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

Sihang Wang[1,2], Bin Yuan[1,2,*], Caihong Wu[1,2], Chaomin Wang[1,2], Tiange Li[1,2], Xianjun He[1,2], Yibo Huangfu[1,2], Jipeng Qi[1,2], Xiao-Bing Li[1,2], Qing'e Sha[1,2], Manni Zhu[1,2], Shengrong Lou[3], Hongli Wang[3], Thomas Karl[4], Martin Graus[4], Zibing Yuan[5*], Min Shao[1,2]

[1] Institute for Environmental and Climate Research, Jinan University, Guangzhou 511443, China

[2] Guangdong-Hongkong-Macau Joint Laboratory of Collaborative Innovation for Environmental Quality, Guangzhou 511443, China

[3] State Environmental Protection Key Laboratory of Formation and Prevention of Urban Air Pollution Complex, Shanghai Academy of Environmental Sciences, Shanghai 200233, China

[4] Department of Atmospheric and Cryospheric Sciences, University of Innsbruck, Innsbruck, Austria

[5] College of Environment and Energy, South China University of Technology, University Town, Guangzhou 510006, China

*Correspondence to: Bin Yuan (byuan@jnu.edu.cn) and Zibing Yuan (zibing@scut.edu.cn)

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 being 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 total VOC emissions for gasoline vehicles, 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% of 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 them 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. After-treatment devices commonly used in light-duty gasoline vehicles are three-way catalyst (TWC) and gasoline particulate filter (GPF) (Lyu et al., 2020). These devices have been improved with the stricter emission standards. 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. 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 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

196 determination of hydrocarbons emitted from various vehicles. All the canisters were
197 sent to the laboratory for analysis by an offline GC-MS/FID system, with a total 95
198 hydrocarbons calibrated by Photochemical Assessment Monitoring Stations (PAMS)
199 and TO-15 standard mixtures (Table S5). We compared emission factors from PTR-
200 ToF-MS and the offline canister-GC-MS/FID (Fig. S6c-d), obtaining generally
201 consistent results, considering the large variation of VOC emissions for driving
202 conditions and the difficulty to control the fill time for canisters.

203 An instrument based on Hantzsch reaction-absorption method was used to
204 measure formaldehyde (Zhu et al., 2020). Good agreement for formaldehyde between
205 PTR-ToF-MS and the Hantzsch instrument was obtained (Fig. S6a). An iodide-adduct
206 time-of-flight chemical ionization mass spectrometer (I^- ToF-CIMS, Aerodyne
207 Research, Inc.) (Wang et al., 2020c;Ye et al., 2021) was used to measure organic acids,
208 hydrogen cyanide (HCN), and isocyanic acid (HNCO) from vehicles (Li et al., 2021).
209 As shown in Fig. S6b, formic acid measured by PTR-ToF-MS and I^- ToF-CIMS showed
210 reasonable agreement.

211 ## 2.4 Emission factors and emission ratios calculation

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

220 The average emission factors for various types of vehicles are determined from
221 arithmetic means for different emission standards of vehicles. As for diesel vehicles,
222 the average emission factors are obtained from the arithmetic means of LDDT, MDDT,
223 HDDT, and bus. Besides, we also calculate emission factors and emission ratios from
224 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 of 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 on emissions in diesel vehicles is much lower than gasoline vehicles. This may be explained by 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, namely benzene and toluene, from the diesel vehicle. These higher OVOC concentrations in diesel vehicle exhausts are in line with the higher 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 vehicles 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. The emission factors of the representative VOC species are highest for China II gasoline vehicles rather than China I vehicles, which can be explained by the China II vehicles having the highest mileage of the test vehicles. Emission factors of the four species for China VI vehicles are 12 to 25 times lower than emission factors 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·km^{-1} for acetaldehyde and 0.8 to 10.0 mg·km^{-1} for acetone) than almost all gasoline vehicles (a maximum of 3.9 mg·km^{-1} for acetaldehyde and a maximum of 3.2 mg·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·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 present in the combustion cylinder (i.e., overall fuel-lean conditions) 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).

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. S8). 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 for a number of species occupying 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 (Gentner et al., 2017) and the after-treatment devices aim for VOCs control for gasoline vehicles, the strong correlation and significantly lower than unity slope in Fig. 7a suggest that unburned fuel are the major contributor for exhaust emissions of gasoline vehicles, which has been previously shown in California, U.S. (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 being more volatile than diesel fuel (US NRC, 1996). We further explore the effects of emission standards on VOC 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. S9) and between China III and China V for LDDT (Fig. 7d, also see China III versus China V for MDDT and HDDT in Fig. S9). Fig. 7c show that the chemical compositions of VOC emissions are comparable between different emission standards for abundant VOC species from gasoline vehicles, indicating after-treatment devices may not affect the relative fractions of VOC components for gasoline vehicles (Drozd et al., 2019;Lu et al., 2018;Zhao et al., 2017). In comparison, the results between different emission standards for diesel vehicles (Fig. 7d) are somewhat more scattered than in gasoline vehicles. 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 that are 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 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 showed 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 differences in 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 for most OVOC species. For example, formic acid is found to be one of the most significant species emitted by diesel vehicles, with emission factors being three orders of magnitude higher than those from 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. S10a). 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. S10b) 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 significant decrease for n_C>15. Based on Fig. 9, we determine that emissions of aromatics with n_C≥10 in gasoline and diesel vehicles account for 14% and 63% of total aromatic emissions, respectively, again suggesting 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 increases for both gasoline and diesel vehicles. The extent of this decrease is observed to be comparable for C_1-C_6 carbonyls in gasoline (97.6%) and diesel vehicles (97.4%). However, as n_C>6, the decrease in carbonyl emission factors for diesel vehicles become smaller, resulting 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 used 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·mg^{-1} (corresponding to 0.57 and 1.46 ppb·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 significantly higher emission factors of C_{14} aromatics from diesel vehicles suggest that diesel vehicles can be a significant or even dominant source of higher molecular-weight 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 to 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 different vehicles are summarized in Fig. 11. As shown in Fig. 11a, the determined average mileage-based emission factors of total VOC ions from diesel vehicles were much higher than gasoline and LPG vehicles. Fig. 11b-d quantified the proportions of different categories of ions measured by PTR-ToF-MS. The determined average mileage-based emission factors of C_xH_y accounted for the largest fraction in gasoline vehicles (84% ± 5.9%), and lower fractions in diesel (47% ± 16%) and LPG vehicles (32% ± 0.7%). OVOCs account for larger fractions in diesel (49% ± 16%) and LPG vehicles (58% ± 3.7%), while they only account for 13% ± 6.1% of emissions from gasoline vehicles. The fractions of different OVOC groups generally demonstrate a downward trend from $C_xH_yO_1$ to $C_xH_yO_{\geq 3}$, and OVOCs with more than two oxygen atoms only occupy small percentages (0-7%) in vehicle exhausts, indicating low emissions of these species.

Combined with measurements of other VOCs from canisters measured by GC-MS/FID, the fractions of OVOCs in total VOC emissions can be determined for different vehicles (details in Sect. 6 in the Supplement) (Fig. 12). OVOCs account for 9.4% ± 5.6% of total VOC emissions for gasoline vehicles. The OVOC fractions for gasoline vehicles are generally comparable for different emission standards and cold/hot start, except somewhat higher fractions for China VI from hot start (Fig. S11). The OVOC fractions obtained in this study for gasoline vehicles are generally consistent with previous results (Cao et al., 2016;Wang et al., 2020b) (Fig. 12). Among

these studies, the OVOC fractions determined for gasoline with 10% ethanol (E10) (Roy et al., 2016) (22% ± 11%) are apparently higher. The fractions of OVOCs in total VOC emissions for diesel vehicles are 71% ± 20%, 65% ± 22%, 52% ± 18%, and 56% ± 26% for LDDT, MDDT, HDDT, and bus, respectively. The variations of OVOC fractions with emission standards are observed to be mixed among different types of diesel vehicles (Fig. S11). The OVOC fractions from diesel vehicles are obviously higher than those in gasoline vehicles, indicating the importance of OVOCs in VOC emissions from diesel vehicles. Compared to previous studies (Tsai et al., 2012;Qiao et al., 2012;Cao et al., 2016;Mo et al., 2016), determined OVOC fractions for diesel 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 a previous study (Wang et al., 2020b) where only carbonyls and a few esters/alcohols were 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 also 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 the total VOC emissions from gasoline vehicles, while the fractions are significantly higher for diesel vehicles (52-71%), highlighting the importance to measure 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.

Acknowledgement

This work was supported by the National Key R&D Plan of China (grant No. 2019YFE0106300, 2018YFC0213904), the National Natural Science Foundation of China (grant No. 41877302, 42121004), Guangdong Natural Science Funds for Distinguished Young Scholar (grant No. 2018B030306037), Guangdong Basic and Applied Basic Research Fund Project (grant No. 2020A1515110085), and Guangdong Innovative and Entrepreneurial Research Team Program (grant No. 2016ZT06N263). This work was also supported by Special Fund Project for Science and Technology Innovation Strategy of Guangdong Province (Grant No.2019B121205004). TK and MG were supported by OEAD grant CN 05/2020. The authors would like to thank Prof. Junyu Zheng for providing many resources during vehicle measurements and allowing to use PEMS and formaldehyde data in this study.

References

Permissible Exposure Levels for Selected Military Fuel Vapors, The National Academies Press, Washington, DC, 1996.

