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,

Xin Li and Co-authors.

College of Environmental Sciences and Engineering
Peking University
100871 Beijing China
E-mail: li_xin@pku.edu.cn
Tel: +86-185 1358 6831

In this manuscript, the authors investigate evaporative emissions from in-use light-duty gasoline vehicles under China's latest regulatory standards. They quantify and compare emission characteristics—including emission factors, chemical composition, and total hydroxyl radical reactivity (k_{OH})—across three processes (HSL, DBL24h, and DBL48h) for vehicles compliant with the China VI and China V standards. The study identifies key reactive volatile organic compound (VOC) species contributing to atmospheric photochemical processes.

The methodology of this paper is innovative, through the collection of on-site observation data, combined with mass spectrometry and other qualitative and quantitative methods, the study integrates the use of online and offline techniques, making the analysis more comprehensive. This study fills the gap of evaporative emission data under the new emission standard, provides a high-precision scientific basis for the control of motor vehicle evaporative emission, and has an important reference value for motor vehicle pollution control policy. The manuscript deserves to be published in the journal after the authors address the concerns below.

Response: We appreciate the great efforts and elaborate work of the reviewers. Based on the comments, we have made corresponding revisions. In the following, 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.

Specific comments:

The authors note significant discrepancies in evaporative emission components and emission factors across different studies, attributing these differences primarily to the number of species measured (P4, Lines 105–112). However, the discussion lacks further analysis of other potential influencing factors such as vehicle operation conditions, fuel formulation, temperature variations, or carbon canister aging. It is recommended to include a more comprehensive discussion of these aspects in this section.

Response: We appreciate your comment and apologize for the problem in our description. In the revision, we have added analysis and discussion. The following revised content is in the third paragraph of the section 1 in the manuscript.

The chemical composition of VOCs emitted by vehicle evaporation mainly consists of alkanes, alkenes, aromatics and oxygenated VOCs (OVOCs) (Man et al., 2020; Liu et al., 2022). However, there are significant differences in chemical composition understanding in different studies. For example, some studies suggest that the proportion of alkanes in the DBL process reaches 68.5 - 91.6% (China IV and T2), while others suggest it was 55.3% and 51.1% (China IV and V). This difference was mainly due to the different number of species being focused on, with the former testing 57 VOCs and the latter testing 115 VOCs, measuring the number of species directly affects the understanding of the composition of emission components (Yue et al., 2017; Zi et al., 2023). In the study of evaporative emissions, measurement procedures corresponding to national standards are usually used to ensure consistency in measurement methods. However, the fuel formulation is also a factor that affects the chemical composition of evaporative emissions. For example, the use of ethanol gasoline has increased the contribution of low-carbon species(Li et al., 2024). In addition, in the testing of China VI vehicles, there is a significant difference in the contribution results of OVOCs, through comparison, it was found that there are significant differences in fuel formulation and vehicle condition (Liu et al., 2022; Zi et al., 2023). In the study of gasoline evaporation, branched chain alkenes (BC-alkenes) were considered as important OH radical reactive species in gasoline evaporation (Wu et al., 2015). In addition, emissions of BC-alkenes have also been observed in oil sands facilities, such as 2-methyl-2-butene and 2-methyl-1-butene (Li et al., 2017). Measurement of BC-alkenes emissions was also noted in early studies on evaporative emissions (Liu et al., 2008; Lu et al., 2003; Zhang et al., 2013). However, there are currently few measurements of this species in research on vehicles in China VI and V. At present, GC-MS/FID (Gas Chromatography-Mass Spectrometry/Flame Ionization Detection) is commonly used for measuring VOCs, with reference gases such as PAMS (Photochemical Assessment Monitoring Stations) and TO-15 (Toxic Organics-15) (Liu et al., 2022; Zi et al., 2023; Yue et al., 2017). However, there is still insufficient attention paid to the measurement of BC-alkenes, which directly affects the understanding of the evaporation and emission characteristics of China VI and V vehicles. Therefore, improvements can be made in the measurement method by determining the measurement species based on the characteristics of evaporative emission sources, and obtaining a more comprehensive VOCs emission source profiles. Moreover, in terms of emission factors, the DBL24 emissions of in-use vehicle and new vehicle in China V were 5.27 g/test and 0.81 g/test, respectively, indicating that in use vehicles may have significantly increased emissions due to aging vehicle configurations (Liu et al., 2022). However, previous study has also suggested that the in-use vehicle of China V (DBL24) was 0.55 g/test (Yue et al., 2020). This significant difference in chemical composition and emission factors also lead to inconsistent understanding of evaporative emissions. Improvements can be made in measurement techniques and experimental procedures, such as adding measurement methods, customizing experimental fuel formulation, and selecting test vehicles, to ensure a complete and accurate understanding of evaporation emissions. Therefore, further research is needed on the composition of chemical components and emission factors, especially on the China VI vehicles after the revision of evaporative emission standards, which are still relatively rare compared to vehicle research in China V and before.

