

**Analysis of
atmospheric
molecular clusters**

K. Lehtipalo et al.

Analysis of atmospheric neutral and charged molecular clusters in boreal forest using pulse-height CPC

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

We measured the size distribution of atmospheric neutral and charged clusters and particles down to mobility diameter around 1.5 nm by applying pulse-height CPC technique at SMEAR II station in Hyytiälä, southern Finland during spring 2007 and May 2008. The concentration of molecular clusters smaller than 3 nm seems to be highly variable in boreal forest environment. The concentration varied typically between 500–50 000 cm⁻³, the medians being 8060 cm⁻³ in year 2007 and 3380 cm⁻³ in 2008. By comparing to concentrations measured with ion spectrometers, we conclude that ion clusters and neutral clusters produced by ion-ion recombination are usually not sufficient to explain all of the observed clusters; the median fraction of recombination products from all neutral clusters was 4.9%. Before and during most new particle formation events the cluster formation rate rose only slightly, or remained close to stable. Nocturnal formation of clusters was also frequently observed.

1 Introduction

Aerosol particles affect the climate both directly by scattering and absorbing solar radiation and indirectly via cloud processes. The net radiative forcing of particles is currently believed to be negative (i.e. cooling), but the level of scientific understanding is still relatively low (IPCC, 2007). Detailed knowledge of nucleation process is needed to include secondary aerosol particles to climate models. Nucleation events have been proven to affect the regional and global particle budget significantly (Spracklen et al., 2006). Additionally, aerosol particles enter the human respiratory system, where particles may cause adverse immediate and chronic health effects (e.g. Brunekreef and Holgate, 2002).

The existence of stable neutral atmospheric clusters and their role in new particle formation is the key question in understanding atmospheric nucleation process. New particle formation has been observed on numerous locations around the world (Kul-

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Analysis of atmospheric molecular clusters

K. Lehtipalo et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



mala et al., 2004a), but the exact mechanisms how particles are formed from precursor vapors are still under debate. The prevailing nucleation mechanism, at least in boreal forest environment, is suggested to be activation of neutral atmospheric clusters approximately 1–2 nm in diameter (Kulmala et al., 2000; 2006; and 2007a). Theoretical arguments and laboratory experiments support the existence of neutral clusters (e.g. Kulmala et al., 2005; Hanson and Eisele, 2002). The proposed candidates for the chemical compounds involved in forming clusters include sulphates (e.g. Vehkamäki et al., 2004; Kulmala et al., 2004b), ammonia (Torpo et al., 2007) and organics (Bonn et al., 2008). Ion-ion recombination is also known to produce neutral clusters (Turco et al., 1998).

Due to instrumental limitations direct observations of neutral clusters in the atmosphere have been sparse. Weber et al. (1995) and Kulmala et al. (2005) showed that clusters were present during nucleation events. Ion clusters in the size range below 1.5 nm can be easily detected and have been proven to exist practically all time in the atmosphere (Hörrak et al., 1998). The concentration of ion clusters is, however, typically not high enough to explain the observed atmospheric particle formation rates (e.g. Laakso et al., 2004; Iida et al., 2006). The contribution of ion-induced nucleation to new particle formation in Hyytiälä seems to be less than 10% (Gagné et al. 2008). A significant effort has recently been put into developing instruments capable of measuring neutral particles below 3 nm, which is the lower detection limit of the current commercial instruments. With newly developed measurement techniques, like Neutral Cluster and Air Ion Spectrometer (NAIS) and CPC-based applications, Kulmala et al. (2007a) and Sipilä et al. (2008, 2009) observed a persistent pool of neutral sub-3 nm clusters in boreal forests.

In this work we will, for the first time, present a continuous time series of atmospheric neutral cluster concentrations. We also study the diurnal variation of cluster concentration in boreal forest, which gives insight into their production mechanisms. By measuring simultaneously both charged and neutral clusters with various independent instruments we aim at estimating the significance of ions in producing neutral

Analysis of atmospheric molecular clusters

K. Lehtipalo et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏮

⏭

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



clusters.

2 Material and methods

2.1 Site description and instrumentation

The measurements took place at SMEAR II station (61° 51' N, 24° 17' E, 181 m a.s.l.) in Hyytiälä, southern Finland. The station is surrounded by coniferous Scots pine-dominated forest. For detailed site description see e.g. Hari and Kulmala (2005).

The particle size-distribution from 3 to 1000 nm was measured with a basic twin-DMPS system (Aalto et al., 2001). For measuring the ion mobility distribution a Balanced Scanning Mobility Analyzer (BSMA, Tammet, 2006) and an Air Ion Spectrometer (AIS, Mirme et al., 2007) were used. Both of the ion spectrometers are manufactured by Airel Ltd., and their mobility ranges are $0.032\text{--}3.2\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ ($\sim 0.8\text{--}7.6\text{ nm}$ in mobility diameter) and $0.0013\text{--}2.4\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ ($\sim 0.9\text{--}42\text{ nm}$), respectively. Neutral Cluster and Air Ions Spectrometer (NAIS) is based on the AIS, but equipped with a unipolar charger to measure also neutral particles. The size range of the charger ions sets the lower size limit of the NAIS to about 2 nm depending on polarity and cluster concentration (Asmi et al., 2008). The size distribution of neutral and charged clusters $\sim 1.2\text{--}5\text{ nm}$ (equivalent ion mobility diameter) was measured with a pulse-height CPC (PH-CPC, discussed in Sect. 2.2).

