Aliphatic Carbonyl Compounds (C_8-C_{26}) in Wintertime Atmospheric Aerosol in London, UK

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ABSTRACT

Three groups of aliphatic carbonyl compounds, the n-alkanals (C_8-C_{20}), n-alkan-2-ones (C_8-C_{26}) and n-alkan-3-ones (C_8-C_{19}) were measured in air samples collected in London from January-April 2017. Four sites were sampled including two roof-top background sites, one ground-level urban background site and a street canyon location on Marylebone Road in central London. The n-alkanals showed the highest concentrations followed by the n-alkan-2-ones and the n-alkan-3-ones, the latter having appreciably lower concentrations. It seems likely that all compound groups have both primary and secondary sources and these are considered in the light of published laboratory work on the oxidation products of high molecular weight n-alkanes. All compound groups show relatively low correlation with black carbon and NOx in the background air of London, but in street canyon air heavily impacted by vehicle emissions, stronger correlations emerge especially for the n-alkanals. It appears that vehicle exhaust is likely to be a major contributor for concentrations of the n-alkanals whereas it is a much smaller contributor to the n-alkan-2-ones and n-alkan-3-ones. Other primary sources such as cooking or wood burning may be ~~significant~~contributors for the ketones but were not directly evaluated. It seems likely that there is also a significant contribution from photo-oxidation of n-alkanes and this would be consistent with the much higher abundance of the n-alkan-2-ones relative to the n-alkan-3-ones if the formation mechanism were to be through oxidation of condensed phase alkanes. Vapour-particle partitioning fitted the Pankow model well for the n-alkan-2-ones but less well for the other compound groups, although somewhat stronger relationships were seen at the Marylebone Road site than at the background sites. The former observation gives support to the n-alkane-2-ones being a predominantly secondary product, whereas primary sources of the other groups are more prominent.

Keywords: Carbonyl compounds; n-alkanals; n-alkan-2-ones; n-alkan-3-ones; organic aerosol; partitioning;

1. INTRODUCTION

Carbonyl compounds are classified as polar organic compounds, constituting a portion of the oxygenated organic compounds in atmospheric particulate matter (PM). Aliphatic carbonyl compounds are directly emitted into the atmosphere from primary biogenic and anthropogenic sources (Schauer et al., 2001, 2002a, b), as well as being secondary products of atmospheric oxidation of hydrocarbons (Chacon-Madrid et al., 2010; Zhang et al., 2015; Han et al., 2016).

The most abundant atmospheric carbonyls are methanal (formaldehyde) and ethanal (acetaldehyde), and many studies have described their emission sources and chemical formation in urban and rural samples (Duan et al., 2016). Long-chain aliphatic carbonyl compounds have been identified in PM and reported in few published papers (Gogou et al., 1996; Andreou and Rapsomanikis, 2009), and these compounds are considered to be formed from atmospheric oxidation processes affecting biogenic emissions of alkanes. Anthropogenic activity is also considered to be a significant contributor to the aliphatic carbonyls. Appreciable concentrations of aliphatic carbonyl compounds have been identified in emissions from road vehicles (Schauer et al., 1999a; 2002b), coal combustion (Oros and Simoneit, 2000), wood burning (Rogge et al., 1998) and cooking processes (Zhao et al., 2007a,b), spanning a wide range of molecular weights. Furthermore, chamber studies (Chacon-Madrid and Donahue, 2011; Algrim and Ziemann, 2016) have demonstrated that the aliphatic carbonyl compounds are very important precursors of secondary organic aerosol (SOA) when they react with OH radicals in the presence of NO_x.

The oxidation of n-alkanes by hydroxyl radical is considered to be an important source of aliphatic carbonyl compounds. It was believed that the n-alkanals with carbon atoms numbering less than 20 indicate oxidation of alkanes, whereas the higher compounds were usually considered to be of direct biogenic origin (Rogge et al., 1998). The homologues and isomers of n-alkanals and n-alkanones have been identified as OH oxidation products of n-alkanes in many chamber and flow tube studies (Zhang et al., 2015; Schilling Fahnestock et al., 2015; Ruehl et al., 2013; Yee et al., 2012), although not all studies identified the position of the carbonyl group. The commonly accepted oxidation pathways of n-alkanes generally divide into functionalization and fragmentation. Functionalization occurs when an oxygenated functional group ($–ONO_2$, –OH, –C=O, –C(O)O– and –OOH) is added to a molecule, leaving the carbon skeleton intact. Alternatively, fragmentation involves C−C bond cleavage and produces two oxidation products with smaller carbon numbers than the reactant. The chamber studies of dodecane oxidation ~~have identified 1-undecanal, hexan-3-one, octan-3-one, heptan-2-one, nonan-2-one and decan-2-one as Oh~~include observations of aldehydes and ketones as oxidation products (Schilling Fahnestock et al., 2015; Yee et al., 2012).

In London, with a high population density and a large number of diesel engine vehicles, the aliphatic hydrocarbons constitute an important fraction of ambient aerosols. Anthropogenic activities and secondary formation ~~favour~~ contribute to the emission and production of carbonyl compounds within the city. The objectives of the present study were the identification and quantification of aliphatic carbonyl compounds in particle and vapour samples collected in London from January to April 2017. This work has aided an understanding of the concentrations and secondary formation of carbonyls in the London atmosphere. Spatial and temporal variations of the studied carbonyl compounds were

assessed and used to infer sources. One of the main objectives was to provide gas/particle partitioning coefficients of identified carbonyls under realistic conditions. Diagnostic criteria were used to estimate the sources of identifiable atmospheric carbonyl compounds. Additionally, for the first time, concentrations of particulate and gaseous n-alkan-3-ones are reported.

2. MATERIALS AND METHODS

2.1 Sampling Method and Site Characteristics

Three sampling campaigns were carried out between 23 January and 18 April 2017 at four sampling sites (Figure 1) in London. The first campaign used two sampling sites, one located on the roof of a building (15 m above ground) of the Regent's University (51°31′N, -0°9′W), hereafter referred to as RU, sampled from 23 January 2017 to 19 February 2017, the other located on the roof (20 m above ground) of a building which belongs to the University of Westminster on the southern side of Marylebone Road (hereafter referred to as WM), sampled from 24 January 2017 to 20 February 2017. The third sampling site was located at ground level at Eltham (51°27′N, 0°4′E), hereafter referred to as EL, sampled from 23 February 2017 to 21 March 2017, which is located in suburban south London, and the fourth sampling site was located at ground level on the southern side of Marylebone Road (51°31′N, -0°9′W), hereafter referred to as MR, sampled from 22 March 2017 to 18 April 2017. Marylebone Road is in London's commercial centre, and is an important thoroughfare carrying 80-90,000 vehicles per day through central London. The Regent's University site is within Regent's Park to the north of Marylebone Road. The Eltham site is in a typical residential neighbourhood, 22 km from the MR site. Earlier work at the Marylebone Road and a separate Regent's Park site is described by Harrison et al. (2012).

The particle samples were collected on polypropylene backed PTFE filters (47 mm, Whatman) which preceded stainless steel sorbent tubes packed with 1cm quartz wool, 300 mg Carbograph 2TD 40/60 (Markes International, Llantrisant, UK) and sealed with stainless-steel caps before and after sampling. Sampling took place for sequential 24-hour periods at a flow rate of 1.5 L min^{-1} using an in-house developed automated sampler. Field blank filters and ~~adsorption~~ sorbent tubes were prepared for each site, and recovery efficiencies were evaluated. After the sampling, each filter was placed in a clean sealed petri dish, wrapped in aluminium foil and stored in the freezer at -18ºC prior to analysis. Black carbon (BC) was simultaneously monitored during the sampling period at RU and WM sites using an aethalometer (Model AE22, Magee Science). Measurements of BC and NO_x at MR and NO_x at EL were provided by the national network sites of Marylebone Road, and Eltham (https://uk-air.defra.gov.uk/).