References:

Li, R.;Zhong, C.;Ning, Y.;Liu, Y.;Song, P.;Xu, R.;Mao, H. Exhaust and evaporative volatile organic compounds emissions from vehicles fueled with ethanol-blended-gasoline, Environ. pollut., 357, 124163, https://doi.org/10.1016/j.envpol.2024.124163, 2024.

Li, S.-M.;Leithead, A.;Moussa, S. G.;Liggio, J.;Moran, M. D.;Wang, D.;Hayden, K.;Darlington, A.;Gordon, M.;Staebler, R.;Makar, P. A.;Stroud, C. A.;McLaren, R.;Liu, P. S. K.;O'Brien, J.;Mittermeier, R. L.;Zhang, J.;Marson, G.;Cober, S. G.;Wolde, M.;Wentzell, J. J. B. Differences between measured and reported volatile organic compound emissions from oil sands facilities in Alberta, Canada, Proc. Natl. Acad. Sci., 114, E3756-E3765, 10.1073/pnas.1617862114, 2017.

Liu, Y.;Shao, M.;Fu, L.;Lu, S.;Zeng, L.;Tang, D. Source profiles of volatile organic compounds (VOCs) measured in China: Part I, Atmos. Environ., 42, 6247-6260, https://doi.org/10.1016/j.atmosenv.2008.01.070, 2008.

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.

Lu, S.;Bai, Y.;Zhang, G.;Ma, J. Study on the Characteristics of VOCs Source Profiles of Vehicle Exhaust and Gasoline Emission, Acta Sci. Nat. Univ. Pekin., 39, 507-511, 10.13209/j.0479-8023.2003.077, 2003.

Man, H.;Liu, H.;Niu, H.;Wang, K.;Deng, F.;Wang, X.;Xiao, Q.;Hao, J. VOCs evaporative emissions from vehicles in China: Species characteristics of different emission processes, Environ. Sci. Ecotechnol., 1, 100002, https://doi.org/10.1016/j.ese.2019.100002, 2020.

Wu, Y.;Yang, Y.;Shao, M.;Lu, S. Missing in total OH reactivity of VOCs from gasoline evaporation, Chin. Chem. Lett., 26, 1246-1248, https://doi.org/10.1016/j.cclet.2015.05.047, 2015.

Yue, T.;Yue, X.;Chai, F.;Hu, J.;Lai, Y.;He, L.;Zhu, R. Characteristics of volatile organic compounds (VOCs) from the evaporative emissions of modern passenger cars, Atmos. Environ., 151, 62-69, https://doi.org/10.1016/j.atmosenv.2016.12.008, 2017.

Yue, T.;Wang, M.;Huang, Z.;Wang, X.;Wang, Z.;Wang, B.;Zhang, L.;Wang, S. Characteristics of evaporative emissions from light-duty vehicles and effects of ambient temperature on evaporative emissions of light-duty vehicles, Res. Environ. Sci., 33, 73-81, 10.13198/j.issn.1001-6929.2019.07.25, 2020.

