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Nucleation events detected at the high altitude site of the Puy de Dôme Research Station, France

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Aerosol and ion number size distributions were measured at the top of the Puy de Dôme (1465 m above the sea level) for a three-month period. The goals were to investigate the vertical extent of nucleation in the atmosphere and the effect of clouds on nucleation. Nucleation and new-particle formation events were classified into four classes: (1) burst of cluster ions, (2) large ion formation starting from 10 nm, (3) burst of cluster ions followed by large ion formation with a gap of intermediate ions, and (4) burst of ions with continuous growth to the sizes > 10 nm. All together these events were observed during nearly half of the analyzed days. Concentrations of cluster ions (< 1.4 nm) varied typically between 100 and 1000 cm^{-3}. Intermediate ion (1.4–6 nm) concentrations were usually lower than 500 cm^{-3} but could exceed 3000 ions cm^{-3} during nucleation events. Large concentrations of intermediate ions seem to be appropriate to detect the occurrence of most of nucleation events. In clouds, the aerosol condensation sink and cluster ions concentrations were lower, presumably because of scavenging by cloud droplets, but the intermediate ion concentrations remained unchanged. We observed that large ion formation starting at 10 nm (class 2 events) and continuous growth of ions (class 4 events) occurred preferably under clear-sky conditions, and that all except class 2 events could be observed under cloudy conditions.

Introduction

Atmospheric aerosols play an important role in the radiative balance of the Earth. The first effect of the particles on the climate is through the absorption and scattering of the solar radiation. The second effect arises from the fact that these particles act as cloud condensation nuclei (Hobbs 1993). Consequently, it is urgently needed to be able to predict the aerosol size distribution in time and space, and hence to understand the formation mechanisms under various environments. Primary marine and dust aerosol sources have been extensively studied and characterized regarding their relationship with the environmental factors such as wind speed (Andreas 2002, Marticorena and Bergametti 1995). On the other hand, the sources of sub-micron secondary aerosol particles in various environments are much less understood, even though they account for a high fraction of particle number concentrations.

Ultrafine aerosols formation, i.e. nucleation events, have been observed in many environments, such as the boreal atmosphere (Mäkelä *et al*. 1997, Kulmala *et al*. 1998), Antarctic environment (Ito 1993), free troposphere and near clouds (Clarke 1992, Perry and Hobbs 1994, Keil and Wendisch 2001), as well as coastal environments around Europe (O'Dowd *et al.* 1999). A review of nucleation events observations was published by Kulmala *et al.* (2004a). Most of the nucleation events mentioned in the literature have been detected by observing the number size distribution of aerosol particles with the SMPS or DMPS technique. However, these techniques have not, up to now, been able to detect aerosol particles in natural environments down to sizes below 3 nm. The use of the Air Ion Spectrometer (AIS) (0.4–44 nm ion size distribution) brings new information on new particle formation processes. Firstly, the instrument gives us access to sizes that are intermediate stages between the gas and particulate phases. Second, it provides measurements of the charged fraction of the clusters and particles, and hence gives indications on the role of ions in the nucleation process. This paper deals with first measurements made at a high-altitude site during a three-month period using the AIS device. We propose to describe and classify nucleation events observed during the spring period at the site of the Puy de Dôme, central France. The Puy de Dôme station is located at 1465 m above the sea level and lies in a region where both the upper part of the boundary layer (BL) and the free troposphere (FT) can be sampled. It is likely that the interface between the BL and FT is of interest, since there clean air from the FT mixes with polluted air from the BL. The advantage of such a site is mainly the possibility to document the vertical extend of nucleation in the atmosphere and better characterize the role of vertical mixing in the nucleation process. Additional information can be provided on the occurrence of nucleation in the presence of clouds. A particular interest will be given here to precursors in the new particle formation events by studying the total concentrations of cluster ions (0.4–1.4 nm diameter) and their relation with the presence of clouds.

Materials

Measurement site

The Puy de Dôme research station is located at 1465 m above the sea level in central France (45°46´N, 2°57´E). The station is surrounded mainly by a protected area where fields and forests are predominant, the city of Clermont-Ferrand (300 000 inhabitants) being located 16 km east of the station. Meteorological parameters, including the wind speed and direction, temperature, pressure, relative humidity and radiation (global, UV and diffuse), atmospheric trace gases (O_3, NO_x, SO_2, CO_2) and particulate black carbon (BC) are monitored continuously throughout the year. A small military base is located north of the station, where fuel is used to generate electricity under stormy winter conditions. Winter temperatures vary typically from –10 to +10 °C. Westerly and northerly winds are dominant. During the November–April period, the road access to the station is restricted to experimental work preventing from local contamination. Despite its relatively low elevation, long-term records of gases and meteorological parameters indicate that, in winter, the site is mainly located in the free troposphere. This has been confirmed by comparing of the aerosol load and composition between our site and other sites located at higher elevation in the Alps (Jungfraujoch, Sonnblick, Zugspitze) (Sellegri *et al.* 2003).

The data discussed in this paper are based on samplings achieved during three months from March to May 2006. During this period, a complete set of aerosol instrumentations (twin-SMPS, filters, low-pressure impactors and AIS) were deployed at the site.

Instrumentation

Because the Puy de Dôme station is more than 50% of the time in clouds, the aerosol sampling is performed through a whole air inlet (WAI) which ensures efficient sampling of both cloud droplets and interstitial aerosol in the presence of clouds. The WAI samples air at 12 m above the ground through a heated inlet that avoids ice formation. Wind velocity around the inlet head is lowered by a wind-shield to ensure efficient sampling even at elevated wind speeds. Air is sucked into a 12-cm-diameter PVC tube at a flow rate of 30 m^3 h^{-1}, subsequently sub-sampled inside the PVC tube with a 5 cm-diameter stainless-steel tube ensuring iso-kinetic sub-sampling. The stainless-steel section of the inlet is equipped with a heated section to evaporate cloud droplets and to maintain the relative humidity of sampled air at ~50%. Interstitial aerosols and evaporated cloud residues are sampled simultaneously at a constant relative humidity and can be compared in size regardless of the environmental conditions. Temperature never exceeded 25 °C to limit aerosol volatilization. A Twin-SMPS (Scanning Mobility Particle Sizer), consiting of nano-SMPS and SMPS, measured the particle number size distribution (3–500 nm) at the top of the Puy de Dôme station through the WAI continuously since May 2005. The twin-SMPS data will be used in this work to evaluate the charged-to-neutral ratio of particles detected during nucleation events. The nano-SMPS flow rate is 1.5 l min^{-1} and for the SMPS it is 1 l min^{-1}. Condensation particle counter used are TSI-3025 and TSI-3010. Differential mobility analyser (DMA) columns are the small TSI-3085 and the long TSI-3081 for the nano-SMPS and SMPS, respectively. The scanning time for the twin-SMPS is three minutes.

