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On-board measurements of gaseous pollutant emission characteristics under real driving conditions from light-duty diesel vehicles in Chinese cities

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ABSTRACT

A total of 15 light-duty diesel vehicles (LDDVs) were tested with the goal of understanding the emission factors of real-world vehicles by conducting on-board emission measurements. The emission characteristics of hydrocarbons (HC) and nitrogen oxides (NO_x) at different speeds, chemical species profiles and ozone formation potential (OFP) of volatile organic compounds (VOCs) emitted from diesel vehicles with different emission standards were analyzed. The results demonstrated that emission reductions of HC and NO_x had been achieved as the control technology became more rigorous from Stage I to Stage IV. It was also found that the HC and NO_x emissions and percentage of O₂ dropped with the increase of speed, while the percentage of CO₂ increased. The abundance of alkanes was significantly higher in diesel vehicle emissions, approximately accounting for 41.1%–45.2%, followed by aromatics and alkenes. The most abundant species were propene, ethane, *n*-decane, *n*-undecane, and *n*-dodecane. The maximum incremental reactivity (MIR) method was adopted to evaluate the contributions of individual VOCs to OFP. The results indicated that the largest contributors to O₃ production were alkenes and aromatics, which accounted for 87.7%–91.5%. Propene, ethene, 1,2,4-trimethylbenzene, 1-butene, and 1,2,3-trimethylbenzene were the top five VOC species based on their OFP, and accounted for 54.0%–64.8% of the total OFP. The threshold dilution factor was applied to analyze the possibility of VOC stench pollution. The majority of stench components emitted from vehicle exhaust were aromatics, especially *p*-diethylbenzene, propylbenzene, *m*-ethyltoluene, and *p*-ethyltoluene.

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Introduction

The changes of the gaseous pollutant contents in the atmospheric environment have been associated with the growth of China's vehicle population (Chan and Yao, 2008).

The motor vehicle population was 208 million in 2011 in China, with automobiles, light-duty trucks, and motorcycles accounting for 44.7%, 5.9%, and 49.4%, respectively. The automobile category was divided into gasoline vehicles and diesel vehicles, and the contribution ratios to nitrogen oxides

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(NO_x) and hydrocarbons (HC) were 90% and 70% of the total motor vehicle population, respectively (MEP, 2011). Vehicle emissions have gradually been recognized as a significant source of ambient volatile organic compounds (VOCs) (Huang et al., 2011), which play an important role in atmospheric chemistry and urban air quality. An investigation showed that vehicle emissions accounted for more than 50% of the ambient VOCs in some cities (Liu et al., 2008a). In order to control the vehicle exhaust pollution and improve the urban air quality, national governments have implemented numerous control measures, including promoting clean transportation fuel, improving exhaust after-treatment technology as well as enacting strict emission standards (Yao et al., 2007). Among them, implementing vehicle exhaust emission standards has become one of the main measures of urban motor vehicle pollution control at home and abroad. Various vehicle emission standards were implemented in different stages in China. However, the desired ambient air quality has not been achieved due to the rapid increase of vehicles and kilometers driven (Huo et al., 2012a). Gaseous pollutants have still remained at a higher level of pollution in urban atmospheres.

Pollutants discharged from vehicles are complicated, and mainly come from incomplete combustion of fuels. The exhaust measurements show that the main composition consists of carbon monoxide (CO), HC, NO_x, sulfur oxides (SO_x), and particulate matter (PM) (Fu, 2009). The HC and NO_x are major pollutants in vehicle emissions. As mobile pollution sources, vehicles often accumulate in flourishing areas and the pollutants have toxic effects on atmospheric chemistry (Tsigaridis and Kanakidou, 2007) and adverse health effects (Zhang et al., 2008). First of all, VOCs are important HC of vehicle exhaust pollution, which include a variety of carcinogenic substances (Louie et al., 2013). They can stimulate the visual and olfactory organs and result in anemia and even acute poisoning. Additionally, VOCs can convert into secondary organic aerosols (SOA) through photochemical oxidation, which also has significant influence on human health (Pachauri et al., 2013). Last but not least, VOCs can react with NO_x generated in the process of combustion and form the secondary pollutant ozone (O₃) under strong light (Suthawaree et al., 2012).

