# Response to reviewers' comments

**Reviewer #1**

*Overview*

*The authors have made many significant improvements to the manuscript. Both the text and the figures have improved significantly. However, some important edits largely related to the presentation and interpretation of results should be still addressed.*

Reply: We would like to thank the reviewer for the insightful comments, which helped us tremendously in improving the quality of our work. Please find the response to individual comments below.

*1. The discussion of the consistency in composition across emissions standards is problematic. For gasoline vehicles the authors' results are consistent with previous findings1–3, which should be referenced on line 358. For diesel vehicles, the author's interpretation of the data is either misleading or in error, based on Figure 7d. The blue line showing the fit to the data passes through very few of the points. (The opposite is true for gasoline, in which the line seems to pass through the spread of the data points). For diesel, it thus appears that either a small number of compounds heavily impact the fit, or the fit is somehow in error. Thus the authors should not claim that diesel emissions are not changing with emissions standards, because it would appear only a few major compounds are not varying, but the others could vary significantly. The argument based on the questionable R-squared value is not acceptable in this case, because the distribution of the data about the fit is very far from normal.*

Reply: We thank the reviewer for the comment. We agree with the reviewer that the discussions of the consistency in composition across emissions standards for diesel vehicles are not appropriate. We have revised the text added at lines 359-362 in the latest version manuscript. We appreciate the reviewer for providing these useful references.

The sentences in the Section 3.2 (line 360-366) are modified to:

**Fig. 7c show that the chemical compositions of VOC emissions are**

**comparable between different emission standards for abundant VOC species from gasoline vehicles, indicating after-treatment devices may not affect the relative fractions of VOC components for gasoline vehicles (Drozd et al., 2019;Lu et al., 2018;Zhao et al., 2017). In comparison, the results between different emission standards for diesel vehicles (Fig. 7d) are somewhat larger than in gasoline vehicles.**

*2. A similar problem exists for the cold-start vs. hot-start emissions. In general the argument that unburned fuel dominates the emissions for gasoline vehicles seems consistent with previous literature, although the BTEX compounds are a notable exception with different ratios in emissions vs. fuel4, which should be noted. How can the authors make the same claim for diesel, when such a large fraction of the diesel emissions is reported to be OVOCs? Diesel fuel is not more than 50% OVOC, so despite any data analysis here, the major claim of the manuscript concerning OVOC fractions in emissions, does not allow for the emissions to be comprised of unburned fuel. This statement must be removed, and some alternative explanation for the correlation of cold-start and hot-start emissions must be suggested. Perhaps the OVOC may be derived from particular fuel components, yet still the authors have no information on fuel composition, the largest fault in this study.*

Reply: We thank the reviewer for the insightful comment. We have revised description in the manuscript on the unburned fuel dominates the emissions for gasoline vehicles. For diesel vehicles, we have removed related description. Explanation for the correlation of cold-start and hot-start emissions have described in Lines 339-346 of the revised manuscript. The information on fuel composition had been added in the Sect. 1 in the supplement in the last version manuscript, and the high emissions of OVOCs from diesel vehicles may be related to combustion processes in diesel vehicles, with more excess air (i.e., under overall fuel-lean conditions) into combustion cylinder (Gentner et al., 2017), we had claim about it in the lines 293-297 in the revised manuscript.

The sentences in the Section 3.2 (line 346-350) are modified to:

**As cold start emissions are richer in unburned fuel than other hot-running conditions (Gentner et al., 2017) and the after-treatment devices aim for VOCs control for gasoline vehicles, the strong correlation and significantly lower slope than unity in Fig. 7a infer that unburned fuel are the major contributor for exhaust emissions of gasoline vehicles, which has been previously shown in California, U.S. (Gentner et al., 2013).**

*3. Finally, the manuscript needs to be carefully reviewed for grammar and syntax again. A couple egregious issues are noted below.*

*Line 263 "Intestinally, the emission factors of the representative VOC species are highest for China II gasoline vehicles rather than China I vehicles, coincidence with largest mileage of the test vehicles. This sentence should be changed to: "The emission factors of the representative VOC species are highest for China II gasoline vehicles rather than China I vehicles, which can be explained by the China II vehicles having the highest mileage of the test vehicles."*

*Line 445 "The remarkable larger emission factors of C14 aromatics from diesel vehicles suggest that diesel vehicles can be a significant or even predominated source for higher molecular aromatics" This sentence should be changed to: "The significantly higher emission factors of C14 aromatics from diesel vehicles suggest that diesel vehicles can be a significant or even dominant source for higher molecular-weight aromatics"*

We thank the reviewer for the comment. We corrected all these comments and checked the grammar and syntax throughout the manuscript.

