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Title: Aliphatic Carbonyl Compounds (C8–C26) in Wintertime Atmospheric Aerosol in London, UK

Author(s): Ruihe Lyu et al.

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RESPONSE TO REVIEWERS

We thank the reviewers for their very detailed and insightful reviews which have led to many enhancements to the paper.

REVIEWER #1

General Comment:

This manuscript by Lyu et al. describes measurements of three groups of aliphatic carbonyl compounds (n-alkanals, n-alkan-2-ones and n-alkan-3-ones) in air samples collected in London during winter time. The application of the work sampled at four different sites which included roof-top background, ground-level urban background and street canyon background. The authors found that the concentrations from high to low ordered by n-alkanals, n-alkan-2-ones and n-alkan-3-ones. Both primary and secondary sources contribute the formation of all compound groups and black carbon and NO_x has relatively low correlation with the products. Vehicle emissions have a strong impact on the air in street canyon location, it is suggested as a major contributor for n-alkanals. Overall, the results are interesting and solid. However, I have some major comments that the authors should address before considered publishable at ACP.

Main Comments:

1. Apparently, the authors have analyzed carbonyl compounds with a limited range of carbon number. The authors should try to provide the range in the abstract or the last paragraph of the introduction. Otherwise, the description at the beginning of the paper is inconsistent with the findings.

RESPONSE: The carbon number range of carbonyl compounds is now described in the abstract.

2. From Line 207 to Line 247. The manuscript spent a lot of effort comparing results between this study and previous reports. But this part is less well organized and little information if provided in terms of what such a big difference exists.

RESPONSE: The text has been lightly edited, and explanations for the differences from earlier work provided.

3. To comprehensively discuss gas-particle partitioning, it is very important to provide information of total organic particle loading at the sampling sites. With that information, one can have a reasonable idea of the fractions of n-alkanes and their products in the particle phase vs. the gas phase. This manuscript starts implying gas-particle partitioning at Line 282, without providing the mass loading information. At typical ambient aerosol loading, C14-C18 n-alkanes should primarily be in the gas phase based on their high vapor pressure. If they observe a > 50% fraction in the particle phase for C14 alkane, it is strongly against the vapor pressure estimates and partitioning theory. It is either from measurement uncertainty or more surprisingly slow evaporation rates after emission from particles. Was this high particle-phase fraction for the “IVOC”-ranged C14-C18 n-alkanes observed at all 4 sites?

RESPONSE: We regret that an incorrect dataset for the condensed phase was described in the first version of the paper. This has now been replaced with new data, and PM mass loading data are also provided in Table S5.

4. Starting from Line 286, the manuscript discussed ratios between the n-alkanes, 2ketones, and 3-ketones, but it is unclear if these ratios are from gas-phase data? Particle-phase data? Or combined? In addition, some conclusions drawn from the ratios, such as the ones at Line 299-302, are not obviously clear. More explanation is needed.

RESPONSE: The ratios between n-alkanes, 2-ketones, and 3-ketones were from the sum of concentrations of gas and particle phases. This is now clarified in the text.

Line 299-302,

RESPONSE: This sentence has been re-worded to provide clarification.

5. CPI usage. The mathematical expression of CPI does not immediately explain what the CPI values mean. The authors should try to provide a little more details, especially information like, what CPI ranges suggesting what sources.

RESPONSE: An explanatory sentence has been added.

6. Ratios of alkanes/alkanals. The authors compare ratios of C12-C18 alkanes/alkanals at each carbon number between direct diesel vehicle emission data and their particle-phase data. The similarity between the emission data and the MR site measurement suggests a diesel source of the alkanals at MR. However, it is unclear what the ratios of C8-C10 alkanes/alkanals are compared to and how the authors came to a conclusion of the gasoline source (Line 374-378). In addition, the higher ratios at the other 3 sites may indicate a relatively aged air mass being sampled, as the authors pointed out that alkanals react faster than alkanes. Thus the higher ratios cannot rule out the alkanals at the other sites also have diesel source.

RESPONSE: A reference to literature data for C8-C10 compounds from gasoline engines is now included. Commentary on the higher ratios at other sites is now added.

7. Gas-particle partitioning. Line 451-452. It is problematic to assume this. Based on the SIMPOL.1 estimates of vapor pressure, C16 alkanal has a C* of 75 ug/m³, and C19 alkanone has a C* of 11 ug/m³. These species are in the SVOC range and should have substantial fraction in the gas phase.

RESPONSE: We thank the reviewer for raising this. The vapor concentrations are unlikely to be zero, but were below detection limit. An explanatory note has been added at the bottom of Table 2.

Minor Comments:

Line 70. Should be "...an important source of aliphatic carbonyl"

RESPONSE: Amended as suggested.

Line 117. Change "adsorption tubes" to "sorbent tubes" to be consistent with the context.

RESPONSE: Amended as suggested.

Line 188 and 194. The same information was repeated twice.

RESPONSE: The second expression of this information has been deleted.

Line 225-226. A reference is needed here.

RESPONSE: The following references are now cited: Simoneit, B. R. T., Cox, R. E., and Standley, L. J.: Organic matter of the troposphere - IV. Lipids in Harmattan aerosols of Nigeria, *Atmos. Environ.*, 22, 983-1004, [https://doi.org/10.1016/0004-6981\(88\)90276-4](https://doi.org/10.1016/0004-6981(88)90276-4), 1967. Gogou, A., Stratigakis, N., Kanakidou, M., and Stephanou, E. G.: Organic aerosols in Eastern Mediterranean: components source reconciliation by using molecular markers and atmospheric back trajectories, *Org. Geochem.*, 25, 79-96, [https://doi.org/10.1016/S0146-6380\(96\)00105-2](https://doi.org/10.1016/S0146-6380(96)00105-2), 1996.

Line 330. Cmax is defined after already used a few times. The same for CPI.

RESPONSE: We do not feel that this is problematic, and may occasionally assist the reader (not all of which start reading at page 1).

Line 249-253. These discussion should be moved before Line 229.

RESPONSE: Moved as recommended.

Line 270. It is unclear from these two references that whether OH quickly attacks H at the one position.

RESPONSE: This has been clarified by removing the word “quickly”.

Section 3.2 is too short to be an individual topic. Not much discussion is on this part anyway. Suggest merge it into other sections.

RESPONSE: Agreed. Now merged into 3.1.

Line 413-414. How can a “moderate” correlation indicate a “substantial” source?

RESPONSE: The sentence has been modified to resolve this contradiction.

REVIEWER #2

Review of, “Aliphatic Carbonyl Compounds (C8-C26) in Wintertime Atmospheric Aerosol in London, UK”

General Comments:

This study provides measurements of three groups of carbonyls: n-alkanals, n-alkan-2-ones, and n-alkan-3-ones across a wide range of carbon numbers in both the gas and particle phases at one urban and three background sites of London. The n-alkanal concentrations were observed to be the highest at all sites, followed by those of the n-alkan-2-ones, and n-alkan-3-ones. Homologue distributions are presented and tracer correlations are explored to infer anthropogenic emissions as the primary source for alkanals. Empirical gas-particle partitioning coefficients are also provided. While generally this dataset has value and would be of interest to ACP readership, the manuscript’s writing needs to be greatly improved before publication. Improvements in terms of organization, focus, and precision of discussions when comparing to previous literature are suggested in the specific comments below. Regarding organization, authors should consider reordering some sections as results or statements are made as fact without support until much later in the manuscript (e.g. alkanals are said early on to be from anthropogenic emissions, yet measurements and analysis support of this are discussed near end).

Specific Comments:

1. Lines 117-118: What were the recovery efficiencies? Was breakthrough of the PTFE filters addressed? Specifically, semi-volatile components in particles that make it to the sorbent tubes?

RESPONSE: Filter artefacts were not evaluated, but this kind of sampling train is in widespread use. Provided pressure drops are modest, loss from the particles should be minimal. A breakthrough test was made on the sorption tubes and showed a minimal breakthrough for alkanes $\geq C_{11}$.

2. Line 246: CPI has not been introduced properly to discuss here out of context.

RESPONSE: An explanation of CPI values is now included.

3. Presentation of literature should be more precisely worded regarding use of Zhang, Ruehl, Schilling Fahnestock, and Yee et al. references:

a. Line 74-75: Add Yee et al., 2012 with this group.

