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Air Ion Concentrations in Various Urban Outdoor Environments

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Abstract

Atmospheric ions are produced by many natural and anthropogenic sources and their concentrations vary widely between different environments. There is very little information on their concentrations in different types of urban environments, how they compare across these environments and their dominant sources. In this study, we measured airborne concentrations of small ions, particles and net particle charge at 32 different outdoor sites in and around a major city in Australia and identified the main ion sources. Sites were classified into seven groups as follows: park, woodland, city centre, residential, freeway, power lines and power substation. Generally, parks were situated away from ion sources and represented the urban background value of about 270 ions cm^{-3}. Median concentrations at all other groups were significantly higher than in the parks. We show that motor vehicles and power transmission systems are two major ion sources in urban areas. Power lines and substations constituted strong unipolar sources, while motor vehicle exhaust constituted strong bipolar sources. The small ion concentration in urban residential areas was about 960 cm^{-3}. At sites where ion sources were co-located with particle sources, ion concentrations were inhibited due to the ion-particle attachment process. These results improved our understanding on air ion distribution and its interaction with particles in the urban outdoor environment.

Keywords: small ions, aerosol, charged particle, urban environment.

1. Introduction

Atmospheric ions are formed mainly by ionization of air molecules by cosmic rays from space and alpha radiation from natural radioactive materials such as Rn-222 emanating from the ground and its airborne progeny. These ions are soon attracted to water molecules in the air to form singly-charged molecular clusters smaller than about 1 nm in size, known as ‘small ions’ (Iribarne et al, 1980). Once produced, small ions attach to aerosols in the air, producing charged particles in the form of intermediate and large ions in the size range between 2 nm and 1 μm in diameter. Under natural, stable conditions, atmospheric ions are present in concentrations of about 300-400 cm^{-3} but this may increase to a few thousand 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), respectively.

Increased small ion concentrations have been found in forest regions in conjunction with nucleation events that occur during the daytime due to biogenic volatile organic compound precursors such as pinic acid. Vana (2006) found a high percentage of negatively charged particles in the size range 2.6 nm to 5 nm during a nucleation burst at a boreal forest station in Finland. Horrak et al. (2007) investigated small ion concentration and naturally charged nanometre-sized aerosol in a boreal forest at the Hyytiälä SMEAR station in Finland and showed that variations in small ion concentration could be explained by changes in ion loss due to attachment to aerosols. Tammet et al. (2006) measured ionization rates in a coniferous forest, and found values of 5.6 cm^{-3} s^{-1} at 2 m and 3.9 cm^{-3} s^{-1} at 14 m above the tree line with most of the small ions attached to aerosol particles. The origin of these ions in forest environments is uncertain (Suni et al, 2007), and has been attributed to vegetation (Wang et al, 2006) or radon efflux from the ground (Hirsikko et al., 2007), or both.

High voltage components in the power transmission network are a reported source of corona ions. The presence of elevated small ion concentration in the air downwind of power lines has been directly measured with ion monitors (Carter et al., 1988; Jayaratne et al, 2008) and indirectly estimated by measuring the static dc electric fields at the ground (Fews et al, 1999, 2002). Carter (1988) measured air ion concentrations near a 500 kV dc test line and found small ion concentraion of up to 1.5 x 10^5 cm^{-3} and particle charge concentrations of a few tens of thousands cm^{-3}. Similarly, Suda and Sunaga (1990) measured large ion concentrations near a 750 kV dc test line and found concentrations as high as 10^4 ions cm^{-3} at a distance of 200 m downwind of the line. Grabarczyk et al. (2004) measured ion concentrations near high voltage ac lines using a Gerdien-type intermediate/large ion counter. They reported concentrations of the order of 10^3 cm^{-3} near two 110 and 220 kV lines and of the order of 10^4 cm^{-3} near a 400 kV line. Jayaratne et al (2008) measured net small ion concentrations under power lines at 41 sites and reported that the absolute small ion concentrations at approximately 76% of the sites exceeded the absolute mean urban outdoor value.

Combustion sources, hot surfaces and flames are all reported sources of ions (Maricq, 2006; Fialkov, 1997; Peineke and Schmidt-Ott, 2008). Therefore, it is not surprising that motor vehicle exhausts produce significant quantities of small ions and charged particles (Yu et al, 2004; Jung and Kittelson, 2005; Maricq, 2006) These studies on diesel and petrol vehicles showed that ions of both signs were emitted at roughly equal rates. Approximately 60-80% of the emitted soot particles were electrically charged, with near equal numbers of positive and negative charges. Israelsson and Lelwala (1999) measured space charge concentrations as a function of horizontal distance from a highway used by gasoline engine vehicles. They found maximum concentrations of 625 ions cm^{-3} at the roadside, decreasing exponentially to 125 cm^{-3} at a downwind distance of 1 km from the highway. Hirsikko et al (2007) measured small ion concentration at an urban location about 100 m away from a major road, and reported that median positive and negative small ion concentrations during weekdays were 590 and 630 cm^{-3} respectively, and 632 and 696 cm^{-3} respectively over the weekends. These values, devrived by Hirsikko et al (2007), may be compared with the positive and negative small ion concentrations of 248 and 208 cm^{-3} and 280 and 231 cm^{-3} , respectively, found at rural outdoor locations by Fews et al (2005) and Horrak et al (1998). Small ion concentrations in polluted environments are generally lower than in clean environments due to attachment to particles. For example, Retalis et al (2009) analysed 17 years of data obtained in Athens, Greece, and reported mean concentrations of 189 and 151 cm^{-3} for positive and negative small ions respectively. Horrack et al (2000) monitored air ions at a sparsely populated rural location in Estonia and reported that both the mean mobility and the total small ion concentration showed a marked diurnal variation of a single wave shape with a maximum in the nighttime and a minimum in the afternoon. The nocturnal high concentrations were attributed to the accumulation of radon and thoron near the ground under calm atmospheric conditions.

It is clear that small ions are affected by a range of conditions and vary between different locations in the urban environment. However, there is very little information on their concentrations in different types of urban environments, how they compare across these environments and their dominant sources. This study was conducted in a large urban area with the aim of addressing these gaps in our knowledge. These specific aims were: (1) to investigate the differences in ion concentrations in different types of outdoor environments, (2) to identify specific sources that give rise to relatively high concentrations of ions and (3) to study how aerosol particle concentrations affect the small ion concentration.

2. Methods

2.1 Measurement Sites

Positive/negative and total small ions concentrations (hereafter denoted n_+/n_- and n_t), particle number and charge concentrations were measured in real time at 32 different outdoor sites in and around a major city in Australia over a period of two years. The sites were classified into groups as shown in Table 1 together with the total number of sites in each group.

Monitoring was carried out for up to 12 h at each site. The main aim of this study was to compare air ion concentrations at several diverse location types and to identify the main sources of these ions in the urban environment. Atmospheric ion concentrations show a marked diurnal variation with higher values and higher standard deviations during the night than the daytime (Horrack et al, 2000). In order to avoid these variations, all measurements reported in this paper were restricted to daylight hours. Sampling was carried out at a height of about 1 m above the ground under fair weather conditions, with the air temperature between 20ºC to 30ºC. A brief description of the various sites and location groups follows.

