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.

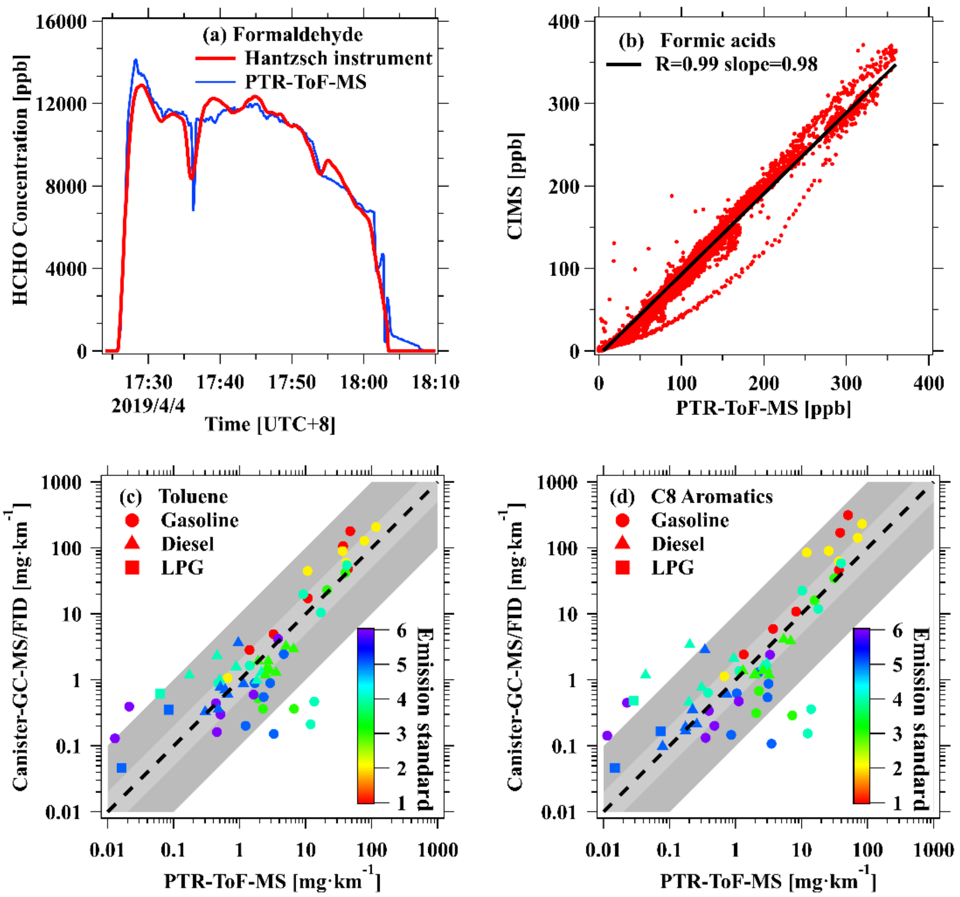

Figure S6. (a) Time series of formaldehyde measured by PTR-ToF-MS and the Hantzsch instrument. (b) Scatterplot of the concentration of formic acid between PTR-ToF-MS and the CIMS. Scatterplot of the emission factor of (c) toluene and (d)C_8 aromatics calculated by the data detected by PTR-ToF-MS and 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).

