Oxygenated VOCs as significant but varied contributors to VOC emissions from vehicles

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Abstract:

Vehicular emission is an important source for volatile organic compounds (VOCs) in urban and downwind regions. In this study, we conducted a chassis dynamometer study to investigate VOC emissions from vehicles using gasoline, diesel, and liquefied petroleum gas (LPG) as fuel. Time-resolved VOC emissions from vehicles are chemically characterized by a proton-transfer-reaction time-of-flight mass spectrometry (PTR-ToF-MS) with high frequency. Our results show that emission factors of VOCs generally decrease with the improvement of emission standard for gasoline vehicles, whereas variations of emission factors for diesel vehicles with emission standards are more diverse. Mass spectra analysis of PTR-ToF-MS suggest that cold start significantly influence VOCs emission of gasoline vehicles, while the influences are less important for diesel vehicles. Large differences of VOC emissions between gasoline and diesel vehicles are observed with emission factors of most VOC species from diesel vehicles were higher than gasoline vehicles, especially for most oxygenated volatile organic compounds (OVOCs) and heavier aromatics. These results indicate quantification of heavier species by PTR-ToF-MS may be important in characterization of vehicular exhausts. Our results suggest that VOC pairs (e.g. C_{14} aromatics/toluene ratio) could potentially provide good indicators for distinguishing emissions from gasoline and diesel vehicles. The fractions of OVOCs in total VOC emissions are determined by combining measurements of hydrocarbons from canisters and online observations of PTR-ToF-MS. We show that OVOCs contribute 9.4% ± 5.6% of gasoline vehicles of the total VOC emissions, while the fractions are significantly higher for diesel vehicles (52-71%), highlighting the importance to detect these OVOC species in diesel emissions. Our study demonstrated that the large number of OVOC species measured by PTR-ToF-MS are important in characterization of VOC emissions from vehicles.

1. Introduction

Volatile organic compounds (VOCs) are important trace components in the troposphere, as important precursors of ground-level ozone (Shao et al., 2009) and secondary organic aerosol (SOA) (Seinfeld and Pandis, 2006;Kansal, 2009;Ziemann and Atkinson, 2012). As the result, it is particularly important to identify emission sources of VOCs in the atmosphere. Vehicular emission is an important source of VOCs in cities around the world (Liu et al., 2008;Parrish et al., 2009), contributing approximately 25% to total VOC emissions in China (Ou et al., 2015;Wu et al., 2016;Sun et al., 2018). In order to control atmospheric pollution in urban and surrounding regions, it is necessary to understand source profiles and emission characteristics of VOCs from vehicles.

Emissions of VOCs from vehicles have been investigated extensively from tunnel studies (Cui et al., 2018;Zhang et al., 2018;Song et al., 2020), on-road mobile measurements (Li et al., 2017), and chassis dynamometer tests (Guo et al., 2011;Wang et al., 2013;Yang et al., 2018). Previous studies demonstrated that fuel types of vehicles strongly impact VOC emissions. Aromatics along with other hydrocarbons are known as compounds with high emissions in exhausts of gasoline vehicles (Wang et al., 2013;Ly et al., 2020). Some carbonyl compounds contribute significantly to emissions of diesel vehicles, at fractions much higher than gasoline vehicles (Tsai et al., 2012;Qiao et al., 2012;Yao et al., 2015;Mo et al., 2016). Moreover, there are still a large number of unidentifiable compounds in diesel vehicles (May et al., 2014). Furthermore, VOC emissions from vehicles significantly decreased in China due to stricter emission standards (Liu et al., 2017;Sha et al., 2021). In order to reduce emissions of most primary pollutants, more stringent emission standards and after-treatment devices have been implemented. The emission standard of China VI has already been implemented in July of 2019 in a few key cities in China and in July of 2021 nationwide. 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). With the continuous development of engine and exhaust after-treatment technologies, emission

characteristics of VOCs from vehicles may change and need to be frequently updated.

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). Traditionally, VOCs are collected in the canister or Tedlar bags, and then analyzed by gas chromatography-mass spectrometer/flame ionization detector (GC-MS/FID), mainly reporting emissions of hydrocarbons (Wang et al., 2017;Qi et al., 2019). Previous work usually collected 2,4-dinitrophenyhydrazine (DNPH) cartridges and analyzed using high-performance liquid chromatography (HPLC) for carbonyls (aldehydes and ketones), which are both time-consuming and prone to contaminations (Mo et al., 2016;Han et al., 2019).

The large variability of VOC emissions under different engine activities or driving conditions require characterization of vehicular emissions at higher time resolution. Proton-transfer-reaction mass spectrometry (PTR-MS) has been used in a number of studies for measurements of vehicle emissions. VOCs from vehicle exhausts under various driving and operational modes were measured by PTR-MS onboard a mobile laboratory (Zavala et al., 2006;Zavala et al., 2009). Drozd et al. (2016) used a PTR-MS to emphasize the importance of cold start for vehicles, concluding that VOC emissions during cold start were equal to a 200 miles distance of driving during hot stabilized condition. Proton-transfer-reaction time-of-flight mass spectrometry (PTR-ToF-MS) can provide more powerful detection of various VOCs, thanks to the measurements of whole mass spectra and high mass resolution (Cappellin et al., 2012;Yuan et al., 2017). More OVOC species could be quantified from the measured mass spectra based on parameterization methods for sensitivity of instrument (Sekimoto et al., 2017;Wu et al., 2020).

In this study, we applied a PTR-ToF-MS along with a suite of other instruments to measure VOCs emitted from gasoline, diesel, and liquefied petroleum gas (LPG) vehicles. We investigated emission factors from different fuel types and emission standards for representative VOC species exhausted from these vehicles. We used the

dataset to analyze contributions of various VOC groups to total VOC emissions in different types of vehicles.

2. Materials and methods

2.1 Tested vehicles and the chassis dynamometer study methods

In this study, we conducted chassis dynamometer measurements to investigate VOC emissions from vehicles using gasoline, diesel, LPG as fuel. All gasoline vehicles are light-duty-gasoline-vehicle (LDGV) with the emission standards from China I to China VI, whereas diesel vehicles can be classified into light-duty-diesel-truck (LDDT), middle-duty-diesel-truck (MDDT), heavy-duty-diesel-truck (HDDT), and bus associated with emission standards of China III to China V. In addition, the test vehicles using LPG are all taxis, which are under mandatory scrappage after 8 years of driving in China; as a result only China IV and China V for LPG vehicles were tested. The fractions of gasoline and diesel vehicles with different emission standards in China are shown in Table S1 (MEEPRC, 2019;Li et al., 2021). Among the 38 vehicles we tested, a fraction of vehicles was measured several times, with a total of 62 experiments measured. The detailed information for test vehicles is summarized in Sect. 1 in the Supplement, Table S2 and Table S3.

The short transient driving cycle (GB 18285-2018, Figure S1a), as one of the widely used test methods for vehicle emissions in China (Li et al., 2012;Wang et al., 2013), was used for measurements of gasoline vehicles and LDDT, each running for three to five times. The short transient driving cycle methods were initially adapted based on emission regulations of the Economic Commission for Europe (ECE) cycle (Yao et al., 2003), which is developed and used in European countries (Laurikko, 1995). The short transient driving cycle consist of four conditions, namely idling, acceleration, deceleration and uniform speed, as shown in Fig. S1. For the MDDT and HDDT, we customized a step-by-step test method, in which the vehicle accelerates to 20 $km \cdot h^{-1}$, 40 $km \cdot h^{-1}$ and 60 $km \cdot h^{-1}$ in sequence after the engine activates, keeping at 20 $km \cdot h^{-1}$ and 40 $km \cdot h^{-1}$ for 2 minutes, and 60 $km \cdot h^{-1}$ for 1 minute, respectively (Fig. S1) (Li et al., 2021;Liu et al., 2021;Liao et al., 2021). In addition, the cold start was tested for a

number of vehicles after a cold soak for more than 12 hours at ambient temperature (20-25 ℃) before engine started. The measurements of cold start are compared to measurements of hot start after a ~10 minutes break for the vehicles after previous measurement. More details about cold start and hot start in this campaign can be found in Li et al. (2021).

A custom-built sampling and dilution system for vehicles combining online and offline sampling techniques was used in this study. As shown in Fig. S2, a portable emission measurement system (PEMS, SEMTECH-DS, Sensors. USA) was employed to measure emissions of CO, CO_2, NO_X, and total hydrocarbon (THC) directly from the tailpipe of vehicles. A custom-built dilution system (Li et al., 2021;Liao et al., 2021) was used for dilution of vehicular emissions, achieving dilution ratios of 10-100 for different vehicles. After dilution, CO_2 and CO were measured using a Li-840A CO_2/H_2O Gas Analyzer (Licor, Inc. USA) and a Thermo 48i-TLE analyzer (Thermo Fisher Scientific Inc. USA), respectively. Measurements of CO_2 before and after the dilution system was used to determine the dilution ratio for each test (see details in Fig. S3).

