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A comparison of new particle formation events in the boundary layer at three different sites in Europe

Antti Jaatinen[1)], Amar Hamed[1)], Jorma Joutsensaari[1)], Santtu Mikkonen[1)], Wolfram Birmili[2)], Birgit Wehner[2)], Gerald Spindler[2)], Alfred Wiedensohler[2)], Stefano Decesari[3)], Mihaiela Mircea[3)], Maria C. Facchini[3)], Heikki Junninen[6)], Markku Kulmala[6)], Kari E. J. Lehtinen[1)4)] and Ari Laaksonen[1)5)]

[1)] *Department of Physics, University of Kuopio, P.O. Box 1627, FI-70211 Kuopio, Finland*
[2)] *Leibniz-Institute for Tropospheric Research, D-04318 Leipzig, Germany*
[3)] *Istituto di Scienze dell'Atmosfera e del Clima Consiglio Nazionale delle Ricerche, I-40129 Bologna, Italy*
[4)] *Finnish Meteorological Institute, Kuopio Unit, P.O. Box 1627, FI-70211 Kuopio, Finland*
[5)] *Finnish Meteorological Institute, P.O. Box 503, FI-00101 Helsinki, Finland*
[6)] *Department of Physics, P.O. Box 64, FI-00014 University of Helsinki, Finland*

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In this study, we compare new particle formation (NPF) in the boundary layer at different sites in Europe: Melpitz, Germany (central Europe), San Pietro Capofiume, Italy (southern Europe) and Hyytiälä, Finland (northern Europe) for the period of two years (July 2003–June 2005). NPF was studied based on observations of the particle size distribution, meteorological and gas-phase parameters. Nucleation was found to occur frequently at all stations, however seasonal differences were observed for every station. These differences have a clear correlation with the annual variation of estimated formation rate values. The growth rate reached its maximum values during summer at all three stations. In Hyytiälä the formation and growth of the particles was characterized by low pre-existing condensation sink and most likely high biogenic VOC concentrations associated with the growth season, and in Melpitz and San Pietro Capofiume by the high level of pollution arriving from the nearby industrial and agricultural sources.

Introduction

The radiative balance of the Earth is affected by the absorbing, scattering and cloud condensation nuclei (CCN) forming properties of atmospheric aerosols. The magnitude of the aerosol radiative forcing still has major uncertainties associated with it (IPCC 2007), partly because the sources of atmospheric aerosols are unknown. Development of aerosol size distribution measurement techniques has enabled scientists to understand the formation of secondary aerosol particles. During recent decades, observations made at different sites around the world have shown that new secondary particle formation bursts occur frequently in the Earth's atmosphere (Kulmala *et al*. 2004). It is not yet possible to exactly predict rates at which particles are formed and grow,

or even to know with certainty which chemical species or meteorological parameters influence new particle formation. Therefore, nucleation is an active area of atmospheric research and better understanding of processes concerning the formation and growth of new particles has certainly become important.

Secondary aerosol formation from gas phase precursors is considered an important source of tropospheric aerosols. Considerable attention has been paid to sources and sinks of the atmospheric particles. Particularly the number concentration of freshly formed particles has been of great concern due to their effects on global radiative forcing and on human health (Charlson *et al*. 1987, Donaldson *et al*. 1998). New particle formation has been observed almost everywhere in the atmosphere, in clean areas, rural, coastal and polluted areas (Kulmala *et al*. 2004).

A variety of different nucleation mechanisms have been suggested for the atmosphere. From the present knowledge it is not possible to decide what is the most significant mechanism. It may be that more than one nucleation process is operating in the atmosphere. The most studied mechanisms are the homogeneous binary water–sulfuric acid nucleation (e.g. Kulmala and Laaksonen 1990), homogeneous ternary water–sulfuric acid–ammonia nucleation (e.g. Kulmala *et al*. 2000, Napari *et al*. 2002), ion-induced nucleation of binary (water–sulfuric acid) or ternary vapors, or of organic vapors (e.g. Yu and Turco 2000, Eisele *et al*. 2005, Vana *et al*. 2006, Laakso *et al*. 2007), barrierless (kinetically controlled) homogeneous nucleation (McMurry and Friedlander 1979, Kulmala *et al*. 2003) and activation nucleation (Kulmala *et al*. 2006). Altogether, the driving force for both nucleation and the growth of freshly formed particles is the sufficient amount of non-volatile vapors, such as sulfuric acid and some organic compounds formed by photochemical oxidation reactions involving precursor gases (Kulmala *et al*. 2004).

Most measurements performed so far support the idea (Kulmala *et al*. 2000) that new particle formation and growth of these particles are uncoupled under atmospheric conditions (Kulmala *et al*. 2004). Observations made in the free troposphere are consistent with the binary water–sulfuric acid nucleation, whereas in the boundary layer a third nucleating component, such as ammonia, or a totally different nucleation mechanism is needed (Weber *et al*. 1997, Sihto *et al*. 2006). Also the possibility of ion-induced nucleation in the boundary layer is evident. Growth rates of the nucleated particles cannot usually be explained by the condensation of sulfuric acid and associated inorganic compounds. Organic compounds having a very low saturation vapor pressure are the most likely candidates for the growth of nucleated particles (Kulmala *et al*. 2004).

Several studies have compared new particle formation at different measurement stations. For example Dal Maso *et al*. (2007) studied new particle formation bursts at four different stations all located in a relatively clean area in Scandinavia (Hyytiälä, Värriö and Pallas in Finland and Aspvreten in Sweden). Since all of these stations are located in similar environments, it has been found that also the parameters concerning NPF are more or less similar with only minor discrepancies. The idea of our study was to examine atmospheric nucleation in as many entirely different environments as possible. To accomplish this we selected three measurement stations in three very different environments: a highly polluted area in southern Europe, a moderately polluted area in central Europe and a relatively clean area in northern Europe. To study the similarities and differences in different parameters during new particle formation events among these stations, we selected a two-year data set including aerosol size distribution, meteorological and gas phase parameter data. Our aim was to bring out new information on conditions that favor nucleation and, on the other hand, what kind of conditions inhibit the new particle formation process.

Material and methods

Site descriptions and instrumentation

In this study, we present an analysis of aerosol size distribution data concerning new particle formation in the boundary layer at three sites in Europe: Melpitz, eastern Germany, a moderately rural area (central Europe), San Pietro Capofiume in the Po Valley, a highly polluted rural area (southern Europe), and Hyytiälä

station in Finland, a clean forest area (northern Europe) for the period of two years (July 2003–June 2005). Henceforth we refer to San Pietro Capofiume as SPC, Melpitz as MEL and Hyytiälä as HYY.

San Pietro Capofiume, Italy

The SPC station (44°39´N, 11°37´E, 10 m a.s.l.) is located about 30 km northeast from the city of Bologna, in the Po Valley. The Po Valley is densely populated, highly industrialized and known to have relatively high level of anthropogenic pollution (for more details *see* Hamed *et al*. 2007). The particle size distribution measurements at SPC were carried out using a twin Differential Mobility Particle Sizer (DMPS) system. In addition to particle size measurements, several gas and meteorological parameters were measured at the station: SO_2, NO, NO_2, NO_x, O_3, temperature, relative humidity, wind direction, wind speed, global radiation, precipitation, and atmospheric pressure (Hamed *et al*. 2007).

Melpitz, Germany

The MEL station (51°32´N, 12°54´E, 87 m a.s.l.) is located in northern Saxony, 41 km northeast of Leipzig near Torgau. The station itself is on an old flat meadow surrounded by agricultural land and the site can be described as situated in a rural polluted continental area. MEL is equipped with *in-situ* meteorological instrumentation as well as continuous gas (O_3, NO, NO_2, and SO_2) and aerosol measurements are carried ou there. The particle size distribution was determined using a twin DMPS system, the first system detects particles from 3 nm in diameter and the second one from 11 nm, maximum detectable diameter being 800 nm (for more details *see* Birmili and Wiedensohler 2000 and Spindler *et al*. 2004).

Hyytiälä, Finland

The HYY (SMEAR II) station (61°51´N, 24°17´E, 170 m a.s.l.) is located in southern Finland, about 50 km northeast of Tampere. The station is in the middle of the boreal forest and can therefore be described to be situated in a relatively clean area (for details *see* Hari and Kulmala 2005). The particle size distribution measurements were performed using a twin DMPS system similar to those in the two other stations. Particles are measured in the size range of 3–500 nm. The station has also facilities to measure gases such as CO_2, H_2O, SO_2, O_3 and NO_x concentrations as well as temperature, wind speed and direction, radiation, rain, relative humidity and air pressure (for more details *see* e.g. Kulmala *et al*. 1998, Dal Maso *et al*. 2005).

