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Ions in Motor Vehicle Exhaust and Their Dispersion near Busy Roads

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Abstract

Measurements in the exhaust plume of a petrol-driven motor car showed that molecular cluster ions of both signs were present in approximately equal amounts. The emission rate increased sharply with engine speed while the charge symmetry remained unchanged. Measurements at the kerbside of nine motorways and five city roads showed that the mean total cluster ion concentration near city roads (603 cm^{-3}) was about one-half of that near motorways (1211 cm^{-3}) and about twice as high as that in the urban background (269 cm^{-3}). Both positive and negative ion concentrations near a motorway showed a significant linear increase with traffic density (R^2=0.3 at $p<0.05$) and correlated well with each other in real time (R^2=0.87 at $p<0.01$). Heavy duty diesel vehicles comprised the main source of ions near busy roads. Measurements were conducted as a function of downwind distance from two motorways carrying around 120-150 vehicles per minute. Total traffic-related cluster ion concentrations decreased rapidly with distance, falling by one-half from the closest approach of 2m to 5m of the kerb. Measured concentrations decreased to background at about 15m from the kerb when the wind speed was 1.3 m s^{-1}, this distance being greater at higher wind speed. The number and net charge concentrations of aerosol particles were also measured. Unlike particles that were carried downwind to distances of a few hundred metres, cluster ions emitted by motor vehicles were not present at more than a few tens of metres from the road.

Keywords: vehicle emissions, cluster ions, charged particles.

1. Introduction

Although, particle emissions from motor vehicles have been extensively studied, there are only a few reports of their charge characteristics. The same is true concerning air quality monitoring near busy roads where, while there are many reports of particle mass and number concentrations, there are only a handful of papers reporting ion and charged particle concentrations.

It is not commonly known that most surfaces emit charged nanoparticles when heated to a high temperature. Jeon et al (2003) showed that copper heated to close to its melting temperature emitted positively charged nanometer-sized clusters. Peineke and Schmidt-Ott (2008) repeated these experiments with a range of metals and showed that the sign of charge depended on the metal. For example, silver emitted only positive charge, while palladium emitted both positive and negative charges. The negative particle charge was attributed to thermoemission of electrons and positive particle charge to surface ionization of impurity atoms with low ionization energy. More widely known is flame ionization where charged soot particles are emitted by hydrocarbon flames. Fialkov (1997) showed how the charged species in such a flame may be manipulated by the application of an external electric field. Maricq (2004) showed that a substantial fraction of the soot particles from a flame are electrically charged, predominantly with a single charge per particle and with equal numbers of positive and negative particles.

It is informative to compare the flame soot results with the charged particle concentrations found in emissions from combustion sources. Kittelson et al (1986) showed that about 80% of the particles in diesel emissions are charged with roughly equal amounts of positive and negative charge. The number of charges per particle increased with particle size from one charge at 40 nm to four charges at 300 nm. Two different processes, possibly acting together, have been attributed to the generation of ions in the engine cylinder during the combustion process (Reinmann et al, 1997; Kubach et al, 2004). In chemiionisation, chemical reactions between neutral species generate sufficient energy to ionize the reaction products, and thermal ionization where the energy from the reaction heats the burned gases. Peak ion concentrations in the exhaust gases are of the order of 10^6 - 10^7 ions cm^{-3} for petrol engines and 10^8 ions cm^{-3} for diesel engines (Collings et al, 1988; Yu et al, 2004). Recent experiments have shown that almost all the charge resides on soot particles in the accumulation mode with very little in the nucleation mode (Jung and Kittelson, 2005; Maricq, 2006; Lahde et al, 2009), suggesting that the semivolatile nanoparticles are not formed by ion-induced nucleation.

In the natural environment, ions are produced from many sources including the ionization of air molecules by cosmic rays and alpha radiation from natural radioactive materials such as Rn-222 in the ground. These ions readily attach to water molecules in the air to form singly-charged molecular clusters smaller than about 2 nm in size. They are also known as ‘small ions’ and exist in concentrations of about 300-400 cm^{-3} under stable atmospheric conditions and are known to rapidly attach to aerosol particles in the air, especially when the number concentration of the particles is high (Reiter, 1992). Particle number emissions from light and heavy duty vehicles are of the order of 10^5 and 10^7 cm^{-3} (Ristovski et al, 2005, Jayaratne et al, 2009). As such, it is expected that cluster ions emitted by motor vehicles would not last very long in the high particle number concentration exhaust plumes. Therefore, near busy roads, most of the emitted charge would be expected to reside on soot particles.

Israelson and Lelwala (1999) measured space charge near a highway carrying about 700 vehicles per hour in Sweden. They found maximum ion concentrations of about 625 ions cm^{-3} nearest the road, decreasing exponentially to 125 cm^{-3} at a downwind distance of 1 km. They reported elevated values at distances of up to 2 km from the road. Titta et al (2007) monitored cluster ions and charged particles at a location 10 m away from a busy motorway carrying 14,000-16,000 vehicles per day in Finland. Average cluster ion (0.3-1.8 nm) concentrations were around 320 cm^{-3} and 280 cm^{-3} for negative and positive ions respectively. The corresponding charged particle (1.8-40 nm) concentrations were 750 cm^{-3} and 510 cm^{-3}, respectively. They compared these values with measurements obtained around the same time at a rural, clean air station and showed that the cluster ion concentration at this site was about three-times higher than that at the traffic site, while the particle charge concentration was only about one-third as much. Hirsikko et al (2007) measured cluster ion concentrations at an urban location about 100 m away from a major road, and reported that median positive and negative ion concentrations during weekdays were 590 and 630 cm^{-3} respectively, and 632 and 696 cm^{-3} respectively over the weekends. These values may be compared with the positive and negative cluster 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). Cluster 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.

The presence of ions and charged particles in the air is of concern as it has been suggested that they may be linked to several adverse health effects such as respiratory and cardiological conditions (Fews et al, 1999; Henshaw, 2002). Vehicle emissions are the main source of air pollution in urban environments and, since the particles are accompanied by significant concentrations of ions, it is important to investigate the nature and concentration of these charges near roads and to determine how far they would be carried from a road and for how long they would last in the environment. Our understanding of these factors is highly limited and, in this paper, we report findings that address these gaps in knowledge. Moreover, many roads and highways pass through high density residential areas and, therefore, these results are of paramount interest to exposure studies.

