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Characteristics of new particle formation events and cluster ions at K-puszta, Hungary

Taina Yli-Juuti[1)], Ilona Riipinen[1)], Pasi P. Aalto[1)], Tuomo Nieminen[1)], Willy Maenhaut[2)], Ivan A. Janssens[3)], Magda Claeys[4)], Imre Salma[5)], Rita Ocskay[5)], András Hoffer[6)], Kornélia Imre[6)] and Markku Kulmala[1)]

[1)] *Department of Physics, P.O. Box 64, FI-00014 University of Helsinki, Finland*
[2)] *Department of Analytical Chemistry, Ghent University, Proeftuinstraat 86, B-9000 Gent, Belgium*
[3)] *Department of Biology, University of Antwerp, Universiteitsplein 1, B-2610 Antwerpen, Belgium*
[4)] *Department of Pharmaceutical Sciences, University of Antwerp, Universiteitsplein 1, B-2610 Antwerpen, Belgium*
[5)] *Institute of Chemistry, Eötvös University, P.O. Box 32, H-1518 Budapest, Hungary*
[6)] *Department of Earth and Environmental Sciences, University of Pannonia, P.O. Box 158, H-8201 Veszprém, Hungary*

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Atmospheric new particle formation events were analyzed based on particle size distributions measured with a Differential Mobility Particle Sizer (DMPS) and an Air Ion Spectrometer (AIS) during the BIOSOL (Formation mechanisms, marker compounds, and source apportionment for biogenic atmospheric aerosols) campaign on 22 May–29 June 2006 at the K-puszta measurement site in Hungary. The particle size distribution data were classified into different new particle event classes and growth and formation rates of the particles were calculated. New particle formation was observed on almost all days and the median diameter growth rates of nucleation mode particles increased with increasing particle size. The observed formation rate of 10 nm particles was typically somewhat larger than 1 cm^{-3} s^{-3} (median 1.2), and the growth rate for sub 3 nm particles was 1.7 nm h^{-1} and for nucleation mode 6 nm h^{-1}. The ambient concentrations of gases or meteorological data were not able to explain the differences in the growth and formation rates or in the particle formation between the days. However, 0.3–1.8 nm cluster ion concentrations correlated negatively with wind speed.

Introduction

New particle formation events, i.e. the formation of new secondary aerosol particles from vapours by nucleation and their subsequent growth by vapour condensation, have been observed in the atmosphere worldwide in a variety of urban and rural sites (Kulmala *et al*. 2004b), including boreal forests (Mäkelä *et al*. 1997), polluted megacities (Stanier *et al*. 2004, Mönkkönen *et al*. 2005) as well as coastal, Antarctic, alpine and savannah environments (Weingartner *et al*. 1999,

Koponen *et al*. 2003, O'Dowd and Hoffmann 2005, Laakso *et al*. 2008). These particles likely have a significant effect on regional and global climate patterns directly and by acting as cloud condensation nuclei if they reach sufficient sizes (e.g. Lohmann and Feichter 2005, Spracklen *et al*. 2006). The exact magnitude of this effect, however, is still among the largest single uncertainties in atmospheric radiative forcing calculations (IPCC 2007).

To quantify the global aerosol source provided by secondary particle formation, it is necessary to further characterise the variety of environments in which new particle formation and subsequent particle growth take place. Also, information on the formation and growth mechanisms and the atmospheric vapours participating in them is needed. Although there have been several studies on atmospheric secondary particle formation, the reasons and mechanisms behind these events are still not completely known (Kulmala 2003). In many environments sulphuric acid has been identified as a potential component in atmospheric aerosol formation (Weber *et al*. 1996, Korhonen *et al*. 1999, Kulmala *et al*. 2006, Sihto *et al*. 2006, Riipinen *et al*. 2007). However, sulphuric acid is typically not solely able to explain the growth of the particles (Boy *et al*. 2005) and therefore the role of organic vapours on atmospheric particle formation and growth has also been investigated in many studies (e.g. Kulmala *et al*. 2004a). In particular the growth rates of the newly formed particles have been observed to correlate with the emissions of biogenic organic vapours (e.g. Dal Maso *et al*. 2005, Tarvainen *et al*. 2007).

Atmospheric neutral and charged clusters below 3 nm have been proposed to be key players in atmospheric particle formation processes (Kulmala *et al*. 2000, Kulmala *et al*. 2005). Observations on neutral atmospheric clusters are still scarce due to the lack of suitable commercial instrumentation (for the first observations of atmospheric neutral clusters, *see* e.g. Kulmala *et al*. 2007a, 2007b, Sipilä *et al*. 2008). Charged clusters, however, can be observed with ion spectrometers such as the Balanced Scanning Mobility Analyzer (BSMA, Tammet 2006) and Air Ion Spectrometer (AIS, Mirme *et al*. 2007). Although the concentrations of ion clusters are highly dependent on the ionisation intensity of the atmosphere, they can be used to give an indication on the evolution of neutral clusters since their sinks are similar.

New particle formation event classification is used to gain information about the mechanisms behind atmospheric new particle formation events. In many cases, event classification is done on day-to-day basis separating days into event and non-event days. The event days may also be divided into different subgroups. Comparing atmospheric parameters during event and non-event days and event frequencies at various measurement sites may indicate which parameters are controlling or are involved in new particle formation. Recently, several new particle formation event classification studies became available and the event classification schemes used in them slightly differ (*see* e.g. Dal Maso *et al*. 2005, Hirsikko *et al*. 2007, Boy *et al*. 2008, Suni *et al*. 2008, Svenningsson *et al*. 2008, Vana *et al*. 2008).

In this study, we analyse the characteristics of new particle formation events during the BIOSOL measurement campaign in the early summer of 2006 at the K-puszta measurement site on the Great Hungarian Plain. First, we study the frequency and intensity of secondary particle formation and growth based on size distributions of both neutral and naturally charged aerosol particles. Second, we compare the characteristics of particle formation events with ambient conditions and available gas and particle phase data measured at the site (e.g. Maenhaut *et al*. 2008a). Third, we study the behaviour of atmospheric ion clusters during the measurement period. The methods followed in this study are to a large extent the same as those previously applied to the data from the SMEAR II (Station for Measuring Ecosystem–Atmosphere Relations) forest station which is situated in a rural boreal forest environment in Hyytiälä, southern Finland (for the site description *see* Hari and Kulmala 2005). Thus, to put our observations into perspective, the results from this study are compared with corresponding results from Hyytiälä and with the results obtained in recent studies from a few other sites where the same or similar methods were used.