RESPONSE: This reference has been added.

b. Only reference Zhang et al., 2015 and Ruehl et al., 2013 positively identify carbon position of the carbonyl groups. Other references sum isomers together/propose structures of compounds with some of the ketone group positions listed in lines 80-82, but they were not specifically isolated as authors suggest. Probably better to simply delete those lines.

RESPONSE: The lines have been amended to indicate that carbon positions of carbonyl groups were not identified in all studies.

i. Lines 80-82 should be revised to read more along the lines of, "...chamber studies of dodecane oxidation include observation of aldehydes and ketones as oxidation products...".

RESPONSE: Amended as recommended.

ii. In lines 250-253, to generally say that these compounds with "few carbon atoms are believed mainly to originate as the fragmental products from n-alkanes" and that "higher compounds are mainly generated from functional pathways" as an extension to the atmosphere is not actually supported by these references. Further, what is the cutoff for "few carbon atoms"? It seems that the authors instead are inferring this in the context of their results. It may be possible for their measurements to address this question in fact, which would be interesting and should be brought to more focus in the Introduction if so. Authors should at minimum revise the wording to "*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; SchillingFahnestock et al., 2015) or as functionalized products from heterogeneous oxidation of particle-bound alkanes (Ruehl et al., 2013; Zhang et al., 2015).*"

RESPONSE: The suggested wording has been added to the text.

4. Lines 260-278: This discussion seems more relevant to put in the introduction as motivation for why measurement of carbonyls and the specific carbon position of ketones is important. If the authors can restructure the writing, it seems that they are trying to utilize their measurements to infer sources of the measured carbonyls from homogenous/gas-phase oxidation and heterogeneous oxidation which is told by ketone number position. Though, this is not rigorously addressed using the measurements in the same way Zhang et al., 2015 do. So, either limit the specificity on the literature that is presented here and change language throughout the manuscript to "lightly" suggest chamber and flow tube measurements as supporting the trends in the presented measurements or do a more rigorous analysis to focus on the phase of oxidation and ratios of ketone carbon number position. This is further difficult to address with the measurements presented as is because there are no n-alkane distributions provided. The authors need to adjust the certainty in language used when describing that something must derive from gas or heterogeneous oxidation.

RESPONSE: The text has been substantially revised.

5. Line 280: Are there references that can be added to support anthropogenic activities as a source of aldehydes and to what degree? Cite Table S3 here. This becomes addressed later in the manuscript, so it seems odd to state with such certainty early-on without providing the measurements and discussions up front.

RESPONSE: Lines 280-282 have been revised to include references.

6. Line 284: Where do these numbers come from? Include the particulate form % for the low MW n-alkanes here to compare with that of C14-C36. Why are these not included along in an SI Table like Table 2 or with Table 2?

RESPONSE: The n-alkane data will be published elsewhere. The text has been amended to reflect this.

7. Lines 265, 288, 297 (and any others throughout manuscript): Replace "homogeneous" with "gas-phase". Homogeneous reaction should not be used to synonymously refer to the gas-phase reaction of alkane (gas) + OH (gas). One could have a homogeneous reaction in the particle phase as well (both reactants are in the particle phase). Heterogeneous reaction across phases: OH (gas) reacting with alkane (particle phase) in some contexts presented in the manuscript.

RESPONSE: Amended as recommended.

8. Lines 287-289: The authors should provide context as to what these ratios mean, what ranges are expected for meaning what (primarily gas-phase vs heterogeneous oxidation, etc.).

RESPONSE: As implied by the previous sentence, a ratio of >1 can be taken to imply a heterogeneous mechanism in the absence of primary sources.

9. Lines 289-290: Provide additional support from literature or from the conducted measurements for this claim of 2-ketones being from primary emission sources that are supported. For example, Table S3 provides some support for alkanals correlation with BC and NO_x, but why is this analysis not done with the 2-ketones as well? Correlations are provided much later in manuscript. Why not provide similar Table S3 for ketone groups?

RESPONSE: A reference to primary emissions has been added at this point. The section on correlations addresses 3-ketones as well as 2-ketones. See Section 3.2.3.

10. Lines 290-292: Are the photochemical conditions (e.g. NO_x conditions) during the field studies close enough to those of the cited chamber studies (low-NO_x) from Yee et al. 2012 and Schilling Fahnstock et al., 2015 to be applicable here as plausible mechanisms? It seems that in non-rural environments, well-established mechanisms of ketone formation as in Lim et al., 2009 for alkane oxidation in the presence of NO_x would be another/more applicable route of formation to explain these products. Further, what are the actual NO_x levels in the current study?

RESPONSE: The average NO_x concentrations were EL(23.35 µg/m³), MR(202 µg/m³) and were not measured at the RU and WM sites. The concentrations of NO_x (RU, WM, EL, MR) during our sampling period were between the low-NO_x (Yee et al., 2012; Schilling Fahnstock et al., 2015) and high-NO_x condition (Lim and Ziemann, 2009). Additional text is now included which discusses the mechanistic implications of the presence of NO, and now includes reference to the work of Lim and Ziemann.

11. Line 303: This claim is too strong as the measurements might be indicative of such, but there are no measurements that actually verify this. Change "...were attributed to...", to "might be explained by" and "...reactions were expected..." to "would be the expected dominant pathway."

RESPONSE: Agreed. Amended as suggested.

12. Section 3.2: This is oddly placed and should really be placed at the beginning of the Results and Discussion section as Section 3.1. Figure 3 should come before Figure 2.

RESPONSE: Moved, as recommended.

13. Line 330: It would be beneficial to the readers to include a brief sentence orienting the range in CPI values that is traditionally assumed to be indicative of anthropogenic/biogenic sources. Same with C_{max}. Also, lines 330-331 do not make sense as written. C_{max} is merely the carbon number of the carbonyl with the highest concentration, correct?

RESPONSE: A brief explanation of CPI has been added. We thank the reviewer for pointing out the meaningless nature of lines 330-331 and have now amended the sentence.

14. Lines 337-338: Seems that in arguing for any carbonyl to be an oxidation product, fragment, or primary emission, the authors should present C_{max} and CPI values for distributions of regular n-alkanes.

RESPONSE: The n-alkane data will be presented elsewhere. A sentence has been added to summarise the homologue distributions (C_{max}) and CPI values) of the n-alkanes.

15. Lines 380-384: This paragraph is out of place and does not provide value to the manuscript (at least is not further placed in context or expanded upon).

RESPONSE: This material has been edited and moved to the first paragraph of this section.

16. Lines 388-390: Not sure what is meant here.

RESPONSE: Now amended to clarify.

17. Lines 427-438: Do the diesel engine laboratory tests show indications of ketones in the exhaust as well to support some of the hypotheses made here?

RESPONSE: Ketones were below detection limit in the diesel exhaust. This information has been added to this section.

18. Lines 451-453: Why was this assumption made when measurements of these compounds were actually performed to get empirical K_p?

RESPONSE: This statement has been modified in the light of comments from both reviewers.

19. Table 2: It would be helpful in interpretation of the results here to show TSP values as well (For example: why is % in particle phase higher for similar carbon #'s at EL site?)

RESPONSE: The values are as below. These have been added to the SI. We have an explanation for the % particle phase being higher at EL.

Sites	PM ₁₀ Range, µg/m ³	PM ₁₀ Mean µg/m ³	Note
RU and WM	10.8-72.4	34.1	The sampling period was dominated by southerly winds and the data from London, North Kensington were used as this is an upwind urban background site.
EL	4.37-27.1	19.3	The PM ₁₀ data was obtained from the London North Kensington site (Defra), because the EL only have PM _{2.5} data, and the PM _{2.5} data of two site (EL and London North Kensington) were close to each other.
MR	12.6-78.7	30.7	MR site

20. Lines 487-491: These sentences seem contradictory pointing to heterogeneous n-alkane oxidation vs anthropogenic primary sources as origin of the ketones. Perhaps just language needs to be changed to not make it seem like one source dominates over the other.

RESPONSE: We agree that this was contradictory and have amended it to provide greater clarity.

