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Composition and Emission Factors of Traffic-Emitted Intermediate Volatility and Semi-Volatile Hydrocarbons (C_{10}-C_{36}) at a Street Canyon and Urban Background Sites in Central London, UK

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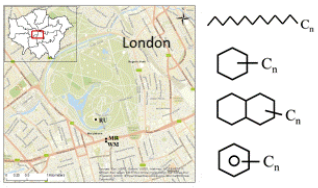

TOC CAPTION: The measurements of I/SVOCs in the London Campaign 2017.

ABSTRACT

Hydrocarbons in both gas and particle phases from C_{10} to C_{36} (I/SVOCs) were analysed at sites in central London. Samples were collected from a street canyon, Marylebone Road (MR), a rooftop site (WM) above MR, and a site in the adjacent Regent's Park (RU), north of MR to evaluate the change in composition of I/SVOCs during advection from the traffic to the cleaner atmosphere of the urban background. Groups of compounds identified and quantified in gas and particle phases include C_{13}-C_{36} n-alkanes and branched alkanes, C_{12}-C_{25} monocyclic alkanes, C_{13}-C_{27} bicyclic alkanes and C_{10}-C_{24} monocyclic aromatics. The similarities found in the aliphatic and aromatic region above C_{12} in urban air and diesel exhaust demonstrate the impact of diesel-powered vehicles on urban air quality. Diesel exhaust is suggested to be the dominant emission source, while small differences between sites indicate the possibility of other sources which are also discussed. The ambient concentrations of I/SVOCs in the street canyon at MR were highest when the southerly winds brought the traffic emitted pollutants to the sampler. Emission factors (EFs) for all compound groups were estimated from the concentrations at the MR site. Particle-phase n-alkane EFs are broadly similar to those measured elsewhere in the world, despite differences in traffic fleet composition. A comparison between n-alkane EFs estimated from field measurements and those measured from diesel engines in the laboratory suggests a large contribution from vehicles with higher emissions than recent passenger cars to London air.

Key Words: Hydrocarbon; semi-volatile; diesel emission; street canyon; emission factor

1. INTRODUCTION

Particulate matter is the air pollutant with the greatest public health impact, and its effects are likely to depend upon particle size and composition (Rissler et al., 2012; Masiol et al., 2012). As a major emission source within the urban environment, particulate matter originated from traffic has generated major interest over the last few decades. The majority of traffic-emitted fine particles are carbonaceous, directly emitted as primary organic aerosol (POA) and elemental carbon, oxidation of the former leading to production of secondary organic aerosol (SOA) (Jimenez et al., 2009). A substantial fraction of the organic compounds in exhaust emissions of gasoline and diesel vehicles are semi-volatile (May et al., 2013a,b). While intermediate volatility organic compounds (IVOCs) exist mainly in the vapour phase, semi-volatile organic compounds (SVOCs) partition directly between gas and particulate phases under ambient conditions (May et al., 2013a; Robinson et al., 2007; Donahue et al., 2012). SVOCs refer to organic species with an effective saturation concentration C^* between 1 and 10^3 μg m^{-3} while IVOCs refer to species with C^* between 10^4 and 10^7 μg m^{-3} (Robinson et al., 2007).

I/SVOC emissions from traffic mainly comprise aliphatic and aromatic hydrocarbons typically ranging between C_{12} and C_{35} (Worton et al., 2014; Gentner et al., 2012; Alam et al., 2018; Weitkamp et al., 2007). Most of the gasoline emitted organic compounds are volatile organic compounds (VOCs) while some aromatics can extend to the intermediate-volatile range. Only 30% of diesel emitted hydrocarbons are VOCs and most of them are less volatile (mainly I/SVOCs) (Gentner et al., 2012). Gasoline engine emissions are typically in the carbon number range below C_{12} while diesel engine emissions are mainly in the range from C_8 to C_{25} (Gentner et al., 2012). Detailed emission information for these diesel-derived organic compounds (above C_{12}) in the atmosphere is not widely available (Dunmore et al., 2015) although the greatest roadway emitters of particles per vehicle are diesel powered. In the UK, 40% of licensed passenger cars were using a diesel engine in 2017 (Fleet News, 2018). Diesel exhaust contains primarily unburned fuel (C_{15}-C_{23}

organics), unburned lubricating oil (C_{15}-C_{36} organics) and sulfate (Jacobson et al., 2005). A recent study investigated the hydrocarbon composition of diesel exhaust using gas chromatography coupled with time-of-flight mass spectrometry and concluded that the diesel fuel contributes up to C_{20} hydrocarbons whilst engine lubricating oil contributes primarily to the C_{18} to C_{36} range of compounds (Alam et al., 2016a).

Despite huge research interest and many contributions over the last decades, many uncertainties remain regarding the identities and chemical composition of traffic emitted I/SVOCs. A key reason is that the vast majority of I/SVOC mass cannot be separated and characterised by the traditional one-dimensional gas-chromatography (1D-GC) based analytical techniques (Schauer et al., 1999; 2002; Jathar et al., 2012). A mixture of cyclic, linear, and branched hydrocarbons is present in a typical chromatogram as an unresolved complex mixture (UCM) (Mandalakis et al., 2002). The UCM is often observed in samples associated with the use of fossil fuels (Nelson et al., 2006; Frysinger et al., 2003; Ventura et al., 2008), and comprises more than 80% of the semi-volatile hydrocarbons emitted from diesel and gasoline derived engines (Schauer et al., 2002; 1999; Chan et al., 2013). A number of studies have reported the chemical components of organic emissions in traffic influenced regions by using one dimensional chromatography coupled with mass spectrometry (GC-MS) or comprehensive two-dimensional gas chromatography coupled with mass spectrometry (GC×GC -MS) (Lewis et al., 2000; Hamilton and Lewis, 2003; Omar et al., 2007; Chan et al., 2013; Hamilton et al., 2004; Worton et al., 2014; Dunmore et al., 2015). However, the homologous series that have been reported in most of the studies only represent a small fraction of the total organic mass that is emitted from traffic, with a consequent lack of information on I/SVOC composition.

Emissions from road traffic are known to make a large contribution to total particulate matter (van Deursen et al., 2000) and vapour concentrations in urban areas. It is important to understand the magnitude and characteristics of I/SVOC emissions from vehicles, especially in megacities like London. Measurements on laboratory-based diesel engines (Schauer et al., 1999; Perrone et al., 2014) allow the determination of exhaust emissions under controlled test conditions but these tests often cover a limited set of vehicles due to the high costs. These tests cannot fully represent the large variation in engine types and driving modes in different environments (Charron et al., 2019), and are not able to give an accurate estimation on the dilution of I/SVOCs (Kim et al., 2016) and do not include non-exhaust emissions (Pant et al., 2013). Therefore, estimates deriving from concentration measurements at a near-road site are considered to offer a realistic simulation for the emission factors, which currently comprise both tunnel and roadside measurements (Hwa et al., 2002; Kawashima et al., 2006; He et al., 2008, Staehelin et al., 1998).

In this study, samples were collected in central London at the roadside of the heavily trafficked Marylebone Road (MR), and two rooftop sites (WM and RU) during different times from January to April 2017 in London. The samples were analysed by using comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (TD-GC×GC-ToF-MS) combined with a mapping and grouping methodology to classify, identify and quantify the compounds classes. I/SVOCs (C_{10}-C_{36}) were identified and quantified in both the gas phase and particle phase, to offer a more comprehensive understanding of the chemical composition of traffic emitted particulate matter. The concentrations of four main I/SVOC groups are reported and discussed, including alkanes (n+i) (defined as the sum of n-alkanes and branched alkanes), monocyclic alkanes, bicyclic alkanes and monocyclic aromatics. The effect of wind direction on the dispersion of traffic emitted pollutants in the street canyon and the spatial distribution of I/SVOCs in different locations are discussed. Emission factors for n-alkanes and the main I/SVOC groups are estimated for traffic on Marylebone Road. Oxygenates, which are both important primary emissions from road traffic, and are formed by atmospheric oxidation of hydrocarbons have been addressed in an earlier paper (Lyu et al., 2019).

