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Interactive comment on “Secondary organic aerosol formation from photochemical aging of light-duty gasoline vehicle exhausts in a smog chamber” by T. Liu et al.

Anonymous Referee #1

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This paper presents an experimental study of SOA formation from dilute exhaust from two gasoline powered vehicle (Euro I and Euro 4) operated on Euro 3 gasoline. The vehicles were tested at idle. A total of five experiments were performed. The dilute exhaust was photo-oxidized in a smog chamber and substantial SOA was formed (exceeding the primary organic aerosol emissions). The paper calculated effective yields (~ 3 to 17%) and evaluated SOA mass closure (50-90% of SOA could be explained with measured precursors).

The basic experiments are quite similar to other recent papers on SOA formation from gasoline vehicle exhaust. The results also fall within the range of results from hose

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previous paper. It does expand the dataset on gasoline vehicle exhaust. The paper emphasizes the Chinese context as novel (“first” experiments performed in China). Not clear how important it is to perform these experiments in China, since China follows European emissions and fuel standards. The very small number of vehicles (2) and limited tests (5) all performed at idle (a very limited operating mode) makes it hard to draw much insight into SOA formation from in use vehicle operations. Therefore, the paper contributes little new knowledge.

The paper is well organized and the experiments were performed with high quality instrumentation.

Specific comments:

The exhaust was transferred through Teflon transfer line and a GAST rotary vane pump (not clear if the system was heated). This set up likely caused substantial losses of both PM and VOCs before the chamber (we never use Teflon lines for PM sampling). Were these losses characterized? If not, it makes the results largely qualitative and every presentation of effective yield or mass closure needs to be qualified with this substantial uncertainty. Presumably there is less issues with the composition information (Figure 8).

The high, end of experiment SOA/POA ratios (Table 4) could largely be an artifact of substantial POA losses in the sampling system.

This paper focuses on organic aerosol. What about total PM (that is what is regulated no organic aerosol)? Were there substantial refractory (e.g. BC) emissions?

It does not appear that seed particles were used in the experiment. Therefore there is likely substantial loss of condensable vapors to the chamber walls (Zhang et al. PNAS 2014). This will reduce the SOA production.

Blanks – Did they run any blank experiments (with no vehicle exhaust) to quantify contamination?

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“alkanes shared about 42.9 and 66.2% of the total speciated NMHCs measured with the GC-FID/MSD by mass, respectively, dominating the NMHCs emissions in gasoline vehicle” not sure what “shared” means? Contributed might be a better word. It is not clear that alkanes dominate NMHC emissions, only NMHCs that were speciated in this study. This needs to be rephrased.

“emission factors of NMHCs and aromatic hydrocarbons for vehicle I were 2.1 and 0.8 g kg⁻¹, approximately 1.3 and 0.5 times lower than those for vehicle II, respectively” Not clear what 0.5 times lower means. Does this mean the aromatic emissions were actually higher for the newer vehicle. Also these seem like pretty modest emission reductions between a Euro 1 and a Euro 4 vehicle. I am not familiar with these specific standards but suspect that the expected reduction in NMHC emissions would be much greater than a factor of 2. This may reflect the fact that the experiments were performed at idle. Idle exhaust temperature are relatively low and therefore may not be sufficient to fully activate the catalytic converter. This further complicates interpreting the results (e.g. at idle, Euro 1 and Euro 4 vehicles may have similar emissions).

“ approximately 10 min, indicating dramatic new particle formation. After nucleation occurred, the mean diameter increased from 20 to 60nm in about 1.5 h. Because particles with diameters larger than 50nm can act as cloud condensation nuclei (CCN) (McFiggans et al., 2006) and influence the radiative forcing, SOA from vehicle” The nucleation underscores the weakness of not having seed aerosol. The reference to McFiggans and CCN is misleading since in the atmosphere there is substantial existing particle mass which will likely suppress nucleation of gasoline vehicle exhaust.

“aromatics and naphthalene accounted for 51–90% of the measured SOA, comparable to the estimation that classical C6–C9 light aromatics were” Claiming this level of mass closure is very problematic since they do not account for loss of condensable vapors to the walls. This seems more like the maximum amount of SOA they can explain.

“The wall-loss rate constant was determined separately for each experiment by fitting

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the SMPS and AMS data when no new particles were formed.” I do not understand this. No new particles formed suggests to me no nucleation. I suspect they mean before there is any photo-oxidation – needs to be clarified in the text.

“The $w = 1$ wall-loss correction is not suitable for the experiments here in which nucleation occurred and no seed particles were added” I do not understand why this is the case. The ~ 1 hr induction period before SOA formation could simply reflect loss of condensable vapors to the walls. I can understand why the $w=1$ case may not be representative of the vapor losses, but it seems incorrect (based on the results of Zhang) to ignore the wall losses of vapors. Also, wall losses with vapors will mean that you likely underestimate the amount of SOA production and therefore that your mass closure analysis estimates the maximum amount of SOA that can be explained with single ring aromatics.

“Table 5. Chemical compositions of the aromatic hydrocarbons in the exhaust of different vehicles, listed as weight percentages.” Weight percentages of what? Speciated NMHCs?

“Figure 2. Particle number (left) and mass (right) distributions for a typical smog chamber experiment (experiment). The right hand panel suggests that there is substantial mass in the nucleation mode (much more than the 3% suggested in the text). Wall loss of these very small particles is more rapid than the larger particles. How was this corrected for?”

Figure 4 – Mass fraction of what?

Figure 6. They attribute lower yields measured here compared to Nordin et al. to not using seed particles, which leads to higher losses of vapors to the smog chamber walls. That seems like a reasonable explanation. If that is the case then the amount of unexplained SOA is twice what they report. This caveat needs to be included in the text. Also, did Nordin have the same or higher OH exposures. This might also impact the yield.

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The effective yields are defined based on a relatively small number of single ring aromatics. Did Nordin use the same set of compounds to define their effective yield? If not, is it fair to compare the new results with Nordin et al. results based on yields. The fact that the effective yield was defined relative to this small subset of compounds needs to more clearly stated in paper, including the presentation of the effective yield results and in the caption of Figure 6.

Figure 7 – is this just plotting numbers in Table 3? If so, Table 3 could go into the supplemental.

Given that they only have two vehicles; I would refer to them in the text by their certification standard, not Vehicle 1 and Vehicle 2. I had to keep looking up which one is which.

“In this study, the SOA yield of benzene and other single-ring aromatics were estimated using the two-product model curves taken from Borrás et al. (2012) and Odum et al. (1997), respectively. While the SOA yield of naphthalene was taken from Shakya et al. (2010).” How representative are these yields of the rest of the literature. E.g. I think that the Odum yields are on the low end of the literature yields for single ring aromatic (in part because they did not use seed aerosols). Do conclusions about the mass closure change if the analysis is done with different yields. Were the yields taken from the literature measured under similar experimental conditions as these experiments (e.g. VOC/NO_x, OA concentration). Given the uncertainty in the yields, the analysis should be repeated with different published yield data to generate error bars in the mass closure estimates (51 to 90%).

Page 10555 line 15 – “form” should be “from”

Table 2 – Is this supposed to be ppbv carbon for NMHCs?

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