On-road tailpipe emission characteristics and ozone formation potentials of VOCs from gasoline, diesel and liquefied petroleum gas fueled vehicles

Menglei Wang\textsuperscript{a,b,1}, Shunyi Li\textsuperscript{a,1}, Rencheng Zhu\textsuperscript{a,*}, Ruiqin Zhang\textsuperscript{a}, Lei Zu\textsuperscript{c}, Yunjing Wang\textsuperscript{c}, Xiaofeng Bao\textsuperscript{c}

\textsuperscript{a} School of Ecology and Environment, Zhengzhou University, Zhengzhou, 450001, China
\textsuperscript{b} School of Chemical Engineering, Zhengzhou University, Zhengzhou, 450001, China
\textsuperscript{c} State Environmental Protection Key Laboratory of Vehicle Emission Control and Simulation, Chinese Research Academy of Environmental Sciences, Beijing, 100012, China

HIGHLIGHTS

- VOCs from various types of vehicles were investigated systematically with the PEMS.
- Aromatics and alkanes were the dominant VOC groups from in-use vehicle exhaust.
- Aromatics were the major contributors of the total OFPs, accounting for 49.6–93.4%.
- Naphthalene was the most abundant VOC species emitted by HDDT, accounting for 31.8%.
- Road conditions had great impacts on tailpipe VOC emissions.

ARTICLE INFO

Keywords:
Volatile organic compound (VOC)  
Ozone formation potential (OFP)  
Portable emission measurement system (PEMS)  
Gasoline vehicle  
Diesel truck  
Liquefied petroleum gas bus

ABSTRACT

Volatile organic compounds (VOCs) of motor vehicles contribute greatly to ground-level ozone formation, especially in the megacity regions. While the variations of tailpipe VOC emissions along with the vehicle technologies and road conditions are rarely investigated systematically. Thus, on-road tailpipe VOC emissions from in-use vehicles, including light-duty gasoline vehicles (LDGV), light-duty diesel trucks (LDDT), heavy-duty diesel truck (HDDT) and liquefied petroleum gas-electric hybrid bus (LPGB), were sampled with a combined portable emission measurement system (PEMS). A total of 102 individual VOC species were quantified by a gas chromatography mass spectrometry detector (GC-MSD), and the maximum incremental reactivity (MIR) scale was used to calculate the ozone formation potentials (OFPs). Results showed that aromatics and alkanes were the major VOC groups regardless of the vehicle type, accounting for 68.1–98.0%. For the LDGV, \textit{i}-pentane, acetone, and propane were the top three VOC species. Naphthalene, dodecane and \textit{n}-undecane were main VOC constituents in the diesel exhaust. Acetone was the most abundant VOC species for the LPGB, followed by \textit{i}-pentane, \textit{i}-butane and \textit{n}-butane. Road conditions had a significant impact on the VOC emission factors. Specifically, emission factors on urban roads were 3.3–7.0 times those on the highway. The OFPs were 70.7, 128.1, 2189.4 and 124.7 mg O\textsubscript{3}/km for the LDGV, LDDT, HDDT and LPGB, respectively; aromatics were the main contributors, occupying 49.6–93.4% of the total OFPs. Results indicated that emission factors and dominant species of VOCs were strongly affected by vehicle technologies and road conditions, but aromatics were the major group for both VOC composition and OFPs.

1. Introduction

Volatile organic compounds (VOCs) are of particular interest because many of them have high chemical reactivity and behave as important precursors of ground-level ozone (Song et al., 2019). Macromolecular VOCs have been identified to be the major contributors to the formation of atmospheric secondary organic aerosols (Dai et al., 2010). A growing body of evidence suggests that some VOCs, such as benzene, toluene,
ethylbenzene and xylene (BTEX), have harmful effects on human health (e.g. irritant, carcinogenic, mutagenic and teratogenic) (Hao et al., 2018; Ke et al., 2018). In recent years, automobile exhaust has become a major anthropogenic air pollution source, especially in the urban areas (Garzon et al., 2015; Hui et al., 2018; Li et al., 2018). Considering the sustained and rapid growth of the vehicle population in China and the increasing vehicle-use intensity (Huo et al., 2012), a better understanding of VOC emissions from vehicle exhaust is desirable for the control of severe atmospheric pollution in the megacity regions.