2. Methods

2.1 Instrumentation

Cluster ion concentrations were measured with two battery-operated Alphalab air ion counters. This instrument operates by drawing ambient air at a rate of 0.8 L s^{-1} between the plates of a parallel plate capacitor. One plate has a voltage applied so that it repels the ions of the same sign into the other plate which is connected to ground through a sensitive electrometer. The current in the electrometer is a measure of the charge of the cluster ions in the sampled air. The voltage on the plate provides a minimum characterisable mobility of 0.5 cm^2 V^{-1} s^{-1}, ensuring that ions larger than 1.6

nm, which includes charged particles, are not detected. The minimum detectable charge concentration is 10 ions cm^{-3} and the response time is 2s at the sampling rate used. The instrument has the capability of monitoring negative and positive ions separately, but not simultaneously. Hence, in the present study, two instruments were used to measure both positive and negative cluster ions simultaneously. Both instruments were factory-calibrated immediately prior to the measurement campaign.

The net particle charge concentration was measured with a TSI 3068 aerosol electrometer. The instrument operates by drawing ambient air at a known flow rate through a particle filter attached to a sensitive electrometer. The filter traps all particles in the size range 2 nm to 5 μm and the total net charge present on aerosol particles is measured by the electrometer. 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 6 nm in number concentrations up to 5×10^4 cm^{-3}. The time response of the instrument is less than 3s.

The aerosol electrometer and the CPC were powered by a portable petrol-powered ac voltage generator which was placed at least 10 m away in the downwind direction from the instruments. All data were logged at 1 s intervals and stored on a laptop computer. Wind speed was estimated using a hand-held anemometer, while the wind direction was noted on a fixed weather vane. Traffic density was estimated manually by counting the number of light and heavy-duty vehicles passing in each 1 min period at intervals of five minutes. Air temperature and humidity were also recorded at regular intervals over the measurement periods.

2.2 Motor Vehicle Emissions

In the first part of the study, we measured the charge in the exhaust emissions from a 3-year old Ford Falcon station wagon, operating on unleaded petrol. The vehicle was stationed on a level ground and the emissions were directed into a 0.4 m^3 box, placed about 0.5 m from the tailpipe. The exhaust plume entered the box through an open window on the side of the box and exited through the top of the box that was left open. In doing so, the plume mixed with clean ambient air such that the temperature of the gas in the box was not more than 50ºC. Positive and negative small ions, particle number and charge concentrations were measured in the box in real time.

2.3 Roadside Measurements

Field measurements were carried out at 14 different sites near busy roads in a major city in Australia. Of these, nine were near major motorways with an average of 120-140 vehicles min^{-1} with 5-15% consisting of heavy-duty diesel vehicles. Five sites were by city roads with roughly 40-90 vehicles min^{-1} of which more than 90% were petrol cars. The instruments were placed on a folding table of height 0.8 m, 2-5 m away from the edge of the road. Concentrations were also measured at four urban parks, situated well-away from roads and built-up areas. These were treated as 'urban background values'. Three of the motorway sites, denoted A, B and C, were selected for conducting measurements as a function of downwind distance from the road, taking into account that they comprised a stretch of level ground with short grass cover and were well away from trees and other obstacles. The instruments were placed on a trolley that was moved along a line normal to the road. Measurements were obtained at regular intervals along this line. A reference point was selected, usually at a distance of about 10 m from the road. Readings were obtained for periods of 10-15 min at each location, followed by 5 min at the reference location before moving to the next location. All readings were standardized with respect to the nearest reading at the reference location. Measurements were also obtained on the upwind side of each road immediately before and after the experiments and these were treated as the respective background values. Traffic-related cluster ion concentrations were derived by subtracting the upwind value from the measured values. At sites A and B, the measurements were concentrated more at close distances to the road, from a nearest approach of 2m up to 18m and 15m, respectively, at intervals of about 2m. Site C allowed measurements to be carried out to a greater distance of 150 m from the road. The nearest approach to the motorway kerb in this instance was 10 m. Measurements at site C were conducted as for the two sites A and B above but at distances of 10, 20, 30, 40, 50, 100 and 150 m from the kerb.

We hypothesized that the ion concentrations would increase with traffic density. In order to investigate this, at Site B, the instruments were located 2m from the kerb and the traffic in both directions was manually counted at 1 min periods. At the prevalent wind speed of 2.5 m s^{-1}, it was estimated that the ions took approximately 1 s to reach the instruments from the passing vehicles and this time lag was taken into account in computing the average cluster ion concentrations during each 1 min period.

2.4 Data analysis

All data were obtained at 1 s intervals. In deriving representative values of the parameters at a given location, median values were used instead of mean values because both the particle number and charge concentrations monitored near the roads showed sharp but large spikes, generally coinciding with the passage of vehicles. When comparing magnitudes between different locations, mean values were used so that the data points could be treated statistically using the 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 regression analyses were estimated at a confidence level of 95%.

3. Results and Discussion

3.1 Motor Vehicle Emissions

The exhaust emissions contained cluster ions of both signs in approximately equal quantities. Fig 1 shows an example of a typical time series of positive and negative cluster ion concentrations measured in the exhaust plume of the Ford Falcon petrol car at three engine speeds: 750, 2000 and 3000 revolutions per minute (rpm). Fig 1(a) 750 rpm corresponds to the idle condition with the foot off the accelerator. Fig 1(b) and 1(c) show the time series for 2000 rpm and 3000 rpm, respectively. The arrows show the times at which the engine speed was increased to the required rate by stepping on the accelerator and where the foot was taken off the accelerator. Fig 2 shows the mean positive and negative cluster ion concentrations found under these three conditions. The error bars show standard deviations about the means. Despite the large variations that were mostly due to air turbulence, two clearly important results emerged: (1) At the two higher engine speeds, the concentration of positive ions and negative ions were not significantly different from each other, as confirmed by the t-test analysis. Note also the near mirror image patterns of the positive and negative ion time series in Figs 1 (b) and (c). This pattern became more pronounced at the higher engine speed. (2) The concentrations of ions of both signs increased sharply with engine speed, with the t-test analysis showing significant differences between each pair of engine conditions. Ion concentrations of both signs showed an approximate order of magnitude increase from idle to 2000 rpm and again from 2000 rpm to 3000 rpm.

Fig 1

Fig2

These results agree broadly with Kittelson et al (1986) and Maricq (2006) who found approximately equal numbers of positively and negatively charged particles in the exhaust of motor vehicle engines. As stated earlier, exhaust plumes contain 10^5 to 10^7 particles cm^{-3} when motor vehicles are being driven at normal speed. Since cluster ions are known to have a strong affinity to particles in the air, it is expected that their numbers in the exhaust plume will be rapidly diminished after emission with most of the charge residing on the particles. While the maximum cluster ion concentration in the exhaust plume of the vehicle in the present study was of the order of 2×10^4 cm^{-3}, typical particle charge concentrations found in other studies have exceeded this figure by three orders of magnitude (Collings et al, 1988; Yu et al, 2004; Ma et al, 2008).