21. The conclusions section is written more like a results and discussion section with specific correlations, ratios, and comparisons of these ratios to fuel sources. Rewrite to focus more on bigger implications. For example, what are the implications of 2-ketones regression of log K_p vs vapor pressure having a better fit compared to the alkanals and the 3-ketones? Seems like this should say something about equilibrium vs non-equilibrium conditions and the timescales of aging, oxidation, and partitioning. Is this indicative of specific chemical pathways and/or uncertainties not properly accounted for the alkanals and 3-ketones source?

RESPONSE: The reviewer raised a good point for which we add new text.

Technical Corrections:

1. No need to repeat lines 176-178 from lines 141-143.

RESPONSE: Agreed and amended.

2. Lines 192-194: Seems unnecessary to make this separate paragraph.

RESPONSE: Agreed and amended.

3. It does not seem convention to specify the C1 position for aldehyde names as in:

a. Line 80, "1-undecanal" should just be undecanal

b. Figure 3 caption. "1-" for alkanals

c. Line 280

RESPONSE: Agreed and amended.

4. Line 274: Change subscripted reference 18 to proper format.

RESPONSE: Agreed and amended.

5. Line 355: repetitive C_{max} information on MR can be deleted.

RESPONSE: We do not find any repetition.

6. Line 440: Suggest renaming this section to “Gas and Particle Phase Partitioning”

RESPONSE: Agreed and amended.

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3 **Aliphatic Carbonyl Compounds (C₈-C₂₆) in Wintertime**
4 **Atmospheric Aerosol in London, UK**
5

6 **Ruihe Lyu^{1,2}, Mohammed Salim Alam¹, Christopher Stark¹**

7 **Ruixin Xu¹, Zongbo Shi¹, Yinchang Feng² and Roy M. Harrison^{†*1}**
8

9 **¹ Division of Environmental Health and Risk Management**
10 **School of Geography, Earth and Environmental Sciences, University of**
11 **Birmingham Edgbaston, Birmingham B15 2TT, UK**
12

13 **² State Environmental Protection Key Laboratory of Urban Ambient Air**
14 **Particulate Matter Pollution Prevention and Control, College of Environmental**
15 **Science and Engineering**
16 **Nankai University, Tianjin 300350, China**
17
18
19

20 **† Also at: Department of Environmental Sciences / Centre of Excellence in Environmental**
21 **Studies, King Abdulaziz University, PO Box 80203, Jeddah, 21589, Saudi Arabia.**
22

23 **Corresponding authors:**

24 E-mail: r.m.harrison@bham.ac.uk (Roy M. Harrison)
25

26 **ABSTRACT**

27 Three groups of aliphatic carbonyl compounds, the n-alkanals (C₈-C₂₀), n-alkan-2-ones (C₈-C₂₆) and
28 n-alkan-3-ones (C₈-C₁₉) were measured in air samples collected in London from January-April 2017.
29 Four sites were sampled including two roof-top background sites, one ground-level urban background
30 site and a street canyon location on Marylebone Road in central London. The n-alkanals showed the
31 highest concentrations followed by the n-alkan-2-ones and the n-alkan-3-ones, the latter having
32 appreciably lower concentrations. It seems likely that all compound groups have both primary and
33 secondary sources and these are considered in the light of published laboratory work on the oxidation
34 products of high molecular weight n-alkanes. All compound groups show relatively low correlation
35 with black carbon and NO_x in the background air of London, but in street canyon air heavily impacted
36 by vehicle emissions, stronger correlations emerge especially for the n-alkanals. It appears that
37 vehicle exhaust is likely to be a major contributor for concentrations of the n-alkanals whereas it is a
38 much smaller contributor to the n-alkan-2-ones and n-alkan-3-ones. Other primary sources such as
39 cooking or wood burning may be significant contributors for the ketones but were not directly
40 evaluated. It seems likely that there is also a significant contribution from photo-oxidation of n-
41 alkanes and this would be consistent with the much higher abundance of the n-alkan-2-ones relative
42 to the n-alkan-3-ones if the formation mechanism were to be through oxidation of condensed phase
43 alkanes. Vapour-particle partitioning fitted the Pankow model well for the n-alkan-2-ones but less
44 well for the other compound groups, although somewhat stronger relationships were seen at the
45 Marylebone Road site than at the background sites. The former observation gives support to the n-
46 alkane-2-ones being a predominantly secondary product, whereas primary sources of the other groups
47 are more prominent.

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

50 1. INTRODUCTION

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

56

57 The most abundant atmospheric carbonyls are methanal (formaldehyde) and ethanal (acetaldehyde),
58 and many studies have described their emission sources and chemical formation in urban and rural
59 samples (Duan et al., 2016). Long-chain aliphatic carbonyl compounds have been identified in PM
60 and reported in few published papers (Gogou et al., 1996; Andreou and Rapsomanikis, 2009), and
61 these compounds are considered to be formed from atmospheric oxidation processes affecting
62 biogenic emissions of alkanes. Anthropogenic activity is also considered to be a significant
63 contributor to the aliphatic carbonyls. Appreciable concentrations of aliphatic carbonyl compounds
64 have been identified in emissions from road vehicles (Schauer et al., 1999[a](#); [2002b](#)), coal combustion
65 (Oros and Simoneit, 2000), wood burning (Rogge et al., 1998) and cooking processes (Zhao et al.,
66 [2007a,b](#)), spanning a wide range of molecular weights. Furthermore, chamber studies (Chacon-
67 Madrid and Donahue, 2011; Algrim and Ziemann, 2016) have demonstrated that the aliphatic
68 carbonyl compounds are very important precursors of secondary organic aerosol (SOA) when they
69 react with OH radicals in the presence of NO_x.

70

71 The oxidation of n-alkanes by hydroxyl radical is considered to be an important source of aliphatic
72 carbonyl compounds. It was believed that the n-alkanals with carbon atoms numbering less than 20
73 indicate oxidation of alkanes, whereas the higher compounds were usually considered to be of direct
74 biogenic origin (Rogge et al., 1998). The homologues and isomers of n-alkanals and n-alkanones have
75 been identified as OH oxidation products of n-alkanes in many chamber and flow tube studies (Zhang
76 et al., 2015; Schilling Fahnstock et al., 2015; Ruehl et al., 2013; Yee et al., 2012), although not all
77 studies identified the position of the carbonyl group. The commonly accepted oxidation pathways of
78 n-alkanes generally divide into functionalization and fragmentation. Functionalization occurs when
79 an oxygenated functional group ($-\text{ONO}_2$, $-\text{OH}$, $-\text{C}=\text{O}$, $-\text{C}(\text{O})\text{O}-$ and $-\text{OOH}$) is added to a molecule,
80 leaving the carbon skeleton intact. Alternatively, fragmentation involves C–C bond cleavage and
81 produces two oxidation products with smaller carbon numbers than the reactant. The chamber studies
82 of dodecane oxidation ~~have identified 1-undecanal, hexan-3-one, octan-3-one, heptan-2-one, nonan-~~
83 ~~2-one and decan-2-one as~~ Oh include observations of aldehydes and ketones as oxidation products
84 (Schilling Fahnstock et al., 2015; Yee et al., 2012).

85

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

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

97

98 **2. MATERIALS AND METHODS**

99 **2.1 Sampling Method and Site Characteristics**

100 Three sampling campaigns were carried out between 23 January and 18 April 2017 at four sampling
101 sites (Figure 1) in London. The first campaign used two sampling sites, one located on the roof of a
102 building (15 m above ground) of the Regent's University (51°31'N, -0°9'W), hereafter referred to as
103 RU, sampled from 23 January 2017 to 19 February 2017, the other located on the roof (20 m above
104 ground) of a building which belongs to the University of Westminster on the southern side of
105 Marylebone Road (hereafter referred to as WM), sampled from 24 January 2017 to 20 February 2017.
106 The third sampling site was located at ground level at Eltham (51°27'N, 0°4'E), hereafter referred to
107 as EL, sampled from 23 February 2017 to 21 March 2017, which is located in suburban south London,
108 and the fourth sampling site was located at ground level on the southern side of Marylebone Road
109 (51°31'N, -0°9'W), hereafter referred to as MR, sampled from 22 March 2017 to 18 April 2017.
110 Marylebone Road is in London's commercial centre, and is an important thoroughfare carrying 80-
111 90,000 vehicles per day through central London. The Regent's University site is within Regent's
112 Park to the north of Marylebone Road. The Eltham site is in a typical residential neighbourhood, 22
113 km from the MR site. Earlier work at the Marylebone Road and a separate Regent's Park site is
114 described by Harrison et al. (2012).

