A review of the characteristics of nanoparticles in the urban atmosphere and the prospects for developing regulatory controls

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Abstract

The likely health and environmental implications associated with atmospheric nanoparticles have prompted considerable recent research activity. Knowledge of the characteristics of these particles has improved considerably due to an ever growing interest in the scientific community, though not yet sufficient to enable regulatory decision making on a particle *number* basis. This review synthesizes the existing knowledge of nanoparticles in the urban atmosphere, highlights recent advances in our understanding and discusses research priorities and emerging aspects of the subject. The article begins by describing the characteristics of the particles and in doing so treats their formation, chemical composition and number concentrations, as well as the role of removal mechanisms of various kinds. This is followed by an overview of emerging classes of nanoparticles (i.e. manufactured and bio–fuel derived), together with a brief discussion of other sources. The subsequent section provides a comprehensive review of the working principles, capabilities and limitations of the main classes of advanced instrumentation that are currently deployed to measure number and size distributions of nanoparticles in the atmosphere. A further section focuses on the dispersion modelling of nanoparticles and associated challenges. Recent toxicological and epidemiological studies are reviewed so as to highlight both current trends and the research needs relating to exposure to particles and the associated health implications. The review then addresses regulatory concerns by providing an historical perspective of recent developments together with the associated challenges involved in the control of airborne nanoparticle concentrations. The article concludes with a critical discussion of the topic areas covered.

Keywords: Airborne nanoparticles; Bio–fuel; Manufactured nanomaterials; Number and size distributions; Street canyons; Ultrafine particles

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1. Introduction

This review addresses the characteristics of airborne nanoparticles and the prospects for developing appropriate regulatory controls, subjects that have recently attracted substantial attention from the air quality management and scientific communities. Here, we focus mainly on man-made nanoparticles in urban atmospheres, as this is where nearly all exposure to particle pollution occurs and is consequently the target for regulatory action. We refer to natural sources of nanoparticles (e.g. in marine or forest environments) only where necessary to set urban conditions in context. The focus implies that the dominant source is road transport. There are, of course, likely to be specific urban locations, perhaps near demolition or building sites (Hansen et al., 2008), airports (Hu et al., 2009) or ports and harbours (Isakson et al., 2001; Saxe and Larsen, 2004), where other sources are important. Specifically including these in the review is not feasible as their influence is localised (becoming a site-specific issue) whereas road traffic is widespread.

Nanoparticles are basically particles in the nanometre size range (i.e. $<1\ \mu\text{m}$). However, currently used definitions in the literature for the term ‘nanoparticle’ differ. For example, it is sometimes employed as a description of particle sizes $<100\ \text{nm}$ (regardless of mode), sometimes $<50\ \text{nm}$, at times for any particle $10\ \text{nm}$ or less and occasionally $<1\ \mu\text{m}$ (Anastasio and Martin, 2001; BSI, 2005; EPA, 2007). Here, we define nanoparticles as particles of size $<300\ \text{nm}$ as this size range includes more than 99% of the total *number* concentration of particles in the ambient atmospheric environment (see Fig. 1) (Kumar et al., 2008a,b,c, 2009a). In what follows, the terms airborne, atmospheric and ambient are used interchangeably as are the terms particles and aerosols (according to context).

The first question arises is why might we need to control nanoparticles? The reasons could include their probable negative impact on human health (Murr and Garza, 2009), urban

visibility (Horvath, 1994) and global climate (IPCC, 2007; Strawa et al., 2010), as well as their influence on the chemistry of the atmosphere, through their chemical composition and reactivity opening novel chemical transformation pathways (Kulmala et al., 2004). Atmospheric particles are currently regulated in terms of mass concentrations in the size ranges ≤ 10 μm (PM_{10}) and ≤ 2.5 μm ($\text{PM}_{2.5}$) but this does not address particle *number* concentrations. Thus the major proportion of vehicle emissions that contribute significantly to number concentrations remains unregulated through ambient air quality standards.

If atmospheric nanoparticles are to be controlled, what would be the best metric to represent their toxic effects? This question cannot be answered precisely as several generic and specific characteristics of particles (i.e. chemical composition, size, geometry, mass concentration or surface area, etc.) have been proposed but without a consensus being reached. However, recent toxicological (Donaldson et al., 2005; Murr and Garza, 2009) and epidemiological (Ibald-Mulli et al., 2002) studies associate exposure to ultrafine particles (those below 100 nm in diameter) with adverse health effects, though there are uncertainties about the exact biological mechanisms involved. The studies however suggest that particle *number* concentrations are an important metric to represent the toxic effects. This is because ultrafine particles have (i) a higher probability of suspension in the atmosphere and hence a longer residence time (AQEG, 2005; Kittelson, 1998), (ii) a larger likelihood of penetration and deposition in respiratory or cardiovascular systems (see Fig. 1) (Donaldson et al., 2005; ICRP, 1994), and (iii) a higher surface area per unit volume than larger particles that increases the capability to adsorb organic compounds, some of which are potentially carcinogenic (Donaldson et al., 2005; EPA, 2002). Note that the ultrafine size range comprises the major proportion (about 80%) of the total number concentration of ambient nanoparticles, but negligible mass concentration (AQEG, 2005; Kittelson et al., 1999, 2008c).

1 While the above potential impacts motivate control of nanoparticles, several important
2 questions related to their characteristics, sources and measurement remain unanswered. While
3 several new sources (e.g. from bio-fuel emissions and particle manufacture) continue to
4 emerge, conventional-fuelled vehicles remain the dominant anthropogenic source in urban
5 areas (Johansson et al., 2007; Rose et al., 2006; Schauer et al., 1996; Wahlin et al., 2001). All
6 else being equal, diesel-fuelled vehicles contribute about 10 to 100 times more in terms of
7 both mass and number concentrations compared with petrol-fuelled vehicles (Kittelson et al.,
8 2004). However, the latter emit a higher proportion of small-sized particles, by number,
9 under high speed and load conditions (CONCAWE, 1999; Kittelson et al., 2004; Wehner et
10 al., 2009). The use of bio-fuels in vehicles has been promoted as a result of strict emission
11 standards and intentions to secure fossil fuel supplies. Particle mass emissions from bio-
12 fuelled vehicles have decreased significantly, but possibly at the expense of an increase in
13 particle number emissions (Cheng et al., 2008a), leading to some confusion as to whether
14 such vehicles can meet the particle number based emissions standards included in Euro-5 and
15 Euro-6 (EU, 2008; see Section 7 for details). Furthermore, new types of nanoparticles (i.e.
16 manufactured, engineered or synthesized) have recently appeared for which there is limited
17 background knowledge of their concentrations, characteristics, health and environmental
18 effects (Kumar et al., 2010a). These may have relatively smaller concentrations than other
19 nanoparticles in the atmosphere but may pose larger health risks (Andujar et al., 2009).
20 Whether the increased use of manufactured nanoparticles will complicate existing regulatory
21 concerns over other atmospheric nanoparticles remain uncertain.

22 Concentrations of nanoparticles can vary by up to five or more orders of magnitude (from 10^2
23 to 10^7 # cm^{-3}) depending on environmental conditions and source strengths (see Section 3).
24 Urban street canyons lead the table for greatest concentrations as they can act as a trap for
25 pollutants emitted from vehicles. This is enhanced by the surrounding built-up environment

1 that limits the dispersion of exhaust emissions (Van Dingenen et al., 2004). For example, a
2 street canyon study by Kumar et al. (2008c) found that 20 s averaged nanoparticle
3 concentrations increased by up to a factor of a thousand from the overall hourly averaged (i.e.
4 from about 10^4 to 10^7 # cm⁻³) because a diesel lorry was parked near the sampling location
5 with its engine idling for a few tens of seconds. Such events are common in urban areas but
6 are generally overlooked either because of the limited sampling frequencies of instruments
7 (see Section 5) or the general practice to analyse air quality data on a minimum of a half-
8 hourly or an hourly basis. Exposure to such peak concentrations may aggravate existing
9 pulmonary and cardiovascular conditions (Brugge et al., 2007) and hence require regulatory
10 attention.

11 Reliable characterisation of nanoparticles in the air is vital for developing a regulatory
12 framework. A number of instruments have recently emerged but progress to measure
13 concentrations and distributions has been limited by a lack of standard methodologies and
14 application guidelines (see Section 4).

15 This article aims to address the following areas that are important for developing a regulatory
16 framework for atmospheric nanoparticles: (i) the characteristics of atmospheric nanoparticles,
17 providing an overview of their formation, chemical composition and loss mechanisms, (ii)
18 conventional and emerging sources (e.g. bio-fuels and manufacturing) and their contribution
19 to atmospheric particle levels, (iii) the current state-of-the-art for measuring number and
20 size distributions, (iv) dispersion modelling of nanoparticles and associated challenges, (v)
21 health and environmental implications, (vi) an historical perspective of recent developments
22 in regulation and policy, and (vii) a discussion of the critical findings and future research
23 needs.

2. Characteristics of atmospheric nanoparticles

Fig. 1 summarises the terminology commonly used to represent particle size ranges. For example, toxicologists use terms like ultrafine (particle sizes below 100 nm), fine (below 1000 nm) and coarse particles (above 1000 nm) (Oberdörster et al., 2005a). On the other hand, regulatory agencies use terms such as PM_{10} , $PM_{2.5}$ and PM_1 (PM is referred to particulate matter and the subscripts show cut-off sizes in μm).

In aerosol science, atmospheric particles are discussed in terms of modes (i.e. nucleation, Aitken, accumulation and coarse). Each has distinctive sources, size range, formation mechanisms, chemical composition and deposition pathways (Hinds, 1999). It is important to define the particle size range for each mode as definitions currently used differ, as summarised in Table 1. Each mode is described below in the context of the polluted urban atmosphere.