During spring 2007 (15 March–26 June) all of the above mentioned instruments were measuring simultaneously in Hyytiälä as a part of the EUCAARI campaign. From spring 2008 (1–31 May) PH-CPC, DMPS and BSMA data were available. All particle measurements were conducted inside the forest canopy from a height of c 2 m above the ground. All reported diameters are non-reduced mobility diameters, and all times are local wintertime.

Analysis of atmospheric molecular clusters

K. Lehtipalo et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



2.2 PH-CPC

The pulse height analysis technique (Saros et al., 1996) relies on detecting the intensity of light scattered by particles after their condensational growth in the CPC. Due to supersaturation gradient inside the condenser, particles activate for growth at different axial positions depending on their size. The smaller the particle, the later it will be activated leading to smaller final droplet sizes. Clearly there is an upper size limit, after which only total concentration, but no size information of particles can be achieved, since all bigger particles are activated almost simultaneously. Pulse height analysis method has been used in size distribution measurements between 3 and 10 nm (Weber et al., 1995; 1998) as well as to determine the composition of freshly nucleated nanoparticles (O'Dowd et al., 2002; Hanson et al., 2002). Recently Sipilä et al. (2008) applied of this method to detect atmospheric clusters.

The PH-CPC used in this study comprises a TSI-3025A ultrafine CPC with modified optics (Dick et al., 2000) and a multichannel analyzer. For increasing the detection efficiency of small particles, the supersaturation inside the condenser was increased from nominal until homogenous nucleation appeared. The pulse height analysis technique allowed us to distinguish homogenous nucleation from activation of clusters and resolve the size distribution of particles below 5 nm. Detailed description of data inversion is published by Sipilä et al. (2009).

The PH-CPC's size response and detection efficiency has been calibrated using positive ions (silver and 241-Am charger generated ions) only, due to lack of reference instrument for neutral particles below 3 nm. Winkler et al. (2008) showed that charged clusters are activated in lower supersaturations than neutral ones, and negative ones before positive. When PH-CPC is used for measuring atmospheric aerosol, we therefore tend to slightly underestimate the size and concentration of neutral particles. The activation probability of particles depends also on their composition (e.g. O'Dowd et al., 2002, 2003; Kulmala et al., 2007b). For these reasons the size scale of our results should not be considered as actual diameters, but rather the equivalent activation

Analysis of atmospheric molecular clusters

K. Lehtipalo et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



mobility diameter of insoluble positive ions.

Furthermore, the activation probability depends on the total particle concentration activated inside the condenser due to the vapour consumption of the growing droplets. At concentrations larger than $4000\text{--}5000\text{ cm}^{-3}$ homogenous nucleation is almost completely suppressed compromising the method. Cluster concentrations measured during strong nucleation events and pollution episodes are therefore not considered reliable, and normally excluded from the analyses. The factors affecting the size and concentration response of the PH-CPC are further discussed by Sipilä et al. (2009).

From spring 2007 to 2008 the measurement method was modified in a way that instead of assuming a symmetrical homogenous nucleation mode, we measured the homogenous nucleation level after each ambient measurement. For retaining a similar background concentration, a diffusion tube (c. 2 m, i.d. 8 mm copper tubing, flow rate of 3 lpm) was applied for filtering the clusters and smallest particles away. Additionally, an ion trap (7 cm coaxial tube i.d. 8 mm with a voltage of 32 V between the electrodes) was applied after each diffusion tube measurement to get rid of charged clusters. In 2007 the ion trap and a diffusion battery were applied irregularly.

2.3 Data analysis

2.3.1 Neutral clusters

In 2007 the concentration of neutral particles was calculated by subtracting the ion clusters of corresponding size range measured with the BSMA from the total cluster concentration measured with the PH-CPC. As the concentration of intermediate ions larger than 1.5 nm is typically very low, $<200\text{ cm}^{-3}$ except during nucleation events (Hirsikko et al., 2005), the effect should be minor. The neutral cluster concentration in 2008 can be achieved solely from PH-CPC data by subtracting the diffusion tube measurement from the ion trap measurements.