Results and discussion

Event classification

For further data analysis, the days were divided into event, non-event and undefined days. The classification method we used here is based on the methods described by Mäkelä *et al*. (2000) and Dal Maso *et al*. (2005). A day is considered an event day when the formation of new aerosol particles starts at the lowest measurable particle size (diameter 3 nm) and subsequent growth of the newly formed particles is observed for several hours. The nucleation event classification used here is based on event clarity, i.e. the number concentrations of the freshly formed particles, and their formation and growth rates (for more details *see* Hamed *et al*. 2007). The nucleation event classes 1, 2 and 3 refer to strong, intermediate, and weak events, respectively. However, because of the subjectivity of the event classification method some overlapping within the classes may occur. To minimize the uncertainty of the classification method the weak class 3 events were excluded from some calculations, which will be detailed below. The days with no particle formation are classified as non-event days. The days which do not fulfill the criteria to be classified as the event or non-event days were combined into one group, called undefined days.

Event frequencies

We analyzed two years of data from SPC, MEL

and HYY. During this period, the DMPS instrument in SPC was operational on 513 days. This is about 70% of all days during the whole period. For the rest of the days, the data are either missing or of poor quality. From those operational days, the data include 158 (~31%) event days (classes 1, 2 and 3), 209 (~41%) non-event days, and 146 (~28%) undefined days. The respective numbers for MEL are 614 operational days (~84% of all days), 158 (~26%) event days, 353 (~57%) non-event days, and 103 (~17%) undefined days; and for HYY: 706 operational days (~97% of all days), 248 (~35%) event days, 320 (~45%) non-event days, and 138 (~20%) undefined days (*see* Tables 1–3).

Monthly frequencies of NPF events at the stations ranged from 0% to 50% depending on location and season (Fig. 1). In spring, it was common that new particle formation days were more frequent. For HYY, the maximum event frequency (on average ~40%) was observed from March to May, while for SPC it was seen in the late spring ~45% (May) and summer ~43% (July) and for MEL in the late summer ~36% (August) and early autumn ~37% (September). In November, no particle formation was observed at SPC and MEL; at HYY only few event days were seen. Minimum values of event frequencies occurred in winter at all three sites. In winter, the driving force of nucleation events

Table 1. Number of nucleation-event days (class 1, 2 and 3 events), undefined (UD) days, non-event days (NE), missing data (MD) days, and the days during which the DMPS instrument was fully operational (oper. days) during two years of measurements at the San Pietro Capofiume station.

Month	Class 1	Class 2	Class 3	UD	NE	MD	Oper. days
Jan	0	2	2	20	36	2	60
Feb	4	4	6	21	22	0	57
Mar	1	5	4	24	28	0	62
Apr	1	5	9	17	19	9	51
May	9	5	10	4	3	31	31
Jun	3	2	4	3	2	46	14
Jul	10	16	14	12	9	1	61
Aug	1	5	16	13	14	13	49
Sep	2	0	9	4	5	40	20
Oct	0	4	1	11	19	27	35
Nov	0	0	1	6	23	30	30
Dec	0	2	1	11	29	19	43
Total	31	50	77	146	209	218	513

Table 2. Number of nucleation event days (class 1, 2 and 3 events), undefined (UD) days, non-event days (NE), missing data (MD) days, and the days during which the DMPS instrument was fully operational (oper. days) during two years of measurements at the Melpitz station.

Month	Class 1	Class 2	Class 3	UD	NE	MD	Oper. days
Jan	0	1	2	2	54	3	59
Feb	0	2	1	8	43	3	54
Mar	3	3	1	6	38	11	51
Apr	4	2	4	7	14	29	31
May	1	5	4	8	19	25	37
Jun	6	9	12	14	16	3	57
Jul	4	5	11	14	21	7	55
Aug	7	17	14	9	12	7	59
Sep	13	9	8	14	15	1	59
Oct	2	5	6	7	28	14	48
Nov	0	0	0	5	44	11	49
Dec	0	0	1	9	49	3	59
Total	40	54	64	103	353	117	614

— solar radiation — is of course less intense, which could be one reason for the low winter frequencies of nucleation events at those sites.

Nucleation event start and end times

The atmospheric nucleation has been observed to occur at particle sizes 1.5–2.0 nm (*see* Kulmala *et al*. 2007), and the particles need time to grow to 3 nm which is the minimum detectable size for the aerosol instruments used in this study. This time varies under different atmospheric conditions (Kulmala *et al*. 2004). However, because the exact growth time was not known, the observed start of the particle formation was used as the start of nucleation and the observed end of the formation was used as the end time of nucleation. In practice, the MATLAB program was used to determine visually these times. Accordingly, the duration of the NPF event was estimated as the difference between these two times.

New particle formation events tended to, on average, start about an hour earlier at MEL than at SPC and HYY (MEL and SPC times are UTC+1 and HYY UTC+2) (*see* Table 4). Also the duration of an event was the shortest at MEL, about 1.5-h shorter than at SPC and about 3-h shorter than at HYY. There seems to be a connection between long-lasting NPF events and relatively clean areas and, on the other hand, a connection between shorter event durations and polluted areas. Furthermore it was found that event durations were slightly shorter during summer. That could be due to high afternoon temperatures at the stations during the summer and/or as a result of the pre-existing aerosol population's capability to scavenge the freshly formed clusters more efficiently in summer.

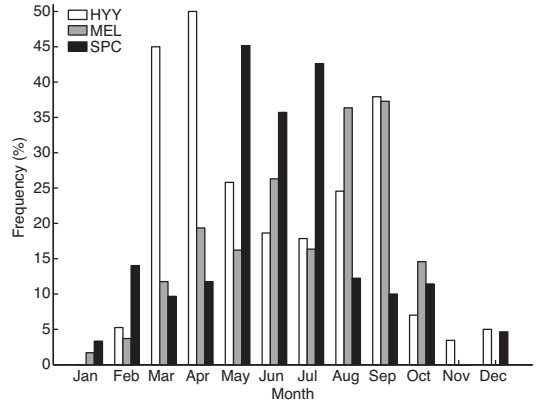

Fig. 1. Monthly frequency of nucleation events (classes 1 and 2) at Hyytiälä (HYY), Melpitz (MEL) and San Pietro Capofiume (SPC). (Note: June and September for SPC were poor).

Particle formation and growth rates

The particle formation rate, FR (particles cm^{-3} s^{-1}), and particle growth rate, GR (nm h^{-1}), were esti-

Table 3. Number of nucleation event days (class 1, 2 and 3 events), undefined (UD) days, non-event days (NE), missing data (MD) days, and the days during which the DMPS instrument was fully operational (oper. days) during two years of measurements at the Hyytiälä station.

Month	Class 1	Class 2	Class 3	UD	NE	MD	Oper. days
Jan	0	0	2	12	48	0	62
Feb	1	2	8	10	36	0	57
Mar	10	17	11	9	13	2	60
Apr	11	19	11	7	12	0	60
May	8	8	16	8	22	0	62
Jun	1	10	14	12	22	1	59
Jul	2	8	3	15	28	6	56
Aug	5	9	12	12	19	5	57
Sep	7	15	8	8	20	2	58
Oct	2	2	7	19	27	5	57
Nov	0	2	7	13	36	2	58
Dec	0	3	7	13	37	2	60
Total	47	95	106	138	320	25	706

mated from the measured particle size distributions. In this study, we estimated the formation rate at 3 nm from the increase of 3–25 nm particle number concentration between the start of the event and the time when the particle concentration exhibited a maximum during the event. Note that in our FR calculations removal of particles via coagulation was not taken into account. We determined the growth rates visually from the DMPS data plots. The reliability of our methods in determining the FR and GR was checked by Hamed *et al*. (2007) by comparing results from our method with those using the method described by Dal Maso *et al*. (2005). The conclusion was that the values for FR and GR estimated with both methods were very similar.