In this case, determining the emission characteristics of vehicles in real-world conditions, especially for policy makers, is an intractable issue in controlling the vehicle emissions more effectively. During the past several years, the majority of sampling methods have mainly included remote sensing techniques (Carslaw and Rhys-Tyler, 2013), traffic tunnel measurements (Ho et al., 2009), dynamometer tests (Tsai et al., 2006), and roadside sampling (Phuleria et al., 2007). For instance, Ho et al. (2013) collected samples at roadside locations, and the most abundant VOC was ethane, which accounted for 9.5%–29.0% of the total quantified VOCs. However, these methods show great differences from real driving conditions on account of limitations of technology and equipment. Investigations on driving patterns (Tong et al., 2000) have reported that the actual driving pattern emissions were generally higher than those derived from dynamometer tests if the effect of the operating conditions of the vehicles is neglected. It is also clear that research on the emission characteristics of various vehicle models is relatively scarce

and limited. In addition, the problems caused by diesel vehicle emissions have gradually become more prominent with better control of gasoline vehicle emissions (Fu, 2009). Therefore, in order to reveal the vehicle emission characteristics of China's diesel vehicles under real traffic conditions, a total of 15 light-duty diesel vehicles (LDDVs) were employed to collect HC, nitrogen oxides (NO_x), and VOC samplings using a developed dilution sampling system for vehicle exhaust under real driving conditions during 2013 and 2014 in the cities of Tangshan and Hengshui in Hebei province of China. The objectives of this study mainly include: (1) investigating the HC and NO_x emission characteristics and the influence of vehicle speed on HC and NO_x emissions; (2) analyzing the chemical profiles of VOCs emitted from LDDVs in real conditions; and (3) evaluating the ozone formation potential (OFP) and stench index of VOCs emitted from LDDVs.

1. Experimental methods

1.1. Sampling system for vehicle exhaust

The majority of sampling methods discussed above have not considered real driving conditions and the transformation of gaseous pollutants to secondary fine particles when the exhaust is cooled and diluted with the ambient atmosphere. This might overestimate the VOC emission due to the high temperature of vehicle exhaust. The flue gas temperature should be at 42°C or lower according to the dilution sampling standard proposed by the International Organization for Standardization (ISO 25597:2013). However, the temperatures of vehicle exhaust measured in this study were all above 42°C. Therefore, an on-board emission measurement system containing an exhaust gas dilution system was employed to collect samplings from diesel vehicles under real driving conditions (Fig. 1).

This system mainly includes the following parts: (1) A flow meter was used to measure instantaneous exhaust flow rate and temperature from test vehicles. (2) A heated inlet line was used to ensure that the temperature of exhaust gas did not drop from the flow meter to the mixing chamber. (3) A five-gas analyzer (Gasboard-5030, Wuhan Cubic Optoelectronics Co., Ltd., China) was utilized to measure the real-time emissions of gaseous pollutants, such as percent by volume of oxygen (O₂), carbon dioxide (CO₂), and the concentration of HC and NO_x every 3 sec. To ensure the accuracy of the data, the five-gas analyzer was checked for tightness and zeroed in the atmosphere before use. (4) A global position system (GPS) device (Columbus V-990, CDH Electronic Technology Co., Ltd., China) was applied to monitor the instantaneous speed and location of test vehicles. (5) A zero gas generator was used to provide pure air mixed with exhaust in the mixing chamber to simulate the rapid cooling and dilution processes after hot exhaust exited the tail pipe. Finally, the temperature of the air mixture was dropped to below 42°C. (6) A computer was used to control the software, and data including the dilution ratios, the flow of diluent air, and other parameters could be recorded and exported after the sampling. The sampling equipment was always placed inside the vehicles in the process of testing (Huo et al., 2012c). Due to the different