2.1 Nucleation mode

Nucleation (or nuclei) mode particles (typically defined as the 1 to 30 nm range) are predominantly a mixture of two or more mutually exclusive aerosol populations (Lingard et al., 2006). These are not present in primary exhaust emissions, but are thought to be formed through nucleation (gas-to-particle conversion) in the atmosphere after rapid cooling and dilution of emissions when the saturation ratio of gaseous compounds of low volatility (i.e. sulphuric acid) reaches a maximum (Charron and Harrison, 2003; Kittelson et al., 2006a). Most of these particles comprise sulphates, nitrates and organic compounds (Seinfeld and Pandis, 2006). These particles are typically liquid droplets primarily composed of readily volatile components derived from unburned fuel and lubricant oil (i.e. the solvent organic fraction: *n*-alkanes, alkenes, alkyl-substituted cycloalkanes, and low molecular weight poly-

aromatic hydrocarbon compounds) (Lingard et al., 2006; Sakurai et al., 2003; Wehner et al., 2004).

Nucleation mode particles are found in high number concentrations near sources. Collisions with each other and with particles in the accumulation mode are largely responsible for their relatively short atmospheric life time. Dry deposition, rainout or growth through condensation are the other dominant removal mechanisms (Hinds, 1999).

2.2 Aitken and accumulation modes

The Aitken mode is an overlapping fraction (typically defined as the 20 to 100 nm range) of the nucleation and accumulation mode particles (Seinfeld and Pandis, 2006). This mode is not clearly visible in many ambient measurements as is the case in Fig. 1 (Kumar et al., 2008a,b,c), but can be separated using mode fitting statistical analysis (Agus et al., 2007; Leys et al., 2005; Lingard et al., 2006). Particles in this mode arise from the growth or coagulation of nucleation mode particles as well as by production in high numbers by primary combustion sources such as vehicles (Kulmala et al., 2004). These particles are mainly composed of a soot/ash core with a readily absorbed outer layer of volatilisable material (Lingard et al., 2006).

Accumulation mode particles (typically defined as the 30 to 300 nm size range and sometimes referred to as the ‘soot mode’) are carbonaceous (soot and/or ash) agglomerates. They derive mainly from the combustion of engine fuel and lubricant oil by diesel–fuelled or direct injection petrol–fuelled vehicles (Graskow et al., 1998; Wehner et al., 2009), as well as from the coagulation of nucleation mode particles (Hinds, 1999). Most of these particles are formed in the combustion chamber (or shortly thereafter) with associated condensed organic matter (Kittelson et al., 2006b). They are mainly composed of two or more distinct

components that are either co-joined or exist with one component adsorbed on to the surface of another, forming an outer layer and inner core (Lingard et al., 2006). These particles are not removed efficiently by diffusion or settling, as they coagulate too slowly, but rainout or washout is an effective removal mechanism (Hinds, 1999). Thus, they tend to have relatively long atmospheric life times (typically days to weeks) and hence can travel over very long distances in the atmosphere (Anastasio and Martin, 2001). More importantly, particles in this mode are of sizes comparable with the wavelengths of visible lights, and hence account for much of the man-made visibility impairment problem in many urban areas (Seinfeld and Pandis, 2006).

Nanoparticles discussed in this review are combination of all three of the above modes.

3. Sources and concentrations of atmospheric nanoparticles

This section describes the key anthropogenic sources of nanoparticles in urban areas but includes a brief introduction of natural sources to set this in context. Particle emissions from shipping, like those from other diesel vehicles, are dominated by the ultrafine particle size range (Saxe and Larsen, 2004). These can contribute substantially to the background concentrations in the cities with major port or harbour facilities (Isakson et al., 2001). Nevertheless, sources such as trains, ships and aircraft are not covered in this review as attention is focused on the dominant urban source (e.g. road vehicles). However, emerging sources (i.e. bio-fuel derived and manufactured) are included as these may become important as a target for regulatory action.

3.1 Anthropogenic nanoparticles

A recent source apportionment study for Barcelona city by Pey et al. (2009) found vehicular emissions (mean value $1.14 \times 10^4 \text{ \# cm}^{-3}$) and regional-urban background ($0.43 \times$

$10^4 \text{ \# cm}^{-3}$) to be the largest contributors (65 and 24% respectively) to total particle number concentrations in the 13–800 nm size range. These were followed by photochemically induced nucleation ($0.59 \times 10^3 \text{ \# cm}^{-3}$; 3%), industrial sources ($0.31 \times 10^3 \text{ \# cm}^{-3}$; 2%), sea spray ($0.31 \times 10^3 \text{ \# cm}^{-3}$; 2%), mineral dust ($0.25 \times 10^3 \text{ \# cm}^{-3}$; 1%) and other unaccounted sources (3%). The following sections add some details to these figures.

3.1.1 Manufactured nanoparticles

These differ from other airborne nanoparticles in numerous aspects, such as their sources, composition, homogeneity or heterogeneity, size distribution, oxidant potential and potential routes of exposure and emissions (Xia et al., 2009; Kumar et al., 2010a). Small size and relatively large reactive surface areas are the novel properties of manufactured nanoparticles that encourage their increased production and use in various technologic applications (e.g. in electronics, biomedicine, pharmaceuticals, cosmetics, energy and materials) (Helland et al., 2007). For instance, Maynard (2006) projected that the worldwide production of nanomaterials will rise from an estimated 2000 tons in 2004 to 58,000 tons by 2020. Dawson (2008) reported that by 2014 more than 15% of all products in the global market will have some sort of nanotechnology incorporated in their manufacturing process. The major class of these particles falls in the categories of fullerenes, carbon nanotubes, metal oxides (e.g. oxides of iron and zinc, titania, ceria) and metal nanoparticles (Ju-Nam and Lead, 2008). Silver nanoparticles, carbon nanotubes and fullerenes are the most popular classes of nanomaterials currently in use (HSE., 2007). This benefits industry and the economy but is likely to increase population exposure and may affect human health (Xia et al., 2009).

Manufactured nanoparticles are not intentionally released into the environment, though a release may occur in the production, use and disposal phases of nanomaterial–integrated

1 products (Bystrzejewska–Piotrowska et al., 2009). Unexpected sources are also emerging;
2 e.g. Evelyn et al. (2002) reported carbon nanotube–like structures in diesel–engine emissions,
3 leading to concern about their potential impact if widely emitted into the atmosphere.
4 Furthermore, carbon nanotubes are widely used in mass consumer products such as batteries
5 and textiles (Köhler et al., 2008). Life cycle studies indicate that these particles can enter the
6 environment by wear and tear of products or through the municipal solid waste stream where
7 only incineration above 850 °C is thought to eliminate them (Köhler et al., 2008). Similarly,
8 fullerenes and carbon black can enter the environment during storing, filling and weighing
9 operations in factories (Fujitani et al., 2008; Kuhlbusch et al., 2004). Because of their size,
10 effects of gravitational settling are small and a long lifetime in air is expected. Muller and
11 Nowack (2008) report rare data on mass concentrations of manufactured nanoparticles (about
12 $10^{-3} \mu\text{gm}^{-3}$) in the atmosphere in Switzerland. However, knowledge of the current
13 background concentrations and distributions (on a number basis) of air–dispersed
14 manufactured nanoparticles is very limited. Despite this, a substantial forecast production and
15 their supposed persistence against degradation imply increasing human and environmental
16 exposure (Donaldson and Tran, 2004; Helland et al., 2007). Unquestionably, understanding
17 of the nature and behaviour of this class of particles has improved in recent years (Nowack,
18 2009) but a number of unanswered questions remain, related to emission routes, atmospheric
19 life time, dispersion behaviour and background concentrations.

20 To generalise the toxicity of these particles is difficult because of the great variability in the
21 materials used (e.g. titanium dioxide, silver, carbon, gold, cadmium and heavy metals among
22 others) (Donaldson et al., 2006; Duffin et al., 2007). Other factors such as size, shape, surface
23 characteristics, inner structure and chemical composition also play an important role in
24 determining toxicity and reactivity (Maynard and Aitken, 2007). For instance, some

1 manufactured nanoparticles (e.g. carbon nanotubes, nanowires, nano-whiskers and
2 nanofibres, etc.) have large aspect ratios (i.e. length to diameter) compared to most others
3 (e.g. nanosphere, nanocubes, nanopyramids, etc.), introducing uncertainties in their
4 measurement once they are mixed with ambient nanoparticles. Carbon nanotubes show the
5 most variability in aspect ratio because of their extended diameter (2.2 to 10's nm) and length
6 ranges (up to 100's nm) (Iijima, 1991). Occupational exposure to manufactured nanoparticles
7 is possible during recycling processes and in factory environments (Andujar et al., 2009).
8 Chemical characteristics suggest a possible accumulation along the food chain and high
9 persistence (Donaldson et al., 2006). Many questions remain largely unanswered, e.g., the
10 best metric to evaluate toxicity, the precise biological mechanisms affecting human health,
11 the potential for accumulation in the environment and organisms, biodegradability, long-term
12 effects, exposure pathways, measurement methods and associated environmental risks.

13 Further information on manufactured nanoparticles can be found in Handy et al. (2008a;
14 2008b), Valant et al. (2009), Bystrzejewska-Piotrowska et al. (2009) and Kumar et al.
15 (2010a).

16 **3.1.2 Nanoparticle emissions from conventional-fuelled vehicles**

17 In the UK, the average traffic fleet share of diesel-fuelled vehicles over the period
18 between 1999 and 2008 was about 26% (DfT, 2008, 2009). This figure is lower in London
19 but, despite this, Colvile et al. (2001) found that PM₁₀ emissions from diesel-engine vehicles
20 were far greater (about 67% of total) than from petrol-fuelled vehicles (about 11%). More
21 generally, many mass-unit based studies show that vehicular sources can comprise up to 77%
22 of total PM₁₀ in urban environments (AQEG, 1999), although some recent studies have
23 reported smaller contributions (Vardoulakis and Kassomenos, 2008).

