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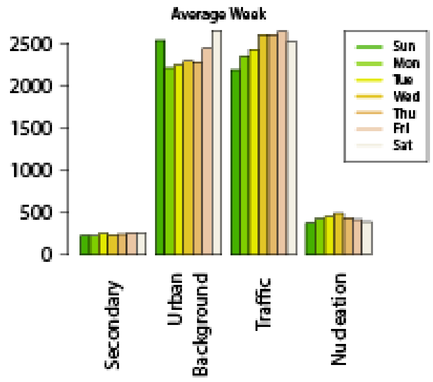
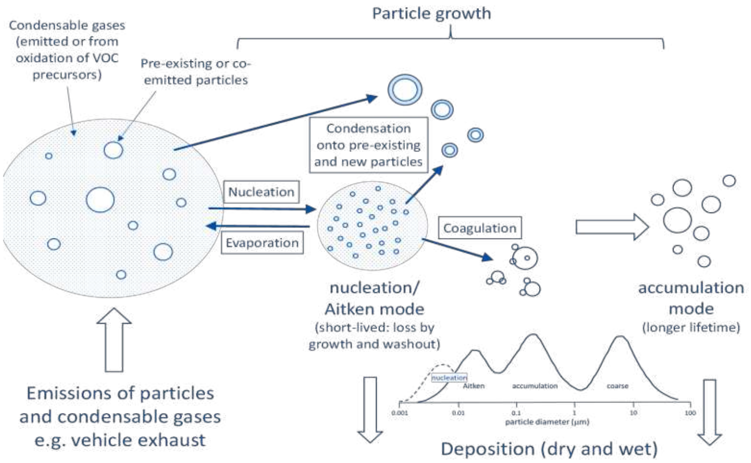
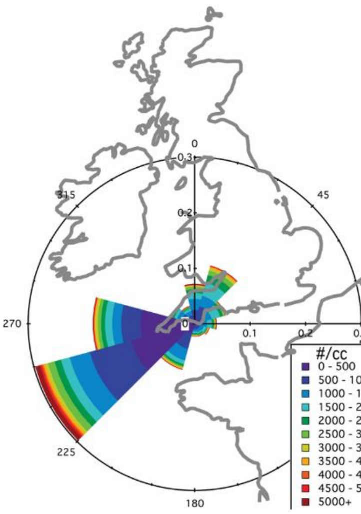
AIR QUALITY EXPERT GROUP

Ultrafine Particles (UFP) in the UK







Prepared for:
Department for Environment, Food and Rural Affairs;
Scottish Government; Welsh Government; and
Department of the Environment in Northern Ireland

AIR QUALITY EXPERT GROUP

Ultrafine Particles (UFP) in the UK

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This is a report from the Air Quality Expert Group to the Department for Environment, Food and Rural Affairs; Scottish Government; Welsh Government; and Department of the Environment in Northern Ireland, on ultrafine particles in the UK. The information contained within this report represents a review of the understanding and evidence available at the time of writing.

Front cover image credit: Defra/Air Quality Expert Group

United Kingdom air quality information received from the automatic monitoring sites and forecasts may be accessed via the following media:

Freephone Air Pollution Information Service 0800556677

Internet http://uk-air.defra.gov.uk

PB14510

Terms of Reference

The Air Quality Expert Group (AQEG) is an expert committee of the Department for Environment, Food and Rural Affairs (Defra) and considers current knowledge on air pollution and provides advice on such things as the levels, sources and characteristics of air pollutants in the UK. AQEG reports to Defra's Chief Scientific Adviser, Defra Ministers, Scottish Ministers, the Welsh Government and the Department of the Environment in Northern Ireland (the Government and devolved administrations). Members of the Group are drawn from those with a proven track record in the fields of air pollution research and practice.

AQEG's functions are to:

- Provide advice to, and work collaboratively with, officials and key office holders in Defra and the devolved administrations, other delivery partners and public bodies, and EU and international technical expert groups;

- Report to Defra's Chief Scientific Adviser (CSA): Chairs of expert committees will meet annually with the CSA, and will provide an annual summary of the work of the Committee to the Science Advisory Council (SAC) for Defra's Annual Report. In exception, matters can be escalated to Ministers;

- Support the CSA as appropriate during emergencies;

- Contribute to developing the air quality evidence base by analysing, interpreting and synthesising evidence;

- Provide judgements on the quality and relevance of the evidence base;

- Suggest priority areas for future work, and advise on Defra's implementation of the air quality evidence plan (or equivalent);

- Give advice on current and future levels, trends, sources and characteristics of air pollutants in the UK;

- Provide independent advice and operate in line with the Government's Principles for Scientific Advice and the Code of Practice for Scientific Advisory Committees (CoPSAC).

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Executive Summary

Background

Ultrafine particles (UFP) are defined as those with one dimension less than 100 nanometres. They are therefore the smallest group of particles in the atmosphere and comprise a minor component of $PM_{2.5}$ and PM_{10}. However, although their contribution to particle mass is generally very small, they typically contribute the greatest number of particles per unit volume relative to the total number of particles present in the atmosphere.

UFP are both primary (directly emitted into the atmosphere from sources such as road traffic and coal combustion) and secondary (formed from chemical reactions in the atmosphere). Because of their very small size, UFP typically undergo rapid dynamic transformations in the atmosphere due to processes such as coagulation, condensational growth, evaporation and deposition. The concentrations therefore vary greatly in time and space, especially close to sources of emission.

UFP are believed to contribute to the toxicity of airborne particulate matter but the magnitude of their contribution is currently unclear. Whilst it is possible that their small size and large surface area may make them particularly harmful to health, the available evidence is limited and as yet no air quality guideline has been set for their concentration.

Emissions of UFP arise primarily from combustion sources and especially transport-related sources which burn sulphur-containing fuels. Emissions from road transport affect all areas with major roads, emissions from shipping are important on the main shipping routes, and emissions from aviation are significant in the vicinity of major airports. Some possibly important sources such as domestic wood burning are currently poorly quantified.

Secondary UFP which arise from new particle formation within the atmosphere are very important in southern Europe but less so in the UK. Regional nucleation processes are believed to account for around 10% on average of the particle count at a background site in London.

Measurement

There are established methods to measure ultrafine particles which can be determined by mass, but are more usually measured by number. Only three long-term sites are operating in the UK for the measurement of UFP and these operate at a roadside, urban background and rural location.

Time series of measurements of UFP at UK sites show a general decline in concentrations, which fell steeply at roadside when the sulphur content of motor fuels was reduced. A continuing gradual reduction in airborne concentrations is most probably associated with the increasing penetration of motor vehicles fitted with diesel particle filters. UFP correlate with other traffic-generated pollutants, although the relationships tend to be site specific. There is a sharp reduction in UFP concentrations on moving away from major roads which is mainly due to dilution but also due in part to the evaporation of semi-volatile compounds. There have been few studies of the chemical composition of UFP but this tends to be similar to that of $PM_{2.5}$, with significant regional variations.

Models

Numerical models of urban dispersion processes can give reasonable estimates of particle number concentrations in urban areas, when the emissions are well characterised; however, the incorporation of aerosol dynamical processes is needed to give more accurate estimates of concentration and to allow the simulation of particle size distributions. Such models have to date not been used routinely in the UK.

Receptor models which use atmospheric measurements to infer the sources of particles have attributed UFP in the urban background of London to four major sources, i.e. urban background representing mainly aged traffic exhaust and wood smoke particles, local traffic, secondary particles and regional nucleation.

Abatement

Policies and actions to control ambient $PM_{2.5}$ and PM_{10} will not always control UFP.

There are no emissions standards for UFP other than for diesel and gasoline-direct injection engine road vehicles which must meet a type approval standard for non-volatile particles of >23 nanometre diameter.

Some of the technologies routinely used by industry for abatement of particulate matter emissions are efficient for the removal of UFP. For instance, there have been a number of studies of municipal waste incinerators which show highly effective removal of UFP by their pollution control systems.

Road vehicle emissions can be controlled through the use of diesel particle filters, while reduction of emissions from shipping and aviation depends primarily upon the use of low sulphur fuels.

Recommendations

Continuous monitoring of UFP concentrations and size distributions currently takes place at only three UK sites, all of which are in the southeast of England. The current measurement strategy is focused on the urban and traffic sources. It is insufficient to determine exposure from poorly understood UFP emission sources such as airports and shipping / ports, and also the way in which existing policies to reduce PM_{10} and $PM_{2.5}$ are affecting UFP exposure.

The group therefore recommends monitoring in other parts of the country, including the establishment of at least one permanent site monitoring in the vicinity of a major airport. There is also a need for research to further understand the chemical composition of ambient UFP, as well as enhanced numerical models to simulate and predict the behaviour of UFP in the atmosphere.

1 Introduction

1.1 Key Points

Ultrafine particles (with one dimension smaller than 100 nm diameter) contribute little to the mass of particles in the atmosphere, but typically dominate the total number of particles in polluted air.

Ultrafine particles are both primary (directly emitted into the atmosphere) and secondary (formed from chemical reactions in the atmosphere).

Ultrafine particles undergo many dynamic transformations in the atmosphere due to processes such as coagulation, condensational growth, evaporation and deposition.

As the sources and behaviour of ultrafine particles in the atmosphere differ in substantial ways from the main component particles contributing to $PM_{2.5}$ and PM_{10} mass, their spatial patterns and temporal trends cannot be inferred from $PM_{2.5}$ or PM_{10} mass measurements.

1.2 Purpose of this Report

The purpose of this report from the Air Quality Expert Group is to summarise what is currently known about the impact of the ultrafine particle (UFP) component on UK ambient air quality. This is considered particularly in respect of differences between UFP and the $PM_{2.5}$ and PM_{10} quantities that are also used to characterise airborne particulate matter, and which have been the subject of previous reports by AQEG (2005; 2012).

Ultrafine particles refer to particulate matter that has at least one dimension less than 100 nanometres (nm). The term nanoparticles is also used to refer to the same entity. UFP are currently not the direct subject of any regulation of their emissions or ambient concentration, but measures designed to mitigate concentrations of $PM_{2.5}$ and PM_{10}, of which they are part, may also affect UFP. Like $PM_{2.5}$ and PM_{10}, UFP are both emitted directly to the atmosphere and formed by chemical reactions within the atmosphere.

It is typical for >90% of the number of particles in the air to be in the UFP size range; but the contribution of these particles to the mass of particles in the air is very small. This is because very small particles individually have very little mass; for example, one million particles of diameter 10 nm are equivalent in mass to only one particle of diameter 1 µm (1000 nm) of the same density. The sources, behaviour and impacts of UFP in the atmosphere can differ from those of the substantially fewer, larger particles that dominate the currently regulated $PM_{2.5}$ and PM_{10} size fractions. In particular, due to their very small size, UFP can penetrate deep into the human lung.

They also undergo atmospheric transformations at rates considerably more rapid than that of the larger particles which are the main contributors to $PM_{2.5}$ mass. However, beyond the immediate proximity of source, UFP concentrations and size distributions become more stable and point measurements are representative of a larger area.

The next section lists policy relevant questions that set the scope for this report. The remainder of the Introduction provides a general overview of the sources and characteristics of UFP in the atmosphere (including engineered UFP), their health effects, and relevant current legislation, as context to the greater detail specific to the UK presented in subsequent chapters.

1.3 Manufactured UFP/Nanoparticles

There has been a substantial growth in recent years in the deliberate manufacture of nanoparticles for incorporation in a wide range of products (sometimes also referred to as engineered nanoparticles). These include nanoparticles of silver, which because of their anti-microbial action, are incorporated into clothing, and zinc oxide and titanium dioxide which are used in sun screens. Cerium dioxide is used in motor fuel additives, and carbon nanotubes are used in electronic products, and many others. There are essentially four ways in which these engineered nanoparticles can enter the atmosphere:

i. by release from manufacturing processes. Such releases should be minimal from a properly operated plant;

ii. through attrition of products in which they are incorporated. Thus nanoparticles might be lost from items of outer clothing into the atmosphere or from construction materials during demolition processes. There is currently little evidence for this;

iii. release possibly in modified form from use as a combustion additive.

iv. by accidental release, for example due to spillage in road traffic accidents.

Cerium dioxide is used in a number of modes for the control of particulate matter emissions from diesel engines. It can be added to the fuel of vehicles which are not fitted with a particle trap, in which case the emissions contain largely carbonaceous particles in which cerium-rich nanoparticles are embedded. Although the properties are changed, the cerium remains in nanoparticle form, probably attached to a larger nanoparticle. In some applications they are added to the fuel but the vehicle is fitted with a particle filter which retains the cerium oxide where its catalytic activity is valuable in oxidising carbonaceous particles. Catalytic elements such as cerium can also be included in particle traps during their manufacture, which may lead to loss of nanoparticles through attrition during use of the filter.

Currently, none of these processes is expected to give rise to appreciable atmospheric concentrations of nanoparticles, especially compared with the carbonaceous particles that are formed normally in combustion processes. However, estimates have been made of the airborne concentrations and size distributions of particle-associated cerium that could arise from more widespread use of cerium additives in motor fuel (Gantt et al., 2014).

This report does not consider further the issue of manufactured nanoparticles in ambient air.

1.4 Sources and Characteristics of UFP

As noted above, the UFP/nanoparticle fraction of airborne particulate matter carries very little particle mass, but a very large number of particles, as shown in Figure 1. This figure shows that most particles by number lie below 0.1 µm (100 nm) and are therefore UFP. However, when their volume is summed, they contribute very little to the volume of the particles, which lies mostly between 0.1 and 1 µm, and 2 µm and 10 µm. This leads to the situation in the air quality field in which UFP are usually quantified by their number concentration (per unit volume of air), whereas particle distributions that include particles with diameters greater than a few hundred nm, are generally characterised by their mass concentration, e.g. the mass-based concentrations per unit volume of air associated with the PM_{10} and $PM_{2.5}$ metrics. The boxed text provides definition of the $PM_{2.5}$ and PM_{10} metric. Emissions from road vehicles are measured by number using the PMP protocol (Section 1.5) which excludes smaller semi-volatile particles (<23 nm after heating to 300ºC) before the counter.

Definitions of PM_{10} and $PM_{2.5}$

In principle, PM_{10} and $PM_{2.5}$ are the mass concentrations of airborne particles with an aerodynamic diameter of <10 μm or <2.5 μm, respectively, where the volume of air is its volume at ambient conditions, rather than at standardised temperature and pressure. (A particle's aerodynamic diameter is the diameter of the spherical particle of unit density that has the same aerodynamic properties.) The sizes of 10 μm and 2.5 μm are chosen because of their relevance for inhalation into the human lung, as set out in the document ISO 7708:1983 *Air quality – particle size fraction definitions for health related sampling*. Specifically, PM_{10} corresponds to the 'thoracic convention' – the size fraction of inhaled particles that penetrate beyond the larynx, whilst $PM_{2.5}$ corresponds to the 'high risk respirable convention' – the size fraction that penetrate to the unciliated airways (essentially to the gas-exchange surfaces) and is of particular concern for high risk groups (children, the elderly and infirm). In practice it is not possible to design a collector that has a step change between zero and 100% collection efficiency at the required aerodynamic particle diameter so the PM_{10} and $PM_{2.5}$ size fractions are defined by adherence to specified separation efficiency curves as a function of particle diameter that have midpoints (50% separation efficiency) at diameters of 10 μm and 2.5 μm, respectively. The standardised sampling curves for regulatory purposes are specified in European CEN standard EN 12341:2014. Furthermore, some but not all, emission measurement techniques capture the "condensable and semi-volatile" component of PM. This inconsistency has led to complications associated with the use of the PM_{10} and $PM_{2.5}$ metrics in emission inventories (see Chapter 2.1).

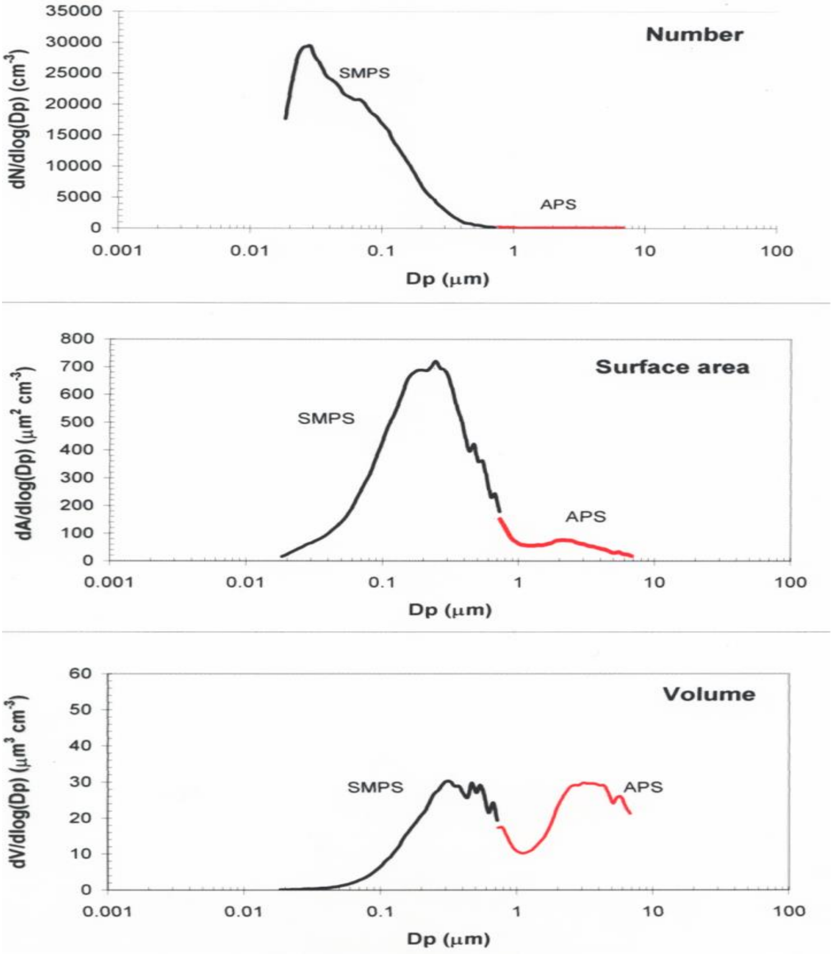

Figure 1. Particle distributions as a function of aerodynamic diameter measured in Birmingham expressed by particle number, particle surface area and particle volume. The latter is equivalent to a mass distribution when variation in densities of the particles is small.

The UFP size range encompasses a number of sub-sets or modes of particle sizes, whose presence largely reflects their sources and formation processes (Figure 2). The nucleation and Aitken modes typically encompass particles of <30 nm and 30–100 nm, respectively. The UFP size range also includes part of the accumulation mode, which comprises particles in the size range 50–1000 nm. However, none of these latter classifications are strictly defined. For UFP measurements taken at urban background or roadside sites, the nucleation and Aitken modes contribute most to the total particle number concentration (Kumar et al., 2011). This contribution would be greater if particles below 10 nm, which are difficult to measure, are taken into account.

As for the whole particle ensemble, UFPs can be classified as ‘primary’ or ‘secondary’.

1.4.1 Primary UFP

Natural sources of primary UFP include marine aerosol and volcanic particles, which only have a small UFP component, and forest fires for which the UFP component is larger.

Anthropogenic sources of UFPs include transport (on- and off-road vehicles, diesel trains, shipping, and aircraft activities at airports), combustion in industries such as power plants and waste incineration, construction and demolition, biomass burning, agricultural processes, cooking and cigarette smoke.

In urban environments, road vehicles are the major source of UFP emissions. This means that the roadside increment for UFP is greater than for larger PM size fractions. A source apportionment study for Marylebone Road in London reported contributions to total particle number concentrations from vehicle exhaust emissions, brake dust, resuspension and urban background sources of 65%, 2%, 5% and 18%, respectively (Harrison et al., 2011). Similar proportions for vehicle exhaust and background contributions were derived from measurements in Barcelona (Pey et al., 2009).

Diesel engines dominate exhaust emissions of UFP, with average emission factors about two orders of magnitude greater than for gasoline engines (Beddows and Harrison, 2008). Particles formed by condensation of semi-volatile vapours upon less volatile nuclei during dilution of the engine exhaust plume in the first seconds after emission are still generally referred to as primary emissions. Various studies have implicated sulphuric acid derived from oxidation of fuel sulphur in the nucleation process, consistent with observations of a reduction in the abundance of nucleation mode particles in the atmosphere of London (Jones et al., 2012) and Copenhagen (Wahlin, 2009) when diesel fuel composition changed from ultra-low (<50 ppm) to zero (<10 ppm) sulphur content. By application of Positive Matrix Factorization (PMF) to particle size distributions measured at roadside in London, Harrison et al. (2011) were able to separately quantify the normally overlapping semi-volatile particle number mode centred upon 20 nm from the graphitic solid particle mode centred upon 50 nm also emitted from road traffic. The former accounted for 38% of the on-road particle number emissions, with the latter contributing 53%.

Although UFP are usually quantified by number concentration, the UK inventory of primary UFP emissions published by the National Atmospheric Inventory is mass based (effectively a $PM_{0.1}$ inventory), being derived from the NAEI PM_{10} inventory by application of source-specific mass-based factors of the fraction of particle mass in particles smaller than 0.1 µm (100 nm) in diameter. However, particle number emission factors have been developed independently and used by TNO to derive a PN emission inventory for the UK (see Section 2.1.2).

1.4.2 Secondary UFP

Secondary formation of UFP occurs via atmospheric photochemistry of gaseous precursors and condensation of semi-volatile vapours (Holmes, 2007; Kulmala et al., 2013) (see Figure 2). The most common atmospheric formation mechanism involves nucleation of sulphuric acid, which in turn derives from oxidation of emitted S-containing compounds such as SO_2 and dimethylsulphide (CH_3SCH_3) - the latter is emitted from marine phytoplankton (Kulmala et al., 2004). Other natural nucleation pathways include oxidation of terpenes and other biogenic VOC emitted by vegetation (Ehn et al., 2014) and oxidation of iodine-containing compounds emitted at coastal margins (McFiggans et al., 2004). However, particle nucleation is widely observed in polluted atmospheres, with anthropogenic SO_2 and VOC apparently playing a role in the formation and growth of new particles, or anthropogenic O_3 promoting nucleation from natural VOC.

New particle formation events generally occur during high global radiation, low wind speed and relative humidity, and low pre-existing particle surface area (Rimnacova et al., 2011). The increased prevalence of the latter in polluted air tends to inhibit nucleation, although new particle formation in urban areas can still be significant (Kumar et al., 2014), particularly in warmer, sunnier climates (Reche et al., 2011). Typical formation rates of 3 nm size particles are in the ranges 0.01–10, up to 100, 10^4–10^5 and 10^4–10^5 $cm^{-3}\,s^{-1}$ for the atmospheric boundary layer, urban areas, coastal areas and industrial plumes, respectively (Kulmala et al., 2004).

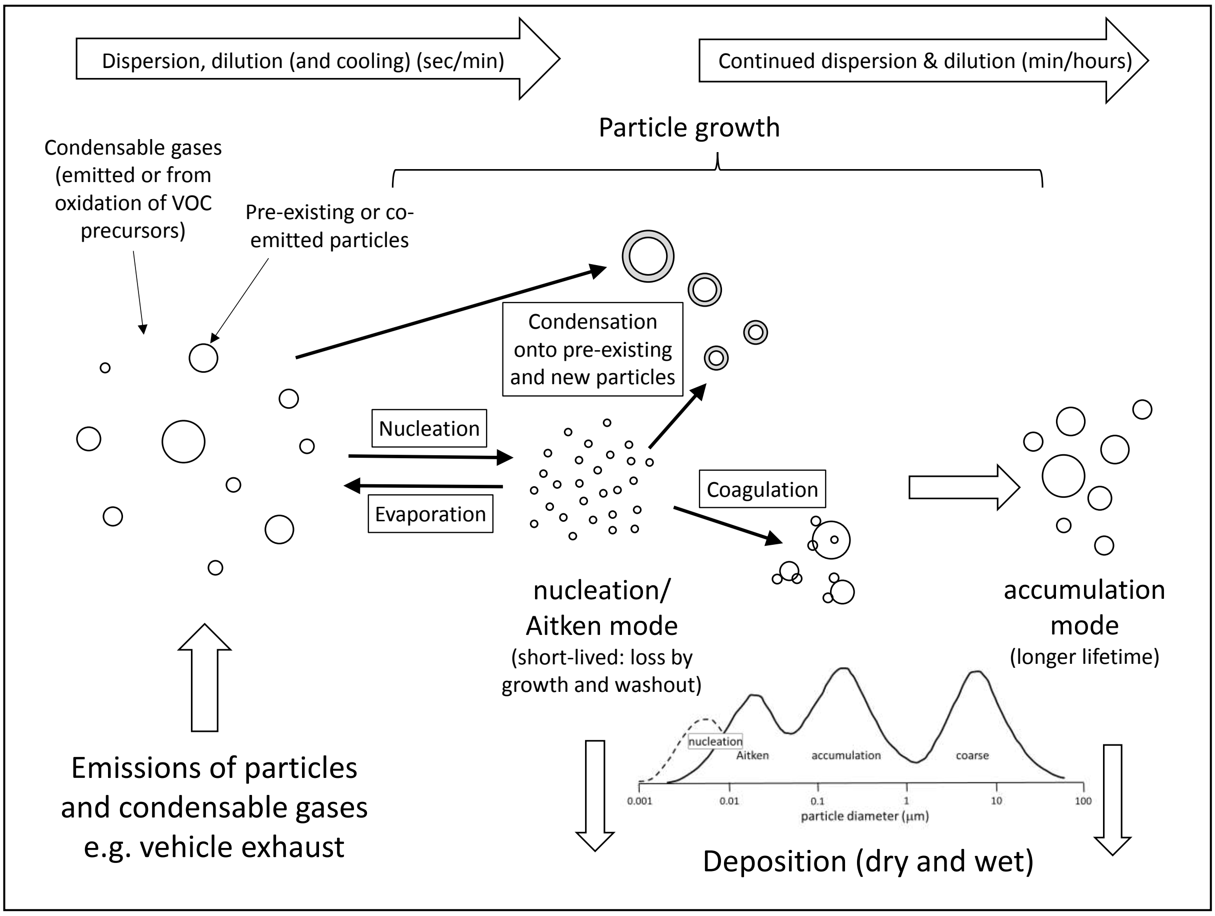

Figure 2. Schematic of processes affecting particle formation, growth and size distributions.

1.4.3 UFP dynamics

The UFP size distribution, in the urban environment in particular, is highly dynamic due to the competing influences of processes such as dilution, nucleation, condensation, coagulation, evaporation, and deposition (dry and wet). A schematic of some of these processes is shown in Figure 2. Net particle growth rates are typically a few nm h^{-1} (Kulmala et al., 2004). From analysis of a pan-European dataset of UFP observations, Beddows et al. (2014) concluded that as particles move across the European atmosphere they grow in diameter at a rate of ~0.6-0.9 nm h^{-1}. Spatial variation in UFP concentrations can exceed an order of magnitude within metres of distance under certain circumstances, but temporal variations may reach several orders of magnitude within seconds. Factors that affect the rate of particle transformation include variability in the emission strength (e.g. vehicle speed), meteorological conditions (e.g. temperature, humidity, wind speed, solar radiation), and urban topography. These factors also affect the turbulence levels which in turn affect the mixing and dilution.

Despite the dominant influence of traffic upon UFP in urban areas, a review of measurements of mass, number and black carbon concentrations across seven urban areas in Europe concluded that UFP variability was not equally influenced by the same emission sources and atmospheric processes, and does not always reflect the impact of road traffic on air quality (Reche et al., 2011). A separate study of UFP at 24 background sites across Europe also reported variability in complexity of UFP size distributions, especially when impacted by local sources or a variety of different air masses (Beddows et al., 2014). It should be noted that although UFP grow into larger particles in the atmosphere, this does not affect the airborne mass of chemical constituents which they carry, as this simply becomes associated with larger particles.

1.4.4 UFP composition

Chemical composition of UFPs in different environments is still comparatively under-studied, which is important from the perspective of source apportionment and studies of their impacts on health.

Nucleation mode particles originating from unburned fuel and lubricating oil consist of organic compounds, sulphates and nitrates from the condensation of vapour during the rapid cooling of exhaust gases (Charron and Harrison, 2003; Kittelson et al., 2006). Aitken mode particles are mainly made of a soot/ash core with an adsorbed layer of volatilisable material including PAHs, carboxylic acids and hopanes (Kulmala et al., 2004; Chow and Watson, 2007).

Secondary particles are generally comprised of sulphuric acid, ammonium sulphates and nitrates, organic compounds and a range of trace metals.

1.5 Health concerns of ambient UFP

UFP penetrate deep into the respiratory system, allowing interactions with lung tissue and potential translocation into the blood stream. This, together with the hypothesis that the toxicity of particulate matter is governed by the surface area of the particles rather than their mass, has led to suggestions that ultrafine particles may be particularly harmful to health (HEI, 2013).

Recent authoritative reviews (WHO, 2013; HEI, 2013) have noted that few epidemiological studies investigating concentration-effect relationships for UFP are available, because of insufficient measurements of UFP metrics such as particle number concentration. The World Health Organization (WHO, 2013) concluded that the epidemiological data are currently too scarce to evaluate or to use as the basis for recommending an air quality guideline for UFP.

Nonetheless, in the light of evidence that UFP act (in part) through mechanisms not shared with larger particles and can contribute to the health effects of PM, they recommended that efforts to reduce the numbers of UFP in engine emissions should continue (WHO, 2013). The Health Effects Institute (HEI, 2013) considered that the current evidence did not convincingly support the suggestion that UFPs alone can account in substantial ways for the adverse effects that have been associated with ambient pollutants such as $PM_{2.5}$. However, they noted that independent effects of UFP could not be ruled out, given the limitations of the current evidence base.

1.6 Legislation pertaining to ambient UFP

There are no ambient air quality standards for UFP in the UK or anywhere else in the world.

However, the EU (and consequently also the UK) has particle number emission standards for new vehicles. This is currently the only such legislation worldwide. The Euro 5 and Euro 6 standards specify a PN emission limit of 6.0×10^{11} solid particles per test-cycle km for compression ignition (diesel) vehicles (EC Directive, 2008). Euro 6 standard also places a similar limit (6.0×10^{11} solid particles per km) for direct injection gasoline vehicles, exempted to 6.0×10^{12} solid particles per km for the first three years of its implementation date in September 2014 (EC Directive, 2008). These limit values apply to non-volatile particles of >23 nm diameter after heating at 300 °C. The lower particle cut–off is to exclude semi-volatile nucleation mode particles in order to enhance the prospects of repeatability in measurements. It also helps minimise particles losses during sampling.

The lower cut-off set by the Euro standards means that more than ~30% of the smallest UFP in urban environments may not be included (Wehner and Wiedensohler, 2003).

Whilst these regulations limit the emissions of UFPs to the environment from one key source, they do not in themselves regulate the exposure of the public to UFPs.

1.7 Chapter 1 References

AQEG. Particulate Matter in the United Kingdom. Air Quality Expert Group, UK Department for Environment, Food and Rural Affairs, London, 2005. PB10580. Accessible at: http://uk-air.defra.gov.uk/library/reports?report_id=269

AQEG. Fine Particulate Matter (PM2.5) in the United Kingdom. Air Quality Expert Group, UK Department for Environment, Food and Rural Affairs, London, 2012. PB13837. Accessible at: http://uk-air.defra.gov.uk/library/reports?report_id=727

Beddows, D., Dall'Osto, M., Harrison, R., Kulmala, M., Asmi, A., Wiedensohler, A., Laj, P., Fjaeraa, A., Sellegri, K., Birmili, W., Bukowiecki, N., Weingartner, E., Baltensperger, U., Zdimal, V., Zikova, N., Putaud, J. P., Marinoni, A., Tunved, P., Hansson, H., Fiebig, M., Kivekas, N., Swietlicki, E., Lihavainen, H., Asmi, E., Ulevicius, V., Aalto, P., Mihalopoulos, N., Kalivitis, N., Kalapov, I., Kiss, G., de Leeuw, G., Henzing, B., O'Dowd, C., Jennings, S., Flentje, H., Meinhardt, F., Ries, L., van der Gon, H. and Visschedijk, A. Variations in tropospheric submicron particle size distributions across the European continent 2008-2009. Atmos. Chem. Phys., 14, 4327-4348, 2014.

Beddows, D. C. S., Harrison, R. M. Comparison of average particle number emission factors for heavy and light duty vehicles derived from rolling chassis dynamometer and field studies. Atmos. Environ., 42, 7954-7966, 2008.

Charron, A., Harrison, R. M. Primary particle formation from vehicle emissions during exhaust dilution in the roadside atmosphere. Atmos. Environ., 37, 4109-4119, 2003.

Chow, J.C., Watson, J. G. Review of measurement methods and compositions for ultrafine particles. Aerosol Air Qual. Res., 7, 121-173, 2007.