2.2 Analytical Instrumentation

The particle samples were analyzed using a 2D gas chromatograph (GC, 7890A, Agilent Technologies, Wilmington, DE, USA) equipped with a Zoex ZX2 cryogenic modulator (Houston, TX, USA). The first dimension was equipped with a SGE DBX5, non-polar capillary column (30.0 m, 0.25 mm ID, 0.25 mm – 5.00% phenyl polysilphenylene-siloxane), and the second-dimension column equipped with a SGE DBX50 (4.00 m, 0.10 mm ID, 0.10 mm – 50.0% phenyl polysilphenylene-siloxane). The GC × GC was interfaced with a Bench-ToF-Select, time-of-flight mass spectrometer (ToF-MS, Markes International, Llantrisant, UK). The acquisition speed was 50.0

Hz with a mass resolution of >1200 fwhm at 70.0 eV and the mass range was 35.0 to 600 m/z. All data produced were processed using GC Image v2.5 (Zoex Corporation, Houston, US).

2.3 Analysis of Samples

Standards used in these experiments included 19 alkanes, C_8 to C_{26} (Sigma-Aldrich, UK, purity >99.2%); 12 n-aldehydes, C_8 to C_{13} (Sigma-Aldrich, UK, purity ≥95.0%), C_{14} to C_{18} (Tokyo Chemical Industry UK Ltd, purity >95.0%); and 10 2-ketones, C_8 to C_{13} and C_{15} to C_{18} (Sigma-Aldrich, UK, purity ≥98.0%) and C_{14} (Tokyo Chemical Industry UK Ltd, purity 97.0%).

The filters were spiked with 30.0 µL of 30.0 µg mL^{-1} deuterated internal standards (dodecane-d_{26}, pentadecane-d_{32}, eicosane-d_{42}, pentacosane-d_{52}, triacontane-d_{62}, butylbenzene-d_{14}, nonylbenzene-2,3,4,5,6-d_5, biphenyl-d_{10}, p-terphenyl-d_{14}; Sigma-Aldrich, UK) for quantification and then immersed in dichloromethane (DCM), and ultra-sonicated for 20.0 min at 20.0ºC. The extract was filtered using a clean glass pipette column packed with glass wool and anhydrous Na_2SO_4, and concentrated to 50.0 µL under a gentle flow of nitrogen for analysis using GC × GC-ToF-MS. 1 µL of the extracted sample was injected in a split ratio 100:1 at 300ºC. The initial temperature of the primary oven (80.0ºC) was held for 2.0 min and then increased at 2.0 ºC min^{-1} to 210ºC, followed by 1.5 ºC min^{-1} to 325 ºC. The initial temperature of the secondary oven (120ºC) was held for 2.0 min and then increased at 3.0ºC min^{-1} to 200ºC, followed by 2.00ºC min^{-1} to 300ºC and a final increase of 1.0ºC min^{-1} to 330 ºC to ensure all species passed through the column. The transfer line temperature was 330 ºC and the ion source temperature was 280ºC. Helium was used as the carrier

gas at a constant flow rate of 1.0 mL min^{-1}. Further details of the instrumentation and data processing methods is given by Alam et al. (2016a,b).

The sorbent tubes were analyzed by an injection port thermal desorption unit (Unity 2, Markes International, Llantrisant, UK) and subsequently analyzed using GC × GC-ToF-MS. Briefly, the tubes were spiked with 1 ng of deuterated internal standard for quantification and desorbed onto the cold trap at 350ºC for 15.0 min (trap held at 20.0ºC). The trap was then purged onto the column in a split ratio of 100:1 at 350ºC and held for 4.0 min. The initial temperature of the primary oven (90.0ºC) was held for 2.0 min and then increased to 2.0ºC min^{-1} to 240ºC, followed by 3.0ºC min^{-1} to 310ºC and held for 5.0 min. The initial temperature of the secondary oven (40.0ºC) was held for 2.0 min and then increased at 3.0ºC min^{-1} to 250ºC, followed by an increase of 1.5ºC min^{-1} to 315ºC and held for 5.0 min. Helium was used as carrier gas for the thermally desorbed organic compounds, with a gas flow rate of 1.0 mL min^{-1}.

Qualitative analysis

Compound identification was based on the GC×GC-TOFMS spectra library, NIST mass spectral library and in conjunction with authentic standards. Compounds within the homologous series for which standards were not available were identified by comparing their retention time interval between their homologues, and by comparison of mass spectra to the standards for similar compounds within the series, by comparison to the NIST mass spectral library and by the analysis of fragmentation patterns.

Quantitative analysis

An internal standard solution (~~including dodecane-d_{26}, pentadecane-d_{32}, eicosane-d_{42}, pentacosane-d_{52}, triacontane-d_{62}, nonylbenzene-2,3,4,5,6-d_5, butylbenzene-d_{14}, biphenyl-d_{10}, p-terphenyl-d_{14})~~ (~~Sigma-Aldrich, Uk~~outlined above) was added to the samples to extract prior to instrumental analysis. Five internal standards (pentadecane-d_{32}, eicosane-d_{42}, pentacosane-d_{52}, triacontane-d_{62}, nonylbenzene-2,3,4,5,6-d_5) were used in the calculation of carbonyl compound concentrations.

The quantification for alkanes, aldehydes and 2-ketones was performed by the linear regression method using seven-point calibration curves (0.05, 0.10, 0.25, 0.50, 1.00, 2.00, 3.00 ng μL^{-1}) established between the authentic standards/internal standard concentration ratios and the corresponding peak area ratios. The calibration curves for all target compounds were highly linear (r^2>0.99, from 0.990 to 0.997), demonstrating the consistency and reproducibility of this method. Limits of detection for individual compounds were typically in the range 0.04–0.12 ng m^{-3}. 3-ketones were quantified using the calibration curves for 2-ketones. This applicability of quantification of individual compounds using isomers of the same compound functionality (which have authentic standards) has been discussed elsewhere and has a reported uncertainty of 24% (Alam et al., 2018). Alkan-2-ones and alkan-3-ones were not well separated by the chromatography. These were separated manually using the peak cutting tool, attributing fragments at m/z 58 and 71 to 2-ketones and m/z 72 and 85 to 3-ketones. ~~The calibration for 2-ketones was applied to quantification of the 3-ketones.~~ Field and laboratory blanks were routinely analysed to evaluate analytical bias and precision. Blank levels of individual analytes were normally very low and in most cases not detectable. Recovery efficiencies were determined by analyzing the blank samples spiked with standard compounds. Mean

recoveries ranged between 78.0 and 102%. All quantities reported here have been corrected according to their recovery efficiencies.

3. RESULTS AND DISCUSSION

3.1 Mass Concentration of Particle-Bound Carbonyl Compounds

The study of temporal and spatial variations of air pollutants can provide valuable information about their sources and atmospheric processing. The time series of particle-bound n-alkanals, n-alkan-2-ones, and n-alkan-3-ones are plotted in Figure ~~3~~2. It is clear that the concentrations of n-alkanals varied substantially with date, and were always higher than n-alkanones at four sites. It is also clear from Figure ~~2~~3 that concentrations were broadly similar at the background sites, RU, WM and EL, but are elevated, especially for the n-alkanals, at MR. This is strongly indicative of a road traffic source.

Carbonyls including n-alkan-2-one and n-alkan-3-one homologues could result as fragmentation products from larger alkane precursors during gas-phase oxidation (Yee et al., 2012; Schilling Fahnestock et al., 2015) or as functionalized products from heterogeneous oxidation of particle-bound alkanes (Ruehl et al., 2013; Zhang et al., 2015). While carbonyl compounds are expected to be amongst first generation oxidation products of alkanes, product yields are not well known, and are highly dependent upon the chemical environment in which oxidation occurs. Yee et al. (2012) show substantial yields of mono-carbonyl product, the position of substitution undefined, in the low-NO_x oxidation of n-dodecane. Ruehl et al. (2013) report the production of 2- through 14-octacosanone

from the oxidation of octacosane, giving relative, but not absolute yields. Schilling Fahnestock et al. (2014) report oxidation products of dodecane formed in both low-NO and high NO environments (<d.l and NO = 97.5 ppb respectively). A singly substituted unfragmented ketone product is reported only from the low-NO oxidation, and in relatively low yield amongst many products. Lim and Ziemann (2009) propose a reaction scheme for the OH-initiated oxidation of alkanes in the presence of NO_x. They express the view that first generation carbonyl formation is negligible at high NO concentrations for linear alkanes with C_n>6 since reactions of an alkylperoxy radical with O_2 are to slow to compete with isomerisation, which leads ultimately to hydroxynitrate and hydroxycarbonyl products. Ziemann (2011) also shows a substantial yield of alkylnitrates from OH-initiated oxidation of n-alkanes from C_{10}-C_{25} in the presence of NO. The NO concentrations in the background air of London are <12 ppb typically (UK-Air, 2018), and hence lie between the low and high NO environments of experiments in the literature, therefore most probably permitting some oxidation to proceed through pathways leading to first generation carbonyl products.