Materials and methods

Site description and particle size distribution measurements

The data used in this work was obtained at the K-puszta measurement site (46°58´N, 19°35´E, 125 m a.s.l.) in Hungary during the BIOSOL (Formation mechanisms, marker compounds, and source apportionment for biogenic atmospheric aerosols) campaign between 22 May and 29 June 2006. K-puszta is a rural measurement site located on the Great Hungarian Plain (Horváth and Sutton 1998), 15 km northwest from the nearest town Kecskemét, and 80 km southeast from Budapest. The surroundings of the measurement site are dominated by mixed forest (62% coniferous, 28% deciduous) and grassland (10%), while the soil around the site is sandy. The site is characterised by intensive solar radiation during summer. The station is involved in the Global Atmospheric Watch (GAW) network and the European Monitoring and Evaluation Programme (EMEP) and it is equipped with a variety of instrumentation measuring trace gases and the composition of particulate matter (*see* http://www.nilu.no/projects/ccc/sitedescriptions/hu/index.html for a detailed description of the site).

Maenhaut *et al*. (2008a) studied the composition of atmospheric particulate matter during the BIOSOL campaign and observed that the campaign time could be divided into two periods: from the start of the campaign until 11 June 2006 when it was unusually cold with daily maximum temperatures between 12 and 23 °C, and from 12 June 2006 onward when the temperatures were considerably higher with daily maxima ranging from 24 to 36 °C. During the cold period the air masses came mainly from the northwest over the North Sea or the Atlantic Ocean whereas after 12 June 2006, i.e. during the warm period, the air masses were continental. The atmospheric concentrations of the PM and most species and elements were higher during the warm period. There was also a difference in atmospheric concentrations of trace gases and selected particulate species: daily average concentrations of SO_2, SO_4^{2-}, NH_4^+, NH_3, and HNO_3 were higher during the warm period than during the cold period, although the concentrations started to rise already on 8 June 2006 On the other hand, NO_2 and NO_3^- concentrations did not clearly differ between the two periods. The amounts of NO_3^- and SO_4^{2-} were measured by ion chromatography, while those of SO_2 and HNO_3 were determined by ion chromatography as sulphate and nitrate. Concentrations of NH_3, NH_4^+ and NO_2 were determined using a spectrophotometric method. Ambient concentrations of isoprene and monoterpenes were measured with the high-frequency proton transfer reaction mass spectrometry technique (PTR-MS, IONICON, Innsbruck, Austria), which was calibrated with a standard gas mixture (Ozon precursor mix, RESTEK, US) containing 57 VOCs including isoprene at a concentration of 40 ppb. Concentrations of both isoprene and monoterpenes were higher during the warm than the cold period (Maenhaut *et al*. 2008b).

The main experimental data set used in this study was the aerosol particle size distribution data. The size distributions of aerosol particles 10–1000 nm in diameter were measured with a self-made Differential Mobility Particle Sizer (DMPS) (Aalto *et al*. 2001). DMPS is classifying particles according to their electrical mobility. Aerosol samples were taken from the height of two meters, one meter away of the station wall. No special inlet was used, just a rain cover, and the sampling line was 4 mm diameter copper tubing. The aerosol was dried with a Topas aerosol drier and neutralized with a self-made neutralizer containing a 370 MBq Ni-63 beta source (Nycomed Amersham model NBC3). The aerosol classifier was a copy of a Hauke-type differential mobility analyzer (DMA). The sample and sheath flow rates were 1 and 5 LPM, respectively. One size spectrum was measured in six and half minutes. The particle counter was a TSI model 3010 condensation particle counter (CPC). Since a drier is used, the DMPS measures the dry size of the particles.

In order to also obtain information on particles smaller than 10 nm, we utilized the size distributions of naturally charged aerosol particles i.e. air ions in the mobility range 3.2–0.0013 $cm^2\ V^{-1}\ s^{-1}$ which corresponds to 0.34–40 nm in Tammet diameters (Mäkelä *et al*. 1996) measured with an Air Ion Spectrometer (AIS) (Mirme *et al*. 2007). The AIS has two identical cylindri-

cal aspiration-type DMAs, one for each polarity, that have 21 insulated collectors which measure the electric current carried by the ions. The sample flow rate in each DMA was 30 LPM and the sheath flow rate was 60 LPM.

Classification of new particle formation events

The days during the measurement period were classified with respect to whether or not new particle formation (NPF) was observed. To identify NPF event days from the DMPS data we used the criteria established by Dal Maso *et al*. (2005). To classify the AIS data with respect to particle formation, we introduced a modified classification scheme and combined the criteria developed by Dal Maso *et al*. (2005), Hirsikko *et al*. (2007) and Vana *et al*. (2008). Hirsikko *et al*. (2007) classified NPF events detected with a Balanced Scanning Mobility Analyzer (BSMA) measuring the size distribution of air ions in the size range 0.4–7.5 nm (Tammet 2006) and Vana *et al*. (2008) classified NPF events detected with an AIS. (For classification scheme and examples of particle size distributions in different classes *see* Table 1 and Fig. 1, respectively.)

Compared with the event classifications of Dal Maso *et al*. (2005) and Hirsikko *et al*. (2007), Vana *et al*. (2008) used three new classes: 'mixed-type', 'apple' and 'hump'. 'Mixed-type' days are days when some new particle formation is detected but the day does not satisfy the criteria of any other event class. This new class is added to reduce the number of days when particle formation is clearly detected but the day is classified into class 'undefined' because the event does not satisfy criteria of any other event class. 'Apples' refer to bursts of small,

Table 1. Criteria for classifying days with respect to new particle formation.

Class and the instrument(s)	Criteria
Class Ia (DMPS and AIS)	There is a new mode with growing mean diameter smaller than 25 nm. The mode is homogeneous enough to further analyse the event (e.g. to calculate particle growth and formation rates). The event starts from cluster sizes (AIS) or from about lower detection limit 10 nm (DMPS) and continues over 25 nm. These are the "model" events.
Class Ib (DMPS and AIS)	There is a new mode with growing mean diameter smaller than 25 nm. The mode is homogeneous enough to further analyse the event (e.g. to calculate particle growth and formation rates). The event does not have to start from cluster mode or continue over 25 nm, or there might be a gap (temporary very low particle concentration) in the growth of the mode.
Class II (DMPS and AIS)	There is a new mode with growing mean diameter smaller than 25 nm. Due to disturbances in the data or unclear shape of the event it is not necessarily possible to analyse the growth and formation rates.
Apple (AIS)	There is a new mode in the size range between clusters and 25 nm but the mean diameter of the mode does not grow. There is a clear gap (i.e. very low concentration) between the new mode and other modes. The event lasts more than two hours.
Hump (AIS)	There is a nucleation burst starting from the cluster mode but the growth does not continue to larger sizes than 10 nm.
Rain (AIS)	Rain-induced ion bursts in nucleation mode size range.
Mixed-type (AIS)	There are new particles in the size range smaller than 25 nm. The day does not have features of class I, II, apple or hump, or it has features of many of these classes. For example those ion bursts that cannot be explained by rain.
Non-event (DMPS and AIS)	No new particle mode in the size range less than 25 nm in diameter.
Undefined (DMPS and AIS)	Days when it cannot be said whether there is an event or not. Uncertainty can be caused, for example, by disturbances in data or by rapid changes in particle concentrations.
Bad data (DMPS and AIS)	More than 8 hour data missing or the data has a lot of disturbances. If there is data missing but a clear particle formation event is seen, the day is classified according to the event.

