1 PERSPECTIVE

2 Technical challenges in tackling regulatory concerns for 3 urban atmospheric nanoparticles

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13 Abstract

14 Recent Euro-5 and Euro-6 vehicle emission standards are the first ever initiative to
15 control particles on a *number* basis at the source. Related standards are also desirable
16 for *ambient* nanoparticles (taken in this article to be those below 300 nm) to protect
17 against possible adverse impacts on public health and the environment. However,
18 there are a number of technical challenges that need to be tackled before developing a
19 regulatory framework for atmospheric nanoparticles. Some of the challenges derive
20 from a lack of standardisation of the key measurement parameters, including
21 sampling, necessary for robust evaluation of particle number concentrations,
22 especially in the context of insufficient knowledge of the physicochemical
23 characteristics of emerging sources (i.e. bio-fuel derived and manufactured
24 nanoparticles). Ideally, ambient concentrations of primary particles could be linked to
25 primary particle emissions by use of nanoparticle dispersion models, and secondary
26 nanoparticles using photochemical modelling tools. The limitations in these areas are
27 discussed. Although there is inadequate information on the exact biological
28 mechanism through which these particles cause harm, it is argued that this should not
29 in itself delay the introduction of regulation. This article reviews the missing links
30 between the existing knowledge of nanoparticle *number* concentrations and the
31 advances required to tackle the technical challenges implied in developing
32 regulations.

33 **Keywords:** Airborne and manufactured nanoparticles; Particle number concentrations;
34 Size distributions; Street canyons; Ultrafine particles; Vehicle emissions

35 1. Introduction

36 The dominant pathway for population exposure to nanoparticles is through the
37 inhalation of polluted air. Toxicological studies associate exposure to nanoparticles
38 with adverse health effects (Murr & Garza, 2009) and show that a significant number

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of mortalities may result in megacities (Kumar, Gurjar, Nagpure, & Harrison, 2011). Nanoparticles readily coagulate with larger sized particles and grow to sizes where their optical properties may adversely affect urban visibility (Horvath, 1994). They also affect global climate, both through direct optical effects and indirect effects via cloud formation (Buseck & Adachi, 2008). The main source of primary particles in urban air is vehicle emissions, followed by emissions from industry. Secondary particles, formed through photochemically induced nucleation from gaseous precursors, can dominate concentrations when an episode is in progress (Holmes, 2007).

It is important to identify the size range that is most relevant to atmospheric particles from the number concentration point of view. Particles below 300 nm (referred to here as nanoparticles) appear to be by far the most numerous (i.e. over 99% of the total particle number concentrations) in urban atmospheric environments (Kumar, Fennell, & Britter, 2008; Kumar, Garmory, Ketzel, Berkowicz, & Britter, 2009), with the ultrafine range (those below 100 nm) being the main contributor (at about 80% of the total) (Kumar, Fennell, Hayhurst, & Britter, 2009). Consistent with this, Tuch et al. (1997) and Wehner and Wiedensohler (2003) found negligible number concentrations for particles sizes greater than 500 nm in European urban environments. The relevant lower size limit is more contentious. Significant numbers of particles are expected down to 1 nm and below. However, accurate measurements become more difficult below about 20 nm due to instrumentation and sampling losses.

The distributions of concentrations in the size ranges of interest vary dramatically with time and location. For example, Charron and Harrison (2003) observed that particles in the 11–100 nm size range represented 71 to 95% of total number concentrations in central London. Similar results were reported by Woo, Chen, Pui, & McMurry (2001) for Atlanta (USA), showing up to 89% of total particle numbers in the size range below 100 nm. It is important to note that a significant contribution to these concentrations derives from particles below 10 nm that typically arise from secondary formation (Kulmala et al., 2004). This contribution was found to be in the range of 36–44% at road sides in Birmingham, UK (Shi, Evans, Khan, & Harrison, 2001) and generally about 25% in urban areas of Pittsburgh, USA (Stanier, Khlystov, & Pandis, 2004) and Atlanta, USA (Woo, Chen, Pui, & McMurry, 2001). Likewise, Wehner and Wiedensohler (2003) found 16 to 24% of total number concentrations in the 3 to 10 nm range in Leipzig (Germany) and Kumar et al. (2009) reported slightly smaller contributions (4 to 12%) in Cambridge (UK) for the 5 to 10 nm size range.