Parks: These four sites were located outside the city centre and consisted of open grassy areas away from trees. They were at least 200 m away from the nearest vehicular traffic and residential areas with no power lines in the vicinity.

Woodlands: These sites were generally wooded environments within suburban areas. The instruments were placed in small clearings surrounded by eucalyptus and stringybark trees, at least 500 m away from the nearest human activities.

City Centre: These five sites were all within the central business district, close to busy roads, intersections and surrounded by buildings.

Residential: These three sites were situated within residential areas. One site was situated close to the city centre and the other three sites in the suburbs. All sites were surrounded by residential dwellings.

Freeways: These seven sites were all located 2-5 m away from the edge of multi-lane freeways carrying 100-150 vehicles min^{-1} of which 10% to 25% consisted of heavy duty diesel vehicles. The measurements reported here, were carried out on the downwind sides of the roads.

Power lines: These five sites were all near overhead high voltage ac power lines. These lines were double circuit, strung on steel lattice towers, running along creek valleys, open parkland and cleared pathways through forest and bush land. The energized voltage was in the two ranges 220 to 330 kV (transmission voltage) and 110 to 132 kV (sub-transmission voltage). Line heights varied between 10 and 25 m. All measurements were carried out in the downwind directions, at a distance of 20-30 m from the power lines.

Power substations: These measurements were carried out immediately outside the perimeter fences of high voltage substations, about 30 m away from the high voltage transformers in the downwind direction. The environments near three such substations were monitored.

2.2 Instrumentation

Small ion concentrations were measured by two Alphalab air ion counters that were factory-calibrated just prior to the measurement campaign. This instrument has a dynamic range of 10 – 10^6 ions cm^{-3} with a minimum detectable charge concentration of 10 ions cm^{-3} and a response time of 2 s at a sampling rate of 0.8 L s^{-1}. 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. The instrument has the capability of monitoring negative and positive ions separately, but not simultaneously. Hence, two instruments were used to measure both n_+ and n_- separately at each measurement point.

A TSI 3068 aerosol electrometer was used to measure the net particle charge concentration. This instrument draws ambient air through a particle filter and determines the total net charge present on aerosol particles in the size range 2 nm to 5 μm. Particle charge concentration is estimated under the assumption that each charged particle carries a unit charge. The nominal response time is about 1 s. 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 x 10^4 cm^{-3}. The time response of the instrument is less than 3s. Particle number size distributions were measured at some of the sites with a TSI 3936 scanning mobility particle sizer (SMPS), using a TSI electrostatic classifier and CPC. Particles in the size range from 4 to 160 nm were measured in 100 size bins.

In this study, all data were logged at 1 s intervals and stored on a laptop computer.

2.3 Data analysis

Median values of each of the four parameters - positive and negative small ions, particle number and charge concentrations were calculated for each location group, together with their respective 1st and 3rd quartile (Q1 and Q3) values. The relationship between n_+ and n_- were tested using a simple linear regression analysis. The differences between the regression coefficients of the groups were compared. The differences between the group means were tested using a Students t-test.

3. Results and Discussion

Fig 1 shows typical example time series of n_+ and n_- at four different sites. In addition to the type of source, measured air ion concentrations at a point is expected to depend on a wide range of conditions such as the distance to the source, wind conditions and humidity. Although, it was not the aim of this study to acquire long-term data to predict complete temporal variations at each type of site or to investigate the effects of all parameters that control the concentrations, our results illustrated some important features and showed some consistent differences between the different types of sites. The lowest concentrations were found at the parks, with average n_+ and n_- values of 50 and219 cm^{-3}, respectively. This yielded a net n_- of 169 cm^{-3} and an n_t of 269 cm^{-3}. The maximum n_t were found at the power line and substation sites. We measured ions at five power line sites. Only one of these sites showed the small ion concentration and particle charge concentration that were significantly higher than background, indicating that the line at this site contained a corona ion source. At the other four sites, the concentrations were close to the parks values, suggesting that negligible ion emissions were present. Considering the clear difference in small ion concentration measured at these sites, we classified them into two groups: power line sites with corona (PC) and power line sites with negligible or no-corona (PNC). At site PC, the corona was clearly of one sign (positive) as shown in Fig 1(b). Jayaratne et al (2008) investigated small ion concentrations at 41 different power line sites and showed that less than 1 in 4 sites exhibited concentrations that were more than double the background values.

Table 2 gives a site summary of n_+ and n_- as measured by the air ion counters, the net particle charge concentration as measured by the aerosol electrometer and the aerosol particle number concentration as measured by the CPC. For each of the sites, we determined the median values of each of the four parameters. Median values were considered more appropriate than mean values because they imparted less importance to the presence of concentration spikes that were recorded, especially when sampling close to ion sources such as power lines and freeways (Fig 1). Note that the net particle charge concentration is the difference between the number concentrations of positively and negatively charged particle concentrations and is not representative of the total number of charged particles. The values shown in Table 2 are median values for the 1 s data points at all the sites in each group. Also shown are the respective Q1 and Q3 values.

In discussing the results shown in this table, we look at each type of site in turn:

Parks: Sites in this group most closely approximated what may be termed the 'urban background'. This is reflected by the relatively low median values of particle number concentration (3890 cm^{-3}), n_+ (50 cm^{-3}) and n_- (219 cm^{-3}) observed. The variance in the time series of the parameters was also lower than in the other groups, indicating the absence of nearby ion and particle sources.

Woodlands: Although sites in this group were more distant from anthropogenic sources than in all other groups, a relatively high particle number concentration and small ion concentration were recorded. Compared to the urban background (in the parks), n_- (424 cm^{-3}) was not significantly different but n_+ (301 cm^{-3}) was significantly higher. The high particle number concentration is indicative of nanoparticles formed from volatile organic and biogenic precursors in the atmosphere during the daytime as has been reported by many workers (Mäkelä et al, 1997; Kulmala et al, 1998; Suni et al, 2007). Fig 2 shows a particle number size distribution obtained at a site surrounded by eucalyptus trees during one of the monitoring sessions using the SMPS close to mid-day. Note the normal background accumulation mode at about 50 nm together with the nucleation mode at about 18 nm that was observed only during this time of the day, confirming that the high particle number concentration was due to enhanced nucleation. At this stage, we have no reason to link the high n_t and the particle number concentration, although there is some evidence for such an association in the literature (Laakso et al, 2004; Suni et al, 2007).

City Centre: All five sites in this group showed above background small ion concentration of both signs with a preponderance of negative ions. This was also reflected by the net negative charge carried on particles. The n_+ value, although lower than n_-, was significantly higher than background.

Residential: Residential areas generally include ion and particle sources related to human activities such as motor vehicles, cooking and electrical appliances like transformers and air conditioners and it is expected that ion and particle number concentrations in these areas are mostly determined by these processes. Sites in this group showed n_+ and n_-, and particle concentrations significantly higher than that of the urban background. The average concentrations were: n_+: 601 cm^{-3}, 12 times higher than background; n_-: 361 cm^{-3}, 1.8 times higher than background; and particle number 1.78 x 10^4 cm^{-3}, 4.5 times higher than background. The Student's t-tests showed that each of these parameters was significantly higher than the corresponding background values at the confidence level of 99%.