2.2 VOC measurements using PTR-ToF-MS

In this study, a Proton Transfer Reaction Quadrupole interface Time-of-Flight Mass Spectrometer (PTR-QiToF-MS) (Ionicon Analytik, Innsbruck, Austria) with H_3O^+ chemistry was used to measure VOCs (Sulzer et al., 2014). The mass spectra of PTR-ToF-MS was recorded every 1 s as to capture characteristics of VOC species from vehicle exhausts in real-time. Background measurements of the instrument were performed using sampled air through a custom-built platinum catalytical converter heated to 365 °C for 30 s before vehicle starts in each test. The more detailed setting parameters for the instrument can be found elsewhere (Wu et al., 2020;Wang et al., 2020a;He et al., 2022). Data analysis of PTR-ToF-MS was performed using the Tofware software package (version 3.0.3, Tofwerk AG, Switzerland) (Stark et al., 2015).

A 23-component gas standard (Linde Spectra) was used for daily calibration of PTR-ToF-MS during the campaign. VOC sensitivities from automatical calibrations

indicated quite stable instrumental performance for most of the VOC species (Fig. S4). Another gas standard with 35-component VOCs (Apel Riemer Environmental Inc.) was used for calibrations during the later period of this campaign to include more VOC species in the calibration. The Liquid Calibration Unit (LCU, Ionicon Analytik, Innsbruck, Austria) was used to calibrate a total of 11 organic acids and nitrogen-containing species (Table S4). The limits of detection for calibrated VOC species are below 100 ppt for the 1-s measurement, except for ethanol (423 ppt) and formic acid (166 ppt). Additionally, the humidity dependence for a few VOC species in PTR-ToF-MS (Yuan et al., 2017;Koss et al., 2018) were corrected using humidity-dependence curves determined in the laboratory, as previously shown in Wu et al. (2020). To quantify the ion signals without calibration, we determine the sensitivities based on the kinetics of proton-transfer reactions of H_3O^+ with VOCs (Cappellin et al., 2012;Sekimoto et al., 2017). The relationship between VOCs sensitivity and kinetic rate constants for the same instrument has been reported in Wu et al. (2020) and He et al. (2022). The corrected sensitivities as a function of kinetic rate constants for proton-transfer reactions of H_3O^+ with VOCs during this campaign is shown in Fig. S5. The fitted line is used to determine sensitivities of uncalibrated species, and the uncertainty of the concentrations for uncalibrated species are determined to be around 50%.

2.3 Other VOC measurements

Whole air samples were collected using canisters after the dilution system for determination of hydrocarbons emitted from various vehicles. All the canisters were sent to the laboratory for analysis by an offline GC-MS/FID system, with a total 95 hydrocarbons calibrated by Photochemical Assessment Monitoring Stations (PAMS) and TO-15 standard mixtures (Table S5). 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.

An instrument based on Hantzsch reaction-absorption method was used to measure formaldehyde (Zhu et al., 2020). Good agreement for formaldehyde between

PTR-ToF-MS and the Hantzsch instrument was obtained (Fig. S6a). An iodide-adduct time-of-flight chemical ionization mass spectrometer (I^- ToF-CIMS, Aerodyne Research, Inc.) (Wang et al., 2020c;Ye et al., 2021) was used to measure organic acids, hydrogen cyanide (HCN), and isocyanic acid (HNCO) from vehicles (Li et al., 2021). As shown in Fig. S6b, formic acid measured by PTR-ToF-MS and I^- ToF-CIMS showed reasonable agreement.

2.4 Emission factors and emission ratios calculation

In this study, we determine emission factors of VOC species in two different approaches: the mileage-based emission factors ($mg \cdot km^{-1}$) as the mass of these VOCs exhausted per kilometer driving of vehicles, and the fuel-based emission factors ($mg \cdot kg_{fuel}^{-1}$) as the mass of VOCs per kilogram of fuel burned by the vehicles. In addition, emission ratios of VOCs to combustion tracers (usually CO) are widely applied in vehicle emissions in urban regions, as the result we determine emission ratios to CO in $ppb \cdot ppm^{-1}$ as well. More details about the determination of emission factors and emission ratios can be found in Sect. 2 in the Supplement.

The average emission factors for various types of vehicles are determined from arithmetic means for different emission standards of vehicles. As for diesel vehicles, the average emission factors are obtained from the arithmetic means of LDDT, MDDT, HDDT, and bus. Besides, we also calculate emission factors and emission ratios from weighted means based on the fractions of gasoline and diesel vehicles with different emission standards in China (MEEPRC, 2019;Li et al., 2021) (see Sect. 2 in the Supplement for details). In order to evaluate the uncertainties of obtained emission factors, the average limit of detection for VOC species are used to estimate the limit of detection for the determined emission factors (more details can be found in Sect. 3 in the Supplement).

3. Results and discussions

3.1 Characteristics of the VOC emissions in the vehicles

Time series of several aromatics and OVOC species measured by PTR-ToF-MS for a selected gasoline vehicle associated with emission standard of China I and a LDDT

associated with China IV emission standard are shown in Fig. 1. Both tests started with cold engines for the two vehicles. Benzene and toluene are typical aromatic species emitted by vehicles. As shown in Fig. 1a, high concentrations of benzene and toluene exhausted by the gasoline vehicle were observed as the engine started. The concentrations of the two species continued to increase until ~2 min after the engine started, and then dropped rapidly before a minor increase during the acceleration condition. These observations are similar to the previous results from PTR-MS measurements in Drozd et al. (2016). Acetaldehyde and acetone are important OVOC species emitted from vehicles. They show similar temporal variations as benzene and toluene. However, concentrations of acetaldehyde and acetone were much lower than the two aromatics after engine started. Compared to the concentrations at engine start-up for the gasoline vehicle (the first cycle), concentrations of the VOCs are 3.0 to 40 times lower during the gasoline vehicle running at hot stabilized condition (the third cycle). As shown in Fig. 1 for the diesel vehicle, enhanced emissions from cold start are minor, which is different from the gasoline vehicle. The concentration of these VOCs at engine start-up for the diesel vehicle are only 1.3 to 2.5 times higher than the periods as the diesel vehicle running at hot stabilized condition. It indicates that the impact of the engine start-up in diesel vehicles on emissions is much lower than gasoline vehicles. 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). In contrast to the gasoline vehicle, we observe higher concentrations of the two OVOC species than the two aromatics species from the diesel vehicle. These higher OVOC concentrations in diesel vehicle exhausts are in line with the observations of organic acids using the I- ToF-CIMS from the same campaign (Li et al., 2021).

Based on the high time-resolution measurements of PTR-ToF-MS, we determined emission factors of various VOC species from different vehicles. Fig. 2 shows the determined average mileage-based emission factors of benzene, toluene, acetaldehyde, and acetone for various types of vehicles (also tabulated in the Supplement table). 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. Emission factors of the four species for China VI vehicles are 12 to 25 times lower than emissions for China I vehicles, indicating that newer emission standards successfully reduced VOC emissions of gasoline vehicles. The decline of emission factors for the four species with newer emission standards for diesel vehicles are in the range of 1.1 to 7.4 times from China III to China V, compared to 4.5 to 5.4 times reduction from China III to China V for gasoline vehicles. Emission factors of benzene and toluene from diesel vehicles are in the range of 0.8 to 7.4 $mg \cdot km^{-1}$ and 0.3 to 5.8 $mg \cdot km^{-1}$, which are comparable to emission factors from gasoline vehicles with China IV to China VI emission standards. This is different from observations of the two OVOC species (acetaldehyde and acetone), with much higher emission factors from diesel vehicles (8.0 to 27.9 $mg \cdot km^{-1}$ for acetaldehyde and 0.8 to 10.0 $mg \cdot km^{-1}$ for acetone) than almost all gasoline vehicles (a maximum of 3.9 $mg \cdot km^{-1}$ for acetaldehyde and a maximum of 3.2 $mg \cdot km^{-1}$ for acetone). Higher emission factors from diesel vehicles are also observed for many other common OVOC species, as shown in Fig. 4. As the largest OVOCs emitted from gasoline vehicles (4.6 ± 5.1 $mg \cdot km^{-1}$), 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). The high emissions of OVOCs from diesel vehicles may be related to combustion processes

in diesel vehicles, with more excess air (i.e., under overall fuel-lean conditions) into combustion cylinder resulting in higher oxygen contents and more oxidation processes during fuel combustion (Pang et al., 2008;Qiao et al., 2012;Gentner et al., 2017). Finally, the determined emission factors of the four VOC species from LPG vehicles are much lower than both gasoline and diesel vehicles.

3.2 Analysis of PTR-ToF-MS mass spectra to evaluate VOCs speciation

In addition to typical VOC species shown above, PTR-ToF-MS detected abundant signals for a large number of ions. The determined average mileage-based emission factors for all detected VOC species are shown as mass spectra in Fig. 4. VOC species measured by PTR-ToF-MS were divided into groups according to chemical formula, namely hydrocarbon species only containing C and H atoms (C_xH_y), OVOCs ($C_xH_yO_z$), species containing nitrogen and/or sulfur atoms (N/S-containing), and some other ions (others). We observe similar mass spectra of emission factors for gasoline vehicles with different emission standards (Fig. S7). Highest emission factors from gasoline vehicles (Fig. 5a) are detected as hydrocarbons, including C_6 to C_{10} aromatics. A few OVOC species, namely methanol, ethanol, formaldehyde, acetaldehyde and acetone, are also observed as the largest emissions. In contrast to gasoline vehicles, the largest emissions from diesel vehicles were attributed to a few low-molecular-weight OVOC species, including formaldehyde, acetaldehyde, formic acid, and acetic acid, followed by a large number of hydrocarbon species. Comparison between the mass spectra of gasoline and diesel vehicle emissions suggest that emissions from diesel vehicles are more evenly distributed among different VOC species, as reflected by 50 and 140 species contributing more than 1‰ of the total emissions for gasoline and diesel vehicles, respectively. As shown in Fig. 5b, many hydrocarbon ions in the range of m/z 150-200 still account for significant fractions of emissions from diesel vehicles, whereas only one species in this m/z range contribute more than 1‰ of emissions from gasoline vehicles. These results demonstrate that diesel vehicles emit more heavier hydrocarbons than those from gasoline vehicles, which is consistent with observations

in previous studies (Gentner et al., 2012;Erickson et al., 2014). It should be noted that the signals of $C_{16}H_{22}O_4H$ (m/z=279) were higher during the tests based on determined emission factors. However, we suspect that it may be emitted artifacts from the sampling or dilution system as it mainly showed higher signals in the latter period of each test when sampling materials absorb more heat from vehicle exhausts (Fig. S8), and thus it is not included in Fig. 5 (details in the Sect. 3 in the Supplement).