Analysis of atmospheric molecular clusters

K. Lehtipalo et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



2.3.2 Recombination products

A neutral cluster may result if two ions of opposite charge collide and form a stable entity; this is called recombination. An estimate for the steady-state concentration of these recombination products can be obtained by setting the balance equation

$$5 \quad \frac{dN_{n,\text{rec}}}{dt} = a\alpha N_i^+ N_i^- - \beta N_{n,\text{rec}}(N_i^+ + N_i^-) - \text{Coag}S(N_{n,\text{rec}})N_{n,\text{rec}} \quad (1)$$

to zero. The subscript n refers to neutral clusters and i to ion clusters. a is the fraction of stable recombination products, α the ion-ion recombination coefficient and β the aerosol-ion attachment coefficient. Thus the first term on the right hand side represents recombination source, the second and the third loss of neutral particles by charging and coagulation, respectively. For α we used a value of $1.6 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ and for β $0.01 \times 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ (Tammet and Kulmala, 2005). To obtain a maximum estimate, a was set to unity. The ion cluster concentrations were taken from the BSMA data. As we were interested in recombination products in the size range of the PH-CPC, only collisions between ions large enough to produce particles about 1.5–2 nm in diameter were accounted for. The corresponding BSMA channels were chosen using mass-mobility relation by Mäkelä et al. (1996, based on experimental data by Kilpatrick (1971)).

2.3.3 Formation rates

The formation rate of 1.5 nm clusters can be calculated from (as in Kulmala et al., 2007a, supporting material)

$$20 \quad J_{1.5} = \frac{dN_{1.5-2}}{dt} + \text{Coag}S_{1.5-2} \cdot N_{1.5-2} + \frac{GR_{1.5-2}}{0.5} N_{1.5-2} \quad (2)$$

The coagulation loss is calculated for 2 nm particles from the DMPS data. We left the last term out, reaching again a minimum estimate for cluster formation rate. The

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



equation can be written separately for neutral particles, ion clusters and for particles formed by recombination.

3 Results and discussion

3.1 Cluster concentrations

5 According to PH-CPC data from spring 2007 and May 2008, there is a pool of molecular clusters present in Hyytiälä practically all the time. Due to uncertainties regarding the size of these clusters discussed in Sect. 2.2, we hereafter usually refer to total concentration below 3 nm, even though our measurements inevitably have a lower size limit corresponding to activation of positive 1.2 nm ions. Most probably we were able
10 to see only the upper size section of the cluster band. Figure 1 presents the total cluster concentration from year 2007 and Fig. 2 neutral cluster concentration from 2008. The concentration of these clusters ranged typically from 500 cm^{-3} to $50\,000\text{ cm}^{-3}$, the lowest values usually coinciding with high coagulation sink. The median concentration of clusters below 3 nm was 8060 cm^{-3} in spring 2007 and 3380 cm^{-3} in May
15 2008. In 2008 the homogenous nucleation level inside the PH-CPC was lower than in 2007 indicating lower supersaturation, which could at least partly explain the difference in median concentration. When the temperature difference between saturator and condenser was increased on 15 May, we began to see slightly higher cluster concentrations.

20 In Fig. 3 we compared the total concentrations measured with the PH-CPC to the ones measured with the NAIS on 31 March–3 April 2007. In the size range 3–5 nm the measurement agree remarkably well, especially on the negative charging side of the NAIS. In the 1.5–3 nm range concentrations are of similar order, but either the NAIS is not sensitive enough to variations in cluster concentration or then again the PH-CPC
25 detection efficiency is too sensitive to background aerosol concentration.

In Fig. 4 the fraction of neutral clusters from 2007 is compared to recombination

Analysis of atmospheric molecular clusters

K. Lehtipalo et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



products ($\sim 1.5\text{--}2\text{ nm}$) and ion cluster concentrations. It seems that the concentration of neutral clusters is one order of magnitude higher than recombination product and cluster ion ($\sim 0.8\text{--}1.3\text{ nm}$) concentrations, and two orders of magnitude higher than the concentration of ions of the corresponding size ($\sim 1.3\text{--}3.2\text{ nm}$). The scatter plot of neutral clusters as a function of recombination clusters, Fig. 5, further affirm, that we are able to see the $1.5\text{--}2\text{ nm}$ neutral particles produced by recombination, but that is not the single source of neutral clusters. The values below the unity line are explained by measurement noise and overestimation of recombination products. The median fraction of recombination clusters from all neutral clusters was 4.9%, but the values varied from less than 0.1% to more than 100%. This is in accordance with Kulmala et al. (2007a), who calculated that recombination should usually account for less than 10% of neutral clusters in Hyytiälä conditions.

It is hard to give a certain accuracy estimate for our measurements, since clearly the uncertainties regarding size and concentration increase with decreasing particle size. As discussed in Sect. 2.2, most instrumental factors tend to lower the detection efficiency of clusters, so the concentration can be considered a minimum estimate. The measured cluster concentrations are indeed a bit lower than the ones predicted for Hyytiälä from formation rates of $2\text{--}3\text{ nm}$ particles, $7000\text{--}50\,000\text{ cm}^{-3}$ (Kulmala et al., 2007a). Sipilä et al. (2009) stated that the error in diameter due to unknown cluster composition and charge can be as large as $\sim 0.5\text{ nm}$ and the uncertainty in detection efficiency several percents.

