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Analysis of the air pollution climate of a central urban roadside supersite

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DOI: 10.1016/j.atmosenv.2021.118479

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Document Version Peer reviewed version

Citation for published version (Harvard):

Kamara, AÁ & Harrison, RM 2021, 'Analysis of the air pollution climate of a central urban roadside supersite: London, Marylebone Road', *Atmospheric Environment*, vol. 258, 118479. https://doi.org/10.1016/j.atmosenv.2021.118479

Link to publication on Research at Birmingham portal

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4	Analysis of the Air Pollution Climate of a
5	Central Urban Roadside Supersite:
6	London, Marylebone Road
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ABSTRACT. The London Marylebone Road monitoring site is a roadside supersite adjacent to a 17 highway carrying 80-90,000 vehicles per day on six lanes in a street canyon. Data from the 18 Automatic Urban and Rural Network (AURN), Black Carbon Network, Automatic Hydrocarbon 19 20 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 21 22 seasonal) and long-term variations and geographic source attribution. The contribution of roadside 23 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 24 the particulate matter fractions (-4.0%; -3.93%/yr for $PM_{2.5}$ and PM_{10} respectively) and gas phase 25 pollutants associated with vehicular emissions (-5.5%; -1.22% and -2.1%/yr for CO, NO_x and NO₂ 26 respectively), although concentrations of SO₂ and O₃ have remained relatively constant over the 27 years. Equivalent Black carbon (eBC) and total particle number count have also declined over the 28 years whereas the heavy metals show mixed results (only Cu, Ni and V shows significant 29 downward trends). The inorganic ionic components of the PM₁₀ fraction, elemental (EC) and 30 31 organic carbon (OC) and the volatile organic compounds all generally show declining trends over 32 the period. Assessment of the diurnal variations shows elevated concentrations of the particulate matter fractions, the nitrogen oxides, CO and SO₂ at periods corresponding to the traffic rush hours, 33 34 whereas O₃ 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 35 traffic influence. Cl, Mg, K and Na levels show no systematic pattern throughout, with their 36 presence likely controlled by meteorological conditions, and Ca showing high concentrations in the 37 afternoon because of resuspension of deposited dust resulting from turbulence created by vehicular 38 39 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-40 volatile nature, with sulphate producing a peak around mid-day. The VOCs, with the exception of 41 ethane, give the bimodal peaks typical of traffic related emission in the diurnal plots and their 42

pattern is more similar to CO than the other traffic emitted gaseous pollutants. Ethane is associated 43 with leakages from gas supply pipes. The weekday plots show weekday (Monday – Friday) 44 increases in traffic-related pollutants and a decline over the weekends due to lower traffic volumes, 45 46 with the reverse observed for O₃. K and the marine aerosol components show relatively similar concentrations on all days of the week, while Ca, NH_4^+ , NO_3^- and SO_4^{2-} all show a weekday 47 maximum and decline over the weekend. The pollutants show seasonal variations; O₃ shows a 48 49 springtime maximum, with the traffic-emitted pollutants (NO, NO_x, CO, EC, OC etc) giving a winter maximum due to increase in emission, lower mixing depth and poor dispersion. Particulate 50 matter fractions and total particle count show lower concentrations in summertime reflective of the 51 52 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. 53 NH_4^+ , NO_3^- and SO_4^{2-} show lowest levels in summer and maximum springtime concentrations. The 54 traffic-related VOCs show a summertime minimum and wintertime maximum, while isoprene 55 shows increased concentrations during summertime. The street canyon circulation causes the 56 57 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 58 exhaust (particulate matter mass fractions, particle number and eBC) and non-exhaust emissions 59 60 (heavy metals). However, roadside increments of inorganic species, which include Ca, marine aerosol components and the secondary particulate matter components, are not significant, indicating 61 that they are mainly controlled by regional transport of the pollutants. Polar plots show strong local 62 contributions for the regulated gas phase pollutants and the carbon components (EC and OC), with 63 O₃ concentrations enhanced mainly from the northerly direction. The long-range contribution from 64 65 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 66 EC than OC. 67

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

69 INTRODUCTION

London is the largest and most populated city in the UK and has a history of severe pollution events 70 such as the notorious 1952 London smog that precipitated an increased awareness of air quality 71 72 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 73 74 and policy development. Bigi and Harrison (2010) analysed 13 years of hourly data from a central 75 urban background site in London for particulate matter and gas phase pollutants in terms of long-76 term trends, annual, weekly and diurnal cycles. The analysis showed generally declining trends for all the pollutants considered, with the exception of O₃ which exhibited a steady increase over the 77 78 period. Clear seasonal variations were observed, with CO, NO, NO₂ and SO₂ showing a summer and winter maximum and a pattern associated with traffic emissions (for CO, NO and NO₂). O_3 79 showed a maximum in May and a minimum in winter, and the particle number count was at a 80 minimum in August and a maximum in winter. Colette et al. (2011) investigated air quality trends 81 in Europe over the past decade by looking at pollutants such as NO₂, O₃ and PM₁₀ from urban 82 83 background, suburban background and rural background stations. They observed a general decline in NO₂ for the majority of the monitoring stations, with a slight increase of O₃ observed (especially 84 at urban sites) due to a decrease in NO_x emissions. PM₁₀ levels declined over the decade in UK and 85 86 Germany. Analysis of 18 years of data from Fresno (California) using time series and multiple linear regression models showed that the concentrations of NO_x, EC and ammonium nitrate had 87 halved since 2000, but the PM_{2.5} levels had not declined significantly (de Foy and Schauer, 2019). 88 Similarly, in Los Angeles, an assessment of the effectiveness of regulations to reduce tail pipe 89 90 emission was undertaken by investigating the trend in PM_{2.5} mass concentration and chemical 91 species concentrations for the period 2005 - 2015 (Altuwayjiri et al., 2021). The study reported an overall significant downward trend in mass concentration of EC and OC (major contributors to the 92 PM_{2.5} mass concentration). Data from 18 sites for the period 1999-2016 analysed for Seoul also 93 94 showed a decrease in the long-term measurements of PM₁₀ due to a reduction in the local source

contribution, and an increase in O_3 from local secondary production, with NO_2 and SO_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_{10} and primary gaseous pollutant concentrations with migratory high-pressure systems that enhance regional transport and local accumulation during warmer periods.

