

Composition and emission factors of traffic- emitted intermediate volatility and semi-volatile hydrocarbons (C₁₀–C₃₆) at a street canyon and urban background sites in central London, UK

Xu, Ruixin; Alam, Mohammed S.; Stark, Christopher; Harrison, Roy M.

DOI:

[10.1016/j.atmosenv.2020.117448](https://doi.org/10.1016/j.atmosenv.2020.117448)

License:

Creative Commons: Attribution-NonCommercial-NoDerivs (CC BY-NC-ND)

Document Version

Peer reviewed version

Citation for published version (Harvard):

Xu, R, Alam, MS, Stark, C & Harrison, RM 2020, 'Composition and emission factors of traffic- emitted intermediate volatility and semi-volatile hydrocarbons (C₁₀–C₃₆) at a street canyon and urban background sites in central London, UK', *Atmospheric Environment*, vol. 231, 117448.
<https://doi.org/10.1016/j.atmosenv.2020.117448>

[Link to publication on Research at Birmingham portal](#)

General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.

Download date: 03. May. 2024

1
2
3
4 **Composition and Emission Factors of Traffic-**
5 **Emitted Intermediate Volatility and Semi-Volatile**
6 **Hydrocarbons (C₁₀-C₃₆) at a Street Canyon and**
7 **Urban Background Sites in Central London, UK**
8

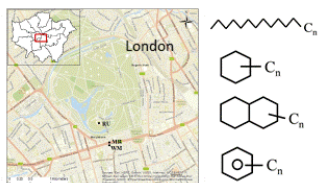
9
10 **Ruixin Xu, Mohammed S. Alam, Christopher Stark and**
11 **Roy M. Harrison*[†]**
12

13 **Division of Environmental Health and Risk Management,**
14 **School of Geography, Earth and Environmental Sciences**
15 **University of Birmingham**
16 **Edgbaston, Birmingham B15 2TT**
17 **United Kingdom**
18
19

* To whom correspondence should be addressed.

Tele: +44 121 414 3494; Fax: +44 121 414 3709; Email: r.m.harrison@bham.ac.uk

[†]Also at: Department of Environmental Sciences / Center of Excellence in Environmental Studies, King Abdulaziz University, PO Box 80203, Jeddah, 21589, Saudi Arabia



20

21

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

23

24

25

26

27

28 **ABSTRACT**

29 Hydrocarbons in both gas and particle phases from C₁₀ to C₃₆ (I/SVOCs) were analysed at sites in
30 central London. Samples were collected from a street canyon, Marylebone Road (MR), a rooftop
31 site (WM) above MR, and a site in the adjacent Regent's Park (RU), north of MR to evaluate the
32 change in composition of I/SVOCs during advection from the traffic to the cleaner atmosphere of
33 the urban background. Groups of compounds identified and quantified in gas and particle phases
34 include C₁₃-C₃₆ n-alkanes and branched alkanes, C₁₂-C₂₅ monocyclic alkanes, C₁₃-C₂₇ bicyclic
35 alkanes and C₁₀-C₂₄ monocyclic aromatics. The similarities found in the aliphatic and aromatic
36 region above C₁₂ in urban air and diesel exhaust demonstrate the impact of diesel-powered vehicles
37 on urban air quality. Diesel exhaust is suggested to be the dominant emission source, while small
38 differences between sites indicate the possibility of other sources which are also discussed. The
39 ambient concentrations of I/SVOCs in the street canyon at MR were highest when the southerly
40 winds brought the traffic emitted pollutants to the sampler. Emission factors (EFs) for all compound
41 groups were estimated from the concentrations at the MR site. Particle-phase n-alkane EFs are
42 broadly similar to those measured elsewhere in the world, despite differences in traffic fleet
43 composition. A comparison between n-alkane EFs estimated from field measurements and those
44 measured from diesel engines in the laboratory suggests a large contribution from vehicles with
45 higher emissions than recent passenger cars to London air.

46

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

48 1. INTRODUCTION

49 Particulate matter is the air pollutant with the greatest public health impact, and its effects are likely
50 to depend upon particle size and composition (Rissler et al., 2012; Masiol et al., 2012). As a major
51 emission source within the urban environment, particulate matter originated from traffic has
52 generated major interest over the last few decades. The majority of traffic-emitted fine particles are
53 carbonaceous, directly emitted as primary organic aerosol (POA) and elemental carbon, oxidation
54 of the former leading to production of secondary organic aerosol (SOA) (Jimenez et al., 2009). A
55 substantial fraction of the organic compounds in exhaust emissions of gasoline and diesel vehicles
56 are semi-volatile (May et al., 2013a,b). While intermediate volatility organic compounds (IVOCs)
57 exist mainly in the vapour phase, semi-volatile organic compounds (SVOCs) partition directly
58 between gas and particulate phases under ambient conditions (May et al., 2013a; Robinson et al.,
59 2007; Donahue et al., 2012). SVOCs refer to organic species with an effective saturation
60 concentration C^* between 1 and $10^3 \mu\text{g m}^{-3}$ while IVOCs refer to species with C^* between 10^4 and
61 $10^7 \mu\text{g m}^{-3}$ (Robinson et al., 2007).

62
63 I/SVOC emissions from traffic mainly comprise aliphatic and aromatic hydrocarbons typically
64 ranging between C_{12} and C_{35} (Worton et al., 2014; Gentner et al., 2012; Alam et al., 2018;
65 Weitkamp et al., 2007). Most of the gasoline emitted organic compounds are volatile organic
66 compounds (VOCs) while some aromatics can extend to the intermediate-volatile range. Only 30%
67 of diesel emitted hydrocarbons are VOCs and most of them are less volatile (mainly I/SVOCs)
68 (Gentner et al., 2012). Gasoline engine emissions are typically in the carbon number range below
69 C_{12} while diesel engine emissions are mainly in the range from C_8 to C_{25} (Gentner et al., 2012).
70 Detailed emission information for these diesel-derived organic compounds (above C_{12}) in the
71 atmosphere is not widely available (Dunmore et al., 2015) although the greatest roadway emitters of
72 particles per vehicle are diesel powered. In the UK, 40% of licensed passenger cars were using a
73 diesel engine in 2017 (Fleet News, 2018). Diesel exhaust contains primarily unburned fuel (C_{15} - C_{23}

74 organics), unburned lubricating oil (C₁₅-C₃₆ organics) and sulfate (Jacobson et al., 2005). A recent
75 study investigated the hydrocarbon composition of diesel exhaust using gas chromatography
76 coupled with time-of-flight mass spectrometry and concluded that the diesel fuel contributes up to
77 C₂₀ hydrocarbons whilst engine lubricating oil contributes primarily to the C₁₈ to C₃₆ range of
78 compounds (Alam et al., 2016a).

79

80 Despite huge research interest and many contributions over the last decades, many uncertainties
81 remain regarding the identities and chemical composition of traffic emitted I/SVOCs. A key reason
82 is that the vast majority of I/SVOC mass cannot be separated and characterised by the traditional
83 one-dimensional gas-chromatography (1D-GC) based analytical techniques (Schauer et al., 1999;
84 2002; Jathar et al., 2012). A mixture of cyclic, linear, and branched hydrocarbons is present in a
85 typical chromatogram as an unresolved complex mixture (UCM) (Mandalakis et al., 2002). The
86 UCM is often observed in samples associated with the use of fossil fuels (Nelson et al., 2006;
87 Frysinger et al., 2003; Ventura et al., 2008), and comprises more than 80% of the semi-volatile
88 hydrocarbons emitted from diesel and gasoline derived engines (Schauer et al., 2002; 1999; Chan et
89 al., 2013). A number of studies have reported the chemical components of organic emissions in
90 traffic influenced regions by using one dimensional chromatography coupled with mass
91 spectrometry (GC-MS) or comprehensive two-dimensional gas chromatography coupled with mass
92 spectrometry (GC×GC -MS) (Lewis et al., 2000; Hamilton and Lewis, 2003; Omar et al., 2007;
93 Chan et al., 2013; Hamilton et al., 2004; Worton et al., 2014; Dunmore et al., 2015). However, the
94 homologous series that have been reported in most of the studies only represent a small fraction of
95 the total organic mass that is emitted from traffic, with a consequent lack of information on I/SVOC
96 composition.

97

98 Emissions from road traffic are known to make a large contribution to total particulate matter (van
99 Deursen et al., 2000) and vapour concentrations in urban areas. It is important to understand the

100 magnitude and characteristics of I/SVOC emissions from vehicles, especially in megacities like
101 London. Measurements on laboratory-based diesel engines (Schauer et al., 1999; Perrone et al.,
102 2014) allow the determination of exhaust emissions under controlled test conditions but these tests
103 often cover a limited set of vehicles due to the high costs. These tests cannot fully represent the
104 large variation in engine types and driving modes in different environments (Charron et al., 2019),
105 and are not able to give an accurate estimation on the dilution of I/SVOCs (Kim et al., 2016) and do
106 not include non-exhaust emissions (Pant et al., 2013). Therefore, estimates deriving from
107 concentration measurements at a near-road site are considered to offer a realistic simulation for the
108 emission factors, which currently comprise both tunnel and roadside measurements (Hwa et al.,
109 2002; Kawashima et al., 2006; He et al., 2008, Staehelin et al., 1998).