The situation with particle *number* emissions from road vehicles is not much different. Numerous studies conclude that road vehicles are a major source of nanoparticles in urban areas (Johansson et al., 2007; Keogh et al., 2009; Shi et al., 2001). Their contribution can be up to 86% of total particle number concentrations (Pey et al., 2009). This arises because the majority of particles emitted from diesel- and petrol-fuelled vehicles are of sizes below 130 nm and 60 nm, respectively (Harris and Maricq, 2001; Kittelson, 1998). Diesel-fuelled vehicles, though fewer in number, make by far the greatest contributions to total number concentrations. However, emissions from petrol-fuelled vehicles are more uncertain as they are highly dependent on driving conditions (Graskow et al., 1998). Typical driving in unsteady and stop-start conditions in urban areas leads to storage and release of volatile hydrocarbons during acceleration (Kittelson et al., 2001) and petrol-fuelled vehicles then emit at rates similar to modern heavy duty diesel-fuelled vehicles (CONCAWE, 1999; Graskow et al., 1998).

3.1.3 Nanoparticle emissions from bio-fuelled vehicles

As illustrated in Fig. 2, bio-fuels are liquid or gaseous fuels that are produced from organic material through thermochemical or biochemical conversion processes (Hart et al., 2003). They are seen as one of the means by which targets within the Kyoto Protocol could be met by reducing the transport sector's 98% reliance on fossil fuels (EEA Briefing, 2004). Among those shown in Fig. 2, bio-diesel and bio-ethanol are largely the preferred alternative fuel for road vehicles (Agarwal, 2007; Demirbas, 2009). Their use has significantly decreased particle mass and gaseous (e.g. CO, CO₂ and HC) emissions but has increased the particle *number* emissions (see Table 2). The main reasons for this include (i) a shift in size distributions towards smaller particle sizes, (ii) the reduced available surface area of pre-existing particles in emissions that favours nucleation over adsorption (Kittelson, 1998), (iii) the lower calorific values of bio-fuels (typically 37 MJ kg⁻¹ for rapeseed methyl ester bio-

diesel (RME) compared with 42.6 MJ kg^{-1} for ultra-low sulphur diesel, ULSD), resulting in increased fuel flow rates, and (iv) a higher density of bio-diesel (typically 883.7 kg m^{-3} for RME compared with 827.1 kg m^{-3} for ULSD), resulting in increased rate of fuel mass used (Lapuerta et al., 2008; Mathis et al., 2005; Tsolakis, 2006).

Irrespective of the type of bio-fuel (pure or blended) and engine used, most studies indicate relatively higher particle number emissions for bio-fuels than for diesel or petrol fuels (see Table 2). Some of the observations (e.g. by Fontaras et al. (2009) for passenger cars and by Lee et al. (2009) for non-DPF (diesel particulate filter) cars) indicate problems in meeting the particle number emission regulations enacted by Euro-5 and Euro-6 emission standards, which limit number emissions to $6.0 \times 10^{11} \text{ \# km}^{-1}$. Fontaras et al. (2009) found that particle number emissions can increase up to twofold under certain driving cycles when the blend of bio-diesel in petroleum-diesel is increased from 50 to 100%. Munack et al. (2001) found an increase in particle number emissions in the 10–120 nm size range from rapeseed oil bio-diesel compared with emissions from diesel fuel. Similarly, Krahel et al. (2003; 2005) observed an increase in number concentrations below 40 nm for bio-diesel fuels relative to those for low and ultra-low sulphur diesel fuels. The increased nanoparticle emission rates arise mainly from a shift in the overall particle number distributions towards smaller size ranges (see Table 3). The magnitude of the change depends on a number of factors such as driving conditions, type of bio-fuel and engine. A few studies have found large decreases (up to 10-fold) in mean particle diameter when bio-diesels were compared with standard diesel (Hansen and Jensen, 1997). The reasons for these variations are not well understood but need to be resolved.

In contrast, some studies find similar total particle number concentration emissions from both the bio- and diesel fuelled vehicles (see Bagley et al. (1998) for the ‘rated power’ case in

Table 2). Others actually record a decrease in particle number emissions when bio-fuels were replaced with petrol or diesel fuels (e.g. Cheng et al. (2008a) for low and medium engine loads; Bunger et al. (2000) for idling conditions; Bagley et al. (1998) with an oxidation catalytic converter; see Table 2). In line with this, Jung et al. (2006) observed about a 38% decrease in number concentrations for soy-based bio-diesel as compared with emissions from standard diesel, attributing these decreases partly due to easy oxidation of bio-fuel derived particles. Very low or nil sulphur contents in bio-diesel could be another reason for the decrease, as sulphur has often been found to be associated with the formation of nucleation mode particles (Kittelson, 1998).

Most studies agree on the overall reduction in particulate mass emissions from combustion of bio-fuels, mainly due to reduced emissions of solid carbonaceous particles and the lower sulphur content (Lapuerta et al., 2008). For example, Aakko et al. (2002) tested bio-fuels in a Euro 2 Volvo bus engine equipped with an oxidation catalytic converter and a continuously regenerating particulate trap. They observed that rapeseed oil derived bio-diesel (blended 30% into reformulated diesel fuel) emissions contained a lower mass of particulates in the main peak area (around 100 nm) than EN590 (European diesel with sulphur content below 500 ppm) or RFD (Swedish Environmental Class 1 reformulated diesel) fuels. Similar results were found by Bunger et al. (2000) and Lapuerta et al. (2002) for rapeseed oil based bio-diesels and by Jung et al. (2006) for soy-based bio-diesel.

The above observations suggest that use of bio-fuels in road vehicles considerably reduces emissions of total particle mass. However, this does not seem to be the case with number concentrations, which lead to difficulties in meeting the recently introduced number based limits of the European vehicle emission standards. Better understanding of the performance of these fuels is needed so that appropriate considerations can be made in developing a

regulatory framework for atmospheric nanoparticles. Further information on bio-fuels can be found in Agarwal (2007), Hammond et al. (2008), Basha et al. (2009), Balat and Balat (2009) and Kumar et al. (2010b).

3.1.4 Tyre and road surface interaction

It is generally believed that tyre and road surface interactions generate about 70% of particles by mass mainly in the 2.5 to 10 μm size range (AQEG, 1999). A number of studies have focused on this source to analyse its contribution towards $\text{PM}_{2.5}$ and PM_{10} mass concentrations (Aatmeeyta et al., 2009; Gustafsson et al., 2008; Hussein et al., 2008; Kreider et al., 2010), but less attention has been paid to particle number emissions. Studies indicate considerable nanoparticle emissions, depending on surface, vehicle and driving conditions. For example, Gustafsson et al. (2008) found the generation of 1.81 to $2.65 \times 10^4 \text{ \# cm}^{-3}$ (against background of 0.13 to $0.17 \times 10^4 \text{ \# cm}^{-3}$) particles in the 15 to 700 nm range at a vehicle speed of 70 km h^{-1} . Similarly, Dahl et al. (2006) found generation of particle number concentrations between 0.37 and $3.2 \times 10^{12} \text{ \# veh}^{-1} \text{ km}^{-1}$ in the 15 to 50 nm range. They found that the emission factors for particles (on a number basis) originating from the road-tyre interaction were similar in magnitude to those for some classes of vehicles using liquefied petroleum gas fuel. Thus this source may be a significant contributor to particle number emissions from both conventionally fuelled and ultra-clean vehicles (see Section 3.1.3), though there is insufficient information to quantify this in general.

3.2 Natural sources

The main natural sources of nanoparticles in many regions of the world (e.g. Northern Europe) are forests, oceans and atmospheric formation. Particle number concentrations in marine and forest environments are typically 2 to 3 orders of magnitude smaller than those in urban areas. However, given the total area covered by such environments their contribution

towards the global nano-sized particle load is nevertheless substantial (O'Dowd et al., 1997). New particles are formed in the atmosphere through condensation of semi-volatile organic aerosols (O'Dowd et al., 2002), photo-chemically induced nucleation and/or nucleation through gas-to-particle conversion (Holmes, 2007; Kumar et al., 2009a; Vakeva et al., 1999). The rates of formation and the concentrations attained vary, as shown in Table 4. The great variability in particle formation and growth rates in different environments leads to significant differences in number concentrations and consequent challenges for their modelling (Section 5). Episodic contributions from a number of events such as forest fires (Makkonen et al., 2010), dust storms (Schwikowski et al., 1995) and volcanic eruptions (Ammann and Burtscher, 1990) may well be very large but generally are short-lived. These are briefly mentioned here because of their general relevance and to set the discussion of the urban atmosphere in context. A full review of such sources is however beyond the scope of this article. Further details can be found in Kulmala et al. (2004) and Holmes (2007) and references therein.

4. Current state of the art for nanoparticle number measurements

Atmospheric nanoparticles display a variety of shapes (e.g. tabular, irregular, aggregated or agglomerates), rather than an ideal sphere, and this causes difficulty in their measurement. Aerodynamic equivalent (D_a), Stokes (D_s) or electrical mobility equivalent (D_p) diameters are used to classify particles when the focus is on the behaviour of particles in moving air. D_a is currently used within regulatory limits; it is defined as the diameter of a spherical particle of unit density (1000 kg m^{-3}) and settles in the air with a velocity equal to that of the particle in question. D_s has a similar definition but uses the true density of the particle (Hinds, 1999). The main concern with using D_s is keeping account of the density of each particle as it moves through the atmosphere. D_p is widely used in instruments and is defined as the diameter of a spherical particle that has the same electrical mobility (i.e. a

measure of the ease in which a charged particle will be deflected by an electric field) as the irregular particle in question. It implicitly takes into account the particle characteristics such as shape, size and density.

A review of the capabilities and limitations of most advanced commercially available instruments that are currently used for nanoparticle monitoring is given below, with Table 5 providing a summary of their characteristics. The operating principles of optical, aerodynamic and electrical mobility analysers can be found in Flagan (1998), McMurry (2000a; 2000b) and Simonet and Valcarcel (2009).

4.1 Scanning mobility particle sizer (SMPS)

The SMPSTM (TSI Inc. www.tsi.com) system uses an electrical mobility detection technique to measure number and size distributions. It consists of three components, (i) a bipolar radioactive charger for charging the particles, (ii) a differential mobility analyser (DMA) for classifying particles by electrical mobility, and (iii) a condensation particle counter (CPC) for detecting particles (Stolzenburg and McMurry, 1991; Wang and Flagan, 1989; Wiedensohler et al., 1986).