The net particle charge concentrations indicated by the aerosol electrometer at 2000 and 3000 rpm were $+100 \pm 50$ cm^{-3} and -1000 ± 500 cm^{-3}, respectively. These values are around 5% of the total cluster ion concentrations and, as we expect the particle charge concentrations in the exhaust to exceed the cluster ion concentrations, it strongly suggests that the positive and negative charge concentrations carried by the exhaust particles are also nearly equal. Although we had no way of confirming this observation, it is consistent with Kittelson et al (1986) and Maricq (2006).

3.2 Roadside Measurements

3.2.1 Ion concentrations near the kerb

Table 1 shows the measured mean positive, negative and total cluster ion concentrations at the four urban background, nine motorway and five city road sites. The uncertainties indicate the standard deviations about the means. All nine motorway sites showed cluster ions of both signs with concentrations well above the mean urban background value. The mean total ion concentration near the motorways (1211 cm^{-3}) was 4.5 times higher than the mean urban background value. The mean total ion concentration near the city roads (603 cm^{-3}) was about one-half of the motorway value and about twice as high as the urban background value.

Table 1.

The left half of Fig 3 shows a 15-min time series of the positive and negative cluster ion concentrations measured 2 m away from the edge of a busy motorway. The instruments were placed on the downwind side of the road, the wind speed at the time was 2.1 ± 0.7 m s^{-1} and the traffic density was 115 ± 20 min^{-1} which included 18 min^{-1} heavy-duty diesel trucks. The mean positive and negative cluster ion concentrations at this site were 740 ± 300 and 598 ± 289 cm^{-3}, respectively. Note that both the positive and negative time series showed sharp concentration spikes, up to four times as high as the average values. This was typical at all motorway sites and accounted for the relatively large standard deviations observed. Visual observations confirmed that these spikes generally coincided with the passage of heavy duty diesel trucks. It is interesting to note that the positive and negative spikes often coincided in time, suggesting that they were from the same source. This is consistent with the finding in section 3.1 that motor vehicles emit cluster ions of both signs at roughly equal rates. Similarly, as shown by Kittelson et al (1986) and Maricq (2006), motor vehicle exhaust contains approximately equal numbers of positively and negatively charged particles. Our measurements of the net particle charge using the aerosol electrometer yielded a mean value of about -50 cm^{-3}. 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 instrumentation did not permit us to measure this quantity. 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

The right half of Fig 3 shows a 15-min time series of the positive and negative cluster ion concentrations measured close to the kerb of a busy city road carrying approximately 80 vehicles min^{-1}. Not more than 5 min^{-1} of these were heavy duty vehicles. The instruments were again situated on the downwind side of the road and the wind speed at the time was less than 2 m s^{-1}. The mean positive and negative cluster ion concentrations at this site were 396 ± 90 and 217 ± 137 cm^{-3}, respectively. Note that, unlike in the motorway results, there are no sharp concentration spikes evident here. This also ensured that the standard deviations were lower than for the motorways. The mean cluster ion concentration near city roads was approximately one-half that near the motorways.

Fig 4 shows the second-by-second positive cluster ion concentration plotted against the simultaneous negative value at one of the motorway sites over a period of 15 min. A regression analysis showed a strong relationship between the two parameters (R^2=0.87; P<0.01), suggesting that ions of both signs were emitted from the same source. This correlation was much higher than the corresponding value of R^2=0.48 obtained at the background site.

Fig 4

3.2.2 Ion concentration as a function of traffic density

The positive and negative cluster ion concentrations at 2 m from the kerb at Site B were computed for each 1 min interval in time and are plotted as a function of the corresponding traffic density in Fig 5. Both the positive and negative cluster ion concentrations showed an increase with traffic density. Although there was a fair amount of scatter (R^2 = 0.56), a linear regression analysis showed both increases to be statistically significant at $p<0.05$.

Fig 5

3.2.3 Ion concentrations as a function of distance to the road

Traffic-related cluster ion concentrations were determined at the two motorway sites, A and B, as a function of downwind distance from the road. In both cases, the closest approach to the road was 2m with the wind blowing normal to the road. Table 2 shows some of the parameters pertaining to the two sites and some measurements obtained. Fig 6 shows the traffic-related positive and negative cluster ion concentrations as a function of distance at the two sites. The values shown are medians at each distance with the error bars showing the first and third quartile values. Fig 7 shows the total cluster ion concentrations at the two sites as a function of distance.

Table 2.

Fig 6

Fig 7

At the closest approach point to the road (2 m), the median traffic-related positive and negative cluster ion concentrations were 309 and 459 cm^{-3} at Site A and 667 and 390 cm^{-3} at Site B, giving total concentrations of 768 and 1057 cm^{-3}, respectively. The site-difference between these values was statistically significant and we attribute it to the higher traffic density at Site B over Site A. At both sites, total, positive and negative ion concentrations decreased sharply with distance away from the road. From 2m to 5m of the kerb, the total concentrations fell by approximately one-half. The variation of total cluster ion concentration (N cm^{-3}) with distance from the kerb (d in m) approximated best to a power function of the form $N = T d^{-v}$, where T and v are constants at a given site. The corresponding best-fit values of the two constants and the power-law regression coefficients for Sites A and B are shown in the graph legend in Fig 7. We hypothesize that the constant T is mainly controlled by the traffic density while the constant v determines the rate of decrease of ions with distance and is mainly controlled by the wind speed.

We conclude that cluster ions are concentrated near the road and deplete rapidly with distance and approach background values, meaning upwind values, within a short distance from the kerb. At Site A, the measured concentration decreased to the background value at a distance of about 15m from the kerb while, at Site B, it was still greater. We attribute this difference to the higher mean wind speed and traffic density at Site B (2.5 m s^{-1} and 140 min^{-1}) over Site A (1.3 m s^{-1} and 120 min^{-1}).

It is pertinent to compare the rate of decrease of cluster ion concentration with distance with the corresponding pattern for particles emitted by motor vehicles. Several studies have investigated particle number concentrations as a function of distance from busy motorways and approximated the decrease to be exponential (Hitchins et al, 2000; Zhu et al, 2002a,b). In Fig 8, we show the particle number concentrations measured at Sites A and B as a function of distance from the road. Two observations can be immediately made. First, the particle number concentration at the closest point to the motorway is higher at Site B than at Site A. This is easily attributable to the difference in traffic density between the two sites. Secondly, at Site B, the rate of decrease with distance is much greater than at Site A. We attribute this to the higher wind speed at Site B. Higher wind speeds result in greater dilution of the exhaust as it is carried downwind. Hitchins et al (2000) reported this effect on their measurements of particle number concentration as a function of distance from a busy motorway.

