

QUT Digital Repository:
<http://eprints.qut.edu.au/>



Morawska, Lidia and Ristovski, Zoran and Jayaratne, Rohan and Keogh, Diane U. and Ling, Xuan (2008) Ambient nano and ultrafine particles from motor vehicle emissions: characteristics, ambient processing and implications on human exposure. *Atmospheric Environment* 42(35):pp. 8113-8138.

© Copyright 2008 Elsevier

Ambient nano and ultrafine particles from motor vehicle emissions: characteristics, ambient processing and implications on human exposure

L. Morawska*, Z. Ristovski, E.R. Jayaratne, D.U. Keogh and X. Ling

International Laboratory for Air Quality and Health, Queensland University of Technology, 2 George Street, Qld 4001, Australia

Abstract

The aim of this work was to review and synthesize the existing knowledge on ultrafine particles in the air with a specific focus on those originating due to vehicles emissions. This constitutes Part II of a literature review on ultrafine (UF) particles, with industrial and power plant emissions covered in Part I. As the first step, the review considered instrumental approaches used for UF particle monitoring and the differences in the outcomes they provide. This was followed by a discussion on the emission levels of UF particles and their characteristics as a function of vehicle technology, fuel used and after treatment devices applied. Specific focus was devoted to secondary particle formation in urban environments resulting from semi volatile precursors emitted by the vehicles. The review discussed temporal and spatial variation in UF particle concentrations, as well as particle chemical composition and relation with gaseous pollutants. Finally, the review attempted to quantify the differences between UF particle concentrations in different environments. These, as well as other aspects of UF characteristics and dynamics in the air, were discussed in the context of human exposure and epidemiological studies as well as in relation to management and control of the particles in vehicle affected environments.

1. Introduction

Ultrafine and nano particles present in the air due to natural sources and processes, as well as those resulting from anthropogenic activities have attracted an increasing level of interest in the last decade.

Ultrafine particles (UF) are defined as those with diameters smaller than 0.1 μm , and their subset, nanoparticles as smaller than 0.05 μm . Both these terms constitute a somewhat arbitrary classification of particles in terms of their size, indicating the significant role of this physical characteristic on particle fate in the air. Also health and environmental effects of particles are strongly linked to particle size, as it is the size which is a determinant (in a probabilistic sense) of the region in the lung where the particles would deposit or the outdoor and indoor locations, to which the particles can penetrate or be transported. In addition, sampling of particles and choice of an appropriate instrumentation and methodology is primarily based on particle size. Airborne concentration of UF and nanoparticles is most commonly measured and expressed in terms of number concentrations of particles per unit volume of air, in contrast to larger particles, which are measured in terms of mass concentration.

The size of particles, however, depends on the multiplicity of sources and processes which lead to their formation, and therefore, on the material from which the particles were formed, with the complex scientific knowledge behind these processes still containing many significant gaps. The recent interest in UF particles is to a large extent due to the impact of anthropogenic processes, resulting in unprecedented increases in particle concentration, often by one or two orders of magnitude above their natural concentrations. The most significant are the various outdoor anthropogenic combustion sources, including vehicles (and other forms of transport), as well as industrial and power plants, all utilising fossil fuels. Another significant combustion source is biomass burning, including controlled and uncontrolled forest and savannah fires. There are also indoor combustion sources such as stoves and heaters utilising fossil fuels and biomass, as well as tobacco smoking.

The interest in UF particles has resulted in a large body of literature published in recent years, reporting on various aspects and characteristics of these particles. Therefore, the aim of this work was to review and synthesize the existing knowledge and to draw conclusions as to the picture emerging with regard to

these particles in atmospheric systems. Out of the two main outdoor anthropogenic sources, this paper is focused on vehicle emissions, while the companion paper targets industrial and power plants as sources of UF particles. Not included in this review is the contribution of biomass burning (controlled and uncontrolled fires), and incineration of refuse to local or global UF particle concentrations. Both are topics for independent reviews.

2. Capabilities and limitations of particle number measurement methods

A full review of the instrumental methods for measuring of UF particle properties is outside the scope of this review paper and the reader is directed to several recent publications addressing this topic, e.g. (McMurry 2000). However, it is important to consider the existing methods for particle number and size distribution measurements, since it is the very nature of the instrumental method which determines the measurement outputs and in turn their compatibility with those obtained utilising different methods. The majority of the published studies reporting on particle number and number size distribution applied electrostatic classifiers (EC) and condensation particle counters (CPC) manufactured by TSI Incorporated (www.tsi.com), with a much smaller number using other instruments, for example GRIMM (www.dustmonitor.com), or air ion mobility spectrometers, which have enabled measurements down to 0.4 nm (Mirme et al. 2007). The latter measures only naturally charged particles, and have been used only in a handful of studies.

When referring to UF or nanoparticles, an unspoken assumption is made that the instrumental methods used provide information on particles in the two specific size ranges (<0.05 and <0.1 μm , respectively). This is possible if the instrumental method enables measurements of particle number size distribution, usually in a broader range, from which the sections of data encompassing UF or nanoparticles is extracted. Such methods are most commonly based on electrostatic classifiers operating in combination with particle counters as differential/scanning mobility particle sizers (DMPS or SMPS, respectively)

(Baron and Willeke 2001). The lower end of the size window is determined both by instrumental factors and operator decisions. In the first instance, the lower size limit is determined by the capability of the CPC and ranges from 2-10 nm. However, most commonly the DMPS/SMPS lower end of the window is set to a value above this, in the range from 10 – 20 nm. The reason for setting it up to 10 nm higher than the achievable lower limit is that this provides a compromise as to the overall size of the window. Losing the few nanometres at the lower end enables a significant extension of the window at the upper end, which in most cases is a preferable option, unless a study specifically focuses on the nucleation mode.

If, rather than employing instrumentation for particle size distribution measurement, only a particle counter is used, the outcome of the measurement is the total particle number concentration in the detection size range of the instrument. There are two important implications of this to the interpretation of this value as a measure of UF particles. Firstly, this means that the outcomes of the measurements are not specifically UF or nano particle concentrations, unless specific inlets are used which restrict the range of particles entering the detecting arm of the instrument. While it is true that in most typical environments particle number concentration is dominated by UF particles, which is, thus, usually a good approximation of the total particle number concentration, it is important to keep in mind that these are not the same, that there are environments where there are significant particle modes outside the UF range (see section 5.1, below) and therefore the two concentrations (UF and total number) differ significantly. Secondly, and even more significantly, the condensation particle counters often detect particles in the range extending to lower sizes than the window set by the DMPS/SMPS. This means that the counters are capable of detecting particles in the earlier stages of nucleation, and the presence of the nucleation mode which is below the size detection limit set by the DMPS/SMPS. Therefore in most situations, the counters would detect more particles than the DMPS/SMPS, and significantly more in the environments where a nucleation mode is frequently present.

The above points are important when comparing particle number concentrations reported in different papers and when specifically considering UF or nanoparticles. Since different studies use different sets of instrumentation and investigate a different size range window, comparison of the total particle number concentrations reported should be conducted with caution. In order to develop at least a broad understanding of the impact which these differences have on the measured particle concentrations, data from 52 studies reporting total particle number concentrations for a range of different environments was compiled and then the results grouped according to the measurement technique used: CPC or DMPS/SMPS.

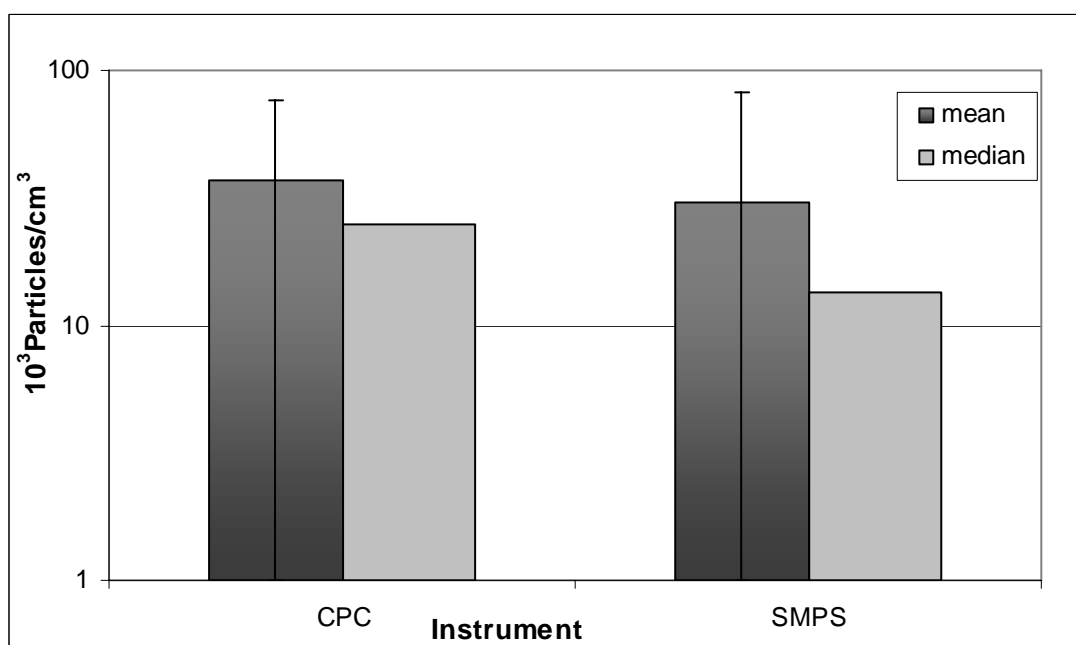


Figure 1. Comparison of reported particle number concentrations measured by CPC or DMPS/SMPS*.

* These CPC and SMPS results were extracted from the following papers: Aalto et al. (2001), Harrison et al. (1999), Kittelson et al. (2004) and Shi et al. (2001a) who used both the CPC and SMPS; Vakeva et al. (1999), Zhu et al. (2004), Imhof et al. (2005a), Paatero et al. (2005) and Westerdahl et al. (2005) who used only the CPC and McMurry and Woo (2002), Tuch et al. (1997), Morawska et al. (1999a), Hitchins et al. (2000), Junker et al. (2000), Jamriska and Morawska (2001), Pitz et al. (2001), Ruuskanen et al. (2001), Cheng and Tanner (2002), Molnar et al. (2002), Morawska et al. (2002), Thomas and Morawska (2002), Wehner et al. (2002), Zhu et al. (2002a), Zhu and Hinds (2002b), Ketzler et al. (2003), Longley et al. (2003), Tunved et al. (2003), Wehner and Wiedensohler (2003), Gidhagen et al. (2004), Gramotnev and Ristovski (2004), Gramotnev et al. (2004), Hussein et al. (2004), Jamriska et al. (2004), Janhall et al. (2004), Jeong et al. (2004), Ketzler et al. (2004), Morawska et al. (2004), Stanier et al. (2004a), Gidhagen et al. (2005), Holmes et al. (2005), Imhof et al. (2005b), Rodriguez et al. (2005), Janhall et al. (2006), Virtanen et al. (2006), Wahlin et al. (2001), Woo et al. (2001b), Abu-Allaban et al. (2002), Laakso et al. (2003), Hussein et al. (2005a) and Mejia et al. (2007a) who used only the SMPS. Other studies, such as (Hameri et al. 1996; Kaur et al. 2006), which measured particle concentration without using a CPC or SMPS (e.g. P-trak etc.) were not included in Figure 1, nor were the four tunnel studies (Abu-Allaban et al. 2002; Gouriou et al. 2004; Jamriska et al. 2004; Imhof et al. 2005b) (see comments in relation to tunnels in section 8.4 below).

The mean concentrations measured by the CPC's and DMPS/SMPS's are $36.8 \times 10^3/\text{cm}^3$ and $30.6 \times 10^3/\text{cm}^3$, respectively, and the median concentrations are $24.9 \times 10^3/\text{cm}^3$ and $13.5 \times 10^3/\text{cm}^3$, respectively. In other words, the mean and the median CPC measurements are 32% and 56%, higher than DMPS/SMPS's measurements, respectively. The difference in the means was tested using a Students t-test and found to be statistically significant at a confidence level of over 99%.

The overall comparison of the differences between the total particle concentration values measured by CPCs and DMPS/SMPSs has some shortcomings. In particular, the differences for specific environments could vary, where larger differences are expected for environments where a nucleation mode is present and smaller where aged aerosol dominates. Moreover, corrections for particle losses within the two instruments may play a significant role. Nevertheless, the comparison shows what overall magnitude of differences can be expected when comparing results using these different measuring techniques. It is important to keep these differences in mind when attempting to establish quantitative understanding of variation in particle concentrations between different environments, which is of significance for human exposure and epidemiological studies.

It is worth mentioning that large discrepancies have also been observed when comparing the results of particle number concentrations measured directly from vehicle exhaust. While particle volume/mass showed reasonable reproducibility in between different studies, results of particle number measurements were difficult to reproduce, even in the same study. Some artefacts and poor reproducibility in vehicle emission measurements were due not only to the different instruments used but also to the fact that the majority of particles (in terms of number) belonged to the nucleation mode and were formed in the process of dilution. The number of particles formed in the nucleation mode is very sensitive to the dilution conditions and any slight changes (of the dilution temperature, for example) can result in a significant change in particle number concentration. A detailed discussion on the effects of dilution

conditions on sampling and measurements of particle numbers in vehicle emissions can be found in Kasper (2005). In order to develop a method that could be used in a reproducible and comparable manner in laboratories around the world, the UNECE-GRPE Particulate Measurement Program (PMP) was formed. This program focused on future regulation of nano-particle emissions from light duty vehicles and heavy duty engines with the goal to amend existing approval legislation to stipulate an extensive reduction of particle emissions from mobile sources (Mohr and Lehmann 2003). Based upon the recommendation of the PMP, the European Commission has added a particle number limit to its Euro 5/6 proposed emission standards for light-duty vehicles. Only solid particles are counted, as volatile material is removed from the sample, according to the PMP procedure.

3. Sources of particles in natural environment

While the main focus of this review is on the impact of vehicle emissions on ambient characteristics of UF and nanoparticles, for completeness, and in order to fully understand this impact, firstly natural sources and their contributions are discussed, as they result in the natural background of the particles in ambient air. Vehicle emissions increase particle concentrations over this background and result in an overall change of particle characteristics.

Of particular importance in natural environments is the formation of new particles, of which the main mechanism is nucleation of low-volatile gas-phase compounds, followed by their growth into small particles. It is not the intention of this review to go into great detail about the mechanisms of particle formation (both natural and anthropogenic). For more details on this topic, the reader is referred to several recent literature reviews (Kulmala et al. 2004; Holmes 2007). There were a number of observations of new particle formation in natural environments ranging from very clean environments such as the arctic (Birmili and Wiedensohler 2000), boreal forests in the northern hemisphere (O'Dowd et al. 2002; Tunved et al. 2006), eucalypt forests of Australia (Suni et al. 2007) and a large number of studies in the coastal areas (see for example a review by Kulmala et al (2004)). In general, there are a

much larger number of observations from the northern hemisphere than from the southern hemisphere. Observations were also made from a variety of platforms ranging from ground based to ships and aeroplanes. In most of these observations the measurements were made such that the platform was not moving along with the same air parcel. Therefore observations of new particle formation may be biased by spatial variations of constituents in different air parcels (Kulmala et al. 2004).

In remote environments particle formation events are preceded by an increase in the atmospheric concentration of sulphuric acid, with the increase in the particle number occurring about 1–2 h after an increase in sulphuric acid was measured (Weber et al. 1997). This is followed by a relatively small particle growth rate between 1 and 2 nm h⁻¹ (Weber et al. 1996; Marti and Weber 1997; Weber et al. 1997; Birmili and Wiedensohler 2000). These events showed a linear relationship between the number of newly formed particles and the production rate of sulphuric acid indicating the importance of sulphuric acid. The question still remains: Is the binary nucleation solely responsible for the formation of these particles or is a third species such as ammonia or an organic involved? Birmilli and Wiedensohler (2000) estimated that the concentration of sulphuric acid needed to achieve the same nucleation rates through binary nucleation was over two orders of magnitudes higher than that measured. Napari et al. (2002) using their observations and parameterisation of the ternary nucleation rate with an atmospheric ammonia concentration of 20 pptv and the measured sulphuric acid concentration obtained good agreement with the observed nucleation rates.

In forests the sources of new particle formation are different. The mechanisms responsible for the formation and growth of these particles are still uncertain. Although sulphuric acid is one of the most likely candidates thought to be responsible for the formation of the initial nanometer-sized particles (Riipinen et al. 2007), sulphur chemistry does not sustain enough sulphuric acid in the atmosphere to explain more than a small fraction of the observed particle-size growth rate. To explain the observed

growth, which is up to a diameter of 50 to 100 nm, other compounds are required. O'Dowd et al (2002) showed that particle formation can commonly occur from biogenic precursors. A recent study by Tunved et al. (2006) showed a direct relation between emissions of monoterpenes and gas-to-particle formation over these regions which were substantially lacking in anthropogenic aerosol sources. Therefore, secondary organic aerosol formation from monoterpenes is an important source in these environments. Further, the authors show that the forest provides an aerosol population of $1-2 \times 10^3 \text{ cm}^{-3}$ of climatically active particles during the late spring to early fall period, presenting a substantial source of global importance.

Proposed particle production mechanisms in the marine environment include the seawater bubble-burst process (O'Dowd et al. 2004), ternary nucleation producing a reservoir of undetectable particles upon which vapours can condense (Kulmala et al. 2000), free tropospheric production with mixing down to the boundary layer (Raes 1995), and the generation of coastal iodine particles from macroalgal iodocarbon emissions (Raes 1995; Kulmala et al. 2000; O'Dowd et al. 2004; O'Dowd and Hoffmann 2005). While iodine-containing particles were found in large numbers at Mace Head research station in Ireland, they are not likely to play an important role globally (McFiggans 2005). Wind-produced bubble-burst particles containing salt are ubiquitous in the marine environment (Ayers and Gras 1991), but these represent less than 10% of particle numbers. The majority of particles are much smaller than these salt particles and their origins remain only partially explained.

Several conclusions can be derived from this brief review. Firstly, particles are formed in the environment due to natural processes and therefore are always present at some background concentration levels. Therefore, when considering particle concentrations in urban environments it is important to compare them to the background levels in order to assess the magnitude of the anthropogenic impacts (see Section 7.6 below). Secondly, the mechanisms of new particle formation

exhibit similar complexities in both types of environments (natural and vehicle affected), strongly depend on local meteorological factors, and therefore a complete picture of the dynamics of particle formation in urban environments must include all factors involved. These issues are further discussed in Section 8.6 below.

