Papers

Observations of new particle formation events in the south-eastern Baltic Sea*

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Abstract

New particle formation and growth were observed at a coastal site (Preila station, Lithuania) during 1997 and 2000–2002. The total amount of data analysed covers 291 one-day periods, 45 (15%) of which were long-term, new particle formation days. Short-term nucleation events (from a few minutes to one hour) and long-term events (from one to eight hours) were identified. The mean particle growth rate, condensation sink and condensable vapour source rate during nucleation events were 3.9 nm h^{-1}, 1.45×10^{-3} cm^{-3} s^{-1} and 7.5×10^{4} cm^{-3} s^{-1} respectively. The average formation rate J_{10} was 0.4 cm^{-3} s^{-1}. The nucleation events were accompanied mainly by air masses transported from the north (43%) and north-west (19%). Meteorological parameters and trace gas (O_3, SO_2, NO_2) concentrations were also analysed. It was found that nucleation events are related to high levels of solar radiation.

1. Introduction

Coastal regions are areas where new particle formation takes place: this involves the production of nanometre (nm)-sized particles by nucleation and their growth to detectable sizes (O'Dowd et al. 2002, Kulmala et al. 2004, 2008, Holmes 2007). However, long-term measurements at these sites have shown that the formation of ultrafine particles a few nm in diameter and their subsequent growth to about 100 nm are noticeably rarer than under continental conditions (Kulmala et al. 2004). In the coastal marine environment new particle formation has been observed in Western Europe along the Scottish, Irish, English and French coasts (O'Dowd et al. 2002, De Leeuw et al. 2002), and also in the Mediterranean coastal zone (Lazaridis et al. 2006). Furthermore, coastal nucleation has been studied in Asia (the west coasts of Korea and China (Gao et al. 2009) and Japan (Shiobara et al. 2007)) as well as in the Arctic Ocean pack ice region (Xi et al. 2006). Recently, intensive and long-lasting ultrafine aerosol formation was studied in coastal areas of countries around the Baltic Sea. Most often these nucleation events occurred during spring and autumn, with 95% of cases in the daytime and under the calm, sunny conditions typical of an anticyclone, when polar air was flowing towards the measurement site. In some cases aerosol nucleation occurred over large areas (distances of several hundred kilometres) on the same days, suggesting that the scale of the process can extend from the microphysical to the synoptic (Ulevicius et al. 2002, Plauškaitė et al. 2003, 2005).

In order to understand the nucleation process, the atmospheric perturbations predominantly responsible for it have to be identified. Generally speaking, the probability of new particle formation is related to the pre-existing particle concentration, the relevant precursors, cloudiness, air advection, etc. Nilsson et al. (2001), Kulmala (2003) and Sogacheva et al.

(2005) associated nucleation events with the advection of North Atlantic air and especially to outbreaks of cold polar air. Nilsson & Kulmala (1998) explained that a strong potential temperature gradient indicative of vertical mixing was favourable to new particle formation. Despite intensive research extending over several decades, the fundamental mechanism leading to new particle formation remains uncertain (Birmili et al. 2000). The binary homogeneous nucleation mechanism of water and sulphuric acid, which has generally been presumed to be the principal mechanism of new particle formation in the atmosphere, is in many cases insufficient to explain the observed nucleation rates. Alternatively, ternary homogeneous nucleation, also involving ammonia (Korhonen et al. 1999), has been suggested as a means of accelerating the nucleation process (Weber et al. 1998, Clarke et al. 1998, Kulmala et al. 2000a, b). However, besides the physical and chemical processes leading to new particle formation, as yet to be determined, it is important to know the local environmental conditions of nucleation events and their frequency at a specific site, and the possible effect of such ultrafine particles on climate change using regional or global models. The processes of new particle formation vary significantly between different sites in the Baltic Sea region, i.e. southern Finland (boreal forest) and western Lithuania (coastal zone) (Plauškaitė et al. 2003). It was found that the mean rate of new particle formation was almost three times faster in the continental environment than in the coastal zone (0.41 and 0.14 cm^{-3} respectively; Plauškaitė 2008). However, nucleation events were clearly correlated with high levels of solar radiation at both sites. In addition, observations suggested that a low concentration of pre-existing particles and clean air mass transfer were the other conditions necessary for nucleation to occur (Plauškaitė et al. 2003, Pugatshova et al. 2007). Comparison of investigations of the properties and frequency of nucleation events in southern Scandinavia and high-latitude Nordic areas (Dal Maso et al. 2007) showed a higher frequency in southern Sweden. Nucleation events were most frequent during spring and autumn and clearly more distinctive at stations situated at lower latitudes. Generally however, the frequency of all nucleation events and the relative number concentration of newly formed nucleation mode particles were higher in cleaner cold air masses from the North Atlantic (O'Dowd et al. 2001, Dal Maso et al. 2007).

The aim of this work was to analyse the atmospheric conditions that could be responsible for new particle formation and growth in western Lithuania in the coastal zone of the Baltic Sea (Preila station). We tried to relate nucleation events to the measurements of meteorological parameters (relative humidity, wind speed, solar radiation) and the movement of air masses from different directions towards the investigation site. Backward air

mass trajectories were used to determine the dependence of aerosol particle size spectra on air mass origin, which could be responsible for new particle formation and growth. Also, the concentrations of trace gases (ozone (O_3), nitrogen oxides (NO_2) and sulphur dioxide (SO_2)) were analysed together with air mass transfer as an indication of their pollution level.

The observed nucleation mode growth, the source rate of condensable material during nucleation and growth events were evaluated using equations describing the rate of change in the vapour concentration, aerosol particle number concentration and particle growth.

