Charging State of Aerosols during Particle Formation Events in an Urban Environment and its Implications for Ion-Induced Nucleation

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Abstract

The aim of this study was to investigate the charging state of atmospheric ions during particle formation (PF) events in an urban environment. We measured small ion (charged cluster) and large ion (charged particle) concentrations over a period of 13 months in Brisbane, Australia, using a neutral cluster and air ion spectrometer (NAIS) and obtained 245 complete days of data. PF events were observed on 110 days which count as 45% of the total. On the average, the positive small ion concentration was 40% higher than the negative. The positive large ion concentration was 20% higher than the negative. Generally, small ion concentrations peaked during the night, while large ion concentrations were a maximum during the day. Next, we classified the results into days on which there was a PF event and when there was not. We showed that PF events have a profound effect on small and large ion concentrations in the environment; the small ion concentrations decreased by about 30% while large ion concentrations increased by up to 100%. We identified two phenomena that have a bearing on ion-induced nucleation. Firstly, the fraction of particles that were charged consistently decreased during PF events and rarely exceeded the equilibrium value, suggesting that the formation process was not significantly influenced by an ion-induced mechanism. Secondly, small ion concentrations were higher in the pre-dawn hours of PF event days than on other days, while the fraction of clusters that were charged often showed an increase immediately prior to a PF event, both observations supporting an ion-induced mechanism of PF. This study serves as basis for future work explaining these observations.

Keywords: Ion, Charged particle, Secondary particles, Particle formation, Nucleation

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INTRODUCTION

Particles and ions are omnipresent in the atmosphere. While the properties of particles have been thoroughly investigated, the same cannot be said about environmental ions, their concentrations, temporal variation and their interaction with particles. For example, while particle formation (PF) events are frequently observed in urban environments, the role of atmospheric ions in this process is largely unknown. Furthermore, there are few reports of the diurnal variation of ion concentrations, especially charged particles.

Atmospheric ions are formed by ionization of air molecules by cosmic radiation and radioactive materials in the environment. ‘Small ions’, which are charged molecular clusters smaller than 1.6 nm, are naturally found in concentrations of 200-2500 cm$^{-3}$ in unpolluted environments (Hirsikko et al., 2011). Their concentrations may be elevated in the presence of anthropogenic sources of ions such as overhead power lines (Buckley et al., 2008; Jayaratne et al., 2008) and motor vehicles (Jayaratne et al., 2010). Small ions have a limited lifetime as they are soon lost by recombination or attachment to aerosol particles in the air. Thus, while their concentrations are high in clean environments, in polluted urban environments they may be as low as 200-400 cm$^{-3}$ (Hirsikko et al., 2011; Ling et al., 2010; Retalis et al., 2009). In stable ambient air with no ion sources, approximately 1 in 3 ultrafine particles carry a charge, the vast majority being a single charge (Hirsikko et al., 2011). These charged particles are larger than 1.6 nm and are also known as ‘large ions’. In areas away from ion sources, large ions are found in concentrations of 500-1000 cm$^{-3}$. However, in the presence of an ion source, this may increase to several thousand cm$^{-3}$, with many particles carrying more than one charge (Jayaratne et al., 2011; Lee et al., 2012).