Zhang, Y.;Wang, X.;Zhang, Z.;Lu, S.;Shao, M.;Lee, F. S. C.;Yu, J. Species profiles and normalized reactivity of volatile organic compounds from gasoline evaporation in China, Atmos. Environ., 79, 110-118, https://doi.org/10.1016/j.atmosenv.2013.06.029, 2013.

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.

The study highlights the critical role of branched-chain alkenes (BC-alkenes) in accounting for missing OH reactivity, emphasizing the need for their inclusion in chemical analysis. However, the Introduction section does not mention this rationale. It is suggested to include a relevant discussion in the Introduction to better justify the novelty and significance of the study.

Response: We appreciate your comment and have added the relevant discussion content. The following revised content is in the third paragraph of the section 1 in the manuscript.

In the study of gasoline evaporation, branched chain alkenes (BC-alkenes) were considered as important OH radical reactive species in gasoline evaporation (Wu et al., 2015). In addition, emissions of BC-alkenes have also been observed in oil sands facilities, such as 2-methyl-2-butene and 2-methyl-1-butene (Li et al., 2017). Measurement of BC-alkenes emissions was also noted in early studies on evaporative emissions (Liu et al., 2008; Lu et al., 2003; Zhang et al., 2013). However, there are currently few measurements of this species in research on vehicles in China VI and V. At present, GC-MS/FID (Gas Chromatography-Mass Spectrometry/Flame Ionization Detection) is commonly used for measuring VOCs, with reference gases such as PAMS (Photochemical Assessment Monitoring Stations) and TO-15 (Toxic Organics-15) (Liu et al., 2022; Zi et al., 2023; Yue et al., 2017). However, there is still insufficient attention paid to the measurement of BC-alkenes, which directly affects the understanding of the evaporation and emission characteristics of China VI and V vehicles. Therefore, improvements can be made in the measurement method by determining the measurement species based on the characteristics of evaporative emission sources, and obtaining a more comprehensive VOCs emission source profiles.

References:

Li, S.-M.;Leithead, A.;Moussa, S. G.;Liggio, J.;Moran, M. D.;Wang, D.;Hayden, K.;Darlington, A.;Gordon, M.;Staebler, R.;Makar, P. A.;Stroud, C. A.;McLaren, R.;Liu, P. S. K.;O'Brien, J.;Mittermeier, R. L.;Zhang, J.;Marson, G.;Cober, S. G.;Wolde, M.;Wentzell, J. J. B. Differences between measured and reported volatile organic compound emissions from oil sands facilities in Alberta, Canada, Proc. Natl. Acad. Sci., 114, E3756-E3765, 10.1073/pnas.1617862114, 2017.

Liu, Y.;Shao, M.;Fu, L.;Lu, S.;Zeng, L.;Tang, D. Source profiles of volatile organic compounds (VOCs) measured in China: Part I, Atmos. Environ., 42, 6247-6260, https://doi.org/10.1016/j.atmosenv.2008.01.070, 2008.

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.

Lu, S.;Bai, Y.;Zhang, G.;Ma, J. Study on the Characteristics of VOCs Source Profiles of Vehicle Exhaust and Gasoline Emission, Acta Sci. Nat. Univ. Pekin., 39, 507-511, 10.13209/j.0479-8023.2003.077, 2003.

Wu, Y.;Yang, Y.;Shao, M.;Lu, S. Missing in total OH reactivity of VOCs from gasoline evaporation, Chin. Chem. Lett., 26, 1246-1248, https://doi.org/10.1016/j.cclet.2015.05.047, 2015.

Yue, T.;Yue, X.;Chai, F.;Hu, J.;Lai, Y.;He, L.;Zhu, R. Characteristics of volatile organic compounds (VOCs) from the evaporative emissions of modern passenger cars, Atmos. Environ., 151, 62-69, https://doi.org/10.1016/j.atmosenv.2016.12.008, 2017.