Chemical profiles of VOCs are usually expressed as the weight fractions of the individual species relative to the total VOCs emissions. Accurate and reliable VOC profiles are the basic data for source apportionment, health exposure assessment and air quality models (Qiao et al., 2012; Ou et al., 2014). To this end, an increasing number of studies have been conducted to investigate characteristics of VOC emissions from different vehicles. For example, Cao et al. (2016) investigated the characteristics of VOC emissions from gasoline cars with a PEMS. Ayoko et al. (2014) compared the emission characterization of VOCs from LPG and passenger cars on a chassis dynamometer. Some other researches also investigated VOCs from diesel vehicles (Yao et al., 2015a; Wang et al., 2016; Jung et al., 2019). However, all these studies were conducted under different conditions with various test methods. As far as we know, systematical studies about tailpipe VOC emissions from different types of automobiles are still rare. Wang et al. (2017) summarized the on-road VOC profiles of different vehicle categories in China based on references from 2001 to 2016, but the differences in fuel quality, test methods and VOCs species in different studies might lead to great uncertainties to the understanding of VOC profiles from different vehicle categories. Thus, systematical research based on the same test method is necessary to be conducted to have a further understanding of the tailpipe VOCs emission characteristics from different types of vehicles.

Various methods have been developed to investigate the emission characteristics of a single vehicle or the entire fleet. Tunnel studies and roadside measurements have been proved to be the robust methods to obtain the fleet-average emission factors under real-world driving conditions, while they may be interfered by the evaporative emissions or other sources (Araizaga et al., 2013; Li et al., 2017; Zhang et al., 2018). Bench test is always used to investigate the influence of a single factor, such as fuel property, vehicle type and driving cycle for its good repeatability. However, this result may not reflect the actual on-road tailpipe emissions (Pang et al., 2014; Chen et al., 2018). Thus, the California Air Resources Board developed the portable emission measurement system (PEMS) for on-road vehicle emission measurements (CARB, 1996). The PEMS was used to detect the instantaneous tailpipe gaseous emissions under the real-world running situation, and now some unregulated pollutants could also be tested or sampled with the instrument upgrade. In recent years, PEMS has been widely used in the measurement of tailpipe CO, CO₂, NOₓ, and THC emissions from different types of vehicles (Huang et al., 2013; Koussoulidou et al., 2013; May et al., 2014; Wang et al., 2016; Bishop et al., 2019). However, reports referring to VOC emissions measured with PEMS were still limited, and most of them were mainly focused on gasoline vehicles (Cao et al., 2016; Yao et al., 2016; Hao et al., 2018). Only several publications referred to the on-road VOC emission characteristics of diesel vehicles with the PEMS system, while the quantity of VOC species and results were not always consistent. For example, results from Yao et al. (2015a, 2015b) showed the formaldehyde and acetaldehyde were the dominant VOC species, but report by Wang et al. (2016) showed that the abundance of alkanes was significantly higher in diesel vehicle emissions, followed by aromatics and alkenes.

In this study, a PEMS system combined with a VOC sampling unit was used to sample the on-road tailpipe VOCs emissions from different types of vehicles, including gasoline cars, diesel trucks and liquefied petroleum gas-electric hybrid bus. Chemical profiles and emission characteristics of the tailpipe VOCs were investigated, and then OFPs of VOC species were evaluated with the MIR scale. The results would be of importance to further understand the VOC characteristics of modern vehicles and provide implications for mitigating ozone pollution in urban areas.

2. Materials and methods

2.1. Test vehicles and routes

Considering those heavy-polluting vehicles are eliminated gradually, seven typical in-use vehicles complying with China III-V were selected in this study, including two gasoline cars (LDGV), three light-duty diesel trucks (LDDT), one heavy duty diesel truck (HDDT) and a liquefied petroleum gas-electric hybrid bus (LPGB). Detailed information for each test vehicle is summarized in Table 1.

Two routes (route A and route B) were designated according to the different uses of these tested vehicles. Specifically, route A was selected for the tests of LDDT, HDDT and LDGV, and route B was for LPGB. As shown in Fig. S1, the total length of route A was approximately 68 km, including urban roads (in red), suburban roads (in yellow) and highway roads (in blue). Considering that trucks are mainly responsible for the intercity transportation in the urban agglomerations, VOC emissions were only sampled when trucks travelled on the urban and highway roads, respectively. For the gasoline cars, three canisters were used for samplings of VOCs on the urban, suburban and highway roads, respectively. Route B (in green) was the route of No. B12 bus in Zhengzhou, China, and the single trip was approximately 18 km, including 29 stations. To simulate the passengers getting on and off, the tested bus was required to stop for 10 s at each station. Two canisters were used for the VOCs sampling of the bus test, one for the trip from the starting station to terminus, and the other for the return trip. Each vehicle was tested twice to enhance the reliability of the results. A total of 30 samples were obtained during the VOC sampling campaign. To ensure these vehicles could run under the ordinary conditions, each vehicle was driven by its owner throughout the test, and all the fuels meeting the China VI standards were from a local PetroChina gas station. Analysis showed that uncertainties of the majority of VOCs (65.7%–86.3%) were under the tolerance level of 45% for concentrations at ppb levels (10⁻⁷) (Hortwitz, 1982; Ayoko et al., 2014). The bigger deviations of the residual VOC species were mainly attributed to the very low concentrations (10⁻¹³–10⁻¹¹).