Particle burst events are commonly observed in urban environments (Woo et al., 2001). These events fall into two broad types. The first type is when large numbers of particles are formed at a
distant location and transported to the monitoring site. Such instances are generally not accompanied by particle growth at the monitoring location. The second type of event involves the in-situ rapid formation of secondary particles by the homogeneous nucleation of gaseous precursors such as sulfuric acid, ammonia and organics from motor vehicle exhaust and industrial emissions. Nucleation is facilitated by photo-oxidation and occurs when solar radiation and ozone concentrations are high, generally during the middle of the day. These particles continue to grow from the same or other precursor gases, exhibiting the well-known ‘banana-shaped’ particle size distribution contour plots. During such events, ultrafine particle number concentrations (PNC) in the environment can increase from a few thousand cm\(^{-3}\) to over \(1 \times 10^5\) cm\(^{-3}\) (Woo et al., 2001). PF is mostly attributed to binary nucleation, generally involving water vapour and sulphuric acid. Although this process is enhanced in the presence of ammonia (Korhonen et al., 1999; Weber and McMurry, 1998; Yu, 2006), it is still not sufficient to account for the high nucleation rates observed in the atmosphere (Birmili and Wiedensohler, 2000). For this reason, additional mechanisms have been proposed. One of these mechanisms is ion-induced nucleation (Iida et al., 2006; Yu and Turco, 2000). Several studies have attempted to detect the rate of change of cluster ions during PF events (Laakso et al., 2007; Manninen et al., 2009; Vana M., 2006). While ion-induced nucleation was sometimes seen to contribute to new PF, many of the PF events were clearly dominated by neutral nucleation (Kulmala et al., 2007). However, recent studies, such as Herrmann et al. (2013) and Gonser et al. (2014) have observed increased cluster ion concentrations during PF events which indicate that ion-induced nucleation may play a role in PF. A measure of ion-induced nucleation is the so-called ‘overcharging’ of particles in the atmosphere (Kerminen et al., 2007; Laakso et al., 2007). This is when particles, especially in the size range below 10 nm, carry charges greater than they normally would in stable equilibrium.
The aim of this study was to investigate the charging state of atmospheric ions at an urban location, particularly during PF events. We monitored small and large ion concentrations and neutral PNC over a period of 13 months using a neutral cluster and air ion spectrometer (NAIS) in Brisbane, Australia. This paper summarizes our findings and, in particular, presents the diurnal variations of small ions and charged particles, and derives important conclusions on their behavior during PF events.

METHODS

Instrumentation

The instrument used in this study was the neutral cluster and air ion spectrometer (NAIS) developed by Airel Ltd, Estonia (Manninen et al., 2009; Mirme et al., 2007). It contains two parallel spectrometer columns, one for each charge polarity. As the air is drawn into the instrument, particles are charged and passed through the two columns where they are classified by a pair of cylindrical differential mobility analyzers. Ions are deflected in a radial field and collected on 21 electrically isolated electrometer rings according to their electrical mobilities. The ion currents from the rings are measured with electrometers, providing ion and particle number distributions in selected size fractions in the range 0.8 to 42 nm. In equilibrium, almost all charged particles in this size range carry a single charge. Controlled charging and electrostatic filtering enables the NAIS to differentiate neutral aerosols from charged ions. Although this works well at larger sizes, it has been shown that there can be some uncertainty in discriminating between charged and uncharged particles in the size range below about 3 nm (Asmi et al., 2009; Manninen et al., 2009; Mirme and Mirme, 2013). Therefore, all data obtained by the NAIS below 3 nm should be treated with some caution.
Switching between ion and neutral particle modes is enabled by cycling the operation of the chargers and electrostatic filters in user-defined time periods. In this study, we set the NAIS to operate in a cycle of 2.5 min including ion and neutral particle sampling periods of 1.0 min each, the remaining 0.5 min being an offset period which is required to neutralize and relax the electrodes. Readings were logged at 1 min intervals, thus providing one ion and particle measurement in each 2.5-min cycle.

The upper size detection limit of the NAIS effectively restricts it to the nanoparticle size range, which has somewhat arbitrarily been defined as smaller than 50 nm (Morawska et al., 2009). Particles in vehicle emissions, particularly soot, have a mode between 50 and 100 nm. Larger particles can carry a greater charge than smaller particles so that a substantial portion of the charges reside on particles larger than 42 nm that are not detected by the NAIS. Therefore, the particle charges reported in this study may be considered to be lower limits and not the total charges carried by the particles present.

