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Kamara, Adams A.; Harrison, Roy M.

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Analysis of the Air Pollution Climate of a Central Urban Roadside Supersite: London, Marylebone Road

Adams A. Kamara and Roy M. Harrison*†

School of Geography, Earth and Environmental Sciences
University of Birmingham
Edgbaston, Birmingham B15 2TT
United Kingdom

* To whom correspondence should be addressed (Email: r.m.harrison@bham.ac.uk)
†Also at: Department of Environmental Sciences / Center of Excellence in Environmental Studies, King Abdulaziz University, PO Box 80203, Jeddah, 21589, Saudi Arabia
ABSTRACT. The London Marylebone Road monitoring site is a roadside supersite adjacent to a highway carrying 80-90,000 vehicles per day on six lanes in a street canyon. Data from the Automatic Urban and Rural Network (AURN), Black Carbon Network, Automatic Hydrocarbon Network, Heavy Metal Network, Particle Size and Number and Particle Composition Network covering the period from 2009-2018 were analysed to determine short-term (diurnal, weekly and seasonal) and long-term variations and geographic source attribution. The contribution of roadside emissions relative to background sites (roadside increment) to the pollution climate was also investigated. The long-term trend analysis shows significant decline in regulated pollutants such as the particulate matter fractions (-4.0%; -3.93%/yr for PM$_{2.5}$ and PM$_{10}$ respectively) and gas phase pollutants associated with vehicular emissions (-5.5%; -1.22% and -2.1%/yr for CO, NO$_x$ and NO$_2$ respectively), although concentrations of SO$_2$ and O$_3$ have remained relatively constant over the years. Equivalent Black carbon (eBC) and total particle number count have also declined over the years whereas the heavy metals show mixed results (only Cu, Ni and V shows significant downward trends). The inorganic ionic components of the PM$_{10}$ fraction, elemental (EC) and organic carbon (OC) and the volatile organic compounds all generally show declining trends over the period. Assessment of the diurnal variations shows elevated concentrations of the particulate matter fractions, the nitrogen oxides, CO and SO$_2$ at periods corresponding to the traffic rush hours, whereas O$_3$ peaked in the afternoon when there is less titration due to lower NO concentrations. The diurnal pattern of eBC and Total Particle Number Count are similar to NO$_x$ and show strong traffic influence. Cl, Mg, K and Na levels show no systematic pattern throughout, with their presence likely controlled by meteorological conditions, and Ca showing high concentrations in the afternoon because of resuspension of deposited dust resulting from turbulence created by vehicular movement, and eroded road-surface material. Ammonium and nitrate show their lowest concentrations during the day when the temperature is high, probably reflective of their semi-volatile nature, with sulphate producing a peak around mid-day. The VOCs, with the exception of ethane, give the bimodal peaks typical of traffic related emission in the diurnal plots and their
pattern is more similar to CO than the other traffic emitted gaseous pollutants. Ethane is associated with leakages from gas supply pipes. The weekday plots show weekday (Monday – Friday) increases in traffic-related pollutants and a decline over the weekends due to lower traffic volumes, with the reverse observed for O₃. K and the marine aerosol components show relatively similar concentrations on all days of the week, while Ca, NH₄⁺, NO₃⁻ and SO₄²⁻ all show a weekday maximum and decline over the weekend. The pollutants show seasonal variations; O₃ shows a springtime maximum, with the traffic-emitted pollutants (NO, NOₓ, CO, EC, OC etc) giving a winter maximum due to increase in emission, lower mixing depth and poor dispersion. Particulate matter fractions and total particle count show lower concentrations in summertime reflective of the semi-volatile nature of some components. Ca shows less seasonal variability, with marine aerosol components showing a maximum winter concentration driven by higher wind speed conditions. NH₄⁺, NO₃⁻ and SO₄²⁻ show lowest levels in summer and maximum springtime concentrations. The traffic-related VOCs show a summertime minimum and wintertime maximum, while isoprene shows increased concentrations during summertime. The street canyon circulation causes the sampling of North London air on northerly winds, but enhanced traffic pollution when winds have a southerly component. There is a sizeable roadside increment above the local background for both exhaust (particulate matter mass fractions, particle number and eBC) and non-exhaust emissions (heavy metals). However, roadside increments of inorganic species, which include Ca, marine aerosol components and the secondary particulate matter components, are not significant, indicating that they are mainly controlled by regional transport of the pollutants. Polar plots show strong local contributions for the regulated gas phase pollutants and the carbon components (EC and OC), with O₃ concentrations enhanced mainly from the northerly direction. The long-range contribution from mainland Europe to the particulate matter fractions is significant and occurs mainly as secondary aerosol. Ratios of OC/EC in particles have shown a steady increase due to a more rapid reduction of EC than OC.

Keywords: Air quality; trends, particulate matter; gaseous pollutants; roadside site; traffic pollution.
INTRODUCTION

London is the largest and most populated city in the UK and has a history of severe pollution events such as the notorious 1952 London smog that precipitated an increased awareness of air quality issues within the city. Investigating the trends, seasonality and cyclic patterns exhibited by air pollutants gives insights into their sources and properties, and is important for health considerations and policy development. Bigi and Harrison (2010) analysed 13 years of hourly data from a central urban background site in London for particulate matter and gas phase pollutants in terms of long-term trends, annual, weekly and diurnal cycles. The analysis showed generally declining trends for all the pollutants considered, with the exception of \( \text{O}_3 \) which exhibited a steady increase over the period. Clear seasonal variations were observed, with \( \text{CO}, \text{NO}, \text{NO}_2 \) and \( \text{SO}_2 \) showing a summer and winter maximum and a pattern associated with traffic emissions (for \( \text{CO}, \text{NO} \) and \( \text{NO}_2 \)). \( \text{O}_3 \) showed a maximum in May and a minimum in winter, and the particle number count was at a minimum in August and a maximum in winter. Colette et al. (2011) investigated air quality trends in Europe over the past decade by looking at pollutants such as \( \text{NO}_2 \), \( \text{O}_3 \) and \( \text{PM}_{10} \) from urban background, suburban background and rural background stations. They observed a general decline in \( \text{NO}_2 \) for the majority of the monitoring stations, with a slight increase of \( \text{O}_3 \) observed (especially at urban sites) due to a decrease in \( \text{NO}_x \) emissions. \( \text{PM}_{10} \) levels declined over the decade in UK and Germany. Analysis of 18 years of data from Fresno (California) using time series and multiple linear regression models showed that the concentrations of \( \text{NO}_x \), \( \text{EC} \) and ammonium nitrate had halved since 2000, but the \( \text{PM}_{2.5} \) levels had not declined significantly (de Foy and Schauer, 2019). Similarly, in Los Angeles, an assessment of the effectiveness of regulations to reduce tail pipe emission was undertaken by investigating the trend in \( \text{PM}_{2.5} \) mass concentration and chemical species concentrations for the period 2005 – 2015 (Altuwayjiri et al., 2021). The study reported an overall significant downward trend in mass concentration of \( \text{EC} \) and \( \text{OC} \) (major contributors to the \( \text{PM}_{2.5} \) mass concentration). Data from 18 sites for the period 1999-2016 analysed for Seoul also showed a decrease in the long-term measurements of \( \text{PM}_{10} \) due to a reduction in the local source
contribution, and an increase in O\textsubscript{3} from local secondary production, with NO\textsubscript{2} and SO\textsubscript{2} not showing significant trends (Seo et al., 2018). This study also looked at short-term variability in pollutant concentrations, and was able to associate high PM\textsubscript{10} and primary gaseous pollutant concentrations with migratory high-pressure systems that enhance regional transport and local accumulation during warmer periods.

This study examined data generated by different monitoring networks at the roadside London, Marylebone Road supersite, one of the most investigated roadside locations in Europe, with data from the North Kensington and the Westminster background sites utilised as required for comparison. Changes in the short and long-term trends of regulated pollutants, geographic source apportionment and roadside contribution increments were investigated. A similar analysis was also conducted for unregulated pollutant metrics (i.e. eBC, heavy metals, hydrocarbon and particle numbers). The results are consider as likely to be representative of heavily trafficked roadside locations across Europe, as over the relevant period, the UK was subject to EU Directives which applied also across many other countries in the region. This is especially true of vehicle emission standards which are applied to vehicles across Europe, even outside of the EU. Consequently, although there will be differences due to local source emissions and differing meteorology, there are broadly similar air pollution climates across Europe, especially in relation to road vehicle emissions.

**METHODOLOGY**

Marylebone Road is an important thoroughfare in central London. It runs east to west from the Euston Road at Regent's Park, to the A40 Westway at Paddington. The road, which has three lanes in both directions, is part of the London Inner Ring Road and as such forms part of the boundary of the zone within which the London congestion charge applies. As part of the Ring Road, it is a feeder route to the A40 (and hence the M40 motorway to the west) and the A5 and M1
motorway (to the north). Air sampling equipment is housed in a large kerbside cabin on the sidewalk of this busy central London street canyon. The adjacent six-lane highway carries around 80,000 vehicles per day. The highway is relatively straight and at this point runs almost due east—west (angle 80º from north). The buildings on either side of the highway are around six storeys in height, giving a street canyon aspect ratio of approximately 1:1 (Harrison et al., 2019).

