations of 100–200 cm⁻³. The evolution of nighttime growth events is different compared with daytime events. The mechanism behind nighttime events is still unclear, but the behaviour can be described by the hypothesis of activation of clusters.

1. Introduction
Formation of new aerosol particles in the atmosphere is a complicated series of chain reactions, including the production of nanometre-size clusters from precursor vapours, the growth of these clusters to detectable sizes by condensation of, for instance, sulphuric acid and organic vapours and the simultaneous removal of clusters by coagulation with the pre-existing aerosol particle population (e.g. Kerminen et al., 2001; Kulmala, 2003). Once formed, the aerosol particles need to grow further to sizes above 50–100 nm in diameter to be able to influence climate by scattering solar radiation or by being activated into cloud droplets. At smaller sizes, the particles may have a direct effect on human health (Ibald-Mulli et al., 2002; Pope and Dockery, 2006; Weschler et al., 2006) and atmospheric composition.

Over the past decade or so, aerosol formation has been observed at a large number of sites around the world (Kulmala et al., 2004a). Such observations have been performed on different platforms (on the ground, on ships, on aircrafts) and over different time periods (focus campaigns or continuous measurements). In the continental boundary layer, regional nucleation events are common. Such events increase particle concentrations over a distance of hundreds of kilometres.

Although there are some atmospheric observations on nighttime new particle formation (NPF) (e.g. Wiedensohler et al., 1997; Vehkamäki et al., 2004; Lee et al., 2008; Suni et al., 2008), studies reporting this phenomenon are sparse. On the other hand, many of the nighttime NPF events may start from the cluster ion pool, the existence of which has been known for decades (e.g. Kulmala and Tammet, 2007 and references therein). Recently, Kulmala et al. (2007b) observed a constant pool of neutral clusters also. Because of their unique capability to detect ions and charged particles down to < 1 nm sizes, the new ion spectrometers, as used in these cited studies, can provide new insight also to nighttime NPF events.

Here we investigate episodes of nocturnal cluster ion growth during 2003–2006 in a pine forest in southern Finland, where clear NPF has been frequently observed during the daytime (e.g. Mäkelä et al., 1997; Kulmala et al., 2001; Dal Maso et al., 2005, 2007). Our main aim is to examine nighttime NPF events and discuss their possible connections to day time NPF events.
2. Material and methods

2.1. Site description

Our measurements took place in Hyytiälä, southern Finland, at the station for measuring forest ecosystem (SMEAR II, 61°51′N, 24°17′E, 181 m asl), research site operated by the University of Helsinki. Several continuous measurements have been performed at SMEAR II. The station is located at a rural site, surrounded by pine-dominated forests. The station is equipped with extensive instrumentation for atmospheric measurements (for a detailed description, see e.g. Kulmala et al., 2001; Hari and Kulmala, 2005). Precipitation measurements used in this study were measured above the forest at the height of 18 m, with precipitation meter FD12P Weather sensor (Vaisala Oyj, Helsinki, Finland).

2.2. Atmospheric observations with ion spectrometers

We measured size distributions of atmospheric ions and charged aerosol particles with the balanced scanning mobility analyzer (BSMA; Tammet, 2004) and the air ion spectrometer (AIS; Mirme et al., 2007), both manufactured by Airel Ltd, Estonia. The BSMA consists of two plain aspiration-type differential mobility analysers, one for positive and the other for negative ions. The measured electric mobility range is 0.032–3.2 cm² V⁻¹ cm⁻¹. The mobility distribution is converted to a size distribution using an algorithm (Tammet, 1995), with the resulting size distribution range from 0.4 to 6.3 nm. The AIS is based on the same principle, but measures particles with diameters from 0.34 to 40 nm. The operation period used in the present study was from 1 April 2003 to 21 December 2006.

2.3. NPF event classification

First, we plotted the AIS and BSMA data as surface plots to see the development of particle and cluster size distribution as a function of time (Fig. 1). To better identify nighttime behaviour, we plotted two subsequent days in one figure. Since the observed events were very different from corresponding daytime events, we modified the visual method described by Dal Maso et al. (2005, 2007) for classification of daytime NPF events. Besides surface plots, we plotted cluster concentrations in the BSMA channel 5 (size range 1.3–1.8 nm in Tammet diameter, see Tammet, 1995) for each classified day. This size class usually represents the upper size limit of the cluster ion pool. Therefore, an increase of the ion concentration in this size channel is indicative of an increased average size of cluster ions and therefore the growth event.