3.2 Particle formation

An example of a new particle formation event on 10 May 2008 seen by the PH-CPC and DMPS is presented in Fig. 6. The number concentration of clusters starts to rise a little before 9 o'clock, and 3 nm particles appear about two hours later both in DMPS and PH-CPC. When total particle concentration reaches circa 4000 cm^{-3} , the cluster concentration starts declining due to increased coagulation sink and declining supersaturation inside the instrument. In the evening a second process seems to take

Analysis of atmospheric molecular clusters

K. Lehtipalo et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



place, as the concentration of clusters rises again strongly peaking around 20 o'clock at $15\,000\text{ cm}^{-3}$. These nocturnal clusters reach the size of $\sim 3\text{ nm}$, but disappear gradually as they are scavenged mainly by coagulation (Kerminen et al., 2001). The upper range of these clusters is also visible in the DMPS figure just above the detection limit of the instrument.

No consistent pattern of cluster concentrations during nucleation events can be attained from the data. Clear growth from cluster band towards bigger particles was seen only rarely. Often the particles seemed to emerge at sizes close to 3–4 nm, and the cluster concentration rose simultaneously, or remained close to stable. This indicates that the actual particle formation might not happen in the near vicinity of our measurement place, but the air mass with newly formed particles is brought to the site by vertical or horizontal mixing. However, as strong particle formation changes the supersaturation inside the instrument rapidly, these events cannot be further studied using the present method.

The median diurnal variation of cluster concentration and neutral cluster formation rate is presented in Fig. 7 for spring 2007. Figure 8 presents median concentration of neutral clusters and 3–5 nm particles in May 2008. Days are classified into event, non-event and undefined days according to Dal Maso et al. (2005), excluding strong events with background aerosol concentration reaching over 5000 cm^{-3} . Interestingly, the highest cluster concentration were not measured during daytime nucleation events, but in the evenings a little after sunset. This is partly due to lower night-time boundary layer, but as the formation rate and mean size also grew, we conclude, that there is a cluster source near ground in the night-time.

Favorable conditions for night-time cluster formation prevailed especially during late May 2008, as a distinct rise in concentration could be seen almost every night (Fig. 9). During this time period only weak (class II) events were observed in the daytime. Recently Junninen et al. (2008) studied nocturnal particle formation from ion data (AIS and BSMA) in Hyytiälä. They conclude that most strong nocturnal ion formation events are associated with rain, and that a nucleation event during daytime enhances particle

Analysis of atmospheric molecular clusters

K. Lehtipalo et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



formation in the following night. In the contrary, nocturnal formation of neutral clusters does not depend on rain and seems to be slightly higher on non-event days. The latter could although be a consequence of higher background concentration on event days. The characteristics of cluster formation was found to be very similar than the nocturnal event types identified by Junninen et al. (2008). Both the neutral and charged clusters persisted for hours and could sometimes reach sizes around 4–5 nm, but never grew any larger. The simultaneous rise in ion cluster concentration was much less pronounced, which suggests that nocturnal growth of ion clusters could result mostly from charging of the neutral ones.

4 Conclusions

We observed number concentrations of molecular clusters ranging from less than a thousand to tens of thousands per cubic centimeter by directly measuring the cluster band in boreal forest environment during four months in spring 2007 and 2008. The size scale of PH-CPC measurements depend on the charge and composition of the measured particles. Since the concentration goes rapidly down after ~2 nm, we can nonetheless safely conclude, that the signal comes from clusters or molecules smaller than 3 nm, which are thus beyond traditional aerosol instrumentation.

The data set presented in Sect. 3 is unique. Earlier reports on neutral clusters in boreal forest are mainly qualitative (Sipilä et al., 2008) or just examples from field are given (Sipilä et al., 2009). The measurements confirm the continuous existence of neutral clusters in Hyytiälä. Since the uncertainties regarding cluster concentrations are still large, the reported concentrations should be considered as our best estimates. However, the diurnal and day-to-day variation of clusters can be studied; a distinct diurnal variation with a clear night-time maximum was indeed found.

The number of neutral clusters seems to considerably exceed the charged ones, as the measured cluster concentrations were usually at least one order of magnitude higher than total ion cluster concentrations. On most days, also the contribution of ion-

Analysis of atmospheric molecular clusters

K. Lehtipalo et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



ion recombination products to total neutral cluster concentration was found to be minor. For neutral clusters we cannot rely on any reference instrument, but the concentration of 3–5 nm particles measured with PH-CPC correspond usually well to the NAIS and DMPS.

5 Our results support the concept that formation of clusters and their activation for growth are two distinct processes (Kulmala et al., 2000). Neutral clusters are readily formed in the night-time, when no particle formation is observed. The connection to daytime particle formation events remained still somewhat uncertain: on average the cluster concentration and formation rate remained close to stable during the event. The applicability of PH-CPC method to study new particle formation is however limited by
10 its sensitivity to background aerosol concentration.

