Response to Reviewers

Reviewer #1

Overview

This manuscript characterizes gaseous emissions from a number of vehicles meeting a wide range of Chinese emissions standards, to include gasoline, diesel, and liquified petroleum gas (LPG), as measured using a chassis dynamometer setup. Measurements are primarily presented for those using a PTR-ToF-MS, and included canister sampling with GC-MS/FID analysis and a few species by Iodide CIMS, along with common measurements (CO_2, etc.) using a portable emissions measurement system. Oxygenated VOC's (OVOC) are indicated to be molecules with less than 18 carbons.

This work shows the strong influence of OVOC in diesel exhaust (>50% by mass) compared to a much smaller influence in gasoline vehicles (~15%). Clear differences between cold-start and hot-start emissions are also observed, notably they are much more significant for gasoline vehicles than for diesel vehicles, and aromatics and OVOC had similar temporal profiles. Some ratios of emissions (e.g. toluene to larger aromatics) are unique between gasoline and diesel vehicles, and are suggested as potentially useful for emissions attribution.

Overall the work as presented is quite thorough, and the intended goals of the work are clearly made. The insights from the work are a good contribution to the field. There are a few details that should be addressed, however prior to suitability for publication, notably quality control.

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.

General Comments

1. It is concerning that the agreement between canister with GC-MS/FID and PTR-ToF measurements for toluene are so disparate in more than 20% of the tested vehicles, as shown in Figure S6c. These discrepancies are essentially ignored in the manuscript.

How can canister measurements be near-zero while PTR-ToF measurements are 250 mg/km, and vice versa? Perhaps this might cold occur for more exotic species, but for toluene I would expect agreement at least within a factor of 2 in all cases, as it is a high volatility species that is easily ionized in PTR and observed with GC-MS/FID. Perhaps in some cases one or the other measurement was not made and simply reported as zero? This issue should be clarified. Furthermore, agreement between generally accepted canister measurements and PTR-ToF measurements must be reported for a wider variety of species, to include oxygenated species and larger aromatics.

Reply: We thank the reviewer for the comment. We also found this issue when we analyzed data for preparing the original manuscript, but we did not pay enough attention to it. We re-checked all the data and found a mistake in alignment of data points between offline canister-GC-MS/FID and PTR-ToF-MS for several gasoline vehicles and diesel vehicles. We have modified the corresponding data points, and added comparison of C_8 aromatics between two measurements (Fig. S6), obtaining generally consistent results, considering large variations of VOC emissions for driving conditions and the difficulty to control the fill time for canisters. We also revised related figures (Fig. 12 and Fig. S12) and description in the manuscript on the fractions of OVOCs in total VOC emissions in various types of vehicles. These modifications do not change any conclusion in the manuscript.

The sentence in the Section 2.3 (line 194-197) is modified to:

We compared emission factors from PTR-ToF-MS and the offline canister-GC-MS/FID (Fig. S6c-d), obtaining generally consistent results, considering the large variation of VOC emissions for driving conditions and the difficulty to control the fill time for canisters.

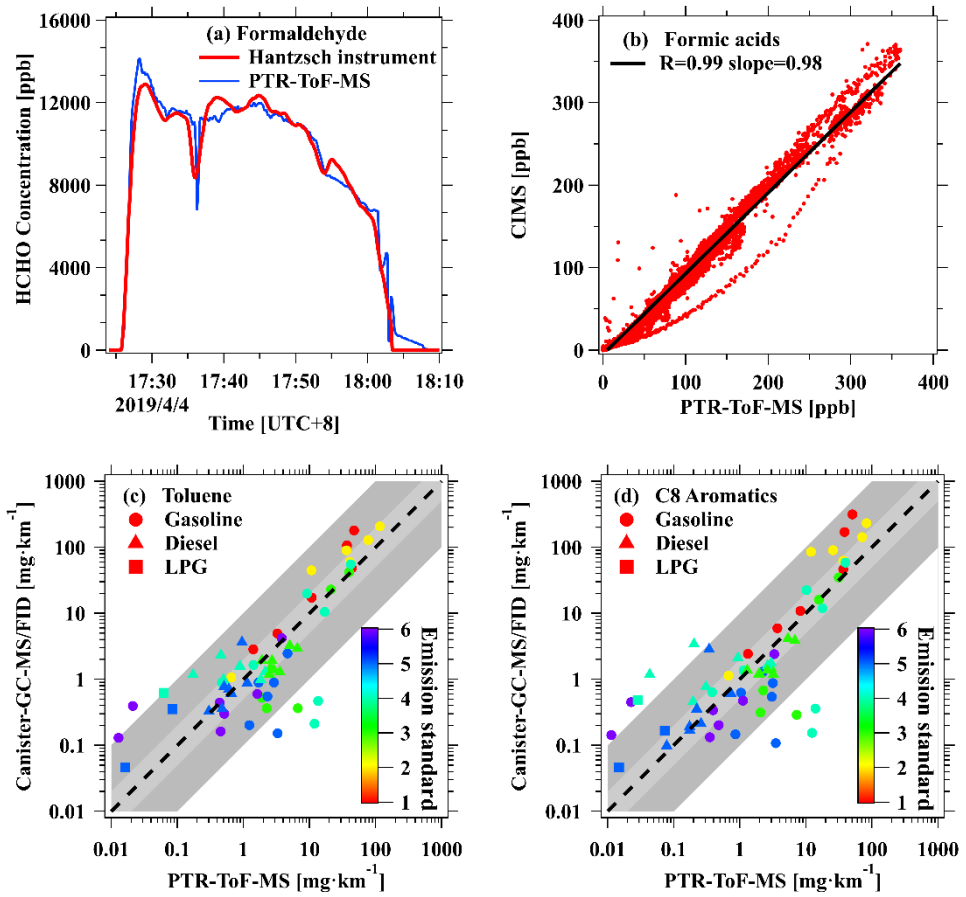


Figure S6. (a) Time series of formaldehyde measured by PTR-ToF-MS and the Hantzsch instrument. (b) Scatterplot of the concentration of formic acid between PTR-ToF-MS and the CIMS. Scatterplot of the emission factor of (c) toluene and (d)C_8 aromatics calculated by the data detected by PTR-ToF-MS and Canister-GC-MS/FID. The black dashed lines represent 1:1 ratio, and the shaded areas represent ratios of a factor of 2 and 10 in (c) and (d).

