Investigation of speciated VOC in gasoline vehicular exhaust under ECE and EUDC test cycles

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HIGHLIGHTS
► EFs and compositions of VOC emission from passenger cars under different driving cycles were studied.
► EFs of VOC ranged from 0.10–0.25 g km−1 (ECE cycle) and 0.01–0.02 g km−1 (EUDC cycle).
► Ethylene, toluene, and benzene were the most abundant VOCs in exhaust gas.
► OFP of VOC emission at the ECE cycle was much higher than that at the EUDC cycle.

1. Introduction

Volatile organic compounds (VOC) are defined as a group of carbon-containing compounds that evaporate readily at room temperature (USEPA, 2012). Biogenic and anthropogenic VOC in ambient air affect the air quality in both regional and long-distance scales worldwide (Kim et al., 2008; Parra et al., 2009; Schürmann et al., 2007; Zemankova and Brechler, 2010). VOC are well known as ground level ozone precursors from photochemical reactions which pose health hazards (Armor John, 1994; Finlayson-Pitts and Pitts, 1993). They also contribute to the formation of photochemical smog, including secondary organic aerosol (SOA) (Derwent et al., 2010; Volkamer et al., 2006). A lot of VOC are carcinogenic, mutagenic, and teratogenic. Previous source apportionment studies demonstrated that the major emission sources of VOC comprise of natural sources, solvent utilization, biomass burning, and automobile especially gasoline vehicles (Brown et al., 2007; Cai et al., 2010; Lau et al., 2010; Srivastava et al., 2005). To properly address the related air quality and health effect problem, reliable source data of VOC are critical for developing effective control technologies and setting strategies. Speciated VOC emission source profile is also useful for simulation and prediction of secondary pollutant formation, such as secondary organic aerosol (Kanakidou et al., 2005; Seinfeld and Pandis, 2006).
The most important VOC emission source in an urban area is on-road vehicular emission (Kwangsam, 2006; Na et al., 2005; Parra et al., 2009; Parrish, 2006; Schmitz et al., 2000; Schürmann et al., 2007; USEPA, 2011). In recent decades, numerous studies have been conducted on measuring total VOC from road traffic by using tunnel, roadside, remote-sensing, and chassis dynamometer studies (Bergvall and Westerholm, 2009; Fraser et al., 1994; Graham, 2005; Graham et al., 2008; Kwangsam, 2006; Schmitz et al., 2000; Sjödin and Andréasson, 2000). Schmitz et al. (2000) determined the compounds of VOC emission from five cars using a chassis dynamometer. Graham et al. (2008) conducted the studies on VOC emission from engines operated on low blend ethanol gasoline. Most of those studies focused on total VOC or categories of VOC (e.g., alkanes, aromatics, and phenols). However, reports on typical in-use gasoline passenger cars were absent and the numbers of individual VOC reported were limited.

Previous studies demonstrated that the concentration and type of VOC depend on the car type, engine condition, and many other factors (Heeb et al., 2002, 2003; Saxer et al., 2006). Among all the technologies to measure vehicular emissions from vehicles, the chassis dynamometer is commonly employed to acquire a uniform source profile for vehicle evaluation and regulatory purpose (Beddows and Harrison, 2008; Durbin et al., 2002; Huai et al., 2004). The chassis dynamometer can simulate various engine operation conditions using different test cycles. A typical driving cycle should consist of a series of accelerations, decelerations, and frequent stops. The Federal Test Procedure 75 (FTP-75) is mandatory for new light duty vehicles in the United States while the Motor Vehicle Emissions Group A (MVEG-A), also known as the ECE/EUDC cycles, is used in European countries (Degobert, 1995) and has been adopted in China (An et al., 2011). The ECE cycle represents driving conditions such as low average speed, low engine load, and low exhaust temperature. The EUDC cycle is a supplemental for the ECE, to address emissions under a much more aggressive driving condition. The EUDC cycle is a supplemental for the ECE and the EUDC will give an accurate emission data for the urban driving style. Table 1 gives a summary of representative parameters of different driving cycles.