The scatterplot of carbon oxidation states ($\overline{OS_C}$) as a function of carbon number (n_C) provides a framework for describing bulk chemical properties of organics (Kroll et al., 2011). The details of $\overline{OS_C}$ calculation is included in Sect. 4 in the Supplement. The results from gasoline and diesel vehicles are compared in Fig. 6 (LPG vehicles are shown in Fig. S9). It is apparent that ions with carbon oxidation states between -2.0 to 0 comprise main emissions for each carbon number for both gasoline and diesel vehicles. It is interesting to observe that averaged $\overline{OS_C}$ for n_C>6 increase as the carbon number decrease for both gasoline and diesel vehicles, whereas the opposite trends are observed for n_C<5. The averaged $\overline{OS_C}$ in diesel vehicles for n_C between 1 and 5 are significantly higher than those in gasoline vehicles, as the result of high emissions of C_2 to C_5 low-molecular-weight OVOCs. Fig. 6c further shows that emission factors of most VOC species from diesel vehicles were higher than gasoline vehicles, except a number of species occupying in the right-bottom corner of the two-dimensional space.

The determined mass spectra of PTR-ToF-MS in terms of emission factor for different types of vehicles can be used to explore the dependence of various VOC emissions to different factors. Fig. 7a-b shows scatterplots of the average mileage-based emission factors of VOCs between cold start and hot start for gasoline and diesel vehicles, respectively. 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). It is obvious that emission factors of VOCs during cold start are significantly higher than those during hot start for gasoline vehicles (slope=0.40), whereas similar emissions factors between cold start and hot start are derived for diesel vehicles (slope=0.84). These results suggest that gasoline vehicles are more significantly influenced by cold start, as the result of compositions in gasoline fuel are more volatile than diesel fuel (US NRC, 1996). We further explore the effects of emission standards to VOCs emission factors by comparing determined emission factors between China I and China V for gasoline vehicle (Fig. 7c, also see China III versus China V and China V versus China VI in Fig. S10) and between China III and China V for LDDT (Fig. 7d, also see China III versus China V for MDDT and HDDT in Fig. S10). 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. Furthermore, comparison of both gasoline and diesel vehicles demonstrate newer emission standards successfully decreased VOC emissions. Based on the derived slopes, we obtain VOCs emission factors reduced by a factor of 10 for gasoline vehicles from China I to China V (a factor of 5 reduction from China III to China V and a factor of 2.5 reduction for China V to China VI), and a factor of 2 reduction for LDDT from China III to China V (a factor of 1.5 and 8 reduction for MDDT and HDDT from China III to China V). The reduction ratio for gasoline vehicles from China I to China V are generally similar for most VOC species, except that some OVOC species with smaller reduction ratios. The reduction ratios for LDDT vehicles from China III to China V show large variability for different species. The lowest reduction ratios (a factor of ~2) are observed for the low-molecular weight OVOC species associated with largest emissions, while the reduction ratios for hydrocarbons and higher-molecular weight OVOCs are in the range of a factor of 10-100. 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).

3.3 Non-target analysis for comparison between gasoline and diesel vehicles

As shown in the previous section, the analysis of PTR-ToF-MS mass spectra provide rich information on understanding the influences of VOC emissions from vehicles. This detailed information provided by the PTR-ToF-MS also offer an opportunity to systematically compare emissions between gasoline and diesel vehicles. The scatterplot of the determined average emission factors of various VOC species between gasoline and diesel vehicles is shown in Fig. 8. Large difference of VOC compositions emitted from gasoline and diesel vehicles are observed, as indicated by the low correlation of the data points (R=0.24). A limited number of VOC species, including C_6-C_{10} aromatics and some N/S-containing species (e.g. C_7H_5N) are associated with higher emission factors from gasoline vehicles, whereas the obtained emission factors of most VOC species emitted from diesel vehicles are higher, especially most OVOC species. For example, formic acid is found to be one of the most significant emission species in diesel vehicles, with emission factors three orders of magnitude higher than that of gasoline vehicles. In addition, emission factors of HCN from gasoline vehicles are similar to those from diesel vehicles. These results are consistent with the measurements using the I^- ToF-CIMS from the same campaign, as shown in Li et al. (2021).

The scatterplot shown in Fig. 8 can also be expressed in terms of the determined fuel-based emission factors between gasoline and diesel vehicles (Fig. S11a). 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. Furthermore, the difference between the slopes reflects the different average mileage for the same weight of fuel between gasoline (9.7 $km \cdot kg_{fuel}^{-1}$) and diesel vehicles (7.1 $km \cdot kg_{fuel}^{-1}$), as demonstrated for emission factors of CO_2 in Table S6.

Comparing gasoline and diesel vehicles, we can also observe profound differences in relative changes of emission factors for analogous compounds series. The emission factors of C_6-C_{10} aromatics are apparently higher for gasoline vehicles than diesel vehicles, whereas emission factors for larger aromatics (n_C>11) from diesel vehicles start to exceed gasoline vehicles. 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). As shown in Fig. 9, emission factors of aromatics from gasoline vehicles start to rapidly decrease at n_C=10 (a factor of 5 for each additional carbon for C_{10}-C_{15}), while the emission factors of aromatic for diesel vehicles demonstrate a relatively flat pattern between C_6 and C_{15}, only with significantly decrease for n_C>15. Based on Fig. 9, we determine that emissions of aromatics with n_C≥10 in gasoline and diesel vehicles are account for 14% and 63% of total aromatic emissions, again suggest the importance of heavier aromatics in emissions from diesel vehicles. It also highlights that quantification of these heavier species by PTR-ToF-MS may be important in characterization of vehicular exhausts, especially diesel vehicles.

In addition to aromatics, the relative changes of emission factors for carbonyls with carbon number are apparently different between gasoline and diesel vehicles (Fig. 8 and Fig. 9b). Emission factors of carbonyls tend to decrease as carbon number increase for both gasoline and diesel vehicles. The decrease magnitudes are observed to be comparable from C_1-C_6 carbonyls for gasoline (97.6%) and diesel vehicles (97.4%). However, as n_C>6, the decrease of carbonyl emissions factors for diesel vehicles become smaller, result in larger emissions factors than gasoline vehicles for this range of carbon number.

The above discussions demonstrate that emission characteristics of aromatics and OVOCs are significantly different between gasoline and diesel vehicles. As the result, the ratios of VOC pairs can be identified to distinguish emissions of gasoline and diesel vehicles. Fig. 10 shows the scatterplots of four representative VOCs (benzene, C_{14}

aromatics, formaldehyde, and acetaldehyde) versus toluene based on the determined emission factors. The data points for each VOCs pair clearly show distinct separation between gasoline vehicles and diesel vehicles, with apparently higher slopes for diesel vehicles than gasoline vehicles, as the result of much larger emission factors of toluene from gasoline vehicles and lower emission factors of the four representative VOCs from diesel vehicles. The benzene/toluene ratio in gasoline and diesel vehicle are determined as 0.48 and 1.24 $mg \cdot mg^{-1}$ (corresponding to 0.57 and 1.46 $ppb \cdot ppb^{-1}$ that are more widely used in ambient studies). The difference of benzene/toluene ratio between gasoline and diesel vehicles has been reported in previous studies, and our results are generally consistent with these previous results (Chan et al., 2002;Barletta et al., 2005;Qiao et al., 2012;Kumar et al., 2020). Compared to benzene/toluene ratio, the difference of C_{14} aromatics/toluene ratio between gasoline and diesel vehicles are more substantial (a factor of 3800). The remarkable larger emission factors of C_{14} aromatics from diesel vehicles suggest that diesel vehicles can be a significant or even predominated source for higher molecular aromatics. 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). Similar discrepancies are observed for formaldehyde/toluene and acetaldehyde/toluene ratios between gasoline and diesel vehicles. These ratios may not be able to be used as indicators for distinguish gasoline and diesel vehicles in ambient studies, since secondary sources may complicate the observed ratios in ambient air. However, these results strongly suggest that diesel vehicles can be important in emissions of these OVOC species, though the number of diesel vehicles are smaller than gasoline vehicles in many countries, e.g. China and U.S (Wallington et al., 2013;Yao et al., 2015;Huang et al., 2021).