2. Methods

All measurements were performed at the Preila environmental pollution research station (55°55′N, 21°00′E, 5 m above sea level) in the coastal/marine environment during 1997, 1998, 2000–2002 (Figure 1). This station is located on the Curonian Spit, which separates the Curonian Lagoon from the Baltic Sea. The Curonian Lagoon, the largest coastal bay on the Baltic Sea, is a highly eutrophic water body. It is an enclosed shallow (mean depth – 3.7 m) bay connected to the Baltic Sea by the narrow (width 400–600 m) Klaipėda strait. One of the nearest industrial cities, Klaipėda, is about 40 km to the north of Preila, and the other major city in the region, Kaliningrad, is 90 km to the south. The aerosol particle number concentrations and size distributions in the 10 to 200 nm range were measured at the Preila station using the differential mobility particle sizer (ELAS-5Mc) developed at the Environmental Physics and Chemistry Laboratory, Institute of Physics, Lithuania. An inlet system with a silica gel dryer was used to reduce the relative humidity (for more information on this, see Ulevicius et al. 2002). The air samples were collected over a 24-hour interval for the analysis of chemical compounds. Sulphur dioxide (SO_2) was collected on a Whatman 40 filter impregnated with potassium hydroxide (KOH), which followed the Whatman 40 filter for particle retention in the 2-stage filter pack. The flow rate was 16.7 dm^3 min^{-1}. The SO_2 in the extracts from the filter was analysed as sulphate using ion chromatography. Nitrogen dioxide (NO_2) was collected on a sodium iodide impregnated glass sinter filter (flow rate = 0.5 dm^3 min^{-1}). A solution of triethanolamine was used to extract NO_2 from the glass sinter filter. NO_2 was analysed as nitrite by spectrophotometry. Surface ozone concentration was measured by UV absorption using an O_3 41M commercial ozone analyser. Meteorological data (solar radiation, relative humidity, wind speed) were provided by the Atmospheric Pollution Research Laboratory, Institute of Physics, Lithuania. Average hourly and diurnal solar radiation data (W m^{-2}) at Preila were applied to analyse environmental conditions for the event and non-event

Figure 1. Location of the Preila environmental pollution research station

days during 1997 and 2000. The series of 48 h and 96 h backward air mass trajectories for Preila were calculated for June–August 1997, June 2000, May 2001 and March, June–October 2002 using the Hybrid Single-Particle Lagrangian Integrated Trajectories model Version 4 (HYSPLIT) (NOAA, http://www.arl.noaa.gov/ready.html). Initially the back trajectories were calculated every 8 hours (06:00, 14:00 and 22:00 UTC) at three different altitudes (1000, 500 and 20 m above ground level) for the 48 h series. The trajectories were plotted on maps and divided into 9 classes, corresponding to 8 directions (N, NW, W, SW, S, SE, E, NE) and one class for trajectories of uncertain origin (coded UNC). To avoid the uncertain origin that occurs as a result of the complex synoptic situation when an air mass can change its direction several times en route to its recipient, and also to obtain better statistics when analysing the source and transport pathways of air masses arriving at Preila, the back trajectories were calculated every 6 hours (00:00, 06:00, 12:00 and 18:00 UTC) at a 250 m arrival height above the ground level for the 96 h series. The model runs of both series were carried out using the Global FNL meteorological archive with a spatial resolution of 191×191 km. Using the 96 h back trajectory series, the mean position of the air parcel at reference time back steps -12, -24, -48, -72 and

−96 hours was calculated for each 45° sector, starting from 22.5° to cover each direction, and was presented in the form of contour lines of distant points at different time steps. For each patch, delimited by the direction and reference time, we calculated the frequency of the trajectory passing through the patch.

For each nucleation event, the growth rate was calculated graphically from the contour plots (such as in Figures 2a and 3a); furthermore, the concentration of condensable vapour could be estimated from the growth rate. Since the exact identity of the condensable vapour was unknown, the concentrations were estimated by using transport values of sulphuric acid. The characteristics of nucleation event days during the investigation at the Preila station were calculated using equations (1)–(4): the results are presented in Figures 4–7. A log-normal fitting of the aerosol particle size distribution was performed. The separate aerosol particle size modes in the results analysis were investigated according to the accepted mode ranges: nucleation (10–25 nm), Aitken (25–90 nm) and accumulation (90–200 nm) (Mäkelä et al. 2000). The observed nucleation mode growth, the source rate of condensable material and the changes of hygroscopic properties during the nucleation and growth events were analysed using three equations describing the rate of change of the vapour concentration, and the aerosol particle number concentration and particle growth were analysed using the method of Dal Maso et al. (2005). If condensable vapour molecules are assumed to be of species X, the time dependence of vapour concentration C can be expressed (Kulmala et al. 1998) by

$$\frac{dC}{dt} = Q - CS\ C, \tag{1}$$

where Q is the source rate of vapour and CS is its condensation sink rate for the pre-existing aerosol. The time evolution of the aerosol number concentration N in size class i can be expressed by (Kulmala et al. 2001)

$$\frac{dN_i}{dt} = J_i - CoagS\ N_i, \tag{2}$$

where J_i is the formation rate of particles and $CoagS$ is the coagulation sink rate for size i particles. The growth rate can be expressed by (Kulmala 1988)

$$\frac{dr}{dt} = \frac{m_v \beta_m DC}{r\rho}, \tag{3}$$

where r is the particle radius, m_v is the molecular mass of condensable vapour, β_m is the transitional correction factor for mass flux, D is the