110

111 In this study, samples were collected in central London at the roadside of the heavily trafficked
112 Marylebone Road (MR), and two rooftop sites (WM and RU) during different times from January
113 to April 2017 in London. The samples were analysed by using comprehensive two-dimensional gas
114 chromatography time-of-flight mass spectrometry (TD-GC×GC-ToF-MS) combined with a
115 mapping and grouping methodology to classify, identify and quantify the compounds classes.
116 I/SVOCs (C₁₀-C₃₆) were identified and quantified in both the gas phase and particle phase, to offer a
117 more comprehensive understanding of the chemical composition of traffic emitted particulate
118 matter. The concentrations of four main I/SVOC groups are reported and discussed, including
119 alkanes (n+i) (defined as the sum of n-alkanes and branched alkanes), monocyclic alkanes, bicyclic
120 alkanes and monocyclic aromatics. The effect of wind direction on the dispersion of traffic emitted
121 pollutants in the street canyon and the spatial distribution of I/SVOCs in different locations are
122 discussed. Emission factors for n-alkanes and the main I/SVOC groups are estimated for traffic on
123 Marylebone Road. Oxygenates, which are both important primary emissions from road traffic, and
124 are formed by atmospheric oxidation of hydrocarbons have been addressed in an earlier paper (Lyu
125 et al., 2019).

126 **2. EXPERIMENTAL**

127 **2.1 Field Measurements in London Campaign, 2017**

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

140 **2.2 Sample Collection**

141 An in-house auto-sampler was designed to collect sequential 24 h duration samples (Figure S3).
142 The sampler has seven channels and is turned to the next channel automatically. A pump draws air
143 through a polypropylene backed PTFE filter (47 mm, 1 µm pore, Whatman, Maidstone, UK) to
144 collect the particulate phase, and then through a stainless steel thermal adsorption tube packed with
145 1 cm quartz wool and 300 mg Carbograph 2TD 40/60 (Markes International) to collect the gas
146 phase. The flowrate was calibrated by a calibrator (Gilian Gilibrator-2 NIOSH Primary Standard
147 Air Flow Calibrator, Sensidyne, Schauenburg, Germany) and set at 1.5 L/min during the field
148 measurements. The inlet to the sampler was through a downward facing ¼ inch o.d. stainless steel
149 tube giving an estimate cut point of around 4 µm (Harrison and Perry, 1986). After 24h duration
150 sampling, filters were transferred to pre-cleaned filter cases which are then enclosed with
151 aluminium foil. Adsorption tubes were capped firmly. Both filter cases and tubes were stored under

152 conditions of approximately -18°C prior to extraction and GC×GC-ToF-MS analysis. Adsorption
153 tube breakthrough was evaluated in the field with two tubes in series, and vapour concentrations are
154 reported only for compounds for which collection was quantitative.

155

156 **2.3 GC×GC ToF MS Analysis**

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

163

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

177

178 **2.4 Classification of Organic Compounds**

179 Recently studies have reported that the diesel fuel derived organic compounds are predominantly
180 found from C₁₃-C₂₀, while compounds derived from lubricating oil are predominantly within the
181 range C₁₈-C₃₅. Both are part of an unresolved complex mixture (UCM) in traditional GC (Dunmore
182 et al., 2015; Alam et al., 2016a,b). The number of possible structural isomers increases with the
183 number of carbon atoms (Goldstein and Galbally, 2007), and beyond around C₉ it is a challenge to
184 identify the structure of all compounds present in the ambient air (Dunmore et al., 2015). However,
185 it is possible to assign individual compounds to particular chemical classes and functionalities based
186 on their retention behaviour in two-dimensional chromatography. The physicochemical similarities
187 within compound classes and their steady changes with the increasing chain length and /or
188 molecular sizes enables the further identification of the ordered appearance of compounds in the
189 chromatogram. This allows the identification of species without unique mass spectra but based on
190 the pattern of the database. This study grouped the chemical compounds into isomer sets based on
191 their carbon number and functional group (Figure 1). Natural standards were chosen for calibration
192 and quantification, including n-alkanes (C₁₁-C₃₆), phytane and pristane (Sigma Aldrich, UK), n-
193 alkyl-cyclohexanes (C₁₁ -C₂₅), n-alkylbenzenes (C₁₀, C₁₂, C₁₄, C₁₆ and C₁₈), tetralin, alkyl-tetralins
194 (methyl-, di-, tri- and tetra-), cis- and trans-decalin, alkyl-naphthalenes (C₁₁, C₁₂, C₁₃ and C₁₆)
195 (Chiron AS, Norway) and 13 polycyclic aromatic hydrocarbons (Thames Restek UK Ltd). The
196 authentic standard mixture (72 natural standards and 9 internal standards) was expected to cover as
197 much of the whole chromatogram as possible and can be applied to calibrate the quantification of
198 the isomer groups with the same functionality and molecular ions. Briefly, known amounts of
199 natural and internal standard were injected into the GC×GC -MS system prior to the sample
200 analysis to determine the response of target compounds. The identification of individual compounds
201 is described by Alam et al. (2016b). Groups of isomers were quantified by adopting an individual
202 compound with the same carbon number and functionality as a surrogate. For instance, the response
203 for n-tridecane, (*m/z* 184) was used to quantify all isomers identified within the C₁₃ alkane polygon.

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

208 209 **2.5 Supporting Data**

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

214
215 London Heathrow airport, located west of central London, is the closest station to provide
216 comprehensive meteorological information for the sampling sites above the roof. Daily mean wind
217 direction data from London Heathrow airport (Met Office, 2006) were used to sort the 24 h duration
218 I/SVOC samples into north wind (N), south wind (S) and undefined wind (Duffy and Nelson, 1996)
219 based on the predominant direction during each sampling interval. The wind angles 300-360° and
220 0-60° are defined as a north wind while wind angles 120-240° are defined as a south wind in this
221 study. North wind and south wind are both cross-canyon flows, whilst an undefined wind (Duffy
222 and Nelson, 1996) represents the along-street flows, including wind angles 60–120° (east wind)
223 and 240-300° (west wind). The Heathrow site is within 25 km of the London sampling sites. Using
224 data from UK sites, Manning et al. (2000) show that wind data from airfield sites are representative
225 of wind fields up to 40 km from the site. The Heathrow data represent winds above the street
226 canyon; those within the canyon are very different. Harrison et al. (2019) show diagrammatically
227 the circulations within the Marylebone Road canyon.

228
229

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 C₁₃-C₃₆ alkanes (n+i), C₁₂-C₂₅ monocyclic alkanes, C₁₃-C₂₇ bicyclic alkanes, C₁₀-C₂₄ monocyclic aromatics, C₁₀-C₁₅ naphthalenes, C₁₃-C₁₅ biphenyls, C₁₄-C₁₅ fluorenes, C₁₅-C₁₆ phenanthrenes/anthracenes and C₁₂-C₁₃ tetralins. Lyu et al. (2019) further identified alkanals (C₁₀-C₁₄), alkan-2-ones (C₁₀-C₁₈) and alkan-3-ones (C₁₀-C₁₆) 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 C₂₀) 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.

256 The carbon distribution of I/SVOCs in Figure 2 is in broad agreement with the carbon distribution
257 of diesel fuel reported by Gentner et al. (2012), who demonstrated a sharp peak at around C₁₀ to C₁₃
258 and a broader peak at around C₁₆-C₂₀. A correlation analysis was carried out between the I/SVOCs
259 measured in the London air and diluted emissions from a light-duty diesel engine designed to a
260 Euro 5 standard under three different operation modes (low-speed/low-load, high-speed/low-load
261 and high-speed/high load), without or with aftertreatment by a diesel oxidation catalyst (DOC) and
262 diesel particulate filter (DPF) (Alam et al., 2019). Total I/SVOCs (sum of acyclic alkanes, cyclic
263 alkanes and aromatics in the gas phase and particle phase) ranging from C₁₃ to C₃₆ collected at MR
264 and RU correlated strongly with the diesel exhaust (Table S3), indicating that the I/SVOCs
265 measured in London air have a similar carbon distribution and composition as those measured in the
266 diesel exhaust. The I/SVOCs at the roadside site MR ($r^2=0.71-0.81$) generally correlated better with
267 the diesel exhaust than those sampled at the background site RU ($r^2=0.56-0.76$). The on-road light-
268 duty diesel fleet includes older vehicles without abatement devices, vehicles with only DOC, and
269 vehicles with both a DOC and DPF (Alam et al., 2019). The correlation between I/SVOCs in
270 London air and diesel exhaust emitted under different operation conditions without or with
271 aftertreatment varies little. Compounds observed in the gas phase of diesel emissions are similar to
272 those identified in diesel fuels (mainly below C₂₀) while compounds in the particle phase are similar
273 to lubricating oil (mainly C₂₁-C₂₇) (Alam et al., 2018). The similarities found in the I/SVOC profiles
274 in urban air and diesel exhaust clearly demonstrate the impact of diesel-powered vehicles upon
275 urban air quality.

276

277 While London has a high percentage of diesel vehicles, it is likely that there are other sources of
278 I/SVOCs that are contributing to urban air besides diesel- exhaust. The majority of IVOCs emitted
279 from gasoline engines have volatility similar to C₁₂-C₁₄ n-alkanes and comprise aliphatic and
280 aromatic compounds with published work reporting a large fraction of unspciated UCM (Drozd et
281 al., 2019; Zhao et al., 2016). I/SVOCs below C₁₈ 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.

296

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

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

310

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

320

321 **3.1.3 Monocyclic alkanes and bicyclic alkanes**

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

327

328 Monocyclic alkanes ranging from C₁₂ to C₁₈ were detected in the particulate and gas phases while
329 C₁₉ to C₂₅ were detected only in the particle phase (Figure 3). Alkyl-cyclopentane, alkyl-
330 cyclohexane and alkyl-cycloheptane and their derivatives were observed in the monocyclic alkane
331 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 C₁₃ to C₁₇ were detected in the particulate and gas phases while C₁₈ to C₂₇ 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 C₁₂ to C₂₅ 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 C₁₀ to C₁₉ were detected in the particulate and gas phase air samples while C₂₀ to C₂₄ 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 C₁₀ homologue was the most abundant in the gas phase with a further peak at C₁₅ while the particle phase distribution was steady throughout C₁₀ to C₁₉ with an increase for C₁₉ and above (Figure 3). Monocyclic aromatics ranging from C₁₀ to C₁₁ 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

358 street canyon) (Kumar et al., 2008). The MR sampling site is at the kerbside on the southern side of
359 the heavily trafficked Marylebone Road, which is relatively straight and oriented in the west–east
360 direction. The buildings on either side of Marylebone Road are around six storeys in height giving a
361 street canyon aspect ratio of approximately 1:1 (Harrison et al., 2019). Typically, winds can set up
362 a single vortex in a regular street canyon (aspect ratio ~ 1) when the wind is across the canyon (wind
363 direction to the street axis exceeds 30°) with a wind speed above 1.5 m s^{-1} (Kumar et al., 2008;
364 DePaul and Sheih, 1985).