We excluded data that were measured during the malfunctioning or maintenance of the instruments. A nighttime NPF event was defined as an increase in concentration in the 1.3–1.8 nm size class and a simultaneous, visually apparent growth of clusters. An increase in the ion concentration alone is not a sufficient criterion because the mixing volume in the nocturnal boundary layer (NBL) is smaller than that of the daytime boundary layer. This would lead to increased nighttime ion concentrations even if the total number of ions were constant inside the boundary layer. In addition, an important ion source, radon, accumulates close to the ground during the night and can, thereby, increase ion concentrations (e.g. Hirsikko et al., 2007b). For each nighttime NPF event, we determined the characteristics and duration of the intermediate ion burst or the growth of the clusters and classified the events as follows: Class I—‘hump’ shaped formation events; Class II—‘apple’ shaped formation events and Class III—very strong events where intermediate ions up to several nanometres

![Fig. 1. Example of Class I nocturnal NPF event. (a) Number concentration of negative air ions measured with AIS on 30 April 2007–1 May 2007. The nocturnal event is highlighted. (b) Absolute number concentrations of negative, 1.3–1.8 nm cluster ions measured with AIS (solid) and BSMA (dashed). (c) Same as (a), but measured on 4 June 2004–5 June 2004. (d) Same as (b), but measured on 4 June 2004–5 June 2004.](image-url)
Fig. 2. Example of Class II nocturnal NPF event. (a) Number concentration of negative air ions measured with AIS on 27 November 2003–28 November 2007. The nocturnal event is highlighted. (b) Absolute number concentrations of negative, 1.3–1.8 nm cluster ions measured with AIS (solid) and BSMA (dashed). (c) Same as (a), but measured on 15 December 2004–16 December 2004. (d) Same as (b), but measured on 15 December 2004–16 December 2004.

Fig. 3. Example of Class III nocturnal NPF event. (a) Number concentration of negative air ions measured with AIS on 7 October 2003–8 November 2007. The nocturnal event is highlighted. (b) Absolute number concentrations of negative, 1.3–1.8 nm cluster ions measured with AIS (solid) and BSMA (dashed). (c) Same as (a), but measured on 5 December 2004–6 December 2004. (d) Same as (b), but measured on 5 December 2004–6 December 2004.

in size appear suddenly and persist, with no observable growth, for many hours.

Classes I–III describe the three most common nighttime NPF types observed from the data set. Class I portrays the most frequent type, a clear 'shoulder' above the cluster mode in the surface plot and a clear increase in 1.3–1.8 nm cluster concentration in the BSMA data (Fig. 1). Class II events are characterised by a roundish-shaped particle burst from 1.3 to approximately 8–10 nm, (Fig. 2). Class III (Fig. 3) events are the strongest and produce a large number of intermediate ions up to several nanometres, which persist for many hours and then suddenly disappear. These events bear some resemblance to the nocturnal events seen in a Eucalypt forest in Tumbarumba and South-East Australia (Suni et al., 2008). However, we never observed any banana-type events, which are typical for daytime (Dal Maso et al., 2005).

3. Results and discussion

Table 1 shows the number of nighttime NPF events and nights with no formation (non-events) in 2003–2006. The most numerous are Class I events: they occurred on approximately 1/6 of the nights. The length of Class I events varied from 2 to 20 h, with median length for positive clusters 6.9 h and for negative ones 8.6 h (see Fig. 4).

The annual variation of the nighttime NPF nights was apparent. The event frequency peaked clearly in May, decreased towards autumn and reached the minimum in winter (Figs. 5a
Table 1. Distribution of classified nights to non-events and events

<table>
<thead>
<tr>
<th>Year</th>
<th>Non-event</th>
<th>Event</th>
<th>MD</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>2003</td>
<td>176</td>
<td>69</td>
<td>120</td>
<td>50</td>
<td>3</td>
<td>1</td>
<td>41</td>
</tr>
<tr>
<td>2004</td>
<td>258</td>
<td>99</td>
<td>9</td>
<td>65</td>
<td>5</td>
<td>3</td>
<td>64</td>
</tr>
<tr>
<td>2005</td>
<td>246</td>
<td>77</td>
<td>42</td>
<td>54</td>
<td>6</td>
<td>1</td>
<td>63</td>
</tr>
<tr>
<td>2006</td>
<td>255</td>
<td>99</td>
<td>11</td>
<td>73</td>
<td>11</td>
<td>1</td>
<td>63</td>
</tr>
</tbody>
</table>

Three event classes are separated for negative and positive ions. For non-events, only the night when there is no event in positive or negative ions are counted. Events are counted if any of charges have event of any class. MD – missing data.