Figure~~.~~ ~~2~~ 3 shows the average total concentrations of particle-bound 1-alkanals, n-alkan-2-ones, and n-alkan-3-ones from January to April at four measurement sites, and the particle and gaseous phase concentrations are detailed in the Table S1 (Supporting Information). Total n-alkanals was defined as the sum of particle-bound n-alkanals ranging from C_8 to C_{20}. The particulate n-alkanals at the MR site accounted for 75.2% of the measured particle carbonyls with the average total concentration of 682 ng m^{-3}, and concentrations at the other sites were 167 ng m^{-3} at EL, 117 ng m^{-3} at WM and 82.6 ng m^{-3} at RU, accounting for 57.0%, 57.9% and 56.3% of the measured particulate carbonyls, respectively. The n-alkanals identified in this study differed ~~in some aspects~~substantially from those

previously reported in samples collected from Crete (Gogou et al., 1996) and Athens (Andreou and Rapsomanikis, 2009) in Greece. The n-alkanals from London presented narrower ranges of carbon numbers and a higher concentration than rural and urban samples from Crete. The concentrations of n-alkanal homologues (C_8-C_{20}) ranged from 5.50 to 141 ng m^{-3} (average 52.0 ng m^{-3}) at MR which were far higher than 1.48-28.6 ng m^{-3} (average 6.44 ng m^{-3}) at RU, 1.42-50.3 ng m^{-3} (average 9.03 ng m^{-3}) at WM and 3.29-53.0 ng m^{-3} (average 13.0 ng m^{-3}) at EL (Table S1), unlike Crete where the concentrations were 0.9-3.7 ng m^{-3} in rural (C_{15}-C_{30}) and 5.4-6.7 ng m^{-3} in urban (C_9-C_{22}) samples, and the average concentration of all four sites was much higher than the 0.91 ng m^{-3} measured in Athens (Andreou and Rapsomanikis, 2009) (C_{13}-C_{20}). This is a clear indication of a road traffic, most probably diesel source which is greater in London.

As part of the CARBOSOL project (Oliveira et al., 2007), air samples were collected in summer and winter at six rural sites across Europe. The particulate n-alkanals ranged from C_{11} to C_{30} with average total concentrations between 1.0 ng m^{-3} and 19.0 ng m^{-3}, with higher concentrations in summer than winter at all but one site. ~~These concentrations fall well below those measured in the present study, although the range of compounds differed.~~ Maximum concentrations at all sites were in compounds >C_{22} indicating a source from leaf surface abrasion products and biomass burning (Simoneit et al., 1967; Gogou et al., 1996). This far exceeds the C_{max} values seen in the particulate fraction at our sites.

~~Atmospheric concentrations of long-chain n-alkan-3-ones have not previously been reported in the literature. The n-alkan-2-one and n-alkan-3-one homologues with few carbon atoms are believed~~

~~mainly to originate as the fragmental products of n-alkanes (Yee et al., 2012; Schilling Fahnestock et al., 2015), whereas the higher compounds are mainly generated from functional pathways (Zhang et al., 2015; Ruehl et al., 2013).~~

The n-alkan-2-one homologues measured in London ranged from C_8 to C_{26}, and the average total particulate fraction concentration was 58.5 ng m^{-3} at RU, 75.1 ng m^{-3} at WM, 112 ng m^{-3} at EL and 186 ng m^{-3} at MR, approximately accounting for 39.9% (RU), 37.0% (WM), 38.1% (EL) and 20.5% (MR) of the total particulate carbonyls, respectively (Figure~~.~~ ~~2~~3). The published data from Greece indicated that the concentrations of n-alkan-2-ones were independent of the seasons, and an average of 5.40 ng m^{-3} (C_{13}-C_{29}) was measured in August and 5.44 ng m^{-3} in March at Athinas St, but 12.88 ng m^{-3} was measured in March at the elevated (20 m) AEDA site in Athens (Gogou et al.,~~ ~~(~~1996). Concentrations in Crete for alkan-2-ones (C_{10}-C_{31}) were 0.4-2.1 ng m^{-3} at the rural site and 1.9-2.6 ng m^{-3} at the urban site (Andreou and Rapsomanikis, 2009). The CARBOSOL project also determined concentrations of n-alkan-2-ones, between C_{14} and C_{31} with a C_{max} at C_{28} or C_{29} at all but one site. Average concentrations ranged from 0.15 ng m^{-3} (C_{17-29}) to 3.35 (C_{14}-C_{31}), very much below the concentrations at our London sampling site. Cheng et al. (2006) measured concentrations of n-alkan-2-ones in the Lower Fraser Valley, Canada, in $PM_{2.5}$. Samples collected in a road tunnel showed the highest concentrations, total 1.8-12.6 ng m^{-3} for C_{10}-C_{31}, and were higher in daytime than nighttime. Concentrations at a forest site were 1.1-7.2 ng m^{-3} without a diurnal pattern. Values of C_{max} ranged from C_{16-17} at the road tunnel to C_{27} (secondary maximum) at the forest site. Values of CPI averaged across sites from 1.00 to 1.34, giving little evidence for a substantial biogenic input

from higher plant waxes. These data clearly suggest a road traffic source in London, but less influential than for the n-alkanals for which the increment at the roadside MR site is much greater.

~~Atmospheric concentrations of long-chain n-alkan-3-ones have not previously been reported in the literature. The n-alkan-2-one and n-alkan-3-one homologues with few carbon atoms are believed mainly to originate as the fragmental products of n-alkanes (Yee et al., 2012; Schilling Fahnestock et al., 2015), whereas the higher compounds are mainly generated from functional pathways (Zhang et al., 2015; Ruehl et al., 2013).~~ The n-alkan-3-one homologues identified in the samples ranged from C_8 to C_{19}, and the average of individual compound concentrations was 0.52 ng m^{-3} at RU, 0.94 ng m^{-3} at WM, 1.37 ng m^{-3} at EL and 3.34 ng m^{-3} at MR. The concentrations of n-alkan-3-ones at the four sites were lower than the n-alkanals and n-alkan-2-ones, and MR had the highest average total mass concentrations 39.4 ng m^{-3}, followed by 14.3 ng m^{-3} at EL, 10.4 ng m^{-3} at WM and 5.65 ng m^{-3} at RU, respectively.

The isomeric carbonyls formed via OH-initiated heterogeneous reactions of n-octacosane (C_{28}) exhibit a pronounced preference at the 2-position of the molecule chain (Ruehl et al., 2013). The n-octacosan-2-ones have the highest relative yield (1.00), followed by n-octacosan-3-ones (0.50), while other isomeric carbonyl yields were lower than 0.20. The same results were found in the subsequent chamber studies of n-alkanes (Zhang et al., 2015) (C_{20}, C_{22}, C_{24} but not C_{18}). The main probable reason was that a large fraction of C_{18} evaporated into the gas phase, and OH oxidation happened in the gas phase (homogeneous reaction). This may be supported by the evidence from previous studies (Kwok and Atkinson, 1995; Ruehl et al., 2013), which found that the isomeric distribution of

oxidation products of n-alkanes depends upon whether the reaction occurs in the gas phase or at the particle surface (Kwok and Atkinson, 1995; Ruehl et al., 2013). The homogeneous gas-phase oxidation occurs fast, and H-abstraction by OH radicals occurs at all carbon sites. The fractions of the OH radical reaction by H atom abstraction from n-decane at the 1-, 2-, 3-, 4- and 5-positions are 3.10%, 20.7%, 25.4%, 25.4%, and 25.4%, respectively, and the products from gas phase (homogeneous) reaction were generally in accord with structure-reactivity relationship (SRR) predictions (Kwok and Atkinson, 1995; Aschmann et al., 2001). Zhang et al. (2015) report on the competition between homogeneous and heterogeneous oxidation of medium to high molecular weight alkanes. They express the view that in the atmosphere, compounds typically classified as semi-volatile evaporate sufficiently rapidly that homogeneous gas phase oxidation is more rapid than oxidation in the condensed phase. ~~Recently published studies have found that the isomeric distribution of first-generation oxidation products of n-alkanes depends strongly upon whether the reaction occurs in the gas phase or at the particle surface (Kwok and Atkinson, 1995; Ruehl et al., 2013). The homogeneous gas-phase oxidation occurs fast, and H-abstraction by OH radicals occurs at all carbon sites. The fractions of the OH radical reaction by H atom abstraction from n-decane at the 1-, 2-, 3-, 4- and 5-positions are 3.10%, 20.7%, 25.4%, 25.4%, and 25.4%, respectively, and the products from homogeneous reaction were generally in accord with structure-reactivity relationship (SRR) predictions (Kwok and Atkinson, 1995; Aschmann et al., 2001). Reaction of particulate n-alkanes is dominated by heterogeneous reactions with OH, and the H-abstraction occurs preferentially at the 2-position of the carbon chain (Zhang et al., 2015; Ruehl et al., 2013). The n-alkanes diffuse from the inner particle to the surface, where the OH will quickly attack the H atom of 1 and 2 position carbons. The intermediate products at the 2-position are relatively more stable than at the 1-position,~~