The mobility distributions of atmospheric positive and negative ions are measured with the AIS (Air Ion Spectrometer, AIREL Ltd., Estonia), providing the ion size distribution in the diameter range 0.4–44 nm (mobility range: 3.162–0.0013 cm^2 V^{-1} s^{-1}). The AIS sampling principle is based on the simultaneous selection of 21 different sizes of atmospheric ions of each polarity (negative and positive) along two differential mobility analysers and their subsequent simultaneous detection using electrometers in parallel. The conversion from mobility to diameter is calculated according to the Tammet's inversion (Tammet 1995). The sample flow rate of the AIS is 60 l min^{-1} and the integration time is five minutes. The AIS sampling is performed through a different inlet, directly through the station front facade, in order to avoid the re-combination of ions in the sampling line. The size-cut of large ions sampled through the AIS inlet is 10 μm for a wind speed of 2 m s^{-1} and 2 μm for a wind speed of 5 m s^{-1} wind speed. As a result, few droplets should enter the inlet, except at wind speeds smaller than 5 m s^{-1} which is rare at the station. The sampling with the AIS was performed between 25 February and 31 May 2006.

Results

Classification of nucleation events with AIS data

The size distributions of ions at the Puy de Dôme station were similar to those observed in other environments: high concentrations of small clusters of both positive and negative charges were observed nearly continuously (Horrak *et al.* 2003, Hirsikko *et al.* 2005). Peak concentrations of positive clusters were observed for diameters in the range 0.6–1.2 nm while negative clusters were smaller with highest concentrations found for sizes between 0.4 and 1 nm.

Cluster ions were sometimes observed to grow into larger sizes (> 1.4 nm) on time scales of a few hours. This rapid growth will be referred to as a "burst" of ions. The growth of cluster ions into larger sizes was often followed by a nucleation event, but not always. During the three months of sampling (97 days), nucleation event and/or ion bursts occurred on 42 days. Consequently, nearly half of the sampling days are available for investigating the link between the burst of small ion clusters and the formation of new particles. Classification of nucleation events can be found in the literature for the boreal atmosphere (Dal Maso *et al.* 2005, Hirsikko *et al.* 2007) and the marine atmosphere (O'Dowd *et al.* 2002). Because each environment has different features regarding nucleation events, we chose to classify the 42 nucleation days observed at the Puy de Dôme station into the four classes explained below.

Class 1 (6 days): a burst of ions was detected but it was not followed by a significant particle formation event (Fig. 1). The reasons for this kind of observation could be multiple. One possible explanation for this phenomenon could be that the low volatility compounds responsible for the growth of the cluster ions stopped being produced, because of changes in photochemical conditions at the site. We do not have information on the mixing ratios of organic compounds at the Puy de Dôme station to investigate this possibility. Another explanation could be that the air mass sampled at the Puy de Dôme was horizontally inhomogeneous. The first stages of the burst of small ions are usually observed during

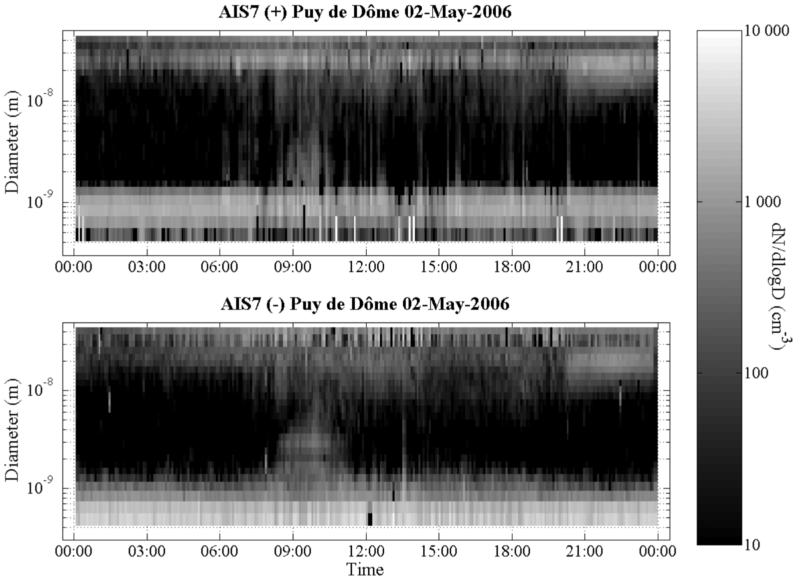

Fig. 1. Example of class 1 event: burst of ions without particle formation. The growth of ions stops at approximately 4 nm. A high concentration of small ions < 2 nm (small positive ions are larger than the negative) can be seen.

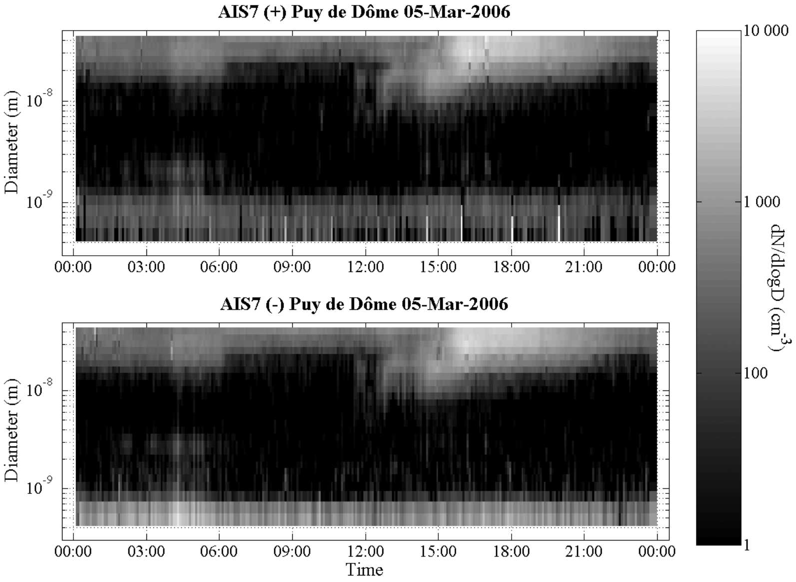

Fig. 2. Example of the class 2 event: nucleation without an ion burst. No ions between 1 and 10 nm were detected.

the morning starting from 09:00. At this time, the Puy de Dôme is still in the free troposphere but we can not exclude inputs from the boundary layer, which is one more explanation for these bursts of ions to occur. The last explanation is that the nucleated particles were scavenged by larger pre-existing particles before they grew into sizes of a few nanometers. The role of the condensational sink will be shortly investigated in later sections.

Class 2 (12 days): formation of large ions starting at 10 nm diameter. In cases belonging to this class, large ions of 10 nm grew into larger sizes during the day, but no ions below 10 nm were detected prior to the formation of 10 nm particles (Fig. 2). Once again, this could be due to an inhomogeneous air mass transported to the Puy de Dôme station. In this class, however, the newly-formed particles were observed at around mid-day, thus they were more likely the results of a transport from the boundary layer where nucleation had occurred earlier during the day.