2.2. Exhaust sampling system

A SEMTECH ECOSTAR PLUS (Sensors Inc., USA) combined with an additional VOC sampling unit was employed to measure the exhaust emissions from vehicles under real-world driving conditions. The scheme of the on-board emission measurement system is shown in Fig. S2.

The SEMTECH ECOSTAR PLUS mainly contained three units: a gas analyzer, a micro proportional sampling system (MPS) and a particulate matter (PM) analyzer. The gas analyzer was used to measure NOₓ, with a nondispersive ultraviolet (NDUV) analyzer, THC with a hydrogen flame ion detector (FID), and CO and CO₂ with a nondispersive infrared (NDIR) analyzer. The SEMTECH-FEM (Sensors Inc., USA) and SEMTECH-HTF (Sensors Inc., USA) were used to measure the exhaust flow rate. A weather probe (WP) and a global position system (GPS) were used to record actual ambient humidity, temperature and instantaneous latitude and longitude. All the data were collected at a 1-s time resolution and delivered to a laptop in real time.

The MPS is a partial flow dilution system, which was used to dilute the sampled exhaust from the SEMTECH-FEM tube. The diluted exhaust was divided into two strands, one into the SEMTECH-PFM module for PM filter sampling, and the other into the SEMTECH-CPM module for instantaneous PM monitoring. The VOC sampling unit was connected to the SEMTECH ECOSTAR PLUS via the SEMTECH-CPM module. Some...
could capture all condensable substances, including all VOCs, moisture. The VOC samples were pre-concentrated using a 3600DS Autosampler (Nutech, USA) and an 8900DS pre-concentrator (Nutech, USA) with a three-stage restriction valve at approximately 0.10 L/min for tested vehicles driving on route A and approximately 0.08 L/min for tested bus driving on route B. To reduce the adsorption of VOCs in the sampling process, Teflon tubes were used for the junctions.

3.2 Vacuum Summa canisters (Entech Inst., USA) were used for VOC emission sampling. The sampling flow rate was controlled by a passive restriction valve at approximately 0.10 L/min for tested vehicles driving on route A and approximately 0.08 L/min for tested bus driving on route B. To reduce the adsorption of VOCs in the sampling process, Teflon tubes were used for the junctions.

2.3 VOC analysis

The VOC samples were analyzed by a gas chromatography-mass spectrometry detector (7890 GC-5975 MS, Agilent Technologies, USA) based on the Method TO-15 (U.S. EPA, 1999). Firstly, VOC samples were diluted to approximately 85% of the atmospheric pressure before analysis with an automatic diluter (model 2201A, Nutech, USA). Then, the samples were pre-concentrated using a 3600DS Autosampler (Nutech, USA) and an 8900DS pre-concentrator (Nutech, USA) with a three-stage cryotrap. The first cryotrap is a traditional glass bead cryotrap, which could capture all condensable substances, including all VOCs, moisture and CO₂. The second cryotrap is a Tenax multimedia trap, which had strong adsorption capacity for VOCs but did not absorb the moisture. The working temperature of the second cryotrap was only set to approximately 10 °C and CO₂ could not be condensed at that environment. Thus, moisture and CO₂ would be removed when samples transferred from the first cryotrap to the second cryotrap. The third was a traditional cryo-focus trap. VOCs would be further condensed and then be heated rapidly to enter the column for chromatographic analyses through the hot desorption injection.

The movement speed of each VOC species in the column was different after a certain period due to its different adsorption capacity for each component. Therefore, the components were separated in the column, and then were detected and recorded sequentially in the detector. The target compounds were qualitatively analyzed based on the chromatographic retention time and mass spectrometry diagram, and the samples concentrations were calculated with the external standard method. In total, 102 VOCs were identified and measured, and the species are shown in Table S1.

2.4 Quality assurance and quality control (QA/QC)

Strict QA/QC procedure of the sampling and analysis was conducted according to the criteria mentioned in Method TO-15 to assure the data quality (U.S. EPA, 1999). Before sampling, all canisters were flushed at least five times by repeatedly filling and evacuating humidified zero air using a canister cleaner (Model 2101DS, Nutech, USA). In order to check if there was any contamination in the canisters, a canister was evacuated after the cleaning procedures, re-filled with pure nitrogen, stored in the laboratory for at least 24 h, and then analyzed as the same way of field samples to make sure that all the target VOC compounds were not present or below the detection limits.