2. EXPERIMENTAL

2.1 Field Measurements in London Campaign, 2017

Simultaneous measurements were conducted on the roof of the University of Westminster (WM) and a roof of Regent's University (RU) from 24 January 2017 to 19 February 2017. The WM sampling site was located on the roof of a Westminster University building (around 26 metres high) on the south side of the road overlooking the ground-level Marylebone Road (MR) monitoring station. The RU sampling site was located on the roof (around 16 metres high) of Regent's University located in Regent's Park, which is about 380 m north of Marylebone Road (see Figures S1 and S2). Samples were also collected at the kerbside MR Supersite on the south side of Marylebone Road from 22 March to 18th April 2017. Marylebone Road has three traffic lanes for each direction and the traffic flow is over 80,000 vehicles per day. The instruments were housed in a large cabin placed on the sidewalk of Marylebone Road with an inlet around 2.5 metres above ground level.

2.2 Sample Collection

An in-house auto-sampler was designed to collect sequential 24 h duration samples (Figure S3). The sampler has seven channels and is turned to the next channel automatically. A pump draws air through a polypropylene backed PTFE filter (47 mm, 1 µm pore, Whatman, Maidstone, UK) to collect the particulate phase, and then through a stainless steel thermal adsorption tube packed with 1 cm quartz wool and 300 mg Carbograph 2TD 40/60 (Markes International) to collect the gas phase. The flowrate was calibrated by a calibrator (Gilian Gilibrator-2 NIOSH Primary Standard Air Flow Calibrator, Sensidyne, Schauenburg, Germany) and set at 1.5 L/min during the field measurements. The inlet to the sampler was through a downward facing ¼ inch o.d. stainless steel tube giving an estimate cut point of around 4 µm (Harrison and Perry, 1986). After 24h duration sampling, filters were transferred to pre-cleaned filter cases which are then enclosed with aluminium foil. Adsorption tubes were capped firmly. Both filter cases and tubes were stored under conditions of approximately -18℃ prior to extraction and GC×GC-ToF-MS analysis. Adsorption tube breakthrough was evaluated in the field with two tubes in series, and vapour concentrations are reported only for compounds for which collection was quantitative.

2.3 GC×GC ToF MS Analysis

A two-dimensional approach separating compounds in a mixture by volatility and polarity was adopted. The analytical instruments and calibration methods have been described in earlier papers from our group (Alam et al., 2016a,b; Alam and Harrison 2016, Alam et al., 2018). Nine deuterated internal standards namely, dodecane-d26, pentadecane-d32, eicosane-d42, pentacosane-d52, triacontane-d62, biphenyl-d10, n-butylbenzene-d14, n-nonylbenzene-2, 3, 4, 5, 6-d5 (Chiron AS, Norway) and p-terphenyl-d14 (Sigma Aldrich, UK) were used in this study.

Adsorption tubes were spiked with 1 ng of deuterated internal standard for quantification. Then the tubes were desorbed onto a cold trap at 350ºC for 15 min (trap held at 20ºC), and then the trap released chemicals into the column with a split ratio of 100:1 (split ratio changed based on sampling sites) at 350ºC. Carrier gas was helium at a constant flow rate of 1 ml/min. Whole PTFE filters were spiked with 5 µl internal standards (1 ng/µL) for quantification, and were extracted with dichloromethane (HPLC grade), using ultrasonic agitation at room temperature (20ºC) for 20 mins. The filtrate was concentrated using a stream of dry nitrogen gas, to a volume of approximately 50 µl. 1 µL of the extracted sample was injected with a split ratio of 100:1 (split ratio changed based on sampling sites) at 300ºC. A modulation time of 11s was applied while a total run time for each sample was 120 min. Subsequent data processing was conducted using GC Image_v2.6 (Zoex Corporation). Blank filters were prepared, processed, and analysed in the same manner as the real particle phase samples to mitigate the analytical bias and precision. More details of the instrument settings and sample analysis methods are given by Alam et al. (2016a,b).

2.4 Classification of Organic Compounds

Recently studies have reported that the diesel fuel derived organic compounds are predominantly found from C_{13}-C_{20}, while compounds derived from lubricating oil are predominantly within the range C_{18}-C_{35}. Both are part of an unresolved complex mixture (UCM) in traditional GC (Dunmore et al., 2015; Alam et al., 2016a,b). The number of possible structural isomers increases with the number of carbon atoms (Goldstein and Galbally, 2007), and beyond around C_9 it is a challenge to identify the structure of all compounds present in the ambient air (Dunmore et al., 2015). However, it is possible to assign individual compounds to particular chemical classes and functionalities based on their retention behaviour in two-dimensional chromatography. The physicochemical similarities within compound classes and their steady changes with the increasing chain length and /or molecular sizes enables the further identification of the ordered appearance of compounds in the chromatogram. This allows the identification of species without unique mass spectra but based on the pattern of the database. This study grouped the chemical compounds into isomer sets based on their carbon number and functional group (Figure 1). Natural standards were chosen for calibration and quantification, including n-alkanes (C_{11}-C_{36}), phytane and pristane (Sigma Aldrich, UK), n-alkyl-cyclohexanes (C_{11} -C_{25}), n-alkylbenzenes (C_{10}, C_{12}, C_{14}, C_{16} and C_{18}), tetralin, alkyl-tetralins (methyl-, di-, tri- and tetra-), cis- and trans-decalin, alkyl-naphthalenes (C_{11}, C_{12}, C_{13} and C_{16}) (Chiron AS, Norway) and 13 polycyclic aromatic hydrocarbons (Thames Restek UK Ltd). The authentic standard mixture (72 natural standards and 9 internal standards) was expected to cover as much of the whole chromatogram as possible and can be applied to calibrate the quantification of the isomer groups with the same functionality and molecular ions. Briefly, known amounts of natural and internal standard were injected into the GC×GC -MS system prior to the sample analysis to determine the response of target compounds. The identification of individual compounds is described by Alam et al. (2016b). Groups of isomers were quantified by adopting an individual compound with the same carbon number and functionality as a surrogate. For instance, the response for n-tridecane, (*m/z* 184) was used to quantify all isomers identified within the C_{13} alkane polygon.

More mapping details are given in Supplementary Information, Section 2.The quantification of isomer sets has been discussed in Alam et al., (2018), who reported the overall uncertainties of this method as 24% by comparing the difference between concentrations estimated with authentic standards and generic standards.

2.5 Supporting Data

The DEFRA air quality network (https://uk-air.defra.gov.uk/networks/) measures black carbon (BC), NO_x and benzene concentrations at the Marylebone Road monitoring station (MR) used in this study. Measurements of BC at the roof sites WM and RU were carried out using aethalometers (2 Wavelength Magee Aethalometer AE22) simultaneously with I/SVOC measurements.

London Heathrow airport, located west of central London, is the closest station to provide comprehensive meteorological information for the sampling sites above the roof. Daily mean wind direction data from London Heathrow airport (Met Office, 2006) were used to sort the 24 h duration I/SVOC samples into north wind (N), south wind (S) and undefined wind (Duffy and Nelson, 1996) based on the predominant direction during each sampling interval. The wind angles 300-360° and 0-60° are defined as a north wind while wind angles 120-240º are defined as a south wind in this study. North wind and south wind are both cross-canyon flows, whilst an undefined wind (Duffy and Nelson, 1996) represents the along-street flows, including wind angles 60−120° (east wind) and 240-300° (west wind). The Heathrow site is within 25 km of the London sampling sites. Using data from UK sites, Manning et al. (2000) show that wind data from airfield sites are representative of wind fields up to 40 km from the site. The Heathrow data represent winds above the street canyon; those within the canyon are very different. Harrison et al. (2019) show diagrammatically the circulations within the Marylebone Road canyon.