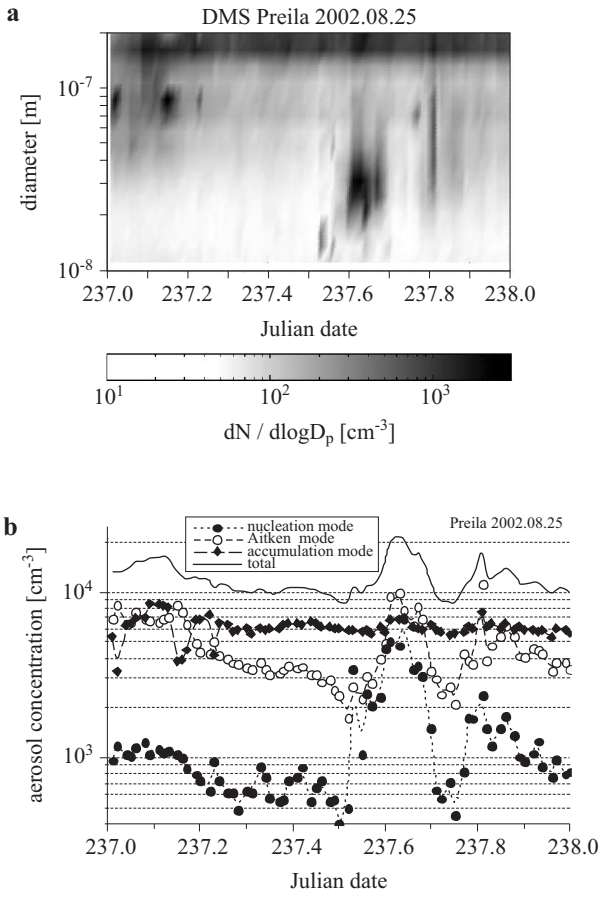

Figure 2. Time evolution of aerosol particle size distribution (a), modal aerosol concentration (b) and backward air mass trajectories (c) at the Preila station on 25 August 2002

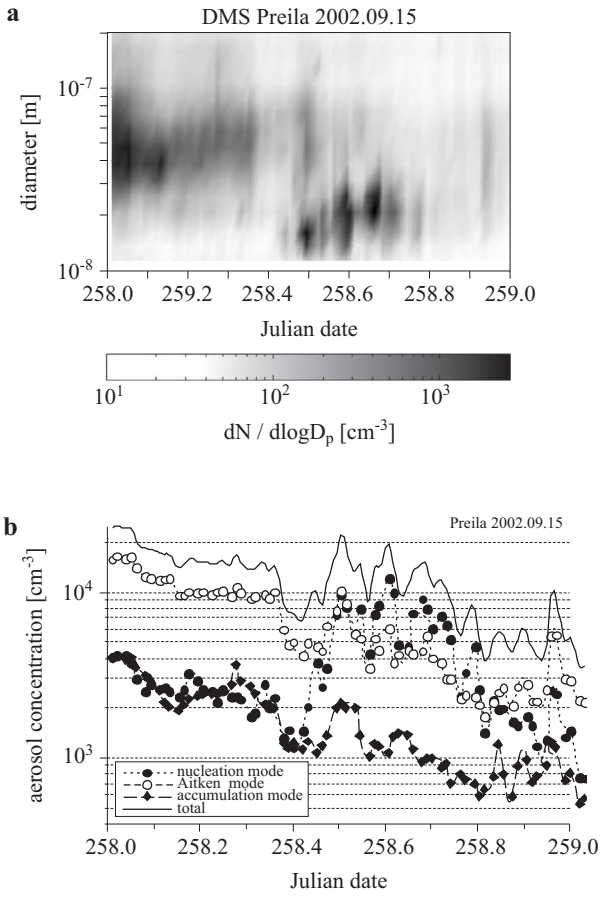

Figure 3. Time evolution of aerosol particle size distribution (a), modal aerosol concentration (b) and backward air mass trajectories (c) at the Preila station on 15 September 2002

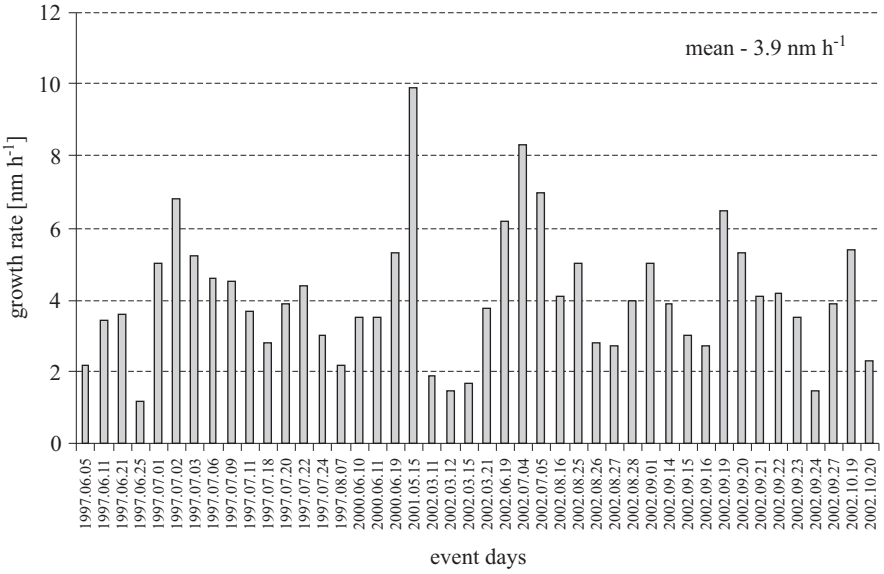

Figure 4. New particle growth rates at the Preila station during the measurement period

