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Processes affecting concentrations of fine particulate matter ($PM_{2.5}$) in the UK atmosphere

Roy M. Harrison [a,c,*], Duncan Laxen [b], Stephen Moorcroft [b], Kieran Laxen [b]

[a] Division of Environmental Health & Risk Management, School of Geography, Earth & Environmental Sciences, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK
[b] Air Quality Consultants, 23 Coldharbour Road, Bristol BS6 7JT, UK
[c] Centre of Excellence in Environmental Studies, King Abdulaziz University, PO Box 80203, Jeddah (21589), Saudi Arabia

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ABSTRACT

$PM_{2.5}$ is now subject to a limit value and exposure-reduction targets across the European Union. This has led to a rapid expansion in $PM_{2.5}$ monitoring across Europe and this paper reviews data collected in the United Kingdom in 2009. The expected gradient between rural, urban background and roadside sites is observed, although the roadside increment is generally rather small except for heavily trafficked street canyon locations. $PM_{2.5}$:PM_{10} ratios decline from around 0.8 in southeast England to below 0.6 in Scotland consistent with a higher contribution of secondary particulate matter in southeast England. Average diurnal profiles of $PM_{2.5}$ differ around the UK but have a common feature in a nocturnal minimum and a peak during the morning rush hour. Central and southern UK sites also show an evening peak following a concentration reduction during the mid afternoon which is not seen at northern UK sites and is attributed to evaporation of semi-volatile components, particularly ammonium nitrate. Concentrations of $PM_{2.5}$ are typically highest in the winter months and lowest in the mid-summer consistent with better mixing and volatilisation of semi-volatile components in the warmer months of the year. Directional analysis shows a stronger association of $PM_{2.5}$ with easterly winds associated with air masses from the European mainland than with the direction of local traffic sources.

1. Introduction

Particulate matter (PM) in ambient air is a complex mixture of organic and inorganic substances. It is derived from a wide variety of sources, both natural and anthropogenic, and displays a range of physical and chemical properties. Particles are termed either ‘primary’, where they are emitted directly into the atmosphere, or ‘secondary’, where they are formed in the atmosphere by reactions between gases.

During the late 1980s and early 1990s the results of epidemiological studies in the USA identified PM less than 10 μm diameter (PM_{10}) as a key pollutant metric related to acute (short-term) and chronic (long-term) health effects. More recently, the growing body of research has pointed towards the smaller particles within PM_{10} as being the most significant in relation to health outcomes. In particular, attention has focused on PM less than 2.5 μm diameter ($PM_{2.5}$) as a metric more closely associated with adverse health effects than PM_{10}, although there is still considerable debate as to whether it is actually the ultrafine fraction ($PM_{0.1}$), or indeed a non-mass metric, e.g. particle number, that is primarily responsible for the effects. A number of studies have also identified long-term exposure to PM as being more significant than the short-term (daily) exposure to higher levels that had first been linked to health effects (Pope and Dockery, 2006). These long-term effect studies have formed the basis for calculation of health outcomes from exposure to PM in the UK and Europe, which are not insubstantial (COMEAP, 2010).

The emphasis has thus shifted from the PM_{10} metric to $PM_{2.5}$, although it is recognised that there are also health effects associated with exposure to the coarser particles within PM_{10}, termed either $PM_{2.5-10}$ or PM_{coarse} (USEPA, 2009). A recent paper (Liu and Harrison, 2011) has reviewed current knowledge of PM_{coarse} behaviour in the UK atmosphere. Until recently, however, the UK monitoring network has included relatively few measurements of $PM_{2.5}$, and the data are still limited in terms of duration and geographical coverage.

Legislation to control exposure to PM developed during the 1990s. The focus was initially on controlling exposure to short-lived peak concentrations, as the epidemiological evidence at the time indicated that health effects were primarily associated with these peaks. A 24-h standard for PM_{10} of 50 μg m^{-3} was therefore introduced by both the European Union and the UK government.

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* Corresponding author. Tel.: +44 121 414 3494; fax: +44 121 414 3709.
E-mail address: r.m.harrison@bham.ac.uk (R.M. Harrison).

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The use of such air quality standards has meant that control strategies have primarily been aimed at reducing pollutant concentrations at so-called ‘hot spots’, where monitoring has shown the standard can be exceeded. These hot spots have most commonly been identified alongside busy roads, especially in major urban areas.

The re-orientation of attention towards $PM_{2.5}$, coupled with the evidence that long-term concentrations are more significant in health terms than short-term peaks, has led to changes in legislation. The UK introduced the idea of a $PM_{2.5}$ standard in its Air Quality Strategy update (Defra, 2007). This was followed shortly after by the EU introducing its Clean Air for Europe (CAFE) Directive in 2008, which also included standards for $PM_{2.5}$ (Official Journal, 2008). In both cases a new approach was introduced in recognition of the absence of a threshold for exposure to PM. This new approach involves a reduction in the overall exposure of the urban population to $PM_{2.5}$, based on the concept that greater benefits can be obtained from this general reduction in exposure than by a policy aimed at reducing exposure at hot spots (Laxen and Moorcroft, 2005). Under the CAFE directive, exposure to $PM_{2.5}$ in Europe will be constrained principally by the exposure-reduction target that will involve a reduction in the 3-year average urban background concentrations of between 0% and 20% between 2010 and 2020. The precise value for the reduction to be applied in the UK has yet to be announced, but is expected to be 10% or 15%. This is supplemented by an annual mean target value of 25 $\mu g\ m^{-3}$ (to be met in 2010) a limit value of 25 $\mu g\ m^{-3}$ (to be met in 2015) and a 3-year average urban background concentration of 20 $\mu g\ m^{-3}$ (to be met by 2015). The limit value is mandatory, while the target is non-mandatory.

In order to implement the new legislation, a network of $PM_{2.5}$ monitoring sites has been established across the UK. This paper examines the $PM_{2.5}$ results for 2009 in order to provide a better understanding of the implications of the processes affecting concentrations of $PM_{2.5}$ in the UK atmosphere. This understanding is crucial to the development of effective strategies to meet the obligations of the new standards.

2. Measurement of $PM_{2.5}$

The reference methods for the determination of concentrations of PM_{10} and $PM_{2.5}$ for comparison with the limit values are described in European Standards EN12341 and EN14907 respectively (CEN, 1999, 2005). The approaches are founded on filter-based gravimetric measurements, in which PM is sampled by drawing air at ambient temperature and pressure through a filter. The filter is subsequently weighed in a laboratory, after conditioning at a specified temperature and humidity, to determine the PM mass. Any losses of semi-volatile PM, or any artefacts associated with particle-bound water are deemed to be zero by convention.

