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Charged particle size distributions and analysis of particle formation events at the Finnish Antarctic research station Aboa

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We measured the size distributions of positively and negatively charged particles in the size range 0.34–40 nm at the Finnish Antarctic research station Aboa from 14 December 2004 to 30 January 2005 with an Air Ion Spectrometer (AIS). Our focus was to study secondary particle formation in a clean environment. Therefore, we classified the 48 measurement days either as a particle formation event day, an undefined day or a non-event day. Approximately 23% of the days were particle formation event days, a fraction similar to that observed at a boreal forest site. The median diameter growth rates of negatively charged particles in size classes 1.3–3, 3–7 and 7–20 nm were 1.1, 1.5 and 4.3 nm h^{-1}, respectively, and somewhat lower for positively charged particles. Furthermore, we observed a clear positive correlation between the wind speed and cluster and intermediate ion concentrations, which suggests that ions were produced by friction processes in fast moving snow and ice crystals during the periods with strong winds. Cluster ions (diameter < 1.6 nm) were present during the whole measurement period. The average (± SD) positive and negative cluster ion concentrations were 557 ± 974 and 587 ± 543 cm^{-3}, respectively.

Introduction

The cleanest continent, Antarctica, is also the continent with the least amount of vegetation. Measurements in Antarctica provide information on natural background concentrations and aerosol processes to be compared with corresponding data from polluted latitudes in the north and data from regions having vegetation. Antarctic measurements are also important for assessing the direct and indirect aerosol climate forcing in the continent, and to increase our understanding of interactions between air and snow. Measurements of aerosol number concentrations, chemical size distributions and chemical properties have been conducted at several stations around Antarctica, including Terra Nova Bay (e.g. Hillamo *et al.* 1998), Aboa (Teinilä *et al.* 2000, Virkkula *et al.* 2006a, 2006b), Dumont d'Urville (Jourdain and Legrand 2002), Halley (Rankin and Wolff 2003), Mawson (Gras 1993), South Pole (e.g. Bergin *et al.* 1998, Arimoto *et al.* 2004) and Neumayer

(Jaenicke *et al*. 1992). Most studies on Antarctic aerosols have concentrated on the chemical composition and transport of aerosol particles and their deposition onto snow.

Formation of new atmospheric aerosol particles by nucleation has been observed at several measurement sites around the world (Kulmala *et al*. 2004b). One of the most important open questions in this regard is the role of different nucleation mechanisms. It has been known for some time that binary homogeneous nucleation of water and sulfuric acid cannot explain nucleation observed in the troposphere (e.g. Weber *et al*. 1996, Clarke *et al*. 1998). Other nucleation mechanisms have been proposed, such as ternary homogeneous nucleation of water, sulfuric acid and ammonia, ion-induced or ion-mediated nucleation involving inorganic and/or organic vapors, and homogeneous nucleation of iodide compounds in coastal environments (e.g. Korhonen *et al*. 1999, O'Dowd *et al*. 2002, Kulmala 2003, Laakso *et al*. 2004a, 2004b, 2007, Yu 2006, Kulmala *et al*. 2006 and references therein). Another open question is how aerosol particles grow in size after their formation by nucleation. Observations on growth of particles as a function of their size yield information on possible growth mechanisms (Kulmala *et al*. 2004c). So far very few studies on the nucleation and growth of secondary atmospheric particles in Antarctica have been conducted. Koponen *et al*. (2003) measured the formation and growth of aerosol particles with a high time resolution at the Finnish Antarctic research station Aboa (73°03´S, 13°25´W, 470 m above the sea level) using a Twin Differential Mobility Particle Sizer (Twin-DMPS) in the size range of 3–700 nm during the Antarctic summers 1999/2000 and 2000/2001. Several particle formation and growth events were observed. Particles formed during these events grew typically at the rate of 0.3–2.7 nm h^{-1}, which are the slowest growth rates reported by Kulmala *et al*. (2005).

The particles that were observed by Koponen *et al*. (2003) were larger than 3 nm in diameter, so the particles had already grown from the size range of stable clusters (~1 nm). In order to study the initial steps of aerosol formation and growth, measurements have to be extended to sizes close to 1 nm. In order to investigate further the particle formation mechanisms, we measured air ion size distributions in the size range 0.34–40 nm at the Finnish Antarctic Research station Aboa in Queen Maud Land, Antarctica, during the FINNARP-2004 expedition from 14 December 2004, to 30 January 2005. The purpose of the measurements was also to provide data on air ion concentrations at a site, in which ionization by soil-emitted radon and thoron is negligible. The site is surrounded by glaciers so galactic cosmic rays are the primary ionization source. In this work we present the first simultaneous measurements of air ion and aerosol particle (neutral + charged) number size spectra, as well as the first analysis of the formation events of intermediate ions (1.6–8.0 nm in diameter) and their further growth in Antarctica.