**Sampling techniques**

The instrument was located in a laboratory on the top floor of a six-floor building at the Gardens Point Campus of the Queensland University of Technology. Monitoring was conducted between 16 November 2011 and 20 December 2012. The site was well-represented as an urban location as it bordered the main city centre and a large city park and was situated about 100 m away from a busy freeway. The air was sampled from outside a window through a conductive rubber tube of length 1.1 m and diameter 17 mm. A steel mesh was placed at the inlet of the tube to trap any windblown debris and insects, such as flies and mosquitoes, from being sucked into the instrument in the high air flow. The instrument was operated by the software provided on an online computer which also stored the data acquired in real time.
Data analysis

The NAIS was operated continuously during each period of measurement. One minute average readings of ion and particle number concentrations were obtained in each 2.5 min cycle, giving 24 readings of each parameter every hour. In deriving diurnal variations, average values were calculated for each 30-min period. Differences between means of samples were estimated statistically using a Student’s t-test. Linear regression analyses were used to investigate significant increases or decreases of parameters. All significant differences in both the t-tests and the linear regression analyses were estimated at a confidence level of 95%.

PF events were identified based on the rate of increase of the PNC, dN/dt, where N is the number of particles in the size range 1.6-10 nm. Events with dN/dt > 15,000 cm$^{-3}$ h$^{-1}$ were classified as PF events in accordance with the method employed by Zhang et al. (2004). Days with no such events were classified as non-event days.

Molecular clusters are smaller than 1.6 nm and can be either neutral or charged. Charged clusters are also known as ‘small ions’. The percentages of clusters and particles that were charged were calculated as the ratios small ion concentration / cluster concentration and charged particle concentration / total particle concentration, respectively.

RESULTS AND DISCUSSION

During the monitoring period, the instrument was unavailable on some days due to other projects. It was also removed for cleaning on 5 days. Allowing for such interruptions, we were able to acquire complete 24-hour data on 245 days. Of these days, at least one PF event was observed on 110 days, which counts as approximately 45% of the total. On such days, the higher PNCs had a
profound effect on the small and large ion concentrations, as we will show later. PF events were more likely to occur during the hot summer months (November-February, approximately 65% of the days) than during the cold summer months (June-August, approximately 30% of the days). A complete analysis of the frequency and variation of PF events in this study and the conditions that give rise to them are outside the scope of this paper and, here, we shall restrict ourselves to the impact of PF events on the small and large ion concentrations observed in the environment.

*Relationship between positive and negative ion concentrations*

The results showed a consistent relationship between the concentrations of positive and negative ions at all times of the day. Both small and large ions coexisted in the air, with a small excess of positive over negative ion concentrations at all times. For example, Fig 1 shows the data for the calendar month of May 2012 where data were available for a full 30 days. Each point in the graph is a 1 min data point and the straight line shows equality. We see that the positive ion concentration was generally higher than the negative for both small (a) and large (b) ions. The coefficient of unipolarity (COU) is defined as the ratio of the positive to the negative ion concentration (Gefter, 2002; Kolarž et al., 2009) and is given by the slope of the best line in these graphs. In Fig 1, the COU’s or slopes of the two lines for (a) small and (b) large ions were 1.37 and 1.17, respectively. These two values were consistent right through the monitoring period; the corresponding means and standard deviations being 1.4 ± 0.4 and 1.2 ± 0.2, respectively.

The magnitudes and COU of the small ion concentrations are consistent with that found by Ling et al. (2013) at close proximity to the present monitoring location using two Alphalab air ion counters. They found COU’s for small ions of 1.40 at a site very similar to the present site, about 2 km away, and 1.30 at an urban residential site located about 9 km to the north of the present site. An excess of positive small ions has also been observed in several other studies at urban
locations. For example, Retalis et al. (2009) observed a COU of 1.25 in Athens, Greece. Kolarž et al. (2009) reported a COU of 1.06 in downtown Belgrade, Serbia. A notable exception within urban environments is Hirsikko et al. (2007) who did not find a significant difference between the small ion concentrations of the two polarities in Helsinki, Finland. In this study, however, the excess of positive small ions over negative may be explained in terms of the higher mobility of negative ions. Consequently, negative ions have a higher efficiency of ion neutralization and, therefore, their lifetime and concentration are generally lower than positive ions in stable environments (Kolarž et al., 2009). For example, Tammet et al. (2006) estimated the average lifetimes of small positive and negative ions in a forest station in Finland to be 130 s and 110 s, respectively. They calculated the COU’s to be 1.17 at the top of the tree canopy and 1.20 close to the ground. The lifetimes of small ions are significantly reduced in more polluted environments where ions with the higher mobility (negative) will be neutralized faster due to attachment to particles and the COU will be much higher.

