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Spatial and Temporal Trends in Carbonaceous Aerosols in the United Kingdom

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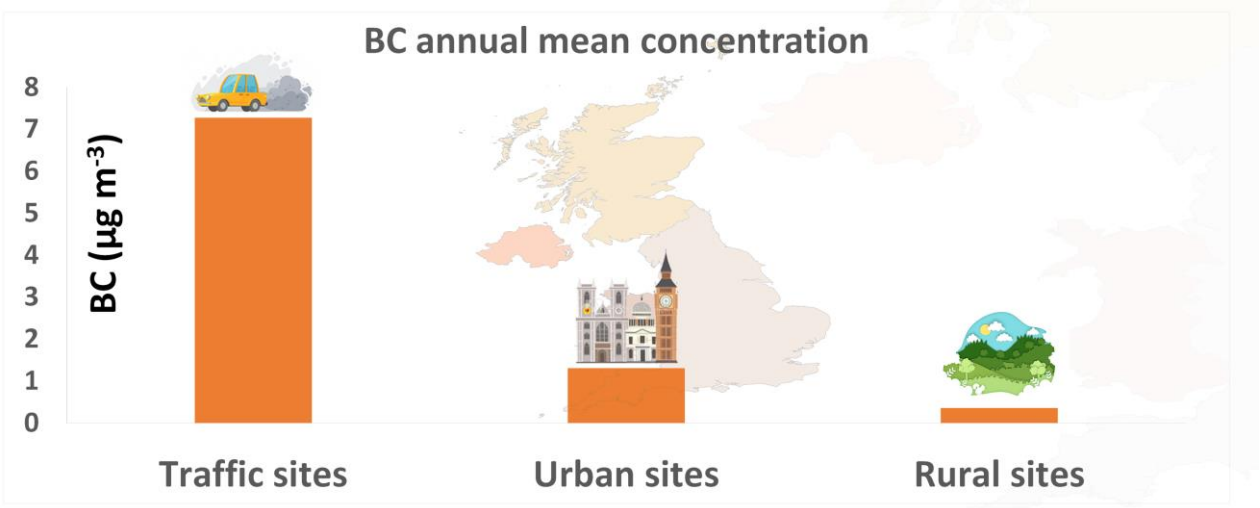
GRAPHICAL ABSTRACT:



Caption: A substantial spatial gradient in black carbon is seen between traffic, urban background and rural sites.

ABSTRACT

There is an increasing scientific interest in carbonaceous aerosols due to their effects on local air quality and climate. The database of the UK air monitoring networks from 2009 to 2017 was analysed to examine the trends in black carbon (BC), brown carbon (BrC), elemental carbon (EC) and organic carbon (OC) at 11 sites with different classifications over the UK. The concentrations increased from rural to urban background to kerbside sites. BC showed the strongest variation, with maxima at kerbside (> 9.0 µg m^{-3}) and minima at rural sites (below 1.0 µg m^{-3}). On the other hand, BrC showed no clear variation according to site classification. BrC increased as domestic emissions of wood smoke increased at weekends. Total OC and secondary OC showed a winter maximum at urban and kerbside sites, while BC increased during the winter at urban sites and in autumn at kerbside sites. Secondary Organic Carbon is dominated by regional transport processes. All pollutants revealed a decreasing long-term trend in the UK, the most significant reduction was observed in BC levels, particularly at the kerbside site (-0.87 µg m^{-3} yr^{-1}), with lesser rates of decline (-0.08 to -0.13 µg m^{-3} yr^{-1}) at urban background sites. The general behaviour of BrC was consistent with a major contribution from regional transport. As expected, EC shows similar behaviour to BC, and OC/EC ratios have increased with time as diesel particle filters have reduced EC emissions more than OC, and other sources of primary OC have not changed markedly.

Keywords: Elemental carbon; Organic carbon; Black Carbon; BrC; Emission trends; Carbonaceous aerosols

1. INTRODUCTION

1.1 Overview

Carbonaceous aerosols (CAs) are ubiquitous in the atmosphere (Hand et al., 2013). The component chemical species include Black Carbon (BC), Brown Carbon (BrC or UVPM; the two terms are used interchangeably in this paper), Organic Carbon (OC) and Elemental Carbon (EC). Generally, carbonaceous aerosols are accountable for 20%-50% of the total atmospheric Particulate Matter (PM) mass (Contini et al., 2018). CAs contribute to the adverse health effects of particulate matter exposure; reduce visibility and impact the atmosphere by scattering and absorbing solar radiation. Thus, they contribute to climate forcing, which increases the scientific interest of these species (Hand et al., 2013).

OC is a fraction of CAs that has light scattering properties, and thus has a cooling effect on climate (Bahadur et al., 2012), it is typically 3–12 times higher than BC in mass in background air (Chen et al., 2010). OC is considered a primary pollutant when it is emitted directly from incomplete combustion of biomass and organic matter (Jones and Harrison, 2005). The emission factor from combustion processes depends on combustion conditions and the type of fuel. Secondary organic carbon (SOC) is formed in the atmosphere by gas to particle phase conversion of volatile organic compounds (VOCs), which may be emitted from natural sources, burning of organic matter and evaporation from fuel (Jones and Harrison, 2005). The key stage of SOC formation is the oxidation of a VOC molecule to form a less volatile compound which then condenses (Hallquist et al., 2009).

Brown carbon is defined as the component of OC which absorbs light in the ultraviolet wavelength region (Lack et al, 2014). BrC has both primary and secondary sources; it comprises emissions from biomass burning, in the UK predominantly domestic wood burning, in addition to humic-like substances arising from gas-phase oxidation of VOCs (Liu, et al., 2013; Chakrabarty et al., 2010). BrC has a wide range of physicochemical properties that are difficult to be generalized (Andreae

and Gelencsér, 2006), and includes water-soluble and insoluble components. BrC (also referred to as Delta-C in some studies) is often taken as representing wood-burning emissions, but this is often not an accurate interpretation (Harrison et al., 2013).

The refractory light absorbing component of CAs is named BC or EC according to the quantification method employed. The term EC is used when thermal optical methods are applied, while BC is used when light absorption techniques are applied (Contini et al., 2018). When BC is measured using an instrument such as an aethalometer it is called equivalent black carbon (eBC) (Sharma et al., 2017). The term total carbon (TC) is defined as the sum of EC and OC measured by thermal optical analysis (Petzold et al., 2013). BC and EC are emitted directly from incomplete combustion processes, including on-road and off-road automotive sources (especially diesel vehicles), domestic combustion of coal and public electricity power stations, in addition to waste incineration and stationary combustion in manufacturing industries (Richmond et al., 2020).

These light-absorbing carbonaceous aerosols are driving forces for global warming (Andreae and Gelencsér, 2006), and contribute to adverse health effects (WHO, 2012) and have high ability to absorb and adsorb a range of toxic chemicals (Wang et al., 2014).

BC and EC have a relatively short lifetime in the atmosphere (between a few days to a few weeks) compared to greenhouse gases (GHG), which have a much longer lifetime (ranges from several to thousands of years). Therefore, any abatement strategies for BC and EC emissions will have a more immediate effect on the regional scale to control climate change and reduce global warming (Chen et al., 2012; Ramanathan and Carmichael, 2008).