Based on our calculations, the estimated mean value for the FR was ~0.7 cm^{-3} s^{-1} at HYY, ~4.6 cm^{-3} s^{-1} at MEL, and ~3.6 cm^{-3} s^{-1} at SPC. A clear gradient was found between the more polluted sites (SPC and MEL) that exhibited high formation rates and less polluted site (HYY) that exhibited low formation rates. Generally, the particle formation rates were higher at all stations in spring and summer than in winter (Fig. 2a). At HYY, the trend of the formation rates in different seasons was almost the same as the nucleation event frequency trend, i.e. the maximum mean values were found in the spring and early autumn. At MEL and SPC, the highest monthly formation rates were found in July and April but nucleation events were not most frequent during this months.

The mean growth rate of the nucleation mode particles was ~2.9 nm h^{-1} at HYY, ~6.2 nm h^{-1} at MEL, and ~6.1 nm h^{-1} at SPC. This is not a surprise, since it is known that low growth rates are typical for clean areas (e.g. Dal Maso *et al*. 2007). The high value of GR at SPC and MEL might possibly be due to the relatively large degree of pollution. Since the evolution of the nucleation mode size distribution results from competition between growth and scavenging onto background aerosols, fast growth is needed for particle formation. Otherwise, nucleated particles would be scavenged before growing into detectable sizes (Kerminen and Kulmala 2002, Lehtinen *et al*. 2007).

The monthly-mean growth rates values did not follow same pattern as the nucleation event frequency, as the growth rates were in general higher from mid-spring to mid-autumn than during the rest of the year (Fig. 2b). This may be due to the more intensive solar radiation during the summer, providing more efficient photochemistry that leads to formation of condensable

Table 4. Monthly means of event start and end times and event duration for nucleation events together with minimum (Min), maximum (Max) and mean for the whole study period and for each station. MEL and SPC times are UTC+1 and HYY UTC+2. NC means no strong events were observed in that month. Note: during June and September the DMPS was operational for only ~23% and ~33% of the time, respectively, hence there are fewer SPC data.

	HYY			SPC			MEL		
Month	Start	End	Duration	Start	End	Duration	Start	End	Duration
Jan	NC	NC	NC	11:33	19:53	8:20	9:09	13:09	4:00
Feb	11:09	18:43	7:34	10:42	17:10	6:28	9:39	12:59	3:20
Mar	11:15	18:20	7:05	10:43	16:05	5:22	9:17	13:11	3:54
Apr	9:34	17:25	7:51	10:00	16:22	6:22	10:10	14:23	4:14
May	9:18	16:36	7:18	9:20	13:14	3:54	8:53	13:21	4:28
Jun	8:56	15:09	6:13	7:21	12:27	5:06	8:47	11:56	3:09
Jul	9:18	14:59	5:41	9:18	14:47	5:29	8:16	13:35	5:19
Aug	10:11	15:51	5:41	10:07	16:09	6:02	8:50	12:30	3:41
Sep	9:50	16:38	6:48	9:20	17:00	7:40	8:43	13:03	4:19
Oct	11:41	18:31	6:50	10:11	16:33	6:23	10:14	13:57	3:42
Nov	11:41	17:16	5:35	NC	NC	NC	NC	NC	NC
Dec	11:36	17:22	5:46	8:50	15:30	6:40	NC	NC	NC
Min	8:56	14:59	5:35	8:50	14:47	3:54	8:16	11:56	3:09
Max	11:41	18:43	7:51	11:33	19:53	8:20	10:14	14:23	5:19
Mean	10:02	17:00	6:59	9:45	15:12	5:27	8:58	12:58	4:00

species such as low volatility organics and sulfuric acid. Note however, that the annual cycle of GR was much more pronounced at HYY as compared with that at SPC and MEL. A probable reason for this is that the dominant condensable species at HYY are biogenic in origin. Emission of biogenic VOC's, precursors of the condensable species, follows the temperature and light intensity, peaking in the summer. At SPC and MEL, anthropogenic organics and sulfuric acid, whose precursors' emissions may not show a similar annual cycle, are likely to contribute more to particle growth than at HYY.

Meteorological and gas phase parameter influence on new particle formation

In order to study the relationship between nucleation events and numerous parameters (meteorological and gas phase concentrations parameters), we analyzed a two-year set of meteorological data for the three stations. We will present the analysis seasonally. In addition, the differences between event and non-event hourly-average values were studied individually for every station.

Higher temperatures, on average, were associated with nucleation events at all stations (*see* Fig. 3). However in summer at SPC and spring at HYY, non-event days had higher temperatures than event days. At least for HYY, an explanation for this might be that nucleation events tend to occur when the air masses arrive from the north (Dal Maso *et al*. 2005). In this case, northern air masses are colder, but also cleaner resulting in a lower condensation sink. At MEL the temperature was higher on event days as compared with that on non-event days during all the seasons except in winter. Especially in the autumn, when the event frequency was highest at MEL, the temperature was much higher on event days. This is a clear indication that a high temperature (as a result of high intensity of radiation) at MEL favors NPF. At the moment we do not have an unambiguous explanation for the apparent opposite behavior of temperature during nucleation events in different environments, but most likely the origin of the air masses plays a crucial role in this feature. The hourly-average temperature was

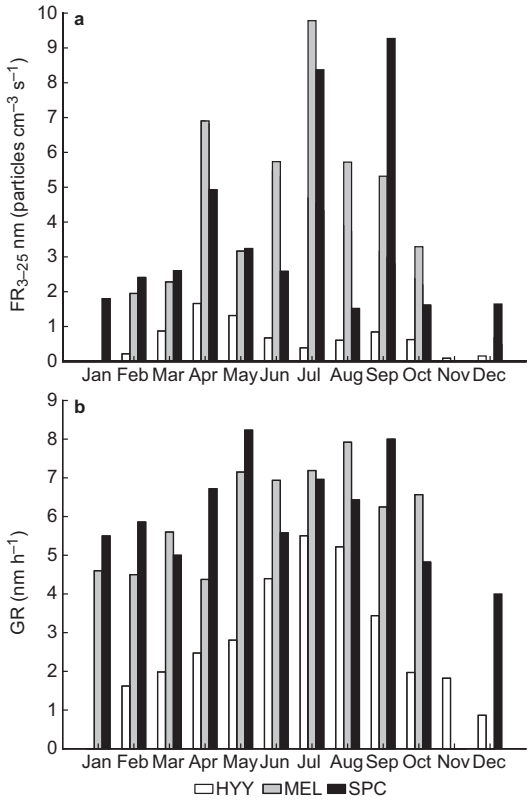

Fig. 2. Monthly averages of (**a**) FR (cm^{-3} s^{-1}) and (**b**) GR (nm h^{-1}) at Hyytiälä (HYY), Melpitz (MEL) and San Pietro Capofiume (SPC). Note: during June and September the DMPS was operational for only ~23% and ~33% of the time, respectively, hence there are fewer SPC data.

at its maximum around noon at all three stations (Fig. 3), which is the most common time of day for nucleation events to take place. It is not a surprise that, overall, the temperature was higher at SPC and MEL than at HYY because of their location.

The intensity of global radiation was higher on event days as compared with that on non-event days in all the seasons and in all the stations. This is not a surprise, since having stronger solar radiation intensity during event days than non-event days has been the main feature found in all long term nucleation studies. This clearly shows that photochemistry, most probably due to the formation of the hydroxyl radicals, produces the nucleating and/or condensing species involved in NPF (Harrison *et al*. 2000). The maximum value of the intensity of radiation is around noon. Again, the intensity