Data for this study were downloaded from the Automatic Urban and Rural Network for the regulated pollutants (gas phase and particulate matter), as well as for heavy metals, black carbon, particle number size distributions and hydrocarbons from the respective networks. The heavy metals data are based on an integrated 1-month period sampling of the PM$_{10}$ fraction, while the other parameters are measured automatically and recorded over hourly periods. Quality assurance and quality control procedures follow the standards for the Automatic Urban and Rural Network (AURN) instruments, including regular span and zero checks, and every six months full servicing and an inter-calibration audit (https://uk-air.defra.gov.uk). Details of the instruments appear in Table S1. Data recovery is high (mostly >80%) for the hourly measurements especially for the regulated pollutants, not requiring any adjustments. For annual averages, as in the calculation of roadside increments, only periods with data availability at both locations are included.

The data were analysed mostly using the Openair package in the R software; see Carslaw (2015) for details of the analysis procedures. Long-term variability in measured concentrations of different pollutants were investigated using the Theil-Sen function, whereas the relative shorter time variations (diurnal, weekdays and monthly) used the Time Variation functions. Polar plots are used to identify geographical sources of pollutant origins. Roadside increments were investigated by subtracting the value for background location measurement from that of the London Marylebone Road (LMR) monitoring station measurement. The London North Kensington (LNK) station is use
as the background site for the estimation of the roadside increment for the particulate matter
fractions, equivalent black carbon and the inorganic species whereas the London Westminster (LW)
background site is use for the heavy metals estimation. The term “background site” is used to
describe sampling locations where the pollution level is not influenced significantly by any single
source or street, but rather by the integrated contribution from all sources upwind of the station. The
surroundings of the LNK site are mainly residential with the closest road being usually quiet and no
major highway in the vicinity. The nearest road to the LW site is about 17 metres away, and the
surrounding area has mixed commercial and residential use.”

Using a median wind speed, the typical atmospheric transport time from the background sites to the
LMR site is 19 minutes. This is insufficient to justify any time shift in hourly mean data.

RESULTS AND DISCUSSION

Long-Term Trends in Pollutant Concentrations

Investigating long-term trends in pollutant concentrations is an asset in evaluating the effectiveness
of control measures put in place for given pollutants. Monitoring of regulated pollutants and other
pollutants of interest has taken place for a long time at the London Marylebone Road site leading to
the accumulation of a huge dataset, suitable for such investigation.

Over the period 2009 – 2018 a significant decrease in the levels of the different particulate matter
fractions, the nitrogen oxides (NO\textsubscript{x} and NO\textsubscript{2}) and carbon monoxide (Table 1) was observed. CO
exhibits the highest rate of decline followed by the PM fractions and then the nitrogen oxides. The
levels of O\textsubscript{3} and SO\textsubscript{2} have remained relatively constant, as they show an overall insignificant
increase and decrease in trend respectively. At the London Marylebone Road, SO\textsubscript{2} arises mainly
from road traffic. Low emissions of SO\textsubscript{2} from the transport sector is because of the introduction of
low sulphur content (<50 ppb) diesel and petrol introduced in 1999 and 2001 respectively, with an
even lower sulphur content fuel of <10 ppb few years later (Boulter and Latham, 2009). The
reduction in motor fuel sulphur to “zero sulphur” levels (<10ppm S) occurred in 2007, which is why
concentrations and the traffic increment have remained low and fairly constant since. Road
transport is one of the key emitters of air pollutants in urban areas, and this sector has been
regulated for tail pipe emissions since the early 1990s by the Euro emission standards. According
to Matthaios et al. (2019), the widespread use of the three-way catalyst in gasoline vehicles has
brought about significant reduction in tail pipe emissions. Many diesel vehicles were fitted with an
oxidation catalyst to meet the Euro 3 standard, introduced in 2000 leading to oxidation of CO and
hydrocarbons but also to oxidation of NO leading to an increase in NO₂ emissions, corrected
subsequently by a variety of technologies. These emission standards, introduced from 1992
onwards, applied only to new vehicles, so changes in air quality occur only gradually as new
technology vehicles enter the fleet. Studies to determine the effectiveness of control measures to
reduce exhaust emissions in London are available. Font and Fuller (2016) investigated 65 roadside
showed a significant downward trend in roadside PM₂.₅ for most of the sites with a mixed result for
PM₁₀, but with most of the sites closer to the city centre showing a downward trend in PM
attributed to use of diesel particle filters. The upward trends observed for PM₁₀ in some of the sites
is linked to an increase in the coarse particulate fraction (largely non-exhaust emissions). The study
further reported an increase in NO₂ and NOₓ concentration during 2005 – 2009 and attributed this to
the increased proportion of light duty diesel vehicles. The decrease in levels of NOₓ at most of the
roadside sites between 2010 – 2014 was concluded to be the result of reduction in vehicle fleet
number, and the introduction of the London Low Emission Zone, applying at that time to heavy
duty vehicles. The reduction in roadside increment of PM levels, which is associated with the use of
Diesel Particle Filters (DPF) from Euro 5, is also reported by Harrison and Beddows (2017), in a
paired site study of London Marylebone Road and London North Kensington (2009 – 2015), a
period during which no significant change in traffic flow and vehicle types was observed. The more
stringent measures introduced by the Euro 6 standard (from 2014 with subsequent strengthening)
and the London Ultra-low Emission Zone from 2019 will have led to further reductions in NOx emissions.

The instances of exceedances of European Union air quality standards are indicated in Supplementary Table S2. From 2012 to date, PM10 has not exceeded the 24 hrs mean Limit Value of 50 µg/m³ (not to be exceeded more than 35 times per year) set for the protection of human health, with the number of exceedances per year decreasing over time. It has also stayed below the annual mean Limit Value for the past ten years, as is the case for PM2.5 (the mean annual PM2.5 concentration is below 25 µg/m³ for the period 2009-2018). The levels of gas phase pollutants and particulate matter concentrations have been reported to be in decline across Europe for several years, with the reduction assumed to be the result of implementing abatement strategies and the introduction of the Integrated Pollution Prevention and Control (IPPC) directive (Cusack et al., 2012). Similarly, Sicard et al. (2021) in an investigation of the air quality status of European cities for the period 2000 – 2017, reported a significant decline in the emission of all primary pollutants at national level, even though the population exposures for some pollutants were found to be high in some cases i.e. exceeding limits set by EU Directives. On the other hand, for NO2, the 200 µg/m³ one-hour limit that should not be exceeded more than 18 times a year was exceeded for the entire period, with the least exceedance number of 31 times recorded in 2018. The annual mean limit of 40 µg/m³ was also exceeded throughout this period. For O3, the 8 hr mean limit of 100 µg/m³ was not exceeded throughout the period under consideration. This is expected as there will be sufficient NO present from traffic emissions to suppress O3 concentrations at this location.

There is a steady downward trend exhibited in the monthly mean NO2 and CO concentrations throughout the period. The highest monthly levels for NO2 were measured in 2009 (>120 µg/m³), and these were <100 µg/m³ by 2018. CO also had its highest monthly mean concentration of 0.9 mg/m³ recorded in 2009. For NOx, even though the lowest peaks (monthly average) occurred in
most recent times, the highest monthly concentrations occurred during the period 2012-2016. The particulate matter fractions (PM$_{2.5}$, PM$_{10}$ and PM$_{\text{coarse}}$) like NO$_2$, show a steady decline, with the maximum monthly peaks occurring during 2011-2012. The maximum monthly mean concentrations for the PM fractions are 35 µg/m$^3$, 52 µg/m$^3$ and 18 µg/m$^3$ for PM$_{2.5}$, PM$_{10}$ and PM$_{\text{coarse}}$ respectively. There was a relatively constant level of O$_3$ and SO$_2$ concentrations from one year to the next during this period. For O$_3$, the maximum monthly peak concentrations >30 µg/m$^3$ have occurred since 2010 and are still observed for measurements as recently as 2018. SO$_2$ on the other hand showed maximum monthly peaks (≈11 µg/m$^3$) between 2014-2016 and is declining in the most recent measurements. The downward trend shown by the pollutants based on real time measurements is in line with the National Atmospheric Emissions Inventory in which there have been significant declines in emissions over the years, due to measures which reduced or eliminated the sources of such emissions (Figure S1). However, for most of these pollutants, the decline is either slowing down or has levelled off. For instance, since 2010 the decline in the oxides of nitrogen and SO$_2$ have slowed down (appearing to level off from 2020) while those of the regulated particulate matter fractions had started levelling off by 2015 (Defra, 2019).