The SMPS (3034 TSI Inc.) measures D_p between 10 and 487 nm using 54 size channels (32 channels per decade) for number concentrations in the range from 10^2 to 10^7 # cm^{-3} . This model takes 180 s to analyse a single scan. The later SMPS model (3934 TSI Inc.) uses up to 167 size channels (up to 64 channels per decade) to measure particle diameters between 2.5 and 1000 nm at a minimum sampling time of 30 s. Adjusting of the sampling flow rate from 0.2 to 2 l min^{-1} allows it to measure the number concentrations in the 1 to 10^8 # cm^{-3} range (TSI, 2008). The SMPS is regarded as a standard instrument by which other ultrafine particle sizers are compared; though it has its own limitations (see Table 5).

4.2 Electrical low pressure impactor (ELPI)

The ELPITM (Dekati Ltd. www.dekati.com) is a real-time particle size spectrometer with a sampling time of 1 s; the instrument time constants being 2 to 3 s. It measures number and size distributions of particles in the 0.03 to 10 μm range, which can be extended down to 7 nm by a backup filter accessory (Keskinen et al., 1992). The ELPI combines aerodynamic size classification with particle charging and electrical detection of charged particles. It operates on three main principles: (i) charging by a corona charger, (ii) inertial classification using a low pressure cascade impactor, and (iii) electrical detection of the aerosol particles by a multi-channel electrometer (ELPI, 2009). The impactor collection principle also allows size-dependent particle analysis using chemical, scanning electron microscopy (SEM) or transmission electron microscopy (TEM) methods. Further details of the ELPI can be found in Keskinen et al. (1992) and Marjamäki et al. (2000).

4.3 Aerodynamic particle sizer (APS)

The APSTM (model 3320 or 3321 TSI Inc. www.tsi.com) uses a time-of-flight technique for real-time measurements of D_a (Agarwal and Remiarz, 1981). It can measure the particle number distributions in the 0.5 to 20 μm range at a sampling rate of 1 s. Particle size distributions are obtained by using an optical detector (i.e. photomultiplier) to measure the speed acquired by each particle in an accelerated sample air-stream in which they are suspended. Further details can be found in TSI (2009a) and Leith and Peters (2003).

4.4 Differential mobility spectrometer (DMS)

The DMS500 (Cambustion, www.cambustion.com) offers fast response measurement of particle number distributions based on D_p . It uses a differential mobility classifier that provides the fastest time response (200 ms $T_{10-90\%}$, at a data rate of 10 Hz) available in any currently available (i.e. November 2009) ultrafine particle sizer. It is capable of measuring

over two size ranges, namely 5 to 1000 nm and 5 to 2500 nm; see Kumar et al. (2009c) for an example of its application in ambient measurements. Each of these ranges requires different set-points for the instrument's internal flows, voltage and pressure. The instrument uses primary and secondary dilution stages. The primary stage is used to dilute the sample flow with compressed air at the point of sampling; this is generally suitable for ambient measurements. The secondary dilution is used for the sampling of concentrated aerosols (e.g. engine emissions) to bring concentrations within the dynamic range of the instrument (Cambustion, 2003-9). A sample flow rate of 8 l min^{-1} is used when working in the 5–1000 nm size range, decreasing to 2.5 l min^{-1} for the 5–2500 nm size range. Further details of the DM5500 and comparison of its results with other instruments (SMPS and ELPI) can be found in Biskos et al. (2005), Cambustion (2008), Collings et al. (2003) and Symonds et al. (2007).

Cambustion Instruments has recently produced a mobile version of this instrument, the DMS50, based on the same working principle as the DMS500. The DMS50 can measure D_p in the 5 to 560 nm range at a sampling frequency up to 10 Hz but is considerably smaller and can be battery operated (Cambustion, 2009).

4.5 Fast mobility particle sizer (FMPS)

The FMPSTM (model 3091, TSI Inc. www.tsi.com) provides particle number distribution measurements based on D_p up to a sampling frequency of 1 Hz. It can measure particles in the 5.6 to 560 nm range using 32 channels (16 channels per decade of size) (see Table 5). A high sample flow rate (10 l min^{-1}) helps to minimise particle sampling losses due to diffusion (Kumar et al., 2008d) and operation at ambient pressure prevents evaporation of volatile and semi-volatile particles (TSI, 2009d). It uses an electrical mobility detection technique similar to that in the SMPS (see Section 4.1). As opposed to the SMPS, which uses CPC, the FMPS uses multiple, low-noise electrometers for particle detection.

4.6 Ultrafine particle (UFP) monitor

The UFP monitor (model 3031, TSI Inc. www.tsi.com) measures particle number distributions based on D_p at a time resolution of 10 min with 1 min additional zeroing time. It can measure particles in the 20 to 1000 nm range using 6 size channels at a 5 l min⁻¹ sample flow rate (TSI, 2009d). It is designed for operation in a range of meteorological conditions (e.g. temperature 10–40 °C, humidity 0–90%, ambient pressures 90–100 kPa) and for unattended long duration use. It can measure concentrations in the 500 to 10⁶ # cm⁻³ range at 20 nm and 50 to 10⁶ # cm⁻³ range at 200 nm. Further details of the UFP monitor and comparisons of its results with other instruments can be seen in Medved et al. (2000) and TSI (2009b).

4.7 Laser aerosol spectrometer (LAS)

The LAS (model 3340, TSI Inc. www.tsi.com) is a recently commercialised particle spectrometer. It operates on an optical detection system using wide angle optics and an intracavity laser (McMurry, 2000b) and can measure particles in the 0.09 to 7.5 µm range and concentrations up to 1.8×10^4 # cm⁻³ at a sample flow rate 0.1 l min⁻¹. Size distributions of particles can be measured at a sampling time of about 1 s, with up to 100 user configurable size range channels (TSI, 2009c).

4.8 GRIMM nanoparticle measuring systems

GRIMM Aerosol Technik (www.grimm-aerosol.com) produces a number of instruments that measure particle number concentrations and distributions using combinations of SMPS, DMA and CPC systems. The model SMPC+C includes DMA with a CPC to measure particles in the 5 to 1110 nm size range in 44 channels. The model WRAS (wide range aerosol spectrometer) incorporates an additional GRIMM aerosol spectrometer and can measure particles up to 32 µm with 72 channels. The model GRIMM SMPS+E is an

integration of a DMA and a Faraday Cup Electrometer. It can measure particles in the 0.8 to 1100 nm in 44, 88 or 176 size channels with a very fast sampling frequency (T90 response: 0.2 s; T90 is the time taken for the output to reach 90% of its final value). The time response and measuring capacity of these instruments are summarised in Table 5. Detailed information can be found in GRIMM (2009).

4.9 Analysis of the capabilities of the instruments and future needs

Table 5 summarises the capabilities of the instruments described above; see also Keogh et al. (20010) for the application of these instruments. Issues that need to be considered in using such instruments in any regulatory framework include their portability, time response, detection limits, robustness for unattended operation over long durations, cost, calibration and maintenance requirements. Although most instruments claim to overcome many of these issues, reproducibility of data still remains a major issue; see Asbach et al. (2009) for a comparison of a number of mobility analysers. An initiative is needed for evaluating the performance of nanoparticle monitoring instruments, similar to the UN–ECE Particle Measurement Programme that aims to establish new systems and protocols for assessing nanoparticle emissions from vehicles (EU, 2008).

Noise level of an instrument generally increases with the increase in sampling rate. Therefore, selection of an appropriate instrument and sampling frequency critically depends on the objectives of an individual study and noise level of an instrument. A recent study by Kumar et al. (2009c) concluded that a relatively low sampling frequency (i.e. 1 Hz or lower), which can be achieved by almost all the instruments mentioned in Table 5, would be appropriate for urban measurements unless the study rely critically on fast response data. It will not only improve the performance of an instrument by reducing the effects of its noise but will also help to keep the data files in more manageable sizes.

Most instruments are not capable of detecting particles below 3 nm, a size range that is important for secondary particle formation. Further advances in performance are needed to address this deficiency and enable real-time determination of nanoparticle physio-chemical properties and related gas phase species involved in nucleation and growth (Kulmala et al., 2004). Development of robust and cost-effective instruments that have high sampling frequencies and cover a wide range of particle sizes (from nanoparticle to PM₁₀) is needed so that individual and population exposure to particulate pollution in urban environments may be characterised. These capabilities are not currently met by a single particle monitoring instrument and use of more than one instrument is required to obtain such information.

5. Dispersion modelling of nanoparticles and associated challenges

The full range of dispersion model types (e.g. Box, Computational Fluid Dynamics (CFD), Gaussssian, Lagrangian, Eulerian) is available for particulate and gaseous pollutants but only a few are appropriate for the prediction of particle number concentrations. A review of these models can be found in Holmes and Morawska (2006) and Vardoulakis et al. (2003; 2007). The intention here is not to describe them in any detail but briefly to address the challenges associated with them.

The challenges in modelling nanoparticle number concentrations grow with the inclusion of the complex dilution and transformation processes that occur after their release into the atmosphere (Holmes, 2007; Ketzel and Berkowicz, 2004). Model development and evaluation has been limited by insufficient measurements of number and size distributions (see Section 4) and lack of detailed information on emission factors. Information on particle number emission factors (as distinct from mass) for individual types of vehicles under a range of driving conditions is not abundantly available for routine applications. Studies of particle number emission factors show up to an order of magnitude difference for a given vehicle type

under near-identical conditions (Jones and Harrison, 2006; Keogh et al., 2010; Kumar et al., 2008b). Such uncertainty will generally affect the predictions of any model to a similar degree. Model inter-comparison studies have been carried out for ‘conventional’ vehicle emissions (e.g. see Lohmeyer et al. (2002)) but not for particle number concentration prediction. Currently, there are several particle dispersion models available that include particle dynamics e.g. MAT (Ketzel and Berkowicz, 2005) which uses a multi-plume scheme for vertical dispersion and routines of the aerodynamics model AERO3 (Vignati, 1999), MATCH (Gidhagen et al., 2005) which is an Eulerian grid-point model and includes aerosol dynamics, MONO32 (Pohjola et al., 2003) and AEROFOR2 (Pirjola and Kulmala, 2001) – both include gas-phase chemistry and aerosol dynamical processes. Some operational models disregard particle dynamics e.g. OSPM (Berkowicz, 2000) which uses a combination of a plume model for the direct contribution and a box model for the re-circulating pollution part in the street canyon; several others are described in Holmes and Morawska (2006). Performance evaluation of such particle number concentration models against validation data is essential if they are to be used for developing mitigation policies.