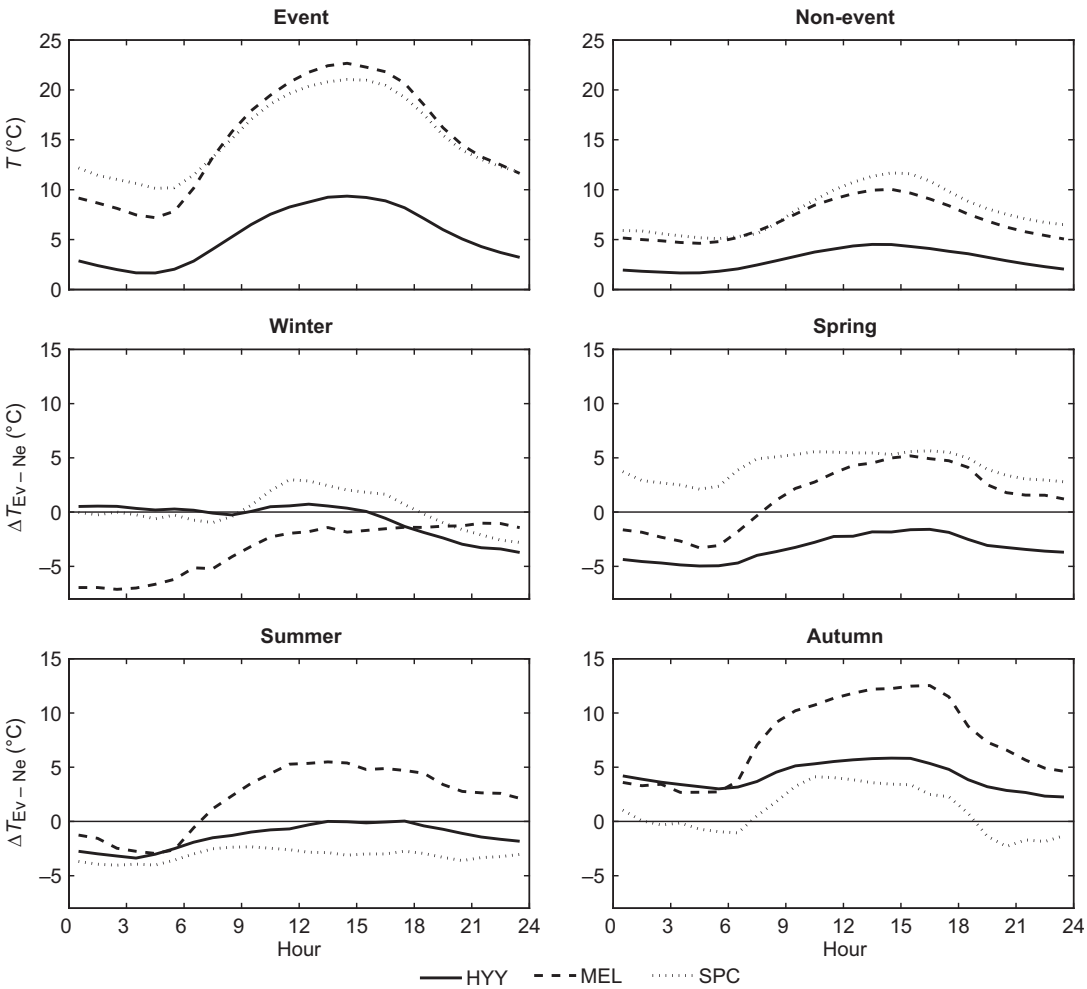

Fig. 3. Hourly-mean values of temperature T (°C) on event and non-event days, as well as the differences between event and non-event day values, for different seasons and stations over the whole two year period. ΔT_{Ev-Ne} = non-event day values subtracted from event day values.

of radiation was higher at SPC and MEL than at HYY (Fig. 4). There is, of course, a strong correlation between the high intensity of global radiation and low relative humidity, at least at the three stations in question. Therefore, the hourly-average relative humidity followed the opposite temporal pattern as that of the intensity of global radiation (Fig. 5). The relative humidity (RH) reached its minimum at about 15:00. The RH was lower on event days than on non-event days throughout the year and at all stations. Surprisingly, although the intensity of global radiation was higher and RH was lower on event days as compared with those on non-event days at SPC in the summer, the difference between these two values was not as significant as in the other seasons. This supports the fact that also the temperature was lower on event than non-event days in the summer at SPC.

The hourly-average SO_2 concentration was observed to be clearly higher on event than on non-event days at MEL all year round. Also at SPC, the SO_2 concentration was slightly higher on event days, especially in the winter and spring (*see* Fig. 6). The natural interpretation for this is that SO_2 is needed for production of sulfuric acid, which participates in the nucleation and growth of stable nm-sized clusters (Kerminen and Kulmala 2002, Lehtinen *et al*. 2007). However, at HYY, SO_2 concentrations seemed to be

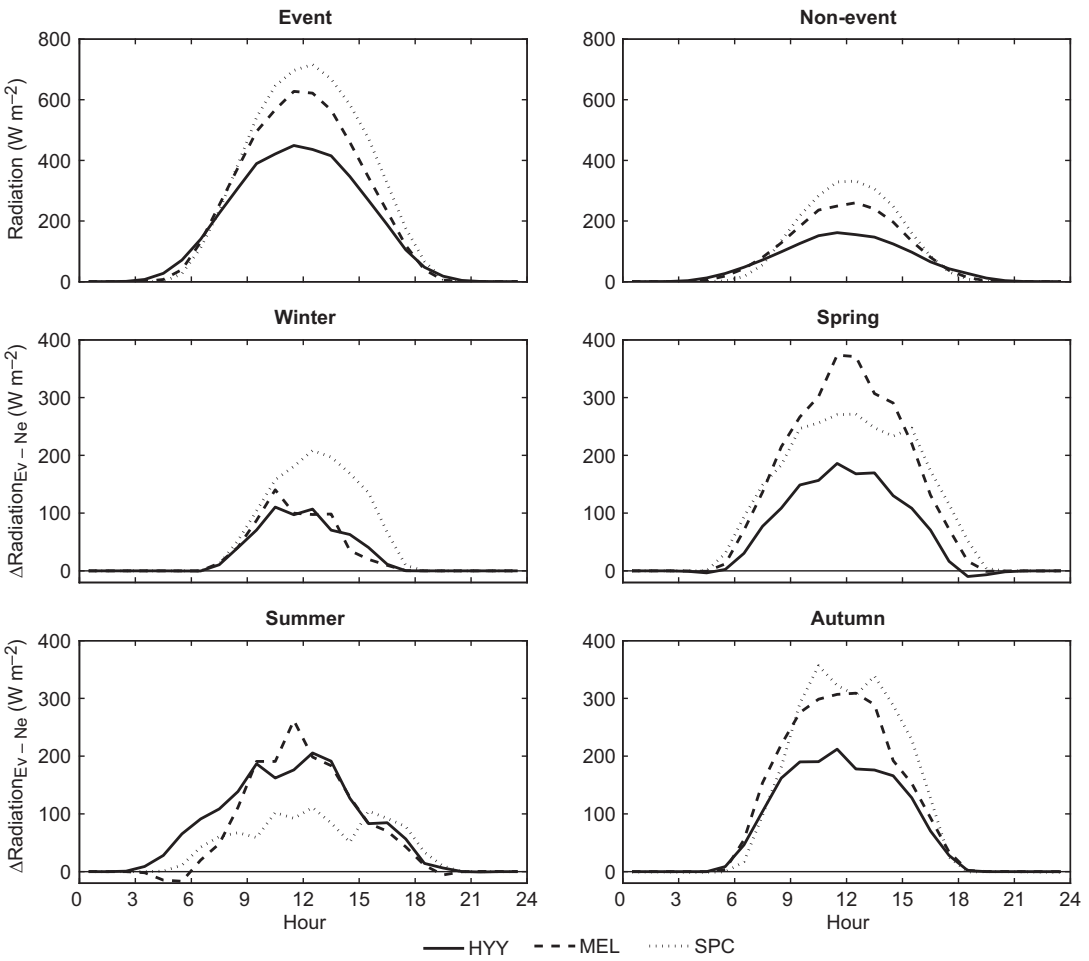

Fig. 4. Hourly-mean values of radiation (W m^{-2}) on event and non-event days, as well as the differences between event and non-event day values, for different seasons and stations over the whole two year period. $\Delta Radiation_{Ev-Ne}$ = non-event day values subtracted from event day values.

higher on non-event days. As noted above, this is in accord with the fact that at HYY, nucleation often takes place in clean air when condensation sink is lower (we will discuss this more below, in connection with the different nucleation parameters). SO_2 concentrations were very low at HYY where the maximum hourly-average SO_2 concentration was ~0.8 μg m^{-3}, while at MEL and SPC it was ~9.3 μg m^{-3} and ~3.5 μg m^{-3}, respectively. Because of the poor quality of SO_2 data in SPC, there are no data points for strong event days in the autumn.