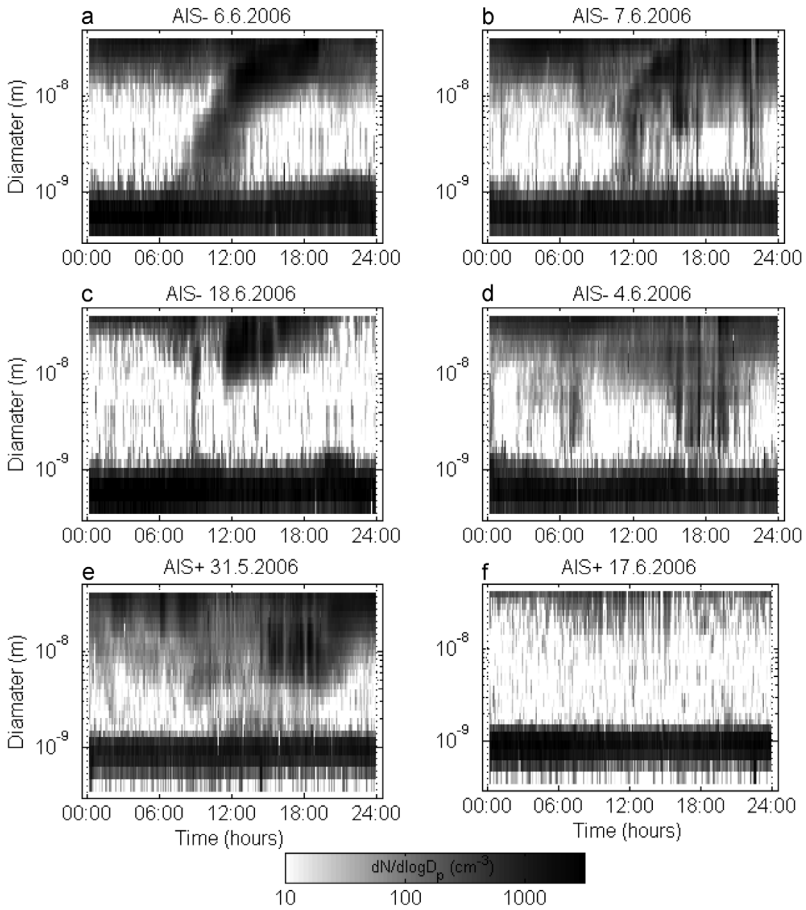

Fig. 1. Examples of size distribution spectra measured with the AIS, and classified with respect to particle formation and growth according to the criteria given in Table 1. (**a**) class Ia event, (**b**) class Ib event, (**c**) class II event, (**d**) rain-event, (**e**) mixed-type, (**f**) non-event.

less than 25 nm in diameter, particles that form a new mode but do not show clear growth (contrary to class I and II, so called 'banana'-type events; e.g. Heintzenberg *et al*. 2007) and are not connected to the continuous ion cluster pool at sizes 0.5–1.8 nm. 'Humps' are growth episodes of the cluster mode that never, however, reach sizes over a few nanometer. However, in order to have for AIS data a compatible classification with DMPS data we do not use the classification scheme of Vana *et al*. (2008) as such since they did not divide the 'banana'-type events into subgroups like Dal Maso *et al*. (2005) and Hirsikko *et al*. (2007).

The event classification was done visually from the surface plots of particle size distribution for one day at the time. It was done by a panel of three researchers to minimize the subjectiveness of the classification. When the days are classified according to whether or not NPF is observed, a day can belong only to one class. The criteria summarized in Table 1 were gone through from the top to the bottom. First, it was considered whether the day belongs to class Ia. If this was not the case, it was considered whether the day belongs to class Ib and so on, until the class 'undefined', which contains all days that do not fulfil the criteria of any other class. The days during which particle size distribution data was missing for more than 8 hours were put in the class 'bad data' and removed from the days to be further analysed unless a clear class Ia, Ib or II event was detected.

Particle growth rates

To study the amount of atmospheric vapours condensing to the particles, we determined the particle growth rates during the NPF events with

the method reported by Hirsikko *et al*. (2005). Particle growth rate (GR) refers here to the growth rate of the average diameter of the particles. The method is based on determining the moment in time when the concentration in each size fraction reaches its maximum. The growth rate of different-sized particles was obtained by fitting a line to the particle sizes as a function of the timing of the maximum concentration for the size classes. We calculated the growth rates from the AIS data for the same size classes as Hirsikko *et al*. (2005) used, i.e. 1.3–3 nm, 3–7 nm and 7–20 nm in mobility equivalent diameter, for both polarities separately. As the DMPS setup had the lower measuring limit at 10 nm, we calculated the growth rates from the DMPS data only for the size class 10–20 nm. The magnitudes of the growth rates were compared with ambient meteorological and trace gas data.

Particle formation rates and condensation sink values

The intensity of particle formation is characterised by the rate at which new particles are formed. We calculated the formation rates of nucleation mode particles larger than 10 nm (J_{10}) and condensation sink (CS) based on the DMPS data with the same methods as used by Dal Maso *et al*. (2005). The formation rate is thus expressed as

$$J_{10} = \frac{dN_{10-25}}{dt} + F_{Coag} + F_{GR}, \quad (1)$$

where N_{10-25} is the concentration of nucleation mode particles in size range 10–25 nm, t is time, and F_{Coag} and F_{GR} represent the losses due to coagulation and growth out of the considered size range. The method to calculate J_{10} thus takes into account the change of number concentration of nucleation mode particles, the rate of loss of particles due to coagulation and the flux of particles out of the nucleation mode size range due to condensational growth.

We calculated the CS based on the dry size of the particles measured with DMPS since there was no data available on the hygroscopicity of the particles at K-puszta. The CS values reported here thus represent a minimum estimate for the real condensation sink. The particle formation rate and condensation sink values were compared to ambient meteorological and trace gas data.

