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The relationship between airborne small ions and particles in urban environments

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HIGHLIGHTS

- Real life confirmation of small ions being suppressed by particles in the air.
- Their concentrations are inversely related in urban environments.
- There is no such relationship in clean environments.
- Their concentrations are suppressed during particle formation events.
- Positive small ion concentrations are 10%–40% greater than negative concentrations.

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ABSTRACT

Ions play an important role in affecting climate and particle formation in the atmosphere. Small ions rapidly attach to particles in the air and, therefore, studies have shown that they are suppressed in polluted environments. Urban environments, in particular, are dominated by motor vehicle emissions and, since motor vehicles are a source of both particles and small ions, the relationship between these two parameters is not well known. In order to gain a better understanding of this relationship, an intensive campaign was undertaken where particles and small ions of both signs were monitored over two week periods at each of three sites A, B and C that were affected to varying degrees by vehicle emissions. Site A was close to a major road and reported the highest particle number and lowest small ion concentrations. Precursors from motor vehicle emissions gave rise to clear particle formation events on five days and, on each day this was accompanied by a suppression of small ions. Observations at Site B, which was located within the urban airshed, though not adjacent to motor traffic, showed particle enhancement but no formation events. Site C was a clean site, away from urban sources. This site reported the lowest particle number and highest small ion concentration. The positive small ion concentration was 10%–40% higher than the corresponding negative value at all sites. These results confirm previous findings that there is a clear inverse relationship between small ions and particles in urban environments dominated by motor vehicle emissions.

1. Introduction

Atmospheric ions are formed due to ionization of air molecules by cosmic rays from space and radiation from airborne radioactive materials such as Rn-222 and its daughter products. These ions are soon attracted to hydrous molecules in the air and readily form singly-charged molecular clusters that can continue to grow by further attachment. Molecular clusters that are smaller than 1.6 nm in size are known as 'small ions' (Iribarne and Cho, 1980). Small ions are lost from the atmosphere due to two main processes – recombination of oppositely charged ions and attachment to aerosol particles larger than about 2 nm. Charged aerosols, formed by the above attachment process, are found in the size range 2 nm to 1 μm and are termed 'large ions'. Hirsikko et al. (2011) reviewed 93 publications including data on the spatial and temporal distributions of small ions and concluded that, under steady conditions in the natural atmosphere, average positive and negative small ion concentrations varied widely, from about 100 cm^{-3} in clean environments to over 2500 cm^{-3} in the presence of natural and anthropogenic ion sources such as waterfalls (Laakso et al., 2006) and overhead power lines (Fews et al., 1999; Jayaratne et al., 2008). Therefore, it is expected that the small ion concentration in the environment is strongly affected by the aerosol number

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concentration. While previous studies demonstrate an inverse relationship between particle number concentration and small ion concentration, the picture is not very clear in urban environments where motor vehicles comprise a common source of particles as well as small ions. It is well known that the majority of airborne particles in the urban environment originate in motor vehicle emissions (Shi et al., 1999). However, it has also been shown that motor vehicles emit large quantities of small ions and charged particles (Jayaratne et al., 2010). Thus, Retalis (1977) and Retalis et al. (2009) found an inverse relationship between small ion concentration and smoke in the air above Athens, Greece. Ling et al. (2010) showed that, at sites where ion sources were co-located with particle sources, small ion concentration was inhibited due to the attachment process. Hirsikko et al. (2007) measured daily outdoor ion concentration at an urban site approximately 100 m from a busy road and showed that the highest concentrations of large ions were observed when the wind blew from the road. Titta et al. (2007) measured ion concentrations near a busy freeway and showed that small ion concentrations were three times lower than that at a rural station where the air was cleaner.

The aim of the present study was to investigate the relationship between small ion and particle concentrations in the urban environment which is generally dominated by pollution from motor vehicle emissions. In order to achieve this aim, measurements of small ions and particles were carried out at two urban sites, one dominated by motor vehicle emissions and the other being some distance away from busy roads but, nevertheless, within the same urban airshed. The results were compared with that obtained at a third site, which was well away from urban traffic, to investigate whether a lower particle number concentration would result in a higher small ion concentration.

