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Jayaratne, Rohan, Ling, Xuan, & Morawska, Lidia
(2014)
Suppression of cluster ions during particle formation events in the atmosphere. In
15th International Conference on Atmospheric Electricity (ICAE 2014), 16-20 June 2014, Norman, Oklahoma.

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Suppression of Cluster Ions during Particle Formation Events in the Atmosphere

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ABSTRACT: Charged and neutral cluster and particle number concentrations (PNC) in the size range 1.6 to 42 nm were monitored using a neutral cluster and air ion spectrometer (NAIS) over a period of 13 months in Brisbane, Australia. The study yielded 242 complete days of usable data, of which particle formation events were observed on 101 days. During these events, the PNC, which was normally lower than 1×10^4 cm^{-3}, often exceeded 5×10^4 cm^{-3} with occasional values over 1×10^5 cm^{-3}. Small ions (charged clusters) generally occurred in number concentrations between 400 and 600 cm^{-3} but decreased to about 300 cm^{-3} during particle formation events. This was accompanied by an increase in the large ion (charged particle) concentration. 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. In the diurnal cycle, small ion concentration was highest during the second half of the night while large ion concentrations were a maximum during the day. A positive correlation between PNC and large ion concentration and a negative correlation between PNC and small ion concentration were observed on most days.

INTRODUCTION

Nucleation from trace vapors is now recognized as a major process of particle formation in the atmosphere [Curtius, 2006]. Particle formation events are commonly observed in urban environments where the gaseous precursors are generally sulfuric acid, ammonia and organic compounds from motor vehicle and industrial emissions [McMurry et al, 2005; Stanier et al, 2004]. Particle formation generally occurs in bursts with formation rates as high as 100 cm^{-3} s^{-1} often observed in urban areas [Kulmala et al, 2004]. These burst events occur during the daytime when the oxidation of gaseous precursors is facilitated by solar radiation and increased concentration of ozone in the troposphere.

Although, much work has been carried out, the precise mechanism of nucleation has not been identified. The known mechanisms such as binary (sulfuric acid and water) and ternary (ammonia, sulfuric acid and water) are not able to explain the rates of new particle formation in many atmospheric situations [Kirkby et al, 2011]. An alternative mechanism that has been suggested is ion-induced nucleation, where charged clusters initiate nucleation of gaseous precursors [Yu and Turco, 2000; Iida et al, 2006]. There has been much controversy regarding ion-induced nucleation and it is still open to debate [Enghoff and Svensmark, 2008; Manninen et al, 2009; Kirkby et al, 2011].

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Most of the ions in the lower atmosphere are formed by galactic cosmic radiation and radioactivity at the ground. These ions attach to molecular clusters that remain stable up to a size of 1.6 nm. These charged clusters are also known as cluster ions or small ions. Small ions have a limited lifetime in air as they soon attach to aerosol particles to form large ions [Hirsikko et al, 2009]. Therefore, the concentration of small ions is severely affected by the PNC in the environment. Although they fall into the class of large ions, ions in the size range 1.6 to 7.5 nm are also classified as Intermediate Ions [Horrak et al, 2003].

METHODS

The neutral cluster and air ion spectrometer (NAIS) was developed by Airel Ltd, Estonia (Mirme et al., 2007; Manninen et al., 2009). The NAIS measures positive, negative and neutral cluster and charged particle concentrations simultaneously in the size range 0.8 to 42 nm. In the present study, the NAIS was set 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.

Ambient air was sampled from outside a laboratory on the sixth floor of a building in the Gardens Point Campus of the Queensland University of Technology, Brisbane, Australia, between November 2011 and December 2012. The site borders the main city centre and a large city park.

Particle formation 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 particle formation events in accordance with the method employed by Zhang et al. [2004]. Days with no such events were classified as non-event days.

RESULTS

During this study period, we were able to obtain 242 complete days of usable data, of which particle formation events were observed on 101 days (41.7%). On a typical non-event day, the PNC ranged from $5x10^3$ to $2x10^4$ cm^{-3} and the small ion concentration varied between 400 and 600 cm^{-3}. The average positive small ion concentration was 40% higher than the negative. The positive large ion concentration was 20% higher than the negative. In the diurnal cycle, small ion concentration was highest during the second half of the night while large ion concentrations were a maximum during the day.