Ion cluster concentrations

We calculated the ion cluster concentrations between 0.3–1.8 nm based on the AIS size distribution data. The cluster concentrations were compared to ambient measurements on meteorological data and trace gas species to find indications of conditions that are favourable for cluster ions.

Sulphuric acid proxy

Sulphuric acid is likely to play a role in atmospheric particle formation and growth (e.g. Weber *et al*. 1996, Sihto *et al*. 2006, Riipinen *et al*. 2007), hence it is interesting to compare the concentrations of gaseous sulphate with the determined formation and growth rates. As there were no sulphuric acid measurements done at K-puszta during the period analysed in this study, we calculated a simple proxy for sulphuric acid using measurements of gaseous SO_2 and global radiation.

H_2SO_4 is formed in the atmosphere from the oxidation of SO_2 by OH. OH, on the other hand, is formed in the reaction between H_2O and excited oxygen atom $O(^1D)$ which results from the photolysis of O_3 (Seinfeld and Pandis 2006). Thereby, a rough proxy for the behaviour of H_2SO_4 vapour concentration ($[H_2SO_4]$) was calculated by (Petäjä *et al*. 2008)

$$[H_2SO_4] \propto \frac{[SO_2]\mathrm{GlobR}}{\mathrm{CS}}, \quad (2)$$

where $[SO_2]$ is the sulphur dioxide concentration, GlobR is global radiation intensity and CS is the condensation sink. Equation 2 does not, of course, give the absolute value of the H_2SO_4 concentration nor does it even have the right units for $[H_2SO_4]$, since reaction coefficients are not included. However, Eq. 2 can be used to compare the possible concentrations of H_2SO_4 vapour on different days.

The SO_2 concentration data were available as 24-hour averages (period starting at 09:00 CET) (Fig. 2a). Meteorological data were available with 10-minute time resolution but for calculating the daily average approximation of $[H_2SO_4]$ 24-hour averages (from 00:00 to 24:00) (Fig. 2c) were calculated from the global radiation data (Fig. 2b) with 10-min time resolution and the same kind of average was calculated for the condensation sink. By doing so, GlobR and CS did not have the same averaging time periods as $[SO_2]$, but this selection was reasonable as the period from midnight to midnight is more suitable when analysing NPF events due to the fact that new particle formation is sometimes observed to start already in the early hours of the morning. The sulphuric acid proxy obtained was then compared with the calculated particle growth and formation rates, condensation sink and ion cluster concentrations.

Results and discussion

New particle formation event statistics

The median number concentrations of negative and positive nucleation mode ions (i.e. ions in size range 1.8–25 nm) were 111 cm^{-3} and 90 cm^{-3}, respectively, reaching values higher than 500 cm^{-3} during new particle formation events (Fig. 2e and f). The median total number concentration of nucleation mode particles (10–25 nm) calculated from DMPS data was 521 cm^{-3} reaching values between 3000–30 000 cm^{-3} during new particle formation events (Fig. 2g). The *x*-axis in Fig. 2 is divided into two at 12 June 2006, following the division of the data into the cold and warm periods (*see* Fig. 2d) by Maenhaut *et al*. (2008a). It seems that the nucleation mode ion concentrations were on average slightly lower during the warm period than during the cold period.

There was new particle formation during more than half of the analysed days (Table 2). We observed new particle formation and subsequent growth according to the DMPS data on a total of 26 days. The corresponding numbers according to data from the AIS were 20 and 18 for negative and positive particles, respectively. There was only one day which was classified as a non-event day according to data from both DMPS and AIS (both polarities). The difference in the observed number of event days between DMPS and AIS is logical since DMPS detects all the particles where as AIS detects only naturally charged particles.

In the classification of the AIS data there were 9 and 12 days for negative and positive polarities, respectively, while no class Ia, Ib or II event was observed but there was clearly some kind of particle formation below the 25 nm size limit. Seven of these days are explained by rain and the other days are classified as 'mixed-type'. During the rainy days there were new ions observed in sizes from cluster ions to over 25 nm in diameter simultaneously with the rain. These kinds of rain-induced ion bursts have been observed also at other sites, e.g. Hyytiälä (Hirsikko *et al*. 2007, *see* also Tammet *et al*. 2009 for a possible explanation of the phenomenon). The reasons behind the 'mixed-type' events are not known but one possible explanation could be, for example, a local pollution burst.

The observed event frequency is large, for instance compared to results from measurements done at the boreal forest site in Hyytiälä, where on average 25% of the days each year are typically classified as event days (Dal Maso *et al*. 2005, Hirsikko *et al*. 2007), or in the coastal site Mace Head, where on 57% of days new particle formation is detected with AIS, of which 12% are banana-type events (Vana *et al*. 2008). On

Table 2. NPF event classification statistics.

Event class	Number of days according to		
	DMPS	AIS neg.	AIS pos.
Class Ia	2	1	1
Class Ib	14	16	15
Class II	10	3	2
Apple	Not classified	0	0
Hump	Not classified	0	0
Rain	Not classified	7	7
Mixed-type	Not classified	2	5
Non-event	1	3	3
Undefined	9	3	2
Bad data	1	4	4