For a variety of practical reasons, the European reference samplers (or other filter-based gravimetric samplers) have not been widely used in the UK. Their use is labour-intensive (requiring pre- and post-sampling weighing of filters) and they only provide information on 24-h mean PM concentrations. In addition, they cannot provide real-time information on PM concentrations to the public. The FDMS (Filter Dynamics Measurement System) analyser is an airborne PM monitor based on the TEOM (Tapered Element Oscillating Microbalance) technology, but with the ability to measure both ‘core’ and volatile fractions of particles (Green et al., 2009; Harrison et al., 2006). The analyser draws ambient air through a size-selective inlet (PM_{10} or $PM_{2.5}$). This air then passes through a drier to remove water, before entering the sensor unit where the PM is collected onto a filter held at 30 °C, and weighed. The analyser samples in this ‘base cycle’ mode for 6 min, during which there will be losses of volatile particles. The sample flow is then switched, so that it passes through a cooled chamber held at 4 °C, and then through a filter which removes all of the PM in the airstream. This cooled, scrubbed air is then returned to the sensor unit. During this ‘reference’ or ‘purge’ cycle (which also runs for 6 min) volatile particles will continue to evaporate from the sensor unit filter, such that the average PM concentration measured during the purge cycle will normally be negative. This reference, or purge cycle concentration provides an estimate for the volatile particle concentration (designated as V_{10} or $V_{2.5}$) that is being lost, which can then be added onto the base concentration to give an overall PM mass concentration. The total PM concentration for each 12 min cycle is thus equal to the base concentration minus the purge concentration (the latter is normally a negative value and so the purge concentration is in effect added). It should be recognised that the loss of volatile particles occurs relatively slowly, thus the loss during any individual cycle will include volatile material collected in previous cycles. This is manifest as a time shift of a few hours in the purge concentration. The FDMS analyser has now been widely deployed into the UK networks to measure both PM_{10} and $PM_{2.5}$ concentrations.

3. UK measurements in 2009 and analysis

The $PM_{2.5}$ data analysed in this paper are all taken from measurements made using FDMS analysers, unless otherwise stated. Hourly data for UK sites have been obtained for sites that form part of the UK Automatic Urban and Rural Network (AURN), the London Network and the Northern Ireland Air Quality Network (available at: uk-air.defra.gov.uk, www.londonair.org.uk and www.airqualityni.co.uk/). Quality assurance protocols are described by AEAT (2009). Annual means have been calculated from the hourly data sets. Valid annual means have been taken to be those with >90% data capture. In some instances the criteria have been relaxed to a data capture >75%. The following analyses are based on hourly-mean $PM_{2.5}$ concentrations measured in 2009 at 37 urban background sites (27 with data capture >90%), seven roadside/kerbside sites, three industrial sites and one rural background site. Reference is also made to nitrate concentrations measured using a Rupprecht and Patashnick 8400N Nitrate Analyser with a $PM_{2.5}$ sampling inlet (Rattigan et al., 2006).

Certain of the analyses have been carried out with the Openair software package (Carslaw and Ropkins, 2011) using the R language (R Development Core Team, 2011). The temporal plots of concentrations averaged by hour-of-the-day have been prepared using local time, i.e. they take account of the change from winter (GMT) to summer (BST) time. The plots show average concentrations for the hour beginning, i.e. the value for 23:00 h is the average over the period 23:00–24:00 h. Wind data from eight meteorological stations have been used in this analysis (listed in the Supplementary Information). Polar plots show the measured concentrations by colour shading as a function of wind direction and wind speed. The wind speed increases from zero at the centre of the plot, to typically around 15 $m\ s^{-1}$ at the edge. Polar annulus plots show concentrations as a function of both wind direction and time-of-day. The time-of-day runs from 00:00–01:00 h on the inside of the circle through the day to 23:00–24:00 h on the outside of the circle.

4. Discussion of measured data

During 2009 results were only available for one rural site, Auchencorth Moss, which is located to the south of Edinburgh in Scotland. This recorded the lowest annual mean $PM_{2.5}$

concentration of all UK sites in 2009, at 3.4 μg m^{-3}. This cannot be taken to be representative of UK rural background sites. This is evident from the 12-month mean over the period August 2009–2010 of 10.4 μg m^{-3} at Harwell, a rural site in southern England.

Annual mean concentrations in 2009 at the 37 urban background sites are set out in Table S1 (in Supplementary Information). The majority of the concentrations fall in the 12–14 μg m^{-3} range. The highest concentrations in 2009 were 17.6, 15.5 and 14.8 μg m^{-3} respectively at London Eltham in East London, Lisburn in Northern Ireland and Stoke-on-Trent Centre in the Midlands. The lowest was 8.5 μg m^{-3} in Edinburgh, Scotland. The presence of the highest concentration in London is not unexpected, given that the site is in the largest UK urban area. The high concentration at the Lisburn site is believed to be due to the continued use of domestic solid fuel in the area around this site (see also discussion below). The reason for the high annual mean concentration at the Stoke-on-Trent Centre site remains unclear. These concentrations lie well within the range of annual means typical of north western Europe, and scale according to site type in the same way (Querol et al., 2004; Putaud et al., 2010).

The urban enhancement over the regional (rural) background cannot be derived rigorously, due to the paucity of rural data. However, the Edinburgh urban background site recorded an annual mean concentration that was around 5 μg m^{-3} higher than that measured at the nearby Auchencorth Moss rural site, while the London Eltham concentration was around 7 μg m^{-3} higher than the regional background (using the result for the rural site at Harwell), although more typically the urban background sites in London were around 3–6 μg m^{-3} above concentration at Harwell.

Results are only available for seven roadside/kerbside sites in 2009, five of which were in London (Table S2). In the UK, kerbside is defined as within 1 m of the kerb, while roadside is between 1 m and 10 m from the kerb. The results for roadside and background sites in London are shown as box-plots in Fig. 1. The roadside sites had annual mean concentrations that were on average 0.9 μg m^{-3} higher than the background. In addition to this general comparison for roadside sites in London three roadside/kerbside sites have been paired with a nearby background site to allow the roadside increment to be calculated:

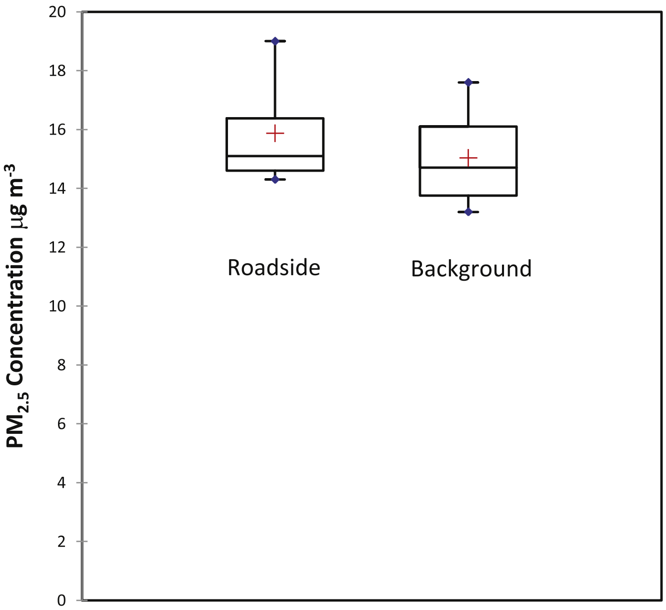

Fig. 1. Summary of $PM_{2.5}$ concentrations (μg m^{-3}) in 2009, at roadside (n = 4) and urban background (n = 6) sites in London with >90% data capture. The box-and-whisker plots are made up as follows: The box shows the median and the upper and lower quartiles, with the mean shown by the cross. The lines extending from the box represent the upper and lower bounds of the data for data points that fall within the range of the upper interquartile + 1.5 times the interquartile range and the lower interquartile − 1.5 times the interquartile range.