Freeways: All seven sites near freeways showed ions of both signs with concentrations well above background values. The observed median n_+ and n_- were

481 cm^{-3} and 589 cm^{-3}, respectively. The n_t (1070 cm^{-3}) was three times higher than background. The time series showed sharp n_+ and n_- peaks, up to four times of the average values (see Fig 1a and Fig 3) and observations showed that these excursions generally coincided with the passage of heavy duty trucks. It is interesting to note that n_+ and n_- spikes often coincided with each other in time, suggesting that they were from the same source. This is consistent with the experimental studies that have shown that vehicles emit ions of both signs at roughly equal rates (Yu et al, 2004; Jung and Kittelson, 2005; Maricq, 2006). This is further confirmed by the low net charged particle concentrations recorded by the aerosol electrometer. As explained earlier, the net particle charge concentration is the difference between the number concentrations of positively and negatively charged particle concentrations and is not representative of the total number of charged particles. Thus, for example, although the total charged particle concentration near a freeway is expected to be large, our measured median value is only -50 cm^{-3} which is relatively low when compared to the other groups. From our data, we can only infer that the number of negatively charged particles exceeded the positively charged particles by 50 cm^{-3}. Fig 3 shows examples of 15 min time series of n_+ and n_- obtained at four of the freeway sites.

Power lines: Fig 4 shows typical 10-min time series of n_+ and n_- observed at the four power line sites. Sites 1, 2 and 3 refer to power line sites with no corona, PNC, while PC is the site with the strong positive corona source. The n_+ and n_- values at the PNC sites were similar to the woodland sites and this was not surprising as these three sites were not very far from wooded areas. At site PC, n_+ was well above background with median values nearly 70 times higher than in the parks. The positive sign of ions is consistent with observations under other ac power lines, such as Fews et al (2002).

The time series showed large fluctuations with spikes of magnitude 400 times higher than the urban background. These spikes very often coincided with wind gusts and their origin is discussed in Jayaratne et al (2009). The n_- value was only marginally higher than background. Consequently, the net charged particle concentration was also positive and of magnitude 1000-2000 cm^{-3}. The n_- value at site PC was very similar to that at the PNC sites and, so, has not been shown in Fig 4. Note the stark difference when a corona source is present.

Substations: All three substation sites showed small ion concentrations well above background values with a predominantly negative sign. This was in contrast to the power line PC site which was clearly positive. A possible explanation for this difference is that, unlike a power line, the substations included many high voltage electrical devices such as transformers and capacitors that may exhibit different corona initiation processes to power lines.

Total Ion Concentration and Comparison between Groups

Fig 5 is a graphical display that enables a comparison of n_t of the various groups. Assuming that parks represented the urban background, we see that woodlands, cities, residential, freeways, power lines PNC, power line PC and substations showed median n_t that were 280%, 160%, 350%, 400%, 190%, 1360% and 400% higher. The difference between each of these groups and the background was tested using a Students t-test and all of them were found to be statistically significant at a confidence level exceeding 99%. As described in the previous section, the higher n_t in the woodland, power line and substation groups have possible explanations. However, the observation of the higher n_t of the residential group over the city centre group requires an explanation. We noted that the particle number concentration in the city centre group (3.91 x 10^4 cm^{-3}) was significantly higher than in the residential group (1.78 x 10^4 cm^{-3}). This may be attributed to a higher density of traffic in the city centre in comparison to the residential area. In the presence of large concentrations of particles in the air, small ions are likely to be attached, forming charged particles that are not detected by the air ion counters. This observation is also consistent with Retalis et al (2009) and Hirsikko et al (2007) in other polluted urban locations who found that n_t decreased when particle charge concentrations increased during the rush hour. The n_t values at the substation and power line PC sites were respectively 8 and 13 times higher than background. The results proved the existence of strong ion sources in these two groups. Power line PNC sites were not significantly different to the background.

Correlation between n_+ and n_-

Fig 6 shows n_- plotted against the simultaneous value of n_+ at four different sites - urban background (park) group, freeway group, power line PC group and substation group. Compared to the background site (R^2=0.48), the freeway site showed a high correlation coefficient (R^2=0.68), suggesting that both sign of ions were emitted from the same source. A regression analysis showed a strong relationship between the two parameters ($P<0.01$). Nevertheless, the power line PC and substation site showed the least significant correlations between the positive and negative ions, with R^2 values of 0.0039 and 0.0089 respectively. These results indicate the presence of only one strong unipolar ion source at each of these two sites.

It is clear that the sign and magnitude of the small ion concentrations in different environments are determined mainly by the type and intensity of both ion and particle sources that are present. Once produced, small ions are depleted by recombination and by attachment. While some sources of ions such as power lines are unipolar, others such as motor vehicles are bipolar. Thus, near busy roads, small ion concentrations are severely reduced due to both recombination and ion-particle attachment. On the other hand, ions associated with corona emission from power lines are less likely to neutralise quickly because their oppositely charged partners are not available. The effect of ions from power lines has been detected at distances of over 500 m (Fews et al, 1999).

In order to understand and assess these effects better, in Fig 7, we present the particle number concentration and n_t for the different sites in the same figure. The substation and power line PC produced the highest n_t, while the highest particle number concentrations were observed near freeways and in the city centre, which is to be expected owing to the dominant impact of motor vehicle traffic in these areas. Compared to the park (urban background), both the residential and woodlands groups showed higher n_t and particle concentrations as discussed previously. It is interesting to look at the ratio of n_t to particle number concentration, together with the regression coefficient R^2 of n_+ versus n_- relationships for the various groups. An intense ion source in the absence of a particle source, such as at power lines and substations, have a large ion/particle ratio while, in the presence of a particle source, irrespective of an ion source, such as near a freeway and in the city centre, this ratio is small. A large R^2 value implies that there is a bipolar ion source, such as near a freeway.

The results in Fig 7, together with the information on the ion/particle ratios and the regression coefficients R^2 of the n_+ versus n_- relationships for the various groups are summarised in Table 3. Based on this summary, we classified the eight location groups into three categories. The first two categories were clearly different to each other and to the rest. To the first category we assigned the freeway and city centre groups as they both showed high particle number concentrations (> $3x10^4$ cm^{-3}) and bipolar ion sources with relatively high R^2 values (>0.25). The power line PC and substation groups were assigned to the second category as they both showed n_t that were significantly higher than all other groups (>$2x10^3$ cm^{-3}) with a high ion/particle ratio (>0.2) and relatively low R^2 values (<0.05) indicating the presence of a strong unipolar ion source with no significant particle source. The rest of the groups, with relatively low values of all parameters, we assigned to the third category.

To summarize our findings, sample 15-min time series of n_t at eight different sites with the readings averaged over 1 min intervals are shown in Fig 8. The figure illustrates the relative n_t to be expected. The power line graphs for PC (power lines with corona) and PNC (power lines with no corona) are shown separately. The three upper traces are consistent relative to each other and clearly stand out from the other five groups. While, there was always some overlap in n_t between these five groups, in general the parks showed the lowest n_t with the other three groups in-between the parks and the freeway values. The mean n_t ranged from 270 cm^{-3} at parks to 3650 cm^{-3} at power line PC.