365

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

382

383

384 **3.3 Spatial Distribution of Concentrations**

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

394
395 In order to better understand the spatial distribution of I/SVOCs, scaling of the MR I/SVOC
396 concentrations was applied to estimate the I/SVOC concentrations as if MR had been sampled
397 simultaneously with WM/RU (January-February 2017) by taking account of BC as a dispersion
398 marker. In London, BC arises very largely from vehicle traffic (Harrison and Beddows, 2017;
399 Harrison et al., 2019) and the major fraction of BC measured at the roadside site MR comes from
400 traffic emissions. The sum of I/SVOCs in the gas phase and particle phase correlated moderately
401 with BC at MR during the MR campaign period (average $r^2=0.40$) below C_{28} while there was a
402 weaker correlation for I/SVOCs above C_{28} (average $r^2=0.20$). I/SVOCs at MR during the WM/RU
403 sampling campaign were estimated based on the original MR I/SVOC concentrations multiplied by
404 the ratio of MR BC during the WM/RU sampling period to that during the MR sampling period
405 (estimation details in Supplementary Information Section 5). The concentrations of alkanes,
406 monocyclic alkanes, bicyclic alkanes and monocyclic aromatics at WM and RU during January to
407 February 2017 and scaled data from MR (sum of the gas phase and particle phase) are shown in
408 Figure 5. Expectedly, MR concentrations were the highest of all sites as it is a heavily trafficked
409 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 ($\text{PM}_{2.5}$, $\text{PM}_{2.5-10}$, PM_{10}) correlated most strongly with roadside NO_x , which is frequently used as a dispersion tracer (Jones and Harrison, 2006). The EFs of

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

443
444 The emission factor of NO_x on Marylebone Road for the mixed fleet was estimated as 0.82 g (NO_x
445 as NO₂) veh⁻¹ km⁻¹, based upon the mean concentrations during the MR sampling period. A major
446 change in the fleet composition between the early 2000s and the present day is that the proportion
447 of diesel-powered light-duty vehicles (LDVs) has grown. The numbers of gasoline-powered LDVs
448 and diesel-powered LDVs are similar in the UK currently while most of the heavy-duty vehicles
449 (HDVs) in Europe are diesel-powered (Carslaw et al., 2011; Hassler et al., 2016). Diesels contribute
450 the majority of burned fuel for transportation in the UK (Dunmore et al., 2015). Since only the
451 gasoline-powered vehicles have shown a remarkable reduction in NO_x emissions in the past two
452 decades, and the NO_x emission from diesel vehicles have not declined much during the same time
453 period (Carslaw and Rhys-Tyler, 2013), the roadside NO_x emission have remained stable in the UK
454 (Carslaw et al., 2011; Hassler et al., 2016) Carslaw et al. (2011) reported that the NO_x EFs were
455 variable based on different estimates. The UK NAEI assumes a much lower proportion of Euro
456 1/Euro 2 for petrol vehicles than that suggested by RSD (remote sensing detector) and does not
457 differentiate the age of vehicles by area/road type (e.g. urban area and motorways). The differences
458 in the fleet composition and vehicle age assumed in the NAEI and observed by RSD are important
459 factors affecting the NO_x emission estimates.

460

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

468

469 The n-alkane emission factors estimated in this study are shown in Table S7 and compared with
470 several previous roadside studies and lab tests although the comparisons between EFs measured
471 under different conditions is not straightforward The three roadside studies are the Zhujiang Tunnel
472 study in China (He et al., 2008), the roadside study of Route 467 in Fujisawa, Japan (Kawashima et
473 al., 2006) and the roadside study of Grenoble Ring Road in Grenoble, France (Charron et al., 2019).
474 The background information on these studies can be seen in Table S8, including sampling date,
475 vehicle speed, traffic volume and the proportion of light duty vehicles (LDVs) and heavy-duty
476 vehicles (HDVs). The emission factors of n-alkanes measured in the gas phase in this study were
477 markedly lower than in the roadside study in Japan (Kawashima et al., 2006), while the emission
478 factors of particle phase n-alkanes ranging from C₁₉-C₂₆ showed a broad agreement with the tunnel
479 study in China (He et al., 2008) and the roadside study in France (Charron et al., 2019), all of which
480 showed a similar order of magnitude and a broad peak at around C₂₁-C₂₅. Greater particle-phase
481 emissions of long chain n-alkanes (above C₂₇) were detected in this study compared with the
482 Zhujiang Tunnel study in China (He et al., 2008).

483

484 Vehicle fleet composition varies appreciably between countries. There are far fewer light duty
485 diesel powered vehicles in China and Japan than in the EU. Gasoline engines are typically used in
486 light-duty vehicles (LDVs) in these former countries whilst diesel engines dominate in heavy-duty

487 vehicles (HDVs). There has been a significant shift to diesel engines in the small vehicle market in
488 recent years, especially in several European countries (EMEP/EEA, 2016). Diesel vehicles
489 represented 40% of the vehicles in 2017 in the UK (Fleet News, 2018) while accounting for 72% of
490 vehicles in 2011 in France (Charron et al., 2019). In contrast, light duty gasoline vehicles represent
491 a large percentage of the Chinese vehicle fleet and the share increased rapidly from less than 50% in
492 2002 to 70% in 2009 (Huo et al., 2012). In Japan, the ratio of diesel-powered small trucks to
493 gasoline powered vehicles is 8.1% (Kawashima et al., 2006). Gentner et al. (2012) measured the
494 carbon distribution of straight and branched chain alkanes from gasoline and diesel-powered
495 vehicles, finding a predominant contribution of gasoline combustion to the lighter alkanes (up to
496 C₁₂). Diesel emissions are mainly comprised of heavier aliphatic hydrocarbons containing primarily
497 unburned fuel (up to C₂₀) and unburned lubricating oil (C₁₈ to C₃₆) (Alam et al., 2016a). Therefore,
498 greater emissions of light alkanes might be expected in the gas phase in Japan as gasoline powered
499 vehicles dominate the market. The composition of lubricants may explain the difference in the long
500 chain n-alkane (above C₂₇) emissions in this study and the Zhujiang Tunnel study in China (He et
501 al., 2008). The differences of the EFs in these studies are probably mainly caused by variations in
502 the vehicle type and the composition of fuel/oil in use, as well as the road conditions and vehicle
503 speed.

504

505 Also included in Table S7 are the emission factors for particle-phase hydrocarbons measured by
506 chassis dynamometer tests for diesel-powered passenger cars of Euro 2, Euro 3, Euro 4, and Euro 4
507 with a particle trap (Charron et al., 2019; Perrone et al., 2014). Perrone et al. (2014) reported the n-
508 alkane EFs from Euro 2 decreased to one-fifth of Euro 1, and declined further to Euro 3, indicating
509 the n-alkane EFs have a strong association with the technological development of the LDVs. The
510 fleet average on-road emission factors measured both in this work and by Charron et al. (2019) in
511 Table S7 generally exceed the values for Euro 3 vehicles (Charron et al., 2019; Perrone et al., 2014)
512 but are closer to Euro 2 without an emission control device (Perrone et al., 2014), despite the fact

513 that most vehicles would have been built to more recent Euro standards at the time of sampling, and
514 many would be fitted with a diesel particle filter (DPF). This suggests a major contribution from the
515 heavy-duty vehicles and/or many high emission vehicles with malfunctions in their emissions
516 control devices, or an unrepresentative test cycle in the laboratory work.

517

518 The C₂₀-C₃₂ n-alkane EF profiles detected in the particle-phase of diesel emissions show a
519 maximum n-alkane EF at C₂₀-C₂₂ and a decrease in EF with the increase of carbon number
520 (Charron et al., 2019; Perrone et al., 2014). Past studies have reported a similar profile of n-alkane
521 EFs in diesel exhaust of medium-duty trucks (Schauer et al., 1999), heavy-duty vehicles (Shah et
522 al., 2005) and Euro 4 vehicle tested for the urban cycle with cold start (Kim et al., 2016). The
523 difference between the n-alkane EFs from the ambient air of London roadside and the laboratory
524 measurements of diesel-powered vehicles may be attributed to the presence of other emission
525 sources in London air, such as the exhaust from gasoline-powered vehicles and non-exhaust sources
526 (e.g. asphalt-related paving). The carbon number distribution of n-alkane EFs in the particle phase
527 can also be affected by dilution ratio (DR) which may differ from the laboratory tests (typically
528 lower DR) to measurements in ambient air (higher DR) (Perrone et al, 2014). Fujitani et al. (2012)
529 reported that the distribution of n-alkane EFs ranging from C₁₂ to C₃₃ between the gas phase and
530 particle phase in diesel exhaust varied with DR, since the gas-particle partitioning depends strongly
531 on DR and vapour pressure.