100

101 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 102 from the North Kensington and the Westminster background sites utilised as required for 103 104 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 105 conducted for unregulated pollutant metrics (i.e. eBC, heavy metals, hydrocarbon and particle 106 numbers). The results are consider as likely to be representative of heavily trafficked roadside 107 locations across Europe, as over the relevant period, the UK was subject to EU Directives which 108 109 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, 110 although there will be differences due to local source emissions and differing meteorology, there are 111 broadly similar air pollution climates across Europe, especially in relation to road vehicle 112 emissions. 113

114

115 **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 80° 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).

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> Data for this study were downloaded from the Automatic Urban and Rural Network for the 127 regulated pollutants (gas phase and particulate matter), as well as for heavy metals, black 128 carbon, particle number size distributions and hydrocarbons from the respective networks. 129 The heavy metals data are based on an integrated 1-month period sampling of the PM_{10} 130 fraction, while the other parameters are measured automatically and recorded over hourly 131 periods. Quality assurance and quality control procedures follow the standards for the 132 Automatic Urban and Rural Network (AURN) instruments, including regular span and zero 133 checks, and every six months full servicing and an inter-calibration audit (https://uk-134 air.defra.gov.uk). Details of the instruments appear in Table S1. Data recovery is high 135 (mostly >80%) for the hourly measurements especially for the regulated pollutants, not 136 requiring any adjustments. For annual averages, as in the calculation of roadside increments, 137 only periods with data availability at both locations are included. 138

139

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

147 as the background site for the estimation of the roadside increment for the particulate matter

148 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

151 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
- 154 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.

157

158 **RESULTS AND DISCUSSION**

159 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.

164

Over the period 2009 - 2018 a significant decrease in the levels of the different particulate matter 165 fractions, the nitrogen oxides (NO_x and NO₂) and carbon monoxide (Table 1) was observed. CO 166 exhibits the highest rate of decline followed by the PM fractions and then the nitrogen oxides. The 167 levels of O₃ and SO₂ have remained relatively constant, as they show an overall insignificant 168 increase and decrease in trend respectively. At the London Marylebone Road, SO₂ arises mainly 169 from road traffic. Low emissions of SO₂ from the transport sector is because of the introduction of 170 low sulphur content (<50 ppb) diesel and petrol introduced in 1999 and 2001 respectively, with an 171 even lower sulphur content fuel of <10 ppb few years later (Boulter and Latham, 2009). The 172

reduction in motor fuel sulphur to "zero sulphur" levels (<10ppm S) occurred in 2007, which is why 173 concentrations and the traffic increment have remained low and fairly constant since. Road 174 transport is one of the key emitters of air pollutants in urban areas, and this sector has been 175 176 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 177 178 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 179 hydrocarbons but also to oxidation of NO leading to an increase in NO2 emissions, corrected 180 subsequently by a variety of technologies. These emission standards, introduced from 1992 181 onwards, applied only to new vehicles, so changes in air quality occur only gradually as new 182 technology vehicles enter the fleet. Studies to determine the effectiveness of control measures to 183 reduce exhaust emissions in London are available. Font and Fuller (2016) investigated 65 roadside 184 monitoring sites in London for the period 2005 - 2009 and 2010 - 2014. The study generally 185 showed a significant downward trend in roadside PM_{2.5} for most of the sites with a mixed result for 186 187 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 188 is linked to an increase in the coarse particulate fraction (largely non-exhaust emissions). The study 189 further reported an increase in NO_2 and NO_x concentration during 2005 – 2009 and attributed this to 190 the increased proportion of light duty diesel vehicles. The decrease in levels of NO_x at most of the 191 roadside sites between 2010 - 2014 was concluded to be the result of reduction in vehicle fleet 192 number, and the introduction of the London Low Emission Zone, applying at that time to heavy 193 duty vehicles. The reduction in roadside increment of PM levels, which is associated with the use of 194 195 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 196 period during which no significant change in traffic flow and vehicle types was observed. The more 197 198 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 NO_x
emissions.

201

202 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 203 of 50 μ g/m³ (not to be exceeded more than 35 times per year) set for the protection of human health, 204 205 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 PM_{2.5} (the mean annual PM_{2.5} 206 concentration is below 25 μ g/m³ for the period 2009-2018). The levels of gas phase pollutants and 207 208 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 209 introduction of the Integrated Pollution Prevention and Control (IPPC) directive (Cusack et al., 210 2012). Similarly, Sicard et al. (2021) in an investigation of the air quality status of European cities 211 for the period 2000 - 2017, reported a significant decline in the emission of all primary pollutants at 212 213 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 μ g/m³ 214 one-hour limit that should not be exceeded more than 18 times a year was exceeded for the entire 215 period, with the least exceedance number of 31 times recorded in 2018. The annual mean limit of 216 $40 \,\mu g/m^3$ was also exceeded throughout this period. For O₃, the 8 hr mean limit of $100 \,\mu g/m^3$ was 217 not exceeded throughout the period under consideration. This is expected as there will be sufficient 218 NO present from traffic emissions to suppress O₃ concentrations at this location. 219