5.1 Importance of transformation and loss processes in dispersion models

Table 6 summarises the effect of transformation and loss processes on particle number concentrations. A simple qualitative description of the nature of any change is included. *Coagulation* acts to reduce the number of particles in the atmosphere (Hinds, 1999). Gidhagen et al. (2005) used a three dimensional Eulerian grid-point model for calculating distributions of particle number concentrations over Stockholm. They found the overall loss to be up to 10% due to coagulation when compared with inert particles. Ketzel and Berkowicz (2005) observed a similar effect (up to 10% loss) by coagulation in Copenhagen. However, other studies found the effect of coagulation too slow to affect number

1 concentrations in either a car exhaust plume or under typical urban conditions (Pohjola et al.,
2 2003; Zhang and Wexler, 2002).

3 *Nucleation* and *dilution* promote the formation of new particles that may offset the loss
4 mechanisms. For instance, pseudo-simultaneous measurements in a Cambridge street canyon
5 indicated about a five times greater formation rate of new particles at rooftop level than at
6 street level (Kumar et al., 2009a), attributed to less efficient scavenging mechanisms
7 (Kerminen et al., 2001) and favourable conditions for gas-to-particle conversion (Kulmala et
8 al., 2000) at rooftop. Other processes such as *condensation* and *evaporation* have negligible
9 effects (Zhang and Wexler, 2004).

10 *Dry deposition* occurs when a particle is removed at an air-surface interface as a result of
11 particle Brownian diffusion. This can remove the smaller particles (i.e. nucleation mode)
12 more efficiently due to their higher diffusion coefficient compared with that for large
13 particles (i.e. accumulation mode). The deposition velocity will be relatively high for small
14 particles and for high friction velocities (Hinds, 1999). For example, Kumar et al. (2008c)
15 estimated dry deposition losses of vehicle emitted particles onto a road surface in a
16 Cambridge street canyon. The relative removal of total particle number concentrations in the
17 10–30 nm range was estimated to be about 19% larger than the particles in the 30–300 nm
18 range at the road surface compared to concentrations at 1 m above the road level. Likewise,
19 city scale model calculations in Stockholm by Gidhagen et al. (2005) found up to 25% loss of
20 total particle number concentrations in about 3 to 400 nm size range at certain locations, and
21 up to 50% in episodic conditions. Dry deposition is therefore an important loss process that
22 can reduce total particle number concentrations considerably. The effect of dry deposition at
23 various spatial scales should be treated appropriately in particle dispersion models.

1 Current knowledge is insufficient to describe behaviour of transformation processes at
2 different spatial scales in any detail. Therefore the above figures may vary in different
3 settings; e.g. in vehicle-wakes (Kumar et al., 2009c; Minoura et al., 2009), street canyons
4 (Kumar et al., 2009a; Pohjola et al., 2003), urban areas (Wehner et al., 2002) or globally
5 (Raes et al., 2000). The combined effect of particle transformation processes may also vary
6 with setting and scale depending on meteorological conditions, source terms and the
7 background concentrations of particles and gas phase species.

8 Does performance of dispersion models suffer if particle dynamics are disregarded? Particle
9 dynamics can probably be neglected for street scale modelling (Ketzel and Berkowicz, 2004;
10 Kumar et al., 2008c); e.g. as in existing dispersion models such as OSPM. Recent work by
11 Kumar et al. (2009b) supports this conclusion. Particle dynamics were disregarded and
12 particle number concentrations predicted by using a modified Box model (Kumar et al.,
13 2009b), OSPM (Berkowicz, 2000), and the CFD code FLUENT (Solazzo et al., 2008).
14 Particle number concentrations predicted by all three models were within a factor of three of
15 the measured values. However, a number of studies indicate that particle dynamics should be
16 included in city scale models where they may affect the total number concentrations
17 considerably (Gidhagen et al., 2005; Ketzel and Berkowicz, 2004; Ketzel et al., 2003; Kumar
18 et al., 2009a). Changes in total particle number concentrations due to the combined effects of
19 transformation and loss processes can lie between a loss of 13 and 23% compared to an inert
20 treatment (Ketzel and Berkowicz, 2005).

21 The above observations highlight a number of challenges associated with dispersion
22 modelling of particle number concentrations and the role of particle dynamics at various
23 spatial scales. Extensive measurements of nanoparticle concentrations would be helpful in

evaluating dispersion model performance and hence supporting the modelling that is required for the evaluation of mitigation policies.

6. Effect of nanoparticles on health and the environment

This section summarises recent advances concerning the impact of atmospheric nanoparticles on human health and urban visibility and highlights some remaining research requirements.

6.1 Health effects

The ultrafine size range of nanoparticles has the potential for the largest deposition rates in the lungs (Fig. 1). They can enter the body through the skin, lung and gastrointestinal tract and can also penetrate epithelial cells and accumulate in lymph nodes (Nel et al., 2006). Nemmar et al. (2002) observed that ultrafine particles could rapidly pass through the blood circulation system and accumulate in the lungs, liver and bladder. Only about 20% of nanoparticles are removed once deposited in alveolar regions in animal subjects after 24 h exposure, in contrast to about 80% removal for particles above 500 nm (Oberdörster et al., 2005b). In related work, Chalupa et al. (2004) found about 74% deposition of carbon ultrafine particles in asthmatic human subjects for a 2 hour exposure.

A number of generic and specific properties (e.g. particle number or mass concentrations, chemical composition, size, geometry or surface area) are important in characterising the toxicity of nanoparticles (McCawley, 1990). Nowack and Bucheli (2007) demonstrate that particle size plays an important role in defining toxicity but little is known about the effects of size on particle behaviour and reactivity. Tetley (2007) notes that some of the particular properties of nanoparticles (i.e. high surface reactivity and ability to cross cell membranes) increase their negative health impact. Likewise, Limbach et al. (2007) showed that chemical composition plays a significant role in defining effects on human lung epithelial cells.

1 Some studies favour particle surface area as a suitable metric to quantify human exposure
2 whilst many others support particle number concentrations. For example, Maynard and
3 Maynard (2002) found that the higher surface area to mass ratio of ultrafine particles (relative
4 to coarse particle) allows greater contact for adsorbed compounds to interact with biological
5 surfaces. On the other hand, epidemiological studies discussed below support number
6 concentration as a metric. Pekkanen et al. (1997) demonstrated associations between deficits
7 in peak expiratory flow among asthmatic children and exposure to ultrafine particles.
8 Likewise, other studies associate this form of exposure with cardiovascular events such as
9 heart attacks and cardiac-rhythm disturbance (Nel et al., 2006; Oberdörster et al., 2005a;
10 Seaton et al., 1999; Wichmann et al., 2000). Penttinen et al. (2001) demonstrated a negative
11 correlation between the ultrafine-dominated fraction of daily mean particle number
12 concentrations and peak expiratory flow. Similarly, Delfino et al. (2005) showed indirect
13 epidemiologic evidence linking the ultrafine-dominated fraction of fossil-fuel combustion
14 particles with adverse cardiovascular effects. Peters et al. (2004), Pope III and Dockery
15 (2006), Sioutas et al. (2006) and Brugge et al. (2007) found that while short-term exposure to
16 nanoparticles exacerbated existing pulmonary and cardiovascular disease, long-term repeated
17 exposure increased the risk of cardiovascular disease and death. Seaton et al. (1995)
18 hypothesised that nanoparticles can penetrate the lung wall inducing inflammation that
19 stimulates the production of clotting factors in the blood which are responsible for
20 exacerbating ischemic heart disease in susceptible individuals. This hypothesis has been
21 further supported by panel studies with coronary heart disease patients (Ruckerl et al., 2006).
22 Panel studies with patients suffering from chronic pulmonary diseases have also been
23 performed in Germany, Finland and the United Kingdom (Ibald-Mulli et al., 2002). Overall, a
24 decrease of peak expiratory flow and an increase of daily symptoms and medication use were
25 found for elevated daily fine and ultrafine particle concentrations. More recently, Stölzel et

al. (2007) found statistically significant associations between elevated nanoparticle number concentrations (10-100 nm) and daily total as well as cardio-respiratory mortality using time-series epidemiological analysis. Likewise, several toxicological and panel studies present similar evidence, favouring number concentrations as an appropriate metric for assessing health effects (Nel et al., 2006; Peters et al., 1997; Xia et al., 2009).

Ultrafine particles carry considerable levels of toxins that are expected to induce inflammatory responses through reactive oxygen species or other mechanisms (Sioutas et al., 2005). Kim et al. (2002) performed chemical characterisation of ambient ultrafine particles and found that a major fraction comprised organic and elemental carbon, which is a primary product of diesel-fuelled vehicle emissions. Large concentrations of such particles are expected in close proximity of mobile sources (Minoura et al., 2009), resulting in increased susceptibility of the health of children and asthmatic patients (Chalupa et al., 2004; Peters et al., 1997).

It can be concluded from the above discussions that particle number concentration is an important indicator of toxicity, presenting a strong contention for a potential regulatory metric. Exposure of nanoparticle number (or surface area) concentrations adversely affect human health (Stölzel et al., 2007). When such particles are inhaled, their behaviour differs from coarse particles as they become more reactive and toxic due to larger surface areas, leading to detrimental health effects such as oxidation stress, pulmonary inflammation and cardiovascular events (Buseck and Adachi, 2008; Nel et al., 2006). To date, understanding of the exact biological mechanisms through which such particles cause disease or death are not yet fully understood. This is clearly an area of nanoparticle research that requires more epidemiological and toxicological evidence.