3. RESULTS AND DISCUSSION

3.1 I/SVOC Measured at MR and RU

3.1.1 Chemical composition and distribution

The identified and quantified chemical groups were C_{13}-C_{36} alkanes (n+i), C_{12}-C_{25} monocyclic alkanes, C_{13}-C_{27} bicyclic alkanes, C_{10}-C_{24} monocyclic aromatics, C_{10}-C_{15} naphthalenes, C_{13}-C_{15} biphenyls, C_{14}-C_{15} fluorenes, C_{15}-C_{16} phenanthrenes/anthracenes and C_{12}-C_{13} tetralins. Lyu et al. (2019) further identified alkanals (C_{10}-C_{14}), alkan-2-ones (C_{10}-C_{18}) and alkan-3-ones (C_{10}-C_{16}) sampled during the London Campaign, 2017. Average concentrations of grouped compounds appear in Table S1, and of specific compounds in Table S2. Figure 2 shows the organic compound composition, expressed as the relative abundance in total mass concentration (sum of gas and particle phase) collected at MR and RU. Acyclic alkanes (57%) are the most abundant hydrocarbons followed by monocyclic alkanes (17%) and monocyclic aromatics (16%) at RU. At MR, acyclic alkanes were still dominant but dropped to 36% as there was a greater contribution from monocyclic alkanes (24%), bicyclic alkanes (15%) and monocyclic aromatics (18%). Isaacman et al. (2012) reported that the diesel fuel which they analysed consisted of 73% aliphatic hydrocarbons and 27% aromatics. Alkanes accounted for nearly half (41%) of the observed mass fraction of diesel fuel, followed by 14% cycloalkanes, 11% bicyclic alkanes and 6% benzenes (Isaacman et al., 2012), broadly consistent with our own analyses (Alam et al., 2018). SVOCs (above C_{20}) emitted from gasoline and diesel-powered engines derive mainly from engine oil (Drozd et al., 2019; Alam et al., 2016b). Studies of the contribution of different components in engine lubricating oil have reported that the most abundant groups are straight, branched and cyclic alkanes (≥80%) with the largest contribution from cycloalkanes (≥27%) (Worton et al., 2014; Sakurai et al., 2003). The chemical composition of diesel fuel and lubricating oil in the literature well explain the overwhelming presence of acyclic alkanes, monocyclic alkanes and bicyclic alkanes in the urban air samples.

The carbon distribution of I/SVOCs in Figure 2 is in broad agreement with the carbon distribution of diesel fuel reported by Gentner et al. (2012), who demonstrated a sharp peak at around C_{10} to C_{13} and a broader peak at around C_{16}-C_{20}. A correlation analysis was carried out between the I/SVOCs measured in the London air and diluted emissions from a light-duty diesel engine designed to a Euro 5 standard under three different operation modes (low-speed/low-load, high-speed/low-load and high-speed/high load), without or with aftertreatment by a diesel oxidation catalyst (DOC) and diesel particulate filter (DPF) (Alam et al., 2019). Total I/SVOCs (sum of acyclic alkanes, cyclic alkanes and aromatics in the gas phase and particle phase) ranging from C_{13} to C_{36} collected at MR and RU correlated strongly with the diesel exhaust (Table S3), indicating that the I/SVOCs measured in London air have a similar carbon distribution and composition as those measured in the diesel exhaust. The I/SVOCs at the roadside site MR (r^2=0.71-0.81) generally correlated better with the diesel exhaust than those sampled at the background site RU (r^2=0.56-0.76). The on-road light-duty diesel fleet includes older vehicles without abatement devices, vehicles with only DOC, and vehicles with both a DOC and DPF (Alam et al., 2019). The correlation between I/SVOCs in London air and diesel exhaust emitted under different operation conditions without or with aftertreatment varies little. Compounds observed in the gas phase of diesel emissions are similar to those identified in diesel fuels (mainly below C_{20}) while compounds in the particle phase are similar to lubricating oil (mainly C_{21}-C_{27}) (Alam et al., 2018). The similarities found in the I/SVOC profiles in urban air and diesel exhaust clearly demonstrate the impact of diesel-powered vehicles upon urban air quality.

While London has a high percentage of diesel vehicles, it is likely that there are other sources of I/SVOCs that are contributing to urban air besides diesel- exhaust. The majority of IVOCs emitted from gasoline engines have volatility similar to C_{12}-C_{14} n-alkanes and comprise aliphatic and aromatic compounds with published work reporting a large fraction of unspeciated UCM (Drozd et al., 2019; Zhao et al., 2016). I/SVOCs below C_{18} measured at MR correlated more strongly with the gasoline-tracer benzene (r^2=0.46-0.71) rather than those above C_{18} (r^2=0.005-0.10), indicating a substantial gasoline emission contribution to the more volatile organics. Some organic markers (i.e. n-alkanes and PAHs) have been detected in on-road non-exhaust emissions, such as from tyre and brake lining wear and in road dust (Rogge et al., 1993; Pant and Harrison, 2013; Kwon and Castaldi, 2012; El Haddad et al., 2009). The use of volatile chemical products (VCPs) (e.g. pesticides, coating, cleaning and personal care products) can contribute to urban organic emissions, and that mineral spirits commonly used in solvent-borne coatings can be a source of nonoxygenated IVOCs (McDonald et al., 2018).Khare and Gentner (2018) suggest that asphalt-related road paving and repair could also be a source of I/SVOCs. Aliphatic and aromatic VOCs and IVOCs up to C_{18}, with minor SVOCs present, were detected in paving-related products. During the paving processes (i.e. hot storage, application and surfacing), the degradation of larger organic compounds in heated asphalts can generate lighter compounds ranging from C_7 to C_{30}, such as alkanes, cyclic alkanes and single-ring aromatics that may also contribute to the I/SVOC roadside concentrations due to their long emission timescales after application.

3.1.2 Acyclic alkanes

Figure 3 shows the split between gas and particle concentrations for the I/SVOC classes. Alkane homologues including linear n-alkanes and branched alkanes were grouped depending on their carbon number. Alkanes from C_{13} to C_{31} were detected in both the particulate and gas phase while C_{32} to C_{36} were detected only in the particulate phase. A number of studies have distinguished the origin of n-alkanes by applying the carbon preference index (CPI), calculated by the summation of odd carbon number n-alkanes over a carbon range divided by the summation of even carbon number n-alkanes over the same carbon range (Cincinelli et al., 2007; Andreou and Rapsomanikis, 2009; Simoneit, 1999). The I/SVOCs emitted from natural sources (e.g. plant wax) present CPI >1 while from fossil fuel sources (e.g. vehicle emission) present CPI close to or lower than 1

(Simoneit, 1999). The CPI values for alkanes at RU (average CPI=1.13) and MR (average CPI=1.05) indicate an origin mainly from fossil fuel sources, such as vehicle emissions, and are discussed in more depth in a companion paper (Xu et al., 2020.

The distribution of the acyclic alkanes in Figure 3 has been correlated with diesel engine emissions and is similar to that reported for gas-phase (r^2=0.64 at MR; r^2=0.56 at RU) and particle-phase diesel exhaust (r^2=0.64 at MR; r^2=0.42 at RU) measured by Alam et al.(2019), showing diesel exhaust is the potential emission source for acyclic alkanes, in agreement with the CPI results. The distribution of alkanes shown in Figure 3 bears a strong similarity to that for n-alkanes reported from Delhi by Gupta et al. (2017), but differs from measurements in Guangzhou (Bi et al., 2003) and Athens (Mandalakis et al., 2002) which lack the mode at lower carbon numbers, presumably because of a lower abundance of diesel vehicles. A larger mode at lower carbon numbers in this study might also due to the lighter and more volatile hydrocarbons found in gasoline emissions.

3.1.3 Monocyclic alkanes and bicyclic alkanes

In most previous studies, the mixture of cyclic alkanes and branched alkanes has typically been observed as a part of the unresolved complex mixture (UCM) (Mandalakis et al., 2002) or classified as groups of compounds (Dunmore et al., 2015). This study has separated the monocyclic alkane and bicyclic alkane components (structure of chemicals shown as Figure S5-S6) from UCM based on their retention behaviour in the 2D chromatography.