1.2 Trends in carbonaceous aerosols

Several studies have investigated the spatial and temporal trends of CAs in Europe and worldwide (Luoma et al., 2020; Zheng et al., 2020; Sun et al., 2020; Sommer et al. 2019; Kucbel et al., 2017; Titos et al., 2017; Cavalli et al., 2016; Ahmed et al., 2014; Sandrini et al., 2014; Tiwari et al., 2013; Querol et al., 2013; Backman et al., 2012; Sahu et al., 2011). CAs concentration was found to increase significantly on moving from Scandinavia to Central Europe as a result of the atmospheric pollution dilution (Cavalli et al., 2016). In Spain, maximum levels of eBC and BrC were observed in Granada during a cold winter as a result of biomass burning, this influence was stronger in suburban areas compared to the city centre (Titos et al., 2017). The same pattern was observed in OC and EC concentrations in the Czech Republic by Mbengue et al. (2018) and at different urban and rural locations across the Italian peninsula (Sandrini et al., 2014), whereas at rural sites in the Northeastern United States, BC peaked in late summer (Ahmed et al., 2014).

Trends of BC over the UK have been investigated by Singh et al. (2018) over the period 2009–2016; the analyses showed a decreasing trend in BC at 7 locations out of the 21 study locations. The highest decrease in BC concentration was seen at Marylebone Road in London. Harrison and Yin (2008) found that in the U.K. West Midlands, EC increased significantly on moving from rural to urban to roadside sites, while the levels of OC at different sites showed a much smaller difference. A chemical mass balance receptor model developed by Yin et al. (2010) detected the presence of organic aerosols which were not related to primary sources and were attributed to secondary organic aerosols (SOA).

Jones and Harrison (2005) reported that OC and EC did not show any systematic seasonal pattern with one exception at the urban site of London North Kensington. It was clear that the non-traffic sources of SOC and POC were predominant in the urban background at all times. At urban sites, the concentrations of OC and EC were higher during weekdays compared to weekends (Jones and Harrison, 2005). According to the analysis conducted by Charron et al. (2013), SOC could be

considered as regional pollutant. This is due to the uniformity shown by SOC across different sites in the UK. The concentration field maps revealed that mainland European areas were important sources for SOC at the study sites. Charron et al. (2013) emphasised the strong effect of air mass back trajectories on EC levels at the rural Harwell site.

Most of published work and studies have focussed on one or two components of CAs, OC and EC or BC in most cases. Moreover, a limited number of studies have been conducted in the UK related to long-term temporal and spatial trends of different carbonaceous aerosols. Thus, this study aims to investigate the long-term trends in CAs in the UK and examines seasonal, day of the week and diurnal patterns for all metrics (BC, BrC, OC, SOC, POC and EC). A comparison of the concentrations by site type is carried out and spatial patterns across the UK are investigated. Finally, the long-term, seasonal and day of the week diurnal patterns in the traffic and urban increments are examined.

2. MATERIALS AND METHODS

2.1 Sampling and Analysis Methods

Datasets from UK air monitoring networks for BC, BrC (UVPM), EC and OC were downloaded from the UK-Air website (DEFRA, 2019) for use in this study. BC and BrC were monitored by the Black Carbon Network, while OC and EC were monitored by the Particles Concentration Network. Both monitoring networks are managed by the National Physical Laboratory and the Quality Assurance protocols are provided in their reports (National Physical Laboratory, 2016a;b).

BC is measured using Magee scientific model AE22 aethalometers (Beccaceci et al, 2013). The basic principle of this instrument is to measure absorption during transmission of light through a sample collected on a filter tape. The aethalometers operate at two different wavelengths, 880 nm and 370 nm. The first wavelength (880 nm) is used to quantify the concentration of BC, while the

second wavelength (370 nm) is used to measure BrC (Butterfield et al., 2016). The concentration of the UV component is calculated by subtracting the concentration of BC measured at the 880 nm wavelength from the concentration measured at 370 nm (Beccaceci et al, 2013).

The Thermo Partisol 2025 sequential air sampler is used for daily sampling of EC and OC PM_{10} components (Beccaceci et al, 2013). The samples are collected on ultrapure quartz filters, and a thermal/optical analyser is used to carry out the analysis of EC and OC based on the National Institute for Occupational Safety and Health (NIOSH) protocol (PD CEN/TR 16243, 2011), where the sample is heated first in a helium atmosphere to 870°C in order to remove OC, before it is heated again up to 890°C in the presence of oxygen to detect EC (Beccaceci et al, 2013).

2.2 Sampling Sites

The number of BC Network sites has changed over the years (Butterfield et al., 2013). This has created some gaps in the collected data and has limited the value of the data for comprehensive analysis. For this study, and in order to achieve a high level of reliability, sites with the longest measuring period and of significant importance were chosen. The start and end dates for the trend analysis were not the same for all sites because they operated in different years.

The study focused on 11 sites in the BC and BrC monitoring network spread across different regions of the UK. Regarding the EC and OC components of PM_{10}, the only monitoring sites in the network are Harwell, London North Kensington and London Marylebone Road. Table 1 provides a brief description of the study sites and lists the monitoring period for each site, and Figure 1 shows the location of each site. Site details are available from (https://uk-air.defra.gov.uk/).

2.3 Data Analysis

190 The Open-air model was adopted through the different stages of this study to analyse the CA dataset.
191 One of Open-air's functions that was used in this study is the time variation function. This function
192 is used to find the diurnal, day of the week and monthly patterns in pollutant concentrations. It is
193 based on the 95% confidence interval, which is calculated by bootstrap re-sampling (Carslaw and
194 Ropkins, 2012). Another function is the PolarPlot function. This function plots the concentration of
195 pollutants on a polar coordinate, which is very useful to find the spatial distribution of pollutants
196 based on wind speed and direction (Carslaw and Ropkins, 2012). The TheilSen function was used for
197 long term trend analysis. This function uses the Mann-Kendall method with a linear regression in the
198 analysis process. The confidence interval for the TheilSen function is 95% (Carslaw and Ropkins,
199 2012). This method is insensitive to outliers and bootstrap-resampling is used to estimate the
200 parameters such as median (Agustine, 2017; Carslaw, 2015).

201 In order to compare EC and BC concentrations, the reduced major axis regression method (RMA)
202 was applied to the measurements (Garrett, 2018). RMA takes into consideration the uncertainty in
203 both x and y variables. In the case of pollutant concentrations, the error can occur in both x and y
204 directions because of uncertainty in measurements of both variables. Thus, RMA is preferable when
205 comparing EC and BC concentrations to least-squares regression which minimises the sum of squares
206 of the errors in the vertical direction (y) (Butterfield et al., 2016; Ayers, 2001).

207

208 For use in the EC tracer method to estimate the $(OC/EC)_{min}$ ratio the scatterplot function was used,
209 where OC and EC concentrations (in μg m^{-3}) of a given year were used to produce the scatterplot
210 with OC on the y-axis and EC on the x-axis. Then the slope of the line which passes through the
211 origin and the lowest points was calculated. This slope represents $(OC/EC)_{min}$ for that year (Pio et
212 al., 2011). Any points above this line indicate the formation of SOC. Then the daily values of POC
213 and SOC for each year were calculated according to the following equations:

214 $$POC = (OC/EC)_{min} \times EC + OC_{non\text{-}combustion} \quad (1)$$

$$SOC = OC - POC \quad (2)$$

where $(OC/EC)_{min}$ is the ratio of OC to EC from primary sources at the study area, $OC_{non\text{-}combustion}$ is primary OC from non-combustion sources (Lin et al., 2009). In this study it was assumed that $OC_{non\text{-}combustion}$ equals zero. This was conducted year by year as the composition of primary aerosol and hence $(OC/EC)_{min}$ can change with time.

The urban increment was calculated by subtracting simultaneous measurements at Harwell (rural) from North Kensington (urban background) data, while the roadside increment was calculated by subtracting simultaneous measurements at North Kensington from Marylebone Road (roadside).