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Analysis of atmospheric molecular clusters

K. Lehtipalo et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Analysis of atmospheric molecular clusters

K. Lehtipalo et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Analysis of atmospheric molecular clusters

K. Lehtipalo et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Analysis of atmospheric molecular clusters

K. Lehtipalo et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Analysis of atmospheric molecular clusters

K. Lehtipalo et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Analysis of
atmospheric
molecular clusters**

K. Lehtipalo et al.

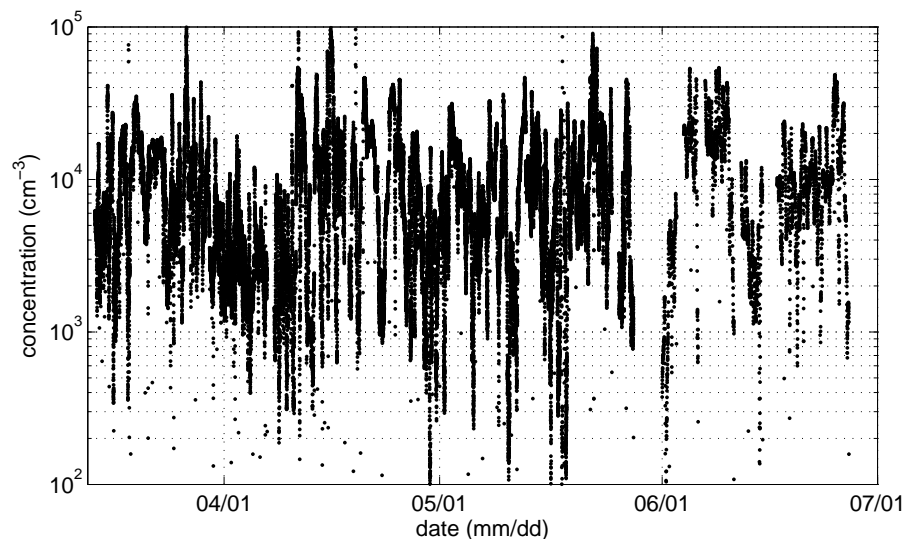


Fig. 1. Total number concentration of <3 nm clusters measured with PH-CPC in Hyytiälä 14 March–26 June 2007.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

**Analysis of
atmospheric
molecular clusters**

K. Lehtipalo et al.

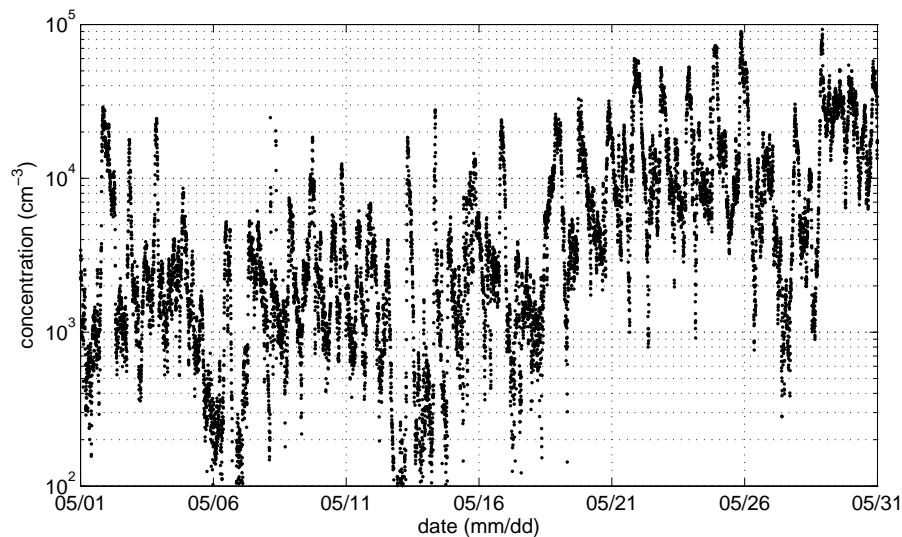


Fig. 2. Total number concentration of <3 nm neutral clusters measured with PH-CPC in Hyytiälä 1–31 May 2008.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Analysis of
atmospheric
molecular clusters