220

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 μ g/m³), and these were <100 μ g/m³ by 2018. CO also had its highest monthly mean concentration of 0.9 mg/m³ recorded in 2009. For NO_x, even though the lowest peaks (monthly average) occurred in

most recent times, the highest monthly concentrations occurred during the period 2012-2016. The 225 particulate matter fractions (PM_{2.5}, PM₁₀ and PM_{coarse}) like NO₂, show a steady decline, with the 226 maximum monthly peaks occurring during 2011-2012. The maximum monthly mean concentrations 227 for the PM fractions are 35 μ g/m³, 52 μ g/m³ and 18 μ g/m³ for PM_{2.5}, PM₁₀ and PM_c respectively. 228 There was a relatively constant level of O_3 and SO_2 concentrations from one year to the next during 229 this period. For O₃, the maximum monthly peak concentrations $>30 \mu g/m^3$ have occurred since 230 2010 and are still observed for measurements as recently as 2018. SO₂ on the other hand showed 231 maximum monthly peaks ($\approx 11 \ \mu g/m^3$) between 2014-2016 and is declining in the most recent 232 measurements. The downward trend shown by the pollutants based on real time measurements is in 233 234 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 235 such emissions (Figure S1). However, for most of these pollutants, the decline is either slowing 236 down or has levelled off. For instance, since 2010 the decline in the oxides of nitrogen and SO₂ 237 have slowed down (appearing to level off from 2020) while those of the regulated particulate matter 238 239 fractions had started levelling off by 2015 (Defra, 2019).

240

The long-term trend for other pollutants has also been investigated (Table S3). For black carbon 241 (BC), there has been a steady decline in the concentration of BC at an overall rate of 12.44%/year (p 242 < 0.001). An average maximum concentration of 8 μ g/m³ was observed in 2014, with monthly 243 average concentrations generally below $4 \mu g/m^3$ measured in 2018 (i.e. decreasing by a factor of 244 more than two). Trends in carbonaceous aerosol components across the UK are examined in more 245 detail elsewhere (Jafar and Harrison, 2020). Total number particle count (TNC) shows a 246 statistically significant (p < 0.001) downward trend in monthly mean concentration for the period 247 2011-2018. The average monthly total particle count was $\approx 65,000$ count cm⁻³ in 2011 and has 248 reduced to below 30,000 count cm^{-3} in 2018. The trends for the heavy metals for the period 2011-249 2018 give mixed results. Metals such as Cu (-3.59%/yr, p < 0.05), Pb (-2.92%/yr, p < 0.05), Ni (-250

5.33%/yr, p < 0.001) and V (-7.21%/yr) show significant downward trends, whereas As has 251 increased at a rate of 3.91%/yr (p < 0.05). The upward trend exhibited by arsenic is possibly due to 252 increased emissions arising from domestic combustion of coal and treated wood for which data are 253 254 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. 255 256 Goddard et al. (2019) also reported similar long-term trends (based on off-line ICP-MS analysis) of 257 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., 258 2010). The inorganic ionic components of the PM_{10} fraction show declining trends in most cases. 259 260 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 261 marked downward trend in sea salt component concentrations is probably explained by a decreased 262 average speed of south-westerly winds, which declined by 1.99% per year between 2011 and 2018, 263 as the generation of sea salt is strongly wind speed dependent. An alternative possibility is a 264 265 reduced use of deicing salt, but we have been unable to obtain data to test the latter hypothesis. 266 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 267 268 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 269 270 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 NH₄⁺ shows an almost 271 constant level and non-significant change, NO_3^- and SO_4^{2-} showed a significant downward trend (p 272 < 0.001) at an overall rate of -7.91%/yr and -10.98%/yr respectively. These trends are also seen in 273 those of the precursor molecules (NO_x and SO₂ respectively). However, the rate of decrease of NO_x 274 275 (-2.17%/yr) and SO₂ (-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 276

investigation. The decrease in the concentrations of the primary pollutants are in line with the 277 reductions observed in the emissions of the pollutants as illustrated by the National Atmospheric 278 Emissions Inventory (Figure S1). It was reported that between 2002 to 2004, regional background 279 280 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 281 282 secondary aerosol components may be the combined outcome of a decline in long-range transport 283 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 284 use, consumer products, transport (combustion and evaporation) and leakages from gas pipes in 285 286 urban areas showed a declining trend. With the exception of isoprene and ethane that showed a nonsignificant downward trend i.e., levels being relatively constant, the other nine VOCs show 287 significant downward trends. 1.3-Butadiene, which is one of the VOCs with an air quality guideline 288 in the UK showed the highest rate of decline at -12.59%/yr. Both 1,3-butadiene and benzene have 289 annual averages below the limits stated in the National Air Quality Objectives of 2.25 μ g/m³ and 5 290 $\mu g/m^3$ respectively. 291