~~and the products are dominated by oxidation of the 2-position. The isomeric carbonyls formed via OH-initiated heterogeneous reactions of n-octacosane (C_{28}) exhibit a pronounced preference at the 2-position of the molecule chain[18]. The n-octacosan-2-ones have the highest relative yield (1.00), followed by n-octacosan-3-ones (0.50), while other isomeric carbonyl yields were lower than 0.20. The same results were found in the subsequent chamber studies of n-alkanes (Zhang et al., 2015) (C_{20}, C_{22}, C_{24}) but not C_{18}. The main reason was that OH oxidation of C_{18} was dominated by the homogeneous reaction as a large fraction of C_{18} evaporated into the gas phase.~~

During the field experiment, the n-alkanal homologues were abundant in all samples, and this is probably attributable to the primary emission sources, including diesel vehicles (Schauer et al., 1999a), gasoline cars (Schauer et al., 2002b), wood burning (Rogge et al., 1998) and cooking aerosol (Schauer et al., 1999b). Correlations with other largely vehicle-generated pollutants (see later) support this interpretation. ~~During the field experiment, the 1-alkanal homologues were abundant in all samples, and this could be explained by a strong impact of anthropogenic activities. Thus, the n-alkanals are considered to arise mainly from primary emission sources. Furthermore, t~~The particulate form of the n-alkane homologues (C_{14}-C_{36}) identified in the samples ~~ranged from 50-100%~~dominated for >C_{25} ~~in contrast to~~and there was a significant particulate fraction for all but the low MW n-alkanes (unpublished data~~C_{11}-C_{13}~~). The H-abstraction by OH radicals may therefore have been dominated by heterogeneous reactions generating the higher concentrations of n-alkan-2-ones than n-alkan-3-ones that were found in all samples. The ratio of n-alkan-2-ones/n-alkan-3-ones (C_{11}-C_{18}) with the same carbon atom number ranged from 2.35-11.3 at four measurement sites. Surprisingly, although the n-alkane (C_{11}-C_{13}) oxidation was expected to be dominated by

homogeneous gas phase reactions, the n-alkan-2-one/n-alkan-3-one ratios were still greater than 2.00. The probable reason was that the lower molecular weight n-alkan-2-ones were significantly impacted by primary emission sources such as cooking (Zhao et al., 2007a,b). Another likely reason is that the n-alkan-2-one and n-alkan-3-one homologues with lower carbon atom numbers originated in part from the fragmental products of higher n-alkanes (Yee et al., 2012; Schilling Fahnestock et al., 2015).

The ratios of n-alkan-2-ones/n-alkanes, n-alkan-3-ones/n-alkanes (with same carbon numbers) were calculated and are reported in Table S2. The n-alkan-3-ones with carbon numbers higher than C_{20} were not identified in the samples, indicating that both the ~~homogeneous~~ gas phase and heterogeneous reactions of higher molecular weight n-alkanes were slow, the former probably due to the low vapour phase presence of n-alkanes. The ratios of n-alkan-3-ones/n-alkanes at four measurement sites gradually increased from $C_{11,}$ and then decreased from C_{17}, while higher ratios of n-alkan-2-ones/n-alkanes were observed in the range from C_{17} to C_{22}, probably indicating a shift from homogeneous reactions to heterogeneous reactions with the increase of carbon numbers. The low ratios of n-alkan-2-ones/n-alkanes with carbon numbers from C_{23} to C_{26} ~~were attributed to~~might be explained by the low diffusion rate from the inner particle to the surface with the increasing carbon number of n-alkanes, even though heterogeneous reactions ~~were~~ would be the expected dominant pathway.

~~**3.2 Temporal and Spatial Variations**~~

~~The study of temporal and spatial variations of air pollutants can provide valuable information about their sources and atmospheric processing. The time series of particle-bound n-alkanals, n-alkan-2-ones, and n-alkan-3-ones are plotted in Fig. 3. It is clear that the concentrations of n-alkanals varied~~

~~substantially with date, and were always higher than n-alkanones at four sites. It is also clear from Figure 2 that concentrations were broadly similar at the background sites, RU, WM and EL, but are elevated, especially for the n-alkanals, at MR. This is strongly indicative of a road traffic source.~~

3.~~3~~ 2 Sources of Carbonyl Compounds

3.~~3~~2.1 Homologue distribution and carbon preference index (CPI)

Figure~~.~~ 4 shows the average concentrations, and molecular distributions of particle-bound carbonyl compounds at the four sites. The values of carbon preference index (CPI) were calculated to estimate the origin of carbonyl compounds, according to Bray and Evans (1961):

$$\mathrm{CPI} = \frac{1}{2}\left(\frac{\sum_4^m C_{2i+1}}{\sum_4^m C_{2i}} + \frac{\sum_4^m C_{2i+1}}{\sum_5^{m+1} C_{2i}}\right)$$

For n-alkanals and n-alkan-3-ones (m=9): $\mathrm{CPI} = \frac{1}{2}\left(\frac{\sum odd(C_9-C_{19})}{\sum even(C_8-C_{18})} + \frac{\sum odd(C_9-C_{19})}{\sum even(C_{10}-C_{20})}\right)$

For n-alkan-2-ones (m=12): $\mathrm{CPI} = \frac{1}{2}\left(\frac{\sum odd(C_9-C_{25})}{\sum even(C_8-C_{24})} + \frac{\sum odd(C_9-C_{25})}{\sum even(C_{10}-C_{26})}\right)$

where *i* takes values between 4 and *m*, and 5 and *m* as in the equation, and

m = 9 for n-alkanal and n-alkan-3-ones

m = 12 for n-alkan-2-ones

The carbon ~~maximum~~ number of the homologue of highest concentration (C_{max}) ~~was used to evaluate the relative contribution~~can be indicative of the source. ~~and exhibit the homologue distribution of~~

~~highest concentration.~~ Table. 1 presents the CPI and C_{max} of particle-bound carbonyl compounds calculated in the current and other studies. A CPI of ≤1 is an indication of an anthropogenic source, while a CPI of 1-5 shows a mixture of anthropogenic and biogenic sources and a CPI >5 suggests a biogenic (plant wax) source.

The n-alkanes which are potential precursors of the oxygenates described typically showed two C_{max} values, the first at C_{13} (the lowest MW compound measured), and at C_{23}. The CPI values for the n-alkanes were between 0.97-1.02 at the four measurements sites (unpublished data).

According to the low CPI (0.41-1.07) at the four sites, the n-alkanal homologues with carbon number from C_8 to C_{20} mainly originate from anthropogenic emissions or OH oxidation of ~~anthropogenic~~ fossil-derived hydrocarbons. The particle-bound n-alkanals exhibited a similar distribution of carbon number from January to April at four sites, and they had the same C_{max} at C_8 with concentration 28.6 ng m^{-3} at RU, 50.3 ng m^{-3} at WM, 53.0 ng m^{-3} at EL and 141 ng m^{-3} at MR, respectively. This compound may be a fragmentation product, oxidation product or primary emission. In addition, the distribution of n-alkanals had a second concentration peak at C_{15} (MR) and C_{18} (RU, WM, and EL). The C_{18} compound was observed accounting for the highest percentage of the total mass of n-alkanals in some rural aerosol samples (Gogou et al., 1996) in Crete. Andreou and Rapsomanikis reported the C_{max} as C_{15} or C_{17} in Athens (Andreou and Rapsomanikis, 2009) and attributed this to the oxidation of n-alkanes. However, a C_{max} at C_{26} or C_{28} in urban Crete (Gogou et al., 1996) was observed, suggestive of biogenic input. The homologue distribution and CPI of n-alkanals in this study differed from those previous reports, and demonstrated weak biogenic input and a strong

impact of anthropogenic activities in the London samples.

