Atmos. Chem. Phys. Discuss., 15, C2454–C2460, 2015
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Atmospheric Chemistry and Physics Discussions

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 #2

Received and published: 11 May 2015

Dear Editor, dear Authors,

I have read and evaluated the manuscript

Atmos. Chem. Phys. Discuss., 15, 10553–10592, 2015, www.atmos-chem-phys-discuss.net/15/10553/2015/, doi:10.5194/acpd-15-10553-2015,

with the title "Secondary organic aerosol formation from photochemical aging of light-duty gasoline vehicle exhausts in a smog chamber" by T. Liu, X. Wang, W. Deng, Q. Hu, X. Ding, Y. Zhang, Q. He, Z. Zhang, S. Lü, X. Bi, J. Chen, and J. Yu.

Please find my comments below.

A) General Remarks:

The manuscript fits the scope of the journal and is of scientific relevance to the community. As the manuscript title suggests, the study provides insight into organic aerosols as emitted primarily from gasoline vehicles (1x Euro 4 and 1x Euro 1) and reports on the secondarily formed organic aerosol (SOA) mass upon photo oxidation in a smog chamber. The tested gasoline vehicles are operated in China with Euro III compliant gasoline fuel. Modern state-of-the art instrumentation is used in the investigations.

The article is well structured, and provides additional data for the community, adding to the statistics on gasoline vehicle SOA formation. This is of significance, as previous publications (Nordin et al., 2013, Platt et al., 2013, Platt et al., 2014, Gordon et al., 2014, May et al. 2013ab, and others) have shown large error bars on gasoline vehicle SOA formation estimations, and additional data help to constrain gasoline vehicle SOA formation further. However, I disagree with the repeated statements in the abstract, introduction and conclusions, that these experiments are representative of Chinese vehicles compared to previous experiments, due to (1) limited experimental conditions, and (2) the limited number of tests conducted (5 tests with 2 vehicles). However, in general, the results lie within previous findings (note that I do feel that an extended comparison with existing literature is recommended, see references mentioned above) and support the overall statistical quality of the data, despite the fact, that no significantly new conclusions are found. I believe before publication the authors should clearly state that the numbers reported are only valid for the tested cars and more data would be required to constrain the Chinese vehicular emissions.

B) Specific Remarks: Experimental Methods and Data Analysis:

While the data support the current literature, the experimental methods and sample size lead to limited results that are not globally representative and should not be used to draw global conclusions, e.g. on the vehicle fleet in China. The reason for stating the limited scope of the study is, that it relies on replicates (2 - 3x) of only two mea-

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surements of idling gasoline vehicles (1x Euro 4, 1x Euro 1), excluding the influence of different driving behavior and technologies. In addition, problems with the experimental set-up and the data processing have to be pointed out. The following major points regarding the experimental set up and data analysis must be addressed before I could recommend publication:

- Sampling lines were unheated Teflon, and samples were taken through a pump: this will lead to losses of (1) primary particles through electrostatic losses, and (2) VOCs, IVOCs and SVOCS via adsorption on the Teflon surface; In addition, there might be significant losses in the pump. Could the authors add estimations for particle and gas-phase losses in the sampling system, or give more information on the operation of the pump and how this will affect the sample taken into the smog chamber? (Losses are potentially indicated by the small starting particle number concentration in the smog chamber). Please provide starting concentrations in SI. - Nucleation is observed upon photooxidation, which points to the fact that there was not enough seed aerosol surface available in the smog chamber; potential losses of vapors to chamber walls should be taken into account. Can the authors estimate the starting seed aerosol surface? (Section 3.2, Page 10565, Line 11 – 17, "As shown in Fig. 5c, the total particle number concentration increased fast from 82 to 116 143 cm-3 in approximately 10 min, indicating dramatic new particle formation. After nucleation occurred, the mean diameter increased from 20 to 60 nm)." - Problems with the AMS/SMPS analysis are indicated: Figure 2 presents SMPS size distribution from a HR-ToF-AMS. Likely a big fraction of the mass as measured with the HR-ToF-AMS is actually outside the optimum transmission efficiency of the lens. No direct correction for lens transmission was applied, but the authors scaled AMS data with SMPS data. However, lens transmission issues are not discussed in section 2.2. and 2.4.2. I recommend adding this to the manuscript. Additionally, I would like to ask the authors to clarify how refractory particulate matter (elemental carbon) has been taken into account in the analysis, or discuss, why it was assumed that the vehicle exhaust studied in the smog chamber consist only of non-refractory material. - Offline samples were taken with different systems (e.g. aluminum

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foil bags, stainless steel containers). Please clarify which systems were applied when, and which analysis was performed. I expect significant losses for SOA precursors on stainless steel surfaces (see e.g. section 2.4.3, page 10563, line 13). Did results from offline samples compare well with online HR-PTR-ToF-MS results (please add this to section 3.1). - Estimation of yields: Relatively low yields are found (3 – 17%), compared to previous publications on gasoline vehicles tested on driving cycles. Please provide extended discussion on potential reasons, and clarify how significant losses of IVOCs and SVOCs compared to VOCs in the unheated Teflon lines used for sample introduction and in the stainless steel containers used for sample collection would skew these results.

B) Specific Remarks: Language / Formulations:

Abstract: - Please remove the sentence “However, there are still no chamber simulation studies in China on SOA formation from vehicle exhausts” (Line 4-5) as it is not of significance in which country laboratory experiments are performed. - Please add “operated” to “in China” in Line 7, so that the sentence reads “. . . operated in China . . .” - Please reformulate “at the quite similar OH exposure” to “at comparable OH exposure”.