3. RESULTS AND DISCUSSION

3.1 Time Variation Analysis

The diurnal profile of BC at the roadside site of Marylebone Road followed the traffic flow over the day. This is expected because the main source for BC in the European cities is incomplete fuel combustion in automobiles, particularly diesel vehicles (Sommer et al., 2019). All days of the week showed the same pattern where BC levels increased substantially between 6:00 and 18:00, but at weekends the levels were lower compared to weekdays (Figure 2), as also observed by Singh et al. (2018). This is attributed to a drop in traffic flow, especially in heavy diesel vehicle numbers during weekends at Marylebone Road (Butterfield et al., 2016). Similar weekly cycles were observed at traffic stations across Germany (Kutzner et al., 2018) and at traffic sites in Zurich and Bern, Switzerland (Zotter et al., 2017; Reche et al., 2011). BC revealed weak seasonality dependence, where the lowest concentrations (less than 6.5 μg m^{-3}) were in spring and the highest (above 8.0 μg m^{-3}) were in autumn (Figure 3). This is unlikely to be due to changes in traffic emissions between spring and autumn, but due to the change in the relative amounts of southerly and northerly winds

between the seasons, where northerly winds were dominant in spring; the effect of wind direction is discussed in Section 3.3.

BrC revealed an opposite behaviour to BC at Marylebone Road, where the concentration decreased to less than zero in daytime and increased at night (Figure S1). These negative concentrations were observed by Harrison et al. (2013) at Marylebone Road and by Butterfield et al. (2016) at different sites over the UK, especially roadside sites. The cause of these negative spikes might be the semi-volatile organic species from vehicle-exhaust, which are collected on the filter and increase UV absorption. These semi-volatile aromatic organic species may evaporate over time and cause negative artefact concentrations of BrC at roadside sites in particular. The elevated BrC levels at night during all days of the week are likely because of higher emissions from wood burning, enhanced condensation of semi-volatile components, and more stable atmospheric conditions which trap the pollutants due to less effective dispersion. BrC measurements during weekends were higher than weekdays, and peaked in winter (Figure 3) due to residential heating and winter-time inversions. This study is consistent with Titos et al. (2017) where BrC levels over Granada, Spain, increased in winter. Similar seasonality as well was recorded at different sites over Europe by Lukács et al. (2007).

At urban background sites, Birmingham Tyburn, North Kensington and Cardiff, the morning BC peak was around 09:00 local time coinciding with the traffic morning rush hour (Figures S2, S3 and S4). BC levels also increased during the evening due to a conjunction of heavy traffic and a decrease in boundary layer depth. Elevated levels of BC were recorded on weekdays compared to weekends, which reflects a traffic signature on BC profiles at these sites. The BrC component at the three sites showed a slight increase in the morning and a rapid increase over the night (Figures S5, S6 and S7), which could be related to a night-time inversion, secondary home heating and the formation of secondary BrC due to night-time chemistry.

The urban sites in Northern Ireland revealed the same patterns in BC and BrC concentrations and the two metrics had similar behavior (as illustrated in Figure S8, S9, S10) for BC, and Figures S11, S12, S13 for BrC). A small peak due to morning rush-hour traffic was observed in the diurnal profiles and the concentrations of BC and BrC increased at night to peak at around 20:00 at Strabane and Ballymena, while the peak at Kilmakee was two hours later. The reason for this increase is likely to be less effective mixing and dispersion at night, and residential heating, which is predominantly by solid and liquid fossil fuel at Strabane and natural gas at Ballymena and Kilmakee. No difference was noticed between BrC and BC measurements at weekdays and weekends (except for the rush-hour effect which disappeared at weekends), because the dominant source of BC at these sites is mainly domestic emissions which do not vary during the week as traffic flow does.

At Belfast Urban Centre, the traffic-based signature was clearly seen due to elevated levels in BC coinciding with the morning rush-hour, after which the concentration was fairly constant between 17:00-23:00 (Figure S14). BrC levels dropped in daytime and increased at night, which could be because of residential heating and night-time atmospheric processes (Figure S15). On Saturday evenings and Sunday early mornings, BC and BrC concentrations increased slightly, probably due to traffic and biomass burning respectively. Apart from this, no difference was observed between trends at weekends and weekdays.

BrC and BC revealed seasonal dependence at urban background sites and Belfast Urban Centre (Figures S16, S17, S18, S19, S20, S21, S22). Both metrics showed elevated levels in winter and low levels in summer. This is attributed to less effective atmospheric mixing in winter and higher local emissions, particularly from domestic heating compared to summer, as is the case in other European urban areas where biomass burning is a significant source for CAs (Kutzner et al., 2018; Titos et al., 2017).

Similar diurnal, weekly and seasonal profiles of BC were observed in previous studies at urban and sub-urban sites in the UK (Singh et al., 2018; Harrison et al., 2013), in urban sites across Germany (Sun et al., 2020) and at urban areas in Barcelona and Granada, Spain (Viana et al., 2013; Titos et al., 2017). The diurnal and seasonal profiles of BrC are consistent with Harrison et al. (2013) and are in line with the maximum levels of BrC that were observed during Vienna and Granada cold winters as a result of biomass burning, where the influence was stronger in suburban areas compared to the city centre (Sommer et al., 2019; Titos et al., 2017).

At rural sites, the lowest BC levels were recorded compared to other study sites. However, a small effect of the morning rush-hour was still evident (Figures S23, S24, S25). Due to this very weak effect of traffic, BC levels showed a relatively flat weekly cycle. Both BC and BrC (Figures S26, S27, S28) increased at night which could be due to a night-time inversion and shallower PBL, beside stronger local wood burning emissions at night. Since BrC is not directly affected by traffic (which has higher emissions at weekdays compared to weekends), the concentrations were fairly constant over the week.

Most rural sites showed low levels of BrC in summer and high levels in winter (Figures S29, S30, S31), which seems to be due to less effective mixing in winter and higher emissions from wood burning for heating. However, BC concentrations at Detling and Auchencorth Moss revealed no seasonal dependence, while Harwell showed very weak seasonality.

Regarding EC, OC, SOC and POC at Marylebone Road, these pollutant metrics decreased sharply at weekends (Figures S32 and S33) due to reduced traffic flows on Sundays and Saturdays, which is a major source for EC and POC at this site. EC revealed the same seasonal pattern as BC, as the two pollutants are emitted from the same sources, but are operationally defined (Figure S34). OC in general showed maxima in winter and minima in summer, the levels of SOC showed the same

trend, while POC displayed elevated levels in autumn and low levels in spring (Figure S35). Moreover, the concentrations of SOC were higher than simultaneous concentrations of POC. The low levels of SOC in summer may be attributable to semi-volatile SOA compounds which change to the gaseous-phase at higher temperatures. The high levels in winter may be attributed to an increase in anthropogenic precursor emissions and less effective dispersion compared to summer, whereas, elevated POC concentrations in autumn and low levels in spring could be related to changes in the relative amounts of southerly and northerly winds between the seasons rather than a change in traffic emissions. It is important to remember that the graphical method used for separating the two components of OC is far from perfect. It is likely that even at the lowest OC/EC ratios, there is still some SOC, and there is no situation in the UK where there is no SOC (Jones and Harrison, 2005). This is a flaw in the technique and there is no way of allowing for it.