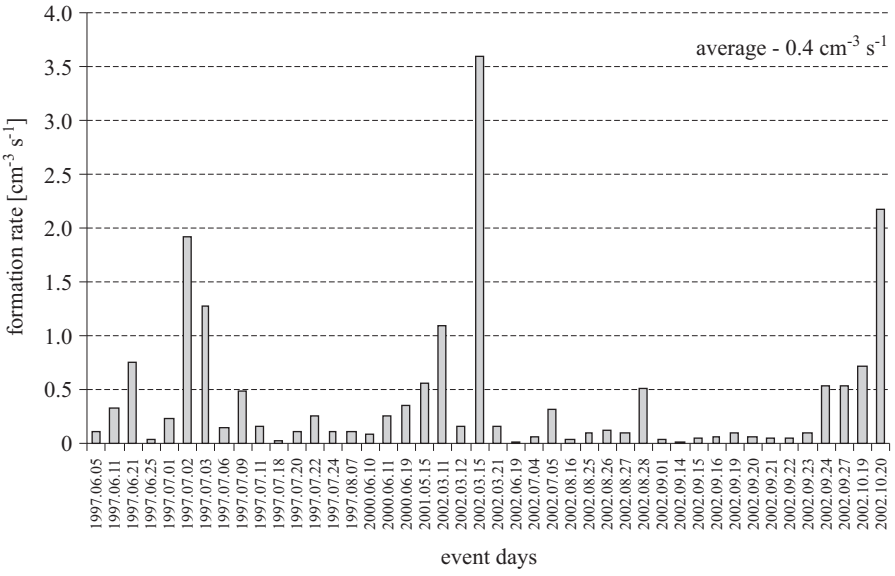

Figure 5. New particle formation rates at the Preila station during the measurement period

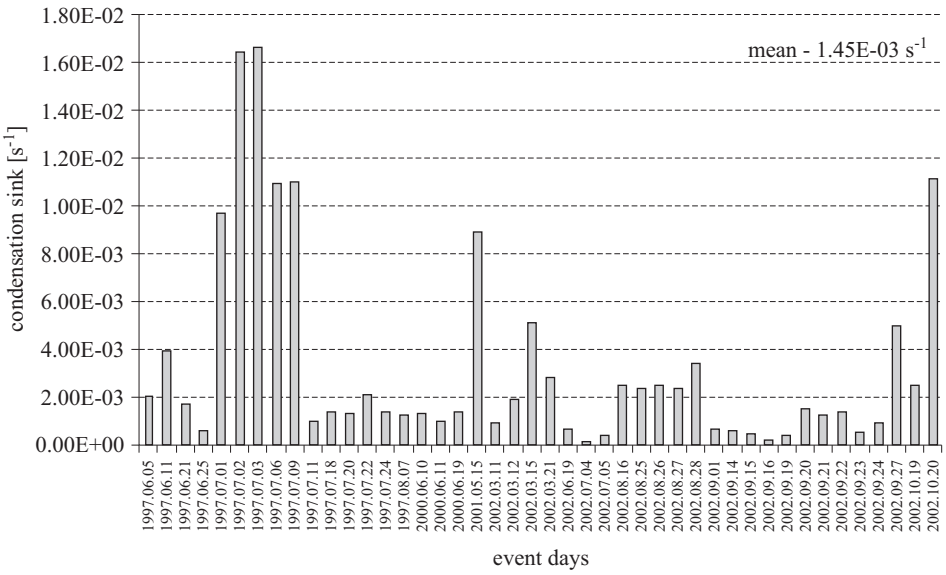

Figure 6. Aerosol particle condensation sink at the Preila station during the measurement period

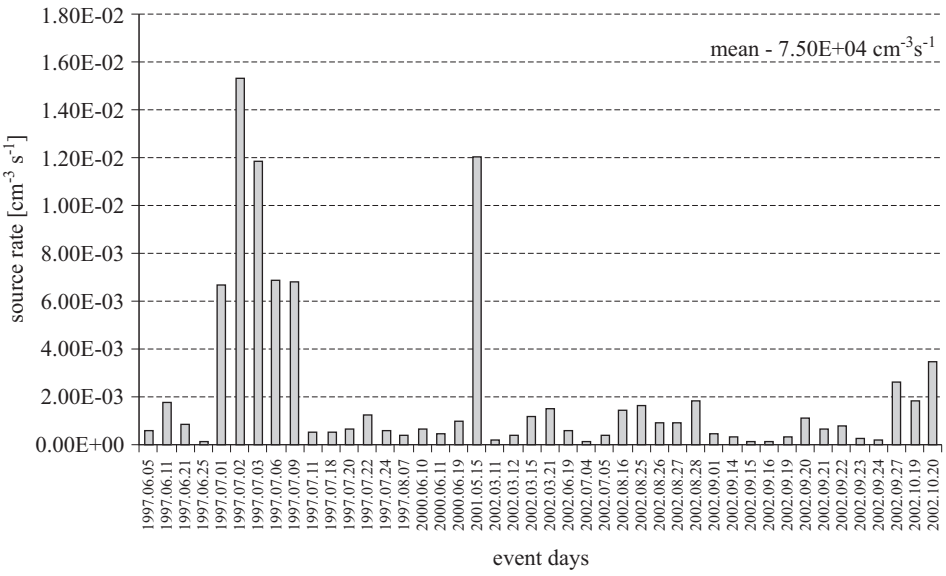

Figure 7. Condensable vapour source rate at the Preila station during the measurement period

diffusion coefficient, and ρ is the particle density. Equation (3) can be integrated from r_0 to r to obtain:

$$C = \rho \left\{ \frac{r^2 - r_0^2}{2} + [4/(3\alpha) - 0.623]\lambda(r - r_0) + \right.$$
$$\left. + 0.623\lambda^2 \ln \frac{\lambda + r}{\lambda + r_0} \right\} \Big/ \Delta t D m_v, \tag{4}$$

where α is the mass accommodation coefficient (i.e. sticking probability) and λ is the mean free path. The parameters dr/dt, CS, $CoagS$, $dN_{10\ \mathrm{nm}}/dt$, $N_{nucleation\,mode}$ and the soluble fraction can be obtained directly from measurements of the aerosol size distribution changes and hygroscopicity properties. A detailed analysis of these equations can be found in Dal Maso et al. (2005).