EC Directive: Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe, 2008. Accessible at: http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32008L0050:EN:NOT

Ehn, M., Thornton, J.A., Kleist, E., Sipila, M., Junninen, H., Pullinen, I., Springer, M., Rubach, F., Tillmann, R., Lee, B., Lopez-Hilfiker, F., Andres, S., Acir, I. H., Rissanen, M., Jokinen, T., Schobesberger, S., Kangasluoma, J., Kontkanen, J., Nieminen, T., Kurten, T., Nielsen, L. B., Jorgensen, S., Kjaergaard, H. G., Canagaratna, M., Dal Maso, M., Berndt, T., Petaja, T., Wahner, A., Kerminen, V.M., Kulmala, M., Worsnop, D. R., Wildt, J., Mentel, T. F. A large source of low-volatility secondary organic aerosol. Nature, 506, 476-479.

Gantt, B., Hoque, S., Willis, R. D., Fahey, K. M., Delgado-Saborit, J. M., Harrison, R. M., Erdakos, G. B., Bhave, P.V., Zhang, K., Kovalcik, K., Pye, H.O. Near-Road modeling and measurement of cerium-containing particles generated by nanoparticle diesel fuel additive use. Environ. Sci. Technol., 48, 10607-10613, 2014.

Harrison, R. M., Beddows, D. C. S., Dall'Osto, M. PMF analysis of wide-range particle size spectra collected on a major highway. Environ. Sci. Technol., 45, 5522-5528, 2011.

HEI. Understanding the health effects of ambient ultrafine particles. HEI Perspectives 3. HEI Review Panel on Ultrafine Particles, Health Effects Institute, Boston, MA USA. 2013. Accessible at: http://pubs.healtheffects.org/view.php?id=394,

Holmes, N. A review of particle formation events and growth in the atmosphere in the various environments and discussion of mechanistic implications. Atmos. Environ., 41, 2183-2201, 2007.

Jones, A. M., Harrison, R. M., Barratt, B., Fuller, G. A large reduction in airborne particle number concentrations at the time of the introduction of "sulphur free" diesel and the London Low Emission Zone. Atmos. Environ., 50, 129-138, 2012.

Kittelson, D., Watts, W., Johnson, J. On-road and laboratory evaluation of combustion aerosols - Part 1: Summary of diesel engine results. J. Aerosol Sci., 37, 913-930, 2006.

Kulmala, M., Kontkanen, J., Junninen, H., Lehtipalo, K., Manninen, H. E., Nieminen, T., Petaja, T., Sipila, M., Schobesberger, S., Rantala, P., Franchin, A., Jokinen, T., Jarvinen, E., Aijala, M., Kangasluoma, J., Hakala, J., Aalto, P. P., Paasonen, P., Mikkila, J., Vanhanen, J., Aalto, J., Hakola, H., Makkonen, U., Ruuskanen, T., Mauldin, R. L., Duplissy, J., Vehkamaki, H., Back, J., Kortelainen, A., Riipinen, I., Kurten, T., Johnston, M. V., Smith, J. N., Ehn, M., Mentel, T. F., Lehtinen, K. E. J., Laaksonen, A., Kerminen, V. M., Worsnop, D.R. Direct observations of atmospheric aerosol nucleation. Science, 339, 943-946, 2013.

Kulmala, M., Vehkamaki, H., Petaja, T., Dal Maso, M., Lauri, A., Kerminen, V. M., Birmili, W., McMurry, P. H. Formation and growth rates of ultrafine atmospheric particles: a review of observations. J. Aerosol Sci., 35, 143-176, 2004.

Kumar, P., Robins, A., Vardoulakis, S., Quincey, P. Technical challenges in tackling regulatory concerns for urban atmospheric nanoparticles. Particuology, 9, 566-571, 2011.

Kumar, P., Morawska, L., Birmili, W., Paasonen, P., Hu, M., Kulmala, M., Harrison, R. M., Norford, L., Britter, R. Ultrafine particles in cities. Environ. Int., 66, 1-10, 2014.

McFiggans, G., Coe, H., Burgess, R., Allan, J., Cubison, M., Alfarra, M. R., Saunders, R., Saiz-Lopez, A., Plane, J. M. C., Wevill, D. J., Carpenter, L. J., Rickard, A. R., Monks, P. S. Direct evidence for coastal iodine particles from Laminaria macroalgae - linkage to emissions of molecular iodine. Atmos. Chem. Phys., 4, 701-713, 2004.

Pey, J., Querol, X., Alastuey, A., Rodriguez, S., Putaud, J.P., Van Dingenen, R. Source apportionment of urban fine and ultra-fine particle number concentration in a Western Mediterranean city. Atmos. Environ., 43, 4407-4415, 2009.

Reche, C., Querol, X., Alastuey, A., Viana, M., Pey, J., Moreno, T., Rodriguez, S., Gonzalez, Y., Fernandez-Camacho, R., Sanchez de la Campa, A., de la Rosa, J., Dall'Osto, M., Prevot, A., Hueglin, C., Harrison, R.M., Quincey, P. New considerations for PM, black carbon and particle number concentration for air quality monitoring across different European cities. Atmos. Chem. Phys., 11, 6207-6227, 2011.

Rimnacova, D., Zdimal, V., Schwarz, J., Smolik, J., Rimnac, M. Atmospheric aerosols in suburb of Prague: The dynamics of particle size distributions. Atmos. Res., 101, 539-552, 2011.

Wahlin, P. Measured reduction of kerbside ultrafine particle number concentrations in Copenhagen. Atmos. Environ., 43, 3645-3647, 2009.

Wehner, B., Wiedensohler, A. Long term measurements of submicrometer urban aerosols: statistical analysis for correlations with meteorological conditions and trace gases. Atmos. Chem. Phys., 3, 867-879, 2003.

WHO. Review of evidence on health aspects of air pollution – REVIHAAP Project: Technical Report, World Health Organisation, Copenhagen, Denmark, 2013. Accessible at:

http://www.euro.who.int/__data/assets/pdf_file/0004/193108/REVIHAAP-Final-technical-report-final-version.pdf

2 Sources of UFP

Key Points

- Emissions inventories show that combustion sources, and especially those related to residential wood burning and transport (road traffic, aircraft, shipping) are the main sources of ultrafine particle emissions in the UK and Europe.
- Reductions in fuel sulphur content and the use of diesel particle filters is leading to a reduction in emissions from transport sources.
- Emission factors are more uncertain than for particle mass metrics ($PM_{2.5}$ and PM_{10}).
- Emissions from some potentially important sources such as domestic wood burning are very poorly known.
- Future projections show an increasingly important contribution of UFP from aviation.
- Regional nucleation is also a source of ultrafine particle formation in the atmosphere and accounts for ~10% of the particle count at a background site in London.

2.1 Emission Inventories for UFP

2.1.1 Emission inventories by mass

National emission inventories report annual totals of emissions of particulate matter by mass from anthropogenic sources. Emissions are estimated for source sectors defined for the purposes of reporting inventories to international bodies such as the UNECE Convention on Long-Range Transboundary Air Pollution (CLRTAP). Inventories are constructed following guidelines specified in the EMEP/EEA Emissions Inventory Guidebook and generally entail estimations of emissions using source-specific emission factors and activity data combined with emission rates directly measured by operators and reported to regulatory authorities such as the Environment Agency. Directly reported emissions are usually restricted to emissions from major industrial sources.

2.2 Emission Factors

Emission factors are usually derived from measurements of a given source, sometimes for research purposes as well as to meet regulatory requirements. They are not always measured specifically for the benefit of emission inventories, and may have been derived using different measurement techniques and procedures. This means that factors gathered together from different sources may not always be comparable with each other which makes it difficult for authors of inventory guidebooks to develop consistent and representative emission factors. It also makes it difficult to compare inventories reported by different countries where different approaches and sources of information have been used. One specific consequence of this is uncertainty into the extent that inventories for different source sectors include condensable and semi-volatile components in the PM mass emissions that are reported. Including this component can increase the emission factor by up to a factor of five (Denier van der Gon, 2015).

The UN/ECE Task Force on Emission Inventories and Projections (TFEIP) is currently working with the Task Force on Modelling and Monitoring (TFMM) to address this issue under the CLRTAP. The first step is to better understand what information Parties are using in their current emissions inventories, and what the emission factor information in the UN/ECE Air Pollutant Emissions Inventory Guidebook actually represents. This work is on-going. Once this information has been compiled, the TFEIP will make a recommendation as to whether the CLRTAP should standardise the definition of PM with or without the condensable and semi-volatile fraction, and hence provide information on the UN/ECE Air Pollutant Emissions Inventory Guidebook that is consistent with this definition. Standardising emission factors in the UN/ECE Air Pollutant Emissions Inventory Guidebook so that they are fully consistent is a complex task, and it is expected that it will be several years before this can be achieved. It may be necessary to chemically speciate the PM emissions from different sources to estimate the contribution from low, medium and high volatility components, and hence derive emission factors that include the condensable and semi-volatile component.

2.3 UK Reporting for International Conventions and Directives

Countries are currently only required to report emissions of PM_{10} and $PM_{2.5}$ as well as Total Suspended Particulates; reporting of black carbon is voluntary, but is reported by the UK's National Atmospheric Emissions Inventory (NAEI). Emission reduction targets are in place for $PM_{2.5}$ under the Gothenburg Protocol of the CLRTAP specifying a 30% reduction in national emissions from the UK to be achieved by 2020 relative to a 2005 baseline.

The CLRTAP's TFMM have indicated that they would ideally like PM emission estimates to be reported by volatility categories. This would allow improved air pollutant transport and chemical modelling of PM and other pollutants. However, the TFEIP have indicated that this is generally seen as being unrealistic in the foreseeable future, and that the priority is to move towards the standardisation of the definition of PM in emission inventories. However, it is not yet known whether this standardisation of the PM metric will, or will not, include the condensable and semi-volatile component.

There is currently no requirement to report a national emissions inventory of UFPs to international bodies such as the UNECE Convention on Long Range Transport of Air Pollutants (CLRTAP). There are currently no emissions ceilings or emission reduction targets set on UFPs. Consequently, there are no guidelines or common sources of emission factors of UFPs to enable inventories to be developed on a consistent basis and any emissions data that are reported are likely to come from ad-hoc research studies.

The NAEI does include an inventory of fine particulate matter mass in the sub-1 micron and sub-0.1 micron size range (PM_1 and $PM_{0.1}$) for anthropogenic sources in the UK. These are reported and updated annually so as to be consistent with reported inventories for PM_{10} and $PM_{2.5}$. The inventories therefore exclude emissions from natural sources and sources such as cooking. The inventories for PM_1 and $PM_{0.1}$ are developed by applying simple sector-specific mass fractions to the inventories for PM_{10} or Total Suspended Particulates (TSP), in much the same way as the inventories for $PM_{2.5}$ are developed. This does mean they cover the same source sectors and cover the same time-series as the inventories for TSP, PM_{10} and $PM_{2.5}$. The vast majority of the PM fractions used in the NAEI come from a TNO (1997) report or from the AP-42 emission factor source developed by the USEPA (1995). The factors are therefore old, not necessarily applicable to current fuels and technologies and subject to high levels of uncertainty.

The mass fractions are applied to each of the ~400 sources included in the NAEI inventory for PM. When grouped into the main source categories, the overall mass fractions for $PM_{0.1}$, PM_1 and $PM_{2.5}$ relative to PM_{10} are shown in Figure 3. These fractions may conceal differences between many different sub-category sources and fuels and are effectively a weighting of the fractions for all the detailed sources contributing to each main source category shown here for 2015. However, these charts indicate that for the finer particle sizes, smaller mass fractions are applied to non-combustion sources and larger fractions applied to combustion sources reflecting (in mass terms) the size distributions of particulates emitted by each source. It also shows how combustion sources with solid fuels tend to have smaller fractions of the finer particle sizes than combustion with gaseous and liquid fuels.

Figure 4(a) shows the share of overall $PM_{0.1}$ emissions in the UK by source sector in 2015. These are consistent with the inventories for PM_{10} and $PM_{2.5}$ developed by the NAEI and reported to CLRTAP in early 2017. The share in $PM_{2.5}$ emissions is shown in Figure 4(b) for comparison.

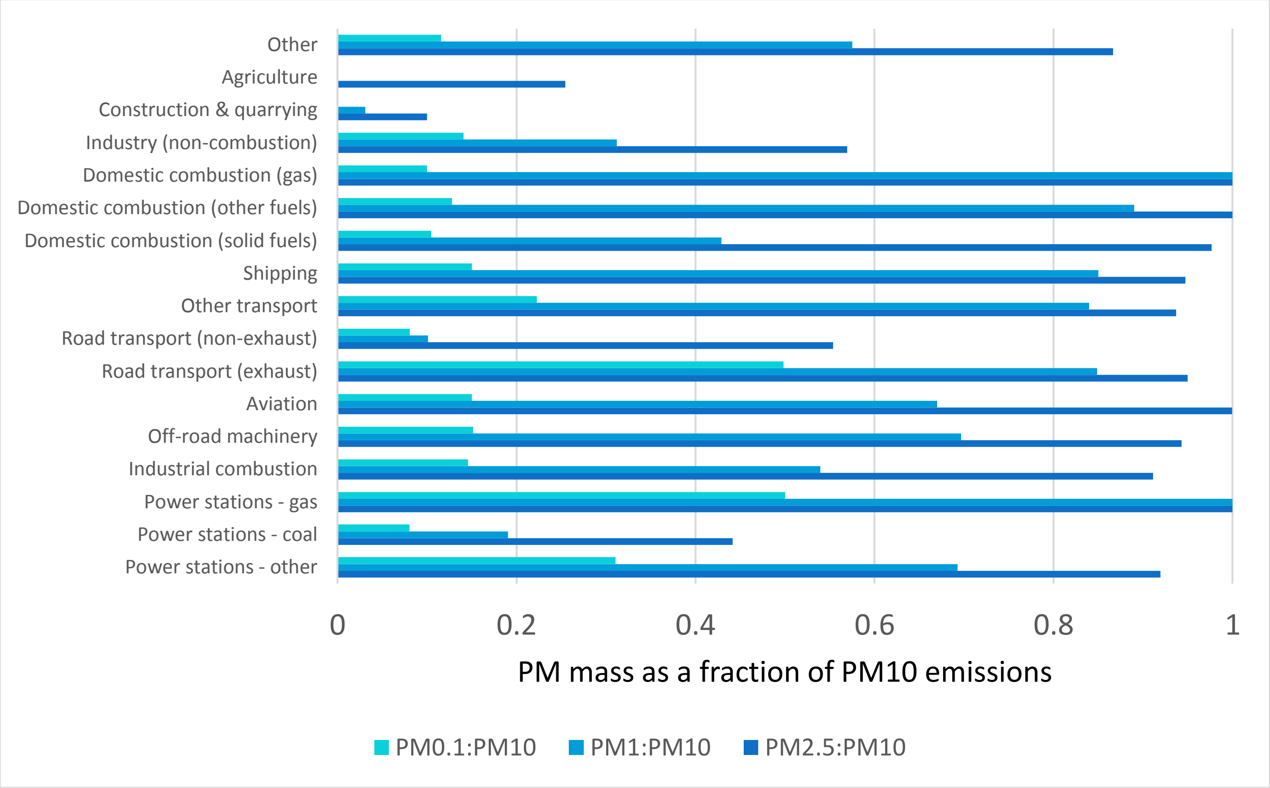

Figure 3. Mass fraction of PM0.1, PM1 and PM2.5 relative to PM10 for emission source groups in 2015.

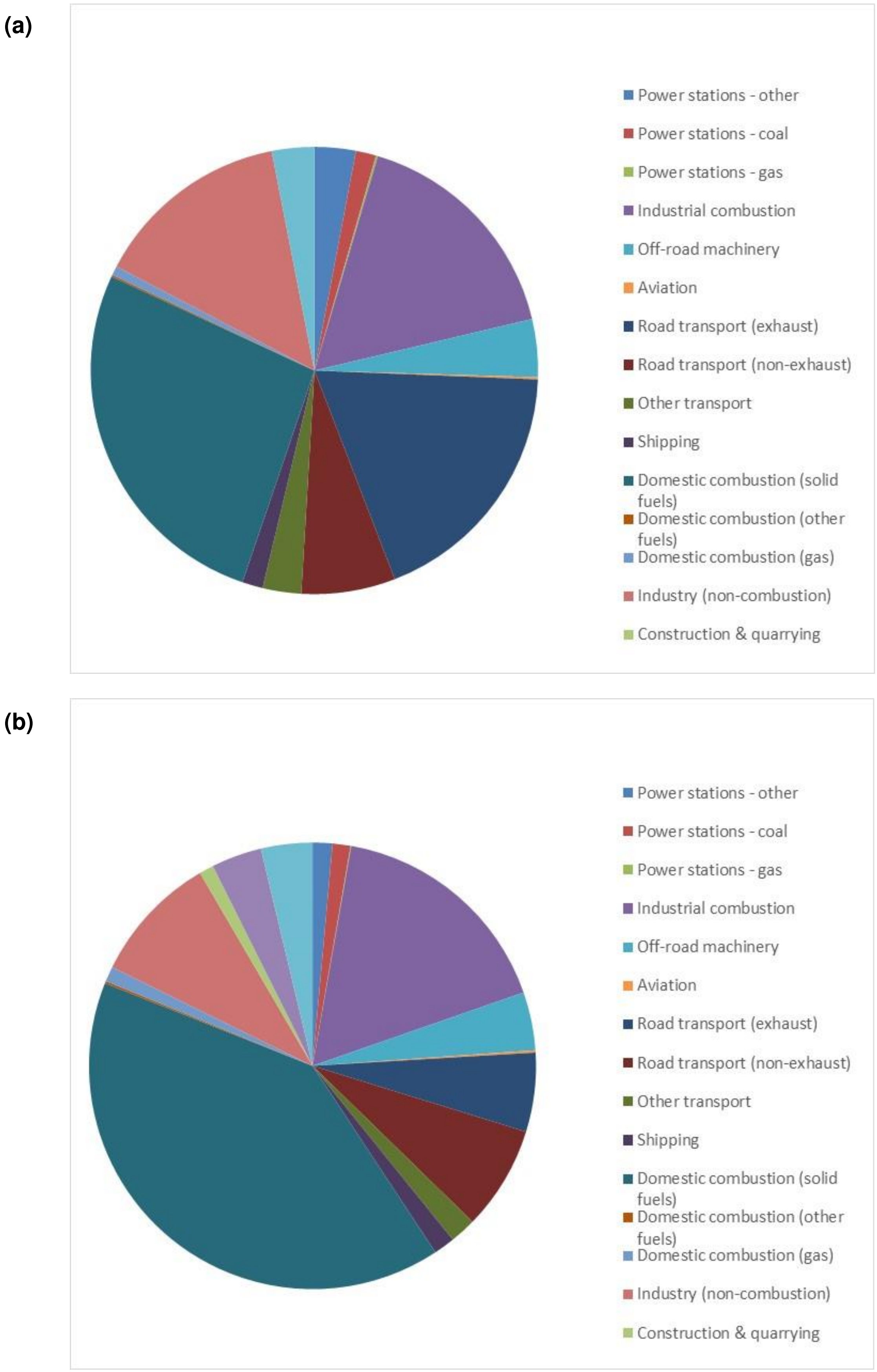

Figure 4. (a) Proportion of UK PM0.1 emissions in 2015 by emission source according to the 2015 version of the NAEI. (b). Proportion of UK PM2.5 emissions in 2015 by emission source according to the 2015 version of the NAEI.

The main differences between these two charts are in the share attributed to road transport exhaust emissions and residential solid fuel combustion emissions. The road transport exhaust share increases from 6% for $PM_{2.5}$ to 19% for $PM_{0.1}$ whereas for residential solid fuel combustion the share decreases from 40% for $PM_{2.5}$ to 27% for $PM_{0.1}$. The reason for this is largely a reflection of the different fuels used in road transport and residential combustion.

The relatively clean petroleum-based fuels used in road transportation produce a relatively high proportion of the particle mass in the nucleation mode. In contrast, a high proportion of the particle mass emissions from residential solid fuel combustion in the UK come from solid fuels (coal, wood) burned under less optimum combustion conditions with high proportions of fly ash emitted in coarser particle size ranges. Consequently, the net contribution of residential solid fuel combustion to $PM_{0.1}$ mass emissions compared with other combustion sources using liquid and gaseous fuels is smaller than for $PM_{2.5}$. The smaller fraction of PM mass emitted in the $PM_{0.1}$ range from residential solid fuel combustion is evident in Figure 3. However, it should be noted that the PM size fractions used for road transport in the NAEI come from the TNO (1997) source so pre-date the introduction of sulphur-free fuels, thus contributing to the high levels of uncertainty in these estimates. Combustion in the energy and other industries make a large contribution in both PM size ranges.

A recent study on ambient measurements of particle number concentrations under the landing approach near airports in the U.S. suggests significant emissions of UFPs occur from aircraft, particularly under low load conditions (Riley et al., 2016). This may indicate that the $PM_{0.1}$ mass fraction for aviation should be higher than shown in Figure 3.

There are considerable uncertainties and gaps in the inventories for UFPs which will be discussed in Section 2.1.6.

2.3.1 Trends in UK UFP mass emissions

Using the trends in the UK inventory for PM_{10} from 1990-2015 by each source sector, trends in inventories for $PM_{0.1}$, PM_1 and $PM_{2.5}$ have been developed. Figure 5(a) shows the time-series trend for $PM_{0.1}$ split by each main source category. Figure 5(b) shows the corresponding trend for $PM_{2.5}$.

These figures show that between 1990 and 2015, $PM_{0.1}$ emissions have decreased by 57% compared with a decrease of 47% for $PM_{2.5}$. Most of the fall in $PM_{2.5}$ and $PM_{0.1}$ emissions has been due to reductions in power generation, road transport and industrial combustion and machinery emissions.

(a)

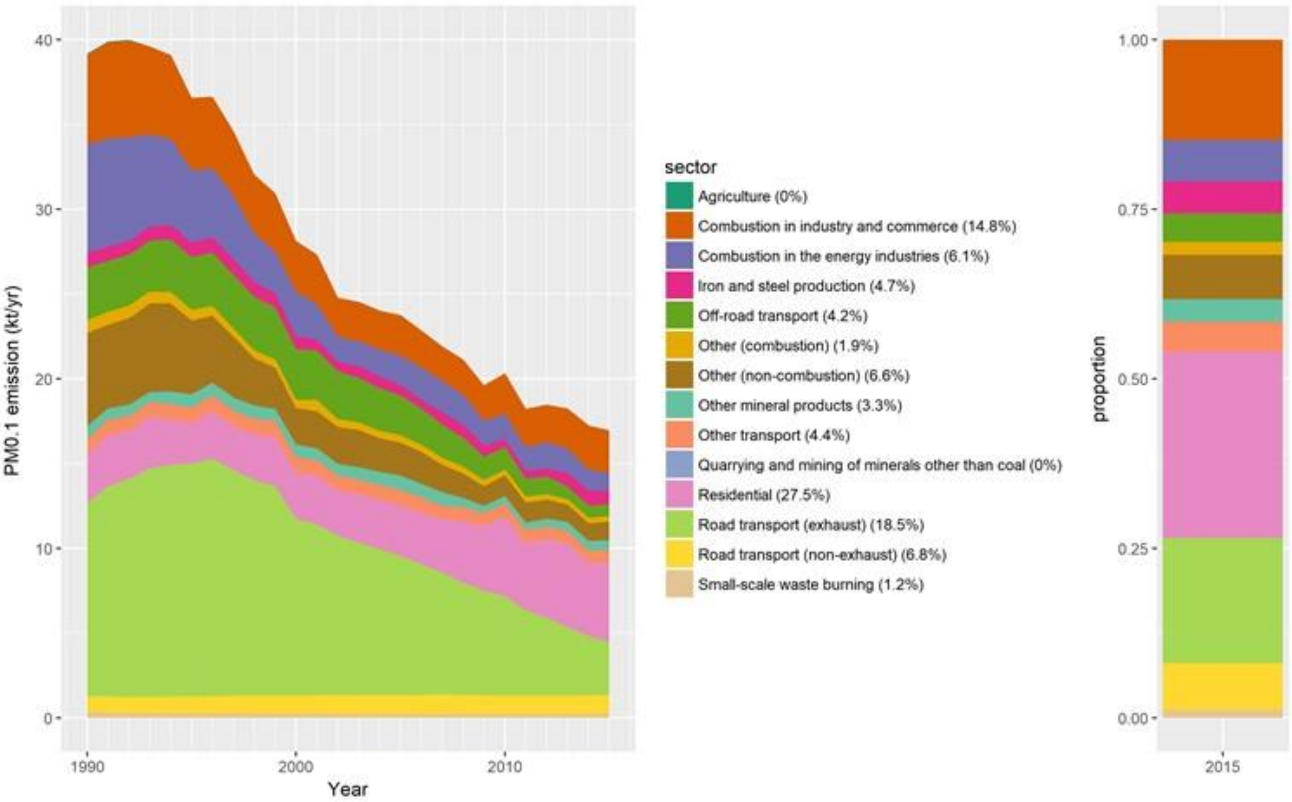

Figure 5(a). Trend in UK emissions of PM0.1 from 1990-2015 by source sector. The bar on the right shows the contribution of the different sources in 2015, which are shown as percentages in the figure caption.

(b)

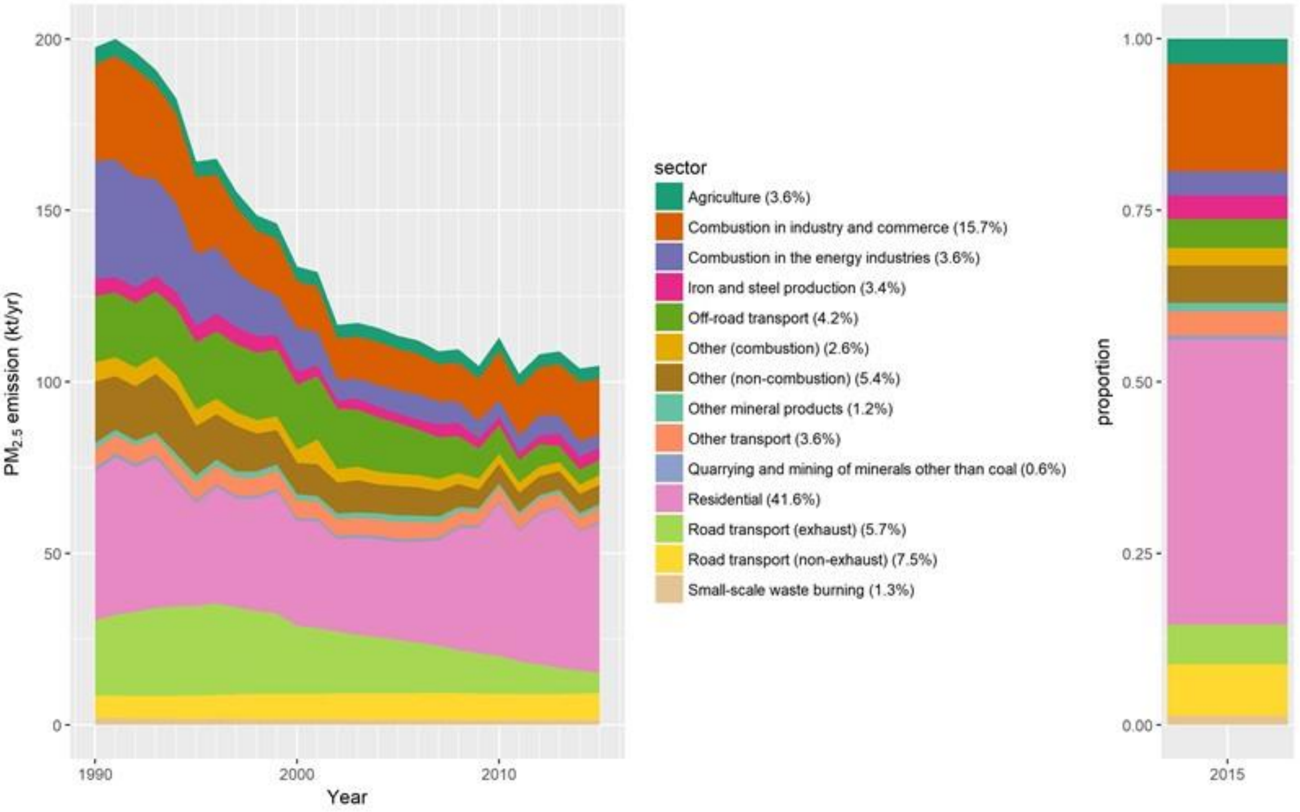

Figure 5(b). Trend in UK emissions of PM2.5 from 1990-2015 by source sector. The bar on the right shows the contribution of the different sources in 2015 which are shown as percentages in the figure caption.

2.3.2 Chemically-speciated PM emission inventories

Particulate matter (PM) emitted directly into air is a complex mixture of various components including inorganic sulphates, nitrates, metals, elemental carbon (EC) and organic carbon (OC) aerosols. The composition of particulate matter is dependent on the emission source and its general operation mode. Development of a chemically speciated PM emissions inventory is outside the scope of the current NAEI programme as it is not required for reporting of emissions to CLRTAP or to EMEP. However, advanced numerical air quality models require that particulate matter emissions are speciated into specific chemical components in order to reproduce the chemical composition of ambient PM and allowing a direct comparison with measurements.

The NAEI is currently developing a chemically speciated PM inventory using source-specific PM profiles taken from a review of information available in Europe. In particular, information from the SPECIEUROPE Database was used for many combustion and industrial sources supplemented by information on vehicle exhaust emissions derived by Ricardo and other sources from TNO and IIASA. Rather than develop a full speciation profile as unique chemical entities, the PM species are grouped according to their physical and chemical parameters to correspond with the inorganic and secondary organic aerosol modules used in chemistry schemes within chemical transport air pollution models, thus:

- Elemental carbon
- Organic carbon

- Sulphates
- Nitrates
- Coarse particles
- Fine fraction (the sum of other inorganic components that make up the fine fraction, including metals)

The profile will split the NAEI $PM_{2.5}$ inventory into these components for emission sources at the SNAP 1 sector level as commonly used in air pollution models.

2.3.3 Particle number and particle mass emission factors for road transport

Compared with other emission sources, the particulates from road vehicle exhausts have been relatively well characterised. This information could be used to improve the mass emissions inventory for road transport for the sub-micron particulates and inform an inventory on particle number emissions for this sector.

There is currently a disagreement between the trend in the UK emission inventories for $PM_{0.1}$ (which is based on fairly crude emission factors relative to PM_{10}) and ambient particle number concentrations. The concentrations show a sharp drop at sites in London in 2007, not shown by the inventory which has been linked to a drop in fuel sulphur content not accounted for in the inventory. The $PM_{0.1}$ emission factors used in the NAEI are based on an old study by TNO which pre-dated the introduction of lower sulphur road fuels and no data has since been published on the dependence of vehicle emissions of UFP on fuel sulphur content at the sub-100ppm level.

Figure 6 shows the sulphur content of pump fuels in the UK since 2000 when the EU Fuel Quality Directive came into effect, based on information provided by the UK Petroleum Industry Association. Fuels with sulphur content below 50ppm were available well before they were required by legislation (2005). By 2001, nearly all fuel sold in the UK was <50ppm S. Refineries also started to gear up to the further EU regulation 2003/17/EC for <10ppm S limit on road fuels that came into effect in January 2009 and the period between 2005 and 2008 did see a sharp reduction in the sulphur content of diesel; for petrol the change came a little later (2008 to 2009).

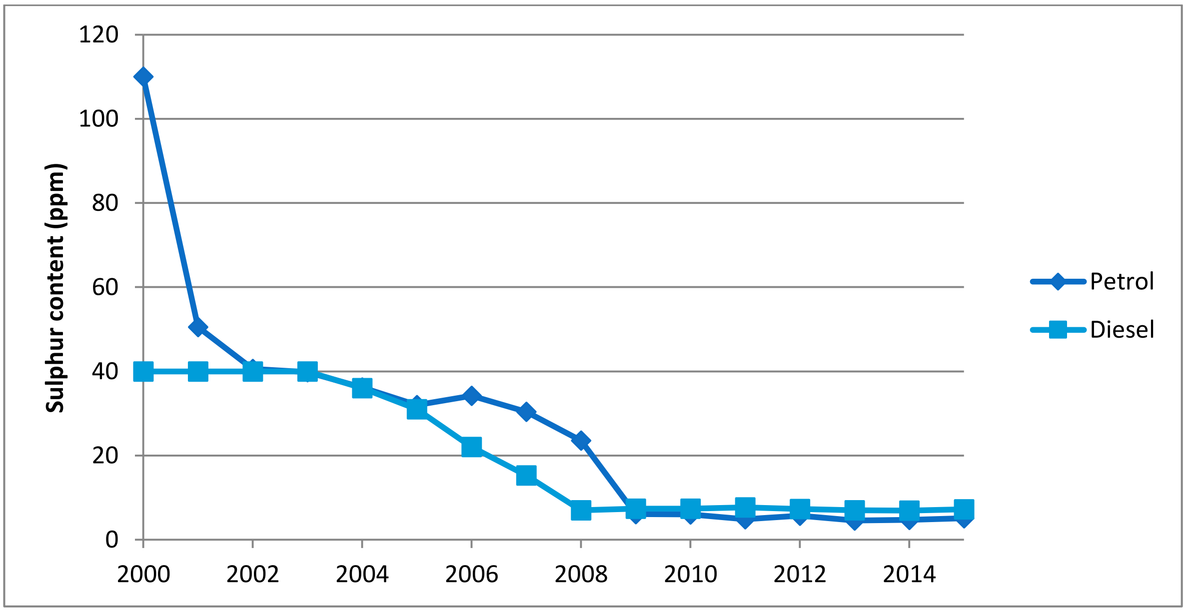

Figure 6. Sulphur content of road fuels sold in the UK. Source: UKPIA.