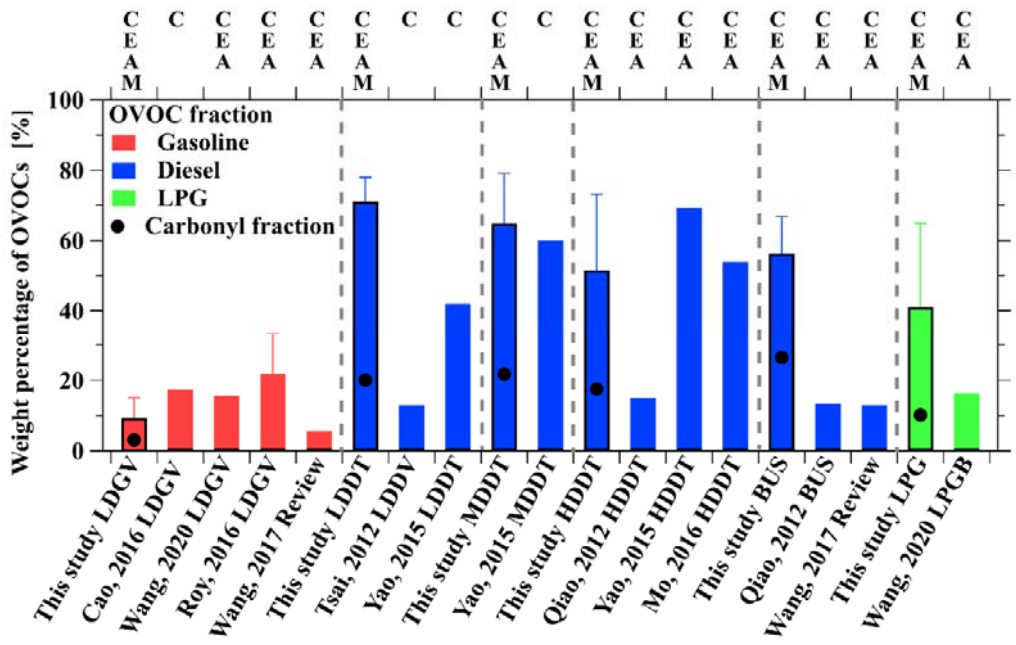


Figure 12. Comparison of OVOCs fractions determined in this study and those in previous studies. Error bars represent the standard deviations of the weight percentage of OVOCs. The C, E, A, M above the top axis represent the four groups of OVOCs measured in this study or previous studies, including Carbonyl: C, Ester/Ether: E, Alcohol: A, Multiple-functional: M.

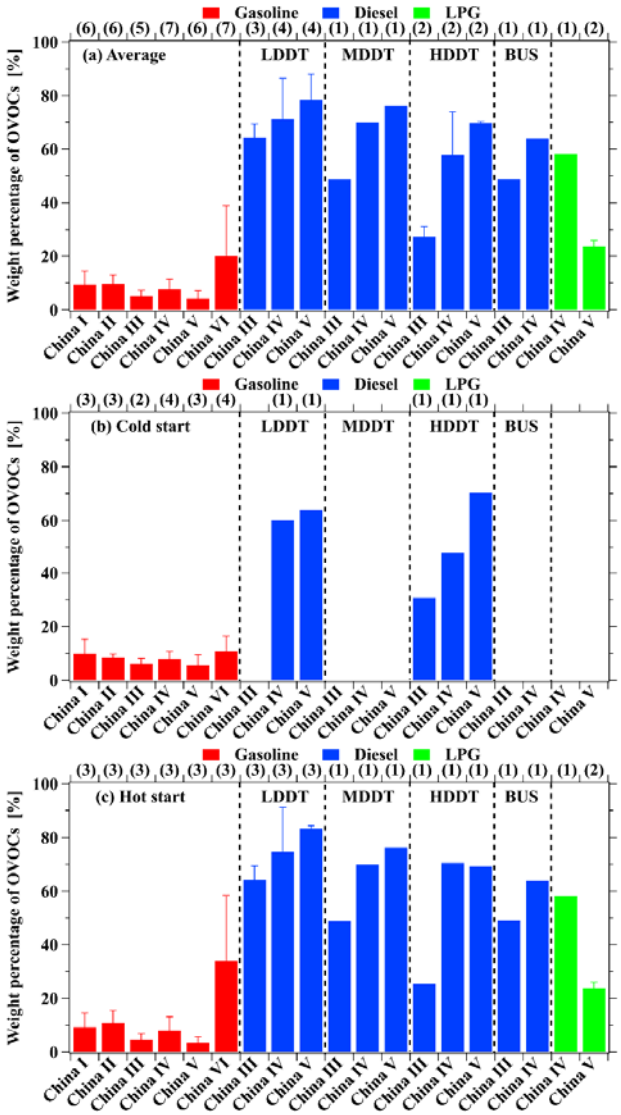


Figure S12. (a) Average OVOC fractions for vehicles with different emission standards, and some difference between (b) cold start and (c) hot start. Error bars represent the standard deviations of the fraction of OVOCs.

2. The mileage of the vehicles tested is quite variable, are there any correlations in your data with mileage, are these different for gasoline vs. diesel?

Reply: We thank the reviewer for the comment. The mileage of the vehicles is one of determining factors of emissions from the vehicles. We also found that the emission factors for the representative VOC species in China II gasoline vehicles are higher than other emission standards, which may be explained by the higher mileage of them than other vehicles (Fig. 3). Strong positive correlations between emission factors

and mileage are obviously for both gasoline and diesel vehicles. We added some description in the Section 3.1 and Fig. 3 with scatterplot of the emission factor of (a)-(b) toluene and (c)-(d) acetone during the hot start based on the odometer for each gasoline and diesel vehicle.

The sentences in the Section 3.1(line 258-270) are modified to:

In general, we observe a downward trend for emissions factors of gasoline vehicles from China I to China VI emission standards for the four representative VOC species. This is consistent with the results in previous studies with lower emissions for newer emission standards (Wang et al., 2017;Sha et al., 2021). In addition, the dependence of VOCs emission versus emission standard may also be attributed to the history of vehicle usage, i.e., the mileage traveled by the vehicles, as lower mileages of vehicles are usually associated with vehicle with newer emission standards. As shown in Fig. 3, we observe strong positive relationship between toluene emission factors and vehicle odometers for both gasoline and diesel vehicles, indicating the mileages of vehicles can significantly affect VOCs emission factors for vehicles tested in this study. 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.