The sentence in line 272-274 in the revised manuscript is modified to:

**The emission factors of the representative VOC species are highest for China II gasoline vehicles rather than China I vehicles, which can be explained by the China II vehicles having the highest mileage of the test vehicles.**

The sentence in line 453-455 in the revised manuscript is modified to:

**The significantly higher emission factors of $C_{14}$ aromatics from diesel vehicles suggest that diesel vehicles can be a significant or even dominant source for higher molecular-weight aromatics.**

*References*

*(1) Lu, Q.; Zhao, Y.; Robinson, A. L. Comprehensive Organic Emission Profiles for Gasoline, Diesel, and Gas-Turbine Engines Including Intermediate and Semi-Volatile Organic Compound Emissions. Atmos. Chem. Phys. Discuss. 2018, 18, 1–28.*

*(2) Drozd, G. T. G. T.; Zhao, Y.; Saliba, G.; Frodin, B.; Maddox, C.; Chang, M.-C. O. O.; Maldonado, H.; Sarder, S.; Weber, R. J. R. J.; Robinson, A. L.; et al. Detailed Speciation of Intermediate Volatility and Semivolatile Organic Compound Emissions from Gasoline Vehicles: Effects of Cold-Starts and Implications for Secondary Organic Aerosol Formation. Environ. Sci. Technol. 2019, 53 (3), 1706–1714.*

*(3) Zhao, Y.; Saleh, R.; Saliba, G.; Presto, A. A.; Gordon, T. D.; Drozd, G. T.; Goldstein, A. H.; Donahue, N. M.; Robinson, A. L. Reducing Secondary Organic Aerosol Formation from Gasoline Vehicle Exhaust: Precursors and NOx Effects. Proc. Natl. Acad. Sci. 2017, 114 (27), 6984–6989.*

*(4) Drozd, G. T.; Zhao, Y.; Saliba, G.; Frodin, B.; Maddox, C.; Weber, R. J.; Chang, M.-C. O. C. O.; Maldonado, H.; Sardar, S.; Robinson, A. L.; et al. Time Resolved Measurements of Speciated Tailpipe Emissions from Motor Vehicles: Trends with Emission Control Technology, Cold Start Effects, and Speciation. Environ. Sci. Technol. 2016, 50 (24), 13592–13599.*

**Reviewer** #2

*Wang et al. present a revised manuscript that addresses many of the comments in my previous review. I appreciate the authors works, and I am satisfied by the responses. Overall, I support publication. There is one remaining comment that I would appreciate if the authors could address, as I believe it will help clarify a question that I posed in my initial review. I've also made a number of comments on the new content in the SI that I think will help to clarify the material.*

Reply: We would like to thank the reviewer for the insightful comments, which helped us tremendously in improving the quality of our work. Please find the response to individual comments below.

*Main Comment*

*Lines 359 - 362: This new text is confusing, and I believe this was added to address comments 5 and 8 of my previous review. Admittedly, my initial questions may have not been clear. In my previous review, I asked whether Figures 7a-b could provide information about the effects of the after treatment process on VOC profiles. I presumed that the comparison between coldstart emissions and hot-start emissions were sufficient to address this question. Really, my aim was to hear more from the authors about the source of VOC emissions, and I think the authors now effectively address this at lines 346-349 with the discussion of unburnt fuel.*

*In the new text, the authors point to Figures 7c-d to argue that the after treatment process has little effect on VOC profiles. I do not agree that these panels provide strong evidence for this conclusion. Figure 7d shows significant scatter, and the correlation coefficient derived from these data seem to be driven by a select number of high emission VOCs. Furthermore, after rereading this section, this new text conflicts with the statement at lines 375-377, which suggest that the "after-treatment device for diesel vehicles may effectively reduce emissions of some heavier VOC species."*

*I think this can be resolved by simply removing the text at lines 359 - 362. Ultimately, I don't think this text adds much to the discussion. I appreciate the efforts by the authors* *to address my comments.*

Reply: We thank the reviewer for the comment. We agree with the reviewer that the discussions of the consistency in composition across emissions standards for diesel vehicles are not appropriate. We have revised the text added at lines 359-362 in the latest version manuscript.