- London Marylebone Road (kerbside) paired with London North Kensington;
- Birmingham Tyburn Roadside paired with Birmingham Tyburn; and
- Glasgow Kerbside paired with Glasgow Centre.

The results have been examined for matched periods and the mean roadside enhancements calculated as 8.1 μg m^{-3}, 1.2 μg m^{-3} and 7.2 μg m^{-3} respectively. The London Marylebone Road and Glasgow Kerbside sites are on the edge of busy canyon-like roads in built up areas, with the monitors 1 m from the kerb, while the Birmingham Tyburn Roadside site is alongside a wide dual-carriageway road in a mainly residential area of Birmingham, and around 7 m from the kerb. The greater distance of the Birmingham Tyburn Roadside site from the carriageway and the more open setting, together with the lower traffic flow, will account for the lower road contribution to $PM_{2.5}$ at this site, which is more consistent with the general roadside increment apparent in London (Fig. 1). Further data analyses from the Marylebone Road site are available in Charron and Harrison (2005), Jones and Harrison (2006) and Harrison et al. (2011), and the pollution climate of the North Kensington site is described by Bigi and Harrison (2010).

Annual mean concentrations are also available for three industrial sites in 2009, with values of 8.6 μg m^{-3} at Grangemouth (a site near an oil refinery), 14.0 μg m^{-3} at Salford Eccles (a site in a general industrial area within Greater Manchester) and 8.1 μg m^{-3} at Port Talbot (a site near to a major steelworks in Wales (Dall'Osto et al., 2008)). The low concentrations at two sites in relation to the typical urban background values, which are in the range 12–14 μg m^{-3}, will be due to these sites being in parts of the UK with lower regional background concentrations, and to the industrial areas being in a generally rural setting. The Salford Eccles site is within the Greater Manchester urban area, and this will account in large part for the higher concentration. The results indicate that industrial sources do not make a major contribution to local annual mean $PM_{2.5}$ concentrations, although this observation is based on a limited dataset for industrial sites.

A detailed review has recently been carried out of monitoring around the steelworks complex at Port Talbot in Wales (Hayes and Chatterton, 2009). The focus was on PM_{10}, but some $PM_{2.5}$ monitoring was also reported. The report included polar plots for a monitoring site around 300 m to the northeast of the steelworks, which showed that while PM_{10} concentrations were elevated to above 80 μg m^{-3} during periods with winds >5 m s^{-1} blowing from the south-southwest, i.e. from the steelworks, the $PM_{2.5}$ concentrations were only elevated to around 15 μg m^{-3} under these conditions. The steelworks is thus a more significant source of coarse PM, i.e. $PM_{2.5-10}$ than of $PM_{2.5}$. Coarse particle data from UK sites are analysed by Liu and Harrison (2011).

4.1. Ratios between $PM_{2.5}$ and PM_{10}

Reliable ratios can only be derived from measurements made with reference equivalent instruments. This essentially confines the examination of $PM_{2.5}$–PM_{10} ratios to results from FDMS instruments. During 2009 there were 23 network sites where both $PM_{2.5}$ and PM_{10} were monitored and data capture was >75% (13 of the sites had >90% data capture for both pollutants – it was considered helpful to extend the number of sites by relaxing the criterion to

>75% data capture). Average $PM_{2.5}$:PM_{10} ratios for each site were derived as the mean of the hourly ratios, to ensure matched periods were used.

The results are summarised as box-and-whisker plots for urban background, roadside and industrial sites in Fig. S1. The mean values are fairly similar, but there is much greater variability in the industrial sites and a suggestion that the ratio is higher for roadside sites. However, as shown below the latter suggestion is not borne out when examining the results in more detail.

The $PM_{2.5}$:PM_{10} ratios at urban background sites in 2009 are shown across the UK in Fig. S2. There is no immediately clear pattern, although the highest ratio is in central London, while the lowest is in Glasgow Centre. In a further analysis, the results have been plotted as a function of distance from Dover (Fig. S3) (Dover is in the extreme south-eastern corner of the UK and was selected as it is known that background concentrations decline from the southeast towards the northwest of the UK (Laxen et al., 2010)). There is a statistically significant relationship ($p = 0.15$), with ratios declining from around 0.8 in Southeast England to below 0.6 in Scotland. The fine fraction of PM thus becomes more important on moving towards continental Europe, which is consistent with secondary PM being more significant in southeast England, as noted in earlier studies (AQEG, 2005). The scatter around the line will relate in part to the varying contributions of sea salt and resuspended dust from agricultural and construction activities, as these sources will have a more prominent coarse PM component, tending to reduce the $PM_{2.5}$:PM_{10} ratio. $PM_{2.5}$:PM_{10} ratios across Europe generally lie within the range 0.51–0.90 without any clear relationship to the type of site or its location in Europe (Putaud et al., 2010).

Also shown in Fig. S3 are the ratios at roadside sites, plotted against distance from Dover. There are only three sites, but there is no evidence that the ratio for roadside sites differs systematically from the urban background pattern. This implies there is no particular enhancement of either the coarse or the fine fraction of PM at roadside sites. Industrial sites show much greater variability in the $PM_{2.5}$:PM_{10} ratios, which will relate to the differing proportions of fine and coarse PM being emitted from the industrial sources. The very low ratio in Fig. S3 is for the site at Port Talbot, near to the major steelworks complex, which shows that coarse PM is a major component of the emission from these works (see above).

4.2. Relationship of $PM_{2.5}$ to other pollutants

There are a number of sites in the national network measuring a range of pollutants in addition to $PM_{2.5}$. The correlations between $PM_{2.5}$ and these pollutants have been derived using hourly data for each site with >75% data capture in 2009. The correlation coefficients of the hourly-mean data are summarised as box-and-whisker plots in Fig. S4, separated into background (mostly urban background), roadside and industrial sites.

There is a strong consistency in the correlation coefficients at the different sites, especially in the case of the urban background sites. The highest correlation at all sites is unsurprisingly between $PM_{2.5}$ and PM_{10} (correlation coefficients typically 0.8–0.9) (this is in large part because $PM_{2.5}$ accounts for a major proportion of PM_{10}). $V_{2.5}$ concentrations are also highly correlated with $PM_{2.5}$ (correlation coefficient typically 0.7–0.8). $V_{2.5}$ is a measure of the volatile $PM_{2.5}$, derived from FDMS monitors as the 'purge' concentration. The correlation with V_{10} is not as strong (correlation coefficient typically 0.4–0.7), suggesting that the volatile component of PM_{10} (V_{10}) is somewhat different to that associated with $PM_{2.5}$. The NO_x and NO_2 concentrations are also fairly highly correlated with $PM_{2.5}$ (correlation coefficient 0.5–0.6), at all site types. The correlation with CO is weaker at background and industrial sites (correlation coefficient ~0.4), but is similar to that for NO_x and NO_2 at the one roadside site for which CO results are available (Marylebone Road in London). The correlation with SO_2 is lower still at background and industrial sites (correlation coefficient ~0.3), but is much higher at the one roadside site (which is probably due to the SO_2 associated with the residual sulphur in vehicle fuels). The correlation with O_3 is negative (correlation coefficient ~−0.4), thus lower O_3 concentrations are associated with higher $PM_{2.5}$ concentrations. This will be due to increased concentrations of $PM_{2.5}$ being associated with increased NO_x, which leads to lower O_3 concentrations. There may be short periods when $PM_{2.5}$ and O_3 are positively correlated during photochemical episodes, when both $PM_{2.5}$ and O_3 are generated by the photochemical activity, but on an annual basis these are swamped by the negative correlation.