Very small particles (generally <30 nm diameter) are formed from semi-volatile compounds which condense when the exhaust gases cool on mixing with ambient air. Fuel sulphur plays a role in this by providing sulphate nuclei on which the semi-volatile compounds can condense. The processes are strongly dependent upon the dilution ratio of the exhaust with ambient air, and are difficult to replicate in the laboratory. For this reason the UNECE Particle Measurement Programme (PMP) protocol was developed, and depends upon removing the semi-volatile particles before counting the solid particles in the exhaust.

The PMP developed a repeatable protocol for measuring “solid” particles in engine exhaust. In this context, “solid” particles refer to particles with a diameter between 23 nm and 2.5 μm which survive a residence time of 0.25s at 300^0 C, designed to evaporate volatile particles. Exhaust gases are sampled from a constant volume dilution tunnel sampler through a cyclone size separator (2.5 μm cut), through a volatile particle remover (hot dilution at 150^0 C followed by heating to 300^0 C) and a condensation particle counter. A specialised condensation particle counter with a 50% efficiency lower size cut at 23± 3 nm is used. The PMP method was evaluated by Johnson et al. (2009) who found that there were many solid particles <23 nm diameter which are not counted, and that at high engine load, particles were forming after the diesel particle filter.

Unlike other source sectors, for road transport the EMEP/EEA Emissions Inventory Guidebook provides emission factors for several particle characteristics besides the PM_{10} and $PM_{2.5}$ metrics (EMEP/EEA, 2014). This includes ‘active surface area’ (in cm^2/km), the ‘total particle number’ (in #/km), and the ‘solid particle number’ (in #/km) divided into three different size bands (< 50 nm, 50–100 nm, 100–1,000 nm). Factors are available for diesel cars, petrol cars with gasoline direct injection (GDI), buses and three different weight classes of HGVs equipped with and without different types of exhaust aftertreatment systems (DPF and SCR). Factors are given for emissions under urban, rural and highway cycles. The values of factors given in the Guidebook are said to be obtained from the EU PARTICULATES (2005) project under laboratory conditions which were expected to maximise the concentrations, hence they should be considered to represent near-maximum emission rates.

For light duty vehicles, the Guidebook factors only cover vehicles up to Euro 3 standards which is likely to reflect the era in which the measurements were made, i.e. during the early 2000s, although it does include factors for a Euro 3 diesel car with a DPF and a Euro 3 petrol car with gasoline direct injection (GDI). However, the Euro 5 and 6 standards for diesel cars specify a particle number emission limit of 6×10^{11} solid particles per km. The same limit also applies to Euro 6 GDI petrol cars. Factors are given in the Guidebook for different types of heavy duty vehicles up to Euro V, but do not appear to be complete (e.g. no factors for a Euro V with DPF). The incompleteness of the PN factors in the Guidebook, prohibits a complete inventory for UK road transport PN emissions, but the factors themselves do show some interesting trends, as demonstrated for the Euro 1-3 passenger cars which might shed some light on the expected trend in UK emissions of PN over the 2000-2010 period.

Figures 7 and 8 show emission factors for PM and PN for Euro 1-3 diesel and petrol cars taken from the latest Guidebook. The factors are shown on a log scale for comparisons and refer to urban conditions (PM mass emissions are in ng/km). Figure 7 also shows the limit value for PN that applies to both Euro 6 diesel and petrol cars

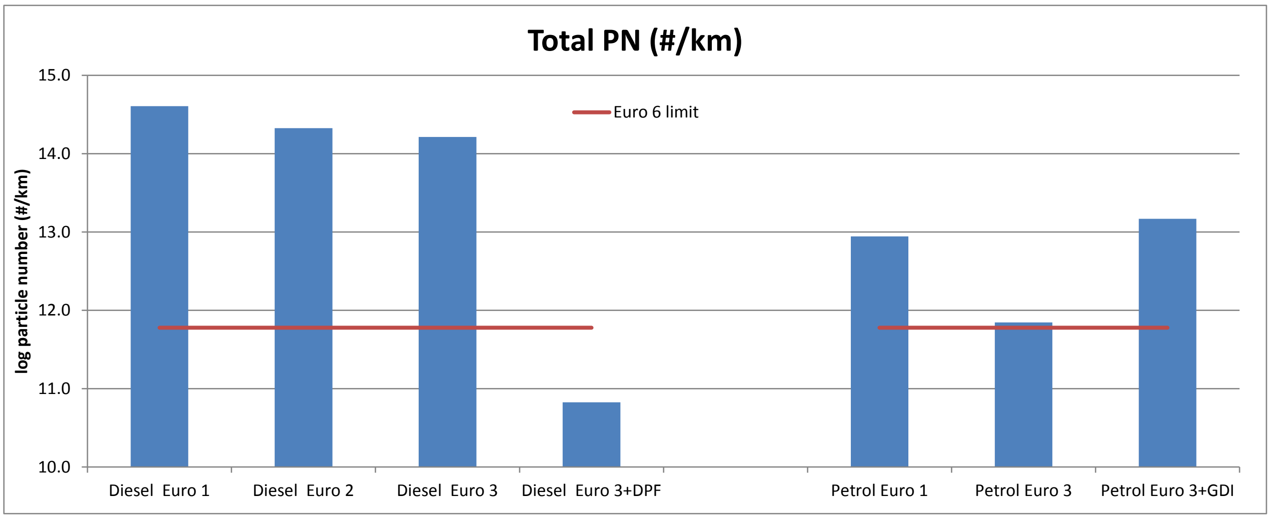

Figure 7. Particle number urban emission factors for passenger cars. Source EMEP/EEA Emissions Inventory Guidebook (2013).

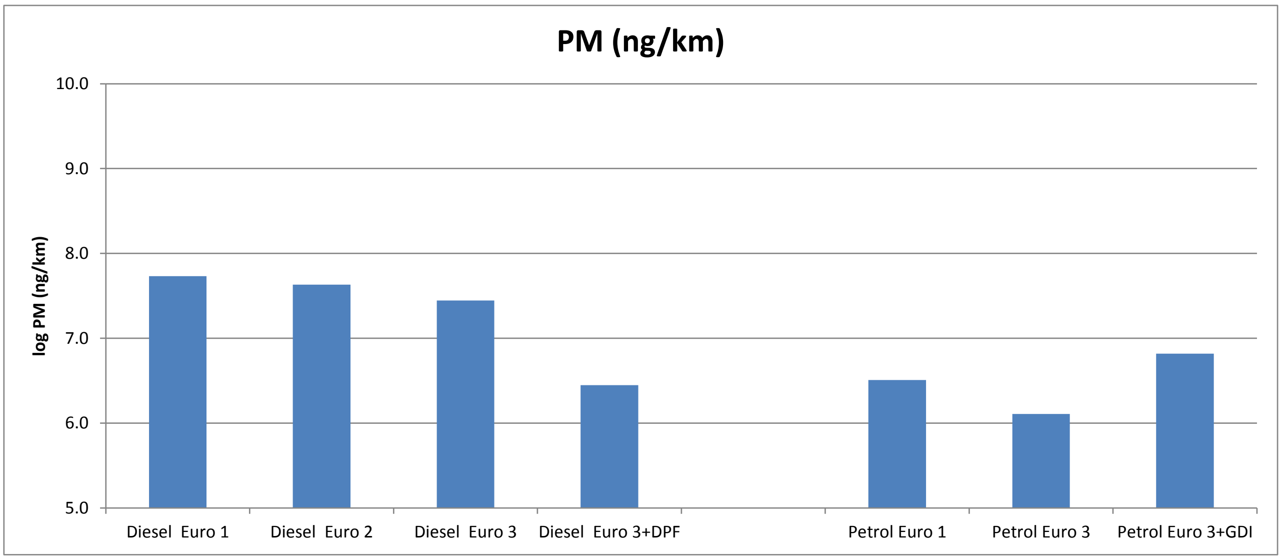

Figure 8. Particle mass urban emission factors for passenger cars. Source EMEP/EEA Emissions Inventory Guidebook (2013).

The main point to note from these plots is that the drop in particle number emissions for a diesel car with a DPF appears to be far greater than the drop in particle mass emissions. Although not complete, the factors in the Guidebook for heavy duty vehicles do show the same trend with much lower PN emissions (by several orders of magnitude) from early Euro standard vehicles fitted with a DPF compared with those of the same Euro class without a DPF. The PN factors shown here refer to “total particle number emitted from the vehicle”. Details of the PN measurements do not appear in the Guidebook, but it does make the comment that the factors were obtained in the laboratory under conditions which were expected to maximise the concentrations of volatile particles, hence they should be considered to represent a near-maximum emission rate.

The Guidebook also provides particle number factors for solid particles in three different size bands: <50nm, 50-100nm and 100-1000nm. These all show the same trend as total particle number.

Whilst diesel particulate filters (DPF) have been effective in reducing PM emissions from diesel vehicles, there is increased concern about emissions of PM from petrol cars with gasoline direct injection (GDI). Emission tests have shown that petrol cars with GDI can emit 5-40 times more particles (by mass) than a conventional port fuel-injected petrol engine, although still less than a diesel engine without a filter (SAE, 2014; ICCT, 2011; T&E, 2013; Karjalainen et al., 2014; Zhao et al., 1999; Maricq et al., 1999). In terms of particle number, PM emissions from a GDI engine can be several orders of magnitude higher than a conventional petrol engine (T&E, 2013). Injecting fuel directly into the hottest part of the engine cylinder enables better fuel efficiency and lower CO_2 emissions than a conventional petrol engine, but can produce higher PM emissions due to incomplete fuel volatilisation and partially fuel-rich zones in the combustion chamber and impingement of fuel on piston and cylinder surfaces (SAE, 2014). Most emissions typically occur during cold starts and high load transient cycles during warming.

The higher PM emissions from a GDI vehicle are reflected in the emission factor figures for PM mass and PN emissions given in the EMEP/EEA Emissions Inventory Guidebook for a Euro 3 petrol car with GDI, shown in Figures 7 and 8. However, this performance should not necessarily be indicative of the effect of GDI on a more modern Euro 6 car which has to meet strict limit value on PN emissions. This can be achieved by use of a Gasoline Particulate Filter (GPF), similar in principle to a DPF, which can reduce PN emissions from a GDI engine by 80-90% (SAE, 2014). Other engine management methods can reduce engine-out emissions through optimising combustion design and fuel injection timing, targeting and metering, although these are less effective in reducing overall PM emissions than exhaust after treatment using a GPF (see Chapter 6).

2.3.4 Emissions from aircraft engines

Direct measurements of aircraft engines have shown that the UFP produced are of two types; non-volatile black carbon (BC) and nucleated sulphurous particles (Petzold et al., 2011). The observations reported by Timko et al. (2010) noted that while the BC is found to be emitted directly by the engine, the sulphurous particles are formed immediately downwind as the plume cools and mixes with surrounding air. The biggest factor in the concentration of sulphurous particles is the sulphur content of the fuel. They also found that the highest mass concentrations of BC per unit fuel burned are emitted during higher engine powers such as during climbout and takeoff, although the behaviour of number concentrations versus power were less consistent across engine modes; as with all UFP, aircraft emissions are also subject to complex dynamical effects post-formation (Wong et al., 2008; Dakhel et al., 2007).

Greater detail on studies of emissions of particles form aircraft is given in Masiol and Harrison (2014).

2.3.5 Emissions inventories by particle number

TNO has developed an emission inventory for the UK by particle number. For each transport sector a bottom-up calculation is made, including gap-filling for unknown technologies or activities. To approximate the future year emissions for the non-transport sectors, scaling factors are used based on the IIASA Primes baseline scenario for $PM_{2.5}$ (http://gains.iiasa.ac.at/). Hence it is assumed that PN emissions for the non-transport sectors would follow the trend in $PM_{2.5}$ emissions. Total PN emissions for the UK are presented in Figure 9. Transport is by far the dominant sector. The transport emissions are further broken down in Figure 10. The emissions of land-based transport change significantly over time, especially road transport declines strongly (Figure 11).

The base year of the study was 2005, and the implementation of diesel particulate filters caused a steep reduction in PN emissions going from 2005 to 2020. In the inventory aviation is now recognized as a significant source of (semi-volatile) PN. PN emissions are projected to halve in the future. International shipping is a dominating source in 2005, but is expected to decline due to the introduction of low sulphur fuels. This is not prominent in Figure 9 and Figure 10 because these only include UK based sources. International shipping on the North Sea is not included here.

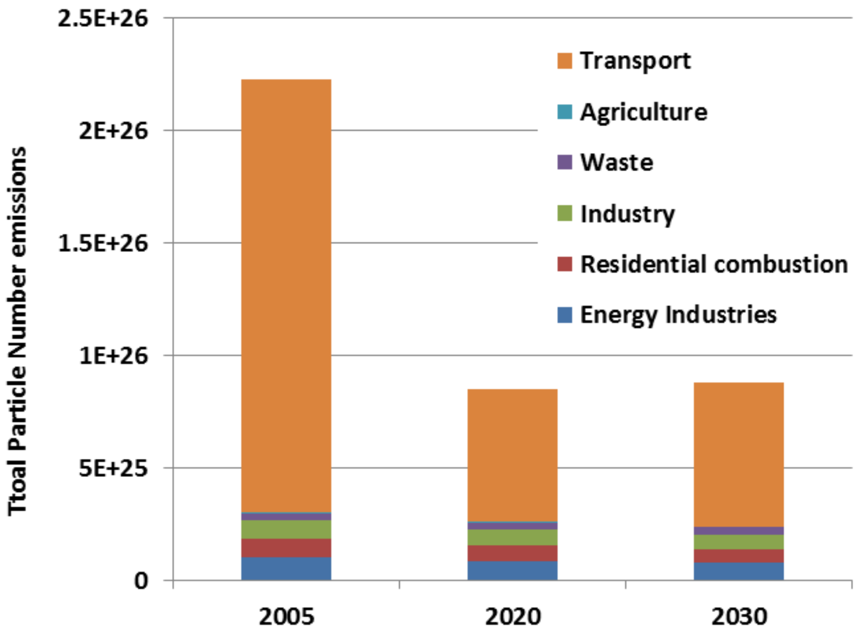

Figure 9. Total particle number emissions for 2005, 2020 and 2030 for the UK by source sector (data from TNO).

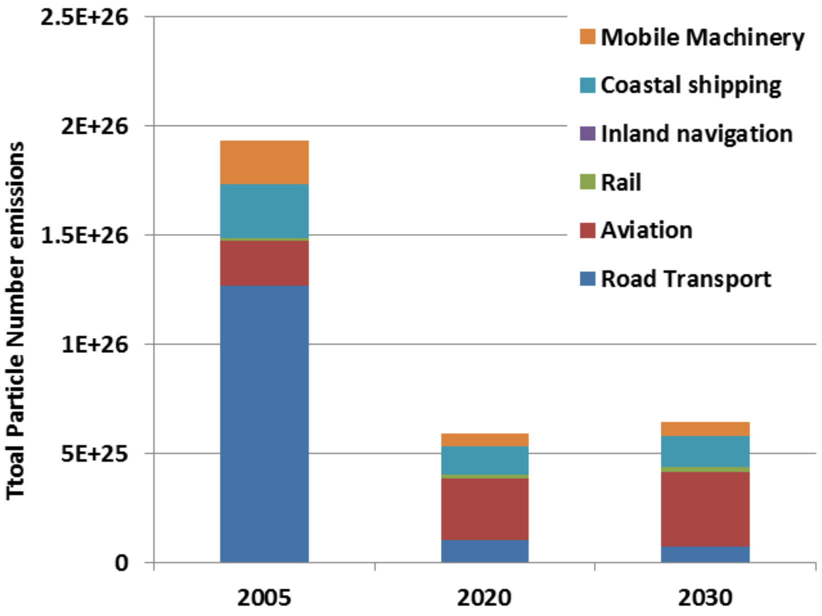

Figure 10. U.K. transport sector total particle number emissions in 2005, 2020 and 2030 excluding International shipping. (Aviation = airport LTO's up to 1000 m) (data from TNO).

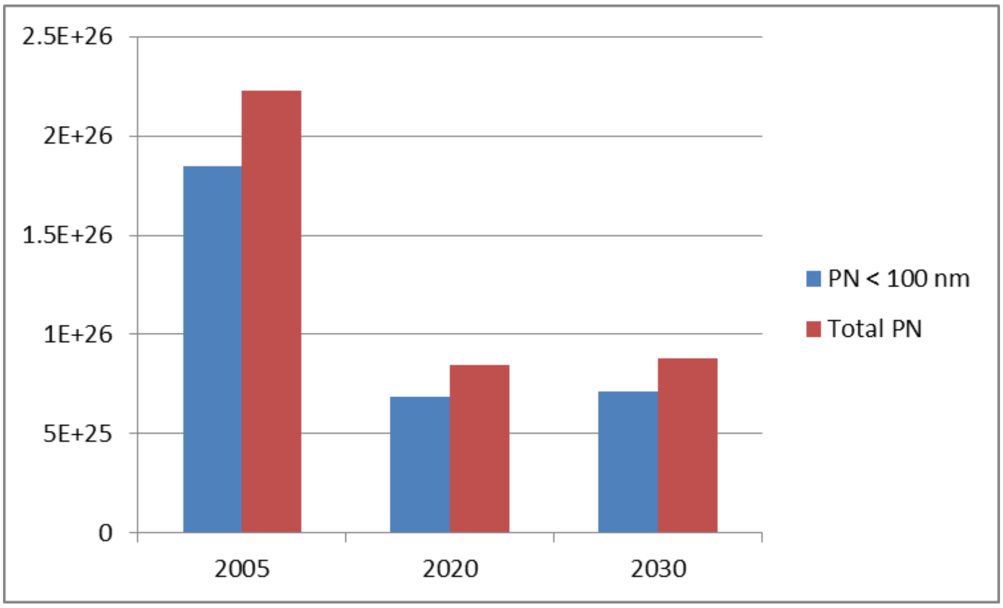

Figure 11. Total particle number emissions and particle number emissions < 100nm for the UK in 2005, 2020 and 2030.

Figure 11 shows the inventory totals for both UFP (<100 nm diameter) and total particle number. Clearly, the total number count is a good reflection of UFP abundance.

PN emissions due to fuel combustion in road transport and shipping, are expected to change significantly from 2005 as a consequence of motor and fuel modifications, such as low-sulphur fuels and particulate matter filters. This impact is reflected in the 2020 and 2030 projections. Another remarkable change compared to the previous inventory by Denier van der Gon et al. (2010) is that aviation is a stronger source of UFP than previously assumed; most of these are not solid PN and may have escaped attention in previous emission factor measurements. The UK emissions decline strongly in future years, due to implementation of emission standards in road transport and the phase-out of the older vehicles with less stringent emission limits. Both inland shipping and coastal shipping emissions are expected to decline, due to limits placed on the sulphur content of marine fuels.

The NAEI has not developed an emissions inventory for the UK by particle number as PN emissions are not required for reporting to CLRTAP. However, given that the vehicle activity data are available as used in generation of the PM_{10} and $PM_{2.5}$ inventories and particle number emission factors are available for road vehicles, it would be relatively straightforward to generate PN inventories for at least road transport sources in the UK.

2.3.6 Inventory uncertainties and gaps

The emission inventories for UFPs are subject to very high levels of uncertainty, but these cannot be quantified. As explained earlier, there are no requirements for reporting national inventories of UFP mass or particle number emissions, to any of the international bodies to which countries report emissions of other pollutants. Consequently, there are no (or very few) emission factors or methodologies for estimating UFP emissions provided in official inventory Guidebooks published by the EU and UNECE. The UK's inventory for $PM_{0.1}$ emissions is provided for information purposes on a voluntary basis, but no resources have been used to improve on the very simple method used to derive it, based on old sources of PM size fraction information applied to current PM_{10} inventories.

Uncertainties in emission inventories are generally high for PM_{10} and $PM_{2.5}$, particularly for non-combustion and diffuse fugitive sources, as documented in previous AQEG reports. In addition, since these reports, the important issue of the Guidebooks providing emission factors that are inconsistent regarding the inclusion of the condensable and semi-volatile component of PM has been identified. Any inventories for $PM_{0.1}$ based on applying PM size fractions to PM_{10} inventories, must have even higher levels of uncertainty because of the added uncertainties in the size fractions themselves. There are several factors that must significantly contribute to the uncertainties in the PM size fractions. One of these is the lack of measurements of UFP emissions for current fuels and technologies done on a consistent basis across the range of sources. The TNO and AP-42 sources of PM size fractions were published in the 1990s and so may not be appropriate for contemporary sources in the UK. Many of the factors would have been based on measurements made in the U.S.

On the face of it, a UFP mass inventory for vehicle exhaust emissions may be thought to be of relatively low uncertainty, at least compared with other sources, simply because much of the particle mass is emitted in the 100nm range, but there are still likely to be a number of contributory factors that cast considerable uncertainty in factors derived by TNO in the 1990s. One of these is the change in fuel composition, notably the significant reduction in sulphur content of road fuels from levels above 100ppm to <10ppm today. Another factor is the change in vehicle engine technology and exhaust aftertreatment systems, such as exhaust gas recirculation, diesel particulate filters, oxidation catalysts and other catalytic systems, as well as a variety of fuel injection systems, including gasoline direct injection. All of these may lead to different quantities of particles being emitted in the UFP range. Another area of uncertainty stems from the increased use of biofuels. These have significantly higher oxygen content than fossil fuels, as well as some other differences in fuel properties that can affect the formation of solid particles and the condensation of semi-volatile vapours. Changes in lubricant formulation may be another reason why UFP factors measured in the 1990s are not valid for current years.

PM size fractions used in inventories may also be affected by changes in properties of fuels used by other sources. For example, fuels used for shipping and other non-road mobile sources have seen significant reductions in sulphur content over the past decade. The AQEG report on biomass emphasised the importance of PM emissions from domestic wood burning sources which are being increasingly used in urban areas. Real-world emission factors of PM for different biomass fuels and combustion devices, have not been well-characterised and this would be even further the case for emissions of UFPs. A recent study suggests that residential wood burning following the Greek financial crisis is leading to elevated particle number concentrations in Thessaloniki during winter evenings (Vouitas et al., 2015).

As well as gaps in the knowledge of UFP emissions from known sources, there are further gaps for sources not currently covered in inventories at all for PM. These have been discussed in previous AQEG reports on PM, but include sources such as cooking and traffic-induced resuspension.

As with inventories for other pollutants, it is also the case for primary UFP emissions that the spatial representation of the emissions will be more uncertain than the national emission totals. This is because there are fairly good statistical data on source activities at national level, but far less information on emissions at specific locations and times, apart from major point sources such as power stations and refineries. For most pollutants, the relative change in emissions over a time-series may be known with greater certainty than at an absolute level, again because of fairly good and consistent trends in statistical data on activities. However, the time-series in the $PM_{0.1}$ inventory shown above, may not be so robust because of the greater uncertainty in the relevance of emission size fractions measured in the 1990s to current sources. The NAEI has not produced projections of future $PM_{0.1}$ emissions, but it further follows that these would also be of greater uncertainty.

Whilst further research on primary emissions of UFPs from all major sources would be welcomed as a means to reduce the uncertainties in inventories for UFPs, some progress may well be gained from a critical review of the scientific literature that currently exists. Without the impetus from national inventory reporting obligations, this has not been undertaken in a manner that provides a single compilation resource of emission factors suitable for estimating inventories for UFPs. Such a review would need to consider current and future sources, and aim to produce representative emission factors on a consistent basis, so that inventories developed from them can be understood and interpreted by the air quality research community, examining trends in concentrations of UFPs measured in ambient air. This would require a thorough understanding of the techniques used to measure UFP emissions from different sources so that the emissions can be compared on a consistent basis. An example would be the extent to which an emission factor for a given source includes semi-volatiles or not. This is not immediately clear from most current sources of factors such as those used for the $PM_{0.1}$ inventory developed by the NAEI.

2.4 Chapter summary

There are few direct measurements of UFP emission factors for sources done on a consistent basis.

Emission factors measured for different sources by different techniques, may not always be comparable with each other, particularly in regard to the extent that condensable and semi-volatile components are included in the PM mass emissions.

The fact that there is no requirement for reporting UFP emission inventories under international conventions such as the CLRTAP, has not provided the impetus for measuring UFP emission factors for inventory purposes

PM size fractions that are used to scale inventories for PM_{10} and $PM_{2.5}$ emissions to finer PM sizes are very old and may not be applicable to current fuels and technologies.

Changes in fuel sulphur content, increased use of biofuels, changes in engine design and fuel injection technologies, particulate traps and other exhaust aftertreatment systems may have led to significant changes in UFP emission factors for mobile sources since early measurements were made, and may show high degrees of variability according to precise design and operational details

Domestic wood combustion is making an increasing contribution to $PM_{2.5}$ emissions in the UK. There is a need for greater understanding and measurements of UFP emissions from the wide range of old and modern solid fuel burning stoves and appliances used in homes and commercial premises.

To fully understand the contribution of different sources to UFP emissions in the future, will require a continuous and consistent programme of measurements of UFP emission factors, for an increasingly diverse range of combustion technologies and fuels (including gaseous and biofuels) as they develop and are used on mobile and stationary sources.

2.4.1 Formation of Ultrafine Particles by Regional Nucleation Processes

It has long been known that high concentrations of very small ultrafine particles can arise spontaneously in the atmosphere from nucleation processes in which new particles are formed. Some of the earliest comprehensive observations were made in clean marine air in the coastal environment (Allen et al., 1999; O'Dowd et al., 2002). Subsequent observations have demonstrated nucleation in a wide range of generally less polluted environments and there has been intensive research on the mechanisms of new particle formation which goes well beyond the scope of this report.

Some of the earliest observations of new particle formation in the UK were made by Alam et al. (2003) in Birmingham. Alam et al. (2003) measured particles in the 3-7 nm diameter range which they interpreted as being newly formed. They were able to identify periods with huge and rapid increases in the number of particles in this size range, but a careful analysis of their dataset showed unequivocal evidence of nucleation on only eight out of 232 days, with a further four days possibly attributable, accounting for only 3-5% of all measurement days. Charron et al. (2007) examined factors influencing new particle formation at the Harwell site analysing a three year dataset from 1999-2001. Around 10% of hourly particle number size distributions showed a nucleation mode, but a close examination of the data showed only 26 daily episodes, representing 5.2% of observation days. All episodes apart from three occurred when clean cool arctic or polar maritime air masses were accompanied by high solar radiation and thin cloud cover. Nucleation tended to be associated with higher concentrations of sulphur dioxide and higher relative humidity, suggesting a role of sulphuric acid formation in the nucleation process (Charron et al., 2007).

Using a more recent dataset from 2011-2012, Beddows et al. (2015) applied the Positive Matrix Factorization receptor modelling algorithm (described in Section 5.7), to particle number size distribution data collected at the London, North Kensington site, and associated the particles between 16 and 604 nm diameter with four different predominant sources, which were secondary particles, the urban background, local traffic and regional nucleation. The factor associated with nucleation showed a mode in the size distribution at around 20 nm and peaked around 12 noon in association with peak solar intensities. It occurred more frequently in the summer months and accounted for 7.8% of the total particle count, which compared with 44.8% for traffic, 43.0% for the urban background, and 4.4% associated with secondary particles (Beddows et al., 2015). Figure 12 shows the number particle size distributions, their average diurnal cycles, and the explained variation of each particle size associated with this source category.

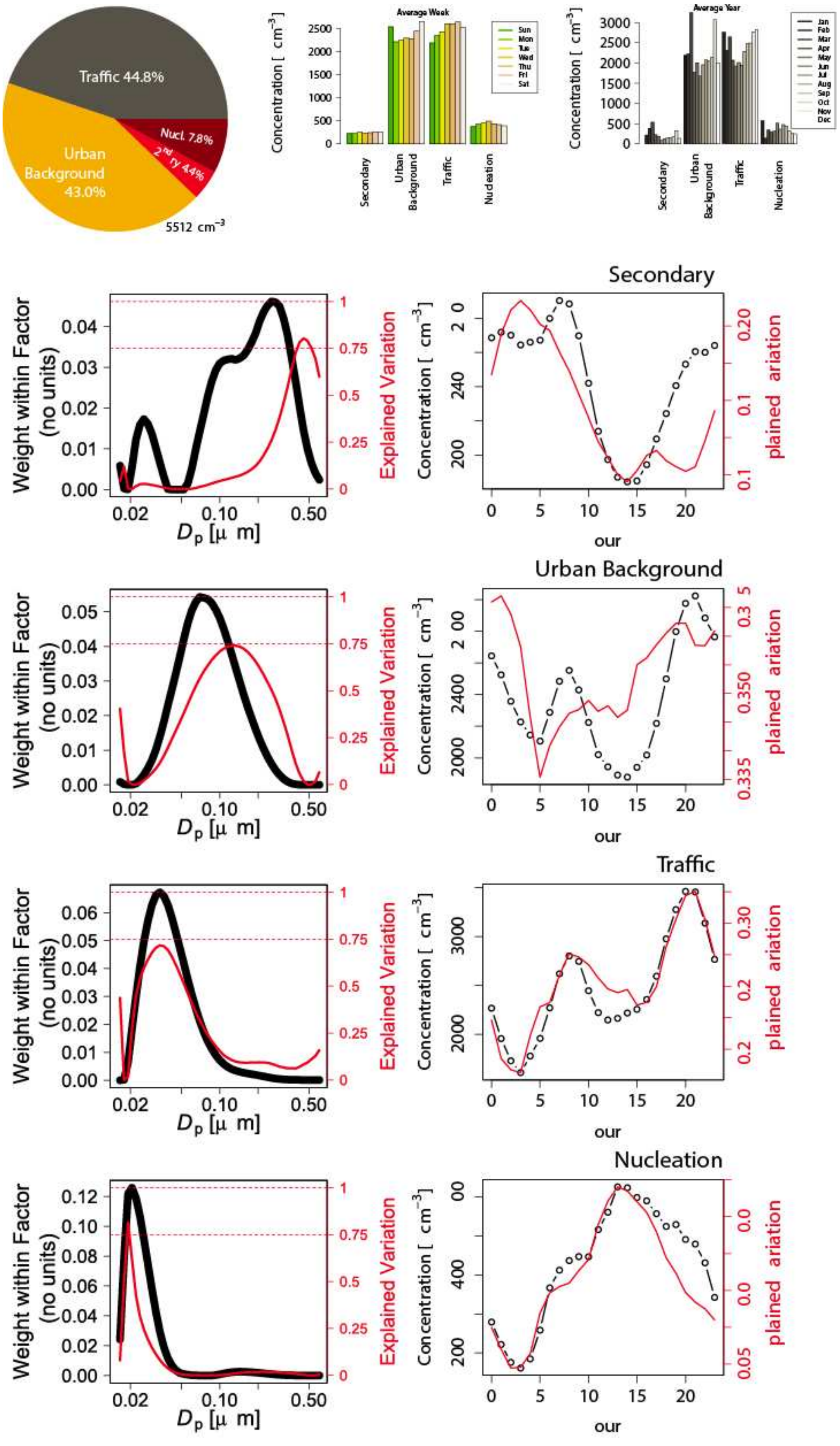

Figure 12. Factors outputted from PMF2 run on the Particle Number Size Distribution showing the size distribution from each source (black line in left hand panels) and Explained Variation (percentage of number count at each size) of each metric (red line). The right hand panels show the diurnal variation in each source factor and its percentage contribution at different particle sizes.

Reche et al. (2011) studied the diurnal variation in particle number count in a number of European cities. In most of the northern European cities including the North Kensington, London site, the diurnal variation of particle number count very closely paralleled that of black carbon, taken as a tracer of diesel road traffic emissions. In contrast, diurnal profiles from southern European cities typically showed morning and evening peaks in particle number count associated with road traffic, but also a large midday peak in particle number count which was not seen for black carbon. This was attributed to particle nucleation. Subsequent work in Barcelona (Dall'Osto et al., 2013) and more widely in high insolation-developed world cities (Brines et al., 2015) has shown road traffic and nucleation events to account for a large proportion of the ultrafine particle number count in the atmosphere. It is, however, clear that nucleation processes which are prevalent in high insolation environments are comparatively rare in the UK atmosphere, as a consequence of high pre-existing particle loadings (also seen in southern Europe) and much lower insolation than in southern Europe. However, a reduction in concentration of PM_{10} which acts as a sink for condensing vapours, would favour increased nucleation in the UK atmosphere.