Barletta, B., Meinardi, S., Sherwood Rowland, F., Chan, C.-Y., Wang, X., Zou, S., Yin Chan, L., and Blake, D. R.: Volatile organic compounds in 43 Chinese cities, Atmospheric Environment, 39, 5979-5990, 10.1016/j.atmosenv.2005.06.029, 2005.

Cao, X., Yao, Z., Shen, X., Ye, Y., and Jiang, X.: On-road emission characteristics of VOCs from light-duty gasoline vehicles in Beijing, China, Atmospheric Environment, 124, 146-155, 10.1016/j.atmosenv.2015.06.019, 2016.

Cappellin, L., Karl, T., Probst, M., Ismailova, O., Winkler, P. M., Soukoulis, C., Aprea, E., Mark, T. D., Gasperi, F., and Biasioli, F.: On quantitative determination of volatile organic compound concentrations using proton transfer reaction time-of-flight mass spectrometry, Environmental Science & Technology, 46, 2283-2290, 10.1021/es203985t, 2012.

Chan, C. Y., Chan, L. Y., Wang, X. M., Liu, Y. M., Lee, S. C., Zou, S. C., Sheng, G. Y., and Fu, J. M.: Volatile organic compounds in roadside microenvironments of metropolitan Hong Kong, Atmospheric Environment, 36, 2039-2047, https://doi.org/10.1016/S1352-2310(02)00097-3, 2002.

Cui, L., Wang, X. L., Ho, K. F., Gao, Y., Liu, C., Hang Ho, S. S., Li, H. W., Lee, S. C., Wang, X. M., Jiang, B. Q., Huang, Y., Chow, J. C., Watson, J. G., and Chen, L.-W.: Decrease of VOC emissions from vehicular emissions in Hong Kong from 2003 to 2015: Results from a tunnel study, Atmospheric Environment, 177, 64-74, 10.1016/j.atmosenv.2018.01.020, 2018.

Drozd, G. T., Zhao, Y., Saliba, G., Frodin, B., Maddox, C., Weber, R. J., Chang, M. O., Maldonado, H., Sardar, S., Robinson, A. L., and Goldstein, A. H.: Time Resolved Measurements of Speciated Tailpipe Emissions from Motor Vehicles: Trends with Emission Control Technology, Cold Start Effects, and Speciation, Environmental Science & Technology, 50, 13592-13599, 10.1021/acs.est.6b04513, 2016.

Drozd, G. T., Zhao, Y., Saliba, G., Frodin, B., Maddox, C., Oliver Chang, M. C., Maldonado, H., Sardar, S., Weber, R. J., Robinson, A. L., and Goldstein, A. H.: Detailed Speciation of Intermediate Volatility and Semivolatile Organic Compound Emissions from Gasoline Vehicles: Effects of Cold-Starts and Implications for Secondary Organic Aerosol Formation, Environ Sci Technol, 53, 1706-1714, 10.1021/acs.est.8b05600, 2019.

Erickson, M. H., Gueneron, M., and Jobson, B. T.: Measuring long chain alkanes in diesel engine exhaust by thermal desorption PTR-MS, Atmospheric Measurement Techniques, 7, 225-239, 10.5194/amt-7-225-2014, 2014.

Gentner, D. R., Isaacman, G., Worton, D. R., Chan, A. W., Dallmann, T. R., Davis, L., Liu, S., Day, D. A., Russell, L. M., Wilson, K. R., Weber, R., Guha, A., Harley, R. A., and Goldstein, A. H.: Elucidating secondary organic aerosol from diesel and gasoline vehicles through detailed characterization of organic carbon emissions, Proc Natl Acad Sci U S A, 109, 18318-18323, 10.1073/pnas.1212272109, 2012.

Gentner, D. R., Worton, D. R., Isaacman, G., Davis, L. C., Dallmann, T. R., Wood, E. C., Herndon, S. C., Goldstein, A. H., and Harley, R. A.: Chemical Composition of Gas-Phase Organic Carbon Emissions from Motor Vehicles and Implications for Ozone Production, Environmental Science & Technology, 47, 11837-11848, 10.1021/es401470e, 2013.

Gentner, D. R., Jathar, S. H., Gordon, T. D., Bahreini, R., Day, D. A., El Haddad, I., Hayes, P. L., Pieber, S. M., Platt, S. M., de Gouw, J., Goldstein, A. H., Harley, R. A., Jimenez, J. L., Prevot, A. S., and Robinson, A. L.: Review of Urban Secondary Organic Aerosol Formation from Gasoline and Diesel Motor Vehicle Emissions, Environ Sci Technol, 51, 1074-1093, 10.1021/acs.est.6b04509, 2017.

George, I. J., Hays, M. D., Herrington, J. S., Preston, W., Snow, R., Faircloth, J., George, B. J., Long, T., and Baldauf, R. W.: Effects of Cold Temperature and Ethanol Content on VOC Emissions from Light-Duty Gasoline Vehicles, Environ Sci Technol, 49, 13067-13074, 10.1021/acs.est.5b04102, 2015.

Guo, H., Zou, S. C., Tsai, W. Y., Chan, L. Y., and Blake, D. R.: Emission characteristics of nonmethane hydrocarbons from private cars and taxis at different driving speeds in Hong Kong, Atmospheric Environment, 45, 2711-2721, 10.1016/j.atmosenv.2011.02.053, 2011.

Han, C., Liu, R., Luo, H., Li, G., Ma, S., Chen, J., and An, T.: Pollution profiles of volatile organic compounds from different urban functional areas in Guangzhou China based on GC/MS and PTR-TOF-MS: Atmospheric environmental implications, Atmospheric Environment, 214, 10.1016/j.atmosenv.2019.116843, 2019.

He, X., Yuan, B., Wu, C., Wang, S., Wang, C., Huangfu, Y., Qi, J., Ma, N., Xu, W., Wang, M., Chen, W., Su, H., Cheng, Y., and Shao, M.: Volatile organic compounds in wintertime North China Plain: Insights from measurements of proton transfer reaction time-of-flight mass spectrometer (PTR-ToF-MS), Journal of Environmental Sciences, 10.1016/j.jes.2021.08.010, 2022.

Huang, J., Yuan, Z., Duan, Y., Liu, D., Fu, Q., Liang, G., Li, F., and Huang, X.: Quantification of temperature dependence of vehicle evaporative volatile organic compound emissions from different fuel types in China, Sci Total Environ, 813, 152661, 10.1016/j.scitotenv.2021.152661, 2021.

http://e.jmrb.com/m/2008/11/17/10/m_182226.shtml, Access on 2009-12-10, 2008.

Kansal, A.: Sources and reactivity of NMHCs and VOCs in the atmosphere: a review, J Hazard Mater, 166, 17-26, 10.1016/j.jhazmat.2008.11.048, 2009.

Koss, A. R., Sekimoto, K., Gilman, J. B., Selimovic, V., Coggon, M. M., Zarzana, K. J., Yuan, B., Lerner, B. M., Brown, S. S., Jimenez, J. L., Krechmer, J., Roberts, J. M., Warneke, C., Yokelson, R. J., and de Gouw, J.: Non-methane organic gas emissions from biomass burning: identification, quantification, and emission factors from PTR-ToF during the FIREX 2016 laboratory experiment, Atmospheric Chemistry and Physics, 18, 3299-3319, 10.5194/acp-18-3299-2018, 2018.

Kroll, J. H., Donahue, N. M., Jimenez, J. L., Kessler, S. H., Canagaratna, M. R., Wilson, K. R., Altieri, K. E., Mazzoleni, L. R., Wozniak, A. S., Bluhm, H., Mysak, E. R., Smith, J. D., Kolb, C. E., and Worsnop, D. R.: Carbon oxidation state as a metric for describing