London, North Kensington revealed a slight decrease in OC, SOC, POC and EC over weekends (Figure S36 and S37), because it is an urban background site that is affected by traffic movement through the week. EC, OC and POC revealed maxima in winter and minima in summer (Figure S38 and S39), which might be due to higher emissions and especially less effective mixing in winter. However, SOC did not display any seasonality, one possible explanation is the SOA semi-volatile nature, which causes some volatilisation at high summer temperatures, despite more effective photochemical formation in summer. Another reason could be the increase in residential precursor emissions in winter, mainly from heating and wood burning. The latter is known to oxidise rapidly to SOA after emission. Concentrations at Harwell were fairly constant over the whole week (Figure S40 and S41), because the site is dominated by sources other than traffic, such as the regional background, and local domestic and biogenic emissions from surrounding sources. These emissions do not vary over the week to the same extent as traffic flow. SOC was the only metric which revealed seasonal dependence at this site (Figure S42 and S43), where maximum levels were recorded in summer, which is consistent with Charron et al. (2013). This might be the result of high

biogenic precursor concentrations and photochemical activity which increase in the warmer months and enhance the formation of SOC by gas-particle conversion. The same seasonal pattern was observed in OC and EC concentration across Germany (Kutzner et al., 2018), the Czech Republic (Mbengue et al., 2018), in Granada, Spain (Titos et al., 2017), and at different urban and rural locations across the Italian peninsula (Sandrini et al., 2014).

A substantial spatial variation in BC, EC, OC, POC and SOC was clearly seen amongst the study sites. The concentrations increased from rural to urban background to kerbside sites. BC showed the strongest variation, The highest annual mean concentration of BC amongst the 12 sites was 7.28± 2.32 μg m^{-3} at Marylebone Road, and the concentration decreased with respect to distance from BC emission sources to reach minima at rural sites (0.36± 0.15 μg m^{-3}), while the urban background sites recorded an annual mean concentration of 1.31± 0.25 μg m^{-3}, which is in line with the Singh et al. (2018) findings in the U.K.. Similar trends in BC variation have been reported across Europe; in Finland, Germany and Italy (Luoma et al., 2020; Kutzner et al., 2018; Sandrini et al., 2014). The annual mean concentrations of BC for traffic, urban background, and rural sites were close to those reported by Kutzner et al. (2018) in Germany.

Urban increment

The urban increment is related to emission sources in the city. The urban increment of BC in London, provides an evidence of the effect of commuter traffic movement on BC levels at North Kensington, since the increment shows a peak coinciding with the morning rush-hour and a slight drop at weekends as traffic flow decreased (Figure S44), while the increase in the increment at night-time indicates the presence of domestic heating emissions. Since BrC is often taken as representing wood-burning emissions, the increase in the urban increment of BrC at night (Figure S45) emphasizes the presence of domestic heating emissions at night-time in North Kensington. The EC increment shows the same behaviour as the BC increment (Figure S46), since they have the

same emission sources. Both increments increased in November and decreased from May to July (Figure S47). The OC increment was fairly constant over the week (Figure S46), which means traffic is not the dominant source of OC at North Kensington, and it increased in winter due to higher residential heating emissions and fell in summer (Figure S48), which indicates the strong effect of the heating season on OC levels in the London urban background just as at urban background sites in Granada and Barcelona in Spain (Titos et al., 2017; Viana et al., 2013), Paris in France (Weimer et al., 2009) and in Germany (Kutzner et al., 2018) where the effect of biomass burning is evident on CA levels during the heating season.

Roadside increment

The roadside increment makes it easier to separate the changes in concentrations due to regional processes (such as dynamics of PBL, meteorological conditions and regional emissions) from those of local traffic emissions. The roadside increment in BC followed the expected profile of daily traffic flow (Figure S49), where elevated levels were seen in the morning and evening rush-hours, and low concentrations at weekends, which provides evidence of vehicle emissions as a major source for BC at Marylebone Road similar to other traffic sites across Europe in Finland, France, Austria, Germany, Switzerland and Italy (Luoma et al., 2020; Font et al., 2019; Sommer et al., 2019; Kutzner et al., 2018; Zotter et al.,2017; Sandrini et al., 2014; Reche et al., 2011). The diurnal and day of the week profiles of roadside increment of BrC were clearly affected by the negative concentrations of BrC observed at Marylebone Road (Figure S50). The EC roadside increment showed the same pattern as the BC increment due to similar sources (Figure S51). The EC and BC traffic-related increment displayed elevated levels from July to October and minima in spring (Figure S52), for which the possible explanation is a change in the relative amounts of southerly and northerly winds between the seasons at Marylebone Road (Figure S53), which is discussed in Section 3.3. The roadside increments in OC at weekends were lower than weekdays (Figure S51), due to drop in the vehicle fleet size on Sundays and Saturdays. Moreover, the OC increment

revealed no clear seasonal dependence, but increments in autumn and winter were generally higher compared to spring and summer (Figure S54). This emphasizes the effect of other factors besides traffic emissions on OC levels at Marylebone Road, such as domestic heating. The roadside increment of EC/OC ratio in London was higher than 1.0 on all days of the week (Figure S55) which suggests that in vehicle emissions at Marylebone Road, the levels of EC exceed OC, whereas at rural and urban background sites OC is typically predominant. All months except November showed a roadside increment ratio of EC/OC higher than 1.0 (Figure S56). The low increment ratio in November (about 0.8), is due to a slight drop in EC roadside increment coinciding with an increase in OC increment during that month.

3.2 Long Term Trend Analysis

The largest decrease in BC levels over the period 2009-2017 was recorded at Marylebone Road (-0.87 µg m^{-3}/year, Figure 4). This significant reduction is attributed to effective policies and standards for vehicle exhaust emissions, and implementation of low emission zones, besides promotion of walking and cycling. The reduction in roadside increment of BC in London strengthens this explanation (Figure S57 (A)). The findings of Singh et al. (2018) emphasise the effect of traffic-emissions abatement policies to reduce BC levels significantly in London as suggested by the current study. The urban background sites showed a downward trend in BC ranged between -0.08 and -0.13 µg m^{-3}/year (Figures S58, S59, S60, S61, S62), except for Strabane where the decreasing trend was not significant. The levels at rural sites revealed a lower decrease in BC compared to kerbside and urban background sites (Figure S63). This could be attributed to the sources of BC that are dominant at each site, for example at the kerbside site the main source is traffic, thus any restriction on vehicle emissions will directly reduce BC levels. Urban background sites are still affected by traffic emissions beside the local and regional sources, so the effect of vehicle emissions control is still evident at these sites, but rural sites are the least affected by traffic

emissions and more influenced by the regional background, which declines more slowly over the years.

In the broader context, decreasing trends in BC mass concentration were also reported at different sites in Germany, Austria and Finland (Luoma et al., 2020; Sun et al., 2020; Sommer et al., 2019; Kutzner et al. 2018). The highest decrease was at traffic sites which is most likely due to the efforts of the European Union to mitigate anthropogenic emission through various policies and programmes (Luoma et al., 2020; Sommer et al., 2019; Sun et al., 2020), especially the requirement for diesel particle filters on new vehicles.

The BrC component at Marylebone Road revealed an upward trend (+ 0.04 µg m^{-3}/year, Figure 4) over the study period. This increase seems likely to be due to local residential emissions of wood smoke, since the levels of both BC and BrC dropped slightly at North Kensington (Figure S58 (B)), which is affected by domestic emissions more than traffic relative to Marylebone Road. Moreover, looking on the trends in urban and roadside increments of different metrics in London, the roadside increment of EC, BC and OC decreased (Figure S57), while the urban increment was fairly constant over time (Figure S64). All urban background sites showed a downward trend in BrC levels, but this change was not significant, except at Birmingham Tyburn and Ballymena (Figures S58 (A) and S60), probably due to a reduction in local wood smoke emissions, whereas the levels at rural sites were fairly constant over the study period, which provides strong evidence of long-range transport of BrC which is in line with Viana et al. (2013) where the source apportionment analysis showed evidence of the contribution of regional transported SOA and biomass burning contributors to the CA load at a rural site in Barcelona, Spain, and agrees with what has been reported in a rural area in the Czech Republic, where the high pollution episodes of CAs were mainly associated with continental air masses (Mbengue et al., 2018).