2.5 Long-Range Transport of Ultrafine Particles

Beddows et al. (2014) examined particle size distributions measured at 24 sites across Europe. They were able to cluster the measured particle size distributions into nine separate clusters of which two appeared to be associated with nucleation processes and two other clusters represented either road traffic emissions or aged nucleated particles. When air masses were tracked across Europe, particles were seen to grow in size at a rate of around 0.6 to 0.9 nm h^{-1}. This appears to be the result of condensation of low volatility vapours onto particle surfaces. In the more aged air masses, a large proportion of particles had grown beyond the ultrafine size range.

Further evidence of particle aging is seen in data from the BT Tower measured as part of the REPARTEE campaigns (Harrison et al., 2012) and shown in Figure 13. Particle number size distributions were measured at a height of 160 metres on the BT Tower and are presented in Figure 13 as averages for different atmospheric mixing depths in three ranges: less than 105 metres, 105-250 metres and greater than 250 metres. In the latter case, the boundary layer is well mixed to above the height of the sampling point on the Tower and the size distribution clearly shows a substantial abundance of particles in the lower part of the size range. When the mixing depth falls below 105 metres, the sampling point on the Tower experiences long-range transported air which has been cut off from recent ground-level emissions. As such, the size distribution is shifted towards coarser sizes lacking the nucleation mode seen at around 20 nm in the well mixed (greater than 250 metre) case. This demonstrates that nucleation mode particles are present in the regionally transported air but at much reduced concentrations and coarser sizes than seen in air freshly polluted with ultrafine particles.

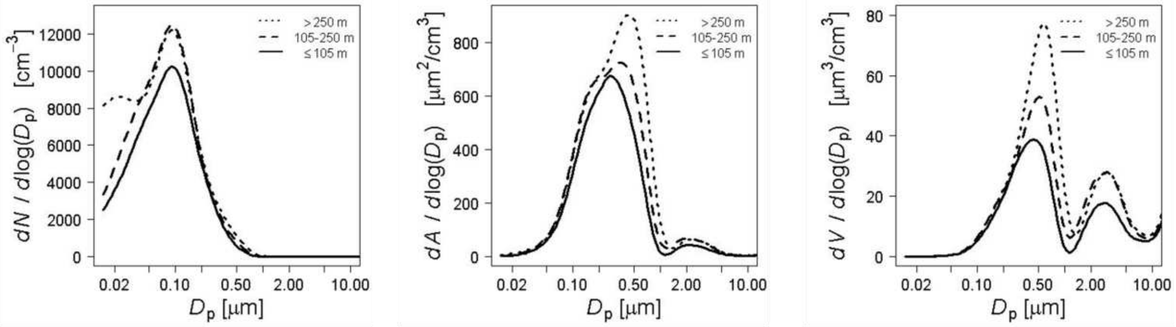

Figure 13. Particle count data measured at the BT Tower presented as number, surface area and volume and according to the boundary layer height.

2.6 Chapter 2 References

Alam, A., Shi, J. P., Harrison R. M. Observations of new particle formation in urban air. J. Geophys. Res., 108, 4093-4107, 2003. doi:10.1029/2001JD001417

Allen, A. G., Grenfell, J. L., Harrison, R. M., James, J., Evans, M. J. Nanoparticle formation in marine airmasses: Contrasting behaviour of the open ocean and coastal environments. Atmos. Res., 51, 1-14,1999.

Beddows, D. C. S., Dall'osto, M., Harrison, R. M., Kulmala, M., Asmi, A., Wiedensohler, A., Laj, P., Fjaeraa, A.M., Sellegri, K., Birmili, W., Bukowiecki, N., Weingartner, E., Baltensperger, U., Zdimal, V., Zikova, N., Putaud, J.-P., Marinoni, A., Tunved, P., Hansson, H.-C., Fiebig, M., Kivekäs, N., Swietlicki, E., Lihavainen, H., Asmi, E., Ulevicius, V., Aalto, P.P., Mihalopoulos, N., Kalivitis, N., Kalapov, I., Kiss, G., De Leeuw, G., Henzing, B., O'Dowd, C., Jennings, S.G., Flentje, H., Meinhardt, F., Ries, L., Denier Van Der Gon, H. A. C., Visschedijk, A. J. H. Variations in tropospheric submicron particle size distributions across the European continent 2008-2009. Atmos. Chem. Phys., 14, 4327-4348, 2014.

Beddows, D.C.S., Harrison, R.M., Green, D., Fuller, G. Receptor modelling of both particle composition and size distribution data from a background site in London UK, Atmos. Chem. Phys., 15, 10107-10125, 2015.

Brines, M., Dall'Osto, M., Beddows, D. C. S., Harrison, R. M., Gómez-Moreno, F., Núñez, L., Artíñano, B., Costabile, F., Gobbi, G.P., Salimi, F., Morawska, L., Sioutas, C., Querol X. Traffic and nucleation events as main sources of ultrafine particles in high insolation developed World cities. Atmos. Chem. Phys., 15, 5929-5945, 2015.

Charron, A., Birmili, W., Harrison, R. M. Factors influencing new particle formation at the rural site, Harwell, United Kingdom. J. Geophys. Res., 112, D14210. doi:10.1029/2007JD008425, 2007

Dakhel, P., Lukachko, S. P., Waitz, I. A., Miake-Lye, R.C., Brown, R. C. Postcombustion evolution of soot properties in an aircraft engine. J. Propul. Power, 23, 942-948. 10.2514/1.26738, 2007

Dall'Osto, M., Querol, X., Alastuey, A., O'Dowd, C., Harrison, R. M., Wenger, J., Gómez Moreno, F. J. On the spatial distribution and evolution of ultrafine particles in Barcelona. Atmos. Chem. Phys., 13, 741-759, 2013.

Denier van der Gon, H. A. C., Bergstrom, R., Fountoukis, C., Johansson, C., Pandis, S. N., Simpson, D., Visschedijk, A. J. H. Particulate emissions from residential wood combustion in Europe – revised estimates and an evaluation. Atmos. Chem. Phys., 15, 6503-6519, 2015.

Denier van der Gon, H. A. C., Visschedijk, A., Johansson, C., Ntziachristos, L., Harrison, R. M. Size-Resolved Pan-European Anthropogenic Particle Number Inventory. International Aerosol Conference, 29/8-3/9 2010, Helsinki, 2010.

EMEP/EEA. Air pollutant emission inventory guidebook – 2013 (updated July 2014). Part B. 1A Combustion. 1A3bi-ib Exhaust Emissions from Road Transport, 2014. Accessible at: http://www.eea.europa.eu/publications/emep-eea-guidebook-2013

EU PARTICULATES. Characterisation of Exhaust Particulate Emissions from Road Vehicles, 2005. Accessible at: http://lat.eng.auth.gr/particulates/

Harrison, R. M., Dall'Osto, M., Beddows, D. C. S., Thorpe, A. J., Bloss, W. J., Allan, J. D., Coe, H., Dorsey, J. R., Gallagher, M., Martin, C., Whitehead, J., Williams, P.I., Jones, R. L., Langridge, J.

M., Benton, A. K., Ball, S. M., Langford, B., Hewitt, C.N., Davison, B., Martin D., Petersson, K., Henshaw, S. J., White, I. R., Shallcross, D. E., Barlow, J. F., Dunbar, T., Davies, F., Nemitz, E., Phillips, G. J., Helfter, C., Di Marco, C.F., Smith, S. Atmospheric chemistry and physics in the atmosphere of a developed Megacity (London): An overview of the REPARTEE experiment and its conclusions. Atmos. Phys. Chem., 12, 3065-3114, 2012.

ICCT. Estimated Cost of Gasoline Particulate Filters, Working Paper 2011-8, Sept 2011. http://www.theicct.org/sites/default/files/publications/GFPworkingpaper2011.pdf

Johnson, K. C. Durbin, T. D., Jung H., Chaudhary, A., Cocker, D.R., Herner, J. D., Robertson, W. H., Huai, T., Ayala, A., Kittelson, D. Evaluation of the European PMP methodologies during on-road and chassis dynamometer testing for DPF equipped heavy duty vehicles. Aerosol Sci. Technol., 43, 962-969, 2009.

Karjalainen, P., Pirjola, L., Heikkila, J., Lahde, T., Tzamkiozis, T., Ntziachristos, L., Keskinen, J., Ronkko, T. Exhaust particles of modern gasoline vehicles: A laboratory and an onroad study. Atmos. Environ., 97, 262-270, 2014.

Maricq, M., Podsiadlik, D., Brehob, D., Haghgooie, M. Particulate Emissions from a Direct-injection Spark-Ignition (DISI) Engine, SAE Technical Paper 1999-01-1530,1999. doi:10.4271/1999-01-1530

Masiol, M., Harrison R. M. Aircraft engine exhaust emissions and other airport-related contributions to ambient air pollution: A review. Atmos. Environ., 95, 409-455, 2014.

O'Dowd, C. D., Jimenez, J. L., Bahreini, R., Flagan, R. C., Seinfeld, J. H., Hameri, K., Pirjola, L., Kulmala, M., Jennings, S. G., Hoffmann, T. Marine aerosol formation from biogenic iodine emissions. Nature, 417, 632-636, 2002.

Petzold, A., Marsh, R., Johnson, M., Miller, M., Sevcenco, Y., Delhaye, D., Ibrahim, A., Williams, P., Bauer, H., Crayford, A., Bachalo, W. D., Raper, D. Evaluation of methods for measuring particulate matter emissions from gas turbines. Environ. Sci. Technol., 45, 3562-3568, 2011.

Reche, C., Querol, X., Alastuey, A., Viana, M., Pey, J., Moreno, T., Rodriguez, S., Gonzalez, Y., Fernandez-Camacho, R., Sanchez de la Campa, A. M., de la Rosa, J., Dall'Osto, M., Prevot, A. S. H., Hueglin, C., Harrison, R. M., Quincey, P. New considerations for PM, black carbon and particle number concentration for air quality monitoring across different European cities. Atmos. Chem. Phys., 11, 6207-6227, 2011.

Riley, E. A., Gould, T., Hartin, K., Fruin, S.A., Simpson, C. D., Yost, M. G., Larson, T. Ultrafine particle size as a tracer for aircraft turbine emissions. Atmos. Environ., 139, 20-29, 2016.

SAE. Attacking GDI engine particulate emissions. SAE International, 2014. Accessible at: http://articles.sae.org/13624/

T&E. Particle emissions from petrol cars. Transport & Environment Briefing, 2013. Accessible at: http://www.transportenvironment.org/sites/te/files/publications/GDI%20Briefing_final_T&E.pdf

Timko, M. T., Onasch, T. B., Northway, M. J., Jayne, J. T., Canagaratna, M. R., Herndon, S. C., Wood, E. C., Miake-Lye, R. C., and Knighton, W. B. Gas Turbine Engine Emissions - Part II: Chemical properties of particulate matter. J. Eng. Gas Turb Power, 132, 061505-061505, 2010. 10.1115/1.4000132

TNO. Particulate matter emissions (PM_{10}, $PM_{2.5}$, $PM_{0.1}$) in Europe 1990-1993, Berdowski et al. TNO Institute of Environmental Sciences, Energy Research and Process Innovation, Report TNO-MEP-R96/472,1997.

USEPA. Compilation of Air Pollutant Emission Factors AP-42, Fifth Edition, 1995. United States Environmental Protection Agency, 1995. Emission factors currently accessible at: http://www3.epa.gov/ttn/chief/ap42/index.html

Vouitsis, I., Amanatidis, S., Ntziachristos, L., Kelessis, A., Petrakakis, M., Stamos, I., Mitsakis, E., Samaras, Z. Daily and seasonal variation of traffic related aerosol pollution in Thessaloniki, Greece, during the financial crisis. Atmos. Environ., 122, 577-587, 2015.

Wong, H.-W., Yelvington, P. E., Timko, M. T., Onasch, T. B., Miake-Lye, R. C., Zhang, J., Waitz, I. A. Microphysical modeling of ground-level aircraft-emitted aerosol formation: Roles of sulfur-containing species. J. Propul. Power, 24, 590-602, 2008.

Zhao, F., Laia, M.-C., Harrington, D. L. Automotive spark-ignited direct-injection gasoline engines. Prog. Energy Combust. Sci., 25, 437-562, 1999.

3 Measuring Ultrafine Particles

Key Points

- Ultrafine particles can be measured by mass or number, with number counts generally easier to implement.
- Particle number counts and size distributions are currently made continuously at three UK sites representative of roadside, urban background and rural atmospheres.
- Particle emissions from road vehicles are measured according to a special procedure (the PMP Protocol) to evaluate compliance with regulatory limits.

3.1 Introduction

Although they are typically defined as particles below 100 nm in diameter, measurements of ultrafine particles are in practice constrained by the techniques and instrumentation available, and the upper size limit is not usually a critical factor.

Unlike fine particles ($PM_{2.5}$, those less than 2.5 μm in diameter), or PM_{10} (less than 10 μm), which also include coarse particles, the mass of a sample of ultrafine particles would be too small to be measured accurately by normal PM methods. Ultrafine particles are therefore not generally measured as a mass concentration “$PM_{0.1}$”, in μg m^{-3}. Instead, the most common measurement is of particle number concentration. For historical reasons, this is given in units of particles per cubic centimetre (cm^{-3}).

Particle number concentration of ultrafine particles is measured with a Condensation Particle Counter (CPC), described in more detail below. Because the great majority of airborne particles are below 100 nm in size, there is no attempt to remove particles larger than 100 nm before the sample is measured.

The other common measurement instrument is the Mobility Particle Size Spectrometer (MPSS), often known as a Scanning Mobility Particle Sizer (SMPS). This will typically produce a size distribution (numbers of particles in each size fraction) in the range 15 nm to 800 nm. Because the results are presented as a continuous distribution, with the x-axis being logarithmic size (log D_p, where D_p is the particle diameter), the y-axis represents $dN/d(\log D_p)$, where N is the number concentration. Other instruments such as the Electrical Lower Pressure Impactor (ELPI), DMS and Fast Mobility Particle Sizer (FMPS) are used in engine test studies, but rarely in ambient air measurements.

Samples of ultrafine particles can be collected for chemical analysis using impaction, as described below.

3.1.1 Challenges of ultrafine particle measurement

Measurements of airborne particles are inherently more complex than of pollutant gases, because the metric needs supplementary parameters to be fully defined, and will therefore be instrument-dependent unless these parameters are agreed by convention. Consequently, particle diameters measured by an electrical mobility technique are not the same as those measured by an aerodynamic method, but may be converted if other particle properties are known.

In terms of particle number concentration in ambient air, the key additional parameters are:

Lower particle size cut-off, i.e. the smallest particle size that is to be included in the count;

Allowed hygroscopic growth (water absorption) within the sampling system. Although more important for the size distribution, if the humidity is not controlled, significant numbers of “below cut-off size” particles could grow large enough to be counted;

Allowed particle losses within the sampling system. Losses by impaction to the walls, which can be a problem for PM_{10}, will not be a problem for ultrafine particles. However, losses to the walls by diffusion can be very significant for particles below around 20 nm.

Retention or removal of semi-volatile particles. Some particles containing, for example, low-boiling point organic compounds or ammonium nitrate, can be volatilised within the sampling system. Where a representative measurement is required, this must be minimised. Alternatively, if semi-volatile particles form a high but unstable background concentration, as in vehicle emission measurements, they can be deliberately removed.

3.2 Standardisation of Ultrafine Sampling and Measurement In Ambient Air and Vehicle Emissions

3.2.1 Ambient air

As measurements of particle number concentration will vary depending on the conventions used, several groups have standardised all or part of the measurement process at a European level. Much initial work, especially on sampling, was carried out within the EUSAAR (European Supersites for Atmospheric Aerosol Research) project, which ran between 2006 and 2011 http://www.eusaar.net/. This work has continued within the ACTRIS (Aerosols, Clouds, and Trace gases Research Infra Structure) network http://www.actris.eu/. The World Meteorological Organisation - Global Atmospheric Watch (WMO-GAW) World Calibration Centre for Aerosol Physics, hosted by TROPOS in Leipzig, is a key partner in these activities. Their recommendations are included in Wiedensohler et al. (2012).

Standardisation of the measurement process for regulated air pollutants is carried out by CEN (the European Committee for Standardisation). This is taking place for ultrafine particles within CEN TC 264 WG 32, with direct input from ACTRIS partners. This group is close to publishing a Technical Specification (CEN TS 16976) for well-defined measurements of particle number concentration in ambient air, including humidity control during sampling, limits on diffusion losses, specified calibration methods, and a low-size cut-off of 7 nm.

It should be noted that the sampling requirements are different to those for PM_{10} and $PM_{2.5}$, which have no humidity control in the sampling line, so that the measured sample of particulate matter will not be exactly the same in the two cases. As there is no formal standardisation for these measurements in place as yet, the comparability of UK network data with those from other sources will be less good than for regulated air pollutants.

3.2.2 Vehicle emissions

Measurement methods for particle number concentrations in vehicle emissions were developed independently and in advance of the ambient methods. In part this was to encourage the early adoption of Diesel Particulate Filters (DPFs); by setting emissions limits in terms of number concentration rather than mass concentration, a lower limit, needing DPFs, could be set within legislation without running into the lower limit of detection of the mass concentration methods. This required a workable standard method for number concentration, and this was developed by the

Particle Measurement Programme, which was run by the United Nations Economic Commission for Europe.

This measurement protocol for particle number concentrations (Regulation No 83, 2012) is very different to that being put in place for ambient measurements. There is a heating and dilution stage in the sampling line to remove semi-volatile particles, and a low-size cut-off of 23 nm (see also Chapter 2). Both of these steps were designed to produce a more reproducible metric, as the large concentrations of small semi-volatile particles in vehicle exhausts close to the tailpipe are very sensitive to small changes in the sampling system. Comparisons between ambient concentrations and concentrations modelled from emissions must therefore be treated with care.

3.3 Methods used to produce the Ultrafine Particle Data in this Report

Most of the data used in the report were produced within the Defra-funded UK Particle Counting Network.

The Network was established in 1998 and was originally set up and operated on behalf of Defra by Stanger (now part of Bureau Veritas), with operation being transferred to NPL and King's College London (KCL) in 2005. Originally, the ultrafine part of the Network consisted of seven urban background sites monitoring number concentration, primarily for epidemiology, and three size distribution sites, providing urban roadside, urban background and rural measurements in and around London. The sites were rationalised in 2007 to the three London sites plus an urban background site in Birmingham.

The Network also carries out monitoring of other non-ultrafine particle metrics, specifically anions, cations, elemental carbon and organic carbon.

Data from the Network are available through http://uk-air.defra.gov.uk/data/particle-data and http://uk-air.defra.gov.uk/data/data_selector.

3.3.1 Current routine measurements of particle number count and particle size distribution in the UK particle counting network

Particle number count and particle size distribution measurements are currently made at three sites: London Marylebone Road, London North Kensington, and Chilbolton, a rural site in Hampshire that has recently taken on the rural measurements previously made at Harwell in Oxfordshire.

A fourth site, providing particle number concentrations at an urban background site in Birmingham, was operational over the period November 2004 to September 2013, when the instrument failed. Replacement of the instrument will take place when CPCs complying with the new requirements of CEN TS 16976 become available.

There are far fewer monitoring sites producing routine ultrafine particle data than there are for $PM_{2.5}$, for example, which number about 75 across the United Kingdom. This is because many $PM_{2.5}$ monitoring sites are required to meet EU Air Quality Legislation requirements, whereas ultrafine particle measurements are not mandatory. These sites therefore produce much less monitoring data with which to assess spatial variations, investigate sources and underpin models.

Further information about the current Network is given in the network Annual Reports, available through http://uk-air.defra.gov.uk/library/reports?section_id=5.

3.3.1.1 The sampling system

Ambient air is taken in to the monitoring cabin via a TSP head and a PM_1 cyclone. Within the cabin, the humidity of the sample air going to the instruments is controlled and monitored through Nafion drier units.

3.3.1.2 The condensation particle counter

Particle number concentrations are measured using a Condensation Particle Counter (CPC) TSI model 3022A. This works by passing the sample through a heated tube saturated with butanol and then cooling the airstream to set up supersaturated conditions. The butanol vapour then condenses on particles down to very small size, enabling them to be counted optically. CPCs are sensitive to particles from 7 nm up to several micrometres in size, and have a concentration range from zero to 10^7 cm^{-3}. At lower concentrations, each particle is individually counted, and at higher concentrations (from 10^4 cm^{-3}) an optical integrating mode is used.

3.3.1.3 The mobility particle size spectrometer

Particle size distributions are measured using an instrument known commercially as a Scanning Mobility Particle Sizer (SMPS). This consists of a CPC (TSI model 3775) combined with an electrostatic classifier (TSI model 3080). The electrostatic classifier consists of a charge neutraliser (incorporating a Kr-85 radioactive source) and a Differential Mobility Analyser (DMA – TSI model 3081). The former brings the particles in the sample to a known steady state charge distribution and the latter allows particles of a single electrical mobility (a quantity related to particle diameter) to pass to the CPC. By varying the operating voltage of the DMA, the size of particles sent to the CPC can be varied and a size distribution obtained.

3.3.1.4 Quality assurance/quality control procedures.

A summary of the principal quality assurance and quality control procedures used during the measurement and ratification process on the Network is given below:

- Regular communication with the Local Site Operators (LSOs).
- A Duty Officer at King's College, London is available to advise LSOs 365 days per year.
- Data collection is automated by the MONNET system at King's College, London, allowing daily automatic and manual data validation.
- Scheduled instrument services and calibrations (see below).
- An annual audit of all sites and instruments conducted by NPL.
- Final datasets are produced following rigorous ratification procedures using all available information.

Data quality circle meetings are held at least annually to review the data. This may lead to tracking back through the measurements and analytical procedures to confirm the validity of specific measurements. Other measurements made in this monitoring programme and in other Defra monitoring programmes are also used to check the validity of the measurements.

The 3022A and 3775 CPCs are serviced and calibrated at NPL, who received ISO 17025 accreditation for this calibration in 2008. The SMPS instruments are also serviced and calibrated at NPL.

3.3.2 Electrometer-based instruments

There have been a number of instruments come available that utilise electrical (rather than optical) detection of particles to measure UFP. Particles are subjected to an ionisation source (e.g. a corona discharge) and detected as pulses on an electrometer. By exploiting the size-dependent charging properties of particles, information concerning the size of the particles can also be derived, e.g. the particle surface area. These instruments have the advantage of not using working fluids (like the CPC) and can be very compact, meaning handheld versions of this technology (e.g. DiSCmini, NanoTracer, Partector) are popular within the exposure science community for personal exposure measurements and pollutant mapping. However, the exact technologies vary from manufacturer to manufacturer, with no central standard.

Furthermore, when compared with an SMPS and/or CPC as a reference, their accuracy has found to be limited (Todea et al., 2017), owing to the charging model needed, so they are not as well suited for atmospheric monitoring. While instruments marketed for monitoring using this general technology have recently come onto the market (e.g. the Pegasor Urban), they have yet to become validated by the general scientific community.

3.3.3 $PM_{0.1}$ measurement by impaction

PM_{10} and $PM_{2.5}$ are usually measured as the mass concentration of airborne particles (µg/m^3) after the removal of the particles larger than the desired cut-off size. This is done with a size-selective inlet, which removes the larger particles using a combination of inertia and drag, so that the lower size fraction can be collected on a filter, for example.

The same principle can be applied to ultrafine particles, with a size-selective inlet designed to remove particles above 100 nm in diameter, to give $PM_{0.1}$. However, the aerodynamic behaviour at these sizes is such that the cut-off size is much less well defined. Moreover, the mass of material collected by this method is very much less than for PM_{10} and $PM_{2.5}$, so that subsequent chemical analysis needs to be very sensitive and free from artefacts. Consequently, $PM_{0.1}$ measurements are not often made.

3.4 Methods Used to Produce Data for Other Metrics in this Report

3.4.1 Electron microscopy

Transmission electron microscopy is able to provide resolution to below 1 nm, and hence should be well suited to characterisation of ultrafine particles. There are, however, limitations which arise from the volatility of many particles in the high vacuum of the microscope, the difficulties of obtaining secondary X-ray emission spectra (EDAX) on the smallest particles, and the problems of characterising a sufficient number of particles to be statistically meaningful. Maynard (2000) gives an overview of the methods available, and their capabilities. He reports that high resolution transmission electron microscopy can provide structural information to <0.2 nm resolution and that electron energy loss spectroscopy (EELS) and X-ray emission allows characterisation at nanometre sizes. Smith et al. (2012) used transmission electron microscopy to characterise size-fractionated particles in the atmosphere of London finding only very refractory particle types, including carbonaceous diesel particles and various types of metallic particles. Particles containing iron and titanium were particularly prominent, although many were coarser than the ultrafine size range.

3.4.2 Characterisation of bulk samples of ultrafine particles

This is rarely carried out, but due to the small amounts of analyte present, Good Laboratory Practice involving very clean working is required. The analytical techniques are broadly comparable to those used in analysis of other size ranges such as $PM_{2.5}$ and PM_{10}, although enhanced sensitivity is beneficial provided the blanks are low or have minimal variation.

3.4.3 Individual particle studies

The ability of electron microscopy to characterise particles as small as a few nanometres has led to many studies of nanoparticle size, morphology and chemical composition. The method is not well suited to quantification of airborne concentrations and may also not be representative of the full diversity of atmospheric nanoparticles, as in general it is only possible to examine tens of particles, and the atmosphere typically contains tens of thousands per cubic centimetre of air.

Many studies (e.g. Shi et al., 2000; Murr and Bang, 2003) have characterised diesel exhaust particles in the engine laboratory or ambient air. Murr and Bang (2003) also studied the morphology and composition of both carbonaceous and non-carbonaceous particles from brake wear, including copper-rich particles, carbon nanotubes and fullerene-related nanocrystals, titania clusters and jet engine exhaust.

There have been a few studies conducted in the U.K. Gantt et al. (2015) studied particles emitted from an automotive diesel engine using fuel containing a nanoparticulate cerium oxide additive. Both individual ceria particles, and particles in which ceria was internally mixed with carbon were identified. Cerium-containing particles collected in the atmosphere were typically ~75 nm diameter and the fraction of CeO_2 associated with soot particles averaged around 40% (Gantt et al., 2015).

Sanderson et al. (2016) sampled airborne nanoparticles from the atmosphere using a nano-MOUDI instrument as sampler. They found an abundance of iron-containing particles, which could be classified as either within a Fe-rich type with ~90% iron in the presence of alloying elements, or a type with ~75% iron, typically, with a significant fraction of silicon and manganese. The former group were aggregates of primary spherules of median diameter ~27nm, and the latter were also aggregated with a primary sphere size of ~37 nm. They appear to originate from the wear of vehicle engines, and were shown to be in an iron oxide form.

3.5 Chapter 3 References

Gantt, B., Hoque, H., Fahey K. M., Willis, R. D., Delgado-Saborit, J. M., Harrison, R. M., Zhang, K. M., Jefferson, D. A., Kalberer, M., Bunker, K. L., Conny, J. M., Bhave, P. V., Weinstein, J. P., Pye, H. O. Factors affecting the ambient physiochemical properties of cerium-containing particles generated by nanoparticle diesel fuel additive use. Aerosol Sci. Technol., 49, 371-380, 2015.

Maynard, A. D. Overview of methods for analysing single ultrafine particles. Phil. Trans. R. Soc. Lond. A., 358, 2593-2610, 2000.

Murr, L. E., Bang, J. J.,. Electron microscope comparisons of fine and ultra-fine carbonaceous and non-carbonaceous, airborne particulates. Atmos. Environ., 37, 4795-4506, 2003.

Sanderson, P., Su, S. S., Chang, I. T. H., Delgado-Saborit, J. M., Kepaptsoglou, D. M., Weber, R. J. M., Harrison, R. M. Characterisation of iron-rich atmospheric submicrometre particles in the roadside environment. Atmos. Environ., 140, 167-175, 2016.

Shi, J. P., Mark, D., Harrison, R. M. Characterisation of particles from a current techology heavy-duty diesel engine. Environ. Sci. Technol., 34, 748-755, 2000.

Smith, S., Ward, M., Lin, R., Brydson, E., Dall'Osto, M., R. M. Harrison. Comparative study of single particle characterisation by transmission electron microscopy and time-of-flight aerosol mass spectrometry in the London atmosphere. Atmos. Environ., 62, 400-407, 2012.

Regulation No 83 of the Economic Commission for Europe of the United Nations (UN/ECE). Uniform provisions concerning the approval of vehicles with regard to the emission of pollutants according to engine fuel requirements, Official Journal of the European Union, 2012.

Todea, A. M., Beckmann, S., Kaminski, H., Bard, D., Bau, S., Clavaguera, S., Dahmann, D., Dozol, H., Dziurowitz, N., Elihn, K., Fierz, M., Lidén, G., Meyer-Plath, A., Monz, C., Neumann, V., Pelzer, J., Simonow, B. K., Thali, P., Tuinman, I., van der Vleuten, A., Vroomen, H., Asbach, C. Inter-comparison of personal monitors for nanoparticles exposure at workplaces and in the environment. Sci. Tot. Environ., 605-606, 929-945, 2017.

Wiedensohler, A., Birmili, W., Nowak, A., Sonntag, A., Weinhold, K., Merkel, M., Wehner, B., Tuch, T., Pfeifer, S., Fiebig, M., Fjäraa, A.M., Asmi, E., Sellegri, K., Depuy, R., Venzac, H., Villani, P., Laj, P., Aalto, P., Ogren, J.A., Swietlicki, E., Williams, P., Roldin, P., Quincey, P., Hüglin, C., Fierz-Schmidhauser, R., Gysel, M., Weingartner, E., Riccobono, F., Santos, S., Grüning, C., Faloon, K., Beddows, D., Harrison, R., Monahan, C., Jennings, S. G., O'Dowd, C. D., Marinoni, A., Horn, H.-G., Keck, L., Jiang, J., Scheckman, J., McMurry, P.H., Deng, Z., Zhao, C. S., Moerman, M., Henzing, B., de Leeuw, G., Löschau, G., Bastian, S. Mobility particle size spectrometers: harmonization of technical standards and data structure to facilitate high quality long-term observations of atmospheric particle number size distributions. Atmos. Meas. Tech., 5, 657-685, 2012.

4 Concentrations, Size Distribution and Composition of Ultrafine Particles.

Key points

- Overall, PNC concentrations have reduced considerably since 2006 and in particular at Marylebone Road in London. The main driver affecting the reduction in concentration is related to the introduction of sulphur-free road fuels in December 2007.
- There has been a further reduction in the concentration of PNC, black carbon, $PM_{2.5}$ and PM_{10} since about 2010. An important factor contributing to the decline in particle concentrations since that time is likely to be the increased penetration of diesel particulate filters in the vehicle fleet.
- PNC concentrations tend to be highly correlated with other common air pollutants (including black carbon, NO_x, PM_{10} and $PM_{2.5}$) at roadside locations, and vary with sampling location (e.g. distance from road).
- Similar to PNC, black carbon concentrations have also decreased considerably in recent years at Marylebone Road, reflecting the influence of diesel particulate filters.
- PNC tends to be better correlated with combustion gases and black carbon than PM_{10} or $PM_{2.5}$, which could have implications for health studies, where for example, the combustion gases may provide a better marker for PNC health effects than other measures of particulate matter such as PM_{10} or $PM_{2.5}$.
- The chemical composition of UFP is broadly similar to that of $PM_{2.5}$, with some studies showing enhanced concentrations of organic compounds and trace metals.
- Measurements of UFP close to airports suggest that aircraft are an important source of UFP that can result in elevated PN concentrations tens of km from airports. Mobile UFP measurements from non-UK locations also suggest that UFP concentrations can be elevated due to landing aircraft. More comprehensive measurements of UFP concentrations close to airports is required to better understand the distribution and magnitude of UFP concentrations in the vicinity of airports.

4.1 Particle Number Counts (PNC)

4.1.1 Trends in PNC

The trends in PNC are considered in detail for Marylebone Road in London from 2006 to 2015 (the most recent year data are available). Previous analysis of trends by Jones et al. (2012), showed there was a large reduction in PNC at Marylebone Road and Birmingham Tyburn around 2007 to 2008. During that period there were several factors that could potentially affect PNC concentrations close to roads in London, including the introduction of sulphur free fuel, the London Low Emission Zone (LEZ), other specific changes to the London bus and taxi fleet and ongoing changes to vehicle fleets in general due to fleet turnover. The LEZ was enforced for heavy goods vehicles (HGVs) greater than 12 tonnes from February 2008, and for other goods vehicles, buses and coaches greater than 3.5 tonnes from July 2008. Jones et al. (2012) reasoned that because reductions in PNC concentrations were also observed in Birmingham, it was likely that reductions in concentrations were dominated by fuel sulphur changes rather than the London LEZ.