Class 3 (13 days): burst of ions followed by the formation of large ions without intermedi-

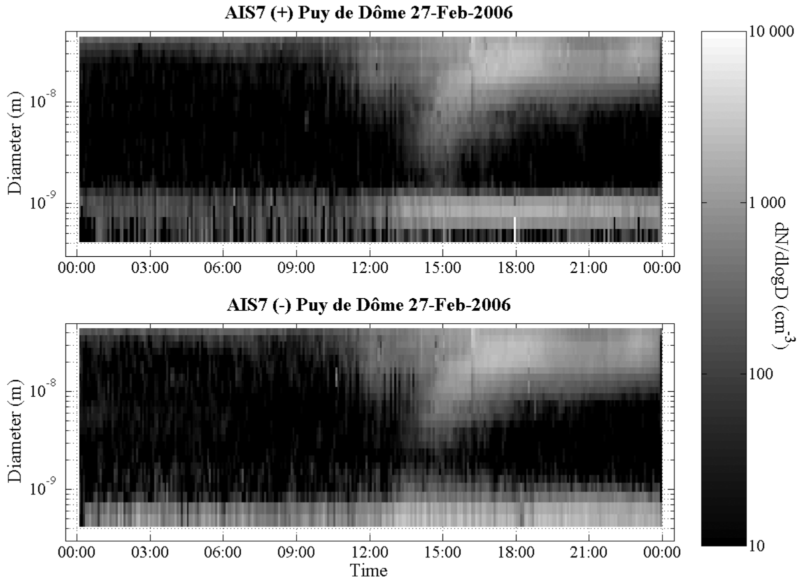

Fig. 3. Example of the class 3 event: concentration of small ions increased at 13:00. The growth of ions is quite visible although there were no intermediate ions around 2–3 nm.

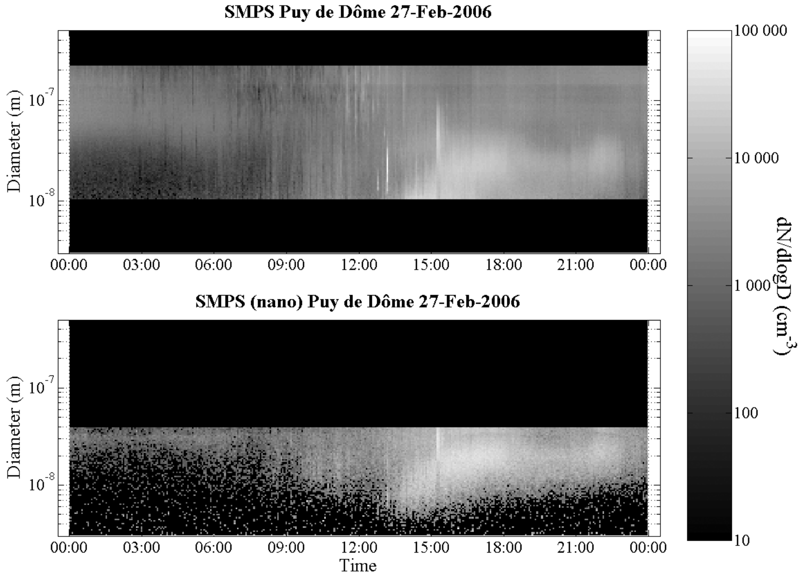

Fig. 4. The same day as Fig. 3 but measured with the twin-SMPS. No particles were detected below 4 nm. For this nucleation event there was a significant lack of ions/particles between 1 and 4–5 nm.

ate ions. In cases belonging to this class, a burst of ions up to 3 nm occured, followed later by a nucleation event of large ions of 4 to 8 nm. However, intermediate sizes between cluster ions and large ions were not observed (Fig. 3). The explanation for this "gap" of ions during the growth of ion clusters is not clear. In order to study the possibility of ion recombination in this size range specifically, the measurements of total number concentration of particles using the twin-SMPS were compared with the AIS data (Fig. 4). Neither the twin-SMPS nor AIS detected particles below 5 nm, thus excluding a recombination artefact in the AIS. Here again, nucleation may have taken place in several places but not homogeneously, or this class can be a combination of classes 1 and 2, i.e. a burst of ions produced in the free troposphere followed by newly-formed particles brought from the boundary layer.

Class 4 (11 days): continuous growth of cluster ions into large ions. In this class ions were observed to grow from 0.4 nm to at least 10–20 nm in a continuous manner (Fig. 5). In this class, we can calculate a growth rate of ions from clus-

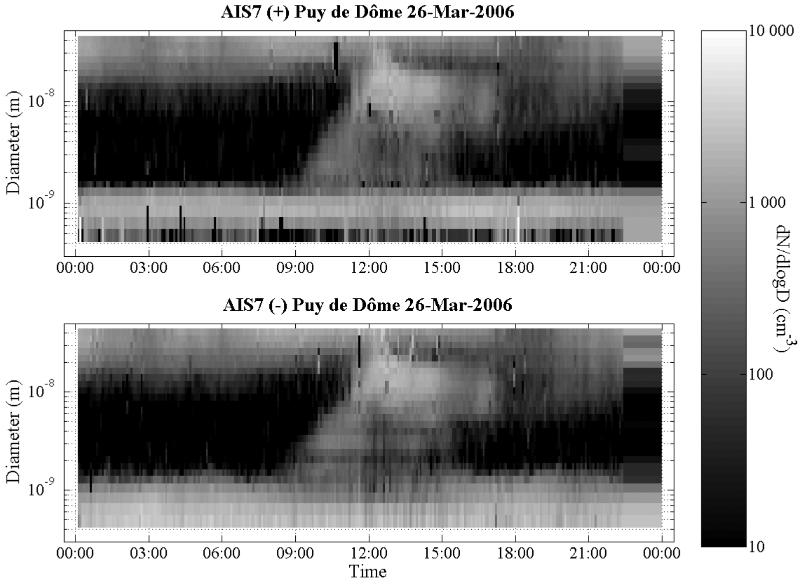

Fig. 5. Example of the class 4 event: continuous growth of ions with particles formation.