Monocyclic alkanes ranging from C_{12} to C_{18} were detected in the particulate and gas phases while C_{19} to C_{25} were detected only in the particle phase (Figure 3). Alkyl-cyclopentane, alkyl-cyclohexane and alkyl-cycloheptane and their derivatives were observed in the monocyclic alkane groups. Alkenes were observed but not well separated from the monocyclic alkane polygons. The observed alkenes had very low concentrations, consistent with the finding of Gentner et al. (2012), so that the influence of alkenes on the group concentration was estimated as negligible. Bicyclic alkanes ranging from C_{13} to C_{17} were detected in the particulate and gas phases while C_{18} to C_{27} were detected only in the particle phase (Figure 3). Isaacman et al. (2012) reported the semi-volatile organic compound composition of diesel fuel, and cycloalkanes accounted for a more significant fraction of diesel fuel (14%) than bicyclic alkanes (11%), broadly consistent with the air samples. Alkyl-cyclohexanes from C_{12} to C_{25} were also quantified in this study and shown in Table S2. Concentrations of alkyl-cyclohexanes presented similar patterns to those for grouped monocyclic alkanes in Figure 3 and on average accounted for around 30% of the monocyclic alkane groups.

3.1.4 Monocyclic aromatics

Approximately 30% of gasoline mass and 20% of diesel fuel mass are aromatics while the remaining components are comprised largely of alkane classes (acyclic and cyclic) (Gentner et al., 2013). Monocyclic aromatics ranging from C_{10} to C_{19} were detected in the particulate and gas phase air samples while C_{20} to C_{24} were detected only in the particle phase. Monocyclic aromatic homologues occupied the third largest percentage of the total chemicals (18% at MR and 16% RU).. The C_{10} homologue was the most abundant in the gas phase with a further peak at C_{15} while the particle phase distribution was steady throughout C_{10} to C_{19} with an increase for C_{19} and above (Figure 3). Monocyclic aromatics ranging from C_{10} to C_{11} represent a large fraction of the IVOC emission of gasoline exhaust (Drozd et al., 2019), suggesting that the light monocyclic aromatics in the gas phase may derive from both gasoline and diesel-powered vehicles.

3.2 The Influence of Wind Direction

The air flow within a street canyon is strongly influenced by street orientation and the wind conditions. Wind direction is the most important factor affecting the flow and mixing processes in the street canyon and the consequent I/SVOC concentrations (arising from emissions within the street canyon) (Kumar et al., 2008). The MR sampling site is at the kerbside on the southern side of the heavily trafficked Marylebone Road, which is relatively straight and oriented in the west–east direction. The buildings on either side of Marylebone Road are around six storeys in height giving a street canyon aspect ratio of approximately 1:1 (Harrison et al., 2019). Typically, winds can set up a single vortex in a regular street canyon (aspect ratio ~1) when the wind is across the canyon (wind direction to the street axis exceeds 30°) with a wind speed above 1.5 m s^{-1} (Kumar et al., 2008; DePaul and Sheih, 1985).

There were 25 daily samples collected at MR, including eight south wind days, six north wind days and 11 mixed flow days. The average concentrations of the main I/SVOC groups during the north wind and south wind have been calculated and compared (Figure 4). In a street canyon, air exchange between the street level and the atmosphere on the rooftop level is limited. The traffic emitted pollutants in the street are less diluted due to the buildings at the roadside, especially in winter as a result of a more stable weather conditions (Wehner et al., 2002; Gromke et al., 2008). A schematic diagram from our previous work of the wind flows in the street canyon of Marylebone Road shows how southerly winds and northerly winds transport the pollutants from Marylebone Road to MR and WM monitoring sites respectively (Harrison et al., 2019). During the south wind, the sampler at the southern side of Marylebone Road was heavily exposed to the freshly emitted traffic pollutants from the road. During the north wind, the MR sampler was exposed mainly to incoming air from the background atmosphere of north London, resulting in a reduced concentration of I/SVOCs compared to the average concentrations of the entire campaign. This is seen clearly for alkanes (n+i) in Figure 4, and shows that the hydrocarbon distribution in background north London air is very similar to that in the air heavily polluted by vehicle emissions when the wind is in the southerly sector (r^2=0.90)

3.3 Spatial Distribution of Concentrations

Samples were collected at WM and RU simultaneously from 24 January to 19 February 2017, and after that MR sampling was run from 22 March to 18th April 2017. The difference of sampling period makes comparability between these sites more difficult. The concentrations of organic compounds are typically higher in winter than in summer, attributed to the differences in meteorological parameters as well as the strength of seasonal particulate emissions, such as from residential heating, and lower breakdown rates. SOA formation from urban emissions in winter can be as efficient as the SOA production observed in summer (Schroder et al., 2018). The significant variation in seasonal concentrations of particulate matter has been reported in several studies (Fu et al., 2008; Pant et al., 2015; Singh et al., 2011; Yadav et al., 2013.

In order to better understand the spatial distribution of I/SVOCs, scaling of the MR I/SVOC concentrations was applied to estimate the I/SVOC concentrations as if MR had been sampled simultaneously with WM/RU (January-February 2017) by taking account of BC as a dispersion marker. In London, BC arises very largely from vehicle traffic (Harrison and Beddows, 2017; Harrison et al., 2019) and the major fraction of BC measured at the roadside site MR comes from traffic emissions. The sum of I/SVOCs in the gas phase and particle phase correlated moderately with BC at MR during the MR campaign period (average r^2=0.40) below C_{28} while there was a weaker correlation for I/SVOCs above C_{28} (average r^2=0.20). I/SVOCs at MR during the WM/RU sampling campaign were estimated based on the original MR I/SVOC concentrations multiplied by the ratio of MR BC during the WM/RU sampling period to that during the MR sampling period (estimation details in Supplementary Information Section 5). The concentrations of alkanes, monocyclic alkanes, bicyclic alkanes and monocyclic aromatics at WM and RU during January to February 2017 and scaled data from MR (sum of the gas phase and particle phase) are shown in Figure 5. Expectedly, MR concentrations were the highest of all sites as it is a heavily trafficked site. The concentrations of hydrocarbons at WM were higher than RU presumably reflecting a greater distance of RU from the source of emissions. The carbon distribution of these I/SVOC groups presented in Figure 5 was similar at the three sampling sites and presented $r^2 \geq 0.58$ (Table S4), implying the dispersion of traffic emission to the downwind area. While traffic, especially diesel emissions, was suggested as the dominant emission sources for the I/SVOCs identified in the current study, small differences between sites indicate the likely presence of other sources, such as roadside dusts and the use of VCP.

Results in the current study were compared with a recent gas-phase I/SVOC study (Dunmore et al., 2015) at North Kensington (NK) in London, which is classified as an urban background site by the UK automatic air quality network (Dall'Osto et al., 2011). Dunmore et al. (2015) grouped alkanes, alkenes and cycloalkanes as aliphatic compounds, suggesting approximately 5600 ng/m^3 for C_{13} in January/February. To compare with the NK study (Dunmore et al., 2015), gas phase concentrations of the alkane groups and monocyclic alkane groups in MR during January-February were summed, reporting a very much lower concentration for C_{13} (282 ng/m^3). The degree of traffic pollution, as represented by the BC concentration was however higher in the Dunmore et al. (2015) study.

3.4 Estimation of the Emission Factors (EFs) of I/SVOCs Detected at MR

MR is a congested urban street canyon where vehicle speeds vary greatly over short distances (Jones and Harrison, 2006) and the traffic flow is over 80,000 vehicles per day. Jones and Harrison (2006) estimated the fleet-average emission factors (EFs) of NO_x at Marylebone Road (MR) in 2002/2003 based on the fleet composition and traffic emissions from the National Atmospheric Emissions Inventory (NAEI) database. The NO_x EF at MR during the MR campaign 2017 was estimated by scaling the NO_x EF in 2002/2003 reported by Jones and Harrison (2006) by the ratio of NO_x concentrations (minus background) in the two periods accounting also for the traffic mix and flows. The roadside increments ($PM_{2.5}$, $PM_{2.5-10}$, PM_{10}) correlated most strongly with roadside NO_x, which is frequently used as a dispersion tracer (Jones and Harrison, 2006). The EFs of

I/SVOC groups were estimated based on the assumption that the I/SVOCs and NO_x in the traffic increments (minus background) come from the common traffic source and disperse similarly in the ambient air, enabling the EFs of I/SVOC to be estimated from the ratio of their concentrations to those of NO_x (minus background) (see Supplementary Information, Section 6). A number of previous studies have applied this method (Johansson et al., 2009; Ketzel et al., 2003; Omstedt et al., 2005; Wåhlin et al., 2006) or assumption (Gietl et al., 2010; Gidhagen et al., 2005) to estimate the EFs of pollutants.