Fig 8

However, we note that the cluster ions fall off with distance much more rapidly than particles. For example, at Site A, from 2m to 12m of the road, the cluster ion concentration falls by more than 70% (Fig 7) while the particle number concentration falls by just 10%. At Site B, where the wind speed is much higher, the drop in particle number is 40% (Fig 8), which is still much lower than the corresponding drop in cluster ions over the same distance. Moreover, when we compare the variation of cluster ion concentration with distance at the two sites (Fig 7), we see the opposite effect, with the rate of decrease with distance at Site A being greater than at Site B. It suggests that, unlike for particles, dilution is not the dominant factor controlling the decrease in cluster ion concentration with distance. It is known that cluster ions quickly attach to particles and the particle number concentration near the motorways is very high (several tens of thousands cm^{-3}). Cluster ions are also lost by recombination and we know that ions of both signs are present in motor vehicle emissions. Both attachment and recombination are enhanced by the greater turbulent exchanges that occur at higher wind speeds together with shorter times available for the ions to attach to particles or recombine with ions of the opposite sign (Mareev et al., 1996). The wind speed at Site B was approximately twice the value at Site A. Therefore, the time available for attachment and recombination before the ions reached a given downwind location was twice as long at Site A than at Site B. Hence, our results suggest that the effect of the wind speed in determining the distance to which cluster ions are transported is controlled not so much by dilution as the associated lifetimes of the ions.

Measurements at Site C, carried out from a distance of 10m to 150m of a motorway carrying 135 vehicles min^{-1} showed no significant drop in cluster ion concentration ($p=0.64$) within this distance range. However, over the same distance, in good agreement with Hitchins et al. (2000), the particle number concentration decreased by over 50%. Overall, we have shown that, unlike particles that are carried downwind to distances of a few hundred metres of busy roads, cluster ions emitted by motor vehicles are not carried to more than a few tens of metres.

Finally, we compare our results with previous measurements of ions near roads. The total average cluster ion concentration at a distance of 10 m from a busy road in Finland reported by Titta et al (2007) was 600 cm^{-3}. This value is higher than the corresponding value of 250-400 cm^{-3} found in the present study but may have been influenced by emissions from another motorway nearby. Moreover, considering that the Finland study was carried out over a longer period during which the wind speed and direction varied widely, the agreement is reasonable. Israelson and Lelwala (1999) reported maximum traffic-related space charge density of 625 ions cm^{-3} near a road carrying about 700 vehicles per hour in Sweden. This traffic density was much less than in the present study. They did not report the exact distance of the measurement point to the road and it should also be kept in mind that their result may include the charge carried by particles and so a direct comparison is not possible.

4. Summary and Conclusions

Positive and negative cluster ion concentrations, net particle charge concentration and particle number concentrations were measured in the exhaust plume of a motor car and by the kerbside of nine busy motorways and four city roads in a major city in Australia. Measurements were also carried out as a function of distance from the road at three of the motorway sites.

The main findings of this study are as follows:

1. Motor vehicles emit ions of both signs in roughly equal numbers. The cluster ion concentration from a 3-year old Ford Falcon station wagon, operating on unleaded petrol, increased sharply with engine speed, showing an approximate order of magnitude increase from idle to 2000 rpm and again from 2000 rpm to 3000 rpm.
2. Cluster ions of both signs are found near busy roads in roughly equal numbers. Concentration spikes at the kerb coincide with the passage of vehicles and are dominated by heavy-duty diesel trucks. Mean cluster ion concentration of each sign showed a linear increase with traffic density.
3. The mean positive and negative ion concentrations measured 2-5 m downwind of the motorways were 569 ± 316 cm^{-3} and 642 ± 269 cm^{-3}, respectively, where the uncertainties indicate the standard deviations about the mean. The mean total ion concentration near the motorways was 4.5 times higher than background.
4. The mean positive and negative cluster ion concentrations at the five city road sites were 309 ± 172 cm^{-3} and 294 ± 218 cm^{-3}, respectively. The mean total ion concentration near the city roads (603 ± 252 cm^{-3}) was about one-half of the motorway value and about twice as high as the background.
5. Cluster ion concentrations decreased sharply with downwind distance from the motorways. The rate of decrease with distance was significantly higher than for particles. At one site investigated, from 2m to 12m of the road, the cluster ion concentration decreased by more than 70% while the particle number concentration decreased by just 10%. No further decrease in cluster ion concentration was observed beyond this distance, as it merged with the

background value. At another site, no decrease in cluster ion concentration was observed from 10m to 150m of the motorway, while the particle number concentration decreased by over 50%.

6. The distance to which cluster ions are transported from the road increases with increasing wind speed. We attribute this to the shorter time available for recombination or attachment to particles that dominate over dilution and turbulence effects that control the decrease of particle concentrations with distance from a source.
7. The results suggest that, unlike particles that are carried downwind to distances of a few hundred metres of busy roads, cluster ions emitted by motor vehicles recombine or attach to particles within a very short time and are, therefore, not transported to more than a few tens of metres.

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Table 1: Mean positive, negative and total cluster ion concentrations at the urban background, motorway and city road sites.

	Number of Sites	Mean Concentrations (cm^{-3})		
		Positive	Negative	Total
Urban Background	4	50 ± 17	219 ± 97	269 ± 109
Motorway Kerbside	9	569 ± 316	642 ± 269	1211 ± 315
City-Road Kerbside	5	309 ± 172	294 ± 218	603 ± 252

Table 2: Some parameters and measurements at the two motorway sites.

Site	**A**	**B**
Traffic count (min^{-1})	120	140
Percentage heavy-duty vehicles	12	15
Wind speed ($m\ s^{-1}$)	1.3±0.3	2.5±0.5
Nearest approach to road (m)	2	2
Furthest measurement point from road (m)	18	15
Median total ion concentration at 2m downwind	1148	1660
Median total ion concentration at upwind	380	610
Median traffic-related total ion concentration at 2m downwind	768	1050

Figure Captions

Fig 1: Time series of cluster ion concentrations measured in the exhaust plume of a Ford Falcon petrol car at three engine speeds: (a) 750 rpm (b) 2000 rpm and (c) 3000 rpm.

Fig 2: Mean values of cluster ion concentrations measured in the exhaust plume of a Ford Falcon petrol car at three engine speeds. The error bars indicate the standard deviations.

Fig 3: Typical 15-min time series of positive and negative cluster ion concentrations near the kerb of a motorway (left) and a city road (right).

Fig 4: Positive cluster ion concentration plotted against the simultaneous negative concentration at one of the motorway sites.