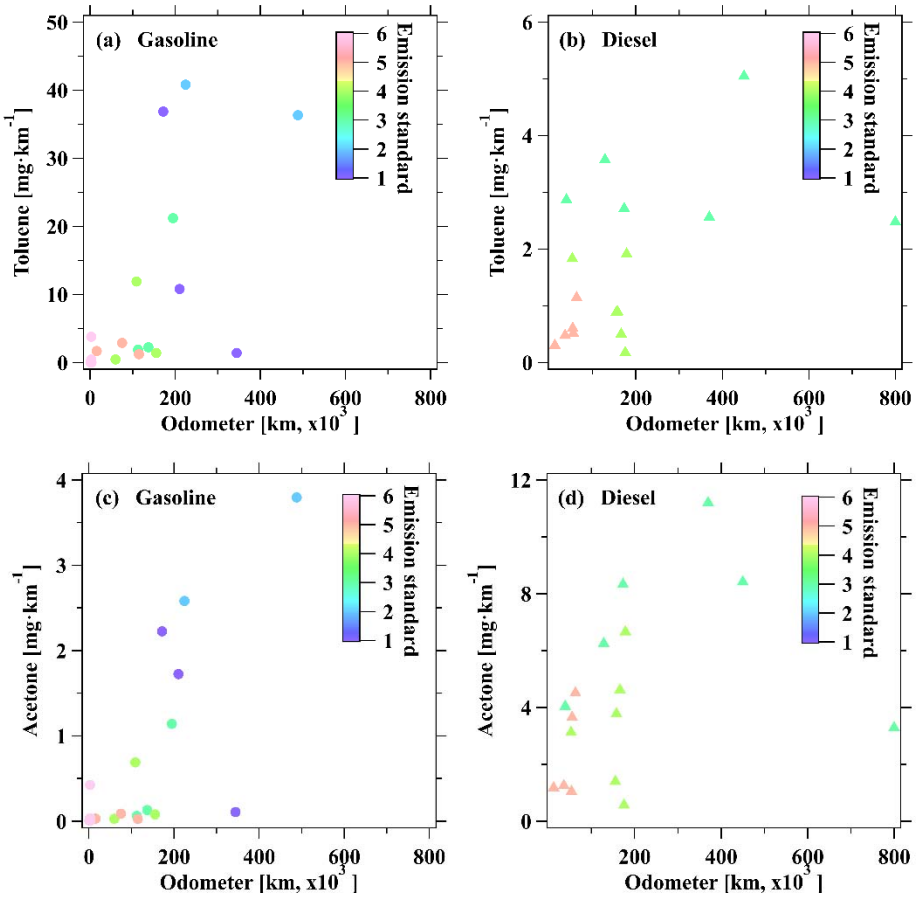


Figure 3. Scatterplot of the emission factor of toluene in (a) gasoline and (b) diesel vehicles, and acetone in (c) gasoline and (d) diesel vehicles during the hot start based on the odometer for each vehicle.

3. Was any analysis of the fuels done? To make clear sense of the emissions, the compositions of each fuel type, in terms of saturates (linear and cyclic), aromatics (BTEX and others), and oxygenates should be given. This is especially important for the diesel fuel, which can vary significantly in terms of aromatic content. Were the fuels summer or winter blends? The results presented have much narrower significance without clearer information on the fuel composition. Did the gasoline fuel have any ethanol content, as might be expected for gasoline in China after 2017? Ethanol content will have significant effects on small OVOC emissions. The discussion beginning on line 377 is well explained by the difference in aromatic content of the two fuels.

Reply: Thanks for the reviewer's advice. Fuel composition is one of determining factor for VOCs emissions from vehicles (Gentner et al., 2017). However, the

compositions of fuel were not measured during the tests, as most of the test vehicles are mainly from the local automobile quality supervision test center in this study. A fraction of vehicles is from a car rental company, with full tank of fuel before the test. In response to the reviewer's comment, we conducted some literature review and added a discussion in Section 1 in the Supplement to provide some information about chemical compositions of gasoline and diesel fuel in China, and added some description of difference in aromatic content of the two fuels in the Section 3.3. Furthermore, gasoline and diesel fuel are summer blends, and the gasoline fuel does not content ethanol in this study.

The sentence in the Section 2.1 (line 126-127) is modified to:

The detailed information for test vehicles is summarized in Sect. 1 in the Supplement, Table S2 and Table S3.

The Section 1 in the Supplement is modified to:

Fuel composition is one of determining factor for VOCs emissions from vehicles (Gentner et al., 2017). The gasoline fuel used in China is mainly comprised of C_4-C_7 hydrocarbons. The chemical compositions of gasoline fuel are alkanes (55%-62%), alkenes (12%-17%), aromatics (27%-32%), and methyl tert-butyl ether (MTBE, 1%-4%) (Tang et al., 2015;Sun et al., 2021;Qi et al., 2021;Huang et al., 2022). Heavy hydrocarbons, namely C_8-C_{10} alkanes and aromatics, contributed most in diesel fuel. The chemical compositions of diesel are alkanes (70%-79%), alkenes (1%-7%), and aromatics (21%-25%) (Wang et al., 2015;Yue et al., 2015;Hou and Jiang, 2018;Liu and Zhang, 2015). Gasoline and diesel fuel are summer blends, and the gasoline fuel does not content ethanol in this study.

The sentences in the Section 3.3(line 416-420) are modified to:

This interesting behavior is the result of different variations of emission factors for gasoline and diesel vehicles as carbon number increases. This may be attributed to the differences of chemical compositions of gasoline and diesel fuel, such as higher fractions of polycyclic aromatic hydrocarbons (PAHs) in the diesel fuel (Yue et al., 2015;Gentner et al., 2017).

4. When considering the usefulness of ratios between emitted species as diagnostic for diesel vs. gasoline species, you should also consider their atmospheric lifetimes for oxidation.

Reply: We thank the reviewer for the suggestion. It is necessary to consider the atmospheric lifetime of C_{14} aromatics and toluene for oxidation when used the C_{14} aromatics/toluene ratio as diagnostic for diesel versus gasoline vehicles. Here, we consider the change of C_{14} aromatics/toluene ratio with the OH reaction in the atmosphere (de Gouw et al., 2005) (Figure R1):

$$\frac{[C_{14}\ \text{aromatics}]}{[Toluene]} = ER \times exp[-(k_{C14} - k_{Toluene})[OH] \times t] \quad (6)$$

Where $[C_{14}\ \text{aromatics}]$ and $[Toluene]$ are the concentrations of C_{14} aromatics and toluene, respectively. ER is the emission ratio of C_{14} aromatics versus toluene (1.42 in diesel vehicles and 3.7E-4 in gasoline vehicles). $[OH]$ is the concentration of OH radicals (mole·cm^{-3}). k is the rate constant of the OH reaction with toluene (5.63 ×10^{-12} cm^3·mole^{-1}·s^{-1}) (Atkinson and Arey, 2003) and C_{14} aromatics, respectively. t is the photochemical age. Here, an averaged OH concentration in the PRD, China with 1.5×10^6 mole·cm^{-3} is used (Wang et al., 2020;Tan et al., 2019). Due to the rate constant for C_{14} aromatics did not report in previous study, we used the averaged rate constant for C_{12} aromatics (hexamethylbenzene) to estimate the reaction rate (1.33 ×10^{-10} cm^3·mole^{-1}·s^{-1}) (Alarcon et al., 2015;Berndt and Böge, 2001), which may be a little lower than the real value of C_{14} aromatics rate constant.

Based on the Equation (6), the C_{14} aromatics/toluene ratio emitted from diesel vehicles will be higher than emission ratio of gasoline vehicles for photochemical reactions shorter than 12 h. Therefore, the C_{14} aromatics/toluene ratio could be applied to the ambient measurements in urban or downwind regions, especially for roadside measurements or tunnel study to distinguish the emission of diesel and gasoline vehicles. Therefore, we conclude that the C_{14} aromatics/toluene ratio should be applied for distinguishing emissions of gasoline and diesel vehicles in ambient measurements of urban or downwind regions, especially for roadside measurements or tunnel study to

distinguish the emission of diesel and gasoline vehicles.