3. Results and discussion

3.1. Nucleation events

At the coastal site (Preila station) we observed two types of nucleation events, i.e. short-term and long-term particle bursts. The aerosol size distributions were plotted as they evolved with time throughout each nucleation event day. Examples of such plots, together with the number concentrations of each mode and air mass back trajectories, are shown in Figure 2 for 25 August 2002 and in Figure 3 for 15 September 2002, which were typical long-term nucleation event days at Preila (Plauškaitė et al. 2005). A similar analysis of the aerosol particle number size distribution at the Preila site was carried out by Kikas et al. (2008). Long-term nucleation events occur mostly in the daytime and last from one to eight hours. Short-term nucleation events occur all the year round, both during the day and at night, lasting from only a few minutes to one hour, but the particle number concentrations during these nucleation events are comparable to some of the long-term nucleation events. Some short-term nucleation events were also observed during rainfall or soon afterwards. The generation of negative cluster ions (or multiply charged nanometer particles with the same mobility as cluster ions) was often recorded during rain (Laasko et al. 2004). The formation mechanism of charged nanometer particles during rainfall is not well known (Hoppel & Frick 1990).

The total amount of data analysed covers 291 one-day periods (1997, 2000–2002), 45 (15%) of which were long-term nucleation event days. The percentage of observation days that were nucleation event days at other measurement stations in the coastal/marine zone of the Baltic Sea was

similar – 15% (Aspvreten, Sweden; Dal Maso et al. 2007) and 11–14% (Utö, Finland; Hyvärinen et al. 2008). In the continental region around the Baltic Sea 27% of the observation days were classified as nucleation event days as regards new particle formation (Hyytiälä, Finland; Dal Maso et al. 2007), 36% in southern Sweden (Kristensson et al. 2008) and 19% in Värriö (Finland; Dal Maso et al. 2007). In our previous work (Plauškaitė et al. 2003) it was shown that nucleation events at a boreal forest site (Hyytiälä station) could be described by plots of the aerosol size distributions as they evolve with time that have the classical, well known, 'banana' shape. The majority of the nucleation events at the coastal site (Preila station) were characterised by a clear formation process followed by the sudden disappearance of the nucleation mode particles, perhaps explainable by specific peculiarities in the coastal/marine atmospheric circulation.

That the Preila nucleation events are not as straightforward to analyse, especially in terms of growth rates, is evident from Figures 2a and 3a. There is a clear formation of nucleation mode particles at the lower end of the detection limit (10 nm), when the mode shows very distinct growth (Figures 2b and 3b). During the new particle formation event on 25 August 2002 (Figure 2a, b) it was mainly such processes that were observed: no sooner were particles formed than they disappeared. This type of nucleation appears to be characteristic of the coastal/marine environment (O'Dowd et al. 2002). Analysis of the backward air mass trajectories at different altitudes (1000, 500 and 20 m above ground level) showed that on 25 August 2002 (Figure 2c) there was a steady advection of continental air masses at all the heights in the atmosphere from higher latitudes. In this case the environmental parameters in the coastal zone may have been influenced more by the peculiarities of the continental air mass than by the marine boundary layer and disrupted the development of long-term new particle formation. In the second case (Figure 3c), advection of polar air masses, which were transported along coastal regions of the Baltic Sea from Finland to the Preila site, was observed. In Figure 3c we can see that, before reaching Preila, the air masses at 1000 and 500 m altitudes were transported mainly in the lower layers of the atmosphere above the Baltic Sea and could have influenced the evolution of long-term new particle formation.

Moreover, before the start of a nucleation event, pre-existing particle concentrations were observed to decrease at Preila; this may have been another necessary condition for nucleation to occur. The investigation showed that the pre-existing particle concentration decreased in 60% of all the cases of long-term new particle formation events at Preila.

The formation of new aerosol particles appears to be highly correlated with the intensity of solar radiation, which is usually ca 50–75% higher than

the levels recorded on non-nucleation event days. There are few nucleation events when levels of solar radiation are low; these are recorded when 10 nm particles are detected in the afternoon or evening. In recognition of the fact that particles need some time to grow from 2–3 nm to 10 nm (Plauškaitė et al. 2003), the solar radiation was averaged for about 2–3 hours before the nucleation event time. These levels were also well above the non-nucleation event day averages. For example, during the event on 24 July 1997 the average hourly solar radiation was 610 W m^{-2}, while during the non-event period on the same day it was 390 W m^{-2}; on 19 June 2000 the respective levels were 590 W m^{-2} and 290 W m^{-2} (Plauškaitė et al. 2003).