Fig 5: Positive and negative cluster ion concentrations measured near the kerb of the motorway at Site B as a function of traffic density.

Fig 6: Traffic-related cluster ion concentrations as a function of distance from the road at two motorway sites.

Fig 7: The total cluster ion concentrations at the two sites as a function of distance from the road.

Fig 8: Particle number concentrations as a function of distance from the road.

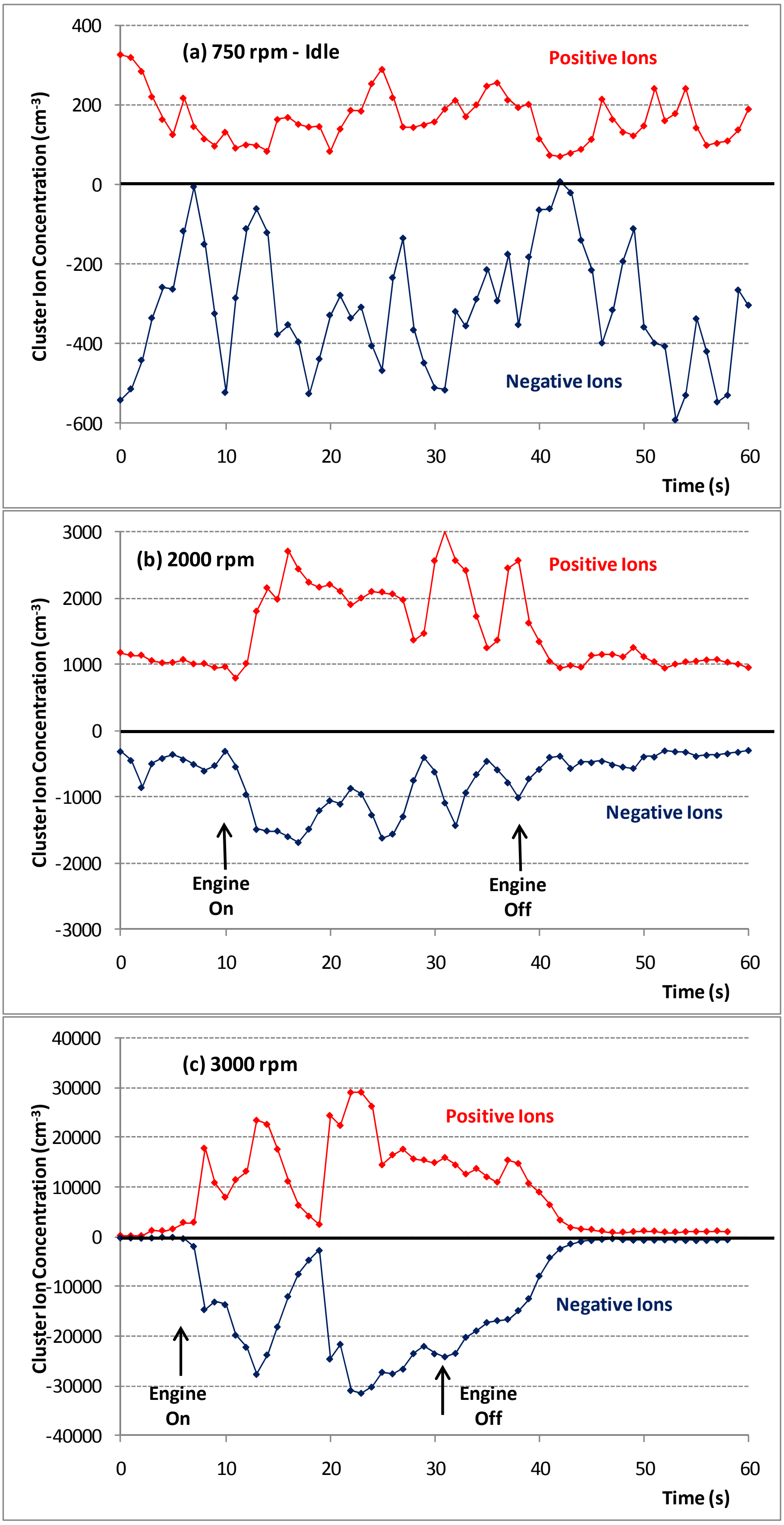

(a) 750 rpm - Idle
Positive Ions
Negative Ions
Cluster Ion Concentration (cm-3)
Time (s)
400
200
0
-200
-400
-600
0
10
20
30
40
50
60
(b) 2000 rpm
Positive Ions
Negative Ions
Engine On
Engine Off
Cluster Ion Concentration (cm-3)
Time (s)
3000
2000
1000
0
-1000
-2000
-3000
0
10
20
30
40
50
60
(c) 3000 rpm
Positive Ions
Negative Ions
Engine On
Engine Off
Cluster Ion Concentration (cm-3)
Time (s)
40000
30000
20000
10000
0
-10000
-20000
-30000
-40000
0
10
20
30
40
50
60