In order to provide a clearer understanding of trends in PNC and the timing of important changes in concentration, the data from Marylebone Road have been analysed using a technique to 'remove' meteorological variation (Carslaw and Taylor, 2009). The analysis provides the expected trend for 'average' meteorology over the period 2006 to 2015. Hourly meteorological data were used from the London Heathrow site. Briefly, a statistical model was developed to explain PNC concentrations in terms of many meteorological and other variables and the resulting model run 100s of times based on randomly selecting meteorology from the 2006 to 2015 period. The simulations were then averaged to provide a single 'meteorologically averaged' time series. Figure 14 shows the trends in PNC with meteorological variation removed. It is clear that at Marylebone Road that PNC decreased sharply from about 90,000 cm^{-3} to about 30,000 cm^{-3} over a period from mid-2007 to early 2008. It is much less clear from the raw data when the changes in PNC occurred.

According to the UK Petroleum Industry Association, diesel and super unleaded petrol met the sulphur free (defined as < 10 ppm sulphur) limit by 4 December 2007 (UKPIA, 2016). The introduction of sulphur free fuels was well ahead of the deadline of January 2009, contained in the EU Directive. The pattern of change seen in Figure 14 is consistent with a move to sulphur-free fuel by December 2007 (98/69/EC and 98/70/EC) – see Section 2.1.4.

Also shown in Figure 14 is a consistent decrease in PNC from around the beginning of 2010, which coincides with the introduction of Euro 5 diesel cars fitted with diesel particulate filters, but could also be affected by other changes to the vehicle fleet. Unlike the decrease in PNC coinciding with the introduction of sulphur free fuels, the decrease in since 2010 is much less abrupt and corresponds to less of an absolute change in PNC concentration. A less steep decrease would be expected in PNC due to the introduction of particle filters because these vehicles take time to penetrate vehicle fleets. Overall, it seems that the introduction of sulphur-free fuel has had the greatest impact in reducing PNC concentrations over the past decade. Sulphur free fuel is an 'enabling technology', which makes it possible for DPF to operate efficiently and avoid catalyst poisoning by sulphur.

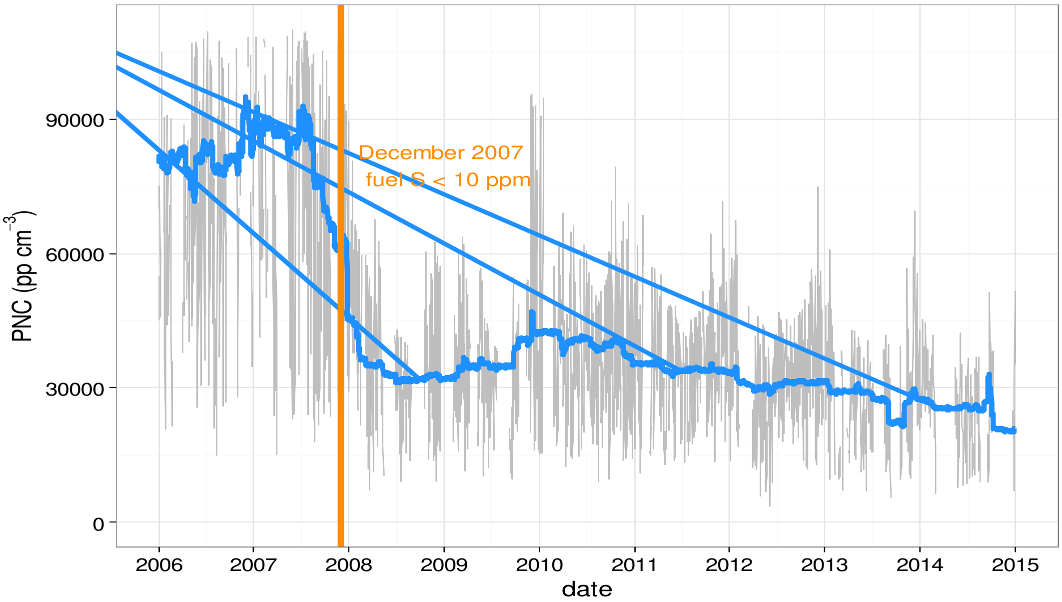

Figure 14. Trend in PNC at Marylebone Road. The grey line shows the raw daily mean data and the blue line the trend with the meteorology removed. The vertical orange line shows the date when sulphur-free diesel and petrol were introduced.

4.1.2 Relationship of PNC with other pollutants

PNC data from four AURN sites (Marylebone Road roadside, North Kensington urban background, Birmingham Tyburn urban background and Harwell rural), have been compared with other common pollutants including NO_x, CO, PM_{10}, $PM_{2.5}$ and black carbon (BC). The annual mean trends have been calculated from 2009 to 2015. The results shown in Figure 15 reveal some interesting characteristics of PNC compared with the other species. For all pollutants Marylebone Road has the highest concentrations, showing that road vehicle emissions of all these pollutants are important.

The relative importance of vehicle sources varies across the different pollutants. NO_x for example is considerably higher at Marylebone Road than at the other sites, illustrating the dominant effect of vehicle emissions from the road itself. The situation for PNC and BC are similar to NO_x in that the roadside site has considerably higher concentrations. For PM_{10} and $PM_{2.5}$ there is less difference between the sites, which reflects the importance of urban and regional background concentrations for those pollutants. A shorter time series of PNC at Blackwall Tunnel (from about 2012 to 2014) shows similar concentrations to Marylebone Road.

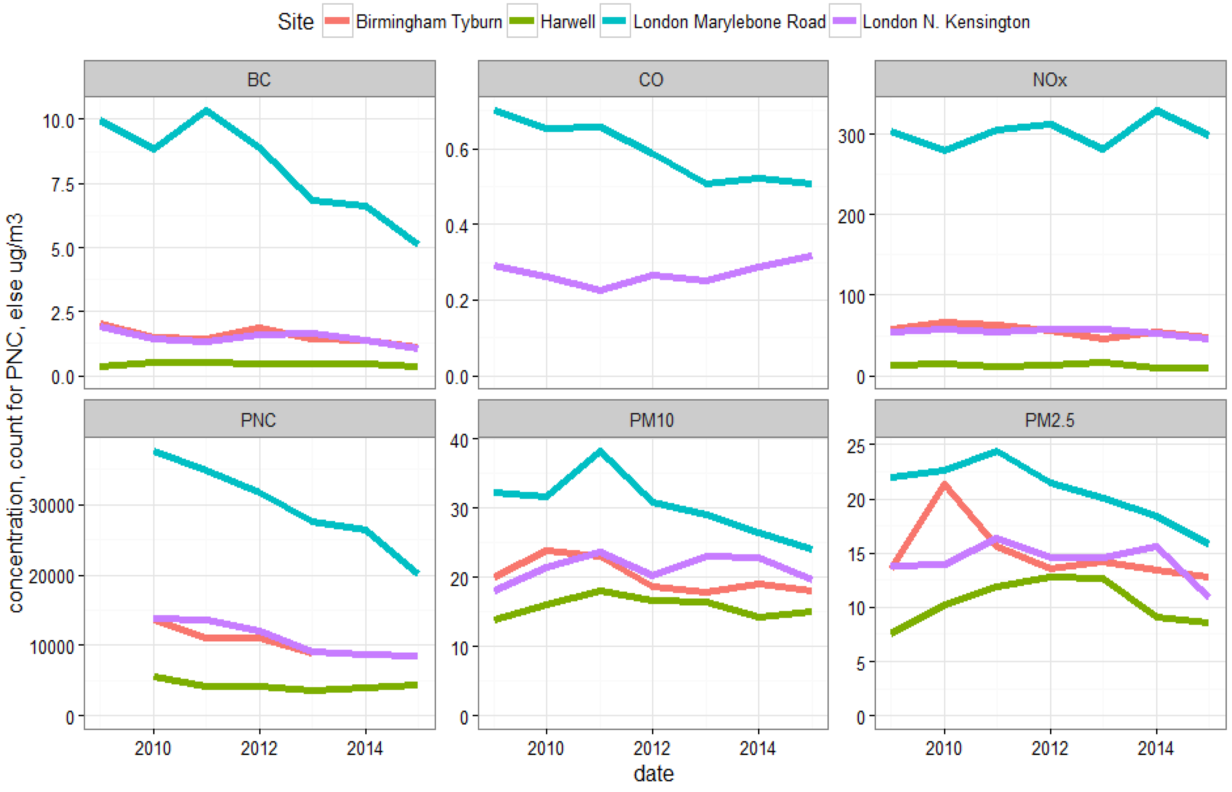

Figure 15. Trends in PNC and other common pollutants at four sites across the UK.

In terms of the trends for the different pollutants, the following can be seen from Figure 15. Concentrations of NO_x have changed little over the past seven years at most sites. For Marylebone Road, all particle measurements (PNC, BC, PM_{10} and $PM_{2.5}$) have shown decreases in recent years – and in particular from 2012. For some species these decreases have been substantial e.g. for BC where there has been a 50% reduction from 2011 to 2015.

While the data capture for PNC is not as high as the other pollutants it is also clear that roadside PNC concentrations have also decreased considerably since 2010. The reduction in roadside concentrations of all PM species reflects will reflect a reduction in diesel vehicle emissions. Over the period of 2010 to 2015 an increased proportion of diesel vehicle in the fleet (light and heavy) would have been fitted with particulate filters. These filters are known to be highly efficient at removing particle mass and reducing particle number concentrations. The evidence from the limited number of sites considered in Figure 15 is consistent with the effective control of vehicular particle emissions.

4.1.3 Temporal variations and episodes

Figure 16 shows the temporal variations of PNC and other common pollutants at the Marylebone Road site. The concentrations have been normalised by dividing by their mean values to highlight the pattern of variation. In general, the species behave in a similar way to one another, reflecting the strong road vehicle source of many of these components. The PM_{10} and $PM_{2.5}$ monthly variation highlights springtime peaks from regional episodes not seen for the other pollutants.

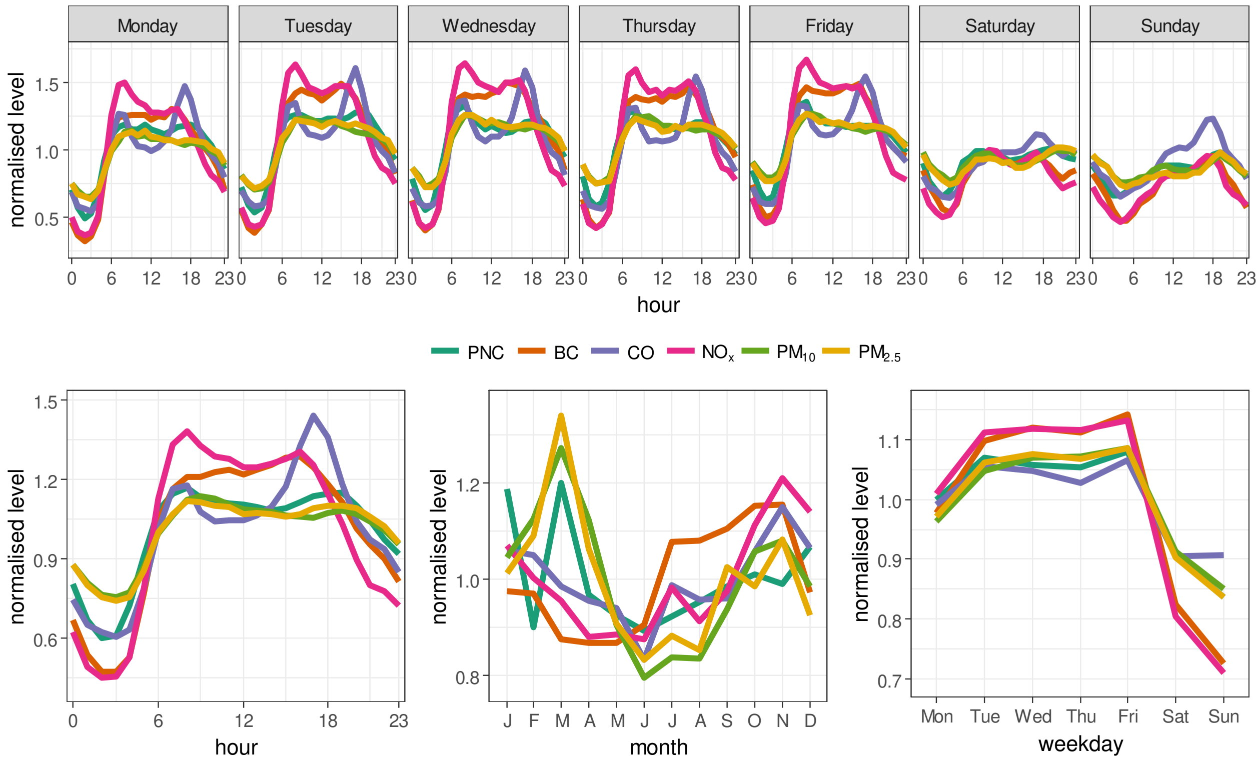

Figure 16. Temporal variations in PNC and other pollutant concentrations at Marylebone Road based on data from 2009 to 2015.

The temporal variations at North Kensington (Figure 17) share some of the similarities with Marylebone Road, but also show a stronger influence of meteorology. For example, the diurnal variations show relatively higher concentrations of most species around 6 am when both the source strength is high and the atmosphere is more stable – with a similar pattern later on in the day around 6 pm. Similarly, the seasonal variation shows a characteristic dip during the summer months and peak during the winter months; again reflecting more stable atmospheric conditions. There is a much stronger day of the week variation for NO$_x$ and BC, which are relatively much lower than the other species during weekends.

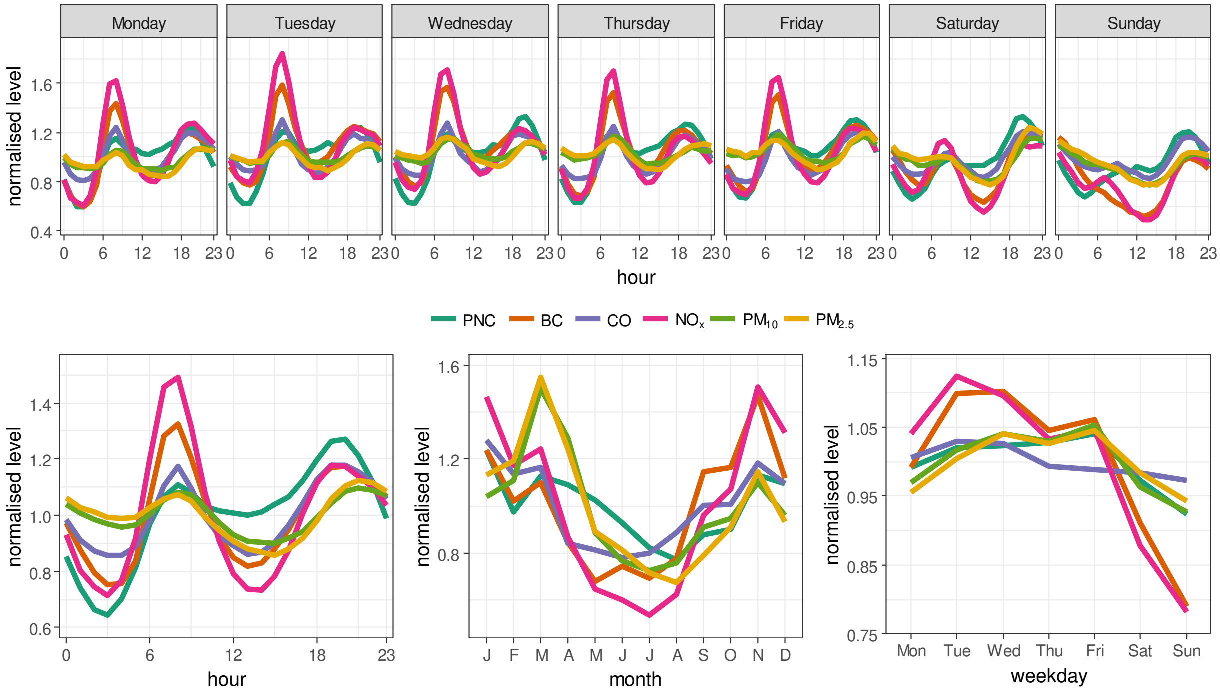

Figure 17. Temporal variations in PNC and other pollutant concentrations at North Kensington based on data from 2009 to 2015.

Harwell (Figure 18) shares many similarities with North Kensington. The most significant difference between Harwell and the other sites (and other species at Harwell) is the variation of PNC diurnally and seasonally.

Concentrations tend to increase throughout the day at a time when most other species decrease in concentration. This variation is characteristic of nucleation as a source of new particles. It is also evident that PNC shows no day of the week variation, suggesting that local sources of PNC are unimportant compared with other species.

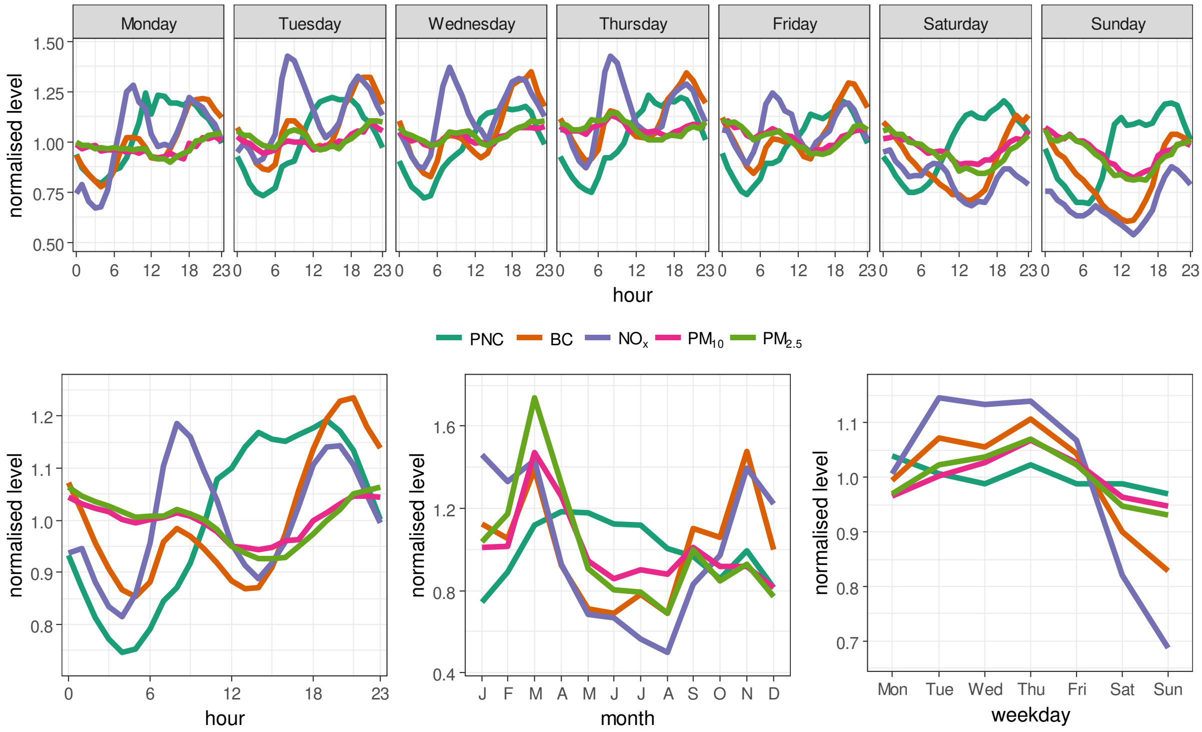

Figure 18. Temporal variations in PNC and other pollutant concentrations at Harwell based on data from 2009 to 2015.

The nature of pollution episodes of PNC differs between the site types. Overall, periods of elevated concentration of PNC are most prevalent at Marylebone Road, where concentrations are highest and least prevalent at Harwell, where concentrations are lowest. This behaviour broadly reflects the importance of local vehicle sources in controlling the periods of highest PNC concentrations. At Marylebone Road the periods of highest concentration are coincident with periods when other road source emissions are also high and which are also influenced by the street canyon nature of the site. Typically, these periods are during wintertime.

Similar to Marylebone Road, North Kensington tends to have periods of high PNC concentration during wintertime – but there are also frequent periods of elevated concentrations during springtime. Finally, at the rural Harwell site the highest concentration period of PNC tends to occur in spring and summer, where nucleation processes will be more important.

An indication of the periods when PNC are high is shown in Figure 19 where 3-day rolling mean concentrations are shown for 2011 (when data capture across all three sites was highest).

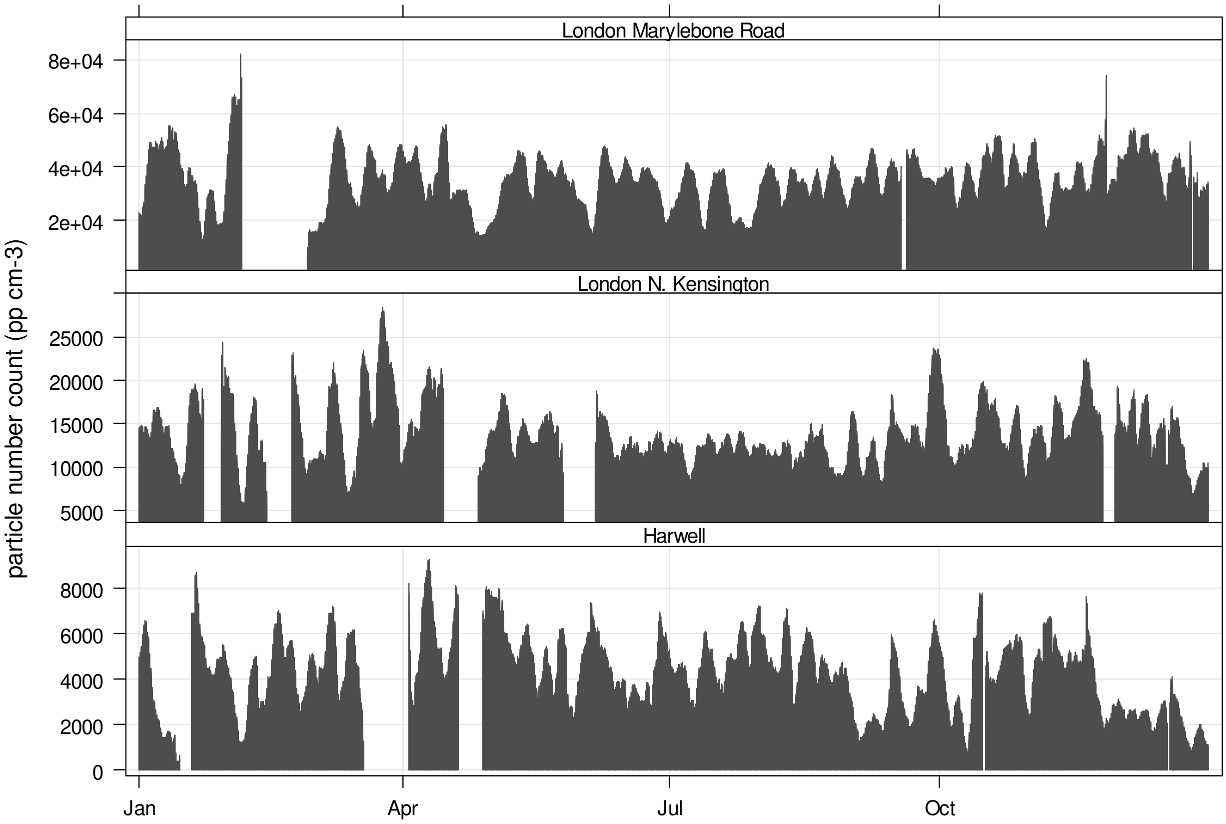

Figure 19. Rolling 3-day mean concentrations of PN at Marylebone Road, North Kensington and Harwell for 2011.

4.1.4 Correlation between species

Figures 20, 21 and 22 show respectively the correlations between pollutants at the national network sites, Marylebone Road (roadside), North Kensington (urban background) and Harwell (rural) for the period 2009-2015.

At the Marylebone Road site (Figure 20) all the species considered in the analysis tend to be highly correlated with one another in both winter and summer. PNC tend to be most closely related to NO_x and BC, reflecting the strong influence of nearby vehicle emissions rather than other particle measurements (PM_{10} and $PM_{2.5}$).

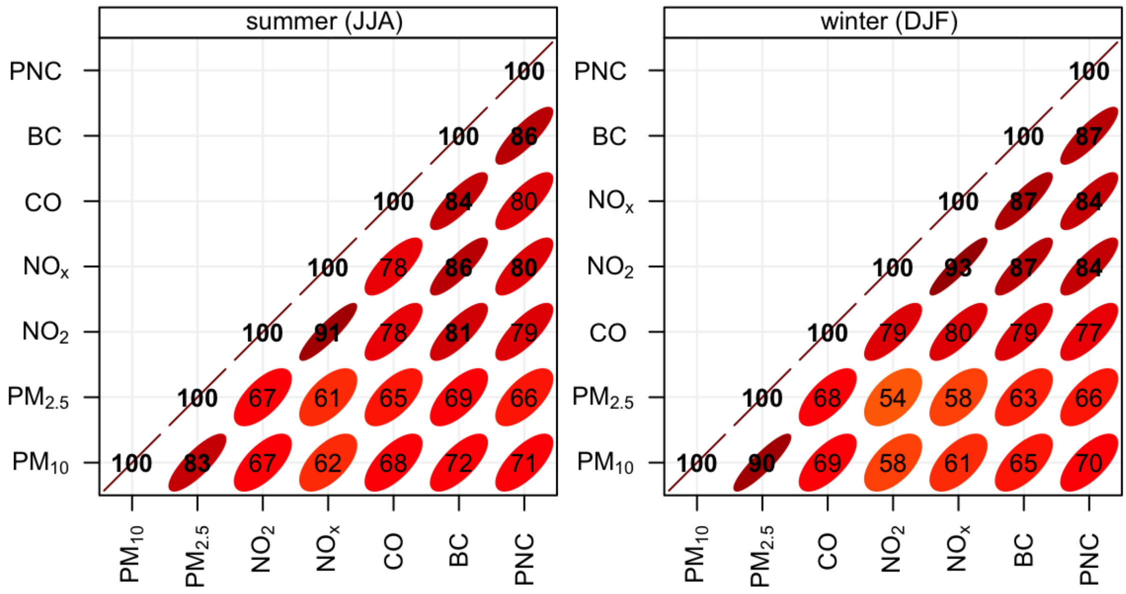

Figure 20. Correlation between different pollutants at Marylebone Road split by winter and summer months for data from 2009 to 2015. The plot shows the Pearson correlation coefficients expressed as 0 to 100 (no correlation to perfect correlation). Hierarchical cluster analysis has also been applied to the correlation coefficients such that pollutants that are next to each other behave most similarly e.g. PM_{10} *and* $PM_{2.5}$*.*

At North Kensington (Figure 21), PNC tends to be strongly correlated with BC, CO and NO_x in winter and less well correlated with any other species during summertime.

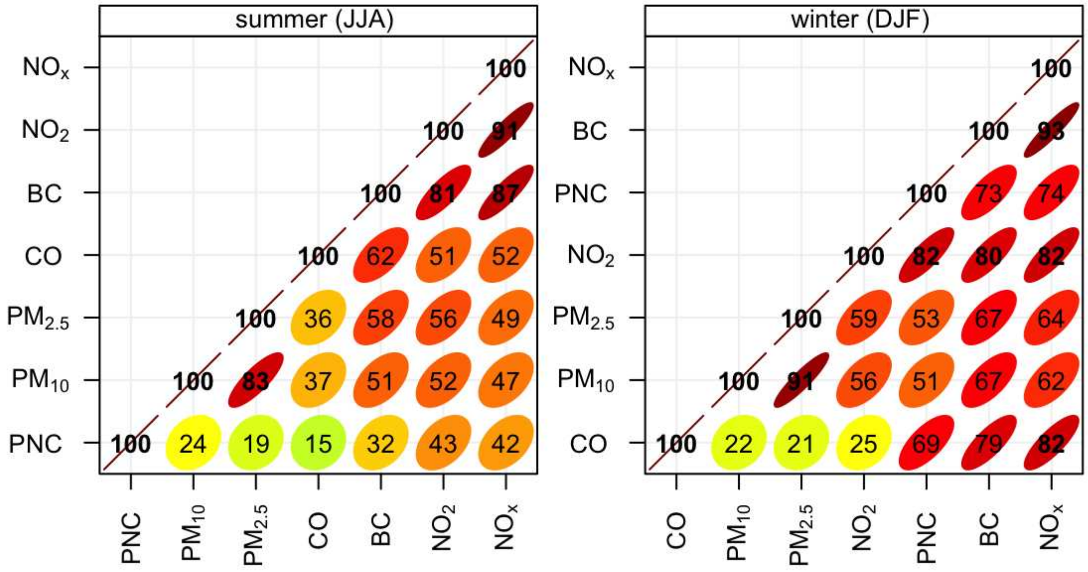

Figure 21. Hourly correlation between different pollutants at London North Kensington split by winter and summer months for data from 2009 to 2015. The plot shows the Pearson correlation coefficients expressed as 0 to 100 (no correlation to perfect correlation). Hierarchical cluster analysis has also been applied to the correlation coefficients such that pollutants that are next to each other behave most similarly e.g. PM_{10} and $PM_{2.5}$.

The correlations at the rural Harwell site show a different behaviour compared with Marylebone Road and North Kensington. In the winter months PNC tends to be most strongly correlated with BC and NO_x (similar to Marylebone Road and North Kensington). However, during the summer months PNC has very little correlation with any other species reflecting processes such as nucleation.

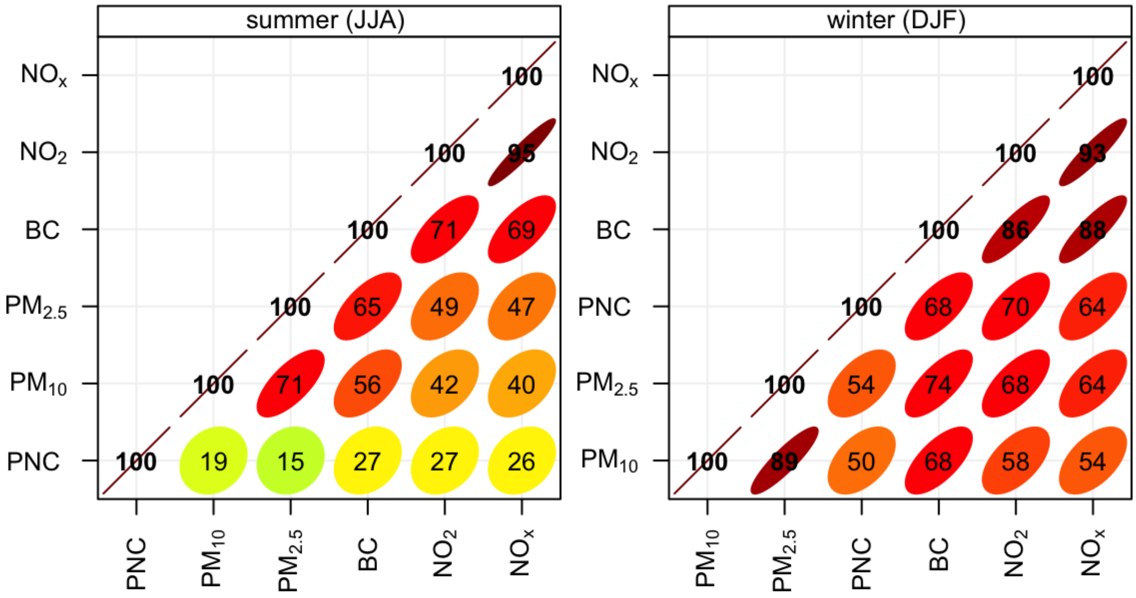

Figure 22. Correlation between different pollutants at Harwell split by winter and summer months for data from 2009 to 2015. The plot shows the Pearson correlation coefficients expressed as 0 to 100 (no correlation to perfect correlation). Hierarchical cluster analysis has also been applied to the correlation coefficients such that pollutants that are next to each other behave most similarly e.g. PM_{10} *and* $PM_{2.5}$.

Figure 23 shows the results of correlations for air sampled in Leicester in 2014 and 2015. Correlations tend to be strongest in winter when the atmosphere is generally more stable leading to less mixing of traffic-generated pollutants.

Although it is evident from Figures 20 to 23 that the ultrafine particle number count (PNC) can be highly correlated with other pollutants, the gradient of such correlations is both site- and season-dependent, and liable to change with time as pollutant sources change. As a consequence, it is important to measure concentrations of UFP directly, rather than attempting to infer their concentrations from measurements of other pollutants.