3.4 OVOC fractions in VOC emissions

Emission factors of various VOC species measured by PTR-ToF-MS from

462 different vehicles are summarized in Fig. 11. As shown in Fig. 11a, the determined
463 average mileage-based emission factors of total VOC ions from diesel vehicles were
464 much higher than gasoline and LPG vehicles. Fig. 11b-d quantified the proportions of
465 different categories of ions measured by PTR-ToF-MS. The determined average
466 mileage-based emission factors of C_xH_y accounted for the largest fraction in gasoline
467 vehicles (84% ± 5.9%), and lower fractions in diesel (47% ± 16%) and LPG vehicles
468 (32% ± 0.7%). OVOCs account for larger fractions in diesel (49% ± 16%) and LPG
469 vehicles (58% ± 3.7%), while they only account for 13% ± 6.1% of emissions from
470 gasoline vehicles. The fractions of different OVOC groups generally demonstrate a
471 downward trend from $C_xH_yO_1$ to $C_xH_yO_{\geq 3}$, and OVOCs with more than two oxygen
472 atoms only occupy small percentages (0-7%) in vehicle exhausts, indicating low
473 emissions of these species.

474 Combined with measurements of other VOCs from canisters measured by GC-
475 MS/FID, the fractions of OVOCs in total VOC emissions can be determined for
476 different vehicles (details in Sect. 6 in the Supplement) (Fig. 12). OVOCs account for
477 9.4% ± 5.6% of total VOC emissions for gasoline vehicles. The OVOC fractions for
478 gasoline vehicles are generally comparable for different emission standards and
479 cold/hot start, except somewhat higher fractions for China VI from hot start (Fig. S12).
480 The OVOC fractions obtained in this study for gasoline vehicles are generally
481 consistent with previous results (Cao et al., 2016;Wang et al., 2020b) (Fig. 12). Among
482 these studies, the OVOC fractions determined for gasoline with 10% ethanol (E10)
483 (Roy et al., 2016) (22% ± 11%) are apparently higher. The fractions of OVOCs in total
484 VOC emissions for diesel vehicles are 71% ± 20%, 65% ± 22%, 52% ± 18%, and 56%
485 ± 26% for LDDT, MDDT, HDDT, and bus, respectively. The variations of OVOC
486 fractions with emission standards are observed to be mixed among different types of
487 diesel vehicles (Fig. S12). The OVOC fractions from diesel vehicles are obviously
488 higher than those in gasoline vehicles, indicating the importance of OVOCs in VOC
489 emissions for diesel vehicles. Compared to previous studies (Tsai et al., 2012;Qiao et
490 al., 2012;Cao et al., 2016;Mo et al., 2016), determined OVOC fractions for diesel
491 vehicles in this study are higher. 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 (Fig. 12), since most previous studies only detected carbonyls among various types of OVOCs. Finally, we determine that OVOCs account for 41% ± 10% of total VOC emissions for LPG vehicles, which is also higher than in one previous study (Wang et al., 2020b) with only carbonyls and a few esters/alcohols included. These results stress that the large number of OVOCs measured by PTR-ToF-MS are important in characterization of VOC emissions from vehicles. It should be noted that the OVOC fractions obtained here only reflect exhaust emissions. Evaporative emissions may be associated with different fractions of various VOC groups, which may be more related to fuel compositions (Rubin et al., 2006;Huang et al., 2021).

4. Conclusions

In this work, we conducted a chassis dynamometer study to measure VOC emissions from gasoline, diesel, and LPG vehicles using PTR-ToF-MS along with other offline and online measurement techniques. Using this dataset, we provide emission factors of many VOCs from these three different types of vehicles associated with various emission standards in China. Our results show that emission factors of VOCs generally decrease with the increased stringency of emission standards for gasoline vehicles, whereas variations of emission factors for diesel vehicles with emission standards are more diverse. Mass spectra analysis of PTR-ToF-MS suggest that cold start significantly influence VOCs emission of gasoline vehicles, while the influences are smaller for diesel vehicles.

We observe large differences of VOC emissions between gasoline and diesel vehicles based on PTR-ToF-MS measurements. Emission factors of most VOC species from diesel vehicles were higher than gasoline vehicles, especially for most OVOCs and heavier aromatics. The substantially larger emission factors of some OVOCs emission factors for diesel vehicles indicate potentially dominant emissions of these species from diesel vehicles among vehicular emissions. Our results suggest that VOC pairs (e.g. C_{14} aromatics/toluene ratio) could potentially provide good indicators for

distinguishing emissions between gasoline and diesel vehicles.

Based on measurements of PTR-ToF-MS, C_xH_y ions account for the largest fraction in gasoline vehicles (84% ± 5.9%), whereas OVOC ions are the largest contributor in the mass spectra of emissions from diesel (49% ± 16%) and LPG vehicles (58% ± 3.7%). In the end, the fractions of OVOCs in total VOC emissions are determined by combining hydrocarbons measurements from canister results and online measurements of PTR-ToF-MS. We show that OVOCs contribute 9.4% ± 5.6% of gasoline vehicles of the total VOC emissions, while the fractions are significantly higher for diesel vehicles (52-71%), highlighting the importance to detect these OVOC species in diesel emissions.

This study shows significant contributions of OVOCs in VOC emissions from various vehicles, especially diesel vehicles. As a consequence, vehicular emissions may account for considerable proportions for primary emissions of these OVOCs in urban regions. Emissions of many OVOC species are currently not fully represented in emission inventories of VOCs, which may in turn affect the prediction ability of air quality models in urban regions. In this study, OVOC species are mainly quantified from PTR-ToF-MS measurements by taking into account all signals in the mass spectra, which stress that the large number of OVOC species measured by PTR-ToF-MS are important in characterization of VOC emissions from vehicles.

Data availability

Data are available from the authors upon request.

Author contribution

BY designed the research. ZBY, BY, QES organized vehicle test measurements. SHW, CHW, CMW, TGL, JPQ, QES, and MMZ contributed to data collection. SHW performed the data analysis, with contributions from TGL, XJH, YBH, XBL, and QES. SHW and BY prepared the manuscript with contributions from other authors. All the authors reviewed the manuscript.

Competing interests

The authors declare that they have no known competing financial interests or

personal relationships that could have appeared to influence the work reported in this paper.

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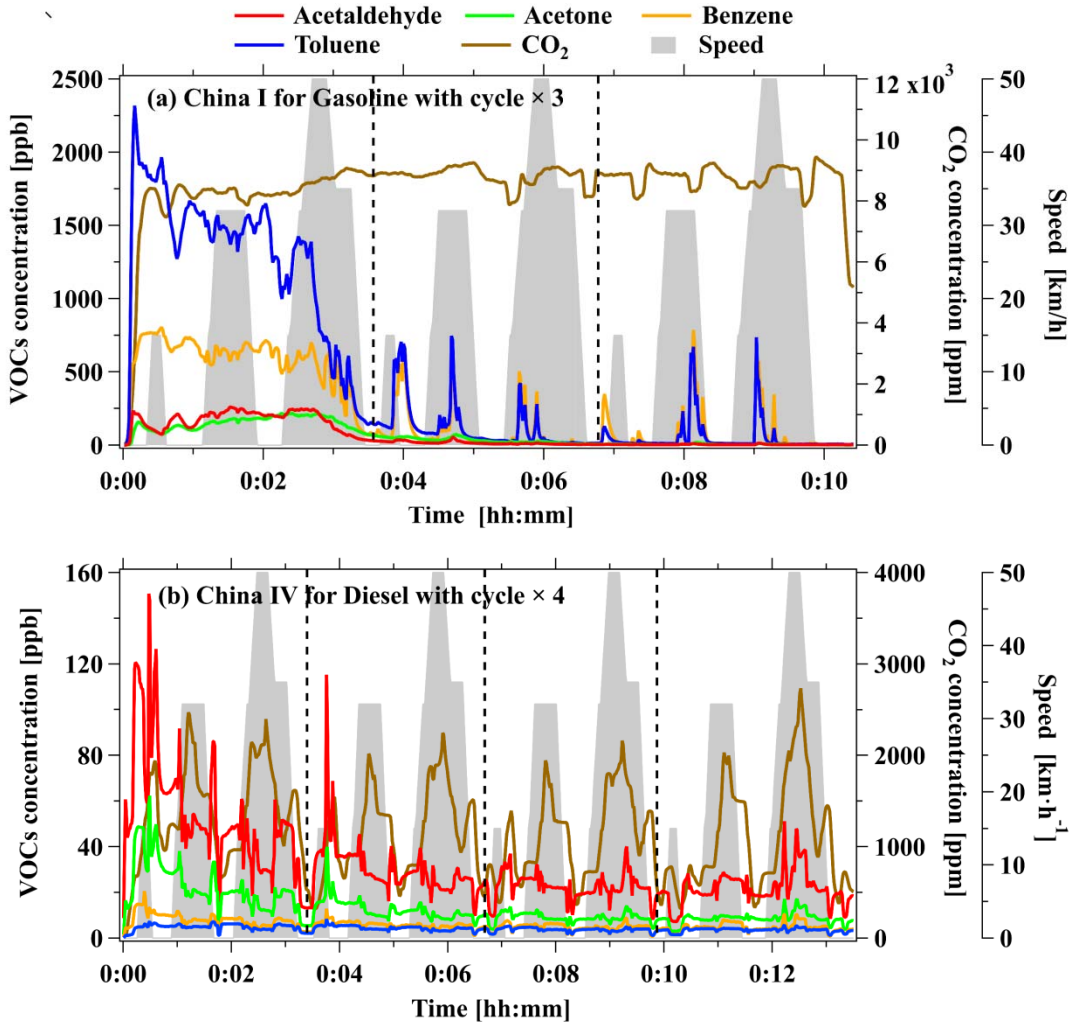