K. Lehtipalo et al.

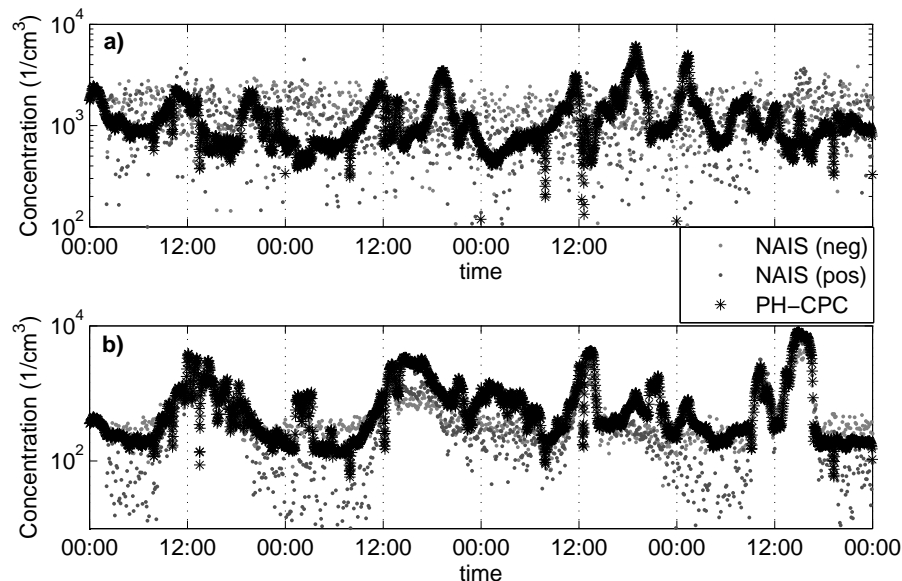


Fig. 3. Total number concentration of **(a)** clusters 1.5–3 nm and **(b)** particles 3–5 nm measured with PH-CPC (black stars) and NAIS (gray dots) on 31 March–3 April 2007 in Hyytiälä.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

**Analysis of
atmospheric
molecular clusters**

K. Lehtipalo et al.

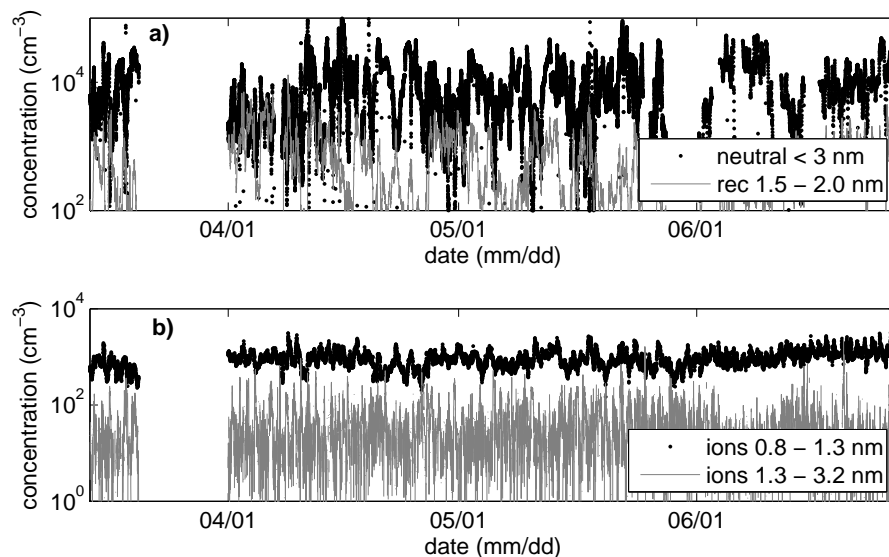


Fig. 4. (a) Number concentration of <3 nm neutral clusters (black dots) and 1.5–2 nm recombination products (gray line), (b) concentration of ions 0.8–1.3 nm (black dots) and 1.3–3.2 nm (gray line). Data are calculated from PH-CPC and BSMA measurements in March–June 2007 in Hyttiälä.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

**Analysis of
atmospheric
molecular clusters**

K. Lehtipalo et al.

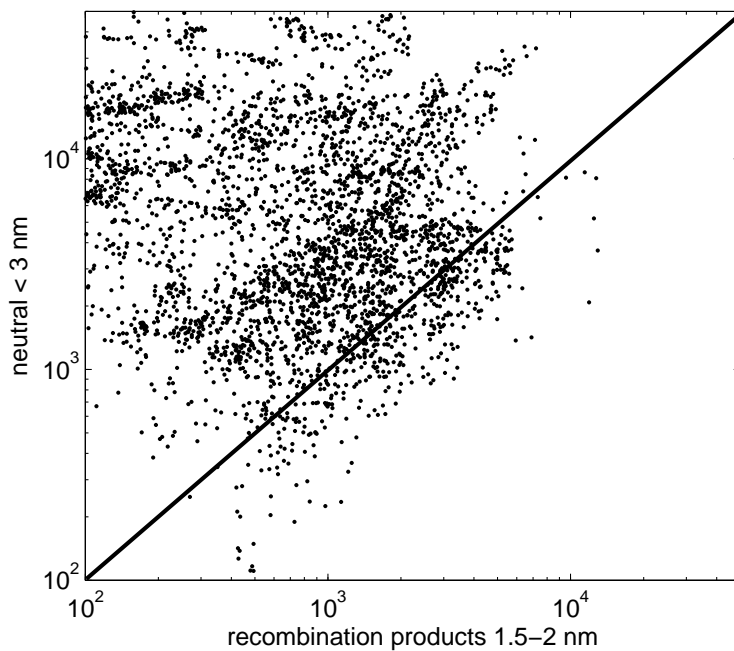


Fig. 5. Neutral <3 nm clusters compared to 1.5–2 nm recombination products. Data are calculated from PH-CPC and BSMA measurements in April 2007 in Hyytiälä.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Analysis of atmospheric molecular clusters