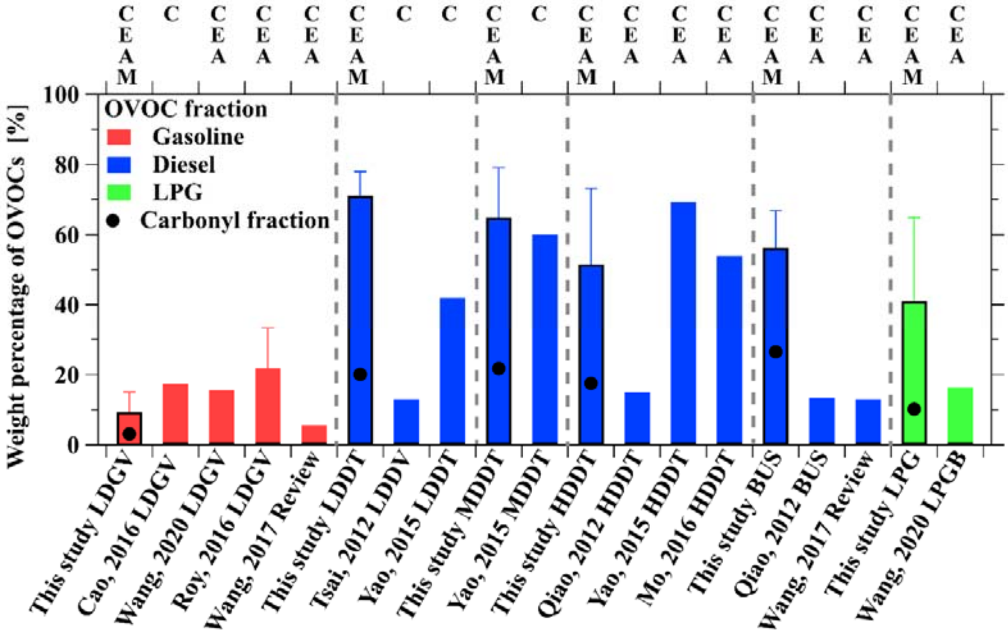

Figure 12. Comparison of OVOCs fractions determined in this study and those in previous studies. Error bars represent the standard deviations of the weight percentage of OVOCs. The C, E, A, M above the top axis represent the four groups of OVOCs measured in this study or previous studies, including Carbonyl: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

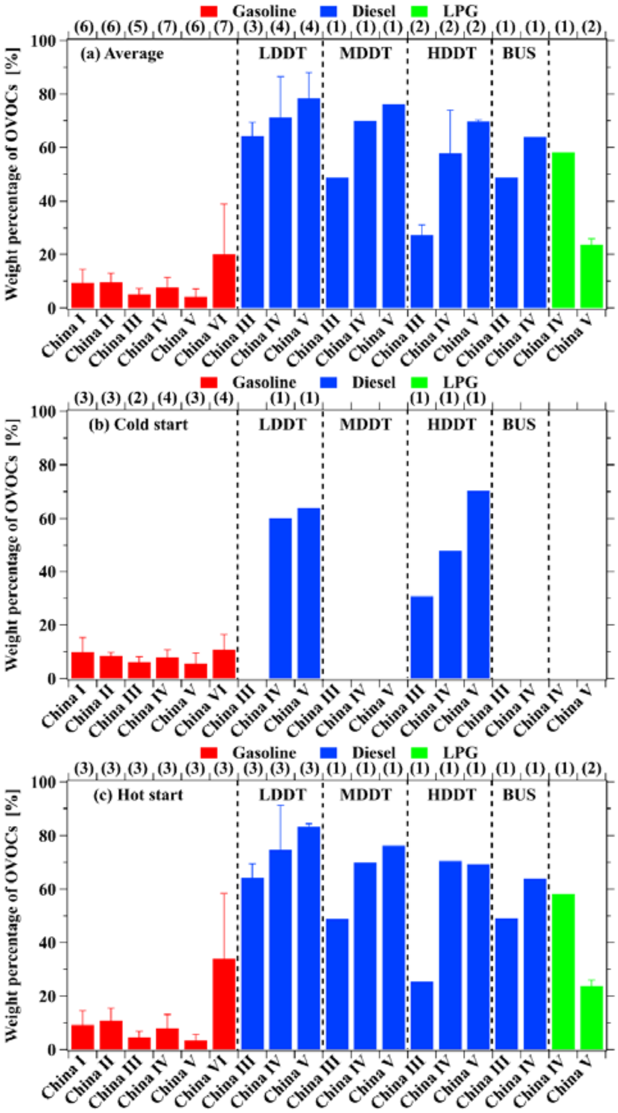

Figure S12. (a) Average OVOC fractions for vehicles with different emission standards, and some difference between (b) cold start and (c) hot start. Error bars represent the standard deviations of the fraction of OVOCs.