Section 1, Introduction: - Section 1, Page 10557, Line 13: please reformulate or remove; see comments on Abstract. - Section 1, Page 10557, Line 26, please reformulate; see comments on Abstract.

Section 2, Materials and methods: - Please add a section on derivation of OH exposure to Materials and methods. - Section 2.4.2., please move Fig 2 and 3. to SI and provide the integrated OH exposure as additional time axis. - Section 2.4.2, please clarify how refractory particulate matter (elemental carbon) has been taken into account in the analysis, or discuss, why you assume that the vehicle exhaust studied in the smog chamber consist only of non-refractory material. - Section 2.4.2, please clarify that the discrepancy between SMPS and AMS derived mass in the presented experiments also results from different size-dependent measurement cut-offs (you mention very small

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particle size of at least the primary particles, which are well below the optimum lens transmission of the AMS), and not only from AMS collection efficiency. - Section 2.4.2, page 10562, line 12: please remove “the two”, the sentence should read: “However, both methods have limitations”. - Section 2.4.3, line 13 (page 10563), please specify “simulating air”.

Section 3, Results and discussion: - For all data presented in Tables and Figures: where data are available, please add error bars to the data and indicate which kind of averaging method has been applied to the data of different experiments. - Please use either NMHC or VOC in the manuscript for purpose of consistency, and specify the measurement principle (GC-FID or GC-MSD or HR-ToF-PTR-MS where needed, e.g. in Table 2, 3, 5, and Figure 4 and 5). - Section 3.1, line 11-13 and line 18-19, please compare the results with Huang et al., 2015, ACPD (doi:10.5194/acpd-15-7977-2015), and other literature to narrow down whether fuel, vehicle type or emission standards are causing the difference in the two vehicles, or whether the difference lies within the statistical range. Previous publications have shown a wide spread in vehicle emissions for different vehicles and test conditions, and a comparison of 1 vehicle to another to conclude for a whole class of vehicles from one emission standard is not justified. - Section 3.1, the authors have used a HR-ToF-PTR-MS in the course of the study. I suggest adding a comparison of GD-FID/MSD data with HR-ToF-PTR-MS data to this section. - Section 3.1, I suggest to include information in Table 5 into Figure 4, and remove Table 5 or provide in SI. - Section 3.2, Fig 5ab: please provide also the integrated OH exposure as time axis in addition to the “time since lights on” in the Fig. - I suggest to discuss Fig. 5c and the statement in section 3.2, page 10565, line 11 – 14, “As shown in Fig. 5c, the total particle number concentration increased fast from 82 to 116 143 cm-3 in approximately 10 min, indicating dramatic new particle formation. After nucleation occurred, the mean diameter increased from 20 to 60 nm in about 1.5 h” as a potential limitation of the study, rather than a result. Rather than this being a significant result of the investigations, the fact that nucleation occurs during these experiments points to experimental weakness of the study, which is, that no sufficient aerosol seed

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surface is provided. This can lead to significant losses of vapors to chamber walls, as demonstrated in recent publications (Zhang, et al., 2014). In addition, the small starting particle number concentration in the smog chamber (82 cm-3), points to significant losses during sampling into the smog chamber. - The statement in section 3.2, page 10565, line 14 – 17 “Because particles with diameters larger than 50 nm can act as cloud condensation nuclei (CCN) (Mc Figgans et al., 2006) and influence the radiative forcing, SOA from vehicle exhausts may has climate effects to a certain extent as well as air quality effects.” should be removed, unless the authors can provide experimental evidence. - Section 3.2, page 10565, please reformulate Line 18 to “SOA production factors (PF) for the LDGVs tested in this study” instead of “for LDGVs in China”. - Section 3.2, page 10565, Line 25 onwards (“Decay of toluene . . .”): the section on estimation of OH exposure should be moved to “Materials and methods”. - Section 3.3: Table 3 and Figure 7 present essentially the same information. Please include additional information provided in Table 3 into Figure 7 and remove Table 3 or provide Table 3 in SI. - Section 3.3: Table 4: please provide some extended discussion on why the yields observed in the smog chamber are around 3% for vehicle II and 10 – 20% for vehicle I. Please link the difference in the yield with the chemical composition of the precursor gases to find an explanation.

Section 4, Conclusions: I recommend removing this section fully, as no real conclusions are drawn and a summary of the results and discussion section is superfluous.

References: Gordon TD, et al., (2014) Atmos. Chem. Phys., 14, 4661-4678, doi:10.5194/acp-14-4661-2014; Huang C, et al., (2015) Atmos. Chem. Phys. Discuss., 15, 7977–8015, 2015, doi:10.5194/acpd-15-7977-2015; May AA, et al., (2013a) Atmos Env., 77, 128-139, doi: 10.1016/j.atmosenv.2013.04.060; May AA, et al., (2013b) Env Sci Technol, 47, 8288-8296, doi: 10.1021/es400782j; Nordin EZ, et al., (2013) Atmos. Chem. Phys., 13, 6101–6116, doi:10.5194/acp-13-6101-2013; Platt SM, et al., (2013) Atmos. Chem. Phys., 13, 9141–9158, doi:10.5194/acp-13-9141-2013; Platt SM, et al., (2014) Nature Communications 5, 3749, doi:10.1038/ncomms4749; Zhang X, et al.

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(2014) PNAS, 111, 5802–5807, doi: 10.1073/pnas.1404727111;

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 10553, 2015.