4. Conclusions

Both n_+ and n_-, net particle charge and fine particle number concentrations were measured at several urban sites. The sign of net particle charge generally followed the sign of the dominant small ions. The net particle charge was high when ions of only one sign were produced (power line PC, substations), and low when ions of both signs were produced (freeways). The relatively high n_t found near freeways suggested that the corresponding total particle charge was also relatively high.

The highest n_t was found at the power line PC site, followed by substations, freeways and residential. Both signs of charge were observed near freeways and in the city while predominantly one sign was observed under corona emitting power lines and substations. Positive and negative ions were strongly correlated when they both originated from the same source (motor vehicles). Woodlands exhibited a special pattern that may be attributed to a nucleation process from biogenic precursors from vegetation. This generally occurs around mid-day when the number of nanoparticles increases sharply together with n_t in the atmosphere, although the connection between these two is not very clear at this time.

In summary, small ion concentration varies among different locations in the urban outdoor environment. Motor vehicles and power transmission systems are believed to be the two major ion sources in the urban environment. Fewer ions were observed at sites where ion sources coexisted with particle sources due to ion-particle attachment effects. These results improved our understanding of the concentration and distribution of small ions and their interaction with particles in the urban outdoor environment.

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References

Carter, P.J., Johnson, G.B., 1988. Space charge measurements downwind from a monopolar 500 kV HVDC test line. IEEE Transactions on Power Delivery 3(4): 2056–2063.

Fews, A.P., Henshaw, D.L., Wilding, R.J., Keitch, P.A., 1999. Corona ions from power lines and increased exposure to pollutant aerosols. International Journal of Radiation Biology. 75 (12): 1523–1531.

Fews, A.P., Wilding, R.J., Keitch, P.A., Holden, N.K., Henshaw, D.L., 2002. Modification of atmospheric DC fields by space charge from high-voltage power lines. Atmospheric Research 63: 271–289.

FewsA.P., Holden N.K., Keitch P.A., Henshaw D.L., 2005. A novel high-resolution small ion spectrometer to study ion nucleation of aerosols in ambient indoor and outdoor air. Atmospheric Research. 76: 29–48.

Fialkov A.B., 1997. Investigations on ions in flames. Progress in Energy and Combustion Science. 23(5): 399-528.

Grabarczyk, Z.J., Berlinski, J., 2004. Charging of atmosphere aerosols by AC HV power lines. Journal of Aerosol Science. 35 (Suppl. 1): 251–262.

Hirsikko A.,Juuti T.Y., Nieminen T., Vartiainen E., Laakso L., Hussein T., Kulmala M., 2007. Indoor and outdoor air ions and aerosol particles in the urban atmosphere of Helsinki: characteristcs, sources and formation. Boreal Environment Research. 12: 295-310.

Hõrrak U., Mirme A., Salm J., Tamm E., Tammet H., 1998. Air ion measurements as a source of information about atmospheric aerosols. Atmospheric Research. 46: 233–242.

Hõrrak U., Salm J., Tammet H., 2000. Statistical characterization of air ion mobility spectra at Tahkuse Observatory: Classification of air ions. Journal of Geophysical Research. 105 (D7): 9291-9302.

Hõrrak U., Aalto P.P., Salm J., Komsaare K., Tammet H., Mäkelä J. M., Laakso L., and Kulmala M., 2007. Characterization of positive air ions in boreal forest air at the Hyytiälä SMEAR station. Atmospheric Chemistry and Physics Discussions. 7: 9465-9517.

Iribarne, J.V., Cho, H.R., 1980. Atmospheric Physics. Reidel, Holland.

Israelsson S., Lelwala R., 1999. Space charge density measurements downwind from a traffic route. Atmospheric Research. 51: 301–307.

Jayaratne E.R., J-Fatokun F.O., Morawska L., 2008. Air ion concentrations under overhead high-voltage transmission lines. Atmospheric Environment. 42: 1846–1856.

Jung H.J. Kittelson D.B., 2005. Measurement of electrical charge on diesel particles. Aerosol Science and Technology. 39: 1129-1135.

Kulmala M., Toivonen A., Mäkelä J.M., Laaksonen A., 1998. Analysis of the growth of nucleation mode particles observed in Boreal forest. Tellus. 50B: 449-462.

Laakao L., Hirsikko A., Grönholm T., Kulmala M., Luts A., Parts T. E., 2007. Waterfalls as sources of small charged aerosol particles. Atmospheric Chhemistry and Physics. 7: 2271-2275.

Mäkelä J.M., Kulmala M., Aalto P., Toivonen A., Pohja T., 1997. Continuous measurements of submicron particle size distribution at boreal forest station in southen Finland. Journal of Aerosol Science. 28(suppl.1): S403-S404.

Maricq M.M., 2006. On the electrical charge of motor vehicle exhaust particles. Aerosol Science 37: 858–874.

Peineke C., Schmidt-Ott A., 2008. Explanation of charged nanoparticle production from hot surfaces. Aerosol Science. 39: 244-252

Retalis A., Nastos P., Retalis D., 2009. Study of small ions concentration in the air above Athens, Greece. Atmospheric Research. 91: 219–228.

Suda, T., Sunaga, Y., 1990. An experimental study of large ion density under the Shiobara HVDC test line. IEEE Transactions on Power Delivery 5: 1426–1435.

Suni T., Kulmala M., Hirsikko A., Bergman T., Laakso L., Aalto P.P., Leuning R., Hõrrak U., Mirme S., Mirme A., Twining J., Tadros C., Cleugh H., Zegelin S., Hughes D., Gorsel E. van, Kitchen M., Vana M., 2007. Formation and characteristics of ions and charged aerosol particles in a native Ausralian Eucalypt forest. Atmospheric Chemistry and Physics Disscussions. 7: 10343–10369

Tammet, H., Hõrrak, U., Laakso, L., Kulmala, M., 2006. Factors of air ion balance in a coniferous forest according to measurements in Hyytiala, Finland. Atomspheric Chemistry and Physics. 6: 3377-3390.

Vana M., Tamm E., Hõrrak U., Mirme A., Tammet H., Laakso L., Aalto P.P., Kulmala M.. 2006. Charging state of atmospheric nanoparticles during the nucleation burst events. Atmospheric Environment. 82: 536-546.

Wang J.B., Ren J., Ruan L., Wei S.L., Wu Y.J., Yu Z.L., 2006. Study on the contribution of winter-season crops to negative air ion. Journal of Anhui Agriculture science. 34(6): 1131-1133.

Yu F.Q., Lannib T., Frank B. P., 2004. Measurements of ion concentration in gasoline and diesel engine exhaust. Atmospheric Environment. 38: 1417–1423.

Table 1: List of site type groups.