2. Methods

2.1. Measurement sites

Measurements were carried out for two weeks at each of three sites, details of which are provided in Table 1. The site locations in relation to the city of Brisbane are shown in the satellite image in Fig S1 (supplementary material). Mean meteorological conditions during the monitoring periods at the three sites are shown in Table S1 (supplementary material). All three sites were primary schools within the greater Brisbane area in South–East Queensland, Australia. Brisbane is a city with a population of approximately 2 million, situated on the eastern coast of Australia. The entire urban area extends about 30–40 km in the north-south direction and is sandwiched between the sea and a low range of hills located about 30 km inland. The air quality in this region is dominated by emissions from motor vehicles.

Site A was located about 2 km from the city centre, approximately 35 m from a major urban arterial road carrying two lanes of traffic in either direction. The highest traffic flow was observed during the weekday morning and late afternoon rush hours with about 100 vehicles min^{-1} in both directions. Most of these vehicles were petrol cars with heavy duty vehicles accounting for about 10% of the total traffic.

Site B was located in a school play ground surrounded by a large urban residential area, 9 km north of the city centre. The instruments were placed about 140 m from a major road carrying about 50 vehicles min^{-1} in both directions. The highest traffic flow was observed during the morning rush hour. Most of the vehicles were petrol cars with less than 5% being heavy duty vehicles and these were mostly buses.

Site C was situated near the coast, away from the urban sprawl, about 20 km north–east of the city centre. This area did not have any significant pollution sources and therefore, it was considered a 'clean' site, especially when the wind was blowing directly from the ocean.

Table 1
Details of the three measurement sites.

Site	Location lat (S) long (E)	Monitoring dates	Distance to nearest major road (m)	Traffic density (min^{-1} in both directions)
A	27°27′ 153°01′	1–8 Mar and 22–29 Mar 2010	35	100
B	27°22′ 153°01′	18 Oct–01 Nov 2010	140	50
C	27°17′ 153°04′	15–29 Nov 2010	500	80

2.2. Instrumentation

Small ion concentrations were measured with two Alphalab air ion counters that were factory-calibrated prior to the measurement campaign. Although this instrument has the capability of monitoring both negative and positive small ions, the operational principle does not permit them to be measured simultaneously. Hence, two instruments were used to monitor positive and negative small ions at the same time. The ion counter is battery-operated and samples by drawing air at a rate of 0.8 L s^{-1} through a parallel plate polarization electric field. The ion concentration is determined by measuring the plate current. The output signal was fed into a computer and the data was logged in real time at 1 s intervals. The instrument has a dynamic range of 10–10^6 ions cm^{-3} with a minimum detectable charge concentration of 10 ions cm^{-3}. The minimum characterisable mobility of the unit is 0.5 cm^2 V^{-1} s^{-1}, which corresponds to a detectable maximum ion size of 1.6 nm, thus restricting the measured charge to small ions.

Aerosol particle number concentration was monitored with a TSI-3782 water-based condensation particle counter (CPC) that can detect airborne particles down to a size of 10 nm in number concentrations up to 5×10^4 cm^{-3}. The time response of the instrument is less than 3 s and data were recorded every 1 s. In addition, particle number size distributions were measured with a TSI 3036 scanning mobility particle sizer (SMPS) which consisted of a TSI 3080 electrostatic classifier with a TSI 3085 nano-DMA and a TSI 3025 CPC. The nano-DMA was used in order to detect the smaller sized particles during formation events. Particle formation events were most common at Site A. Therefore, the detectable particle size range of the SMPS was set to 5–100 nm at Site A and 9–160 nm at the other two sites. A complete size scan was obtained every 3 min. Particle size was represented by the count median diameter (CMD) of the particles in each scan. Particle number concentration was separated into the nucleation mode (smaller than 50 nm) and Aitken mode (larger than 50 nm).

A monitor sensor automated weather station with uSmart series sensors and data logger was used to monitor meteorological parameters such as the air temperature, relative humidity and wind speed and direction.

2.3. Data analysis

For the time series analysis, the 1 s data were separated into 30 min sections and the corresponding median values calculated. Median values were considered to be more representative than mean values as the latter were affected by sharp, brief concentration peaks in the data. Such peaks are commonly observed near roads with motor vehicle traffic (Jayaratne et al., 2010).