In this study, n-alkan-2-ones have similar homologue distributions and C_{max} (C_{19} or C_{20}) (Table 2) at RU, WM and EL sites, and the total concentration from C_{16} to C_{23} accounts for 76.0%, 76.1% and 68.0% of ∑n-alkan-2-ones, respectively. The CPI values for n-alkan-2-ones ranged from 0.57 to 1.23 at the RU, MR and WM sites and were not indicative of major biogenic input, and were considered to mainly originate from anthropogenic activities and OH oxidation of anthropogenic n-alkanes. It is however notable that the CPI values for both the 2-ketones and 3-ketones exceed those for the alkanals (see Table 1), suggesting a contribution from contemporary biogenic sources, possibly wood smoke and cooking. At EL, the CPI of 1.57 is ~~probably~~ clearly indicative of a biogenic contribution in suburban south London. A difference was observed at the MR site, the n-alkan-2-ones with carbon atoms numbering from C_{12} to C_{18} accounting for 72.0% of ∑n-alkan-2-ones, with the C_{max} being at C_{16}. These data suggest a contribution of primary emissions from traffic at MR, but a dominant background, probably substantially secondary, at the other sites. The C_{max} of n-alkan-3-ones was at C_{16} at the MR site, at EL, C_{max} = C_{16}, WM, C_{max} = C_{17} and at RU, C_{max} = C_{17}, respectively.

3.~~3~~2.2 The ratios of n-alkanes/n-alkanals

Diesel engine emission studies have been conducted previously in our group; details of the engine set up and exhaust sampling system are given elsewhere (Alam et al., 2016b). Briefly, the steady-state diesel engine operating conditions were at a load of 5.90 bar mean effective pressure (BMEP) and a

speed of 1800 revolutions per minute (RPM), and samples (n=14) were collected both before a diesel oxidation catalyst (DOC) and after a diesel particulate filter (DPF). The n-alkanes (C_{12} - C_{37}) and 1-alkanals (C_9 - C_{18}) were quantified in the particle samples, while n-alkanones were not identified because their concentrations were lower than the limits of (detection 0.01–0.15 ng m^{-3}). The emission concentrations of n-alkanals ranged from 7.10 to 53.2 µg m^{-3} (before DOC) and 1.20 to 11.5 µg m^{-3} (after DPF), respectively, and the ratios of alkanes/alkanals (~~C_{12}~~C_{13}-C_{18}) with the same carbon atom numbers ranged from 0.15 to 0.23 (before DOC) and 0.52 to 7.60 (after DPF). The n-alkane/n-alkanal (~~C_{12}~~C_{13}-C_{18}) ratio at MR ranged from 0.~~92~~ 30 to 5.7~~03~~, while average ratios of ~~27.6~~14.9 (RU), ~~22.1~~11.5 (WM) and ~~15.1~~14.7 (EL) were obtained, respectively. The similarity of the n-alkanes/n-alkanal ratio between MR and the engine studies (after DPF) strongly suggests that diesel vehicle emissions were the main source of ~~1-~~alkanals at MR. The higher ratios at the other sites may be due to greater airmass aging and loss of alkanals due to their higher reactivity (Chacon-Madrid and Donahue, 2011; Chacon-Madrid et al., 2010).

The emission factors of total alkanes from diesel engines are reported to be 7 times greater than gasoline engines (Perrone et al., 2014), with n-alkanals with carbon atoms numbering lower than C_{11} being quantified in the exhaust from gasoline engines (Schauer et al., 2002b; Gentner et al., 2013). The n-alkane/n-alkanal (C_8-C_{10}) ratio with the same carbon numbers ranged from 5.60 to 14.3 (Schauer et al., 2002b), suggesting that gasoline combustion may be another potential source of atmospheric n-alkanals.

~~Studies of n-alkanals showed that aldehydes have high reactivity when the OH radical attacks the aldehyde moiety (Chacon-Madrid and Donahue, 2011; Chacon-Madrid et al., 2010), and the rate constants are more than 3 times those of n-alkanes with the same carbon number. The mechanism and rate constants of H-abstraction by OH detailed in the Master Chemical Mechanism (MCM, v3.3.1), were obtained via http://mcm.leeds.ac.uk/MCM, and used in the evaluation of our data.~~

3.~~3~~2.3 Correlation analysis

Insights into the sources of carbonyls can be gained from intra-site ~~from~~ correlation analysis with black carbon (BC) and NO_x. This ~~has the advantage of comparing relative concentrations of pollutants, rather than absolute concentrations. The latter~~is more informative than comparisons between sites when sampling did not take place simultaneously, as concentrations are strongly affected by weather conditions, making inter-site comparisons difficult to interpret ~~when sampling did not occur simultaneously~~. In London, both black carbon and NO_x arise very substantially from diesel vehicle emissions (Liu et al., 2014; Harrison et al., 2012; Harrison and Beddows, 2017), and hence these are good measures of road traffic activity. The concentrations of BC were simultaneously determined by the online instruments during the sampling periods, with the average concentrations of 1.34, 1.94 and 3.58 μg m^{-3} at the RU, WM and MR sites, respectively. The data for NO_x were provided by the national network sites, with the average concentrations of 23.4 and 202 μg m^{-3} at the EL and MR sites, respectively. At the MR site, the concentrations of BC and NO_x averaged 5.00 μg m^{-3} and 281 μg m^{-3} when southerly winds were dominant compared to 2.60 and 128 μg m^{-3} for northerly winds. All correlations were carried out with the sum of particle and vapour phases for the carbonyl compounds, and strong (r^2 = 0.87) and weak (r^2 = 0.12) correlations between

BC and NO_x were obtained when the southerly and northerly winds were prevalent at MR, respectively. Marylebone Road is a street canyon site where a vortex circulation is established by the wind. The effect is that on northerly wind sectors the sampling site on the southern side of the road samples near-background air, while on southerly wind sectors, the traffic pollution is carried to the sampling site, leading to elevated pollution levels affected heavily by the traffic emissions. The strong correlation between BC and NO_x with southerly wind sectors is a reflection of their emission from road traffic. In addition, the correlations between n-alkanals (C_8-C_{20}) and BC, and between n-alkanals (C_8-C_{20}) and NO_x were calculated to assess the contribution of vehicular emissions (Table S3). The results showed that the correlations (r^2) between n-alkanals and BC gradually decreased from 0.61 (C_9) to 0.34 (C_{20}) at MR when the southerly winds were prevalent, indicating that the distribution of n-alkanals, and especially the lower MW compounds, was significantly impacted by the vehicular exhaust emissions. The average correlations at MR (southerly winds) between n-alkanals and BC, and between n-alkanals and NO_x were $r^2 = 0.47$ and $r^2 = 0.32$, respectively. These moderate correlations demonstrated that the vehicular emissions were a ~~substantial~~ source of n-alkanals at MR, and ~~result in~~contribute to the high background concentrations of n-alkanals in London. The other probable sources of n-alkanals include cooking emissions, wood burning, photooxidation of hydrocarbons and industrial emissions. Poorer correlations between n-alkanals and BC (average $r^2 = 0.15$), and between n-alkanals and NO_x (average $r^2 = 0.15$) were observed at MR in the north London background air sampled when northerly winds were prevalent. There were very weak correlations (average $r^2 < 0.10$) between n-alkanals and BC, and between n-alkanals and NO_x at the RU, WM and EL sites, which may be attributable to the high chemical reactivity of n-alkanals. High concentrations of furanones (γ-

lactones) are generated via the photo-oxidation reaction of n-alkanals (Alves et al., 2001), and the total concentrations (particle and gas) were up to 376, 279, 347 and 318 ng m^{-3} at RU, WM, WL, and MR, respectively for the sum of furanone homologues (from 5-propyldihydro-2(3H)-furanone to 5-tetradecyldihydro-2(3H)-furanone).