Before analysis, the GC-MS system was calibrated using U.S. EPA TO-15 standard gas and U.S. EPA Photochemical Assessment Monitoring Stations (PAMS) standard gas (Nutech, USA) with five concentrations, i.e. 0.5, 1, 5, 15 and 30 ppbv. The calibration curves were obtained by running the five diluted standards plus humidified zero air in the same way as the field samples, and the relative standard deviation of response factor of each point shall be within 30%. Analyze one parallel sample every 10 samples to ensure that the deviations of target components in the parallel sample are within 30%. In general, the detection limits of the target NMHCs ranged from 7 to 141 pptv and the accuracy of the measurements was about 1%-10%.

25. Data analysis

The measured concentrations (ppbv) were converted to emission factors (g/km) with exhaust flow rates and traveling distances during each test. The instantaneous data of the exhaust flow rate, dilution ratio and velocity were time-aggregated. Formula (1) was used to calculate the emission factors of the total VOCs.

$$EF_{TVOC} = \sum_{i=1}^{n} C_i \times M_i \times \frac{\sum_{j=1}^{n} (V_i \times DR_j)}{22.4 \times \sum_{j=1}^{n} S_j}$$  \hspace{1cm} (1)

where $EF_{TVOC}$ is the emission factor of total VOCs, mg/km; $C_i$ is the concentration of VOC species i (i = 1, 2, 3 ... n), ppbv; $M_i$ is the molar mass of VOC species i, g/mol; $V_i$ is the instantaneous exhaust flow rate, $m^3$/s; $DR_j$ is the instantaneous dilution ratio of MPS; $S_j$ is the distance travelled at second (j = 1, 2, 3 ... t) m, and equals to the value of the instantaneous velocity at second (j = 1, 2, 3 ... t) recorded by the GPS system, m/s; and $n$ is the amount of the VOC species, n = 102. t is the total time of the corresponding experiment, s. The volume and concentration data were all normalized to the standard ambient temperature and pressure conditions (273.12 K, 101.33 kPa).

To estimate the OFP of individual VOC species from vehicle exhaust, the maximum incremental reactivity (MIR) scale was adopted (Carter W. P. L., 1994, 2010; Li et al., 2014). OFP of individual VOC species was calculated as Formula (2):

$$OFP_i = EF_i \times MIR_i$$  \hspace{1cm} (2)

where $OFP_i$ (mg O₂/kg) represents the ozone formation potential of VOC species i; $EF_i$ (mg/km) is the emission factor of VOC species i; and MIR is the maximum incremental reactivity of VOC species i, mg O₂/mg VOC. The total OFP of the VOCs were the sum of the each OFP.

3. Results and discussion

3.1 Source profiles of tailpipe VOCs from different vehicles

102 individual VOC species were classified into six groups, alkanes, aromatics, halocarbons, carboxyls and others. All detected VOC components and the detail VOCs concentrations, emission factors
and profiles of LDGV, LDDT-1, LDDT-2, LDDT-3, HDDT and LPGB were provided in the Supplementary Excel. Emission factors of total VOCs were $20.1 \pm 10.8$ mg/km, $82.2 \pm 45.0$ mg/km, $706.7 \pm 107.0$ mg/km and $42.5 \pm 3.4$ mg/km for LDGV, LDDT, HDDT and LPGB, respectively. The corresponding emission factors of THC measured by PEMS with FID method were $39.4 \pm 19.6$ mg/km, $227.4 \pm 129.8$ mg/km, $76.6 \pm 35.4$ mg/km for LDGV, LDDT and LPGB, respectively. That is, the identified VOCs species accounted for $36.1$–$55.5\%$ of THC in this study, which were slightly lower compared with $50$–$82.1\%$ reported in previous studies (Chiang et al., 2007; Tsai et al., 2012; Araizaga et al., 2013). A plausible explanation was that C2 hydrocarbons, such as ethane, ethene, and ethyne, were not detected in this study.