The long-term trend for other pollutants has also been investigated (Table S3). For black carbon (BC), there has been a steady decline in the concentration of BC at an overall rate of 12.44%/year ($p$ < 0.001). An average maximum concentration of 8 µg/m$^3$ was observed in 2014, with monthly average concentrations generally below 4 µg/m$^3$ measured in 2018 (i.e. decreasing by a factor of more than two). Trends in carbonaceous aerosol components across the UK are examined in more detail elsewhere (Jafar and Harrison, 2020). Total number particle count (TNC) shows a statistically significant ($p$ < 0.001) downward trend in monthly mean concentration for the period 2011-2018. The average monthly total particle count was ≈ 65,000 count cm$^{-3}$ in 2011 and has reduced to below 30,000 count cm$^{-3}$ in 2018. The trends for the heavy metals for the period 2011-2018 give mixed results. Metals such as Cu (-3.59%/yr, $p$ < 0.05), Pb (-2.92%/yr, $p$ < 0.05), Ni (-
5.33%/yr, p < 0.001) and V (-7.21%/yr) show significant downward trends, whereas As has increased at a rate of 3.91%/yr (p < 0.05). The upward trend exhibited by arsenic is possibly due to increased emissions arising from domestic combustion of coal and treated wood for which data are highly uncertain. Fe, Mn and Zn have shown an upward trend, although such increases are not statistically significant, with Cd, Co, Cr and Se also showing a non-significant downward trend.

Goddard et al. (2019) also reported similar long-term trends (based on off-line ICP-MS analysis) of metals at UK sites and attributed a recent increase in Mn to an increase in biomass fuel burning. Fe is the most abundant metal due to emissions of brake wear particles from road traffic (Gietl et al., 2010). The inorganic ionic components of the PM$_{10}$ fraction show declining trends in most cases. Sodium and chloride ions are associated with marine aerosol and show a significant declining trend (p < 0.001) at similar rates i.e. at an overall rate of -7.77%/yr and -7.62%/yr respectively. The marked downward trend in sea salt component concentrations is probably explained by a decreased average speed of south-westerly winds, which declined by 1.99% per year between 2011 and 2018, as the generation of sea salt is strongly wind speed dependent. An alternative possibility is a reduced use of deicing salt, but we have been unable to obtain data to test the latter hypothesis.

Ca and to some extent K ions have declined over the period, but the reasons are unclear. A reduction in the biomass burning source seems unlikely as concentrations of Brown Carbon at this site have increased (Jafar and Harrison, 2020). Mg is the only element that shows some semblance of an increasing trend even though it is not significant. The anthropogenic secondary aerosol components (ammonium, nitrate and sulphate) all show downward trends, and this decline will account in part for the decline in the particulate matter concentrations. While NH$_4^+$ shows an almost constant level and non-significant change, NO$_3^-$ and SO$_4^{2-}$ showed a significant downward trend (p < 0.001) at an overall rate of -7.91%/yr and -10.98%/yr respectively. These trends are also seen in those of the precursor molecules (NO$_x$ and SO$_2$ respectively). However, the rate of decrease of NO$_x$ (-2.17%/yr) and SO$_2$ (-2.67%/yr) are significantly lower than those of the secondary products, which are 7.91%/year and 10.98%/year for nitrate and sulphate respectively, for the period under
investigation. The decrease in the concentrations of the primary pollutants are in line with the reductions observed in the emissions of the pollutants as illustrated by the National Atmospheric Emissions Inventory (Figure S1). It was reported that between 2002 to 2004, regional background levels of secondary inorganic aerosol accounted for 88% and 92% of nitrate and sulphate respectively in Central London (Young et al., 2015). Therefore, the higher rate of decline of secondary aerosol components may be the combined outcome of a decline in long-range transport of secondary aerosol and a decline in the local emissions of the precursor molecules, but predominantly the former. Volatile Organic Compounds (VOCs) which are emitted from solvent use, consumer products, transport (combustion and evaporation) and leakages from gas pipes in urban areas showed a declining trend. With the exception of isoprene and ethane that showed a non-significant downward trend i.e., levels being relatively constant, the other nine VOCs show significant downward trends. 1,3-Butadiene, which is one of the VOCs with an air quality guideline in the UK showed the highest rate of decline at -12.59%/yr. Both 1,3-butadiene and benzene have annual averages below the limits stated in the National Air Quality Objectives of 2.25 µg/m³ and 5 µg/m³ respectively.

At the London, Marylebone Road (also for the background site at North Kensington), there is a significant decline in both Elemental Carbon (EC) and Organic Carbon (OC) for the period 2011-2018 at an overall rate of -7.54%/yr (p < 0.001) and -3.52%/yr (p < 0.001) respectively. For EC, the monthly average was ≈9 µg/m³ in 2010 which reduced to a value of 2 µg/m³ in 2018, whereas OC showed a monthly peak value of 9.8 µg/m³ in 2011 which declined to 4.5 µg/m³ at the start of 2018 (however it rose to ≈7 µg/m³ later in the year). The OC/EC ratio, however, exhibited a significant upward trend at a rate of 8.77%/yr for the same period (rising from 0.5 to 2.9 by 2018). The yearly average OC/EC ratio is 1.2-2.4 at the site (Table S4). With the exception of 2018 with the highest ratio of 2.4, all the other years give values less than 2. Several studies have utilized the value of the OC/EC ratio to determine the sources contributing carbonaceous components to particulate matter.

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pollution. A ratio of 1.1 has been attributed to a contribution mainly of fossil fuel combustion to EC and OC (i.e. primary emissions), whereas a ratio of up to 2.8 or more is because of a contribution of secondary organic aerosol formation to OC (Zhang et al., 2009; Mbengue et al., 2018). The OC/EC ratio values for the period under investigation for the Marylebone Road data indicates even though primary emissions may have been the major contributor to carbonaceous emissions, there has been a gradual shift to SOA being a major component of the OC fraction. This SOA may be from aged materials transported over long distance to the monitoring station. However, such interpretations risk being over-simplistic and the more likely explanation is an increased OC/EC ratio in vehicle emissions due to the increasing use of diesel particle filters which remove involatile EC more effectively than OC, much of which is semi-volatile (Beddows and Harrison, 2018; Alam et al., 2019).

**Diurnal, Weekday and Seasonal Variations**

Figure 1 gives the time series plots for some of the regulated pollutants with the left, middle and right panels showing diurnal, seasonal and weekday variations in pollutant concentrations (normalised) respectively. The level of the pollutants on any given day shows a strong traffic influence i.e. a bimodal diurnal distribution corresponding to the early and late traffic rush hours (Kendrick et al., 2015). The concentrations of the nitrogen oxides, PM fractions, CO and SO₂ all give maximum concentrations during the period of the traffic rush hours. There are two visible peaks for each of these pollutants corresponding to the early traffic rush hours (08:00-10:00 hrs) and the late rush hours (after 18:00 hrs). During these periods of the day, less dispersion of pollutants from a stable weather condition (low wind and a lower mixing depth) may also enhance concentrations. For CO, the evening peak has a higher amplitude than the early rush hour peak, which contrasts with the other traffic related pollutants. The reason for this is uncertain, but may be related to the relative amounts of gasoline vehicle traffic in the westbound and eastbound lanes. Generally, there is a relatively high constant concentration of the traffic related pollutants during the
day, i.e. between the traffic peak hours, due to a continuous high vehicular volume flow at the London Marylebone Road, as the characteristic ‘afternoon dip’ observed at many sites during daytime is almost missing. On the other hand, O$_3$ levels are at a maximum during periods with least NO emissions, with limited O$_3$ titration reaction and vice-versa. The O$_3$ peaks before 06:00 hrs in the morning and at around 15:00 hrs in the afternoon. However, absolute concentrations of ozone at the roadside are expected to be low as there is a sufficient supply of nitrogen oxide from vehicle exhaust to attenuate the concentrations.

The diurnal plot for eBC shows a typical traffic dependence of the pollutant concentration (similar to the pattern exhibited by other traffic emission related pollutants discussed above), with maximum levels observed between 08:00 hr to 18:00 hr, indicating continuous vehicular movement throughout this period. eBC is a major component of PM$_{2.5}$ emanating from tail pipes of vehicles in urban areas. However, a relatively weak correlation ($R^2 = 0.24$) exists between the two variables at this site. This may be because of other potential source contributions to PM$_{2.5}$ to this location.

There is significant contribution by secondary aerosol transported from mainland Europe to PM$_{2.5}$ concentrations in southern England during easterly or southeasterly wind conditions (Harrison et al., 2012a). To understand the correlation between BC and PM$_{2.5}$ at the site better, a plot of the two variables as a function of wind direction produces a feature that explains how wind conditions contribute to the BC levels and distinguishes it from the other sources of BC at the London, Marylebone Road site (Figure 2). This shows higher eBC concentrations are associated with higher PM$_{2.5}$ concentration in the south-westerly wind direction and this is where the street canyon vortex carries fresh vehicle emissions to the air sampler (Harrison et al., 2019). There is also such strong correlation in higher concentrations of the species during easterly wind conditions. The northerly winds direction shows a stronger relationship with lower concentrations. This observation of the source contribution of BC to the PM$_{2.5}$ size fraction is also the dominant feature discussed in relation to the polar plots presented later. The low BC/PM$_{2.5}$ ratios in northerly wind sectors are
reflective of background air composition in those sectors without appreciable influence of local
traffic emissions (see below).