115

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

127

128 **2.2 Analytical Instrumentation**

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

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

138

139 **2.3 Analysis of Samples**

140 Standards used in these experiments included 19 alkanes, C₈ to C₂₆ (Sigma-Aldrich, UK, purity
141 >99.2%); 12 n-aldehydes, C₈ to C₁₃ (Sigma-Aldrich, UK, purity ≥95.0%), C₁₄ to C₁₈ (Tokyo
142 Chemical Industry UK Ltd, purity >95.0%); and 10 2-ketones, C₈ to C₁₃ and C₁₅ to C₁₈ (Sigma-
143 Aldrich, UK, purity ≥98.0%) and C₁₄ (Tokyo Chemical Industry UK Ltd, purity 97.0%).

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145 The filters were spiked with 30.0 µL of 30.0 µg mL⁻¹ deuterated internal standards (dodecane-d₂₆,
146 pentadecane-d₃₂, eicosane-d₄₂, pentacosane-d₅₂, triacontane-d₆₂, butylbenzene-d₁₄, nonylbenzene-
147 2,3,4,5,6-d₅, biphenyl-d₁₀, p-terphenyl-d₁₄; Sigma-Aldrich, UK) for quantification and then
148 immersed in dichloromethane (DCM), and ultra-sonicated for 20.0 min at 20.0°C. The extract was
149 filtered using a clean glass pipette column packed with glass wool and anhydrous Na₂SO₄, and
150 concentrated to 50.0 µL under a gentle flow of nitrogen for analysis using GC × GC-ToF-MS. 1 µL
151 of the extracted sample was injected in a split ratio 100:1 at 300°C. The initial temperature of the
152 primary oven (80.0°C) was held for 2.0 min and then increased at 2.0 °C min⁻¹ to 210°C, followed by
153 1.5 °C min⁻¹ to 325 °C. The initial temperature of the secondary oven (120°C) was held for 2.0 min
154 and then increased at 3.0°C min⁻¹ to 200°C, followed by 2.00°C min⁻¹ to 300°C and a final increase
155 of 1.0°C min⁻¹ to 330 °C to ensure all species passed through the column. The transfer line
156 temperature was 330 °C and the ion source temperature was 280°C. Helium was used as the carrier

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

159

160 The sorbent tubes were analyzed by an injection port thermal desorption unit (Unity 2, Markes
161 International, Llantrisant, UK) and subsequently analyzed using GC × GC-ToF-MS. Briefly, the
162 tubes were spiked with 1 ng of deuterated internal standard for quantification and desorbed onto the
163 cold trap at 350°C for 15.0 min (trap held at 20.0°C). The trap was then purged onto the column in
164 a split ratio of 100:1 at 350°C and held for 4.0 min. The initial temperature of the primary oven
165 (90.0°C) was held for 2.0 min and then increased to 2.0°C min⁻¹ to 240°C, followed by 3.0°C min⁻¹
166 to 310°C and held for 5.0 min. The initial temperature of the secondary oven (40.0°C) was held for
167 2.0 min and then increased at 3.0°C min⁻¹ to 250°C, followed by an increase of 1.5°C min⁻¹ to 315°C
168 and held for 5.0 min. Helium was used as carrier gas for the thermally desorbed organic compounds,
169 with a gas flow rate of 1.0 mL min⁻¹.

170

171 *Qualitative analysis*

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

178

179 *Quantitative analysis*

180 An internal standard solution (~~including dodecane-d₂₆, pentadecane-d₃₂, eicosane-d₄₂, pentacosane-~~
181 ~~d₅₂, triacontane-d₆₂, nonylbenzene-2,3,4,5,6-d₅, butylbenzene-d₁₄, biphenyl-d₁₀, p-terphenyl-d₁₄)~~
182 ~~(Sigma-Aldrich, UK outlined above)~~ was added to the samples to extract prior to instrumental analysis.

183 Five internal standards (pentadecane-d₃₂, eicosane-d₄₂, pentacosane-d₅₂, triacontane-d₆₂,
184 nonylbenzene-2,3,4,5,6-d₅) were used in the calculation of carbonyl compound concentrations.

185

186 The quantification for alkanes, aldehydes and 2-ketones was performed by the linear regression
187 method using seven-point calibration curves (0.05, 0.10, 0.25, 0.50, 1.00, 2.00, 3.00 ng μL^{-1})
188 established between the authentic standards/internal standard concentration ratios and the
189 corresponding peak area ratios. The calibration curves for all target compounds were highly linear
190 ($r^2 > 0.99$, from 0.990 to 0.997), demonstrating the consistency and reproducibility of this method.

191 Limits of detection for individual compounds were typically in the range 0.04–0.12 ng m^{-3} . 3-ketones
192 were quantified using the calibration curves for 2-ketones. This applicability of quantification of
193 individual compounds using isomers of the same compound functionality (which have authentic
194 standards) has been discussed elsewhere and has a reported uncertainty of 24% (Alam et al., 2018).

195 Alkan-2-ones and alkan-3-ones were not well separated by the chromatography. These were separated
196 manually using the peak cutting tool, attributing fragments at m/z 58 and 71 to 2-ketones and m/z 72
197 and 85 to 3-ketones. ~~The calibration for 2 ketones was applied to quantification of the 3 ketones.~~

198 Field and laboratory blanks were routinely analysed to evaluate analytical bias and precision. Blank
199 levels of individual analytes were normally very low and in most cases not detectable. Recovery
200 efficiencies were determined by analyzing the blank samples spiked with standard compounds. Mean

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

203

204 3. RESULTS AND DISCUSSION

205 3.1 Mass Concentration of Particle-Bound Carbonyl Compounds

206 The study of temporal and spatial variations of air pollutants can provide valuable information about
207 their sources and atmospheric processing. The time series of particle-bound n-alkanals, n-alkan-2-
208 ones, and n-alkan-3-ones are plotted in Figure- 32. It is clear that the concentrations of n-alkanals
209 varied substantially with date, and were always higher than n-alkanones at four sites. It is also clear
210 from Figure 23 that concentrations were broadly similar at the background sites, RU, WM and EL,
211 but are elevated, especially for the n-alkanals, at MR. This is strongly indicative of a road traffic
212 source.

213

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

222 from the oxidation of octacosane, giving relative, but not absolute yields. Schilling Fahnestock et
223 al. (2014) report oxidation products of dodecane formed in both low-NO and high NO environments
224 (<d.l and NO = 97.5 ppb respectively). A singly substituted unfragmented ketone product is
225 reported only from the low-NO oxidation, and in relatively low yield amongst many products. Lim
226 and Ziemann (2009) propose a reaction scheme for the OH-initiated oxidation of alkanes in the
227 presence of NO_x. They express the view that first generation carbonyl formation is negligible at
228 high NO concentrations for linear alkanes with C_n>6 since reactions of an alkylperoxy radical with
229 O₂ are too slow to compete with isomerisation, which leads ultimately to hydroxynitrate and
230 hydroxycarbonyl products. Ziemann (2011) also shows a substantial yield of alkylnitrates from OH-
231 initiated oxidation of n-alkanes from C₁₀-C₂₅ in the presence of NO. The NO concentrations in the
232 background air of London are <12 ppb typically (UK-Air, 2018), and hence lie between the low and
233 high NO environments of experiments in the literature, therefore most probably permitting some
234 oxidation to proceed through pathways leading to first generation carbonyl products.