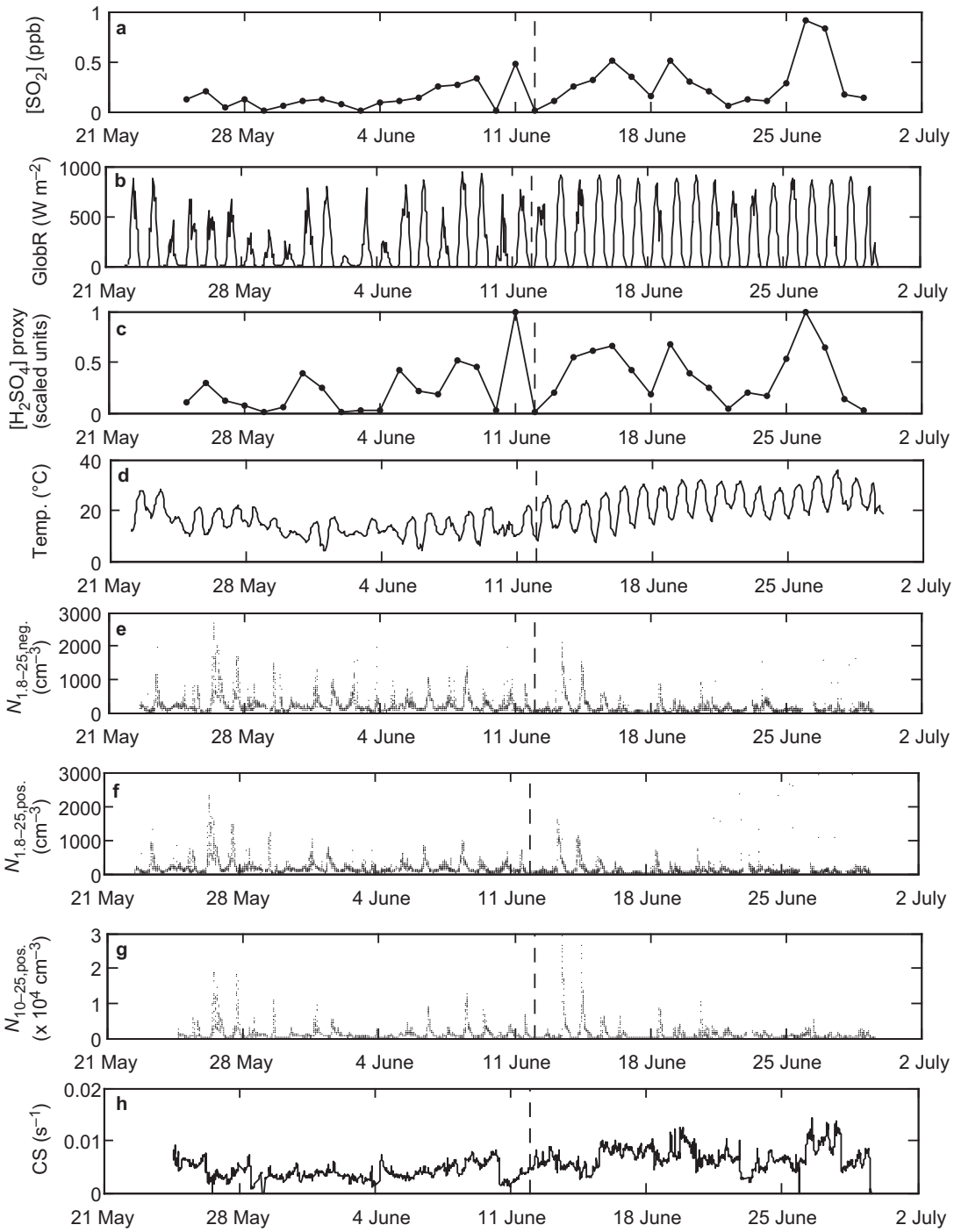

Fig. 2. Time series of (**a**) the concentration of sulphuric dioxide, (**b**) global radiation, (**c**) sulphuric acid proxy [H_2SO_4] (units scaled with maximum value), (**d**) temperature, (**e**) negative and (**f**) positive nucleation mode ions from AIS data, (**g**) total concentration of nucleation mode particles from DMPS data, and (**h**) condensation sink in May–June 2006. The *x*-axes are divided into the cold and warm periods by a line at 12 June.

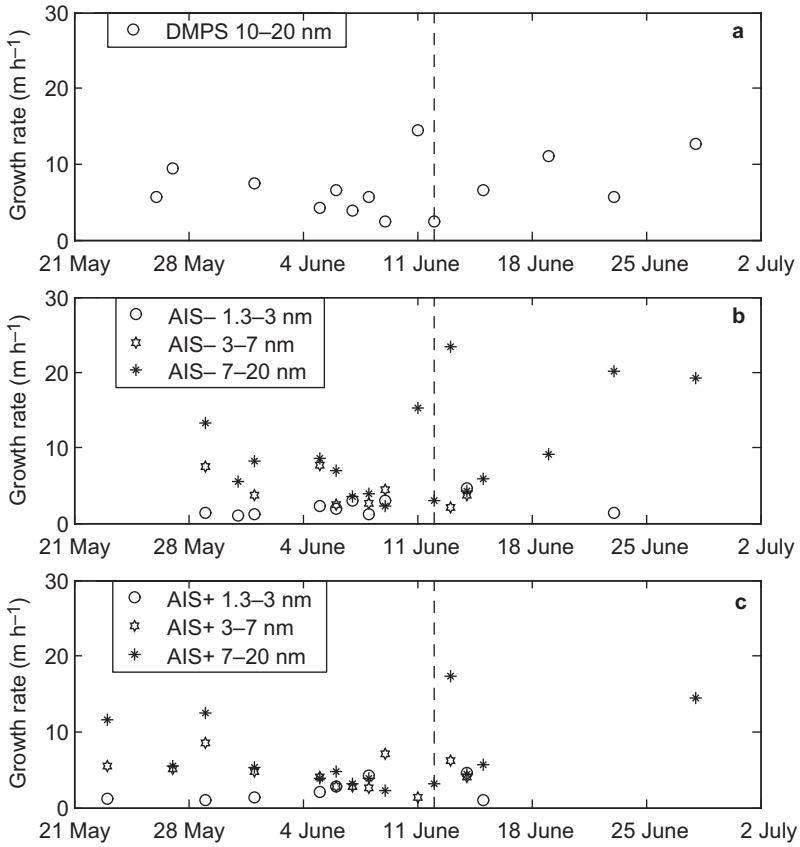

Fig. 3. Daily mean growth rates of different size nucleation mode particles in May–June 2006 calculated from the data from (**a**) DMPS, (**b**) AIS for negative ions, and (**c**) AIS for positive ions. The *x*-axes are divided into the cold and warm periods by a line at 12 June.

the other hand, at the Australian Eucalypt forest site Tumbarumba according to AIS measurements NPF events corresponding to our classes Ia, Ib and II take place on average 52% of days (Suni *et al*. 2008). It thus seems that the conditions at the K-puszta site are favourable to secondary particle formation. However, in this study the measurement period was too short to draw general conclusions about e.g. the annual mean of the number of event days.

Growth rates of particles

We calculated the growth rates (GR) of the particles from the AIS data for three size classes: 1.3–3 nm, 3–7 nm and 7–20 nm, and from the DMPS data for one size class which was 10–20 nm. In this analysis only class Ia and Ib days were included. The median growth rate was 1.7 nm h^{-1} for sub 3 nm particles (ions), about 4 nm h^{-1} for 3–7 nm particles (ions) and about 6 nm h^{-1} for nucleation mode (7–20 nm) particles (Table 3). The growth rates were slightly larger during the warm period than during the cold one (Fig. 3).

On average, there was a size dependency in the particle growth rates so that the larger the

Table 3. Median, minimum and maximum values of growth and formation rates of particles and condensation sink.