4. Vehicle emissions as a source of ultrafine particles

4.1 Introduction

As discussed previously, many studies have conclusively shown that motor vehicle emissions constitute the major source of ultrafine particle pollution in urban environments (Harrison et al. 1999; Shi and Harrison 1999; Shi et al. 1999; Shi et al. 2001a; Wahlin et al. 2001). Particles emitted from diesel engines are in the size range 20-130 nm (Kittelson 1998; Morawska et al. 1998a; Harris and Maricq 2001; Ristovski et al. 2006) and from petrol engines in the range 20-60 nm (Harris and Maricq 2001; Ristovski et al. 2006). Therefore, it is not surprising that a large fraction of the particle number concentration in urban air is found in the UF size range (Morawska et al. 1998b). Overall, it has been shown that in urban environments the smallest particles make the highest contribution to the total particle number concentrations, while only a small contribution to particle volume or mass. A US study by Stanier et al. (2004a) showed that 25% of the aerosol number is less than 10 nm and 75% of the aerosol number is less than 50 nm. Similarly Woo et al. (2001b) showed that 26% of particle number is smaller than 10 nm and 89% smaller than 100 nm. Zhang et al. (2004b) showed that the number concentrations of particles the size ranges of 0.011-0.050 μm and 0.011-0.1 μm accounted for approximately 71% and 90%, respectively of the total number concentration. However, particles smaller than 0.050 μm contributed only 3% to the total volume concentration, while the largest contribution of 87% was from particles larger than 0.1 μm . In Europe Junker et al. (2000) found that the highest in terms of number were concentrations of particle $<0.1 \mu\text{m}$, averaging between 82–87% of the total particle numbers $<0.421 \mu\text{m}$ while the accumulation mode (0.1–2.8 μm) made up for most of the particle

mass (mean >82%). Shi et al. (2001a) showed that particles smaller than 10 nm contributed more than 36-44% of the total particle number concentration in an urban roadside location and particles within the size range 3–7nm accounted for 37% of total measured particles. Charron and Harrison (2003) showed that particles ranging from 11 to 100 nm represent from 71% to 95% (median 88.7%) of the particle number between 11 and 450 nm. Pirjola et al. (2006) reported that in winter in Helsinki, Finland, 90–95%, and in summer, 86–90% of particles were smaller than 50 nm, while Virtanen et al. (2006) estimated for the same data set that particles smaller than 63 nm made up ~90% of particles in the winter and ~80% of particles in summer. Peak concentrations often exceeded $2 \times 10^5 \text{ cm}^{-3}$ and sometimes reached $1 \times 10^6 \text{ cm}^{-3}$. In Australia, Mejia et al. (2007a) showed that UF contributed to 82-90% of the particle number and nanoparticles to around 60-70%, except at a site mainly influenced by heavy duty diesel vehicles, where the nanoparticle contribution dropped to 50%.

A large fraction of these ultrafine particles come from heavy-duty diesel vehicles. Kirchstetter et al. (1999) measured particle emissions from light and heavy duty vehicles in a roadway tunnel and showed that heavy-duty diesel trucks emitted 24, 37 and 21 times more fine particles, black carbon and sulphate mass per unit fuel mass burned than light duty vehicles. Heavy-duty vehicles also emitted 15-20 times the number of particles per unit mass of fuel burned compared to light-duty vehicles. In general, a heavy duty diesel truck or bus exhibits particle number emission factors that are one to two orders of magnitude larger than a typical petrol car (Morawska et al. 2005; Ristovski et al. 2005; Ristovski et al. 2006). The only exception was observed by Graskow et al. (1998) who found that when petrol vehicles were driven at higher velocities (~120 km/h) or with higher loads, i.e. during acceleration, the particle number emissions from petrol vehicles came close to that observed from diesel vehicles.

In general, particles from vehicle emissions can be divided into two broad categories, depending on the location of their formation. They can be formed in the engine or tailpipe (primary particles) or they can be formed in the atmosphere after emission from the tailpipe (secondary particles).

4.2 Primary Particles

Primary particles are generated directly from the engine and are mostly submicrometer agglomerates of solid phase carbonaceous material ranging in size from 30 to 500 nm and residing mainly in the accumulation mode. They may also contain metallic ash and adsorbed or condensed hydrocarbons and sulphur compounds. Metallic ash is generally derived from lubricating oil additives and from engine wear. The size distribution of particles in the accumulation mode are very well represented by lognormal distributions, with an almost constant standard deviation of 1.8–1.9 (Harris and Maricq 2001), and it does not vary significantly between measurements from a given vehicle under different operating conditions. Repeated measurements from a diesel engine, in particular, can be very consistent (Kasper 2005; Ristovski et al. 2006). For this reason, the primary solid particle number limit has been added to the European Commissions proposed Euro 5/6 emission standards for light-duty vehicles.

4.3 Secondary Particles

As the hot exhaust gases are expelled from the tailpipe of a vehicle, they cool and condense to form large numbers of very small particles in the air. They are volatile and consist mainly of hydrocarbons and hydrated sulphuric acid. These, so-called secondary particles, are generally in the nanoparticle size range below 30 nm and compose the nucleation mode, which have been commonly observed near busy freeways, especially carrying a large fraction of heavy duty diesel vehicles (Harrison et al. 1999; Kittelson et al. 2002; Charron and Harrison 2003; Sturm et al. 2003; Gramotnev and Ristovski 2004; Zhu et al. 2004; Rosenbohm et al. 2005; Westerdahl et al. 2005; Ntziachristos et al. 2007). They have also been observed in on-road studies, such as when a vehicle is being followed by a mobile laboratory

(Vogt et al. 2003; Kittelson et al. 2004; Pirjola et al. 2004; Gieshaskiel et al. 2005; Kittelson et al. 2006a; Ronkko et al. 2006; Casati et al. 2007). However, while sometimes present, they are not commonly observed in dynamometer measurements where dilution tunnels are used to cool and dilute the exhaust gases (Rickeard et al. 1996; Khalek et al. 1999, 2000; Kittelson et al. 2006a; Ristovski et al. 2006).

It has been shown that the conditions necessary for the production of these volatile nanoparticles are strongly affected by the dilution conditions such as the dilution rate, dilution ratio, temperature and residence time (Khalek et al. 1998, 1999; Shi and Harrison 1999; Khalek et al. 2000; Kawai et al. 2004; Mathis et al. 2004; Kasper 2005). Lyrranen et al (2004) investigated particle number distributions obtained from a turbo-charged diesel off-road engine using several different dilution systems and concluded that nucleation modes were observed when the dilution process involved rapid cooling and mixing of the exhaust. Casati et al. (2007) measured particle emissions from a diesel passenger car in field and laboratory conditions and concluded that the nucleation mode was strongly affected by dilution conditions and decreased when the exhaust was more diluted.

Similarly, on-road dilution of the exhaust plume is very important in the generation of secondary particles in the exhaust plume. Ronkko et al. (2006) studied particle size distributions in emissions from an on-road heavy-duty diesel vehicle and demonstrated that the formation of the nucleation mode 5m behind the vehicle was favoured by low ambient temperatures and high relative humidity. For smaller distances no nucleation modes were observed neither by Ronkko et al (2006) or Morawska et al (2007b) for a diesel vehicle. During on-road measurements using light duty spark ignition (SI) vehicles, Kittelson et al (2006b) did not observe a significant particle signature above background under highway cruise conditions. Much higher number emissions were observed during acceleration, at high-speed cruise, and during cold starts.

In addition to the dilution and cooling effects, there is another factor that plays an important role in determining the concentration of secondary particles. The gaseous precursors condense or adsorb on to the surface of carbon particles in the accumulation mode. If the concentration of carbon particles is low, the gases will nucleate homogeneously, giving rise to large concentrations of volatile nanoparticles. This has been clearly observed with diesel vehicles equipped with particle filters (Burtscher 2001), where the accumulation mode has been removed by the particle filter leading to large nucleation modes. The presence of a large accumulation mode will act to suppress the formation of the nuclei mode because the carbonaceous agglomerates scavenge volatile material reducing the likelihood of nucleation. Older vehicles with excess soot emissions are less likely to exhibit nucleation modes. Therefore, the number concentration of the nucleation mode particles, unlike the accumulation mode particles, is highly unstable and unpredictable. Further, as in some instances, as many as 90% of the total particle number may occur in the nucleation mode, total particle number emissions from similar types of motor vehicles may vary by over an order of magnitude (Ristovski et al. 2004).

4.4 Role of Fuels

Particle emissions from motor vehicles are significantly affected by the nature of the fuel used and thus a considerable effort is being devoted to investigations of fuel properties and their impacts on particle emissions.

Sulphur in Diesel Fuel: The main source of chemically-bound sulphur in diesel fuel is that which occurs naturally in crude oil and is in a volatility range which leads to its incorporation in the diesel fuel fraction. The presence of sulphur is useful as it increases the lubricating properties of the fuel. During combustion, a fraction of this sulphur is oxidised to sulphur trioxide which binds with water to form sulphuric acid that contributes to total particle emissions. However, the presence of sulphur in diesel has

several other adverse effects such as the corrosion of the exhaust system and increased wear and tear on engine parts. For these reasons, measures have been taken to progressively reduce the sulphur content in diesel fuel worldwide. Currently, most industrialised countries use diesel fuel with a sulphur level of 5 to 50 ppm. In addition, it should be noted that sulphur compounds are also present in lubricating oils.

Several studies were conducted to investigate the effect of reducing the sulphur content in diesel on particle number emissions. Bagley et al. (1996) found a significant reduction of the number of nucleation mode particles from a heavy duty engine when the sulphur levels were reduced from 3200ppm to 100ppm. Andersson et al. (2001) investigated three heavy duty vehicles using diesel fuel of three sulphur levels: 340 ppm, 53 ppm, and less than 10 ppm, and showed that, while changes in accumulation mode particles could be attributed to changes in engine technology, the variation in nanoparticle number was more likely influenced by fuel properties. The fuel containing the highest sulphur content (340 ppm) showed the highest nanoparticle emissions for the 'weighted cycle' (where each stage of the cycle was weighted according to the time it contributed to the overall cycle), while the fuel with the lowest sulphur content (<10ppm) showed the lowest. They also concluded that the influence of the fuel sulphur content could not be fully decoupled from other chemical and physical effects within the tested fuels, such as the total aromatic content which varied between the fuels.

Ristovski et al. (2006) reported particle emissions from a fleet of twelve in-service buses fuelled by 50 and 500 ppm sulphur diesel at four driving modes on a chassis dynamometer and showed that particle number emission rates were 30-60% higher with the 500 ppm over the 50 ppm fuel. Most of the excess particles were smaller than 50 nm and resided in the nucleation mode.

Kittelson et al. (2002) measured nanoparticle emissions from a diesel engine on a dynamometer using fuels with three different levels of sulphur (1, 49 and 325 ppm) and two different lubricating oils (4000 ppm and 385 ppm sulphur). They observed that for conventional lubricating oil (385 ppm) and both 1

ppm and 49 ppm sulphur fuel, there was no significant formation of a nucleation mode. Increasing fuel sulphur to 325 ppm increased nanoparticle emissions, especially at high engine load. Sulphate particles are formed at high temperature conditions, such as at full engine load when more of the fuel sulphur is converted to sulphuric acid. When present, most of the nucleation mode particles were removed when passed through a thermodenuder, suggesting that they were highly volatile. Other researchers have observed nucleation mode particles even with very low sulphur levels (<10ppm) (Vaaraslahti et al. 2004) suggesting that other components, such as unburned hydrocarbons, can have an important role. At the low levels of sulphur in the fuel the amount of sulphur in the lubricating oil can have a major influence. The most surprising result was the large influence of specially formulated lubricating oil (Kittelsohn et al. 2002). Contrary to expectations, low sulphur oil led to an increase in nanoparticle formation in nearly all cases. It is possible that the increase in nanoparticle formation when using low sulphur oil was related to the formulation of the oil necessary to compensate for the removal of sulphur. It could also be due, in part, to the release of volatile components from the oil, related to the lack of oil break-in. Lubricating oil, unburned hydrocarbons from the fuel, as well as PAH's, could also play a critical role in the formation of the nucleation mode (Kittelsohn et al. 2002; Sakurai et al. 2003; Vaaraslahti et al. 2005; Ristovski et al. 2006). On the other hand, Vaaraslahti et al (2005) have observed a clear correlation between the lubricating oil sulphur content and nanoparticle formation only when the engine was equipped with a continuously regenerating diesel particulate filter (CRDPF).

Alternative Fuels: Liquefied petroleum gas (LPG) is generally perceived to be a cleaner fuel than unleaded petrol (Gamas et al. 1999). Ristovski et al. (2005) found that particle number emissions from LPG cars were up to 70% less than from similar unleaded petrol cars. Compressed natural gas (CNG) vehicles are known to emit considerably lower particle mass than equivalent diesel vehicles. However, there is considerable disagreement as to particle number emission levels. This is due to the small number of measurements reported and the difficulties in quantifying the effects of engine operating and testing

conditions and fuel and lubricating oil composition on secondary particle production. In relation to buses, it has been shown that, in general, particle number emissions from CNG buses are smaller than from diesel buses, but there are some exceptions, particularly related to high engine load conditions where large nuclei modes (<10 nm) and ultrafine particle number concentrations have been observed (Holmen and Ayala 2002). In addition, the nuclei mode particles observed at high loads are highly volatile (Meyer et al. 2006).

4.5 Role of After-Treatment Devices

There are two main particulate matter control technologies in use today. They are oxidation catalysts and particle traps.

Oxidation Catalysts: While oxidation catalysts reduce the soluble organic fraction (SOF), they have little effect on the soot or black carbon in the exhaust. Still, some reduction in particle mass emissions is achieved through the removal of the SOF. The maximum total particle mass reduction is dependent on the magnitude of the SOF compared to the carbonaceous portion in the engine-out exhaust, and is usually between 20% and 30% (Harayama 1992). The sulphate fraction of diesel particles (SO₄) is increased in the diesel oxidation catalyst, due to the oxidation of SO₂ with subsequent formation of sulphuric acid. Under certain conditions, however, the SOF decrease can be more than off-set by an increase of sulphate particle mass, leading to an overall increase in total particle mass emission. In general, the effect of oxidation catalysts on particle number emissions is often unpredictable. Total particle number concentrations, especially in diesel emissions, are attributed primarily to nucleation mode particles which are composed mostly of hydrocarbon and sulphuric acid condensates. If the catalyst removes hydrocarbons (gas phase and SOF), it will prevent their subsequent nucleation, thus reducing the particle number concentrations. If, however, the catalyst produces sulphates, an effect more

prominent with high sulphur fuels, and more active noble metal catalysts, the observed particle number concentrations may be higher than with no catalyst due to sulphuric acid nucleation (Vogt et al. 2003).

Particle Traps: Particle traps are very effective in controlling the solid fraction of exhaust particles, including elemental carbon (soot) and the related black smoke emissions. The filtration efficiencies of some commercially available diesel particle traps frequently exceed 90%. In light duty vehicles, Mohr et al (2006) showed a high efficiency of diesel particle filters (DPFs) in curtailing nonvolatile particle emissions over the entire size range. High emissions were observed only during short periods of DPF regeneration and immediately afterwards. However, they have limited effectiveness in controlling the non-solid fractions of particle mass, such as the SOF or sulphate particles that occur mainly in the liquid phase within the hot and humid emissions. For this reason, trap systems designed to control the total particle mass emission are likely to incorporate additional functional components targeting the SOF emission (e.g., oxidation catalysts). More recently, the introduction of ultra low sulphur diesel has helped to improve the efficiency of abatement devices, many of which are poisoned by sulphur. Emissions from diesel fuels containing sulphur levels of less than about 12 ppm will not poison these devices. Very often, volatile material pass through particle traps and nucleate to form nanoparticles that increase the total particle number. To make matters worse, by retaining carbon particles, the trap removes the material, which otherwise acts as a “sponge” for condensates formed in the sampling system. Therefore there is a possibility that in some cases particle traps can increase the formation of nanoparticles through nucleation. In effect, particle traps reduce the numbers of solid agglomeration mode particles by replacing them with liquid nucleation mode nanoparticles (Burtscher 2001).

Vaaraslahti et al (2004) have observed that in heavy duty vehicles at high loads nucleation mode particles form only when the engine is equipped with a continuously regenerating diesel particulate filter (CRDPF). The tests were conducted with two fuels of 2 and 40 ppm sulphur content and the nucleation

mode correlated with the sulphur level in the diesel fuel. In a later publication, Vaaraslahti et al (2006) show that the formation of nucleation modes in heavy duty engines with CRDPF is positively correlated not only with the fuel sulphur level but also with the lubricant sulphur level, suggesting that sulphuric compounds are the main nucleating species in this situation. Formation of nucleation mode particles was also observed on a heavy duty vehicle equipped with a continuously regenerating trap (CRT) during on-road highway cruise conditions (Kittelson et al 2006). The CRT has reduced the concentrations of accumulation mode particles to levels indistinguishable from background while increasing the emissions of particles in the nucleation mode. Similar to the observation by Vaaraslahti et al the increased emissions of nanoparticles was observed at higher engine loads when the exhaust temperature increased above about 300 °C therefore increasing the conversion of SO₂ emitted by the engine to SO₃.

However, the toxicity of these particles has recently been brought into question. Grose et al (2006) showed that nucleation mode particles emitted by a heavy duty diesel engine equipped with a catalytic trap are composed mainly of sulphates. This provides support for the argument that particulate emissions from diesel vehicles equipped with advanced particulate control devices might be less toxic than typical uncontrolled diesel emissions, which contain high concentrations of organic compounds. However, due to the complexity of diesel exhaust and the fact that sulphuric acid enhances polymerisation of organic compounds, as well as solubilises metals, further toxicology studies are required to evaluate the toxicity of these particles.

4.6 Role of Ions

The mechanisms behind particle nucleation in the atmosphere have been discussed in section 3 above, and in particular the role of binary homogeneous nucleation of sulphuric acid and water or ternary homogeneous nucleation involving sulphuric acid, water and ammonia. Theoretical models and experimental observations show that binary homogeneous nucleation alone cannot explain the observed

formation and growth rates of particles in the environment and, while ternary nucleation can explain observed nucleation rates in urban areas, it does not assist in explaining the rates observed in other environments that do not contain sufficiently high concentrations of sulphuric acid (Weber et al. 1996; Clarke et al. 1998; Yu 2001; Kulmala 2003; Alam et al. 2003). However, neither mechanism is capable of explaining the observed growth rates of ultrafine particles to cloud condensation nuclei (CCN) sizes. For example, Weber et al. (1997) demonstrated that growth rates of nanoparticles driven by binary and ternary nucleation is an order of magnitude too low to explain the rapid appearance of fresh ultrafine aerosols during midday. Alam et al (2003), while noting similar observations at urban sites showed that particle formation by homogeneous nucleation occurred on approximately 5% of the days studied and required condensable materials apart from sulphuric acid and water, together with a relatively low pre-existing particle surface area.

An alternative mechanism of particle formation is ion-induced nucleation. It has been shown that ion-induced nucleation occurs at a lower saturation ratio than homogeneous nucleation (Hara et al. 1997, 1998). Homogeneous nucleation can only occur spontaneously in highly supersaturated air. These conditions do not occur naturally in the atmosphere. However, homogeneous nucleation is aided by ions as gas molecules tend to condense and cluster around them. Yu and Turco (2000; 2001) showed that charged molecular clusters can grow significantly faster than neutral clusters and achieve stable observable sizes. Thus, this mechanism can operate under conditions that are unfavourable for binary or ternary nucleation. However, in a recent paper based on results from a study conducted in Hyytiälä, Southern Finland, Kulmala (2007) has argued that ion-induced nucleation cannot explain the large number of neutral clusters that were observed, suggesting that ternary, and not ion-induced, nucleation was probably the dominant process taking place in this Boreal forest environment. On the other hand, Yu and Turco (2008) used a global chemical transport model to show that ion-induced nucleation was an important global source of tropospheric aerosols. From these studies, it is clear that the relative

importance of ion-induced nucleation and neutral nucleation under varying atmospheric conditions remains largely unresolved.

Environmental ions are formed naturally by cosmic rays at a rate of about $2 \text{ ion pairs cm}^{-3} \text{ s}^{-1}$, while the main anthropogenic source of ions is combustion. The ion concentration falls off rapidly with distance from the source due to recombination. Ions generated from hydrocarbon flames play an important role in the formation of nanoparticles (Yu 2001). Positively charged ions have been detected in concentrations of up to $1.6 \times 10^8 \text{ cm}^{-3}$ in jet engine plumes (Arnold et al. 2000) and these might play a key role in the formation of volatile particles in the aircraft wake (Yu and Turco 1997). Also motor vehicle combustion is a significant source of ions that may play an important role in the formation of nanoparticles via ion-induced nucleation during the dilution and cooling of the hot emissions in air, especially in urban environments. Kittelson et al. (1986) monitored electric charges present on diesel emission particles and they showed approximately equal numbers of positively and negatively charged particles with 1-5 units of elementary charge per particle. The charge distribution with respect to size followed a Boltzmann equilibrium relationship equivalent to 1500K.