235

236 Figure- 2-3 shows the average total concentrations of particle-bound 1-alkanals, n-alkan-2-ones, and
237 n-alkan-3-ones from January to April at four measurement sites, and the particle and gaseous phase
238 concentrations are detailed in the Table S1 (Supporting Information). Total n-alkanals was defined
239 as the sum of particle-bound n-alkanals ranging from C₈ to C₂₀. The particulate n-alkanals at the MR
240 site accounted for 75.2% of the measured particle carbonyls with the average total concentration of
241 682 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
242 ng m⁻³ at RU, accounting for 57.0%, 57.9% and 56.3% of the measured particulate carbonyls,
243 respectively. The n-alkanals identified in this study differed ~~in some aspects~~ substantially from those

244 previously reported in samples collected from Crete (Gogou et al., 1996) and Athens (Andreou and
245 Rapsomanikis, 2009) in Greece. The n-alkanals from London presented narrower ranges of carbon
246 numbers and a higher concentration than rural and urban samples from Crete. The concentrations of
247 n-alkanal homologues (C₈-C₂₀) ranged from 5.50 to 141 ng m⁻³ (average 52.0 ng m⁻³) at MR which
248 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
249 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
250 concentrations were 0.9-3.7 ng m⁻³ in rural (C₁₅-C₃₀) and 5.4-6.7 ng m⁻³ in urban (C₉-C₂₂) samples,
251 and the average concentration of all four sites was much higher than the 0.91 ng m⁻³ measured in
252 Athens (Andreou and Rapsomanikis, 2009) (C₁₃-C₂₀). This is a clear indication of a road traffic,
253 most probably diesel source which is greater in London.

254
255 As part of the CARBOSOL project (Oliveira et al., 2007), air samples were collected in summer and
256 winter at six rural sites across Europe. The particulate n-alkanals ranged from C₁₁ to C₃₀ with average
257 total concentrations between 1.0 ng m⁻³ and 19.0 ng m⁻³, with higher concentrations in summer than
258 winter at all but one site. ~~These concentrations fall well below those measured in the present study,~~
259 ~~although the range of compounds differed.~~ Maximum concentrations at all sites were in
260 compounds >C₂₂ indicating a source from leaf surface abrasion products and biomass burning
261 (Simoneit et al., 1967; Gogou et al., 1996). This far exceeds the C_{max} values seen in the particulate
262 fraction at our sites.

263
264 Atmospheric concentrations of long-chain n-alkan-3-ones have not previously been reported in the
265 literature. The n-alkan-2-one and n-alkan-3-one homologues with few carbon atoms are believed

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

270 The n-alkan-2-one homologues measured in London ranged from C₈ to C₂₆, and the average total
271 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
272 186 ng m⁻³ at MR, approximately accounting for 39.9% (RU), 37.0% (WM), 38.1% (EL) and 20.5%
273 (MR) of the total particulate carbonyls, respectively (Figure- 23). The published data from Greece
274 indicated that the concentrations of n-alkan-2-ones were independent of the seasons, and an average
275 of 5.40 ng m⁻³ (C₁₃-C₂₉) was measured in August and 5.44 ng m⁻³ in March at Athinas St, but 12.88
276 ng m⁻³ was measured in March at the elevated (20 m) AEDA site in Athens (Gogou et al., (1996).
277 Concentrations in Crete for alkan-2-ones (C₁₀-C₃₁) were 0.4-2.1 ng m⁻³ at the rural site and 1.9-2.6
278 ng m⁻³ at the urban site (Andreou and Rapsomanikis, 2009). The CARBOSOL project also
279 determined concentrations of n-alkan-2-ones, between C₁₄ and C₃₁ with a C_{max} at C₂₈ or C₂₉ at all
280 but one site. Average concentrations ranged from 0.15 ng m⁻³ (C₁₇₋₂₉) to 3.35 (C₁₄-C₃₁), very much
281 below the concentrations at our London sampling site. Cheng et al. (2006) measured concentrations
282 of n-alkan-2-ones in the Lower Fraser Valley, Canada, in PM_{2.5}. Samples collected in a road tunnel
283 showed the highest concentrations, total 1.8-12.6 ng m⁻³ for C₁₀-C₃₁, and were higher in daytime
284 than nighttime. Concentrations at a forest site were 1.1-7.2 ng m⁻³ without a diurnal pattern. Values
285 of C_{max} ranged from C₁₆₋₁₇ at the road tunnel to C₂₇ (secondary maximum) at the forest site. Values
286 of CPI averaged across sites from 1.00 to 1.34, giving little evidence for a substantial biogenic input

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

289

290 ~~Atmospheric concentrations of long chain n-alkan-3-ones have not previously been reported in the~~
291 ~~literature. The n-alkan-2-one and n-alkan-3-one homologues with few carbon atoms are believed~~
292 ~~mainly to originate as the fragmental products of n-alkanes (Yee et al., 2012; Schilling Farnestock~~
293 ~~et al., 2015), whereas the higher compounds are mainly generated from functional pathways (Zhang~~
294 ~~et al., 2015; Ruehl et al., 2013).~~ The n-alkan-3-one homologues identified in the samples ranged
295 from C₈ to C₁₉, and the average of individual compound concentrations was 0.52 ng m⁻³ at RU, 0.94
296 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
297 the four sites were lower than the n-alkanals and n-alkan-2-ones, and MR had the highest average
298 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
299 ng m⁻³ at RU, respectively.

300

301 The isomeric carbonyls formed via OH-initiated heterogeneous reactions of n-octacosane (C₂₈)
302 exhibit a pronounced preference at the 2-position of the molecule chain (Ruehl et al., 2013). The n-
303 octacosan-2-ones have the highest relative yield (1.00), followed by n-octacosan-3-ones (0.50), while
304 other isomeric carbonyl yields were lower than 0.20. The same results were found in the subsequent
305 chamber studies of n-alkanes (Zhang et al., 2015) (C₂₀, C₂₂, C₂₄ but not C₁₈). The main probable
306 reason was that a large fraction of C₁₈ evaporated into the gas phase, and OH oxidation happened in
307 the gas phase (homogeneous reaction). This may be supported by the evidence from previous studies
308 (Kwok and Atkinson, 1995; Ruehl et al., 2013), which found that the isomeric distribution of

309 oxidation products of n-alkanes depends upon whether the reaction occurs in the gas phase or at the
310 particle surface (Kwok and Atkinson, 1995; Ruehl et al., 2013). The homogeneous gas-phase
311 oxidation occurs fast, and H-abstraction by OH radicals occurs at all carbon sites. The fractions of
312 the OH radical reaction by H atom abstraction from n-decane at the 1-, 2-, 3-, 4- and 5-positions are
313 3.10%, 20.7%, 25.4%, 25.4%, and 25.4%, respectively, and the products from gas phase
314 (homogeneous) reaction were generally in accord with structure-reactivity relationship (SRR)
315 predictions (Kwok and Atkinson, 1995; Aschmann et al., 2001). Zhang et al. (2015) report on the
316 competition between homogeneous and heterogeneous oxidation of medium to high molecular weight
317 alkanes. They express the view that in the atmosphere, compounds typically classified as semi-
318 volatile evaporate sufficiently rapidly that homogeneous gas phase oxidation is more rapid than
319 oxidation in the condensed phase. Recently published studies have found that the isomeric
320 distribution of first-generation oxidation products of n-alkanes depends strongly upon whether the
321 reaction occurs in the gas phase or at the particle surface (Kwok and Atkinson, 1995; Ruehl et al.,
322 2013). The homogeneous gas-phase oxidation occurs fast, and H-abstraction by OH radicals occurs
323 at all carbon sites. The fractions of the OH radical reaction by H atom abstraction from n-decane at
324 the 1-, 2-, 3-, 4- and 5-positions are 3.10%, 20.7%, 25.4%, 25.4%, and 25.4%, respectively, and the
325 products from homogeneous reaction were generally in accord with structure-reactivity relationship
326 (SRR) predictions (Kwok and Atkinson, 1995; Aschmann et al., 2001). Reaction of particulate n-
327 alkanes is dominated by heterogeneous reactions with OH, and the H-abstraction occurs preferentially
328 at the 2-position of the carbon chain (Zhang et al., 2015; Ruehl et al., 2013). The n-alkanes diffuse
329 from the inner particle to the surface, where the OH will quickly attack the H atom of 1 and 2 position
330 carbons. The intermediate products at the 2-position are relatively more stable than at the 1-position,

331 ~~and the products are dominated by oxidation of the 2-position. The isomeric carbonyls formed via~~
332 ~~OH initiated heterogeneous reactions of n-octacosane (C₂₈) exhibit a pronounced preference at the 2-~~
333 ~~position of the molecule chain¹⁸. The n-octacosan 2-ones have the highest relative yield (1.00),~~
334 ~~followed by n-octacosan 3-ones (0.50), while other isomeric carbonyl yields were lower than 0.20.~~
335 ~~The same results were found in the subsequent chamber studies of n-alkanes (Zhang et al., 2015) (C₂₀,~~
336 ~~C₂₂, C₂₄) but not C₁₈. The main reason was that OH oxidation of C₁₈ was dominated by the~~
337 ~~homogeneous reaction as a large fraction of C₁₈ evaporated into the gas phase.—~~