	Median	Min	Max
$GR_{AIS\ positive\ 1.3–3\ nm}$ (nm h^{-1})	1.7	1.0	4.6
$GR_{AIS\ negative\ 1.3–3\ nm}$ (nm h^{-1})	1.7	1.0	4.6
$GR_{AIS\ positive\ 3–7\ nm}$ (nm h^{-1})	4.5	1.4	8.6
$GR_{AIS\ negative\ 3–7\ nm}$ (nm h^{-1})	3.7	2.2	7.7
$GR_{AIS\ positive\ 7–20\ nm}$ (nm h^{-1})	5.0	2.2	17.4
$GR_{AIS\ negative\ 7–20\ nm}$ (nm h^{-1})	7.6	2.2	23.5
$GR_{DMPS\ 10–20\ nm}$ (nm h^{-1})	6.1	2.4	14.4
J_{10} (cm^{-3} s^{-1})	1.2	0.1	9.4
CS ($\times 10^{-3}$ s^{-1})	5.0	0.6	14.4

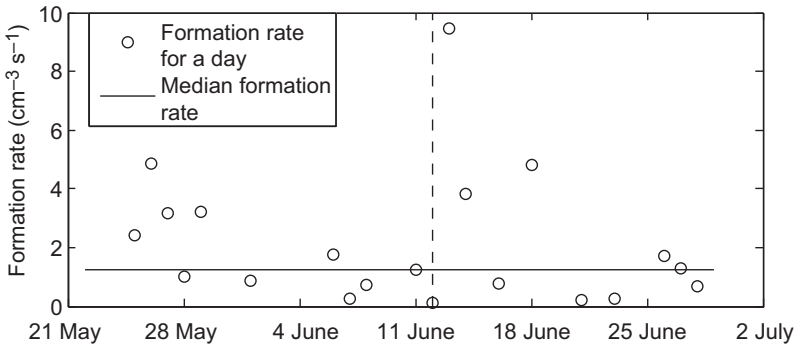

Fig. 4. Daily mean formation rates of nucleation mode particles and the median for them in May–June 2006. The *x*-axis is divided into the cold and warm periods by a line at 12 June.

particle, the larger the growth rate. This kind of size-dependent growth of particles is in line with previous observations from Hyytiälä (Hirsikko *et al*. 2005) and Tumbarumba (Suni *et al*. 2008). The size-dependency in growth rates indicates that there are different factors, for instance different vapours, affecting the growth of different-sized particles. On the other hand, the results may also indicate that there is a time-dependency in the growth of particles. As the growth of larger particles occurs after the growth of smaller particles during the NPF events, the ambient conditions, e.g. concentrations of condensing vapours, may have changed from the initial ones during the growth process. Therefore, the apparent size-dependency in particle growth rates may be a sign of a time-dependency of growth rates.

There also seems to be a difference in the growth rates between different polarities: the negative particles have lower median growth rate than positive particles in size range 3–7 nm but the reverse is seen for the size range 7–20 nm. There is no reason to assume that particles with different polarities have different GRs. Therefore, the difference in calculated GRs between the two polarities is probably due to two factors: first, there is some uncertainty in the method, and, second, it was not possible to obtain the GR for both polarities for all the events. At least in size range 3–7 nm the difference in GR between polarities is small enough to be interpreted as a result of inaccuracy of the method.

Typically GRs of nucleation mode particles vary in range 1–20 nm h^{-1} in midlatitudes (Kulmala *et al*. 2004b). The GRs obtained in this study fall between these values and the variation of GR with respect to size is similar as at Hyytiälä (Hirsikko *et al*. 2005) and Tumbarumba (Suni *et al*. 2008).

Formation rates of 10 nm particles and condensation sink values

The median, minimum and maximum values of the daily formation rates of nucleation mode particles larger than 10 nm (J_{10}) were 1.2, 0.1 and 9.4 cm^{-3} s^{-1}, respectively (Table 3). The formation rates of nucleation mode particles did not differ significantly between the cold and warm periods (Fig. 4). In Hyytiälä, the mean formation rate of nucleation mode particles is 0.8 cm^{-3} s^{-1} and it varies in the range 0.06–5 cm^{-3} s^{-1} (Dal Maso *et al*. 2005); however, it should be noted that the formation rate of nucleation mode particles for Hyytiälä is calculated with a lower limit of 3 nm. Although the maximum J_{10} at K-puszta was 9.4 cm^{-3} s^{-1}, only this one value was higher than formation rates in Hyytiälä. It can be concluded that the intensity of the particle formation in K-puszta during the observed period is at the higher end of the typical rates at remote sites (Kulmala *et al*. 2004b).

The median value of the CS at K-puszta was 5.0×10^{-3} s^{-1}; during days classified as non-event days according to the AIS data, the CS was 6.1×10^{-3}–7.9×10^{-3} s^{-1}, which are typical values for fairly remote continental sites (e.g. Dal Maso *et al*. 2007) (Table 3 and Fig. 2h). The daily average CS during the only day classified as a non-event day according to both the DMPS and the AIS data was 7.9×10^{-3} s^{-1}. The values of the CS obtained in the current study for K-puszta are higher but roughly in the same range as values of

the CS at Hyytiälä, where the average CS without hygroscopic correction is 2.4×10^{-3} s^{-1}.

Comparison between particle formation characteristics and ambient data

We compared the daily average concentrations of trace gases (SO_2, NH_3, HNO_3 and NO_2) and selected particulate species (SO_4^{2-}, NH_4^+ and NO_3^-) and daily average and maximum meteorological conditions with the NPF event classification, but no very clear differences in these data between event and non-event days were found. However, on the only day classified as a non-event day according to both DMPS and AIS the concentrations of NH_3 and NH_4^+ were high as compared with other days, but this was not the case for all non-event days classified according to the AIS data. It should, however, be noted that due to the small number of non-event days during the measurement period it is difficult to conclude whether these observations are representative or not. Furthermore, the condensation sink of dry particles correlated positively with air temperature, global radiation, the concentration of SO_2, HNO_3, NH_3, SO_4^{2-}, NO_3^- and NH_4^+ and product of concentration of ozone and global radiation. The relative humidity correlated negatively with the condensation sink of dry particles. These results are in line with the origin of the air masses: continental air masses during the warm period bring more polluted (both in particles and inorganic trace gases) and drier air to the measurement site.

We also related the particle growth rates to the concentrations of trace gases (SO_2, NH_3, HNO_3 and NO_2) and to the meteorological data, but found no clear correlation. Also, no statistically significant correlations were found between the particle formation rates and gas concentrations or meteorological conditions.

We compared the sulphuric acid proxy with CS, GR and J_{10}. The larger the sulphuric acid proxy was the larger the CS but no clear correlation between sulphuric acid proxy and GR or J_{10} was found. Positive correlation between the CS and sulphuric acid proxy is probably related to the high SO_2 and particulate matter concentrations in the more polluted continental air masses.

