Response to the Comments of the Reviewer

Dear Editor and Reviewer,

We would like to thank you and the reviewer for the great efforts and elaborate work on this manuscript.

We revised the manuscript by responding to each of the suggestions in the reviews. In our response, the questions of the reviewers are shown in ***Italic*** form and the responses in standard form.

We appreciate your help and time.

Sincerely yours,

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This manuscript reports the VOCs and OH reactivity characteristics of vehicle evaporative emissions. The study selected two main emission standard stages from the Chinese vehicle fleet as test objects, which can to some extent reflect the important characteristics of evaporative emissions from Chinese vehicle fleet. The team also improved the measurement method and used direct measurement of OH total reactivity to measure evaporative emissions. The research results are relatively rare and have high scientific significance. Anyway, some revisions need to be made before acceptance.

Response: We appreciate your comments and great efforts on this manuscript. Based on your comments, we have made corresponding revisions. In the response, the reviewer's comments are marked in ***italics***, and the revisions made to the manuscript are in blue standard form. Lastly, we would like to thank you again for your constructive comments.

Major comments:

In the research methodology, the author only selected gasoline vehicles in two emission standard stages, China VI and China V. Why were measurements not conducted on previous emission standard vehicles, such as China IV and China III, according to the China Mobile Source Environmental Management Annual Report (2024), these vehicles still have a high contribution to the emission of air pollutants.

Response: We appreciate your comment and this issue was indeed within the scope of our experimental design considerations. Based on your suggestion, we have made modifications to the description in the methodology. The following revised content is in the first paragraph of the section 2.1 in the manuscript.

In the emission standards of China V and previous stages, the implementation of emission limits is consistent (2 g/test), and the testing methods from China III to China V were also the same. According to statistical data, hydrocarbons emitted by vehicles in the stages of China III to China V are the main source of emissions for gasoline vehicles (Ministry of Ecology and Environment, 2022, 2024). Therefore, in the experimental design of this study, China V vehicles were used as the vehicles for the previous stage of emission standards for testing, in order to compare with China VI emission stage vehicles.

References:

Ministry of Ecology and Environment: China Mobile Source Environmental Management Annual Report, 2022.

Ministry of Ecology and Environment: China Mobile Source Environmental Management Annual Report, 2024.

The description of the method in Section 2.3 is not clear enough and needs to be revised accordingly. The calculation method of emission factors of VOCs species is described. In this experiment, the evaporative emission test using VT-SHED should emphasize whether there is gas exchange during the measurement. In addition, the calculation process of THC should also be given here. The calculation formula can refer to the relevant standard (GB 18352.6-2016).

Response: We appreciate your comment and have made revisions to the issues in the manuscript. The following revised content is in the first paragraph of the section 2.3 in the manuscript.

The emission calculation of THC in the experiment was carried out by the SHED online measurement system, and its calculation method refers to the calculation process of THC in the China VI standard (GB 18352.6-2016). The description is as follows:

$$EF_{THC} = k \times V \times 10^4 \times \left(\frac{C_{THC,f} \times P_f}{T_f} - \frac{C_{THC,i} \times P_i}{T_i}\right) + M_{THC,out} - M_{THC,in} \quad (1)$$

where EF_{THC} is the evaporative emission mass of THC, g; k is a constant, 1.2×(12+H/C), in the HSL and DBL processes, H/C was set to 2.2 and 2.33, respectively; V is the corrected volume of SHED, m^3; $C_{THC,f}$ is the final concentration of THC within SHED, ppm; $C_{THC,i}$ is the initial concentration of THC within SHED, ppm; P_f and P_i are the pressure at the end and start of the sampling process, kPa; T_f and T_i are the pressure at the end and start of the sampling process, K; $M_{THC,out}$ and $M_{THC,in}$ are the amounts of THC emitted and entering SHED during the experiment, respectively; there was no exchange of THC between SHED and the ambient atmosphere during this experiment. Based on this formula, the evaporation emission factors of HSL, DBL24, and DBL48 were calculated separately. In the evaporative emission process, the unit of HSL is g/h, and, the unit of DBL is g/d.

In Section 3.1, in the analysis of emission factors, the measurement results of high emission vehicles (Vehicle I) are noted. This result is different from previous studies. It not only gives the emissions of normal vehicles, but also has abnormal vehicle results. This result has good novelty and scientific value. In this part, the results of high emission vehicles are included in the supplementary materials, which makes the important results not highlighted. It is suggested that the author adjust the content of this part to highlight the results of high emission vehicles.