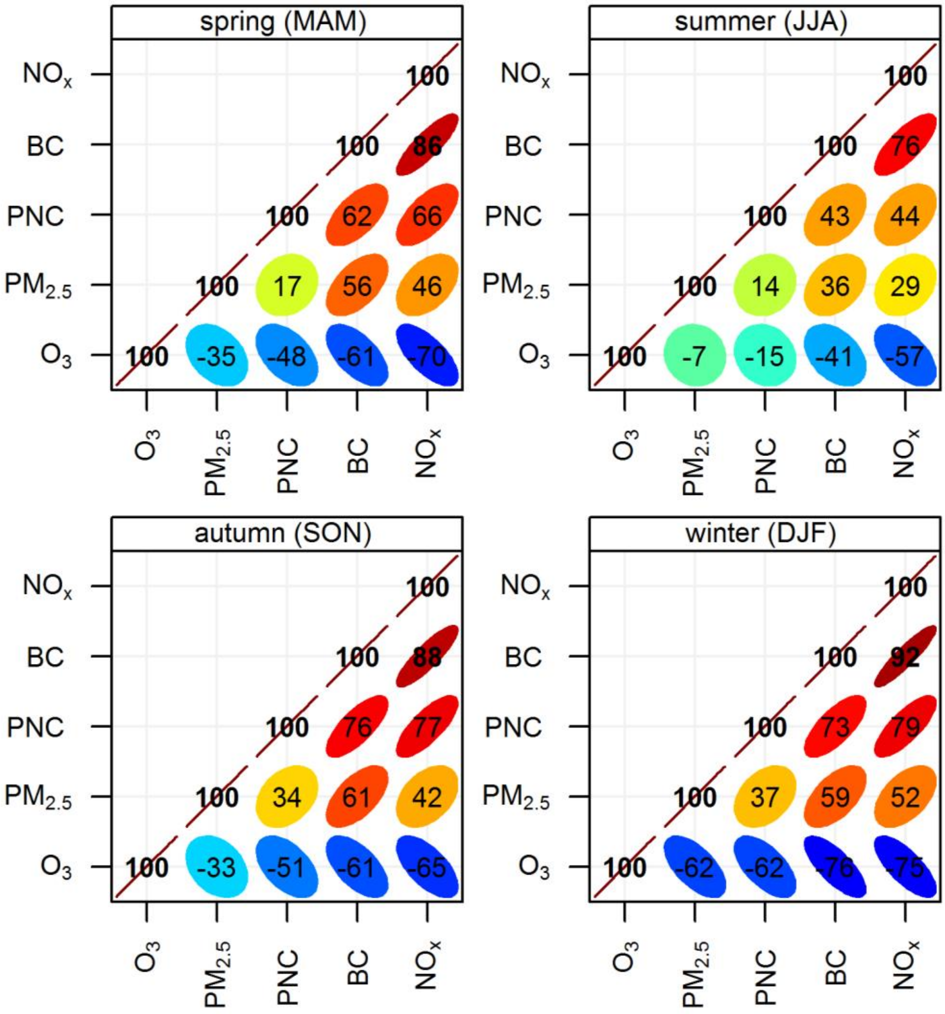

Figure 23. Correlations between pollutants sampled in Leicester in 2014/15 according to season, displayed as in Figures 20-22.

4.2 The German Ultrafine Aerosol Network

The most substantial national network for measurement is in Germany. It is referred to as the German Ultrafine Aerosol Network (GUAN) and comprises 17 sites (Birmili et al., 2015). The site types are classified as roadside (3), urban background (7), rural (4) and mountain (3).

Annual mean concentrations for 20-800 nm particles range from 860 cm^{-3} at an alpine site (2670 metres) to 10,500 cm^{-3} at a roadside site in Leipzig. The lower reporting cut-point of 20 nm is larger than for the UK sites which implies a smaller count due to a more restricted range of sizes included. The particle number count (both 20-800 nm and 20-100 nm) shows a downward trend at all sites with the PNC (20-800 nm) declining at between -8.2% to -0.7% per year with a median of -3.8% between 2009 and 2014.

4.3 Particle Number Size Distributions

The measurement of particle size distributions, and the relationships between distributions expressed in terms of number, surface area, volume and mass are described by Harrison et al.

(2000). Size distributions contain valuable information on the mode of formation and/or the history of the particles, although this can be difficult to extract as size distributions evolve continuously as particles coagulate, deposit, evaporate or grow by condensation. Number size distributions are typically described in terms of four size ranges, the boundaries of which relate to the particle origins and history, and hence may vary between one study and another.

Nucleation range or mode. These are typically <30 nm diameter and arise from new particle formation in the atmosphere, or in high temperature processes in a vehicle engine, industrial or combustion process.

Aitken range or mode. Particles are typically 30-100 nm diameter and mostly arise from growth of nucleation mode particles due to condensation of vapours.

Accumulation range or mode. This is normally assumed to extend over the range 100-1000 nm. Particles enter it through condensational growth or coagulation, or direct emission from an automotive or industrial source. Particles in this size range have a very long atmospheric lifetime as they grow only slowly and are not effectively removed by wet and dry deposition processes. Long-range transported particles are typically found predominantly in the accumulation mode.

Coarse particle range or mode**.** This term describes particles of >1 µm diameter, which typically arise from break-up of bulk materials including wind-blown soil, sea spray and vehicle wear particles.

It is the nucleation and Aitken modes which fall within the ultrafine particle size range. Vu et al. (2015) have reviewed information on the characteristic particle size distributions arising from seven common sources.

4.3.1 Semi-volatility of traffic-generated nanoparticles

Early laboratory research on the number count of particles from diesel engines used very low dilution ratios with clean air, which was unrepresentative of the very high dilutions which occur as exhaust gases enter the atmosphere. When Shi and Harrison (1999) carried out measurements at higher dilution ratios, they found that the number of particles increased substantially as the dilution ratio became greater, with a movement in the particle size distribution towards smaller particles. These processes are now much better understood and arise from the condensation of semi-volatile organic vapours on tiny nuclei of sulphate or trace metals derived from combustion of the fuel or lubricating oil.

These smaller, nucleation mode particles do not form at low dilution ratios as the semi-volatile vapours condense on the high surface area of the larger graphite-based particles, which comprise most of the particle mass and surface area of the emissions. Subsequently, in an analysis of roadside measurements collected at Marylebone Road, London, Charron and Harrison (2003) showed that processes observed with test engines in the laboratory, were also occurring in the atmosphere, with a large number of particles newly formed within the cooling exhaust gases. This process arises because the hot exhaust gases contain organic vapours derived from the fuel and lubricating oil, which become supersaturated when the exhaust gases cool on mixing with ambient air. This, however, has the implication that further dilution of the traffic exhaust, can lead to a situation in which the ambient vapour pressure of the organic compounds, falls below the pressure of vapour in equilibrium with the particle surface, leading to evaporation of the particles. Although the theoretical possibility of this process was realised, it was first seen clearly in ambient air in London by Dall'Osto et al. (2011) who observed that particles emitted on Marylebone Road and subsequently advected into the cleaner air of Regent's Park shrank substantially in size from a modal diameter of around 22 nm to a modal diameter measured in the Park of typically less than 10 nm. This process was analysed subsequently in greater detail by Harrison et al. (2016) who looked carefully at the association with wind direction and the relationship to travel time, clearly again observing the size reduction of particles as they advect into the Park.

This is seen in the average spectra which appear in Figure 24. The highest concentrations at Marylebone Road are associated with southerly winds (135º-270º) when the vortex circulation in the street canyon carries the traffic emissions to the sampler on the south side of the canyon. Southerly wind directions also carry pollutants from the canyon into Regents Park.

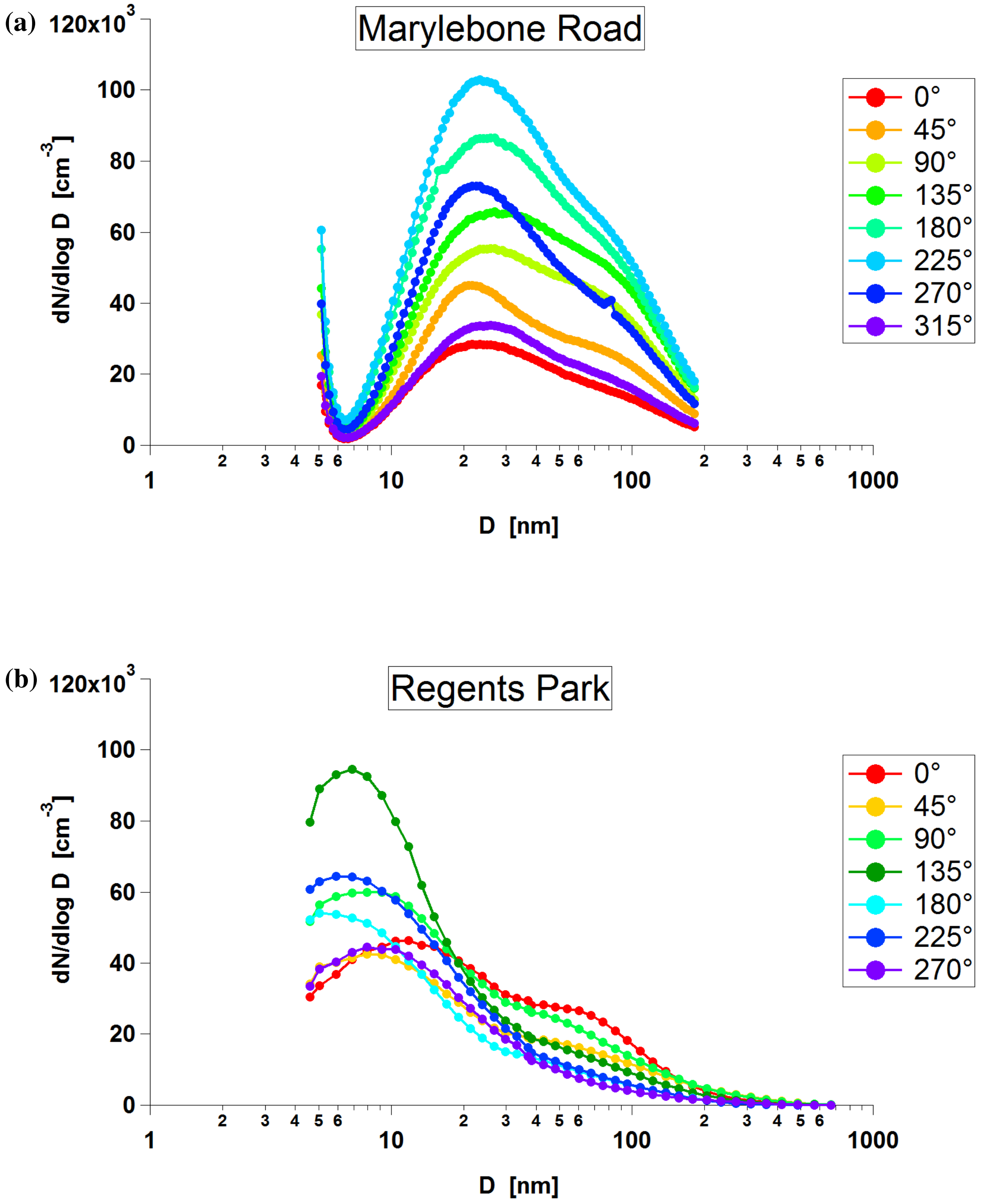

Figure 24. Particle size distributions measured as a function of wind direction at (a) Marylebone Road, and (b) Regent's Park in the REPARTEE experiment.

In a recent study, Alam et al. (2016) have studied the organic component of nanoparticles sampled from diesel engine exhaust in the laboratory. Using current ultra-low sulphur (less than 10 ppm) diesel fuel and fully synthetic motor oil, they find a very wide range of chemical constituents including straight and branch-chained alkanes, cycloalkanes, aromatics, polycyclic aromatics, decalins, steranes and hopanes.

The mixture of compounds can be simulated by mixing different fractions of diesel fuel and engine oil dependent upon the engine operating conditions, but is clearly indicative of a fraction generally less than C20, deriving from diesel fuel and a higher molecular weight fraction, typically covering the range C18-C36 deriving from engine oil. A significant fraction is made up of n-alkanes, and a typical distribution of compounds from C12-C32 measured in engine exhaust particles and vapour appears in Figure 25.

The fraction below circa C19, which is predominantly in the vapour phase, derives mainly from diesel fuel while the fraction greater than C19, which has increasing presence in the particle phase as molecular weight increases, derives predominantly from lubricating oil. It should be emphasised that even the higher molecular weight compounds have a significant vapour pressure and a strong tendency to evaporate as the particles move into cleaner air.

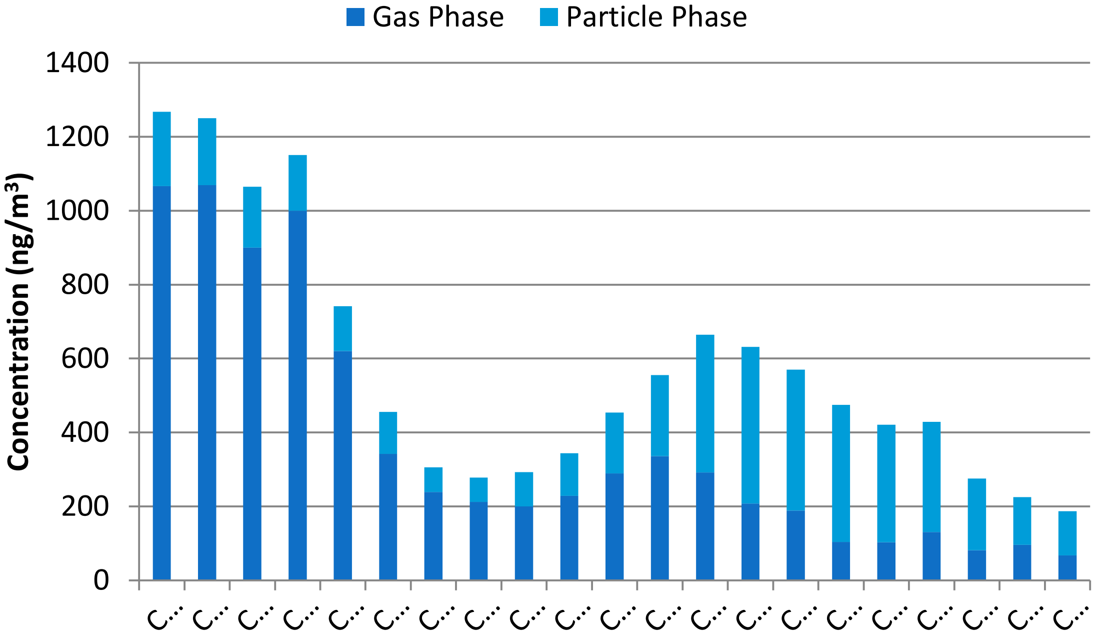

Figure 25. Gas/particle phase distribution of n-alkane concentration as measured in diesel exhaust (from Alam et al., 2016).

The NAEI provides a chemical speciation of NMVOC emissions for all sources in the inventory. For road vehicle emissions, speciation profiles representing the mass fractions of individual VOC species are taken from the EMEP/EEA Emissions Inventory Guidebook. Separate profiles are available for petrol exhaust and evaporative emissions and diesel light duty and diesel heavy duty exhaust emissions. Following the Guidelines these are then applied to the total NMVOC emissions calculated in the inventory using vehicle and fuel specific emission factors also taken from the Guidebook. Only $<C_{10}$ hydrocarbons are treated as individual VOC species in the profiles, whereas larger hydrocarbons are lumped together. Approximately 30% of VOC exhaust emissions from diesel light duty vehicles are assigned to the $>C_{13}$ category (as alkanes and aromatics), and nearly 50% for heavy duty vehicles.

A point to note is whether the speciation profile given in the Guidebook, is consistent with the total VOC exhaust emission factors given in the same Guidebook or whether they are derived under different conditions. The CLRTAP has a precise definition of NMVOCs for inventory reporting*: "NMVOCs comprise all organic compounds except methane which at 273.15 K show a vapour pressure of at least 0.01 kPa or which show a comparable volatility under the given application conditions".* This definition would exclude $>C_{12}$ hydrocarbons. If the NMVOC emission factors given in the Guidebook are intended for national inventory reporting according to this definition, then instead of inferring 30% of VOC emissions from diesel light duty vehicles were $>C_{12}$ (as implied by the Guidebook), the figure would be higher than this by a factor of 100/(100-30).

As discussed in Chapter 2, particle phase VOCs may be captured in the PM emissions inventory depending on the measurement technique used to determine the emission factors.

4.4 UFP from Aviation and Shipping

There have been several measurement campaigns at or close to airports that have reported UFP concentrations. These studies generally report relatively high PN concentrations can be found close to airports, which can often exceed the concentrations of PN close to nearby roads.

Hudda et al. measured concentrations of PN downwind of Los Angeles International Airport (LAX) using a mobile monitoring approach and detected at least a 2-fold increase in PN concentrations over baseline PN concentrations during most hours of the day, in an area of about 60 km^2 that extended to 16 km downwind, and a 4- to 5-fold increase to 8–10 km downwind. Similarly, in Europe, Keuken et al. (2015) made measurements at Adamse Bos, located 7 km from Schiphol, and in 2012 at Cabauw, a regional background site 40 km south of Schiphol. PNC increased during periods in which the wind direction was from Schiphol: at Cabauw by 20% and at Adamse Bos by a factor of three, from 14,100 (other wind directions) to 42,000 cm^{-3} between 06.00 and 23.00. The size distribution of Schiphol-related PNC was dominated by ultrafine particles, ranging from 10 to 20 nm. Four relevant particle number (PN) emission sources at Schiphol were identified as being responsible for the elevated PNC levels at Adamse Bos: take-off and climb-out, planes waiting at the gates, and landing. PN emissions from road traffic at and near the airport were less important than air traffic.

More recently, Riley et al. (2016) measured downwind of two large airports in the USA: LAX and Hartsfield-Jackson International Airport (ATL - Atlanta, GA), using a mobile monitoring platform. Riley et al. (2016) found a 3–5-fold increase in UFP concentrations in transects *under the landing approach* path to both airports, relative to surrounding urban areas with similar ground traffic characteristics. The measurements therefore suggest that aircraft plumes mix downwards to a sufficient extent to be detected at ground-level at concentrations similar in magnitude to road vehicle sources. The implications of this work are potentially important for exposure to UFP concentrations. For example, a location such as Heathrow Airport, where aircraft tend to approach the airport from the east (flying over the London conurbation), there is potential for considerable exposure to UFP from aircraft. It should be stressed however, that there are no measurements of UFP upwind of Heathrow to confirm whether elevated UFP concentration can be detected due to landing aircraft.

It is also the case that it would be more difficult to detect elevated UFP concentrations, due to the influence of other sources (particularly road traffic) than at many other airports where there are fewer sources upwind of the airport. Stacey (2017) has made measurements of particle size distributions at two sites within and adjacent to Heathrow Airport: LHR2 which is within the airport perimeter close to the northern runway, and Oaks Road, just outside the perimeter and close to the southern runway. Average particle size distributions in a measurement campaign in October 2016, showed a substantial elevation in particles of 16-30 nm diameter at both sites, relative to the sites at Marylebone Road (kerbside), North Kensington (urban background) and Chilbolton (rural). Polar plots showed the elevation to originate from the direction of the runways and to be most pronounced during aircraft take-off.

Masiol et al. (2017) carried out winter and summer measurement campaigns at the Harlington site, 1.2 km north of the northern runway of Heathrow Airport. A receptor modelling study using Positive Matrix Factorization found a factor with a size mode of < 20 nm associated with the airport, which accounted for 32% and 33% of particle number count in the warm and cold season campaigns respectively. This was attributed to aircraft emissions. Attribution of road traffic emissions to the airport is more difficult due to the many heavily trafficked roads in the vicinity.

Although shipping is known to be a major source of UFP emissions, Keuken et al. (2012) were unable to distinguish emission from a harbour in Rotterdam from a background affected by aviation and road traffic. However, measurements at Penlee Point, Cornwall exemplified by Figure 26 show distinct peaks in sulphur dioxide and particle number count, apparently associated with the passage of individual ships. At this site, the highest UFP concentrations are associated with the marine air sectors (see Figure 27), suggesting strongly a source from shipping, given the correlation with sulphur dioxide.

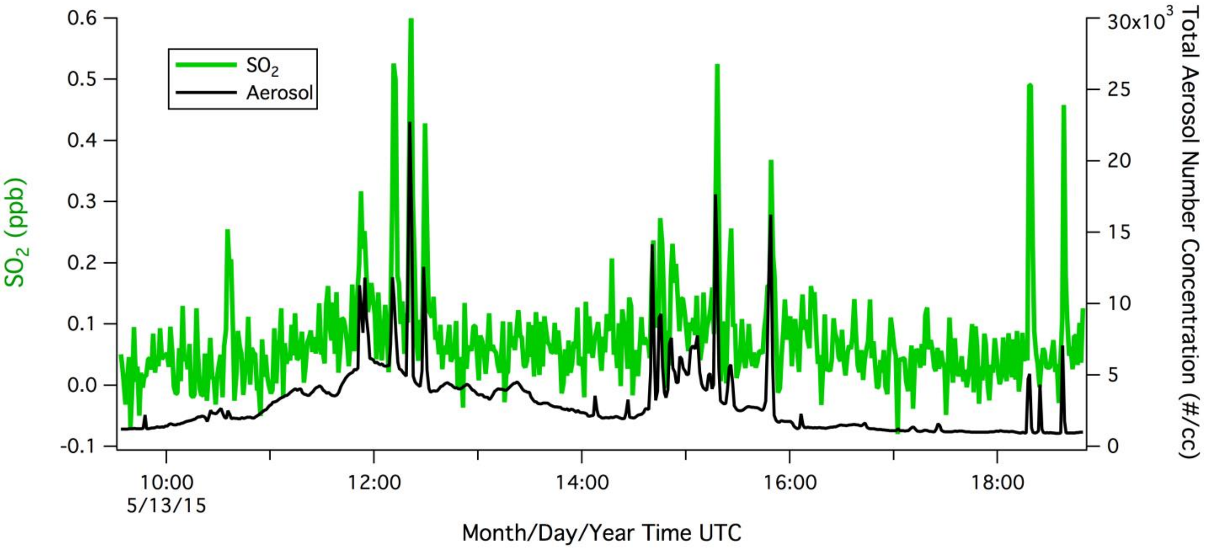

Figure 26. Time series of sulphur dioxide and particle number concentration measured at Penlee Point on 13th May 2015.

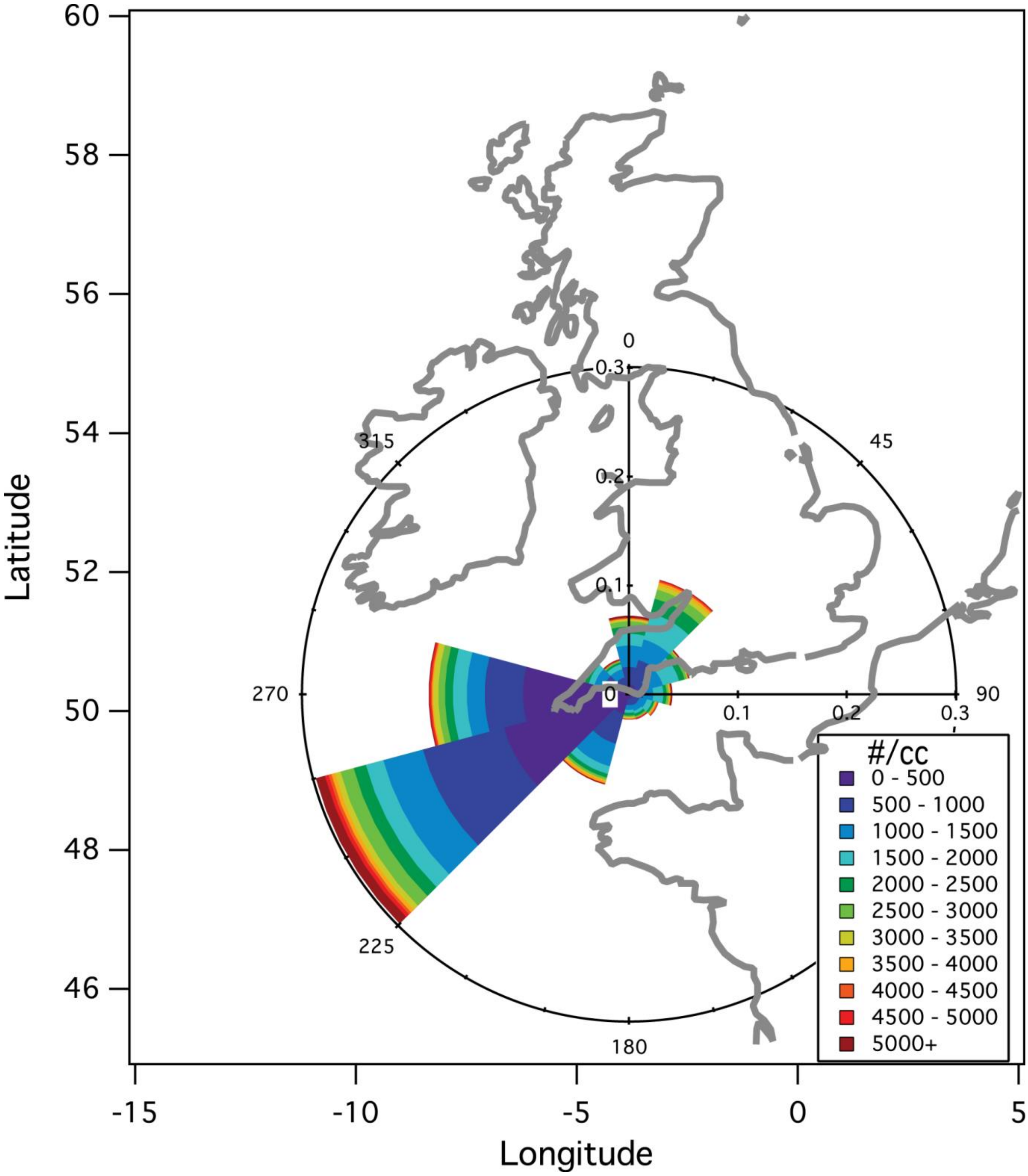

Figure 27. Pollution rose of particle number count measured at Penlee Point between February and November 2016, showing a strong association with the WSW maritime air sector.

Future trends in UFP emissions from coastal shipping and aviation are uncertain as they depend upon activity levels, changes in combustion technology and critically, the sulphur content of the fuels employed.

4.5 Chemical Composition of Ultrafine Particles and Differences between that and $PM_{2.5}$

Measurements of the chemical composition of $PM_{2.5}$ are very abundant and very much more so than those for ultrafine particles. The discrepancy in available information probably results from two drivers:

The regulatory requirements for limiting airborne concentrations of $PM_{2.5}$ necessitate knowledge of sources which can best be inferred from measurements of chemical composition.

Collection of a $PM_{0.1}$ or smaller fraction of particles is not straightforward, although it can be achieved with separation of larger particles by impaction. However, the largest problem is the very small mass of material in $PM_{0.1}$ which provides considerable analytical challenges to obtain high quality data.

The typical composition of $PM_{2.5}$ is as follows:

Major components

Sulphate, typically present within ammonium sulphate

Nitrate, typically present within ammonium nitrate

Ammonium from ammonia neutralisation of airborne acids

Chloride present either as ammonium chloride from atmospheric neutralisation of hydrogen chloride or as sodium chloride from sea salt

Hydrogen ion from residual acidity if airborne acids are not fully neutralised

Elemental carbon from combustion sources and most typically in the UK from diesel vehicle exhaust

Organic compounds which may be primary with a major source in road traffic, or secondary formed from the oxidation of volatile organic compounds

Minor constituents

Various trace elements largely from pollution sources

Mineral particles deriving from rock, soil and road dust and containing species such as Al, Si, Ca, Na, K and Mg along with trace elements, especially if arising from a polluted source.

Since many of the sources and formation mechanisms for constituents of $PM_{2.5}$ also lead to the emission or formation of ultrafine particles (which are a subset of $PM_{2.5}$), there are strong overlaps between the composition of ultrafine particles and that of $PM_{2.5}$. The more important differences arise for two reasons:

Atmospheric particles formed from mechanical disintegration and abrasion processes such as those present in sea spray and wind-blown soils and dusts, are typically rather coarse, and although there is a tail to the size distribution in the fine and ultrafine fractions, their abundance in the ultrafine size range is often extremely low.

The Kelvin effect, which leads to an enhanced vapour pressure for substances in small particles with high surface curvature, leads to enhanced evaporation of semi-volatile components from ultrafine particles. This effect leads to a reduction in the abundance of some hydrocarbon constituents and of ammonium nitrate, both of which have an appreciable vapour pressure at ambient temperatures.

There have been few studies in which the authors have set out directly to determine the entire composition of airborne nanoparticles. One of the early such studies is that of Cass et al. (2000) whose results appear in Table 1. Their data, collected in California, show a predominance of organic compounds in high abundance compared to that of elemental carbon, suggesting that there was a very large secondary component. As anticipated, there is some sulphate which exceeds the nitrate concentration despite the fact that nitrate would far exceed sulphate in $PM_{2.5}$ in southern California. There is a small contribution of sodium and chloride (presumably from sea salt predominantly) and metal oxides make up a disproportionately large contribution relative to $PM_{2.5}$, probably reflecting the very small sizes of trace metals emitted from high temperature processes.

Table 1. Composition measurements of atmospheric nanoparticles from California (from Cass et al., 2000).

	Riverside, 1996	Azusa, California, 1997
Organic compounds	67.2%	51.9%
Elemental Carbon	3.8%	4.9%
Ammonium	1.3%	9.3%
Nitrate	2.8%	1.3%
Sulphate	8.6%	12.0%
Chloride	0.9%	0.1%
Sodium	0.3%	0.4%
Metal oxides	12.0%	20.2%

Specific sources of nanoparticles require consideration. The major proportion of particles emitted in vehicle exhaust when assessed by number are in the ultrafine size range, although their contribution to mass is relatively smaller. These particles comprise two modes, a nucleation mode centred below 30 nm diameter and a soot particle mode at around 60-70 nm diameter. The nucleation mode comprises predominantly condensed hydrocarbons with a very small core of sulphuric acid or involatile trace elements. The composition of the organic matter is discussed in Section 4.2.1. The coarser soot mode particles contain a solid core of graphitic carbon, upon which are adsorbed and condensed a range of organic compounds broadly similar to those in the nucleation mode particles, although chemical composition changes with particle size, with the larger particles able to accommodate more volatile chemical species.

In addition to particles in engine exhaust, nanoparticles are contributed by other combustion and high temperature sources. These include cerium oxide particles derived from cerium-based fuel additives (Gantt et al., 2014), iron-rich particles deriving from engine emissions (Liati et al., 2015) and metal-rich ultrafine particles deriving from brake wear processes, elemental and organic carbon from wood burning, trace metals and carbon arising from combustion of fuel oil and trace metals emitted in coal combustion.

Sanderson et al. (2014) have reviewed measurements of the chemical and physical characteristics of atmospheric metallic nanoparticles. They found a small number of published papers, but concentrations of a very large range of elements both by bulk chemical analysis and by single particle studies were available. They identified very few source apportionment studies which had associated trace constituents with the source categories responsible for them. In studies conducted in the U.S., Saffari et al. (2013) applied a Principal Component Analysis technique, to chemical elements measured in a pseudo-ultrafine $PM_{0.25}$ fraction. They attributed calcium, magnesium, iron, cobalt, titanium and manganese to emissions of road dust, and barium, copper and antimony were associated in a factor attributable to brake wear. Lin et al. (2005) studied a nanoparticle fraction collected by impaction and found elements associated with diesel, gasoline, fuel oil and industrial emissions in Taiwan.

However, techniques based solely upon metal or elemental analysis are liable to miss major contributions from carbonaceous components and major ion components. Kuwayama et al. (2013) analysed a wide range of major and trace constituents in $PM_{0.1}$ samples collected in Sacramento, California and applied receptor modelling by Positive Matrix Factorization. They attributed the particles to five sources: old diesel engines, residential wood smoke, rail, regional traffic and brake wear/paved road dust.

A number of studies have shown a strong influence of vehicle emissions upon the composition of ultrafine particles sampled at urban locations. Fushimi et al. (2008) reported that at a roadside site, elemental carbon represented more than 70% of total carbon in the size fraction 30-60 nm, suggesting a predominance of soot mode particles probably from diesel emissions. In the particles of 30-60 nm aerodynamic diameter, total carbon represented more than 80% of particle mass at a roadside site, and about 50% at a background site. There is a notable lack of UK work in this field.

A further contributor to airborne nanoparticles which can be dominant in terms of numbers but generally not in terms of mass is new particle formation through regional nucleation. There appear to be three main chemical mechanisms of forming substances of very low volatility from vapour phase precursors, which is the prerequisite to particle formation through nucleation. Those chemical mechanisms are as follows:

Formation of sulphuric acid by oxidation of sulphur dioxide and subsequent nucleation in conjunction with water and ammonia or an amine (Kulmala et al., 2000).

There is some evidence that high molecular weight organic compounds including some terpenes from trees form oxidation products which can nucleate (Laaksonen et al., 2008; O'Dowd et al., 2002b).

In the coastal environment, there is strong evidence for iodine compounds leading to nuclei formation through their conversion to oxides (O'Dowd et al., 2002a).