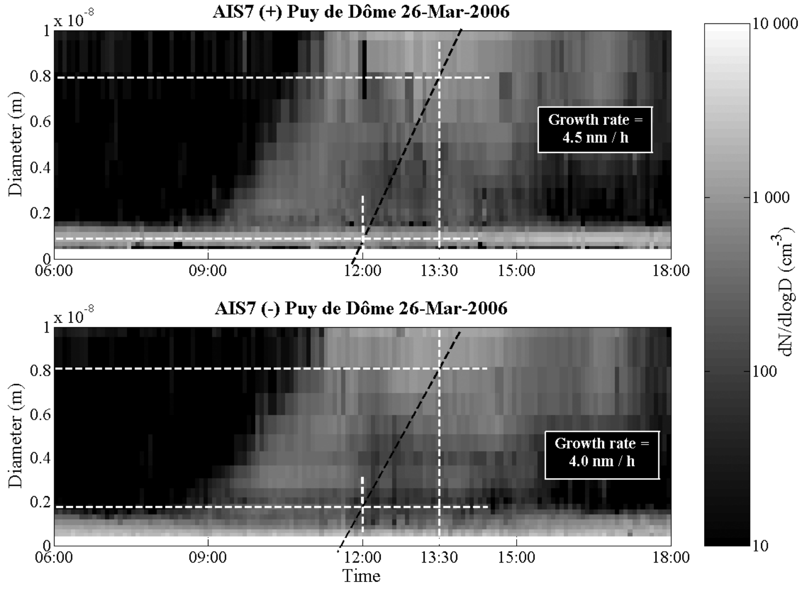

Fig. 6. Example of the growth rate determination for a class 4 event.

ters to large ions. The growth rate was estimated with the three-dimensional contour plots in a linear Y scale (Fig. 6). The growth rate of cluster ions to large ions varied between 2 and 13 nm h^{-1}. These growth rates are similar to those observed at Hyytiälä, Finland (Kulmala *et al.* 2004b). During the class 4 events, it is possible to investigate nucleation both with the AIS and twin-SMPS devices. Figure 7 shows an average size distribution of charged and total particles from 12:00 to 12:30 on a typical day of class 4 (26 March 2006). The formation was always detected with both devices at the same size. The approximate ratio of ions to total particles was 0.01 for the smallest particles (3 nm) and 0.1 for 30 nm particles. This is in agreement with the approximation of the bipolar charge distribution for particles in the submicron size range calculated by Wiedensohler (1988). A more precise calculation of the charging state of particles during nucleation will be performed in a future work. On this three-month measurement period, we did not find

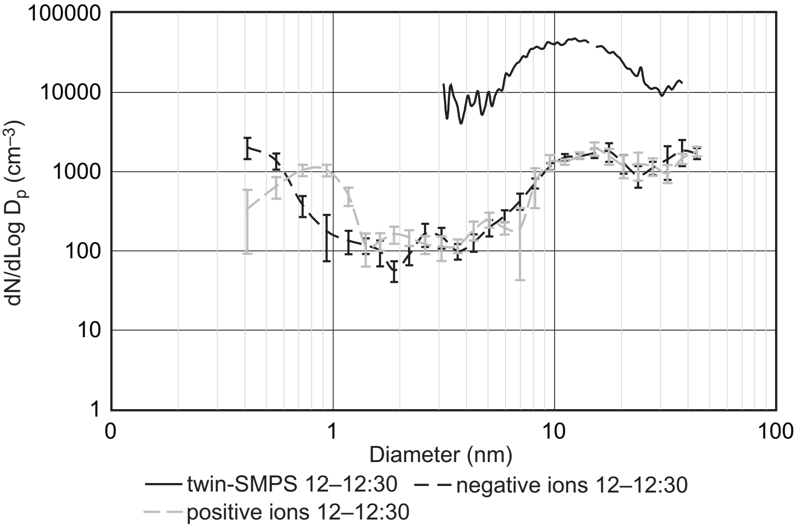

Fig. 7. Comparison between negative and positive ion size distributions (average over half an hour with standard deviation) for a class 4 nucleation event. The total particle number concentration measured with the twin-SMPS is also shown for a comparison.

any difference in frequency between positive and negative ion formation events.

AIS data reduction

The classification of nucleation events presented above is based on the visualization of three-dimensional contour plots as shown in Figs. 1–3 and 5. This classification is quite subjective, hence we investigated whether the time series of a class of ions would be representative of new particle formation. For this purpose, we classified the 28 ion channels of the AIS into three main classes:

- ions clusters: all ions in the diameter range 0.4–1.4 nm,
- intermediate ions: 1.4–6 nm,
- large ions: 6–44 nm.

Over the whole measurement period, correlation plots were made in order to check that the different classes were independent of each other. We found correlation coefficients (R^2) of 0.026 between cluster ions and intermediate ions, of 0.006 between cluster ions and large ions, and of 0.113 between intermediate ions and large ions. Hence we can conclude that the time evolutions of these three classes were not linked with each other and that they represented separate processes.

The concentrations of cluster ions are varied typically between 100 and 1000 cm^{-3}, with medians of 555 cm^{-3} for negative ions and 288 cm^{-3} for positive ions (Fig. 8). This range of concentrations is similar to those in a boreal forest station (Hirsikko *et al*. 2005) and in an Estonian continental station (Horrak *et al*. 2003). However, we found that positive clusters were twice less numerous than negative clusters, contrarily to the other two stations. Positive clusters were less numerous than negative clusters mainly during the periods of low cluster concentrations (Fig. 8). The sources of cluster ions are site dependent according to the Rn emission rate from soils and the intensity of galactic cosmic rays (GCR). Rn concentrations at the Puy de Dôme station are varying between 5 and 30 Bq m^{-3} (corresponding to 1 to 5 ion pairs cm^{-3} s^{-1}), being in the same range as observed in Hyytiälä (Laakso *et al*. 2004). The altitude of the Puy de Dôme station should imply more ions produced by the GCR, but it is also possible that the presence of clouds at the site influences cluster ions concentrations, or that the condensational sink (CS) is higher at Puy de Dôme than in Hyytiälä. These hypotheses will be discussed in the next sections.

The concentrations of intermediate ions were lower than 25 cm^{-3} most of the time, but increase dramatically with bursts up to 300 cm^{-3} (Fig. 9). These values are slightly lower than those observed in bursts in a boreal atmosphere where the intermediate ion concentrations sometimes

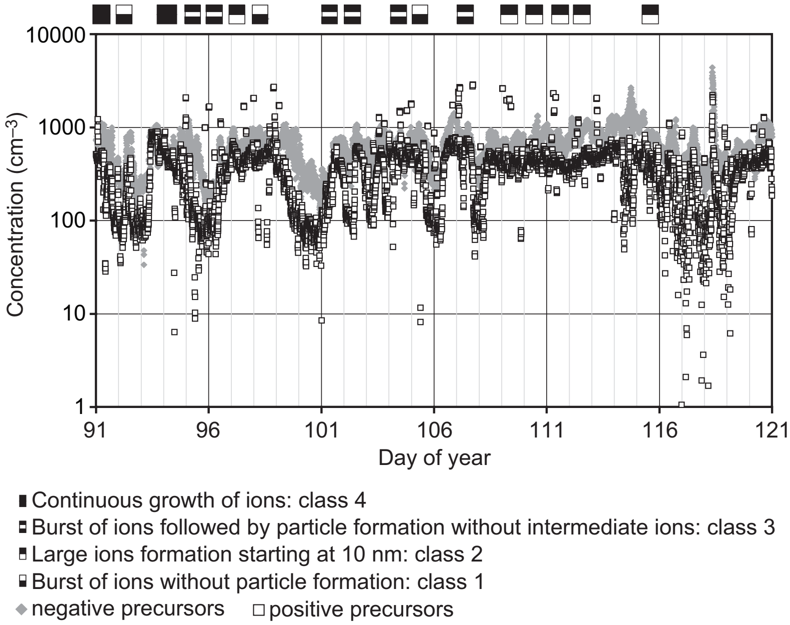

Fig. 8. Concentrations of positive and negative ions between 0.4 and 1.4 nm for April 2006. Indicated at the top are the days when different classes of nucleation were detected (and the kind of particle formation).