The sentences in the Section 3.2 (line 360-366) are modified to:

**Fig. 7c show that the chemical compositions of VOC emissions are comparable between different emission standards for abundant VOC species from gasoline vehicles, indicating after-treatment devices may not affect the relative fractions of VOC components for gasoline vehicles (Drozd et al., 2019;Lu et al., 2018;Zhao et al., 2017). In comparison, the results between different emission standards for diesel vehicles (Fig. 7d) are somewhat larger than in gasoline vehicles.**

*Comments on Supplement:*

*1. Lines 46 - 55 in the Supplement: This information is really useful to the reader in order to understand how the emission control technologies have changed under different standards. I think this section should be elevated to the main text. A good place for this could be at line 121 after the description of the LPG vehicles.*

Reply: We thank the reviewer for the comment. We have removed this section in the Supplement, and added them in the Section 2.1.

The sentences in the Section 2.1 (line 120-129) in the revised manuscript are modified to:

**After-treatment devices commonly used in light-duty gasoline vehicles are three-way catalyst (TWC) and gasoline particulate filter (GPF) (Lyu et al., 2020). They have been improved with the stricter emission standards. For diesel vehicles, typical after-treatment devices include diesel oxidation catalyst (DOC), diesel particulate filter (DPF), and selective catalyst reduction (SCR) (Zhou et al., 2019;Lyu et al., 2020;Shen et al., 2021). The diesel vehicles for China III or prior**

**do not have any after-treatment devices. Light-duty-diesel-truck (LDDT) used DOC and DOC+DPF as after-treatment devices in China IV and V diesel vehicles, respectively. SCR devices are mainly used for heavy-duty-diesel-truck (HDDT) with China IV and V as after-treatment devices.**

*2. Line 26: Please add "the" between "of" and "determining"*

Reply: We add "the" between "of" and "determining".

*3. Line 35: "Content" should be "contain"*

Reply: We replaced "content" with "contain".

*4. Line 37 - 39: Wording is a little awkward, would suggest rephrasing as "… have been recently introduced in China, which applies to light-duty vehicles using gasoline and diesel fuel"*

Reply: We thank the reviewer for the comment. The sentence in the 37-39 in the supplement is modified to:

**The limits and measurement methods for emissions of light-duty vehicles (GB18352.6-2016; known as the China VI standard) have been recently introduced in China, which applies to light-duty vehicles using gasoline and diesel fuel.**

*5. Line 49: Would suggest re-wording "upgrading of emission standard" to say "stricter emission standards*

Reply: We replaced "upgrading of emission standard" with "stricter emission standards".

*6. Line 74: I believe "cycle" should be plural*

Reply: We replaced "cycle" with "cycles".

*7. Line 96 - 97: This reads awkwardly. I suggest revising to read " Here, the limit of detection for VOC mixing ratios were calculated and applied to estimate the limit of detection for emission factors"*

Reply: We thank the reviewer for the comment. The sentence in the 86-88 in the Supplement is modified to:

**Here, the limit of detection for VOC mixing ratios were calculated and applied to estimate the limit of detection for emission factors.**

*8. Line 98: Would suggest removing "kind of"*

Reply: We removed "kind of".

*9. Line 99-102: I don't follow what is written here - are the authors saying that the mass spectra is below the limit of detection for most measurements? I don't fully understand why one vehicle is used here to infer the LOD/Signal ratio here.*

Reply: We thank the reviewer for the comment. In this section, due to the large number of ions measured in the mass spectra, we need to consider whether the corresponding emission factors of all ions are effective. Therefore, we take a China V gasoline vehicle (the emission factors may be sufficiently lower) as an example to calculate the ratio of the emission factor to the limit of detection for emission factor.

*10. Line 106 - 112: I'm not sure why the discussion of C16H22O4H is included here. If the authors do not believe this compound is a part of the tailpipe emissions, then I would remove this from the discussion. If this compound is of interest for other reasons (i.e., some sort of plasticizer?) then I believe the authors should provide some discussion. But to my eye, this seems to be a part of the dynamometer system and can be reasonably discarded.*

Reply: We thank the reviewer for the comment. We have removed this section in the Section 3.2 in the revised manuscript, and revised this section in the Supplement to give an explanation if anyone is interested in this.