659 the chemistry of atmospheric organic aerosol, Nat Chem, 3, 133-139,
660 10.1038/nchem.948, 2011.
661 Kumar, A., Sinha, V., Shabin, M., Hakkim, H., Bonsang, B., and Gros, V.: Non-methane
662 hydrocarbon (NMHC) fingerprints of major urban and agricultural emission sources for
663 use in source apportionment studies, Atmospheric Chemistry and Physics, 20, 12133-
664 12152, 10.5194/acp-20-12133-2020, 2020.
665 Laurikko, J.: Ambient temperature effect on automotive exhaust emissions: FTP and
666 ECE test cycle responses, The Science of Envioment, 169, 195-204, 1995.
667 Li, B., Ho, S. S. H., Xue, Y., Huang, Y., Wang, L., Cheng, Y., Dai, W., Zhong, H., Cao,
668 J., and Lee, S.: Characterizations of volatile organic compounds (VOCs) from vehicular
669 emissions at roadside environment: The first comprehensive study in Northwestern
670 China, Atmospheric Environment, 161, 1-12, 10.1016/j.atmosenv.2017.04.029, 2017.
671 Li, T., Wang, Z., Yuan, B., Ye, C., Lin, Y., Wang, S., Sha, Q. e., Yuan, Z., Zheng, J., and
672 Shao, M.: Emissions of carboxylic acids, hydrogen cyanide (HCN) and isocyanic acid
673 (HNCO) from vehicle exhaust, Atmospheric Environment,
674 10.1016/j.atmosenv.2021.118218, 2021.
675 Li, X., Wu, Y., Yao, X., Zhang, S., Zhou, Y., and Fu, L.: Evaluation of the environmental
676 benefits of the enhanced vehicle inspection /maintenance program based on the short
677 transient loaded mode in Guangzhou (in Chinese), Acta Scientiae Circumstantiae, 32(1),
678 101-108, 10.13671/j.hjkxxb.2012.01.009, 2012.
679 Liao, S., Zhang, J., Yu, F., Zhu, M., Liu, J., Ou, J., Dong, H., Sha, Q., Zhong, Z., Xie,
680 Y., Luo, H., Zhang, L., and Zheng, J.: High Gaseous Nitrous Acid (HONO) Emissions
681 from Light-Duty Diesel Vehicles, Environ Sci Technol, 55, 200-208,
682 10.1021/acs.est.0c05599, 2021.
683 Liu, H., Man, H., Cui, H., Wang, Y., Deng, F., Wang, Y., Yang, X., Xiao, Q., Zhang, Q.,
684 Ding, Y., and He, K.: An updated emission inventory of vehicular VOCs and IVOCs in
685 China, Atmospheric Chemistry and Physics, 17, 12709-12724, 10.5194/acp-17-12709-
686 2017, 2017.
687 Liu, Y., Shao, M., Fu, L., Lu, S., Zeng, L., and Tang, D.: Source profiles of volatile
688 organic compounds (VOCs) measured in China: Part I, Atmospheric Environment, 42,
689 6247-6260, 10.1016/j.atmosenv.2008.01.070, 2008.
690 Liu, Y., Li, Y., Yuan, Z., Wang, H., Sha, Q., Lou, S., Liu, Y., Hao, Y., Duan, L., Ye, P.,
691 Zheng, J., Yuan, B., and Shao, M.: Identification of two main origins of intermediate-
692 volatility organic compound emissions from vehicles in China through two-phase
693 simultaneous characterization, Environ Pollut, 281, 117020,
694 10.1016/j.envpol.2021.117020, 2021.
695 Lu, Q., Zhao, Y., and Robinson, A. L.: Comprehensive organic emission profiles for
696 gasoline, diesel, and gas-turbine engines including intermediate and semi-volatile
697 organic compound emissions, Atmospheric Chemistry and Physics, 18, 17637-17654,
698 10.5194/acp-18-17637-2018, 2018.
699 Ly, B. T., Kajii, Y., Nguyen, T. Y., Shoji, K., Van, D. A., Do, T. N., Nghiem, T. D., and
700 Sakamoto, Y.: Characteristics of roadside volatile organic compounds in an urban area
701 dominated by gasoline vehicles, a case study in Hanoi, Chemosphere, 254, 126749,
702 10.1016/j.chemosphere.2020.126749, 2020.

Lyu, M., Bao, X., Zhu, R., and Matthews, R.: State-of-the-art outlook for light-duty vehicle emission control standards and technologies in China, Clean Technologies and Environmental Policy, 22, 757-771, 10.1007/s10098-020-01834-x, 2020.
May, A. A., Nguyen, N. T., Presto, A. A., Gordon, T. D., Lipsky, E. M., Karve, M., Gutierrez, A., Robertson, W. H., Zhang, M., Brandow, C., Chang, O., Chen, S., Cicero-Fernandez, P., Dinkins, L., Fuentes, M., Huang, S.-M., Ling, R., Long, J., Maddox, C., Massetti, J., McCauley, E., Miguel, A., Na, K., Ong, R., Pang, Y., Rieger, P., Sax, T., Truong, T., Vo, T., Chattopadhyay, S., Maldonado, H., Maricq, M. M., and Robinson, A. L.: Gas- and particle-phase primary emissions from in-use, on-road gasoline and diesel vehicles, Atmospheric Environment, 88, 247-260, 10.1016/j.atmosenv.2014.01.046, 2014.
China Mobile Source Environmental Management Annual Report: http://www.mee.gov.cn/hjzl/sthjzk/ydyhjgl/201909/P020190905586230826402.pdf, 2019.
Mo, Z., Shao, M., and Lu, S.: Compilation of a source profile database for hydrocarbon and OVOC emissions in China, Atmospheric Environment, 143, 209-217, 10.1016/j.atmosenv.2016.08.025, 2016.
Ou, J., Zheng, J., Li, R., Huang, X., Zhong, Z., Zhong, L., and Lin, H.: Speciated OVOC and VOC emission inventories and their implications for reactivity-based ozone control strategy in the Pearl River Delta region, China, Sci Total Environ, 530-531, 393-402, 10.1016/j.scitotenv.2015.05.062, 2015.
Pang, X., Mu, Y., Yuan, J., and He, H.: Carbonyls emission from ethanol-blended gasoline and biodiesel-ethanol-diesel used in engines, Atmospheric Environment, 42, 1349-1358, 10.1016/j.atmosenv.2007.10.075, 2008.
Parrish, D. D., Kuster, W. C., Shao, M., Yokouchi, Y., Kondo, Y., Goldan, P. D., de Gouw, J. A., Koike, M., and Shirai, T.: Comparison of air pollutant emissions among mega-cities, Atmospheric Environment, 43, 6435-6441, 10.1016/j.atmosenv.2009.06.024, 2009.
Qi, L., Liu, H., Shen, X., Fu, M., Huang, F., Man, H., Deng, F., Shaikh, A. A., Wang, X., Dong, R., Song, C., and He, K.: Intermediate-Volatility Organic Compound Emissions from Nonroad Construction Machinery under Different Operation Modes, Environ Sci Technol, 53, 13832-13840, 10.1021/acs.est.9b01316, 2019.
Qiao, Y. Z., Wang, H. L., Huang, C., Chen, C. H., and Huang, H. Y.: Source profile and chemical reactivity of volatile organic compounds from vehicle exhaust(in chinese), Environmental Science, 33, 1071-1079, 2012.
Roy, A., Sonntag, D., Cook, R., Yanca, C., Schenk, C., and Choi, Y.: Effect of Ambient Temperature on Total Organic Gas Speciation Profiles from Light-Duty Gasoline Vehicle Exhaust, Environmental Science & Technology, 50, 6565-6573, 10.1021/acs.est.6b01081, 2016.
Rubin, J. I., Kean, A. J., Harley, R. A., Millet, D. B., and Goldstein, A. H.: Temperature dependence of volatile organic compound evaporative emissions from motor vehicles, Journal of Geophysical Research: Atmospheres, 111, https://doi.org/10.1029/2005JD006458, 2006.

Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R., T.: Measurement of Emissions from Air Pollution Sources. 2. C_1 through C_{30} Organic Compounds from Medium Duty Diesel Trucks, Environmental Science & Technology, 33, 1578-1587, 1999.

Seinfeld, J. H., and Pandis, S. N.: Atmospheric chemistry and physics: from air pollution to climate change, John Wiley & Sons, Inc., Hoboken, 2006.

Sekimoto, K., Li, S.-M., Yuan, B., Koss, A., Coggon, M., Warneke, C., and de Gouw, J.: Calculation of the sensitivity of proton-transfer-reaction mass spectrometry (PTR-MS) for organic trace gases using molecular properties, International Journal of Mass Spectrometry, 421, 71-94, 10.1016/j.ijms.2017.04.006, 2017.

Sha, Q., Zhu, M., Huang, H., Wang, Y., Huang, Z., Zhang, X., Tang, M., Lu, M., Chen, C., Shi, B., Chen, Z., Wu, L., Zhong, Z., Li, C., Xu, Y., Yu, F., Jia, G., Liao, S., Cui, X., Liu, J., and Zheng, J.: A newly integrated dataset of volatile organic compounds (VOCs) source profiles and implications for the future development of VOCs profiles in China, Sci Total Environ, 793, 148348, 10.1016/j.scitotenv.2021.148348, 2021.

Shao, M., Zhang, Y., Zeng, L., Tang, X., Zhang, J., Zhong, L., and Wang, B.: Ground-level ozone in the Pearl River Delta and the roles of VOC and NOx in its production, Journal of Environmental Management, 90, 512-518, 10.1016/j.jenvman.2007.12.008, 2009.

Shen, X., Lv, T., Zhang, X., Cao, X., Li, X., Wu, B., Yao, X., Shi, Y., Zhou, Q., Chen, X., and Yao, Z.: Real-world emission characteristics of black carbon emitted by on-road China IV and China V diesel trucks, Science of The Total Environment, 799, 149435, https://doi.org/10.1016/j.scitotenv.2021.149435, 2021.

Song, C., Liu, Y., Sun, L., Zhang, Q., and Mao, H.: Emissions of volatile organic compounds (VOCs) from gasoline- and liquified natural gas (LNG)-fueled vehicles in tunnel studies, Atmospheric Environment, 234, 10.1016/j.atmosenv.2020.117626, 2020.

Stark, H., Yatavelli, R. L. N., Thompson, S. L., Kimmel, J. R., Cubison, M. J., Chhabra, P. S., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R., and Jimenez, J. L.: Methods to extract molecular and bulk chemical information from series of complex mass spectra with limited mass resolution, International Journal of Mass Spectrometry, 389, 26-38, 10.1016/j.ijms.2015.08.011, 2015.

Sulzer, P., Hartungen, E., Hanel, G., Feil, S., Winkler, K., Mutschlechner, P., Haidacher, S., Schottkowsky, R., Gunsch, D., Seehauser, H., Striednig, M., Jürschik, S., Breiev, K., Lanza, M., Herbig, J., Märk, L., Märk, T. D., and Jordan, A.: A Proton Transfer Reaction-Quadrupole interface Time-Of-Flight Mass Spectrometer (PTR-QiTOF): High speed due to extreme sensitivity, International Journal of Mass Spectrometry, 368, 1-5, 10.1016/j.ijms.2014.05.004, 2014.