Measurements

The Air Ion Spectrometer (AIS, manufactured by AIREL Ltd., Estonia) measured the mobility distribution of air ions (naturally charged clusters and aerosol particles). The mobility range of the AIS for single-charged particles was 3.16–0.00133 $cm^2\ V^{-1}\ s^{-1}$, which corresponds approximately to electrical mobility diameters of 0.34–40 nm at the temperature of 273 K and pressure of 1013 hPa (Tammet 1995, 1998). The spectrometer consists of two identical differential mobility analysers, one for measuring positive ions and the second one for measuring negative ions. The mobility analysers contain 21 collector electrodes connected to electrometers to measure the electric current carried by ions of different mobilities. The time resolution of the measurements was five minutes. For further information about the AIS and its operation principles, the reader is encouraged to consult the paper by Mirme *et al*. (2007).

We measured aerosol particle (neutral + charged) size distributions using a differential mobility particle sizer (DMPS) that consisted of a medium-size, Hauke-type differential mobility analyser (DMA) and TSI 3010 condensation particle counter (CPC). The closed-loop sheath-flow arrangement was used. The time resolution was 10 minutes. The CPC operated with a 25 °C temperature difference between the saturator and

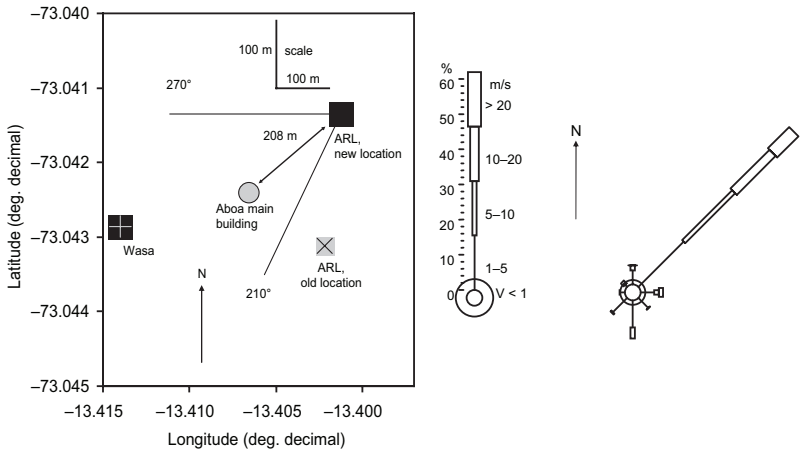

Fig. 1. Location of the aerosol research laboratory (ARL) of Aboa, the contamination sector, and the directional distribution of wind speeds during the FINNARP 2004 expedition.

the condenser, so the 50% detection efficiency was at 5.7 nm (Mertes *et al*. 1995). In principle combined measurements of neutral and charged particles can be used for assessing the contribution of air ions to new-particle formation: if a substantial amount of particles is generated by ion-induced nucleation, then the smallest particles have to be overcharged compared with the steady state situation (Vana *et al*. 2006, Laakso *et al*. 2007). Vana *et al*. (2006) compared size distributions measured with the DMPS and mobility spectrometers that measured charged particles, such as the AIS. They found high percentages of charged particles in the size range 2.6–5 nm during nucleation episodes. However, the DMPS measurements during the campaign presented in this work did not extend to size ranges low enough for this evaluation.

A TSI Model 3007 CPC measured the total number concentration of particles larger than 12 nm in diameter. The CPC was modified for making continuous measurements. A two-wavelength Magee Scientific Aethalometer (AE-20) monitored the black carbon concentration. In this study the aethalometer data, along with the wind data, were used to indicate contamination from the diesel generators in Aboa. The DMPS, aethalometer and CPC 3007 took their sample air from a common inlet. The AIS had a separate copper inlet tube of about 30 cm in length and 16 mm of inner diameter.

The automatic weather station in the aerosol research laboratory provided weather data. The weather station included a Vaisala Milos 500 AWS data logging system and weather sensors that measured the wind direction and velocity (Thies CLIMA Ultrasonic 2D anemometer) 12 m above the ground, relative humidity (Vaisala HMP 45D) and temperature (Pentronic Pt-100) at 2 m above the ground, barometric pressure (Vaisala PTB220) at 1.7 m above the ground, global radiation (heated Kipp & Zonen CM11) and UVB radiation (Solar Light 501A) at 4 m above the ground, as well as the ground temperature (Pentronic Pt-100) at 2, 10, 30 and 60 cm below the surface.

We installed the aerosol instruments in the aerosol research laboratory at a distance of about 200 m from the main building and diesel generator of Aboa. The laboratory was moved approximately 220 m north from the location of the earlier campaigns presented by Koponen *et al*. (2003). Since the new location is on the top of a small hill, the winds measured there are considered to be better representatives of winds at the base. The location is upwind from the pollution sources during the prevailing NE winds (Fig. 1). At Aboa, power is produced with a diesel generator that is a source of small soot particles. We measured a contamination sector: the left edge of the contamination sector (210°) was determined by the measuring the coordinates of the snowmobile route and the right edge (270°) by measuring the coordinates of the northernmost storage area. During the FINNARP 2004 campaign winds blew from the clean sector most of the time and from the contaminated sector approximately 6% of the time (Figs. 1 and 2).