Group	**No of sites**
Parks	4
Woodlands	4
City Centre	5
Residential	3
Freeways	7
Power lines	5
Power substations	3

Table 2: Median concentrations of the measured parameters in each group of sites, together with the respective first quartile (Q1) and third quartile (Q3) values. All values are in cm^{-3}. A negative value in the net charged particle concentration reflects a net negative charge.

Group	Parameter	Median	Q1	Q3
PARKS	n_+	50	36	70
	n_-	-219	-407	-212
	Net Particle Charge	-72	-92	-55
	Particle Number	3,890	2,184	6,080
WOODLANDS	n_+	301	238	336
	n_-	-424	-483	-337
	Net Particle Charge	-69	-102	-49
	Particle Number	11,100	10,800	11,500
CITY CENTRE	n_+	99	68	128
	n_-	-251	-327	-158
	Net Particle Charge	-13	-50	13
	Particle Number	39,100	35,100	44,525
RESIDENTIAL	n_+	601	556	656
	n_-	-361	-406	-304
	Net Particle Charge	-391	-395	-233
	Particle Number	17,800	17,100	18,500
FREEWAYS	n_+	481	413	564
	n_-	-589	-676	-518
	Net Particle Charge	-50	-150	44
	Particle Number	58,000	49,638	70,363
POWERLINES PNC	n_+	59	41	81
	n_-	-449	-511	-375
	Net Particle Charge	-138	-175	-100
	Particle Number	9,950	8,870	10,856
POWERLINE PC	n_+	3,430	2,267	4,544
	n_-	-229	-452	-179
	Net Particle Charge	1,275	865	1,570
	Particle Number	15,400	12,300	19,300
SUBSTATIONS	n_+	67	82	485
	n_-	-1,016	-2,407	-1,232
	Net Particle Charge	-213	-534	-206
	Particle Number	6,495	6,166	8,000

Table 3: Properties of the location groups classified into three types.

Category	**Groups**	**Particle Number Concentration (cm^{-3})**	n_t **(cm^{-3})**	n_t **/Particle Number Ratio**	**R^2 value for n_+ vs. n_-**
1	Freeways City Centre	$>3x10^4$	$<1x10^3$	<0.1	>0.25
2	Power line C Substations	$<2x10^4$	$>2x10^3$	>0.2	<0.05
3	Parks Woodlands Power lines NC Residential	$<2x10^4$	$<1x10^3$	<0.1	0.05-0.25

Figure Captions

Fig 1: Typical time series of n_+ and n_- measured at 1 s intervals at four different sites.

Fig 2: Particle number size distribution measured in a eucalyptus woodland environment close to mid-day, showing the characteristic nucleation mode that is attributed to biogenic precursors.

Fig 3: 15 min time series of n_+ and n_- at four freeway sites.

Fig 4: 10 min time series of n_+ and n_- at three power line sites with no corona source (PNC) and one site with a corona source (PC).

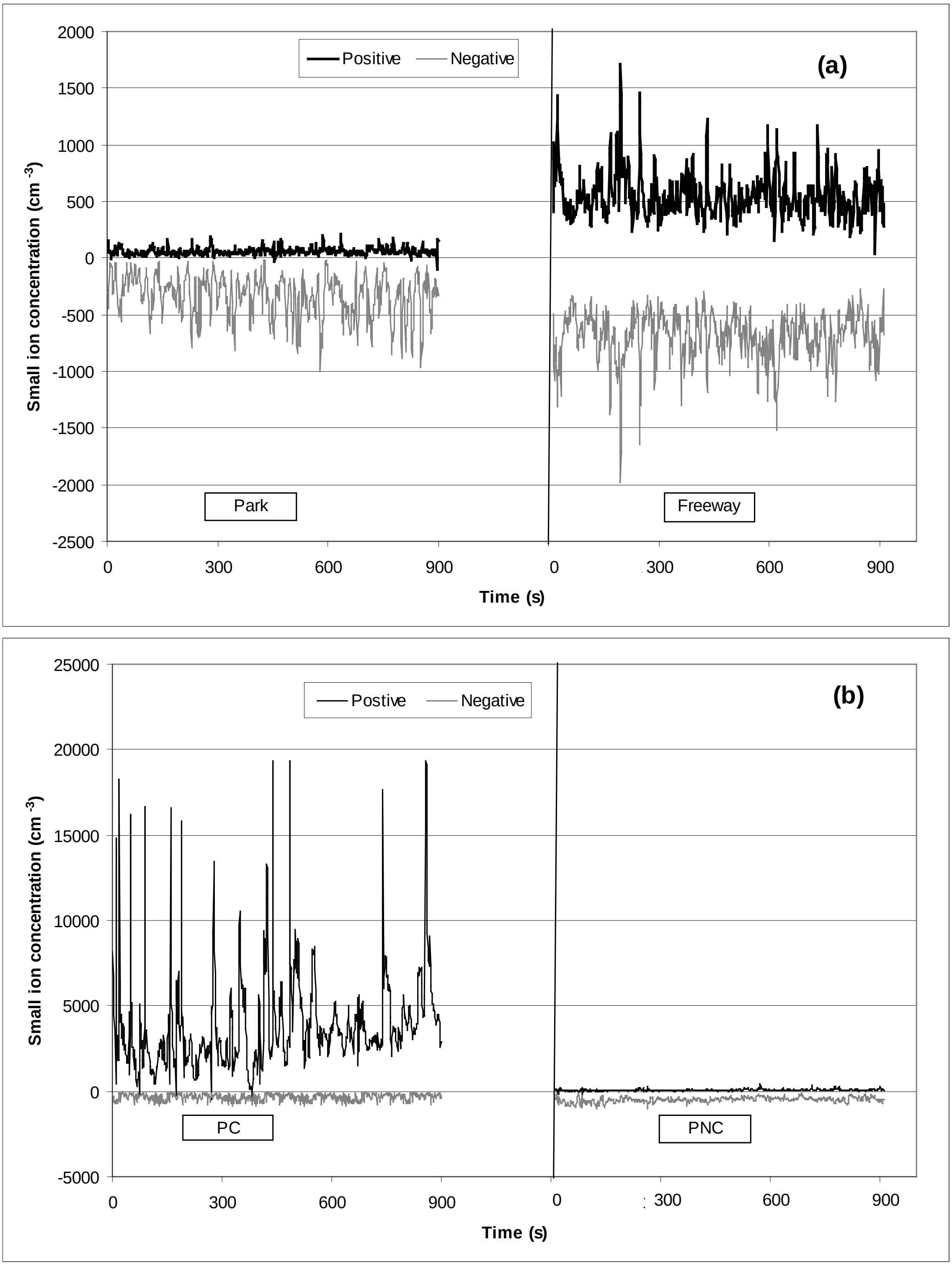
Fig 5: The n_t values (sum of n_+ and n_-) of various groups.

Fig 6: The n_+ and n_- values at four different sites (Note that the X and Y-axes have different scales).

Fig 7: The n_t value and particle number concentration for the different groups.