The VOC profiles of different types of vehicles based on weight percentage (%) are shown in Fig. 1. Overall, aromatics were the most abundant VOC group from the LDGV, accounting for $38.5\%$, followed by alkanes ($29.6\%$), carbonyls ($15.5\%$), halocarbons ($7.1\%$) and others ($7.0\%$). This result was partially consistent with the results obtained by Dai et al. (2010) based on the chassis dynamometer tests. Compared with diesel trucks ($1.0$–$1.4\%$) and LPGB ($3.6\%$), percentage of halocarbon group in total VOCs of the LDGV ($7.1\%$) was relatively higher, especially chlorobenzene, 1,2-dichloroethane, 1,2,4-trichlorobenzene. It is not immediately clear why gasoline vehicle emitted so many halocarbons. One hypothesis is that the content of chlorine in gasoline, which could convert to halocarbons during the combustion, was high because of the poor quality of crude oil and much chlorine would be introduced during the catalytic reforming along with the additives. For LDDTs, alkanes were significantly higher with a fraction of $69.9\%$, followed by aromatics (17.8\%). The top 15 VOC species of these LDDT vehicles complying with China III, China IV and China V, respectively, are shown in Fig. S3. Obviously, weight of dodecane showed decreasing trends as standards tightened, while the variation trends of acetone, 1-butene, 1,2,3-trimethylbenzene, 1,4-diethylbenzene were just opposite. And the residual species did not show obvious variation trends. In sum, emission standards have significant impacts on tailpipe VOC emissions, but the variation trends of most VOC species were not obvious. For the HDDT, aromatics and alkanes were identified as the dominant groups, accounting for $98.0\%$ of the total VOC emissions, which was consistent with the results observed by Wang et al. (2017) and Liu et al. (2008a). For LPGB, alkanes and aromatics were the dominant VOC groups, accounting for $44.2\%$ and $24.5\%$, respectively.
followed by carbonyls (16.3%), alkenes (8.6%), halocarbons (3.7%) and others (2.7%). In general, alkanes and aromatics were the major tailpipe VOC emissions for all tested vehicles, accounting for 68.1–98.0% of the total VOCs. The VOC distributions could be influenced significantly by fuel properties or vehicle types.

The top 10 VOC species of different types of vehicles accounted for approximately 61–91% of the corresponding total VOC emissions, which indicated that the top 10 species might be the major VOCs. Top 10 VOC species of different types of vehicles were listed in Table 2. These vehicles might have the same VOC species, but the abundances were different. For example, 1,4-Diethylbenzene was the top 10 tailpipe VOC species for all test vehicles, but the abundances were 5.6%, 2.7%, 3.0% and 3.8% for LDGV, LDDT, HDDT and LPGB, respectively. The average weight percentage of acetone in LDGV was 8.9%, but for HDDT and LPGB were 31.8% and 14.4%, respectively.

As shown in Table 2, there was obvious difference among the abundant VOC species of different vehicles. To be specific, n-pentane, acetone, propane, and toluene were the major VOC species from LDGV exhaust with weight percentages of 9.8%, 8.9%, 8.1% and 6.2%, respectively. Some of these species were also identified in other studies. For example, n-pentane and toluene were identified as the main VOC species for all test vehicles, but the abundances were 5.6%, 2.7%, 3.0% and 3.8% for LDGV, LDDT, HDDT and LPGB, respectively. The average weight percentage of acetone in LDGV was 8.9%, but for HDDT and LPGB were 31.8% and 14.4%, respectively. In general, alkanes and aromatics were the major tailpipe VOC species for all test vehicles, but the abundances were 5.6%, 2.7%, 3.0% and 3.8% for LDGV, LDDT, HDDT and LPGB, respectively. The average weight percentage of acetone in LDGV was 8.9%, but for HDDT and LPGB were 31.8% and 14.4%, respectively.

As mentioned in section 2.2, route A was designed to test gasoline cars and diesel trucks, and the average speeds on urban, suburban and highway roads were 18.9 km/h, 35.8 km/h and 74.6 km/h, respectively. Tailpipe VOC compositions of LDGV, LDDV and HDDV driving under different road conditions are shown in Fig. 2. In general, aromatics were the most abundant VOC species in LDGV tailpipe emissions, while on different roads, the weight percentages presented different specifics. Specifically, aromatics taken up 35.0% of the tailpipe VOCs under the urban condition, and the percentages increased to 42.7% and 39.4% under suburban and highway conditions, respectively. As the second-most abundant VOC species, weight percentages of alkanes showed just opposite variation trends to the aromatics. The lower air/oil ratio of port fuel injection (PFI) cars under ultra-high-speed working conditions may cause higher aromatic emissions for highway roads in this study. This result was similar with some published references. For example, studies by Wang et al. (2013) and Guo et al. (2011) indicated that as the driving speed increased, the emissions of alkanes had a slight increasing trend, followed by a considerable decrease in the aromatics.