The relationships (r^2 values) between BC and NO_x and the n-alkan-2-ones were low at all sites, but notably higher with southerly winds at MR (average r^2 = 0.33 and 0.35 for BC and NO_x respectively) than for northerly winds (r^2 = 0.16 and 0.03 respectively). This is strongly suggestive of a contribution from vehicle exhaust to n-alkan-2-one concentrations, but smaller than that for n-alkanals. In the case of the n-alkan-3-ones, correlations averaged r^2 = 0.25 with BC and r^2 = 0.21 for NO_x in southerly winds, compared to r^2 = 0.08 and r^2 = 0.05 respectively for northerly winds. This is also suggestive of a small, but not negligible contribution of vehicle emissions to n-alkan-3-ones. The very low correlations observed in background air for both n-alkan-2-ones and n-alkan-3-ones with BC and NO_x are suggestive of the importance of non-traffic sources, probably including oxidation of n-alkanes. Both compound groups were below detection limit in the analyses of diesel exhaust. The considerable predominance ~~for~~ of n-alkan-2-one over n-alkan-3-one concentrations may be indicative of a formation pathway from oxidation of condensed phase n-alkanes, but this is speculative as primary emissions may be dominant.

3.~~4~~ 3 ~~The Partition Between Particle and Gas Phase~~Gas and Particle Phase Partitioning

The partitioning coefficient K_p between particles and vapour was calculated in this study according to the following equation defined by Pankow (1994):

$$K_p = \frac{C_p}{C_g * TSP}$$

Where, C_p and C_g (μg m^{-3}) are the concentration of the compounds in the particulate phase and gaseous phase, respectively. TSP is the concentration of total suspended particulate matter (μg m^{-3}), which was estimated from the PM_{10} concentration (PM_{10}/TSP = 0.80), and daily average PM_{10} concentrations were taken from the national network sites (see Table S5). The partitioning coefficients K_p calculated from our data and the percentages in the particulate form are presented in Table 2. For the three types of carbonyls, the n-alkanals >C_{16}, n-alkan-2-ones >C_{19}, and n-alkan-3-ones > C_{18} ~~were assumed to have negligible~~the vapour concentrations were below detection limit, and the partitioning into the particulate phase gradually increased from C_8 to high molecular weight compounds.

Log Kp was regressed against vapour pressure (VP_T) for the relevant temperature derived from UManSysProp (http://umansysprop.seaes.manchester.ac.uk/) according to the following equation:

$$\text{Log } K_p = \text{m log}(VP_T) + b$$

The calculated log K_p versus log (VP_T) for the three types of carbonyls was calculated for each day, and the results appear in the Table S4. Data from four sites were over the temperature range 0.40–15.3 °C. A good fit to the data for n-alkan-2-ones (r^2 = 0.54–0.94 at RU, 0.64-0.93 at WM, 0.43-

546 0.95 EL and 0.45-0.89 at MR) was obtained. It is notable that the fit to the regression equation as
547 indicated by the r^2 value is appreciably higher at the MR site than at the other sites, especially in the
548 case of the alkan-3-ones. This is not easily explained, except perhaps by an increased particle surface
549 area at the MR site which may enhance the kinetics of gas-particle exchange, leading to partitioning
550 which is closer to equilibrium.

551

552 **4. CONCLUSIONS**

553 Three groups of carbonyl compounds were determined in the particle and gaseous phase in London
554 and concentrations are reported for n-alkanals (C_8-C_{20}), n-alkan-2-ones (C_8-C_{26}) and n-alkan-3-ones
555 (C_8-C_{19}). The Marylebone Road site has the highest concentration of particle-bound n-alkanals, and
556 the average total concentration was up to 682 ng m^{-3}, followed by 167 ng m^{-3} at EL, 117 ng m^{-3} at
557 WM and 82.6 ng m^{-3} at RU. The particulate n-alkanals were abundant in all samples at all four
558 measurement sites, accounting for more than 56.3% of total particle carbonyls. In addition, the
559 average total particle concentrations of n-alkan-2-ones and n-alkan-3-ones at four measurement sites
560 were in the range of 58.5-186 ng m^{-3} and 5.65-39.4 ng m^{-3}, respectively. Diagnostic criteria,
561 including molecular distribution, CPI, C_{max}, ratios and correlations, were used to assess the sources
562 and their contributions to carbonyl compounds. The three groups of carbonyls have similar
563 molecular distributions and C_{max} values at the four measurement sites, and their low CPI values
564 (0.41-1.57) at the four sites indicate a weak biogenic input during sampling campaigns. Heavily
565 traffic-influenced air and urban background air were measured at the MR site when southerly and
566 northerly winds were prevalent respectively; correlations of r^2 = 0.47 and r^2=0.32 were obtained
567 between n-alkanals and BC, and between between n-alkanals and NO_x, respectively in southerly

winds. Vehicle emissions appear to be an important source of n-alkanals, which is confirmed by the similar ratios of n-alkanes/n-alkanals measured at MR (0.30-5.750.92-5.03) and in diesel engine exhaust studies (0.52-7.6), resulting in a high background concentration in London. In addition, the OH-initiated heterogeneous reactions of n-alkanes appear to be important sources of n-alkanones, even though weak contributions from vehicular exhaust emissions were suggested by correlation analysis with BC and NO_x in southerly winds at MR. Anthropogenic primary sources such as cooking (Abdullahi et al., 2013) appear tomay account for a large proportion of the alkan-2-one and alkan-3-one concentrations measured in London, in addition to the secondary contribution from alkane oxidation. Any contribution from cooking or wood combustion is likely to be small, or the CPI would be greater.

In addition, the partitioning coefficients of carbonyls were determined from the relative proportions of the particle and gaseous phases of individual compounds. The results of field measurements of partitioning between particle and vapour phases showed generally a better fit at MR than at the other three sites. The n-alkan-2-ones have a better fit at four sites than the n-alkanals and n-alkan-3-ones, with r^2 = 0.78 72 (0.5449–0.9457) at RU, 0.85 76 (0.6455-0.9387) at WM, 0.74 (0.43-0.95) EL and 0.70 (0.45-0.89) at MR, respectively in a regression of log K_p versus the compound vapour pressure. This most likely reflects the slow formation of the alkan-2-ones as secondary constituents, closer to phase equilibrium than the largely emitted alkanals which would be spatially far more variable. The higher r^2 values for the alkan-2-ones than alkan-3-ones may reflect the higher concentrations, and hence better analytical precision for the former compound group.

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TABLE LEGENDS

Table 1. The carbon preference index (CPI) and C_{max} for n-alkanals, n-alkan-2-ones, and n-alkan-3-ones in this study and published data.

Table 2. Percentages of particle phase form and the partitioning coefficient Kp.

FIGURE LEGENDS

Figure 1. Map of the sampling sites. RU-Regents University (15 m above ground); WM-University of Westminster (20 m above ground); EL-Eltham; MR-Marylebone Road (south side).

Figure 2. The average total concentration of particle-bound n-alkanals (C_8-C_{20}), n-alkan-2-ones (C_8-C_{26}), and n-alkan-3-ones (C_8-C_{19}), for each sampling period and site. The error bars indicate one standard deviation.

Figure 3. Time series of particle-bound ∑~~1~~n-alkanals, ∑n-alkan-2-ones and ∑n-alkan-3-ones at RU, WM, EL, and MR sites.

Figure 4. The molecular distribution of particle-bound carbonyl compounds at four sites (RU, WM, EL, and MR).

Table 1. The carbon preference index (CPI) and C_{max} for n-alkanals, n-alkan-2-ones, and n-alkan-3-ones in this study and published data.