Zhang, Y.;Wang, X.;Zhang, Z.;Lu, S.;Shao, M.;Lee, F. S. C.;Yu, J. Species profiles and normalized reactivity of volatile organic compounds from gasoline evaporation in China, Atmos. Environ., 79, 110-118, https://doi.org/10.1016/j.atmosenv.2013.06.029, 2013.

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.

In the methodology, the China VI test procedure includes the carbon canister loading step after the first refueling. Was this adjustment intended to simulate the initial adsorption state of the canister following long-term vehicle parking? Please clarify the rationale behind this modification and its potential influence on test results.

Response: We appreciate your comment and supplemented the description of this section. As you asked, loading the carbon canister after refueling also reflects to some extent the long-term parking situation of the vehicle. We believe that there are several considerations for this preprocessing, which aims to reflect the evaluation of the control level of vehicle evaporative emissions and the actual emission results. The first process of draining, refueling, and soaking the vehicle is mainly to eliminate the influence of existing oil (unknown source) in the vehicle and reduce its impact on the experimental results. By driving and performing operations such as draining and refueling again, the impact of this situation can be eliminated, allowing the vehicle's fuel to be replaced with customized gasoline. Exclude the impact caused by differences in oil products. The evaporative emissions of vehicles are mainly controlled by the adsorption capacity of carbon canister. Loading and breakdown the carbon canister, while experiencing high temperature soaking, can be considered as the vehicle having been parked for a long time, causing the carbon canister to lose its adsorption capacity. The driving of the vehicle can cause the desorption of hydrocarbons adsorbed in the carbon canister, allowing the canister to regain its adsorption capacity. Therefore, through a unified driving cycle, the carbon canister adsorption capacity of the vehicle can be activated before conducting evaporative emission testing, which can better reflect the actual situation of the vehicle and also help to compare the emission results of different vehicles. This is also the reason why this study uses a unified vehicle testing method for evaporative emissions. Therefore, the following revised content is in the first paragraph of the section 2.1 in the manuscript.

After the vehicle undergoes various processes, such as draining gasoline, refueling, pre-treatment driving, draining gasoline and refueling again, carbon canister loading, and high-temperature driving, etc. The carbon canister of the vehicle's evaporative emission system is loaded and breakdown, and the vehicle is soaking in high temperature. After the evaporative emission control system fails, it undergoes a unified driving cycle, activating the carbon canister's adsorption capacity. At this point, it can reflect the actual situation of the vehicle's ability to control evaporative emissions. Based on this state, conducting evaporative emission testing can obtain the true evaporative emission results of the vehicle. After the vehicle is driven at high temperatures, HSL, DBL24 and DBL48 (emissions on the second day after parking) measurement are conducted in the SHED.

The study emphasizes that BC-alkenes contribute 25.7–39% to OH reactivity (P23, Lines 520–523). However, Section 2.2 only mentions the use of seven BC-alkene standards for calibration (Line 212), without providing validation details. This could

lead to potential over- or underestimation of highly reactive species. It is recommended to include (in the Methods or Supplementary Materials) the standard curve parameters, repeatability test results, and recovery rates from spiked blank matrices, as well as discussion on possible interferences and how they were mitigated.

Response: We appreciate your comment and relevant descriptions were added to the method. The following revised content is in the fourth paragraph of the section 2.2 in the manuscript.