The diurnal variations in the inorganic species show a less obvious traffic dependence of these
pollutants (top and bottom left panels of Figure S2). Ca shows maximum levels during the period
when there is intense vehicular movement. This may be the result of resuspension of mineral matter
deriving from deposited dusts due to turbulence caused by vehicular movement, and attrition of the
road surfacing material itself. These processes may tend to be most efficient around noon when the
road surface is most likely to be dry. The other elements (Cl, Mg, K and Na) remain approximately
constant during the day, with their amount likely to be controlled by meteorological conditions, as
they are most likely not of traffic origin. Na, Cl and Mg are usually from a marine origin, whereas
K is a signature element of biomass burning, but is also present in crustal material such as soil. The
nitrogen containing species (ammonium and nitrate) show a similar pattern with maximum
concentrations around 08:00 hrs in the morning, but show their least concentrations during the
afternoon period, most probably reflecting the semi-volatility of ammonium nitrate (Harrison et al.,
2012a). The sulphate ion on the other hand shows a maximum peak close to mid-day and low,
constant concentrations on either side of this peak (i.e. morning and afternoon to night periods). The
behaviour of these inorganic species shows little traffic influence upon their levels, but formation
and sink processes that may be dominant at a certain time of the day determine their measured
concentrations.

The top and bottom left panels of Figure 3 give the diurnal variation plots for the volatile organic
compounds (VOCs), which show the bimodal peaks indicative of traffic emissions for all the VOCs
with the exception of ethane. Ethane is a major component of natural gas and its main source in the
urban atmosphere can be from gas pipeline leakage, while the other VOCs are either combustion
products from vehicle exhaust or arising from fuel evaporation and solvent use (isoprene can also
be from biogenic sources). The VOCs diurnal patterns (with the exception of ethane) are similar to that of CO with the evening rush hour peak showing a greater amplitude than that of the morning rush hour peak, reflecting a common source in gasoline engine emissions. The mainly traffic related VOCs ethyne, propene, 1,3-butadiene and benzene show high concentrations in the morning and evening periods associated with the traffic rush hours i.e. periods of maximum traffic volume. However, toluene, ethylbenzene and o-xylene although showing strong traffic influences are also major emissions from solvent use, that can also give high concentration during daytime due to higher temperatures. Shin et al. (2013) also report instances of VOCs not associated with traffic emissions (exhaust gases and gasoline vapour) and others showing a diurnal pattern associated with traffic sources, stating that such observations make it difficult to assign the main emission source. Isoprene that is emitted by many species of trees and by traffic shows increasing levels moving through the day, with emissions responding to an increase in ambient temperature. Ethane has a unique diurnal variation which can be easily explained if a constant rate of gas leakage is assumed. The concentration will be higher in the morning with a low mixing depth and a reduction in concentration as the boundary layer deepens during the day. This feature exhibited by ethane can be useful in assessing the emission and dispersion of the other VOCs and gas phase pollutants, with the absolute ethane concentrations used as a normalization factor (Figure S3) i.e. the normalization is done by dividing the hourly concentration of each pollutant by the corresponding hourly ethane concentration. The diurnal patterns of the VOCs, including isoprene, and CO after ethane normalisation are similar suggesting a common source and the probability of them emanating from the same source i.e. road traffic. The bimodal peaks associated with traffic influenced emissions are absent in these plots, and there is a delay in the time maximum levels are observed i.e. showing a distinct difference between the period of maximum emission and that of maximum concentration within the boundary layer.
Total particle number count (TNC) also produces a diurnal pattern associated with traffic emissions with a continuous traffic flow between 08:00 hrs and 20:00 hrs. There is the typical maximum value corresponding to the time of day with intense vehicular activities, and the diurnal plot is very similar to that of eBC (Figure S4). eBC is a good tracer for diesel combustion from traffic sources and a major contributor to particle number count (Reche et al., 2011; Harrison et al., 2019). In this study, the diurnal profile for both parameters is similar, depicting a traffic generated pollutant, and elevated levels of eBC are observed for the southerly wind direction, a condition in which the sampler receives freshly traffic-emitted pollutants.

The weekday plots give the variability of the pollutant during the weekdays (Monday to Friday) and the weekends (see top and bottom left panels in Figures 1 and 2). Pollutants such as the oxides of nitrogen, SO$_2$, CO, the regulated particulate matter fractions, BC and particle total number counts all give maximum values on the weekdays, and the lowest concentrations over the weekend. The pollutant levels are observed to start to increase at the start of the week, attain a relatively constant level, and start to decline as the weekend approaches. These patterns are similar to the traffic volume for London Marylebone Road, which is slightly higher on the weekdays than the weekend (Figure S5), with the traffic profile aligning with that of the traffic related pollutants. Ozone that usually shows lower concentrations with a high NO concentration shows an increased concentration towards the weekends and a decrease to attain minimum levels during the weekdays. The concentrations of the marine aerosol related species and potassium are relatively constant throughout the weekdays in contrast to Ca that shows a maximum during the week and declines over the weekend. NH$_4^+$, and SO$_4^{2-}$ also exhibit a similar weekdays plot as that of Ca. With the exception of ethane, all the VOCs investigated give weekday plots similar to those of the traffic related pollutants. Ethane shows slightly increased levels in the atmosphere on weekdays relative to the weekend, possibly due to increasing usage of the gas in areas close to the monitoring station.

The EC and OC give a similar weekdays pattern with levels higher during the week and a dramatic
approaching the weekend; this observation is indicative of a significant contribution of road traffic emissions to EC and OC. However, the situation is reversed for the OC/EC ratio, with the highest values recorded over the weekend, due to a greater decline in EC than OC.

There is a clear seasonal variability exhibited by the different pollutants investigated in this study. The different seasons and the associated months are defined as follows: Winter (DJF), Spring (MAM), Summer (JJA) and Autumn (SON). The United Kingdom is a net sink for some of these air pollutants, so long-range transport of pollutant will influence the seasonal measurements and patterns observed. For instance, ozone shows a springtime maximum in May (and a minimum in November) similar to observations of the northern hemisphere background at Mace Head, a location reflective of intercontinental and regional long-range transport of the pollutant to the UK (Derwent et al., 2015). It has been suggested that elevated levels of O$_3$ in springtime and summertime may be the result of photochemical reactions of the transported ozone precursor molecules that have accumulated over the winter period (Cristofanelli and Bonasoni, 2009; Vingarzan, 2004). NO and NO$_x$ generally show seasonal fluctuations opposite to those of O$_3$ i.e. winter high and a springtime to summer low. High winter concentrations may result from less mixing in a shallower boundary layer during winter and increased emissions from heating of homes and car usage. NO$_2$ on the other hand shows relatively small seasonal changes. The seasonal change in concentrations of particulate matter is highly influenced by temperatures changes, as the highest values are observed during cooler periods with the lowest measured between June and August when the temperatures are at their highest. The low level of PM in summer is in part due to longer daylight hours and higher temperatures causing vaporization of the semi-volatile components especially the ammonium nitrate-rich aerosol (Harrison et al., 2012a). CO and SO$_2$ both exhibit seasonal patterns similar to those of the particulate matter fractions. Primary pollutants with little seasonal variation in source strength such as BC and NO$_x$ (mainly from local traffic) show higher concentrations in winter due to weaker atmospheric mixing and dispersion. The total particle counts of the PM size fractions
record their least concentrations during summer due to vaporization of volatile components with the
maximum levels recorded during the cooler periods, as ambient concentrations are affected by
ambient temperature (Charron and Harrison, 2003; Sabaliauskas et al., 2012) as well as atmospheric
mixing. During winter, particle number concentrations tend to increase at traffic locations due to
enhanced condensation of the hot tailpipe emission and new particle formation especially for
particle fractions with diameter less than 50 nm (von Bismarck-Osten et al., 2013).

Cl, Mg and Na ions show a winter maximum and a summer minimum. High concentrations of Cl
and Na in winter are due to average higher wind speed leading to increased marine aerosol in the
atmosphere (Twigg et al., 2015; Abdalmogith and Harrison, 2006), and a contribution from road
deicing salt is possible. Ca shows limited seasonal variability while K shows a summer minimum
and a maximum concentration in December, probably related to biomass burning. NH$_4^+$, NO$_3^-$ and
SO$_4^{2-}$ all show a maximum concentration in March and the least amount in summer. There is an
increased nitrate concentration from summer to winter. This increase in concentration in winter can
be explained as an increase in the formation of nitrate on aerosol particles and a longer lifetime of
nitrate in winter than in the summer period, during which there is a high dry deposition velocity of
HNO$_3$ (Fisseha et al., 2006). Frequent regional transport events from mainland Europe are also a
common feature in the spring. Hui et al (2018) state that seasonal variability in VOC
concentrations in the atmosphere depends on the changes in VOC sources, OH radicals and the
atmospheric mixing state. High temperature, strong solar radiation and efficient atmospheric mixing
(i.e. strong convection) during the summer enhances photochemical depletion of the VOCs,
therefore favouring lower concentrations during this period. On the other hand, in the winter period,
the atmospheric boundary layer is shallower; the temperature stratification is more stable leading to
less dilution of the pollutants. All this leads to a lower photochemical consumption in the winter
and maximum pollutant concentrations. Ethane, ethyne, propene, 1,3-butadiene and benzene all
show a summer minimum and a winter maximum. The VOCs more associated with solvent use
(toluene, ethylbenzene and o-xylene), increase in concentration from February and attain their maximum in November. Isoprene gives maximum concentrations in summer due to an increase in both biogenic and evaporative emissions at higher temperatures. There is a strong seasonal change exhibited by EC and OC. EC has a minimum value in April and a maximum value in September, whereas OC shows its least levels during July and maximum in November. The seasonal pattern of the OC/EC ratio has its highest value in March and its lowest value in September. Several studies in Europe have indicated maximum EC and OC concentrations in winter and the minimum in summer (Mbengue et al., 2018; Jones and Harrison, 2005). However, for this study, the maximum levels for both components were recorded in autumn. The reasons are unclear.