There are very few reports of the COU for large ions because instruments that can detect charged particles of both polarities at the exclusion of small ions did not become available until about 15 years ago. Hirsikko et al. (2007) measured weekday and weekend concentrations of 703/784 and 399/433 cm$^{-3}$, respectively, for positive/negative particle charges in the size range 3-40 nm in a car park in Helsinki, Finland (COU = 0.90 and 0.92, respectively). Titta et al. (2007) found corresponding values of 750/510 cm$^{-3}$ at a distance of 10 m from a busy road in Finland (COU = 1.47). The present sampling point was located about 100 m from a busy freeway and our large ion COU of 1.2 is consistent with these two reports. Retalis and Retalis (1998) reported mean positive and negative particle charge concentrations of 8228 and 7075 cm$^{-3}$ over an 8-year period in Athens, Greece, which gives a COU of 1.16, in good agreement with the present value in Brisbane.
In general, the diurnal time series of the small and large ion COUs showed contrasting patterns of variation. While, the large ion COU remained fairly constant right through the day, the small ion COU was observed to increase during and soon after PF events. A typical example is shown in Fig 2 which occurred on 17 November 2011 with a strong PF event between 8-11 am, followed by particle growth into the afternoon. The mean hourly large ion COU and standard deviation on this day were $1.2 \pm 0.1$. The small ion COU remained within $1.5 \pm 0.3$ during the night but increased significantly during PF and growth during the daytime. The larger variations in small ion COU during the night point to the existence of sources of small ions of preferential polarity in the environment. Two of the main sources of small ions in urban environments are motor vehicles and electric power lines. While motor vehicle exhaust contains both polarities in roughly equal numbers (Jayaratne et al., 2010), we have previously shown that ions produced by overhead AC power lines are predominantly of positive polarity (Jayaratne et al., 2008). In contrast, the large ion COU did not show much variation in time. The mean value of 1.2 was consistent on most days. This suggests that the charge distribution on particles is maintained once they attain equilibrium. This is consistent with the idea that, once small ions attach to particles, they remain on the particles for relatively long periods.

The significant increase of small ion COU during PF and growth is explicable in terms of the different mobilities of clusters of the two polarities. Negative clusters have a greater mobility than positive clusters and, therefore, a higher efficiency of ion neutralization and attachment (Kolarž et al., 2009). As a consequence, their lifetime and concentration are generally lower than positive ions in the environments (Tammet et al., 2006). When the PNC increases during a PF event, negative clusters have a greater propensity to attach to particles, leaving a surplus of positive clusters in the atmosphere. This leads to an increase in small ion COU, as observed.
Diurnal variation of positive and negative ion concentrations

Fig 3 shows the average diurnal variations of hourly large and small ions over the monitoring period. The diurnal cycles were distinctly different on PF event days and non-event days and, therefore, we have separated the results into these two categories as shown. In general, the large ion concentration was about 2000 cm$^{-3}$ during the second half of the night when there was minimal activity in the urban environment and increased significantly during the day. The large ion concentration during the day was significantly higher on PF event days over non-event days. Large ions lingered in the atmosphere during the first half of the night on event days. The small ion concentration followed an inverse relationship to the large ion concentration, reaching its maximum value of about 500 cm$^{-3}$ during the night and its minimum during mid day. The daytime minimum value was significantly lower on PF event days over non-event days. These diurnal variations are broadly in agreement with previous studies (Hirsikko et al., 2007; Manninen et al., 2009; Retalis et al., 2009).