The sentences in the 96-100 in the Supplement are modified to:

**It should be noted that the signals of $C_{16}H_{22}O_4H$ (m/z=279) were higher during the tests based on determined emission factors. However, we suspect that it may be emitted artifacts from the sampling or dilution system as it mainly showed higher signals in the latter period of each test when sampling materials absorb more heat from vehicle exhausts (Fig. S12), and thus it is not included in Fig. 5.**

*11. Line 144-146: This reads a bit awkwardly - I would suggest saying "The average rate constant for C14 aromatics has not been reported, so we assume a rate constant similar to representative C12 aromatics"*

Reply: We thank the reviewer for the comment. The sentence in the 132-134 in the Supplement is modified to:

**The average rate constant for $C_{14}$ aromatics has not been reported, so we assume a rate constant similar to representative $C_{12}$ aromatics**.

## Reference:

Drozd, G. T., Zhao, Y., Saliba, G., Frodin, B., Maddox, C., Oliver Chang, M. C., Maldonado, H., Sardar, S., Weber, R. J., Robinson, A. L., and Goldstein, A. H.: Detailed Speciation of Intermediate Volatility and Semivolatile Organic Compound Emissions from Gasoline Vehicles: Effects of Cold-Starts and Implications for Secondary Organic Aerosol Formation, Environ Sci Technol, 53, 1706-1714, 10.1021/acs.est.8b05600, 2019.

Gentner, D. R., Worton, D. R., Isaacman, G., Davis, L. C., Dallmann, T. R., Wood, E. C., Herndon, S. C., Goldstein, A. H., and Harley, R. A.: Chemical Composition of Gas-Phase Organic Carbon Emissions from Motor Vehicles and Implications for Ozone Production, Environmental Science & Technology, 47, 11837-11848, 10.1021/es401470e, 2013.

Gentner, D. R., Jathar, S. H., Gordon, T. D., Bahreini, R., Day, D. A., El Haddad, I., Hayes, P. L., Pieber, S. M., Platt, S. M., de Gouw, J., Goldstein, A. H., Harley, R. A., Jimenez, J. L., Prevot, A. S., and Robinson, A. L.: Review of Urban Secondary Organic Aerosol Formation from Gasoline and Diesel Motor Vehicle Emissions, Environ Sci Technol, 51, 1074-1093, 10.1021/acs.est.6b04509, 2017.

Lu, Q., Zhao, Y., and Robinson, A. L.: Comprehensive organic emission profiles for gasoline, diesel, and gas-turbine engines including intermediate and semi-volatile organic compound emissions, Atmospheric Chemistry and Physics, 18, 17637-17654, 10.5194/acp-18-17637-2018, 2018.

Lyu, M., Bao, X., Zhu, R., and Matthews, R.: State-of-the-art outlook for light-duty vehicle emission control standards and technologies in China, Clean Technologies and Environmental Policy, 22, 757-771, 10.1007/s10098-020-01834-x, 2020.

Shen, X., Lv, T., Zhang, X., Cao, X., Li, X., Wu, B., Yao, X., Shi, Y., Zhou, Q., Chen, X., and Yao, Z.: Real-world emission characteristics of black carbon emitted by on-road China IV and China V diesel trucks, Science of The Total Environment, 799, 149435, https://doi.org/10.1016/j.scitotenv.2021.149435, 2021.

Zhao, Y., Saleh, R., Saliba, G., Presto, A. A., Gordon, T. D., Drozd, G. T., Goldstein, A. H., Donahue, N. M., and Robinson, A. L.: Reducing secondary organic aerosol formation from gasoline vehicle exhaust, Proc Natl Acad Sci U S A, 114, 6984-6989, 10.1073/pnas.1620911114, 2017.

Zhou, H., Zhao, H., Hu, J., Li, M., Feng, Q., Qi, J., Shi, Z., Mao, H., and Jin, T.: Primary particulate matter emissions and estimates of secondary organic aerosol formation potential from the exhaust of a China V diesel engine, Atmospheric Environment, 218, 116987, https://doi.org/10.1016/j.atmosenv.2019.116987, 2019.