Roadside Increments
The contributions of traffic emissions at the London, Marylebone Road site above background pollutant concentrations have been investigated for particulate matter, BC and heavy metal concentrations by subtraction of simultaneously measured concentrations from the London, North Kensington background site, located in a residential area of central London (Bigi and Harrison, 2010). In estimating the roadside increments, it is assumed that the pollution level at the background site is representative of urban background levels and this is not influenced significantly by any single source in the surrounding area, but rather by the integrated contribution from all sources upwind of the station. Therefore, the difference in the pollutant concentration at the roadside and background sites should be solely influenced by traffic emissions. Pollution arising from long-range transport influences both locations to a similar extent.

As expected, there is a higher concentration of particulate matter at the London, Marylebone Road site relative to the background site at North Kensington for the period under investigation. The average yearly increment ranges from 4.5-9.0 µg/m³ for PM$_{2.5}$ and 9.9-16.7 µg/m³ for PM$_{10}$, with 2014 giving the lowest yearly mean for both PM fractions (Table 2). This shows data for
comparison derived from the hourly continuous instrumental data, and from 24-h average data
derived from gravimetric determination of filters. The coarse fraction (PM<sub>c</sub>) also showed a roadside
increment throughout with annual mean values between 4.2 and 9.7 µg/m<sup>3</sup> (daily data). These
increments in the different roadside size fractions can be related to roadside emissions consisting of
both exhaust and non-exhaust contributions (Thorpe and Harrison, 2008; Harrison et al, 2012b).
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annual mean values between 4.2 and 9.7 µg/m<sup>3</sup> (daily data). These
increments in the different roadside size fractions can be related to roadside emissions consisting of
both exhaust and non-exhaust contributions (Thorpe and Harrison, 2008; Harrison et al, 2012b).
The year-to-year variability and apparently anomalous negative value in Table 2 (hourly data) may
be in part attributable to incomplete data recovery (see Table S5 for data recovery data).

Investigation of the long-term trend of the ΔPM<sub>10</sub> shows a significant decline in the monthly mean
value for PM<sub>10</sub> (p < 0.001) with a relatively constant trend exhibited for ΔPM<sub>2.5</sub>. The diurnal plot
for the roadside increment for both PM<sub>2.5</sub> and PM<sub>10</sub> shows a higher increment between the period
08:00 hrs and 18:00 hrs corresponding to the period of the day with greater vehicular movement
(Figure S6). The weekday trend shows the usual higher levels on the weekdays with lowest levels
over the weekend as observed typically for traffic related pollutants. However, there is difference in
trend in the seasonal variation of ΔPM<sub>2.5</sub> and ΔPM<sub>10</sub>. ΔPM<sub>2.5</sub> shows a downward trend from the
start of the year to its minimum value in spring (April) and then a rise to a maximum value in early
autumn (September). In the case of PM<sub>10</sub>, the trough observed for PM<sub>2.5</sub> in April is completely
absent, but rather a rise in value from the start of the year to its first maximum in late spring (May)
and a second one in August are seen. The reasons are not fully clear and issues of incomplete data
recovery may contribute to the divergence in trends.

There is a significant decline in roadside increment for eBC at an overall rate of 13.48%/year (p <
0.001) at the Marylebone Road relative to the urban background site at North Kensington for the
period 2014-2019. A maximum monthly increment >6 µg/m<sup>3</sup> was recorded in 2014 and a minimum
monthly average of <2 µg/m<sup>3</sup> in 2019. The reduction in BC increment is consistent with the
reduction in diesel particle emissions which followed the introduction of diesel particle filters on
Euro 5 vehicles which first entered the market in 2009 (Beddows and Harrison, 2018). The diurnal, weekday and seasonal/monthly variation of the roadside BC increment are similar to those exhibited by $\Delta\text{PM}_{2.5}$, showing a strong exhaust emission contribution to the BC increment (Figure S7).

Roadside emissions of heavy metal species are mainly associated with non-exhaust emissions that derive from the wear of tyres (Zn) and brakes (Cu, Fe) or components of the road surfacing materials and surface dust (Ca, Al, Fe) with Mn attributed to biomass fuel burning by Goddard et al. (2019), although this seems unlikely to apply to the roadside increment. Figure 4 shows Fe as the major component for PM$_{10}$ composition followed by Cu, Zn, Mn, Cr and Pb. This reflects the contributions of brake wear, tyre wear and road surface wear and/or re-suspended road dust.

The roadside increment of metals was investigated by subtracting average yearly metal concentrations from the London, Westminster background site from that of the London, Marylebone Road site for the period 2011-2018. The London, Westminster monitoring station is located within a self-contained housing in the car park of the mortuary and coroner's court. The nearest road is the B323 Horseferry Road approximately 17 metres north of the station. The surrounding area is mixed commercial and residential. Table 3 shows that there is a roadside increment at LMR of all the metals throughout the period under consideration with the exception of 2013-2015 which show a lower level of Pb along the road. The data show that there has not been significant decrease in the concentrations from 2011 to 2018, consistent with the lack of controls on non-exhaust sources.

There are very small roadside increments and decrements in the yearly average for the different inorganic species of the PM$_{10}$ fraction for the period under investigation, i.e. 2011 to 2018 (Table S6) for which the North Kensington site was the background. Such observations illustrate minimal
local contributions to the pollutants but significant concentrations resulting from long-range transport of the pollutants. However, during winter there is some evidence for a higher concentration of Ca, Cl and Mg at the background site relative to the roadside possibly due to a greater usage of de-icing salts (Ca, Mg and Cl are components of de-icing salts). With the exception of Na with four (50%) out of the eight yearly average readings showing a decrement at the roadside, all the other inorganic species give roadside decrements in 62.5%-85.5% of the average yearly readings.

Vehicular activities contribute to elevated levels of both EC and OC at the Marylebone Road site (Table 4). Inspection of the yearly mean values show the yearly mean contribution of EC is declining (maximum increment of 5.89 µg/m$^3$ in 2011 and a value of 1.83 µg/m$^3$ by 2018). The yearly mean roadside increment for OC has decreased slowly throughout the period, consistent with control of diesel particles which contain a predominance of EC relative to OC.

**Geographical Source Attribution of Air Pollutants**

Urban street canyons have a tendency to have high levels of particulate pollution due to restricted dilution resulting from the geometry of such locations (von Bismarck-Osten et al., 2013). At the Marylebone Road site, pollutant levels are highest between the 225 and 270º (or southerly) wind sectors, during which time the sampler receives freshly traffic-emitted pollutants due to the street canyon vortex, and the northerly wind sector is associated with background air from North London (Harrison et al., 2019). The latter point is shown clearly by Figure 5, which plots PM$_{10}$ measurements at Marylebone Road against those for North Kensington for northerly wind sectors, showing very similar concentrations.

A significant contribution of roadside emissions is shown by high concentrations of the nitrogen oxides at both low and high wind speeds (Figure 6). Marylebone Road is an urban street canyon and
the circulation of the air parcel within the street canyon can result in high pollutant concentrations at high wind speeds especially during southerly and south-westerly wind events, as seen in Figure 6. Wind directions are taken from London, Heathrow airport and represent directions above, rather than within the canyon.

For the other gas phase pollutants (Figure S8), CO and SO$_2$ show a significant local source contribution at low wind speeds, with appreciable levels also recorded at high wind speeds for wind originating from the southerly direction. O$_3$ on the other hand shows higher concentrations during high wind speeds from the north and north-east of the monitoring site, corresponding to low NO$_x$ at the site.

The PM$_{10}$ and PM$_{2.5}$ fractions show both a local (w.s. < 2 m/s) and a long-range/regional contribution from the easterly direction at high wind speed (Figure 7). In the UK, several studies have identified long-range transport of fine particulate matter especially from the east (or south-east) comprising air masses originating from continental Europe, with nitrate and sulphate dominating the particle composition (Grange et al., 2016; Bigi and Harrison, 2010). The contribution of PM$_c$ to PM$_{10}$ is greatest during high wind speeds, especially from the easterly and westerly wind directions. This is possibly due to road dust resuspension when the wind direction is parallel to the road.