Relationships between particle number and ion concentrations

In general, we observed a positive correlation between particle number and large ion concentration and a negative correlation between particle number and small ion concentration on most days. The correlations were very strong up to a PNC of about $4 \times 10^4$ cm$^{-3}$ and then deviated at larger concentrations, such as that which occurred during PF events. While the night-time values were consistent on most days, the daytime values were clearly different on PF event and non-event days. Fig 4 shows the relationships on a typical event day (26 April 2012) for all PNC up to $6 \times 10^4$ cm$^{-3}$. The slope of the best line through the points in Fig 4(a) indicated that the percentage of particles that carried a charge was approximately 10% up to a PNC of $4 \times 10^4$ cm$^{-3}$. At higher PNC, especially during PF events, the slope decreased to well below 10%. This was
generally observed during all PF events and will be discussed in the next section. In contrast, the small ion concentration fell sharply with PNC. In this example (Fig 4b), we observed a drop from 1300 to 500 cm\(^{-3}\) as the PNC increased from 1.2 \times 10^4 to 4.0 \times 10^4 cm\(^{-3}\). Similar trends were observed during all PF events.

Fig 5 shows the negative and positive ion size-time contour plots together with the time series of the PNC on this day. Fig 6 shows the corresponding (a) large and (b) small ion concentrations. A strong PF event occurred between 8.30 and 10.30 am. The environment was relatively clean from midnight until about 4:00 am after which morning activities led to an approximate doubling of the PNC, accompanied by an increase of large ion concentration and a decrease of small ion concentration after 5 am. The PF event is evidenced by sharp increases in both PNC and charged particle concentrations. Although the PNC reached its maximum value near 10:30 am, particle growth continued into the late afternoon as observed from the typical banana-shapes of the NAIS contour plots (Fig 5). The growth rate of the particles was computed by tracking the temporal variation of the modal size of the nucleation mode particles. The modal size increased from 5 nm at 9:00h to 25 nm at 13:00h, giving a mean growth rate of 5 nm h\(^{-1}\). The PNC and charged particle concentration reached their maximum values of 1.2 \times 10^5 cm\(^{-3}\) and 7.5 \times 10^3 cm\(^{-3}\), respectively, at 10:30 h. From the start of the PF event to this time, the small ion concentration fell from about 800 cm\(^{-3}\) to about 600 cm\(^{-3}\) (Fig 6c).

**Charged Fractions**

On all days, the percentage of particles that were charged was typically between 10% and 15% during the night, and decreased to between 5% and 10% during the day. The percentage of clusters that were charged showed a wider variation but was generally higher during the night (5% to 75%) than during the day (2% to 10%). The percentages of charged clusters and charged
particles on 26 April are shown over the entire 24-hour period in Fig 7. An interesting observation is that, although the concentration of large ions reached its maximum value at 10 am, the percentage of particles that were charged was a minimum at this time. In order to investigate this observation more closely, in Fig 8 we show the corresponding (a) PNC and (b) percentage of particles charged during the course of the PF event between 8.30-10.30 am. There is a steady decrease in the percentage of particles charged as the PF event progresses. The rate of increase of PNC between 8.30-10.30 am was $6.0 \times 10^4 \text{ cm}^{-3} \text{ h}^{-1}$. During this time, the percentage of particles that were charged fell from 11% to 4%.

This trend was consistently observed during PF events. We have shown two more examples in Fig 9 (17 November 2011) and Fig 10 (21 April 2012). On the 17th November, there were three distinct PF events, beginning at 7.00 am, 9.30 am and 2.00 pm. In each of the three events, the percentage of particles charged decreased while the particle number was increasing. On 21 April, there were two PF events, beginning at 9.00 am and 2.00 pm. The same trend was seen once again.