Response: We appreciate your comment. To highlight the situation of high emission vehicles, we have plotted the results of high emission vehicles in Figure 2.

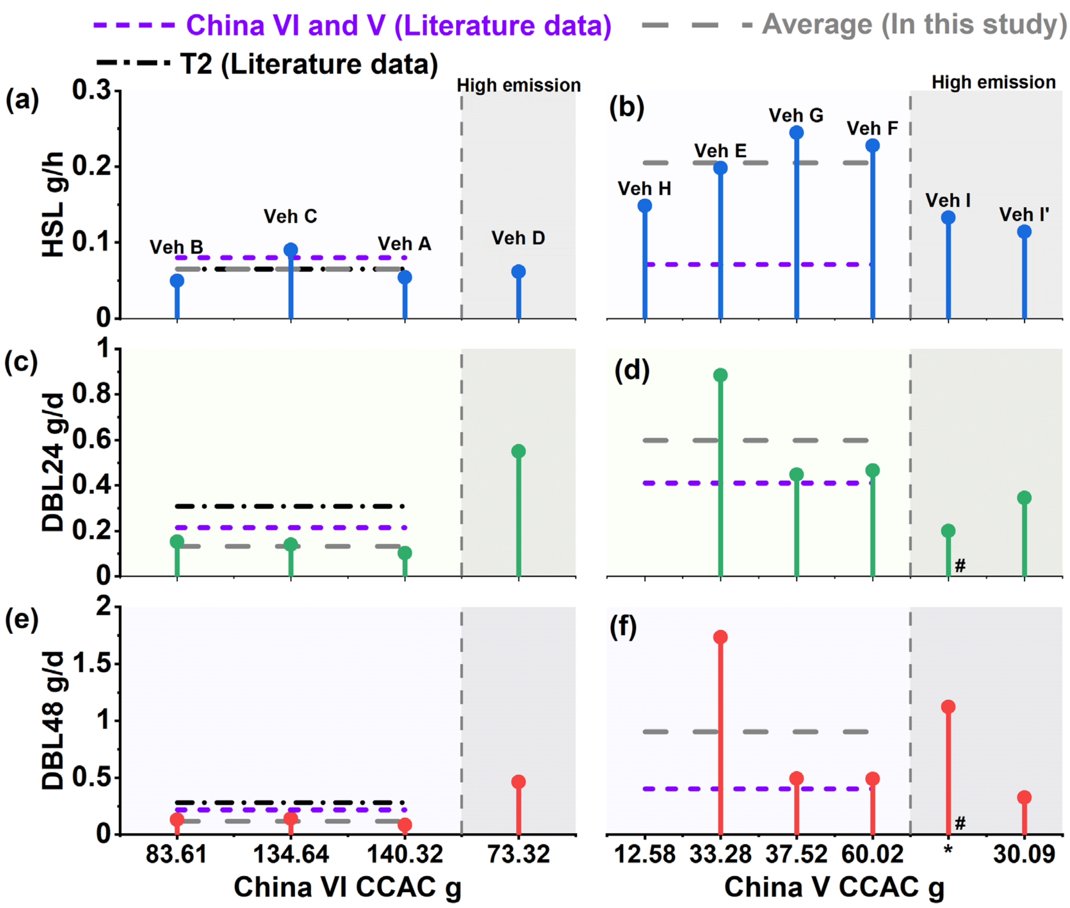

Figure 2. Evaporative emission factors of different vehicles and processes (Liu et al., 2015; Zi et al., 2023). (a) China VI HSL; (b) China V HSL; (c) China VI DBL24; (d) China V DBL24; (e) China VI DBL48; (f) China V DBL48; CCAC: carbon canister adsorption capacity; *: CACC data could not be obtained, please refer to section 2.1 for details; #: the data has been reduced by 10 times.

References:

Liu, H.;Man, H.;Tschantz, M.;Wu, Y.;He, K.;Hao, J. VOC from vehicular evaporation emissions: status and control strategy, Environ. Sci. Technol., 49, 14424-14431, https://doi.org/10.1021/acs.est.5b04064, 2015.

