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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 2 m to 5 m of the kerb. Measured concentrations decreased to background at about 15 m 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.

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.

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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.

Israelsson 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 Hõrrak 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 2 s 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 3 s.

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 50 °C. 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