

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?
2. Line 246: CPI has not been introduced properly to discuss here out of context
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.
 - 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.
 - 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...".
 - 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-3one homologues could result as fragmentation products from larger alkane precursors during gas-phase oxidation (Yee et al., 2012; Schilling-

Fahnestock et al., 2015) or as functionalized products from heterogeneous oxidation of particle-bound alkanes (Ruehl et al., 2013; Zhang et al., 2015).

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.
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.
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?
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.
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.).
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 is 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?
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 Fahnestock 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?

Reference:

Lim, Yong Bin and Ziemann, Paul J. 'Chemistry of Secondary Organic Aerosol Formation from OH Radical-Initiated Reactions of Linear, Branched, and Cyclic Alkanes in the Presence of NO_x', *Aerosol Science and Technology*, 43: 6, 604-619, 2009.

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."
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.
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?
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.
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).
16. Lines 388-390: Not sure what is meant here.
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?
18. Lines 451-453: Why was this assumption made when measurements of these compounds were actually performed to get empirical K_p?
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?)
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.
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?

Technical Corrections:

1. No need to repeat lines 176-178 from lines 141-143.
2. Lines 192-194: Seems unnecessary to make this separate paragraph.
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

4. Line 274: Change subscripted reference 18 to proper format.
5. Line 355: repetitive C_{max} information on MR can be deleted.
6. Line 440: Suggest renaming this section to “Gas and Particle Phase Partitioning”