Zi, T.;Wang, P.;Liu, B.;Zhou, Y.;Shen, X. e.;Zhang, L.;Lu, Y.;Feng, Q.;Yang, Y.;Lang, J. Evaporative emission characteristics of VOCs from in-use light-duty gasoline vehicles, Atmos. Environ., 312, 120024, https://doi.org/10.1016/j.atmosenv.2023.120024, 2023.

There are still some problems in the language description of the manuscript, and the author is suggested to modify the language.

Response: We appreciate your comment and have made language revisions to the manuscript.

Specific comments:

L73 and L83: "Euro4" and "E4" writing need to be unified.

Response: We appreciate your comment and will use "E4" uniformly in the manuscript revision.

L98-101: there is ambiguity in the expression, whether it is pollutant emissions or vehicle population, and please provide the specific time of the data.

Response: We appreciate your comment and have made revisions to this description. The following revised content is in the second paragraph of the section 1 in the manuscript.

Moreover, the stock of gasoline vehicles accounts for 88.7% of the Chinese fleet in 2018, while the stock of diesel vehicles accounts for 41.3% in the European Union in 2015(Environment, 2019; Chossiere et al., 2018).

References:

Chossiere, G. P.;Malin, R.;Allroggen, F.;Eastham, S. D.;Speth, R. L.;Barret, S. R. H. Country- and manufacturer-level attribution of air quality impacts due to excess NOx emissions from diesel passenger vehicles in Europe, Atmos. Environ., 189, 89-97, https://doi.org/10.1016/j.atmosenv.2018.06.047, 2018.

Ministry of Ecology and Environment. China Mobile Source Environmental Management Annual Report, 2019.

L115: "China IV/V" can provide specific explanations to express its meaning.

Response: We appreciate your comment and have made revisions to this description. This "China IV/V" expression refers to the results of testing vehicles in the China IV and V. In the description modification of the introduction, we have made improvements to this section and have avoided the vague expression.

L74, L86 and L117: the author's writing of numbers and units is not standardized, at least consistency should be achieved in the manuscript. Please also check other parts of the manuscript for similar descriptions.

Response: We appreciate your comment and have made revisions to this description. At the same time, we also checked other similar descriptions in the manuscript and made unified modifications.

In Section 2.1, L143-145: the author conducted experiments using customized experimental gasoline. What is the purpose of this experiment and can be highlighted.

Response: We appreciate your comment and have made revisions to this description. The following revised content is in the first paragraph of the section 2.1 in the manuscript.

This experiment compared different emission stages of vehicle models during testing, so by using a uniform gasoline in the experiment, the influence of emission results caused by differences in gasoline products can be avoided.

In Section 3.1, second paragraph, it is noted that abnormal carbon canister can lead to higher THC emissions, which is a significant conclusion and implies an important regulatory target for vehicle evaporative emissions. Suggest the author to conduct in-depth analysis, such as the proportion of this type of vehicle in the actual vehicle fleet.

Response: We appreciate your comment and have made revisions to this description. The following revised content is in the second paragraph of the section 3.1 in the manuscript.

As the evaporation control system of motor vehicles, the working state of the carbon canister determines the control efficiency of evaporation emissions. Previous research has shown that the qualification rate of evaporative emission control systems in fleets was tested, and it was found that the qualification rate of vehicles in the China V stage was between 44 - 75%, and other studies have also shown it to be 33.83% (Lu et al., 2022; Zhang and Hua, 2024). This indicates that abnormal conditions in the evaporative emission control system are a common problem, and also suggests that in the management of VOCs in vehicles, this part of the vehicles should be a key focus of supervision.

References:

Lu, J.;Huang, C.;Xiu, G.;Ma, D.;Li, Y.;Liang, Z.;Lai, Y. Study on leakage test of fuel evaporation control system based on light-duty gasoline vehicle, The Administration and Technique of Environmental Monitoring (Adm. Tech. Environ. Monit.), 34, 45-48, 10.19501/j.cnki.1006-2009.2022.03.008, 2022.

Zhang, Y.;Hua, C. Research on the leakage detection of the operational vehicles fuel evaporation system, Automobile Applied Technology (Automob. Appl. Technol.), 112-115, 10.16638/j.cnki.1671-7988.2024.021.021, 2024.

L396: the writing of "PAMS (Photo Assessment Monitoring Stations)" is incorrect and needs to be corrected.

Response: We appreciate your comment and the description of PAMS (Photochemical Assessment Monitoring Stations) has been modified.