In general, the O_3 concentration was higher on event than on non-event days at all the stations. However, seasonal differences were observed as well. In spring and summer, differences between O_3 concentrations on event days were less significant than in winter and autumn when clear differences appeared in O_3 concentrations between event and non-event days. The differences between event and non-event days were much more significant for O_3 concentrations as compared with those for SO_2 concentrations. A surprising result was that in the summer at SPC, the ozone concentration was a little bit lower on event than on non-event days, being still higher than during other seasons. Also, in the spring at SPC and in the spring and summer at HYY, ozone concentrations were observed to be relative close to each other when comparing

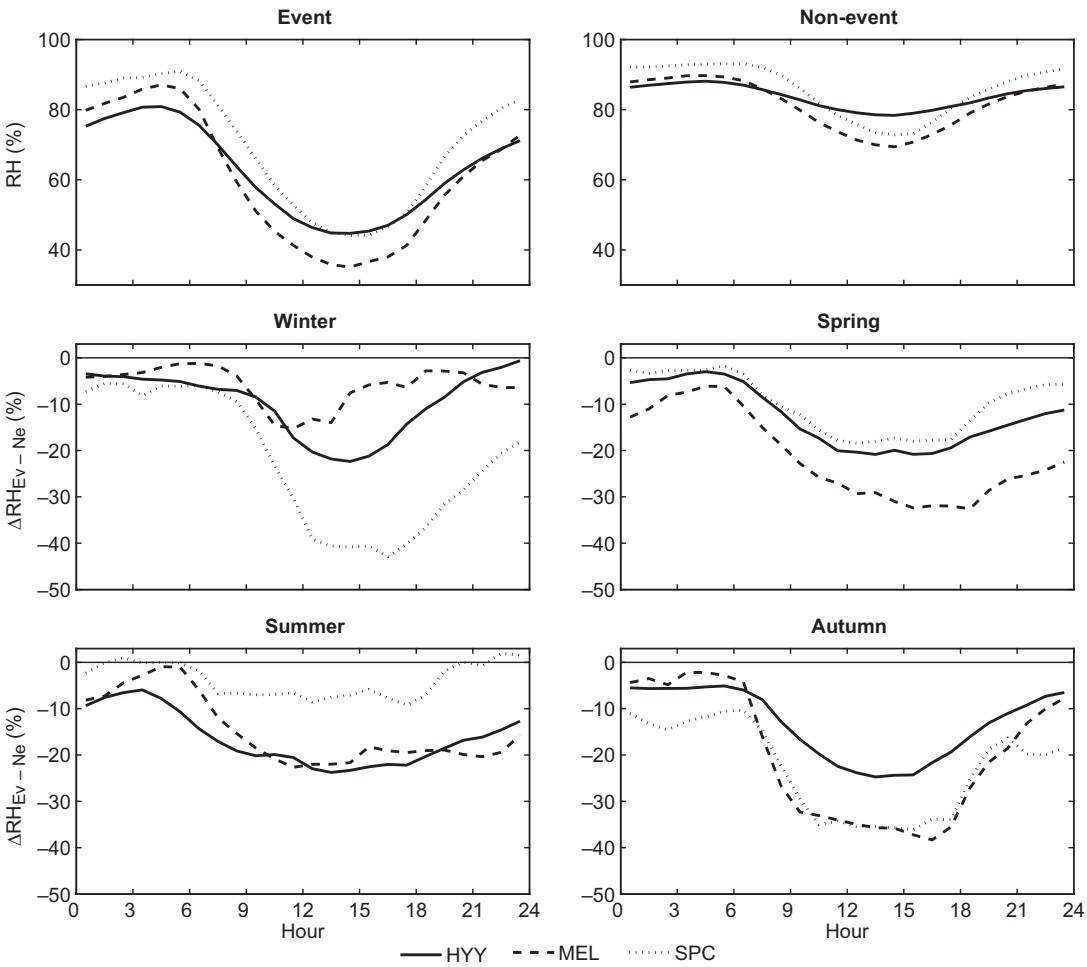

Fig. 5. Hourly-mean values of relative humidity (%) on event and non-event days, as well as the differences between event and non-event day values, for different seasons and stations over the whole two year period ΔRH_{Ev-Ne} = non-event day values subtracted from event day values.

event and non-event days. Throughout the whole two-year period, the hourly-average maximum ozone concentrations were: ~30%, ~25% and ~48% higher on event days than non-event days, at SPC, HYY and MEL, respectively. Overall, O_3 concentrations seemed to be much lower in winter (*see* Fig. 7). This observation suggests that low ozone concentration could be a limiting factor for nucleation event occurrence in the winter. Ozone is responsible for the formation of condensable species through reactions with VOCs, and indirectly by forming other oxidants (OH) upon photolysis (Seinfeld and Pandis 1998). Although condensable organics might not be involved in the actual nucleation, they may be important in speeding up the growth of newly formed molecular clusters so that the clusters survive to detectable sizes before being scavenged by coagulation with larger particles (Kerminen and Kulmala 2002, Lehtinen *et al*. 2007).

Condensation sink

We calculated the condensation sinks for nucleation and non-nucleation days by assuming that condensing vapors have a very low vapor pressure at particle surfaces and that the molecular properties of these vapors are similar to those of sulfuric acid. The calculation method we fol-

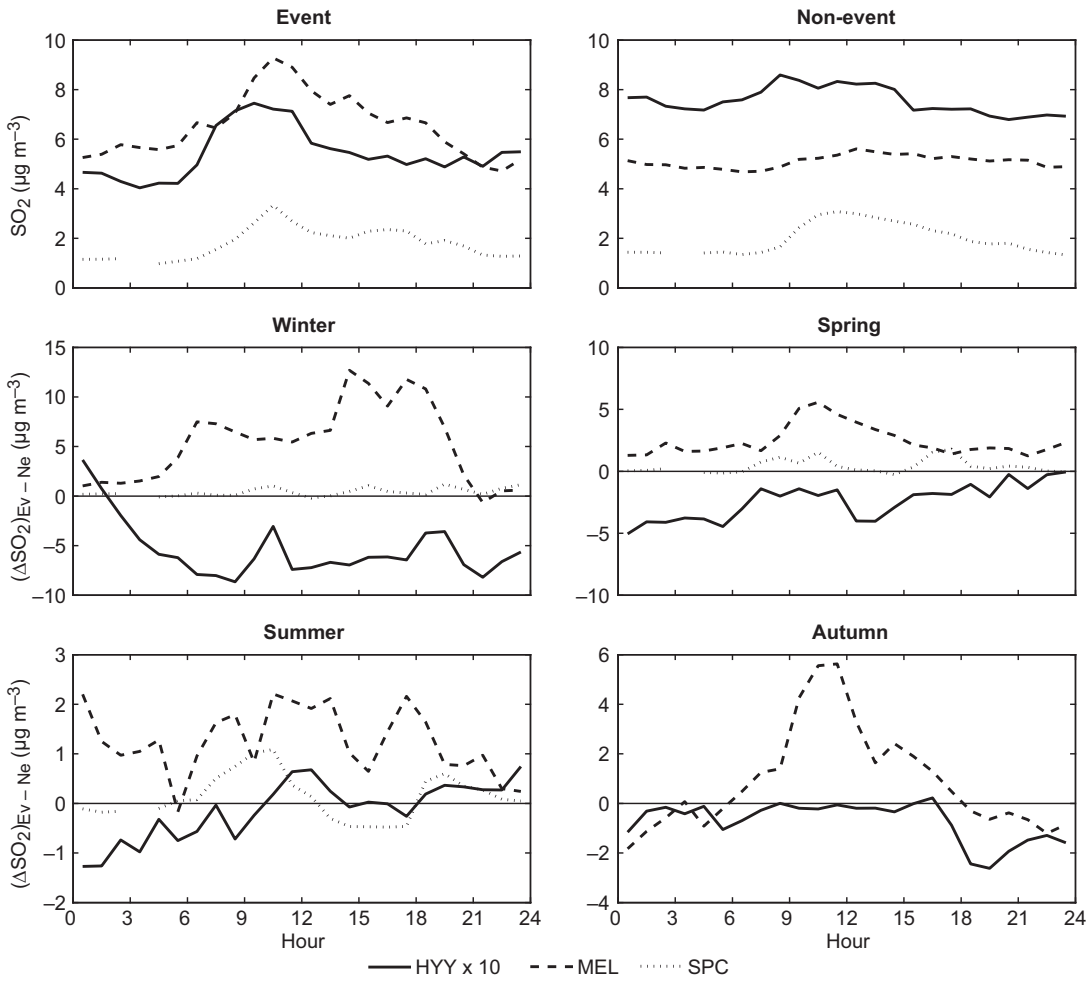

Fig. 6. Hourly-mean values of SO_2 (μg m^{-3}) on event and for non-event days, as well as the differences between event and non-event day values, for different seasons and stations over the whole two year period. $\Delta(SO_2)_{Ev-Ne}$ = non-event day values subtracted from event day values. All calculated values for HYY have been multiplied by the factor of 10 to compensate for the relatively low levels of SO_2 and hence get more information about the diurnal behavior of SO_2 concentrations. Note that *y*-axis scales in the four lower panels differ.

lowed has been described by Pirjola *et al*. (1998) and Kulmala *et al*. (2001).