### Table 2

<table>
<thead>
<tr>
<th>Species</th>
<th>Weight (%)</th>
<th>Species</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDGV</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>i-Pentane</td>
<td>9.8 ±</td>
<td>Dodecane</td>
<td>41.5 ±</td>
</tr>
<tr>
<td>Acetone</td>
<td>8.9 ±</td>
<td>n-Undecane</td>
<td>16.3 ±</td>
</tr>
<tr>
<td>Propene</td>
<td>8.1 ±</td>
<td>Naphthalene</td>
<td>6.4 ±</td>
</tr>
<tr>
<td>Toluene</td>
<td>6.2 ±</td>
<td>Decane</td>
<td>6.2 ±</td>
</tr>
<tr>
<td>1,4-Diethylbenzene</td>
<td>5.6 ±</td>
<td>1-Butene</td>
<td>2.7 ±</td>
</tr>
<tr>
<td>1,2,3-Triethylbenzene</td>
<td>5.3 ±</td>
<td>Propane</td>
<td>2.7 ±</td>
</tr>
<tr>
<td>1,2,4-Triethylbenzene</td>
<td>5.1 ±</td>
<td>Acetone</td>
<td>2.7 ±</td>
</tr>
<tr>
<td>3-Ethyltoluene</td>
<td>4.4 ±</td>
<td>Acrolein</td>
<td>2.4 ±</td>
</tr>
<tr>
<td>2-Butanone</td>
<td>4.3 ±</td>
<td>Nonane</td>
<td>1.9 ±</td>
</tr>
<tr>
<td>i-Propyl alcohol</td>
<td>3.3 ±</td>
<td>1,4-Diethylbenzene</td>
<td>1.7 ±</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>31.8 ±</td>
<td>Diethylbenzene</td>
<td>0.5 ±</td>
</tr>
<tr>
<td>Dodecane</td>
<td>26.0 ±</td>
<td>Acetone</td>
<td>14.4 ±</td>
</tr>
<tr>
<td>n-Undecane</td>
<td>9.2 ±</td>
<td>i-Pentane</td>
<td>7.6 ±</td>
</tr>
<tr>
<td>3-Ethyltoluene</td>
<td>6.5 ±</td>
<td>n-Butane</td>
<td>7.1 ±</td>
</tr>
<tr>
<td>1,4-Diethylbenzene</td>
<td>4.8 ±</td>
<td>Propane</td>
<td>4.8 ±</td>
</tr>
<tr>
<td>1,2,4-Trimehtylbenzene</td>
<td>3.7 ±</td>
<td>n-Undecane</td>
<td>4.5 ±</td>
</tr>
<tr>
<td>1,2,3-Triethylbenzene</td>
<td>3.0 ±</td>
<td>1,4-Diethylbenzene</td>
<td>0.5 ±</td>
</tr>
<tr>
<td>Decane</td>
<td>2.7 ±</td>
<td>1-Butene</td>
<td>3.5 ±</td>
</tr>
<tr>
<td>1-Ethyl-2- methylbenzene</td>
<td>1.7 ±</td>
<td>n-Pentane</td>
<td>3.4 ±</td>
</tr>
<tr>
<td>1,3-Diethylbenzene</td>
<td>1.6 ±</td>
<td>Toluene</td>
<td>2.9 ±</td>
</tr>
</tbody>
</table>

### 3.2 Effect of road conditions on VOC compositions

As mentioned in section 2.2, route A was designed to test gasoline cars and diesel trucks, and the average speeds on urban, suburban and highway roads were 18.9 km/h, 35.8 km/h and 74.6 km/h, respectively. Tailpipe VOC compositions of LDGV, LDDV and HDDV driving under different road conditions are shown in Fig. 2. In general, aromatics were the most abundant VOC species in LDGV tailpipe emissions, while on different roads, the weight percentages presented different specifics. Specifically, aromatics taken up 35.0% of the tailpipe VOCs under the urban condition, and the percentages increased to 42.7% and 39.4% under suburban and highway conditions, respectively. As the second-most abundant VOC species, weight percentages of alkanes showed just opposite variation trends to the aromatics. The lower air/oil ratio of port fuel injection (PFI) cars under ultra-high-speed working conditions may cause higher aromatic emissions for highway roads in this study. This result was similar with some published references. For example, studies by Wang et al. (2013) and Guo et al. (2011) indicated that as the driving speed increased, the emissions of alkanes had a slight increasing trend,
and the emissions of aromatics showed a decreasing pattern. As shown in Fig. 2, aromatics and alkanes from the LDDT presented an opposite tendency related to the LDGV. However, previous studies (Tsai et al., 2012; Cao et al., 2017) reported that low operation speeds resulted in high emission of aromatics and low alkanes. These differences may be due to the complexity of diesel engine combustion and after-treatment devices. Specifically, aromatics emitted by LDDT-3 (equipped with DOC and SCR) increased from 14.8% on urban roads to 27.5% on highway and alkanes decreased from 71.3% to 54.0%. This probably because that DOC + SCR system used for LDDT-3 could be efficient under highway conditions because of the high exhaust temperature, resulting more reduction on alkanes. And it was reported that both the DPF and the SCR systems were capable to reduce many of the n-alkane species emissions by greater than 85% (Liu et al., 2008b). For HDDT, no obvious correlations were observed between road conditions and VOC compositions.