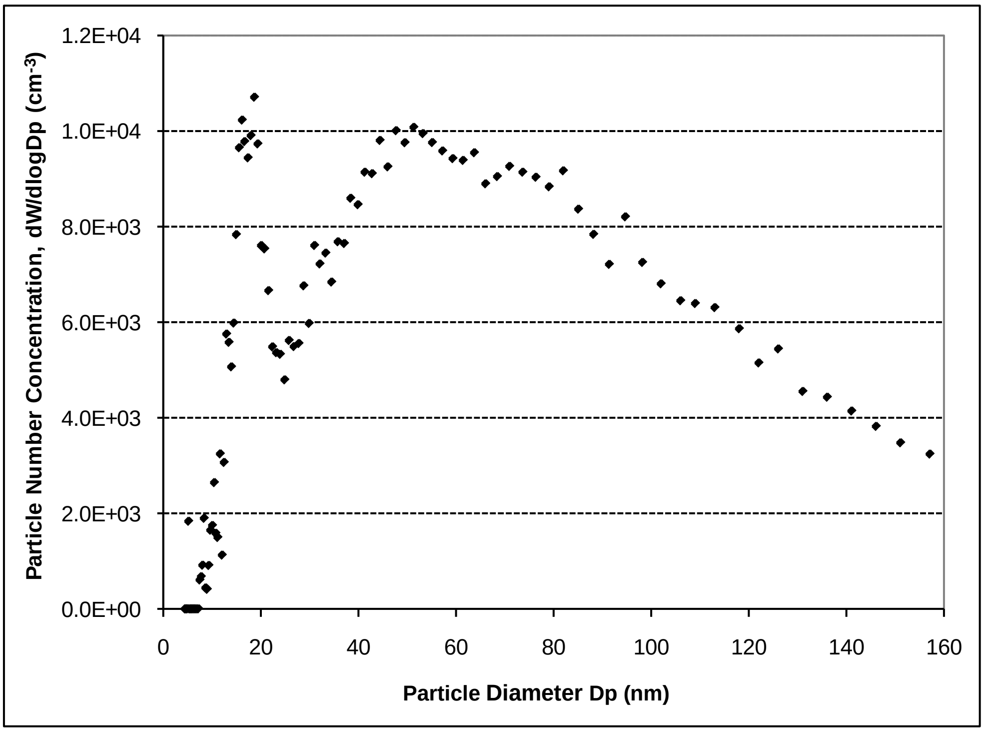
Fig 8: Time series of n_t at eight different sites, shown as 1 min averages.

Fig 1



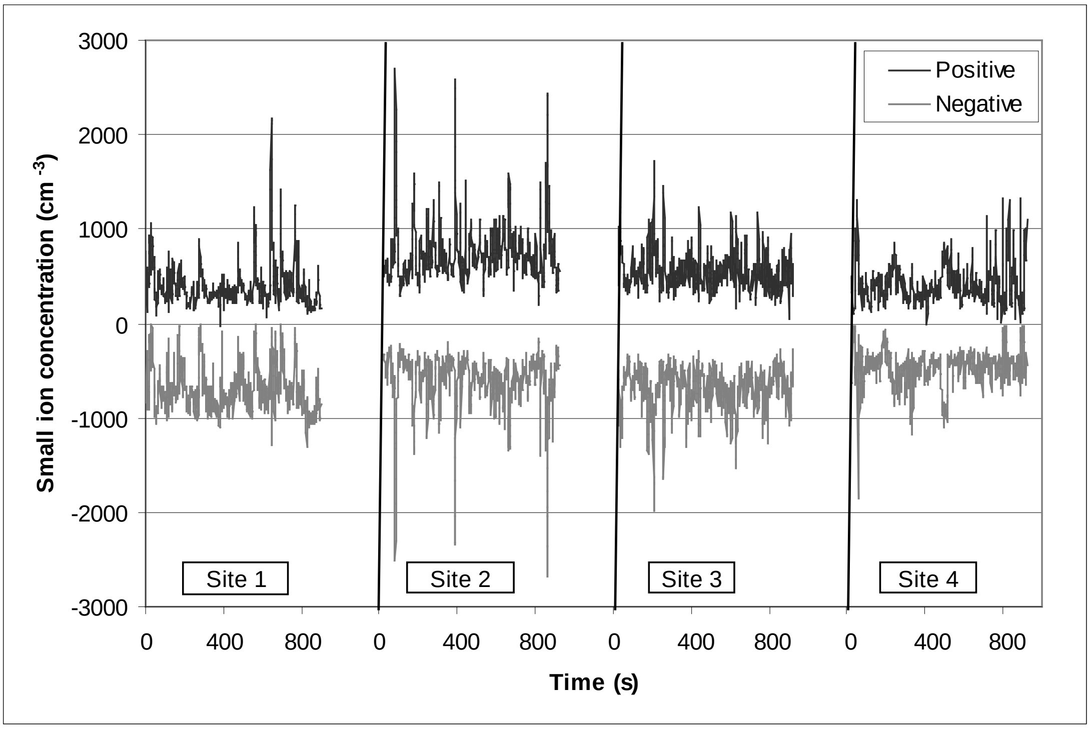
(a)
Positive
Negative
Park
Freeway
Small ion concentration (cm -3)
Time (s)
2000
1500
1000
500
0
-500
-1000
-1500
-2000
-2500
0
300
600
900
(b)
Postive
Negative
PC
PNC
25000
20000
15000
10000
5000
0
-5000

Fig 2



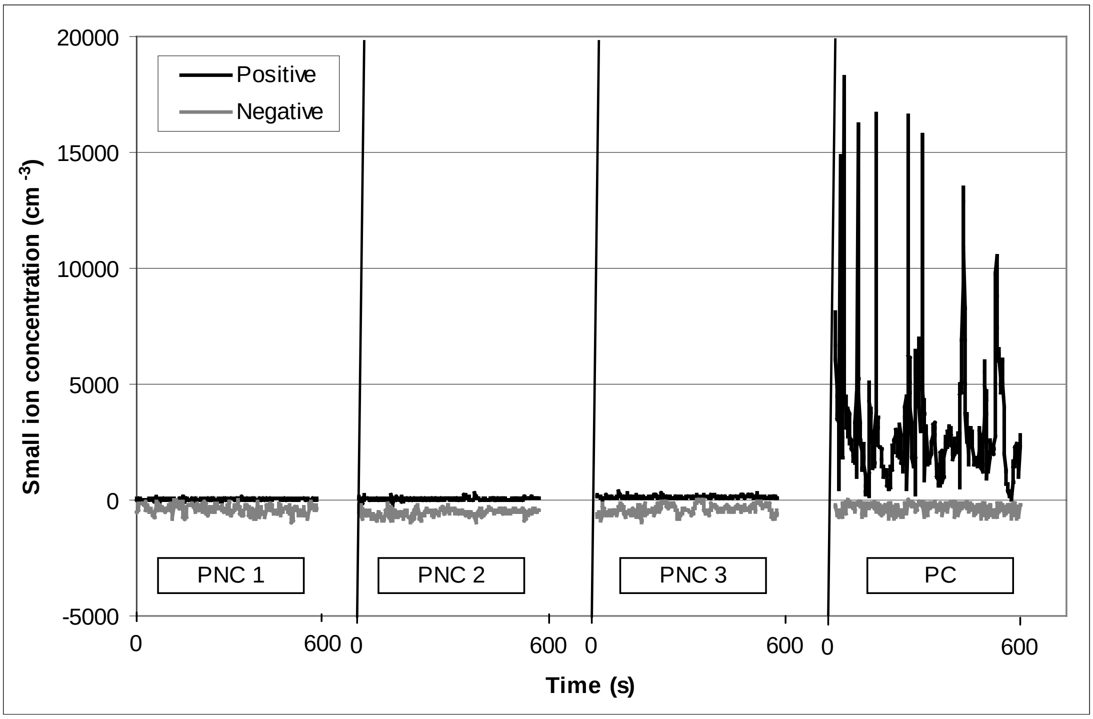
Particle Number Concentration, dW/dlogDp (cm-3)
1.2E+04
1.0E+04
8.0E+03
6.0E+03
4.0E+03
2.0E+03
0.0E+00
0
20
40
60
80
100
120
140
160
Particle Diameter Dp (nm)