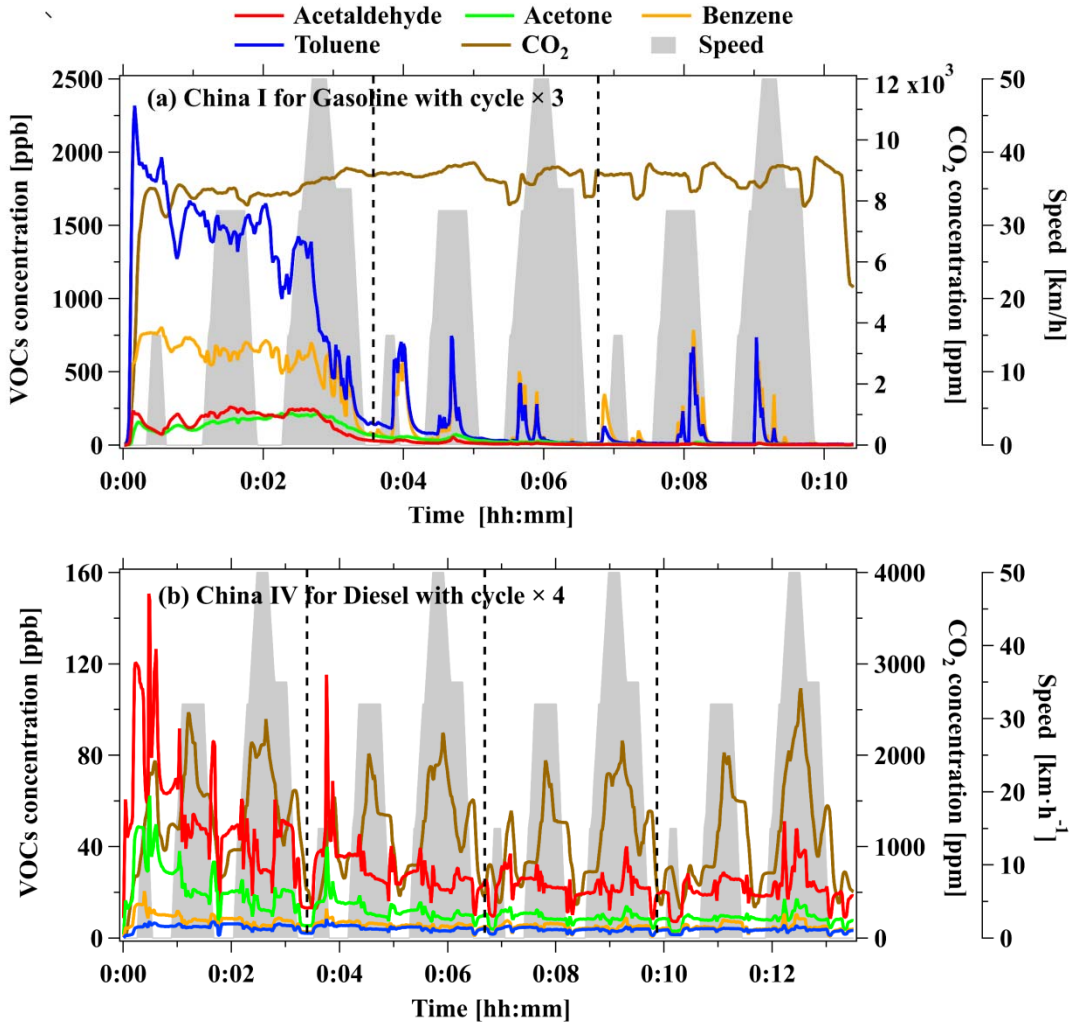
Sun, W., Shao, M., Granier, C., Liu, Y., Ye, C. S., and Zheng, J. Y.: Long-Term Trends of Anthropogenic SO_2, NOx, CO, and NMVOCs Emissions in China, Earth's Future, 6, 1112-1133, 10.1029/2018ef000822, 2018.

Tsai, J.-H., Chang, S.-Y., and Chiang, H.-L.: Volatile organic compounds from the exhaust of light-duty diesel vehicles, Atmospheric Environment, 61, 499-506, 10.1016/j.atmosenv.2012.07.078, 2012.

Wallington, T. J., Lambert, C. K., and Ruona, W. C.: Diesel vehicles and sustainable mobility in the U.S, Energy Policy, 54, 47-53, 10.1016/j.enpol.2011.11.068, 2013.
Wang, C., Yuan, B., Wu, C., Wang, S., Qi, J., Wang, B., Wang, Z., Hu, W., Chen, W., Ye, C., Wang, W., Sun, Y., Wang, C., Huang, S., Song, W., Wang, X., Yang, S., Zhang, S., Xu, W., Ma, N., Zhang, Z., Jiang, B., Su, H., Cheng, Y., Wang, X., and Shao, M.: Measurements of higher alkanes using NO^+ chemical ionization in PTR-ToF-MS: important contributions of higher alkanes to secondary organic aerosols in China, Atmospheric Chemistry and Physics, 20, 14123-14138, 10.5194/acp-20-14123-2020, 2020a.
Wang, H., L. , Jing, S., A. , Lou, S., R. , Hu, Q., Y. , Li, L., Tao, S., K. , Huang, C., Qiao, L., P. , and Chen, C., H.: Volatile organic compounds (VOCs) source profiles of on-road vehicle emissions in China, Sci Total Environ, 607-608, 253-261, 10.1016/j.scitotenv.2017.07.001, 2017.
Wang, J., Jin, L., Gao, J., Shi, J., Zhao, Y., Liu, S., Jin, T., Bai, Z., and Wu, C. Y.: Investigation of speciated VOC in gasoline vehicular exhaust under ECE and EUDC test cycles, Sci Total Environ, 445-446, 110-116, 10.1016/j.scitotenv.2012.12.044, 2013.
Wang, M., Li, S., Zhu, R., Zhang, R., Zu, L., Wang, Y., and Bao, X.: On-road tailpipe emission characteristics and ozone formation potentials of VOCs from gasoline, diesel and liquefied petroleum gas fueled vehicles, Atmospheric Environment, 10.1016/j.atmosenv.2020.117294, 2020b.
Wang, Z., Yuan, B., Ye, C., Roberts, J., Wisthaler, A., Lin, Y., Li, T., Wu, C., Peng, Y., Wang, C., Wang, S., Yang, S., Wang, B., Qi, J., Wang, C., Song, W., Hu, W., Wang, X., Xu, W., Ma, N., Kuang, Y., Tao, J., Zhang, Z., Su, H., Cheng, Y., Wang, X., and Shao, M.: High Concentrations of Atmospheric Isocyanic Acid (HNCO) Produced from Secondary Sources in China, Environmental Science & Technology, 10.1021/acs.est.0c02843, 2020c.
Wu, C., Wang, C., Wang, S., Wang, W., Yuan, B., Qi, J., Wang, B., Wang, H., Wang, C., Song, W., Wang, X., Hu, W., Lou, S., Ye, C., Peng, Y., Wang, Z., Huangfu, Y., Xie, Y., Zhu, M., Zheng, J., Wang, X., Jiang, B., Zhang, Z., and Shao, M.: Measurement report: Important contributions of oxygenated compounds to emissions and chemistry of volatile organic compounds in urban air, Atmospheric Chemistry and Physics, 20, 14769-14785, 10.5194/acp-20-14769-2020, 2020.
Wu, R., Bo, Y., Li, J., Li, L., Li, Y., and Xie, S.: Method to establish the emission inventory of anthropogenic volatile organic compounds in China and its application in the period 2008–2012, Atmospheric Environment, 127, 244-254, 10.1016/j.atmosenv.2015.12.015, 2016.
Wu, Y., Zhang, S., Hao, J., Liu, H., Wu, X., Hu, J., Walsh, M. P., Wallington, T. J., Zhang, K. M., and Stevanovic, S.: On-road vehicle emissions and their control in China: A review and outlook, Sci Total Environ, 574, 332-349, 10.1016/j.scitotenv.2016.09.040, 2017.
Yang, W., Zhang, Q., Wang, J., Zhou, C., Zhang, Y., and Pan, Z.: Emission characteristics and ozone formation potentials of VOCs from gasoline passenger cars at different driving modes, Atmospheric Pollution Research, 9, 804-813, 10.1016/j.apr.2018.01.002, 2018.