4.3. Temporal and spatial patterns of $PM_{2.5}$

Temporal and spatial patterns of $PM_{2.5}$ have been examined using data from FDMS monitors for sites with >75% data capture. The diurnal cycle of $PM_{2.5}$ at urban background sites during 2009 is summarised in Fig. 2 for four geographic areas of the UK (delineation of the four areas and the sites within each area are shown in Fig. S5 in Supplementary Information). All sites show a dip in concentrations in the early morning, between 04:00–06:00 h, then a steep rise to a peak between 07:00–10:00 h. At all sites, apart from those in northern UK, there is then a drop to give the lowest concentrations of the day between about 13:00–17:00 h, before rising to the highest peak of the day between about 20:00–23:00 h. The pattern at northern UK sites is distinctly different, as there is no clear drop during the afternoon, and no evidence of a late evening peak. The diurnal range is, however, relatively limited, averaging around 2.75 $\mu g\ m^{-3}$ at northern UK sites, 2.25 $\mu g\ m^{-3}$ at central UK sites, 2.75 $\mu g\ m^{-3}$ at southern UK sites and 3.25 $\mu g\ m^{-3}$ in London (values quoted to the nearest 0.25 $\mu g\ m^{-3}$). A separate examination of the diurnal pattern at a site measuring $PM_{2.5}$ with a beta attenuation monitor (results not shown) has confirmed this pattern and shows that it is not an artefact of the FDMS analyser. The diurnal pattern over the whole year is retained in all four areas when separated into winter and summer periods (October–March and April–September respectively). Fig. 3 shows the winter/summer results for the southern UK region. The patterns are broadly similar to the annual pattern (*cf.* Fig. 2, 'Southern UK'), although in the summer the afternoon dip is of longer duration, while in winter the evening peak is more prominent. This first observation is consistent with a greater loss of volatile particles from ambient $PM_{2.5}$ during the longer daylight hours in summer months, while the second observation may relate to greater domestic heating emissions during the early part of the night in winter, and greater atmospheric stability trapping primary pollutants.

The pattern during the first half of the day is similar to that seen for most pollutants that are related to typical urban emission sources. The lowest concentrations occur in the early hours, when emissions are at their lowest, with a rise to a peak between 07:00–10:00 h. This peak is usually ascribed to the morning rush-hour traffic, although domestic emissions will also increase at this time. The subsequent decline in the peak is normally related to the greater atmospheric turbulence during the day, as well as to a decline in both traffic flow and domestic heating emissions. Notably for $PM_{2.5}$, this decline continues during much of the daytime to give concentrations in the middle of the afternoon (13:00–17:00 h) that are lower than those in the early morning. This is not expected and is not seen in the results for nitrogen oxides (AQEG, 2004). The most plausible explanation for the afternoon dip is the loss of semi-volatile PM (principally nitrate, with some organic compounds) from the ambient PM, as a result of the higher temperatures during this part of the day.

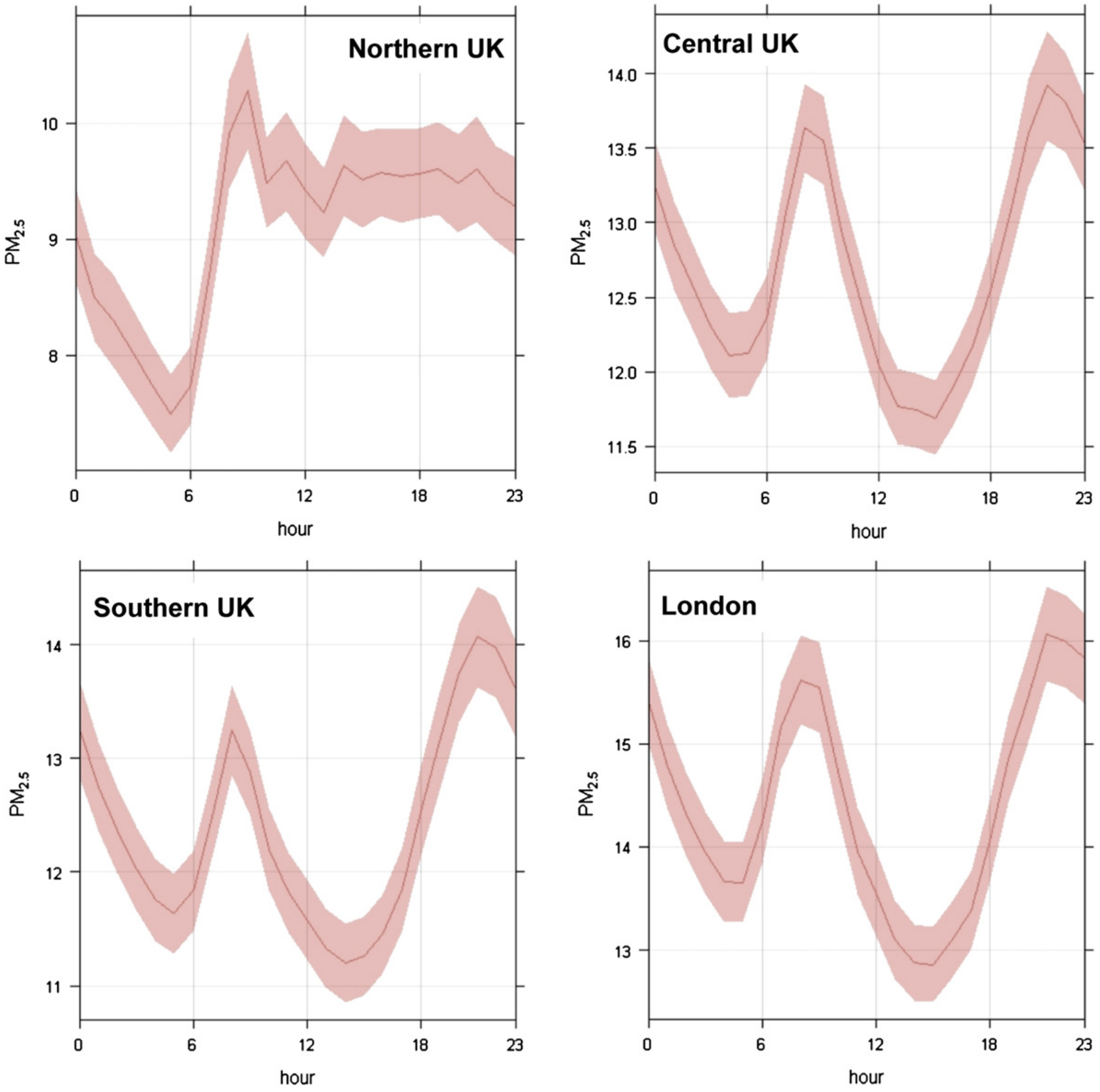

Fig. 2. Variation of $PM_{2.5}$ concentrations (μg m^{-3}) at urban background sites by hour-of-the-day in 2009, at sites in 'Northern UK' ($n = 8$), 'Central UK' ($n = 17$), 'Southern UK' ($n = 8$) and 'London' ($n = 8$). The shading represents the 95% confidence interval. Note different scales.

