

Interactive comment on “Aliphatic Carbonyl Compounds (C₈–C₂₆) in Wintertime Atmospheric Aerosol in London, UK” by 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. A marked up copy of the changes made are in the attached Supplement.

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

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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, 2-alkanones, 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-alkanones, 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

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the SIMPOL.1 estimates of vapor pressure, C16 alkanal has a C^* of 75 $\mu\text{g}/\text{m}^3$, and C19 alkanone has a C^* of 11 $\mu\text{g}/\text{m}^3$. 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 "sor-
bent tubes" to be consistent with the context. RESPONSE: Amended as suggested.

Line 188 and 194. The same information was repeated twice. RESPONSE: The sec-
ond 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., Strati-
gakis, N., Kanakidou, M., and Stephanou, E. G.: Organic aerosols in Eastern Mediter-
ranean: components source reconciliation by using molecular markers and atmo-
spheric 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. C_{max} is defined after already used a few times. The same for CPI. RE-
SPONSE: 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

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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 C₁₁.

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 Fahnstock, 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; Schilling–Fahnstock 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.

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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

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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,

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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.

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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 PM₁₀ Range, $\mu\text{g}/\text{m}^3$ PM₁₀ Mean $\mu\text{g}/\text{m}^3$ 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 PM₁₀ 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 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 ketones regression of $\log K_p$ vs vapor pressure having a better fit compared to the alkanals and the 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 ketones source? RESPONSE: The reviewer raised a good point for which we add new text.

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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. RE-
SPONSE: 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 Cmax 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.

Please also note the supplement to this comment:

<https://www.atmos-chem-phys-discuss.net/acp-2018-769/acp-2018-769-AC1-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2018-769>,
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