The polar plots of the robust slope (Figure S9) of PM$_{2.5}$/PM$_{10}$ and PM$_c$/PM show clearly the predominance of finer particles in the air masses advected from the easterly sector, often attributable to mainland Europe. A similar plot for the BC/PM$_{2.5}$ slope (Figure 8) emphasises the role of traffic on Marylebone Road as a source of PM$_{2.5}$.
All of the inorganic components show elevated concentrations at higher wind speed, which is usually associated with long-range transport of pollutants (Figure S10 and S11). However, some also show in addition to that, higher levels at wind speeds < 2 m/s, indicative of a local emission source contribution. Both Ca and K show elevated concentrations at wind speed ≤ 2 m/s. Local source emissions of Ca include road surface abrasion and resuspension of road surface dust particles. Both local and regional biomass combustion contribute to significant levels of K measured at the site (Harrison et al., 2012b). The components of marine aerosols all show elevated concentrations during high wind speeds. The south-west direction gives the highest concentrations for the chloride ions followed by the easterly direction; Na shows maximum concentrations from the southeast with the southwest quadrant also recording high concentration; the reasons are unclear, but may relate to aged marine aerosol from the southeast. The mass concentrations of Na$^+$ and Cl$^-$ in fresh sea salt are 0.308 g/g and 0.554 g/g respectively (White, 2008), giving an Na$^+/\text{Cl}^-$ ratio of 0.556. Figure S12 shows that this ratio is generally observed on strong winds from the south-westerly direction indicating a contribution of fresh sea salt, whereas the other directions show depleted levels of Cl$^-$ (due to removal by chemical reaction) thereby giving higher ratios. Crilley et al (2017) conducted a source apportionment study at this same location using a combined positive matrix factorization (PMF) and conditional probability function (CPF) approach in which the chlorine level was used to assign two different marine aerosol types i.e. fresh and aged sea salt particles. The study indicated that marine aerosol originated from different wind directions with the south/southwest wind component accounting for the highest contribution of fresh sea salt during high wind speed conditions. The study also identified a significant contribution of marine aerosol originating from the coastline areas in the east, but with greater chlorine depletion.

There are also maximum concentrations for Mg from the east and southwesterly directions. The major components of the anthropogenic secondary inorganic particulate matter (NO$_3^-$, NH$_4^+$ and SO$_4^{2-}$) all show their highest concentrations emanating from the easterly directions indicating
mainland Europe as the dominant source of the pollutants (a similar plot is also observed for the
North Kensington monitoring site). Nitrate, ammonium and sulphate also show some local
contribution to elevated levels. These features exhibited by the species are similar to those of PM$_{10}$
(and PM$_{2.5}$), as they are the major components of particulate matter recorded at this location. The
atmospheric composition is hence strongly influenced by meteorology, with sea salt dominating air
masses from the ocean and secondary inorganic aerosol dominating air masses coming from
mainland Europe (Twigg et al., 2015). Figure 9 shows an important local primary source
contribution (i.e. traffic emissions) for EC and OC concentrations recorded during lower wind
speed conditions (<2 m/s). Elevated concentrations at high wind speed conditions in the
southerly/southwesterly sector can be attributed to emissions within the street canyon. The elevated
concentrations observed from the east and southeasterly directions, especially for OC, are probably
due to long-range transport.

Particle number and size distribution

The long-term plot of total particle count from the condensation particle counter for the Marylebone
Road site shows a statistically significant ($p < 0.001$) downward trend in monthly mean
concentration for the period 2011-2018. The average monthly total particle count averaged $\approx 38,000$
# cm$^{-3}$ in 2011 and has reduced to around 11,000 # cm$^{-3}$ in 2019 (Figure 10).

The diurnal and weekday variations (left and right panels respectively in Figure 11) show a typical
traffic dependence of the total particle number i.e., the typical peaks corresponding to the time of
day with intense vehicular activities. The number count is at its highest during the weekdays and
decreases over the weekends. There is also seasonal variability, with autumn to winter maxima and
the least counts recorded during summer. During winter, particle number concentrations tend to
increase at traffic locations due to enhanced condensation of the hot tailpipe emission and new
particle formation especially for particle fractions with diameter less than 50 nm (von Bismarck-Osten et al., 2013).

These features exhibited for the three different timescales are similar to those shown by both the PM$_{10}$ and PM$_{2.5}$ mass concentration plots. However, a notable difference arises in the seasonal plots in which the time at which the maximum peaks is seen. For all three parameters, there are peaks for both spring and autumn seasons; however, for the particle number count, the highest peak occurs in autumn with the second highest in spring, whereas it is the reverse for PM$_{10}$ and PM$_{2.5}$ concentrations. PM mass is more influenced by regional transport of particles than particle number due to the effects of coagulation and evaporation of traffic particles.

There is an increase of particle number count recorded during both low and high wind speed conditions between 100-270º (Figure 12). In the southerly and southwesterly directions, high concentrations at low wind speed is reflective of direct emission from the road as the location of the monitor favours sampling of fresh materials in this direction. Recirculation of particles within the street canyon can account for elevated concentrations during heavy winds. In addition, a long-range transport effect is observed from the easterly and southeasterly directions. Wind coming from this direction has been identified to carry pollutants originating from continental Europe.

Figure 13 shows a lognormal particle size and number distribution for the average monthly measurement for the period 2010-2018, for particles within the size bins of 16-600 nm. The size distribution is typical of those reported previously for this site (Charron and Harrison, 2003; Jones et al., 2012; Harrison et al., 2019).

The distribution is dominated by ultrafine particles (<100 nm). This feature is common to the distribution curves shown in Figure S9 in the Supplementary Information for each of the years.
under consideration (i.e., 2010-2018) with all the mode(s) in the Aitken range. The modal diameter and curve shape have changed over the years, and a consistent trend is seen in the data (Figure S13).

**Comparison with other sampling sites**

Table 5 summarises literature that contains a number of studies of air sampling sites with long time series of measurements. Similar studies have identified patterns in pollutant concentrations within urban areas with regular cycles established. Local emissions and meteorological conditions are seen to be key factors determining pollutant concentrations during given periods. Long-term trends in concentration reflecting changing emissions have been identified.

**CONCLUSIONS**

All of these studies have identified traffic emissions as a major source of urban pollution. Even though the studies were conducted in different regions, most pollutants showed a decline over time, except O₃ which rose steadily. Wintertime was the most polluted season in these different urban locations.

Broadly similar trends have been observed in this study of the Marylebone Road site, but it is differentiated from the other studies outlined above by:

(i) many more variables/pollutants are investigated;

(ii) the location of the monitoring site is within a street canyon in the centre of London; and

(iii) the specific contribution of vehicular emissions is investigated through calculation of the roadside increment.

The investigation of data from the various monitoring networks shows various processes controlling the pollutant concentrations in the urban atmosphere of Central London. Strong policies and appropriate emission technologies are responsible for the observed decline in the long-term trend
analysis of traffic related pollutants. Emission rates and meteorological conditions are also key in accounting for the relatively short term (diurnal and weekday) and seasonal variations observed for pollutant concentrations. The diurnal plots for the traffic related pollutants show peak concentrations during periods when there are increased vehicular emissions, weaker mixing and poor dispersion accounting for peak levels for pollutant concentrations during the time of the traffic rush hours. The seasonal effect shows winter as generally the most polluted period, a condition enhanced by increased emissions and poor dispersion conditions.

Road traffic emissions (exhaust and non-exhaust) are a major contributor to pollution of urban areas and this is reflected in the roadside increment in particulate matter fractions, BC, EC and OC and heavy metals. Several inorganic species (Ca and those associated with marine aerosol and secondary particulate matter) show measured concentrations being controlled by meteorological conditions, with several periods for which the background site measures greater concentrations. Meteorology strongly influences the composition of the atmosphere at this location, wherein local emissions (vehicular) strongly dominate for the nitrogen oxides, CO and SO$_2$ (and a part of PM), hemispheric and regional transport are dominant for O$_3$, marine aerosol components and particulate matter. The particulate matter (PM$_{10}$ and PM$_{2.5}$) originate from continental Europe mainly as secondary aerosol as is shown by the polar plots for NO$_3^-$, NH$_4^+$ and SO$_4^{2-}$.

The Marylebone Road site exceeds the Limit Values for NO$_2$, although it is worth noting that the extent of these exceedances has been declining over the period under investigation. The annual and 24-hour concentrations of PM$_{10}$ and PM$_{2.5}$ are however largely in compliance with the Limit Values. These results are reflective of the effectiveness of control measures that have been instituted in recent years, although much remains to be done for the protection of public health, especially in relation to non-exhaust emissions of particles, and regional transported secondary particles.
DATA AVAILABILITY

Data supporting this publication are openly available from the UBIRA eData repository at

https://doi.org/10.25500/edata.bham.00000577

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SUPPORTING INFORMATION

Supporting Information provides details of instrumentation, data capture, exceedance of threshold concentrations, OC/EC ratios, as well as further diurnal and polar plots.

CONFLICT OF INTERESTS

The authors declare no competing financial interest.
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TABLES LEGENDS:

Table 1: Long-term trend in pollutant concentrations for the period 2009-2018.

Table 2: Roadside Increment of PM at Marylebone Road for the period 2009-2018.

Table 3: Roadside increment (ng m\(^{-3}\)) for heavy metal concentrations for the period 2011-2018.

Table 4: Roadside increment (µg m\(^{-3}\)) for EC and OC for the period 2010 – 2018 at Marylebone Road.

Table 5: A review of some studies profiling urban air quality status.

FIGURE LEGENDS:

Figure 1: Diurnal, weekly and monthly time series plot for regulated pollutants at Marylebone Road.

Figure 2: 1:1 Scatterplot for BC and PM\(_{2.5}\) by wind direction (right scale, degrees).