Before each sample measurement, a nitrogen sample will be measured to ensure equipment stability before conducting sample testing. The quantitative curve of GC-MS/FID was performed using a customized mixed standard gas of 116 VOCs components. Set five concentration gradients were set during calibration, namely 0.5, 1, 2, 4 and 8 ppb, and repeat each concentration gradient twice. The R^2 of calibration curve was 0.98 or above. The VOCs species were shown in Table S3. For species with overlapping OVOCs components and VOCUS-Eiger measurements, use VOCUS-Eiger measurement results. We have customized 7 BC-alkenes, isobutene, 3-methyl-1-butene, 2-methyl-1-butene, 2-methyl-2-butene, 4-methyl-1-pentene, 2-methyl-1-pentene and 2-methyl-2-pentene. Characteristic ion fragments were considered in the measurement, peak retention times were identified and these fragments were added to the GC-MS/FID measurement method to obtain calibration data, thereby achieving quantitative determination of the sample concentration (Table S4). The establishment of the standard curve is consistent with the 116 VOCs component method mentioned above. The R^2 of the calibration curve can reach 0.99. Considering the measurement of isoprene in 116 VOCs components, a total of 8 BC-alkenes were quantitatively measured in this study.

Figures 4 and 7 present source profile information, but due to the high number of species displayed, it is difficult to identify key components. It is suggested to simplify the figures by grouping similar compounds and highlighting the top 10 individual species, or breaking the figures into subpanels with a clearer focus on critical contributors.

Response: We appreciate your comment and have made revised to Figures 4 and 7 based on your suggestions. In order to better display the key species in the source profiles, we have plotted the key 10 individual species in the source profiles and Figures 4 and 7 with complete source profiles data were included in the supplementary materials (Figures S4 and S5).

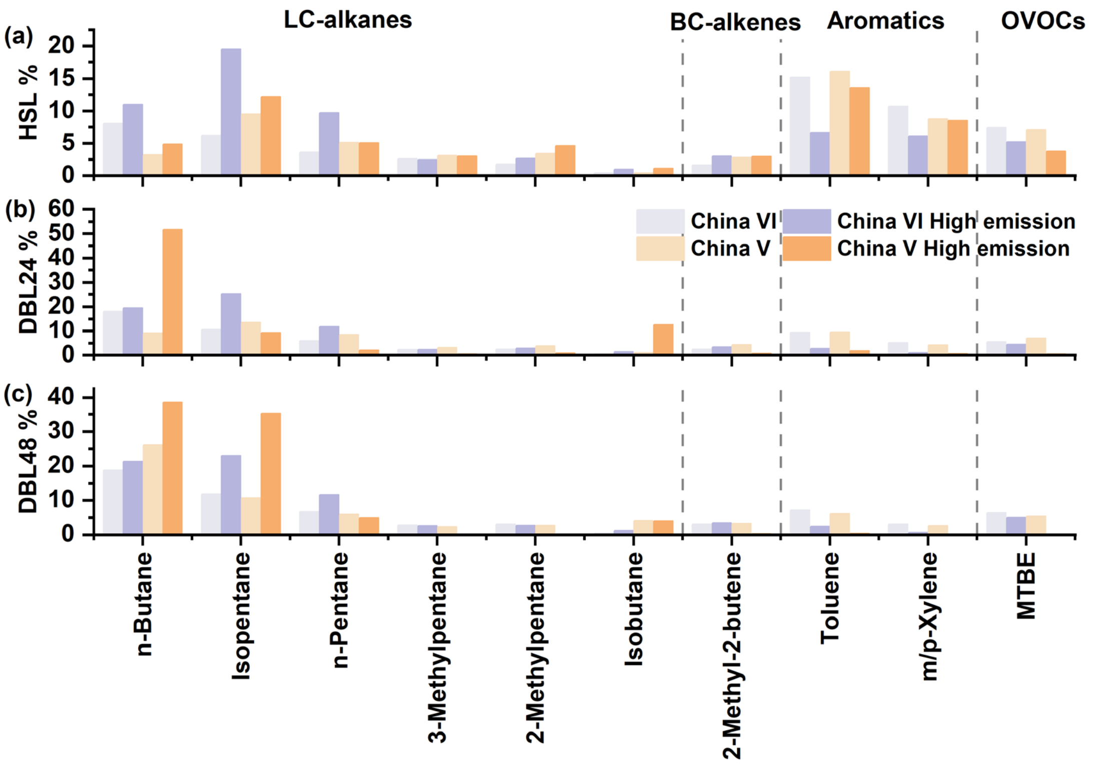

Figure 4. Weight percentage of HSL, DBL24 and DBL48 key species in the source profiles for evaporative emissions; the complete source profiles information is shown in Figure S4 of the supplementary materials.