Yu et al. (2004) measured the ionic emissions from a petrol car and a diesel generator engine. They found that the total ion concentrations from the two engines were about $3.3 \times 10^6 \text{ cm}^{-3}$ and greater than $2.7 \times 10^8 \text{ cm}^{-3}$, respectively. Maricq (2006) studied the electric charge of particles in petrol and diesel vehicle exhaust using single and tandem differential mobility analysis. This method provided the means to sort the particles according to both their size and charge. About 60-80% of the particles were charged but with nearly equal numbers of positive and negative charge, leaving the exhaust electrically neutral. Charge increased with particle size, up to about ± 4 units of charge per particle. At a fixed particle size, charge per particle followed a Boltzmann distribution with temperature range 800-1100 K. Jung and Kittelson (2005) used an electrostatic filter and an SMPS to examine the charged fraction of diesel

particles as a function of their size. They showed that the diesel nanoparticles carried very little charge, while there was a large charged fraction of 60-80%, in the accumulation mode. In summary, these results show that vehicles emit ions of both signs, with the majority of the charges being carried on the larger particles.

4.7 Road-Tyre Interface

So far, tyre wear on the road has been considered to contribute mainly larger size particles ($>10\ \mu\text{m}$) in the air (Pierson and Brachaczek 1974). A recent study by Dahl et al. (2006) showed, however, that road–tire interface can also be a source of sub-micrometer particles. The study conducted in a road simulator showed that the mean particle number diameters were between 15–50 nm. The emission factor increased with increasing vehicle speed, and varied between 3.7×10^{11} and 3.2×10^{12} particles vehicle⁻¹ km⁻¹ at speeds of 50 and 70 km h⁻¹, which corresponds to between 0.1–1% of tail-pipe emissions in real-world emission studies. The authors hypothesised that the particles may originate from three components of the tires: (i) the carbon black reinforcing filler, (ii) small inclusions of excess ZnO or ZnS (ZnO is an activator for organic accelerators that are used to speed up the vulcanization process), (iii) the oils used as softening fillers. The authors suggested that since speed determines the amount of mechanical stress in the tire material it also determines the temperature in the tire, and increased temperature in turn leads to increased emissions of loosely bound reinforcing filler material and evaporation of semi-volatile softening oils. Clearly more research is needed on this topic.

4.8 Emission Factors and Emission Inventories

Emission Factors: An emission factor is the amount of pollutant emitted either when an activity is performed, for example, a vehicle drives a kilometre; or the amount of pollutant emitted per unit of fuel burned. Emission factor values are used for developing inventories for gaseous or particulate motor vehicle emissions, however in order to derive them many issues need to be considered and resolved. In

particular, they depend on motor vehicle type, fuel used, engine load, after-treatment devices fitted, road type, travel speed, road grade and local meteorological conditions. Current methods for deriving emission factor values range from measurement of single vehicles, to vehicle fleets using direct methods, such as measurements on a dynamometer, on or near roadways or in tunnels, or indirect methods such as estimates based on remote sensing or fuel consumption, particularly in relation to UF particles. In addition, a wide range of different instrumentation are used that measure different size ranges (as discussed in section 2). As a result, there are a lot of different values of emission factors published, on different types of measurements, in different parts of the world. This leads to the question as to which values should be used in quantifying and modelling traffic emissions.

Statistical analysis of particle number emission factors around the world: A detailed analysis by Keogh et al. (2007) that included statistical analysis of more than 160 particle number emission factors relating to motor vehicle tailpipe emissions revealed that emission factor values estimated from CPC measurements produced the highest mean values for Fleet, Heavy Duty Vehicle (HDV) and Light Duty Vehicles (LDV) of 7.26, 65 and 3.63×10^{14} particles per vehicle per kilometre respectively. The mean Diesel Bus emission factor value relating to measurements using the SMPS was found to be 3.08×10^{14} particles per vehicle per kilometre.

The review found that there is a significant difference between the means for measured particle number for CPC and SMPS instrumentation (23 and 2×10^{14} particles per vehicle per kilometre respectively); but no significant difference between the means of particle number emission factors for studies conducted in different countries (Australia, Austria, Germany, Sweden, Switzerland, United Kingdom, USA), nor between those for studies conducted on a dynamometer, or near roadways. Particle number emission factors for HDV were found to be significantly higher than the corresponding values from Fleet and LDV.

The range of particle number emission factors reported in four studies, that measured nanoparticle and ultrafine subclasses using the SMPS and DMPS (Gidhagen et al. 2003; Imhof et al. 2005a; Imhof et al. 2005b; Jones and Harrison 2006), are summarised in Table 1 below, where the range given represents the sum of the ranges taken from the four studies. Examination of this table highlights the importance of measuring size ranges < 18nm, where particle numbers tend to be more prolific, and in which the emission factor values are generally larger than those estimated for 18-50nm and 18-100nm.

Table 1. The range of particle number emission factors reported for nano and ultrafine size ranges.

Particle size classification	Size range measured, nm	Fleet 10 ¹⁴ particles per vehicle per km	Heavy Duty Vehicles 10 ¹⁴ particles per vehicle per km	Light Duty Vehicles 10 ¹⁴ particles per vehicle per km
<i>Nanoparticles</i>	< 10	--	14.5	0.63-4.14
	10-30	--	2.14-37.8	0.067-4.87
	18-50	0.59-1.31	1.55-8.2	0.13-0.56
<i>Ultrafine</i>	18-100	0.84-1.55	1.7-10.5	0.37-0.81
	30-100	--	3.19	0.284

Inventories of motor vehicle particle emissions: Estimates of emission inventories for particle number concentration are not available (Jones and Harrison 2006); nor does there exist a comprehensive inventory of vehicle particle emissions covering the full size range emitted by motor vehicles. The one reported inventory is the assessment conducted by Airborne Particles Expert Group (1999). For this assessment emission trends for the years 1970 to 1996 including inventories for PM_{2.5}, PM₁ and PM_{0.1} were estimated based on PM₁₀ UK monitoring data, using mass fractions in this size range available for different emission sources and fuel types and 33 particle number size distribution spectra. It was shown that in all size fractions, vehicle emissions are the major contributor, compared with all other combustion and non-combustion sources in urban areas. With decreasing particle size, the contribution of road transport to the total emissions increases and for PM_{0.1} reaches 60%. Contributions from other combustion sources tend to decrease with decreasing particle size. One of the conclusions from the data presented in the report is that there was a significant decrease in emissions in the PM₁₀ and PM_{2.5} ranges

during the investigated period of time, less in the PM_1 range and very little in the $PM_{0.1}$ range. This could be related to the lack of strategies for decreasing emissions of the UF particles. More effort is needed towards compilation of vehicle emission inventories for UF particles.

5. Transport of particles within urban scale and ambient processing

Vehicle emissions are highly dynamic and consist of reactive mixtures of hot gases and particles. The main factor determining the speed and direction of the pollutant plume away from the emission site is generally the prevalent wind. Other contributing factors include the initial speed of the pollutants emitted from vehicles, turbulence caused by vehicle motion, location of the exhaust, precipitation and the topography of the area. The pollutant plume undergoes dilution with ambient air and is subject to a range of physical and chemical processes, which change its chemical composition, physical characteristics and concentration in the air during the transport process. Also, soon after emission, when the pollutant plume is still concentrated, is the most likely period for secondary particle formation by nucleation involving precursors present in the emission plume, as discussed in section 4.4. Therefore particles measured away from the emission site, and some time after emission, have different characteristics to those measured immediately after formation.

5.1 Role of meteorological factors on particle concentration

The most important factors to consider include wind speed, precipitation, relative humidity and temperature.

Wind speed. Wind speed affects dispersion and dilution and thus atmospheric mixing, but also resuspension of particles. Several studies shown that UF particle concentration decreases, while concentrations of larger particles displays a “U shape” relationship with wind speed (Harrison et al. 2001; Ruuskanen et al. 2001; Molnar et al. 2002; Charron and Harrison 2003). Hussein et al. (2005a)

showed that UF particle number concentrations are best represented by a decreasing exponential function, with the minimum observed during wind speeds $>5\text{ms}^{-1}$, as a result of a higher coagulation rate, better air mixing, and more particle losses due to deposition and scavenging at these wind speeds. Particles larger than 100 nm showed a “U-shape” relationship, best represented by a second-order polynomial, with the minimum during wind speeds between $5\text{--}10\text{ m s}^{-1}$. Similar results were found by Charron and Harrison (2003) as to the trends for particles ranging from 30 to 100 nm and from 100 to 450 nm, as well as a twofold decrease from the weaker to the stronger winds. A decrease of about 10,000 normalised counts per cm^3 was seen for particles in the range from 30 to 100 nm and modal shift toward smaller values with increasing wind speed. However, no obvious relationship with the wind speed was seen for the particles ranging from 11 to 30 nm, and thus no dilution effect was evident for this particle range, which could be explained as characteristic of new particle formation. A study by Hussein et al. (2005a) showed another trend, namely that at some sites, particle number concentrations displayed a linear decrease with wind speed. This was explained by higher summer temperatures, which are accompanied by a high boundary layer and thus mixing of aerosol particles within a bigger volume. Under such conditions, the relative changes of particle concentration with wind speed are smaller compared to a shallow boundary layer and thus smaller volume of air mixing.

Precipitation. In general, precipitation has been shown to have a washout effect, which means removing particles from the atmosphere e.g. (Garcia-Nieto et al. 1994; Morawska et al. 2004) (Jamriska et al. 2007). However, a study by Charron and Harrison (2003) showed an opposite effect in relation to particles below 150 nm, namely an increase of particle numbers during rain, with larger rain drops (more than 0.4 mm) leading to higher particle numbers than smaller ones (0.2 mm). In addition, the highest particle numbers were measured just after a rain event (1 h after). The possible explanation for this phenomenon is an effect of reduced temperatures during precipitation events and thus higher saturation

ratio of semi volatile species combined with low pre-existing surface area of particles, both favouring new particle formation, and thus a significant increase of particle number concentration.

Relative humidity and temperature. These two parameters commonly display diurnal anti-correlation, with the increased temperature during the day accompanied by a decreased relative humidity. In general, both temperature and relative humidity play a role in UF particle number concentration (Charron and Harrison, 2003; Ruuskanen et al. 2001; Jamriska et al. 2007). Kim et al. (2002) showed that during the warmer months, there was some increase in particles smaller than 100 nm, in the afternoon, linked to an increase in temperature. Charron and Harrison (2003) showed that particles in the size range 11-30 nm in a roadside environment peaked during the early morning showing an inverse association with air temperature. Olivares et al (2007) found a distinctive dependence of particle number concentration with ambient temperature in a street canyon in Sweden. They found that the total particle number more than doubled when the temperature decreased from 15°C to -15°C. The variation was most pronounced for particles smaller than 40 nm. Modelling results predicted that the changes in the particle sizes observed were consistent with the condensation of volatile compounds onto pre-existing aerosols. They also showed that nucleation mode particles were largely influenced by relative humidity with high concentrations during high humidity periods. Hussein et al. (2005a) found that the high number concentration of particles larger than 100 nm during the higher summer temperatures was partly due to the growth of aerosol particles in the presence of condensable vapours emitted from the surrounding boreal forest in southern Finland. In general, higher atmospheric water content is expected to favour homogeneous binary nucleation of sulphuric acid and water (Easter and Peters 1994), while ternary nucleation involving ammonia (Korhonen et al. 1999), similarly to nucleation from organic compounds, is expected to be independent of relative humidity. Therefore, in the study by Charron and Harrison (2003) for example, the lack of a dependence on the relative humidity during the daytime was

considered indicative that the binary nucleation from sulphuric acid and water was not a major factor in particle production.

Temperature inversion. Under such conditions, there is little vertical mixing, wind speeds are lower and thus pollution concentration in general is expected to increase. For example, Janhall et al. (2006) showed that morning temperature inversion in Göteborg, Sweden, resulted in significantly elevated concentrations of traffic-related pollutants, including UF particles. Mean particle number concentrations on the days with and without morning inversions were 6500 ± 4800 and 2800 ± 1900 particles cm^{-3} , respectively. However, there was no impact of inversion on PM_{10} concentrations.

5.2 Relative role of various processes

The processes that dominate particle dynamics shortly after emissions by vehicles (i.e. when the concentration of the emission plume, while decreasing due to dilution and mixing, is still high) include: condensation/evaporation, coagulation and new particle formation. Several studies investigated the relative importance of these processes under various meteorological and pollution concentration conditions. During the dilution, when the initially hot mixture of pollutants is cooled down, the saturation ratio of gaseous compounds of low volatility reaches a maximum. This is when two of the above processes are possible: new particles formation by nucleation of vapours, and vapour condensation onto existing particles. The availability of pre-existing particle surface area for the condensation of the semi-volatile vapours along with the dilution rate, since it governs the cooling rate, will determine which of the two processes dominates. Small aerosol concentrations favour new particles formation and their growth to larger sizes (Kulmala et al. 2000), while high concentrations promote the condensation of the vapours on the existing particles and disfavour new particle formation (Kerminen et al. 2001). This is the reason why cleaner air resulting from stronger winds and rain, as discussed above, favour the occurrence of high numbers of UF particles. For example, Charron and Harrison (2003)

showed that large amounts of semi-volatile vapours from vehicle exhausts in the early morning, associated with low pre-existing particle surface area at that time (from about 300 to 500 $\mu\text{m}^2/\text{cm}^3$) favour production of new particles and their growth to detectable sizes (>11 nm). However, during daytime, when the particle surface area ranges from 800 to 1100 $\mu\text{m}^2/\text{cm}^3$, condensation of the condensable gases onto existing particles is likely to dominate. In comparison to the processes discussed above, coagulation appears to be overall a less important process, due to short time available for it to be effective before the high initial concentrations at the road are diluted. Analysis conducted by Shi et al (1999) to estimate the expected effect of coagulation on the decrease of particle number concentration showed that the concentrations between the road and a site 100m away from the road would decrease by less than 11% due to coagulation, compared to a 72% decrease in measured concentrations, implying that dilution with background air is the main mechanism for the rapid decrease in particle number concentration. However, Zhu et al. (2002a) concluded that both atmospheric dilution and coagulation play important roles in the rapid decrease of particle number concentration and the change in particle size distribution with distance away from a freeway. The study by Zhu et al. (2002b) suggested that coagulation is more important than atmospheric dilution for ultrafine particles and the reverse is true for large particles. This contradicts some earlier studies which concluded that the rapid dilution of the exhaust plume made coagulation insignificant (Vignati et al. 1999; Shi et al. 2001a), with the possible reason for this being that the earlier studies assumed a much lower particle number concentration for particles smaller than 15 nm, while this study accurately measured freshly emitted particles down to 6 nm.

Zhang and Wexler (2004a) identified two distinct dilution stages after emission. The first stage, termed tailpipe-to-road, was induced by traffic-generated turbulence and occurred soon after emission, lasting about 1-3 s, when the dilution ratio reached up to 1000. The second stage was mainly dependent on atmospheric turbulence and lasted 3-10 min, with an additional dilution ratio of about 10. In the first

stage, aerosol dynamic processes such as nucleation, condensation and coagulation played major roles. In the second stage, condensation was the dominant mechanism in altering the aerosol size distribution, with coagulation and deposition playing minor roles. Exhaust plumes emitted by different types of engines maintained their characteristics in the first stage but generally mixed with each other in the second stage. A similar conclusion was reached by Pohjola et al. (2003) based on the application of an aerosol process model MONO32. The effect of coagulation was substantial only if the dilution of the exhaust plume was neglected, which is not realistic under most conditions (unless during temperature inversions or a very stable atmosphere). Condensation of an insoluble organic vapor was shown to be important if its concentration exceeds a threshold value of 10^{10} or 10^{11} cm^{-3} for the Aitken ($\sim 50\text{nm}$) and accumulation ($>100\text{nm}$) mode particles, respectively. The importance of condensation or evaporation of water was shown to be strongly dependent on the hygroscopicity of particles. The modeling showed that after a time of 25s, most of the particulate matter transformation processes have already taken place.

It has been suggested that sulphuric acid induced nucleation was the dominant secondary particle production mechanism in the first stage, followed by the condensation of organic compounds (Kittelson 1998; Maricq et al. 2002; Zhang and Wexler 2004a). Schneider et al. (2005) showed that nucleation was mainly due to sulphuric acid and water and low volatile organic species condensed only on pre-existing sulphuric acid/water clusters. However, other studies have suggested that the volatile component of total diesel emission particles was comprised mainly of unburned lubricating oil (Tobias et al. 2001; Sakurai et al. 2003). Recently, Meyer and Ristovski (2007) have shown that ternary nucleation involving ammonia as the third species, is the main nucleating mechanism, followed by the condensation of volatile organic components. Zhang and Wexler (2004a) showed that the first stage of dilution was crucial for the activation of nuclei mode particles due to the high concentration of condensable material during this time.

A deeper insight into the role of the key process was provided by Zhang and Wexler (2004b) whose modelling showed that for particles larger than 0.05 μm , coagulation is too slow to influence number distributions and condensation is the leading process. However, for particles smaller than this, under typical urban conditions, condensation and evaporation, coagulation, nucleation and emissions interact with each other and the Kelvin effect must be considered in modelling. Gravitational settling was shown to significantly affect particle dry deposition, but negligible for vertical turbulent transport; chemical reactions are negligible. It was noted that the relative importance of different mechanisms remains about the same during the day and night time. During the night time, with photochemistry cut off and significantly decreased emissions, concentrations of both volatile or condensable gases and particles is lower leading to the increased time scales for the process, but thus maintaining their relative importance.

In addition to particle growth and dilution, Jacobson et al (2005) showed that that small ($< 15 \text{ nm}$) liquid nanoparticles emit semi volatile organics ($< \text{C-24}$) almost immediately upon emission and that the shrinking of these particles enhances their rates of coagulation by over an order of magnitude. Enhanced coagulation in isolated emission plumes may also affect evolution of particle size distribution. Importantly, they concluded that neither condensation, complete evaporation, coagulation alone, nor preferential small-particle dilution appears to explain the evolution of particle sizes in the vicinity of busy roads.

5.3 Particle size distributions and modal location in urban environments

Particle number size distributions in vehicle emissions often show a characteristic bimodal distribution (Kittelson 1998; Kwon et al. 2003; Vogt et al. 2003; Ristovski et al. 2006). Most of the particulate mass is generally found in the accumulation mode ($> 50\text{nm}$) while a considerable number fraction of the particles may occur in the nucleation mode ($< 30\text{nm}$). Bimodal size distributions have also been observed near busy roads (Pirjola et al. 2006). Distinct ultrafine modes in the particle number

distributions have been found in the size range 10-20 nm on the downwind side but not on the upwind side of busy freeways (Zhu et al. 2002a; Rosenbohm et al. 2005).

A recent literature review of modal locations identified in ambient particle size distributions in a range of worldwide environments (34 studies) found that for particle number modal location values spanned 0.006 to 30 μm , with approximately 98% of these values being $\leq 1 \mu\text{m}$ (Morawska et al. 2007a). Anthropogenic-influenced environments included those in suburban environments in Australia and Finland (Morawska et al. 1999c; Hussein et al. 2005b), urban in Australia, Finland, Germany, Hungary, India and the USA (Morawska et al. 1999c; Salma et al. 2002; Wehner et al. 2002; Wiedensohler et al. 2002; Fine et al. 2004; Hussein et al. 2004; Hussein et al. 2005b; Monkkonen et al. 2005); and traffic-influenced environments in Australia, Finland and Germany and the US (Morawska et al. 1999c; Zhu et al. 2002a; Zhu et al. 2002b; Pirjola et al. 2004; Zhu et al. 2004; Rosenbohm et al. 2005; Zhu et al. 2006).

When considering modes identified in these studies in the $\leq 50\text{nm}$ size range it was found that in anthropogenic-influenced environments they ranged from 8.2-50nm for suburban and urban, and included modes at 7,10, 13, 15, 16, 19, 20, 27 and 30nm in traffic influenced, likely reflecting the influence of motor vehicle emissions. Modes identified in the $> 50 \leq 100\text{nm}$ size range in the anthropogenic-influenced environments were in the range 50.2-65nm in suburban, traffic and urban; and at around 80nm in urban and traffic. Additional modes were found in suburban in the range 92-100nm.