According to our calculations, the mean condensation sink values on event and non-event days at SPC were about 5 and 1.5 times larger than those at HYY and MEL, respectively. Thus, higher condensation sink values seemed to be a feature for the SPC and MEL stations, possibly due to their higher degree of pollution. Furthermore, CS values seemed to be lower on event than on non-event days at SPC and HYY throughout the whole period. This is not a surprise, since a low condensation sink naturally favors nucleation because in this case also the particle growth from 1.5 to 3 nm is possible before their coagulation with larger particles (Hamed *et al*. 2007). On the other hand, it has also been shown in measurements performed in polluted lower-tropospheric conditions, such as those encountered at Heidelberg in central Europe (Fiedler *et al*. 2005), that although a high condensation sink (scavenging rate) can suppress particle formation, nucleation can take place, as long as sulfuric acid concentrations are high enough. This might be one explanation for the fact what our calculations showed — in

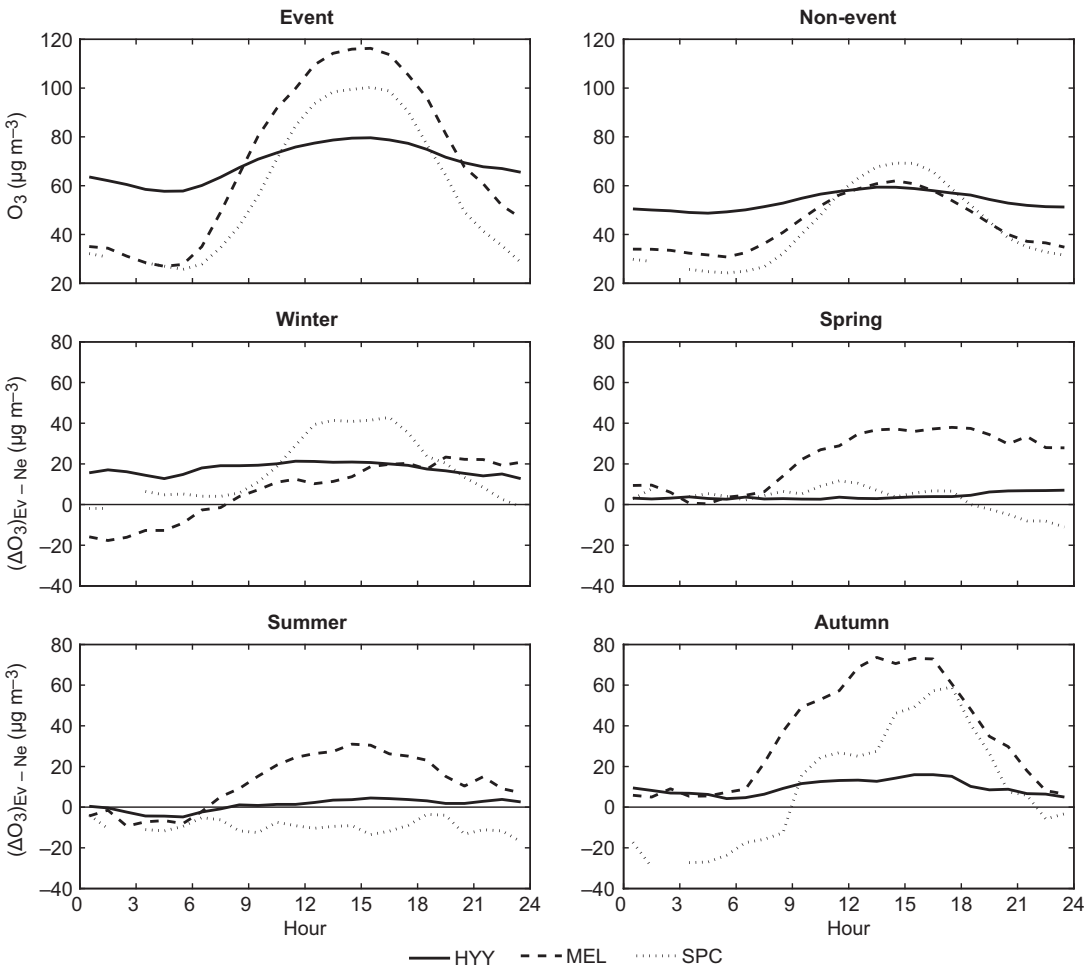

Fig. 7. Hourly-mean values of O_3 (µg m^{-3}) on event and for non-event days, as well as the differences between event and non-event day values, for different seasons and stations over the whole two year period. $\Delta(O_3)_{Ev - Ne}$ = non-event day values subtracted from event day values.

MEL, on average, CS was slightly higher on event than non-event days (*see* Fig. 8).

Nucleation event day prediction

Because of the lack of fully reliable nucleation theories, it is useful to find correlations between environmental variables which could be used to predict whether a nucleation event occurs or not. In this study we compare the methods described by Boy and Kulmala (2002), Stanier *et al*. (2004) and Hyvönen *et al*. (2005). The "nucleation parameter" (NP) of Boy and Kulmala (2002) is given by intensity of UV-A radiation, divided by the product of water vapor concentration and temperature. They studied its performance using nucleation event data obtained at HYY in 1999, and noted that the parameter exceeded a certain threshold on almost all nucleation days, and that on those non-event days when the NP exceeds the threshold, the pre-existing particle concentration was usually high. We calculated the NP for event and non-event days separately for HYY, SPC and MEL as a function of CS (Fig. 9). The event day values were determined at event start time, and the non-event values at noon. We used global radiation instead of UV-A as the latter was not available for all the sites. The conclusions of Boy and Kulmala (2002) made based on HYY