Fig 1

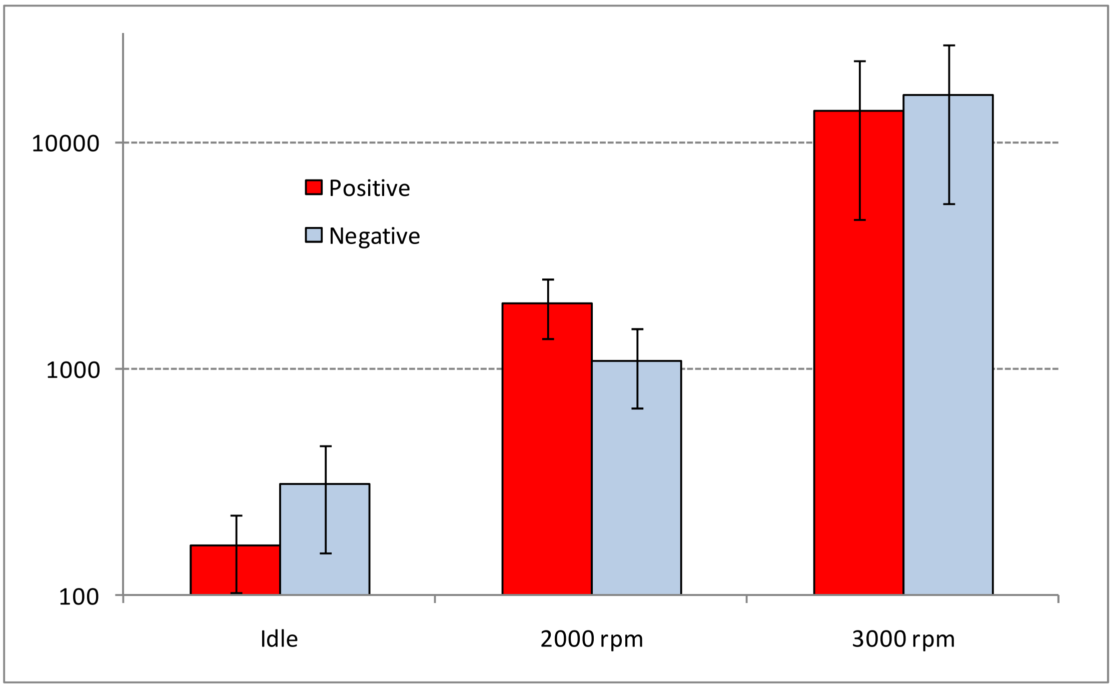


Fig 2

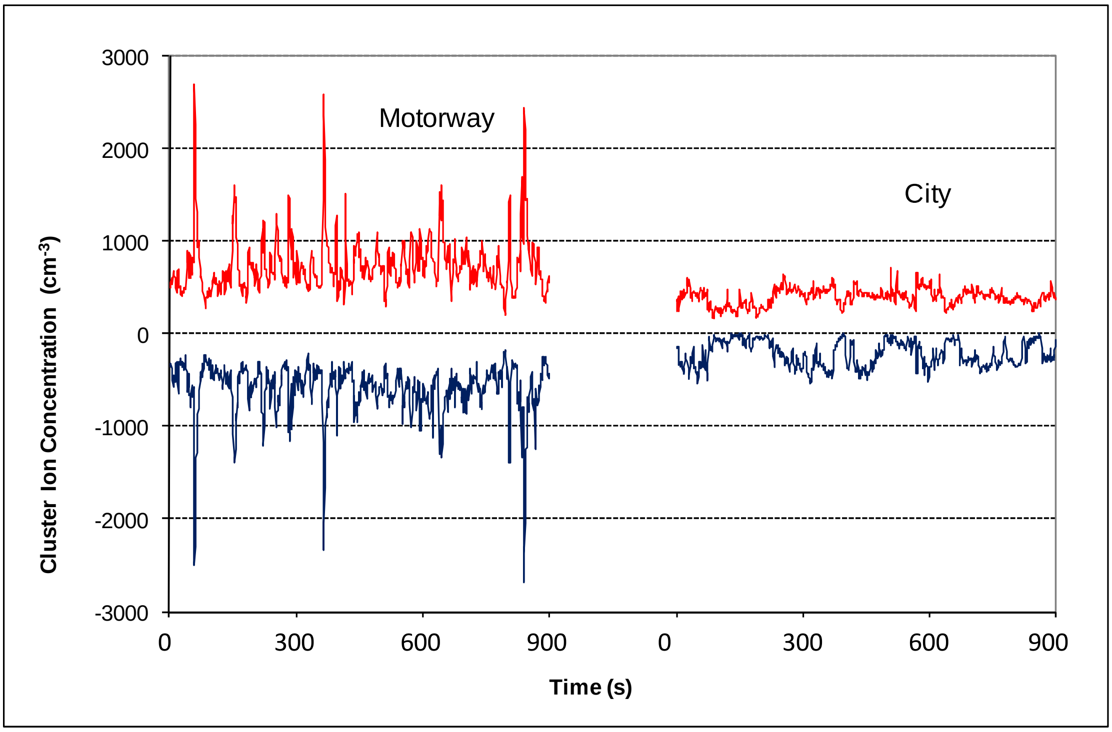
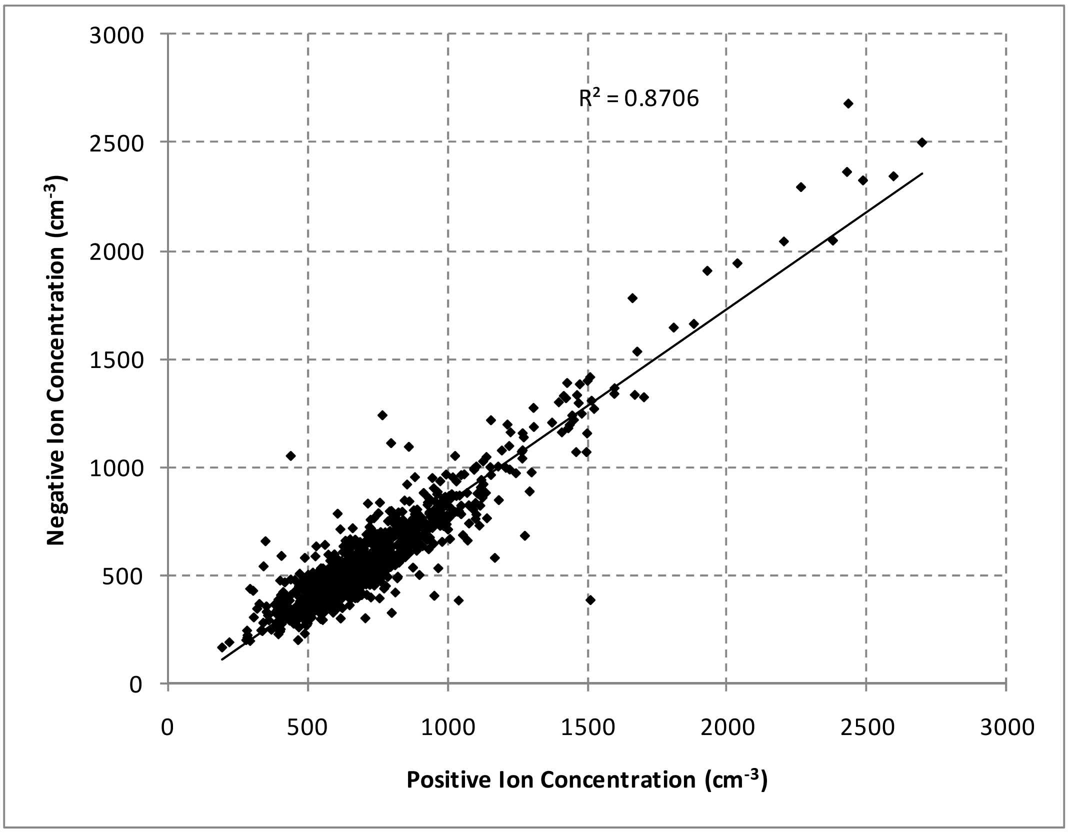
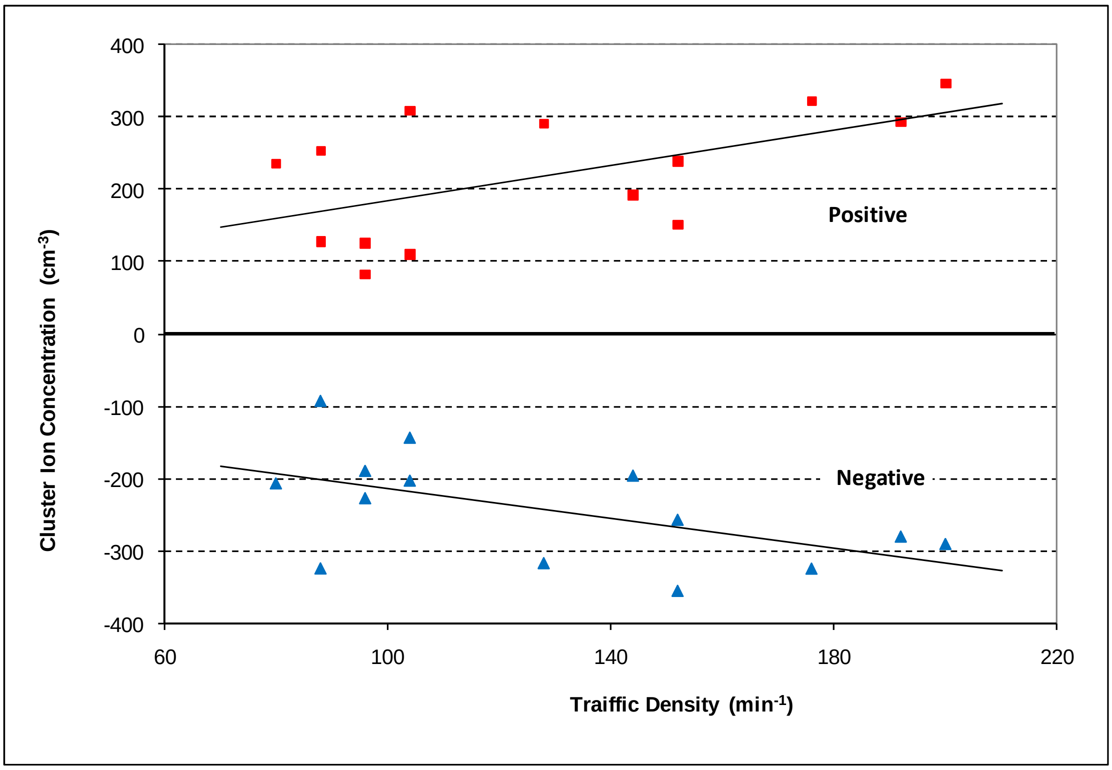