6. Chemical composition of ultrafine particles in different environments

There have been relatively few studies reported, which investigated any aspects of chemical composition of UF particles in ambient air. Moreover, each study was conducted in a different way, sampled particles in a different size range, and focused on different aspects of particle chemical composition. Therefore, at present a comprehensive knowledge on UF particle composition in different environments is not

available. This review summarises the results of the few studies reporting UF particle chemical composition.

As discussed earlier, engine emissions include SO_2 or SO_3 and NO (later converted to NO_2). Transformations in the air of SO_2 , NO_2 and NH_3 from vehicle emissions into SO_4^{2-} , NO_3^- , and NH_4^+ is important for increasing secondary aerosol formation near traffic sites. Three studies investigated these aspects of UF particle chemistry in urban environments. (Kuhn et al. 2005) investigated particle chemical composition in a park 5 km downwind of downtown Pittsburgh. The study showed that UF mass was about $0.6 \mu\text{g m}^{-3}$ and its summer composition was 45% organic matter and 40% salts of ammonium and sulphate, compared to 55% organic matter and 35% of the sum of ammonium and sulphate during winter. This shift was explained as being likely due to higher summertime levels of photochemical activity for oxidation of SO_2 , and increased wood burning and vehicular organic contributions in wintertime. UF chemical composition was also studied by Sardar et al. (2005) and showed a significant seasonal change from summer to winter. Lin et al. (2007) investigated water-soluble ions in nano ($\text{PM}_{0.01-0.056}$) and ultrafine ($\text{PM}_{0.01-0.1}$) size ranges in samples collected near a busy road and at a rural site. Several conclusions were derived from this study. It was shown that the primary, secondary and tertiary peaks of SO_4^{2-} and NH_4^+ were in the fine ($0.56-1.0 \mu\text{m}$), coarse ($3.2-5.6 \mu\text{m}$), and nano ($0.032-0.056 \mu\text{m}$) size ranges, respectively. The second and third peaks of NO_3^- were in the same sizes ranges as those for SO_4^{2-} and NH_4^+ ; however, the primary peak for NO_3^- was in the size range of $1-1.8 \mu\text{m}$ and slightly larger than that of SO_4^{2-} and NH_4^+ . Nano ($\text{PM}_{0.01-0.056}$) and coarse ($\text{PM}_{2.5-10}$) particles exhibited the highest (16.3%) and lowest (8.37%) ratio of nitrate mass to total particle mass, respectively. The mass ratio of NO_3^- was higher than that of SO_4^{2-} (contrary to the trend commonly observed for urban atmospheric particles) and also more variation existed in NO_3^- concentrations for different size range particles at the roadside site than at the rural site. For both sites, NO_3^- concentrations in nano and UF particles were about two times higher than that for coarse particles and the nano NO_3^-

concentration at the roadside site was 1.34 times that at the rural site. The peak of NO_3^- in the ultra-fine size range in this study was attributed mainly to vehicle engines, while the peaks of SO_4^{2-} and NH_4^+ in the nano size range to $(\text{NH}_4)_2\text{SO}_4$ aerosols formed via the interaction of NH_4^+ and SO_4^{2-} . At the two sites, no significant difference in NH_4^+ concentration was found in each of the different size ranges investigated. However, at the rural site, NH_4^+ was highly correlated with SO_4^{2-} in each of the three particle size ranges - nano, ultrafine, and coarse, with R values of 0.89, 0.60, and 0.86, respectively.

Somewhat different aspects of UF particle chemistry were studied by Woo et al. (2001a) who investigated evaluation of outdoor and indoor particle volatility near a freeway by heating particles and detecting changes in their diameters and number concentrations. The study showed that aerosol volatility decreases with increasing distance from the source (in this case the differences between outdoor and indoor particles). Monodisperse distribution was observed for 18 and 27 nm particles with the mode diameter decreasing with increasing heater temperature (thus suggesting that all of these particles are composed mostly of volatile material), and also broadening because not all particles shrink to the same degree due to differences in their chemical composition. Bi-modal distributions were observed for outdoor 45 and 90 nm particles heated to 110°C . In particular the 90 nm mode split into two at heater temperatures of 90°C , with one mode remaining close to the monodisperse mode of the unheated aerosol, while the other shifting to a lower diameter. This bi-modal distribution indicates that a fraction of the 90 nm aerosol consists of particles that are composed of almost entirely non-volatile material and therefore does not change size upon heating, and the remaining fraction contains mostly volatile material and continue to shrink in size with increasing temperature. For temperatures of up to 130°C the diameter of the volatile particles in the whole range investigated (18–90 nm) was still shrinking (at this temperature decreased to about half the diameter compared to the original size at ambient temperature) without a clear evidence of a plateau which would indicate the presence of a non-volatile core; thus if a non-volatile core exists, its diameter will be smaller than that reached by particles at 130°C .

Elemental Carbon (EC) is usually considered a marker of the combustion process; with diesel engines as predominant sources of EC to the urban atmosphere. Sardar et al. (2005) investigated chemical composition of UF particles at two sites (urban and inland). The study showed that organic carbon (OC) ranged from 32 to 69%, EC from 1 to 34%, sulphate from 0 to 24% and nitrate from 0 to 4%. This was somewhat different to the findings from the study by Kim et al. (2002) who showed that OC and EC contribute 35%, sulphate 33%, and nitrate and ammonium 6% and 14%, respectively, with other unknown substances contributing 12%. Kim et al. (2002) also showed that in all cases, a greater fraction of the total mass consists of OC in the UF mode than in the corresponding accumulation mode. Similar conclusions can also be drawn for EC. A distinct OC mode was observed between 18 and 56 nm in the summer and not present in the other seasons, indicating photochemical secondary organic aerosol formation. The EC levels were higher in winter at the source sites and in summer at the receptor sites due to lower inversion heights and increased long-range transport from upwind source areas, respectively. Nitrate was more prevalent in the accumulation mode and almost not measurable in the UF particles. This was related to the process of formation of ammonium nitrate when the nitric acid in photochemical smog in air parcels originating near downtown Los Angeles Basin encounters ammonia. Higher summertime temperatures and lower relative humidity favour the dissociation of particulate ammonium nitrate, which is more pronounced for UF particles due to the Kelvin effect. Sulphate, which similar to nitrate, was only detectable in the size ranges above 56 nm made up greater percentage of the total mass in the accumulation than the UF mode in fall and winter, however a higher proportion in both modes during the summer, likely due to its photochemical origin. It was suggested that the absence of sulphate in the smaller particles indicated that the majority of the particulate sulphate is formed on pre-existing particle surfaces or by liquid-phase reactions of sulphuric acid. The study by Kim et al. (2002) also supported the general findings from an earlier study conducted in the same area by Turpin and Hutzincker (1995), who also investigated the significance of secondary organic aerosol formation by

plotting OC against the EC concentrations. The average ratio of OC to EC at a site affected directly by traffic and at a site downwind from that one estimated from slope of the linear regression, were 3.5 and 8.6, respectively implying the existence of secondary organic aerosols in UF particles at second site.

UF chemistry, including elemental composition was investigated by Pakkanen et al. (2001), including over 40 chemical components of samples from an urban and rural site in the Helsinki area. While the average UF particle mass concentration was higher at the rural (520 ng/m^3) than at the urban site (490 ng/m^3), the average chemical composition of UF particles was similar at the two sites. The most abundant of the measured components were sulphate (32 and 40 ng/m^3 for the urban and rural sites, respectively), ammonium (22 and 25 ng/m^3), nitrate (4 and 11 ng/m^3) and the Ca^{2+} ion (5 and 7 ng/m^3). The most important metals at both sites were Ca, Na, Fe, K and Zn with concentrations between 0.7 and 5 ng/m^3 . Of the heavy metals, Ni, V, Cu, and Pb were important with average ultrafine concentrations between about 0.1 and 0.2 ng/m^3 . Also the organic anions oxalate (urban 2.1 ng/m^3 and rural 1.9 ng/m^3) and methanesulphonate (1.3 and 1.7 ng/m^3) contributed similarly at both sites. The measured species accounted for only about 15-20% of the total UF mass. While not measured, it was estimated that the amount of water was about 10% (50 ng/m^3) and that of carbonaceous material about 70% (350 ng/m^3) at both sites. At both sites the contribution of UF to fine was especially high for Se, Ag, B, and Ni (10-20%) and at the rural site also for Co (20%), Ca^{2+} (16%) and Mo (11%). Enrichment in the UF particles suggests that local sources may exist for these elements. Aitken modes turned out to be useful indicators of local sources for several components. The Aitken modes of Ba, Ca, Mg and Sr were similar in several samples, suggesting a common local combustion source for these elements, possibly traffic exhaust. Co, Fe, Mo and Ni formed another group of elements often having similar Aitken modes, the likely source being combustion of heavy fuel oil.

In summary, it can be concluded from the review of the studies which analyse UF particle composition that almost all the studies focused on different aspects of particle chemistry, with some of them targeting ion or elemental composition, other studies particle volatility, and yet others investigating elemental and organic carbon fractions. It is therefore important that more studies are conducted on particle chemical composition, which would investigate in parallel a range of different aspects to provide a more complete understanding on the chemistry of UF particles and its local variation.

7. Temporal variation of particle characteristics

7.1 Diurnal variation

In urban environments, strong diurnal variation of particle concentration has been reported by many studies and shown to closely follow the temporal variation in traffic density, with the highest levels observed on weekdays during rush hours (Ruuskanen et al. 2001; McMurry and Woo 2002; Charron and Harrison 2003; Paatero et al. 2005; Morawska et al. 2007c). It has been reported that there are differences in the pattern for different weekdays, with for example Friday having higher concentrations, and also between Saturday and Sunday, reflecting different traffic flowrate patterns on different days (Hussein et al. 2004). As shown by many studies (e.g. (Morawska et al. 2002; Hussein et al. 2004)), the daily pattern of aerosols on weekdays is characterized by two peaks coinciding with the traffic rush hours, while on weekends, by a wide peak in the middle of the day. It is, however, the concentration of the nucleation and Aitken modes particles which follows this trend, with far fewer particles in the accumulation mode, indicating exhaust as a major source of UF, but not of larger particles in urban air (Hussein et al. 2004; Hussein et al. 2005a). Stanier et al. (2004a) showed that strong diurnal trends were most apparent in the aerosol number, in contrast to aerosol volume distribution, for which seasonal trends were the strongest. In addition to the impact of traffic emissions, the process of secondary particle formation contributes to the variation in daily pattern of aerosol concentration, with the impact varying during different seasons.

7.2 Seasonal variation

There are several factors contributing to seasonal variation in particle concentration, including those leading to an increase, such as: lower mixing layer height and greater atmospheric stability in winter (due to less dispersion), lower winter temperature (increased nucleation events of combustion exhaust emitted from motor vehicles particularly during morning rush), and increased photochemical particle formation during summer; as well as those leading to a decrease, such as: lower traffic flow rate during summer holiday periods. All the studies investigating seasonal variation in particle concentration in the Northern hemisphere showed that there are clear seasonal trends (Zhang et al. 2004a; Zhang et al. 2004b; Paatero et al. 2005; Pirjola et al. 2006; Virtanen et al. 2006), contrary to a study conducted in the Southern Hemisphere, in Brisbane, Australia, which did not show a trend (Mejia et al. 2007b). While the studies conducted in the Northern Hemisphere were in areas where there are significant meteorological differences between the seasons, and thus seasonal variations in human activities, in subtropical Brisbane there are much smaller differences between the seasons.

With the number of factors affecting particle concentrations it is not surprising that there are differences in the magnitude and time of occurrence of peaks and troughs in the concentrations between different geographical locations. Most of the studies reported the lowest total number concentrations in summer with the highest in winter but sometimes also in other seasons. Pirjola et al (2006) and Virtanen et al. (2006) showed that the average concentrations in winter in Finland were 2–3 times higher, with the highest of $183\,000\text{ cm}^{-3}$ observed in February. Similar results were reported by Wehner and Wiedensohler (2003) in Leipzig, Germany. Zhang et al. (2004b) found the highest monthly mean for N_{11-50} particles for Pittsburgh, USA, in December, with a mean of $7630 \pm 3710\text{ cm}^{-3}$ while lowest of $4280 \pm 2250\text{ cm}^{-3}$ in July. In winter most of the factors leading to the increase in particle concentration tend to occur at the same time: morning traffic rush, when the mixing height is the lowest, coinciding

with the lowest wind speed and temperature. However, Hussein et al. (2004) and Laakso et al. (2003) showed that while the lowest total and nucleation mode particle number concentrations were observed in Helsinki and in northern Finland during summer, the highest were during spring and autumn, and the cleaner the air, the stronger the cycle was. Summer minima were associated with higher temperatures (which limit the nucleation due to temperature dependence of saturation vapour pressures) and better mixing, and in Helsinki, with less traffic in July. Springtime maximum was associated with nucleation of exhaust gases (favoured by low temperatures combined with the low boundary layer height and high radiation) and transport of new particles from cleaner areas.

In general, seasonal daily variation in the accumulation mode particles is less or not significant, while the variation was larger in the UF particles; especially nucleation mode particles (Hussein et al. 2004). Wehner and Wiedensohler (2003) showed that the maximum concentration for both summer and winter occurred for a particle size between 10 and 20 nm. McMurry and Woo (2002) studied ambient aerosols in urban Atlanta, Georgia, and found that for particles between 10 and 100 nm, average concentrations tended to be highest during winter, while concentrations of particles in the 3-10 nm range increased in the summer due to photochemical nucleation, which depends strongly on the intensity of solar radiation. Evidence of summer nucleation was also found by Sardar et al. (2005) and Geller et al. (2002), who showed elevated levels in the mass concentrations in the 32-56 nm size range. Summer nucleation events lead to rapid changes in particle concentrations and as Zhang et al. (2004b) showed, the highest variation was found in July.

7.3 Long term variation

The number of studies investigating long term trends in particle concentrations is limited. Some insight into particle number concentration trends was provided by the studies conducted at different locations in former East Germany, including the city of Erfurt and the counties of Bitterfeld, Hettstedt and Zerbst, during two different campaigns, the first one in the early and the second one in the late 1990's, which found that UF particle number increased between 38.1% (Pitz et al. 2001) and 115% (Ebelt et al. 2001). Wahlin et al (2001) measured particle number concentration and size distributions in a street canyon in Copenhagen over two 2-month campaigns during Jan-Mar 1999 and Jan-Mar 2000 and found a significant decrease in ultrafine particle concentration. This observation was attributed to a 56% fall in the average particle emission from diesel vehicles due to the reduction of the sulphur content in the fuel from approximately 0.05% to less than 0.005% implemented in Denmark in July 1999. A handful of investigations have continuously monitored submicrometer particles for periods of at least one year but no evidence on the long-term trends was reported (Morawska et al. 1998b; Woo et al. 2001a; Wehner and Wiedensohler 2003; Cabada et al. 2004; Paatero et al. 2005; Watson et al. 2005). Exceptions to this are two studies conducted in Finland and in Australia. Hussein et al.(2004), who measured particle number for over a six-year period in Helsinki, found that annual geometric mean particle number concentration increased by 3.2% in 1999, followed by a decrease of 6.7% in 2000, and 17.6% in 2002. Although the monitoring site was moved after the first three years 3km from its original location, thereby influencing the results, their main conclusion was that the annual variation in total particle number was associated with traffic density and the predominance of new vehicles in the Helsinki area. Long trends were investigated over a five-year period in Brisbane, Australia. Particle size distribution was summarized by total number concentration and number median diameter (NMD) as well as the number concentration of the 0.015-0.030 (N_{15-30}), 0.030-0.050 (N_{30-50}), 0.050-0.100 (N_{50-100}), 0.100-0.300 ($N_{100-300}$) and 0.300-0.630 ($N_{300-630}$) μm size classes. Morning and afternoon measurements, the former representing fresh traffic emissions from a nearby freeway (based on the local meteorological

conditions) and the latter well-mixed emissions from the central business district, during weekdays were extracted for time series analysis. Only the morning measurements exhibited significant trends. During this time of the day, total particle number increased by 105.7% over the period of five years and the increase was greater for larger particles, resulting in a shift in NMD by 7.9%. There was no evidence to suggest that traffic flow in the freeway has increased to cause the increase in particle concentration, and it was suggested that the increase was likely due to changes in the composition of the freeway traffic, however, this hypothesis could not be verified. More studies on long term trends are critically needed.

8. Spatial distribution of particle concentrations within urban environment

The three most common approaches to experimental studies concerned with small-scale (urban scale) spatial variation in particle concentration, have generally included: (i) measurements as a function of the distance from a major road; (ii) measurements at a major road or in its immediate vicinity, as well as at side streets; and (iii) measurements at several locations within the city. This section discusses separately the outcomes of each of these types of studies, and concludes with an overall comparison of ultrafine particle number concentration in different environments. Not discussed here are vertical profiles of particle concentrations, of particular importance in relation to urban canyon effects, which are discussed elsewhere (Hitchins et al. 2002; Longley et al. 2003; Vardoulakis et al. 2003; Imhof et al. 2005b).

8.1 Particle concentration as a function of the distance from the road

These studies are ideally conducted in areas where airflow between the road and the monitoring site is undisturbed by buildings or other barriers. As an outcome, such studies provide information about small-scale particle dispersion, where the shape of the dispersion function is similar between the studies, and thus of general applicability to other sites of similar topography. The studies investigated changes to the total particle number concentration as well as to the size distribution, and some of them also compared changes to particle concentrations with the concentrations of gaseous pollutants emitted by vehicles. In general, all such studies showed, as expected, a decrease in particle concentration with distance from the

road, up to about 300 m, beyond which particle concentration levels and size distributions approach the local urban background (Morawska et al. 1999b; Shi et al. 1999; Hitchins et al. 2000; Zhu et al. 2002a).

At the road, particle concentrations range between 10^4 and 10^6 particles cm^{-3} , and show association with vehicle flow characteristics (higher the speed, the greater the particle concentration, and the smaller the particle size), with less variation observed in particle volume compared to particle number size distributions (Kittelson et al. 2004). Virtanen et al.(2006) showed that the total concentrations at roadside were dominated by nucleation mode particles, were increasing with increasing traffic rate and the effect of traffic rate were stronger on particles smaller than 63 nm than on the larger particles. Harrison et al.(1999) reported that at the road significant numbers of particles are in the 3-7 nm size range, with a mode below 10nm, attributable to homogeneous nucleation processes. The roadside measurements show rapid variation, with two modes at 10 and 30 nm, and other modes present at a number of different particle sizes (between 20 and 50 nm and 100 and 200 nm), and changing very quickly between measurements (Harrison et al. 1999; Morawska et al. 2004).

Studies investigating total particle concentration levels showed the decrease with the distance from the road to be exponential or according to the power law. This is similar to the studies investigating gradients of NO_2 concentrations in the vicinity of roads (e.g. (Nitta et al. 1993; Kuhler et al. 1994; Roorda-Knape et al. 1998)), which found them to be curvilinear. Shi et al (1999) showed that total particle number concentration in the size range from 9.6 to 352 nm at the busy road site was 3.6 and 3 times higher, compared to two sites at a distances of 30 and 100m from the road, respectively. A study by Hitchins et al. (2000) conducted for total particle number concentration in the size range from 15 to 697 nm showed that for conditions where the wind was blowing directly from the road, at a distance of approximately 100 - 150 m from the road, the concentration decayed to about half that of the maximum occurring at 15 m from the road (the nearest measuring point to the road), which reduced to 50 – 100 m

for wind blowing parallel to the road. Zhu et al. (2002a) showed that particle number concentration in the size range from 6 to 220 nm as a function of distance from a road ranging from 17 to 300 m displayed an exponential decreasing trend, similarly to the concentrations of CO and black carbon. Pirjola et al. (2006) showed that at a distance of 65 m from the roadside, the average concentration reduced to 39% in winter and to 35% in summer with the wind perpendicular to the road whilst for wind blowing along the road in it decreased to 19% in summer.