exceeded 2000 cm^{-3} (Hirsikko *et al.* 2005). Nucleation events of all types are illustrated in Fig. 9 in order to investigate if intermediate ion concentrations are a good indicator for the new-particle formation. We found that all class 4 events could be characterized by the intermediate ion concentrations larger than 150 cm^{-3}. This holds also for the class 1 nucleation events in 5/6 of the cases. However, class 3 nucleation events had high intermediate ion concentrations in roughly half of the cases (7 times out of 13) and class 2 events in two cases only. Moreover, on seven occasions high concentrations of intermediate ions could be observed without a nucleation event. However, these cases seemed to originate from a local or instrumental artifact (possibly the presence of rain or snow on the site), showing unrealistic values of high concentrations over the whole size spectrum (Fig. 10). Hence high concentrations of intermediate ions can be an indicator of a class 1 or 4 nucleation event. When the new-particle formation took place, concentrations of positive and negative intermediate ions increased at the same time, with a ratio close to one.

The third part of our classification, i.e. large ions, showed concentrations for this size ranging from 100 cm^{-3} up to 1200 ions cm^{-3} (Fig. 11).

Influence of the condensational sink

The condensation sink (CS) due to pre-existing particles was calculated using the full distribution of the Aitken and accumulation modes inferred from the SMPS distribution. Calculation of the condensational sink was performed according to Kulmala *et al.* (2001). Although we do not know what the condensing species are for the first steps of the cluster growth, H_2SO_4 has been used in the calculation in order to be able to compare the values of condensational sink measured at Puy de Dôme with those obtained in other environments. We would like to emphasize here that the calculation of CS does not take into account the cloud droplets distribution. In the presence of clouds, the calculated CS includes cloud interstitial particles and cloud droplet residuals. By doing so, we can separate the role of the clouds from the role of pre-existing particles in scavenging processes.

The values of the CS obtained ranged between 0.00053 and 0.013 s^{-1} with a median of 0.0058 s^{-1}. Cluster ions should be scavenged more efficiently by larger pre-existing particles when the value of CS is higher. The relation between the cluster ion concentration and the value of CS was, however, not very clear (Fig. 12). One can

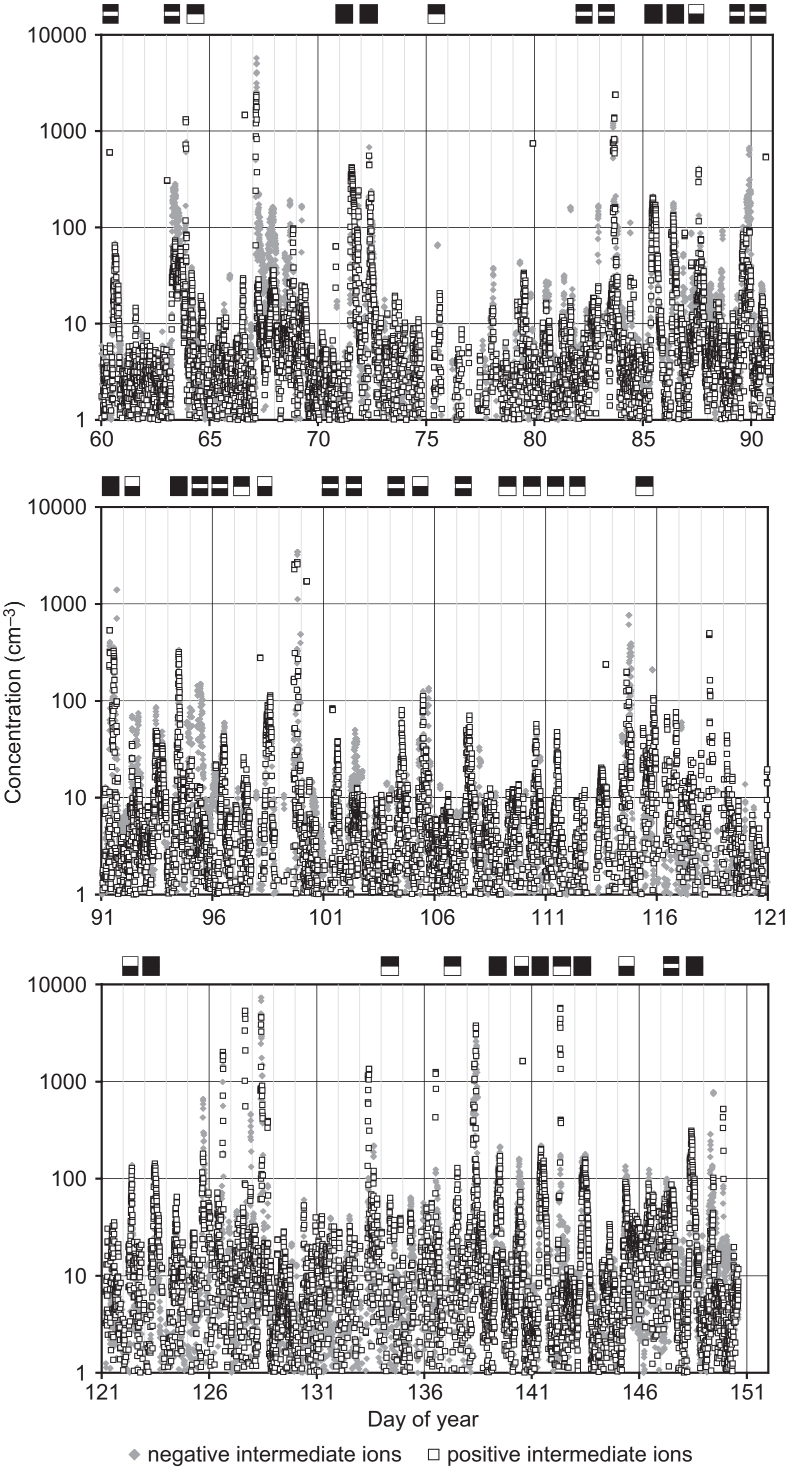

Fig. 9. Variability of intermediate ion concentrations in (**a**) March, (**b**) April and (**c**) May. Depicted at the top of the pictures are the days when nucleation was detected (and the kind of particle formation).