446 The concentration of total OC at Marylebone Road dropped (-0.3 µg m^{-3}/year, Figure S65 (A)) over
447 the period 2009-2017. This decrease is mainly due to reduction in the estimated SOC component (-
448 0.27 µg m^{-3}/year, Figure S66 (A)). A downward trend in the OC roadside increment was also
449 observed (Figure S57). The same trend was revealed at North Kensington, but the reduction was
450 smaller (-0.15 µg m^{-3}/year in OC and -0.1 µg m^{-3}/year in SOC, Figures S65 and S66, respectively),
451 due to a larger influence of other local sources than traffic. A downward trend was also seen at
452 Harwell, but the trend was not significant, emphasizing the contribution of the regional background.
453 However, POC downward trends at the three sites were not significant (Figure S66), which suggests
454 fairly constant regional emissions over the study period as reported by Sun et al. (2020) who
455 analyzed the German Ultrafine Aerosol Network over the period 2009-2018.
456 EC revealed the same temporal and spatial trends as BC, but the downward trends of EC were
457 always smaller (Figure S65). As shown in Section 3.4, the relationship between BC and EC was
458 site-dependent probably reflecting some source-dependency of BC/EC ratios. This would lead to
459 differing spatial and temporal trends as the relative source contributions to BC and EC change with
460 time. The significant reduction in EC at Marylebone Road is directly reflected in the EC/OC ratio
461 (Figure S67), where the ratio decreased by -0.04 /year. The EC/OC ratio at North Kensington and
462 Harwell was fairly constant, due to the slight decrease in both EC and OC at North Kensington and
463 fairly constant concentrations of EC and OC at Harwell over the study period.
464

465 **3.3 Effect of Wind Direction on Concentration**

466 Atmospheric concentration of primary and secondary pollutants can be greatly affected by wind
467 speed and direction. Marylebone Road is different from other sites, it is a street canyon (an urban
468 street, which is surrounded by high buildings on both sides) with an aspect ratio about 0.8 (mean
469 height of buildings to width of street ratio). These characteristics significantly affect the dispersion
470 of pollutants within the street canyon, due to recirculation of air and formation of a vortex that traps
471 the pollutants in the leeward direction inside the canyon in the case of perpendicular wind-flow

(Nataraj et al., 2020; Jones and Harrison, 2005). The road is aligned 255° to 75° (approximately west-east direction) and the monitoring station is to the south of Marylebone Road, which makes it in the leeward direction when the wind above the canyon is from the south. Thus, southerly winds are expected to have the greatest enhancement of pollutant concentrations at Marylebone Road (Jones and Harrison, 2005).

The concentrations of BC, EC and POC at Marylebone Road were enhanced by south and southwest winds (Figures 5, S68 and S69). The BrC component showed the highest levels with easterly and westerly winds. SOC levels increased with southeasterly winds and the concentration of total OC showed a maximum in southerly and near southerly winds, while the lowest levels of all pollutants were observed with northerly winds. These results emphasize the effect of southerly wind perpendicular to the road in enhancing the concentrations of those pollutants emitted at Marylebone Road, due to the location of the monitoring station on the leeward side, as seen in other studies at this site. Northerly winds have the least effect, because in this case the monitoring station is on the windward side and the canyon is filled with background air from north London. The effect of parallel winds (easterly and westerly) is also obvious in increasing the concentrations of BC, EC and POC. As BrC is not an emission within the canyon, it would be expected to show a different directional dependency, more related to local woodsmoke sources.

At North Kensington, the concentrations of all pollutants revealed no dependence on wind direction except for east and south-east winds (Figures S70, S71 and S72). This indicates a combination of local emissions and transport of aged air masses from central London (which is located to the south-east of North Kensington) and the European mainland. SOC was the pollutant which was most enhanced by easterly and south-easterly winds due to the contribution of regional transported SOA

from continental air masses. The influence of these air masses on CAs concentration has also been observed in Barcelona, Spain (Viana et al., 2013).

BC and BrC concentrations at Birmingham Tyburn and Belfast did not reveal a significant dependence on wind direction (Figures S73 and S74), which implies that the predominant source of BC and BrC at these sites is local emissions from all directions. At Cardiff, the concentration of BrC and BC increased with easterly and near easterly winds (Figure S75), which could be attributable to aged air masses from London and mainland Europe affecting the site. At Ballymena, BC did not reveal a variation with wind direction (Figure S76), which suggest local emissions as the main source for BC, while BrC was enhanced by westerly wind, which might be due to regional pollutant transport.

At the Harwell rural site, all pollutants were enhanced by easterly and south easterly winds (Figures S77, S78 and S79), which could be attributable to the emissions from the major A34 highway at a distance of 1.85 km from the station, and air masses from London and the European mainland. The levels of BC at Auchencorth Moss were enhanced by southeasterly winds, and BrC levels increased with easterly winds (Figure S80), which is attributed to a possible effect of the A701 road and regional transport of pollutants. At Detling, southeasterly and easterly winds enhance the concentrations of BC and BrC (Figure 6), which seems likely to be due to regional transport of air masses from mainland Europe.

3.4 Relationship Between BC and EC

Hourly concentrations of BC were measured by the Black Carbon Network, while daily concentrations of EC were measured by the Particles Concentration Network. BC measurements at Marylebone Road, North Kensington and Harwell were converted to daily averages and plotted

against the corresponding EC measurements for the whole study period (2010-2017 at Marylebone Road and North Kensington, 2010-2015 at Harwell). There was a good correlation ($R^2 > 0.7$) between BC and EC at the three sites (Figure 7). The value of R^2 was highest at Marylebone Road ($R^2 = 0.88$), followed by North Kensington ($R^2 = 0.79$) and Harwell ($R^2 = 0.74$). The intercepts at the three sites were relatively small (less than 0.13), and the gradients were respectively 0.70, 0.74 and 0.62.

BC and EC are essentially the same component, but are operationally defined by their measurement procedures, where BC is measured by optical absorption, and EC by combustion. BC is measured by aethalometer, which uses a mass absorption coefficient of 16.6 $m^2\ g^{-1}$ (that is recommended by the manufacturer) to convert the light absorption to BC concentration. According to the regression results, the aethalometer over-estimates BC levels relative to EC, as was also reported by Merico et al. (2019). Similar results were observed by Chang et al. (2017) between collocated aethalometer BC and Sunset Laboratory EC concentrations in Shanghai, China, in all seasons over the period 2009-2014. Also, Merico at al. (2019), working at a Mediterranean site found a measurement protocol-dependence of EC measurements, and a seasonal dependence of OC/EC ratios which may be related to differing ratios of brown to black carbon between the seasons which can influence both optical and thermal measurements in different ways.

3.5 OC/ EC Minimum Ratio

The estimation of $(OC/EC)_{min}$ at Marylebone Road, North Kensington and Harwell has been described above, and is illustrated in the Supplementary Information (Figures S81 to S83), where scatter plots using the measurements of OC and EC for one year of daily data are presented.