The sentence in the Section 3.3 (line 457-461) is modified to:

The enormous difference of C_{14} aromatics/toluene ratio (and also other higher aromatics/toluene) between gasoline and diesel vehicles indicate these ratios could potentially provide good indicators for separation of gasoline and diesel vehicles in ambient or tunnel studies (see discussion in Sect. 5 in the Supplement for details about the feasibility of the ratio using in ambient air).

We added a discussion in Section 5 in the Supplement and Fig. R1 to provide the feasibility of the C_{14} aromatics/toluene ratio used as diagnostic parameter for diesel versus gasoline vehicles. The Section 5 in the Supplement is modified to:

It is necessary to consider the atmospheric lifetime of C_{14} aromatics and toluene for oxidation when used the C_{14} aromatics/toluene ratio as diagnostic for diesel versus gasoline vehicles. Here, we consider the change of C_{14} aromatics/toluene ratio with the OH reaction in the atmosphere (de Gouw et al., 2005):

$$\frac{[C_{14}\ \text{aromatics}]}{[Toluene]} = ER \times exp[-(k_{C14} - k_{Toluene})[OH] \times t] \quad (6)$$

Where $[C_{14}\ \text{aromatics}]$ and $[Toluene]$ are the concentrations of C_{14} aromatics and toluene, respectively. ER is the emission ratio of C_{14} aromatics versus toluene (1.42 in diesel vehicles and 3.7E-4 in gasoline vehicles). $[OH]$ is the concentration of OH radicals (mole·cm^{-3}). k is the rate constant of the OH reaction with toluene (5.63 ×10^{-12} cm^3·mole^{-1}·s^{-1}) (Atkinson and Arey, 2003) and C_{14} aromatics, respectively. t is the photochemical age. Here, an averaged OH concentration in the PRD, China with 1.5×10^6 mole·cm^{-3} is used (Wang et al., 2020;Tan et al., 2019). Due to the rate constant for C_{14} aromatics did not report in previous study, we used the averaged rate constant for C_{12} aromatics (hexamethylbenzene) to estimate the reaction rate (1.33 ×10^{-10} cm^3·mole^{-1}·s^{-1}) (Alarcon et al., 2015;Berndt and Böge, 2001), which may be a little lower than the real value of C_{14} aromatics rate constant.

Based on the Equation (6), the C_{14} aromatics/toluene ratio emitted from

diesel vehicles will be higher than emission ratio of gasoline vehicles for photochemical reactions shorter than 12 h. Therefore, the C_{14} aromatics/toluene ratio could be applied to the ambient measurements in urban or downwind regions, especially for roadside measurements or tunnel study to distinguish the emission of diesel and gasoline vehicles. Therefore, we conclude that the C_{14} aromatics/toluene ratio should be applied for distinguishing emissions of gasoline and diesel vehicles in ambient measurements of urban or downwind regions, especially for roadside measurements or tunnel study to distinguish the emission of diesel and gasoline vehicles.

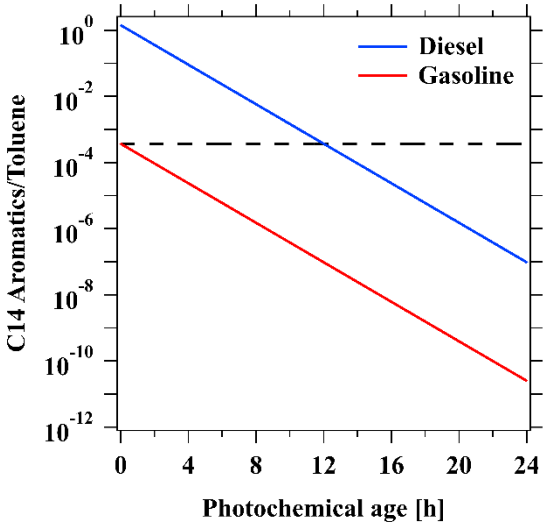


Figure R1. The volume mixing ratios of C_{14} aromatics/toluene in diesel vehicles and gasoline vehicles versus the photochemical age. The black line represents emission ratio of C_{14} aromatics versus toluene in gasoline vehicles.

Specific Comments

1. Figure 9. The fits to your data are poorly presented this way, either for predicting the values through the whole range or for giving physical insight. Perhaps you should make the axes linear rather than logarithmic. At the very least, you should explain that the strange curves to these linear fits in log-log space are due to the y-intercept, or perhaps only plot these fits in the region where they appear linear (where the intercept is small compared to the fit value) and note that you plot only in the region of reasonable fit.

Reply: We thank the reviewer for the comment. Many previous studies have used

the logarithmic axes in plots to better demonstrating the large variability in emission factors for different organic compounds (Gentner et al., 2013;Gentner et al., 2017;Zhao et al., 2016). We also tried to change the plot with linear axes (Fig. R2), with much poor performance for the data points associated with lower emission factor. We added some description in the caption of Fig. 10 in the revised manuscript (Fig. 9 in the original manuscript) about the counterintuitive non-linear curves for a line with non-zero y-intercept in log-log space.

The green and orange line are the fits to gasoline and diesel points in each plot. Note that these linear fits are shown in curves in log-log space as the result of non-zero y-intercept.