The emission factor of NO_x on Marylebone Road for the mixed fleet was estimated as 0.82 g (NO_x as NO_2) veh^{-1} km^{-1}, based upon the mean concentrations during the MR sampling period. A major change in the fleet composition between the early 2000s and the present day is that the proportion of diesel-powered light-duty vehicles (LDVs) has grown. The numbers of gasoline-powered LDVs and diesel-powered LDVs are similar in the UK currently while most of the heavy-duty vehicles (HDVs) in Europe are diesel-powered (Carslaw et al., 2011; Hassler et al., 2016). Diesels contribute the majority of burned fuel for transportation in the UK (Dunmore et al., 2015). Since only the gasoline-powered vehicles have shown a remarkable reduction in NO_x emissions in the past two decades, and the NO_x emission from diesel vehicles have not declined much during the same time period (Carslaw and Rhys-Tyler, 2013), the roadside NO_x emission have remained stable in the UK (Carslaw et al., 2011; Hassler et al., 2016) Carslaw et al. (2011) reported that the NO_x EFs were variable based on different estimates. The UK NAEI assumes a much lower proportion of Euro 1/Euro 2 for petrol vehicles than that suggested by RSD (remote sensing detector) and does not differentiate the age of vehicles by area/road type (e.g. urban area and motorways). The differences in the fleet composition and vehicle age assumed in the NAEI and observed by RSD are important factors affecting the NOx emission estimates.

Four main classes of compounds, including alkanes, monocyclic alkanes, bicyclic alkanes and monocyclic aromatics, accounted for 92% of the gas phase and 99.5% of the particle phase identified emissions. Emission factors of the four main I/SVOC groups by carbon number and phase appear in Figure 6. Particle phase alkanes (n+i) had the highest total emission factor among all particle phase compound classes in this study while the emissions of monocyclic alkanes, bicyclic alkanes, monocyclic aromatics and naphthalene were more abundant in the gas phase than in the particle phase.

The n-alkane emission factors estimated in this study are shown in Table S7 and compared with several previous roadside studies and lab tests although the comparisons between EFs measured under different conditions is not straightforward The three roadside studies are the Zhujiang Tunnel study in China (He et al., 2008), the roadside study of Route 467 in Fujisawa, Japan (Kawashima et al., 2006) and the roadside study of Grenoble Ring Road in Grenoble, France (Charron et al., 2019). The background information on these studies can be seen in Table S8, including sampling date, vehicle speed, traffic volume and the proportion of light duty vehicles (LDVs) and heavy-duty vehicles (HDVs). The emission factors of n-alkanes measured in the gas phase in this study were markedly lower than in the roadside study in Japan (Kawashima et al., 2006), while the emission factors of particle phase n-alkanes ranging from C_{19}-C_{26} showed a broad agreement with the tunnel study in China (He et al., 2008) and the roadside study in France (Charron et al., 2019), all of which showed a similar order of magnitude and a broad peak at around C_{21}-C_{25}. Greater particle-phase emissions of long chain n-alkanes (above C_{27}) were detected in this study compared with the Zhujiang Tunnel study in China (He et al., 2008).

Vehicle fleet composition varies appreciably between countries. There are far fewer light duty diesel powered vehicles in China and Japan than in the EU. Gasoline engines are typically used in light-duty vehicles (LDVs) in these former countries whilst diesel engines dominate in heavy-duty vehicles (HDVs). There has been a significant shift to diesel engines in the small vehicle market in recent years, especially in several European countries (EMEP/EEA, 2016). Diesel vehicles represented 40% of the vehicles in 2017 in the UK (Fleet News, 2018) while accounting for 72% of vehicles in 2011 in France (Charron et al., 2019). In contrast, light duty gasoline vehicles represent a large percentage of the Chinese vehicle fleet and the share increased rapidly from less than 50% in 2002 to 70% in 2009 (Huo et al., 2012). In Japan, the ratio of diesel-powered small trucks to gasoline powered vehicles is 8.1% (Kawashima et al., 2006). Gentner et al. (2012) measured the carbon distribution of straight and branched chain alkanes from gasoline and diesel-powered vehicles, finding a predominant contribution of gasoline combustion to the lighter alkanes (up to C_{12}). Diesel emissions are mainly comprised of heavier aliphatic hydrocarbons containing primarily unburned fuel (up to C_{20}) and unburned lubricating oil (C_{18} to C_{36}) (Alam et al., 2016a). Therefore, greater emissions of light alkanes might be expected in the gas phase in Japan as gasoline powered vehicles dominate the market. The composition of lubricants may explain the difference in the long chain n-alkane (above C_{27}) emissions in this study and the Zhujiang Tunnel study in China (He et al., 2008). The differences of the EFs in these studies are probably mainly caused by variations in the vehicle type and the composition of fuel/oil in use, as well as the road conditions and vehicle speed.

Also included in Table S7 are the emission factors for particle-phase hydrocarbons measured by chassis dynamometer tests for diesel-powered passenger cars of Euro 2, Euro 3, Euro 4, and Euro 4 with a particle trap (Charron et al., 2019; Perrone et al., 2014). Perrone et al. (2014) reported the n-alkane EFs from Euro 2 decreased to one-fifth of Euro 1, and declined further to Euro 3, indicating the n-alkane EFs have a strong association with the technological development of the LDVs. The fleet average on-road emission factors measured both in this work and by Charron et al. (2019) in Table S7 generally exceed the values for Euro 3 vehicles (Charron et al., 2019; Perrone et al., 2014) but are closer to Euro 2 without an emission control device (Perrone et al, 2014), despite the fact that most vehicles would have been built to more recent Euro standards at the time of sampling, and many would be fitted with a diesel particle filter (DPF). This suggests a major contribution from the heavy-duty vehicles and/or many high emission vehicles with malfunctions in their emissions control devices, or an unrepresentative test cycle in the laboratory work.

The C_{20}-C_{32} n-alkane EF profiles detected in the particle-phase of diesel emissions show a maximum n-alkane EF at C_{20}-C_{22} and a decrease in EF with the increase of carbon number (Charron et al., 2019; Perrone et al., 2014). Past studies have reported a similar profile of n-alkane EFs in diesel exhaust of medium-duty trucks (Schauer et al., 1999), heavy-duty vehicles (Shah et al., 2005) and Euro 4 vehicle tested for the urban cycle with cold start (Kim et al., 2016). The difference between the n-alkane EFs from the ambient air of London roadside and the laboratory measurements of diesel-powered vehicles may be attributed to the presence of other emission sources in London air, such as the exhaust from gasoline-powered vehicles and non-exhaust sources (e.g. asphalt-related paving). The carbon number distribution of n-alkane EFs in the particle phase can also be affected by dilution ratio (DR) which may differ from the laboratory tests (typically lower DR) to measurements in ambient air (higher DR) (Perrone et al, 2014). Fujitani et al. (2012) reported that the distribution of n-alkane EFs ranging from C_{12} to C_{33} between the gas phase and particle phase in diesel exhaust varied with DR, since the gas-particle partitioning depends strongly on DR and vapour pressure.

4. OVERVIEW

The comparisons between the composition and carbon number distribution of I/SVOCs in urban air samples with those of diesel exhaust show high similarities, indicating the diesel exhaust is the most probable source of the species identified in this study. Besides diesel fuel, the potential of other emission sources of I/SVOCs in urban air have been discussed, such as gasoline engine emissions, tyre and brake lining wear, the use of volatile chemical products (VCPs) and asphalt-related paving.