Motorway
City
Cluster Ion Concentration (cm-3)
3000
2000
1000
0
-1000
-2000
-3000
0
300
600
900
0
300
600
900
Time (s)

Fig 3



R² = 0.8706
Negative Ion Concentration (cm-3)
Positive Ion Concentration (cm-3)
0
500
1000
1500
2000
2500
3000

Fig 4



400
300
200
100
0
-100
-200
-300
-400
Cluster Ion Concentration (cm^{-3})
Positive
Negative
60
100
140
180
220
Traiffic Density (min^{-1})

Fig 5

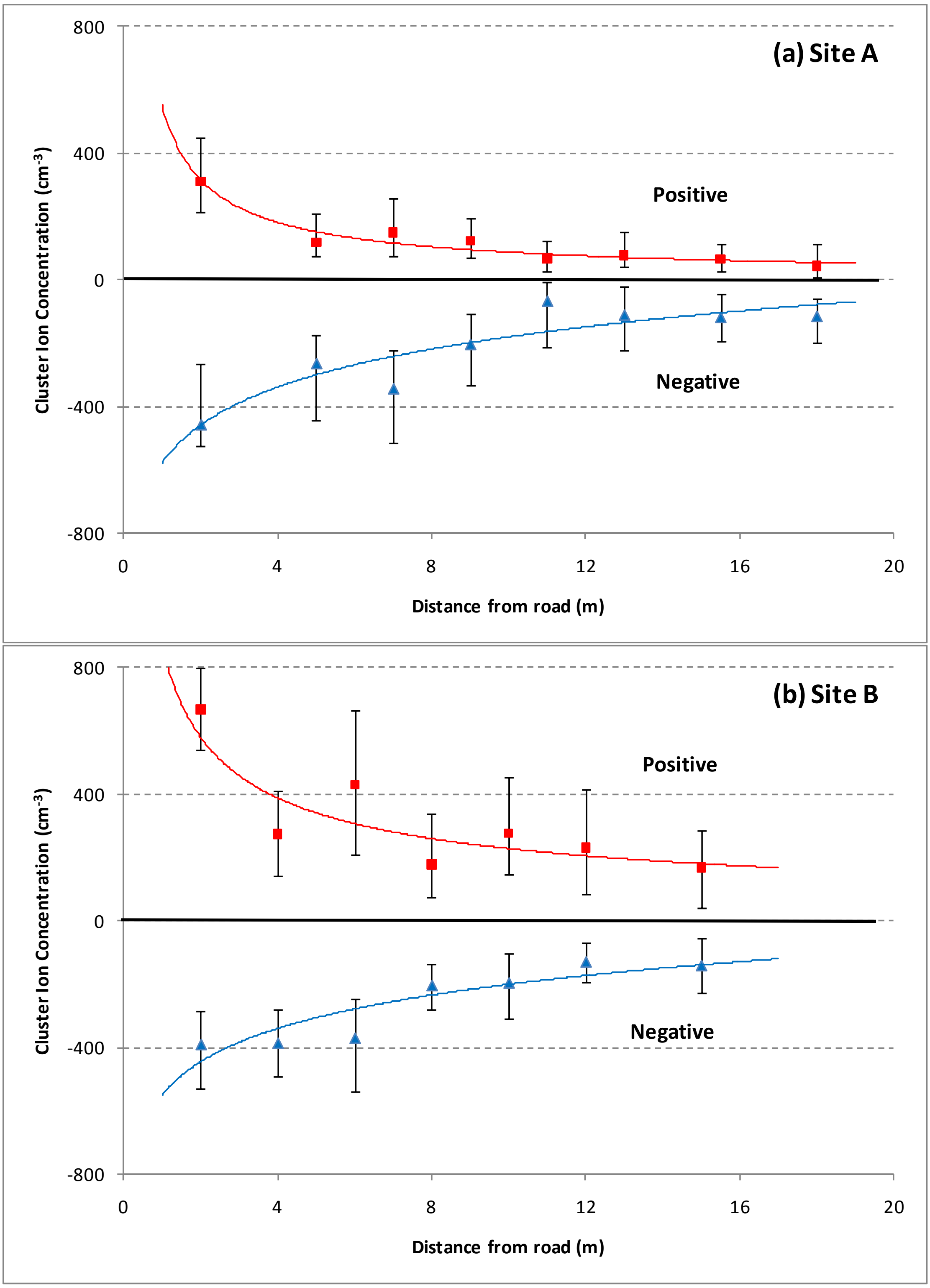

(a) Site A
Positive
Negative
Cluster Ion Concentration (cm⁻³)
Distance from road (m)
800
400
0
-400
-800
0
4
8
12
16
20
(b) Site B
Positive
Negative
Cluster Ion Concentration (cm⁻³)
Distance from road (m)