The ozone formation potential (OFP) is one method to quantify and predict the photochemical ozone formation reactivity of the VOC (Carter, 1994). Concentration of ozone formed from a photochemical reaction between VOC and nitrogen oxides (NOx) is strongly dependent on the VOC/NOx ratio. In addition, Carter indicated that the OFP differs among different individual VOC and VOC mixtures. The maximum incremental reactivity (MIR) scenario was commonly used to predict the highest incremental reactivity of the VOC mixture by adjusting the NOx concentration (CARB, 1991; Czader et al., 2008). Studies have shown the OFP has a good correlation with measured OH reactivity for VOC (Nakashima et al., 2010).

The overall objective of this study is to characterize the VOC emission profile for gasoline vehicles under ECE/EUDC test cycles. The VOC emission was measured in both the emission factors and the VOC speciated source profile. A chassis dynamometer was used to sample exhausts from three different cars. The emission factors of total VOC were identified by gas chromatography–mass spectrometry (GC–MS). Weight percentage of individual VOC was calculated and used to study the ozone formation yield by VOC in gasoline car exhaust.

<table>
<thead>
<tr>
<th>Driving cycles</th>
<th>Lengths (km)</th>
<th>Duration (s)</th>
<th>Mean speed (km h⁻¹)</th>
<th>Max. speed (km h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTP-75</td>
<td>18.02</td>
<td>1877</td>
<td>34.3</td>
<td>91.2</td>
</tr>
<tr>
<td>ECE</td>
<td>4.052</td>
<td>780</td>
<td>18.7</td>
<td>50</td>
</tr>
<tr>
<td>EUDC</td>
<td>6.955</td>
<td>400</td>
<td>62.6</td>
<td>120</td>
</tr>
</tbody>
</table>

Table 2. Specifications of the tested vehicles.

<table>
<thead>
<tr>
<th>ID</th>
<th>Year manufactured</th>
<th>Curb weight (kg)</th>
<th>Mileage (km)</th>
<th>Engine</th>
<th>Transmission</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2007</td>
<td>1600</td>
<td>94,148</td>
<td>4 cylinder 2.4 l</td>
<td>Auto</td>
</tr>
<tr>
<td>2</td>
<td>2008</td>
<td>1700</td>
<td>80,399</td>
<td>4 cylinder 2.4 l</td>
<td>Auto</td>
</tr>
<tr>
<td>3</td>
<td>2009</td>
<td>1300</td>
<td>3559</td>
<td>4 cylinder 1.6 l</td>
<td>Manual</td>
</tr>
</tbody>
</table>

2. Material and methods

2.1. In-use driving conditions

Three in-use light-duty gasoline passenger cars were set on a chassis dynamometer (RPL1220, AVL) to measure the VOC emission in this study. The conditions of the three cars are summarized in Table 2. The vehicles were randomly selected from the fleet in China Automotive Technology and Research Center (CATARC). All the tested vehicles were equipped with an exhaust catalyst and complied with the current Chinese emission regulation (equivalent to Euro III). Due to the strong correlation between the fuel composition and VOC emission, fuel of the same rating (93# RON gasoline) was supplied during the entire study to avoid the interference from a different fuel. In addition, the gasoline used was the representative of average composition and properties in the Chinese fuel market. The vehicles were driven by an experienced technician in CATARC to avoid human artifacts.

The entire driving cycle for one vehicle comprises of four repeated ECE segments without interruption to simulate the urban driving condition, followed by one EUDC segment to simulate the suburban driving condition. The vehicles were kept at 25 °C and the test started without idling to have the cold start condition. Sampling for the ECE and the EUDC test cycles were separated to compare the emission profiles between low speed and high speed conditions.

2.2. Sampling

The exhaust gases were sampled by a constant volume sampler (CVS-2000, HORIBA) connected to the chassis dynamometer. The exhaust gas was diluted by zero-air with a dilution factor of 11.95–29.34 in the system. Fig. 1 shows the schema of the dilution and sampling system.