The particle growth rates at Preila varied between 1.2 and 9.9 nm h^{-1} (mean = 3.9 nm h^{-1}). The average particle growth rates at the other stations were 2.5 nm h^{-1} at Vavihill (southern Sweden; Kristensson et al. 2008), 2.3 nm h^{-1} on Utö (an island in the Baltic Sea; Hyvärinen et al. 2008), 5.9 nm h^{-1} at KGAWC (Korea; Lee et al. 2008), mean growth rate – 3.0 nm h^{-1} at Hyytiälä (Finland; Dal Maso et al. 2005) (Table 1). Unusually high growth rates were recorded on days when air masses arrived at the station from the NW, W and SW. Formation rates J_{10} at Preila varied between 0.01 and 0.36 cm^{-3} s^{-1} (av. = 0.40 cm^{-3} s^{-1}). Values were especially high in spring, and at stations in southern Finland (Dal Maso et al. 2007). Average formation rates of 3 nm particles J_3 of the same order of magnitude (0.09–1.8 cm^{-3} s^{-1}) were registered at rural sites (Wehner et al. 2007): 0.45 cm^{-3} s^{-1} on Utö (Hyvärinen et al. 2008), 1.54 cm^{-3} s^{-1} at Vavihill (Kristensson et al. 2008), 0.4 cm^{-3} s^{-1} at Aspvreten (Sweden), 0.8 cm^{-3} s^{-1} at Hyytiälä, 0.2 cm^{-3} s^{-1} at Värriö and 0.1 cm^{-3} s^{-1} at Pallas (the last two sites are both in Lapland, Finland; Dal Maso et al. 2007). The mean condensation sink at the Preila station was 1.45×10^{-3} s^{-1}. The geometric mean of the condensation sink was ca 3.8×10^{-3} s^{-1} on Utö (Hyvärinen et al. 2008) and 5.4×10^{-3} s^{-1} at Vavihill (Kristensson et al. 2008). The condensation sink at Preila was about 50% lower than at Hyytiälä (2.5×10^{-3} s^{-1}) and Aspvreten (3.3×10^{-3} s^{-1}), and about 50% higher than at Värriö (0.98×10^{-3} s^{-1}) and Pallas (0.72×10^{-3} s^{-1}) (Dal Maso et al. 2007). The mean condensable vapour source rate was 7.5×10^4 cm^{-3} s^{-1} at Preila. Condensable vapour source rates at the Hyytiälä, Värriö, Aspvreten and Pallas stations varied between 3.3×10^4 and 22×10^4 cm^{-3} s^{-1} (Dal Maso et al. 2007). The vapour source rate at Preila varied over larger ranges than at the other stations (0.9×10^4–153×10^4 cm^{-3} s^{-1}). On nucleation event days, when vapour source rates were the highest (118×10^4–153×10^4 cm^{-3} s^{-1}), values of the other calculated characteristics of nucleation events were also high. The higher vapour source rates at Preila led to higher growth and

Table 1. The parameters of nucleation events at Preila and other stations (GR – growth rate, $J_{3\text{ or }10}$ – formation rate, CS – condensation sink, Q – condensable vapour source rate)

Place	GR [nm h^{-1}]	J_3 [cm^{-3} s^{-1}]	CS [s^{-1}]	Q [cm^{-3} s^{-1}]	Reference
Preila (Lithuania)	3.9	0.40 (J_{10})	1.45×10^{-3}	$(0.9 - 153) \times 10^4$	This paper
Aspvreten (Sweden)		0.40	3.30×10^{-3}	$(3.3 - 22) \times 10^{4(b)}$	Dal Maso et al. (2007)
Hyytiälä (Finland)	3.0$^{(a)}$	0.80$^{(b)}$	$2.50 \times 10^{-3(b)}$	$(3.3 - 22) \times 10^{4(b)}$	$^{(a)}$Dal Maso et al. (2005) $^{(b)}$Dal Maso et al. (2007)
Värriö (Finland)		0.20	0.98×10^{-3}	$(3.3 - 22) \times 10^{4(b)}$	Dal Maso et al. (2007)
Pallas (Finland)		0.10	0.72×10^{-3}	$(3.3 - 22) \times 10^{4(b)}$	Dal Maso et al. (2007)
KGAWC (Korea)	5.9				Lee et al. (2008)
Utö (island, Baltic Sea)	2.3	0.45	3.80×10^{-3}		Hyvärinen et al. (2008)
Vavihill (southern Sweden)	2.5	1.54	5.40×10^{-3}		Kristensson et al. (2008)
rural sites		0.09–1.80			Wehner et al. (2007)

formation rates, and ultimately, to more frequent formation events than at the Finnish stations (Dal Maso et al. 2007) (Table 1).

3.2. Air mass transfer, meteorological factors and gases

The frequency of the trajectories of air masses coming from different directions to the Preila station is presented in Figure 8a. As can be seen, air masses arriving at Preila from northerly and westerly directions were dominant during the studied months (especially from the westerly sector). The frequency of trajectories coming from southerly directions was much lower and the distance travelled was much shorter than those of air masses arriving from the Atlantic Ocean. Similar results were obtained at Hyytiälä (Sogacheva et al. 2005). Analysis of the backward air mass trajectories associated with the nucleation events showed that most of the nucleation events were accompanied by air masses advecting from the N (43%) and NW (19%) (Figure 8b). Figure 9 shows the distribution of air mass trajectories on event days in spring, summer and autumn: clearly, on nucleation event days air masses arrive predominantly from the N, especially in autumn. From southerly directions the backward air mass trajectories are almost all twisted northerly, but only in the summer. Therefore, in Figure 8b we can see that the possibility of an event occurring in the −12 and −24 h back step patch of the southerly direction is very high (0.23 and 0.2 respectively), when all but one of the trajectories are actually northerly ones (Figure 9).