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.

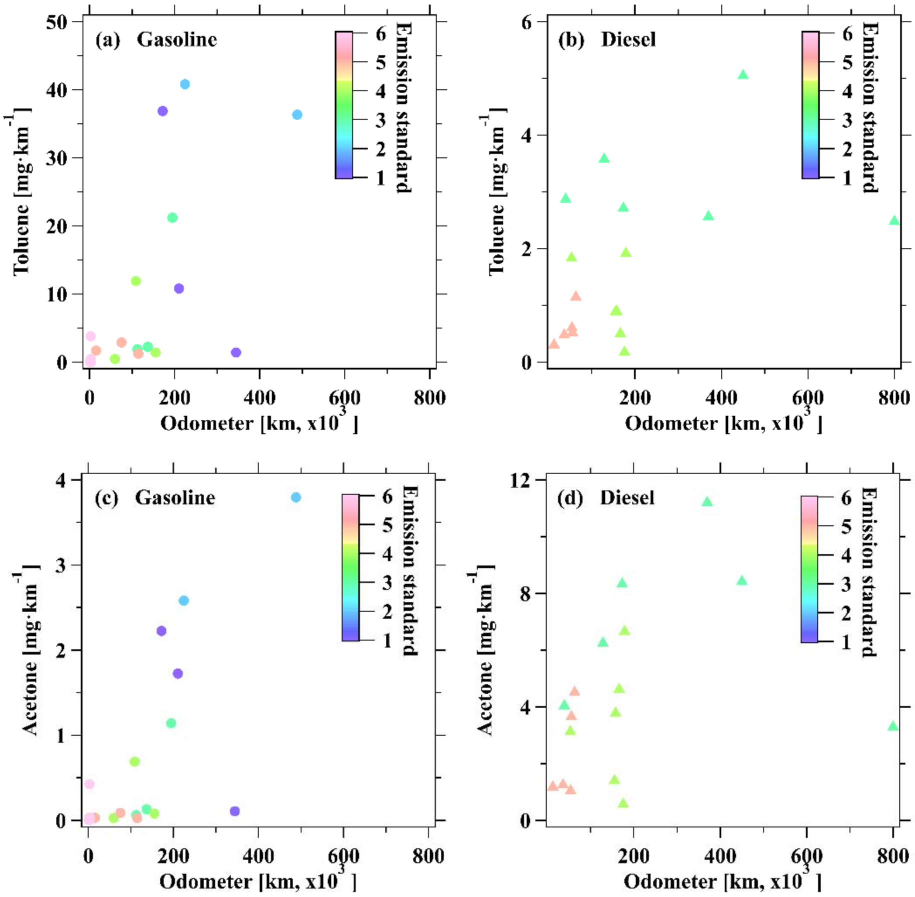

Figure 3. Scatterplot of the emission factor of toluene in (a) gasoline and (b) diesel vehicles, and acetone in (c) gasoline and (d) diesel vehicles during the hot start based on the odometer for each vehicle.

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 $[C_{14}$ 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 ($\text{mole}\cdot\text{cm}^{-3}$). k is the rate constant of the OH reaction with toluene (5.63×10^{-12} $\text{cm}^3\cdot\text{mole}^{-1}\cdot\text{s}^{-1}$) (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 $\text{mole}\cdot\text{cm}^{-3}$ 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} $\text{cm}^3\cdot\text{mole}^{-1}\cdot\text{s}^{-1}$) (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.