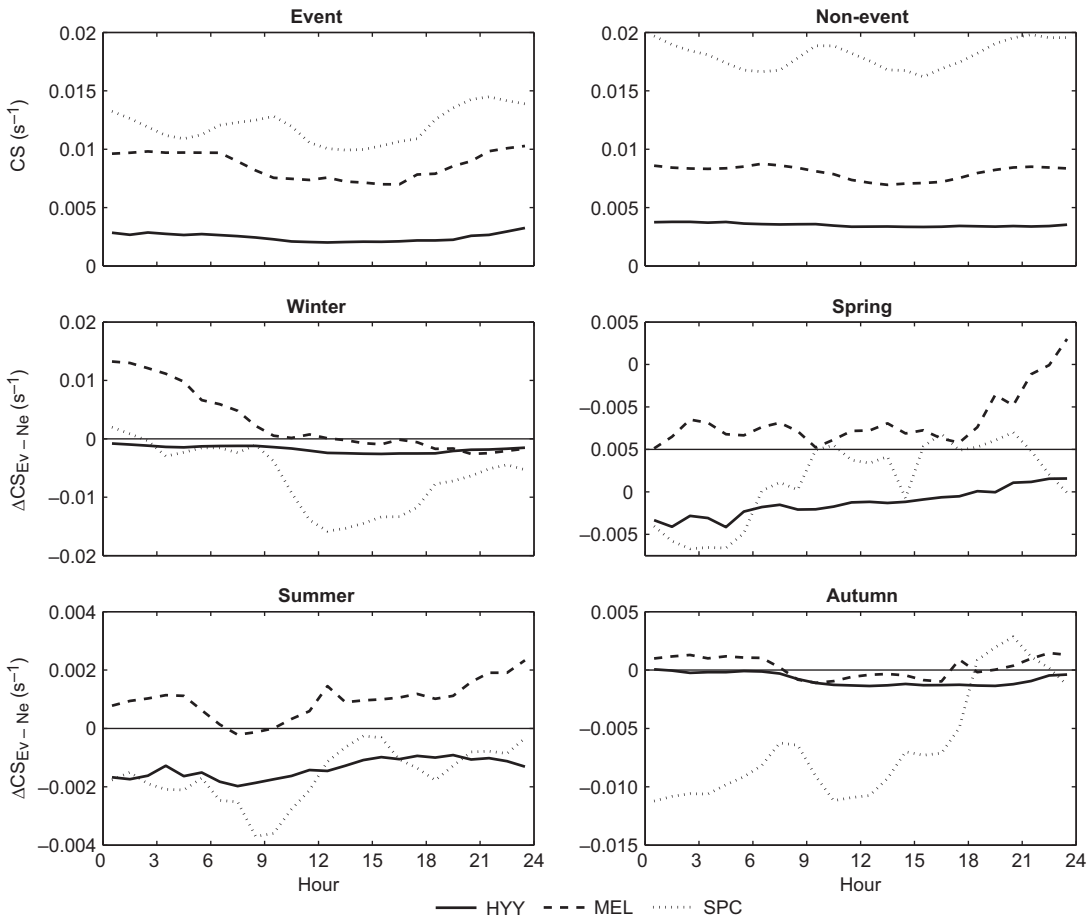

Fig. 8. Hourly-average values of condensation sink (CS) (s^{-1}) for event and non-event days, as well as the differences between event and non-event day values, for different seasons and stations over the whole two year period. ΔCS_{Ev-Ne} = non-event day values subtracted from event day values. Note: *y*-axis scales in the four lower panels differ.

1999 data hold for HYY 2003–2005 as well, with the threshold value at about 5×10^{-24} W m molecules^{-1} K^{-1} (this value is not directly comparable to that given by Boy and Kulmala (2002) because they used UV-A whereas we use global radiation in calculating the NP) (*see* the lower left panel of Fig. 9). However, such a threshold cannot be determined for MEL and SPC (*see* the two upper panels of Fig. 9), nor for the combined dataset (*see* the lower right panel of Fig. 9). That the NP works better for HYY data than for SPC is consistent with the finding of Hamed *et al*. (2007).

Hyvönen *et al*. (2005) showed that nucleation events at HYY can be predicted rather successfully using only two parameters, condensation sink and relative humidity. In our calculation nucleation events at HYY, SPC and MEL, and for the combined dataset we took the CS and RH values at event start-time, and at noon as if the day was a non-event day (Fig. 10), whereas Hyvönen *et al*. (2005) used average daytime values. We tested that this makes only small difference to the result. As with the NP, the separation is best for HYY data. For MEL, there is practically no separation of event and non-event data points except above 80% RH, where there is only non-event data.

Stanier *et al*. (2004) suggested that favorable conditions for new particle formation can be described using a product of SO_2 and incoming UV radiation (its increase indicates the increase

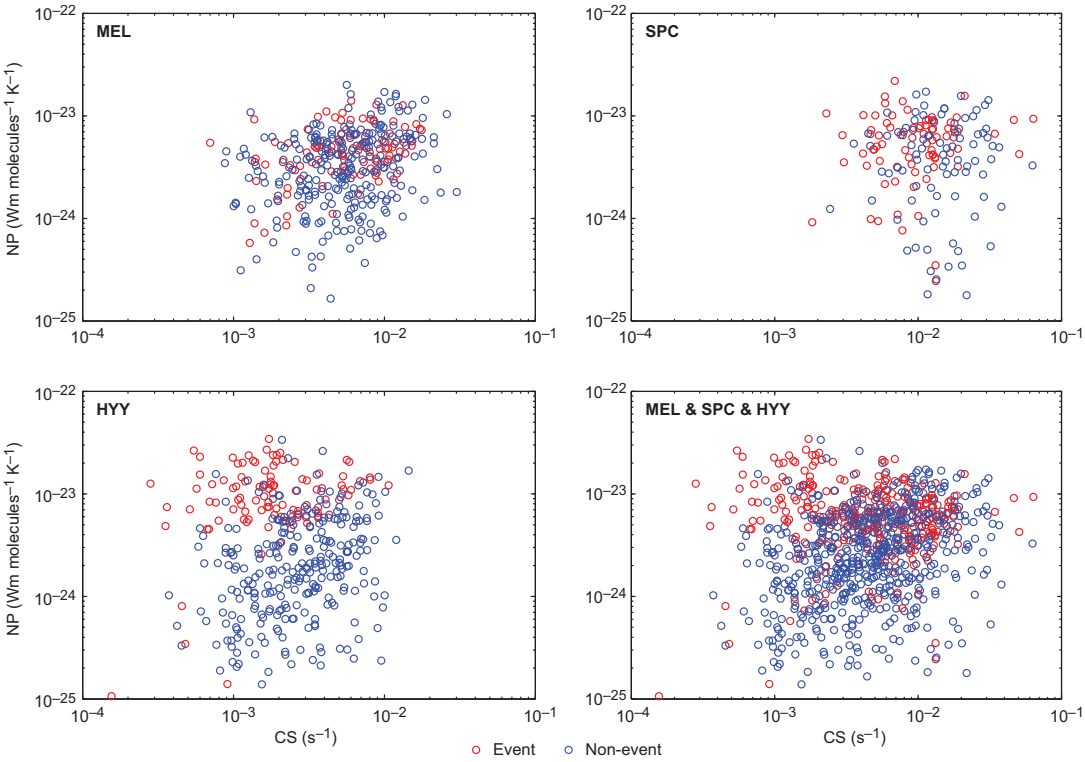

Fig. 9. Nucleation parameter of Boy and Kulmala (2002) as a function of condensation sink. The data from the three stations are combined in the lower right-hand-side panel. Event values for NP and condensation sink (CS) were taken at event start time and non-event values at noon.

of sulfuric acid (H_2SO_4) concentration) and condensation sink. Here, we applied the Stanier way of plotting event and NE data (Fig. 11), but since UV was not measured in all three stations, we used the global radiation instead. As those used for Fig. 10, event values for SO_2, radiation and CS were taken at event start-time and non-event values were taken at noon.

The Stanier-type plot worked well for MEL (Fig. 11). In practice, it separated the event and non-event days and there was only minor overlapping in the event and non-event data points. This suggests that high sulfuric acid together with low condensation sink is a significant factor driving nucleation at MEL. Although the same thing can be said for nucleation at SPC, the separation of the data points was not as clear. At HYY, the correlation between Stanier *et al.* (2004) parameters with new particle formation was not as good as at the other two stations. There was some kind of a separation between event- and non-event-day data points, but no unambiguous separation between them can be done: the overlapping was too great for that. Note that most of the SPC and MEL data are at CS values above 2×10^{-3} s^{-1}, whereas about half of the HYY data are below. Interestingly, this "clean" data showed much more event days below the separation line than the more polluted data with higher CS values. This is a further indication that other factors, such as production of condensable organics capable of speeding up particle formation and growth, are needed to produce a reliable parameterization of the occurrence probability of HYY nucleation events, especially during clean conditions.

Conclusions

A two-year dataset from three different European aerosol measurement stations was analyzed to