Fig 6

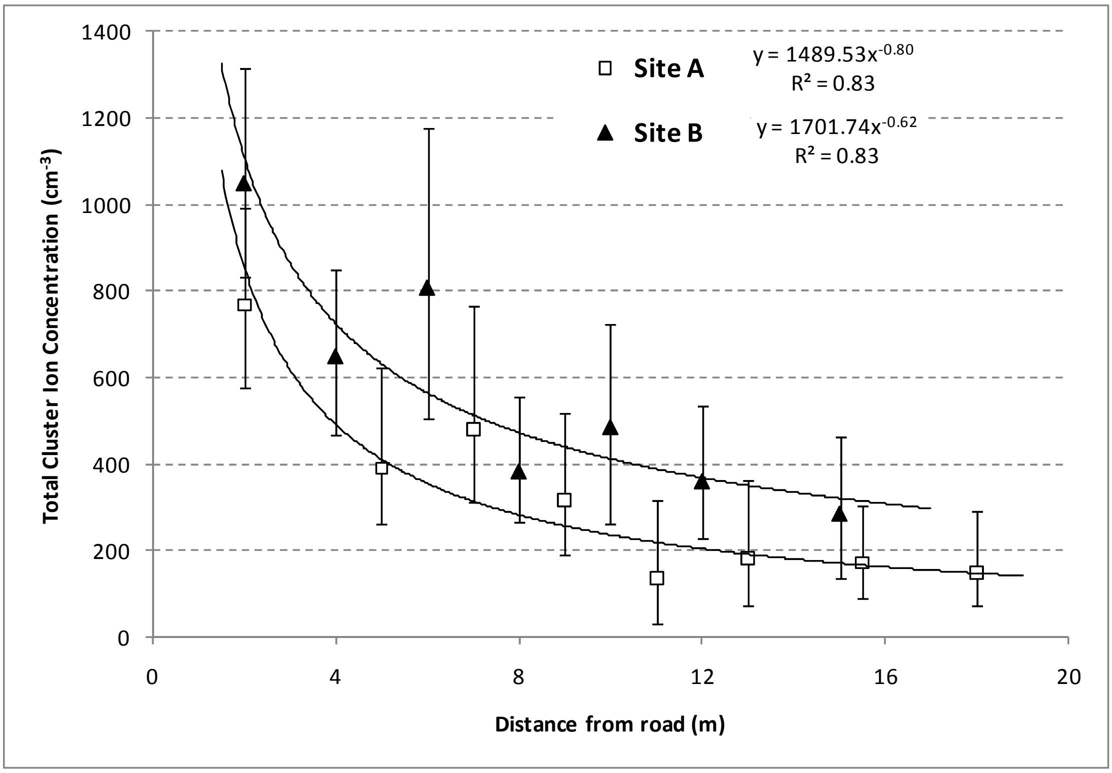

Site A
y = 1489.53x-0.80
R² = 0.83
Site B
y = 1701.74x-0.62
R² = 0.83
Total Cluster Ion Concentration (cm-3)
Distance from road (m)
0
200
400
600
800
1000
1200
1400
0
4
8
12
16
20

Fig 7

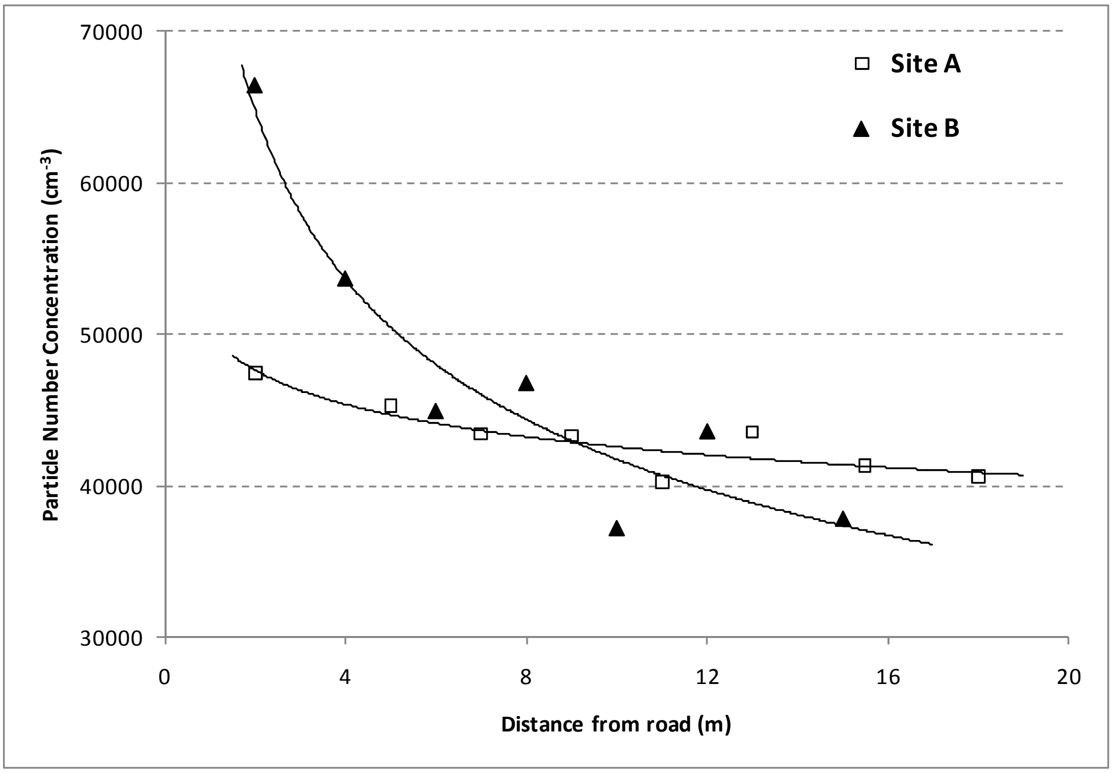

Site A
Site B
Particle Number Concentration (cm⁻³)
70000
60000
50000
40000
30000
0
4
8
12
16
20
Distance from road (m)

Fig 8