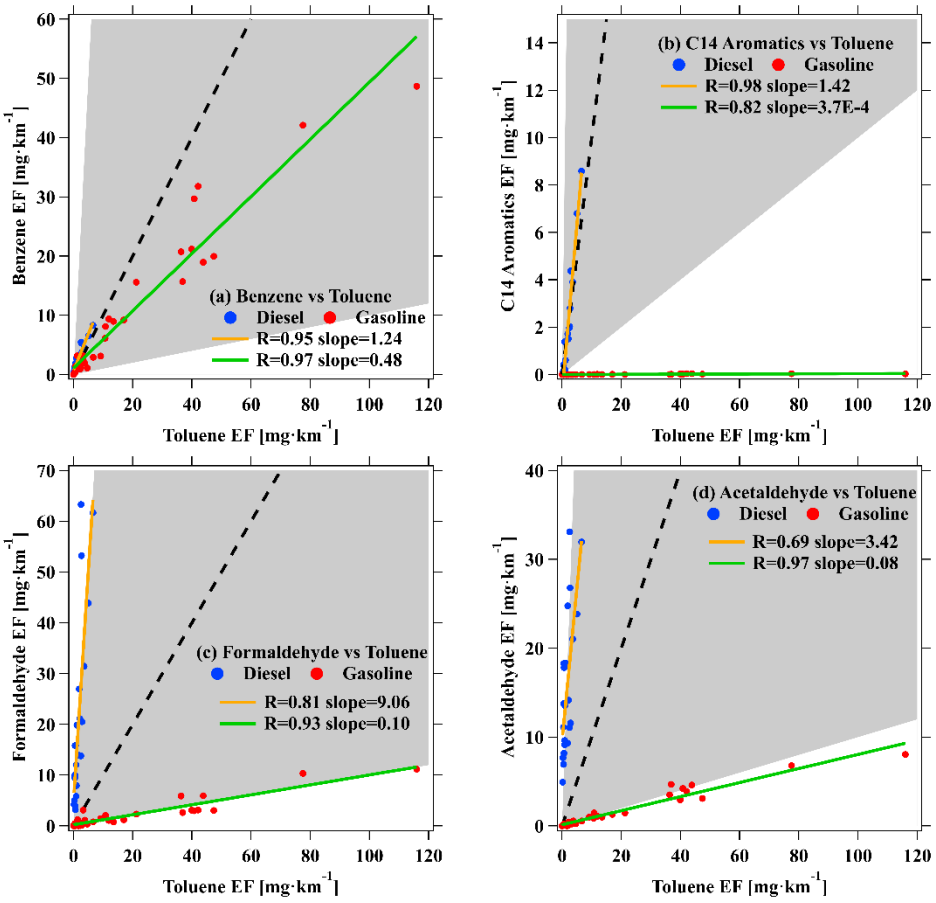


Figure R2. Scatterplots of the determined mileage-based emission factors of (a) benzene versus toluene, (b) C_{14} aromatics versus toluene, (c) formaldehyde versus toluene, and (d) acetaldehyde versus toluene for gasoline and diesel vehicles. Each data point represents each test vehicle in this study. The green and orange lines are the fitted results for gasoline and diesel vehicle. The black line represents 1:1 ratio, and the

shaded areas represent ratio of a factor of 10.

2.Please review again thoroughly for grammar. A few corrections are:

Line 224 "species emitted by vehicles"

Line 377 "Comparing gasoline and diesel vehicles,"

Line 445. "can be determined"

Line 486. "Substantially larger"

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

Reviewer #2

Wang et al. present an analysis of VOC emissions measured from vehicle dynamometer testing for vehicles designed under different emission standards (China I - IV). The authors evaluate total and speciated VOC emissions from both gasoline, diesel, and LPG under a variety of conditions (cold start, warm start, speed, etc). The authors detail the different emission factors between each vehicle, and observe a distinct difference between the OVOCs emitted by gasoline and diesel engines. The latter produces significantly higher fraction of OVOCs than by gasoline, which appears to be at least partly associated with the pollution control technology.

I found the paper to be very well-written, well-reasoned, and full of good information. I appreciated the study as a nice piece of work describing fossil fuel emissions from motor vehicles in China.

My only substantive comment is that I don't have a sense of the fuel composition and how this might contribute to the high OVOCs observed in diesel exhaust. And how do the OVOC emissions compare against diesel exhaust studies reported elsewhere? Gentner et al. (2013) also see elevated OVOC emissions in diesel compared to gasoline. Are these differences comparable to what is observed here, or is there something different between the aftertreatment or fuels that could contribute to any differences?

Reply: We would like to thank the reviewer for the insightful comments, which helped us tremendously in improving the quality of our work. Fuel composition is one of determining factor for VOCs emissions from vehicles (Gentner et al., 2017). We conducted some literature review and added a discussion in Section 1 in the Supplement to provide some information about chemical compositions of gasoline and diesel fuel in China. We also appreciate the reviewer for providing the useful reference. We added some discussions in the Section 3.1 to compare with the result of them.

We also used the fractions of OVOCs in total VOC emissions to compare against diesel exhaust studies reported elsewhere (Fig.12). If only considering carbonyls among various types of OVOCs measured by PTR-ToF-MS, the OVOC fractions determined in this study are more comparable with previous studies. We also discussed higher

OVOC emissions in diesel vehicles and impact on after-treatment devices, please find the response to individual comments below.

The sentence in the Section 2.1 (line 126-127) is modified to:

The detailed information for test vehicles is summarized in Sect. 1 in the Supplement, Table S2 and Table S3.

The Section 1 in the Supplement is modified to:

Fuel composition is one of determining factor for VOCs emissions from vehicles (Gentner et al., 2017). The gasoline fuel used in China is mainly comprised of C_4-C_7 hydrocarbons. The chemical compositions of gasoline fuel are alkanes (55%-62%), alkenes (12%-17%), aromatics (27%-32%), and methyl tert-butyl ether (MTBE, 1%-4%) (Tang et al., 2015;Sun et al., 2021;Qi et al., 2021;Huang et al., 2022). Heavy hydrocarbons, namely C_8-C_{10} alkanes and aromatics, contributed most in diesel fuel. The chemical compositions of diesel are alkanes (70%-79%), alkenes (1%-7%), and aromatics (21%-25%) (Wang et al., 2015;Yue et al., 2015;Hou and Jiang, 2018;Liu and Zhang, 2015). Gasoline and diesel fuel are summer blends, and the gasoline fuel does not content ethanol in this study.

The sentences in the Section 3.1 (line 284-289) are modified to:

As the largest OVOCs emitted from gasoline vehicles (4.6 ± 5.1 mg·km^{-1}), methanol is found to be the only common OVOC species, with lower emission factors from diesel vehicles than gasoline vehicles. The emission factor of other OVOCs (e.g., formaldehyde, acetone) from diesel vehicles are higher than gasoline vehicles, which is consistent with previous results (Gentner et al., 2013).

Comments:

1. Line 70-71 Based on the reference, I presume that the authors are specifically noting the decline of VOCs in urban regions in China? For clarity, I would suggest re-writing this sentence to say "Furthermore, VOC emission significantly decreased in China due to stricter emission standards."

Reply: We thank the reviewer for the comment. We corrected this sentence as

"Furthermore, VOC emissions from vehicles significantly decreased in China due to stricter emission standards (Liu et al., 2017;Sha et al., 2021)".

2. Line 76: Could the authors provide some context on the China VI emission standard? I recognize that the standard is dependent on power ranges, but a few sentences on VOC emissions at max power output would be useful. This would also be useful in the methods (lines 112 - 122) to give readers context as to what the China I - IV standards represent in terms of VOC emissions.

Reply: We thank the reviewer for the comment. China VI emission standard is the newest emission standard for vehicles. Limits on exhaust emissions of gasoline vehicles are tightened by 30% to 50% from China V to China VI for different pollutants (Lyu et al., 2020). China VI emission standard is mainly reflected in the requirements for the emission limits of pollutants (e.g. CO, NOx, THC, etc.). In response to the reviewer's question, power ranges and max power outputs are not directly reflected in China VI emission standard, and rarely reported in previous studies.

We added a discussion in Section 1 in the Supplement to provide some information about the China VI emission standard of vehicles. We added Table S7 with the different emission standards (China I - China VI) for light-duty vehicles (LDV) in gasoline and diesel as fuel, and Table S8 for heavy-duty diesel engines (HDDE) in different emission standards (China I - China V). We also added some discussion in the Section 2.1 to provide the averaged fractions of gasoline and diesel vehicles with different emission standards for the vehicle fleet in China, which is shown in the Table S1 in the revised manuscript (Table S6 in the original manuscript).

The sentences in the Section 1(line 76-78) are modified to:

The emission limits for various air pollutants emitted by vehicles are significantly lower under the China VI emission standard (see details in the Supplement) (Wu et al., 2017).