6.2 Visibility

Visibility impairment is generally caused by a build-up of suspended particles in the atmosphere (Horvath, 2008). It increases with relative humidity and atmospheric pressure and decreases with temperature and wind speed (Tsai, 2005). At high (e.g. 90%) relative humidity, the light scattering cross-sectional areas of particles enlarge by uptake of water. For an ammonium sulphate particle, the increase may be by a factor of five or more above that of the dry particle (Malm and Dry, 2001). In polluted air, light scattering by particles (particularly those containing sulphate, organic carbon and nitrate species) may cause 60 to 95% of overall visibility reduction, whilst carbon particles (e.g. soot) may contribute a 5 to 40% reduction through light absorption (Tang et al., 1981; Waggoner et al., 1981). For example, Horvath (1994) reported that particles were responsible for up to 90% of light scattering and absorption in rural areas of the Austria and up to 99% in urban areas. In comparison, light absorption and scattering by gaseous pollutants is relatively small in polluted air (Jacobson, 2005).

Several local to global scale studies have established strong links between visibility impairment and mass concentrations of both $PM_{2.5}$ and PM_{10} (Chang et al., 2009; Che et al., 2009; Cheng and Tsai, 2000; Noone et al., 1992; Tsai, 2005; Doyle and Dorling, 2002; Mahowald et al., 2007). For example, Doyle and Dorling (2002) analysed the changes in visibility over a period between 1950 and 1997 with respect to particles loading within the atmosphere of eight rural and urban locations in the UK. They reported a strong association of anthropogenically produced and long-range transport of secondary particles (mostly within the nanoparticle size range) with reduction in visibility. This was greatest at urban locations due to the high concentrations of atmospheric particles compared to rural locations, with relative humidity, size and chemical composition of particles also playing important

roles. Particle emissions from diesel–fuelled vehicles contribute more to visibility impairment than emissions from petrol–fuelled vehicles as they absorb more light than they scatter (Kittelson, 1998). Trijonis (1984) noticed that elemental carbon emitted from heavy–duty diesel trucks in California contributed nearly one–half of the state wide elemental carbon emissions and about 5–15% of the state wide visibility reduction.

Nanoparticles play an important role in the growth of coarse particles and in changing their chemical and optical properties that influence urban visibility. Those studies that do relate number concentrations with visibility are limited to coarse particles. For instance, a recent study by Mohan and Payra (2009) analysed fog episodes in Delhi (India) and showed an inverse correlation between urban visibility and particle number concentrations between 0.3 and 20 μm . The relative contributions to visibility improvement from reductions in atmospheric nanoparticle concentrations and the degree to which control of their emissions will bring improvements to urban visibility is largely unknown and requires further research.

7. Progress towards the regulation of atmospheric nanoparticle concentrations

In 1971, the USEPA promulgated the first National Ambient Air Quality Standards for particles in the atmosphere. The primary standard was set for total suspended particulates as 260 and 75 $\mu\text{g m}^{-3}$ for a 24 h and an annual average, respectively. However, in 1987 the USEPA revised the standards by replacing total suspended particulates with PM_{10} . The numerical values were also revised and set to 150 and 50 $\mu\text{g m}^{-3}$ for a 24 h and an annual average, respectively. Then again in 1997, the USEPA revised the standards for the second time and included fine particles (i.e. $\text{PM}_{2.5}$). In the face of a widespread challenge to this development, the US Supreme Court upheld the USEPA’s decision under the Clean Air Act in 2002. Subsequently, the PM_{10} and $\text{PM}_{2.5}$ limits were once more reviewed and changes

made, not to the limit values themselves but to the criteria as summarised in supplementary Table S.1. These standards were chosen as they were regarded as being most appropriate for particles most likely to reach the lung acinus (Li et al., 1996; Schwartz, 1994, 2000; Seaton et al., 1995). However, in December 2006 the USEPA revoked the annual PM₁₀ standard, due to a lack of evidence linking health problems to long-term exposure to coarse particle pollution (Moolgavkar, 2005), but retained the 24 h standard for PM₁₀ (see Table S.1).

The European Union (EU) first air quality daughter directive (1999/30/EC) came into existence in 1999. This set ‘Stage-I’ values for PM₁₀ at levels of 50 and 40 µg m⁻³ for the 24 h and annual mean values, respectively, to be achieved by the member states of the European Community (EC) by the 1st of January 2006. The directive also indicated equivalent ‘Stage-II’ values for PM₁₀ at 50 and 20 µg m⁻³ for 24 h and annual mean values, respectively, with a target date of 1st of January 2010. In September 2005, the EU contemplated its first ever limit for PM_{2.5}. This moved a step closer in May 2008 when a non-binding target value for PM_{2.5} in 2010 was superseded by a binding limit value in 2015 (25 µg m⁻³ annual average for both target and limit values).

In 2005, the EU adopted the “*Thematic Strategy on Air Pollution*” as a consequence of the “Clean Air for Europe” program. This strategy calls for member countries to increase their research activities in the fields of atmospheric chemistry and the distribution of pollutants, and to identify the impact of air pollution on human health and the environment. In July 2008, the UK Department of Transport proposed an emission standard (6×10^{11} # km⁻¹) on a *number* basis for light and heavy duty compression ignition vehicles through their UN-ECE Particle Measurement Programme (Parkin, 2008). These limits were subsequently agreed for inclusion in Euro-5 and Euro-6 emission standards (Table S.2), to become effective from 1st September 2011 for the approval of new types of vehicles and from 1st January 2013 for all

new vehicles sold, registered or put into service in the Community (EU, 2008). The Particle Measurement Programme focuses on the development of new approaches to replace or complement existing mass-based regulatory limits for vehicles and concentrates on the 23–2500 nm size range of solid particles.

At present, there are no legal thresholds for nanoparticle *number* concentrations in *ambient air* and therefore local observation networks do not generally monitor them. A number of technical and practical matters have limited the development of *ambient* particle regulations on a *number* basis. One of the main technical constraints is the lack of standard methods and instrumentation, and the uncertainties in repeatability and reproducibility in measurements (see Section 4). Practical constraints include lack of sufficient long-term monitoring studies that include measurements of nanoparticle concentrations and size distributions, insufficient information on dispersion and transformation behaviour, a shortage of toxicological and epidemiological evidence (see Section 6.1). Nevertheless, it is acknowledged that mass based particle concentration limits do not effectively control the smaller particles that can readily penetrate the alveoli region (Oberdörster et al., 2005a). Therefore, metrics such as particle number concentrations are likely to be considered within future air quality regulation (Maynard, 2004).

8. Discussion and future research

This review has covered the characteristics and sources of ambient nanoparticles, the instrumentation available for their measurements, their modelling, environmental and health impacts, and regulatory implications.

The lognormal distribution is a good fit to the size distribution over a wide particle size range in the nucleation, Aitken, accumulation and coarse modes. Each mode reflects particular

characteristics, indicating sources, chemical composition and sensitivity to particle dynamics. The size ranges quoted for these modes often vary (Section 2), but it is generally agreed that about 80% of total particles, by number, reside in first two modes.

Ambient nanoparticles derive from natural and anthropogenic sources. Road vehicles are the dominant source in urban areas and can raise nanoparticle concentrations by up to three orders of magnitude above the typical levels in natural environments (Section 3). Bio-fuels are seen as an alternate fuel option for controlling vehicle emissions. Their use is being encouraged as a part of international energy policies and to gain social, economic and environmental benefits. The latter are clear as bio-fuelled driven vehicles emit far less particulate mass and gaseous pollutants than conventionally fuelled vehicles, all else being equal. Similar benefits do not seem to be achieved in terms of nanoparticle number emissions (Section 3). In some instances these can fail to satisfy the *number* based limits for vehicles enacted in Euro emission standards, unless, for example, an appropriate emission control system or alternative measures are applied (Grose et al., 2006; Mohr et al., 2006). Moreover, there are still several unanswered technical and social issues pertaining to the use of bio-fuels, including (i) a lack of adequate knowledge about their effect on engine maintenance, efficiency and emissions, and (ii) the social challenges associated with food security and water footprint (Dominguez-Faus et al., 2009).

Manufactured nanoparticles are emerging as an important class of ambient particles and substantial increases in their use in nanomaterials integrated products are predicted. Currently, there is little knowledge of the background concentrations and distributions (on a number basis) of these particles in the atmosphere. Moreover, their sources, emission routes, exposure pathways and potential to affect the environment and human health are poorly understood. Current knowledge of their physico-chemical characteristics, toxicity, release

1 paths (intentional and/or unintentional), sizes, atmospheric lifetime and degradability
2 suggests that their concentrations in ambient air (excluding areas associated with their
3 production or use) are expected to be considerably lower than for other nanoparticles but that,
4 nevertheless, may have substantial impact on health and the environment (Andujar et al.,
5 2009). Many aspects of airborne manufactured nanoparticles need thorough study to enable
6 appropriate controls to be established, both for the indoor (residential, places of production,
7 etc.) and ambient environments, that can be integrated appropriately into potential regulatory
8 frameworks for ambient nanoparticles.

9 A number of advanced instruments have emerged for measuring *number concentrations* and
10 *size distributions*, though standard application guidelines and methods are lacking.
11 Standardising instrument use is a major scientific issue that needs to be resolved before
12 regulations can be reliably imposed for controlling atmospheric nanoparticles. Instrument
13 characteristics and the capabilities for automatic data logging should inform the design of
14 regulatory methods so that data accurately describes local conditions on appropriate time
15 scales. Most available instruments are incapable of measuring particles below 3 nm in
16 diameter – a size range that is crucial in the formation of secondary atmospheric particles.
17 Further advances in instrumentation are desired to address this deficiency and enable real–
18 time determination of physio–chemical properties and the related gas phase species to
19 understand particle transformation processes and their modelling in more detail – both being
20 important for developing regulatory controls.