532

533 4. OVERVIEW

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

539 The lower molecular weight C₁₃ to C₁₈ hydrocarbons were primarily in the gas phase, while the
540 hydrocarbons above C₂₀ were more abundant in the particulate phase. The peak abundance of
541 hydrocarbons of C₁₀-C₂₀ is attributed to diesel fuel, and those of C₂₁-C₂₈ largely to engine oil. As
542 expected, concentrations at MR were the highest of all sites as it is a heavily trafficked roadside.
543 The concentration of hydrocarbons at WM was higher than RU as the emissions were diluted more
544 at an increased distance from the traffic emission source. The alkane concentrations at MR were
545 highest when the south wind brought the traffic emitted pollutants to the MR sampler, while
546 concentrations were lowest when the north wind brought background air from north London.
547
548 Emission factors have been estimated and four classes of compounds, including alkanes (n+i),
549 monocyclic alkanes, bicyclic alkanes and monocyclic aromatics made a dominant contribution to
550 emissions at MR. Although it is a challenge to compare directly the emission factor with other
551 studies conducted under different conditions, the emission factors of n-alkanes estimated in the
552 current study showed a similar order of magnitude and broad agreement with the tunnel study in
553 China (He et al., 2008) and the roadside study in France (Charron et al., 2019). The gas-phase n-
554 alkanes in a roadside study in Japan (Kawashima et al., 2006) were significantly higher than in this
555 study, probably caused by variations in the vehicle type and the composition of fuel/oil in use, as
556 well as the road conditions and vehicle speed. The comparison between the n-alkane EFs estimated
557 in the current study and those measured directly in diesel exhaust indicate a considerable
558 contribution from vehicles with higher emissions than recent diesel passenger cars to London air.
559 Differences in the n-alkane profiles between London air and diesel exhaust may be attributed to a
560 number of factors, such as the presence of gasoline emissions and different dilution ratios (DRs) in
561 real world measurements and lab tests.

565 **DATA ACCESSIBILITY**

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

568

569 **ACKNOWLEDGEMENTS**

570 The authors acknowledge funding from the European Research Council for the FASTER project
571 (ERC-2012-AdG, Proposal No. 320821). The authors acknowledge Dr David Beddows and Dr Ajit
572 Singh for their help during sampling campaigns.

573

574 **SUPPORTING INFORMATION**

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

578

579 **CONFLICT OF INTERESTS**

580 The authors declare no competing financial interest.

581

582

REFERENCE

- Alam, M.S., Zeraati-Rezaei, S., Xu, H., Harrison, R.M., 2019. Characterisation of gas and particulate phase organic emissions (C₉-C₃₇) from a diesel engine and the effect of abatement devices, *Environ. Sci. Technol.*, 53, 11345-11352.
- Alam, M.S., Liang, Z., Zeraati-Rezaei, S., Stark, C., Xu, H., MacKenzie, A.R, Harrison, R.M., 2018. Mapping and quantifying isomer sets of hydrocarbons (≥C₁₂) in diesel exhaust, lubricating oil and diesel fuel samples using GC×GC-ToFMS. *Atmos. Meas. Techn.*, 11, 3047-3058.
- Alam, M.S., Harrison, R.M., 2016. Recent advances in the application of 2-dimensional gas chromatography with soft and hard ionisation time-of-flight mass spectrometry in environmental analysis. *Chem. Sci.*, 7, 3968-3977.
- Alam, M.S., Zeraati-Rezaei, S., Stark, C.P., Liang, Z., Xu, H., Harrison, R.M., 2016a. The characterisation of diesel exhaust particles—composition, size distribution and partitioning. *Faraday Discuss.*, 189, 69-84.
- Alam, M.S., Stark, C., Harrison, R.M., 2016b. Using variable ionisation energy time-of-flight mass spectrometry with comprehensive GC×GC to identify isomeric species. *Anal. Chem.*, 88, 4211-4220.
- Andreou, G., Rapsomanikis, S. 2009. Origins of n-alkanes, carbonyl compounds and molecular biomarkers in atmospheric fine and coarse particles of Athens, Greece. *Sci. Total Environ.*, 407, 5750-5760.
- Bi, X., Sheng, G., Peng, P., Chen, Y., Zhang, Z., Fu, J., 2003. Distribution of particulate- and vapor-phase n-alkanes and polycyclic aromatic hydrocarbons in urban atmosphere of Guangzhou, China. *Atmos. Environ.*, 37, 289-298.
- Carslaw, D. C. and Rhys-Tyler, G., 2013. New insights from comprehensive on-road measurements of NO_x, NO₂ and NH₃ from vehicle emission remote sensing in London, UK. *Atmos. Environ.*, 81, 339-347.
- Carslaw, D.C., Beevers, S.D., Tate, J.E., Westmoreland, E.J., Williams, M. L. 2011. Recent evidence concerning higher NO_x emissions from passenger cars and light duty vehicles. *Atmos. Environ.*, 45, 7053-7063.
- Chan, A.W.H., Isaacman, G., Wilson, K.R., Worton, D.R., Ruehl, C.R., Nah, T., Gentner, D.R., Dallmann, T.R., Kirchstetter, T.W., Harley, R.A., Gilman, J.B., Kuster, W.C., De Gouw, J.A., Offenberg, J.H., Kleindienst, T.E., Lin, Y.H., Rubitschun, C.L., Surratt, J.D., Hayes, P.L., Jimenez, J.L., Goldstein, A.H. 2013. Detailed chemical characterization of unresolved complex mixtures in atmospheric organics: Insights into emission sources, atmospheric processing, and secondary organic aerosol formation. *J. Geophys. Res.: Atmospheres*, 118, 6783-6796.
- Charron, A., Polo-Rehn, L., Besombes, J.-L., Golly, B., Buisson, C., Chanut, H., Marchand, N., Guillaud, G., Jaffrezo, J.-L., 2019. Identification and quantification of particulate tracers of exhaust and non-exhaust vehicle emissions. *Atmos. Chem. Phys.*, 19, 5187-5207, 2019.
- Cincinelli, A., Bubba, M. D., Martellini, T., Gambaro, A., Lepri, L. 2007. Gas-particle concentration and distribution of n-alkanes and polycyclic aromatic hydrocarbons in the atmosphere of Prato (Italy). *Chemosphere*, 68, 472-8.

- Dall'Osto, M., Thorpe, A., Beddows, D.C.S., Harrison, R.M., Barlow, J.F., Dunbar, T., Williams, P.I., Coe, H., 2011. Remarkable dynamics of nanoparticles in the urban atmosphere. *Atmos. Chem. Phys.*, 11, 6623-6637.
- DePaul, F., Sheih, C., 1985. A tracer study of dispersion in an urban street canyon. *Atmos. Environ.*, 19, 555-559.
- Donahue, N.M., Kroll, J., Pandis, S.N., Robinson, A.L. 2012. A two-dimensional volatility basis set–Part 2: Diagnostics of organic-aerosol evolution. *Atmos. Chem. Phys.*, 12, 615-634.
- Drozd, G. T., Zhao, Y., Saliba, G., Frodin, B., Maddox, C., Oliver Chang, M. C., Maldonado, H., Sardar, S., Weber, R. J., Robinson, A. L. & Goldstein, A. H. 2019. Detailed speciation of intermediate volatility and semivolatile organic compound emissions from gasoline vehicles: Effects of cold-starts and implications for secondary organic aerosol formation. *Environ Sci Technol*, 53, 1706-1714.
- Duffy, B.L., Nelson, P.F. 1996. Non-methane exhaust composition in the Sydney Harbour Tunnel: A focus on benzene and 1, 3-butadiene. *Atmos. Environ.*, 30, 2759-2768.
- Dunmore, R., Hopkins, J., Lidster, R., Lee, J., Evans, M., Rickard, A., Lewis, A., Hamilton, J., 2015. Diesel-related hydrocarbons can dominate gas phase reactive carbon in megacities. *Atmos. Chem. Phys.*, 15, 9983-9996.
- El Haddad, I., Marchand, N., Dron, J., Temime-Roussel, B., Quivet, E., Wortham, H., Jaffrezo, J.L., Baduel, C., Voisin, D., Besombes, J.L., 2009. Comprehensive primary particulate organic characterization of vehicular exhaust emissions in France. *Atmos. Environ.*, 43, 6190-6198.
- EMEP/EEA, 2016. Air Pollutant Emission Inventory Guidebook 2016, Technical guidance to prepare national emission inventories. EEA Report No. 21/016, European Environment Agency, Denmark, 2016,
[file:///C:/Users/hardinmt/Downloads/EMEP%20EEA%20air%20pollutant%20emission%20inventory%20guidebook%202016%20Introduction%20\(3\).pdf](file:///C:/Users/hardinmt/Downloads/EMEP%20EEA%20air%20pollutant%20emission%20inventory%20guidebook%202016%20Introduction%20(3).pdf) [last accessed 18 October 2019].
- Fleet News, 2018. Record number of diesel cars now on Britain's roads, says RAC Foundation, <https://www.fleetnews.co.uk/news/manufacturer-news/2018/04/16/diesel-cars-reach-record-number-in-britain> [last accessed 07/02/2019].
- Frysiner, G.S., Gaines, R.B., Xu, L., Reddy, C.M., 2003. Resolving the unresolved complex mixture in petroleum-contaminated sediments. *Environ. Sci. Technol.*, 37, 1653-1662.
- Fu, P., Kawamura, K., Barrie, L. A., 2008. Photochemical and other sources of organic compounds in the Canadian high Arctic aerosol pollution during winter-spring. *Environ. Sci. Technol.*, 43, 286-292.
- Fujitani, Y., Saitoh, K., Fushimi, A., Takahashi, K., Hasegawa, S., Tanabe, K., Kobayashi, S., Furuyama, A., Hirano, S., Takami, A., 2012. Effect of isothermal dilution on emission factors of organic carbon and n-alkanes in the particle and gas phases of diesel exhaust. *Atmos. Environ.*, 59, 389-397.