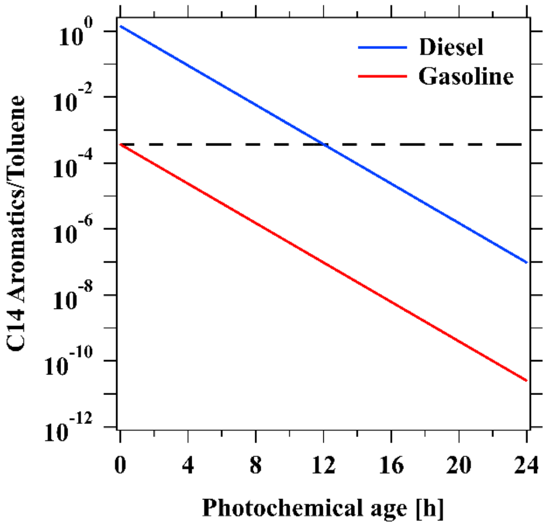

Figure R1. The volume mixing ratios of C_{14} aromatics/toluene in diesel vehicles and gasoline vehicles versus the photochemical age. The black line represents emission ratio of C_{14} aromatics versus toluene in gasoline vehicles.

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.

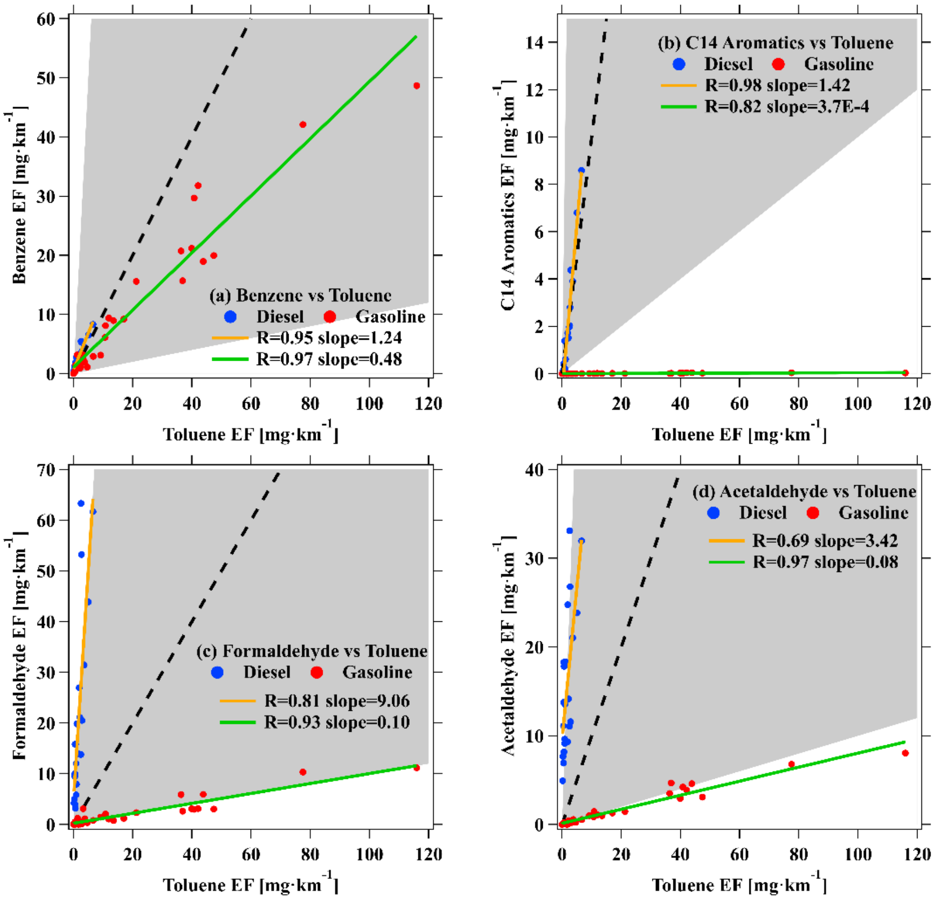

Figure R2. Scatterplots of the determined mileage-based emission factors of (a) benzene versus toluene, (b) C_{14} aromatics versus toluene, (c) formaldehyde versus toluene, and (d) acetaldehyde versus toluene for gasoline and diesel vehicles. Each data point represents each test vehicle in this study. 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.

Reference:

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