The lower molecular weight C_{13} to C_{18} hydrocarbons were primarily in the gas phase, while the hydrocarbons above C_{20} were more abundant in the particulate phase. The peak abundance of hydrocarbons of C_{10}-C_{20} is attributed to diesel fuel, and those of C_{21}-C_{28} largely to engine oil. As expected, concentrations at MR were the highest of all sites as it is a heavily trafficked roadside. The concentration of hydrocarbons at WM was higher than RU as the emissions were diluted more at an increased distance from the traffic emission source. The alkane concentrations at MR were highest when the south wind brought the traffic emitted pollutants to the MR sampler, while concentrations were lowest when the north wind brought background air from north London.

Emission factors have been estimated and four classes of compounds, including alkanes (n+i), monocyclic alkanes, bicyclic alkanes and monocyclic aromatics made a dominant contribution to emissions at MR. Although it is a challenge to compare directly the emission factor with other studies conducted under different conditions, the emission factors of n-alkanes estimated in the current study showed a similar order of magnitude and broad agreement with the tunnel study in China (He et al., 2008) and the roadside study in France (Charron et al., 2019). The gas-phase n-alkanes in a roadside study in Japan (Kawashima et al., 2006) were significantly higher than in this study, probably caused by variations in the vehicle type and the composition of fuel/oil in use, as well as the road conditions and vehicle speed. The comparison between the n-alkane EFs estimated in the current study and those measured directly in diesel exhaust indicate a considerable contribution from vehicles with higher emissions than recent diesel passenger cars to London air. Differences in the n-alkane profiles between London air and diesel exhaust may be attributed to a number of factors, such as the presence of gasoline emissions and different dilution ratios (DRs) in real world measurements and lab tests.

DATA ACCESSIBILITY

Data supporting this publication are openly available from the UBIRA eData repository at https://doi.org/10.25500/edata.bham.00000310.

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SUPPORTING INFORMATION

Supporting Information provides further details of sampling site locations, the 24-hour air sampler, the analysis of 2-D-chromatograms, the specific compound analyses, and the estimation of emission factors.

CONFLICT OF INTERESTS

The authors declare no competing financial interest.

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FIGURE LEGENDS:

Figure 1: Typical TD-GC×GC-ToF-MS chromatogram of a particulate-phase sample collected on the roof of University of Westminster (WM) in Feb 2017, demonstrating the grouping of compounds.

Figure 2: The I/SVOC composition (gas and particle phase) identified at MR and RU in the London Campaign 2017.

Figure 3: Concentrations of alkanes (n+i), monocyclic alkanes, bicyclic alkanes and monocyclic aromatics in the gas phase and particle phase in MR and RU, London Campaign 2017.

Figure 4: The average alkane (n+i) concentrations in MR (sum of gas phase and particle phase) during the MR campaign during southerly and northerly winds.

Figure 5: Concentrations of alkanes (n+i), monocyclic alkanes, bicyclic alkanes and monocyclic aromatics (sum of the gas phase and particle phase) at WM and RU measured simultaneously from January to February 2017, together with MR data adjusted to match the same time period (see text).

Figure 6: Emission factors of alkanes (n+i), monocyclic alkanes, bicyclic alkanes and monocyclic aromatics in the gas phase and particle phase at MR.

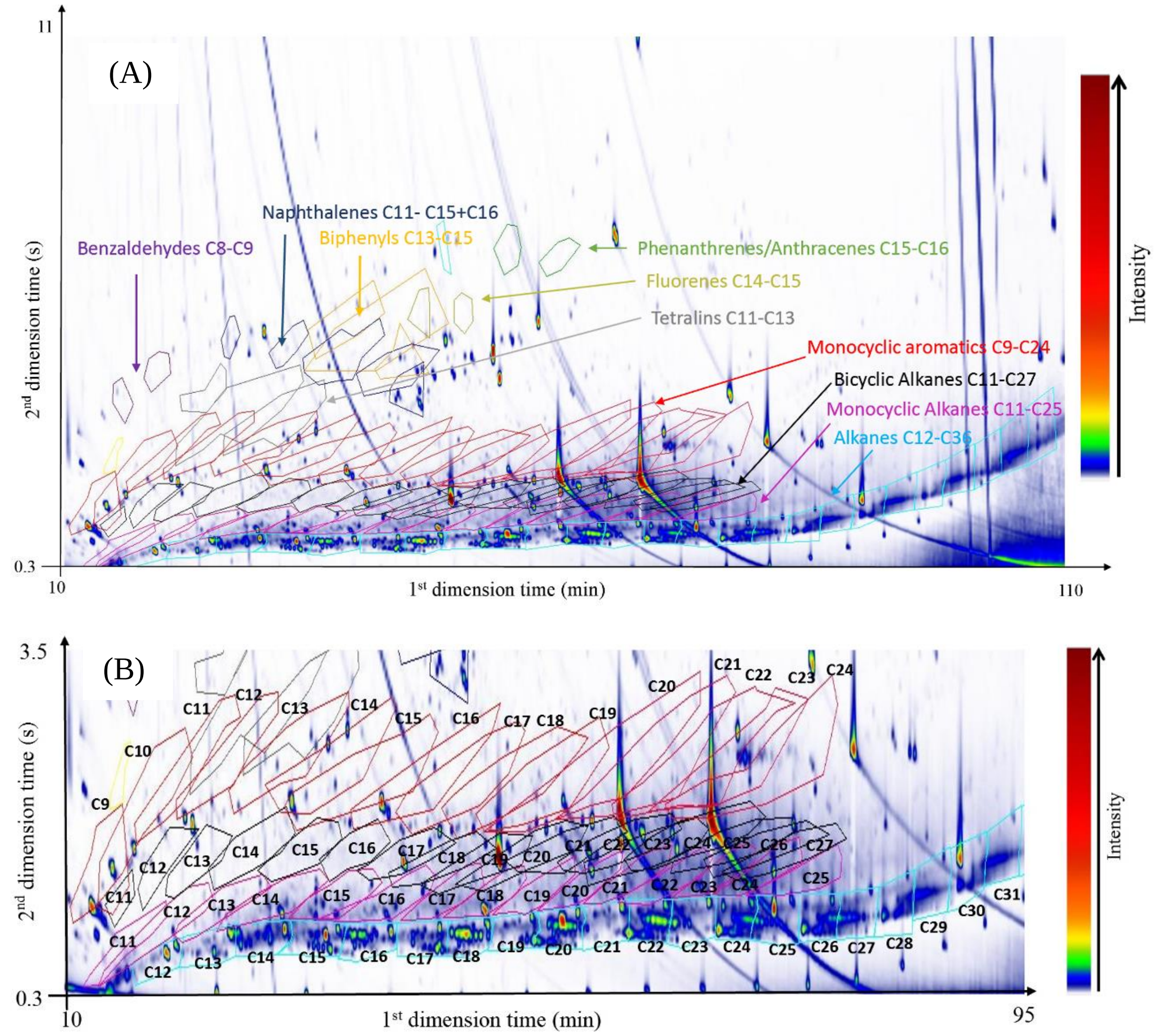


Figure 1: Typical TD-GC×GC-ToF-MS chromatogram of a particulate-phase sample collected on the roof of University of Westminster (WM) in Feb 2017, demonstrating the grouping of compounds. X and y-axis are the retention time on the first and second column respectively, with the intensity of the compounds shown by the coloured contours. Colder colours (i.e. blue) are less intense than the warmer colours (i.e. red). (A) A contour plot (chromatogram) displays C_{12}-C_{36} alkanes, C_{11}-C_{25} monocyclic alkanes, C_{11}-C_{27} bicyclic alkanes, C_9-C_{24} monocyclic aromatics, C_8-C_9 benzaldehydes, C_{11}-C_{16} naphthalenes, C_{13}-C_{15} biphenyls, C_{15}-C_{16} phenanthrenes/anthracenes, C_{14}-C_{15} fluorenes and C_{11}-C_{13} tetralins. Each region fenced by a coloured polygon marks out the grouped isomers of a chemical homologue with a particular carbon number. (B) A zoomed in contour plot displaying the carbon number distribution of grouped alkanes (blue), monocyclic alkanes (pink), bicyclic alkanes (black) and monocyclic aromatics (red).