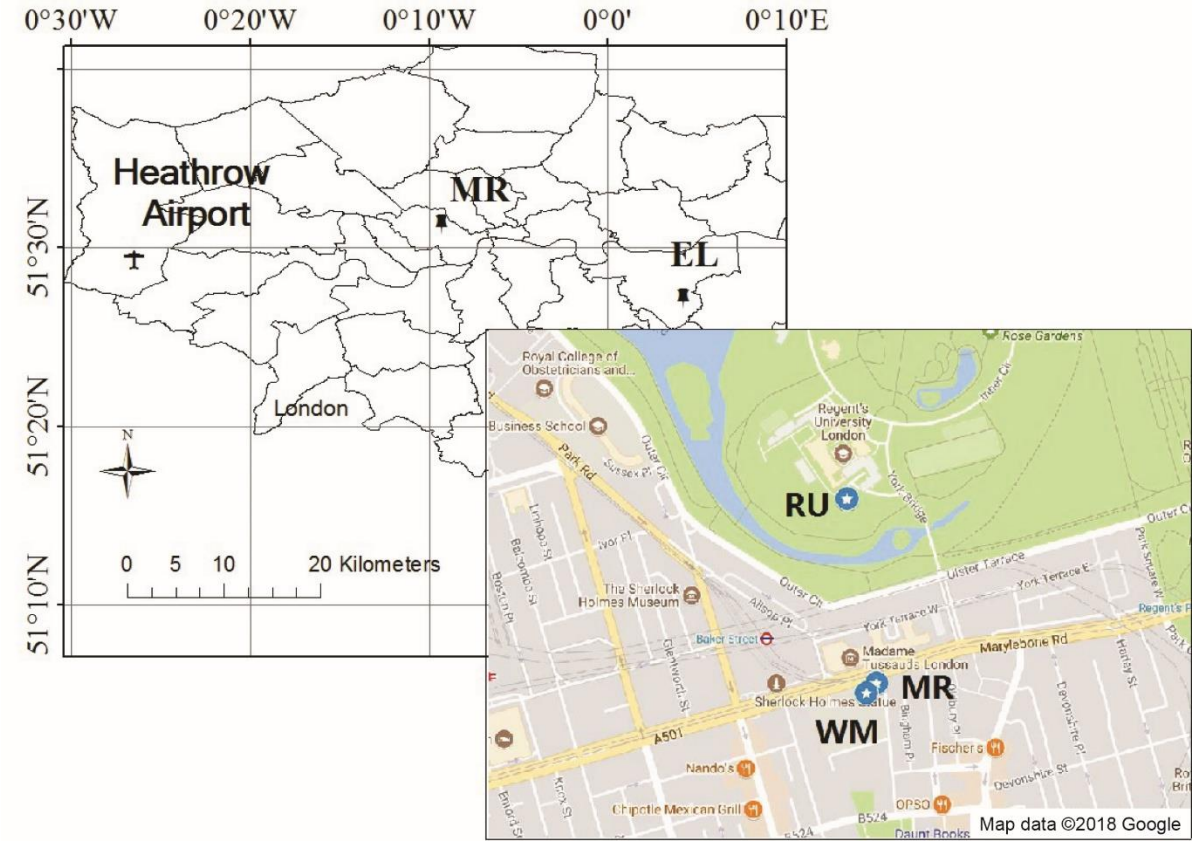
Location	Sampling period	n-alkanals		n-alkan-2-ones		n-alkan-3-ones		Reference
Sampling site		CPI	C_{max}	CPI	C_{max}	CPI	C_{max}	
RU, surrounded by Regent's Park, 15 m above ground	23 Jan - 19 Feb	0.52	C_8	1.23	C_{19}	1.30	C_{17}	Present study
WM, 20 m above ground	24 Jan - 20 Feb	0.41	C_8	0.99	C_{20}	1.26	C_{17}	Present study
EL, suburb of London	23 Feb - 21 Mar	0.71	C_8	1.57	C_{20}	1.04	C_{16}	Present study
MR, adjacent to Marylebone road	22 Mar - 18 Apr	1.07	C_8	0.57	C_{16}	1.12	C_{16}	Present study
Athens, Athinas St.	August	1.49	C_{15}, C_{17}	1.09	C_{18}, C_{21}, C_{19}			(Andreou and Rapsomanikis, 2009)
Urban roadside	March			3.26	C_{21}, C_{19}, C_{20}			
Athens, AEDA, Urban, 20 m above ground	March			2.41	C_{19}, C_{18}, C_{20}			(Andreou and Rapsomanikis, 2009)
Heraklion, Greece Urban 15 m above ground	Spring /summer	0.80–1.40	C_{26}, C_{28}	1.30–1.80	C_{23}, C_{29}, C_{31}			(Gogou et al., 1996)
Vancouver, Canada Roadway tunnel				1.33	C_{17}, C_{19}			(Cheng et al., 2006)
Aveiro, Portugal	Summer		C_{22}, C_{23}, C_{26}		C_{26}, C_{28}, C_{30}			
Suburban	Winter							(Oliveira et al., 2007)
K-Puszta, Hungary	Summer		C_{24}, C_{26}, C_{28}		C_{24}, C_{26}, C_{28}			

Table 2. Percentages of particle phase form and the partitioning coefficient Kp (m^3 μg^{-1}).

	RU						WM					
	n-alkanals		n-alkan-2-ones		n-alkan-3-ones		n-alkanals		n-alkan-2-ones		n-alkan-3-ones	
	%	Kp	%	Kp	%	Kp	%	Kp	%	Kp	%	Kp
C_8	82.9	1.16E-04	18.4	5.37E-06	23.9	7.47E-06	80.2	9.09E-05	13.3	3.43E-06	34.1	1.16E-05
C_9	69.2	5.37E-05	14.5	4.03E-06	16.6	4.74E-06	60.5	3.43E-05	15.6	4.16E-06	28.7	9.05E-06
C_{10}	75.3	7.27E-05	13.6	3.77E-06	7.43	1.92E-06	82.1	1.03E-04	14.4	3.77E-06	23.3	6.82E-06
C_{11}	45.5	1.99E-05	21.4	6.49E-06	12.8	3.49E-06	62.4	3.72E-05	20.1	5.65E-06	36.3	1.28E-05
C_{12}	74.8	7.08E-05	25.0	7.96E-06	31.3	1.09E-05	73.7	6.29E-05	28.8	9.07E-06	22.7	6.60E-06
C_{13}	82.9	1.15E-04	61.0	3.74E-05	35.4	1.31E-05	82.2	1.04E-04	48.9	2.14E-05	62.5	3.74E-05
C_{14}	82.8	1.15E-04	49.5	2.34E-05	35.5	1.31E-05	75.8	7.04E-05	31.8	1.05E-05	25.6	7.74E-06
C_{15}	99.5	5.01E-03	84.1	1.26E-04	50.5	2.44E-05	~~*100~~		85.0	1.27E-04	68.5	4.87E-05
C_{16}	~~100*~~		91.4	2.53E-04	70.3	5.64E-05	~~*100~~		89.6	1.93E-04	91.7	2.47E-04
C_{17}	~~100*~~		91.5	2.55E-04	~~*100~~		~~*100~~		85.9	1.36E-04	91.5	2.42E-04
C_{18}	~~100*~~		94.1	3.80E-04	~~*100~~		~~*100~~		84.8	1.26E-04	99.4	4.02E-03
C_{19}	~~100*~~		99.1	2.69E-03			~~*100~~		~~*100~~			
C_{20}	~~100*~~		~~100*~~				~~*100~~		~~*100~~			
C_{21}			~~100*~~						~~*100~~			
C_{22}			~~100*~~						~~*100~~			
C_{23}			~~100*~~						~~*100~~			
C_{24}			~~100*~~						~~*100~~			
C_{25}			~~100*~~						~~*100~~			
C_{26}			~~100*~~						~~*100~~			

	El						MR					
	n-alkanals		n-alkan-2-ones		n-alkan-3-ones		n-alkanals		n-alkan-2-ones		n-alkan-3-ones	
	%	Kp	%	Kp	%	Kp	%	Kp	%	Kp	%	Kp
C_8	92.7	6.53E-04	24.9	1.72E-05	31.9	2.43E-05	90.0	2.94E-04	28.2	1.28E-05	43.0	2.46E-05
C_9	92.2	6.16E-04	38.0	3.18E-05	44.4	4.15E-05	89.9	2.89E-04	27.0	1.20E-05	39.1	2.09E-05
C_{10}	90.5	4.96E-04	47.6	4.70E-05	47.0	4.59E-05	91.7	3.62E-04	61.1	5.12E-05	20.4	8.33E-06
C_{11}	87.0	3.47E-04	72.3	1.35E-04	81.9	2.34E-04	87.4	2.26E-04	50.2	3.28E-05	33.1	1.61E-05
C_{12}	92.9	6.73E-04	83.4	2.60E-04	66.4	1.02E-04	93.0	4.30E-04	88.5	2.51E-04	28.1	1.28E-05
C_{13}	95.6	1.12E-03	82.2	2.40E-04	65.7	9.92E-05	96.1	8.04E-04	87.7	2.33E-04	46.2	2.79E-05
C_{14}	91.4	5.52E-04	90.3	4.80E-04	59.1	7.48E-05	95.2	6.51E-04	95.9	7.61E-04	72.0	8.38E-05
C_{15}	96.7	1.53E-03	94.5	8.98E-04	84.4	2.80E-04	*100		96.9	1.02E-03	83.8	1.69E-04
C_{16}	*100		96.7	1.41E-03	89.0	4.18E-04	*100		96.4	8.70E-04	88.0	2.38E-04
C_{17}	*100		95.1	1.00E-03	81.5	2.28E-04	*100		96.0	7.73E-04	88.0	2.39E-04
C_{18}	*100		64.6	9.44E-05	85.0	2.93E-04	*100		92.5	4.04E-04	*100	
C_{19}	*100		*100				*100		*100		*100	
C_{20}	*100		*100				*100		*100			
C_{21}			*100						*100			
C_{22}			*100						*100			
C_{23}			*100						*100			
C_{24}									*100			

* For compounds marked with an asterisk, the particulate phase was quantified, but the vapour was below detection limit, and hence K_p is undefined.