Generally, it was observed at Preila that new particle formation usually proceeded at a very low rate during the study period in 2002 (Figure 5), except in March, late September and October. Air mass advection towards Preila in these months was most commonly from the NW, N and NE, in contrast to the summer months (Figure 9). In spring and autumn the observed values of the parameters of new particle formation differed distinctly from those during nucleation events in other months (Figures 4–7). Growth rates in spring and autumn were found to vary from 1.5 to 3.8 nm h^{-1} (mean 2.2 nm h^{-1}) and from 1.5 to 6.5 nm h^{-1} (mean 3.9 nm h^{-1}) respectively. The growth rate in summer (1.2–9.9 nm h^{-1}; mean 4.4 nm h^{-1}) was higher than in spring and autumn. The formation rate was highest in spring, varying from 0.14 to 3.60 $cm^{-3}s^{-1}$ (mean 1.24 cm^{-3} s^{-1}), whereas in autumn and summer it ranged from 0.01 to 2.17 cm^{-3} s^{-1} (mean 0.34 cm^{-3} s^{-1}) and from 0.01 to 1.91 cm^{-3} s^{-1} (mean 0.31 cm^{-3} s^{-1}) respectively. Condensation sink and vapour source rates were also highest in summer: from 1.27×10^{-4} to 1.66×10^{-2} s^{-1} (mean 4.01×10^{-3} s^{-1}) and from 9.27×10^{3} to 1.53×10^{6} cm^{-3} s^{-1} (mean 2.84×10^{5} cm^{-3} s^{-1}) respectively. The condensation sink in spring and autumn varied from

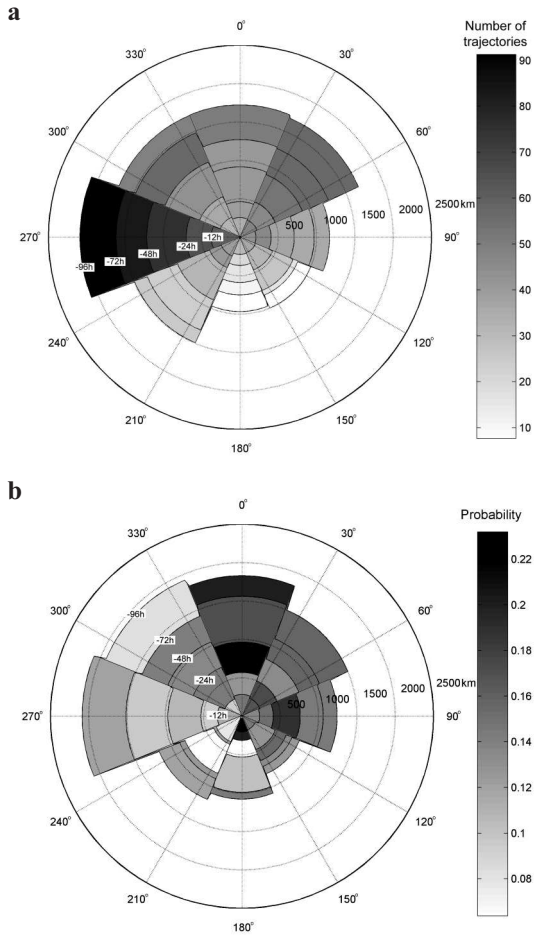

Figure 8. Frequency of 96 h backward air mass trajectories (a) and the probability of a nucleation event for a corresponding trajectory direction (b) in different direction sectors between the corresponding back time steps (contour line for −12 h, −24 h, −48 h, −72 h, −96 h) for the whole investigation period

8.78×10^{-4} to 5.10×10^{-3} s^{-1} (median 2.67×10^{-3} s^{-1}) and from 2.31×10^{-4} to 1.11×10^{-2} s^{-1} (mean 2.03×10^{-3} s^{-1}) respectively. The vapour source rate in spring and autumn ranged from 2.29×10^{4} to 1.46×10^{5} cm^{-3} s^{-1} (mean 8.16×10^{4} cm^{-3} s^{-1}) and from 8.56×10^{3} to 3.50×10^{5} cm^{-3} s^{-1} (mean 9.52×10^{4} cm^{-3} s^{-1}) respectively.

The dependence of solar radiation levels on air mass transport direction was analysed during the summer measurement period. The lowest solar radiation fluxes corresponded to backward trajectories of air masses arriving from the W or SW when cloud cover was high. Solar radiation levels, known

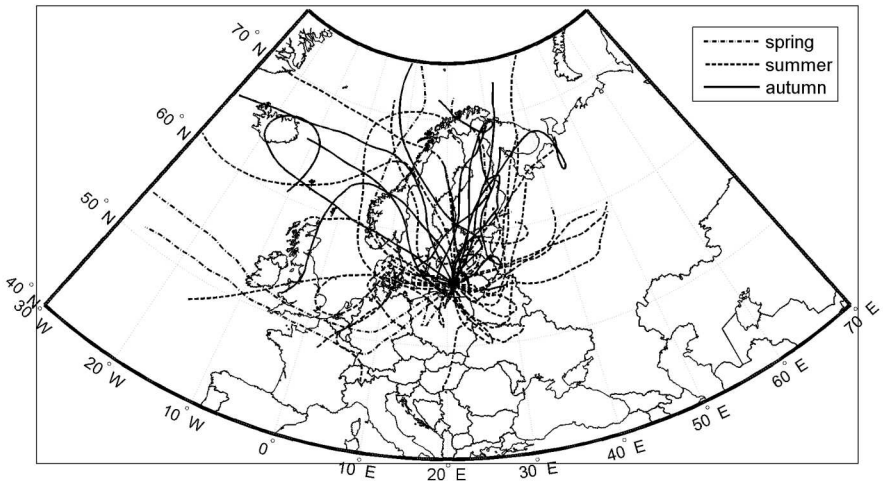

Figure 9. Distribution of 96 h backward air mass trajectories (arrival height above the ground level – 250 m) associated with nucleation event days at the Preila station in spring, summer and autumn