Yao, S., Liu, Z., and Qi, Z.: Test System for Exhaust Pollutants from Light-duty Gasoline Vehicle under Short Transient Driving Cycle (in Chinese), Shanghai Environmental Sciences, 10, 722-728, 2003.
Yao, Z., Shen, X., Ye, Y., Cao, X., Jiang, X., Zhang, Y., and He, K.: On-road emission characteristics of VOCs from diesel trucks in Beijing, China, Atmospheric Environment, 103, 87-93, 10.1016/j.atmosenv.2014.12.028, 2015.
Ye, C., Yuan, B., Lin, Y., Wang, Z., Hu, W., Li, T., Chen, W., Wu, C., Wang, C., Huang, S., Qi, J., Wang, B., Wang, C., Song, W., Wang, X., Zheng, E., Krechmer, J. E., Ye, P., Zhang, Z., Wang, X., Worsnop, D. R., and Shao, M.: Chemical characterization of oxygenated organic compounds in the gas phase and particle phase using iodide CIMS with FIGAERO in urban air, Atmospheric Chemistry and Physics, 21, 8455-8478, 10.5194/acp-21-8455-2021, 2021.
Yuan, B., Koss, A. R., Warneke, C., Coggon, M., Sekimoto, K., and de Gouw, J. A.: Proton-Transfer-Reaction Mass Spectrometry: Applications in Atmospheric Sciences, Chemical Reviews, 117, 13187-13229, 10.1021/acs.chemrev.7b00325, 2017.
Yue, X., Wu, Y., Hao, J., Pang, Y., Ma, Y., Li, Y., Li, B., and Bao, X.: Fuel quality management versus vehicle emission control in China, status quo and future perspectives, Energy Policy, 79, 87-98, https://doi.org/10.1016/j.enpol.2015.01.009, 2015.
Zavala, M., Herndon, S. C., Slott, R. S., Dunlea, E. J., Marr, L. C., Shorter, J. H., Zahniser, M., Knighton, W. B., Rogers, T. M., Kolb, C. E., Molina, L. T., and Molina, M. J.: Characterization of on-road vehicle emissions in the Mexico City Metropolitan Area using a mobile laboratory in chase and fleet average measurement modes during the MCMA-2003 field campaign, Atmospheric Chemistry and Physics, 6, 5129-5142, 10.5194/acp-6-5129-2006, 2006.
Zavala, M., Herndon, S. C., Wood, E. C., Jayne, J. T., Nelson, D. D., Trimborn, A. M., Dunlea, E., Knighton, W. B., Mendoza, A., Allen, D. T., Kolb, C. E., Molina, M. J., and Molina, L. T.: Comparison of emissions from on-road sources using a mobile laboratory under various driving and operational sampling modes, Atmospheric Chemistry and Physics, 9, 1-14, 10.5194/acp-9-1-2009, 2009.
Zhang, Q., Wu, L., Fang, X., Liu, M., Zhang, J., Shao, M., Lu, S., and Mao, H.: Emission factors of volatile organic compounds (VOCs) based on the detailed vehicle classification in a tunnel study, Sci Total Environ, 624, 878-886, 10.1016/j.scitotenv.2017.12.171, 2018.
Zhao, Y., Saleh, R., Saliba, G., Presto, A. A., Gordon, T. D., Drozd, G. T., Goldstein, A. H., Donahue, N. M., and Robinson, A. L.: Reducing secondary organic aerosol formation from gasoline vehicle exhaust, Proc Natl Acad Sci U S A, 114, 6984-6989, 10.1073/pnas.1620911114, 2017.
Zhou, H., Zhao, H., Hu, J., Li, M., Feng, Q., Qi, J., Shi, Z., Mao, H., and Jin, T.: Primary particulate matter emissions and estimates of secondary organic aerosol formation potential from the exhaust of a China V diesel engine, Atmospheric Environment, 218, 116987, https://doi.org/10.1016/j.atmosenv.2019.116987, 2019.
Zhu, M., Dong, H., Yu, F., Liao, S., Xie, Y., Liu, J., Sha, Q., Zhong, Z., Zeng, L., and Zheng, J.: A New Portable Instrument for Online Measurements of Formaldehyde:

From Ambient to Mobile Emission Sources, Environmental Science & Technology Letters, 7, 292-297, 10.1021/acs.estlett.0c00169, 2020.
Ziemann, P. J., and Atkinson, R.: Kinetics, products, and mechanisms of secondary organic aerosol formation, Chem Soc Rev, 41, 6582-6605, 10.1039/c2cs35122f, 2012.



883

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

889

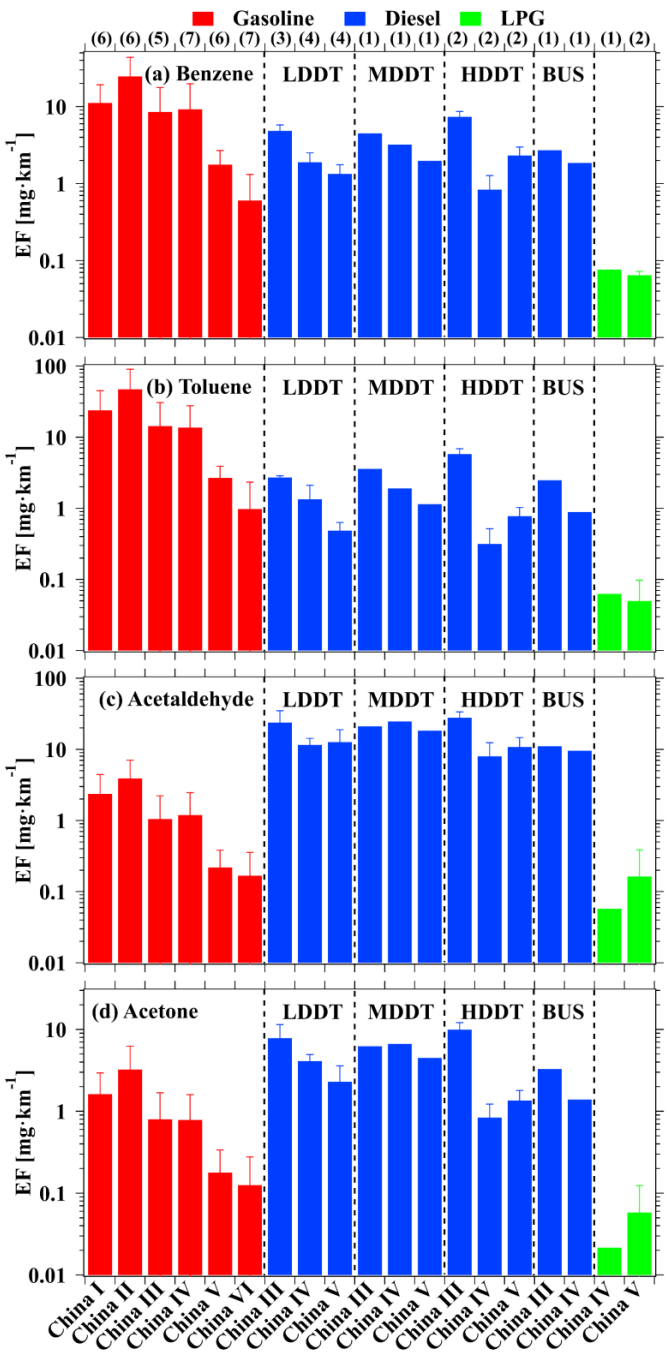


Figure 2. The determined average mileage-based emission factors (mg·km^{-1}) for (a) benzene, (b) toluene, (c) acetaldehyde, and (d) acetone for vehicles with different emission standards. The numbers above the top axis represent the number of all experiments (including multiple measurements for individual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

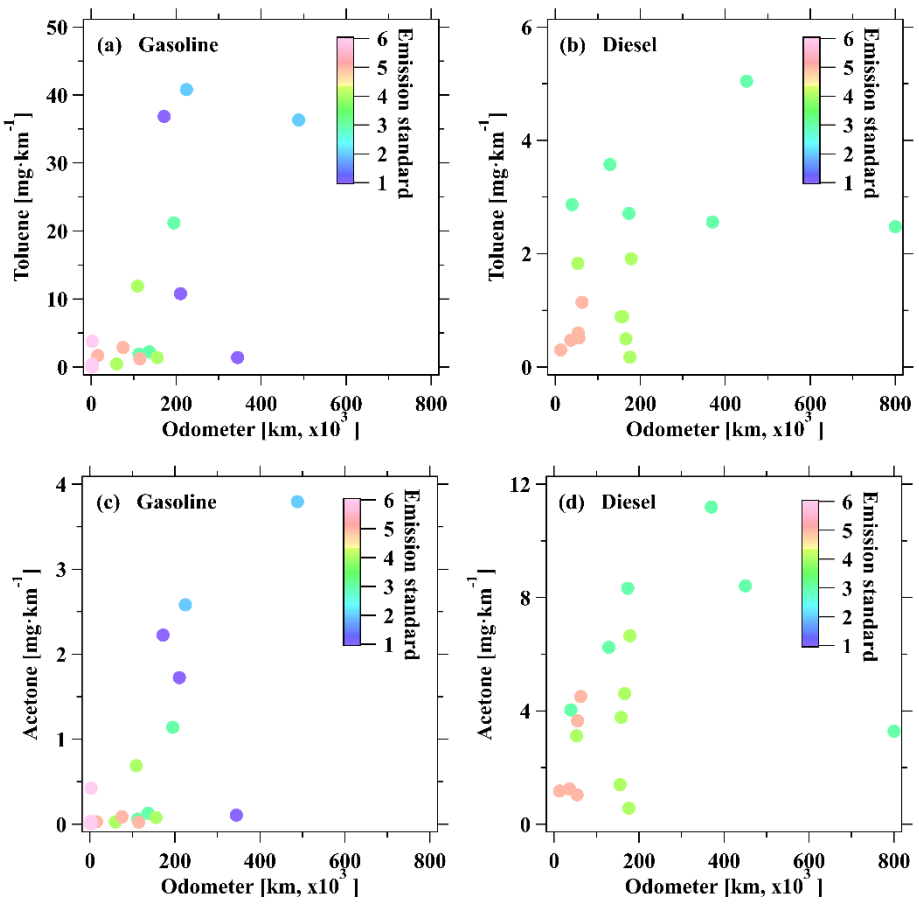


Figure 3. Scatterplot of the emission factor of toluene in (a) gasoline and (b) diesel vehicles, and acetone in (c) gasoline and (d) diesel vehicles during the hot start based on the odometer for each vehicle.