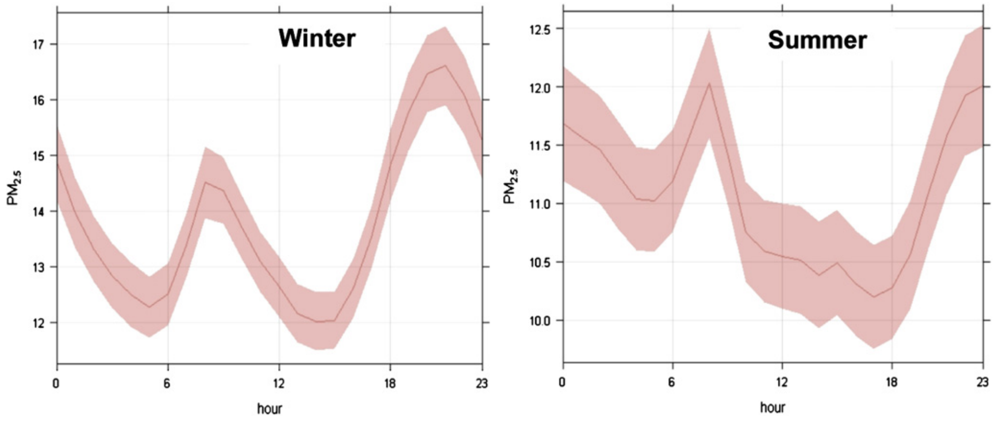

Fig. 3. Variation of $PM_{2.5}$ concentrations (μg m^{-3}) at urban background sites by hour-of-the-day in 2009 at 'Southern UK' sites ($n = 8$) in winter and summer. The shading represents the 95% confidence interval. Note different scales.

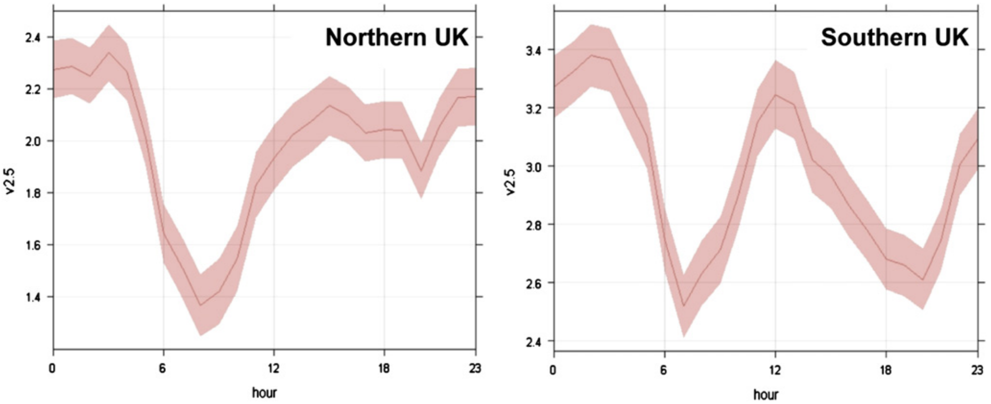

Fig. 4. Variation of volatile $PM_{2.5}$ concentrations ($V_{2.5}$ in μg m^{-3}) at urban background sites by hour-of-the-day in 2009, at sites in 'Northern UK' ($n = 8$) and 'Southern UK' ($n = 8$). The shading represents the 95% confidence interval. Note different scales.

If this dip were due to a loss of semi-volatile PM, then it would be expected that volatile $PM_{2.5}$ ($V_{2.5}$), measured as the purge concentration in the FDMS analysers (see above), would decline during the afternoon, as the ambient particles would have lost their semi-volatile material before they enter the analyser. However, the $V_{2.5}$ results do not show this, as shown in Fig. 4, which presents the average diurnal profile for $V_{2.5}$ at southern UK and northern UK sites (the central UK $V_{2.5}$ results are similar to those in southern UK and are not shown). Both plots show high $V_{2.5}$ concentrations in the early hours of the day, 00:00–04:00 h, and a minimum during the time of the morning $PM_{2.5}$ peak (*cf.* Figs. 4 and 2). During the middle of the day, when $PM_{2.5}$ is at its lowest, $V_{2.5}$ is higher. This would suggest that the purge measurement from the FDMS analyser is not directly related to volatile $PM_{2.5}$. However, it is worth noting that the $V_{2.5}$ plot for southern UK sites is similar in shape to that for $PM_{2.5}$ (*cf.* Fig. 4, 'Southern UK' and Fig. 2, 'Southern UK'), but with the $V_{2.5}$ results showing a time shift forwards of some 3–5 h. This may reflect a delayed loss of volatile PM from the FDMS analyser (which would in turn affect the pattern of total $PM_{2.5}$ concentrations). Green (2007) has reported a 1–2 h time delay in the purge concentration from an FDMS analyser. It is also of note that the variation in $V_{2.5}$ during the day is less than 1 μg m^{-3}, which is much smaller than the diurnal fluctuation of $PM_{2.5}$, which is around 3 μg m^{-3}.

Further insight into the diurnal pattern can be obtained by examining nitrate concentrations. The pattern by hour-of-the-day at two sites in southern England shows a minimum in nitrate concentrations during the afternoon, which supports the view that the afternoon dip in $PM_{2.5}$ concentrations is related to loss of volatile nitrates from ambient $PM_{2.5}$ (Fig. 5). The temperature sensitivity of nitrate concentrations is confirmed by many earlier studies including those in the UK (Allen et al., 1989) and Italy (Bigi and Ghermandi, 2010; Carbone et al., 2010). The different behaviour in the northern UK seen in Fig. 2 may reflect very low levels of NH_4NO_3 in the aerosol with most nitrate being present as less volatile calcium or sodium nitrate.