338

339 During the field experiment, the n-alkanal homologues were abundant in all samples, and this is
340 probably attributable to the primary emission sources, including diesel vehicles (Schauer et al.,
341 1999a), gasoline cars (Schauer et al., 2002b), wood burning (Rogge et al., 1998) and cooking aerosol
342 (Schauer et al., 1999b). Correlations with other largely vehicle-generated pollutants (see later)
343 support this interpretation. ~~During the field experiment, the 1-alkanal homologues were abundant~~
344 ~~in all samples, and this could be explained by a strong impact of anthropogenic activities. Thus, the~~
345 ~~n-alkanals are considered to arise mainly from primary emission sources. Furthermore, t~~
346 ~~particulate form of the n-alkane homologues (C₁₄-C₃₆) identified in the samples ranged from 50-~~
347 ~~100% dominated for >C₂₅ in contrast to and there was a significant particulate fraction for all but the~~
348 ~~low MW n-alkanes (unpublished data C₁₁-C₁₃). The H-abstraction by OH radicals may therefore have~~
349 ~~been dominated by heterogeneous reactions generating the higher concentrations of n-alkan-2-ones~~
350 ~~than n-alkan-3-ones that were found in all samples. The ratio of n-alkan-2-ones/n-alkan-3-ones (C₁₁-~~
351 ~~C₁₈) with the same carbon atom number ranged from 2.35-11.3 at four measurement sites.~~
352 ~~Surprisingly, although the n-alkane (C₁₁-C₁₃) oxidation was expected to be dominated by~~

353 homogeneous gas phase reactions, the n-alkan-2-one/n-alkan-3-one ratios were still greater than 2.00.
354 The probable reason was that the lower molecular weight n-alkan-2-ones were significantly impacted
355 by primary emission sources such as cooking (Zhao et al., 2007a,b). Another likely reason is that the
356 n-alkan-2-one and n-alkan-3-one homologues with lower carbon atom numbers originated in part
357 from the fragmental products of higher n-alkanes (Yee et al., 2012; Schilling Fahnstock et al., 2015).
358
359 The ratios of n-alkan-2-ones/n-alkanes, n-alkan-3-ones/n-alkanes (with same carbon numbers) were
360 calculated and are reported in Table S2. The n-alkan-3-ones with carbon numbers higher than C₂₀
361 were not identified in the samples, indicating that both the homogeneous gas phase and heterogeneous
362 reactions of higher molecular weight n-alkanes were slow, the former probably due to the low vapour
363 phase presence of n-alkanes. The ratios of n-alkan-3-ones/n-alkanes at four measurement sites
364 gradually increased from C₁₁, and then decreased from C₁₇, while higher ratios of n-alkan-2-ones/n-
365 alkanes were observed in the range from C₁₇ to C₂₂, probably indicating a shift from homogeneous
366 reactions to heterogeneous reactions with the increase of carbon numbers. The low ratios of n-alkan-
367 2-ones/n-alkanes with carbon numbers from C₂₃ to C₂₆ ~~were attributed to~~ might be explained by the
368 low diffusion rate from the inner particle to the surface with the increasing carbon number of n-
369 alkanes, even though heterogeneous reactions ~~were~~ would be the expected dominant pathway.

370

371 **3.2 — Temporal and Spatial Variations**

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

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

378

379 **3.3.2 Sources of Carbonyl Compounds**

380 **3.3.2.1 Homologue distribution and carbon preference index (CPI)**

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

384

$$385 \quad \text{CPI} = \frac{1}{2} \left(\frac{\sum_4^m C_{2i+1}}{\sum_4^m C_{2i}} + \frac{\sum_4^m C_{2i+1}}{\sum_5^{m+1} C_{2i}} \right)$$

$$386 \quad \text{For n-alkanals and n-alkan-3-ones (m=9): } \text{CPI} = \frac{1}{2} \left(\frac{\sum \text{odd}(C_9-C_{19})}{\sum \text{even}(C_8-C_{18})} + \frac{\sum \text{odd}(C_9-C_{19})}{\sum \text{even}(C_{10}-C_{20})} \right)$$

$$387 \quad \text{For n-alkan-2-ones (m=12): } \text{CPI} = \frac{1}{2} \left(\frac{\sum \text{odd}(C_9-C_{25})}{\sum \text{even}(C_8-C_{24})} + \frac{\sum \text{odd}(C_9-C_{25})}{\sum \text{even}(C_{10}-C_{26})} \right)$$

388

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

390 $m = 9$ for n-alkanal and n-alkan-3-ones

391 $m = 12$ for n-alkan-2-ones

392

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

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

399
400 The n-alkanes which are potential precursors of the oxygenates described typically showed two C_{\max}
401 values, the first at C_{13} (the lowest MW compound measured), and at C_{23} . The CPI values for the
402 n-alkanes were between 0.97-1.02 at the four measurements sites (unpublished data).

403
404 According to the low CPI (0.41-1.07) at the four sites, the n-alkanal homologues with carbon number
405 from C_8 to C_{20} mainly originate from anthropogenic emissions or OH oxidation of anthropogenic
406 fossil-derived hydrocarbons. The particle-bound n-alkanals exhibited a similar distribution of carbon
407 number from January to April at four sites, and they had the same C_{\max} at C_8 with concentration 28.6
408 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
409 compound may be a fragmentation product, oxidation product or primary emission. In addition, the
410 distribution of n-alkanals had a second concentration peak at C_{15} (MR) and C_{18} (RU, WM, and EL).
411 The C_{18} compound was observed accounting for the highest percentage of the total mass of n-
412 alkanals in some rural aerosol samples (Gogou et al., 1996) in Crete. Andreou and Rapsomanikis
413 reported the C_{\max} as C_{15} or C_{17} in Athens (Andreou and Rapsomanikis, 2009) and attributed this to
414 the oxidation of n-alkanes. However, a C_{\max} at C_{26} or C_{28} in urban Crete (Gogou et al., 1996) was
415 observed, suggestive of biogenic input. The homologue distribution and CPI of n-alkanals in this
416 study differed from those previous reports, and demonstrated weak biogenic input and a strong

417 impact of anthropogenic activities in the London samples.

418

419 In this study, n-alkan-2-ones have similar homologue distributions and C_{\max} (C_{19} or C_{20}) (Table 2)
420 at RU, WM and EL sites, and the total concentration from C_{16} to C_{23} accounts for 76.0%, 76.1% and
421 68.0% of \sum n-alkan-2-ones, respectively. The CPI values for n-alkan-2-ones ranged from 0.57 to
422 1.23 at the RU, MR and WM sites and were not indicative of major biogenic input, and were
423 considered to mainly originate from anthropogenic activities and OH oxidation of anthropogenic n-
424 alkanes. It is however notable that the CPI values for both the 2-ketones and 3-ketones exceed
425 those for the alkanals (see Table 1), suggesting a contribution from contemporary biogenic sources,
426 possibly wood smoke and cooking. At EL, the CPI of 1.57 is ~~probably~~clearly indicative of a
427 biogenic contribution in suburban south London. A difference was observed at the MR site, the n-
428 alkan-2-ones with carbon atoms numbering from C_{12} to C_{18} accounting for 72.0% of \sum n-alkan-2-
429 ones, with the C_{\max} being at C_{16} . These data suggest a contribution of primary emissions from
430 traffic at MR, but a dominant background, probably substantially secondary, at the other sites. The
431 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}
432 = C_{17} , respectively.