During particle formation events, the PNC often exceeded $5x10^4$ cm^{-3}, with occasional values over $1x10^5$ cm^{-3}. This was accompanied by an increase in the large ion (charged particle) concentration, together with a decrease in small ion concentration to about 300 cm^{-3}.

Figure 1 shows a particle formation event with the PNC markers overlaid on the corresponding NAIS particle size–time contour graph showing the typical ‘banana shape’ of a particle formation event which begins soon after 08:00 am. The particle size on the vertical scale ranges from 1 nm at the lower edge of the frame to 42 nm at the top. A second particle formation event begins at about 09:30 and particle growth continues well into mid-day. Close to 11:30, the PNC peaks at about $9x10^4$ cm^{-3}.

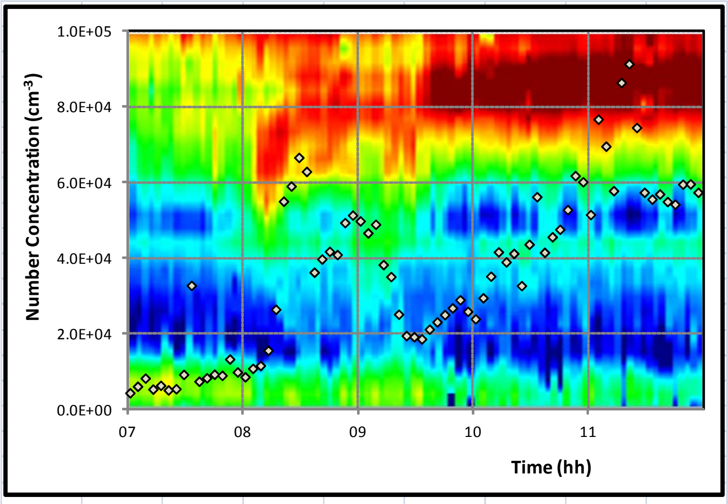

Figure 1

Figure 1: A typical particle formation event obtained by the NAIS, with the PNC markers referenced by the vertical scale. The particle size range is from 1 nm (lower edge) to 42 nm (upper edge).