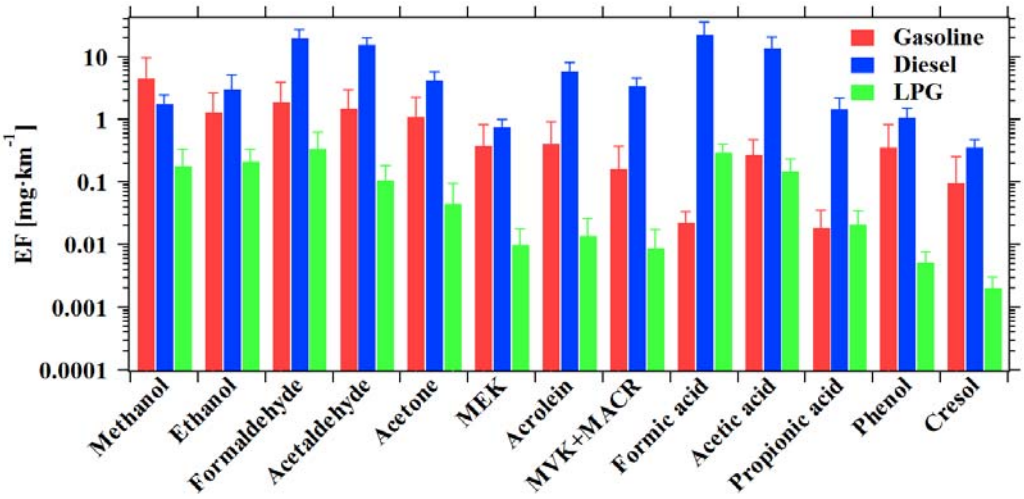
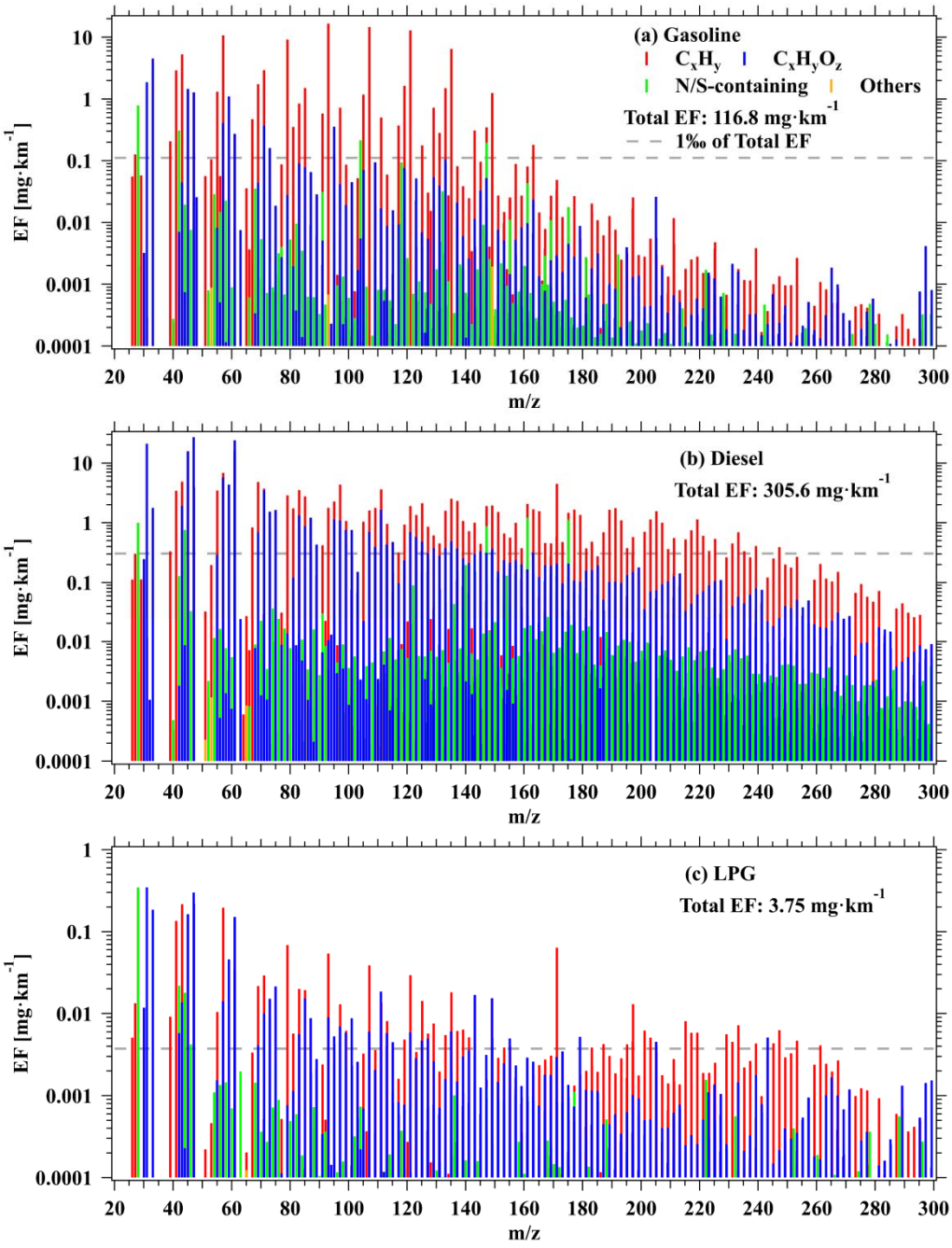


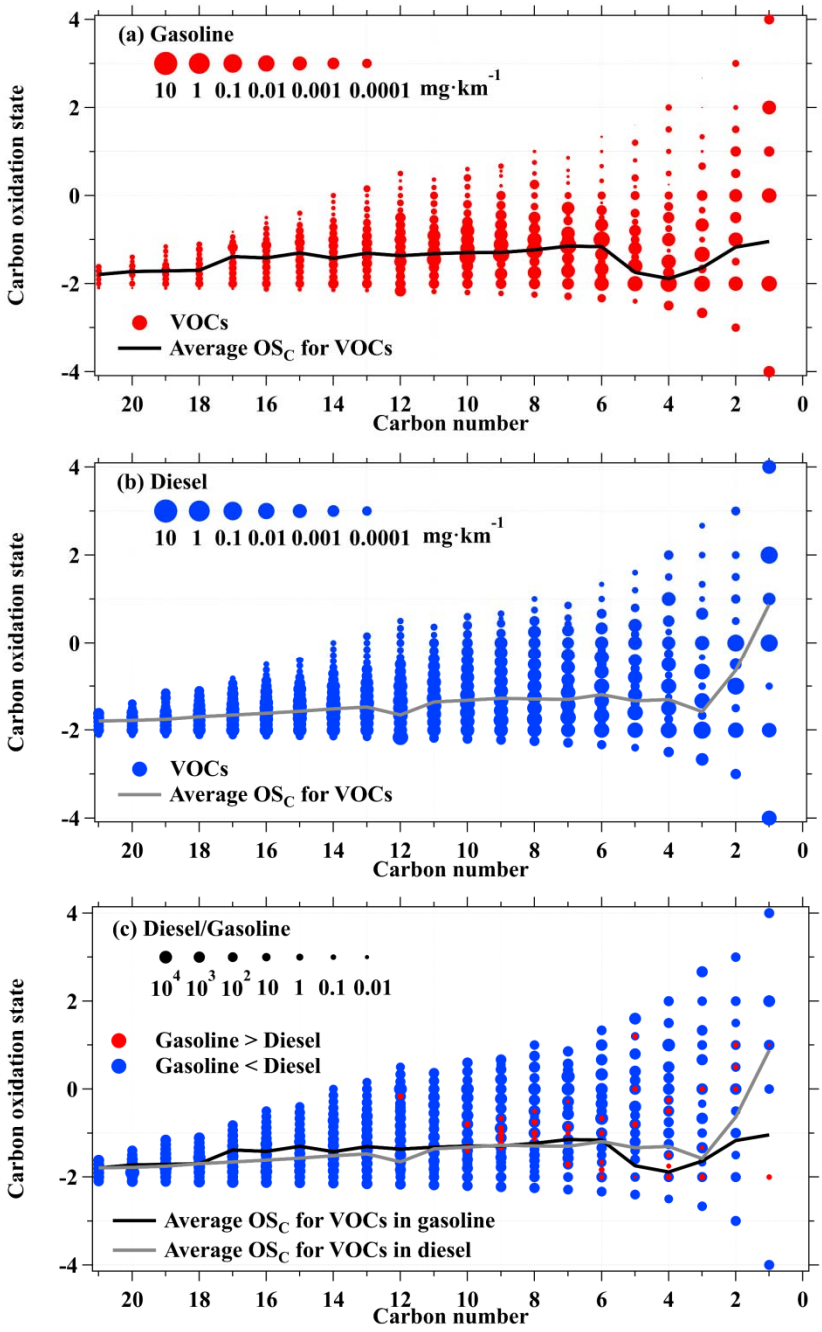
Figure 4. The determined emission factors of representative OVOC species from different types of vehicles. Error bars represent standard deviations of the emission factors for the VOCs.