In theory, road condition was crucial to the emission factor and source profile. However, source profile variations of tailpipe VOCs with different roads were not significant in this study, especially for LDDTs. This might be associated with the actual fuel consumption on different roads. Take LDDTs for example, the fuel consumption of LDDT-1, LDDT-2 and LDDT-3 on urban roads were 12.6 L/100 km, 10.1 L/100 km and 13.1 L/100 km, respectively, while those on highway roads were 13.8 L/100 km, 10.1 L/100 km and 14.6 L/100 km. For both LDGV and HDDV, the fuel consumption on the highway was the lowest and that on the urban was the highest, which was partial consistent with the VOC emission factor and source profile.

3.3. Emission factors of tailpipe VOCs

Emission factors of tailpipe VOCs obtained in this work and some from other references are shown in Table 3. In this study, the average VOC emission factor of HDDT (706.7 mg/km) was the highest, approximately 8.6 times that of LDDT (82.2 mg/km). The serious VOC emission factors under urban conditions were partial consistent with some previous studies. For example, Cao et al. (2012) indicated that the OFP for light duty gasoline vehicles complying with different emission standards varied from 33 mg O$_3$/km to 1300 mg O$_3$/km, and work by Wang et al. (2013) showed that OFP values for gasoline cars were 380–920 mg O$_3$/km. The OFP value of LDGV was partial consistent with previous studies. Furthermore, Cao et al. (2016) indicated that the OFP for light duty gasoline vehicles representing different driving conditions were mainly attributed to the different driving cycle and fuel composition used and VOC species detected. Results from this study indicated that compared with gasoline cars, the OFP caused by diesel vehicles should not be ignored.

Table 3

<table>
<thead>
<tr>
<th>Literature</th>
<th>Vehicle type</th>
<th>Test method</th>
<th>Emission factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>LDGV</td>
<td>PEMS</td>
<td>20.1 ± 10.8</td>
</tr>
<tr>
<td></td>
<td>LDDT</td>
<td>PEMS</td>
<td>20.2 ± 45.0</td>
</tr>
<tr>
<td></td>
<td>HDDT</td>
<td>PEMS</td>
<td>706.7 ± 107.0</td>
</tr>
<tr>
<td></td>
<td>LPGB</td>
<td>PEMS</td>
<td>42.5 ± 3.7</td>
</tr>
<tr>
<td></td>
<td>HDDT</td>
<td>PEMS</td>
<td>73.4 ± 14.7</td>
</tr>
<tr>
<td></td>
<td>MDDT</td>
<td>PEMS</td>
<td>70.3 ± 10.4</td>
</tr>
<tr>
<td></td>
<td>HDDT</td>
<td>PEMS</td>
<td>80.4 ± 36.1</td>
</tr>
<tr>
<td>Yao et al. (2015a)</td>
<td>LDV</td>
<td>Tunnel study</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>HDV</td>
<td>Tunnel study</td>
<td>99</td>
</tr>
<tr>
<td>Zhang et al. (2018)</td>
<td>LDV</td>
<td>Tunnel study</td>
<td>160.8 ± 65.9</td>
</tr>
<tr>
<td></td>
<td>HDV</td>
<td>Tunnel study</td>
<td>358.0 ± 124.9</td>
</tr>
</tbody>
</table>

The average OFP values of total VOC emissions from LDGV, LDDT, HDDT and LPGB were 70.7 mg O$_3$/km, 128.1 mg O$_3$/km, 2189.4 mg O$_3$/km and 124.7 mg O$_3$/km, respectively. The average OFP value of LDGV was partial consistent with some previous studies. For example, Cao et al. (2016) indicated that the OFP for light duty gasoline vehicles complying with different emission standards varied from 33 mg O$_3$/km to 1300 mg O$_3$/km, and work by Wang et al. (2013) showed that OFP values for gasoline cars were 380–920 mg O$_3$/km. The OFP value of LDGV was comparable with those observed by Yao et al. (2015a) that the OFP for LDGV was 306.7 mg O$_3$/km. Moreover, the OFP for HDDT in this study was comparable with results reported by Bermeu et al. (2015) that the OFP of diesel vehicles ranged from 967 to 1281 mg O$_3$/km, but higher than that found by Yao et al. (2015a). The discrepancy of OFP values between this study and the references was mainly attributed to the different driving cycle and fuel composition used and VOC species detected. Results from this study indicated that compared with gasoline cars, the OFP caused by diesel vehicles should not be ignored.

