

#### 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<sub>x</sub> 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.
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 is provided in terms of what such a big difference exists.
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?
4. Starting from Line 286, the manuscript discussed ratios between the n-alkanes, 2-ketones, 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.
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.
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.

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  $75 \text{ ug/m}^3$ , and C19 alkanone has a  $C^*$  of  $11 \text{ ug/m}^3$ . These species are in the SVOC range and should have substantial fraction in the gas phase.

Minor Comments:

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

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

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

Line 225-226. A reference is needed here.

Line 330.  $C_{max}$  is defined after already used a few times. The same for CPI.

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

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

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.

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