909

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

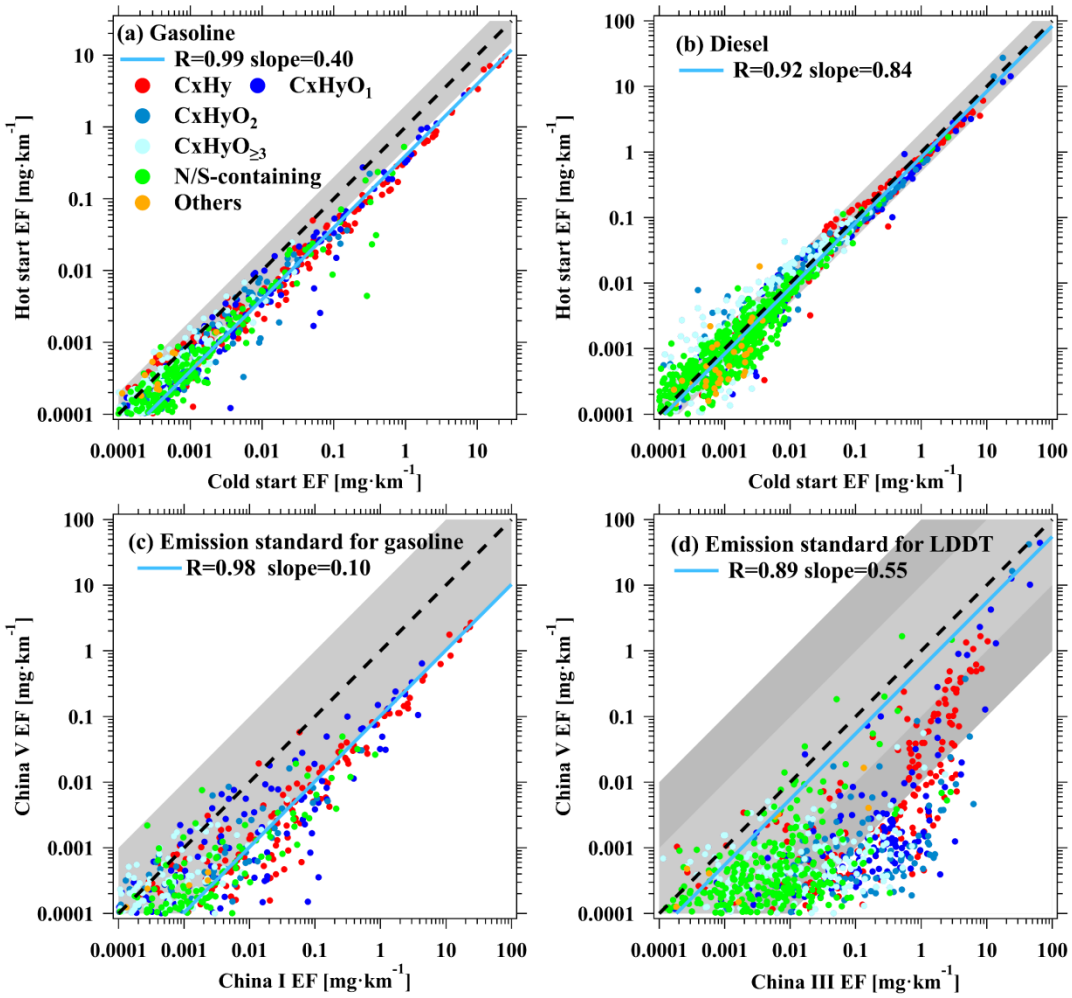
913



914

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

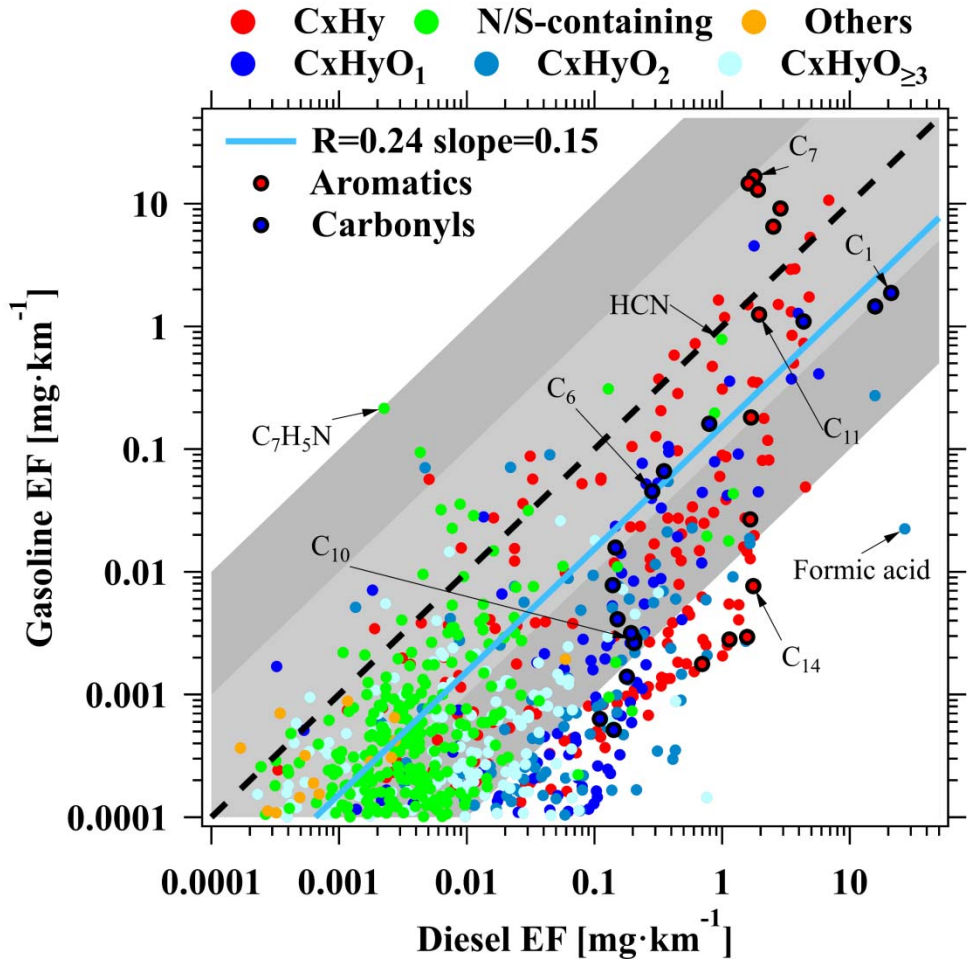
920



921

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

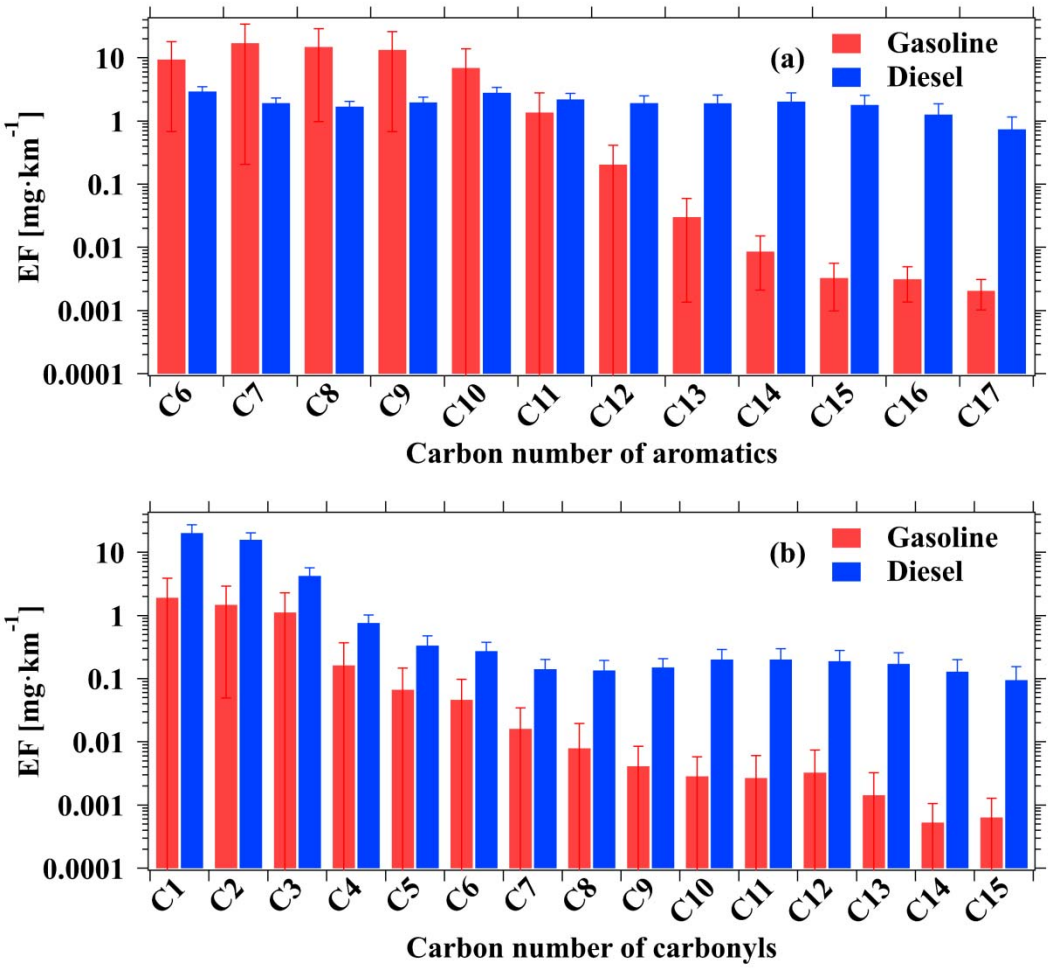
929



930

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

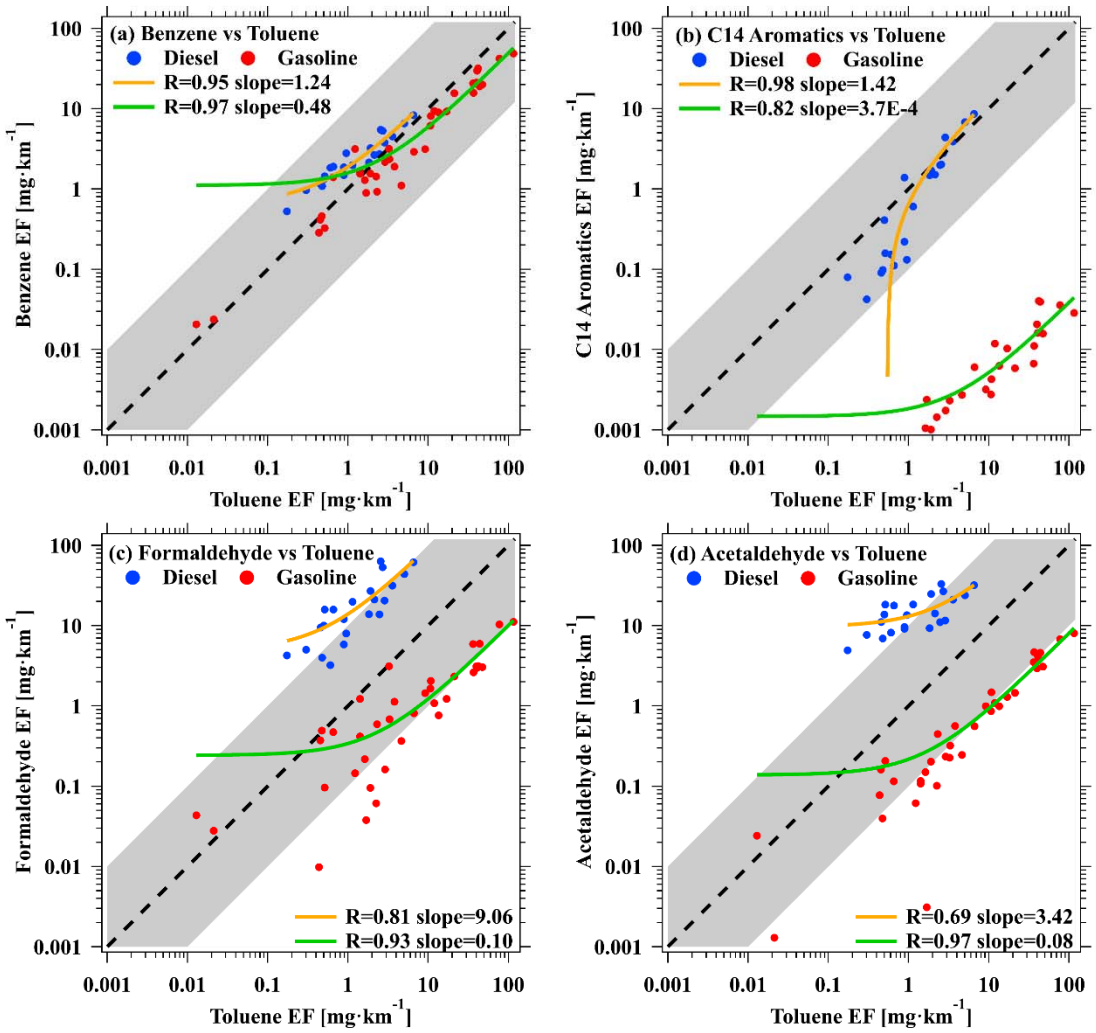
935



936

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

940



941

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

950

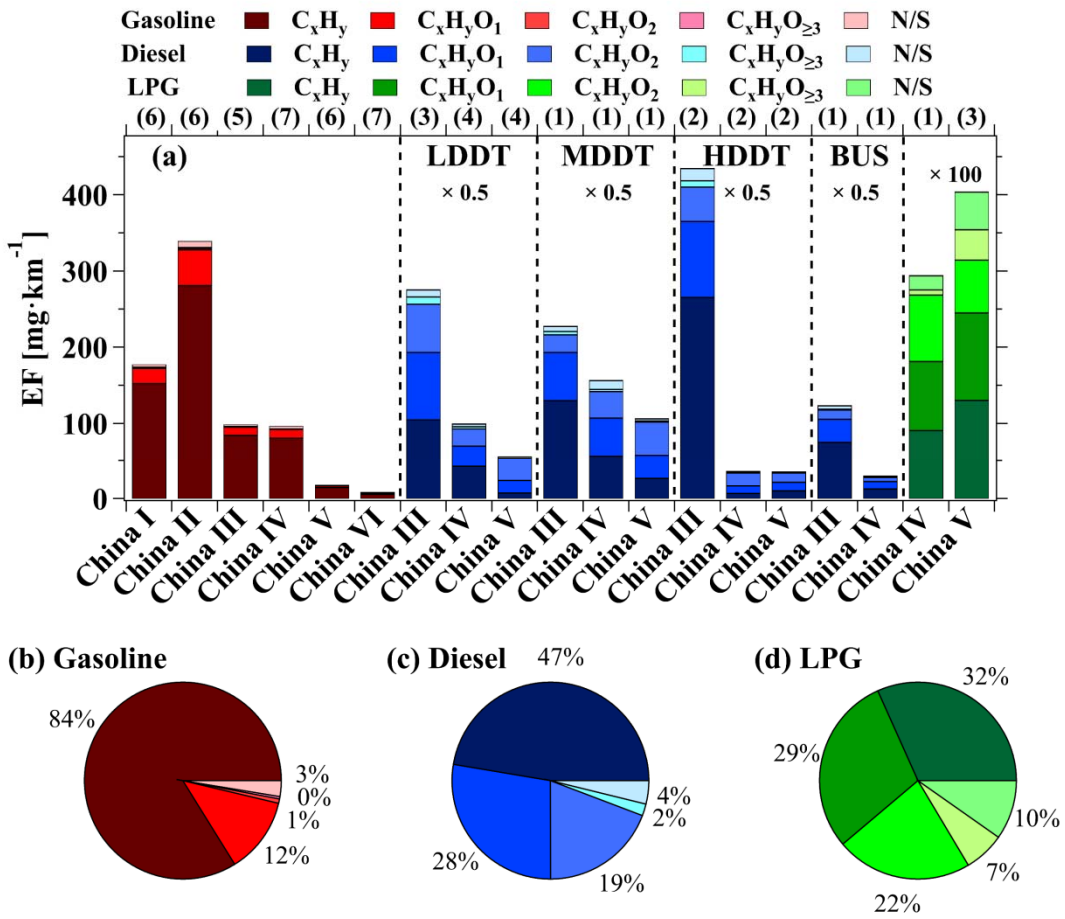