292

At the London, Marylebone Road (also for the background site at North Kensington), there is a 293 significant decline in both Elemental Carbon (EC) and Organic Carbon (OC) for the period 2011-294 2018 at an overall rate of -7.54%/yr (p < 0.001) and -3.52%/yr (p < 0.001) respectively. For EC, the 295 monthly average was $\approx 9 \ \mu g/m^3$ in 2010 which reduced to a value of $2 \ \mu g/m^3$ in 2018, whereas OC 296 showed a monthly peak value of 9.8 μ g/m³ in 2011 which declined to 4.5 μ g/m³ at the start of 2018 297 (however it rose to $\approx 7 \,\mu \text{g/m}^3$ later in the year). The OC/EC ratio, however, exhibited a significant 298 upward trend at a rate of 8.77%/yr for the same period (rising from 0.5 to 2.9 by 2018). The yearly 299 average OC/EC ratio is 1.2-2.4 at the site (Table S4). With the exception of 2018 with the highest 300 ratio of 2.4, all the other years give values less than 2. Several studies have utilized the value of the 301 OC/EC ratio to determine the sources contributing carbonaceous components to particulate matter 302

pollution. A ratio of 1.1 has been attributed to a contribution mainly of fossil fuel combustion to EC 303 and OC (i.e. primary emissions), whereas a ratio of up to 2.8 or more is because of a contribution of 304 secondary organic aerosol formation to OC (Zhang et al., 2009; Mbengue et al., 2018). The OC/EC 305 306 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 307 a gradual shift to SOA being a major component of the OC fraction. This SOA may be from aged 308 309 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 310 emissions due to the increasing use of diesel particle filters which remove involatile EC more 311 effectively than OC, much of which is semi-volatile (Beddows and Harrison, 2018; Alam et al, 312 2019). 313

314

315 Diurnal, Weekday and Seasonal Variations

Figure 1 gives the time series plots for some of the regulated pollutants with the left, middle and 316 317 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 318 influence i.e. a bimodal diurnal distribution corresponding to the early and late traffic rush hours 319 (Kendrick et al., 2015). The concentrations of the nitrogen oxides, PM fractions, CO and SO₂ all 320 give maximum concentrations during the period of the traffic rush hours. There are two visible 321 peaks for each of these pollutants corresponding to the early traffic rush hours (08:00-10:00 hrs) 322 and the late rush hours (after 18:00 hrs). During these periods of the day, less dispersion of 323 pollutants from a stable weather condition (low wind and a lower mixing depth) may also enhance 324 325 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 326 related to the relative amounts of gasoline vehicle traffic in the westbound and eastbound lanes. 327 328 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, O₃ levels are at a maximum during periods with least
NO emissions, with limited O₃ titration reaction and vice-versa. The O₃ 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.

336

The diurnal plot for eBC shows a typical traffic dependence of the pollutant concentration (similar 337 to the pattern exhibited by other traffic emission related pollutants discussed above), with maximum 338 levels observed between 08:00 hr to 18:00 hr, indicating continuous vehicular movement 339 throughout this period. eBC is a major component of PM_{2.5} emanating from tail pipes of vehicles in 340 urban areas. However, a relatively weak correlation ($R^2 = 0.24$) exists between the two variables at 341 this site. This may be because of other potential source contributions to PM_{2.5} to this location. 342 343 There is significant contribution by secondary aerosol transported from mainland Europe to PM_{2.5} 344 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 345 346 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, 347 Marylebone Road site (Figure 2). This shows higher eBC concentrations are associated with higher 348 PM_{2.5} concentration in the south-westerly wind direction and this is where the street canyon vortex 349 carries fresh vehicle emissions to the air sampler (Harrison et al., 2019). There is also such strong 350 351 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 352 source contribution of BC to the PM_{2.5} size fraction is also the dominant feature discussed in 353 354 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 localtraffic emissions (see below).

357

358 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 359 360 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 361 road surfacing material itself. These processes may tend to be most efficient around noon when the 362 road surface is most likely to be dry. The other elements (Cl, Mg, K and Na) remain approximately 363 constant during the day, with their amount likely to be controlled by meteorological conditions, as 364 they are most likely not of traffic origin. Na, Cl and Mg are usually from a marine origin, whereas 365 K is a signature element of biomass burning, but is also present in crustal material such as soil. The 366 nitrogen containing species (ammonium and nitrate) show a similar pattern with maximum 367 concentrations around 08:00 hrs in the morning, but show their least concentrations during the 368 369 afternoon period, most probably reflecting the semi-volatility of ammonium nitrate (Harrison et al., 370 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 371 372 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 373 concentrations. 374

375

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 381 that of CO with the evening rush hour peak showing a greater amplitude than that of the morning 382 rush hour peak, reflecting a common source in gasoline engine emissions. The mainly traffic related 383 384 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. 385 386 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 387 higher temperatures. Shin et al. (2013) also report instances of VOCs not associated with traffic 388 emissions (exhaust gases and gasoline vapour) and others showing a diurnal pattern associated with 389 390 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 391 through the day, with emissions responding to an increase in ambient temperature. Ethane has a 392 unique diurnal variation which can be easily explained if a constant rate of gas leakage is assumed. 393 The concentration will be higher in the morning with a low mixing depth and a reduction in 394 395 concentration as the boundary layer deepens during the day.

396

This feature exhibited by ethane can be useful in assessing the emission and dispersion of the other 397 398 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 399 pollutants by the corresponding hourly ethane concentration. The diurnal patterns of the VOCs, 400 including isoprene, and CO after ethane normalisation are similar suggesting a common source and 401 the probability of them emanating from the same source i.e. road traffic. The bimodal peaks 402 403 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 404 405 emission and that of maximum concentration within the boundary layer.

Total particle number count (TNC) also produces a diurnal pattern associated with traffic emissions 407 with a continuous traffic flow between 08:00 hrs and 20:00 hrs. There is the typical maximum value 408 corresponding to the time of day with intense vehicular activities, and the diurnal plot is very 409 410 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 411 412 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 413 sampler receives freshly traffic-emitted pollutants. 414

415

416 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 417 nitrogen, SO₂, CO, the regulated particulate matter fractions, BC and particle total number counts 418 all give maximum values on the weekdays, and the lowest concentrations over the weekend. The 419 pollutant levels are observed to start to increase at the start of the week, attain a relatively constant 420 421 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 422 (Figure S5), with the traffic profile aligning with that of the traffic related pollutants. Ozone that 423 424 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 425 concentrations of the marine aerosol related species and potassium are relatively constant 426 throughout the weekdays in contrast to Ca that shows a maximum during the week and declines 427 over the weekend. NH_4^+ , and SO_4^{2-} also exhibit a similar weekdays plot as that of Ca. With the 428 exception of ethane, all the VOCs investigated give weekday plots similar to those of the traffic 429 related pollutants. Ethane shows slightly increased levels in the atmosphere on weekdays relative to 430 the weekend, possibly due to increasing usage of the gas in areas close to the monitoring station. 431 The EC and OC give a similar weekdays pattern with levels higher during the week and a dramatic 432

decline 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.