686 Gentner, D.R., Worton, D.R., Isaacman, G., Davis, L.C., Dallmann, T.R., Wood, E.C., Herndon,
687 S.C., Goldstein, A.H., Harley, R.A. 2013. Chemical composition of gas-phase organic carbon
688 emissions from motor vehicles and implications for ozone production. *Environ. Sci. Technol.*, 47,
689 11837-11848.

690
691 Gentner, D.R., Isaacman, G., Worton, D.R., Chan, A.W., Dallmann, T.R., Davis, L., Liu, S., Day,
692 D.A., Russell, L.M., Wilson, K.R., 2012. Elucidating secondary organic aerosol from diesel and
693 gasoline vehicles through detailed characterization of organic carbon emissions. *Proc. Natl. Acad.*
694 *Sci.*, 109, 18318-18323.

695
696 Gidhagen, L., Johansson, C., Langner, J., Foltescu, V.L., 2005. Urban scale modeling of particle
697 number concentration in Stockholm. *Atmos. Environ.*, 39, 1711-1725.

698
699 Gietl, J.K., Lawrence, R., Thorpe, A.J., Harrison, R.M., 2010. Identification of brake wear particles
700 and derivation of a quantitative tracer for brake dust at a major road. *Atmos. Environ.*, 44, 141-146.

701
702 Goldstein, A.H., Galbally, I.E., 2007. Known and unexplored organic constituents in the Earth's
703 atmosphere. *Environ. Sci. Technol.*, 41, 1514-1521.

704
705 Gromke, C., Buccolieri, R., Di Sabatino, S., Ruck, B., 2008. Dispersion study in a street canyon
706 with tree planting by means of wind tunnel and numerical investigations—evaluation of CFD data
707 with experimental data. *Atmos. Environ.*, 42, 8640-8650.

708
709 Gupta, S., Gadi, R., Mandal, T.K., 2017. Seasonal variations and source profile of n-alkanes in
710 particulate matter (PM₁₀) at a heavy traffic site, Delhi. *Environ. Monit. Assess.*, 189, 43.

711
712 Hamilton, J. F., Lewis, A.C. 2003. Monoaromatic complexity in urban air and gasoline assessed
713 using comprehensive GC and fast GC-TOF/MS. *Atmos. Environ.*, 37, 589-602.

714
715 Hamilton, J., Webb, P., Lewis, A., Hopkins, J., Smith, S., Davy, P. 2004. Partially oxidised organic
716 components in urban aerosol using GCXGC-TOF/MS. *Atmos. Chem. Phys.*, 4, 1279-1290.

717
718 Harrison, R.M., Beddows, D.C.S., Alam, M.S., Singh, A., Brean, J., Xu, R., Kotthaus, S. and
719 Grimmond, S., 2019. Interpretation of particle number size distributions measured across an urban
720 area during the FASTER campaign. *Atmos. Chem. Phys.*, 19, 39-55.

721
722 Harrison, R.M., Beddows, D.C. 2017. Efficacy of recent emissions controls on road vehicles in
723 Europe and implications for public health. *Sci. Rep.*, 7, 1152.

724
725 Harrison, R.M., Perry, R., 1986. *Handbook of Air Pollution Analysis*, Second Edition, Chapman
726 and Hall, pp. 634.

727
728 Hassler, B., McDonald, B.C., Frost, G.J., Borbon, A., Carslaw, D.C., Civerolo, K., Granier, C.,
729 Monks, P.S., Monks, S., Parrish, D.D., Pollack, I.B., Rosenlof, K.H., Ryerson, T.B., von
730 Schneidmesser, E., Trainer, M., 2016. Analysis of long-term observations of NO_x and CO in
731 megacities and application to constraining emissions inventories. *J. Geophys. Res. Letts.*, 43, 9920-
732 9930.

733
734 He, L.-Y., Hu, M., Zhang, Y.-H., Huang, X.-F., Yao, T.-T., 2008. Fine particle emissions from on-
735 road vehicles in the Zhujiang Tunnel, China. *Environ. Sci. Technol.*, 42, 4461-4466.

736

737 Huo, H., Yao, Z., Zhang, Y., Shen, X., Zhang, Q., Ding, Y., He, K., 2012. On-board measurements
738 of emissions from light-duty gasoline vehicles in three mega-cities of China. *Atmos. Environ.*, 49,
739 371-377.

740

741 Hwa, M.-Y., Hsieh, C.-C., Wu, T.-C., Chang, L.-F. W., 2002. Real-world vehicle emissions and
742 VOCs profile in the Taipei tunnel located at Taiwan Taipei area. *Atmos. Environ.*, 36, 1993-2002.

743

744 Isaacman, G., Wilson, K.R., Chan, A.W., Worton, D.R., Kimmel, J.R., Nah, T., Hohaus, T., Gonin,
745 M., Kroll, J. H., Worsnop, D. R., 2012. Improved resolution of hydrocarbon structures and
746 constitutional isomers in complex mixtures using gas chromatography-vacuum ultraviolet-mass
747 spectrometry. *Anal. Chem.*, 84, 2335-2342.

748

749 Jacobson, M., Kittelson, D., Watts, W., 2005. Enhanced coagulation due to evaporation and its
750 effect on nanoparticle evolution. *Environ. Sci. Technol.*, 39, 9486-9492.

751

752 Jathar, S.H., Miracolo, M.A., Presto, A.A., Donahue, N.M., Adams, P.J., Robinson, A.L. 2012.
753 Modeling the formation and properties of traditional and non-traditional secondary organic aerosol:
754 problem formulation and application to aircraft exhaust. *Atmos. Chem. Phys.*, 12, 9025-9040.

755

756 Jimenez, J., Canagaratna, M., Donahue, N., Prevot, A., Zhang, Q., Kroll, J. H., Decarlo, P. F.,
757 Allan, J. D., Coe, H., Ng, N., 2009. Evolution of organic aerosols in the atmosphere. *Science*, 326,
758 1525-1529.

759

760 Johansson, C., Norman, M., Burman, L., 2009. Road traffic emission factors for heavy metals.
761 *Atmos. Environ.*, 43, 4681-4688.

762

763 Jones, A.M., Harrison, R.M., 2006. Estimation of the emission factors of particle number and mass
764 fractions from traffic at a site where mean vehicle speeds vary over short distances. *Atmos.*
765 *Environ.*, 40, 7125-7137.

766

767 Khare, P., Gentner, D.R., 2018. Considering the future of anthropogenic gas-phase organic
768 compound emissions and the increasing influence of non-combustion sources on urban air quality.
769 *Atmos. Chem. Phys.*, 18, 5391-5413.

770

771 Kawashima, H., Minami, S., Hanai, Y., Fushimi, A., 2006. Volatile organic compound emission
772 factors from roadside measurements, *Atmos. Environ.*, 40, 2301-2312.

773

774 Ketzel, M., Wåhlin, P., Berkowicz, R., Palmgren, F., 2003. Particle and trace gas emission factors
775 under urban driving conditions in Copenhagen based on street and roof-level observations. *Atmos.*
776 *Environ.*, 37, 2735-2749.

777

778 Kim, Y., Sartelet, K., Seigneur, C., Charron, A., Besombes, J.-L., Jaffrezo, J.-L., Marchand, N.,
779 Polo, L., 2016. Effect of measurement protocol on organic aerosol measurements of exhaust
780 emissions from gasoline and diesel vehicles. *Atmos. Environ.*, 140, 176-187.

781

782 Kumar, P., Fennell, P., Britter, R., 2008. Effect of wind direction and speed on the dispersion of
783 nucleation and accumulation mode particles in an urban street canyon. *Sci. Tot. Environ.*, 402, 82-
784 94.

785 Kwon et al., 2012

786 Kwon, E. E., Castaldi, M. J., 2012. Mechanistic understanding of polycyclic aromatic hydrocarbons
787 (PAHs) from the thermal degradation of tires under various oxygen concentration atmospheres.
788 *Environ. Sci. Technol.*, 46, 12921-12926.