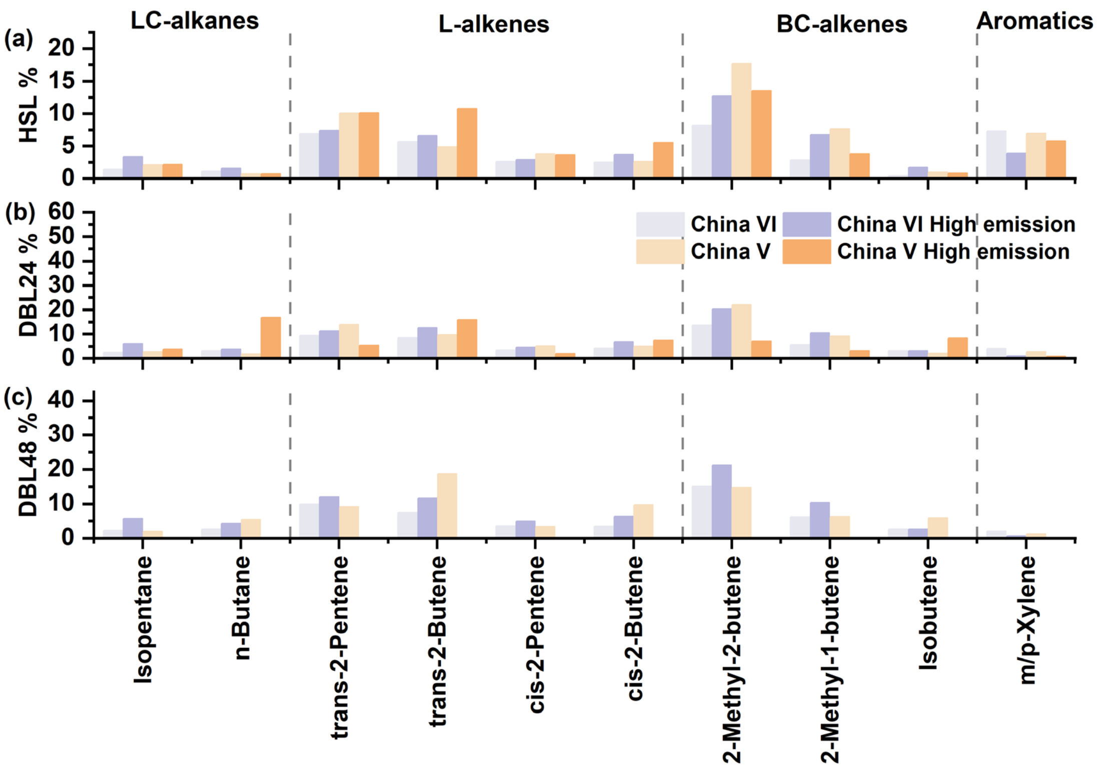

Figure 7. OH reactivity percentage of HSL, DBL24 and DBL48 key species in the source profiles for evaporative emissions; the complete source profiles information is shown in Figure 4 of the supplementary materials.

In the hot soak loss (HSL) test, China VI vehicles were tested at 38 °C after high-temperature driving, whereas China V vehicles were tested at ambient temperatures (23–31 °C). As temperature is a key variable, could this difference confound comparisons between standards? High temperatures promote the volatilization of high-boiling-point VOCs (e.g., aromatics), possibly resulting in a systematic overestimation of China VI emissions and underestimation for China V. (P13, Lines 320–334)

Response: We appreciate your comment. As you mentioned, different temperature settings can lead to differences in evaporative emissions. Due to the modification of the testing temperature setting in the China VI and V standards, we have given particular consideration to the impact of this factor in the experimental design. So, when this study was conducted, the testing procedures for implementing the China VI emission standards for China VI and V vehicles were targeted. Through a unified testing process (China VI), it can more accurately reflect the differences in evaporative emissions of vehicles at different emission stages. The China VI standard has improved the temperature setting for testing compared to China V, and the representativeness of measurement results has also been improved compared to actual environmental conditions (Rodríguez et al., 2019). On this basis, as a comparison, we also chose the same vehicle (vehicle G) and also conducted evaporative emission results for different testing procedures. Therefore, the following revised content is in the third paragraph of the section 3.1 in the manuscript.