K. Lehtipalo et al.

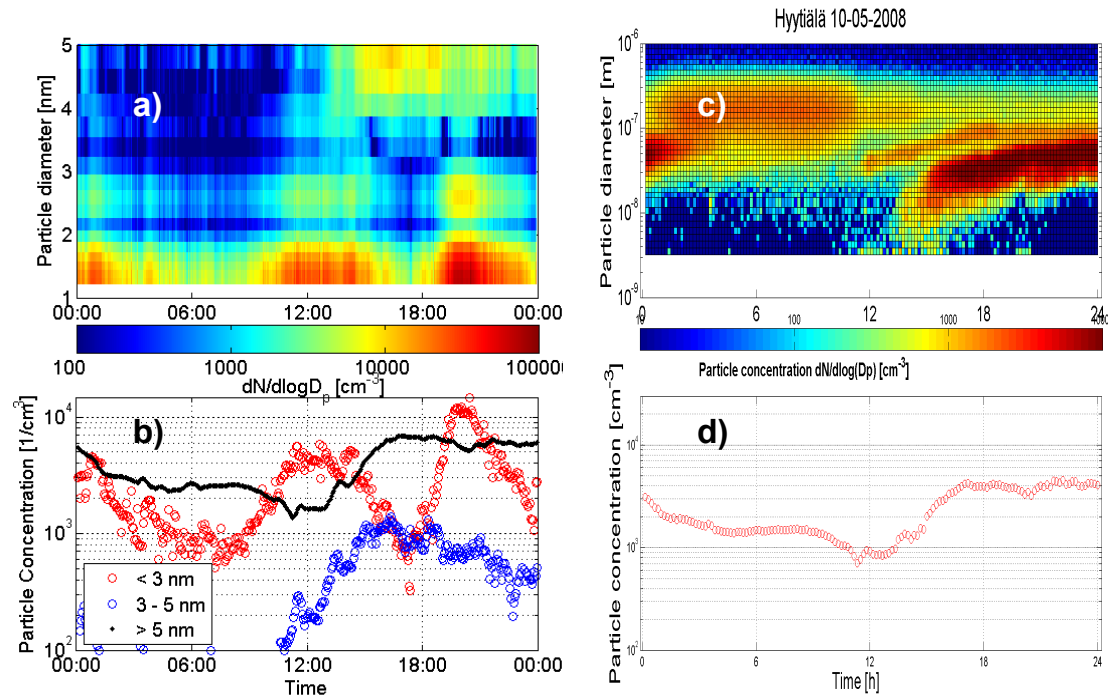


Fig. 6. Example of a new particle formation event day in Hyytiälä, 10 May 2008. **(a)** Number size distribution measured with PH-CPC, **(b)** total number concentration of <3 nm neutral clusters (red circles), 3–5 nm particles (blue circles) and >5 nm particles (black dots) measured with PH-CPC, **(c)** number size distribution measured with DMPS, **(d)** total number concentration measured with DMPS.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Analysis of
atmospheric
molecular clusters

K. Lehtipalo et al.

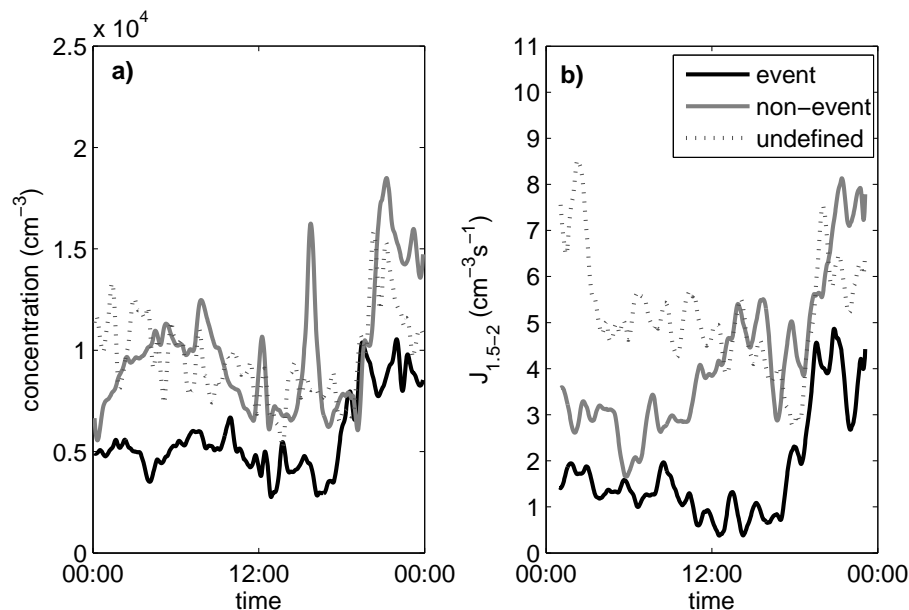


Fig. 7. Median diurnal variation of **(a)** total <3 nm cluster concentration and **(b)** 1.5–2 nm neutral cluster formation rate in April–May 2007 in Hyytiälä. Days are classified into event (black line, 14 days), non-event (gray line, 8 days) and undefined (dashed line, 13 days) according to Dal Maso et al. (2005).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Analysis of
atmospheric
molecular clusters