Figure 3: Diurnal, weekly and monthly time series plot for VOCs at Marylebone Road.

Figure 4a: Yearly mean metal concentrations in PM\(_{10}\) at Marylebone Road.

Figure 4b: Yearly mean metal concentrations in PM\(_{10}\) without Fe at Marylebone Road.

Figure 5: 1:1 Scatter plot for PM\(_{10}\) for both LMR and LNK for the northerly wind direction.

Figure 6: Polar plot for nitrogen oxides showing significance of wind parameters for pollutant dispersion. The direction from the centre of the plot shows the wind direction above the canyon and the distance from the centre is the wind speed (scale in metres per second).

Figure 7: Polar plot for PM fractions showing significance of wind conditions to pollutant dispersion.

Figure 8: Polar plot of the robust slope between PM\(_{2.5}\) and BC for 2013 at London, Marylebone Road.

Figure 9: Polar plot for EC (left) and OC showing the influence of wind direction and speed.

Figure 10: Long-term trend in average monthly total particle number count for London, Marylebone Road.

Figure 11: Diurnal, weekday and monthly variation in total particle count for London Marylebone Road.

Figure 12: Plot of dependence of particle count on wind conditions.
Figure 13: The average particle number size distribution curve for data for the period 2010-2018.

Table 1: Long-term trend in pollutant concentrations for the period 2009-2018.

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<tr>
<td>SO2</td>
<td>-0.42</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>-5.47***</td>
<td></td>
</tr>
<tr>
<td>PM2.5</td>
<td>-4.00***</td>
<td></td>
</tr>
<tr>
<td>PMc</td>
<td>-3.43***</td>
<td></td>
</tr>
<tr>
<td>PM10</td>
<td>-3.93***</td>
<td></td>
</tr>
<tr>
<td>Period</td>
<td>2009 - 2018</td>
<td></td>
</tr>
</tbody>
</table>

Note: the asterisk relates to the statistical significance of the trend estimate: $p < 0.001 = \ast\ast\ast$, $p < 0.01 = \ast\ast$, $p < 0.05 = \ast$ and $p < 0.1 = +$

Table 2: Roadside Increment of PM at Marylebone Road for the period 2009-2018.

<table>
<thead>
<tr>
<th>Year</th>
<th>ΔPM$_{10}$ (µg/m$^3$)</th>
<th>ΔPM$_{2.5}$ (µg/m$^3$)</th>
<th>ΔPM$_c$ (µg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2009</td>
<td>16.7</td>
<td>7.0</td>
<td>9.7</td>
</tr>
<tr>
<td>2010</td>
<td>13.6</td>
<td>8.1</td>
<td>5.6</td>
</tr>
<tr>
<td>2011</td>
<td>16.1</td>
<td>9.0</td>
<td>7.1</td>
</tr>
<tr>
<td>2012</td>
<td>12.7</td>
<td>8.1</td>
<td>4.6</td>
</tr>
<tr>
<td>2013</td>
<td>10.2</td>
<td>5.8</td>
<td>4.4</td>
</tr>
<tr>
<td>2014</td>
<td>10.1</td>
<td>5.9</td>
<td>4.2</td>
</tr>
<tr>
<td>2015</td>
<td>10.1</td>
<td>5.2</td>
<td>4.9</td>
</tr>
<tr>
<td>2016</td>
<td>9.9</td>
<td>4.5</td>
<td>5.3</td>
</tr>
<tr>
<td>2017</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>2018</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

Table 3: Roadside increment (ng m$^{-3}$) for heavy metal concentrations for the period 2011-2018.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>0.127</td>
<td>0.348</td>
<td>0.011</td>
<td>0.136</td>
<td>0.092</td>
<td>0.226</td>
<td>0.123</td>
<td>0.069</td>
</tr>
<tr>
<td>Cd</td>
<td>0.072</td>
<td>0.014</td>
<td>0.013</td>
<td>0.038</td>
<td>0.027</td>
<td>0.029</td>
<td>0.035</td>
<td>0.030</td>
</tr>
<tr>
<td>Cu</td>
<td>67.6</td>
<td>54.6</td>
<td>44.9</td>
<td>46.0</td>
<td>41.7</td>
<td>38.0</td>
<td>48.3</td>
<td>39.2</td>
</tr>
<tr>
<td>Fe</td>
<td>1354</td>
<td>1208</td>
<td>1042</td>
<td>1133</td>
<td>1103</td>
<td>1069</td>
<td>1469</td>
<td>1153</td>
</tr>
<tr>
<td>Mn</td>
<td>10.8</td>
<td>9.90</td>
<td>8.05</td>
<td>8.61</td>
<td>8.39</td>
<td>8.35</td>
<td>11.9</td>
<td>8.94</td>
</tr>
<tr>
<td>Ni</td>
<td>1.33</td>
<td>1.45</td>
<td>0.85</td>
<td>0.62</td>
<td>0.73</td>
<td>0.91</td>
<td>0.99</td>
<td>0.77</td>
</tr>
<tr>
<td>Pb</td>
<td>0.102</td>
<td>2.86</td>
<td>-0.179</td>
<td>-0.626</td>
<td>-0.147</td>
<td>3.303</td>
<td>0.180</td>
<td>0.150</td>
</tr>
<tr>
<td>V</td>
<td>0.188</td>
<td>0.503</td>
<td>0.149</td>
<td>0.270</td>
<td>0.323</td>
<td>0.294</td>
<td>0.336</td>
<td>0.165</td>
</tr>
<tr>
<td>Zn</td>
<td>17.9</td>
<td>30.4</td>
<td>9.34</td>
<td>9.66</td>
<td>11.6</td>
<td>13.3</td>
<td>20.6</td>
<td>16.6</td>
</tr>
</tbody>
</table>
Table 4: Roadside increment (µg m⁻³) for EC and OC for the period 2010 – 2018 at Marylebone Road.

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔEC</td>
<td>5.42</td>
<td>5.89</td>
<td>5.23</td>
<td>3.67</td>
<td>3.89</td>
<td>3.17</td>
<td>2.73</td>
<td>2.50</td>
<td>1.83</td>
</tr>
<tr>
<td>ΔOC</td>
<td>2.64</td>
<td>3.63</td>
<td>3.24</td>
<td>2.47</td>
<td>2.20</td>
<td>2.44</td>
<td>1.90</td>
<td>2.18</td>
<td>2.10</td>
</tr>
</tbody>
</table>

Table 5: A review of some studies profiling urban air quality status

<table>
<thead>
<tr>
<th>No</th>
<th>Outcome</th>
<th>Author and Location</th>
<th>Author and Location</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Investigation of regulated gas phase pollutants and VOCs over a 13-year period (2000-2013) in the Po Valley of Italy. The main emission sources in the region included vehicular, industrial, domestic heating, airport and harbour. The long-term trend analysis of the pollutants showed decreases in the mean concentration of CO, SO₂ and the VOCs, but no significant change in the level of the oxides of nitrogen, while O₃ levels showed a slight increase. The declining trend in some of the pollutants over the period was attributed to a reduction in industries, use of better grade fuel and technological improvement in the emission standards for road vehicles. All of the pollutants showed a seasonal cycle, except SO₂. This unexpected behaviour of SO₂ was due to a very high rate of oxidation i.e. shorter atmospheric residence time. Ozone showed maximum concentrations during the warmest periods while CO, the oxides of nitrogen, VOCs and PM₁₀ produce their highest concentrations in winter, due to an increase in domestic emissions and stable atmospheric conditions. O₃ and SO₂ showed a maximum daily concentration around midday with a greater amplitude in summer. The normal twin peaks corresponding to the morning and evening traffic rush hours were seen for CO, NO, NO₂, NOₓ, PM₁₀ and VOCs. This is a coastal location and the local sea breeze circulation influences the distribution of the pollutants during daytime. The weekday/weekend cycles showed higher weekday concentration of CO, VOCs and the oxides of nitrogen with the reverse observed for ozone. SO₂ and PM₁₀ exhibited a similar pattern throughout the weekdays and weekends.</td>
<td>Masiol et al., 2014</td>
<td>Po Valley, Italy</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>A report of hourly data for PM₂.₅ and O₃ for the period 2006 – 2015 from several stations in Tehran with temporal changes investigated using the Mann-Kendall trend test. The earlier years showed an almost constant annual mean PM₂.₅ concentration, but a significant decline occurred from 2010 to 2015 at a rate of 1.17 µg m⁻³/year. For O₃, there was an initial increase in yearly mean from 2006 – 2008 followed by a significant decline (3.39 µg m⁻³) from 2008 to 2015, with 2015 giving the lowest annual mean concentration. The data show a bimodal diurnal peak for</td>
<td>Faridi et al., 2018</td>
<td>Tehran, Iran</td>
<td></td>
</tr>
</tbody>
</table>
PM$_{2.5}$ corresponding to periods with significant anthropogenic emissions. The first peak occurred around 07:00 to 09:00 corresponding to heavy road traffic in the morning rush hour. The second peak occurred around midnight and beyond correlating with a second traffic rush hour (including heavy-duty diesel vehicles) and construction and demolition activities. Analysis of PM$_{2.5}$ for the different days of the week showed statistically significant higher values during the weekdays over the weekend (Friday). The O$_3$ values showed maximum concentrations at around 3:00 pm and were higher over the weekends than the weekdays. This profile points to the significant contribution of human activities, especially vehicular traffic to poor air quality. There was a seasonal pattern in the concentration of PM$_{2.5}$ with maximum levels in winter and summer months. The high summer PM concentration is because of the Middle East dust events especially in summer, and the winter high is due to stable meteorological conditions (i.e. low mixing depth, low temperatures and weak wind). O$_3$ also showed seasonal variability with maximum monthly concentrations recorded in July due to enhanced photochemical reactions.