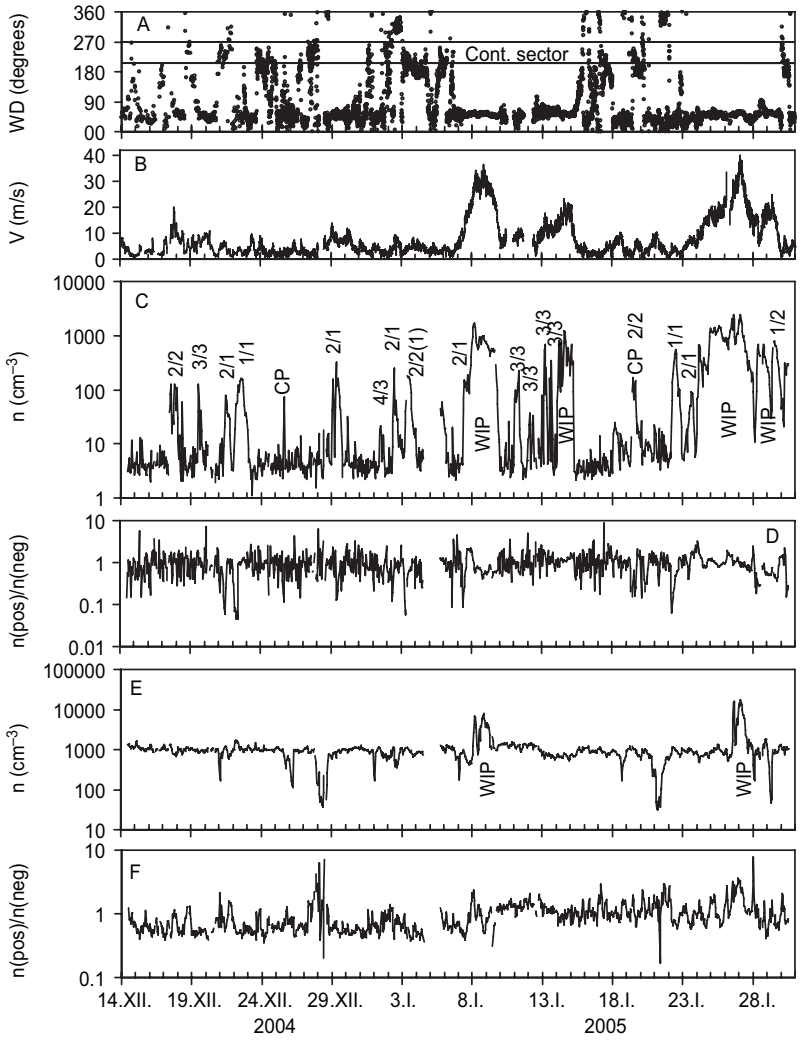

Fig. 2. Wind and air ion data during the campaign. (**A**) wind direction (WD) (Cont. sector = contaminated sector), (**B**) wind speed, (**C**) intermediate ion concentrations (positive + negative ions), (**D**) the ratio of positive and negative intermediate ion concentrations, (**E**) cluster ion concentrations (positive + negative ions), and (**F**) the ratio of positive and negative cluster ion concentrations from top to bottom, respectively. The numbers in panel **C** denote the event type (positive ion event type/negative ion event type). Non-event day classification numbers are not presented. WIP: Wind/snow-induced Particles, CP: Contamination particles.

Event classification

We used ion size distributions for calculating the concentrations of cluster ions (diameter < 1.6 nm) and intermediate ions (1.6 nm < diameter < 8.0 nm). We classified the measurement days as particle formation event days, undefined days or non-event days according to the method described by Dal Maso *et al*. (2005) and Hirsikko *et al*. (2007). The intermediate and large air ion formation events were divided into two main classes 1 and 2. Class 1 contained the most representative events that could be used for studying various particle formation characteristics, such as particle concentrations and growth rates during the event. Dal Maso *et al*. (2005) and Hirsikko *et al*. (2007) divided class 1 events further into sub-classes, but here this was not done. The less representative events, those that are difficult to analyse further, belong to class 2. During class 2 events particles grew in size but the growth rates could not be determined. During some days, we observed high concentrations of intermediate ions for time to time but no growth was visible. These days were classified as undefined. In the tables and figures below these days are put into class 3. Days when cluster ions were the only ions that were observed in significant quantities were classified as non-event days. During these days the size distributions were very stable. In the tables and figures below these days are put into class 4. We made a separate classification for

negative and positive ions. In addition to classes 1–4, an extra class called wind/snow-induced particles (WIP) was introduced here. This class will be discussed in more detail later.

By inspecting the contour plots of size distributions, we classified the DMPS measurement days into class 1 when a distinctly new particle mode appeared in the size range < 10 nm, and this mode was present for several hours and it grew in size (*see* Dal Maso *et al*. 2005). A day was classified into class 2 when the nucleation mode appeared for several hours but no growth could be seen. Undefined days (class 3) could not easily be classified into any other class. Non-event days (class 4) where the ones when the size distribution remained stable and no growing nucleation mode was present.