Fig 3



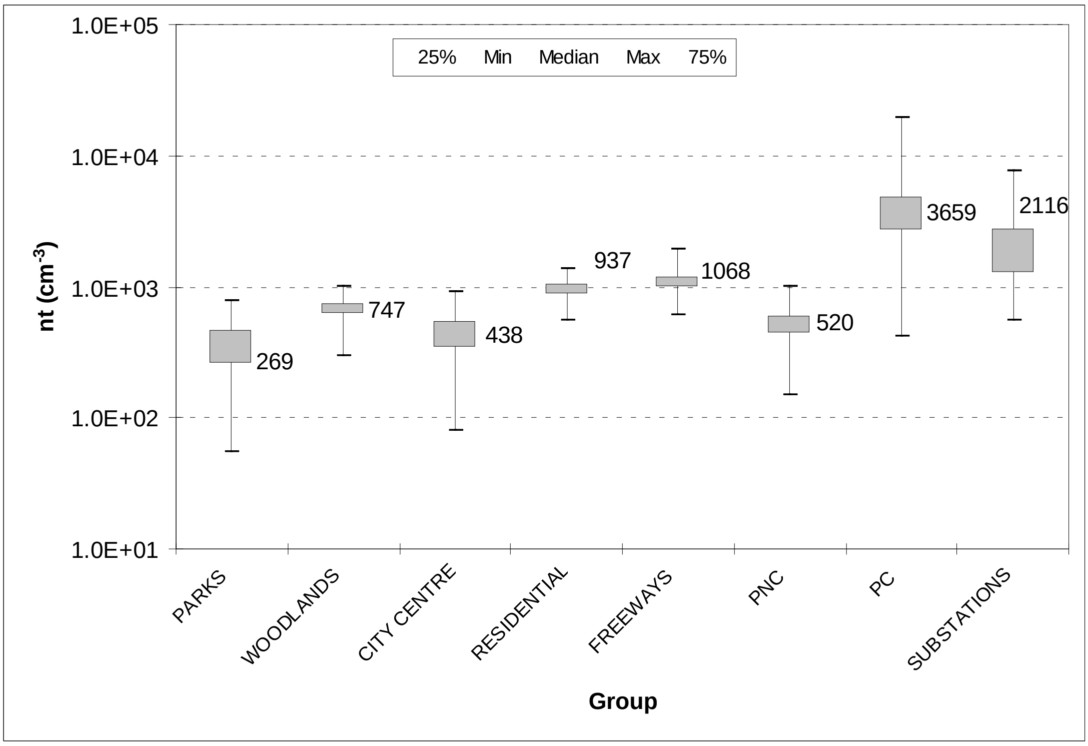
Small ion concentration (cm -3)
3000
2000
1000
0
-1000
-2000
-3000
Positive
Negative
Site 1
Site 2
Site 3
Site 4
0
400
800
Time (s)

Fig 4



Positive
Negative
Small ion concentration (cm -3)
20000
15000
10000
5000
0
-5000
PNC 1
PNC 2
PNC 3
PC
0
600
Time (s)

Fig 5



1.0E+05
1.0E+04
1.0E+03
1.0E+02
1.0E+01
25% Min Median Max 75%
nt (cm-3)
269
747
438
937
1068
520
3659
2116
PARKS
WOODLANDS
CITY CENTRE
RESIDENTIAL
FREEWAYS
PNC
PC
SUBSTATIONS
Group