436

There is a clear seasonal variability exhibited by the different pollutants investigated in this study. 437 438 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 439 pollutants, so long-range transport of pollutant will influence the seasonal measurements and 440 patterns observed. For instance, ozone shows a springtime maximum in May (and a minimum in 441 442 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 443 et al., 2015). It has been suggested that elevated levels of O_3 in springtime and summertime may be 444 the result of photochemical reactions of the transported ozone precursor molecules that have 445 accumulated over the winter period (Cristofanelli and Bonasoni, 2009; Vingarzan, 2004). NO and 446 447 NO_x generally show seasonal fluctuations opposite to those of O₃ i.e. winter high and a springtime to summer low. High winter concentrations may result from less mixing in a shallower boundary 448 layer during winter and increased emissions from heating of homes and car usage. NO₂ on the other 449 hand shows relatively small seasonal changes. The seasonal change in concentrations of particulate 450 matter is highly influenced by temperatures changes, as the highest values are observed during 451 cooler periods with the lowest measured between June and August when the temperatures are at 452 their highest. The low level of PM in summer is in part due to longer daylight hours and higher 453 temperatures causing vaporization of the semi-volatile components especially the ammonium 454 455 nitrate-rich aerosol (Harrison et al., 2012a). CO and SO₂ both exhibit seasonal patterns similar to those of the particulate matter fractions. Primary pollutants with little seasonal variation in source 456 strength such as BC and NO_x (mainly from local traffic) show higher concentrations in winter due 457 to weaker atmospheric mixing and dispersion. The total particle counts of the PM size fractions 458

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).

465

Cl, Mg and Na ions show a winter maximum and a summer minimum. High concentrations of Cl 466 and Na in winter are due to average higher wind speed leading to increased marine aerosol in the 467 atmosphere (Twigg et al., 2015; Abdalmogith and Harrison, 2006), and a contribution from road 468 deicing salt is possible. Ca shows limited seasonal variability while K shows a summer minimum 469 and a maximum concentration in December, probably related to biomass burning. NH₄⁺, NO₃⁻ and 470 SO₄²⁻ all show a maximum concentration in March and the least amount in summer. There is an 471 increased nitrate concentration from summer to winter. This increase in concentration in winter can 472 473 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 474 HNO₃ (Fisseha et al., 2006). Frequent regional transport events from mainland Europe are also a 475 476 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 477 atmospheric mixing state. High temperature, strong solar radiation and efficient atmospheric mixing 478 (i.e. strong convection) during the summer enhances photochemical depletion of the VOCs, 479 therefore favouring lower concentrations during this period. On the other hand, in the winter period, 480 481 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 482 and maximum pollutant concentrations. Ethane, ethyne, propene, 1,3-butadiene and benzene all 483 show a summer minimum and a winter maximum. The VOCs more associated with solvent use 484

(toluene, ethylbenzene and o-xylene), increase in concentration from February and attain their 485 maximum in November. Isoprene gives maximum concentrations in summer due to an increase in 486 both biogenic and evaporative emissions at higher temperatures. There is a strong seasonal change 487 488 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 489 490 the OC/EC ratio has its highest value in March and its lowest value in September. Several studies in 491 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 492 both components were recorded in autumn. The reasons are unclear. 493

494

495 **Roadside Increments**

The contributions of traffic emissions at the London, Marylebone Road site above background 496 pollutant concentrations have been investigated for particulate matter, BC and heavy metal 497 concentrations by subtraction of simultaneously measured concentrations from the London, North 498 499 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 500 background site is representative of urban background levels and this is not influenced significantly 501 502 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 503 roadside and background sites should be solely influenced by traffic emissions. Pollution arising 504 from long-range transport influences both locations to a similar extent. 505

506

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 μ g/m³ for PM_{2.5} and 9.9-16.7 μ g/m³ for PM₁₀, 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_c) also showed a roadside increment throughout with annual mean values between 4.2 and 9.7 μ g/m³ (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).

518

Investigation of the long-term trend of the ΔPM_{10} shows a significant decline in the monthly mean 519 520 value for PM_{10} (p < 0.001) with a relatively constant trend exhibited for $\Delta PM_{2.5}$. The diurnal plot for the roadside increment for both PM_{2.5} and PM₁₀ shows a higher increment between the period 521 08:00 hrs and 18:00 hrs corresponding to the period of the day with greater vehicular movement 522 (Figure S6). The weekday trend shows the usual higher levels on the weekdays with lowest levels 523 over the weekend as observed typically for traffic related pollutants. However, there is difference in 524 525 trend in the seasonal variation of $\Delta PM_{2.5}$ and ΔPM_{10} . $\Delta PM_{2.5}$ 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 526 autumn (September). In the case of PM_{10} , the trough observed for $PM_{2.5}$ in April is completely 527 absent, but rather a rise in value from the start of the year to its first maximum in late spring (May) 528 and a second one in August are seen. The reasons are not fully clear and issues of incomplete data 529 recovery may contribute to the divergence in trends. 530

531

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 μ g/m³ was recorded in 2014 and a minimum monthly average of <2 μ g/m³ 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 $\Delta PM_{2.5}$, showing a strong exhaust emission contribution to the BC increment (Figure S7).