Air pollution in major Chinese cities was investigated for close to a period of one year by monitoring regulated particulate matter and gas phase pollutants (CO, NO$_2$, O$_3$, SO$_2$, PM$_{2.5}$ and PM$_{10}$). There was a winter maximum for all the criteria pollutants, except for ozone. This maximum concentration results from increased emissions and meteorological conditions that limit dispersion of pollutants. Coal combustion and residential heating are major contributors to the increased emissions during wintertime. O$_3$ gave a summer maximum and a winter minimum. The diurnal variation of O$_3$ had a maximum during daytime with the other pollutants giving the lowest concentrations at this time because of higher wind speeds and an increased boundary layer height. Generally, the particulate matter fractions, NO$_2$ and CO produced peaks corresponding to the morning and evening traffic rush hours, while SO$_2$ had a single peak around 11:00 am. Vu et al., (2019) report five year (2013-2017) trends in pollutants averaged across sites in the Beijing area, and corrected for the effects of weather variations. Steady falls in concentrations of all measured pollutants apart from ozone are attributable to an air quality action plan.

Analysis of long-term real time air quality monitoring data (1996-2008) from a background site in central London which showed a general downward trend for several pollutants except ozone, which rose at a steady rate. The downward trends shown by the pollutants were however not uniform and occurred at different rates. For instance, CO and NO showed a close pattern in their trend analysis with a maximum observed around 1996-1998, and a steady decline afterwards, whereas SO$_2$ showed minimal fluctuations, and the concentration remained nearly constant. PM$_{10}$ also showed a pattern that appeared constant.
throughout the period of investigation. Ozone showed the greatest seasonal variability with a maximum in May and a minimum in December, with this pattern influenced by background concentrations. CO, NO and NO$_2$ showed a winter maximum, and minimum values in June and July. PM$_{10}$ showed little seasonal variation. The traffic related pollutants showed a bimodal peak corresponding to the morning and evening traffic rush hour peaks resulting from high traffic volumes and poor dispersion, with PM$_{10}$ and particle count showing lesser amplitudes. Ozone showed a single peak at about 16:00 hrs due to less scavenging of the pollutant in the afternoon and more mixing from aloft in a deeper boundary layer. On average, all the pollutants gave their maximum concentrations in the weekdays and minimum over the weekends, with the reverse observed for O$_3$.

5 Hourly data for nitrogen oxides and particulate matter size fractions for Paris (44 sites) and London (130 sites) for the period 2005 – 2016 were investigated. The annual mean concentration of NO$_2$ exceeded the European Limit Value across all network especially for the roadside locations for both cities with background locations in Paris achieving compliance by 2016. The Limit Value for PM$_{10}$ is mostly attained across the networks in both cities, attributed to controls by the Euro 5 (light duty) and Euro V (heavy duty) standards. There were overall significant declining trends for the pollutants in both cities with the rates higher at the background sites. In 2005 – 2009, there was an increase in roadside increment in NO$_2$ due to an increase in the proportion of diesel vehicles, and with the introduction of the Euro V standard, a significant decline in the roadside increment of the pollutant was recorded between 2010 - 2016. However, for the PM$_{10}$, the roadside increment declined for both periods of measurement with London (especially inner London) showing a greater decrease than Paris. While the roadside increment in PM$_{2.5}$ show a significant downward trend in Paris, it was mostly non-significant in the case of London. The study showed a significant gain made by policies in reducing particulate matter emissions but not as expected in the case of NO$_2$.

6 The chemical composition of non-refractory PM$_{1}$ (by ACSM) and BC (Multichannel Aethalometer) were investigated for Delhi to determine temporal variation in aerosol composition. There was seasonal variability in the PM mass concentration (NR-PM$_{1}$ and C-PM$_{1}$ = NR-PM$_{1}$ + BC), with winter levels giving the highest concentration. The winter values were up to 4 times higher than the warmer periods. There was diurnal variation in the concentrations of the PM and components, with the greatest diurnal swings occurring in winter. Generally, the peak periods occurred in the morning and late evening, with lowest concentrations between 15:00 – 16:00 hrs. The organic component at highest contributed about 50% to C-PM$_{1}$. Ammonium contributed most to the inorganic component balancing the anions, however, chloride exhibited the greatest

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seasonal variability of all these species (winter concentrations up to 20 times the summer concentrations) and with highest global concentrations. Nitrate and sulphate also showed seasonal variation with the nitrate showing the least seasonal and diurnal variability and being the only species that gave elevated levels in the warmer period during daytime. BC concentrations were lower during the day and peaked at night due to high truck traffic passing close to the sampling location at night. The average BC concentration was higher in the winter than summer but contributed 6.4\% of the total mass concentration of C-PM$_1$ in winter as compared to 14\% in the summer.

The study analysed aerosol samples for PM$_{10}$-bound PAHs and heavy metals in Chengdu (China) for a period of 6 years (with ions, OC and EC analysed for source apportionment), with the sampling period divided into wet (Jun - Oct) and dry (Jan – Apr and Dec.) periods. The mean PM$_{10}$ concentration was higher for the dry period, but both periods exceeded the 70µg m$^{-3}$ limit set by the regulatory body in China. The high PM$_{10}$ concentration in the dry period was due to stable weather conditions, low precipitation and higher coal usage. The mean concentration for the 16 PAHs (from coal combustion and vehicle exhaust) also show statistically significant higher values in the dry period compared to the wet. For the heavy metals, As and Ni were higher in the wet period whereas Cr, Co, Cd and Pb were higher in the dry period. However, there was greater variability exhibited by the PAHs with PM$_{10}$ than the heavy metals for the period under investigation. A PMF model analysis for PM$_{10}$ examined 18 elements, 3 ions, OC, EC and 16 PAHs. The first two factors accounted mainly for gasoline and diesel combustion. Coal combustion, industrial sources, crustal dust and secondary aerosol formation were the other sources identified by the model. The percentage contributions of gasoline and diesel combustion were similar in the dry and wet periods, whereas, coal combustion, crustal dust and secondary aerosol formation gave a higher contribution in the dry period (winter) and the contribution by industrial sources was maximised in the wet period.

Trace metal analysis of the PM$_{10}$ fraction using an ICP-AES spectrometer was conducted for aerosol samples collected in Karachi (Pakistan) and PMF analysis conducted for source apportionment. The average PM$_{10}$ concentration recorded of 438µg m$^{-3}$ is comparable to levels reported elsewhere in Asia and some other cities in Pakistan. The mean concentrations of trace metals were categorised into groups: Ca, Al and Fe (13730 – 57260ng m$^{-3}$); Mg and S (7350ng m$^{-3}$ and 6390ng m$^{-3}$ respectively); Zn, P, Cu, Pb, Mn, Ti, Sr and Ba (220 – 830ng m$^{-3}$) and Cr, Ni, Se (50ng m$^{-3}$, 20ng m$^{-3}$ and 10ng m$^{-3}$ respectively). The PMF analysis identified biomass burning, coal combustion, resuspended dust, vehicular emissions and industrial dust as the contributors to the PM$_{10}$ mass concentrations.
**Figure 1:** Diurnal, weekly and monthly time series plot for regulated pollutants at Marylebone Road.

**Figure 2:** eBC pollution rose according to PM$_{2.5}$ concentration range.
**Figure 3**: Diurnal, weekly and monthly time series plot for VOCs at Marylebone Road.
**Figure 4a:** Yearly mean metal concentrations in PM$_{10}$ at Marylebone Road.

**Figure 4b:** Yearly mean metal concentrations in PM$_{10}$ without Fe at Marylebone Road.
Figure 5: 1:1 Scatter plot for PM$_{10}$ for both London Marylebone Road (LMR) and London North Kensington (LNK) for the northerly wind direction.
**Figure 6:** Polar plot for nitrogen oxides showing significance of wind parameters for pollutant dispersion. The direction from the centre of the plot shows the wind direction above the canyon and the distance from the centre is the wind speed (scale in metres per second).

**Figure 7:** Polar plot for PM fractions showing significance of wind conditions to pollutant dispersion.
Figure 8: Polar plot of the robust slope between PM$_{2.5}$ and BC at London, Marylebone Road.
Figure 9: Polar plot for EC (left) and OC showing the influence of wind direction and speed.
Figure 10: Long-term trend in average monthly total particle number count for London, Marylebone Road.

Figure 11: Diurnal, weekday and monthly variation in total particle count for London Marylebone Road.
Figure 12: Plot of dependence of particle count on wind conditions.
Figure 13: The average particle number size distribution curve for data for the period 2010-2018.