$(OC/EC)_{min}$ increased significantly from Marylebone Road to North Kensington to Harwell (Table 2) which emphasize the effect of urban traffic as a main driver of EC emissions at roadside sites and

547 reflects the importance of regional emissions and atmospheric transport on OC concentrations at
548 rural sites. This tendency and similar results have been observed in previous studies in Europe and
549 the UK (Sandrini et al., 2014; Pio et al., 2011; Yin et al., 2010; Yin and Harrison, 2008) despite the
550 difference in measurement and analysis techniques.
551
552 The ratio of $(OC/EC)_{min}$ revealed an increasing trend at Marylebone Road, North Kensington and
553 Harwell over the period 2009-2017 (Figure S84), although the trends were not significant. The
554 $(OC/EC)_{min}$ ratios observed at Marylebone Road (Table 2) are expected to reflect the emissions
555 from road vehicles. The ratios for 2010 – 2012, with a mean ratio = 0.42 are reflective of emissions
556 from diesel engines prior to the mandatory fitting of diesel particle filters (DPF), and are consistent
557 with data derived from a measurement campaign in the UK West Midlands conurbation which
558 reported a typical value of 0.40 (Harrison and Yin, 2008). The data then show a steady increase in
559 $(OC/EC)_{min}$ as the emissions from gasoline engines with a higher particulate OC/EC ratio have
560 become more prominent.
561
562 **4. CONCLUSION AND RECOMMENDATIONS**
563 The dataset was insufficient to define a detailed spatial distribution. However, the concentrations of
564 pollutants showed a marked variation between sites with different characteristics. BC revealed the
565 strongest variation, the highest levels were at Marylebone Road, while the lowest were at rural sites.
566 This is directly related to the large effect of vehicle exhaust emissions at Marylebone Road
567 compared to the other study sites. A weak spatial variation was seen in the BrC component, with the
568 levels at Northern Ireland urban sites higher than other background sites and rural sites, presumably
569 due to greater use of biomass fuels. EC, OC, SOC and POC showed the same tendency as BC
570 indicating a strong influence of anthropogenic emissions. However, $(OC/EC)_{min}$ ratio increased as
571 traffic emissions became less dominant to reach maxima at rural sites (2.7±0.6).
572

The traffic signature was still obvious at urban background and rural sites as well as at the kerbside site, where the concentration of BC showed a peak coinciding with the morning rush hour. At Marylebone Road all pollutants except for BrC showed lower levels at weekends compared to weekdays, reflecting traffic flow variation over the week. Urban background sites revealed the same pattern, excluding sites in Northern Ireland, where the concentration of BC was fairly constant during the week, due to influences from sources other than vehicle emissions. BrC showed elevated levels during weekends at all sites apart from rural sites as these sites are less affected by anthropogenic emissions. As was the case for traffic-related pollutants, OC with its both primary and secondary components decreased at weekends at kerbside and urban sites, whereas it was constant at rural Harwell.

BrC revealed high levels at all study sites during winter (the heating season) and low levels in summer. At urban background sites, BC showed the same seasonality as BrC, while rural sites revealed no seasonal dependence as regional background concentrations are dominant. Primary pollutants and SOC at North Kensington revealed elevated levels during the cold months, whereas SOC was the only pollutant at Harwell which revealed seasonal dependence and was enhanced by photochemistry in summer.

BC levels have dropped in the UK over the years 2009- 2017, the highest decrease in BC being at Marylebone Road which gives strong evidence for the effectiveness of pollution abatement strategies to reduce vehicle emissions, especially in London. On the other hand, BrC increased over the study period at Marylebone Road. All urban background sites showed a downward trend in BrC levels, but this change was not significant, except at Ballymena and Birmingham Tyburn, whereas OC, POC and SOC decreased significantly at kerbside and rural sites, but the POC trend was not significant.

South-easterly and easterly winds were the major wind directions which enhanced the concentrations of pollutants at different sites. This emphasizes the importance of long-range transport from Europe for primary and secondary pollutants levels in the UK, as well as being associated with meteorological conditions which are not conducive to effective dispersion.

The regression analysis of BC and EC revealed that the aethalometer overestimates BC concentrations, and that the mass absorption coefficient should be recalibrated if the data are to be more reflective of EC concentrations.

DATA AVAILABILITY

Data supporting this publication are openly available from the UBIRA eData repository at https://doi.org/10.25500/edata.bham.00000516

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SUPPORTING INFORMATION

Supporting Information provides further details of short and long-term temporal trends of carbonaceous aerosols at all the study sites, together with polar plots of pollutant concentrations in relation to wind speed and direction; in addition to the regression analysis of BC and EC; and the estimation of $(OC/EC)_{min}$.

CONFLICT OF INTERESTS

The authors declare no competing financial interest.

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LIST OF TABLE LEGENDS

Table 1: Study sites classification, government region and monitoring period.

Table 2: The annual $(OC/EC)_{min}$ At Marylebone Road, North Kensington and Harwell Over the Study Period.

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Figure 1: Map of air sampling study sites.

Figure 2: The diurnal and day of the week variation in BC in Marylebone Road.

Figure 3: The monthly variation in BC and BrC in Marylebone Road.

Figure 4: Trends in BC and BrC based on monthly mean concentrations at Marylebone Road. (The solid red line represents the mean trend and the dashed lines represent the 95% confidence interval. The trend and confidence interval are shown at the top as $\mu g\ m^{-3}$/year. The $***$ show that the trend is significant at the $p< 0.001$ level).

Figure 5: Polar plot of mean BC and BrC concentrations at Marylebone Road over the period 2009-2017.

Figure 6: Polar plot of mean BC and BrC concentrations at Detling over the period 2013-2017.

Figure 7: Regression of EC and BC at Marylebone Road, North Kensington and Harwell over the study period. (The black dashed line represents 1:1. while the red dashed line represents the regression line, N is the number of measurements and Fit represents R^2).

904 **Table 1:** Study sites classification, government region and monitoring period.

Site Name	Classification	Government Region	Monitoring Period
London N. Kensington	Urban Background	Greater London	2009-2017
London Marylebone Road	Urban Traffic	Greater London	2009-2017
Birmingham Tyburn	Urban Background	West Midlands	2009-2016
Auchencorth Moss	Rural Background	Central Scotland	2012-2017
Belfast Centre	Urban Background	Northern Ireland	2009-2017
Strabane 2	Suburban Background	Northern Ireland	2009-2017
Ballymena Ballykeel	Urban Background	Northern Ireland	2013-2017
Kilmakee Leisure Centre	Urban Background	Northern Ireland	2013-2017
Cardiff	Urban Background	South Wales	2009-2013
Detling	Rural Background	South East	2013-2017
Harwell	Rural Background	South East	2009-2015

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907 **Table 2:** The annual $(OC/EC)_{min}$ At Marylebone Road, North Kensington and Harwell Over the
908 Study Period.