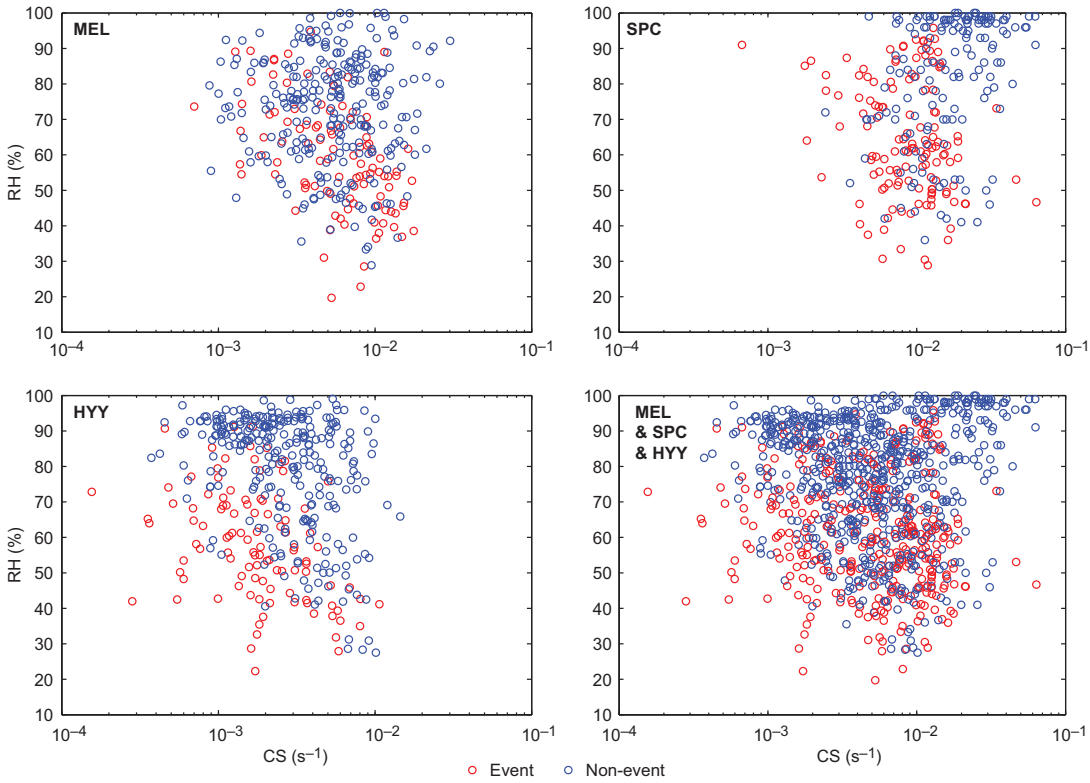

Fig. 10. New particle formation event predicted by a method described by Hyvönen *et al.* (2005). The data from the three stations are combined in the lower right-hand-side panel. Event values for relative humidity (RH) and condensation sink (CS) were taken at event start time and non-event values at noon.

identify new particle formation events and deriving their characteristics. During this two-year period, NPF events were seen on ~31%, ~26% and ~35% of classified days at SPC, MEL and HYY, respectively. Considering these numbers, it can be said that new particle formation in the lower troposphere is a frequent phenomenon all over Europe, from the clean boreal forest areas in northern Europe to the polluted urban areas in southern Europe.

Annual variations in NPF were found at all stations, with maxima in spring and autumn at HYY, in autumn at MEL and in summer at SPC. It was found that event occurrence is slightly more frequent in a clean environment. Although southern and central Europe have higher levels of, for example, radiation and SO_2, the positive effects of these parameters on nucleation is compensated by the high value of condensation sink. The frequency of non-event days was highest at MEL (~57%) and lowest at SPC (~40%). NPF events commonly started a couple of hours before noon at all three stations, at MEL about an hour earlier than at HYY and SPC. On the other hand, the duration of NPF events was longer in the clean environment: at HYY the average duration of a new particle formation event (7 hours) was about 1.5 and 3 hours longer than at SPC and MEL, respectively. Long-lasting NPF events along with low growth and formation rates seem to be characteristics for nucleation in northern Europe (*see* e.g. Dal Maso *et al*. 2007, Kulmala *et al*. 2004).

Based on our calculations, the estimated mean particle formation rates (FR) were clearly higher at MEL and SPC than at HYY. The estimated mean values of the FR were ~0.7 cm^{-3} s^{-1}, ~4.6 cm^{-3} s^{-1} and ~3.6 cm^{-3} s^{-1} at HYY, MEL and SPC, respectively. Also the estimated growth rates were higher at the central and southern European stations. The mean growth rates of the nucleation mode particles were ~2.9 nm h^{-1},

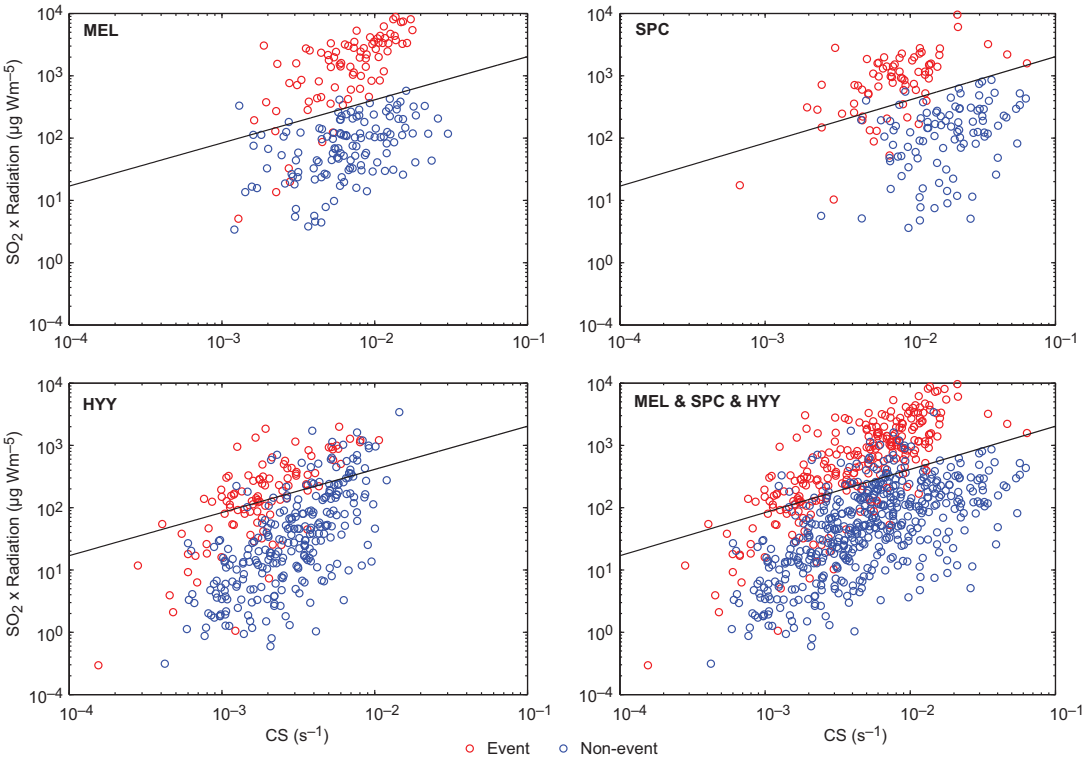

Fig. 11. Nucleation event days predicted by a method described by Stanier *et al.* (2004). The data from the three stations are combined in the lower right-hand-side panel. The same separation line, determined by discriminant analysis from the combined data (lower right-hand-side panel) was drawn in all four panels. Event values for SO_2, radiation and condensation sink (CS) were taken at event start time and non-event values at noon.

~6.2 nm h^{-1} and ~6.1 nm h^{-1} at HYY, MEL and at SPC, respectively. The annual variations of these parameters were as expected, the growth rate being faster with more intense solar radiation and the formation being higher with higher burst frequency. Condensation sinks were higher in the more polluted areas. We found that on event days the mean condensation sinks were ~0.002 s^{-1}, ~0.010 s^{-1} and ~0.007 s^{-1} at HYY, SPC and MEL, respectively. Thus, the hourly-mean condensation sinks were roughly five times higher at SPC than at HYY and about one and a half time higher than at MEL. As compared with that at MEL, the condensation sink seems to have a greater effect as a NPF inhibitor at HYY and SPC, where the differences between event and non-event day values of condensation sink were clear, the sink being lower on event days. At MEL this difference was very small, which suggests that the precursor source might be a more important limiting factor for NPF than condensation sink.

The effects of meteorological parameters and gas phase concentrations on NPF were also studied. Temperature, global radiation and O_3 concentration were all on average higher during the event days than non-event days at all three stations. Also the SO_2 concentration, except that at HYY, was higher during event than non-event days, whereas the relative humidity was found to be lower during event than non-event days at all three stations.

Examination of various parameters concerning nucleation events at HYY, MEL and SPC confirmed that new particle formation is a frequent phenomenon in three very different European environments. At HYY, the formation is characterized by low pre-existing condensation sink and possibly advection of cooler air from the north, while at MEL and SPC by a relatively

high level of pollution arriving from the nearby industrial and agricultural sources. Of the three nucleation event day prediction methods studied (Boy and Kulmala 2002, Stanier *et al*. 2004, Hyvönen *et al*. 2005), the Stanier *et al*. (2004) method worked better for MEL and SPC than for HYY, whereas the two other methods worked to some extent for HYY but did not work at all for MEL and SPC. Overall, the Stanier *et al*. (2004) method was the only one that could be used to make some kind of separation between the event and non-event days when the three datasets were combined. However, there is still no method reliable enough to predict whether a nucleation event occurs or not on a given day. Thus, a better understanding of the nucleation process is needed to be able to develop parameterizations of nucleation events in a larger, universal scale.

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