Fig. 4 presents the contributions of different VOC groups to OFP for the tested vehicles. Clearly, aromatics were the dominant VOC group for OFP of tested vehicles, especially for HDDT, ranging from 49.6 to 93.4%. In addition, alkenes and alkanes also played an important role in the ozone formation of VOC emissions, specifically, accounting for 18.3% and 20.4% for LDGT and 15.0% and 27.5% for LPGB. Compared with LDGT and LPGB, other VOC groups of LDGV and HDDT were less pronounced. Similar results were found in some previous studies. For example, Guo et al. (2011) observed that aromatics were the largest contributor, accounting for more than 80% of the total OFP for gasoline vehicles, and alkenes accounted for approximately 14%. Tsai et al. (2012) found that the fractions of aromatics, carboxylic acids, alkenes, and alkanes were 69%, 16%, 12% and 3.1% for FTP-75 and 69%, 14%, 11%, and 6.1%, respectively, for the highway cycle. The top 10 VOCs species contributed to OFPs were presented in Fig. 5. The top 10 species accounted for approximately 60–90% of the total OFP. For LDGV and HDDT, most of the top 10 species were aromatics, while for LDGT and LPGB, alkenes and alkanes also took up considerable parts. These results indicated that reducing aromatics and alkenes was the key to control the ozone formation of VOC emissions from vehicles.
4. Conclusions

The tailpipe VOC emission characteristics of four types of in-use vehicles were investigated with a combined PEMS, and OFPs were calculated with the MIR method. The main findings are as follows.

(1) Tailpipe VOCs of these tested vehicles were dominated by aromatics and alkanes. However, the detailed composition of VOCs varied with different types of vehicles. i-pentane, acetone and propane were the top three VOC species for LDGV. Diesel trucks had more emissions of naphthalene, dodecane, and n-undecane. Acetone was the most abundant species for the LPGB, followed by i-pentane, i-butene, n-butane and propane. In general, diesel trucks emitted more long-chain hydrocarbons, while LDGV and LPGB were more abundant in short-chain hydrocarbons.

(2) Road conditions had slight influences on the compositions of tailpipe VOCs except for HDDT. More aromatics were found for the LDGV on urban roads, while more alkanes were emitted from the LDDT on urban roads.

(3) Compared with the highway conditions, more VOCs were emitted during the urban roads. Emission factors of tailpipe VOCs from LDGV on urban roads were 1.8 times those on suburban roads and 3.9 times those on highway roads. The emission factors on urban roads were 3.3 and 7.0 times those on highway roads for the LDDT and HDDT, respectively.

(4) OFP of HDDT was much higher compared with other vehicles. The OFPs were approximately 70.7, 128.1, 2189.4 and 124.7 mg O₃/km for the LDGV, LDDT, HDDT and LPGB, respectively. Additionally, aromatics were the main contributors of OFPs, accounting for 49.6–93.4% of the total OFPs.

Despite the conclusions were drawn above, some work still needs to be done. For instance, the LDDT tested in this study had different emission standards, and their VOC compositions varied largely among the vehicles tested. The samples were small for the investigation of emission standards. In addition, we found that the LPGB had considerable VOC emissions. More stringent measurements should be implemented to control the high emissions trucks. Do LPGB reduce VOC emissions compared with traditional LPG buses based on fuel consumption? Thus, additional relative studies could be conducted in the next stage.

Declaration of competing interest

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.
CRediT authorship contribution statement

Menglei Wang: Investigation, Formal analysis, Writing - original draft, Data curation, Visualization. Shunyi Li: Writing - original draft, Supervision, Resources. Rencheng Zhu: Conceptualization, Methodology, Investigation, Writing - review & editing, Validation, Resources, Project administration. Ruqin Zhang: Conceptualization, Funding acquisition, Resources. Lei Zu: Investigation, Data curation. Yunjing Wang: Software, Visualization, Resources. Xiaofeng Bao: Methodology, Resources.

Acknowledgements

This work was supported by the National Key R&D Program of China [No. 2017YFC0212400], the National Natural Science Foundation of China [No. 51808507 & No. 21577135], the China Postdoctoral Science Foundation [No. 2018M632794], the National Engineering Laboratory for Mobile Source Emission Control Technology [No. NELM02018A16], and the Key Scientific Research Project of Colleges and Universities in Henan Province [No. 19A150018]. The authors would like to acknowledge Mr. Xiaoyan Liu, Mr. Yi Li and Mr. Cong Shen of the Chinese Research Academy of Environmental Sciences, and Mr. Xiaoming Zhang for their contributions in conducting the emission tests and Dr. Shijie Yu of Zhengzhou University for detecting VOCs and introducing the VOCs analyses procedures.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2020.117294.

References