Fig 6

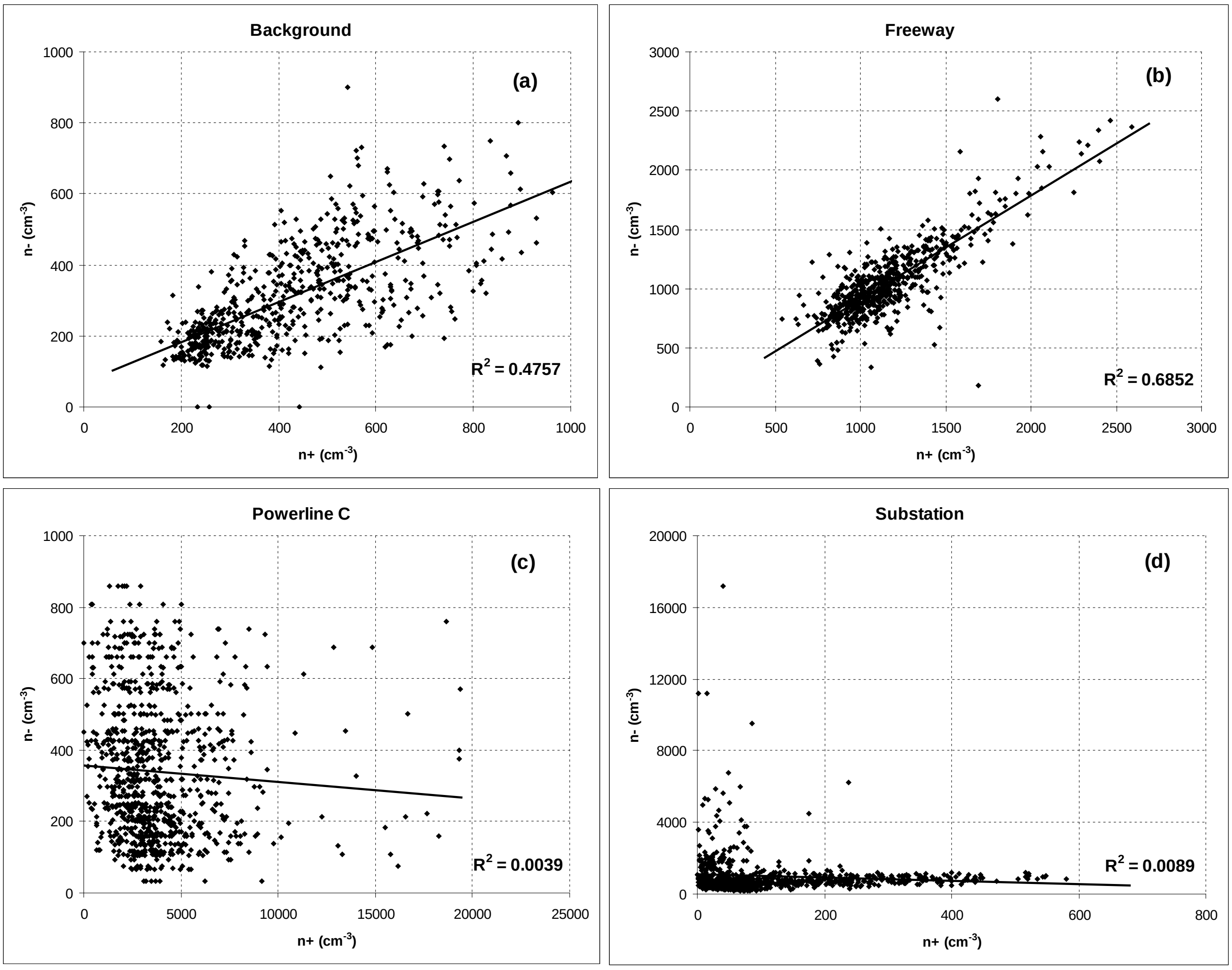
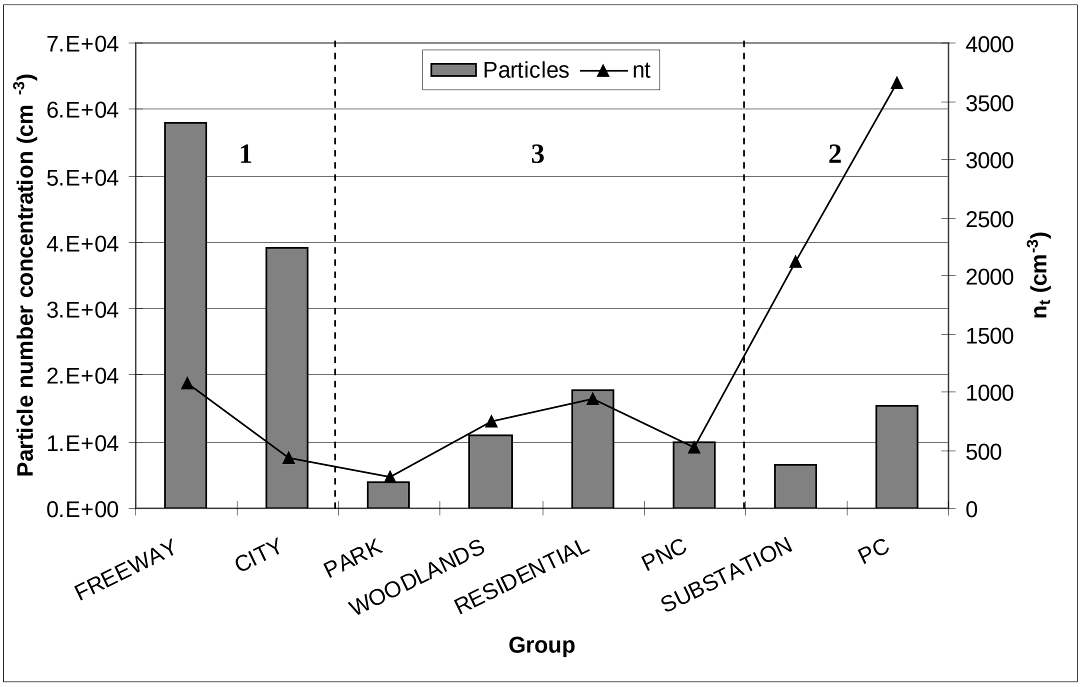
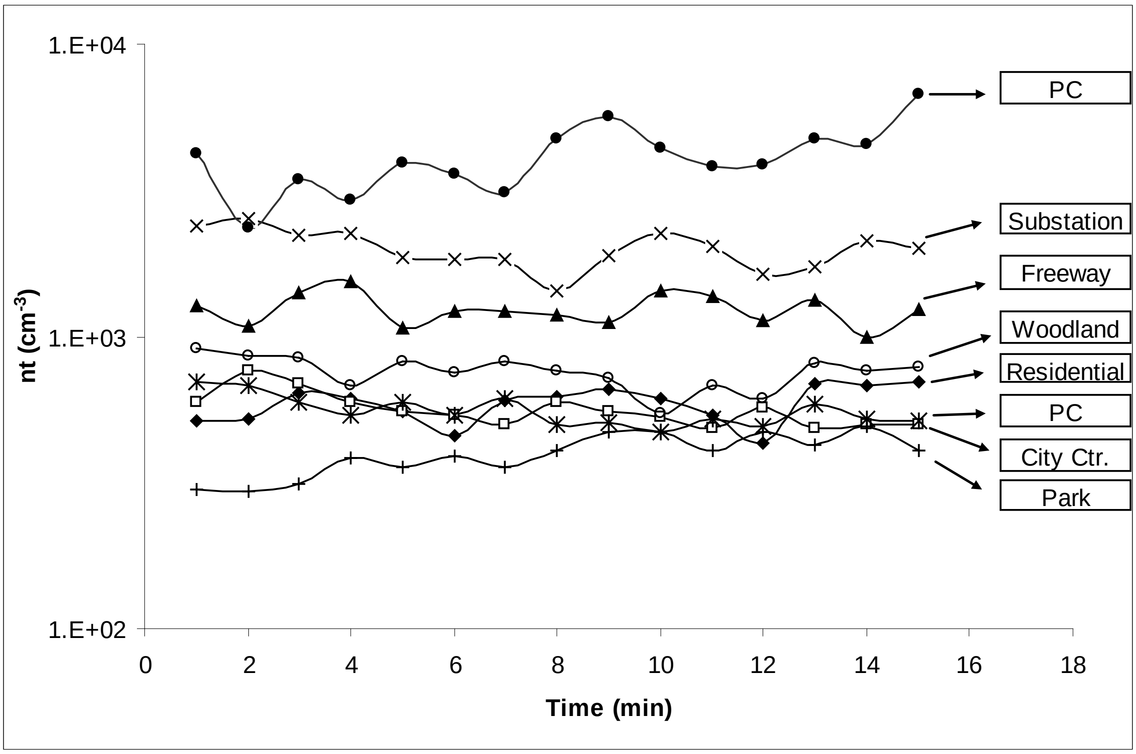

Background
(a)
n- (cm-3)
n+ (cm-3)
R2 = 0.4757
Freeway
(b)
R2 = 0.6852
Powerline C
(c)
R2 = 0.0039
Substation
(d)
R2 = 0.0089

Fig 7



Particles
nt
1
3
2
7.E+04
6.E+04
5.E+04
4.E+04
3.E+04
2.E+04
1.E+04
0.E+00
4000
3500
3000
2500
2000
1500
1000
500
0
Particle number concentration (cm -3)
nt (cm-3)
FREEWAY
CITY
PARK
WOODLANDS
RESIDENTIAL
PNC
SUBSTATION
PC
Group

Fig 8


1.E+04
1.E+03
1.E+02
nt (cm-3)
0
2
4
6
8
10
12
14
16
18
Time (min)
PC
Substation
Freeway
Woodland
Residential
PC
City Ctr.
Park