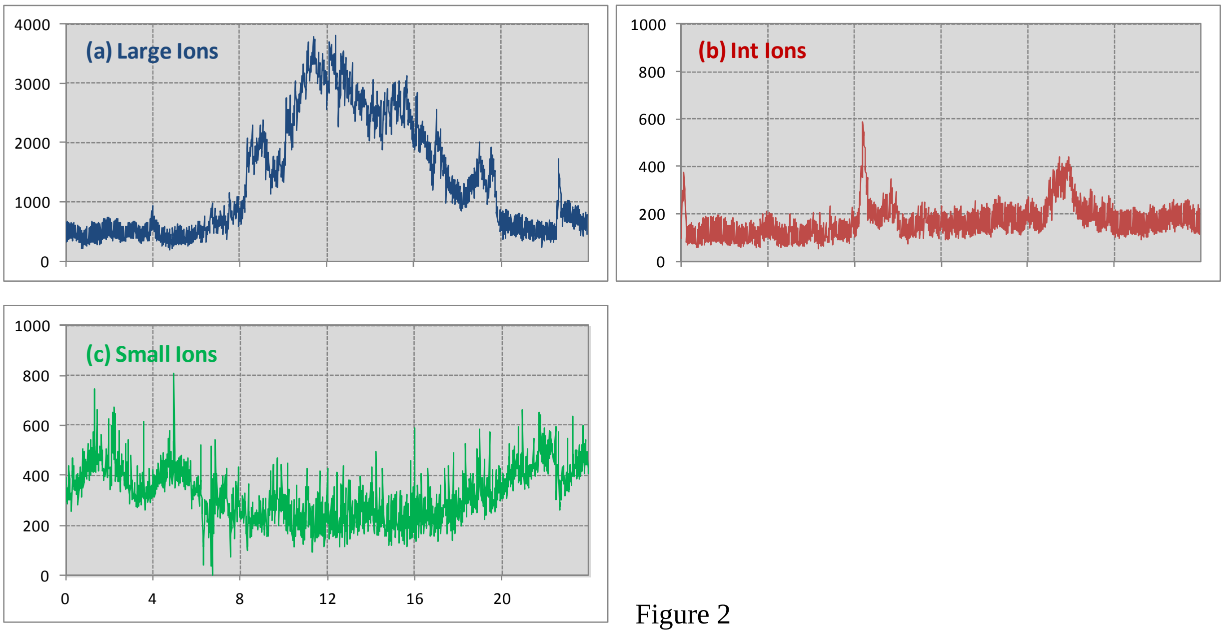

Figure 2

Figure 2 above shows the diurnal variations of positive (a) large (b) intermediate and (c) small ion concentrations corresponding to the day with the particle formation event shown in Figure 1. The negative ion concentrations followed a very similar trend. Of particular interest is the sharp peak in intermediate ion concentration at the inception of the particle formation event at 08:15 which confirms that the particles were being formed in-situ and grew from very small sizes. The second peak at 18:00 is not followed by a high PNC and appears to be due to particles transported from afar rather than being formed at the monitoring location. There is a near-mirror image variation between the large and small ion concentrations. This will be discussed later. 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.

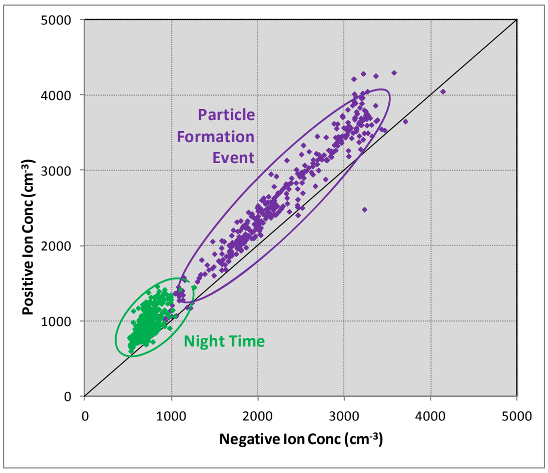

Figure 3

Figure 3 above shows the total positive versus negative ion concentrations during two selected time periods – between 00:00 and 06:00 at night (green) and during the particle formation event between 08:00 and 12:00 (mauve). The straight line indicates equality. The ion concentration during the particle formation event is much higher than during the calm night hours. Note that the total positive charge is always larger than the total negative charge. This may be attributed to the higher mobility of negative ions that enable them to migrate to ground and deposit faster than the positive ions.

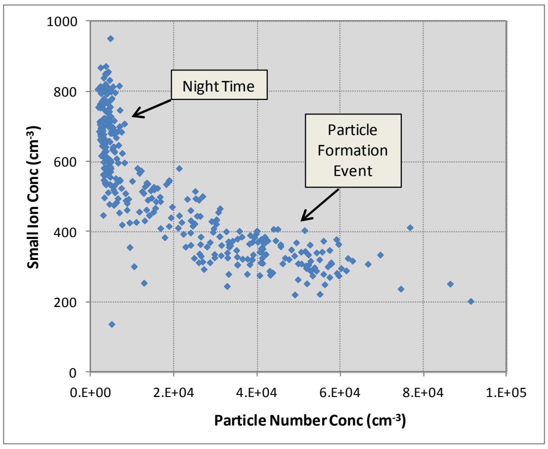

Figure 4

Figure 4 above shows the small ion concentration plotted against the total PNC over the selected period of measurement. This plot adds confirmation to the observation made in Figure 2 where the small ion concentration decreased as the large ion concentration increased. In previous studies we have shown that the large ion concentration is directly proportional to the PNC [Ling et al, 2010, 2013]. Figure 4 shows that the small ion concentration is inversely proportional to the PNC. It is clear that as small ions readily attach to particles, their concentration is suppressed during particle formation events, in this instance decreasing to less than 300 cm^{-3}.

ACKNOWLEDGMENTS

This study was supported by Australian Research Council Discovery Grant DP0985726.

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