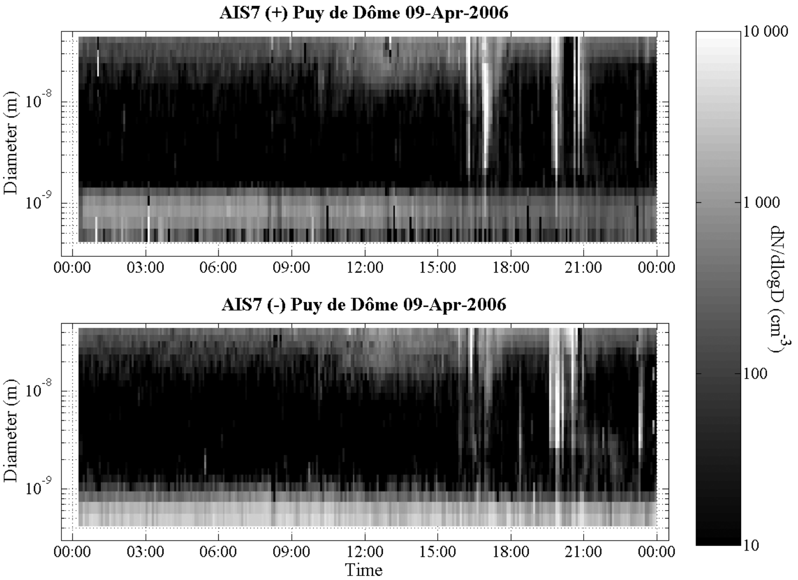

Fig. 10. Contaminated data due to local pollution.

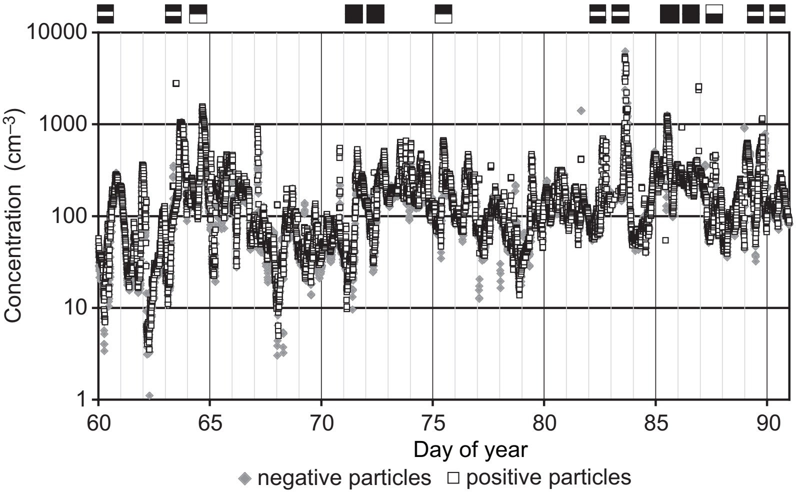

Fig. 11. Variability of large ion (6–44 nm) concentrations measured by the AIS during March 2006.

observe in Fig. 12 two groups of cluster concentrations, one being of the order of 100 cm^{-3} and the other of the order of 500 cm^{-3}. It seems that the group of the lower concentrations corresponds to low CS (smaller than 0.005 s^{-1}) while the highest cluster concentrations are found for high CS. Here we can suppose that both cluster ions and pre-existing particles were scavenged at the same time in a similar process that could imply the presence of a cloud.

During March and April, we found that intermediate ions did not show high concentrations (> 150 cm^{-3} indicative of nucleation events) for values of the condensational sink. However, they could reach concentrations > 150 cm^{-3} for CS as high as 0.017 s^{-1} during May (Fig. 13). This observation might indicate that low-volatility gases responsible for the growth of ions from clusters to intermediate ions were condensing preferably onto pre-existing particles during March and April, whereas during May these gases may have been abundant enough to both condense on pre-existing particles and to participate into the growth of cluster ions to intermediate ions.

The influence of the CS on the occurrence of a specific class (1, 2, 3 or 4) of nucleation events can be further studied by calculating the mean CS value for each class. By doing so, we obtain an equivalent CS value for non-event classes and for

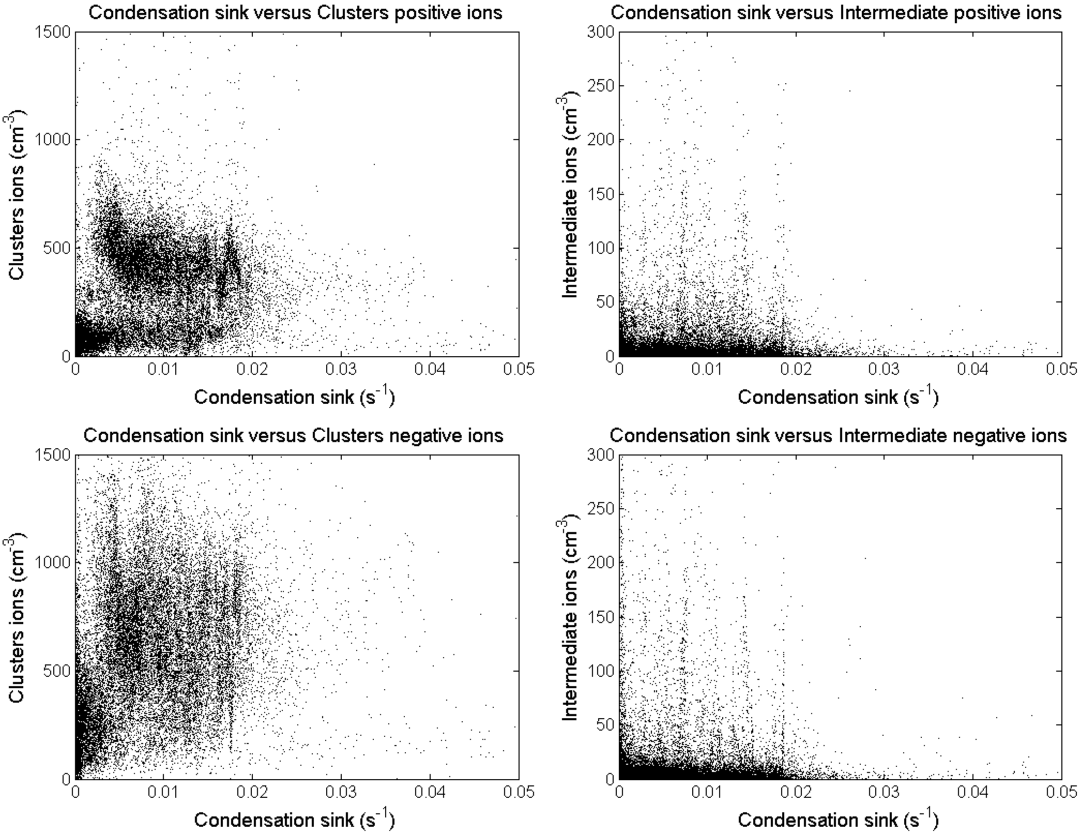

Fig. 12. Relationship between the condensational sink and cluster and intermediate ions for the three-month period.

each event class, except for class 2 which shows a higher CS than all other classes (Fig. 14).