We determined the growth rates of charged particles in different size classes (1.3–3 nm, 3–7 nm, 7–20 nm) with the method presented by Hirsikko *et al*. (2005). The growth rates were calculated for class 1 events for both negative and positive ions.

Results and discussion

Overview of the measurement data

The time series of wind direction and speed, total concentrations of cluster and intermediate ions, as well as the ratio between the positive and negative ion concentrations in different size ranges are presented in Fig. 2. By using the wind speed as a classifier, the campaign could roughly be divided into two distinctly different periods. From 14 December 2004 to 7 January 2005, the wind speed was low (< 10 m s^{-1}) most of the time and its direction varied, whereas in the latter half of the campaign several periods with wind speeds > 10 m s^{-1} were observed (Fig. 2).

Cluster ions were present during the whole campaign. On most days the sum of positive and negative cluster ion concentrations was approximately 1000 cm^{-3}, with higher concentrations of negative ions (Fig. 2 and Table 1). Cluster ion concentrations decreased to below 100 cm^{-3} for several hours on 28 December 2004 and 21 January 2005 (Fig. 2). These days were associated with low wind speeds and high relative humidity (> 95%, not shown in Fig. 2). Aboa was inside low-level clouds during these periods. This observation is similar to that made by Lihavainen *et al*. (2007) at Pallas, a measurement site in northern Finland, where the concentrations of cluster ions were substantially lower inside clouds than in cloud-free air. In our measurements the cloud droplets scavenged negative ions more efficiently than positive ions, as seen in the positive-to-negative ion concentration ratio. Ion concentrations increased clearly during strong winds (Fig. 2). However, much higher winds speeds were needed to enhance cluster ion concentrations than intermediate ion concentrations.

In general, the contamination from the diesel generator did not change the concentrations of cluster or intermediate ions. The contamination was visible in the size range of 20–100 nm and it could clearly been observed in the DMPS data and in the largest size channels of the AIS data. On 21 December there was a clear particle formation event, classified into class 1 for positive ions and class 1 for negative ions, although the wind blew from the contaminated sector and there were particles in the size range of 20–100 nm. There were also contamination periods that could be observed with the DMPS but that had no increase or decrease in the cluster or interme-

Table 1. Average and median concentrations and the 95% range (2.5 and 97.5 percentiles) of positive and negative cluster and intermediate ion concentrations (cm^{-3}) during the whole campaign.

	Positive ions		Negative ions	
	Cluster	Intermediate	Cluster	Intermediate
Mean ± SD	557 ± 974	74 ± 171	587 ± 543	84 ± 181
Median	385	3	524	5
95% range	74–2031	1–630	57–2103	1–621

diate size ion concentrations. This supports the interpretation that the event on 21 December did not result from contamination but was a natural phenomenon.

Event analyses

During non-event days positive and negative intermediate ion concentrations varied around the median values of 3 and 5, respectively (Table 1 and Fig. 2). During class 1 and 2 events, intermediate ion concentrations increased approximately two orders of magnitude (Fig. 2). During these events more negative than positive ions were observed, as can be seen from decreasing ratio between positive and negative ion concentrations (Fig. 2). The AIS operated 48 days and approximately half of the days could be classified as non-event days (Table 2). There were eight event days belonging to class 1, and in all of them there were more negative than positive intermediate ions (Fig. 2).

Table 2. Event-day classification for AIS and DMPS data (*N*/%; *N* = dumber of days; % = fraction of the class of all measurement days: 48 for AIS, 45 for DMPS). Class 1 = Clearest particle formation events, characteristics such as growth rate can be determined. Class 2 = Particle formation and growth observed but unclearly, characteristics difficult to determine. Class 3 = Undefined: intermediate ions observed but no growth. Class 4 = Non-event day: negligble concentrations of intermediate ions, stable size distributions. Class WIP: Wind/snow-induced particles, observed during snow storms.

	Event class				
	1	2	3	4	WIP
AIS+	3/6.3	8/16.7	5/10.4	22/45.8	10/20.8
AIS–	8/16.7	3/6.3	5/10.4	22/45.8	10/20.8
DMPS	14/31.1	4/8.9	5/11.1	22/48.9	0/0

During the periods of strong winds, intermediate ion concentrations increased approximately three orders of magnitude from their non-event-day levels. These concentrations were clearly higher than those during typical class 1 or 2 events, so these periods were classified here as a wind-induced particle (WIP) event, especially because the new particles did not make a growing mode. This topic will be discussed in detail below.

There were more class 1 days in the DMPS data than in the AIS data although the DMPS was operational on 45 days, which is three days fewer than the AIS. A few reasons for this can be found. First, every day that was classified into class 1 for positive or negative ions, was also classified into class 1 for the charged + neutral particles. Second, there were three days when there was a clear nucleation mode that grew in size in the charged + neutral particle data but the ion data were classified as a non-event day. Third, there were three class 1 event days in the charged + neutral particle data that were classified as WIP in the air ion data set. No clear wind-induced particle events were observed with the DMPS (Table 2).