Current regulations in the UK, Europe and elsewhere for controlling atmospheric particulate matter are based on the mass concentrations of particles $\leq 2.5 \mu\text{m}$ ($\text{PM}_{2.5}$) and $\leq 10 \mu\text{m}$ (PM_{10}). These metrics are dominated by larger particles rather than nanoparticles. The Euro–5 and Euro–6 emission standards are first ever regulations for particle numbers, applying to vehicle tailpipe exhausts. The measurement protocols developed by the UNECE GPPE Particle Measurement Programme are an integral part of this regulation, notably including a requirement to remove volatile particles (through heating and dilution), as these would lead to large variations in the results, and a lower size limit of 23 nm, to minimise the effects of both small volatile particles and diffusion losses during sampling. These emission limits will soon be applicable to light duty diesel vehicles used in the European community. One of the reasons to move to number emission standards was that the precision of mass-based

1 method was insufficient to provide reliable regulation of emissions from vehicles with
2 particle traps. These regulations control the emissions of nanoparticle numbers at the
3 source, not at the receptor. Similar standards for atmospheric nanoparticles are
4 desirable to limit public exposure. By analogy with vehicle emission regulation, it is
5 not necessary to have determined the specific cause of health effects before initiating
6 regulation. However, this is still some way off and a number of unanswered issues
7 need to be addressed before a regulatory framework for number concentrations of
8 atmospheric nanoparticles can be proposed.

9 Some of the key issues that are discussed in subsequent sections are: (i) the choice of
10 the most appropriate regulatory metric, (ii) the effect of emerging sources of
11 nanoparticles (e.g. from bio-fuel vehicles and manufactured nanomaterials), (iii)
12 issues affecting the accuracy of measurements, and (iv) the link between emissions
13 and atmospheric concentrations via dispersion modelling. Other important topics such
14 as toxicology and epidemiology policy and governance implications are not covered
15 in detail due to the brevity of the article but the readers are directed towards the
16 relevant literature.

17 **2. Particle number concentration as an appropriate regulatory metric**

18 Metrics for describing the environmental effects of nanoparticles have been a
19 subject of debate for some years, a debate constrained by the limited knowledge of
20 nanoparticle toxicity or even the precise biological mechanisms that affect human
21 health. Adverse health effects have been mainly associated with different fractions of
22 particle mass concentration (e.g. PM₁₀ and PM_{2.5}) although other particle
23 characteristics (number, surface area, shape, size, composition) may be important
24 from a human health point of view. However, consensus has not been reached for the
25 most appropriate metric. Several studies support the contention that particle *number*
26 concentrations are an important indicator of toxicity (Donaldson et al., 2005). These
27 also report evidence of the potential detrimental effects of the ultrafine fraction (<100
28 nm) on human health, though the existing body of epidemiological evidence is
29 insufficient to define an exposure-response relationship. Particle *number*
30 concentration may not be the only important metric but the evidence is that it is
31 clearly an important metric, though whether for the whole size range of nanoparticles,
32 or some sub-range (perhaps the ultrafine size range) is not certain. That being so,
33 improved understanding of nanoparticle size distributions and related health effects is
34 essential. A measure of particle *number* concentration seems to be an appropriate
35 metric for ambient measurements, especially as the *number* based Euro-5 and Euro-6
36 vehicle emission standards will soon be in place (EU, 2008). The importance of
37 defining the required particle size range, the effect of composition on this parameter,
38 and the treatment of volatile particles are discussed in Section 4.