Table 2. Co-occurrence of negative and positive nocturnal NPF events (frequencies)

<table>
<thead>
<tr>
<th>Positive ions</th>
<th>MD</th>
<th>Non-event</th>
<th>Class I</th>
<th>Class II</th>
<th>Class III</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Negative ions</td>
<td>MD</td>
<td>152</td>
<td>25</td>
<td>0</td>
<td>0</td>
<td>177</td>
</tr>
<tr>
<td>Non-event</td>
<td>5</td>
<td>935</td>
<td>67</td>
<td>2</td>
<td>2</td>
<td>1011</td>
</tr>
<tr>
<td>Class I</td>
<td>0</td>
<td>88</td>
<td>151</td>
<td>0</td>
<td>3</td>
<td>242</td>
</tr>
<tr>
<td>Class II</td>
<td>0</td>
<td>23</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>25</td>
</tr>
<tr>
<td>Class III</td>
<td>0</td>
<td>4</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>Total</td>
<td>157</td>
<td>1075</td>
<td>219</td>
<td>4</td>
<td>6</td>
<td>1461</td>
</tr>
</tbody>
</table>

MD – missing data.

Fig. 4. Durations of nocturnal NPF events. Negative ions are represented by grey bars and positive ions by black ones.

Fig. 5. Seasonal variation of nocturnal NPF events for years 2003–2006. (a) all event classes (b) Class I events. Negative ions are represented by grey bars and positive ions by black ones.

and b). Positive ions participated less frequently in nighttime formation in winter and autumn than negative ions. This suggests that negative ions require lower concentrations of condensing vapours than positive ones to start growing to larger sizes (see also Kulmala et al., 2007a). Interestingly, laboratory studies also show that negative sulphuric acid ion clusters are more stable than positive ones (e.g. Kim et al., 1998; Lovejoy et al., 2004). Simultaneous nighttime NPF events of both negative and positive clusters occurred in 48% of Class I cases (Table 2). In 28% of the Class I events, negative clusters grew but positive clusters did not, whereas in 22% of the events only positive clusters grew.

No Class II or III NPF events were observed at relative humidity <80%, a clear indication that these events require high humidity to take place. The production of intermediate ions during rainfall, as well as in waterfall experiments, has been observed in several studies (e.g. Hörrak et al., 2005; Hirskikko et al., 2007; Laakso et al., 2006; Parts et al., 2007). Rain explained 22 out of 25 Class II and III nighttime NPF events. Intermediate clusters in the size range of 2–4 nm appeared when precipitation exceeded 0.1 mm h\(^{-1}\). First, negative intermediate clusters appeared, and if rain lasted long enough (longer than 2 h), positive intermediate clusters also became measurable. These clusters disappeared immediately when the rain stopped.

The three Class II and III events that were not associated with rain, occurred in winter. During these events, night-time temperatures suddenly increased above zero degrees and only negative intermediate clusters appeared. These ions disappeared shortly after the temperature dropped below zero degrees again (Fig. 6). A night with an above-zero temperatures occurs only rarely after a day with subzero temperatures. Therefore, Class II and III events were very rare during winter. However, during spring and autumn, the temperature commonly fluctuates around zero, being negative at night and positive during the day. Formation of ion clusters was observable during such temperature fluctuations, but this phenomenon took place during daytime when many other processes associated with radiation, and thus the expected photochemical reactions, were active. This makes identifying the underlying causes of cluster formation difficult. A few exceptional daytime–nighttime temperature increases during the winter provide a possibility to study intermediate cluster formation in the absence of radiation and photochemistry.

The maximum frequency of nighttime NPF events occurred two months later (May–June) than that of daytime NPF events (March–April; see Dal Maso et al., 2005). In addition, the
seasonal variation of daytime NPF typically has a secondary peak in August–September. The onset of daytime NPF events in spring seems to follow, quite closely, the increase of the product of monoterpane and ozone/OH concentrations (Kulmala et al., 2004b), but no such connection could be identified for nighttime events. These observations together suggest that either the particle formation mechanisms or the vapours participating in these processes are slightly different during the day- and nighttime in Hyytiälä.

To find out a potential link between daytime and nighttime NPF, we grouped the daytime events and non-events (Dal Maso et al., 2005) to those that were followed by a nighttime event and to those that were not. We excluded all unclear days from this analysis. We found 90 daytime events that were followed by a nocturnal event and only 28 daytime non-events that were followed by nighttime events. Since the number of event and non-event days is approximately the same in Hyytiälä (Dal Maso et al., 2007), we can conclude that daytime NPF substantially enhances the probability of NPF during the following night. These findings suggest that the same condensing vapours that cause daytime NPF, could also be responsible for nighttime formation. An alternate explanation is that the general ambient conditions favouring atmospheric NPF tend to prevail more than 12 h at our measurement site.