Gramotnev et al (2003) modelled particle dispersion using a scaling procedure for CALINE4 developed for this purpose, and compared the results with measured total particle concentration in the size range of 0.015 to 0.700 μm at distances between 15 and 265 m from the road. The authors concluded that particle concentration reduces as a power law with the distance from the road, with the typical difference between the theory and average measured concentration being of the order of 10%, which was likely due to processes not included in the modelling, in particular coagulation.

As discussed in Section 5.2, it has been shown that the dynamic pollutant mix evolves during transport from the road: nucleation leads to formation of new particles very soon after emissions, followed by their growth by condensation, diffusion to surfaces and coagulation. Therefore, at the road, particle concentrations are dominated by the smallest particles, with the peak in distribution shifting to the larger sizes at greater distances. Initially these smallest particles are below < 10 nm, and therefore not measured if the instrument window is above this. As they grow with time and thus distance from the road, they become “visible” to these instruments. As this occurs over the distance of about 90 m, there have been particle number increases reported at such distances. In particular Zhang et al. (2004a) showed that a large number of sub-6nm particles emitted from freeways may grow above 10 nm around 30–90 m downwind. Afterwards, some shrink back to sub-10 nm and some continue growing to above the 100nm range. Zhu et al. (2002a) measured particle size distributions in the size range of 6–220nm at

a distance from 17 to 300m downwind of freeway. At 17m downwind from the freeway, the dominant mode was around 10nm with a modal concentration above $3.2 \times 10^5/\text{cm}^3$ and at 20m from the freeway its concentration decreased to $2.4 \times 10^5/\text{cm}^3$. At 30 m its concentration decreased by about 60% with a slight shift in its location. It then kept shifting to larger size ranges with its concentration decreasing for farther sampling locations and to disappear at distance $>150\text{m}$ from the freeway. The second mode at 17m downwind from the freeway was around 20nm with a concentration of $1.5 \times 10^5/\text{cm}^3$ which remained more or less unchanged at 20m, but the mode shifted to 30 nm at 30 m and continued to shift to larger sizes with the distance from the freeway. Number concentrations of particles $<50\text{nm}$, dropped significantly with increasing distances from the freeway, but for those $>100\text{nm}$, number concentrations decreased only slightly. Particles in the size range of 6 to 25nm accounted for about 70% of total UF particle number concentration, which decayed exponentially to about 80% of the roadside value, at 100m, levelling off after 150m. The concentrations in the size ranges 25–50 and 50–100nm, experienced a shoulder between 17 and 150 m. Very similar results were obtained by Zhu et al. (2002b) who also showed that at 30 m downwind from the freeway, three distinct modes were observed with geometric mean diameters of 13, 27 and 65 nm and the smallest mode, with a peak concentration of $1.6 \times 10^5 \text{ cm}^{-3}$, disappeared at distances greater than 90 m.

8.2 Relationship between on-road and urban background particle concentration

A number of studies monitored concentration of particle characteristics in urban sites located at various orientations in relation to the urban traffic, or from mobile laboratories moving around the city. Most commonly the aims of such studies were to compare the differences between local hot spots and urban background locations, rather than to provide a comprehensive characterization of the relationship between the concentrations and the distance from a particular street or traffic flow. In addition, each of the studies was concerned with investigating some other relationship, for example between the parameters measured in relation to the site location. While direct comparison of the results from the

studies is not possible, as the design of each of the studies was different in terms of site locations in relation to traffic areas, and also in terms of parameters measured, some more general conclusions can be drawn from them. In particular the studies showed that:

- Concentration of particle number decreases as the distance of the monitoring site from the street increases e.g. (Buzorius et al. 1999; Kittelson et al. 2004; Westerdahl et al. 2005) and that the difference between close to traffic and away from the traffic concentrations are much larger for particle number than PM_{10} concentrations e.g. (Harrison et al. 1999; Holmes et al. 2005).
- Particle size distribution is much more stable at background urban sites, where it is likely to be unimodal, than close to traffic where it is multimodal and rapidly changing e.g. (Harrison et al. 1999; Morawska et al. 2004).
- Near traffic, the nanometre fraction of UF dominates the total particle number concentrations, and their contribution decreases with distance from traffic (Ketzler et al. 2003; Kittelson et al. 2004).
- Characteristics of UF particles are more closely related to the number of heavy-duty vehicles than to the number of light-duty vehicles (Junker et al. 2000; Holmes et al. 2005; Westerdahl et al. 2005).

All these findings support the findings of studies which investigated particle characteristics as a function of distance from the road (see Section 7.1), which, by their design, controlled better for all the influencing factors. The main significance of studies comparing particle characteristics across different urban areas is in provision of information on the magnitude of local variation in particle concentrations levels as well as size distribution, with less significance for global comparisons.

8.3 Nucleation mode and its impact on urban particle concentrations

The mechanisms and conditions that favour formation of secondary particles by nucleation of condensable species in the air were discussed in general in chapter 4.4. This section will focus on the frequency, temporal variation and the magnitude of the contribution of nucleation events to particle number concentrations. Since during some of these events particle concentrations increase sometimes by

one to two orders of magnitude, their occurrence may have a profound impact on any future approaches to routine monitoring of particle number concentration, interpretation of monitoring results and setting particle number concentration guidelines or standards. Most commonly, nucleation events were observed during: (i) morning rush hours, and (ii) around midday. Therefore, mainly these two types of events and their impact on particle characteristics are discussed here. However, Woo et al.(2001b) reported a third type of event, with particles in the range 35–45 nm, occurring during the late evening on several days in April and September, at an average temperature of 23°C, which showed extraordinarily high concentrations, with an increase by factors ranging from 26 to 350. The source of these particles remains unknown, although elevated levels of SO₂, NO_x and NO_y were also observed, indicating that a plume from a larger source may have passed the measurement site during this time. The presence of elevated SO₂ suggests that an industrial source may have played a role.

Morning rush hours nucleation events, when increased emissions of condensable species from vehicles combined with lower temperatures (particularly during winter months), result in conditions enabling particle nucleation when exhaust mixes with cool ambient air. Occurrence of such events were reported by Wehner et al. (2002), Zhang et al.(2004b) and Zhang and Wexler (2004a). Particles during these events are formed following direct emissions from motor vehicles and thus their concentrations are correlated with CO increases (Zhang et al. 2004b). Woo et al. (2001b) also reported elevated concentrations of SO₂, NO, NO_x, as well as CO (for 12 out of 18 events). Increased concentrations of particles in the size range of 3–10 nm, but mainly 10–100-nm, were reported during these events in urban Atlanta, Georgia (Kittelson et al. 2004), with the average values of particle concentrations in the latter size range being a factor of two to three higher than the average values reported for three European cities (Aalto et al. 2005). Woo et al. (2001b) reported early morning, winter concentrations elevated by a factor of two in the 10–35 nm range, with the average particle size being 51% of the diameter before the event. This was mostly associated with temperatures exceeding 10°C, while for temperatures below

10°C, however, the data showed a pronounced enhancement of particles in the 4–10 nm range. The latter was explained by nucleation that occurs as hot exhaust gases mix with the cool ambient air, however, the study was unable to identify which source or combination of sources was predominant. It is important to mention, that while such events have been reported to occur predominantly in the morning, they have also been observed in the afternoon, during rush hour, particularly in winter when the mixing heights remain low (Woo et al. 2001b; Zhang et al. 2004b).

Midday nucleation events, when increased solar radiation ($>750 \text{ W/m}^2$ (Woo et al. 2001a)), presence of SO_2 and water vapour in the air (Pirjola et al. 1998), and relatively low concentration of pre-existing particles (often occurring under conditions of good atmospheric mixing: higher wind speed and high boundary layer) lead to photo oxidation of SO_2 to sulphuric acid and its subsequent binary nucleation with water and thus formation of sulphuric acid nanoparticles. Shi et al. (2001a) concluded that nucleation events cannot occur without the input of solar radiation, but high solar radiation alone will not necessarily lead to a nucleation event. Wehner and Wiedensohler (2003) found that midday nucleation occurred on weekdays as well as on weekends, concluding that the immediate emission of anthropogenic trace gases is not critical for particle formation in urban areas, or that concentrations of these gases are always sufficiently high to trigger new particle formation. Contrary to other studies, Laakso et al. (2003) showed that nucleation mode particle concentration had a minimum in summer, which was explained as related to high temperatures which limit the nucleation (due to temperature dependence of saturation vapour pressures). Alam et al (2003) reported occurrences of nucleation events on 8 out of 232 days distributed throughout the year at two urban sites in Birmingham, UK, and inferred that both the nucleation and particle growth processes involved condensable molecules other than, or in addition to, sulphuric acid, together with the requirement of a low total particle surface area.

Particle formation may be followed by growth of the newly formed particles, sometimes rapid (Monkkonen et al. 2005), sometimes over longer periods of time of up to 18 h (Zhang et al. 2004b). Ternary nucleation mechanisms involving (H₂SO₄/H₂O/NH₃) have been proposed to account for discrepancies found between calculated binary H₂SO₄/H₂O nucleation rates and experimental results (Stanier et al. 2004b). Woo et al. (2001b) observed that NO_x was typically depleted during these events (while higher before and after the event). The same study also showed that O₃ was elevated during the events. Such events have been reported to occur predominantly in spring and summer (Zhang et al. 2004b), but also in autumn (Laakso et al. 2003; Kittelson et al. 2004). Particles formed through such event have been reported to be very small, mainly in the 3-10 nm range (Harrison et al. 1999; Woo et al. 2001b; Kittelson et al. 2004; Monkkonen et al. 2005). Sardar et al.(2005) showed elevated mass concentrations in the 32-56 nm size range during summer, which may be linked to additional summer nucleation events. Interestingly, the study also showed a mode in organic carbon (OC) between 18 and 56 nm in the summer that was not present in the other seasons, linking it to summertime photochemical secondary organic aerosol formation through hydroxyl radicals, which occurs by the photolysis of ozone, and reacts with organic gases to reduce their volatility. The frequency, intensity, meteorology, and possible chemistry of such new particle formation has been analysed by Stanier et al. (2004b), based on sampling conducted in a park 5 km downwind of downtown Pittsburgh, showing that the nucleation events are associated with photochemical sulphuric acid production and occur on approximately 30% of the study days. The same type of behaviour has also been reported to occur in St. Louis (Shi 2003). Keeler (2004) detected the presence of the noon nucleation peak on 5 out of 11 sampling days in southwest Detroit during the summer. Woo et al. (2001a) observed that 19 of the 23 pronounced noon peaks over 12 months occurred during August and April. During such nucleation events, peaks of SO₂ are strongly associated with the number concentrations of UF (sources are vehicle emissions but also industry). Particle number concentrations during such events can be as high as 3x10⁴ cm⁻³ (Zhang et al. 2004b) and 7.3x10⁴ cm⁻³ (Keeler, 2004). The latter value was 3.5 times higher than the morning peak

concentration. Similarly, Woo et al. (2001a) showed that, during one such mid-day nucleation event, the particle concentration increased by a factor of 50 over the morning peak. McMurry and Woo (2002) concluded that the concentrations produced by the photochemical nucleation event were about an order of magnitude higher than concentration peaks that occurred during both morning and afternoon rush hours.

It is expected that under high concentrations of pre-existing particles new particle formation will not be favoured but rather condensation of condensable species on these particles. For example Vakeva et al. (1999) conducted model calculations, which showed that within a street canyon pre-existing particles prevent new particle formation via the $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ -route, while above roof height (25 m) nucleation potential is much higher. However, studies conducted in highly polluted environments, such as Dunn et al. (2004), also reported occurrence of nucleation events. Monkkonen et al. (2005) also reported some around noon nucleation events in New Delhi (linked to the presence of SO_2), with the formation rate of the particles varying from 3.3 to 13.9 $\text{cm}^{-3} \text{s}^{-1}$, despite the fact that most commonly, the formation and growth of nucleation mode particles were disturbed by high aerosol background concentration.

In general, as concluded by Kittelson et al. (2004), nucleation processes have a greater effect on mean rather than median concentrations, with different trends for particles in different size ranges (thus originating from different nucleation events). For 10–100nm particles, both the median and mean are elevated during the cold months, while mean values for 3–10nm particles are highly variable and can be high both in winter and summer, with the highest mean occurring during summer and the highest median observed in the winter. For example Woo et al. (2001a) observed that annual average concentrations of particles in the 3–10 nm range were elevated due to the appearance of very high concentrations of these particles between 11 am and 2 pm on 23 days of the year.

8.4 Comparison of particle concentration levels between different environments.

Comparison of particle concentration levels reported for different environment was conducted for the purpose of this review by grouping the results from the studies into eight categories according to measurement location including: road tunnel, on-road, road-side (which indicates varying degree of distance from the road), street canyon, urban, urban background, rural, and clean background, and calculating mean and median values for each category. This review only considered those papers that presented concentrations numerically; papers that showed concentrations only graphically have not been included in this comparison since values derived from graphs are of limited accuracy. The majority of the studies reported their results in terms of mean values, and thus for the purpose of this comparison only the reported mean particle number concentrations were considered. Some studies used both CPC and SMPS measurements for the same location; hence there were several overlaps between the number of CPC and SMPS measuring sites. Most of the studies reported multiple measurements at each study site, from which the average was calculated. The overall average for each site was then calculated using the averages for each study. Also, many studies included more than one site. Overall, there were 3 tunnel studies (with 4 sites using the SMPS), 2 on-road studies (with 7 sites using the CPC), 18 road-side studies (with 5 sites using the CPC and 19 using the SMPS), 7 street canyon studies (with 1 site using the CPC and 7 using the SMPS), 24 urban studies (with 1 site using the CPC and 24 sites using the SMPS), 4 urban background studies (with 3 sites using the SMPS), 8 rural studies (with 2 sites using the CPC and 11 sites using the SMPS) and 5 clean background studies (with 9 sites using the SMPS).

Figure 2 presents a comparison of mean and median concentrations for the different environments.

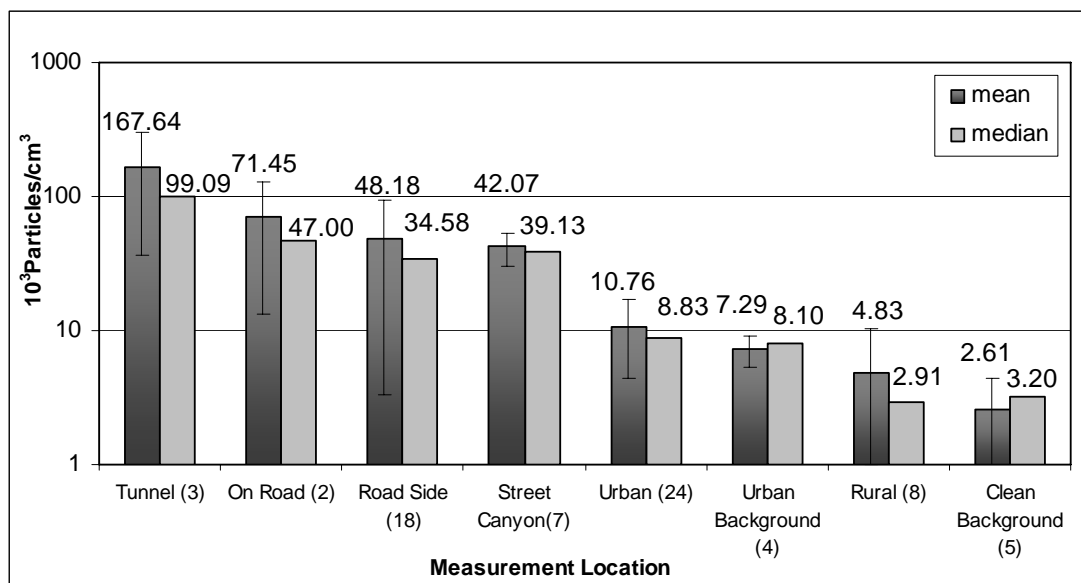


Figure 2. Mean and median particle number concentrations for different environments. In brackets are the numbers of sites for each environment*.

* 3 tunnel studies (Abu-Allaban et al. 2002; Jamriska et al. 2004; Imhof et al. 2005b), 2 on-road studies (Shi et al. 2001b; Westerdahl et al. 2005), 18 road-side studies (Harrison et al. 1999; Morawska et al. 1999b; Hitchins et al. 2000; Shi et al. 2001a; Molnar et al. 2002; Thomas and Morawska 2002; Zhu et al. 2002a; Zhu et al. 2002b; Gramotnev et al. 2003; Ketzel et al. 2003; Gramotnev et al. 2004; Janhall et al. 2004; Ketzel et al. 2004; Kittelson et al. 2004; Morawska et al. 2004; Zhu et al. 2004; Gidhagen et al. 2005; Imhof et al. 2005a), 7 street canyon studies (Vakeva et al. 1999; Jamriska and Morawska 2001; Wählén et al. 2001; Wehner et al. 2002; Longley et al. 2003; Gidhagen et al. 2004; Gidhagen et al. 2005), 24 urban studies (Tuch et al. 1997; Harrison et al. 1999; Hitchins et al. 2000; Junker et al. 2000; Pakkanen et al. 2001; Ruuskanen et al. 2001; Woo et al. 2001a; McMurry and Woo 2002; Morawska et al. 2002; Ketzel et al. 2003; Laakso et al. 2003; Wehner and Wiedensohler 2003; Hussein et al. 2004; Jamriska et al. 2004; Jeong et al. 2004; Ketzel et al. 2004; Morawska et al. 2004; Stanier et al. 2004a; Young and Keeler 2004; Gidhagen et al. 2005; Holmes et al. 2005; Hussein et al. 2005a; Janhall et al. 2006; Mejía et al. 2007a), 8 rural studies 4 urban background studies (Hussein et al. 2004; Ketzel et al. 2004; Virtanen et al. 2006; Hameri et al. 1996), 5 clean background studies (Pitz et al. 2001; Laakso et al. 2003; Tunved et al. 2003; Morawska et al. 2004; Gidhagen et al. 2005;)

It can be seen from Figure 2 that both tunnel and roadside categories have high standard deviations. In relation to the tunnel category, it could be due to the small number of studies conducted. In relation to the roadside category, one reason could be that the studies report concentrations for different distances from the road kerb and many studies had different reference distances, and/or more than one distance, which were difficult to normalize.

The mean concentration measured at both urban and urban background sites were statistically different to that measured at rural and clean background. As such, they were considered as a combined category, the mean of which was compared with the mean of the other site categories (on-road, road side etc), using a Students t-test, and in each case, the differences were found to be statistically significant. The

mean concentration measured at the tunnel sites ($1.67 \times 10^5/\text{cm}^3$) was statistically higher than the means of each of the other categories.

8.5 Exposure to ultrafine particles

There have been very few studies investigating human exposure to UF particles. In general exposure means concentrations experienced over a periods of time spent in different microenvironments. A study by Kaur et al. (2006) investigated exposures of volunteers walking or travelling by bus, car or taxi, along two busy roads with approximate average daily traffic of 83,000 and 18,000 vehicles per day, respectively. The volunteers carried P-TRAK® Ultrafine Particle Counters (TSI Model 8525) and the study showed that different modes of transport resulted in different exposures, with average personal UF particle count exposure (10^4 particles/ cm^3) of 4.61 (walking), 8.40 (cycling), 9.50 (bus), 3.68 (car) and 10.81 (taxi). (Note: the values presented in the paper were rounded for the purpose of this review). Considerable variability was seen in UF particle exposure, of up to an order of magnitude above background, within a few seconds and over a few metres as people moved through the polluted microenvironments, which implies that the influence of time-activity and movement can be easily missed by using averaged results, thus ultimately leading to underestimation of the exposures. Similar conclusions were derived by Gouriou et al. (2004) who showed that particle concentration encountered by car passengers may present high peaks, up to 10^6 particles cm^{-3} . Hourly average exposure is strongly influenced by the frequency with which an individual encounters such exposure events, as well as their severity, and thus mean and median concentrations over a time-averaged period may not reflect all aspects of population exposure patterns.