21 Other technical issues concern the metric used to characterise particle diameter (aerodynamic
22 equivalent, D_a , or electrical mobility equivalent, D_p), the appropriate sampling frequencies
23 and the adequacy of corrections for particle losses in sampling tubes. The existence of
24 sources of high nanoparticle number concentrations that are localised in time and space (e.g.

1 motor vehicles), coupled with imperfect mixing, may result in local concentrations that vary
2 greatly over time scales of a few seconds. To measure such a concentration accurately in a
3 range of environments requires an instrument with a fast response to avoid sampling artefacts
4 in the data. Instruments measuring particles based on D_p may be preferable to those
5 measuring D_a as the aerodynamic measure can be adversely affected by particle
6 characteristics (such as size, shape and density), as most of the particles in the accumulation
7 mode are non-spherical agglomerates (Hinds, 1999; Park et al., 2003a). When attempting to
8 measure non-spherical particles of known density, the shape and orientation of each particle
9 subjected to the accelerating airflow governs the drag force it experiences and hence affects
10 the measured aerodynamic size (Secker et al., 2001). However, measurements of number
11 distributions based on any definition of particle diameter may not differ significantly but their
12 mass distributions do because the density of accumulation mode particles changes rapidly
13 with increased particle diameter (Park et al., 2003a). Another common but somewhat
14 neglected issue is the adequate correction for particle losses in sampling tubes. The limited
15 number of studies that have addressed this suggest that inappropriate correction (or neglect of
16 correction) for such losses may significantly affect the measured number distributions
17 (Kumar et al., 2008d; Noble et al., 2005; Timko et al., 2009). This issue, along with those
18 mentioned above, should be considered while developing a framework for the monitoring and
19 control of atmospheric nanoparticles.

20 Suitable modelling tools for the prediction of nanoparticle concentrations are required for the
21 evaluation of mitigation policies. At present, the development of dispersion modelling faces
22 several challenges, such as a lack of suitable experimental datasets for evaluation purposes,
23 potentially inadequate input information (i.e. emission factors) and insufficient knowledge for
24 treating particle dynamics at all relevant scales. Together, these factors result in inconsistency
25 in the results from particle number concentration models. Laboratory and computational

1 dynamics studies, coupled with long-term field measurements (including number and size
2 distributions), are needed for the development and validation of reliable nanoparticle
3 dispersion models.

4 Although it is difficult to separate the effects of nanoparticles from those of other pollutants
5 and larger particles (Harrison and Yin, 2000; Osunsanya et al., 2001), epidemiological studies
6 suggest that there are health effects of fine and nanoparticles which might be independent of
7 each other (Ibald-Mulli et al., 2002). A number of studies associate high number
8 concentrations in the ultrafine size range with adverse health effects and there are also global
9 climate and urban visibility impacts. Despite considerable toxicological evidence of the
10 potential detrimental effects of these particles on human health, the appropriate metric for
11 evaluating health effects is still not clear. The existing body of epidemiological evidence is
12 thought to be insufficient to define the exposure-response relationship. Nevertheless, recent
13 studies suggest that amongst other characteristics, particle number concentrations are an
14 important indicator of their toxicity. This implies that size distribution information for the
15 entire nanoparticle size range could enhance our ability to assess potential health effects. The
16 measurement of size distributions is thus an important matter that should be considered in
17 potential regulatory frameworks. Whether number concentration based limits should address
18 only the ultrafine size range or the whole nanoparticle range is not clear. Perhaps, covering
19 the nanoparticle size range would be a preferable option as this comprises nearly all the
20 particle number population in the ambient environment.

21 Nanoparticles are major precursors of larger particles, as they promote their growth and
22 modify their optical properties, thereby affecting the radiative properties of the atmosphere.
23 The over effects of the nanoparticle size range on global climate can not currently be
24 determined with any accuracy. It is generally believed that aerosol particles induce a net

negative radiative forcing of -1.2 W m^{-2} which is a combination of direct (-0.5 W m^{-2}) and indirect (-0.7 W m^{-2}) effects (IPCC, 2007), meaning that half of the present global warming from greenhouse gases ($+ 2.5 \text{ W m}^{-2}$; Jacobson, 2001) might be masked by the effects of aerosol particles. On the other hand, carbonaceous particles (e.g. soot) are considered to be one of the major contributors to global warming (i.e. $+0.34 \text{ W m}^{-2}$; IPCC, 2007). Their radiative forcing can increase to about $+0.6 \text{ W m}^{-2}$ if the particles are coated with sulphate or organic compounds, as is common in ambient atmosphere (Chung and Seinfeld, 2005). This impact, together with health and environmental issues (e.g. acid rain, stratospheric ozone depletion (Soden et al., 2002)) associated directly or indirectly with atmospheric nanoparticles illustrates the need for suitable regulatory control.

Visibility impairment has a quite well established link with the light extinction – scattering and absorption – properties (e.g. hygroscopic or hydrophobic nature; Noone et al. (1992), size, chemical composition and concentrations) of coarse atmospheric particles (Che et al., 2009; Cheng and Tsai, 2000). However, the role of nanoparticles in visibility impairment is still unclear. That these particles account for an appreciable number fraction of the carbon and sulphate particles emitted from diesel vehicles and that these particles contribute considerably to visibility reduction, suggests that they play an indirect role in visibility impairment. That being so, improved understanding of nanoparticles role in visibility impairment is essential.

Currently, there is no legal threshold for controlling *number* concentrations of airborne nanoparticles and present mass-based regulations for atmospheric particulate matter are insufficient for their control. Recent Euro-5 and Euro-6 vehicle emission standards include number based limits for nanoparticles (EU, 2008), which is a positive step initiated by the emissions control community. Similar initiatives are needed to control public exposure to

atmospheric particles but their development is hindered by the technical and practical issues discussed in Section 7. Despite these challenges, understanding of ambient nanoparticles (e.g. dispersion behaviour, characterisation and secondary formation) and capabilities for their measurement have increased considerably in recent years. These advances should play a pivotal role in supporting the establishment of regulatory frameworks that focus on a *number* basis. In line with these advances, urban air quality monitoring networks should be encouraged to include nanoparticle number and size distribution measurements in their air pollution monitoring programmes. Such observations can provide the data that will help address the questions summarised above, as well as enable the comprehensive validation of particle dispersion models.

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1 **Figure Captions**

2 Fig. 1. Typical example of number weighted size distributions in a street canyon (Kumar et
3 al., 2008a); also shown are some key definitions regarding atmospheric particles and size
4 dependent deposition in alveolar and tracheo–bronchial regions (ICRP, 1994).

5 Fig. 2. Description of resources and conversion technology used to produce bio–fuels;
6 adapted from Hart et al. (2003).

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1 List of Tables

2 Table 1. Examples showing definitions used to classify particles according to mode.

Particle modes	Size range (nm)	Source
Nucleation mode	<20	Kulmala et al. (2004); Monkkonen et al. (2005); Curtius (2006); Lingard et al. (2006) ; Agus et al. (2007)
	<33	Charron et al. (2008)
	3–30	Kittelson (1998); Kittelson et al. (1999; 2004; 2006a,b); Rickeard et al. (1996); Gouriou et al. (2004); Roth et al. (2008)
	<30	Kumar et al. (2008a,b,c,d, 2009a,b,c)
Aitken mode	20–90	Kulmala et al. (2004); Monkkonen et al. (2005); Curtius (2006); Lingard et al. (2006)
	20–100	Agus et al. (2007)
	33–90	Charron et al. (2008)
	10–100	Seinfeld and Pandis (2006)
Accumulation or soot mode	90–1000	Kulmala et al. (2004); Monkkonen et al. (2005); Curtius (2006); Lingard et al. (2006)
	30–500	Kittelson (1998); Kittelson et al. (1999; 2004; 2006a,b); Rickeard et al. (1996); Gouriou et al. (2004); Roth et al. (2008)
	30–300	Kumar et al. (2008a,b,c,d, 2009a,b,c)
	90–120	Charron et al. (2008)
	100–1000	Agus et al. (2007)

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1 Table 2. Studies comparing emissions of particle number concentrations from both bio- and
2 conventional-fuelled vehicles. The terms DPF, ULSD, OCC and RME stands for diesel
3 particulate filter, ultra low sulphur diesel, oxidation catalytic converter and rapeseed oil
4 methyl ester, respectively.

Source	Bio-fuel	Bio-fuels emissions – number concentrations	Conventional fuel – number concentrations	Remarks
Fontaras et al. (2009)	Neat soybean-oil derived bio-diesel	$1.2\text{--}4.5 \times 10^{14} \text{ \# km}^{-1}$	$0.4\text{--}2.1 \times 10^{14} \text{ \# km}^{-1}$ (Diesel)	Euro 2 diesel passenger car. Note that these are approximate values.
	50% v/v blend with petroleum-diesel	$0.6\text{--}3 \times 10^{14} \text{ \# km}^{-1}$		
Lee et al. (2009)	Ethanol-blended petrol fuel (0, 15 and 85% by volume)	$1.35\text{--}2.14 \times 10^{11} \text{ \# km}^{-1}$	$1.09 \times 10^{11} \text{ \# km}^{-1}$ (Petrol; engine with DPF)	Petrol engine
			$4.17 \times 10^{13} \text{ \# km}^{-1}$ (Petrol; engine with non-DPF)	
Cheng et al. (2008a)	Methanol (fumigation 10, 20 and 30%)	$1.15 \times 10^7 \text{ \# cm}^{-3}$ (10% fumigation; low load)	$1.42 \times 10^7 \text{ \# cm}^{-3}$ (Diesel; low load)	Four-cylinder direct injection diesel engine operating at low (0.19 Mpa), medium (0.38) and high (0.56 MPa) engine loads
		$0.97 \times 10^7 \text{ \# cm}^{-3}$ (20% fumigation; low load)		
		$0.83 \times 10^7 \text{ \# cm}^{-3}$ (30% fumigation; low load)		
		$1.09 \times 10^7 \text{ \# cm}^{-3}$ (10% fumigation; medium load)	$1.22 \times 10^7 \text{ \# cm}^{-3}$ (Diesel; medium load)	
		$0.90 \times 10^7 \text{ \# cm}^{-3}$ (20% fumigation; medium load)		
		$0.71 \times 10^7 \text{ \# cm}^{-3}$ (30% fumigation; medium load)		