L398-400: this sentence description and logical analysis are not reasonable. The author mainly describes the emission characteristics here, and the "high reactivity" mentioned here is ambiguous.

Response: We appreciate your comment and have made revisions to this description. The following revised content is in the second paragraph of the section 3.2 in the manuscript.

In this study, by increasing quantitative measurements of BC-alkenes, it was found that evaporative emissions exhibit distinct characteristics of BC-alkenes emissions, and their contribution levels were also close to those of L-alkenes.

L440-441: the explanation and description here are not sufficient, and the author can emphasize the differences in component composition between DBL process emissions and gasoline headspace.

Response: We appreciate your comment and have made revisions to this description. The following revised content is in the third paragraph of the section 3.2 in the manuscript.

Although LC-alkanes was very important in gasoline headspace and evaporative emissions, there are still differences in the main species. At the same time, there was still significant differences compared to the HSL process, such as aromatics. Gasoline headspace is an important source of evaporative emissions, due to different emission processes, there are also significant differences in its compositions, which reflects the importance of conducting tests on different evaporative emission process.

Line 562: in the title, the beginning letter of "Calculation" needs to be lowercase. It is suggested that the author also check other similar problems in the manuscript.

Response: We appreciate your comment and the description of the manuscript has been revised. The following revised content is in the title of Figure 6 in the manuscript.

Contribution characteristics of the OH reactivity calculation results of the evaporation emission components.

L598 and L635: writing error, the first letter needs to be lowercase.

Response: We appreciate your comment and the description of the manuscript has been revised. The following revised content is in the fourth and sixth paragraph of the section 3.3 in the manuscript.

Compare with DBL process, higher temperature of HSL is beneficial for the volatile emissions of large molecular species (such as aromatics) and can also increase the complexity of components.

When the high emissions of vehicle (the k_{OH} test for the DBL48 process of China V vehicle I failed, so the reactivity source profiles composition was not shown here) was caused by abnormal evaporative emission control system (carbon canister), the changes in reactive species will be different from the high emissions of vehicle D, and the impact of low-carbon species will be more significant.

L607-609: additional references are needed.

Response: We appreciate your comment and the description of the manuscript has been revised. The following revised content is in the fifth paragraph of the section 3.3 in the manuscript.

As shown in Figure 5e, f and g, using the source profiles provided in the related research, focusing on 35 species, it was found that the missed reactivity would further expand (Liu et al., 2022).

Reference:

Liu, Y.;Zhong, C.;Peng, J.;Wang, T.;Wu, L.;Chen, Q.;Sun, L.;Sun, S.;Zou, C.;Zhao, J.;Song, P.;Tong, H.;Zhang, L.;Wang, W.;Mao, H. Evaporative emission from China 5 and China 6 gasoline vehicles: Emission factors, profiles and future perspective, J. Cleaner Prod., 331, 129861, https://doi.org/10.1016/j.jclepro.2021.129861, 2022.

The writing of figure titles in the manuscript is not standardized. In Figures S3 and S5, the initial letters of words are capitalized, which is inconsistent with the titles of other figures.

Response: We appreciate your comment and the description of the manuscript has been revised.

In Section 3.3, the author calculated the emission source profiles based on OH reactivity, and suggested supplementary the species classification and number of reactivity source profiles.

Response: We appreciate your comment and the description of the manuscript has been revised. The following revised content is in the sixth paragraph of the section 3.3 in the manuscript.

Forty-seven VOC species were selected, including 2 HC-alkanes, 8 LC-alkanes, 1 cycloalkane, 9 L-alkenes, 7 BC-alkenes, 11 aromatics and 9 OVOCs, accounting for more than 95% of the k_{OH}^{cal}.

In the conclusion of the Section 4, the first paragraph can supplement the relevant conclusions of high emission vehicles.

Response: We appreciate your comment and the description of the manuscript has been revised. The following revised content is in the first paragraph of the section 4 in the manuscript.

The comparative experiment of carbon canister working conditions shows that in the DBL24 and 48 emission process, the emissions of THC from abnormal conditions (1.987 g/d and 11.209 g/d) were significantly higher than those from normal working conditions (0.345 g/d and 0.326 g/d). The emissions of THC from high mileage vehicles can reach about 4 times the normal emissions. Under high emission conditions, the contribution of LC-alkanes will significantly increase. This conclusion also indicates that in the control of vehicle evaporative emissions, the regulation of high emission vehicles should be a key target for evaporative emission sources.