541

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 PM₁₀ 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.

548

The roadside increment of metals was investigated by subtracting average yearly metal 549 concentrations from the London, Westminster background site from that of the London, 550 551 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 552 nearest road is the B323 Horseferry Road approximately 17 metres north of the station. The 553 554 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 555 2013-2015 which show a lower level of Pb along the road. The data show that there has not been 556 significant decrease in the concentrations from 2011 to 2018, consistent with the lack of controls on 557 non-exhaust sources. 558

559

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.

570

571 Vehicular activities contribute to elevated levels of both EC and OC at the Marylebone Road site 572 (Table 4). Inspection of the yearly mean values show the yearly mean contribution of EC is 573 declining (maximum increment of $5.89 \,\mu g/m^3$ in 2011 and a value of $1.83 \,\mu g/m^3$ by 2018). The 574 yearly mean roadside increment for OC has decreased slowly throughout the period, consistent with 575 control of diesel particles which contain a predominance of EC relative to OC.

576

577 Geographical Source Attribution of Air Pollutants

Urban street canyons have a tendency to have high levels of particulate pollution due to restricted 578 dilution resulting from the geometry of such locations (von Bismarck-Osten et al., 2013). At the 579 580 Marylebone Road site, pollutant levels are highest between the 225 and 270° (or southerly) wind sectors, during which time the sampler receives freshly traffic-emitted pollutants due to the street 581 canyon vortex, and the northerly wind sector is associated with background air from North London 582 (Harrison et al., 2019). The latter point is shown clearly by Figure 5, which plots PM_{10} 583 measurements at Marylebone Road against those for North Kensington for northerly wind sectors, 584 585 showing very similar concentrations.

586

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.

593

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.

599

The PM_{10} and $PM_{2.5}$ fractions show both a local (w.s. < 2 m/s) and a long-range/regional 600 contribution from the easterly direction at high wind speed (Figure 7). In the UK, several studies 601 have identified long-range transport of fine particulate matter especially from the east (or south-602 603 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 604 contribution of PM_c to PM₁₀ is greatest during high wind speeds, especially from the easterly and 605 606 westerly wind directions. This is possibly due to road dust resuspension when the wind direction is parallel to the road. 607

608

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 $PM_{2.5}$.

613

All of the inorganic components show elevated concentrations at higher wind speed, which is 614 usually associated with long-range transport of pollutants (Figure S10 and S11). However, some 615 also show in addition to that, higher levels at wind speeds < 2 m/s, indicative of a local emission 616 617 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 618 619 particles. Both local and regional biomass combustion contribute to significant levels of K 620 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 621 for the chloride ions followed by the easterly direction; Na shows maximum concentrations from 622 623 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⁺ 624 and Cl⁻ in fresh sea salt are 0.308 g/g and 0.554 g/g respectively (White, 2008), giving an Na⁺/Cl⁻ 625 ratio of 0.556. Figure S12 shows that this ratio is generally observed on strong winds from the 626 south-westerly direction indicating a contribution of fresh sea salt, whereas the other directions 627 628 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 629 positive matrix factorization (PMF) and conditional probability function (CPF) approach in which 630 631 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 632 south/southwest wind component accounting for the highest contribution of fresh sea salt during 633 high wind speed conditions. The study also identified a significant contribution of marine aerosol 634 originating from the coastline areas in the east, but with greater chlorine depletion. 635

636

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 640 North Kensington monitoring site). Nitrate, ammonium and sulphate also show some local 641 contribution to elevated levels. These features exhibited by the species are similar to those of PM_{10} 642 643 (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 644 645 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 646 contribution (i.e. traffic emissions) for EC and OC concentrations recorded during lower wind 647 speed conditions (<2 m/s). Elevated concentrations at high wind speed conditions in the 648 southerly/southwesterly sector can be attributed to emissions within the street canyon. The elevated 649 concentrations observed from the east and southeasterly directions, especially for OC, are probably 650 due to long-range transport. 651

652

653 **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).

658

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 declines 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-

666 Osten et al., 2013).

667

668 These features exhibited for the three different timescales are similar to those shown by both the PM₁₀ and PM_{2.5} mass concentration plots. However, a notable difference arises in the seasonal plots 669 670 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 671 autumn with the second highest in spring, whereas it is the reverse for PM₁₀ and PM_{2.5} 672 concentrations. PM mass is more influenced by regional transport of particles than particle number 673 674 due to the effects of coagulation and evaporation of traffic particles. 675 There is an increase of particle number count recorded during both low and high wind speed 676 conditions between 100-270° (Figure 12). In the southerly and southwesterly directions, high 677 concentrations at low wind speed is reflective of direct emission from the road as the location of the 678 679 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 680 transport effect is observed from the easterly and southeasterly directions. Wind coming from this 681 682 direction has been identified to carry pollutants originating from continental Europe. 683 Figure 13 shows a lognormal particle size and number distribution for the average monthly 684

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).

688

The distribution is dominated by ultrafine particles (<100 nm). This feature is common to thedistribution 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).

694 **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.

700

701 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.

706

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

709 (i) many more variables/pollutants are investigated;

710 (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 theroadside increment.

713

714 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.