9. Relationship between different particle metrics and with gaseous pollutants

Many studies in addition to particle number, measured concentrations of particle mass (or mass surrogate) and of gaseous pollutants. The relationship between the measured pollutants was analysed with an aim to gain a better insight into pollution sources or pollution dynamics. In some cases existence

of quantifiable relationship between some of the pollutants would provide justification for using some of the pollutants as a surrogate of others and thus lowering the overall costs of monitoring.

Relationship between particle number, surface area, volume or mass concentrations. Correlations have been considered between total or size classified particle number concentrations and other particle metrics. Harrison and Jones (2005) measured particle number concentrations at eight different urban sites and showed that hourly and daily averaged number concentrations were only weakly correlated to PM_{10} . Harrison et al. (1999) showed that correlation between particle number concentrations and PM_{10} was higher at traffic, than at a background sites. Zhang et al. (2004b) reported that there was no correlation between UF particle number and $PM_{2.5}$ mass concentrations, and modest and good correlation between N_{50-100} and $N_{100-470}$ and $PM_{2.5}$, respectively. Laakso et al. (2003) showed that there was no correlation between particle mass and nucleation mode, total concentration or Aitken mode. Woo et al. (2001b) did not find correlation between the number and surface area or volume concentrations. Ruuskanen et al. (2001) showed that the total and UF number concentrations were poorly correlated with $PM_{2.5}$ levels while the number concentration of accumulation particles showed better correlation. Lin et al. (2007) showed that the ratios of $PM_{0.056}/PM_{10}$ and $PM_{0.1}/PM_{10}$ mass concentrations at the roadside were 0.13 and 0.17, respectively, and were significantly lower at the rural site (0.05 and 0.06, respectively), suggesting that the roadside is exposed to more nano and UF particles than the rural area. Thus in general, while there is some level of correlation between some particle metrics reported by some studies, other studies did not find any correlation. This can be explained by different sources of bigger and smaller particles in different environments, and therefore, without local measurements, the degree, if any, of local correlations cannot be predicted from studies conducted elsewhere.

Relationship between particle number, gaseous pollutant and black carbon concentrations. Most of the studies conducted in the proximity to traffic showed existence of correlations between these pollutants.

Zhu et al. (2002a) and Zhu et al. (2002b) reported that concentration of CO, BC and particle number tracked each other with the increasing distance from the freeway. Ketzler et al. (2003) established that NO_x and total particle number were well correlated at the urban and near-city level indicating a common traffic source. Sardar et al. (2005) showed that during fall and winter (when vehicular emissions become the dominant pollution source) particles greater than 56 nm are correlated well with CO and NO_x, while very low correlations are observed between O₃ and particle number of any size range. Westerdahl et al. (2005), who measured pollutant concentrations from an all-electric mobile platform, found that particles <1µm were highly correlated with BC and NO, while moderately correlated with CO₂ and poorly with CO. The latter was explained by the fact that CO emissions are primarily from gasoline-powered vehicles, and relatively unrelated to those pollutants dominated by diesel vehicles (including particle number). Similar conclusion was derived by Bukowiecki et al. (2002).

Thus, while in general there is a reasonably good correlation between UF particles and traffic emitted gaseous pollutants as well as BC, the existence and the degree of correlation varies. As concluded by Paatero et al. (2005), who estimated levels of particle number concentrations by retrospective modelling using measured air pollution and weather variables, models must be city-specific: associations of particle number concentrations with other pollutants differ between different cities.

10. Conclusions and implications for the exposure and epidemiological studies

This review compiled and synthesized the existing knowledge on UF particles in the air with a specific focus on those originating due to vehicles emissions. As it has been shown in this review, vehicles are a significant sources of UF particles, and it is the vehicle emissions that are commonly the most significant source of air pollution in general in populated urban areas. It is therefore of particular significance to understand the magnitude and characteristics of the vehicle-affected UF particles in

urban air, as it is this type of environment which is the most likely to be considered as a target for future air quality regulations in relation to particle number. Industrial and power plant emissions (covered in Part I) have a significant impact on the environment and climate, but as they often (but not always) occur outside the most populated urban settings, their direct impact on human exposure is lower than the impact of vehicle emissions.

UF particles are most commonly measured in terms of their number concentrations, and unlike particle mass concentration ($PM_{2.5}$, PM_{10}), there is no standard methods for conducting size classified particle number measurement. The review showed that the term “UF particles” is often used imprecisely, meaning various ranges of particle number concentration in a subset of the submicrometer range. In addition, the number concentrations reported depend on the instrument used and its setting. It has been shown by this review that the mean and the median CPC's measurements are 32% and 56%, respectively, higher than DMPS/SMPS's ones. While the differences for specific environments could vary (larger differences expected for the environments where nucleation mode is present and smaller where aged aerosol dominates), it nevertheless shows what overall magnitude of differences can be expected when comparing results using these different measuring techniques. It is important to keep these differences in mind when attempting to establish quantitative understanding of variation in particle concentrations reported by different studies. This also points out the need to develop and utilize standardised measurement procedures, enabling meaningful comparison between the results from different studies, which is of particular significance for human exposure and epidemiological studies.

Despite these differences in reporting measured concentration levels, this review showed that it is possible to quantify the differences between background concentrations of UF particles in clean environments, with the levels in the environments affect by vehicle emissions. It has been shown that the clean background levels are on average of the order of $2.67 \pm 1.79 \times 10^3 \text{ cm}^{-3}$, while levels at urban

sites are 4 times higher and levels at street canyons, roadside, road and tunnel sites [R3] are 27, 18, 16 and 64 times higher, respectively. Thus the range of concentrations between cleans and vehicle effected environments spans over two orders of magnitude. This is very different from particle mass; for example a review by Morawska (2003) showed the decrease in mass concentration between a busy road and urban background ranges only from 0 to about 25–30%. This large variation in particle number concentration across different environments has profound significance in relation to human exposure assessment and epidemiological studies. This means that unless exposure assessment is conducted where the exposures occur and at time scales that elucidates the temporal nature of the exposure, it is unlikely that epidemiological studies would provide answers based only on monitoring in central locations. In other words, central monitoring alone underestimates exposures and may lead to inappropriate management of public health risks.

Lack of answers from epidemiological studies in relation to UF particles (exposure-response relationships) means, that it is not possible to develop health guidelines, a basis for national regulations. In relation to airborne particle mass it has been shown that within the current range of concentrations studied in epidemiological studies there are no threshold levels and that there is a linear exposure-health response relationship. Based on this, in the recent review the World Health Organization Air Quality Guidelines, a new set of guidelines for particulate matter was introduced, with annual mean values for PM_{2.5} and PM₁₀ of 10 and 20 $\mu\text{g m}^{-3}$, respectively. This was based on an American Cancer Society study (Pope et al. 2002) and represents the lowest end of the range over which significant effects on survival have been observed (WHO 2005). It is important to note that these values are not much higher than the concentration levels encountered most commonly in natural environments (while it should be acknowledged that, in some locations and under some circumstances, concentrations in natural environments may be well below or above those cited). If future epidemiological studies report response at lower concentration levels PM_{2.5} and PM₁₀, it is likely that the guideline values will be

lowered even further. While lack of exposure response relationship makes it impossible to propose health guideline for UF particles, it is important to point out that as discussed above, the current levels in environments affected by vehicle emissions are up to an order of magnitude higher than in the natural environments. Thus, if there is also no threshold level in response to exposure to UF particles (or if it is very low), future control and management strategies should target a decrease of these particles in urban environments by more than one order of magnitude. At present there is a long way to go to achieve this.

When considering future management strategies for UF particles, as discussed in this review, there are a few challenges, which include:

1. Currently there are large uncertainties in relation to vehicle emission factors for different particle size ranges and for particle numbers, there are no emission inventories of UF particles from motor vehicles, and there is only very limited data on long term trends in UF particle concentrations in urban environments. All these aspects should attract significant research efforts, as this knowledge is critical for management and control of UF particles.
2. Estimations of pollution concentration in the air are commonly derived based on source emission inventories, which in turn are derived utilizing the source emission factors. However, due to the process of secondary particle formation, estimation of UF particle concentration cannot be derived solely based on vehicle emission factors (which are more likely to reflect emissions of primary particles), but have to include also predictions for secondary particle formation in exhaust plumes and particle formation by nucleation processes in the wider atmosphere.
3. Secondary particle formation results in rapid increase of particle number concentrations by one to two orders of magnitude to the concentration levels of the order of 10^5 particles cm^{-3} . The majority of the new particles are formed by ion-induced or binary nucleation of sulphuric acid and water or

by ternary nucleation involving a third molecule followed by condensation of semi-volatile organics, with photochemistry playing an important role in some of these processes. The mechanisms of new particle formation strongly depend on local meteorological factors, and therefore models of the dynamics of particle formation in urban environments have to include all factors involved and thus must be local area specific.

4. These significant peaks in particle number concentration due to secondary particle formation are a challenge, if there were future regulations considered based on particle number. Issues to resolve include: (i) whether the regulations should be set around the base line concentrations without the peak concentrations, or whether they should include the peaks; and (ii) how to define the peaks. Developing a much better picture of particle formation dynamics in different environments, including those which are influenced by traffic, would greatly assist such regulation formulation.
5. It is not only the particle number concentration, but also particle composition which should be considered when characterising UF particles. The review showed that there have been only a relatively small number of studies focused on UF particle chemistry. There are large differences in particle chemical composition including particle solubility, volatility, elemental composition, etc reported by the studies. The differences depend on many factors, including vehicle technology, fuel used and after treatment devices, but also on the post formation processes occurring atmospheric transport. Since particle composition may be a factor determining particle toxicity there is a need for developing a much better knowledge on UF particle chemistry in different environments.

In summary, the magnitude of the impact of UF particles on human health and the environment has still not been fully quantified (while the picture starts emerging) nor is it fully understood, and the first step in this direction is to develop an in depth understanding of particle concentrations, characteristics, time trends and spatial distribution in clean and anthropogenic modified environments. This knowledge would, in turn, lead to an understanding of the potential impacts of the particles on the environment and

would provide scientific foundation for future studies in the area of human epidemiology. It would also be used as a basis for setting any future emission and air quality standards based on particle number.

Acknowledgements

This work was supported by the EPRI and ARC Linkage Grant LP0775260.

References

- Aalto, P., Hameri, K., Becker, E., Weber, R., Salm, J., Makela, J., Hoell, C., O'Dowd, C., Karlsson, H., Hansson, H., Vakeva, M., Koponen, I., Buzorius, G. and Kulmala, M. (2001). "Physical Characterization of Aerosol Particles During Nucleation Events." *Tellus* **B53**: 344-358.
- Aalto, P., Hameri, K., Paatero, P., Kulmala, M., Bellander, T., Berglind, N., Bouso, L., Castano-Vinyals, G., Cattani, G., Cyrus, J., Von Klot, S., Lanki, T., Marconi, A., Nyberg, F., Pekkanen, J., Peters, A., Sjoval, B., Sunyer, J., Zetzsche, K. and Forastiere, F. (2005). "Aerosol particle number concentration measurements in five European cities using TSI-3022 condensation particle counter over a three year period during HEAPSS (Health Effects of Air Pollution on susceptible Subpopulations)." *Journal of the Air and Waste Management Association* **55**: 1064-1076.
- Abu-Allaban, M., Coulomb, W., Gertler, A., Gillies, J., Pierson, W., Rogers, C., Sagebiel, J. and Tarnay, L. (2002). "Exhaust Particle Size Distribution Measurements at the Tuscarora Mountain Tunnel." *Aerosol Science and Technology* **36**: 771-789.
- Airborne Particles Expert Group (1999). Source apportionment of airborne particulate matter in the United Kingdom. Report for the Department of the Environment, Transport and the Regions, the Welsh Office, the Scottish Office and the Department of the Environment (Northern Ireland).
- Andersson, J., Wedekind, B., Hall, D., Stradling, R. and Wilson, G. (2001). DETR/SMMT/CONCAWE Particulate Research Programme: Light Duty Results. *SAE Technical Paper Series*, Society of Automotive Engineers: No. 2001-01-3577.
- Arnold, F., Kiendler, A., Wiedemer, V., Aberle, S., Stilp, T. and Busen, R. (2000). "Chemion concentration measurements in jet engine exhaust at the ground: implications for ion chemistry and aerosol formation in the wake of a jet aircraft." *Geophysical Research Letters* **27**: 1723-1726.
- Ayers, G. and Gras, J. (1991). "Seasonal Relationship between cloud condensation nuclei and aerosol methanesulphonate in marine air." *Nature* **353**: 834-835.
- Bagley, S. T., Baumgard, K. J., Gratz, L. D., Johnson, J. J. and Leddy, D. G. (1996). Characterization of Fuel and After-Treatment Device Effects on Diesel Emissions, Health Effects Institute: Research Report No. 76.
- Baron, P. A. and Willeke, K., Eds. (2001). Aerosol Measurement: Principles, Techniques and Applications. New York, van Nostrand Reinhold.
- Birmili, W. and Wiedensohler, A. (2000). "Evolution of newly formed aerosol particles in the continental boundary layer: a case study including OH and H₂SO₄ measurements." *Geophysical Research Letters* **27**: 2205-2208.
- Bukowiecki, N., Dommen, J., Prévôt, A. S. H., Richter, R., Weingartner, E. and Baltensperger, U. (2002). "A mobile pollutant measurement laboratory-measuring gas phase and aerosol ambient concentrations with high spatial and temporal resolution." *Atmospheric Environment* **36**: 5569-5579.
- Burtscher, H. (2001). Literature study on tailpipe particulate emission measurement for diesel engines. Particulate Measurement Program BUWAL/GRPE.
- Buzorius, G., Hameri, K., Pekkanen, J. and Kulmala, M. (1999). "Spatial variation of aerosol number concentration in Helsinki city." *Atmospheric Environment* **33**: 553-565.
- Cabada, J. C., Takahama, S., Khlystov, A. Y., Wittig, B., Pandis, S., Rees, S., Davidson, C. I. and Robinson, A. L. (2004). "Mass size distributions and size resolved chemical composition of fine particulate matter at the Pittsburgh Supersite." *Atmospheric Environment* **38**(10): 3127-3141
- Casati, R., Scheer, V., Vogt, R. and Benter, T. (2007). "Measurement of nucleation and soot mode particle emission from a diesel passenger car in real world and laboratory in situ dilution." *Atmospheric Environment* **41**: 2125-2135.
- Charron, A. and Harrison, M. (2003). "Primary Particle Formation from Vehicle Emission During Exhaust Dilution in the Roadside Atmosphere." *Atmospheric Environment* **37**: 4109-4119.
- Cheng, M. and Tanner, R. (2002). "Characterization of Ultrafine and Fine Particles at a Site Near the Great Smoky Mountains National Park." *Atmospheric Environment* **36**: 5795-5806.

- Clarke, A., Davis, D., Kapustin, V. N., Eisele, F. L., Chen, G., Paluch, I., Lenschow, D., Bandy, A. R., Thornton, D., Moore, K., Mauldin, L., Tanner, D. J., Litchy, M., Carroll, M. A., Collins, J. and Albercook, G. (1998). "Particle nucleation in the tropical boundary layer and its coupling to marine sulphur sources." *Science* **282**: 89-92.
- Dahl, A., Gharibi, A., Swietlicki, E., Gudmundsson, A., Bohgard, M., Ljungman, A., Blomqvist, G. and Gustafsson, M. (2006). "Traffic Generated Emissions of Ultrafine Particles from Pavement-Tire Interface." *Atmospheric Environment* **40**: 1314-1323.
- Dunn, M. J., Jimnez, J. L., Baumgardner, D., Castro, T., Mc-Murry, P. H. and Smith, J. N. (2004). "Measurements of Mexico City nanoparticles size distributions: Observations of new particle formation and growth." *Geophysical Research Letters* **31**: L10102.
- Easter, R. C. and Peters, L. K. (1994). "Binary homogeneous nucleation: temperature and relative humidity fluctuations, nonlinearity and aspects of new particle production in the atmosphere." *Journal of Applied Meteorology* **33**: 775-784.
- Ebelt, S., Brauer, M., Cyrus, J., Thomas, T., Kreyling, W. G. and Wichmann, H.-E. (2001). "Air quality in postunification erfurt, East Germany: Associating changes in pollutant concentrations with changes in emissions." *Environmental Health Perspectives* **109**(4): 325-333.
- Fine, P., Shen, S. and Sioutas, C. (2004). "Inferring the sources of fine and ultrafine particulate matter at downwind receptor sites in the Los Angeles basin using multiple continuous measurements." *Aerosol Science and Technology* **38**(S1): 182-195.
- Gamas, E. D., Diaz, L., Rodriguez, R., Lopez-Salinas, E. and Schifter, I. (1999). "Exhaust emissions from gasoline and LPG-powered vehicles operating at the altitude of Mexico City." *Journal of the Air & Waste Management Assoc.* **49**: 1179-1189.
- Garcia-Nieto, P. J., Garcia, B. A., Diaz, J. M. F. and Brana, M. A. R. (1994). "Parametric study of selective removal of atmospheric aerosol by below-cloud scavenging. ." *Atmospheric Environment* **28**: 2335-2342.
- Geller, M. D., Kim, S., Misra, C., Sioutas, C., Olson, B. A. and Marple, V. A. (2002). "A methodology for measuring size-dependent chemical composition of ultrafine particles." *Aerosol Science and Technology* **36**: 748-762.
- Gidhagen, L., Johansson, C., Langner, J. and Foltescu, V. (2005). "Urban Scale Modelling of Particle Number Concentration in Stockholm." *Atmospheric Environment* **39**: 1711-1725.
- Gidhagen, L., Johansson, C., Langner, J. and Olivares, G. (2004). "Simulation of NO_x and Ultrafine Particles in a Street Canyon in Stockholm, Sweden." *Atmospheric Environment* **38**: 2029-2044.
- Gidhagen, L., Johansson, C., Strom, J., Kristensson, A., Swietlicki, E., Pirjola, L. and Hansson, H. (2003). "Model simulation of ultrafine particles inside a road tunnel." *Atmospheric Environment* **37**: 2023-2036.
- Gieshaskiel, B., Ntziachristos, L., Samaras, Z., Scheer, V., Casati, R. and Vogt, R. (2005). "Formation Potential of Vehicle Exhaust Nucleation Mode Particles On-Road and in the Laboratory." *Atmospheric Environment* **39**: 2191-2198.
- Gouriou, F., Morin, J. and Weill, M. (2004). "On Road Measurements of Particle Number Concentrations and Size Distributions in Urban and Tunnel Environments." *Atmospheric Environment* **38**: 2831-2840.
- Gramotnev, G., Brown, R., Ristovski, Z., Hitchins, J. and Morawska, L. (2003). "Determination of average emission factors for vehicles on a busy road." *Atmospheric Environment* **37**(4): 465-474.
- Gramotnev, G. and Ristovski, Z. (2004). "Experimental Investigation of Ultrafine Particle Size Distribution Near a Busy Road." *Atmospheric Environment* **38**: 1767-1776.
- Gramotnev, G., Ristovski, Z. D., Brown, R. J. and Madl, P. (2004). "New methods of determination of average particle emission factors for two groups of vehicles on a busy road." *Atmospheric Environment* **38**(16): 2607-2610.
- Graskow, B., Kittelson, D. B., Abdul-Khalek, I., Ahmadi, M. and Moris, J. (1998). "Characterisation of Exhaust Particulate Emissions from a Spark Ignition Engine." *SAE Paper* **980528**: 155-165.
- Grose, M., Sakurai, H., Savstrom, J., Stolzenburg, M. R., Watts, W. F., Morgan, C. G., Murray, I. P., Twigg, M. V., Kittelson, D. B. and McMurry, P. H. (2006). "Chemical and physical properties of ultrafine diesel exhaust particles sampled downstream of a catalytic trap." *Environmental Science & Technology* **40**: 5502-5507.
- Hameri, K., Kulmala, M., Aalto, P., Leszczynski, K., Visuri, R. and Hamekoski, K. (1996). "The Investigations of Aerosol Particle Formation in Urban Background of Helsinki." *Atmospheric Research* **41**: 281-298.
- Hara, K., Nakae, S. and Miura, K. (1997). "Properties of ion nucleation in the atmosphere." *Atmospheric Electricity* **17**: 53-58.
- Hara, K., Nakae, S. and Miura, K. (1998). "Properties of ion-induced nucleation obtained from mobility measurements." *Journal of Aerosol Science* **29**: S139-140.
- Harayama, N. (1992). Effects of sulfate adsorption on performance of diesel oxidation catalysts. *SAE Technical Paper Series*, Society of Automotive Engineers: No. 920852.
- Harris, S. J. and Maricq, M. M. (2001). "Signature size distributions for diesel and gasoline engine exhaust particulate matter." *Journal of Aerosol Science* **32**: 749-764.
- Harrison, R., Jones, M. and Collins, G. (1999). "Measurements of the Physical Properties of Particles in the Urban Atmosphere." *Atmospheric Environment* **33**: 309-321.
- Harrison, R. M., Yin, J., Mark, D., Stedman, J., Appleby, R. S., Booker, J. and Moorcroft, S. (2001). "Studies of the coarse particle (2.5-10 µm) component in UK urban atmospheres. ." *Atmospheric Environment* **35**: 3667-3679.