39 **3. Effects of emerging sources of nanoparticles**

40 Nanoparticles originate from both natural (biomass burning, volcano, biogenic,
41 etc.) and anthropogenic (road vehicles, power plants etc.) sources. Vehicle emissions
42 are the dominant anthropogenic source and are consequently the target for regulatory
43 action. They can contribute up to ~90% of total particle numbers in polluted urban
44 environments (Pey et al., 2009), where emissions, mostly in the <300 nm size range,
45 can increase number concentrations of nanoparticles by two orders of magnitude or
46 more ($\sim 10^5 \text{ \# cm}^{-3}$) relative to the natural environment ($\sim 10^3 \text{ \# cm}^{-3}$) (Kumar, Fennell,

Langley, & Britter, 2008), though concentrations are highly dependent on meteorological conditions and the formation of secondary particles. These observations clearly indicate a primary need to control vehicle emissions, as enforced through Euro emission standards, in order to limit urban nanoparticle numbers. However, future challenges include tackling emerging sources (e.g. bio-fuel derived and manufactured nanoparticles) that have different physicochemical characteristics to the nanoparticles produced from conventional sources.

3.1 Bio-fuel derived nanoparticles

International energy policy encourages the use of bio-fuels as a substitute for petroleum fuels in vehicles, though socio-economic issues such as food security (Dominguez-Faus, Powers, Burken, & Alvarez, 2009) and resistance from car and components manufacturing companies, private users and local administrations has resulted in a somewhat slow uptake (Lapuerta, Armas, & Fernandez, 2008). The reasons for prompting bio-fuels include energy security, foreign exchange savings, socio-economic issues, such as new employment opportunities, and environmental concerns related to greenhouse gas emissions (Hammond, Kallu, & McManus, 2008). For example, the European directive 2003/30/EC set an immediate legal aim of replacing 5.75% and 20% of conventional fuel in road transportation with bio-fuels by 2010 and 2020, respectively, and use of bio-fuels is on track to meet these aims. However, this has not decreased particle *number* emissions because of (i) a shift in number distributions towards smaller size ranges (Cheng et al., 2008), (ii) the reduced available surface area of pre-existing particles in emissions that favour nucleation over adsorption (Kittelson, Watts, & Johnson, 2004), and (iii) the lower calorific value of bio-fuels, leading to increased fuel usage (Lapuerta, Armas, & Rodríguez-Fernández, 2008). Exhaust-treatment systems, such as diesel particulate filters (DPF), have been found to decrease nanoparticle emissions by up to two orders of magnitude as compared to non-DPF bio-diesel vehicles (Lee, Myung, & Park, 2009), at least in the size range above 23 nm. This can ensure compliance with vehicle emission standards in most cases but does not hide the fact that the use of bio-fuels in vehicles results in an overall increase in nanoparticle numbers when compared to petroleum fuels. Moreover, only somewhat limited and inconsistent information is available on the physicochemical characteristics of bio-fuel derived nanoparticles, such as size, shape, chemical composition and toxicity (Fontarasa et al., 2009; Jung, Kittelson, & Zachariah, 2006). This confounds arguments concerning whether or not bio-fuel derived nanoparticles will complicate existing regulatory concerns with other airborne nanoparticles. The positives about bio-fuel derived nanoparticles are that their physical characteristics (i.e. shape, size) can be assumed to be similar to those from conventional fuels and the same instruments can therefore be applied to measure them (see Section 4.1). However, their chemical characteristics (which relate to toxicity) remain a less understood matter that could significantly influence the development of mitigation strategies (Bunger et al., 2000; Finch et al., 2002). Further details on this topic can be seen elsewhere (Basha, Gopal, & Jebaraj, 2009; Kumar, Robins, & ApSimon, 2010; Lapuerta, Armas, & Rodríguez-Fernández, 2008; and references therein).