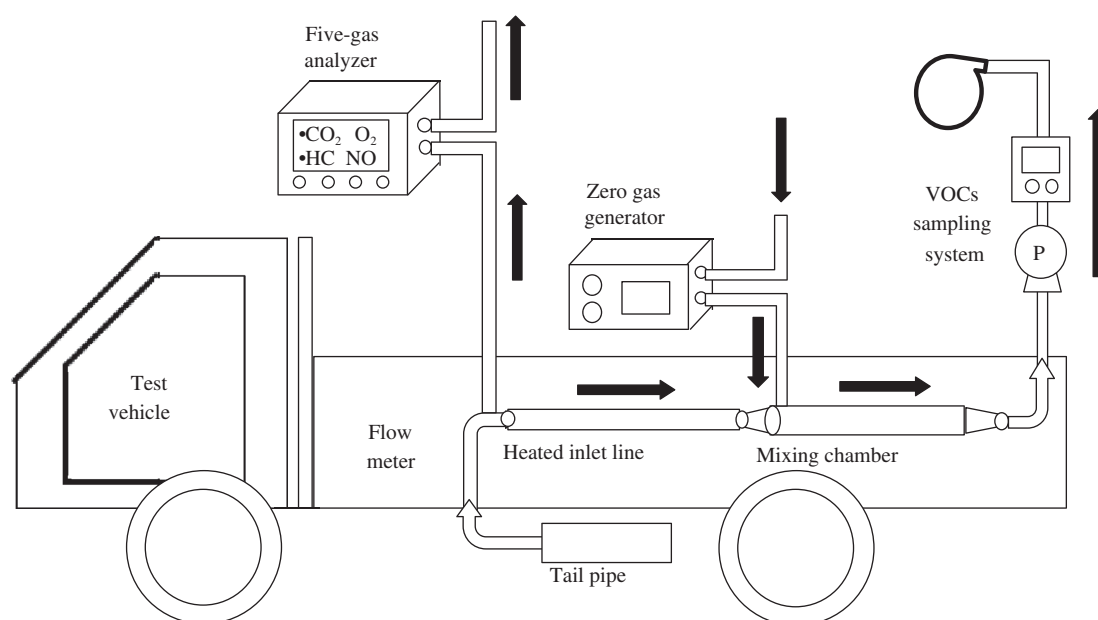


Fig. 1 – Sketch of the on-board emission measurement system. VOCs: volatile organic compounds; P: sampling pump.

discharges of each car, test vehicles should be run for a period of time to expel the remaining gas in pipelines from testing of previous cars before starting the sampling instruments, to reduce the experimental error.

1.2. Testing vehicles

It is well-known that test routes are significant in vehicle emissions and should include different typical road systems. Several studies have discussed the influence of driving pattern on the emission characteristics of diesel vehicles (Yao et al., 2007). The road types are relatively simple in the study cities, and in consequence, we primarily selected arterial roads and residential roads in this study. The motor vehicle population was 1.13 and 0.40 million in Tangshan and

Hengshui, respectively (TSB, 2013; HSB, 2013). A total of 15 LDDVs including Stage I, Stage II, Stage III and Stage IV technologies were tested. Stage I, Stage II, Stage III and Stage IV represent different emission standards of LDDVs. LDDVs tested in this paper were categorized into Stage I, Stage II, Stage III, and Stage IV technologies according to the “Technical guide of on-road motor vehicles emissions inventory compilation” published by Ministry of Environmental Protection (MEP, 2014). Based on the dates of registration, the specific classification of LDDVs followed the rule that LDDVs registered during the period of September 2001–September 2004, September 2004–January 2008, January 2008–July 2013, and July 2013–present conformed to Stage I, Stage II, Stage III, and Stage IV standards, respectively. The diesel fuel quality was Stage III for all cases in Tangshan and Hengshui based on

Table 1 – Basic information of the test vehicles.