- Lewis, A.C., Carslaw, N., Marriott, P.J., Kinghorn, R.M., Morrison, P., Lee, A.L., Bartle, K. D., Pilling, M.J., 2000. A larger pool of ozone-forming carbon compounds in urban atmospheres. *Nature*, 405, 778.
- Lyu, R., Alam, M. S., Stark, C., Xu, R., Shi, Z., Feng, Y., Harrison, R. M. 2019. Aliphatic carbonyl compounds (C8-C 26) in wintertime atmospheric aerosol in London, UK. *Atmos. Chem. Phys.*, 19, 2233-2246.
- Mandalakis, M., Tsapakis, M., Tsoga, A., Stephanou, E. G., 2002. Gas-particle concentrations and distribution of aliphatic hydrocarbons, PAHs, PCBs and PCDD/Fs in the atmosphere of Athens (Greece). *Atmos. Environ.*, 36, 4023-4035.
- Manning, A.J., Nicholson, K.J., Middleton, D.R., Rafferty, S.C., 2000. Field study of wind and traffic to test a street canyon pollution model. *Environ. Monitor. Assess.*, 60, 283-313.
- Masiol, M., Hofer, A., Squizzato, S., Piazza, R., Rampazzo, G., Pavoni, B., 2012. Carcinogenic and mutagenic risk associated to airborne particle-phase polycyclic aromatic hydrocarbons: a source apportionment. *Atmos. Environ.*, 60, 375-382.
- May, A.A., Presto, A.A., Hennigan, C.J., Nguyen, N.T., Gordon, T.D., Robinson, A.L., 2013a. Gas-particle partitioning of primary organic aerosol emissions:(1) Gasoline vehicle exhaust. *Atmos. Environ.*, 77, 128-139.
- May, A.A., Presto, A.A., Hennigan, C.J., Nguyen, N.T., Gordon, T.D., Robinson, A.L., 2013b. Gas-particle partitioning of primary organic aerosol emissions:(2) Diesel vehicles. *Environ. Sci. Technol.*, 47, 8288-8296.
- McDonald, B.C., de Gouw, J.A., Gilman, J.B., Jathar, S.H., Akherati, A., Cappa, C.D., Jimenez, J.L., Lee-Taylor, J., Hayes, P.L., McKeen, S.A., Cui, Y.Y., Kim, S.-W., Gentner, D.R., Isaacman-VanWertz, G., Goldstein, A.H., Harley, R.A., Frost, G.J., Roberts, J.M., Ryerson, T.B., Trainer, M., 2018. Volatile chemical products emerging as largest petrochemical source of urban organic emissions. *Science* 359, 760-764.
- Met Office, 2006. MIDAS: UK Hourly Weather Observation Data. NCAS British Atmospheric Data Centre [Online]. Available: <http://catalogue.ceda.ac.uk/uuid/916ac4bbc46f7685ae9a5e10451bae7c> [Accessed 21 March 2019].
- Nelson, R.K., Kile, B.M., Plata, D.L., Sylva, S.P., Xu, L., Reddy, C.M., Gaines, R.B., Frysiner, G.S., Reichenbach, S.E., 2006. Tracking the weathering of an oil spill with comprehensive two-dimensional gas chromatography. *Environ. Forensics*, 7, 33-44.
- Omar, N.Y. M.J., Abas, M.R.B., Rahman, N.A., Tahir, N.M., Rushdi, A.I., Simoneit, B.R.T., 2007. Levels and distributions of organic source tracers in air and roadside dust particles of Kuala Lumpur, Malaysia. *Environ. Geol.*, 52, 1485-1500.
- Omstedt, G., Bringfelt, B. & Johansson, C., 2005. A model for vehicle-induced non-tailpipe emissions of particles along Swedish roads. *Atmos. Environ.*, 39, 6088-6097.
- Pant, P., Shukla, A., Kohl, S. D., Chow, J. C., Watson, J. G., Harrison, R. M., 2015. Characterization of ambient PM_{2.5} at a pollution hotspot in New Delhi, India and inference of sources. *Atmos. Environ.*, 109, 178-189.

- Pant, P., Harrison, R.M., 2013. Estimation of the contribution of road traffic emissions to particulate matter concentrations from field measurements: a review. *Atmos. Environ.*, 77, 78-97.
- Perrone, M.G., Carbone, C., Faedo, D., Ferrero, L., Maggioni, A., Sangiorgi, G., Bolzacchini, E., 2014. Exhaust emissions of polycyclic aromatic hydrocarbons, n-alkanes and phenols from vehicles coming within different European classes. *Atmos. Environ.*, 82, 391-400.
- Rissler, J., Swietlicki, E., Bengtsson, A., Boman, C., Pagels, J., Sandström, T., Blomberg, A., Löndahl, J.J., 2012. Experimental determination of deposition of diesel exhaust particles in the human respiratory tract. *J. Aerosol. Sci.*, 48, 18-33.
- Robinson, A.L., Donahue, N.M., Shrivastava, M.K., Weitkamp, E.A., Sage, A.M., Grieshop, A. P., Lane, T.E., Pierce, J.R., Pandis, S.N., 2007. Rethinking organic aerosols: Semivolatile emissions and photochemical aging. *Science*, 315, 1259-1262.
- Rogge, W.F., Hildemann, L.M., Mazurek, M. A., Cass, G.R., Simoneit, B.R., 1993. Sources of fine organic aerosol. 3. Road dust, tire debris, and organometallic brake lining dust: roads as sources and sinks. *Environ. Sci. Technol.*, 27, 1892-1904.
- Sakurai, H., Tobias, H. J., Park, K., Zarling, D., Docherty, K. S., Kittelson, D. B., McMurry, P. H., Ziemann, P. J., 2003. On-line measurements of diesel nanoparticle composition and volatility. *Atmos. Environ.*, 37, 1199-1210.
- Schauer, J. J., Kleeman, M. J., Cass, G. R., Simoneit, B. R. Measurement of emissions from air pollution sources. 5., 2002. C1-C32 organic compounds from gasoline-powered motor vehicles. *Environ. Sci. Technol.*, 36, 1169-1180.
- Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R. Measurement of emissions from air pollution sources. 2., 1999. C1 through C30 organic compounds from medium duty diesel trucks. *Environ. Sci. Technol.*, 33, 1578-1587.
- Schroder, J.C., Campuzano-Jost, P., Day, D.A., Shah, V., Larson, K., Sommers, J.M., Sullivan, A.P., Campos, T., Reeves, J.M., Hills, A., Hornbrook, R.S., Blake, N.J., Scheuer, E., Guo, H., Fibiger, D.L., McDuffie, E.E., Hayes, P.L., Weber, R.J., Dibb, J.E., Apel, E.C., Jaeglé, L., Brown, S.S., Thornton, J.A., Jimenez, J.L., 2018. Sources and Secondary Production of Organic Aerosols in the Northeastern United States during winter. *J. Geophys. Res.: Atmospheres*, 123, 7771-7796.
- Shah, S.D., Ogunyoku, T.A., Miller, J.W., Cocker, D.R., 2005. On-Road Emission Rates Of Pah And N-Alkane Compounds From Heavy-Duty Diesel Vehicles. *Environ. Sci. Technol.*, 39, 5276-5284.
- Simoneit, B. R., 1999. A review of biomarker compounds as source indicators and tracers for air pollution. *Environ. Sci. Pollut. Res.*, 6, 159-169.
- Singh, D., Gadi, R., Mandal, T.K., 2011. Characterization of particulate-bound polycyclic aromatic hydrocarbons and trace metals composition of urban air in Delhi, India. *Atmos. Environ.*, 45, 7653-7663.
- Staehelin, J., Keller, C., Stahel, W., Schläpfer, K., Wunderli, S., 1998. Emission factors from road traffic from a tunnel study (Gubrist tunnel, Switzerland). Part III: Results of organic compounds, SO₂ and speciation of organic exhaust emission. *Atmos. Environ.*, 32, 999-1009.

- 891 Van Deursen, M., Beens, J., Reijenga, J., Lipman, P., Cramers, C., Blomberg, J. J., 2000. Group-
892 type identification of oil samples using comprehensive two-dimensional gas chromatography
893 coupled to a time-of-flight mass spectrometer (GC× GC-TOF). *J. High Resol. Chromatogr.*, 23,
894 507-510.
- 895
896 Ventura, G.T., Kenig, F., Reddy, C.M., Frysinger, G.S., Nelson, R.K., Van Mooy, B., Gaines, R. B.,
897 2008. Analysis of unresolved complex mixtures of hydrocarbons extracted from Late Archean
898 sediments by comprehensive two-dimensional gas chromatography (GC× GC). *Org. Geochem.*, 39,
899 846-867.
- 900
901 Wehner, B., Birmili, W., Gnauk, T., Wiedensohler, A., 2002. Particle number size distributions in a
902 street canyon and their transformation into the urban-air background: measurements and a simple
903 model study. *Atmos. Environ.*, 36, 2215-2223.
- 904
905 Weitkamp, E.A., Sage, A.M., Pierce, J.R., Donahue, N.M., Robinson, A. L. 2007. Organic aerosol
906 formation from photochemical oxidation of diesel exhaust in a smog chamber. *Environ. Sci.*
907 *Technol.*, 41, 6969-6975.
- 908
909
910 Wählin, P., Berkowicz, R. & Palmgren, F., 2006. Characterisation of traffic-generated particulate
911 matter in Copenhagen. *Atmos. Environ.*, 40, 2151-2159.
- 912
913 Worton, D.R., Isaacman, G., Gentner, D.R., Dallmann, T.R., Chan, A.W., Ruehl, C., Kirchstetter,
914 T.W., Wilson, K.R., Harley, R.A., Goldstein, A.H., 2014. Lubricating oil dominates primary
915 organic aerosol emissions from motor vehicles. *Environ. Sci. Technol.*, 48, 3698-3706.
- 916
917 Xu, R., Alam, M.S., Stark, C. and Harrison, R.M. 2020. Behaviour of traffic emitted semi-volatile
918 and intermediate volatility organic compounds within the urban atmosphere. *Science of the Total*
919 *Environment*, 137470.
- 920
921 Yadav, S., Tandon, A., Attri, A.K., 2013. Characterization of aerosol associated non-polar organic
922 compounds using TD-GC-MS: a four year study from Delhi, India. *J. Hazard. Mat.*, 252, 29-44.
- 923
924 Zhao, Y., Nguyen, N. T., Presto, A.A., Hennigan, C.J., May, A.A., Robinson, A.L., 2016.
925 Intermediate volatility organic compound emissions from on-road gasoline vehicles and small off-
926 road gasoline engines. *Environ. Sci. Technol.*, 50, 4554-4563.
- 927