3.2 Manufactured or engineered nanoparticles

Manufactured nanomaterials (e.g. carbon nanotubes, nanowires etc.) are another

emerging class of atmospheric nanoparticles. Their production and use are rapidly increasing as new applications emerge. This, combined with their supposed persistence against degradation, implies that human and environmental exposure to so-called engineered nanoparticles will increase (Köhler, Som, Helland, & Gottschalk, 2008). They are not intentionally released into the urban environment but fugitive emissions can arise during production, use and disposal, though source terms are not well understood, neither are potential health effects (Brouwer, 2010; Nowack & Bucheli, 2007). Their physicochemical characteristics differ from atmospheric nanoparticles in numerous ways, such as aspect ratio, size distribution, chemical composition, toxicity and homogeneity (Xia, Li, & Nel, 2009). Recent studies report that inorganic or carbon nanostructures do not cause acute toxic effects at low doses, but prolonged exposure could well lead to adverse human health effects (Casals, Vázquez-Campos, Bastús, & Puentes, 2008). However, the relative toxicity of the two kinds of nanoparticles (atmospheric and manufactured) is currently not well known. Kumar, Fennell, & Robins (2010) recently reviewed the behaviour of manufactured and other airborne nanoparticles and discussed their significance in prioritising research and regulation activities. This concluded that the differences between manufactured and other atmospheric nanoparticles must be understood and specific measurement methods developed for regulatory control. The current knowledge of the characteristics and behaviour of air dispersed manufactured nanoparticles appears to be insufficient to influence any potential regulatory framework for atmospheric nanoparticles as a whole. Though their concentration relative to other atmospheric particles is currently very small, it will continue to grow, driven by the expected widespread use of products incorporating manufactured nanomaterials (e.g. batteries and textiles; Köhler et al., 2008). The current emphasis on developing innovative methods for detecting manufactured nanoparticles in the environment or workplace through exploiting their specific properties (i.e. magnetic, optical, electrical, electrochemical or physical) should eventually provide precise information on their behaviour in the atmosphere.

4. Key challenges in measurements and dispersion modelling of nanoparticle number concentration

There have been substantial advances in instrumentation for measuring nanoparticle number concentrations and size distributions, but there are as yet no *standard* application methods and sampling guidelines for measurement in the urban atmospheric environment. An initiative is needed for urban nanoparticle instrumentation that is similar to the Particle Measurement Programme that is establishing new systems and protocols for assessing nanoparticle emissions from vehicles (EU, 2008). This would seek to harmonise the performance of instruments in different ambient environments and establish standard guidelines for their use.

4.1 Instruments

The generally accepted instrument for measuring particle number concentration is the Condensation Particle Counter (CPC). However, before a CPC-based standard can be proposed, the desired performance characteristics need to be agreed. This mainly applies to the low-size detection cut-off, which itself depends on the particle material, as this affects the condensation of the working fluid around the particle. Within Europe, standardisation is currently underway in the European Committee for Standardisation (CEN) to define a cut-off curve for a specific particle material with a

specific working fluid. At the same time, procedures to determine CPC detection efficiencies are being defined within ISO. The instrumentation aspects of number concentration measurements are therefore being addressed.

In principle, size resolved particle number concentration measurements would be more useful than CPC measurements. There are several instruments available, based on established methods of size selection and detection. These include Scanning Mobility Particle Sizers (SMPS), Electrical Low Pressure Impactors, Aerodynamic Particle Sizers, Differential Mobility Spectrometers, and Laser Aerosol Spectrometers. A comprehensive review of their capabilities and limitations can be seen in Kumar, Robins, Vardoulakis & Britter (2010). Most of the above instruments claim to overcome important issues such as portability, time response, size resolution, robustness for unattended operation over long durations, calibration and maintenance requirements. However, the relative higher cost for widespread deployment and the reproducibility of data still remains as major issues. For example, Asbach et al. (2009) compared a number of mobility analysers with the SMPS that is considered as a benchmark instrument, and found a significant inconsistencies in measured distributions. This is because the different sizing principles would be expected to lead to significant differences for non-spherical particles. Likewise, Watson et al. (2011) compared hourly averaged ambient particle number and size distribution measurements which were taken simultaneously by 4 commercially available SMPS systems. They found similar shape of size distributions but with notable discrepancies in average concentrations for small (5–10 nm) and large (200–300 nm) particle size ranges. Moreover, the SMPS may have its own limitations related to its time response, portability and particle characterisation. For example, an HSE (2006) report observed that under certain circumstances the SMPS has the potential to alter the structure of the sampled particles due to the bi-polar charging process it employs in the size classification of the aerosol. All the above observations make judgement of equipment performance for particle size distribution difficult; e.g. in understanding the repeatability and reproducibility of results from different instruments in nominally identical conditions. Ideally, instruments with high sampling frequencies, covering a wide range of particle sizes (from 3 nm to 10 μ m) and robust enough to operate unattended for long periods at urban monitoring stations are needed at modest cost for widespread deployment to characterise individual and population exposure to nanoparticles at specific sizes in urban environments (Kumar, Robins, Vardoulakis et al., 2010). All these capabilities are not currently met by a *single* particle monitoring instrument and use of more than one instrument is required to obtain such a combination.