The diurnal profiles of $PM_{2.5}$ have been examined in more detail by separating them into two periods: 1) easterly winds (40°–140°) and 2) winds from all other directions. The patterns are similar at sites across England, with an example shown for the site at Leamington Spa in the Midlands (Fig. S6). The strong diurnal pattern with a concentration minimum during the afternoon is seen in the results for all wind directions other than easterly (Fig. S6, 'All other'). When the winds are from the east, concentrations are higher overall, but the pattern is much more uniform, although with a tendency towards higher concentrations during the evening (seen at all four sites considered – not shown). As is discussed below, the high concentrations with easterly winds are likely to be associated with long-range transport of well mixed and spatially homogeneous PM from continental Europe. These observations would suggest that if the low afternoon concentrations are due to loss of semi-volatile PM, then a) semi-volatile PM is not strongly associated with easterly winds and hence not strongly associated

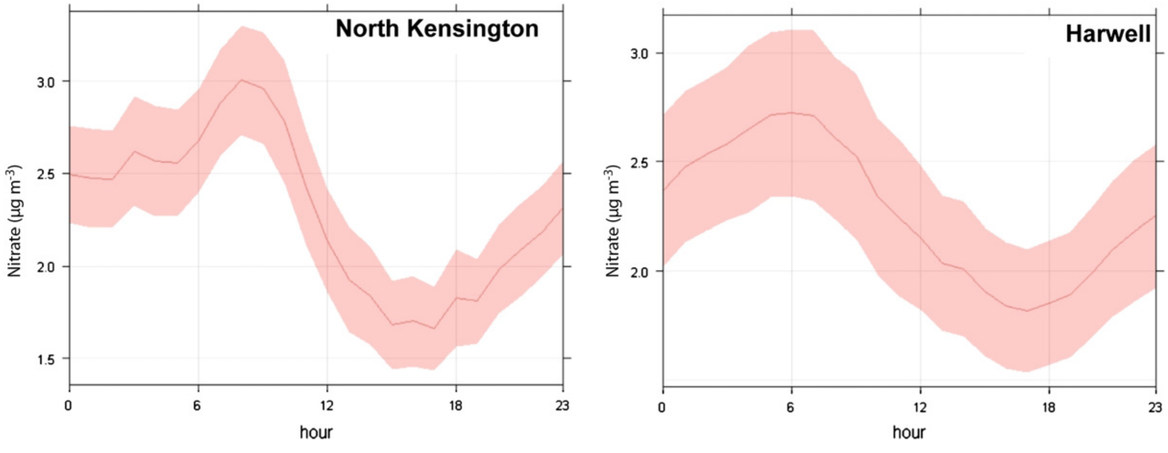

Fig. 5. Variation of nitrate concentrations (μg m^{-3}) by hour-of-the-day in 2009 at 'London North Kensington' (urban background) and 'Harwell' (rural). The shading represents the 95% confidence interval. Note different scales.

with secondary PM, and b) the semi-volatile PM is associated with winds other than those from the east, which will have limited secondary PM. On the other hand, it may be that the loss of semi-volatile PM is not the explanation for the afternoon dip. Clearly, there is currently no unambiguous evidence as to the cause of the $PM_{2.5}$ concentration minimum during the afternoon seen at all southern UK sites.

The other interesting feature of the $PM_{2.5}$ results is the late evening to early night-time (20:00–23:00 h) peak. In part this will be due to reduced dispersion arising from the more stable atmospheric conditions during the night. It may also reflect a contribution from domestic sources, both from heating and cooking. In addition, there may be a contribution of volatile PM condensing on ambient particles with the lower night-time temperatures, an explanation supported by the observation that nitrate concentrations also increase overnight (see Fig. 5).

The diurnal patterns for roadside and industrial sites during 2009 are shown in Fig. S7. The diurnal range is only slightly larger at roadside sites, averaging around 3.75 μg m^{-3} (ranges cited to nearest 0.25 μg m^{-3}) but is substantially less at industrial sites, averaging around 1.5 μg m^{-3}. The afternoon dip is also not as prominent at roadside sites as it is at background sites, nor is the late evening peak (*cf.* Fig. S7, ‘Roadside’ and Fig. 2). There is no clear peak during the evening ‘rush hour’ 16:00–18:00 h, although concentrations during this period are somewhat higher than seen in the pattern at urban background sites, suggesting an influence of the higher traffic flows at this time.

The absence of a clear late evening/early night-time peak at roadside sites is more apparent than real, as the late evening concentrations are elevated above the early morning minimum to a similar extent at roadside and urban background sites; being around 2.25 μg m^{-3} higher, compared with values of around 1.75, 1.75, 2.25 and 2.5 μg m^{-3} for the four background regions (*cf.* Fig. S7, ‘Roadside’ and Fig. 2). This would suggest that the late evening peak is not strongly related to road traffic, it is though being disguised at roadside sites by higher early evening concentrations which are likely to be related to road traffic, i.e. the traffic peak is superimposed on the rising limb of the late evening peak.

The range of diurnal concentrations is much lower at industrial sites (Fig. S7). The morning and evening peaks are still evident, suggesting that the background pattern is playing a role, but the emissions from the industrial sources, which are likely to be more constant throughout the day, and will occur to some extent at night-time, will dampen the background pattern.