928 **FIGURE LEGENDS:**

929

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

933

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

936

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

940

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

943

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

948

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

951

952

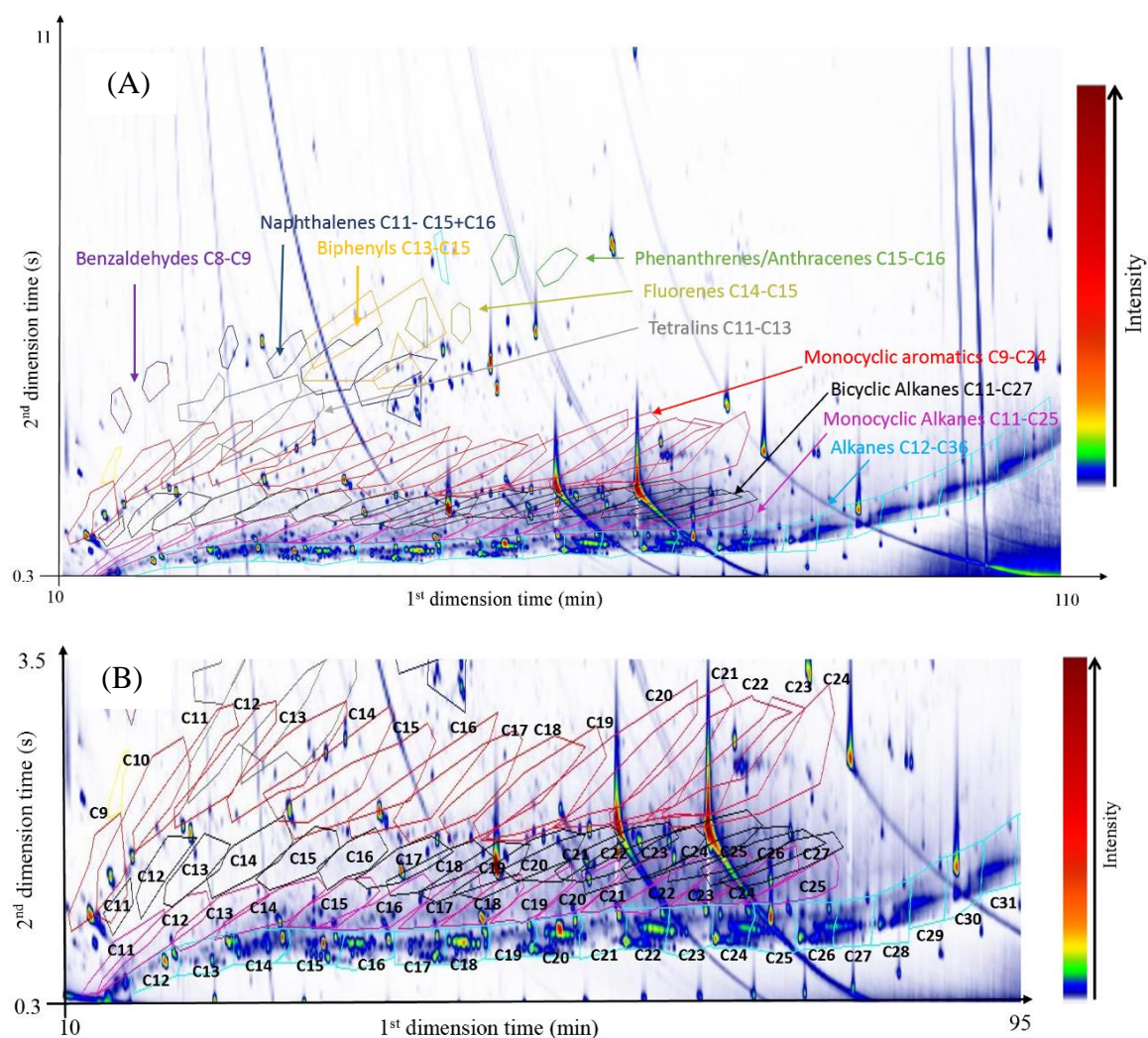
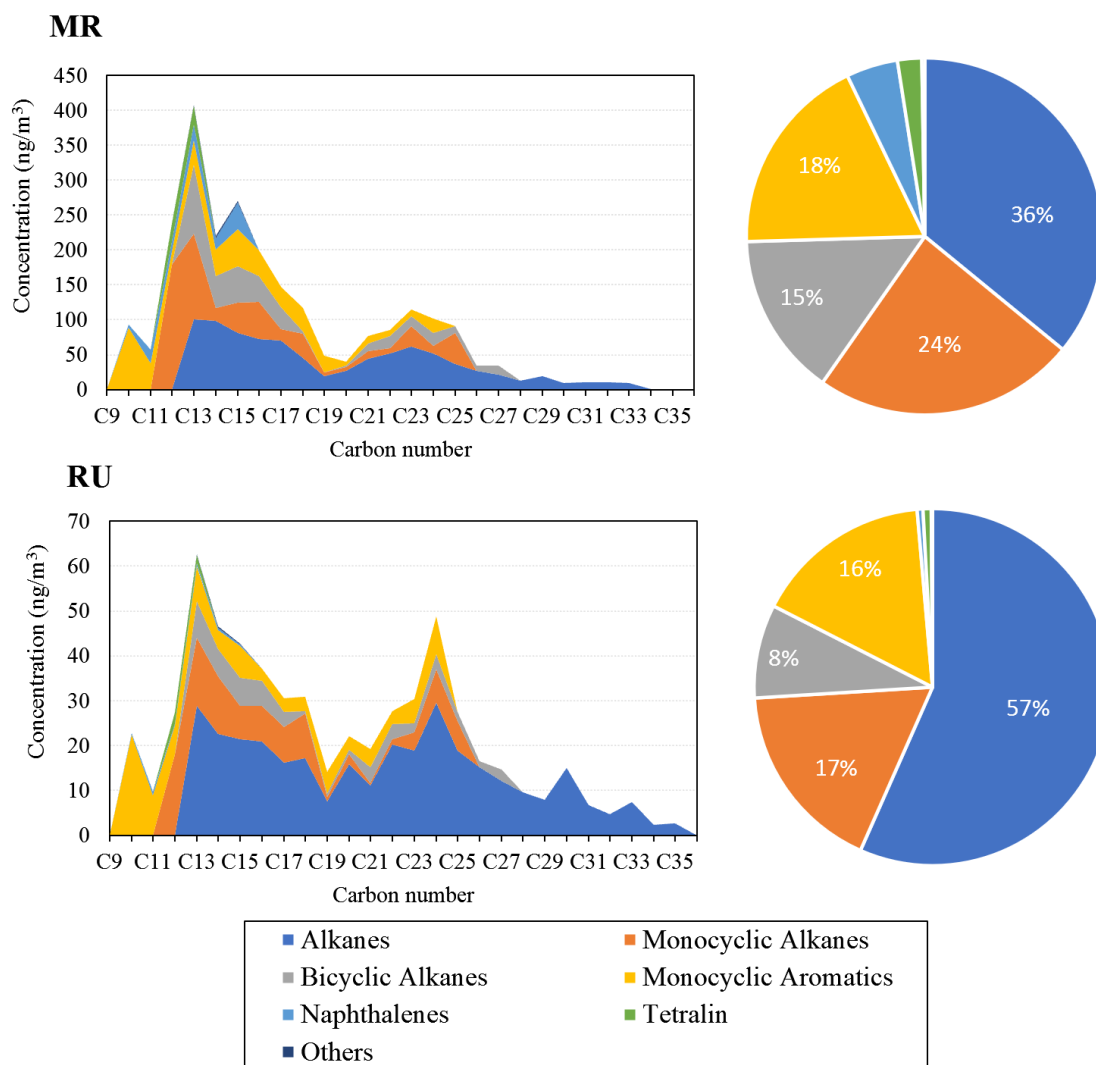


Figure 1: Typical TD-GC×GC-ToF-MS chromatogram of a particulate-phase sample collected on the roof of University of Westminster (WM) in Feb 2017, demonstrating the grouping of compounds. X and y-axis are the retention time on the first and second column respectively, with the intensity of the compounds 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 C₁₂-C₃₆ alkanes, C₁₁-C₂₅ monocyclic alkanes, C₁₁-C₂₇ bicyclic alkanes, C₉-C₂₄ monocyclic aromatics, C₈-C₉ benzaldehydes, C₁₁-C₁₆ naphthalenes, C₁₃-C₁₅ biphenyls, C₁₅-C₁₆ phenanthrenes/anthracenes, C₁₄-C₁₅ fluorenes and C₁₁-C₁₃ 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).