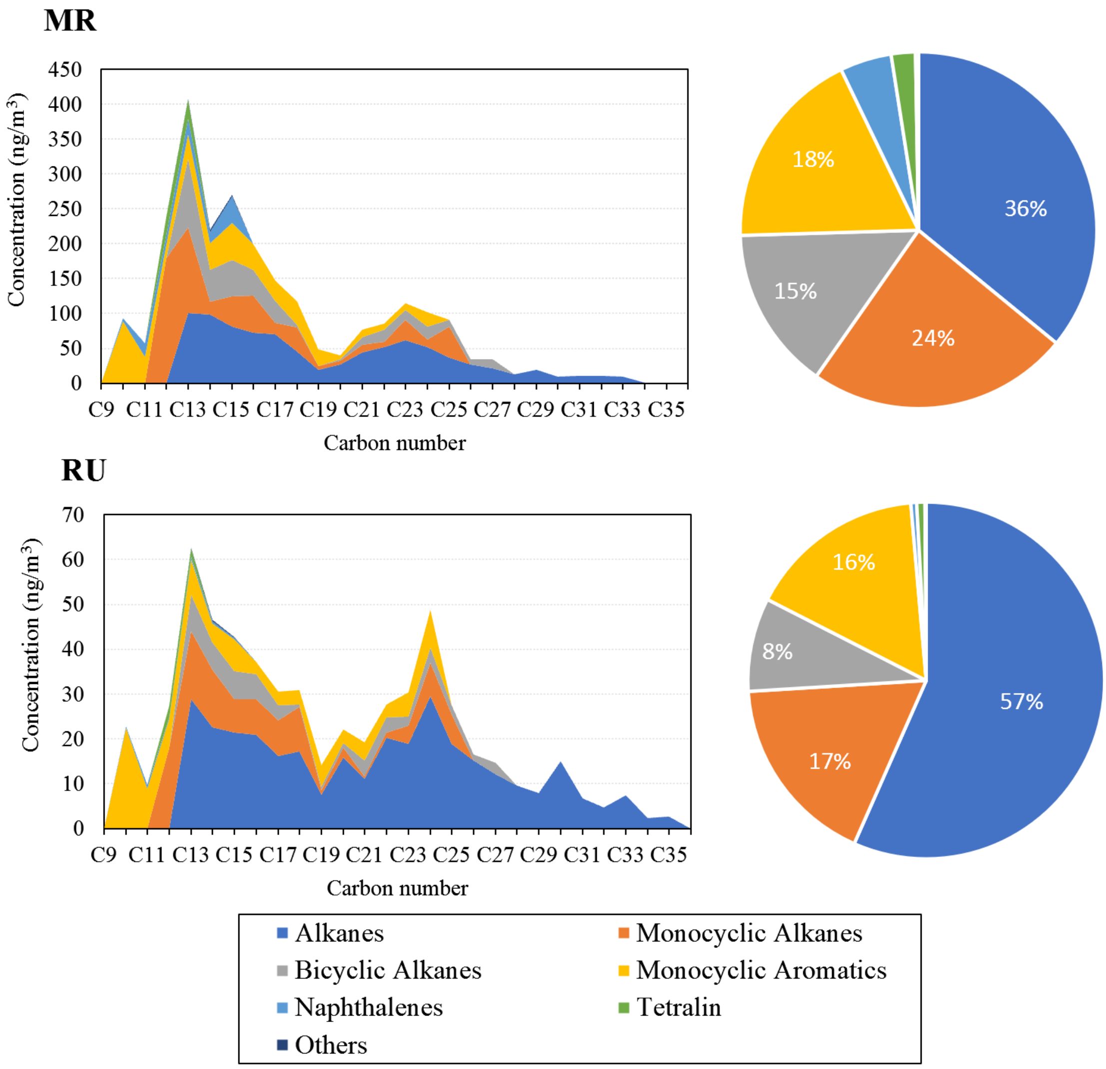


Figure 2: The I/SVOC composition (gas and particle phase) identified at MR and RU in the London Campaign 2017.

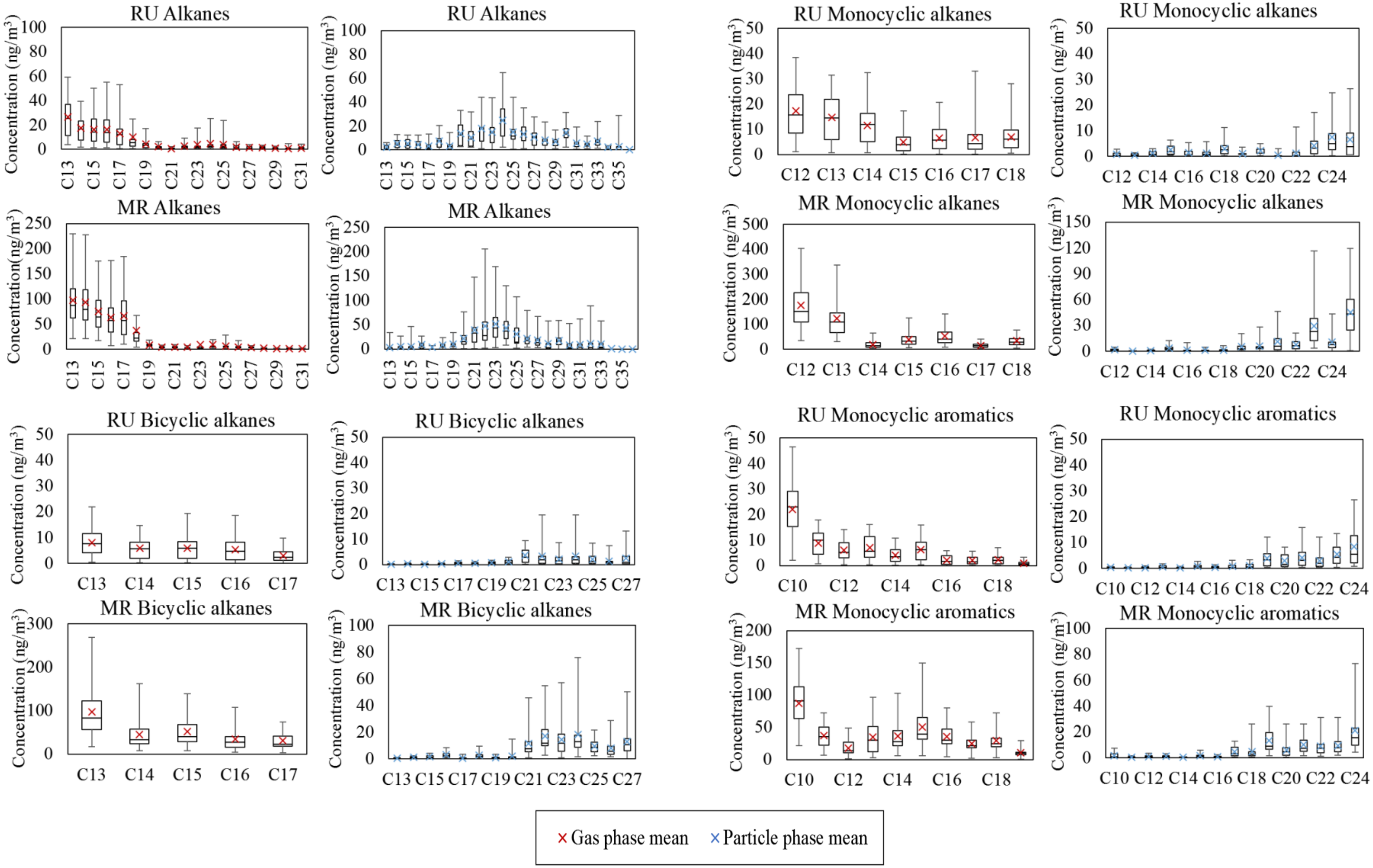


Figure 3: Concentrations of alkanes (n+i), monocyclic alkanes, bicyclic alkanes and monocyclic aromatics in the gas phase and particle phase at MR and RU, London Campaign 2017.