A further important observation is shown in Fig 11, which includes two particle burst events that occurred on 25 April 2012. The event that begins at 10.00 am is a regular PF event and we see the typical decrease in time of the percentage of particles charged. However, the particle burst event between 2.00 pm and 4.00 pm was not a PF event. No banana-shape was observed on the NAIS contour plots and the minimum $dN/dt$ criterion for the identification of a PF event (section 2.3) was not fulfilled. This event did not show the characteristic decrease in percentage of particles charged in time. In fact, the percentage clearly increased with time. We conclude that this was a particle burst event, where aerosols that have formed elsewhere are transported to the sampling site. These particles appear to be already charged when they arrived. No particle formation occurs
near the site. Clearly, the percentage of particles that are charged decreases only when particles are being formed on-site.

When particles form and grow in the atmosphere, their charging state evolves towards unity. If the particles are formed by ion-induced nucleation, their initial charging state would be above unity; that is, the particles would be overcharged. Likewise, if the particles were formed by neutral nucleation, their charging state would be smaller than unity or undercharged (Kerminen et al., 2007). Our observations on the charging state of particles during PF events show that the PF rate is generally too high for the particle charging mechanism to keep pace with the increase. We also observed that the fraction of particles that are charged decreased as the PNC increased. In Fig 12, we have plotted the decrease in the percentage of charged particles h\(^{-1}\) against the PF rate h\(^{-1}\) for the 26 PF events that occurred during the three months May, June and July, 2012. We see a positive correlation between these two quantities. As the PF rate increased, the percentage of charged particles that were charged decreased steadily up to at least \(8 \times 10^4\) cm\(^{-3}\) h\(^{-1}\). The percentage decrease of charged particles increases by 7\% for every \(10^4\) particles cm\(^{-3}\) h\(^{-1}\) increase in PF rate.

As larger particles can carry more charge than smaller particles, it is instructive to determine the size distribution of the fraction of particles that were charged. Under stable conditions, atmospheric particles attain an equilibrium charge distribution due to bipolar diffusion charging. The fraction of particles that are charged increases with particle size, typical values being about 9\% at 10 nm and 35\% at 40 nm (Wiedensohler, 1988). In Fig 13, the line shows the fraction of particles that are charged at equilibrium according to the Wiedensohler model. On the same figure, we show the equivalent fractions on the 17\(^{th}\) November during the night (1-3 am) and during the PF event (8-11 am). During the night, particles smaller than about 5 nm are overcharged, that is they carry a charge that exceeds the equilibrium value, while larger particles
carry a charge that is close to equilibrium. During the PF event, particles smaller than 5 nm are again overcharged but the larger particles are clearly undercharged. Thus, we conclude that, during formation and growth, the particles that are undercharged are overwhelmingly those larger than 5 nm.

Another interesting feature was observed in the charging state of the clusters. Overcharging of clusters was observed during most nights and was particularly high in the pre-dawn hours of PF days. For example, on 26 April 2012, the percentage of clusters that were charged was 10% to 30% during the night but decreased to less than 10% during the day (Fig 7). The cluster ion concentration during the night was also unusually high on this day, over 1200 cm\(^3\). It is interesting to note that Herrmann et al. (2013) have recently reported heightened ion cluster concentrations during the nights before PF event days. The pre-dawn fraction of charged clusters was as high as 60%, on 17 November 2012. Fig 14 shows the percentage of clusters that were charged as a function of time on this day, which included three PF events beginning at 7.00 am, 9.30 am and 2.00 pm (Fig 9). Despite the low percentage of charged clusters during the day and the considerable scatter in the data, there are two peaks at 7.00 am and 2.00 pm, coinciding with the initial stages of PF. At 7.00 am the percentage of charged clusters increased from 20% to 30% and just prior to the event at 2.00 pm, it again increased from 7% to 19%. These increases were statistically tested using linear regression analysis and found to be significant at a confidence interval of 95% (p<0.05). No significant increase was associated with the PF event at 9.30 am. We have no plausible explanation for the absence of a significant increase in this case. However, statistically significant increases were observed during 62% of all PF events that were analysed. This is consistent with the recent study of Gonser et al. (2014) who observed that the occurrence of the ion nucleation mode preceded that of the total particle nucleation mode during PF events suggesting that charged clusters are more likely to form particles than neutral clusters. This may
also explain the occurrence of overcharging of particles smaller than 5 nm during PF events. These observations suggest that cluster ions play a role in nucleation and particle formation.