The statistics of the particle growth rates for class 1 events are presented in Table 3. The average growth rates of negative ions were somewhat higher than those of positive ions in all the size ranges, but for median growth rates the opposite was true in the range 3–7 nm. The comparison between the negative and positive ion growth rates has to be viewed with caution because there were only three class 1 events for positive ions. In the lowest size range no growth rate for positive was obtained. The median growth rates (Table 3) of the ions in the different size ranges were very similar to those found by Hirsikko *et al*. (2005) at a boreal forest site in Hyytiälä, Finland. In Hyytiälä the median growth rates of 1.3–3, 3–7 and 7–20 nm ions were < 2, 2–4 and 4–5 nm h^{-1},

Table 3. Statistics of charged particle growth rates (median, minimum and maximum, in nm h^{-1}) between different size ranges during the class 1 events

	1.3–3 nm	3–7 nm	7–20 nm	3–20 nm
Negative med (min, max)	1.1 (0.9, 2.1)	1.5 (1.0, 9.1)	4.3 (2.0, 4.3)	2.7 (1.6, 19)
Positive med (min, max)		2.3 (1.7, 2.5)	3.5 (2.0, 4.1)	2.8 (2.0, 8.1)

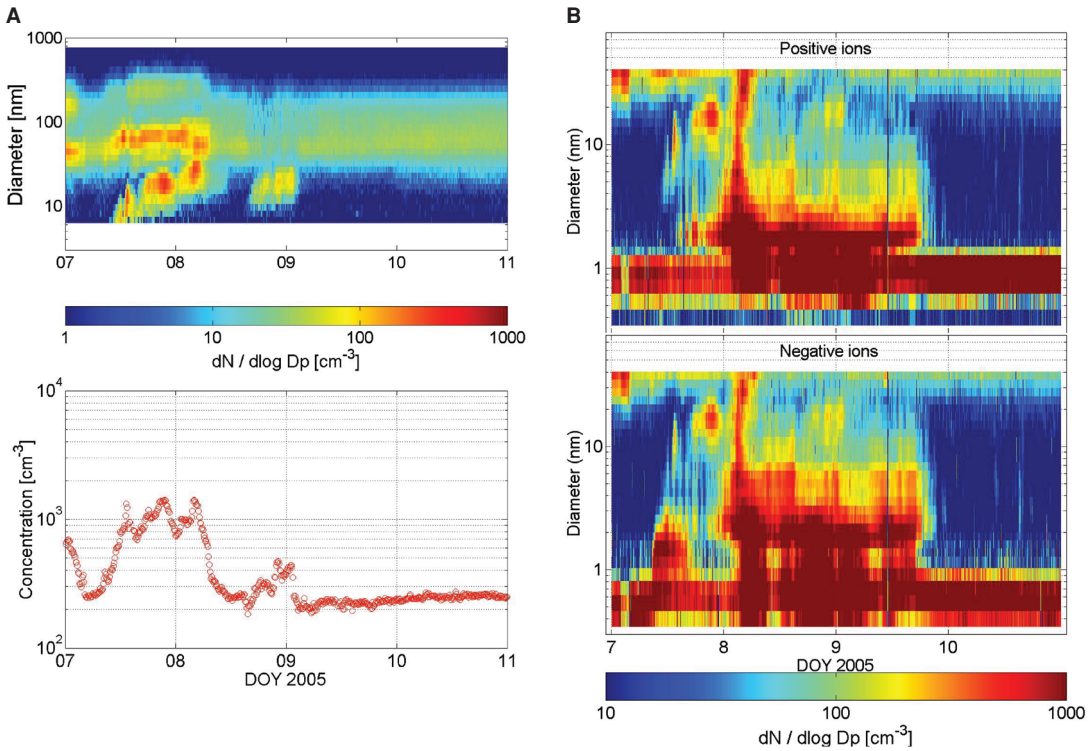

Fig. 3. (**A**) Neutral + charged particle size distributions (upper panel) and concentrations (lower panel) (DMPS measurements), and (**B**) air ion size distributions on 7–10 January 2005.

respectively, between April 2003 and April 2004. The growth rates were higher in summer, being ~5–6 nm h^{-1} for 3–7 nm ions and ~13–14 nm h^{-1} for 7–20 nm ions in July–August (Hirsikko *et al*. 2005). Our measurements were made in Antarctic summer, which is the season of highest particle number concentrations in Antarctica (e.g. Shaw 1988). Therefore, it is likely the particle growth rates in winter Antarctica would be lower than those measured here. In summer, the growth rates were about 50%–70% lower in Aboa as compared with those in Hyytiälä.

The growth rates increased with increasing particle size (Table 3). This is similar to what was observed in Hyytiälä (Hirsikko *et al*. 2005). The theoretical background for the size-dependent growth rate has been analysed by Kulmala *et al*. (2004c). This kind of increase in the growth rate with particles size has been related to multicomponent condensation initialised via a nano-Köhler process (Kulmala *et al*. 2004a).