The Section 1 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) are introduced in the recent years in China, which applies to light-duty vehicles by gasoline or diesel as the fuel. The China VI emission standard continued the EU standard system as the reference with various regulation details integrated from US emissions standards (Lyu et al., 2020). Vehicle emission limits are significantly lower for the China VI standard (Table S7, Table S8). For example, limits on gasoline vehicle exhaust emissions were tightened by 30 to 50% from China V to China VI, and a new particulate number (PN) limit was added in gasoline vehicles (Lyu et al., 2020).

The sentence in the Section 2.1 (line 123-124) is modified to:

The averaged fractions of gasoline and diesel vehicles with different emission standards for the vehicle fleet in China are shown in Table S1 (MEEPRC, 2019;Li et al., 2021).

3. Line 81: Would suggest modifying "group" to say "class of compounds"

Reply: We replaced "group" with "class of compounds".

4. Line 80-83: Are the authors primarily discussing VOC measurements from dynamometer studies, or tunnel studies, or ambient studies? I think the distinction matters given that results from laboratory, tunnel, or ambient measurements can be interpreted differently given differences in co-emitted sources that can convolute the measured signal from tailpipe emissions

Reply: We thank the reviewer for the comment. We modified this sentence in the Section 1 to make it clearly in different vehicle measurement methods.

The sentence in the Section 1(line 82-86) is modified to:

Oxygenated volatile organic compounds (OVOCs) were found to be an important class of compounds in vehicle exhausts, accounting for more than 50% of the total VOC emissions for diesel vehicles from both chassis dynamometer tests (Schauer et al., 1999;Mo et al., 2016) and on-road mobile measurements (Yao et al., 2015).

5. Lines 268-271: Are there also differences in the aftertreatment that might lead to higher OVOC emissions? The authors note the temperature of the device at line 240, and I'm curious if previous work has looked at VOC speciation under different aftertreatment conditions.

Reply: We thank the reviewer for the comment. After-treatment devices in vehicles have been improved associated with the upgrading of emission standards. According to the #8 comment of the reviewer, our results (Fig. 7c-d in the revised manuscript) actually can answer the question of the reviewer in this comment. The two graphs show that the chemical compositions of VOC emissions are comparable between different emission standards for both gasoline and diesel vehicles (R=0.98 and 0.89), indicating after-treatment devices may not affect the relative fraction of VOC components. We added some description and reference in the section 3.2, and added a discussion in Section 1 in the Supplement to provide some information about the after-treatment devices in gasoline and diesel vehicles.

The sentence in the Section 3.2 (line 363-366) is modified to:

Fig. 7c-d show that the chemical compositions of VOC emissions are comparable between different emission standards for both gasoline and diesel vehicles (R=0.98 and 0.89), indicating after-treatment devices may not affect the relative fractions of VOC components.

The sentence in the Section 3.2 (line 379-383) is modified to:

These results indicate the after-treatment device for diesel vehicles (see Sect. 1 in the Supplement for details.) may effectively reduce emissions of some heavier VOC species, though the after-treatment devices do not aim for VOCs control (Gentner et al., 2017).

The Section 1 in the Supplement is modified to:

After-treatment devices commonly used in light-duty gasoline vehicles are three-way catalyst (TWC) and gasoline particulate filter (GPF). They have been improved with the upgrading of emission standard. 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.

6. Figure 1: It would be useful to see the acronyms (LDDT, MDDT, HDDT, and BUS) defined in the caption as a reminder to the reader.

Reply: We thank the reviewer for the comment. We added some description in the caption of Fig. 1about the acronyms (LDDT, MDDT, HDDT, and BUS). We also checked throughout the manuscript, and corrected the caption of Fig.2.

The caption of Fig.1 is modified to:

Figure 1. Real-time concentrations of acetaldehyde, acetone, benzene, toluene, and CO_2 for (a) a gasoline vehicle with emission standard of China I and (b) a light-duty diesel vehicle (LDDV) with emission standard of China IV. The two vehicles were both cold started. The gray shadows represent the speed of the vehicles on the chassis dynamometer.

The caption of Fig.2 is modified to:

Figure 2. The determined average mileage-based emission factors ($mg \cdot km^{-1}$) for (a) benzene, (b) toluene, (c) acetaldehyde, and (d) acetone for vehicles with different emission standards. The numbers above the top axis represent the number of all experiments (including multiple measurements for individual test vehicle) for each emission standard. LDDT, MDDT, HDDT, and BUS represent light-duty-diesel-truck, middle-duty-diesel-truck, heavy-duty-diesel-truck, and bus, respectively. Error bars represent standard deviations of emission factors for the specific emission standard.

7. Title of Section 3.2: The title doesn't quite reflect the discussion that follows. Might I suggest "Analysis of PTR-ToF-MS mass spectra to evaluate VOC speciation"?

Reply: We corrected this title in "Analysis of PTR-ToF-MS mass spectra to evaluate VOCs speciation".

8. Lines 320-323: This is a nice result, and partially addresses my question at lines 268-271. Could the authors point to this figure and discussion to demonstrate that the changes to the VOC distribution isn't significantly different between cold start and normal operation?

Reply: We thank the reviewer for the comment. After-treatment devices have been improved with the upgrading of emission standard. Our results (Fig. 7c-d in the revised manuscript) show that the chemical compositions of VOC emissions are comparable between different emission standards in gasoline and diesel vehicles (R=0.98 and 0.89), indicating after-treatment devices may not affect the relative fraction of VOC components.

Cold start is a major emission source of gasoline vehicles, which occurs after several hours of non-operation of vehicles (Gentner et al., 2017;George et al., 2015). Our results (Fig. 7a-b in the revised manuscript) demonstrate that variation behaviors are similar for different species and thus chemical compositions of VOC emissions are comparable between different start conditions. As cold start emissions are richer in unburned fuel than other hot-running conditions, the observation in Fig. 7a-b also infer that unburned fuel are the major contributor for vehicle exhaust emissions, which has been previously shown in California, US (Gentner et al., 2013). We added some discussions in 3.2 and Section 1 in the Supplement to provide some information about cold start in gasoline and diesel vehicles.

The sentence in the Section 3.2 (line 247-249) is modified to:

It might be a combined effect of cold engine and operation temperature of the after-treatment device (Gentner et al., 2017;George et al., 2015).

The sentences in the Section 3.2 (line 345-353) are modified to:

We observe strong correlation between emission factors from cold start and hot start tests (R=0.99 and 0.92) and generally consistent ratios between cold start and hot start for different types of VOC species for both gasoline and diesel vehicles, indicating that variation behaviors are similar for different species and thus chemical compositions of VOC emissions are comparable between different start conditions. As cold start emissions are richer in unburned fuel than other hot-running conditions, the observation in Fig. 7a-b also infer that unburned fuel are the major contributor for vehicle exhaust emissions, which has been previously shown in California, US (Gentner et al., 2013).