K. Lehtipalo et al.

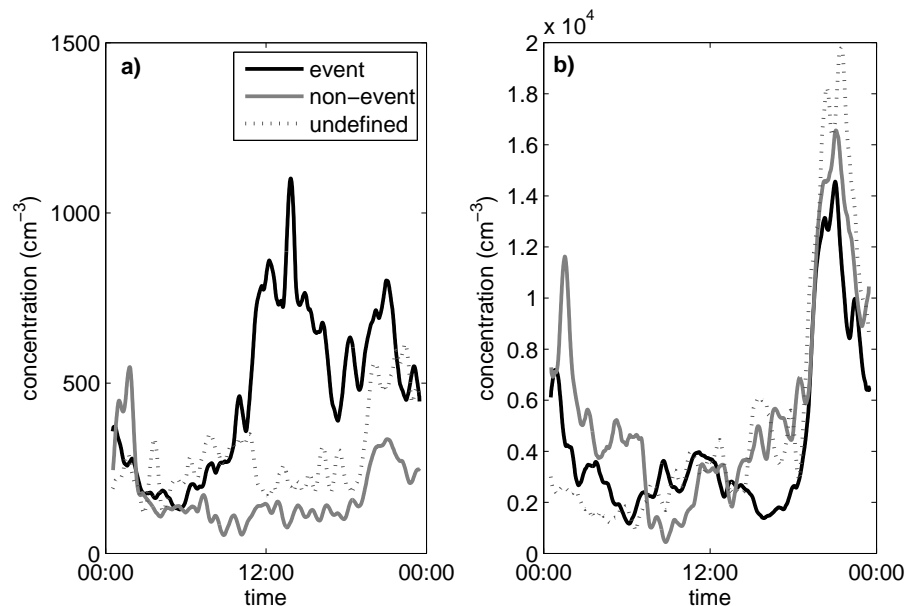


Fig. 8. Median diurnal variation of **(a)** 3–5 nm particle concentration and **(b)** <3 nm neutral cluster concentration in May 2008 in Hyytiälä. Days are classified into event (black line, 16 days), non-event (gray line, 2 days) and undefined (dashed line, 13 days) according to Dal Maso et al. (2005).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Analysis of
atmospheric
molecular clusters

K. Lehtipalo et al.

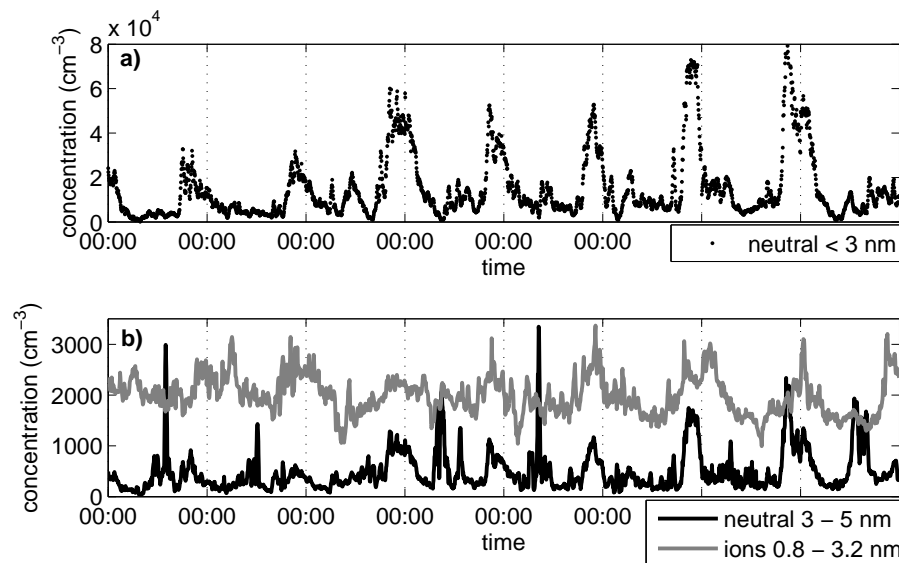


Fig. 9. Nocturnal cluster formation in Hyytiälä 19 May 2008–26 May 2008. Concentrations of **(a)** neutral <3 nm clusters, **(b)** 3–5 nm neutral particles (black line) and 0.8–3.2 nm ions (gray line).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)