Wind/snow-induced particles

In the morning of 7 January, new-particle formation was observed both by the AIS and DMPS (Fig. 3). The new-particle mode prevailed for some hours and the particle grew in size. The growth rates could be determined for negative ions, so it was classified as a class 1 event day. However, soon after new-particle formation the ion concentrations increased rapidly to very high levels. A comparison between the wind speed, cluster ion concentration and intermediate ion concentration showed that the wind speed and intermediate ion concentration coincided remarkably well during this period (Fig. 4). The relative humidity data showed that early in the morning of 8 January, the high wind speed was associated with snow. During high winds there was a lot of snow in air. It is not clear whether this was due to falling new snow or snow blown off from the surface of the surrounding glacier.

A clear positive correlation between the wind speed and cluster and intermediate ion concen-

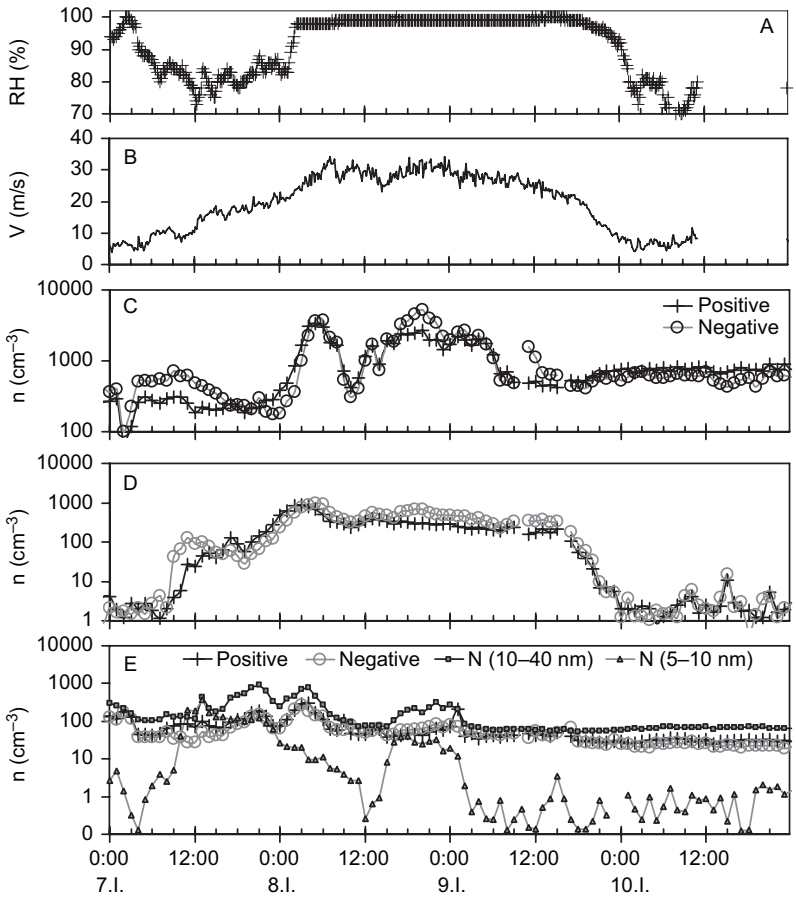

Fig. 4. Weather and air ion data on 7–10 January 2005. (**A**) Relative humidity, (**B**) wind speed, (**C**) cluster ion concentrations, (**D**) intermediate ion concentrations, and (**E**) overlapping range (10–40 nm) air ion concentrations and particle concentrations measured with the DMPS (N(10–40 nm) and N(5–10 nm)).

trations was observed when all data of the campaign were used (Fig. 5). At low wind speeds (< 10 m s^{-1}), intermediate ion concentrations varied by more than two orders of magnitude, since there were days with very different extent of new-particle formation (class 1, 2, 3 or 4 days). The effect of wind speed on ions concentrations could be seen at wind speeds > 15 m s^{-1} for intermediate ions and at wind speeds > 20 m s^{-1} for cluster ions.

There was a clear difference between the wind/snow-induced ions and ions formed during class 1 events. In class 1 events there were always more negative than positive intermediate ions, whereas in wind-induced events the ratio between positive and negative ion concentrations was close to 1 (Fig. 6). The wind process operating at high wind speeds resulted in higher positive than negative cluster ion concentrations (Figs. 5 and 6). The other clear difference between the wind/snow-induced ions and the ions formed during the class 1 events was that in the former case the new particles did not form a growing mode.

The contour plots of the DMPS and AIS data on 26 January 2005 present a clear example of the different behaviour of the two different measurement methods during snow storms (Fig. 7). The DMPS data were classified into class 1 and the AIS data into class WIP. The reason for this is that that there were no clear wind/snow-induced particles in the DMPS data, probably because the DMPS was unable to measure particles in the intermediate-ion size range.