724

Road traffic emissions (exhaust and non-exhaust) are a major contributor to pollution of urban 725 726 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 727 secondary particulate matter) show measured concentrations being controlled by meteorological 728 conditions, with several periods for which the background site measures greater concentrations. 729 Meteorology strongly influences the composition of the atmosphere at this location, wherein local 730 731 emissions (vehicular) strongly dominate for the nitrogen oxides, CO and SO₂ (and a part of PM), 732 hemispheric and regional transport are dominant for O₃, marine aerosol components and particulate matter. The particulate matter (PM₁₀ and PM_{2.5}) originate from continental Europe mainly as 733 secondary aerosol as is shown by the polar plots for NO_3^- , NH_4^+ and SO_4^{2-} . 734

735

The Marylebone Road site exceeds the Limit Values for NO₂, 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 PM₁₀ 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.

743 DATA AVAILABILITY

- 744 Data supporting this publication are openly available from the UBIRA eData repository at
- 745 https://doi.org/10.25500/edata.bham.00000577
- 746

747 ACKNOWLEDGEMENTS

We would like to acknowledge the main sponsor, The Islamic Development Bank (Merit Scholarship Programme for High Technology for Ph.D. Study) for their financial and moral support towards the student's Ph.D. study. We also extend our appreciation to the University of Birmingham (International Recruitment) for facilitating a 30% tuition fee discount. Data for this study was obtained from the Department of Environment, Food and Rural Affairs (DEFRA) website and is gratefully acknowledged.

754

755 SUPPORTING INFORMATION

756 Supporting Information provides details of instrumentation, data capture, exceedance of threshold

concentrations, OC/EC ratios, as well as further diurnal and polar plots.

758

759 CONFLICT OF INTERESTS

760 The authors declare no competing financial interest.

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954 055	TABLES LI	LES LEGENDS:						
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998 999 1000	Figure 10:	Long-term trend in average monthly total particle number count for London, Marylebone Road.						
1000 1001 1002	Figure 11:	Diurnal, weekday and monthly variation in total particle count for London Marylebone Road.						
1003 1004 1005	Figure 12:	Plot of dependence of particle count on wind conditions.						

1006Figure 13:The average particle number size distribution curve for data for the period 2010-10072018.

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

Site name	Site	Parameter (%/year)								
	type	NO _x	NO ₂	O ₃	SO_2	СО	PM _{2.5}	PM _c	PM ₁₀	Period
London Marylebone Road	Urban Traffic	-1.22*	-2.10***	0.63	-0.42	-5.47***	-4.00***	-3.43***	-3.93***	2009 - 2018

0.01 = **, p < 0.05 = * and p < 0.1 = +

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

				Daily	Data					
	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018
$\Delta PM_{10} (\mu g/m^3)$	16.7	13.6	16.1	12.7	10.2	10.1	10.1	9.9	NA	NA
$\Delta PM_{2.5} (\mu g/m^3)$	7.0	8.1	9.0	8.1	5.8	5.9	5.2	4.5	NA	NA
$\Delta PM_c (\mu g/m^3)$	9.7	5.6	7.1	4.6	4.4	4.2	4.9	5.3	NA	NA
				Hourl	y Data					
$\Delta PM_{10} (\mu g/m^3)$	14.2	13.0	14.8	10.4	8.6	4.1	4.3	6.1	7.3	9.9
$\Delta PM_{2.5} (\mu g/m^3)$	8.1	6.6	7.6	6.9	5.0	2.1	4.8	3.8	3.7	6.6
$\Delta PM_c (\mu g/m^3)$	6.1	6.4	7.2	3.4	3.5	2.0	-0.4	2.4	3.6	3.3

		. 2						
1018	Table 3. Roadside increment	$(n\sigma m^{-3})$) for heav	v metal conce	ntrations fo	or the i	neriod 20	11-2018
1010	Tuble 5. Roudblace merement	(ing in	j ioi neuv	y motul conce	intrations it	n une	peniou 20	11 2010

				Ye	ar			
Metals	2011	2012	2013	2014	2015	2016	2017	2018
As	0.127	0.348	0.011	0.136	0.092	0.226	0.123	0.069
Cd	0.072	0.014	0.013	0.038	0.027	0.029	0.035	0.030
Cu	67.6	54.6	44.9	46.0	41.7	38.0	48.3	39.2
Fe	1354	1208	1042	1133	1103	1069	1469	1153
Mn	10.8	9.90	8.05	8.61	8.39	8.35	11.9	8.94
Ni	1.33	1.45	0.85	0.62	0.73	0.91	0.99	0.77
Pb	0.102	2.86	- 0.179	-0.626	-0.147	3.303	0.180	0.150
V	0.188	0.503	0.149	0.270	0.323	0.294	0.336	0.165
Zn	17.9	30.4	9.34	9.66	11.6	13.3	20.6	16.6

Table 4: Roadside increment (μ g m⁻³) for EC and OC for the period 2010 – 2018 at Marylebone Road.

	2010	2011	2012	2013	2014	2015	2016	2017	2018
ΔEC	5.42	5.89	5.23	3.67	3.89	3.17	2.73	2.50	1.83
ΔOC	2.64	3.63	3.24	2.47	2.20	2.44	1.90	2.18	2.10