We also calculated correlation coefficients between the growth rates of particles and vapour concentrations of monoterpenes and isoprene monitored by the PTR-MS (Maenhaut *et al*. 2008b) but found no statistically significant correlation.

It should be noted that the measurement campaign was only 40 days long and on some days there were lack of measured data. Therefore, the measurement period was perhaps too short to find significant correlations between above mentioned data. Also it is possible that it is a certain combination of atmospheric parameters rather than any of the investigated parameters alone that influences the particle formation and growth. In addition, using daily averages of data might lead to loss of information.

Cluster ion concentrations

The median cluster ion (diameter < 1.8 nm) concentrations during the measurement period were 592 cm^{-3} and 413 cm^{-3} for negative and positive ions, respectively. These values are lower than the average cluster ion concentrations in e.g. Hyytiälä, where the monthly mean concentrations vary between 600 and 900 cm^{-3} and where there is no significant difference between the concentrations of negative and positive cluster ions (Hirsikko *et al*. 2005). Also at coastal site Mace Head the average concentrations of negative and positive cluster ions were about the same (Vana *et al*. 2008). However, the concentration of negative cluster ions has been observed to be considerably higher than the concentration of positive cluster ions at Abisko (Svenningsson *et al*. 2008), Tumbarumba (Suni *et al*. 2008), the high altitude site Puy de Dôme Research Station (Venzac *et al*. 2007) and along the Trans-Siberian railroad (Vartiainen *et al*. 2007). At each of these sites average cluster ion concentrations were about the same or higher than those observed in the present study. Air ions are produced by external radiation and airborne radionuclides, mainly radon-222. The external radiation comes from cosmic radiation and gamma radiation from the ground. Hirsikko *et al*. (2007) found that the cluster ion concentration is positively correlated with the ratio of the total ion production rate to the CS. Since the

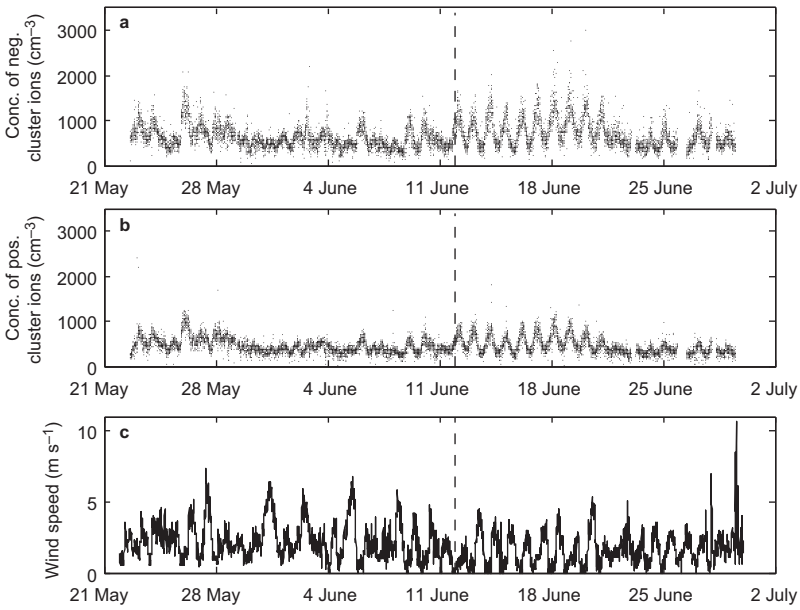

Fig. 5. Concentrations of (**a**) negative and (**b**) positive cluster ions (< 1.8 nm) and (**c**) wind speed in May–June 2006. The *x*-axes are divided into the cold and warm periods by a line at 12 June.

average CS at K-puszta was larger by a factor of 2, and the average cluster ion concentrations were lower only by a factor of less than 2 than those at Hyytiälä, this suggests that the ion production rate is higher at K-puszta than in Hyytiälä. However, we found that the concentrations of cluster ions correlated positively with the CS although negative correlation would be expected due to the fact that cluster ions will be scavenged by existing larger particles.

The cluster ion concentrations show a clear diurnal pattern with higher values during the night than during the day (Fig. 5a and b) as would be expected due to the difference in planetary boundary layer height between day and night. The cluster ion concentrations were reaching higher values and varied more between day and night during the warm period than during the cold period; concentrations started to get higher around 11 June 2006 and lower again after 22 June 2006. At the same time as the cluster ion concentrations increased, the wind speed decreased (Fig. 5c). Especially, the nighttime wind speeds were lower during the warm period as compared with those during the cold period. The correlation coefficients between wind speed and concentrations of negative and positive clusters were –0.33 and –0.24, respectively, with $p < 10^{-10}$ for both polarities. This supports the idea that weak boundary layer mixing and accumulation of radon could be the reasons for higher cluster ion concentrations during the warm period.

The concentrations of isoprene and monoterpenes were higher during the warm period than during the cold period (Maenhaut *et al*. 2008b). The concentration of monoterpenes showed the same diurnal pattern as the cluster ions, with a maximum during the night. The isoprene concentration, on the other hand, had an opposite diurnal behaviour, with maximum during daytime.

On the other hand, the daily average concentrations of the SO_2, NH_3, and HNO_3 gases in the air were also higher during the warm period and could thus have a role in cluster formation. Of these gases, SO_2 resembled most the cluster ion concentrations with lower values after 22 June 2006. Also, the daily average of the simple proxy for sulphuric acid had its highest value during the warm period. However, there were also very low values during that period. This indicates that there may be a connection between the cluster concentrations and sulphuric acid concentration as well. However, to draw any further conclusions, measurements of ambient sulphuric acid concentration or SO_2 concentration data with better resolution than 24 h for the H_2SO_4 proxy calculation would be needed.