**SUMMARY AND CONCLUSIONS**

Thus, in summary, we have two conflicting phenomena that have a bearing on ion-induced nucleation. Firstly, PF events were accompanied by a significant decrease in the percentage of particles that were charged. Particles larger than 5 nm were clearly undercharged during formation and growth. The percentage of charged particles decreased with increasing PF rate, suggesting that the formation process was not significantly influenced by an ion-induced mechanism. Secondly, during the pre-dawn hours of PF event days, the percentage of charged clusters was generally greater than on other days. Immediately prior to the commencement of a PF event, the percentage of clusters that carried a charge often showed a significant increase, supporting an ion-induced mechanism of PF. Further work is clearly required to arrive at a definite conclusion regarding the viability of an ion-induced mechanism of PF in the atmosphere.

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Figure Captions

Fig 1: Relationship between positive and negative concentrations of (a) small and (b) large ions over 30 complete days in May 2012. Each point is a 1 min average value. The best line is shown together with the line of equality which is represented by a broken line.

Fig 2: The diurnal variation of small and large ion COUs on 17 November 2011.

Fig 3: Average diurnal variations of hourly large (◊) and small (∆) ion concentrations on PF event days (filled symbols) and non-event days (open symbols). Error bars indicate the respective standard deviations of the means.

Fig 4: (a) Large and (b) small ion concentrations as a function of PNC up to 6 x 10⁴ cm⁻³ on 26 April 2012.

Fig 5: Negative and positive ion contour plots for 26 April 2012, shown together with the diurnal variation of the PNC. The PF event began at 8 am and, although the PNC began to decrease soon after 10 am, particle growth continued into the afternoon.

Fig 6: Diurnal variations of (a) large ion and (b) small ion concentrations on 26 April 2012.

Fig 7: Time series of the (a) percentage of clusters that were charged and (b) percentage of particles that were charged on 26 April 2012.
Fig 8: Time series of the (a) PNC and (b) percentage of particles that were charged during the PF event on 26 April 2012.

Fig 9: Time series of the (a) PNC and (b) percentage of particles that were charged during the three PF events that occurred on 17 November 2011.

Fig 10: Time series of the (a) PNC and (b) percentage of particles that were charged during the two PF events that occurred on 21 April 2012.

Fig 11: Time series of the (a) PNC and (b) percentage of particles that were charged during the two particle burst events on 25 April 2012.

Fig 12: Percentage decrease of the fraction of charged particles h\(^{-1}\) against the particle formation rate h\(^{-1}\) for the 26 PF events that occurred between May and July, 2012.

Fig 13: Fraction of particles that were charged during the night (1-3 am) and during the PF event (8-11 am) on the 17\(^{th}\) November 2011. The line shows the fraction of particles charged at equilibrium according to the Wiedensohler (1988) model.

Fig 14: Diurnal variation of the percentage of clusters carrying a charge on 17 November 2011. The points are separated by 3 min and the red line shows the hourly mean values. Note the two peaks just prior to the two PF events at 8:00 and 14:00 h.
Fig 1
Fig 2
Fig 3
Fig 4

(a) Large Ion Concentration (cm$^{-3}$) vs. Particle Number Concentration (cm$^{-3}$)

(b) Small Ion Concentration (cm$^{-3}$) vs. Particle Number Concentration (cm$^{-3}$)
Fig 6

(a) Large Ions

(b) Small Ions
Fig 7
Fig 8

(a) Particle Number Concentration (cm$^{-3}$)

(b) Percentage of Particles Charged

Time (h)
Fig 9
Fig 10

(a) Particle Number Concentration (cm$^{-3}$)

(b) Percentage of Particles Charged
Fig 11
Fig 12
Fig 13
Fig 14