- Hitchins, J., Morawska, L., Gilbert, D. and Jamriska, M. (2002). "Dispersion of particles from vehicle emissions around high- and low-rise buildings. ." Indoor Air **12**(1): 64-71.
- Hitchins, J., Morawska, L., Wolff, R. and Gilbert, D. (2000). "Concentrations of submicrometre particles from vehicle emissions near a major road." Atmospheric Environment **34**(1): 51-59.
- Holmen, B. A. and Ayala, A. (2002). "Ultrafine PM emissions from natural gas, oxidation catalyst diesel and particle trap diesel heavy-duty transit buses." Environmental Science & Technology **36**: 5041-5050.
- Holmes, N. (2007). "A Review of Particle Formation Events and Growth in the Atmosphere in the Various Environments and Discussion of Mechanistic Implications." Atmospheric Environment **41**: 2183-2201.
- Holmes, N. S., Morawska, L., Mengersen, K. and Jayaratne, R. (2005). "Spatial distribution of submicrometre particles and CO in an urban microscale environment." Atmospheric Environment **39**(22): 3977-3988.
- Hussein, T., Hameri, K., Aalto, P., Paatero, P. and Kulmala, M. (2005a). "Modal structure and spatial-temporal variations of urban and suburban aerosols in Helsinki-Finland." Atmospheric Environment **39**: 1655-1668.
- Hussein, T., Hameri, K., Heikkinen, M. and Kulmala, M. (2005b). "Indoor and outdoor particle size characterisation at a family house in Espoo, Finland." Atmospheric Environment **39**: 3697-3709.
- Hussein, T., Puustinen, A., Aalto, P., Makela, J., Hameri, K. and Kulmala, M. (2004). "Urban Aerosol Number Size Distributions." Atmospheric Chemistry and Physics Discussions **4**: 391-411.
- Imhof, D., Weingartner, E., Ordonez, C., Gerhig, R., Hill, M., Buchmann, B. and Baltersperger, U. (2005a). "Real World Emission Factors of Fine and Ultrafine Aerosol Particles for Different Traffic Situations in Switzerland." Environmental Science and Technology **39**: 8341-8350.
- Imhof, D., Weingartner, E., Prevot, A., Ordonez, C., Kurtenbach, R., Wiesen, P., Rodler, J., Sturm, P., McCrae, I., Sjodin, A. and Baltersperger, U. (2005b). "Aerosol and NOx Emission Factors and Submicron Particle Number Size Distributions in Two Road Tunnels with Different Traffic Regimes." Atmospheric Chemistry and Physics Discussions **5**: 5127-5166.
- Jacobson, M., Kittelson, D. and Watts, W. (2005). "Enhanced coagulation due to evaporation and its effect on nanoparticle evolution." Environmental Science & Technology **39**: 9486-9492.
- Jamriska, M. and Morawska, L. (2001). "A model for determination of motor vehicle emission factors from on-road measurements with a focus on submicrometer particles." The Science of The Total Environment **264**(3): 241-255.
- Jamriska, M., Morawska, L. and Mengersen, K. (2007). "The Effect of Temperature and Relative Humidity on size Generated Traffic Exhaust Particle Emissions. ." Atmospheric Environment, Submitted.
- Jamriska, M., Morawska, L., Thomas, S. and He, C. (2004). "Diesel bus emissions measured in a tunnel study." Environmental Science & Technology **38**: 6701-6709.
- Janhall, S., Jonsson, A., Molnar, P., Svensson, E. and Hallquist, M. (2004). "Size Resolved Traffic Emissions Factors of Submicrometer Particles." Atmospheric Environment **38**: 4331-4340.
- Janhall, S., Olofson, F., Andersson, P., Pettersson, J. and Hallquist, M. (2006). "Evolution of the Urban Aerosol During Winter Temperature Inversion Episodes." Atmospheric Environment **40**: 5355-5366.
- Jeong, C., Hopke, P., Chalupa, D. and Utell, M. (2004). "Characteristics of Nucleation and Growth Events of Ultrafine Particles Measured in Rochester NY." Environmental Science and Technology **38**: 1933-1940.
- Jones, A. and Harrison, R. (2006). "Estimation of the emission factors of particle number and mass fractions from traffic at a site where mean vehicle speeds vary over short distances." Atmospheric Environment **40**: 7125-7137.
- Jung, H. and Kittelson, D. (2005). "Measurement of electrical charge on diesel particles." Aerosol Science and Technology **39**: 1129-1135.
- Junker, M., Kasper, M., Roosli, M., Camenzind, M., Kunzli, N., Monn, C., Theis, G. and Braun, C. (2000). "Airborne particle number profiles, particle mass distribution and particle bound PAH concentrations within the city environment of Basle: An assessment of the BRISKA project." Atmospheric Environment **43**(19): 3171-3181.
- Kasper, M. (2005). Sampling and measurement of nanoparticle emissions for type approval and field control. SAE Technical Paper Series, Society of Automobile Engineers: No. 2005-26-013.
- Kaur, S., Clark, R., Walsh, P., Arnold, S., Colvile, R. and Nieuwenhuijsen, M. (2006). "Exposure visualisation of ultrafine particle counts in a transport microenvironment." Atmospheric Environment **40**: 386-398.
- Kawai, T., Goto, Y. and Odaka, M. (2004). Influence of dilution process on engine exhaust nanoparticles. SAE Technical Paper Series, Society of Automobile Engineers: No. 2004-01-0963.
- Keeler, G. (2004). "Characterization of ultrafine particle number concentration and size distribution during a summer campaign in southwest Detroit." Journal of the Air and Waste Management Association **54**: 1079-1090.
- Keogh, D., Kelly, J., Mengersen, K., Morawska, L. and Jayaratne, E. R. (2007). "Emission factors for estimating motor vehicle particle emissions in urban areas." Environmental Science & Technology, Submitted.
- Kerminen, V.-M., L., P. and Kulmala, M. (2001). "How significantly does coagulation limit atmospheric particle production?" Journal of Geophysical Research **106**: 24119-24125. .
- Ketzel, M., Wahlin, P., Berkowicz, R. and Palmgren, F. (2003). "Particle and trace gas emission factors under urban driving conditions in Copenhagen based on street and roof-level observations." Atmospheric Environment **37**(20): 2735-2749.

- Ketzel, M., Whalin, P., Kristensson, A., Swietlicki, E., Berkowicz, R., Nielsen, O. and Palmgren, F. (2004). "Particle Size Distribution and Particle Mass Measurement at Urban, Near City and Rural Level in the Copenhagen Area and Southern Sweden." Atmospheric Chemistry and Physics **4**: 281-292.
- Khalek, I. A., Kittleson, D. and Brear, F. (1998). Diesel exhaust particle size: Measurement issues and trends. SAE Technical Paper Series, Society of Automobile Engineers: No. 980525, 133-145.
- Khalek, I. A., Kittleson, D. and Brear, F. (1999). The influence of dilution conditions on diesel exhaust particle size distribution measurements. SAE Technical Paper Series, Society of Automobile Engineers: No. 1999-01-1142.
- Khalek, I. A., Kittleson, D. and Brear, F. (2000). Nanoparticle growth during dilution and cooling of diesel exhaust: Experimental investigation and theoretical assessment. SAE Technical Paper Series 2000, Society of Automobile Engineers: No. 2000-01-0515.
- Kim, S., Shen, S., Sioutas, C., Zhu, Y. and Hinds, W. C. (2002). "Size Distribution and Diurnal and Seasonal Trends of Ultrafine Particles in Source and Receptor Sites of the Los Angeles Basin." Air & Waste Management Association **52**: 297-307.
- Kirchstetter, T. W., Harley, R. A., Kreisberg, N. M., Stolzenberg, M. R. and Hering, S. V. (1999). "On-road measurement of fine particle and nitrogen oxide emissions from light- and heavy-duty motor vehicles." Atmospheric Environment **33**: 2955-2968.
- Kittleson, B. D. (1998). "Engines and Nanoparticles: a Review." Journal of Aerosol Science **29**(5): 575-588.
- Kittleson, D., Watts, W. and Johnson, J. (2006a). "On-road and laboratory evaluation of combustion aerosols - Part 1: Summary of diesel engine results." Journal of Aerosol Science **37**: 913-930.
- Kittleson, D., Watts, W. and Johnson, J. (2006b). "On-road and laboratory evaluation of combustion aerosols - Part 2: Summary of spark ignition engine results." Journal of Aerosol Science **37**: 931-949.
- Kittleson, D. B., Watts, W. F. and Johnson, J. (2002). Diesel Aerosol Sampling Methodology - CRC E-43: Final Report, University of Minnesota, Report for the Coordinating Research Council.
- Kittleson, D. B., Watts, W. F. and Johnson, J. P. (2004). "Nanoparticle emissions on Minnesota highways." Atmospheric Environment **38**: 9-19.
- Kittleson, D., Pui, D. Y. H. and Moon, K. C. (1986). Electrostatic collection of diesel particles. SAE Technical Paper Series, Society of Automotive engineers: No. 860009.
- Korhonen, P., Kulmala, M., Laaksonen, A., Viisanen, Y., McGraw, R. and Seinfeld, J. H. (1999). "Ternary nucleation of H₂SO₄, NH₃, and H₂O in the atmosphere." Journal of Geophysical Research **104**: 26349-26353.
- Kuhler, M., Kraft, J., Bess, H., U., H. and Schurmann, D. (1994). "Comparison between measured and calculated concentrations of nitrogen oxides and ozone in the vicinity of a motorway." Science of the Total Environment **147**: 387-394.
- Kuhn, T., Krudysz, M., Zhu, Y., Fine, P., Hinds, W., Froines, J. and Sioutas, C. (2005). "Volatility of indoor and outdoor ultrafine particulate matter near a freeway." Journal of Aerosol Science **36**: 291-302.
- Kulmala, M., Pirjola, L. and Makela, J. (2000). "Stable sulphate clusters as a source of new atmospheric particles." Nature **404**: 66-69.
- Kulmala, M., Vehkamäki, H., Petaja, T., Dal Maso, M., Lauri, A., Kerminen, V., Birmilli, W. and McMurry, P. (2004). "Formation and Growth Rates of Ultrafine Atmospheric Particles: A Review of Observations." Journal of Aerosol Science **35**: 143-176.
- Kulmala, M. (2003). "How Particles Nucleate and Grow." Science **302**: 1000-1001.
- Kwon, S., Lee, K. W., Saito, K., Shinzaki, O. and Seto, T. (2003). "Size-dependent volatility of diesel nanoparticles: Chassis dynamometer experiments." Environmental Science & Technology **37**: 1794-1802.
- Laakso, L., Hussein, T., Aarino, P., Komppula, M., Hiltunen, V., Viisanen, Y. and Kulmala, M. (2003). "Diurnal and Annual Characteristics of Particle Mass and Number Concentrations in Urban, Rural and Arctic Environments in Finland." Atmospheric Environment **37**: 2629-2641.
- Lin, C., Chen, S., Huang, K., Lee, W., Lin, W., Liao, C., Chung, H. and Chiu, C. (2007). "Water Soluble Ions in Nano/Ultrafine/Fine/Coarse Particles Collected Near a Busy Road and at a Rural Site." Environmental Pollution **145**: 562-570.
- Longley, I., Gallagher, M., Dorsey, J., Flynn, M., Allan, J., Alfarra, M. and Inglis, D. (2003). "A Case Study of Aerosol (4.6 nm < Dp < 10 um) Number and Mass Size Distribution Measurements in a Busy Street Canyon in Manchester, UK." Atmospheric Environment **37**: 1563-1571.
- Lyyranen, J., Jokiniemi, J., Kauppinen, E. I., Backman, U. and Vesala, H. (2004). "Comparison of different dilution methods for measuring diesel particle emissions." Aerosol Science and Technology **38**: 12-23.
- Maricq, M. M. (2006). "On the electrical charge of motor vehicle exhaust particles." Journal of Aerosol Science **37**: 858-874.
- Maricq, M. M., Chase, R. E., Xu, N. and Laing, P. M. (2002). "The effects of the catalytic converter and fuel sulphur level on motor vehicle particulate matter emissions." Environmental Science & Technology **36**: 283-289.
- Marti, J. and Weber, R. (1997). "New particle formation at a remote continental site: assessing the contributions of SO₂ and organic precursors." Journal of Geophysical Research - Atmospheres **102**: 6331-6339.

- Mathis, U., Ristimäki, J., Mohr, M., Keskinen, J., Ntziachristos, L., Samaras, Z. and Mikkanen, P. (2004). "Sampling conditions for the measurement of nucleation mode particles in the exhaust of a diesel vehicle." *Aerosol Science and Technology* **38**: 1149-1160.
- McFiggans, G. (2005). "Atmospheric science: Marine aerosols and iodine emissions." *Nature* **433**(E13).
- McMurry, P. (2000). "A Review of Atmospheric Aerosol Measurements." *Atmospheric Environment* **34**: 1959-1999.
- McMurry, P. and Woo, K. (2002). "Size Distributions of 3-10nm Urban Atlanta Aerosols: Measurements and Observations." *Journal of Aerosol Medicine* **15**: 169-178.
- Mejia, J., Morawska, L. and Mengersen, K. (2007a). "Spatial variation in particle number size distribution in a large metropolitan area." *Atmospheric Chemistry and Physics Submitted for Publication*.
- Mejia, J., Wraith, D., Mengersen, K. and Morawska, L. (2007b). "Trends in size classified particle number concentration in subtropical Brisbane, Australia, based on a five year study." *Atmospheric Environment* **41**: 1064 - 1079.
- Meyer, N., Ristovski, Z. and Jayaratne, R. (2006). *Volatile Properties of CNG and Diesel Bus Emissions Produced During Steady State and Transient Driving Modes*. 10th ETH-Conference on Combustion Generated Nanoparticles.
- Meyer, N. K. and Ristovski, Z. D. (2007). "Ternary Nucleation as a Mechanism for the Production of Diesel Nanoparticles: Experimental Analysis of the Volatile and Hygroscopic Properties of Diesel Exhaust Using the Volatilization and Humidification Tandem Differential Mobility Analyzer" *Environmental Science & Technology* **41**: 7309 - 7314.
- Mirme, A., Tamm, E., Mordas, G., Vana, M., Uin, J., Mirme, S., Bernotas, T., Laakso, L., Hirsikko, A. and Kulmala, M. (2007). "A wide-range multi-channel Air Ion Spectrometer." *Boreal Environmental Research* **12**: 247-264.
- Mohr, M. and Lehmann, U. (2003). Comparison Study of Particle Measurement Systems for Future Type Approval Application, Swiss Contribution to GRPE Particulate Measurement Program (GRPE-PMP CH5). *EMPA Report No. 202779*
- Molnar, P., Janhall, S. and Hallquist, M. (2002). "Roadside Measurements of Fine and Ultrafine Particles at a Major Road North of Gothenburg." *Atmospheric Environment* **36**: 4115-4123.
- Monkkonen, P., Koponen, I., Lehtinen, K., Hameri, K., Uma, R. and Kulmala, M. (2005). "Measurements in a highly polluted Asian mega city: Observations of aerosol number size distribution, modal parameters and nucleation events." *Atmospheric Chemistry and Physics* **5**: 57-66.
- Morawska, L. (2003). Motor vehicle emissions as a source of indoor particles. *Indoor Environment, Airborne Particles and Settled Dust*. L. Morawska and T. Salthammer. Weinheim, Germany, WILEY-VCH.
- Morawska, L., Bofinger, N., Kocis, L. and Nwankowala, A. (1998a). "Submicron and supermicron particulates from diesel vehicle emissions." *Environmental Science & Technology* **32**: 2033-2042.
- Morawska, L., Hofmann, W., Thomas, S., Ristovski, Z. D., Jamriska, M., Rettenmoser, T. and Kagerer, S. (2004). "Exploratory cross sectional investigations on ambient submicrometer particles in the alpine region of Salzburg, Austria." *Atmospheric Environment* **38**(21): 3529-3533.
- Morawska, L., Jamriska, M., Thomas, S., Ferreira, L., Mengersen, K., Wraith, D. and McGregor, F. (2005). "Quantification of particle number emission factors for motor vehicles from on-road measurements." *Environmental Science & Technology* **39**: 9130-9139.
- Morawska, L., Jayaratne, E. R. and Mengersen, K. (2002). "Differences in airborne particle and gaseous concentrations in urban air between weekdays and weekends." *Atmospheric Environment* **36**: 4375-4383.
- Morawska, L., Johnson, G., Ristovski, Z. D. and Agranovski, V. (1999a). "Relation between particle mass and number for submicrometer airborne particles." *Atmospheric Environment* **33**: 1983-1990.
- Morawska, L., Keogh, D., Thomas, S., Mengersen, K. and Wilson, W. (2007a). "Modality in ambient particle size distributions and its potential as a basis for developing air quality regulation." *Atmospheric Environment, Submitted*.
- Morawska, L., Ristovski, Z., Johnson, G., Jayaratne, R. and Mengersen, K. (2007b). "A Novel Method for On Road Emission Factor Measurements Using a Plume Capture Trailer." *Environmental Science & Technology* **41**: 574-579.
- Morawska, L., Thomas, S., Bofinger, N. D., Wainwright, D. and Neale, D. (1998b). "Comprehensive characterisation of aerosols in a subtropical urban atmosphere: particle size distribution and correlation with gaseous pollutants." *Atmospheric Environment* **32**(14/15): 2461-2478.
- Morawska, L., Thomas, S., Gilbert, D., Greenaway, C. and Rijnders, E. (1999b). "A study of the horizontal and vertical profile of submicrometer particles in relation to a busy road." *Atmospheric Environment* **33**(8): 1261-1274.
- Morawska, L., Thomas, S., Jamriska, M. and Johnson, G. (1999c). "The modality of particle size distributions of environmental aerosols." *Atmospheric Environment* **33**(27): 4401-4411.
- Morawska, L., Vishvakarman, D. and Swanson, C. (2007c). "Diurnal variation of PM10 concentrations and its spatial distribution in the South East Queensland airshed." *Clean Air, Submitted*
- Napari, I. and Noppel, M. (2002). "An improved model for ternary nucleation of sulfuric acid-ammonia-water." *Journal of Chemical Physics* **116**: 4221-4227.
- Nitta, H., Sato, T., Nakai, S., Maeda, K., Aoki, S. and Ono, M. (1993). "Respiratory health associated with exposure to automobile exhaust. I. Results of cross-sectional studies in 1979, 1982, and 1983." *Archives of Environmental Health* **48**: 53-58.