The Section 1 in the Supplement is modified to:

Cold start, which occurs after several hours of nonoperation for vehicles (Drozd et al., 2016), is a major source of emissions for gasoline vehicles and have greater emissions due to two issues: (1) low engine temperatures lead to incomplete combustion that allow non/partially combusted fuel compounds to exit engine cylinders. (2) Effective operation of the catalytic converter requires a warm-up period to reach sufficient catalyst operating temperatures (Gentner et al., 2017;George et al., 2015). Due to diesel emissions have emphasized control of primary $PM_{2.5}$ and NO_X emissions, the after-treatment devices of diesel vehicles (e.g. DOC, DPF, SCR etc.) do not aim for VOCs control.

9. Lines 424-425: I like the discussion in this section on using the aromatics to delineate between diesel and gasoline. I agree with the authors that these ratios might be difficult to assess in the ambient owing to additional sources of aromatics (e.g. solvent emissions) and secondary production of formaldehyde and acetaldehyde. Are there any unique masses, with high enough signal in ambient air, that could be used to more definitively separate gasoline vs diesel emissions? I also wonder if ratios to CO or other combustion markers might be insightful.

Reply: We thank the reviewer for the comment. Per the reviewer's comment, we have not found any other unique masses with high enough signals in gasoline or diesel

vehicles that can be used for distinguish the two types of vehicles.

Furthermore, we added a Figure (Fig. S11b) with the emission ratios to CO ($ppb \cdot ppm^{-1}$) between gasoline and diesel vehicles. The result (slope=0.16) is similar to the plot of emission factors between gasoline and diesel vehicles. A limited number of VOC species, including C_6-C_{10} aromatics are associated with higher emission ratios from gasoline vehicles, whereas the obtained emission ratios of most VOC species emitted from diesel vehicles are higher, especially most OVOC species.

The sentences in the Section 3.3 (line 405-408) are modified to:

Generally, similar variability is obtained except the determined slope of the data points, with higher slopes determined from the scatterplot based on fuel-based emission factor (0.19 versus 0.15). The emission ratios to CO between gasoline and diesel vehicles (Fig. S11b) show similar results.

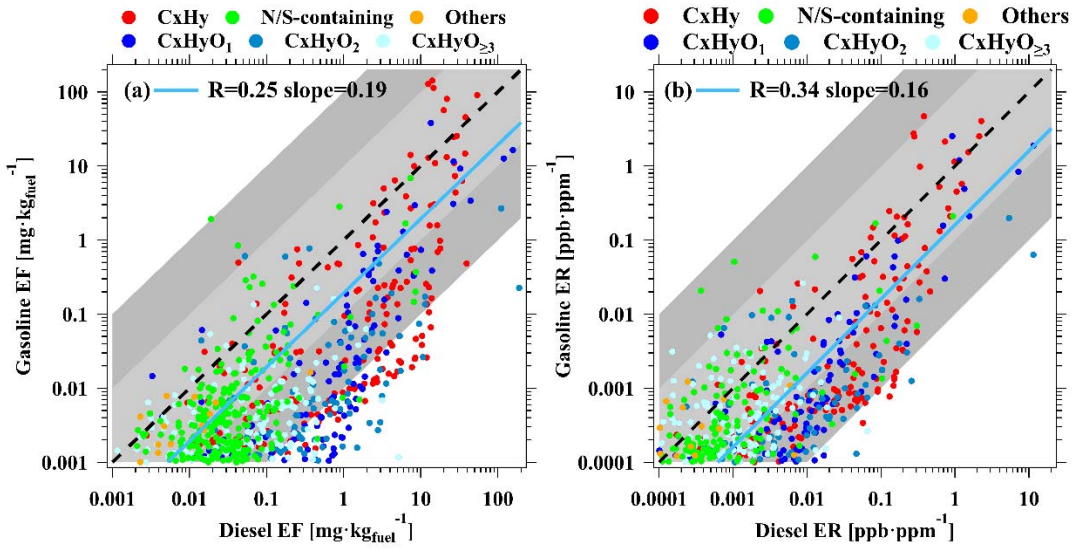


Figure S11. Scatterplot of (a) the determined average fuel-based emission factors ($mg \cdot kg_{fuel}^{-1}$) and (b) the emission ratios to CO ($ppb \cdot ppm^{-1}$) of VOCs between gasoline and diesel vehicles. Each data point indicates a VOC species measured by PTR-ToF-MS. The blue line is the fitted result for all data points. The black line represents 1:1 ratio, and the shaded areas represent ratios of a factor of 10 and 100.

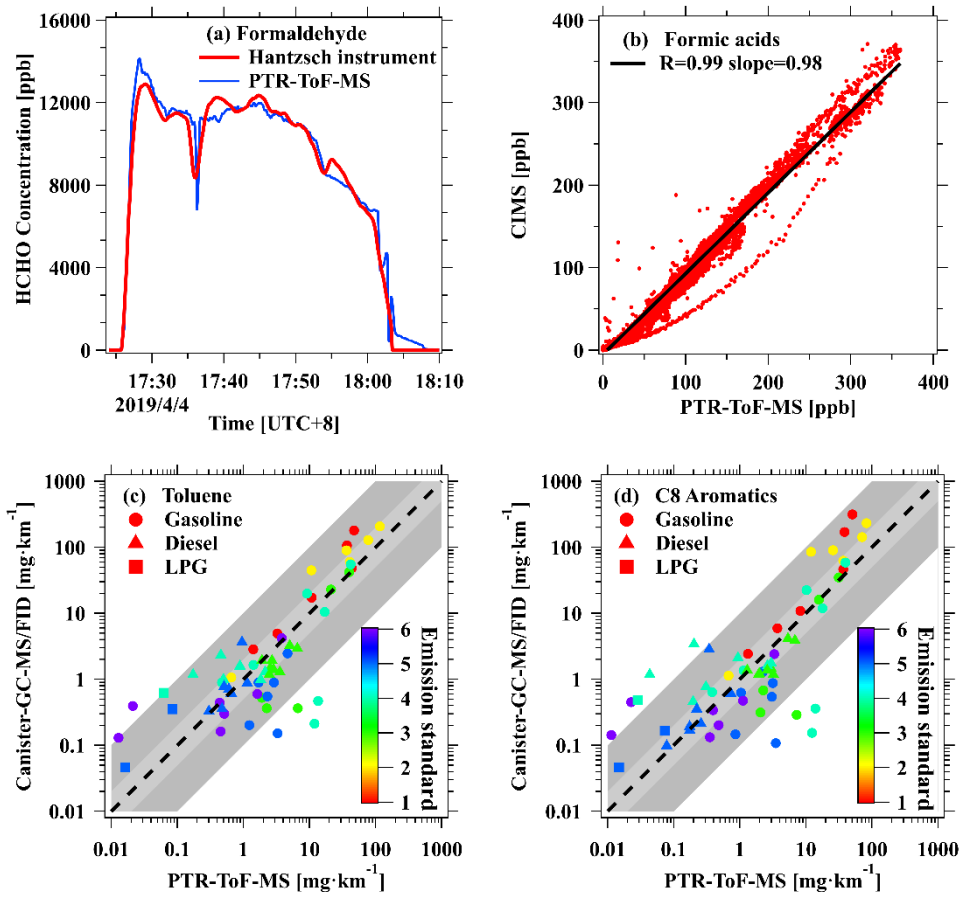
10. Figure S6. The intercomparisons are nice for the fast time-resolution systems, but

there are significant differences between the GC and PTR for toluene - is this due to differences in sampling techniques (e.g., grab sampling artifacts vs real-time sampling), or something due to fragmentation in the PTR to produce a signal at m/z 93? I believe the other reviewer also commented on this, and I agree that some explanation is warranted here.