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Year	Marylebone Road	North Kensington	Harwell
2010	0.50	1.25	2.00
2011	0.41	1.60	2.60
2012	0.36	1.30	3.00
2013	0.51	1.60	3.20
2014	0.51	2.00	2.60
2015	0.68	2.10	2.50
2016	0.60	1.10	
2017	0.83	1.60	

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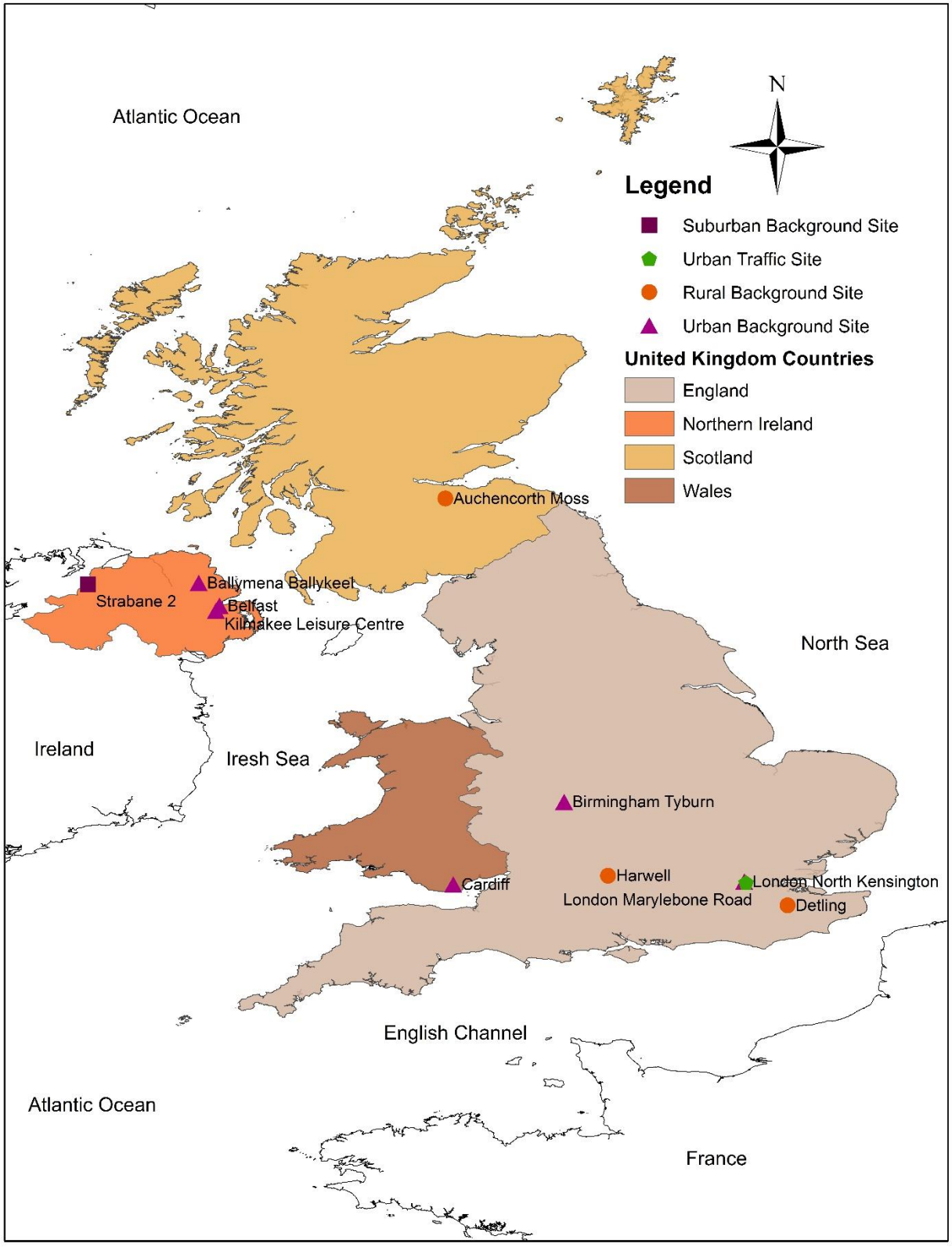

911
912 **Figure 1:** Map of air sampling study sites.

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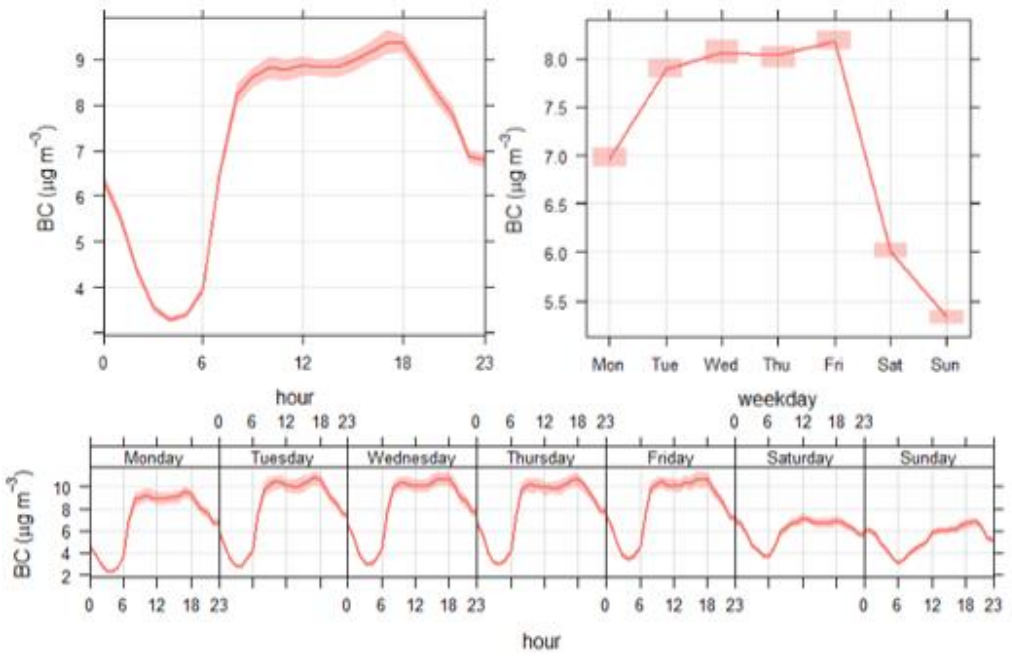


Figure 2: The diurnal and day of the week variation in BC in Marylebone Road.

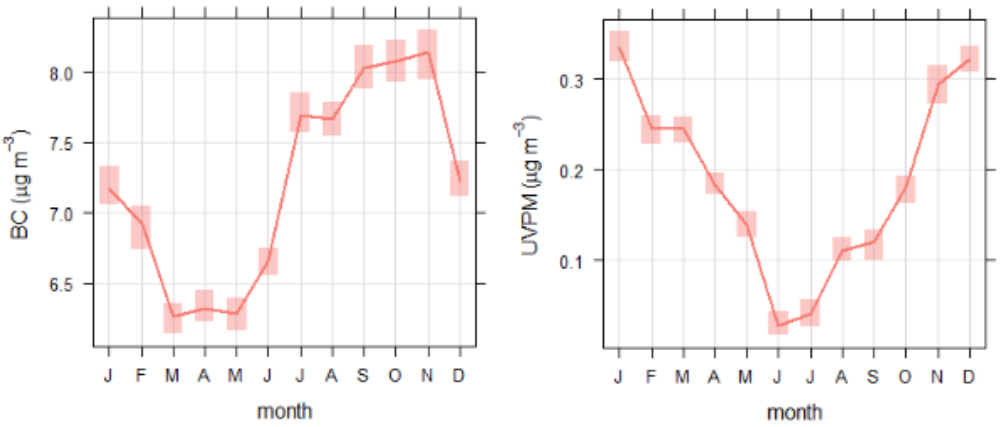


Figure 3: The monthly variation in BC and BrC in Marylebone Road.