Figure 11. (a) The determined average emission factors for different emission standard from gasoline, diesel (×0.5), and LPG (×100) vehicles measured by PTR-ToF-MS. The different ion categories are discussed in the manuscript. Fractions of the determined average emission factors of VOCs ions in different 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.

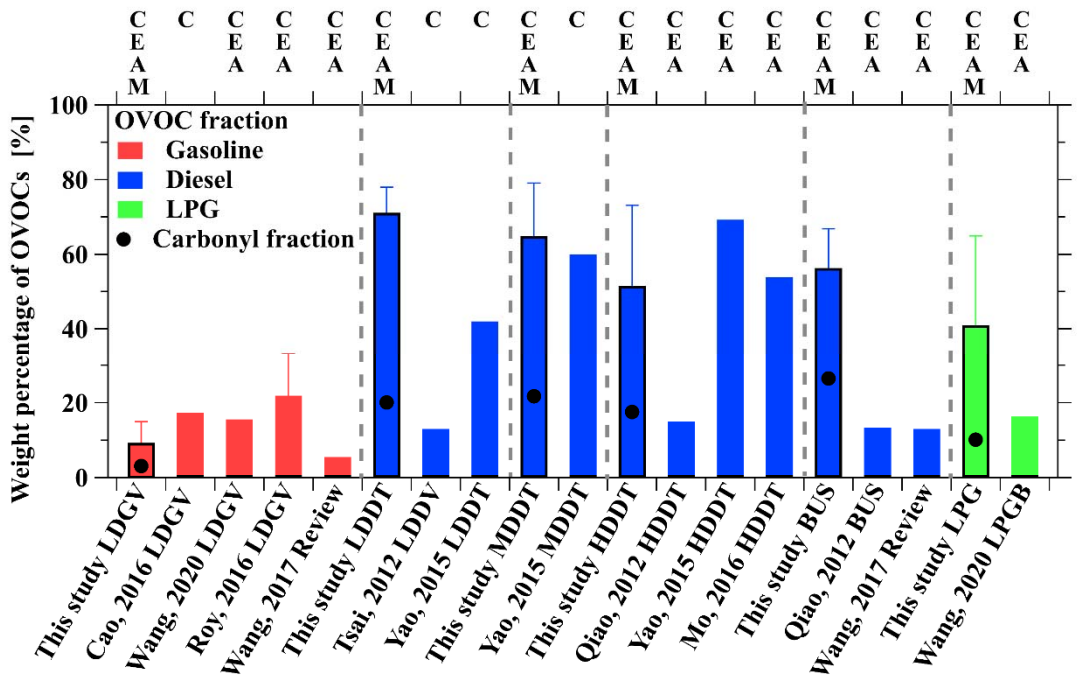


Figure 12. Comparison of OVOCs fractions determined in this study and those in previous studies. Error bars represent the standard deviations of the weight percentage of OVOCs. The C, E, A, M above the top axis represent the four groups of OVOCs measured in this study or previous studies, including Carbonyl: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