The sampling method adopted was based on the EPA standard method TO-15 (USEPA, 1999) through the utilization of a Summa canister (Entech Inst., USA). A Summa canister is a pre-evacuated, passivated, and highly polished stainless steel container. The utilization of Summa canisters can prevent permeation of the VOC through the vessel wall, and degradation during transport to the analytical laboratory. The canisters were washed by deionized water (18 MΩ·cm) and cleaned by ultra-high purity nitrogen. The canisters were evacuated into a vacuum prior to sampling. A flow restrictor was used to spread the diluted exhaust flow over the time periods of the ECE and the EUDC cycles separately. The canisters were sealed and shipped to the analytical laboratory no more than 10 days after sampling, which is in accordance with the EPA TO-15. All the fittings and tubing were made of either stainless steel or polytetrafluoroethylene (PTFE) to provide an inert sampling environment. Zero-air supply was used to dilute the exhaust gas and was collected separately as field blank. No VOC was detected in the field blank. Hence the samples were not subjected to the field blank correction.

2.3. Analysis

The samples collected in the Summa canister were pre-concentrated to an acceptable level for the analytical devices using a 7100A pre-concentrator (Entech Inst., USA) with three cold traps and hot desorb injection. Moisture content in the canister was removed by cooling.
and purifying to a water concentration of 18 ppmv at 25 °C. Concentration of individual VOC in samples was determined by a GC–MS system (QP2010, Shimadzu) following EPATO-15 method. Separation of VOC was achieved through a capillary column (60 m×0.25 mm I.D., 1.4 μm film thickness DB-624, Agilent). The oven temperature was held at 40 °C for 3 min, increasing at 8 °C/min to 90 °C and held for 1 min, then increasing at 6 °C min⁻¹ to 200 °C and held for 9 min. The flow-rate of carrier gas (helium) was held at 1.2 mL/min throughout the GC detector. An ion trap mass spectrometer was employed to detect the VOC compounds with an electron energy of 70 eV and mass range of 45–360 atomic mass units (amu). In total, 108 VOC were analyzed in five replicates for each sample.

The GC–MS system was calibrated using EPA TO-15 standard gas (Spectra Gases, USA) with 64 VOC gas mixtures. Recovery test was done by spiking internal standards, with a total of four times. The recovery for internal standards was over 90%, and relative standard deviations (RSDs) were less than 10%. Laboratory blank test was performed every 10 samples analyzed by inserting ultra-high purity nitrogen gas in order to eliminate interference from residual contamination of devices and pipelines.

2.4. Emission factors calculation

In supplement to measure the weight percentage of individual VOC, the emission factors of total VOC were calculated. The calculations of emission factor of VOC followed Eq. (1) below,

\[
EF = \frac{V \rho C}{10^6 D_S} \tag{1}
\]

where EF is the emission factor, in g km⁻¹; V is the total exhaust gas volume at standard condition (273.2 K, 101.33 kPa), in m³; ρ is the density of hydrocarbon compounds (C:H, 1:1.85) at standard condition and was equal to 0.619 g L⁻¹ in this study; C is the concentration of the VOC in diluted gas, in ppmv (v/v); D_S is the dilution factor and varied for each sampling; and S is the total distance the vehicle traveled, in km.

In addition to the VOC data, emission factors of common gaseous pollutants from gasoline engines such as methane (CH₄), NOx, carbon monoxide (CO), and carbon dioxide (CO₂) were recorded by the on-board monitoring system of the chassis dynamometer.

The statistical significance was determined at the 95% confidence interval using the analysis of variance (ANOVA) t-test. All statistical analyses were performed using statistical software (SAS 9.3).

2.5. Ozone formation potential (OFP) calculation

Carter (1994) developed the maximum incremental reactivities (MIR) scenario which yields the maximum ozone. The MIR for each individual VOC was recorded in unit of gram in Carter's study. The OFP was calculated using the following equation,

\[
OFP = \sum \frac{MIR \times \text{wt} \% \times EF}{EF} \tag{2}
\]

where OFP is the ozone formation potential, in g km⁻¹; MIR is the maximum incremental reactivities of the individual VOC species, in gram ozone formed per gram VOC emitted; wt% is the weight percentage of individual VOC in the total VOC emission; and EF is the emission factor of total VOC, in g km⁻¹.