Once formed, involatile nuclei of about 1 nm diameter can either re-evaporate or grow into larger more easily measured particles. The main origin of substances contributing to the growth of newly formed nanoparticles is through the oxidation of volatile organic compounds to form less volatile secondary species which condense upon the particles leading to their growth (Alam et al., 2003). Much of the knowledge of the composition of such particles is indirect although some direct measurements of the properties of new particles have been made which allow an inference of their composition.

Thus for example, Smith et al. (2005) and Sakurai et al. (2005) have shown that new particles in the size range 6-15 nm sampled in Atlanta, USA were entirely comprised of ammonium sulphate. Zhang et al. (2004) were able to measure the chemical composition of particles down to 30 nm in Pittsburgh, USA, with an Aerodyne Aerosol Mass Spectrometer. They found a predominance of sulphate in the particles that could be most easily characterised. Wehner et al. (2005) suggested that sulphuric acid could explain the growth of nanoparticles up to around 10-20 nm, but that oxidation of organic compounds was necessary to form substances which would then condense onto the surface causing growth, and such secondary organic components, most probably oxidation products of terpenes, have been shown to be major constituents of nanoparticles at rural locations (Laaksonen et al., 2008; Boy et al., 2003).

4.6 Polycyclic Aromatic Hydrocarbons

There is some, limited evidence of enrichment of polycyclic aromatic hydrocarbons in ultrafine particles. Two studies have analysed PAH in airborne particles size fractioned by impaction. Miguel et al. (1998), sampling in the Caldecott tunnel, California, showed the greatest concentration of PAH per unit mass in size fractions of 50-75 and 75-120 nm diameter. For some compounds, but not others, the total mass of PAH in particles of 120 nm to 4 µm diameter exceeded that in the ultrafine (<120 nm) fraction. Ning et al. (2007), using a nano-MOUDI impactor, however showed the highest total abundance of PAH in particles of >200 nm next to a busy Southern California freeway. Also sampling close to Californian freeways, Phuleria et al. (2007) showed higher concentrations of PAH (in ng m^{-3} of air) in particles of <180 nm than in those of 180 nm to 2.5 µm at both freeway and background sites.

Working at a bus station in Brazil, Martins et al. (2012) found higher concentrations (in ng m^{-3} of air) in particles of <250 nm than in larger size fractions, although the aggregate concentration of PAH in size fractions of particles of 250 nm to 10 µm exceeded that in the <250 nm fraction. Szewczyńska et al. (2013) used an Electrical Low Pressure Impactor (ELPI), to sample exhaust emissions under laboratory conditions, from a diesel common rail engine fuelled with both petroleum diesel and biodiesel blends. For diesel emissions in the ultrafine fraction, mainly 3 and 4 ring aromatics were found including phenanthrene, benz(a)anthracene, chrysene, and acenapthene, while for 40% biodiesel blends, mainly 4 and 5 ring aromatics were found including benzo(a)pyrene and benzo(k)fluoranthene.

Two points should be borne in mind in interpreting these data. Firstly, due to their semi-volatile nature, PAH are subject to sampling artefacts and are liable to migrate from larger to smaller particle fractions in a cascade impactor (Delgado-Saborit et al., 2014), which will tend to bias the apparent size distribution. Secondly, as the mass of UFP in the air is usually small, even if the UFP fraction contains more PAH per gram of particles, the PAH per cubic metre of air will be greater in the larger (>100 nm) particles due to their much greater contribution to total mass.

4.7 Chapter 4 References

Alam, A., Shi, J. P., Harrison, R. M. Observations of new particle formation in urban air, J. Geophys. Res. 108, 4093-4107, 2003. doi:10.1029/2001JD001417.

Alam, M. S., Rezaei, S. Z., Stark, C. P., Liang, Z., Xu, H. M., Harrison, R. M. The characterisation of diesel exhaust particles – composition, size distribution and partitioning, Faraday Discuss. 189, 69-84, 2016.

Birmili, W., Sun, J., Weinhold, K., Merkel, M., Rasch, F., Spindler, G., Wiedensohler, A., Bastian, S., Loschau, G., Schladitz, A., Quass, U., Kuhlbusch, T. A. J., Kaminski, H., Cyrys, J., Pitz, M., Gu, J., Peters, A., Flentje, H., Meinhardt, F., Schwerin, A., Bath, O., Ries, L., Gerwig, H., Wirtz, K., Weber, S. Atmospheric aerosol measurements in the German Ultrafine Aerosol Network (GUAN) Part 3: Black carbon mass and particle number concentrations 2009 to 2014. Aerosolmessung, 75, 479-488, 2015.

Boy, M., Rannik, U., Lehtinen, K.E.J., Tarvainen, V., Hakola, H., Kulmala, M. Nucleation events in the continental boundary layer: long-term statistical analyses of aerosol relevant characteristics. J. Geophys. Res. 108, D21, 4667, 2003. doi:10.1029/2003JD003838

Cass, G. R., Hughes, L. A., Bhave, P., Kleeman, M. J., Allen, J. O., Salmon, L. G., 2000. The chemical composition of atmospheric ultrafine particles. In *Mathematical, Physical and Engineering Sciences*. Phil. Trans. R. Soc. Lond. A. 38, No. 1775, 2581-2592.

Carslaw, D. C., Taylor, P. J. Analysis of air pollution data at a mixed source location using boosted regression trees. Atmos. Environ., 43, 3563-3570, 2009.

Charron, A., Harrison, R. M. Primary particle formation from vehicle emissions during exhaust dilution in the roadside atmosphere Atmos. Environ., 37, 4109-4119, 2003.

Dall'Osto, M., Thorpe, A., Beddows, D. C. S., Harrison, R. M., Barlow, J. F., Dunbar, T., Williams, P. I., Coe, H. Remarkable dynamics of nanoparticles in the urban atmosphere. Atmos. Chem. Phys., 11, 6623-6637, 2011.

Delgado-Saborit, J. M., Stark, C., Harrison, R. M., 2014. Use of a versatile high efficiency multiparallel denuder for the sampling of PAHs in ambient air: gas and particle phase concentrations, particle size distribution and artifact formation. Environ. Sci. Technol., 48, 499-507.

Fushimi, A., Hasegawa, S., Takahashi, K. Fujitani, Y., Tanabe, K., Kobayashi, S. Atmospheric fate of nuclei-mode particles estimated from the number concentrations and chemical composition of particles measured at roadside and background sites. Atmos. Environ 42, 949-959, 2008.

Gantt, B., Hoque, S., Willis, R. D., Fahey, K. M., Delgado-Saborit, J. M., Harrison, R. M., Erdakos, G. B., Bhave, P. V., Zhang, K. M., Kovalcik, K., Pye, H. O. T. Near-road modeling and measurement of cerium-containing particles generated by nanoparticle diesel fuel additive use. Environ. Sci. Technol. 48, 10607-10613, 2014.

Harrison, R. M., Shi, J. P., Xi, S., Khan, A., Mark, D., Kinnersley, R., Yin, J.. Measurement of number, mass and size distribution of particles in the atmosphere, Phil. Trans. R. Soc. Lond., A, 358, 2567-2580, 2000.

Harrison, R. M., Jones, A. M., Beddows, D. C. S., Dall'Osto, M., Nikolova, I. Evaporation of traffic-generated nanoparticles during advection from source. Atmos. Environ., 125, 1-7, 2016.

Jones, A. M., Harrison, R. M., Barratt, B., Fuller, G. A large reduction in airborne particle number concentrations at the time of the introduction of "sulphur free" diesel and the London Low Emission Zone. Atmos. Environ., 50, 129-138, 2012.

Keuken, M. P., Henzing, J. S., Zandveld, P., van den Elshout, S., Karl, M. Dispersion of particle numbers and elemental carbon from road traffic, a harbour and an airstrip in the Netherlands. Atmos. Environ., 54, 320-327, 2012.

Keuken, M.P., Moerman, M., Zandveld, P., Henzing, J. S., Hoek, G. Total and size-resolved particle number and black carbon concentrations in urban areas near Schiphol airport (the Netherlands). Atmos. Environ., 104, 132-142, 2015.

Kulmala, M., Pirjola, L., Makela, J. M. Stable sulfate clusters as a source of new atmospheric particles. Nature 104, 66-69, 2000.

Kuwayama, T., Ruehl, C. R., Kleeman, M. J. Daily trends and source apportionment of ultrafine particulate mass ($PM_{0.1}$) over an annual cycle in a typical California city. Environ. Sci. Technol. 47, 13957-13966, 2013.

Laaksonen, A., Kulmala, M., O'Dowd, C. D., Joutsensaari, J., Vaattovaara, P., Mikkonen, S., Lehtinen, K. E. J., Sogacheva, L., Dal Maso, M., Aalto, P., Petaj, T., Sogachev, A., Yoon, Y. J., Lihavainen, H., Nilsson, D., Facchini, M. C., Cavalli, F., Fuzzi, S., Hoffmann, T., Arnold, F., Hanke, M., Sellegri, K., Umann, B., Junkermann, W., Coe, H., Allan, J. D., Alfarra, M. R., Worsnop, D. R., Riekkola, M.-L., Hyotylainen, T., Viisanen Y. The role of VOC oxidation products in continental new particle formation. Atmos. Chem. Physics. 8, 2657-2665, 2008.

Liati, A., Pandurangi, S.S., Boulouchos, K., Schreiber, D., Dasilva, Y.A.R. Metal nanoparticles in diesel exhaust derived by in-cylinder melting of detached engine fragments. Atmos. Environ. 101, 34-40, 2015.

Lin, C.C., Chen, S.-J., Huang, K.-L., Hwang, W.-I., Chang-Chien, G.-P., Lin, W.-Y.

Characteristics of metals in nano/ultrafine/ fine/ coarse particles collected beside a heavily trafficked road. Environ. Sci. Technol. 39, 8113-8121, 2005.

Masiol, M., Harrison, R. M., Vu, T. V., Beddows, D. C. S. Sources of submicrometre particles near a major international airport. Atmos. Chem. Phys., 17, 12379-12403, 2017.

Martins, L. D., da silva Junior, C. R., Solci, M. C., Pinto, J. P., Souza, D. Z., Vasconcellos, P., Guarieiro, A. L. N., Guarieiro, L. L. N., Souza E. T., de Andrade, J. B. Particle emission from heavy-duty engine fuelled with blended diesel and biodiesel. Environ. Monit. Assess., 184, 2663-2676, 2012.

Miguel, A., Kirchstetter, T. W., Harley, R. A. On-road emissions of particulate polycyclic aromatic hydrocarbons and black carbon from gasoline and diesel vehicles. Environ. Sci. Technol., 32, 450-455, 1998.

Ning, Z., Geller, M.D., Sioutas, C.,. Fine, Ultrafine and nanoparticle trace organic compositions near a major freeway with a high heavy duty diesel fraction. SAE paper 2007-24-0108, 2007.

O'Dowd, C. D., Jimenez, J. L., Bahreini, R., Flagan, R. C., Seinfeld, J. H., Hämeri, K., Pirjola, L., Kulmala, M., Jennings, S. G., Hoffmann, T. Marine aerosol formation from biogenic iodine emissions, Nature 417, 632-636, 2002a.

O'Dowd, C. D., Aalto, P., Hmeri, K., Kulmala, M., Hoffmann T. Aerosol formation: Atmospheric particles from organic vapours, Nature 416, 497-498, 2002b.

Phuleria, H. C., Sheesley, R. J., Schauer, J. J., Fine, P. M., Sioutas, C. Roadside measurements of size-segregated particulate organic compounds near gasoline and diesel-dominated freeways in Los Angeles, CA. Atmos. Environ., 41, 4653-4671, 2007.

Riley, E.A., Gould, T., Hartin, K., Fruin, S. A., Simpson, C. D., Yost, M. G., Larson, T. Ultrafine particle size as a tracer for aircraft turbine emissions. Atmos. Environ., 139, 20-29, 2016.

Saffari, A., Daher, N., Shafer, M.M., Schauer, J. J., Sioutas, C. Seasonal and spatial variation of trace elements and metals in quasi-ultrafine ($PM_{0.25}$) particles in the Lost Angeles metropolitan area and characterization of their sources. Environ. Pollut. 181, 14-23, 2013.

Sakurai, H., Fink, M. A., McMurry, P. H., Mauldin, L., Moore, K. F., Smith, J. N., Eisele, F. L., Hygroscopy and volatility of 4-10 nm particles during summertime atmospheric nucleation events in urban Atlanta. J. Geophys. Res. 110, D22S04, 2005. 10.1029/2005JD005918

Sakurai, H., Fink, M. A., McMurry, P.H., Mauldin, L., Moore, K. F., Smith, J.N., Eisele, F.L., Sanderson, P., Delgado-Saborit, J. M., Harrison, R. M. A review of chemical and physical characterisation of atmospheric metallic nanoparticles. Atmos. Environ. 94, 353-365, 2014.

Shi, J. P., Harrison, R. M. Investigation of ultrafine particle formation during diesel exhaust dilution. Environ. Sci. Technol., 33, 3730-3736, 1999.

Smith, J. N., Moore, K. F., Eisele, F. L., Voisin, D., Ghimire, A. K., Sakurai, H., McMurry, P. H. Chemical composition of atmospheric nanoparticles during nucleation events in Atlanta. J. Geophys. Res., 110, D22S03, 2005. doi: 10.1029/2005JD005912.

Stacey, B. Measurement of ultrafine particles at Heathrow Airport – an initial assessment of measurements, September to November 2016, 2017.

Szewczyńska, M., Pośniak, M. and Dobrzyńska, E., Study on individual PAHs content in ultrafine particles from solid fractions of diesel and biodiesel exhaust fumes. J. Chem, Article ID 528471, 2013. http://dx.doi.org/10.1155/2013/528471

UKPIA. Sulphur-free Petrol, Diesel and Non-Road Fuels, 2016. Accessible at: http://www.ukpia.com/industry_issues/fuels/sulphur-free-petrol-diesel-and-non-road-fuels.aspx

Vu, T. V., Delgado-Saborit, J. M., Harrison, R. M. Review: Particle number size distributions from seven major sources and implications for source apportionment studies. Atmos. Environ., 122, 114-132, 2015.

Wehner, B., Petaja, T., Boy, M., Engler, C., Birmili, W., Tuch, T., Wiedensohler, A., Kulmala, M. The contribution of sulfuric acid and non-volatile compounds on the growth of freshly formed atmospheric aerosol, Geophys. Lett. 32, L17810, 2005. doi: 10.1029/2005GL023827.

Zhang, Q., Stanier, C. O., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R., Pandis, S. N., Jimenez, J. L. Insights into the chemistry of new particle formation and growth events in Pittsburgh based on aerosol mass spectrometry, Environ. Sci Technol. 38, 4797-4809, 2004.

5 Modelling Ultrafine Particles

Key Points

- Urban dispersion models can be used to give reasonable estimates of particle number concentration in urban areas if the emissions are well characterized. This means that such models can be used to generate high resolution maps of particle number density. However aerosol dynamics models are required to estimate UFP particle mass and size distribution.

- Receptor modelling has confirmed that road traffic exhaust is the dominant source of UFP in urban areas in the UK.

- Models for UFP have not until now, been used routinely in the UK for future projections or for the development of policy scenarios; this is partly because there are no air quality standards for UFP.

5.1 Introduction

Measurements are able to provide mass, particle number and size distributions of UFP at specific locations, however models are necessary for detailed spatial coverage required for exposure calculations and for future projections required for the development of policies for UFP control. There are no established models used routinely for such calculations as most model developments have only commenced relatively recently. Modelling methodologies applied generally fall into the following categories: mechanistic models which describe aspects of the dispersion and aerosol dynamics; statistical models based on measurements and in some cases also land use; and receptor models which are used to analyse measured concentrations to estimate different source contributions.

5.2 Mechanistic Models

The different processes leading to a particular mass or number concentration of UFP have been described in the Introduction (Section 1). As these processes take place over a very large range of both temporal and spatial scales, it is impractical for models of UFP to take to take account of all of the processes at all scales, but instead assumptions and simplifications are used, so that the models may be used to investigate particular issues or to model UFP at particular scales. A useful discussion of the importance of the different processes in determining number and mass concentrations of UFP is given by Kumar et al. (2011). The relative importance of these at a range of pollutant ages and distances from sources is summarised in Table 2 adapted from Kumar et al.

*Table 2. Relative importance of the different processes affecting UFP number and mass concentration. *** important; ** some importance; * little impact.*

Process	Effects on concentration Number / Mass	Very close to source (secs, metres)	Close to source (10s of seconds/ metres)	Neighbourhood / City scale	Regional Scale
Emissions	+/+	***	***	***	***
Mixing/dilution	-/-	***	***	***	***

Nucleation	+/+	***	**	*	**
Coagulation	-/0	*	*	**	*
Condensation	0/+	***	**	*	**
Evaporation	0,-/-	**	***	**	**
Deposition	-/-	**	**	**	***

Emissions of both UFP and precursor gases and also turbulent mixing and hence dilution, are important at the full range of scales. Very close to sources, for example on a timescale of a few seconds close to vehicle exhausts, high vapour pressures and rapid cooling may result in a supersaturation large enough to cause nucleation, resulting in large relative changes in particle numbers; nucleation is also important in the generation of secondary particulates at regional scale, where chemical reactions can results in species of low volatility. In the presence of large surface area of particles, condensation competes with and inhibits nucleation and results in increase in particle mass. Evaporation is the reverse process compared to condensation resulting in decrease in particle mass; it is typically important in regions of dilution where vapour pressures are much reduced, and in high temperatures where saturation vapour pressures are increased. Coagulation is most efficient between particles of different sizes, changing particle number and size but not total mass; it is typically of less relative importance compared to the other processes. Deposition takes place at all spatial scales; because the rate of loss of UFP due to deposition is slow, compared to rates of emission its relative importance tends to increase with spatial scale.

As Table 2 illustrates it is essential, as with any dispersion model, for a model for UFP to specify emissions and to take account of turbulent mixing and dilution. Whether consideration of these processes only is sufficient, or whether and how other processes need to be accounted for, depends on the purpose for which the model is being utilized. Typically for vehicle emissions, particle distributions input into models are those measured not at the exhaust exit, but at some distance from the source (e.g. at kerbside), where much of the near source nucleation has already occurred. Some model calculations of UFP mass and/or number concentration, especially those investigating UFP over areas with extensive emission sources, such as urban areas or airports, take no subsequent account of particle dynamics, and calculate the evolution of mass and particle number concentration, assuming no change in particle size.

For example Kukkonen et al. (2016) used the regional model LOTOS-EUROS together with local particle emission inventories and urban dispersion models, to calculate particle numbers at 5 European cities; at most sites predicted annual mean particle concentrations were within 25% of observed values. At Schiphol Airport, using a Gaussian plume model, Keuken et al. (2015) used a conversion factor based on measurements of particle number from one site to convert the predictions of inert gas concentrations, into particle number Kumar et al. (2009) used a simplified box model, the street canyon model OSPM and the CFD code FLUENT to calculate particle number at the leeward side of a street canyon. These calculations may provide some support for neglecting particle dynamics in calculations of particle number in street canyons, but it was not possible to distinguish between underlying errors in the models' dispersion algorithms, the assumptions regarding particle emissions and the effect of neglecting aerosol dynamics.

Of the processes listed in Table 2 as well as emissions and dilution, a dispersion model will usually also allow for the treatment of deposition; however nucleation, condensation, evaporation and coagulation are treated by specialist particle process (aerosol dynamics) models. Typically these are ‘box’ models which specify initial concentrations and size distributions, of particles of representative chemical species including condensation nuclei. The models then step forward in time with nucleation, condensation, evaporation and coagulation, determined by rate equations for the different processes (Zhang and Wexler, 2002). The rates depend, amongst other parameters on the partial and saturation vapour pressures of the different species together with the size of the particles. Emissions may be added to the ‘box’ and, to represent mixing of ambient air, a rate of dilution specified which affects both the temperature and the partial pressures of the VOCs being modelled.

Examples of the use of such models include Ketzel et al. (2007) who applied the particle process models AEROFOR and MAT, to study the relative importance of condensation, coagulation and deposition in the evolution of particle number and particle size distribution across an urban area. The emissions were uniformly spaced with size distribution typical of traffic emitted particles. The results were inconclusive being highly dependent on model formulation especially for condensation. Nikolova et al. (2016) simulated the evolution of traffic generated multi-component UFP composed of a non-volatile core, and a representative set of 17 semi-volatile compounds. The simulation used kerbside measurements as input, assumed that nucleation processes had completed and accounted for condensation/ evaporation. Comparison with measurements in a street canyon and at a nearby urban park, showed the modelled particle size distributions were reasonably represented, in particular the large reduction in the nucleation mode peak diameter from 23nm in the street canyon, to 9nm in the park due to evaporation. Zhang et al. (2004a,b) used a multi component model to simulate the evolution of particle size distribution downstream of two Los Angeles freeways.

After initial growth up to 90m downwind of the freeways, evaporation generally reduced particle size in the nucleation mode, although some larger particles continued to grow. This modelling showed that particle dynamic effects were more important in the summer months. Karl et al. (2015) used the detailed particle process model MAFOR together with a simplified box model, for dispersion and dilution to simulate evolution of particle size distributions across Helsinki, Oslo and Rotterdam. Model predictions were broadly consistent with observed size distributions.

MAFOR is one of a number of detailed particle process models being developed to improve representation of aerosols in regional air quality models. Others include the MODE scheme in UKCA and the aerosol scheme in CMAQ (Binkowski et al., 2003). Used in regional models these schemes are unable to account for nucleation, condensation and evaporation occurring close to sources.

5.2.1 Prediction of future trends

Until now the use of UFP models to study the impact of new or proposed technologies on UFP particle numbers and size distribution has been very limited. There are for instance, currently no calculations of $PM_{0.1}$ concentrations across the UK nor their future trends. Toenges-Schuller et al. (2015) have used the aerosol dynamics box model MADE, coupled to a gas phase chemistry and one dimensional transport box model, to simulate particle number concentrations up to 2025 in typical street canyon conditions with high traffic volume in Germany. Their modelling showed that uptake of a high number of Euro 6 vehicles, will reduce particle numbers by 90% compared to 2010. Gantt et al. (2014) have used an extended version of the mode of Zhang and Wexler (2002), to model the impacts of cerium oxide nano-particle additives on particle size numbers, and showed a reduction in particle numbers, except in the nucleation mode, consistent with measured reductions in particle emissions. Further modelling studies for future trends of interest would include the effect of DPFs and the introduction of GDI on particle size distribution, numbers and mass.

5.3 Statistical Models

Statistical models do not consider specific physical processes but are based on the premise that the characteristics of UFP mass, number and size distribution are correlated with meteorological and temporal variables, as well as site type or location and land use. They thus require and are intrinsically linked to measurements, and are therefore most appropriate for historical or current mapping of UFP, but not future projections or planning and policy scenarios. A recent example of a statistical model is that of von Bismarck-Osten et al. (2015). They used multiple linear regression employing 13 meteorological and temporal parameters to estimate size distributions at specific roadside, urban background and rural sites based on measurements at 11 sites in 4 European cities.

The best performance was at road side sites with reasonable transferability to other similar sites. Weichenthal et al. (2016) have developed a land use regression model for ambient UFPs in Toronto, Canada using mobile monitoring data collected during summer/winter 2010–2011 over 405 road segments. The model includes terms for the logarithm of distances to highways, major roads, the central business district, Pearson airport, and bus routes as well as variables for the number of on-street trees, parks, open space, and the length of bus routes within a 100 m buffer. It is able to explain 67% of the spatial variation in the mean number of UFPs (see Figure 28).

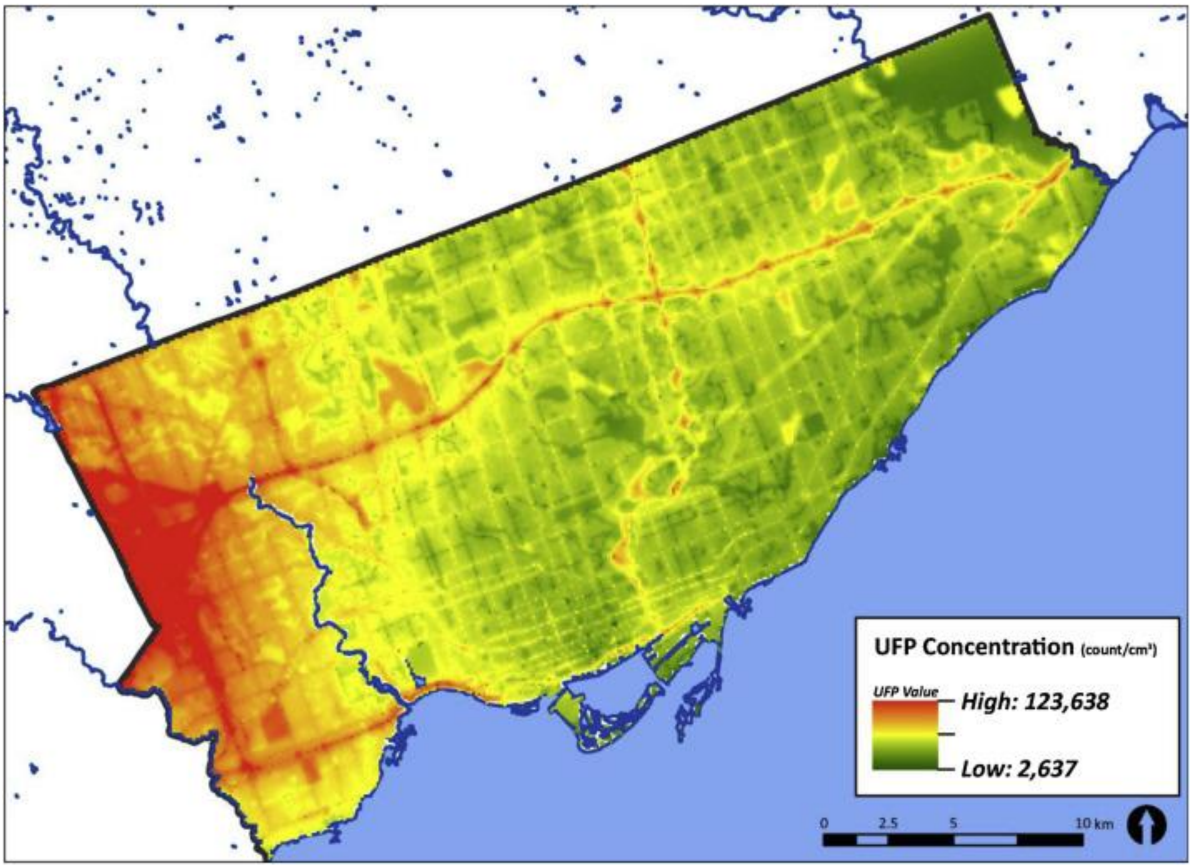

Figure 28. Predicted spatial distribution of ambient UFPs in Toronto, Canada calculated using Land Use Regression Model. From Weichenthal et al. (2016).

5.4 Receptor Modelling

5.4.1 Introduction

Receptor modelling describes the process of analysing measured air quality data to estimate the contribution of a source type to the measured concentrations. A typical outcome from receptor modelling is quantitative source apportionment of the contributors to measured atmospheric concentrations. There are two main generic approaches to receptor modelling, with well development procedures and software available for each (Hopke, 2016). Both methods are based upon a mass conservation approach, i.e.

$$C_{ij} = \sum^{j,k} f_{i,k} \cdot g_{j,k}$$

where $C_{i,j}$ is the concentration of constituent i in sample j

$f_{i,k}$ is the fraction of constituent i in the emissions from source k, and

$g_{j,k}$ is the fractional contribution of source type k to the mass of particles in sample j

In the Chemical Mass Balance modelling approach, a database of source composition ($f_{i,k}$) is used, and values of $g_{j,k}$ are varied to get the best fit to measured values of concentration, $C_{i,j}$ across a range of chemical constituents, i. This approach becomes more difficult when secondary constituents of unknown composition are present, or chemical composition changes between source and receptor, but these issues are tractable.

In the second main receptor modelling approach, multivariate statistical models are used to generate factor (source) profiles from internal correlations within the dataset, which are then fitted to the overall composition of the samples. This approach is better able to deal with unknown and secondary sources, and chemical change within the atmosphere than the Chemical Mass Balance approach. The best known method, Positive Matrix Factorization (PMF) (Paatero and Tapper, 1994) has been widely applied to air quality datasets, often with considerable success. There are also hybrid approaches, such as the Multilinear Engine (ME2) which allow the *a priori* specification of some factor (source) profiles for inclusion in a PMF model.

Receptor modelling methods are most commonly applied to chemical composition data. However, because of the need for multiple samples of $PM_{0.1}$ to be analysed for many chemical constituents, there are very few reported studies of the application of receptor modelling techniques to ultrafine particles. In one of the few such studies, Kuwayama et al. (2013) applied PMF to samples of $PM_{0.1}$ collected in Sacramento, California. They resolved contributions from old-technology diesel engines, residential wood burning, rail, regional traffic and brake wear/road dust.

Receptor models can also be applied to particle number size distribution data, such as that from a Particle Mobility Size Spectrometer which resolves data into many size bins, each of which can be used in a manner analogous to that described for a chemical component. Vu et al. (2015) have reviewed published data on particle size distributions from seven major sources: traffic, industry, biomass burning, cooking, long-range transport, marine aerosol and nucleation. They also consider the effect of atmospheric physical processes in relation to the use of characteristic size distributions in source apportionment studies. Particle size distributions are typically more dynamic than chemical composition which makes the method more difficult to apply, except close to a source. Thus, for example, while the chemical identity of a vehicle exhaust particle is not affected by coagulation with another particle, unless a subsequent chemical reaction leads to modification, coagulation of two particles causes an irreversible change to a particle size distribution.

5.4.2 Receptor modelling of particle number concentrations in the UK atmosphere

Harrison et al. (2011) combined particle size distributions collected with a Scanning Mobility Particle Sizer, with distributions measured with an aerodynamic particle sizer, to give continuous size distributions from 15 nm to 10 µm diameter. By inputting measurements made on Marylebone Road, London into a PMF model, together with gaseous pollutant and traffic count data, they were able to separate contributions into ten source-related factors which are summarised in Table 3.

Table 3. Attribution of mean particle volume and number to tentatively assigned sources.

	Mean Concentration (s.d.) (%)	
	Volume	Number
Marylebone Road Emissions		
Exhaust - solid mode	18.8 (12.1)	38.0 (18.8)
Exhaust - nucleation mode	3.6 (2.8)	27.4 (15.8)
Brake dust	13.7 (10.7)	1.7 (1.5)
Resuspension	4.4 (4.1)	4.8 (4.4)
Sub-total	40.5	71.9
Urban Background		
Accumulation mode	12.8 (10.8)	6.3 (5.6)
Suburban traffic	2.3 (2.0)	7.6 (7.9)
Solid fuel/nitrate	8.4 (7.2)	2.0 (2.3)
Regional	2.5 (3.6)	2.7 (4.1)
Cooking	6.7 (2.6)	6.6 (7.3)
Regional	26.8 (18.1)	3.0 (3.8)
Sub-total	59.5	28.2

The results are expressed both for the number of particles, and the contributions to particle volume, calculated assuming particle spherical geometry. Estimation of contributions to mass would require application of particle density for each source, which is not reliably known. Greater confidence can be placed in the estimates of emissions from Marylebone Road itself, which account for 71.9% of the total particle number measured, and give separate quantification of the solid mode and nucleation mode exhaust particles, brake wear, and resuspension of road surface dust (Table 3). Less confidence can be placed in the attribution of sources to the factors associated with the urban background.

Beddows et al. (2015) applied the PMF model to a two-year time series of particle number size distributions (from 16.5 to 604 nm), collected using a Scanning Mobility Particle Sizer at the London, North Kensington sampling site. The results shown earlier in Figure 12 show that four source-related factors were resolved, attributable to the urban background (43.0% of particle number) – representing mainly aged traffic exhaust and wood smoke particles, local traffic (44.8%), secondary particles (4.4%), and regional nucleation (7.8%). Table 4 shows the matrix of Pearson correlations with six factors derived from application of PMF to a simultaneously collected dataset *of the chemical composition of* PM_{10}.

Table 4. Pearson correlations coefficients between the daily average Number Size Distribution (NSD) and PM10 factors.

FACTORS			NSD			
			1	2	3	4
			Secondary	Urban Background	Traffic	Nucleation
PM_{10}	1	Urban Background	0.60	0.77	0.414	-0.07
	2	Marine	-0.36	-0.35	-0.127	-0.09
	3	Secondary	0.64	0.30	-0.006	-0.15
	4	Non-exhaust Traffic/Crustal	0.47	0.41	0.097	-0.14
	5	Fuel Oil	-0.14	0.02	-0.070	0.28
	6	Traffic	0.53	0.72	0.471	-0.08

Figure 29 shows the air mass back trajectories from the days when each of the four factors made its greatest daily contribution to the particle number size distribution (and hence to ultrafine particles).