- Ntziachristos, L., Ning, Z., Geller, M. D. and Sioutas, C. (2007). "Particle concentration and characteristics near a major freeway with heavy duty diesel traffic." *Environmental Science & Technology* **41**: 2223-2230.
- O'Dowd, C., Aalto, P., Hameri, K., Kulmala, M. and Hoffmann, T. (2002). "Aerosol formation - Atmospheric particles from organic vapours." *Nature* **416**.
- O'Dowd, C., Facchini, M. C., Cavalli, F., Ceburnis, D., Mircea, M., Decesari, S., Fuzzi, S., Yoon, Y. J. and Putaud, J.-P. (2004). "Biogenically driven organic contribution to marine aerosol." *Nature* **431**: 676-680.
- O'Dowd, C. and Hoffmann, T. (2005). "Coastal New Particle Formation: A Review of the Current State-Of-The-Art." *Environmental Chemistry* **2**: 245-255.
- Paatero, P., Aalto, P., Picciotto, S., Bellander, T., Castano, G., Cattani, G., Cyrus, J., Kulmala, M., Lanki, T., Nyberg, F., Pekkanen, J., Peters, A., Sunyer, J. and Forastiere, F. (2005). "Estimating Time Series of Aerosol Particle Number Concentrations in Five HEAPSS Cities on the Basis of Measured Air Pollution and Meteorological Variables." *Atmospheric Environment* **39**: 2261-2273.
- Pakkanen, T., Kerminen, V., Korhonen, C., Hillamo, R., Aarino, P., Koskentalo, T. and Maenhaut, W. (2001). "Urban and Rural Ultrafine (PM_{0.1}) Particles in the Helsinki Area." *Atmospheric Environment* **35**: 4593-4607.
- Pierson, W. and Brachaczek, W. W. (1974). "Airborne particulate debris from rubber tyres." *Rubber Chemistry and Technology* **47**: 1275-1299.
- Pirjola, I., Paasonen, P., Pfeiffer, D., Hussein, T., Hameri, K., Koskentalo, T., Virtanen, A., Ronkko, T., Keskinen, J., Pakkanen, T. and Hillamo, R. (2006). "Dispersion of Particles and Trace Gases Nearby a City Highway: Mobile Laboratory Measurements in Finland." *Atmospheric Environment* **40**: 867-879.
- Pirjola, L., Laaksonen, A., Aalto, P. and Kulmala, M. (1998). "Sulfate aerosol formation in the Arctic boundary layer." *Journal of Geophysical Research* **103**: 8309-8322.
- Pirjola, L., Parviainen, H., Hussein, T., Valli, A., Hameri, K., Aalto, P., Virtanen, A., Keskinen, J., Pakkanen, T., Makela, J. and Hillamo, R. (2004). "'Sniffer' - A novel tool for chasing vehicles and measuring traffic pollutants." *Atmospheric Environment* **38**: 3625-3635.
- Pitz, M., Kreyling, W., Holscher, B., Cyrus, J., Wichmann, H. and Heinrich, J. (2001). "Change of the Ambient Particle Size Distribution in East Germany between 1993 and 1999." *Atmospheric Environment* **35**: 4357-4366.
- Pohjola, M., Pirjola, L., Kukkonen, J. and Kulmala, M. (2003). "Modelling the influence of aerosol processes for the dispersion of vehicular exhaust plumes in a street environment." *Atmospheric Environment* **37**: 339-351.
- Pope, C. A., Burnett, R. T., Thun, M. J., Calle, E. E., Krewski, D., Ito, K. and Thurston, G. D. (2002). "Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution." *Journal of the American Medical Association* **287**(9): 1132-1141.
- Raes, F. (1995). "Entrainment of free tropospheric aerosols as a regulating mechanism for cloud condensation nuclei in the remote marine boundary layer." *Journal of Geophysical Research* **100**: 2893-2904.
- Rickeard, D. J., Bateman, J. R., Kwon, Y. K., McAughy, J. J. and Dickens, C. J. (1996). Exhaust Particulate Size Distribution: Vehicle and Fuel Influence in Light Duty Vehicles, SAE Papers, 961980 97-111.
- Riipinen, S., Kulmala, M., Arnold, F., Dal Maso, M., Birmili, W., Saarnio, K., Teinilä, K., Kerminen, V., Laaksonen, A. and Lehtinen, K. (2007). "Connections between atmospheric sulphuric acid and new particle formation during QUEST III-IV campaigns in Heidelberg and Hyytiälä." *Atmospheric Chemistry and Physics* **7**: 1899-1914.
- Ristovski, Z., Jayaratne, E. R., Lim, M., Ayoko, G. A. and Morawska, L. (2006). "Influence of diesel fuel sulphur on the nanoparticle emissions from city buses." *Environmental Science & Technology* **40**: 1314-1320.
- Ristovski, Z. D., Jayaratne, E. R., Morawska, L., Ayoko, G. A. and Lim, M. (2005). "Particle and carbon dioxide emissions from passenger vehicles operating on unleaded petrol and LPG fuel." *Science of the Total Environment* **345**(1-3): 93-98.
- Ristovski, Z. D., Morawska, L., Ayoko, G. A., Johnson, G., Gilbert, D. and Greenaway, C. (2004). "Emissions from a vehicle fitted to operate on either petrol or compressed natural gas." *Science of the Total Environment* **323**(1-3): 179-194.
- Rodriguez, S., van Dingenen, R., Putaud, J., Martins-Dos Santos, S. and Roselli, D. (2005). "Nucleation and Growth of New Particles in the Rural Atmosphere of Northern Italy - Relationship to Air Quality Monitoring." *Atmospheric Environment* **39**: 6734-6746.
- Ronkko, T., Virtanen, A., Vaaraslahti, K., Koskinen, J., Pirjola, L. and Lappi, M. (2006). "Effect of dilution conditions and driving parameters on nucleation mode particles in diesel exhaust: Laboratory and on-road study." *Atmospheric Environment* **40**: 2893-2901.
- Roorda-Knappe, M. C., Janssen, N. A. H., de Hartog, J. J., van Vliet, P. H. N., Harssema, H. and Brunekreef, B. (1998). "Air pollution from traffic in city districts near major motorways." *Atmospheric Environment* **32**(11): 1921-1930.
- Rosenbohm, E., Vogt, R., Scheer, V., Nielsen, O., Drieseidler, A., Baumbach, G., Imhof, D., Baltensperger, U., Fuchs, J. and Jaeschke, W. (2005). "Particulate size distributions and mass measured at a motorway during the BAB II campaign." *Atmospheric Environment* **39**: 5696-5709.
- Ruuskanen, J., Tuch, T., Brink, H., Peters, A., Khlystov, A., Mirme, A., Kos, G., Brunekreef, B., Wickmann, H., Buzorius, Z., Vallius, M., Kreyling, W. and Pekkanen, J. (2001). "Concentrations of Ultrafine, Fine and PM_{2.5} Particles in Three European Cities." *Atmospheric Environment* **35**: 3729-3738.

- Sakurai, H., Tobias, H., Park, K., Zarling, D., Docherty, K. S., Kittleson, D., McMurray, P. and Ziemann, P. J. (2003). "On-line measurements of diesel nanoparticle composition and volatility." *Atmospheric Environment* **37**: 1199-1210.
- Salma, I., Dal Maso, M., Kulmala, M. and Zaray, G. (2002). "Modal characteristics of particulate matter in urban atmospheric aerosols." *Microchemical Journal* **73**: 19-26.
- Sardar, S. B., Fine, P. M., Mayo, P. R. and Sioutas, C. (2005). "Size-Fractionated Measurements of Ambient Ultrafine Particle Chemical Composition in Los Angeles Using the NanoMOUDI." *Environmental Science and Technology* **39**: 932-944.
- Schneider, J., Hock, N., Weimer, S. and Borrmann, S. (2005). "Nucleation particles in diesel exhaust: Composition inferred from in situ mass spectrometric analysis." *Environmental Science & Technology* **39**: 6153-6161.
- Shi, J., Evans, D., Khan, A. and Harrison, R. (2001a). "Sources and Concentration of Nanoparticles (<10nm Diameter) in the Urban Atmosphere." *Atmospheric Environment* **35**: 1193-1202.
- Shi, J., Harrison, R. and Evans, D. (2001b). "Comparison of Ambient Particle Surface Area Measurement by Epiphaniometer and SMPS/APS." *Atmospheric Environment* **35**: 6193-6200.
- Shi, J. and Harrison, R. M. (1999). "Investigation of ultrafine particle formation during diesel exhaust dilution." *Environmental Science & Technology* **33**: 3730-3736.
- Shi, J. P., Khan, A. A. and Harrison, R. M. (1999). "Measurements of ultrafine particle concentrations and size distribution in the urban atmosphere." *The Science of the Total Environment* **235**: 51-64.
- Shi, Q. (2003). Aerosol size distributions (3 nm to 3 µm) measured at the St. Louis Supersite (4/1/01-4/30/02). . *Department of Mechanical Engineering*. Minneapolis, University of Minnesota.
- Stanier, C., Khlystov, A. and Pandis, S. (2004a). "Ambient Aerosol Size Distributions and Number Concentrations Measured During the Pittsburgh Air Quality Study (PAQS)." *Atmospheric Environment* **38**: 3275-3284.
- Stanier, C., Khlystov, A. and Pandis, S. (2004b). "Nucleation events during the Pittsburgh air quality study: Description and relation to key meteorological, gas phase, and aerosol parameters." *Aerosol Science and Technology* **38 (S1)**: 253-264.
- Sturm, P., Baltensperger, U., Bacher, M., Lechner, B., Hausberger, S., Heiden, B., Imhof, D., Weingartner, E., Prevot, A., Kurtenbach, R. and Wiesen, P. (2003). "Roadside measurements of particulate matter size distribution." *Atmospheric Environment* **37**: 5273-5281.
- Suni, T., Kulmala, M., Hirsikko, A., Bergman, T., Laakso, L., Aalto, P., Leuning, R., Cleugh, H., Zegelin, S., Hughes, D., van Gorsel, E., Kitchen, M., Vana, M., Hörrak, U., Mirme, S., Mirme, A., Twining, J. and Tadros, C. (2007). "Formation and characteristics of ions and charged aerosol particles in a native Australian Eucalypt forest." *Atmospheric Chemistry and Physics Discussions* **7**: 10343-10369.
- Thomas, S. and Morawska, L. (2002). "Size selected particles in an urban atmosphere in Brisbane, Australia." *Atmospheric Environment* **36(26)**: 4277-4288.
- Tobias, H. J., Beving, D. E., Ziemann, P. J., Sakurai, H., Zuk, M., McMurry, P., Zarling, D., Waytulonis, R. and Kittelson, D. B. (2001). "Chemical Analysis of Diesel Engine Nanoparticles Using a Nano-DMA / Thermal Desorption Particle Beam Mass Spectrometer." *Environmental Science & Technology* **35**: 2233-2243.
- Tuch, T., Brand, P., Wichmann, H. and Heyder, J. (1997). "Variation of Particle Number and Mass Concentration in Various Size Ranges of Ambient Aerosols in Eastern Germany." *Atmospheric Environment* **31**: 4193-4197.
- Tunved, P., Hansson, H., Kerminen, V., Strom, J., Dal Maso, M., Lihavainen, H., Viisanen, Y., Aalto, P., Komppula, M. and Kulmala, M. (2006). "High natural aerosol loading over boreal forests." *Science* **312**: 261-263.
- Tunved, P., Hansson, H., Kulmala, M., Aalto, P., Viisanen, Y., Karlsson, H., Kristensson, A., Swietlicki, E., Maso, M., Strom, J. and Komppula, M. (2003). "One Year Boundary Layer Aerosol Size Distribution Data from Five Nordic Background Stations." *Atmospheric Chemistry and Physics Discussions* **3**: 2183-2205.
- Turpin, B. J. and Hutzincker, J. J. (1995). "Identification of Secondary Organic Aerosol Episodes and Quantitation of Primary and Secondary Organic Aerosol Concentrations during SCAQS." *Atmospheric Environment* **29(23)**: 3527-3544.
- Vaaraslahti, K., Keskinen, J., Gieshaskiel, B., Solla, A., Murtonen, T. and Vesala, H. (2005). "Effect of lubricant on the formation of heavy duty diesel exhaust nanoparticles." *Environmental Science & Technology* **39**: 8497-8504.
- Vaaraslahti, K., Virtanen, A., Ristimäki, J. and Keskinen, J. (2004). "Nucleation mode formation in heavy-duty diesel exhaust with and without a particulate filter." *Environmental Science & Technology* **38**: 4484-4890.
- Vakeva, M., Hameri, K., Kulmala, M., Lahdes, R., Ruuskanen, J. and Laitinen, T. (1999). "Street level versus rooftop concentrations of submicron aerosol particles and gaseous pollutants in an urban street canyon." *Atmospheric Environment* **33**: 1385-1397.
- Vardoulakis, S., Fisher, B. E. A., Pericleous, K. and Gonzalez-Flesca, N. (2003). "Modeling air quality in street canyons: a review." *Atmospheric environment* **37**: 155 -182.
- Vignati, E., Berkowicz, R., Palmgren, F., Lyck, E. and Hummelshoj, P. (1999). "Transformation of size distributions of emitted particles in streets." *The Science of The Total Environment* **235**: 37-49.
- Virtanen, A., Ronkko, T., Kannosto, J., Ristimäki, J., Makela, J., Keskinen, J., Pakkanen, T., Hillamo, R., Pirjola, L. and Hameri, K. (2006). "Winter and Summer Time Distributions and Densities of Traffic Related Aerosol Particles at a Busy Highway in Helsinki." *Atmospheric Chemistry and Physics* **6**: 2411-2421.

- Vogt, R., Scheer, V., Casati, R. and Benter, T. (2003). "On-road measurement of particle emissions in the exhaust plume of a diesel passenger car." *Environmental Science & Technology* **37**: 4070-4076.
- Wahlin, P., Palmgren, F., Dingenen, R. and Raes, F. (2001). "Pronounced Decrease of Ambient Particle Number Emissions from Diesel Traffic in Denmark After Reduction of the Sulphur Content in Diesel Fuel." *Atmospheric Environment* **35**: 3549-3552.
- Wählin, P., Palmgren, F. and Van Dingenen, R. (2001). "Experimental studies of ultrafine particles in streets and the relationship to traffic." *Atmospheric Environment* **35**: S63-S69.
- Watson, J. G., Chow, J. C., Lowenthal, D. H., Kreisberg, N. M., Hering, S. V. and Stolzenburg, M. R. (2005). "Variations of nanoparticle concentrations at the Fresno Supersite." *Science of The Total Environment* **358**: 178-187.
- Weber, R., Marti, J. J., McMurray, P., Eisele, F. L., Tanner, D. J. and Jefferson, A. (1996). "Measured atmospheric new particle formation rates: Implications for nucleation mechanisms." *Chemical Engineering Communications* **151**: 53-64.
- Weber, R., Marti, J. J., McMurray, P., Eisele, F. L., Tanner, D. J. and Jefferson, A. (1997). "Measurement of new particle formation and ultrafine particle growth rates at a clean continental site." *Journal of Geophysical Research* **102**: 4375-4386.
- Wehner, B., Birmili, W., Gnauk, T. and Wiedensohler, A. (2002). "Particle number size distributions in a street canyon and their transformation into the urban-air background: measurements and a simple model study." *Atmospheric Environment* **36**(13): 2215-2223.
- Wehner, B. and Wiedensohler, A. (2003). "Long Term Measurements of Submicrometer Urban Aerosols: Statistical Analysis for Correlations with Meteorological Conditions and Trace Gases." *Atmospheric Chemistry and Physics Discussions* **3**: 867-879.
- Westerdahl, D., Fruin, S., Sax, T., Fine, P. and Sioutas, C. (2005). "Mobile platform measurements of ultrafine particles and associated pollutant concentrations on freeways and residential streets in Los Angeles." *Atmospheric Environment* **39**: 3597-3610.
- WHO (2005). Guidelines for Air Quality. World Health Organization.
- Wiedensohler, A., Wehner, B. and Birmili, W. (2002). "Aerosol number concentrations and size distributions at mountain rural, urban-influenced rural and urban-background sites in Germany." *Journal of Aerosol Medicine* **15**(2): 237-243.
- Woo, K. S., Chen, D. R., Pui, D. Y. H. and McMurry, P. H. (2001a). "Measurement of Atlanta Aerosol Size Distributions: Observation of ultrafine particle events." *Aerosol Science and Technology* **34**(1): 75-87.
- Woo, K. S., Chen, D. R., Pui, D. Y. H. and Wilson, W. E. (2001b). "Use of continuous measurements of integral aerosol parameters to estimate particle surface area." *Aerosol Science and Technology* **34**(1): 57-65.
- Young, L. and Keeler, G. (2004). "Characterization of Ultrafine Particle Number Concentration and Size Distribution During a Summer Campaign in Southwest Detroit." *Journal of the Air & Waste Management Assoc.* **54**: 1079-1090.
- Yu, F. (2001). "Chemions and nanoparticle formation in diesel engine exhaust." *Geophysical Research Letters* **28**: 4191-4194.
- Yu, F., Lanni, T. and Frank, B. P. (2004). "Measurements of ion concentration in gasoline and diesel engine exhaust." *Atmospheric Environment* **38**: 1417-1423.
- Yu, F. and Turco, R. P. (1997). "The role of ions in the formation and evolution of particles in aircraft plumes." *Geophysical Research Letters* **24**: 1927-1930.
- Yu, F. and Turco, R. P. (2000). "Ultrafine aerosol formation via ion-mediated nucleation." *Geophysical Research Letters* **27**: 883-886.
- Yu, F. and Turco, R. P. (2001). "From molecular clusters to nanoparticles: Role of ambient ionisation in tropospheric aerosol formation." *Journal of Geophysical Research* **106**(D5): 4797-4814.
- Zhang, K. and Wexler, A. (2004a). "Evolution of Particle Number Distribution Near Roadways Part I: Analysis of Aerosol Dynamics and its Implications for Engine Emission Measurement." *Atmospheric Environment* **38**: 6643-6653.
- Zhang, K. and Wexler, A. (2004b). "Modeling the Number Distributions of Urban and Regional Aerosols: Theoretical Foundations." *Atmospheric Environment* **38**: 1863-1874.
- Zhang, K., Wexler, A., Niemeier, D., Zhu, Y., Hinds, W. and Sioutas, C. (2005). "Evolution of Particle Number Distribution Near Roadways Part III: Traffic Analysis and On-Road Size Resolved Particulate Emission Factors." *Atmospheric Environment* **39**: 4155-4166.
- Zhang, K., Wexler, A., Zhu, Y., Hinds, W. and Sioutas, C. (2004a). "Evolution of Particle Number Distribution Near Roadways Part II: The Road-to-Ambient Process." *Atmospheric Environment* **38**: 6655-6665.
- Zhang, Q., Stanier, C., Canagaratna, M., Jayne, J., Worsnop, D., Pandis, S. and Jiminez, J. (2004b). "Insights into the Chemistry of New Particle Formation and Growth Events in Pittsburgh Based on Aerosol Mass Spectrometry." *Environmental Science and Technology* **38**: 4797-4809.
- Zhu, Y., Hinds, W., Kim, S., Shen, S. and Sioutas, C. (2002a). "Study of Ultrafine Particles Near a Major Highway with Heavy Duty Diesel Traffic." *Atmospheric Environment* **36**: 4323-4335.
- Zhu, Y., Hinds, W., Shen, S. and Sioutas, C. (2004). "Seasonal Trends of Concentration and Size Distribution of Ultrafine Particles Near Major Highways in Los Angeles." *Aerosol Science and Technology* **38**: 5-13.

- Zhu, Y., Hinds, W. C., Kim, S. and Sioutas, C. (2002b). "Concentration and Size Distribution of Ultrafine Particles Near a Major Highway." Journal of the Air & Waste Management Assoc. **52**(9): 1032-1042.
- Zhu, Y., Kuhn, T., Mayo, P. and Hinds, W. (2006). "Comparison of Daytime and Nighttime Concentration Profiles and Size Distributions of Ultrafine Particles Near a Major Highway." Environmental Science and Technology **40**: 2531-2536.