853

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

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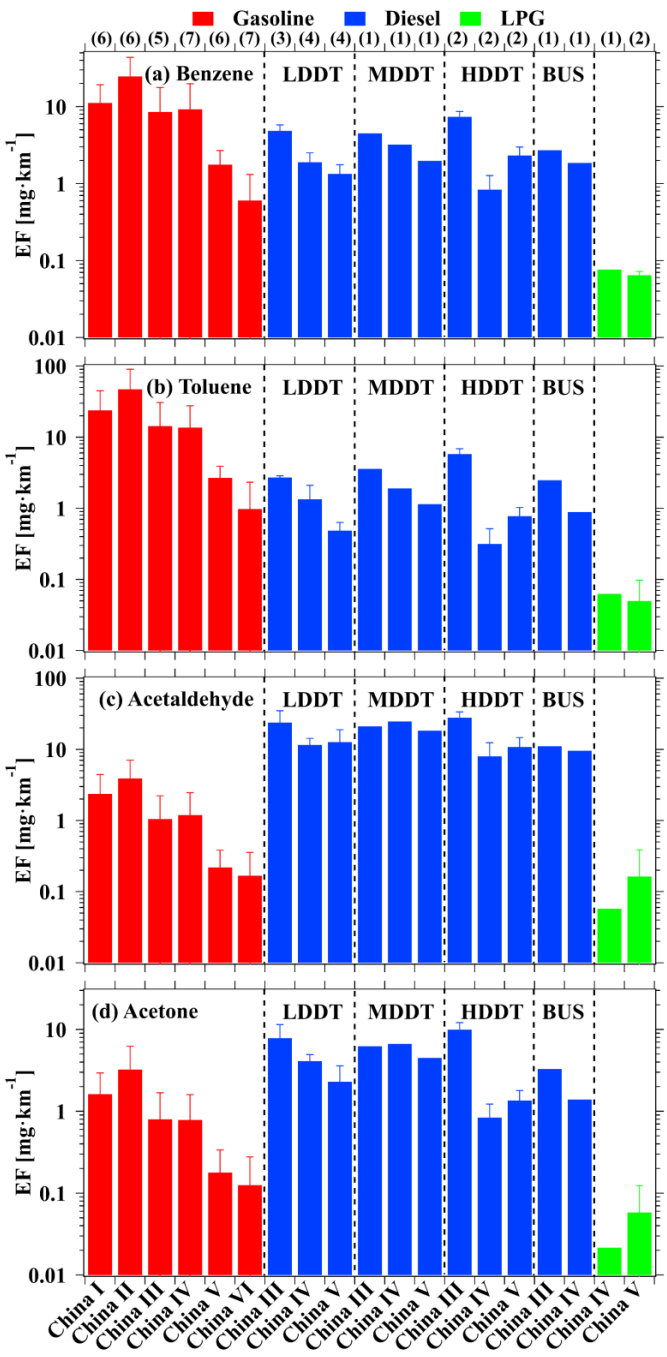


Figure 2. The determined average mileage-based emission factors (mg·km^{-1}) for (a) benzene, (b) toluene, (c) acetaldehyde, and (d) acetone for vehicles with different emission standards. The numbers above the top axis represent the number of all experiments (including multiple measurements for individual 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.

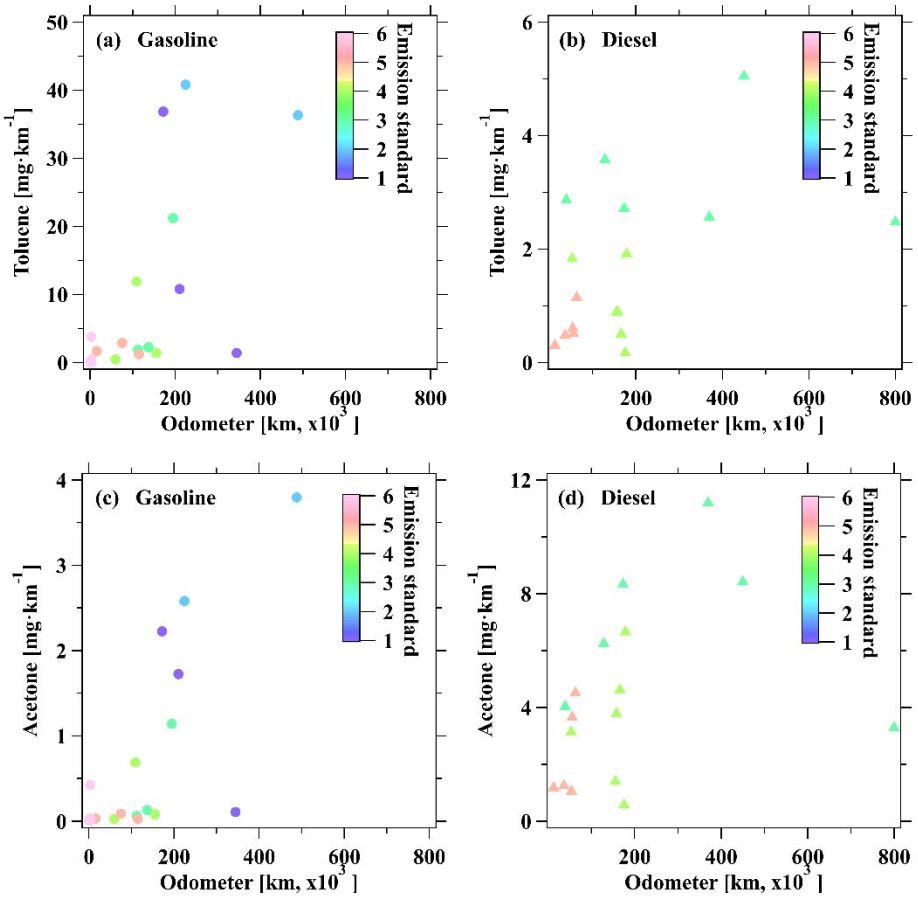
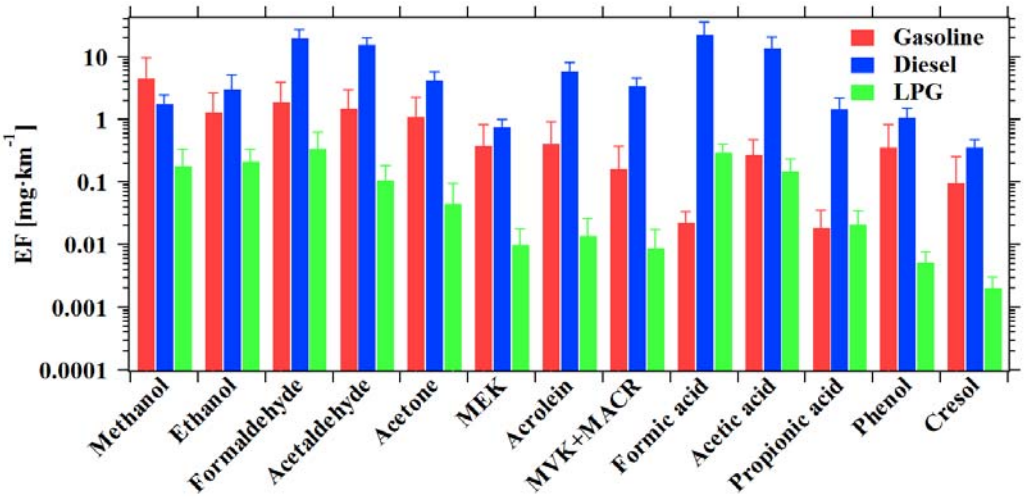


Figure 3. Scatterplot of the emission factor of toluene in (a) gasoline and (b) diesel vehicles, and acetone in (c) gasoline and (d) diesel vehicles during the hot start based on the odometer for each vehicle.



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875 **Figure 4.** The determined emission factors of representative OVOC species from
876 different types of vehicles. Error bars represent standard deviations of the emission
877 factors for the VOCs.