to be an important parameter as regards new particle formation and growth (Birmili & Wiedensohler 2000, Kulmala et al. 2001), were highest when the air masses came from the NE, E and SE, i.e. when anticyclonic weather with a cloudless sky was prevailing. The relative humidity (RH) statistics of the Preila station were evaluated for the entire measurement period. The Preila station is notable for its higher relative humidity owing to its coastal/marine environment (mean = 75–95%). But on many spring days and in July 1997, the relative humidity was higher on nucleation event days than the average on the non-event days of the same month. Nonetheless, the relative humidity on many nucleation event days was lower than the average for non-event days. This negative correlation between new particle formation and relative humidity accords with previous studies (De Leeuw et al. 2002, O'Dowd et al. 2002, Lee et al. 2008). The fact that air mass advection directions and relative humidity were uncorrelated at this location suggests that this may have been due to the small number of data available.

Wind speeds during the measurement period at Preila were high owing the station's location in the coastal/marine environment (mean = 2.1–6.5 m s^{-1}). Wind speed measurements were examined in the context of the backward air mass trajectories recorded there. The highest wind speed was associated with air masses arriving from westerly directions, the lowest with air masses from the easterly sector, when the respective weather conditions were cyclonic and anticyclonic. No direct relationship between wind speed and new particle formation at Preila was found. The wind

speed may have reduced the number of observed nucleation events at Preila in comparison with other measurement stations, where average wind speeds were significantly lower (for example, in boreal regions the mean wind speed was between 0.2 and 0.7 m s^{-1}; Plauškaitė et al. 2003).

The ozone (O_3) concentration data measured over the entire period at Preila can be used as an indicator of when new particle formation is most likely to occur (De Leeuw et al. 2002). The mean O_3 concentration during the measurement period was 64.3 μg m^{-3}. Slightly higher concentrations of O_3 were associated with air masses from the NW at Preila in March and October 2002, which could be due to ozone transfer from overlying atmospheric layers at higher latitudes. However, the higher concentration of O_3 associated with air masses from the E and SW in June, SE and E in July, SE and W in August, S and SE in September was related to boundary layer photochemical reactions. Therefore, when air masses from these directions were transported, nucleation events at Preila were few in number. This suggests that the ozone boundary layer may be a factor limiting the occurrence of nucleation events (Hamed et al. 2007).

Diurnal variations of SO_2 concentrations as a sulphuric acid precursor, which takes part in the new particle formation process (Kulmala et al. 2006, Sihto et al. 2006), were analysed with regard to new particle formation event and non-event days. During the measurement period SO_2 concentrations were high when the air masses were moving in from the SE – W, i.e. when the air masses had passed over central European industrial regions before reaching Lithuania. The highest concentrations of NO_2, especially in March and October, were associated with air masses coming from the S, SE, E and N, when air masses arrived at Preila from more polluted continental regions. In most cases, SO_2 and NO_2 concentrations appear to be a neutral factor as regards nucleation, displaying no significant differences between nucleation event and non-event days. But there were some nucleation event days (northerly air masses) when SO_2 and NO_2 concentrations were two or even three times higher than those on non-event days. Recent findings from observations at the Hyytiälä boreal forest site in Finland (Bonn et al. 2008), on the west coast of South Korea (Lee et al. 2008), at a background station in southern Sweden (Kristensson et al. 2008), on the island of Crete (Greece) and in the eastern Mediterranean (Lazaridis et al. 2006) indicate that the relationship between nucleation events and chemical elements is still an open question, so that in the future, the chemical composition of newly formed particles will have to be elucidated in detail.

4. Conclusions

Experimental results showed that new particle formation and growth is clearly in evidence at a coastal site in the south-eastern Baltic Sea region (Preila, Lithuania). The total number of data analysed covers 291 one-day periods (1997, 2000–2002), 45 (15%) of which were long-term, new particle formation days. Long-term nucleation events occur mostly in the daytime and last from one to eight hours. We also observed short-term nucleation events, which occur all the year round, both in the daytime and at night, lasting from only a few minutes to one hour.

The total aerosol concentration and size distributions were measured and analysed. For each observed nucleation event the growth rate, new particle formation rate, condensation and coagulation sink rates were calculated, and the concentration of condensable vapour was estimated. Growth rates varied between 1.2 and 9.9 nm h^{-1}, formation rates from 0.01 to 4.97 cm^{-3} s^{-1}. The mean condensation sink was 1.45×10^{-3} s^{-1} and the mean condensable vapour source rate was 7.5×10^4 cm^{-3} s^{-1}. The majority of nucleation events at the Preila station involve the evident formation of new aerosol particles, but short-term nucleation events are followed by the sudden disappearance of nucleation mode particles, a typical phenomenon in coastal environments.

Analysis of the backward air mass trajectory directions associated with the nucleation events at Preila showed that nucleation events were accompanied mainly by air masses advecting from the N (43%) and NW (19%).

Meteorological parameters, trace gas and aerosol concentrations measured at the Preila measurement site were analysed and characterised with respect to the air masses arriving there. The formation of new aerosol particles was clearly related to high levels of solar radiation. In most cases, the relative humidity was lower on nucleation event days than the average of non-nucleation event days in the same month. In March and October the higher concentrations of O_3 at Preila were associated with air masses from the NW, i.e. from the direction most closely related to nucleation events, and which could in turn be associated with ozone transfer from overlying atmospheric layers at higher latitudes. Diurnal concentrations of SO_2 and NO_2 did not show any distinct connection with the nucleation process.

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