		$2.05 \times 10^7 \text{ \# cm}^{-3}$ (10% fumigation; high load)	$1.89 \times 10^7 \text{ \# cm}^{-3}$ (Diesel; high load)	
		$1.94 \times 10^7 \text{ \# cm}^{-3}$ (20% fumigation; high load)		
		$1.72 \times 10^7 \text{ \# cm}^{-3}$ (30% fumigation; high load)		
Cheng et al. (2008b)	Cooking oil derived bio- diesel tested at low, medium and high engine loads	$4.92 \times 10^7 \text{ \# cm}^{-3}$ (low load)	$3.90 \times 10^7 \text{ \# cm}^{-3}$ (ULSD; low load)	Direct injection diesel-engine at low (0.19 MPa), medium (0.38 MPa) and high (0.56 MPa) loads
		$5.30 \times 10^7 \text{ \# cm}^{-3}$ (medium load)	$4.67 \times 10^7 \text{ \# cm}^{-3}$ (ULSD; medium load)	
		$7.23 \times 10^7 \text{ \# cm}^{-3}$ (high load)	$6.46 \times 10^7 \text{ \# cm}^{-3}$ (ULSD; high load)	
Tsolakis (2006)	RME bio-diesel	$1\text{--}2.5 \times 10^7 \text{ \# cm}^{-3}$	$0.5\text{--}1.75 \times 10^7 \text{ \# cm}^{-3}$ (ULSD)	Tested at three steady operations modes in a single cylinder diesel- fuelled engine
Bunger et al. (2000)	RME bio-diesel	$1.89 \times 10^5 \text{ \# cm}^{-3}$ at 88 nm (rated power)	$1.26 \times 10^5 \text{ \# cm}^{-3}$ at 105 nm (Diesel; rated power)	Four-stroke direct injection diesel engine in a European test cycle (ECE R49)
		$6.94 \times 10^5 \text{ \# cm}^{-3}$ at 79 nm (idling)	$2.56 \times 10^6 \text{ \# cm}^{-3}$ at 40 nm (Diesel; idling)	
Bagley et al. (1998)	Soyabean and fatty-acid mono-ester derived bio- diesels (given range is for various combinations of RPM and % engine loads)	$8.73\text{--}11.2 \times 10^7 \text{ \# cm}^{-3}$ (without OCC)	$3.48\text{--}11.3 \times 10^7 \text{ \# cm}^{-3}$ (Diesel; engine without OCC)	Indirect injection engine that was equipped with and without an OCC
		$0.85\text{--}1.01 \times 10^8 \text{ \# cm}^{-3}$ (with OCC)	$1.19\text{--}5.64 \times 10^8 \text{ \# cm}^{-3}$ (Diesel; engine with OCC)	

1 Table 3. Studies showing shift in particle number distributions towards smaller size range
2 when bio-fuels are used.

Source	Bio-diesel – mean particle diameters	Conventional fuels - mean particle diameters	Remarks
Cheng et al. (2008a)	78–87 nm (methanol)	93 nm (diesel)	Range of mean diameters represent various tests conducted on low, medium and high engine loads
Cheng et al. (2008b)	47–58 nm (cooking-oil derived bio- diesel)	62–78 nm (ULSD)	Range of mean diameters represent various tests conducted on low, medium and high engine loads
Jung et al. (2006)	62 nm (Soymethylester bio-diesel)	80 nm (diesel)	A medium-duty direct-injection, 4- cylinder, turbocharged diesel engine.
Bunger et al. (2000)	88 nm (RME bio-diesel)	105 nm (diesel)	At ‘rated power’ in an 4–stroke direct injection diesel engine in a European test cycle (ECE R49)
	40 nm (RME bio-diesel)	79 nm (diesel)	At ‘idling’ in an 4–stroke direct injection diesel engine in a European test cycle (ECE R49)
Bagley et al. (1998)	34–64 (soyabean derived bio- diesel)	57–83 (diesel)	Tested without an OCC in an indirect engine; range of mean diameters represent various tests conducted on different speed and loads
	34–50 (soyabean derived bio- diesel)	41–94 (diesel)	Tested with an OCC in an indirect engine; range of mean diameters represent various tests conducted on different speed and loads

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Table 4. Typical range of particle number concentrations according to environment (excluding episodic contributions).

Environment	Typical number concentration range (# cm ⁻³)	Sources
Vehicle wake / exhaust plumes	10 ⁴ –10 ⁷	Kumar et al. (2009c); Wehner et al. (2009); Minoura et al. (2009)
Urban Street canyons	10 ⁴ –10 ⁶	Wehner et al. (2002); Wahlin et al. (2001); (Longley et al., 2004); Kumar et al. (2008a, b, c, 2009a, c)
Forest regions, remote continental, desert and rural (or city background)	10 ³ –10 ⁴	Seinfeld and Pandis (2006); Birmili et al. (2000); Riipinen et al. (2007); O'Dowd et al. (2002); Kulmala et al. (2003); Riipinen et al. (2007); Tunved et al. (2006); Pey et al. (2009); Charron et al. (2008)
Marine, polar and free troposphere	10 ² –10 ³	Seinfeld and Pandis (2006); O'Dowd et al. (2004)

1 Table 5. Selected features of instruments for measuring particle number concentrations and
2 distributions (range of detectable concentrations and sampling rates are obtained through
3 personal communication between May and July 2009). Note that D_a and D_p denote
4 aerodynamic equivalent and electrical mobility equivalent diameters, respectively, indicating
5 an aerodynamic or electrical mobility type of size classification by the instruments.

Instruments	Size range (nm)	Sampling rate (s)	Detected diameter	Detectable (min–max) concentrations ($\# \text{ cm}^{-3}$)
SMPS (model 3034)	10–487 (fixed)	180 (fixed)	D_p	10^2 – 10^7
SMPS (3936 series)	2.5–1000 (variable and dependent on configuration)	30 (upwards rate variable)	D_p	1 – 10^8
ELPI (with filter)	7–10000	1	D_a	50– 1.4×10^7 at 14 nm 0.1 – 2×10^4 at 8400 nm
ELPI(Standard)	30–10000	1	D_a	250 – 6.97×10^7 at 42 nm 0.1 – 2×10^4 at 8400 nm
APS (model 3321)	500–20000 (aerodynamic sizing)	1–64800 (in summed mode)	D_a	Minimum count – 1 Maximum count (without addition of diluter model 3302):
	370–20000 (optical detection)	1–300 (in average mode) 20 (default)	D_a	10^3 at $0.5 \mu\text{m}$ with less than 2% coincidence 10^3 at $10 \mu\text{m}$ with less than 6% coincidence
DMS500	5–1000	0.1	D_p	6671 – 2.26×10^{12} at 5 nm 73 – 2.71×10^{10} at 1000 nm
	5–1000	1	D_p	1840 – 2.26×10^{12} at 5 nm 20 – 2.71×10^{10} at 1000 nm
	5–1000	10	D_p	680 – 2.26×10^{12} at 5 nm 9 – 2.71×10^{10} at 1000 nm
	5–2500	0.1	D_p	7599 – 2.14×10^{12} at 5 nm 47 – 2.33×10^{10} at 2500 nm
	5–2500	1	D_p	1640 – 2.14×10^{12} at 5 nm 18 – 2.33×10^{10} at 2500 nm

DMS50 ^a	5–2500	10	D_p	588– 2.14×10^{12} at 5 nm 9– 2.33×10^{10} at 2500 nm
	5–560	0.1	D_p	8233– 4.97×10^{12} at 5 nm 240– 1.15×10^{11} at 560 nm
	5–560	1	D_p	4209– 4.97×10^{12} at 5 nm 140– 1.15×10^{11} at 560 nm
	5–560	10	D_p	2628– 4.97×10^{12} at 5 nm 72– 1.15×10^{11} at 560 nm
FMPS (model 3091)	5.6–560	1	D_p	10^3 – 10^8 at 5.6 nm 10^1 – 10^6 at 560 nm
UFP Monitor (model 3031)	20–1000 (upper limit set by sampling inlet. Size classes pre set)	600 + 60 (zeroing time)	D_p	500– 10^6 at 20 nm 50– 10^6 at 200 nm
LAS (model 3340)	90–7500	1	Wide angle light scattering using a intracavity laser	Minimum count zero (as <1 particle counted in 5 min; JIS Standard) Maximum count dependent on sample flow rate 1.8×10^4 at $10 \text{ cm}^3 \text{ min}^{-1}$ 3.6×10^3 at $50 \text{ cm}^3 \text{ min}^{-1}$ 1.8×10^3 at $95 \text{ cm}^3 \text{ min}^{-1}$
GRIMM SMPS+C	5–1110	1	D_p	1 – 10^7
GRIMM WRAS	5–32,000	1 (CPC); 110 (DMA); 6 (Aerosol Spectrometer)	D_p and D_a	1 – 10^7
GRIMM SMPS+E	0.8–1110	0.2 (T90)	D_p	100 – 10^8

^aMaximum concentration range assumes maximum dilution used with the DMS50.

Table 6. Transformation and loss processes that modify particle number concentrations in the atmosphere (Ketzel and Berkowicz, 2004).

Process	Sources/Sinks	Change in number concentrations
Coagulation	Collision of particles with each other	loss
Condensation	Aggregation of gaseous phase species onto particle surfaces	none
Dilution and/or mixing	Depending on the concentration in the diluting air mass	gain or loss
Dry deposition	Removal of particles through surface contact	loss
Evaporation	Initially reduction in particle size that leads to complete loss or a residual solid core	none or loss
Nucleation	Formation of new particles through gas-to-particle conversion or photochemical nucleation	gain

Figure 1.ppt

Figure 2.ppt

e-component

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