NPF nights always had low SO₂ concentration (<0.5 ppb) and condensation sink ($3.3 \times 10^{-3} \text{ s}^{-1}$ vs. $4.6 \times 10^{-3} \text{ s}^{-1}$ during non-events) indicative of relatively clean air. No clear differences in the ambient temperature between the event and non-event nights were seen. Both these features are similar to daytime NPF in Hyytiälä (Lyubovtseva et al., 2005). However, contrary to what has been observed during daytime (Sogacheva et al., 2005), the air mass origin seemed to have no effect on the frequency of nighttime NPF events (data not shown). The reason for this is unclear. One possibility is that nighttime events are more local than daytime events, being therefore less sensitive to the air mass origin. Another possibility is the factors controlling nighttime NPF depend weakly on the air mass type.

The concentration of gaseous sulphuric acid was calculated using the method by Boy et al. (2005). In this study, we changed this model to account for nighttime OH-radical production by including an OH-source from the reaction of monoterpenes with ozone, based on the master chemical mechanism (MCM, from the University of Leeds—http://mcm.leeds.ac.uk/MCM/). The yield for the reaction of alpha-pinene with ozone is 0.7 and of beta-pinene, 0.3. For all other terpenes, we used a yield of 0.1.

We found that the calculated sulphuric acid concentrations were substantially higher, frequently by a factor of two, in the NPF nights compared with other nights (Fig. 7). This is an indication that sulphuric acid plays a role in nocturnal NPF.

Our recent analyses suggest that the average contribution of ion-induced nucleation to total NPF is less than 10% during daytime in Hyytiälä (Laakso et al., 2007; Gagné et al., 2008). Here, we found that ion cluster concentrations were clearly higher during event nights compared with non-event nights (Fig. 8). Based on this, it might be tempting to conclude that ions are central to nighttime NPF. One should, however, remember that a significant fraction of neutral clusters become charged during their growth, especially if these clusters grow slowly and were surrounded by many ion clusters (Kerminen et al., 2007). As a result, additional information on the concentrations of neutral clusters during nighttime NPF is necessary before we can state anything.
Fig. 8. Median total concentration of ion clusters (<1.3 nm). Solid lines are for nights with nocturnal NPF event and dashed lines for nights without an event. Black lines are for negative ions and grey lines, for positive ions.

conclusive regarding the involvement of ions or ion-induced nucleation during these nocturnal events.

One major difference between the daytime and nighttime NPF events was that, in nighttime, the clusters never grew to sizes larger than a few nanometres. This can result from a combination of two things. The first is the lower concentrations of condensing vapours during nighttime, which slow to slower particle growth rates. The second is the more efficient coagulation scavenging of the small clusters by the pre-existing particle population; when clusters grow at a slower rate, a larger fraction of them will be scavenged before reaching larger sizes (Kerminen et al., 2001).

4. Conclusions

During our 48 month measurement period, 344 nights had nighttime NPF events whereas 935 nights did not. Majority of nocturnal NPF events belonged to class I, most of which occurred at the same time in both negative and positive polarities (151 cases out of 274 negative and 265 positive ones). Rain and high relative humidity related events, Class II and III are mainly in negative polarity, 31 negative and 10 positive, and often are not occurring at same time in both polarity.

The Class I events were characterised by growth of cluster ions to approximately 2 nm in diameter. These 2-nm particles existed for several hours with no further aerosol growth. The occurrence of Class I events seemed to be independent of ambient weather conditions but were connected to elevated cluster ions and sulphuric acid concentrations. These results suggest that the ions and sulphuric acid have a role in the nocturnal atmospheric nucleation process.

The frequent occurrence of NPF events in the night directly after a daytime event indicates that the same organic vapours or ambient conditions could be responsible for cluster growth in both day- and nighttime processes. However, the differences in seasonal patterns of day- and nighttime formation indicate the opposite. Daytime event frequency had a maximum during the spring recovery of the forest in March–April and a secondary peak in the autumn, whereas the nighttime events peaked during May–June and decreased sharply after that. The role of organic vapours in nighttime formation, therefore, remains unclear. Regardless of the detailed formation mechanism, the above observations are in line with the hypothesis that atmospheric NPF might actually be a two-step process (Kulmala et al., 2000), in which, the first step is the formation of clusters and the second step is the activation of clusters by sulphuric acid and/or organic vapours (Kulmala et al., 2006). The first step can also include the recombination of atmospheric ion clusters into neutral ones. The growth of clusters observed here is probably the starting point of the activation process.

The similarities and differences between daytime and nighttime events give us new insights for finding out the reasons for atmospheric nucleation and initial steps of cluster growth. In particular, the warm nights during the winter provide a means to investigate the formation of intermediate ion clusters without the involvement of radiation and photochemistry. On the other hand, the growth events of cluster ions might reveal information on why particles do not always grow into larger sizes. However, future studies are required to understand the possible mechanisms related to cluster growth and atmospheric nucleation.

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