The strong winds on 8–10 January were associated with high relative humidities. The relative humidity was always high during the storms: at wind speeds > 20 m s^{-1} the average relative humidity was 98% ± 3%. The reason for this was that there was always a lot snow in air during the high wind speeds. On the other hand, as discussed above, there were days with a high

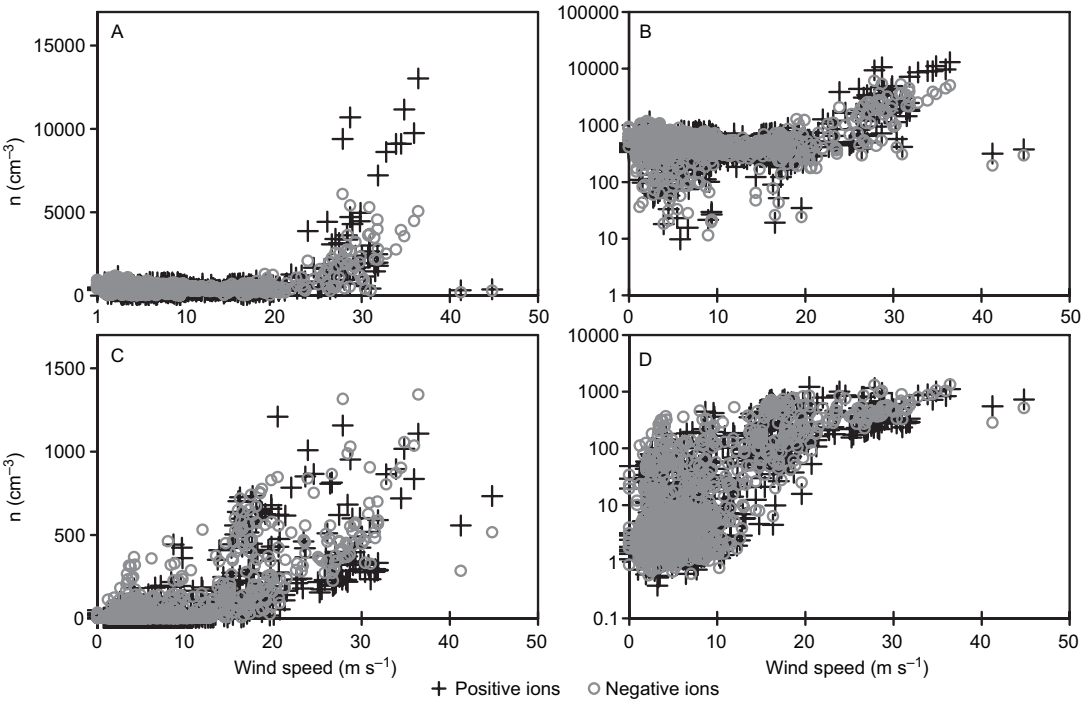

Fig. 5. Cluster (**A** and **B**) and intermediate ion (**C** and **D**) concentrations as a function of wind speed. Left: linear scale; right: logarithmic scale.

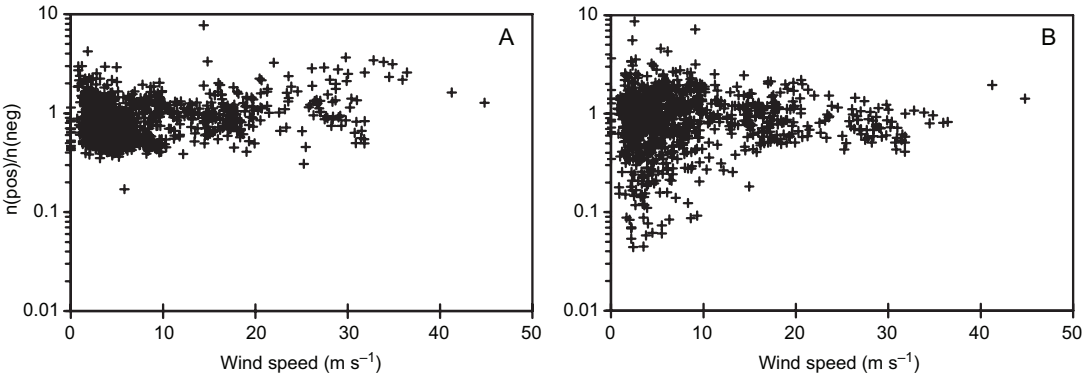

Fig. 6. Ratio between positive and negative ion concentrations as a function of wind speed. (**A**) cluster ions, and (**B**) intermediate ions.

relatively humidity but a low wind speed, i.e. when the site was inside clouds. During these days cluster ion concentrations decreased considerably. These data suggest that the high cluster ion concentrations during the storms were not because of the high humidity but were caused by some friction processes between snowflakes and/or ice crystals.

The observation of wind/snow-induced particles is very similar to that made by Hirsikko *et al*. (2007) in Hyytiälä, Finland, where snowfall-associated intermediate ion bursts with no further growth of the ions were observed. Hirsikko *et al*. (2007) detected snowfall-associated negative intermediate ions slightly more often (24 days) than positive ions (21 days). Hirsikko *et al*. (2007) did not present quantitative concentration data on these snowfall-associated ions, so no comparison between those events and our observations can be made. One clear difference