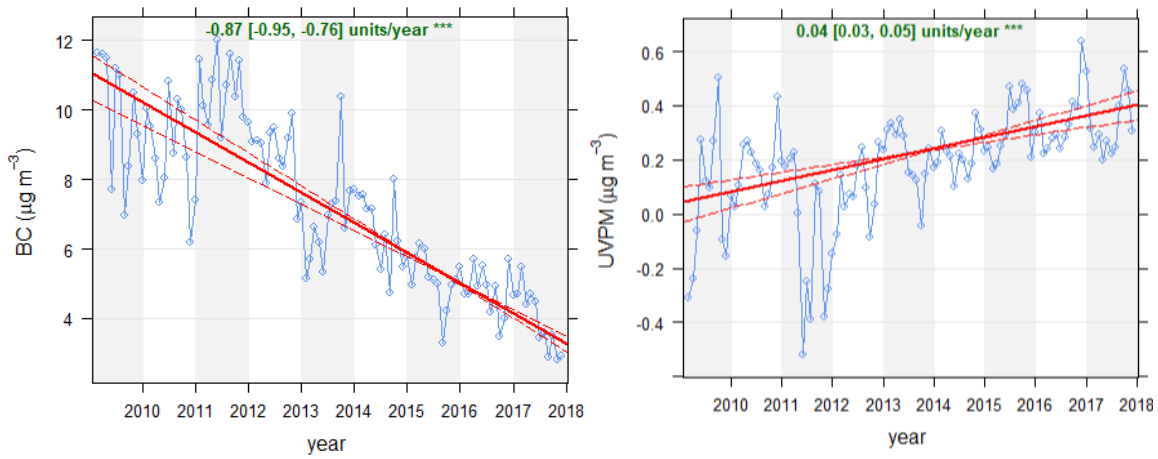


Figure 4: Trends in BC and BrC based on monthly mean concentrations at Marylebone Road. (The solid red line represents the mean trend and the dashed lines represent the 95% confidence interval. The trend and confidence interval are shown at the top as µg m^{-3}/year. The ∗ ∗ ∗ show that the trend is significant at the p< 0.001 level).

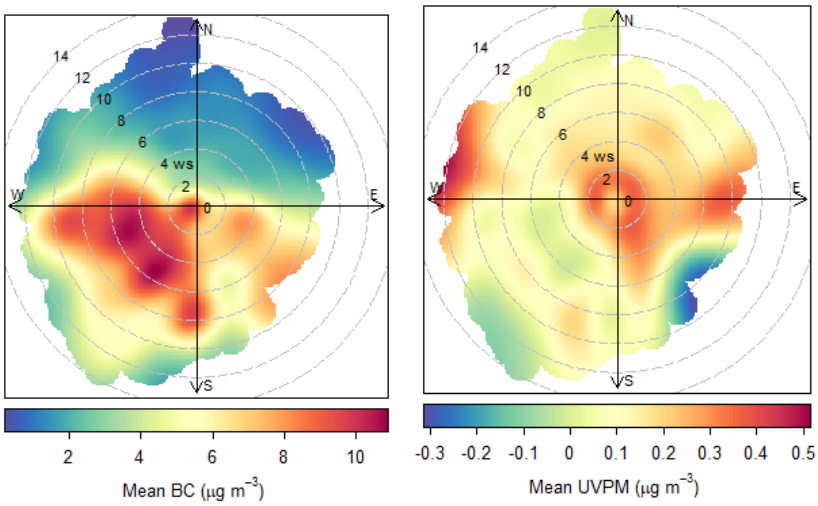
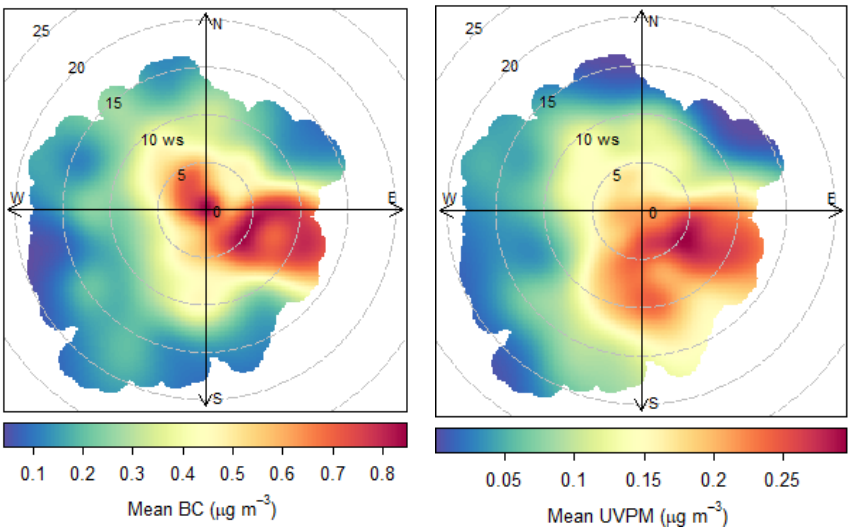


Figure 5: Polar plot of mean BC and BrC concentrations at Marylebone Road over the period 2009-2017.



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943 **Figure 6:** Polar plot of mean BC and BrC concentrations at Detling over the period 2013-2017.

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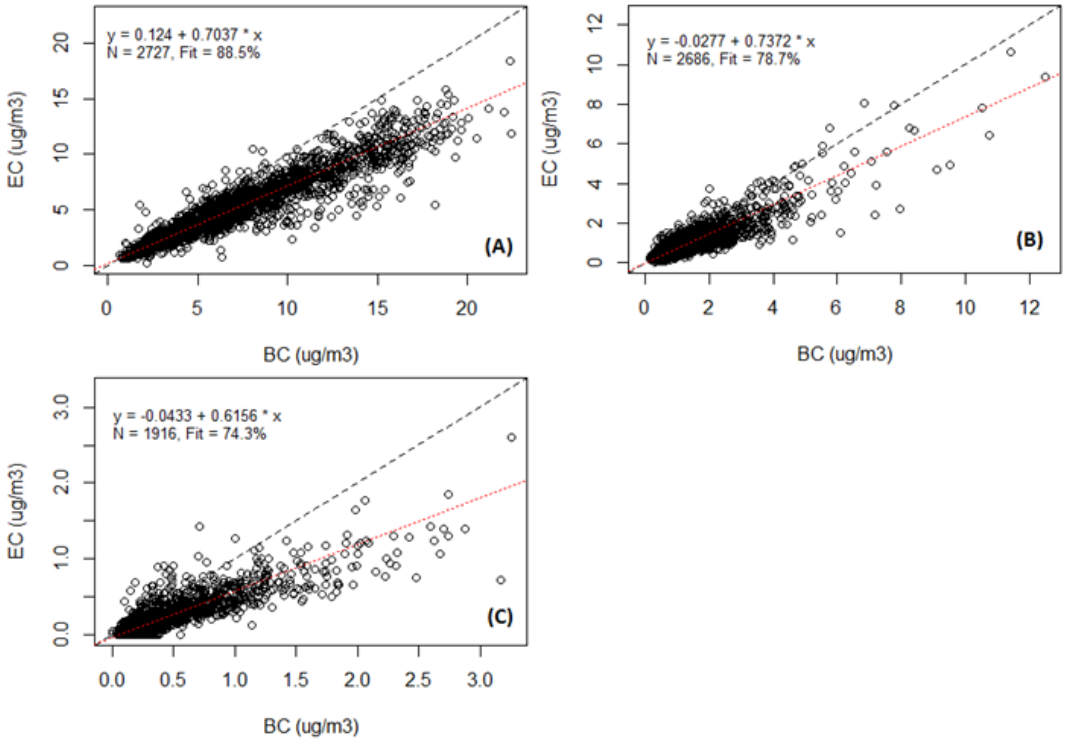

945
946 **Figure 7:** Regression of EC and BC at Marylebone Road, North Kensington and Harwell over the
947 study period. (The black dashed line represents 1:1. while the red dashed line represents the
948 regression line, N is the number of measurements and Fit represents R^2).
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