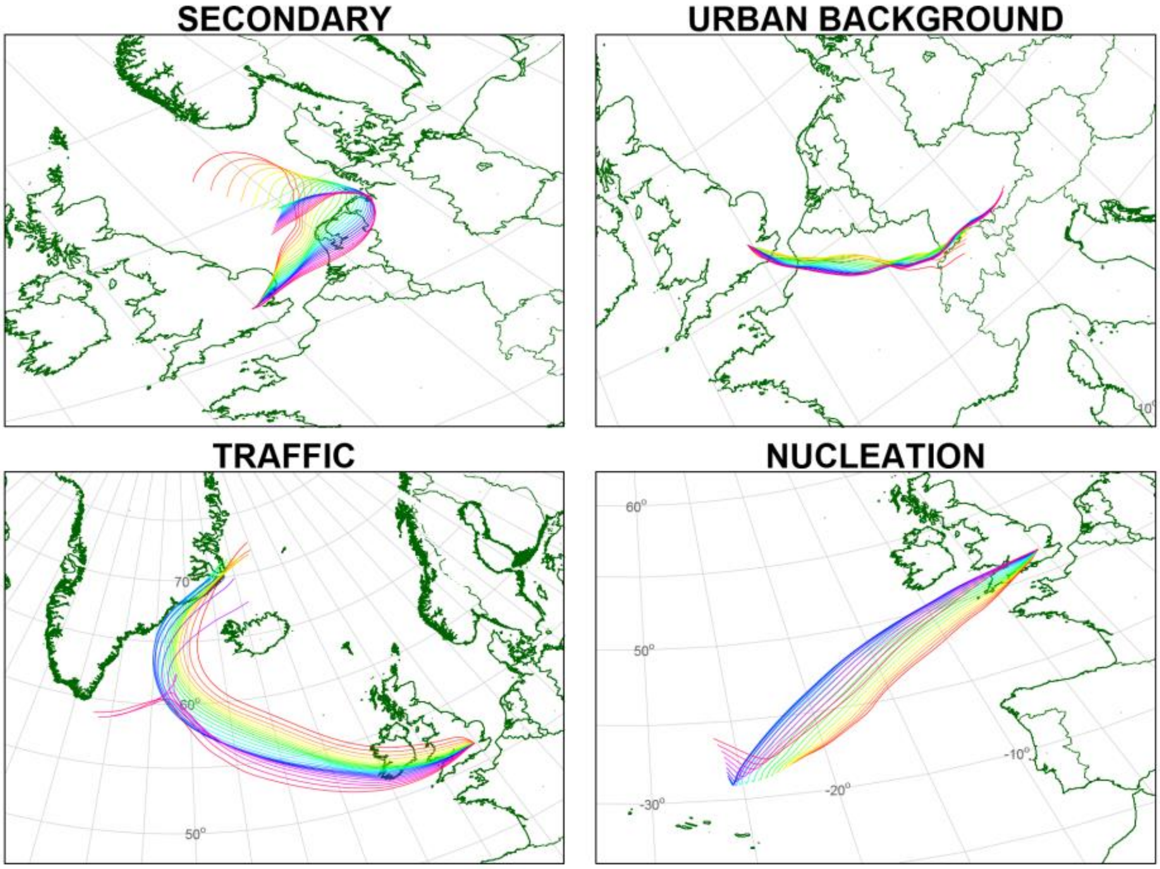

Figure 29. Back mass trajectories corresponding to the day each factor has the highest daily contribution to NSD. [24/03/2012 - Secondary; 01/10/2011 - Urban Background; 27/01/2012–Traffic; 17/07/2012 - Nucleation] (from Beddows et al., 2015).

Most notable are the association of the Nucleation factor with relatively clean air from the Atlantic Ocean, and the Secondary and Urban Background factors with continental air masses, whereas the Local Traffic factor is most prominent in cleaner westerly air masses with a less aged aerosol.

5.5 Key Points Regarding Models

Urban dispersion models can be used to give reasonable estimates of particle number concentration in urban areas if the particle number emissions are well characterized for instance by near source measurements. This means that such models can be used to generate high spatial resolution maps of particle number density. However aerosol dynamics models are required to estimate particle mass and size distribution.

Because local sources dominate particle number concentration statistical models based on land use, meteorology etc together with a network of monitors can also be used to generate maps of number concentration close to sources.

Receptor modelling has proved to be a powerful technique for determining the contributions of different source types to particle number and size. It has confirmed that road traffic exhaust is the dominant source of UFP particle number in urban areas in the UK contributing more than 65% of the total at Marylebone Road.

Models for UFP have not until now been used routinely in the UK for future projections or for the development of policy scenarios; this is partly because there are no air quality standards for UFP.

5.6 Chapter 5 References

Beddows, D. C. S., Harrison, R. M., Green, D., Fuller, G. Receptor modelling of both particle composition and size distribution data from a background site in London UK. Atmos. Chem. Phys., 15, 10107-10125, 2015.

Binkowski, F. S., Roselle S. J. Models-3 Community Multiscale Air Quality (CMAQ) model aerosol component, 1, Model description. J. Geophys. Res., 108, D6, 4183, 2003. doi:10.1029/2001JD001409.

Gantt, B., Hoque, S., Willis, R.D., Fahey, K. M., Delgado-Saborit, J. M., Harrison, R. M., Erdakos, G. B., Bhave, P. V., Zhang, K. M., Kovalcik, K., Pye, H. Near-road modeling and measurement of cerium-containing particles generated by nanoparticle diesel fuel additive use. Environ. Sci. Technol. 2014, 48, 10607-10613, 2014.

Harrison, R. M., Beddows, D. C. S., Dall'Osto, M. PMF analysis of wide-range particle size spectra collected on a major highway. Environ. Sci. Technol., 45, 5522-5528, 2011.

Hopke, P. K. Review of receptor modeling methods for source apportionment. JAWMA, 66, 237-259, 2016.

Karl, M., Kukkonen, J., Keuken, M.P., Lützenkirchen, S., Pirjola, L., Hussein, T. Modelling and measurements of urban aerosol processes on the neighborhood scale in Rotterdam, Oslo and Helsinki. Atmos. Chem. Phys. Discuss., 15, 35157-35200, 2015.

Ketzel, M., Berkowicz, R., Palmgren, F., Glasius, M., Løfstrøm, P., Pohjola, M., Haakana, M., Karppinen, A., Kukkonen, J., Hallquist, M., Janhäll, S., Hansson, H.C., Ström, J., Johansson, C., Tunved, P., Bilde, M., Nielsen, O.J., Swietlicki, E., Massling, A., Simpson, D., Tsyro, S., Denby, B., Berger, J., Tønnesen, D., Lunder, C., Håvard Slørdal, L., Omstedt, G., Gidhagen, L., Kulmala, M., Hussein, T., Pirjola, L. Final Report on the NMR Project: NORPAC Validated Models Describing Nordic Urbanand Regional Concentration of Particles and Organic/Elemental Carbon (OC/EC). Nordic Council of Ministers Working Group Marine & Air 2007. Accessible at: http://www2.dmu.dk/AtmosphericEnvironment/norpac/Downloads/NORPAC_FinalReport_Dec2007.pdf

Keuken, M. P., Moerman, M., Zanveld, P., Henzing, J. S., Hoek, G. Total and size-resolved particle number and black carbon concentrations in urban areas near Schiphol airport. Atmos. Environ., 104,132-142, 2015.

Kukkonen, J., Karl, M., Keuken, M. P., Denier van der Gon, H. A. C., Denby, B. R., Singh, V., Douros, J., Manders, A., Samaras, Z., Moussiopoulos, N., Jonkers, S., Aarnio, M., Karppinen, A., Kangas, L., Lützenkirchen, S., Petäjä, T., Vouitsis, I., Sokhi, R. S. Modelling the dispersion of particle numbers in five European cities. Geosci. Model Dev., 9, 451-478, 2016.

Kumar P., Garmory, A., Ketzel, M., Berkowicz, R., Britter, R. Comparative study of measured and modelled number concentrations of nanoparticles in an urban street canyon. Atmos. Environ., 43, 949-958, 2009.

Kumar, P., Ketzel, M., Vardoulakis, S., Pirjola, L., Britter, R. Dynamics and dispersion modelling of nanoparticles from road traffic in the urban atmospheric environment - A review. J. Aerosol Sci., 42 580–603, 2011.

Kuwayama, T., Ruehl, C.R., Kleeman, M. J. Daily trends and source apportionment of ultrafine particulate mass ($PM_{0.1}$) over an annual cycle in a typical California city. Environ. Sci. Technol., 47*,* 13957-13966, 2013.

Nikolova, I., MacKenzie, R., Cai, X., Alam, M.S., Harrison, R. M. Modelling component evaporation and composition change of traffic-induced ultrafine particles during travel from street canyon to urban background. Faraday Discuss. 189, 529-546, 2016.

Paatero, P., Tapper, U. Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values. Environmetrics, 5, 111-126, 1994.

Toenges-Schuller, N., Schneider, Chr., Niederau, A., Vogt, R., Birmili, W. Modelling particle number concentrations in a typical street canyon in Germany and analysis of future trends. Atmos. Environ., 111, 127-135, 2015.

Von Bismarck-Osten, C., Birmili, W., Ketzel, M., Weber, S. Statistical modelling of aerosol particle number size distributions in urban and rural environments – A multi-site study. Urban Clim., 11 51-66, 2015.

Vu, T. V., Delgado-Saborit, J. M., Harrison, R. M. Review: Particle number size distributions from seven major sources and implications for source apportionment studies. Atmos. Environ., 122, 114-132, 2015.

Weichenthal, S., Van Ryswyk, K., Goldstein, A., Shekarrizfard, M., Hatzopoulou, M. Characterizing the spatial distribution of ambient ultrafine particles in Toronto, Canada: A land use regression model. Environ. Pollut., 208, 241-248, 2016.

Zhang, K. M., Wexler, A. S. Modelling the number distributions of urban and regional aerosols: theoretical foundations. Atmos. Environ., 1863-1874, 2002.

Zhang, K. M., Wexler, A. S. Evolution of particle number distribution near roadways - Part I: analysis of aerosol dynamics and its implications for engine emission measurement. Atmos. Environ., 6643-6653, 2004a.

Zhang, K. M., Wexler, A. S., Zhu, Y. F., Hinds, W. C., Sioutas, C. Evolution of particle number distribution near roadways. Part II: the ‘Road-to-Ambient’ process. Atmos. Environ., 6655-6665, 2004b.

6 Control of Ultrafine Particle Emissions

Key Points

- Particle filters fitted to motor vehicles are highly efficient for removal of UFP, but there is limited data upon the durability and long-term performance.
- Some abatement measures used in industry for control of particle emissions are highly effective in removal of UFP, but others are less effective.
- The abatement plant on modern waste incinerators is highly effective at UFP removal.
- Aviation fuel has a far higher sulphur content than fuels for road vehicles, and the growth of air traffic is likely to cause increased UFP concentrations in the vicinity of airports, unless the fuel sulphur content is reduced.

6.1 Introduction

Most sources which emit particles incorporate abatement plant designed to arrest, or reduce the emission of particulate matter. In general, emission standards for industry are framed in terms of the total mass concentration of particles, irrespective of particle size. Consequently as there are no emissions regulations specific to ultrafine particles, a given plant may be able to meet its targets for abatement of emissions of particulate matter, without necessarily reducing emissions of ultrafine particles.

The extent to which emissions of ultrafine particles are reduced depends largely upon the technology installed upon the source. Some technologies function well for involatile ultrafine particles, while others do not. Electrostatic dust precipitators, fitted to many industrial installations, will not on their own cause much reduction of ultrafine particles, as their operation depends upon imparting an electrical charge to particles, which causes them to migrate in a subsequent electric field. As charging efficiencies fall markedly with particle size, abatement efficiencies for UFP by this technology will be very low. On the other hand, many modern industrial processes use baghouse filters for particulate matter abatement. These force the exhaust gases from the process to pass through a fabric filter where particles are removed.

Contrary to first impressions, fabric filters used to remove particles, do not act like simple sieves and are able to remove particles much smaller than the pore size of the fabric. This is because particles are removed by four separate mechanisms: impaction, interception, diffusive and electrostatic collection (Hinds, 1999). Efficiencies are very high for very small particles (<20 nm) because of their high diffusivity, falling somewhat for particles of around 100 nm, before increasing again as larger particles are trapped by interception (sieving), and impaction. Jones and Harrison (2016) have reviewed studies of UFP emissions from municipal incinerators, which are normally fitted with plant to contact the combustion exhaust gases with a powder or slurry of activated carbon and lime, designed to remove semi-volatile organic compounds (e.g. dioxins) and acid gases (SO_2, HCl, NO_x), followed by a baghouse filter.

Size-specific efficiencies in different studies ranged from over 99.9% at 10 nm and 100 nm diameter, to from < 90% to ca. 99.5% at the efficiency minimum of around 30 µm diameter. The implication of this highly effective removal was that UFP concentrations in incinerator stack gases, were frequently lower than those in the ambient air used in the combustion process (Jones and Harrison 2016). In a review of this same topic, Johnson (2016) comes to a similar conclusion.

The situation may be different where process exhaust contains semi-volatile compounds, which can condense to form UFP, as the exhaust gases cool and mix with ambient air. This is not generally the case with municipal incinerators which have a high burn-out of combustible gases, with both primary air and secondary air injection, as well as abatement plant containing activated carbon to capture such substances by adsorption. However arrestment devices on some other combustion plant may remove involatile particles at high temperatures, but still emit large concentration of UFP forming in the diluting exhaust gases.

Diesel particle filters fitted to road vehicles are typically highly efficient at removing involatile primary particles (> 99%; Yang et al., 2009). However, this does not preclude the formation of UFP after the filter as the exhaust gases cool and mix with the ambient air, and there is evidence of this process occurring (Pedata et al., 2015). Emissions can also occur during regeneration of the filter. The European emission test (referred to as the PMP protocol) is however designed to measure only involatile particles of >23nm diameter, and not to quantify the UFP formed in diluting exhaust gas. Information on DPF durability and long-term performance is limited.

High particulate emissions occur from petrol vehicles with gasoline direct injection engines if control measures are not put in place (Section 2.1.4). It is anticipated that vehicles with GDI will replace conventional port fuel injection engines in new car sales by 2020 (T&E, 2013). The Euro 6 vehicle emission regulations now limit particle number emissions for GDI cars type-approved for sale since 2015, in the same way as diesel cars. Manufacturers have tended to favour engine management approaches to control PN emissions, but gasoline particulate filters (GPFs) are far more effective and proven to reduce PN emissions by a factor of 10-1000 (SAE, 2014). A GPF is similar in principle to a DPF, but the device can be smaller since overall engine-out emissions are lower than a diesel engine, while higher exhaust temperatures prevent accumulation of particles and enable continuous regeneration. A GPF is also cheaper, being smaller and more compact than a DPF.

Some GDI vehicles will be equipped with Exhaust Gas Recirculation (EGR) to reduce emissions. In general, EGR is effective in reducing NO_x emissions, but its effect on PM can be variable and dependent on the EGR strategy. Relatively few studies have looked at the effect of EGR on PM emissions from GDI vehicles, but recent documented research in this area, has come from Southwest Research Institute in the U.S. GDI engines can tolerate a high level of EGR (Zhaoa et al., 1999). Research at SwRI showed that a GDI engine with high levels of EGR showed substantial reductions in PM mass emissions, but a much smaller reduction in PN emissions. It appeared that the more the PM mass emissions were reduced by EGR, the smaller the particles became, but there was little change in total particle number (Khalek et al., 2011).

Hedge et al. (2011) examined PM emissions from a small turbocharged GDI engine operating with different levels of EGR, to determine what strategies would be most effective at reducing engine-out particulate matter. Cooled external EGR was very effective in reducing PM mass by as much as 65%, but solid particle number trends were variable according to engine operation and sometimes showed an opposite trends to PM mass. On the other hand, internal EGR was much more effective than cooled external EGR, in reducing PM mass and solid particle number at light load. EGR increased engine-out volatile particles that are mainly formed during dilution and cooling of hot exhaust, but a three-way catalyst can be very effective in reducing the precursors to volatile particle formation.

Recent studies have found distinct particle size distributions in measurements made under airport descent paths (Riley et al., 2016). The UFPs observed were smaller than particles measured in other urban areas with a large traffic and background contribution, and PN concentrations were 3-5 times higher in aircraft descent paths as far as 5-10km away from the airports than in surrounding areas. Reports on the composition of jet engine exhaust show ultrafine particle size distributions that are dominated by soot particles in the range of 10-40 nm. Nucleation mode particles are also present in exhaust and form when sulfonated and organic gases in the concentrated plume condense and subsequently aggregate (Liati et al., 2014).

The PM emissions from aircraft engines consist of soot and volatile components consisting of sulphur and organic carbon (Kinsey et al., 2010), so emissions will be dependent on the sulphur content of aviation fuel. The current maximum permitted sulphur content of aviation turbine fuels is 3,000 ppm and is set by the U.K/U.S Defence Standard 91-91 and ASTM D1655 (ASTM, 2015). However, the mean fuel sulphur content in the United Kingdom and the United States, is significantly lower than the stipulated maximum value and is about 600-800ppm. The latest figure from UKPIA for aviation turbine fuel in 2015 as used in the NAEI is 798 ppm. This is significantly higher than the current 10ppm S limit for fuels used by road transport and Non-Road Mobile Machinery. There is currently no planned legislation to reduce the sulphur content. The European Aviation Safety Agency (EASA) carried out an assessment of the feasibility, costs and benefits of reducing the sulphur content of aviation fuel, taking into account of the effects on PM emissions (EASA, 2010). It concluded that a reduction from 600ppm to 10ppm levels was feasible and would result in a 0.07% decrease in aircraft landing-take-off (LTO) cycle PM–based mortality. Potential problems of reducing sulphur content were related to reduced lubricity to the engine and fuel systems, but this could be overcome by using fuel additives. It also concluded that reducing the sulphur content would enhance the life of the combustor and associated hardware.

The European Aviation Environmental Report (2016) provided a major review of the current and future environmental performance of the aviation sector in Europe (EASA, EEA and EUROCONTROL, 2016). The report is the first of its kind and was published by EASA, the European Environment Agency and EUROCONTROL. The report gives projections of volatile and non-volatile PM emissions (as well as other pollutants), from aircraft in Europe below 3,000 feet. These were derived from an aviation environmental impact model developed by EUROCONTROL and using aircraft emission indices from the ICAO Database and Manual (ICAO, 2008). In a base forecast scenario with advanced to low technology improvement rate, volatile PM emissions from aviation are forecast to increase by 50%, relative to 2005 levels by 2035 and non-volatile PM emissions by 11%. However, EASA is currently involved with ICAO in developing a new non-volatile PM standard for aircraft engines, which if agreed will be adopted into European legislation. Significant reductions in non-volatile PM (and NO_x) are expected to be achievable and are currently being demonstrated through the Advanced Low Emissions Combustion System (ALECSys) project, centred on lean burn combustion technology.

Another route to changing PM emissions from aviation may be through use of biofuels. Apart from cutting greenhouse gas emissions, if derived from a sustainable source, depending on feedstocks, biofuels contain no aromatics and sulphur leading to reduction in PM and SO_2 emissions relative to conventional aviation turbine fuel. At present, use of sustainable alternative fuels by the aviation sector, has been limited to a few airline demonstration flights, and the proportion of biofuels to total consumption by commercial aviation in Europe, was just 0.05% in 2009 (ICAO, 2008). However, the European Aviation Environmental Report (2016) assumes that these fuels will play a large role in reducing aviation greenhouse gas emissions in the coming decades. The European Advanced Biofuels Flightpath provides a roadmap to achieve an annual production rate of two million tonnes of sustainably produced biofuel for civil aviation by 2020 (ICAO, 2008).

The main biofuel pathways approved for aviation are:

i. Fuels from hydroprocessing of vegetable oils and animals fats such as Hydroprocessed Esters and Fatty Acids / Hydrotreated Vegetable Oils (HEFA/HVO);

ii. Fischer‑Tropsch fuels obtained from biomass;

iii. Synthetic iso‑paraffin fuels obtained from the conversion of sugars.

The first two fuels are approved for blending ratios up to 50% with conventional jet fuel. However, the HEFA/HVO fuels face competition in demand from other transport sectors, and regular production of aviation alternative fuels is projected to be very limited in the next few years, and thus it is unlikely that the roadmap 2020 target will be achieved. Although these biofuels would be largely free of aromatics and sulphur, tests will need to be carried out to fully understand the impact of these fuels on UFP emissions from aircraft engines, operating in different modes.

Domestic wood burning has been highlighted as an important source of $PM_{2.5}$ emissions (AQEG, 2017), although there is less information on the UFP content of the flue gases. A comprehensive report on the control of particle emissions from residential biomass combustion (TU Graz, 2011) concludes that electrostatic precipitators are the most promising approach. However, these have the disadvantages of high capital cost, requirement for an electricity supply, and limited efficacy for very small particles (due to low electric charging efficiencies). There are risks inherent in use of filters as blockage could lead to highly toxic fumes entering the house.

6.2 Chapter 6 References

AQEG. The Potential Air Quality Impacts from Biomass Combustion. Air Quality Expert Group, Defra, 2017.

ASTM. D1655 Standard Specification for Aviation Turbine Fuels, 2015. Accessible at: https://www.astm.org/Standards/D1655.htm,

EASA. Reduction of sulphur limits in aviation fuel standards. European Aviation Safety Agency Report EASA.2008/C11, 2010. Accessible at: https://www.easa.europa.eu/system/files/dfu/2009-SULPHUR-Reduction%20of%20sulphur%20limits%20in%20aviation%20fuel%20standards-Final%20Report.pdf

EASA, EEA and EUROCONTROL. European Aviation Environmental Report 2016. Accessible at: http://ec.europa.eu/transport/sites/transport/files/modes/air/aviation-strategy/documents/european-aviation-environmental-report-2016-72dpi.pdf

Hedge, M., Weber, P., Gingrich, J., Alger, T., Khalek, I. Effect of EGR on particle emissions from a GDI engine. SAE Int. J. Engines, 4, 650-666, 2011.

Hinds, W. C. Aerosol Technology. Wiley, New York, 1999.

ICAO. ICAO Committee on Aviation Environmental Protection Working Group 3 - Emissions Technical, 4th Meeting, 20-24th May 2008, Montreal, Canada. Working Paper: FOA3.0 Guidance Manual for Use By MODTF, CAEP8-WG3-WP08 (FOA3.0 Guidance Manual), 2008.

Johnson, D. R. Nanometer-sized emissions from municipal waste incinerators: A qualitative risk assessment. J. Hazard. Mater., 320, 67-79, 2016.

Jones, A. M., Harrison, R. M. Emission of ultrafine particles from the incineration of municipal solid waste; a review. Atmos. Environ., 140, 519-528, 2016.

Khalek, I. Particle Emissions from Direct Injection Gasoline Engines. Technology Today, 2011. Accessible at: http://www.swri.org/3pubs/ttoday/Summer11/PDFs/ParticleEmissions.pdf

Kinsey, J. S., Dong, Y., Williams, D. C, Logan, R. Physical characterization of the fine particle emissions from commercial aircraft engines during the Aircraft Particle Emissions experiment (APEX) 1-3. Atmos. Environ., 44, 2147-2156, 2010.

Liati, A., Brem, B. T., Durdina, L., Vögtli, M., Arroyo Rojas Dasilva, Y., Dimopoulos Eggenschwiler, P., Wang, J. Electron microscopic study of soot particulate matter emissions from aircraft turbine engines. Environ. Sci. Technol., 48, 10975-10983, 2014.

Pedata, P., Stoeger T., Zimmerman, R., Peters, A., Oberdorster, G., and D'Anna, A. Are we forgetting the smallest sub-10 µm combustion-generated particles? Partic. Fibre Toxicol. 12, 34, 2015.

Riley, E. A., Gould, T., Hartin, K., Fruin, S. A., Simpson, C. D., Yost, M. G., Larson, T. Ultrafine particle size as a tracer for aircraft turbine emissions. Atmos. Environ., 139, 20-29, 2016.

SAE. Attacking GDI engine particulate emissions. SAE International, 2014. http://articles.sae.org/13624/

T&E. Particle emissions from petrol cars. Transport & Environment Briefing, November, 2013. Accessible at: http://www.transportenvironment.org/sites/te/files/publications/GDI%20Briefing_final_T&E.pdf

The European Aviation Environmental Report. European Environment Agency, 2016. Accessible at: https://ec.europa.eu/transport/sites/transport/files/european-aviation-environmental-report-2016-72dpi.pdf

TU Graz. Survey on the present state of particle precipitation devices for residential biomass combustion with a nominal capacity up to 50 kW in IEA Bioenergy Task32 member countries. Graz University of Technology, 2011. Accessible at: http://www.bios-bioenergy.at/uploads/media/Filter-study-IEA-Dez-2011.pdf

Yang, J., Stewart, M., Maupin. G., Herling, D., Zelenyuk, A. Single wall diesel particulate filter (DPF) filtration efficiency studies using laboratory generated particles. Chem. Eng. Sci, 64, 1625-1634, 2009.

Zhaoa, F., Laia, M.-C., Harrington, D. L. Automotive spark-ignited direct-injection gasoline engines. Prog. Energy Combust. Sci., 25, 437-562, 1999.

7 Conclusions and Recommendations

There are two main sources of UFP in the atmosphere of the United Kingdom; direct primary emissions and secondary atmospheric formation. Both the emissions inventories and measurements of atmospheric concentrations show that the major sources are related to combustion of fuels and especially those containing sulphur. In the urban atmosphere, emissions from road traffic and particularly from diesel vehicles dominate the measured concentrations. The UFP concentrations correlate more closely with other traffic-generated pollutants, such as NO_x and black carbon rather than the particulate matter mass metrics $PM_{2.5}$ and PM_{10}. Because of this association with road traffic, roadside concentrations are typically higher than those in the urban background, which in turn exceed those in rural areas. Other primary sources of significance include coastal shipping and aviation. The second major source category is comprised of particles formed within the atmosphere from the oxidation of gases such as sulphur dioxide and VOC. This process, referred to as regional nucleation, does not appear to be a major contributor to UK concentrations, with one study in London suggesting that it accounts for about 8% of the annually averaged UFP concentration. This measurement data show that traffic-generated UFP can shrink in size as they move away from their source of emission, but over greater distances UFP tend to grow in size and hence long-range transport is not an appreciable source of UFP in the UK atmosphere when compared to $PM_{2.5}$.

Airborne concentrations of UFP in the UK have declined sharply in recent years apparently for two major reasons. Firstly, a substantial reduction in the sulphur content of motor fuels in the period 2004-2008 led to a large reduction in emissions from road traffic, and more recently, the requirement to fit diesel particle filters to new diesel vehicles and to gasoline-direct injection engines, will also have contributed to a reduction in emissions. Future trends in UFP concentrations are uncertain, with knowledge of some sectors better than others. Determinants are likely to include activity levels, technology changes and the sulphur content of fuels. Current projections suggest further reductions in emissions from road traffic, declining emissions from shipping due to reductions in the sulphur content of marine fuels, but an increased contribution from aviation emissions for which fuels of relatively high sulphur content are still permitted.

Other industrial and large-scale combustion sources have not been studied in such depth. Incinerators have been the subject of several studies and there is no current evidence of a significant contribution of emissions from incinerators to airborne concentrations. Currently there is also no evidence of significant emissions of manufactured nanomaterials to the atmosphere. Research from mainland Europe and North America indicates that aviation emissions can have an appreciable impact upon particle number concentrations within tens of kilometres of major airports. There is also a concern that growing emissions from residential wood burning may be impacting upon airborne concentrations. Although regional nucleation is currently only a minor source of UFP in the UK atmosphere, it seems very possible that this will increase in future as concentrations of primary particles, which themselves inhibit new particle formation, decline with stricter regulations on $PM_{2.5}$ and PM_{10} emissions.

It is challenging to measure mass concentrations of UFP in the atmosphere as these are very low, but quantification through measurement of the particle number concentration is relatively straightforward. This is accomplished with Condensation Particle Counters which also form part of particle-sizing instrumentation, which reveals the size distribution of particles in the ultrafine range and larger. There are only four sites (and three currently operational) for measurement of UFP concentrations in the UK atmosphere so information on spatial distributions is very sparse. UFP concentrations are typically highly correlated with other traffic-generated pollutants such as NO_x and black carbon. However, it would be most inadvisable to regard these pollutants as surrogates for UFP, as quantitative relationships between the pollutants are liable to change with time as vehicle technologies and fuel quality change.

Numerical models exist to predict UFP concentrations and their spatial distribution, but these have yet to be applied to the UK. Receptor modelling which uses measured airborne particle size distribution data, has proved effective in elucidating sources of particles in the UK atmosphere, but does not provide insights into the spatial distribution. There are no direct standards for UFP emissions, although the methods specified for type approval testing of diesel and gasoline direct-injection engine vehicles, does provide a limit to the emission of involatile particles of > 23 nm diameter. Some of the abatement technologies such as baghouse filters designed to reduce emissions of $PM_{2.5}$, PM_{10} and total suspended particulates from industrial sources, are also efficient at removing UFP.

Other technologies such as electrostatic precipitators, are less efficient for particles in the UFP size range. Filters fitted to diesel and gasoline-direct injection engines are highly efficient at removing UFP when new, but there is limited information on their durability and performance after long-term use. Control of UFP emissions from domestic and other small scale biomass combustion presents a particular problem. Devices based upon electrostatic precipitation have been developed to reduce PM_{10} emissions from domestic wood burning stoves. These are of relatively high capital cost, comparable to that of the stove itself, and require a supply of electricity. Their efficiency for abatement of UFP is likely to be very limited, due to the low electric charging efficiencies of very small particles. They also allow passage of vapour phase constituents, known to oxidise rapidly in the atmosphere to form secondary particles. The use of particle filters similar to those used on diesel vehicles, is considered inadvisable due to concerns over progressive blockage leading to toxic fumes entering the home.

There are currently no air quality standards for UFP in the UK atmosphere and the WHO has not recommended an air quality guideline, although the matter remains under consideration. Authoritative reviews of the health effects of UFP exposure have concluded that although some studies are suggestive of adverse health effects, there is currently insufficient evidence to justify setting a standard for UFP separate from those for $PM_{2.5}$ and PM_{10}. This being the case, it is difficult at present to come to a firm view as to the significance of UFP as a pollutant in the UK atmosphere. However, until such matters are resolved through further research, it will be important to continue to monitor and evaluate the concentrations of UFP in the UK, both to understand better their sources and dynamics and to provide a database for use in health effects research.

7.1 Recommendations

The Group notes that current UK continuous measurements of UFP concentrations are currently only made in the south east at just one roadside, one urban background and one rural site, whilst a site in Birmingham is due to recommence monitoring. We anticipate the main sources of UFP will be similar across the UK however this needs to be verified, therefore the Group recommends the establishment of further monitoring sites for particle number, extending to particle size distributions at a later date, at sites outside the south-east of the country.

Additionally, given the predicted growth in emissions from aviation, it would be prudent to establish a permanent site, monitoring particle number concentration and size distribution in the vicinity of a major airport. There is also a lack of knowledge of the impact of shipping emissions in coastal areas, and there is a strong case for precautionary measurements. Since the lack of long-term datasets is a major limitation on health effects studies, it is important to continue monitoring activities well into the future. Knowledge of the chemical composition of atmospheric UFP derives largely from samples collected overseas and there is a need for analyses of UK samples. Further work is needed to develop reliable numerical models capable of predicting airborne concentrations of UPF.

8 Glossary of Technical Terms

Aerodynamic diameter: The diameter of a particle with the same falling speed as a spherical particle of unit density of that size

CLRTAP: International Convention on the Long-Range Transport of Air Pollutants

Condensation Particle Counter (CPC): A device which grows particles to larger sizes so that their concentration in air can be determined by light scattering

Coarse particles: Particles of aerodynamic diameter between 2.5 and 10 micrometres

Emissions inventory: A collection of quantitative information upon the sources of emissions of a pollutant

Fine particles: Usually used to refer to $PM_{2.5}$ which is particles determined by mass which pass an inlet with a 50% cut-off efficiency at 2.5 micrometres aerodynamic diameter

Micrometre: One millionth (1 in 10^6) of a metre

Mobility diameter: The diameter of a particle measured by determining the rate of movement of an electrically charged particle in an electric field

Nanometre: One billionth (1 in 10^9) of a metre

Nanoparticles: An alternative term for ultrafine particles

$PM_{2.5}$: Particles measured by mass which pass through an inlet with an efficiency of 50% for removing particles of 2.5 micrometres aerodynamic diameter

PM_{10}: Particles measured by mass which pass through an inlet with an efficiency of 50% for removing particles of 10 micrometres aerodynamic diameter

Primary pollutant: An air pollutant emitted to the atmosphere from a source (*c.f.* secondary pollutant

Scanning Mobility Particle Sizer: An instrument which measures particle sizes on the basis of the rate of movement of electrically charged particles in an electric field

Secondary pollutant: An air pollutant formed in the atmosphere by transformation of a gas phase pollutant

Ultrafine particles: Particles of solid or liquid matter with one dimension less than 100 nanometres