433

434 **3.32.2 The ratios of n-alkanes/n-alkanals**

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

438 speed of 1800 revolutions per minute (RPM), and samples (n=14) were collected both before a diesel
439 oxidation catalyst (DOC) and after a diesel particulate filter (DPF). The n-alkanes (C₁₂ - C₃₇) and 1-
440 alkanals (C₉ - C₁₈) were quantified in the particle samples, while n-alkanones were not identified
441 because their concentrations were lower than the limits of (detection 0.01–0.15 ng m⁻³). The emission
442 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
443 (after DPF), respectively, and the ratios of alkanes/alkanals (~~C₁₂C₁₃~~-C₁₈) with the same carbon atom
444 numbers ranged from 0.15 to 0.23 (before DOC) and 0.52 to 7.60 (after DPF). The n-alkane/n-alkanal
445 (~~C₁₂C₁₃~~-C₁₈) ratio at MR ranged from 0.92–30 to 5.703, while average ratios of 27.614.9 (RU),
446 22.411.5 (WM) and 15.414.7 (EL) were obtained, respectively. The similarity of the n-alkanes/n-
447 alkanal ratio between MR and the engine studies (after DPF) strongly suggests that diesel vehicle
448 emissions were the main source of 1-alkanals at MR. The higher ratios at the other sites may be due
449 to greater airmass aging and loss of alkanals due to their higher reactivity (Chacon-Madrid and
450 Donahue, 2011; Chacon-Madrid et al., 2010).

451
452 The emission factors of total alkanes from diesel engines are reported to be 7 times greater than
453 gasoline engines (Perrone et al., 2014), with n-alkanals with carbon atoms numbering lower than C₁₁
454 being quantified in the exhaust from gasoline engines (Schauer et al., 2002b; Gentner et al., 2013).
455 The n-alkane/n-alkanal (C₈-C₁₀) ratio with the same carbon numbers ranged from 5.60 to 14.3
456 (Schauer et al., 2002b), suggesting that gasoline combustion may be another potential source of
457 atmospheric n-alkanals.

458

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

464

465 **3.32.3 Correlation analysis**

466 Insights into the sources of carbonyls can be gained from intra-site ~~from~~ correlation analysis with
467 black carbon (BC) and NO_x. This ~~has the advantage of comparing relative concentrations of~~
468 ~~pollutants, rather than absolute concentrations. The latter is more informative than comparisons~~
469 ~~between sites when sampling did not take place simultaneously, as concentrations~~ are strongly
470 affected by weather conditions, making inter-site comparisons difficult ~~to interpret when sampling~~
471 ~~did not occur simultaneously~~. In London, both black carbon and NO_x arise very substantially from
472 diesel vehicle emissions (Liu et al., 2014; Harrison et al., 2012; Harrison and Beddows, 2017), and
473 hence these are good measures of road traffic activity. The concentrations of BC were
474 simultaneously determined by the online instruments during the sampling periods, with the average
475 concentrations of 1.34, 1.94 and 3.58 µg m⁻³ at the RU, WM and MR sites, respectively. The data
476 for NO_x were provided by the national network sites, with the average concentrations of 23.4 and
477 202 µg m⁻³ at the EL and MR sites, respectively. At the MR site, the concentrations of BC and NO_x
478 averaged 5.00 µg m⁻³ and 281 µg m⁻³ when southerly winds were dominant compared to 2.60 and
479 128 µg m⁻³ for northerly winds. All correlations were carried out with the sum of particle and vapour
480 phases for the carbonyl compounds, and strong ($r^2 = 0.87$) and weak ($r^2 = 0.12$) correlations between

481 BC and NO_x were obtained when the southerly and northerly winds were prevalent at MR,
482 respectively. Marylebone Road is a street canyon site where a vortex circulation is established by
483 the wind. The effect is that on northerly wind sectors the sampling site on the southern side of the
484 road samples near-background air, while on southerly wind sectors, the traffic pollution is carried
485 to the sampling site, leading to elevated pollution levels affected heavily by the traffic emissions.
486 The strong correlation between BC and NO_x with southerly wind sectors is a reflection of their
487 emission from road traffic. In addition, the correlations between n-alkanals (C₈-C₂₀) and BC, and
488 between n-alkanals (C₈-C₂₀) and NO_x were calculated to assess the contribution of vehicular
489 emissions (Table S3). The results showed that the correlations (r^2) between n-alkanals and BC
490 gradually decreased from 0.61 (C₉) to 0.34 (C₂₀) at MR when the southerly winds were prevalent,
491 indicating that the distribution of n-alkanals, and especially the lower MW compounds, was
492 significantly impacted by the vehicular exhaust emissions. The average correlations at MR
493 (southerly winds) between n-alkanals and BC, and between n-alkanals and NO_x were $r^2 = 0.47$ and
494 $r^2 = 0.32$, respectively. These moderate correlations demonstrated that the vehicular emissions were
495 a ~~substantial~~ source of n-alkanals at MR, and ~~result in~~ contribute to the high background
496 concentrations of n-alkanals in London. The other probable sources of n-alkanals include cooking
497 emissions, wood burning, photooxidation of hydrocarbons and industrial emissions. Poorer
498 correlations between n-alkanals and BC (average $r^2 = 0.15$), and between n-alkanals and NO_x
499 (average $r^2 = 0.15$) were observed at MR in the north London background air sampled when
500 northerly winds were prevalent. There were very weak correlations (average $r^2 < 0.10$) between n-
501 alkanals and BC, and between n-alkanals and NO_x at the RU, WM and EL sites, which may be
502 attributable to the high chemical reactivity of n-alkanals. High concentrations of furanones (γ -

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

507

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

521

522 **3.4.3 The Partition Between Particle and Gas Phase Gas and Particle Phase Partitioning**

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

525

$$526 \quad K_p = \frac{C_p}{C_g * TSP}$$

527

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

537

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

540

$$541 \quad \text{Log } K_p = m \log(\text{VP}_T) + b$$

542

543 The calculated log K_p versus log (VP_T) for the three types of carbonyls was calculated for each day,
544 and the results appear in the Table S4. Data from four sites were over the temperature range 0.40–
545 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

568 winds. Vehicle emissions appear to be an important source of n-alkanals, which is confirmed by the
569 similar ratios of n-alkanes/n-alkanals measured at MR (~~0.30-5.75~~~~0.92-5.03~~) and in diesel engine
570 exhaust studies (0.52-7.6), resulting in a high background concentration in London. In addition, the
571 OH-initiated heterogeneous reactions of n-alkanes appear to be important sources of n-alkanones,
572 even though weak contributions from vehicular exhaust emissions were suggested by correlation
573 analysis with BC and NO_x in southerly winds at MR. Anthropogenic primary sources such as
574 cooking (Abdullahi et al., 2013) appear to may account for a ~~large~~ proportion of the alkan-2-one and
575 alkan-3-one concentrations measured in London, in addition to the secondary contribution from
576 alkane oxidation. Any contribution from cooking or wood combustion is likely to be small, or the
577 CPI would be greater.

578

579 In addition, the partitioning coefficients of carbonyls were determined from the relative proportions
580 of the particle and gaseous phases of individual compounds. The results of field measurements of
581 partitioning between particle and vapour phases showed generally a better fit at MR than at the other
582 three sites. The n-alkan-2-ones have a better fit at four sites than the n-alkanals and n-alkan-3-ones,
583 with $r^2 = 0.78\text{-}72$ (~~0.5449-0.9457~~) at RU, $0.85\text{-}76$ (~~0.6455-0.9387~~) at WM, 0.74 (0.43-0.95) EL and
584 0.70 (0.45-0.89) at MR, respectively in a regression of log K_p versus the compound vapour pressure.
585 This most likely reflects the slow formation of the alkan-2-ones as secondary constituents, closer to
586 phase equilibrium than the largely emitted alkanals which would be spatially far more variable.
587 The higher r^2 values for the alkan-2-ones than alkan-3-ones may reflect the higher concentrations,
588 and hence better analytical precision for the former compound group.

589

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764 **TABLE LEGENDS**

765

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

768

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

770

771 **FIGURE LEGENDS**

772

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

776

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

780

781 Figure 3. Time series of particle-bound Σn -alkanals, Σn -alkan-2-ones and Σn -alkan-3-ones at
782 RU, WM, EL, and MR sites.

783

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

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788

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 site	Sampling period	n-alkanals		n-alkan-2-ones		n-alkan-3-ones		Reference
		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. Urban roadside	August March	1.49	C ₁₅ , C ₁₇	1.09 3.26	C ₁₈ , C ₂₁ , C ₁₉ C ₂₁ , C ₁₉ , C ₂₀			(Andreou and Rapsomanikis, 2009)
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 Suburban	Summer Winter		C ₂₂ , C ₂₃ , C ₂₆		C ₂₆ , C ₂₈ , C ₃₀			(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 K_p ($m^3 \mu g^{-1}$).