These observations would lead to the conclusion that cloud droplets, being frequently present at the site, are much better scavengers than aerosol particles. However, these are indirect observations of the effect of clouds on nucleation. Cloud droplet size distributions were not measured during the March to April 2006 period. However, it is possible to have direct information on the effect of clouds by studying relationships between various quantities and the relative humidity.

Effects of the presence of a cloud

Clouds can play an important role in nucleation events as has been shown in different studies (Perry and Hobbs 1994, Keil and Wendisch 2001). Since the top of the Puy de Dôme is half of the time in clouds or near clouds, we have a unique possibility to study the relationship between clouds and nucleation events over a long time period. Cloud droplets can have several effects on atmospheric ion concentrations. The main effect is the scavenging of ions, aerosols and gases by the large surface offered by the cloud droplet population. This could be observed directly as the lower median value of condensation sink at a relative humidity of 100% (0.0027 s^{-1}, in cloud) compared with a relative humidity < 100% (0.0075 s^{-1}, clear sky).

First, we found that the median relative humidity was lowest for class 2 and 4 events compared with all other class events and nonevents (Fig. 15). For classes other 2, a relative humidity of 100% was frequently reached (more than 25% of the time), which indicates that nucleation in classes 1 and 3 and occasionally in class 4 can occur in clouds.

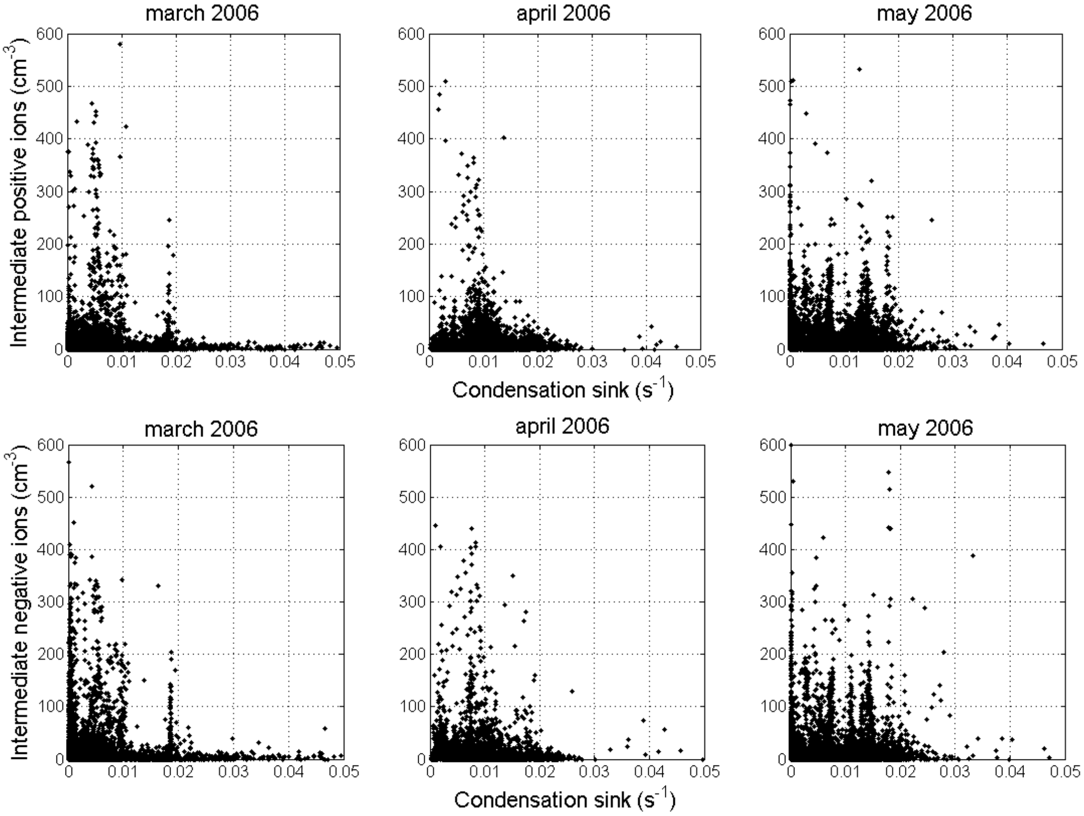

Fig. 13. Relationship between the condensational sink and intermediate ions separately in March, April and May.

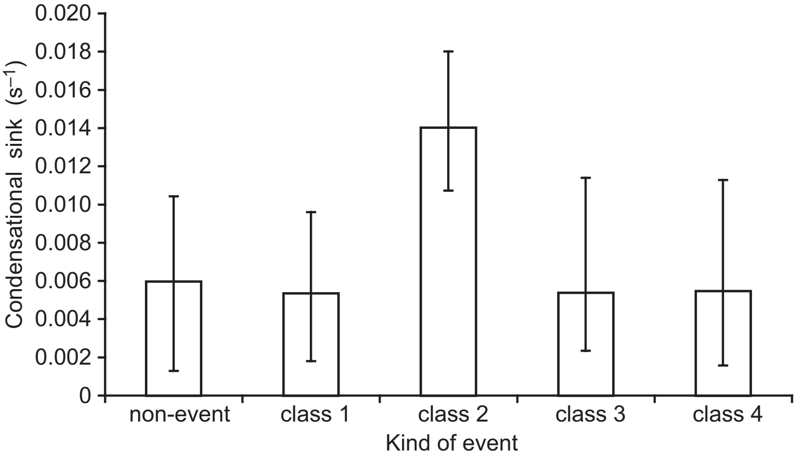

Fig. 14. Median of the condensational sink for the different event classes.

We also found that the median concentration of clusters ions was highest for the class 2 and 4 events, the ones that had the lowest relative humidity. This observation would indicate that cluster ions were efficiently scavenged by cloud droplets. This is confirmed by the calculation of the median cluster and intermediate ions concentrations for cloudy conditions (relative humidity = 100%) and clear sky conditions (relative humidity < 100%). We can observe in Fig. 16a that cluster ions concentrations were significantly lower in cloud compared to clear

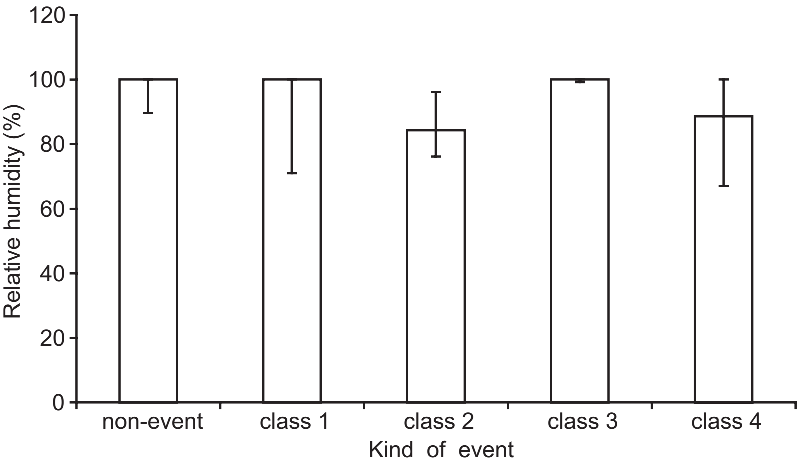

Fig. 15. Median of the relative humidity for the different event classes.

