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Atmospheric Chemistry and Physics Discussions

Interactive comment on "VOC species and emission inventory from vehicles and their SOA formation potentials estimation in Shanghai, China" *by* C. Huang et al.

Anonymous Referee #2

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In this work the authors measured the VOC species from vehicular emissions and calculated the contribution to SOA formation in Shanghai, China. Emissions were characterized at a chassis dynamometer facility, and VOCs are measured by conventional GC techniques. The authors then used literature values for SOA mass yields to compute the emission factors of SOA formation potential relative to CO. This work represents an important effort, as the number of vehicles has increased significantly and will continue to grow in urban China. The topic is of high relevance to ACP. The manuscripts presents a lot of information without detailed discussion, so my comments are generally geared towards elucidating these details to make the manuscript clearer. I also

have a couple of issues regarding how the data were interpreted (regarding how ambient OA is measured, and how to use CO-based emission factors). The manuscript should be considered for publication after major revisions.

Major comments:

1. It is not clear what is the carbon number range considered by the authors for SOA formation calculation. In Figs. 3 and 4, there appears to VOC species measured at C13-C20 for diesel exhaust. However, the authors stated repeatedly in the manuscript that IVOCs are not considered. Does that mean that the alkanes above C12 were measured but not considered quantitative enough for SOA calculation? If so, I suggest removing them from Fig. 3 and 4 because they are misleading and gives the wrong impression.

2. If IVOCs were not considered, I suggest that the authors do a sensitivity analysis: make a best estimate of amounts of different IVOCs based on literature (e.g. can refer to Gentner et al., 2013 for approximate ratios of IVOCs to total VOCs < C12), and vary that by one order of magnitude, and see how that affects the final SOA contribution. That would allow readers to assess whether missing S/IVOCs is more important or other non-vehicular sources are more important, and would guide future research.

3. If the authors did indeed include IVOCs in their calculations, I would raise serious doubts about how quantitative the measurements are, because there seems to be a sharp drop off after C12 (Fig. 4) and the Entech system is likely designed for VOCs < C12. In general, the lack of discussion regarding IVOCs (comments 1 through 3) is a major weakness in the manuscript and it is important that the authors address this issue.

4. Also, it is not clear how the CO-based emission factor is used. The authors noted that vehicles accounted for 27.8% of the total CO emissions. Did the authors take this into account when looking at OA/CO in Fig. 7? The OA production rate of 22.3 ug m-3 ppmv-1 (high NOx, see below about high/low NOx) is OA production per unit

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of *vehicular* CO, not total CO. In the analysis summarized by Fig. 7, one should use a production rate of 22.3 ug m-3 / 0.278ppmv CO, i.e. 80 ug m-3 ppmv-1. If so, the conclusions may change significantly because it would seem like vehicles are responsible almost all of the OA. If the authors did indeed take the 27.8% into account, that should be stately very clearly in the manuscript.

5. I have a hard time reconciling Figs. 7 and 8. Looking at the summer data in Fig. 7, it seems that other than the 10 highest points, there does not seem to be a dependence on photochemical age. The 10 highest points seem like outliers. Are those points associated with one particular day? In Fig. 8, there seems to a very strong correlation between deltaOA/deltaCO vs photochemical age, when viewed as diurnal variations. Can the authors should plot all deltaOA/deltaCO vs photochemical age to see if there truly is a trend, following de Gouw et al., (2008), or redo the diurnal averages Fig. 8 but remove the 10 outliers.

6. The authors should describe how OA is calculated in the ambient data. Is this done by converting OC to OA? If so, what is the OM/OC ratio used? From Section 3.3, it seemed like 1.2 was used for POA, but for SOA it should be higher (likely around 1.3 to 1.6). That would increase the apparent slope of OA vs CO plot and likely decrease the vehicular contribution to OA even further.

7. The treatment of low vs high NOx is too simplistic. In general, high-NOx would be more relevant for urban areas, and the statement that “low-NOx conditions were more realistic in the atmosphere” is not applicable here. At short atmospheric ages (i.e. hours), emissions will not have travelled to areas where NOx is low. Also, measurements are made within the city of Shanghai, where NOx is likely dominating peroxy radical chemistry. Therefore, discussion of low-NOx does not apply here.

Minor comments:

- There are many abbreviations that are never defined in this manuscript. While some (OA, SOA) are obvious, others (ECE driving cycle) need to be defined in order for the

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readers to understand the data. There are even some (e.g. PEMS, MARGA) that are defined but are not important to the overall message of the paper and never used again in the manuscript.

- Abstract line 10: SVOC and LVOC emissions are technically not discussed in this paper. Their reactions do not add OA mass, so it would not be relevant to this study.

- Abstract line 24: “a large number of OA mass” should be “a large amount of OA mass”

- Section 2.1: do the HDDT have aftertreatment technologies? A catalyst or a particulate filter?

- Section 2.3: if MARGA data are not used in the manuscript, I suggest removing it from the discussion

- Pg. 7987 line 6: how is SOA mass yield defined? It seems like discussion and comparison of average SOA mass yields between different studies is of limited utility. It depends on what species are measured and included in SOA yield calculations. I suggest shortening this discussion.

- Pg. 7988 line 9: “analytic method” should be “analytical method”

- Section 3.3: Thousand t is a confusing unit. Perhaps ktonnes?

- Pg. 7989 line 13: typo “respetively" should be “respectively”

- Section 3.4: % iles should be percentiles. Also, why is 97.5 percentile used? Usually 95th percentile is used.

- Section 3.4: To be more precise, t.[OH] should be referred to as “OH exposure”, not photochemical exposure time

- Pg. 7990 line 13: a reference should be cited for the OH rate constants

- Section 3.5: what is the [OH] used to calculate delta t in Eqn (2)? Are there measurements or estimates of OH to support the value used?

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