	RU						WM					
	n-alkanals		n-alkan-2-ones		n-alkan-3-ones		n-alkanals		n-alkan-2-ones		n-alkan-3-ones	
	%	K_p	%	K_p	%	K_p	%	K_p	%	K_p	%	K_p
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			

	EI						MR					
	n-alkanals		n-alkan-2-ones		n-alkan-3-ones		n-alkanals		n-alkan-2-ones		n-alkan-3-ones	
	%	K _p	%	K _p	%	K _p	%	K _p	%	K _p	%	K _p
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		*100	
C ₂₁			*100						*100		*100	
C ₂₂			*100						*100		*100	
C ₂₃			*100						*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.



Fig. 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).

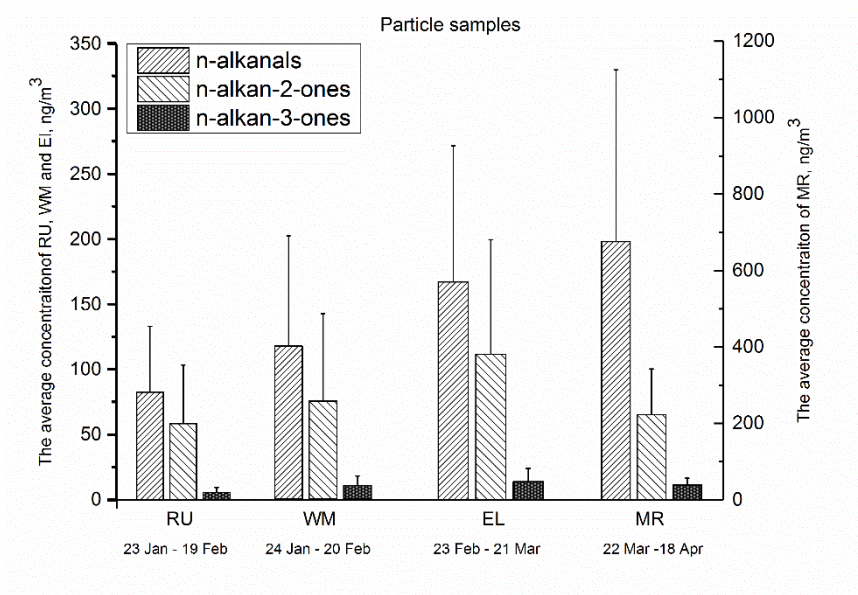


Fig. 2. The average total concentration of particle-bound n-alkanals (C₈-C₂₀), n-alkan-2-ones (C₈-C₂₆), and n-alkan-3-ones (C₈-C₁₉), for each sampling period and site. The error bars indicate one standard deviation.

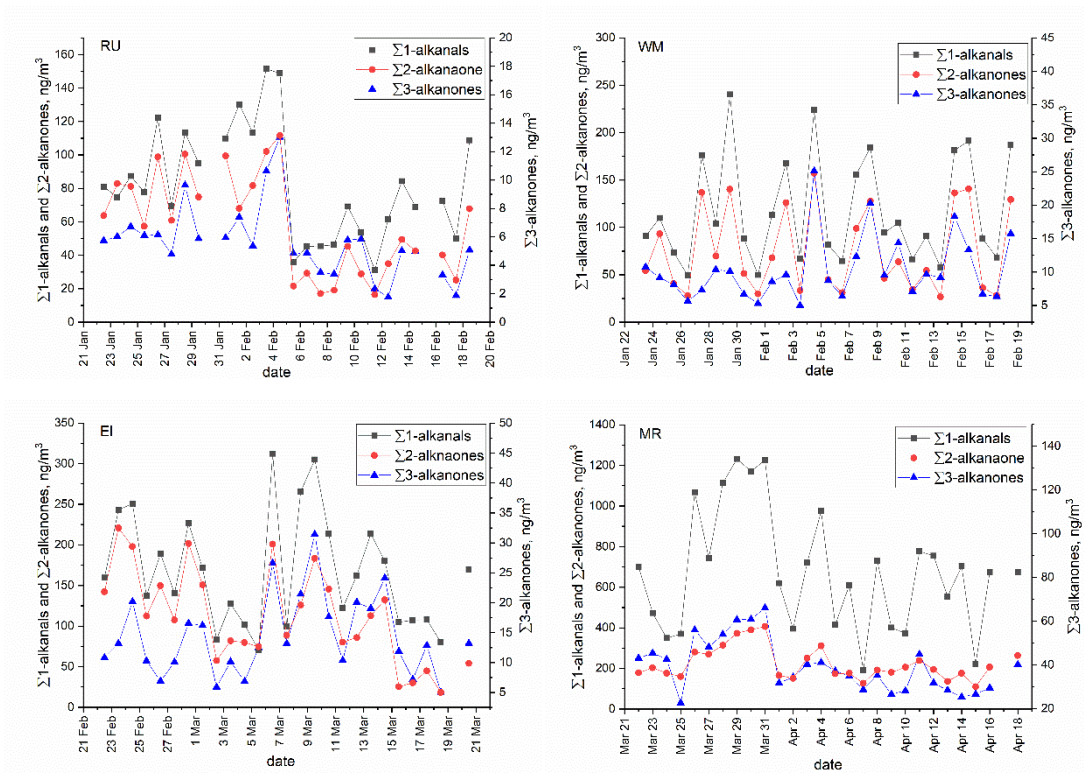


Fig. 3. Time series of particle-bound $\Sigma 1$ -alkanals, $\Sigma 2$ -alkanones and $\Sigma 3$ -alkanones at RU, WM, EL, and MR sites.

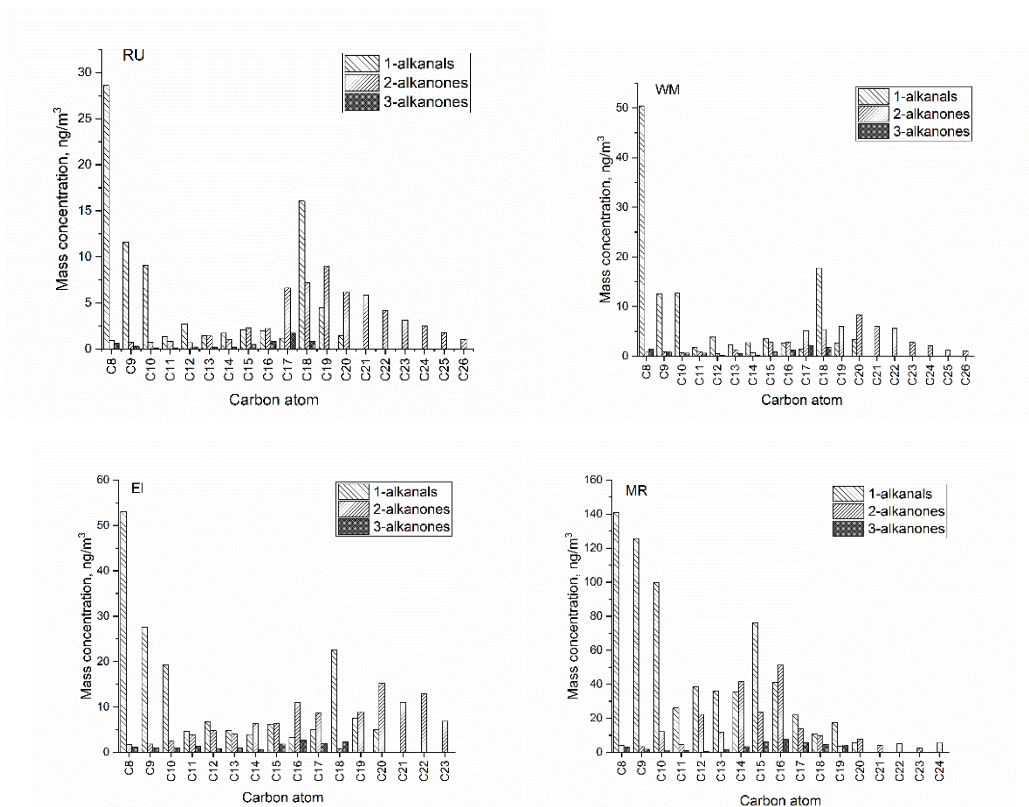


Fig. 4. The molecular distribution of particle-bound carbonyl compounds at four sites (RU, WM, EL, and MR).