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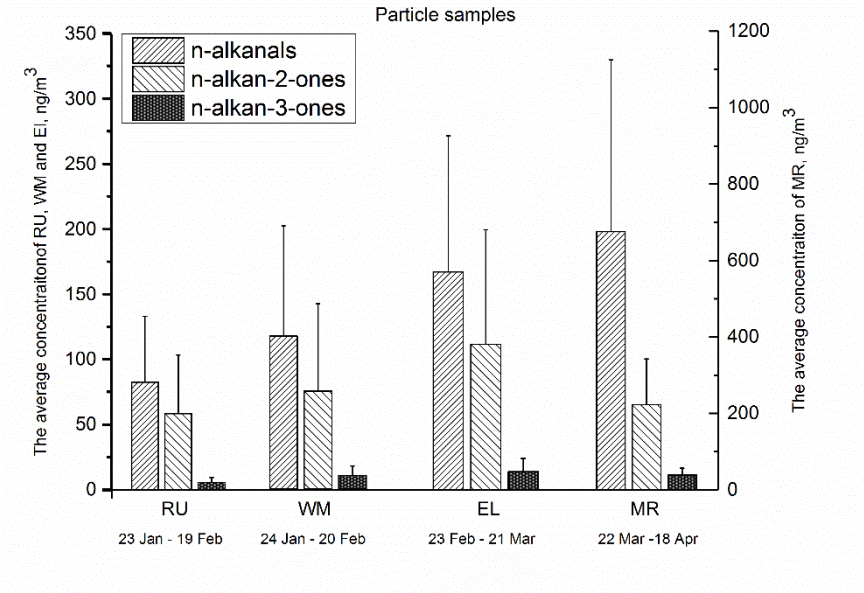

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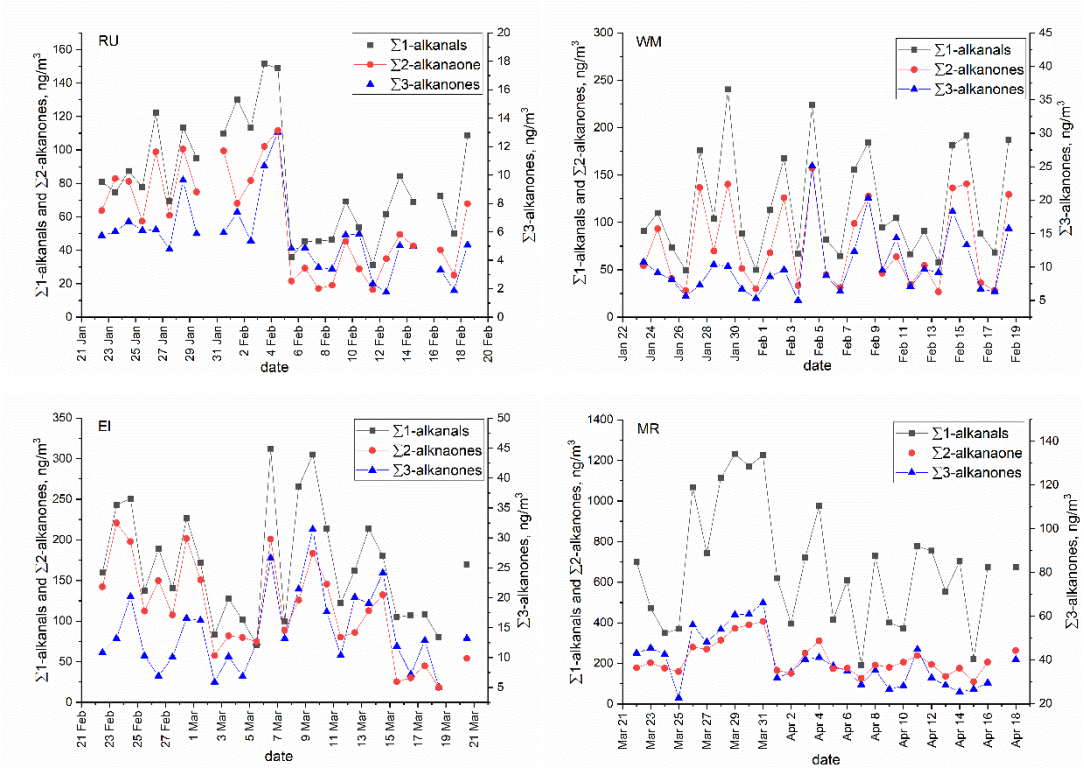

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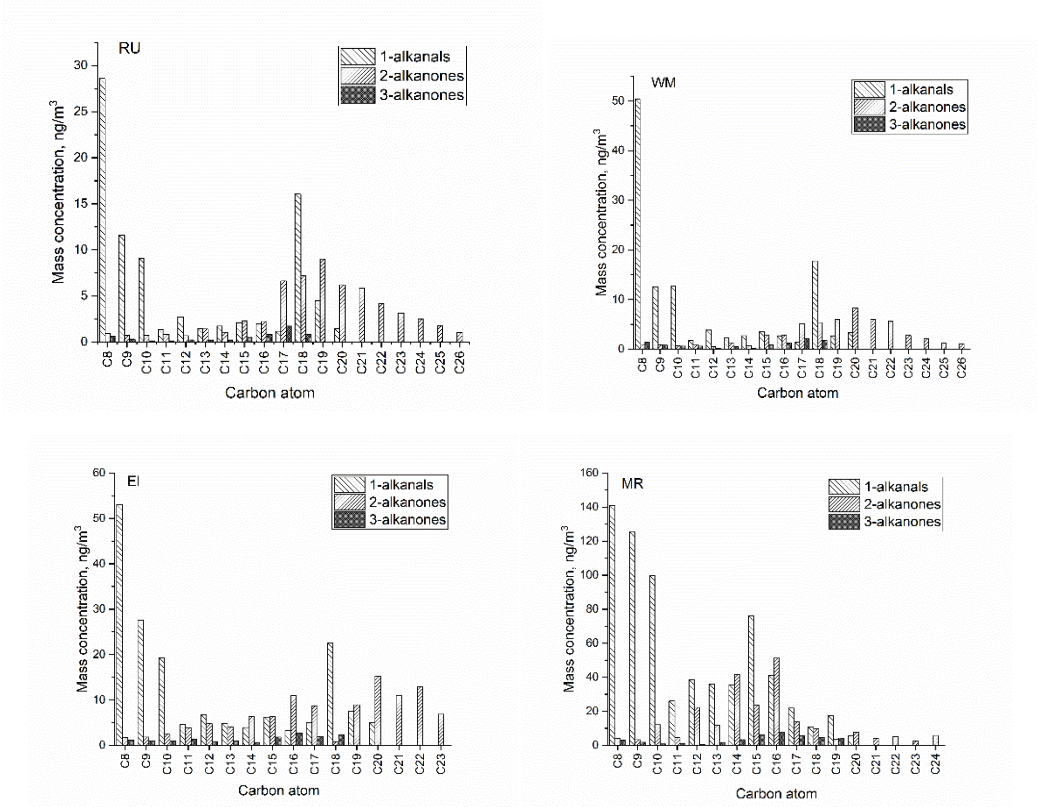

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