4.2 Sampling

Standardisation of sampling methods and data handling is also essential for improving the reproducibility of measurements. For example, Wiedensohler (2010) proposed methods for particle sampling and humidity control during field measurements. Atmospheric particles can undergo significant hygroscopic growth (e.g. ~1.5 time increase in size) at high (~80%) relative humidities (RH) and maintaining the RH below 40–50% in the sampling system is recommended for determining the physical properties of particles. Other recommendations for sampling methods include the use a separate vertical stack for particle measurements with an high sampling efficiency inlet capable of handling wide range of wind speeds; use of

1 weather and sunlight-resistant, conductive and non-corrosive material for sampling
2 tubes; calibrations of size and flow using latex particles and an independent volume
3 flow meter, respectively; and maintaining a laminar flow within the sampling tubes
4 (Reynolds number ~ 2000) to avoid losses of particles due to diffusion and turbulent
5 inertial deposition (Wiedensohler, 2010). Although inertial impaction is in theory only
6 important under turbulent flow conditions and for particles larger than 100 nm (Lee &
7 Gieseke, 1994), particle losses onto the inner surface of the sampling tubes can occur
8 even at low Reynolds number flow in long sampling tubes, as are often required
9 during field measurements, and this can appreciably change the measured number and
10 size distributions. For example, a recent study (Kumar, Fennell, Symonds, & Britter,
11 2008) demonstrated that the turbulent penetration model of Hinds (1999)
12 described particle losses best, even when the flow within the sampling tube during
13 field measurements was in the laminar region (i.e. Reynolds number ~ 461). This was
14 presumably due to the formation of secondary flows and other unknown
15 complications. Losses were found to be greatest for particles below 20 nm, due to the
16 higher diffusivity of smaller particles. The study concluded that an in-situ calibration
17 or comparison is prudent to evaluate the losses of particles in any experimental setup.

18 In contrast to vehicle emissions, there is much less intrinsic benefit in removing
19 volatile particles during the sampling process in ambient air. Unless evidence from
20 health effects requires only non-volatile particles to be measured, the aim should be
21 to minimise volatile losses during sampling. In general, this is not a major problem as
22 sampling and measurement do not involve elevated temperatures.

23 **4.3 Dispersion modelling**

24 Several models are currently available for particle dispersion at various urban
25 scales. These include Box, Gaussian, Lagrangian, Eulerian and Computational Fluid
26 Dynamics models, including models that treat particle dynamics (Holmes &
27 Morawska, 2006; Vardoulakis, Fisher, Pericleous, & Gonzalez-Flesca, 2003).
28 Validation studies for particle number prediction are not abundant because of the lack
29 of both long-term measurements that include size distributions of nanoparticles and
30 accurate input information (i.e. emission factors, meteorology, local traffic and the
31 geometry of the site, etc.). This limits the use of particle dispersion models, which
32 themselves contain both structural (errors in model formation) and parametric (due to
33 model input parameters) uncertainties (COSTAction732, 2010). For example,
34 Lohmeyer (2001) reported that predictions of gaseous pollutants from different
35 models can vary up to a factor of four for identical conditions, depending on the
36 quality of input information. Moreover, the prediction of particles on a *number* basis
37 becomes more complicated when removal (i.e. dry or wet depositions) and
38 transformation (i.e. nucleation, coagulation, condensation and evaporation) processes
39 are incorporated into the models. This is because all chemical and physical processes
40 show a strong non-linear dependency on particle sizes, that itself varies over a very
41 wide range. There is limited information available on the removal and transformation
42 processes that occur after the release of exhaust emissions but play an important role
43 in changing particle size distributions at different urban scales (i.e. in vehicle wake,
44 street canyons and city) (Hinds, 1999; Jacobson & Seinfeld, 2004; Ketzel &
45 Berkowicz, 2004; Kumar, Robins, & Britter, 2009; Pohjola, Pirjola, Kukkonen, &
46 Kulmala, 2003; Wehner, Birmili, Gnauk, & Wiedensohler, 2002). Complex flow and
47 mixing due to intricate networks of streets and buildings, synoptic scale winds,