967

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

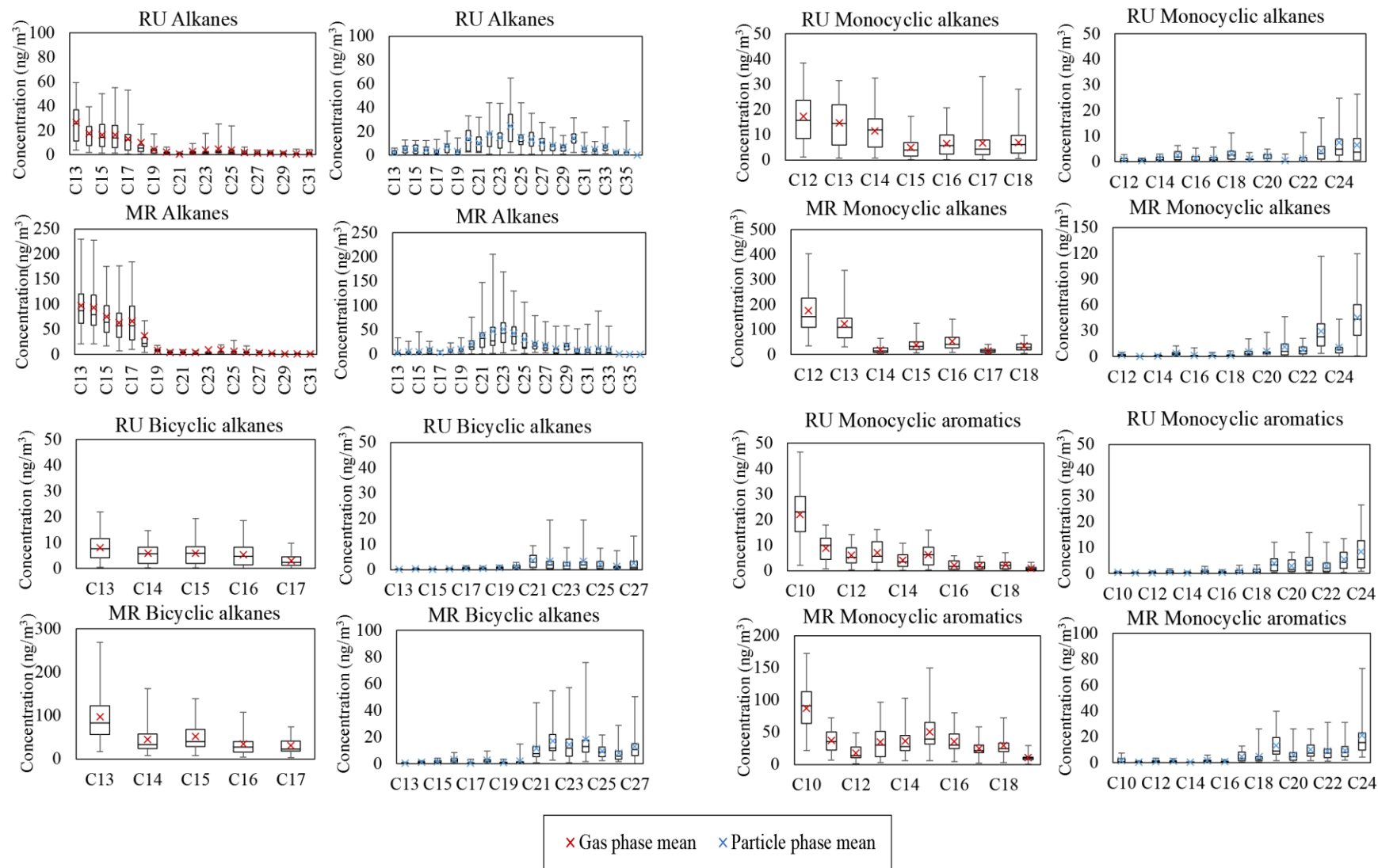
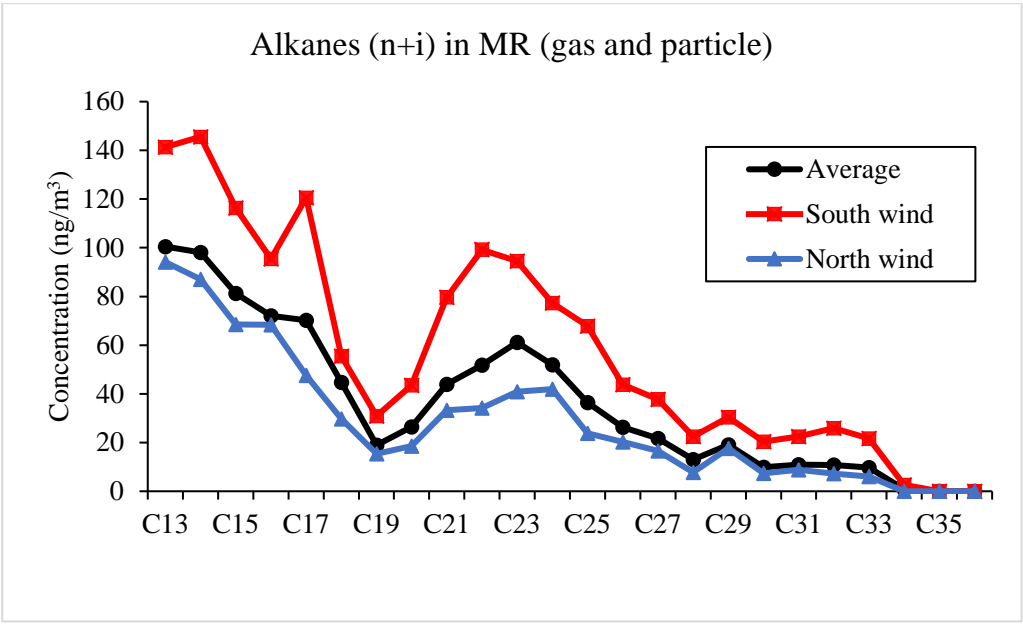


Figure 3: Concentrations of alkanes (n+i), monocyclic alkanes, bicyclic alkanes and monocyclic aromatics in the gas phase and particle phase at MR and RU, London Campaign 2017.

974



975

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

978

979

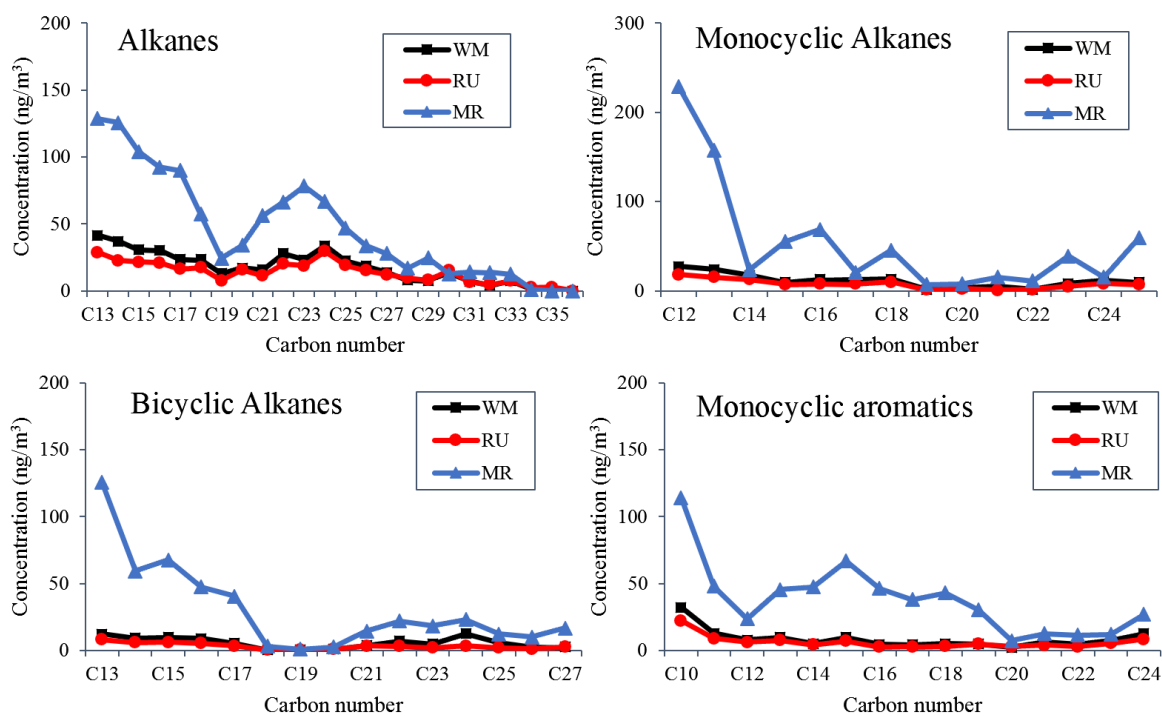


Figure 5: Concentrations of alkanes (n+i), monocyclic alkanes, bicyclic alkanes and monocyclic aromatics (sum of the gas phase and particle phase) at WM and RU measured simultaneously from January to February 2017, together with MR data adjusted to match the same time period (see text).

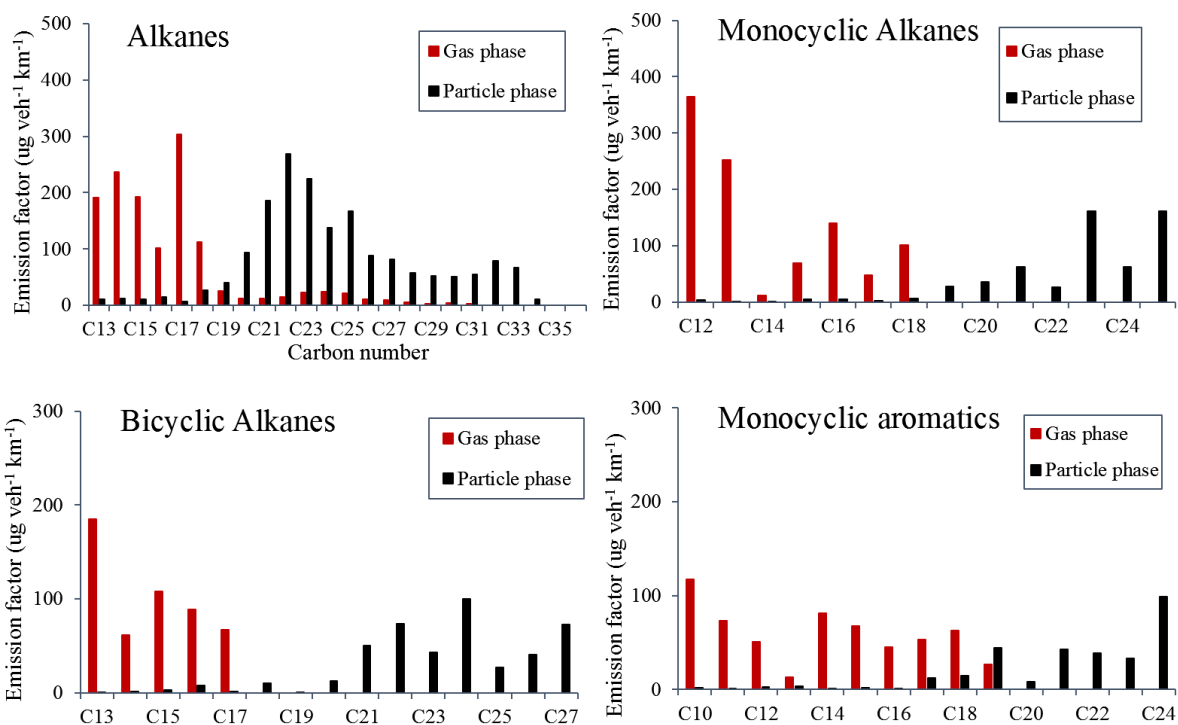


Figure 6: Emission factors of alkanes (n+i), monocyclic alkanes, bicyclic alkanes and monocyclic aromatics in the gas phase and particle phase at MR.