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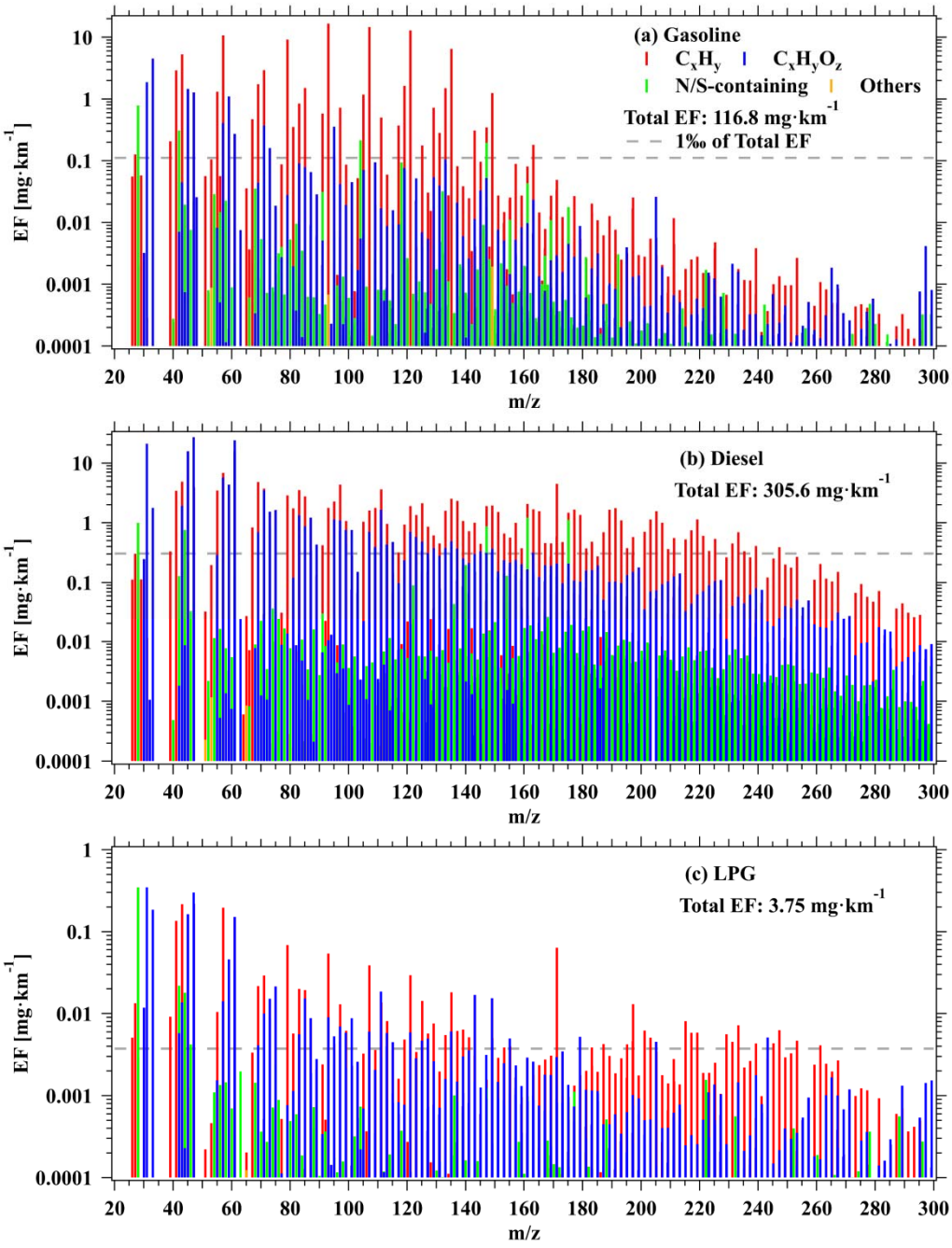

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880 **Figure 5.** The determined average mileage-based emission factors of VOC species
881 measured by PTR-ToF-MS from (a) gasoline, (b) diesel, and (c) LPG vehicles. The
882 gray dashed lines represent 1‰ of total VOCs emission factors.

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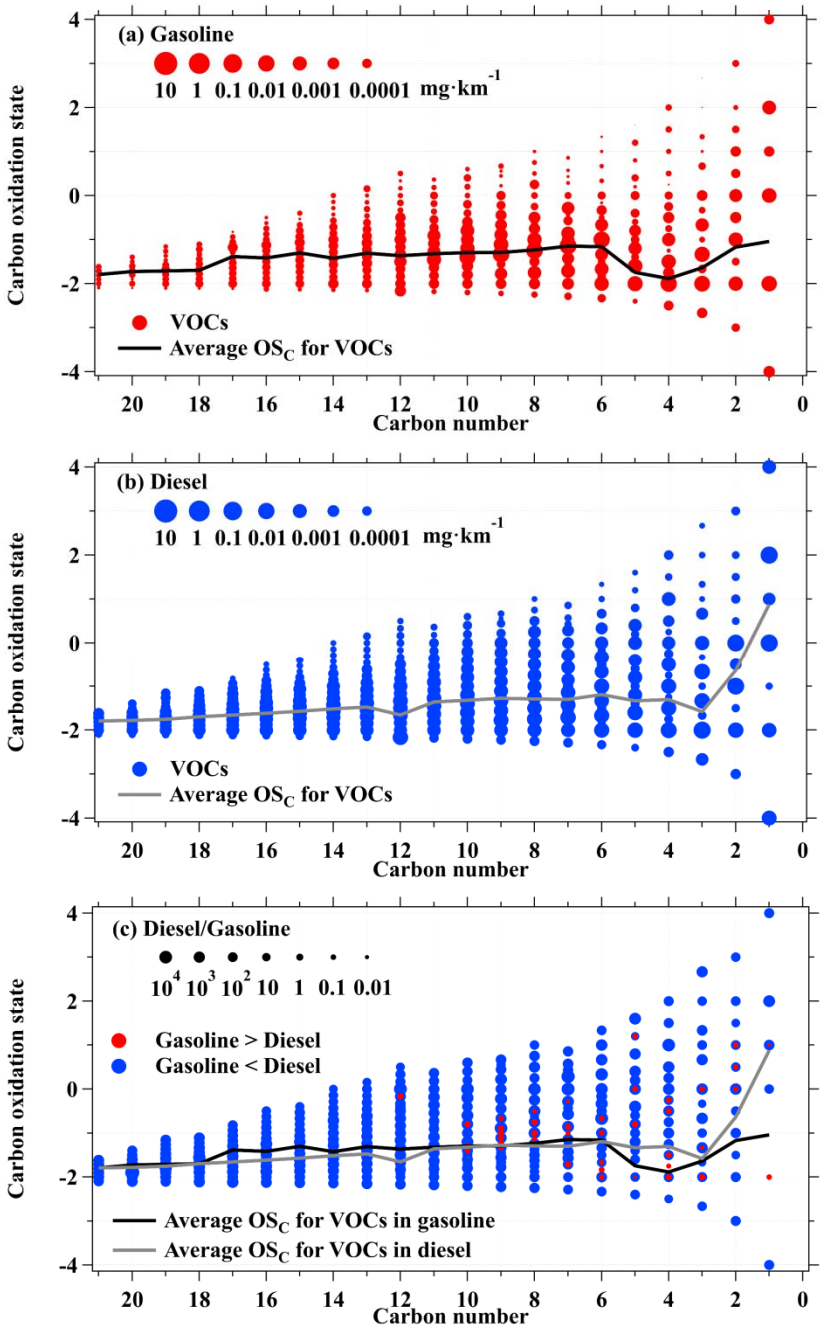

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885 **Figure 6.** The two-dimensional space of $\overline{OS_C} - n_C$ with data points sized coded using
886 emission factors of VOC species from (a) gasoline and (b) diesel vehicles, and (c) the
887 ratio of emission factors of diesel vehicle relative to gasoline vehicle. The black and
888 gray lines are the average $\overline{OS_C}$ of each carbon number for VOC species in gasoline and
889 diesel vehicles, respectively.

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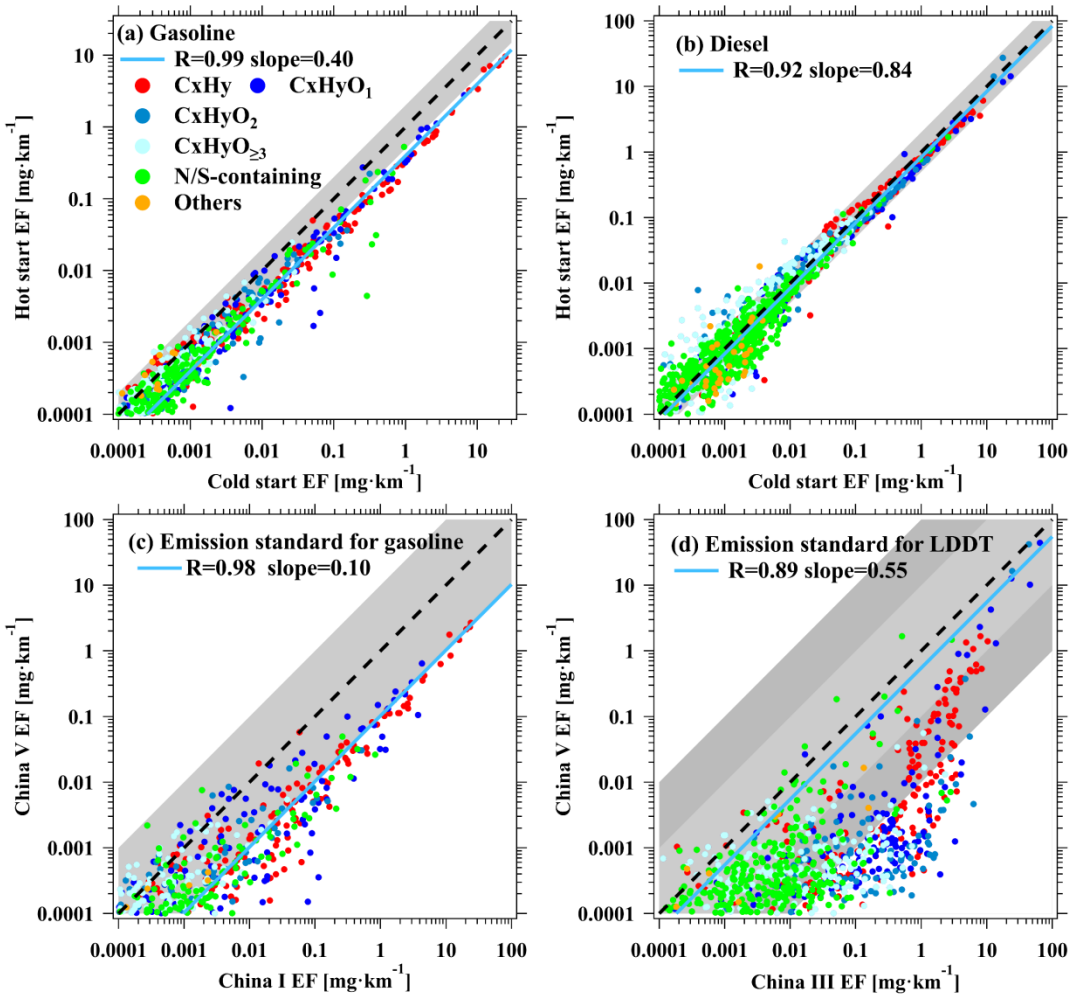

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892 **Figure 7.** Scatterplots of VOCs emission factors between cold start and hot start for
893 gasoline (a) and diesel vehicles (b). Scatterplots of VOCs emission factors between
894 China I and China V emission standard for gasoline vehicles (c) and between China III
895 and China V emission standard for diesel vehicles (d). Each data point indicates a VOC
896 species measured by PTR-ToF-MS. The blue lines are the fitted results for all data
897 points. The black dashed lines represent 1:1 ratio, and the shaded areas represent ratios
898 of a factor of 2 in (a) and (b), and a factor of 10 and 100 in (c) and (d).