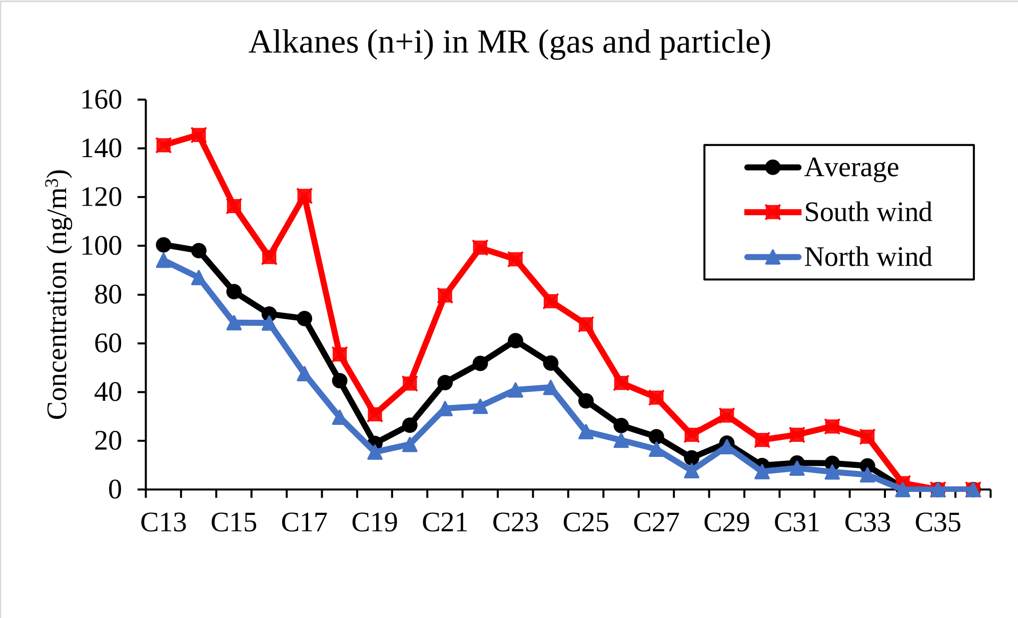
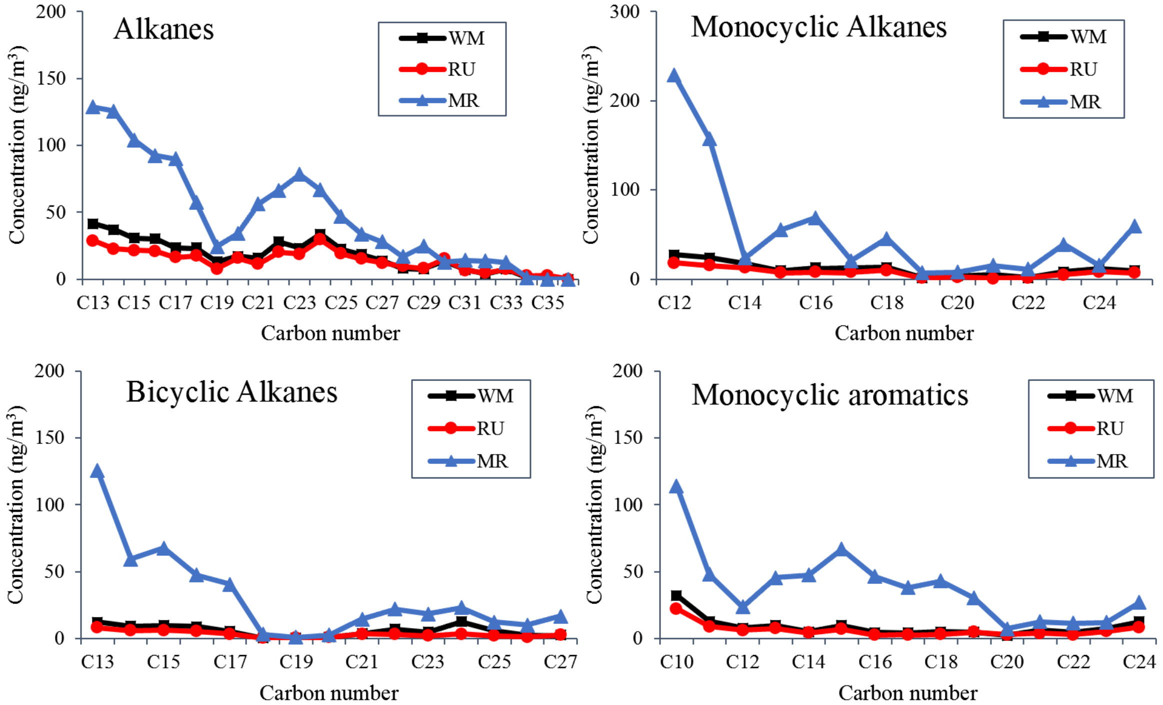


Figure 4: The average alkane (n+i) concentrations in MR (sum of gas phase and particle phase) during the MR campaign during southerly and northerly winds.



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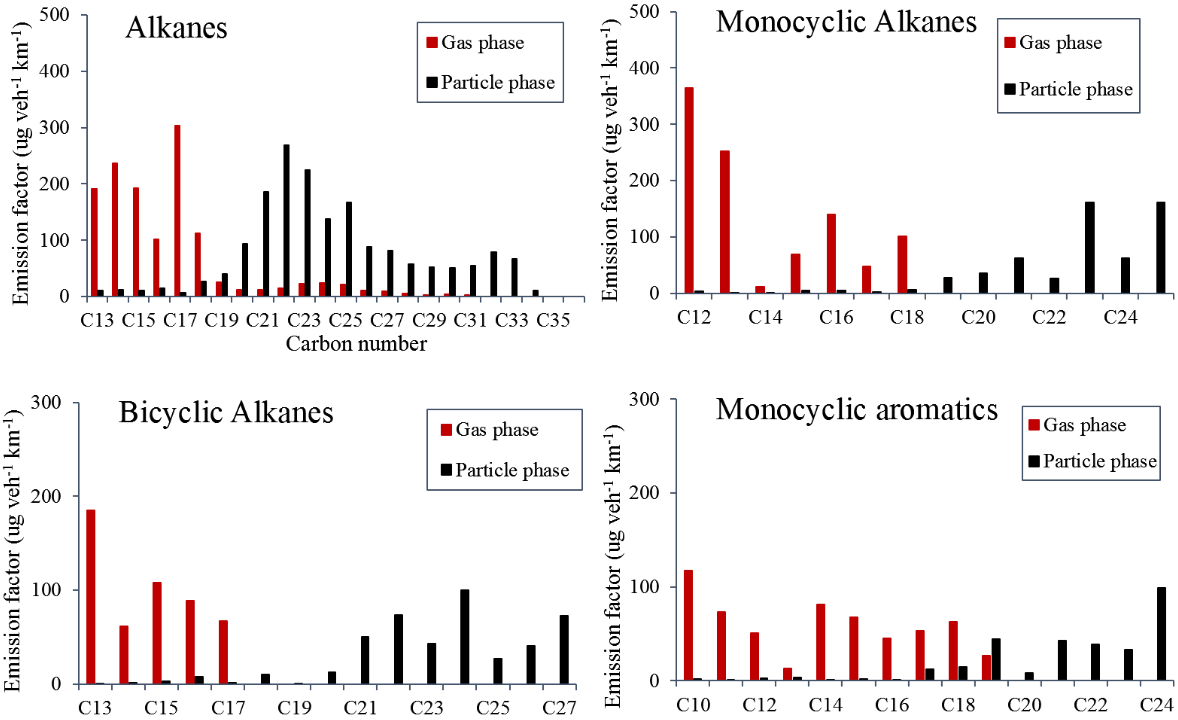

Figure 6: Emission factors of alkanes (n+i), monocyclic alkanes, bicyclic alkanes and monocyclic aromatics in the gas phase and particle phase at MR.