3. Results and discussions

3.1. Common gaseous pollutants

The results of emission factors of common gaseous pollutants at the ECE and EUDC test cycles show statistical difference (p<0.05) in each pollutant category (CH₄, NOx, CO, and CO₂). The averages are summarized in Fig. 2 on a log scale, together with the standard deviation shown as error bars. The emission factors of all the pollutants were the highest at the ECE cycle as expected, which is a relatively low-speed urban condition. The NOx emissions of the EUDC cycle were about 41.5% of the ECE cycle, and a similar pattern was found at the CO₂ emissions (57.6%). The results showed good agreement with the conclusion of Joumard et al. (2000), but Tamsanya and Chungpaibulpatana (2009) found that NOx emissions at the EUDC cycle were higher than those at the ECE cycle. NOx and CO₂ emission factors were generally lower than the previous study on in-use engines.

![Fig. 1. Schematic diagram for the dilution and sampling system.](image)

![Fig. 2. Average emission factors of NOx, CO, and CO2 for different driving cycles.](image)
vehicles \((\text{De Vlieger, 1997})\), which indicated the improvement of the engine and emission technology in recent years.

For CH\(_4\) and CO which are incomplete combustion products from a gasoline engine, the emission factors of the ECE cycle were about 5 times the VOC factors of the EUDC cycle (mean 0.16 g km\(^{-1}\)) compared to the EUDC cycle (high speed) showed that the fuel combustion efficiencies were more speed dependent.

### 3.2. Emission factor of VOC

The total exhaust gas volume, dilution factors, and emission factors are listed in Table 3. Travel distance and other parameters are not included in the table due to the fixed value in the calculation of emission factors. Similar to the common gaseous pollutants, the average emission factors of VOC for the EUDC cycle (mean 0.01 g km\(^{-1}\)) were much less than the ECE cycle (mean 0.16 g km\(^{-1}\)), which means the vehicles have 16 times the VOC emitted during low speed driving condition.

Car 1 has the maximum emission at both the ECE and the EUDC cycles. Car 1 is the oldest and has the highest mileage among three cars. The longer driving history and aging of the engine could play an important role in the emission factor of VOC. The emission of car 2 is higher than car 3 at the ECE cycles, while lower in the EUDC cycles. Driving in the low speed condition, car 2 with an auto transmission emits more VOC. Car 3 which has a manual transmission and a small engine size is more suitable for urban driving with its frequent stops and idles. At high speed driving, car 3 has more emission due to work under high load with a small engine size. Meanwhile, the emission factors can be affected by other factors not surveyed in this study, such as driving history, catalytic converter condition, etc.

### 3.3. VOC compositions from different cars and test cycles

The mean weight percentage of 57 individual VOC detected over total VOC are given in Table 4. The value was an integration of data from both the ECE and the EUDC cycles considering that they were consecutive cycles. In contrast to the emission factors of total VOC, the effect of different cars on the composition of VOC was less pronounced. The compositions of VOC emissions from different cars were relatively identical without a statistically significant difference \((p > 0.1)\), which indicated a similar combustion condition for the formation of individual VOC. Hence, the average weight fraction of three in-use cars of individual VOC could be used to give a better overview of the VOC compositions.

The VOC with weight fraction over 1% are summarized in Fig. 3. Ethylene \((11.80\%)\) was the most abundant VOC followed by toluene \((11.27\%)\) and benzene \((8.83\%)\). However toluene and benzene will draw more attention due to the serious inhalation health risk even at a low exposure level. \(\text{Sweet and Vermette (1992)}\) found that toluene and benzene contributed 7.7% \(\text{(wt)}\) and 3.6% \(\text{(wt)}\) of the total vehicle exhaust, respectively. Their wt.% were less than this study, because they were comparing to total vehicle exhaust not total VOCs. \(\text{Liu et al. (2008)}\) reported a similar emission composition of light duty gasoline vehicles with a slight difference, e.g., the percentage of the alkane ethylene is lower than propylene in Liu’s study.

The 57 VOC detected were grouped into four categories, aromatics, alkanes, alkenes, and others, to give an overview of the influence of test cycles on the VOC compositions. The alkene ethylene was included in the alkene group. The percentage of the VOC group showed a variation at the ECE and the EUDC cycles which is given in Fig. 4.