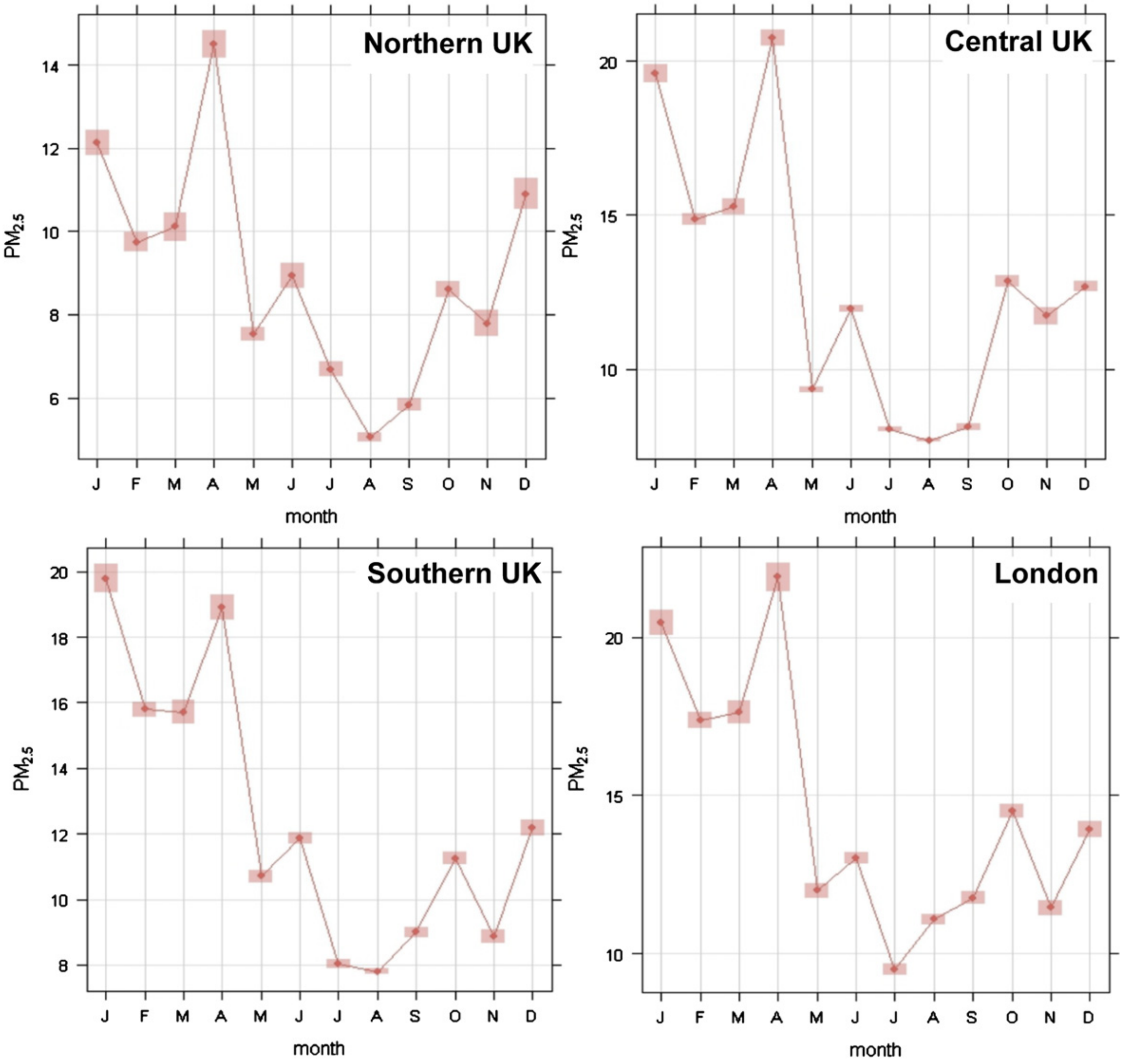

Fig. 6. Variation of $PM_{2.5}$ concentrations (μg m^{-3}) at urban background sites by month of the year in 2009 at sites in ‘Northern UK’ ($n = 8$), ‘Central UK’ ($n = 17$), ‘Southern UK’ ($n = 8$) and ‘London’ ($n = 8$). The shading represents the 95% confidence interval. Note different scales.

It was noted above that the Lisburn site in Northern Ireland was anomalous, with much higher measured $PM_{2.5}$ concentration in 2009 than suggested by the modelled background concentration for this location. The diurnal variation at the Lisburn site reveals a distinctly different pattern, with the range over the day being three times higher than at other urban background sites, at just over 9 μg m^{-3} (Fig. S8). This is primarily due to high overnight concentrations at this site, which peak at a similar time to the peaks seen at other background sites (*cf.* Fig. 2). It is suspected that these high concentrations are due to domestic heating, which is still supplied in part by solid fuel in the area around the monitoring site. This is supported by the observation that the evening peak is much larger during the winter than the summer (not shown).

4.4. $PM_{2.5}$ by season in different parts of the UK

The pattern of $PM_{2.5}$ concentrations by month-of-the-year is summarised in Fig. 6 for urban background sites in four geographic areas of the UK. The pattern during 2009 was broadly similar at all sites (and at roadside and industrial sites – not shown), with the highest concentrations during the first four months of the year (January–April), the lowest concentrations during late summer (July–September), and somewhat higher concentrations during the autumn to early winter (October–December). It will relate to greater emissions of both primary PM and secondary PM precursors during the winter, due to the higher heating load, as well as to reduced dispersion of local sources. It will also relate, in part, to the loss of semi-volatile PM during summer months, which will be less prevalent during winter months. The range of monthly means is substantial, from 5 to 14 μg m^{-3} in northern UK, 5 to 21 μg m^{-3} in central UK, 8 to 20 μg m^{-3} in southern UK and 10 to 22 μg m^{-3} in London. The work of Harrison and Yin (2008), although based upon a different year of observations, shows a substantial elevation in both nitrate and secondary organic carbon in the first four months of the year at a central England site.

4.5. Variation of $PM_{2.5}$ concentrations with wind direction and speed

The relationship between $PM_{2.5}$ and wind direction can provide valuable insight into the sources of the measured concentrations. Two examples are shown in Fig. 7, one for Manchester Piccadilly in the north of England, the other for Reading in the south of England. Both plots show the highest concentrations associated with winds from the east, and in particular with higher wind speeds.

There is a remarkable consistency in the patterns across the UK (see Figs. S9 and S10). Concentrations are generally lower than the annual mean when winds are from the south-southeast clockwise through to north, while they are generally above the annual mean with winds from the northeast through to southeast. There is, however, a subtle difference between sites in the south and those in the north of the UK, with southern sites having the highest concentrations associated with winds from the east through to southeast, while the northern sites, have a more significant component associated with winds from the northeast through to east. These elevated $PM_{2.5}$ concentrations are likely to be due to emissions (mainly of precursors of secondary PM) within continental Europe. Easterly winds in the southern parts of the UK are frequently associated with a blocking high pressure over the Nordic countries that gives rise to an easterly or south-easterly air flow that will transport emissions from eastern Europe, northern Germany, the Netherlands and Belgium to the southern parts of the UK (Barry and Chorley, 2010). In northern parts of the UK the air arriving from the east to southeast sector will not have passed over these same emission sources; hence the lower concentrations associated with these winds in northern UK. On the other hand, the high concentrations associated with more north-easterly winds in the northern parts of the UK are likely to arise when a low pressure runs up the English Channel, drawing air northward across European source areas, out into the North Sea, then around the top of the low pressure to reach the northern parts of the UK from a north-easterly direction (Barry and Chorley, 2010). The highest concentrations with easterly winds are mostly associated with the strongest winds (>10 m s^{-1}), although concentrations are elevated in this wind sector for all wind speeds. This association with higher wind speeds probably relates to the balance between greater dilution at higher wind speeds and the shorter transport times at these higher wind speeds, which allow less time for dispersion and deposition. These observations reinforce the view that urban background $PM_{2.5}$ concentrations are dominated by regional sources, rather than local sources, and that PM derived from sources in continental Europe, probably as secondary PM, plays a significant role in affecting concentrations in the UK.

The 2009 $PM_{2.5}$ monitoring data have been analysed by wind direction and time-of-day for a site near to a busy road,

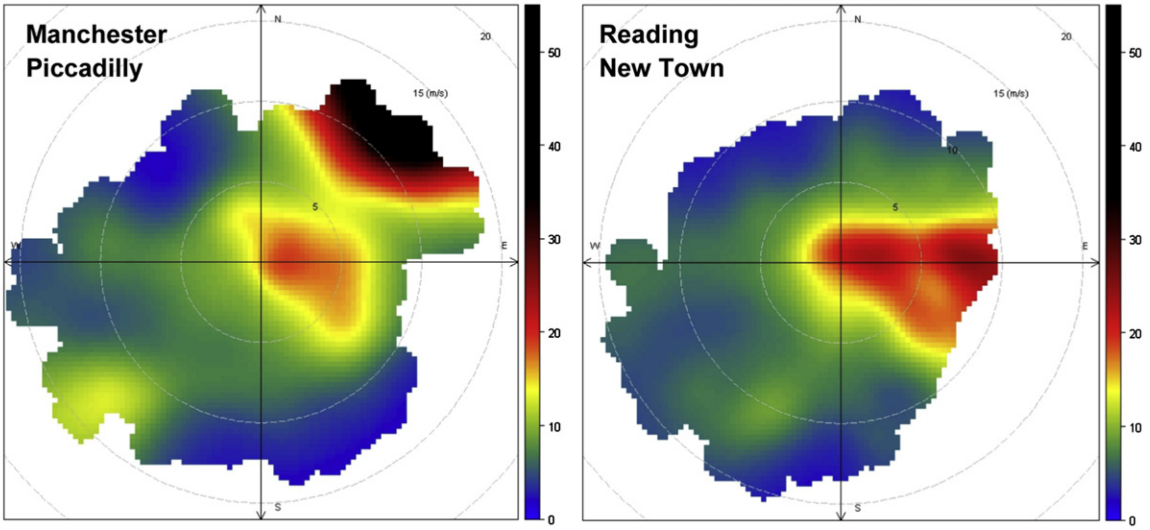

Fig. 7. $PM_{2.5}$ concentrations (μg m^{-3}) at two sites in 2009 as a function of wind direction and wind speed. The circles are at 5 m s^{-1} intervals, with the outer limit at around 15 m s^{-1}.