Reply: We thank the reviewer for the comment. In replying to the comments from the two reviewers, we found an issue in data analysis for preparing the original manuscript. The alignment of data points between offline canister-GC-MS/FID and PTR-ToF-MS for several gasoline vehicles and diesel vehicles was not correct. We have modified the corresponding data points, and added comparison of C_8 aromatics between two measurements (Fig. S6), obtaining generally consistent results, considering large variations of VOC emissions for driving conditions and the difficulty to control the fill time for canisters. We also revised related figures (Fig. 12 and Fig. S12) and description in the manuscript on the fractions of OVOCs in total VOC emissions in various types of vehicles. These modifications do not change any conclusion in the manuscript.

The sentence in the Section 2.3 (line 194-197) is modified to:

We compared emission factors from PTR-ToF-MS and the offline canister-GC-MS/FID (Fig. S6c-d), obtaining generally consistent results, considering the large variation of VOC emissions for driving conditions and the difficulty to control the fill time for canisters.



522

523 **Figure S6. (a) Time series of formaldehyde measured by PTR-ToF-MS and the**
524 **Hantzsch instrument. (b) Scatterplot of the concentration of formic acid between**
525 **PTR-ToF-MS and the CIMS. Scatterplot of the emission factor of (c) toluene and**
526 **(d)C_8 aromatics calculated by the data detected by PTR-ToF-MS and Canister-**
527 **GC-MS/FID. The black dashed lines represent 1:1 ratio, and the shaded areas**
528 **represent ratios of a factor of 2 and 10 in (c) and (d).**

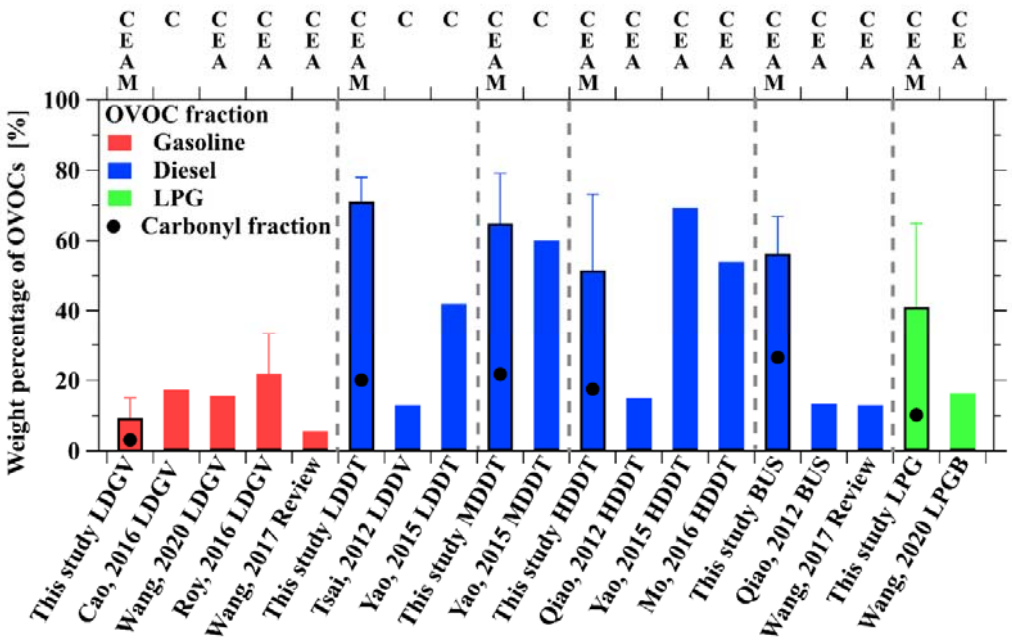


Figure 12. Comparison of OVOCs fractions determined in this study and those in previous studies. Error bars represent the standard deviations of the weight percentage of OVOCs. The C, E, A, M above the top axis represent the four groups of OVOCs measured in this study or previous studies, including Carbonyl: C, Ester/Ether: E, Alcohol: A, Multiple-functional: M.

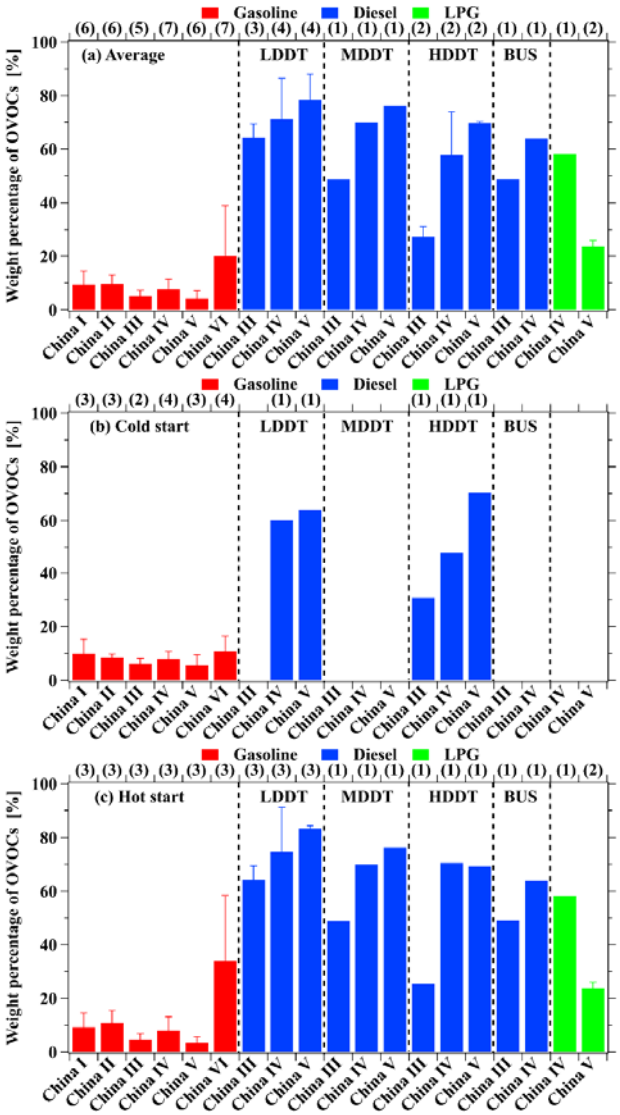


Figure S12. (a) Average OVOC fractions for vehicles with different emission standards, and some difference between (b) cold start and (c) hot start. Error bars represent the standard deviations of the fraction of OVOCs.

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