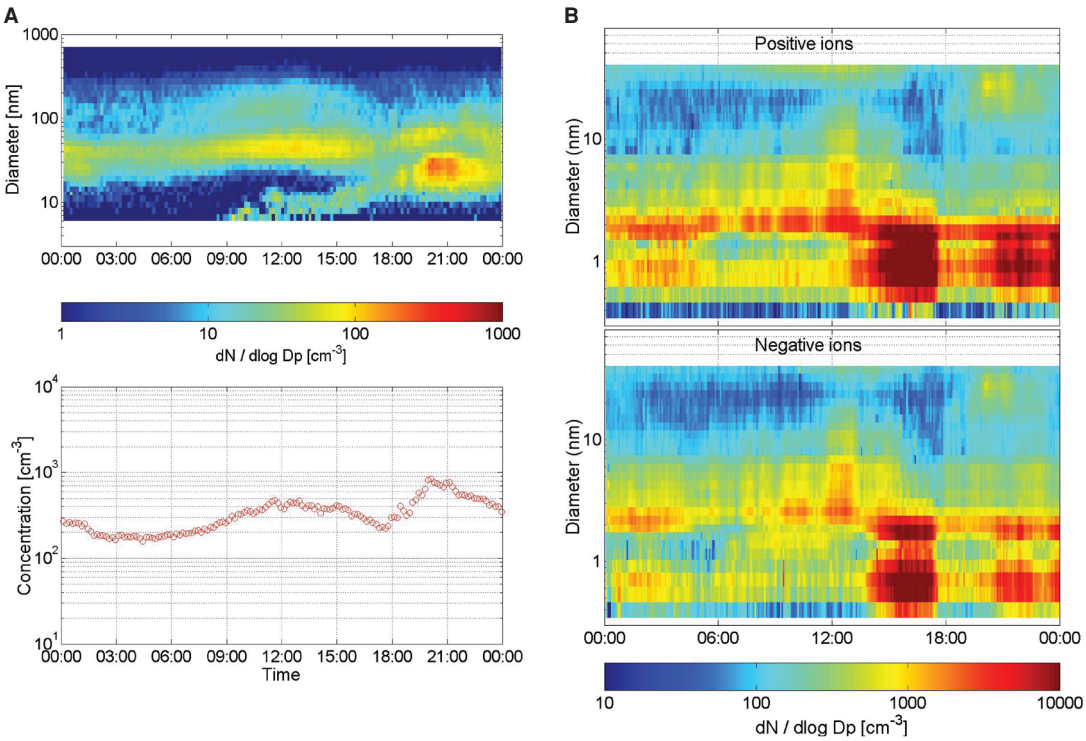

Fig. 7. Example of a day that was classified (**A**) into the event class 1 for the DMPS data but (**B**) into the class WIP for the air ion data.

was that in Hyytiälä the snowfall-associated ions were in the intermediate size range, whereas in Aboa also cluster ions were generated. These observations are, however, consistent because we observed wind-generated cluster ions only at very high wind speeds that were not encountered at the forest site.

Conclusions

The air ion spectrometer measured air ion size distributions in the diameter range of 0.34–40 nm at the Finnish Antarctic research station Aboa between 14 December 2004 and 30 January 2005. The main focus of the measurement campaign was to investigate new-particle formation and growth starting from molecular sizes in a clean environment.

We identified several intermediate ion formation events that could be classified as class 1 or 2 events. The fraction of class 1 and class 2 event days was 16.7% and 6.3%, respectively, giving a total percentage of 23% of days in either class. This fraction is similar to that obtained during a three-year measurement period (2003–2005) at Hyytiälä, Finland (Hirsikko *et al.* 2007). In Hyytiälä the percentage of particle formation event days was about 22%–23% and 25%–27% based on positive and negative ion measurements, respectively. These numbers are annual values, and in spring and autumn there were more events than in winter and summer (Hirsikko *et al.* 2007).

The median growth rates of ion in different size classes in the Aboa formation were comparable to those measured by Hirsikko *et al.* (2005) in Hyytiälä. When looking at the same season (summer), however, ions in Antarctica grew slower than those in Hyytiälä. This result is similar to observations relying on DMPS measurements conducted at different sites around the world (Kulmala *et al.* 2004b): particle growth rates were lowest in Antractica.

Kulmala *et al.* (2004c) showed that an increase in the particle growth rate with increas-

ing particle size over the range 1.5–20 nm is consistent with the nano-Köhler particle growth mechanism. As for the Hyytiälä data, our results also suggest that charge-enhanced growth associated with ion-mediated nucleation plays a minor role in the initial steps of growth, since it would imply a clear decrease of the growth rate with increasing particle size (Kulmala *et al*. 2004c). However, this interpretation is still under debate (e.g. Yu 2006).

High concentrations of intermediate and cluster ions were observed during the storms. This finding is very similar to that made by Hirsikko *et al*. (2007) in Hyytiälä, Finland, where snowfall-associated intermediate ion bursts were observed. A probable explanation is that at strong winds the ions are produced by friction processes in fast moving snow and ice crystals, a process analogous to that in cumulonimbus clouds where this is the process that leads to the thunder. The processes taking place in clouds lead to very large charged particles or droplets, so this does not fully explain the appearance of intermediate or cluster ions. Thus, the formation mechanism of cluster and intermediate ions during snow storms or snowfall remains unclear.

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