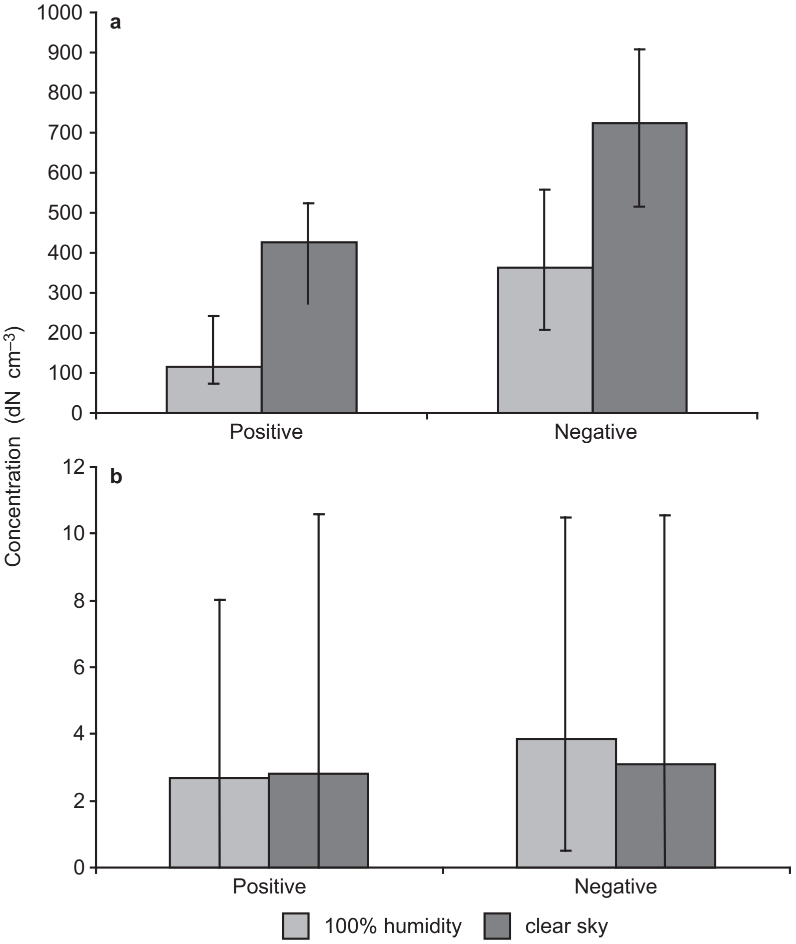

Fig. 16. Median number concentrations during cloudy conditions (relative humidity = 100%) and clear-sky conditions (relative humidity < 100%) at the Puy de Dôme station for (**a**) cluster ions (< 1.4 nm) and (**b**) intermediate ions (1.4–6 nm).

sky conditions, especially for positive ions. In fact, we found that cluster ion concentrations had a maximum during the day (11:00–17:00) and minimum during the night. This is contrary to the observations made by Hõrrak *et al*. (2003) in a continental station in Estonia. This would indicate that, at the Puy de Dôme, the sink by cloud scavenging, maximum at night, is a prevailing parameter controlling the cluster ion concentration and most efficient on positive ions. This result confirms the observations and calculations made by Lihavainen *et al*. (2007) in northern Finland: they found that the main sink for cluster ions was the cloud droplet population during cloudy periods. The mean cluster ion concentrations they found in-cloud was 135 ± 71 cm^{-3} for positive ions and 175 ± 91 cm^{-3} for negative ions, which can be compared with concentrations of 973 ± 346 cm^{-3} for positive ions and 1182 ± 360 cm^{-3} for negative ions during clear sky conditions.

The last important point is that although cluster ions concentrations were lower in cloud, intermediate ions concentrations did not significantly differ between in-cloud and clear-sky conditions (Fig. 16b). This confirms the fact that nucleation can occur in cloud and in clear skies whatever the cluster ion concentration.

Conclusions

The number size distributions of aerosol particles and ions have been measured at the top of the Puy de Dôme (1465 m above sea level) for a three-month period (March 2006–May 2006). Nucleation and new-particle formation events were detected and classified into four classes: (1) burst of cluster ions, (2) large ion formation starting from 10 nm, (3) burst of cluster ions followed by large ion formation with a gap of intermediate ions, and (4) burst of ions with their continuous growth to the > 10 nm sizes. All together, these events occurred in more than one third of the analyzed days, mostly around midday. When a nucleation event occurred, we saw that size distributions of positive and negative ions were different, especially for ions smaller than 5 nm. Although negative cluster ions were more numerous than positive ones during most of the periods (events and non-events), we observed that positive ion concentrations dominated the size range 1.2–2 nm during nucleation, which is the size range representative of the first step of ion cluster growth to intermediate ions.

Since the detection of nucleation/new particle formation events have been, up to now, based on the visual observation of three-dimensional plots, a reduction of the AIS data set was set up. Three size classes of ions were chosen to explain most of the variability in the aerosol signal: cluster ions (0.4–1.4 nm in diameter), intermediate ions (1.4–6 nm) and large ions (6–44 nm). Cluster ion (< 1.4 nm) concentrations varied typically between 100 and 1000 cm^{-3}, being similar to concentrations observed in a boreal forest. Intermediate ion concentrations were lower than 25 cm^{-3} most of the time, but increased dramatically with the burst up to 300 cm^{-3} that are slightly lower values than in the bursts observed in a boreal forest. We found that all class 4 events could be characterized by intermediate ion concentrations larger than 150 cm^{-3}. This holds also for the class 1 nucleation events in 5/6 of the cases. However, class 3 nucleation events had high intermediate ion concentrations in roughly half of the cases (7 times out of 13) and class 2 events in two cases only. Hence high concentrations of intermediate ions can be an indicator of class 1 and 4 nucleation events.

The presence of a cloud at the site had an influence on several parameters. In clouds, the aerosol condensation sink and the concentration of cluster ions were lower, presumably because of scavenging, but the intermediate ions concentrations remain unchanged. We observed that class 2 and 4 events occurred preferably under clear-sky conditions, and that all except class 2 events could be observed in cloudy conditions as well.

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