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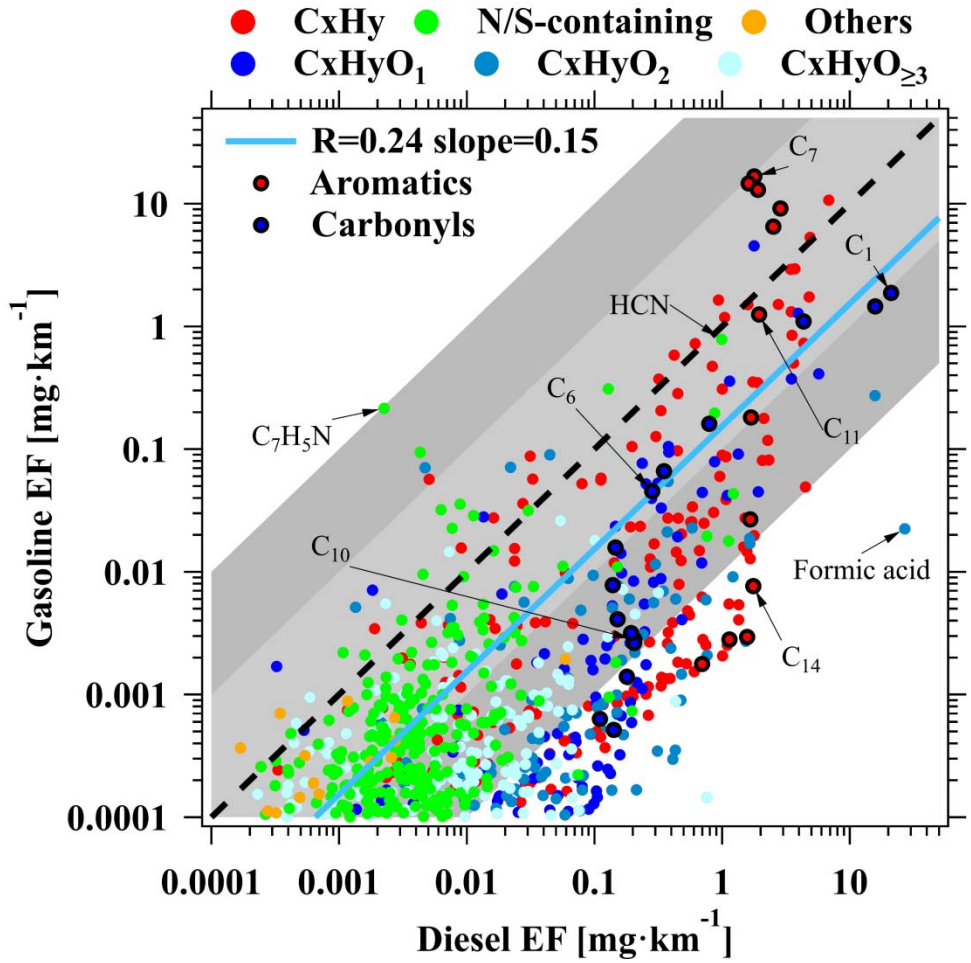

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901 **Figure 8.** Scatterplot of VOCs emission factors between gasoline and diesel vehicles.
902 Each data point indicates a VOC species measured by PTR-ToF-MS. The blue line is
903 the fitted result for all data points. The black line represents 1:1 ratio, and the shaded
904 areas represent ratios of a factor of 10 and 100.

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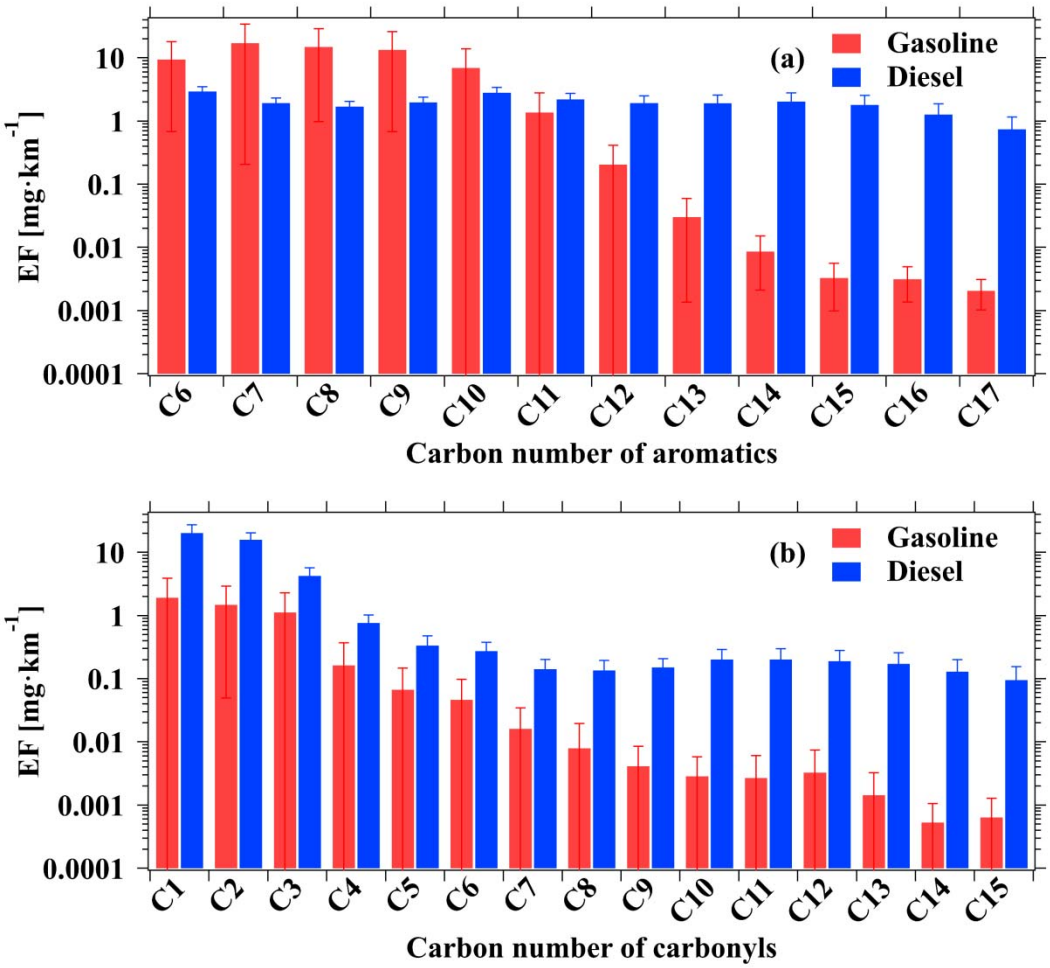
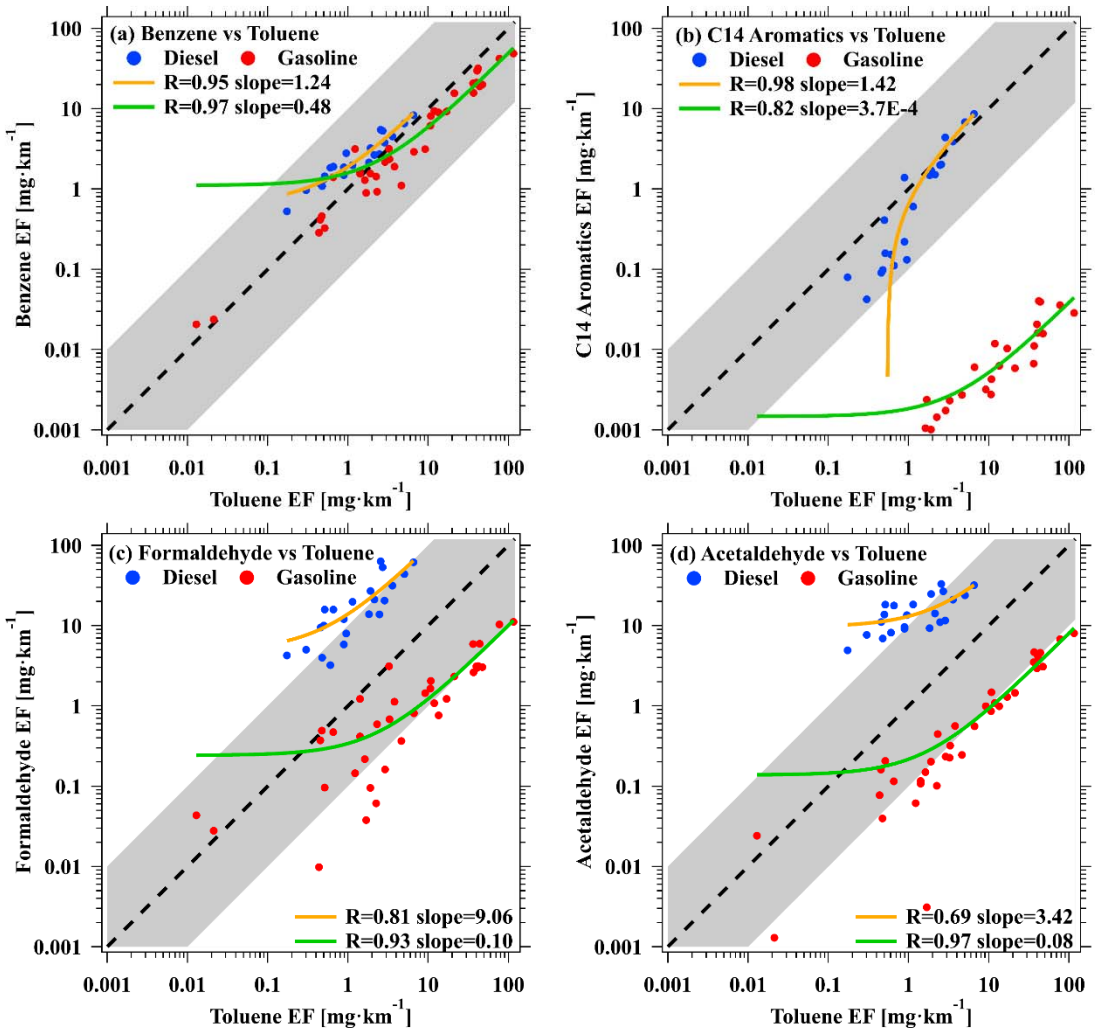