1 surface heating and distributed pollution sources (such as moving traffic in urban
2 areas) make this problem even more challenging (Britter & Hanna, 2003). Detailed
3 information on the dynamics and dispersion modelling of urban atmospheric
4 nanoparticles at different urban scales can be seen in a recent review by Kumar,
5 Ketzel, Vardoulakis, Britter, & Pirjola (2011). Although not strictly necessary for
6 regulation, improved understanding of dispersion modelling at all urban scales would
7 greatly help the development of future strategies to reduce concentrations of urban
8 atmospheric nanoparticles.

9 Despite the limitations imposed by available instrumentation, there has recently been
10 a significant increase in the number of studies of urban nanoparticle concentrations
11 and size distributions, though not sufficient to inform regulatory decision making on a
12 particle *number* basis. Within the United Kingdom, for example, particle number
13 concentration (in the size range from 7 nm up to several micrometers) and size
14 distribution (between about 16 and 600 nm) have been measured continually at
15 several locations for more than 10 years. Typical reported concentrations range from
16 about 5,000 # cm⁻³ at a rural site to 100,000 # cm⁻³ at an urban kerbside site
17 (Beccaceci et al., 2010). Such measurements need to become widespread to provide a
18 comprehensive data-base that can be analysed to understand better the effects of
19 meteorology, traffic volume and particle dynamics as a function of nanoparticle size
20 range. Ideally, this would also cover transformation and transport behaviour from the
21 tailpipe-to-roadside-to-urban background and could serve as validation data for
22 performance evaluation of particle dispersion models (Kumar, Robins, Vardoulakis et
23 al., 2010). It could also be the key to establishing reliable particle number emission
24 factors, one of the most important input parameters for any particle dispersion model.
25 There is currently large associated uncertainty (i.e. up to an order of magnitude for a
26 given vehicle type under nearly identical driving conditions) in both their
27 measurement and estimation (Keogh et al., 2009; Kumar, Ketzel, Vardoulakis, Britter,
28 & Pirjola, 2011). A comprehensive data-base will support the development of better
29 dispersion models for nanoparticle numbers as well as provide the additional input
30 needed for their application.

31 **5. Summary and conclusions**

32 There is presently no legal threshold anywhere in the world for controlling the
33 exposure of the public to airborne particle *number* concentrations in the urban
34 environment. There are several reasons for this, including a lack of standardisation for
35 sampling and measurement, as well as a lack of clear epidemiological evidence (Xia
36 et al., 2009). Properly validated particle dispersion models would also be helpful
37 (Holmes & Morawska, 2006; Vardoulakis et al., 2003). Despite this, understanding of
38 the sources, dispersion and physicochemical characteristics of atmospheric
39 nanoparticles has increased substantially in recent years, as has the availability of
40 suitable monitoring systems. In line with these advances, air quality monitoring
41 networks should be encouraged to use currently available instrumentation to include
42 measurements of number and size distributions of nanoparticles. Such initiatives will
43 provide the data that will help address the issues raised in this article, along with an
44 opportunity for comprehensive validation of particle dispersion models (Kumar,
45 Ketzel, Vardoulakis, Britter, & Pirjola, 2011). The data would also provide a valuable
46 input for decision-makers to help develop research and mitigation strategies for
47 controlling nanoparticles on a *number* basis in the urban environment.

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