Higher ambient temperatures promote evaporative emissions (Huang et al., 2022). The China VI testing method shows a significant improvement in the temperature setting of the testing program compared to the China V testing method. In order to demonstrate the differences in results between different testing methods, the same vehicle (vehicle G) was selected and a comparison was made between the China VI and China V testing methods. Using vehicle G (China VI test method) for testing, the THC of HSL was 1.5 times higher than the corresponding G' (China V test method) values (Figure S3). The testing procedure of China V has a temperature setting of 23 °C - 31 °C (test setting at 25 °C) in the HSL, which may not reflect the actual environmental conditions. By contrast, the 38 °C set by China VI HSL is closer to the environmental characteristics of the summer high temperature weather and also enhances the representativeness of the test results (Rodríguez et al., 2019).

References:

Huang, J.;Yuan, Z.;Duan, Y.;Liu, D.;Fu, Q.;Liang, G.;Li, F.;Huang, X. Quantification of temperature dependence of vehicle evaporative volatile organic compound emissions from different fuel types in China, Sci. Total Environ., 813, 152661, https://doi.org/10.1016/j.scitotenv.2021.152661, 2022.

Rodríguez, F.;Bernard, Y.;Dornoff, J.;Mock, P.: Recommendations for post-Euro 6 standards for light-duty vehicles in the European Union, The International Council on Clean Transportation Europe, 2019.

Section 3.2 establishes source profiles for China V/VI vehicles (Figure 4) and

suggests their applicability in source apportionment and emission inventory improvement (Lines 682–684). However, all measurements were based on a single gasoline type (China VI 95# gasoline, Table S1) and a limited number of vehicles (9 sedans/SUVs). Please clarify the applicability scope of these profiles and suggest boundaries for their use in the Conclusions section.

Response: We appreciate your comment and the description of this part was added in the conclusion section. The following revised content is in the second paragraph of the section 4 in the manuscript.

This study conducted measurements of VOCs components in evaporative emissions from in-use vehicles with different emission standards (two evaporative emission standards in the current fleet) and vehicle conditions (normal emissions and high emissions states) using customized China VI stage gasoline. In the chemical composition, n-butane (3.2 - 26.1%), isopentane (6.2 - 13.5%), n-pentane (3.6 - 8.4%), toluene (6.1 - 16.0%), m/p-xylene (2.5 - 10.7%), MTBE (5.3 - 7.4%) and 4-methyl-2-pentanone (0.4 - 5.8%) were the main contributors. For BC-alkenes and L-alkenes, 2-methyl-2-butene (1.6 - 4.3%), 2-methyl-1-butene (0.7 - 2.0%), and trans-2-pentene (1.6 - 3.4%) were found to be the main components. Simultaneously obtained the source profiles corresponding to high emission vehicles caused by high mileage and abnormal carbon canister. The supplementary measurement of BC-alkenes has also expanded the current understanding of the source profiles evaporative emissions from China VI and China V vehicles. In the analysis of evaporative emission tracer ratio, the n-pentane/ethane and MTBE/B ratio serve as a diagnostic marker to identify evaporative emissions and other vehicle-related sources. The established evaporative emission source profiles and the proposed tracer species ratio in this study can serve as important references for VOCs source apportionment in atmospheric ambient, and further identify the contribution characteristics of evaporative emissions based on vehicle emission sources. It also contributes to the improvement of evaporative emission inventories and the establishment of emission reduction governance systems based on key species.