Figure 9. The determined emission factors of (a) aromatics and (b) carbonyls for each carbon number from gasoline and diesel vehicles. Error bars represent standard deviations of the emission factors for the VOCs of different carbon number.



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912 **Figure 10.** Scatterplots of the determined mileage-based emission factors of (a)
913 benzene versus toluene, (b) C_{14} aromatics versus toluene, (c) formaldehyde versus
914 toluene, and (d) acetaldehyde versus toluene for gasoline and diesel vehicles. Each data
915 point represents each test vehicle in this study. The green and orange lines are the fitted
916 results for gasoline and diesel vehicle. The black line represents 1:1 ratio, and the
917 shaded areas represent ratio of a factor of 10. The green and orange line are the fits to
918 gasoline and diesel points in each plot. Note that these linear fits are shown in curves
919 in log-log space as the result of non-zero y-intercept.

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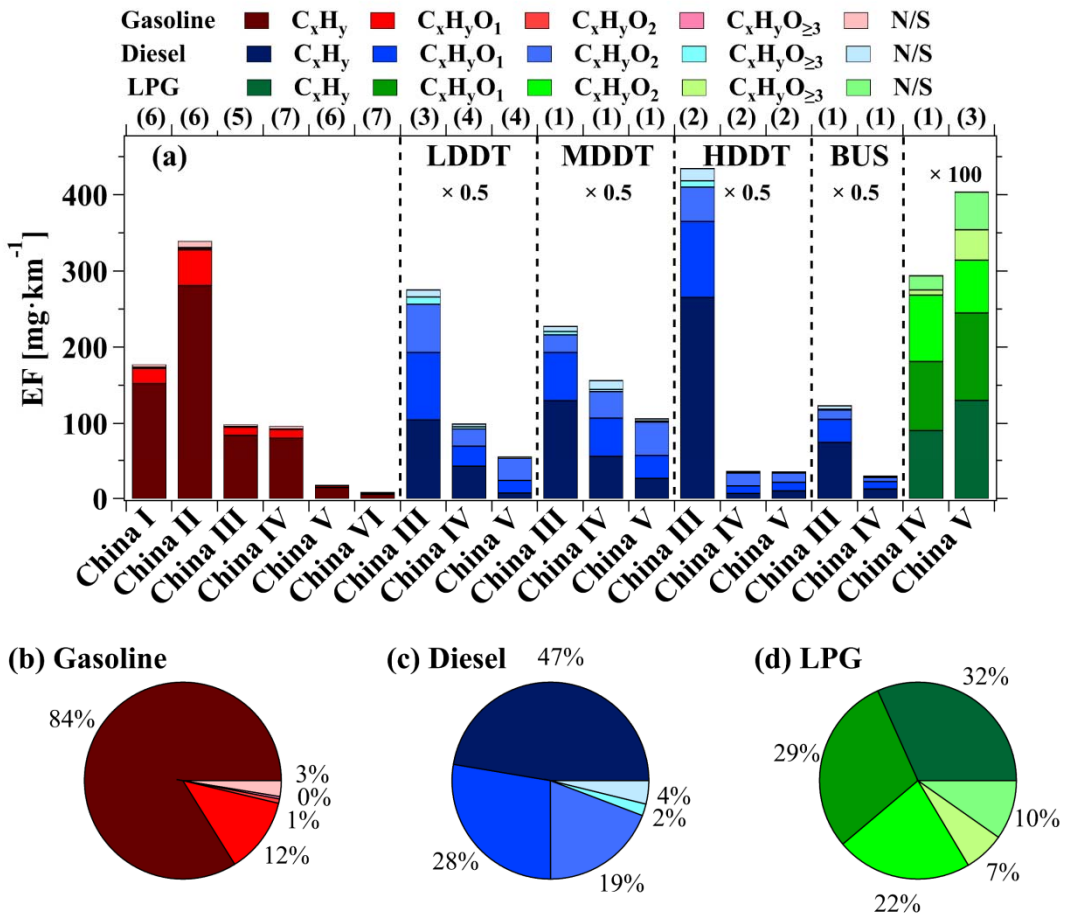

Figure 11. (a) The determined average emission factors for different emission standard from gasoline, diesel (×0.5), and LPG (×100) vehicles measured by PTR-ToF-MS. The different ion categories are discussed in the manuscript. Fractions of the determined average emission factors of VOCs ions in different ion categories from (b) gasoline, (c) diesel, and (d) LPG vehicles. The numbers above the top axis represent the number of all experiments (including multiple measurements for individual test vehicle) for each emission standard.

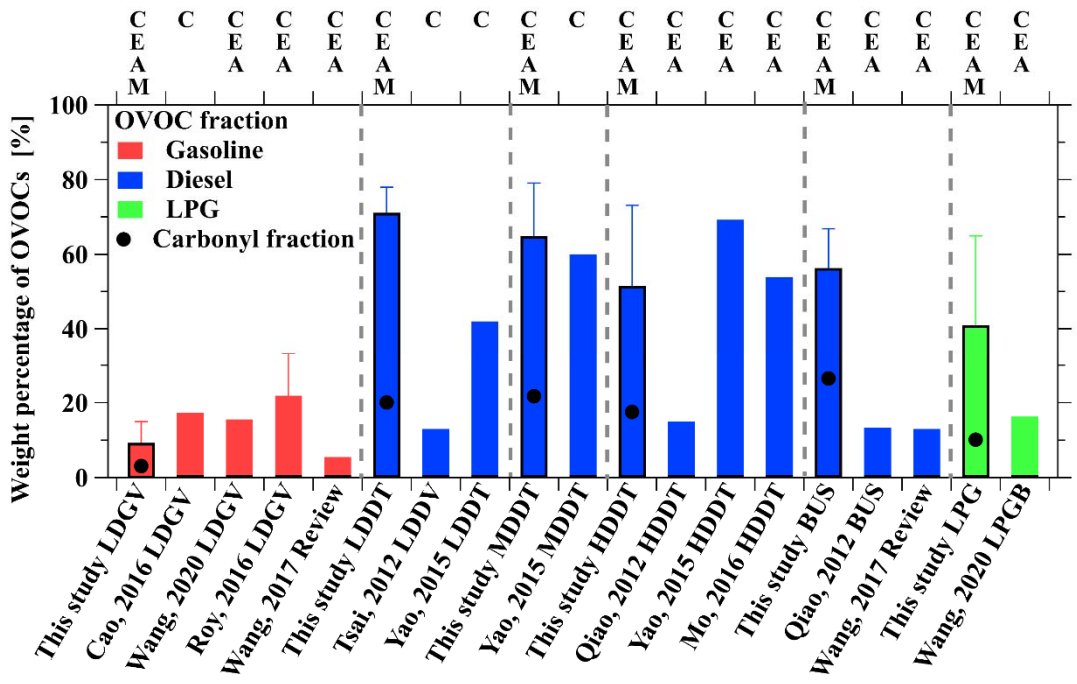

Figure 12. Comparison of OVOCs fractions determined in this study and those in previous studies. Error bars represent the standard deviations of the weight percentage of OVOCs. The C, E, A, M above the top axis represent the four groups of OVOCs measured in this study or previous studies, including Carbonyl: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