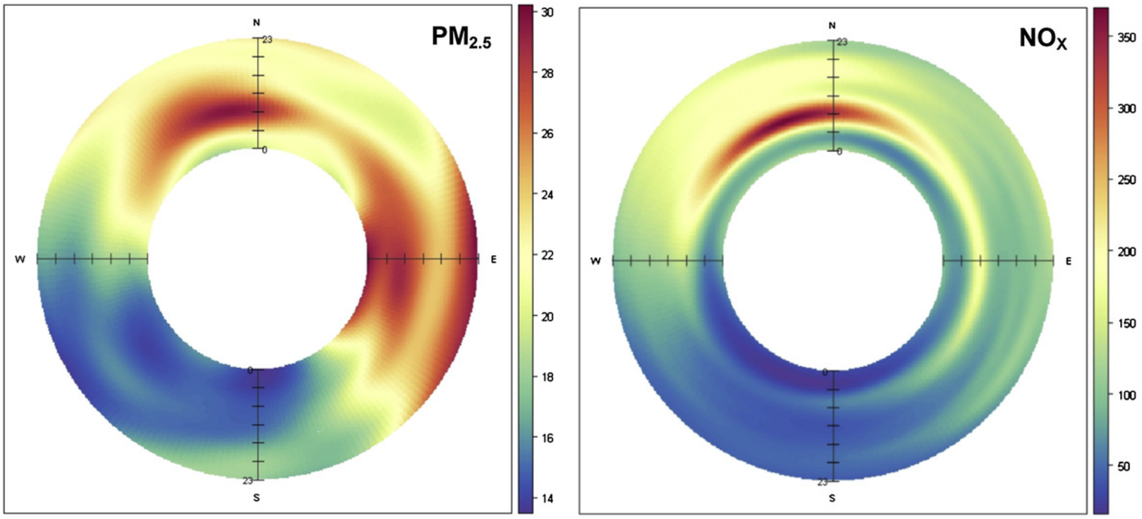

Fig. 8. $PM_{2.5}$, and NO_x concentrations (μg m^{-3}) in 2009 at a near-road site in London, Greenwich as a function of wind direction and time-of-day. Inside of circle is 00:00–01:00 h running through the day to 23:00–24:00.

Greenwich Burrage Grove, which is located around 15 m south of the busy A205 Plumstead Road in east London. Polar annulus plots are presented for $PM_{2.5}$ and NO_x in Fig. 8. The NO_x patterns at both sites are consistent with a major traffic contribution from the nearby road, with the highest concentrations occurring during the morning rush-hour. The pattern for $PM_{2.5}$ is very different, showing the strong easterly predominance to the high concentrations identified in the polar plots. There is limited enhancement of $PM_{2.5}$ linked to air arriving from the nearby roads, suggesting a limited contribution of road traffic to $PM_{2.5}$ at a site near to, but away from the immediate edge of a road. This is consistent with the earlier analysis showing a modest enhancement of $PM_{2.5}$ at roadside sites.

4.6. The overall picture of $PM_{2.5}$ from the monitoring data

Urban background concentrations of $PM_{2.5}$ across the UK fall within a relatively narrow range, generally from 12 to 14 μg m^{-3} and are typically around 3–6 μg m^{-3} above the regional (rural) background. There is some uncertainty in the urban enhancement, as there are currently few rural monitoring stations and insufficient results are available to generate a robust national picture. Kerbside concentrations within 1 m of the kerb of busy urban centre roads can be enhanced by up to 7–8 μg m^{-3} above the urban background. These roadside increments, however, decline rapidly on moving away from the edge of the road (AQEG, 2005), and it would appear that annual mean roadside concentrations of $PM_{2.5}$ are only around 1 μg m^{-3} above the urban background. The limited contribution of road traffic to $PM_{2.5}$ is also evident in the polar annulus plots for a near-road site. From the limited available dataset, there is no evidence that individual industrial operations give rise to annual mean increments of $PM_{2.5}$ of more than a few μg m^{-3}.

Monthly mean concentrations at urban background sites show a substantial range from an early-spring high to a mid-summer low, the range being 5–14 μg m^{-3} at northern UK sites, 5–21 μg m^{-3} at central UK sites, 8–20 μg m^{-3} at southern UK sites and 10–22 μg m^{-3} at London sites. This contrasts with a much smaller diurnal range, which is typically 3 μg m^{-3}.

Analysis of the diurnal patterns of $PM_{2.5}$ concentrations and the patterns related to wind direction has provided strong evidence of a continental European source, probably mainly secondary PM.

4.7. Relationships of monitoring data to air quality objectives and limit values

The EU limit values and targets for $PM_{2.5}$ set out in the EU Directive are all based on annual mean concentrations (Official Journal, 2008). The limit value is 25 μg m^{-3} and is to be met by 2015. The available evidence indicates that it will not be exceeded anywhere in the UK.

The EU Directive exposure-reduction target is based on the Average Exposure Index (AEI) which is calculated as the three-year running annual mean concentration measured at selected urban background sites across the UK. The exposure-reduction target (to be achieved by 2020) ranges from 0% to 20%, and is dependent on the AEI determined for the 2010 reference year. It is unclear at this stage what the EU target reduction for the UK will be, but based on current data, it is expected to be 10% or 15%. Finally, there is an exposure concentration obligation within the Directive, which sets a ceiling of 20 μg m^{-3} for the AEI, to be achieved by 2015. It is expected that the exposure concentration obligation will be met easily.

The UK Government has set its own objectives for $PM_{2.5}$ but these are the same as or more stringent than the EU target (Defra, 2007). The Scottish Government has set its own more stringent annual mean objective for $PM_{2.5}$ of 12 μg m^{-3} to be achieved by 2020 and based on current data there is a risk that this may not be achieved.

It is expected that the exposure-reduction target will be the key driver for UK policy on exposure to $PM_{2.5}$, while the PM_{10} objectives and limit values will supplement this control by driving policy on short-term (daily average) concentrations at hot spots. There may also be a role for the Scottish Government's annual mean $PM_{2.5}$ objective to drive policy in Scotland, although the Scottish Government's PM_{10} objective is likely to be more stringent.

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Appendix. Supplementary information

Supplementary information related to this article can be found online at doi:10.1016/j.atmosenv.2011.10.028.

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