The aromatics dominated the low speed condition (ECE), while they decreased at high speed condition (EUDC). The alkenes dominated the high speed conditions following by alkenes. The amount of VOC in other groups such as carbonyls was typically less than 4% in either condition. The pattern demonstrates the relatively incomplete combustion
under a low speed condition leading to more formation of the aromatics (Mastral and Callén, 2000). However, Schmitz et al. (2000) reported an increase of aromatics with driving speed while the vehicles were equipped with a three way catalyst. The lean or rich air/fuel mixture ratios of test vehicles and speeds can cause a different hydrocarbon conversion efficiency on a catalyst-equipped vehicle, hence this contributed to the VOC group pattern change.

To observe the influence of test cycles on different VOC groups, the individual VOC which has a weight fraction shift from the ECE to the EUDC cycles are summarized in Figs. 5–7. In the aromatics group, an increase in toluene and benzene was found at the EUDC cycle compared to the ECE cycle. 1,2,4-Trimethylbenzene (1.18%) and 4-ethyltoluene (1.45%) dominated the aromatics at the ECE cycle. In the alkane group, ethane was about 9 times at the EUDC cycle compared to the ECE cycle, which clearly showed a more efficient combustion at the high speed condition. It should be noted that isopentane and heptane are major components of gasoline. The presence of isopentane and heptane indicates that possibly a fraction of the VOC was directly emitted from gasoline without combustion. In the alkene group, the difference between test cycles was less pronounced except for ethylene and 1-hexene which were richer in the EUDC cycle.

3.4. Ozone formation potential (OFP)

Because of the variance in the emission factors from different cars, the OFPs were calculated for individual cars. Because of the similar VOC composition among cars, the OFP was mainly dependent on the emission factors of different cars. Car 1 had the highest OFP of 0.92 g km$^{-1}$, while the car 2 and car 3 had 0.46 g km$^{-1}$ and 0.38 g km$^{-1}$, respectively. However, the OFP was an estimation based on Carter's study in California, and different local conditions in China (emissions, meteorology, engine and fuel technology, etc.) will have an impact on the photochemical reaction and the OFP.

Fig. 3. Individual VOC with high fractions from the average of the three cars.

Fig. 4. Average VOC composition under different driving cycles.

Fig. 5. Weight percentage of individual aromatics in the ECE and EUDC driving cycles.
Characterization of the VOC emission factors and weight percentage of individual VOC were carried out in this study. The ECE and EUDC cycle tests were performed to represent both low speed/urban and high speed/suburban conditions, respectively. The measurement of common gaseous pollutants showed that the ECE cycle had a relative high combustion efficiency with the presence of 5 times higher concentration of CH$_4$ and CO compared to the EUDC cycle. The total VOC emission factors for different cars varied. Car 1 with longer history and higher mileage yielded the maximum VOC emission, about 2–4 times that of car 2 and 3. Car 2 with an auto transmission generated more emission than car 3 with a manual transmission during the ECE cycle. During EUDC cycles, the emission of car 3 with a small engine size was higher than car 2. Generally, the emission factors at EUDC cycles were much less than the ECE cycles which has more stops and idles and run at low average speed.

The compositions of VOC among three cars were statistically the same and the average value of each individual VOC was used. The most abundant VOC in the exhaust was ethylene, toluene, and benzene. Looking at different test cycles, the aromatics and the alkanes dominated at the ECE and the EUDC cycles, respectively. The differences among test cycles were induced by different levels of incomplete combustion and catalyst efficiency on hydrocarbon conversion. Increasing percentages of toluene and benzene were found at the EUDC cycle. In addition, the amount of isopentane and heptane gave evidence of directly emitted gasoline without combustion. The OFP, calculated based on a California scenario showed one order of difference in the ECE and the EUDC cycles. The OFP estimation could be a useful regular tool for VOC emissions from a vehicle.

In sum, the results of total VOC emission and composition are similar with several studies done on total VOC emission factors in decades and different countries. The VOC emission factors were lower compared to those studies done prior to 2000 and similar to studies after 2005, which indicated the retrofit of automotive technology. However, the difference in some individual VOC (e.g., alkynes ethyne and propene) exists. Furthermore, the results of this study can be also used for future studies on source apportionment and update of emission inventory.

4. Conclusions

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References


Fig. 6. Weight percentage of individual alkanes in the ECE and EUDC driving cycles.

Fig. 7. Weight percentage of individual alkenes in the ECE and EUDC driving cycles.