1026Table 5: A review of some studies profiling urban air quality status

No	Outcome	Author and Location
1	Investigation of regulated gas phase pollutants and VOCs over a	Masiol et al., 2014
	13-year period (2000-2013) in the Po Valley of Italy. The main	
	emission sources in the region included vehicular, industrial,	Po Valley, Italy
	domestic heating, airport and harbour. The long-term trend	
	analysis of the pollutants showed decreases in the mean	
	concentration of CO, SO ₂ and the VOCs, but no significant	
	change in the level of the oxides of nitrogen, while O ₃ 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 SO ₂ . This	
	unexpected behaviour of SO_2 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 PM_{10} produce their highest	
	concentrations in winter, due to an increase in domestic	
	emissions and stable atmospheric conditions. O_3 and SO_2	
	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, NO ₂ , NO _x , PM_{10} 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. SO_2 and PM_{10} exhibited a similar pattern	
2	A report of hourly data for DM, and Q, for the period 2006	Eartidi at al 2019
	A report of nourly data for PM2.5 and O3 for the period 2000 –	Faridi et al., 2018
	2015 from several stations in Tennah with temporal changes	Tehran Iran
	showed an almost constant annual mean $PM_{2,2}$ concentration	
	but a significant decline occurred from 2010 to 2015 at a rate of	
	1 17 $\mu\sigma$ m ⁻³ /year. For O ₃ there was an initial increase in yearly	
	mean from $2006 - 2008$ followed by a significant decline (3.39)	
	μ m ⁻³) from 2008 to 2015 with 2015 giving the lowest annual	
	mean concentration. The data show a bimodal diurnal peak for	

		PM _{2.5} corresponding to periods with significant anthropogenic emissions. The first peak occurred around 07:00 to 09:00	
		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	
		veckends than the weekdays. This profile points to the	
		traffic to poor air quality. There was a seasonal pattern in the	
		concentration of PM_{25} 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.	
	3	Air pollution in major Chinese cities was investigated for close	Zhao et al., 2016; Vu et
		to a period of one year by monitoring regulated particulate	al., 2019
		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	Chinese cities
		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 altributable to an air quanty action plan.	
ŀ	4	Analysis of long-term real time air quality monitoring data	Bigi and Harrison 2010
	•	(1996-2008) from a background site in central London which	Digi and Harrison, 2010
		showed a general downward trend for several pollutants except	London. England
		ozone, which rose at a steady rate. The downward trends shown	, , ,
		by the pollutants were however not uniform and occurred at	
l		different rates. For instance, CO and NO showed a close pattern	
l		in their trend analysis with a maximum observed around 1996-	
		1998, and a steady decline afterwards, whereas SO ₂ showed	
l		minimal fluctuations, and the concentration remained nearly	
I		constant. PM ₁₀ also showed a pattern that appeared constant	

r		
5	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 .	Font at al. 2010
5	Hourly data for nitrogen oxides and particulate matter size functions for $Partia (44 \text{ site}) = 11 \text{ site} (420 \text{ site}) \int_{0}^{\infty} (400 \text{ site}) dt$	Font et al., 2019
	tractions for Paris (44 sites) and London (130 sites) for the	Dania Engran - 1
	period 2005 – 2016 were investigated. The annual mean c_{0}	Faris, France and
	all network especially for the roadside locations for both cities	London. England
	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	
	showing a greater decrease than Paris. While the roadside	
	increment in PM_{25} 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)	Gani et al., 2019
	and BC (Multichannel Aethalometer) were investigated for	
	Delhi to determine temporal variation in aerosol composition.	Delhi, India
	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	
	umes higher than the warmer periods. There was diurnal variations in the concentrations of the PM and components, with	
	the greatest diurnal swings occurring in winter Generally the	
	neak 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	

	seasonal variability of all these species (winter concentrations up	
	to 20 times the summer concentrations) and with highest global	
	concentrations. Nitrate and suppate also snowed 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	
7	The study analysed aerosol samples for PM ₁₀ -bound PAHs and	Xue et al., 2019
	heavy metals in Chengdu (China) for a period of 6 years (with	
	ions, OC and EC analysed for source apportionment), with the	Chengdu, China
	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	
8	Trace metal analysis of the PM ₁₀ fraction using an ICP AFS	Shahid at al. 2018
0	spectrometer was conducted for aerosol samples collected in	5nama et al., 2010
	Karachi (Pakistan) and PME analysis conducted for source	Karachi Pakistan
	$anortionment$ The average PM_{in} concentration recorded of	Karacin, r akistan
	438 ug m ⁻³ is comparable to levels reported elsewhere in Asia	
	and some other cities in Delvisten. The mean concentrations of	
	and some other cities in Pakistan. The mean concentrations of	
	trace metals were categorised into groups. Ca, AI and Fe (15750 57260 mg m ⁻³). Mg and S (7250 mg m ⁻³ and 6200 ng m ⁻³)	
	-57200 III -57200 III -5720 IIII -5720 III $-$	
	respectively); ZII, P, Cu, PD, NII, 11, Sr and Ba $(220 - 830 \text{ ng m})^{3}$	
	-) and Ur, N1, Se (oung m ⁻ , 20ng m ⁻ and 10ng m ⁻	
	respectively). The PNIF 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.



Frequency of counts by wind direction (%)

Figure 2: eBC pollution rose according to PM_{2.5} concentration range.



1044 Figure 3: Diurnal, weekly and monthly time series plot for VOCs at Marylebone Road.1045







1054 Figure 4b: Yearly mean metal concentrations in PM₁₀ without Fe at Marylebone Road.

 $\mathsf{PM}_{10}_\mathsf{LNK}$ vs. $\mathsf{PM}_{10}_\mathsf{LMR}$ by levels of wind dir.



Figure 5: 1:1 Scatter plot for PM₁₀ for both London Marylebone Road (LMR) and London North
Kensington (LNK) for the northerly wind direction



1072 Figure 6: Polar plot for nitrogen oxides showing significance of wind parameters for pollutant
1073 dispersion. The direction from the centre of the plot shows the wind direction above the canyon and
1074 the distance from the centre is the wind speed (scale in metres per second).



1079 Figure 7: Polar plot for PM fractions showing significance of wind conditions to pollutant1080 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.
1089
1090



1091 ^{year}
1092 Figure 10: Long-term trend in average monthly total particle number count for London,
1093 Marylebone Road.



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



Figure 12: Plot of dependence of particle count on wind conditions.