The correlation between the concentrations of cluster ions and biogenic volatile organic compounds (BVOCs) for nighttime differed from that

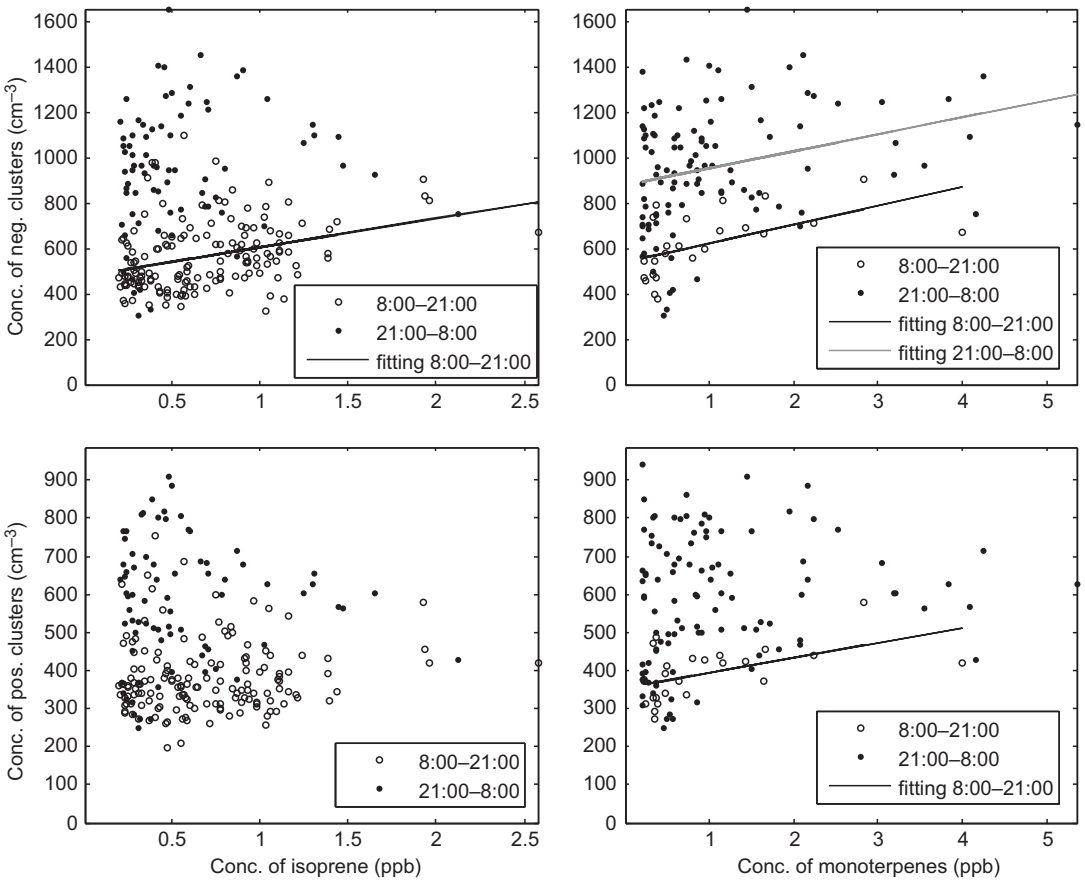

Fig. 6. Correlations between nighttime (21:00–8:00) and daytime (8:00–21:00) concentrations of cluster ions and biogenic volatile organic compounds (*see* also Table 4).

for daytime (Fig. 6 and Table 4). In calculating the correlation coefficients we used only that data where isoprene and monoterpene concentrations were higher than 200 ppt, since below that these concentrations are not very robust. The best correlation was that between daytime concentrations of ion clusters, both negative and positive, and monoterpenes. Concentration of negative ion clusters correlated also with the nighttime monoterpene concentration and the daytime isoprene concentration (Table 4).

Conclusions

Atmospheric particle and ion data measured during 39 days in early summer 2006 at K-puszta, Hungary, were analysed. It was found that there

Table 4. Correlation coefficients between concentrations of cluster ions and biogenic volatile organic compounds, and associated *p* values.

		[isoprene]	[monoterpenes]
Daytime	[negative clusters]	$R = 0.34$, $p = 2.0e{-5}$	$R = 0.55$, $p = 4.0e{-3}$
	[positive clusters]	$R = 0.08$, $p = 0.36$	$R = 0.53$, $p = 6.7e{-3}$
Nighttime	[negative clusters]	$R = 0.13$, $p = 0.25$	$R = 0.30$, $p = 2.2e{-3}$
	[positive clusters]	$R = -0.002$, $p = 0.99$	$R = 0.14$, $p = 0.16$

were many new particle formation event days during that period; formation of new nucleation mode particles and their subsequent growth was observed on more than half of the days, and also during most of the other days particle formation was observed with less pronounced growth. Based on our results, it is reasonable to assume that production of condensable vapours (or activating/nucleating vapours) is high enough to be able to form fresh particles. The chemical production of these vapours is likely to be intense, since K-puszta is characterised by intensive solar radiation in summertime. The ambient SO_2 concentration was not significantly higher than e.g. in Hyytiälä (Lyubovtseva *et al*. 2005). This suggests that the cause for the high event frequency at K-puszta might not be a significantly high sulphuric acid concentration, but presumably the presence of condensable organic vapours, and their clear contribution to new particle formation (e.g. Kulmala *et al*. 2004d).

None of the measured trace gases or meteorological variables was solely able to explain the NPF events since no clear differences in these data were found between event and non-event days. However, the condensation sink reached, as expected, higher values on non-event days than on average, which is in line with other studies (Dal Maso *et al*. 2005).

The observed formation rates of 10 nm particles were somewhat higher than the formation rates observed at Hyytiälä, Finland. We can state that the formation rates are above the median or even at the upper end of formation rates observed in the continental boundary layer (*see* Kulmala *et al*. 2004b). The growth rates of atmospheric nucleation mode particles during NPF events were strongly size-dependent and in the same range as those obtained in other studies at other sites (Kulmala *et al*. 2004b). The size-dependency in growth rates is in line with the findings in previous observational (Hirsikko *et al*. 2005, Suni *et al*. 2008) and phenomenological studies (Kulmala *et al*. 2004c) and suggests that different factors are affecting the growth of different sized particles. This is also indication of increasing importance of organic vapours on growth process as a function of size.

The atmospheric nucleation has been observed to occur at sizes around 1.5–2.0 nm (Kulmala *et al*. 2007a), and it might be related to activation of existing clusters (Kulmala *et al*. 2006). Therefore, the high event frequency and relatively high formation rate could be related to higher number of neutral clusters but even more probably it can be related to high concentration of activated vapours (or nucleating vapours), which might be related to intensive solar radiation. On the other hand, the growth rates of particles were not exceptionally high at K-puszta and therefore the high new particle formation event frequency probably cannot be explained by high concentration of vapours participating in condensational growth.

0.3–1.8 nm ion cluster concentrations were found to correlate clearly with the ambient conditions: during the warm period with continental air masses the diurnal maximum cluster concentrations were significantly higher than during the period with colder and cleaner air masses from the North Sea or the Atlantic Ocean. This could be partly explained by lower wind speed during the warmer period resulting in a weaker boundary layer mixing. It might also point to the role of gaseous precursors in forming atmospheric clusters, since the concentrations of both BVOCs and inorganic trace gases were higher during the warm period. Interestingly, the diurnal variation of the cluster ions was similar to that for the ambient monoterpene concentrations. This could partly be explained by the effect of boundary layer dynamics, but could also point to monoterpenes as a possible source of atmospheric clusters.

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