| No. | City | Model data | Technologies | Fuel type | Curb weight (kg) | Total weight (kg) | Manufacturer | Engine power (kW) | Trip distance (km) |
|-----|----------|----------------|--------------|-----------|------------------|-------------------|--------------|-------------------|--------------------|
| 1 | Tangshan | March 2004 | Stage I | Diesel | 1845 | 2490 | Dongfeng | – | – |
| 2 | Tangshan | March 2004 | Stage I | Diesel | 1845 | 2490 | Dongfeng | 70 | – |
| 3 | Tangshan | June 2004 | Stage I | Diesel | 1495 | 2490 | Dongfeng | 70 | 167,864 |
| 4 | Tangshan | November 2007 | Stage II | Diesel | 3300 | 4450 | Yuejin | – | 155,000 |
| 5 | Tangshan | June 2007 | Stage II | Diesel | 2520 | 4450 | Yuejin | 88 | 190,751 |
| 6 | Tangshan | September 2007 | Stage II | Diesel | 2800 | 4490 | Jinbei | 75 | – |
| 7 | Hengshui | March 2009 | Stage III | Diesel | 2205 | 4390 | Jinbei | 76 | 94,351 |
| 8 | Hengshui | December 2009 | Stage III | Diesel | 2515 | 4495 | Beijing | 68 | 70,000 |
| 9 | Tangshan | April 2011 | Stage III | Diesel | 3400 | – | Beijing | – | 37,400 |
| 10 | Tangshan | August 2011 | Stage III | Diesel | 1760 | 4300 | Jiangling | 75 | 69,528 |
| 11 | Hengshui | February 2012 | Stage III | Diesel | 1405 | 3530 | Jianghuai | 40 | 72,100 |
| 12 | Hengshui | March 2012 | Stage III | Diesel | 1405 | 3530 | Jianghuai | 40 | 60,538 |
| 13 | Tangshan | September 2013 | Stage IV | Diesel | 2800 | 4490 | Yuejin | 75 | 83,471 |
| 14 | Tangshan | December 2013 | Stage IV | Diesel | 2620 | 4195 | Yuejin | 80 | 40,096 |
| 15 | Hengshui | October 2013 | Stage IV | Diesel | 2400 | 4495 | Futian | 75 | 2653 |

Stage I, Stage II, Stage III and Stage IV represent different emission standards of LDDVs; “–” represents data missing.

field investigation during the sampling period. The basic information for each diesel truck is summarized in Table 1, such as city, model year, curb weight, total weight, trip distance and so on. At each state (i.e., idle speed and the actual road), the measurement lasted for 10–15 min to ensure the reliability of the collected data. With the parameters acquired from the on-board emission measurement system, emission factors of LDDVs can be calculated as follows:

$$EF_i = \frac{M_i \times C_i \times 0.001}{22.4} \times \frac{273.15}{273.15 + T} \times \frac{V}{S} \quad (1)$$

where EF_i (g/km) represents the emission factor for pollutant i , M_i and C_i (ppm) represent the molecular weight and concentration for pollutant i , respectively, 22.4 represents molar volume of gas under standard temperature and pressure, S (km) represents the vehicle mileage during the sampling period, and T (°C) and V (m³) represent the exhaust temperature and volume during the sampling period, respectively.

1.3. Sample analytical instrument and method

Vehicle exhausts were first gathered in Tedlar® bags, which were identified as resistant to sorption of organic compounds, and then imported into vacuumed stainless steel canisters (3.2L, Entech Instruments, Inc., USA) for analysis. The Tedlar bags and canisters were pre-cleaned by ultra-pure nitrogen (N₂) (99.999%) to remove water vapor, air, and any organic compounds before sampling (Duan et al., 2008). A total of 121 VOC samples were collected.

This research employed the Environmental Protection Agency (EPA) TO-15 method (US EPA, 1999) to determine VOC concentrations by gas chromatography–mass spectrometry (GC–MS) (7890 A/5975C, Agilent Inc., USA). Firstly, samples were concentrated in the pre-concentrator (7100 A, Entech Instruments Inc., USA) and entered the first cold trap, Module1, which was mainly used to remove H₂O, N₂, CO₂, CO and O₂ contained in samples. The freezing temperature was set to –165°C and the desorption temperature was 10°C. Secondly, the gas desorbed from the Module1 was enriched under –50°C and concentrated in a Tenax adsorption trap, which was used to remove the Ar, CH₄ and CO₂ and trace water. The desorption temperature was 180°C. Thirdly, VOC samples were frozen in cold trap Module3, which was constituted of empty capillaries. The freezing temperature was –160°C. Module3 was warmed up to make the VOC samples vaporize rapidly when the freezing was finished. Under the impetus of the carrier gas helium, samples were desorbed into the GC capillary column for separation and then into the mass spectrometry detector (MSD) for detection, respectively. Finally, photochemical assessment monitoring stations (PAMS) certified gas was used to quantify the target compounds. A calibration curve of each target compound was plotted at four different concentrations, i.e., 0, 5, 10, and 20 ppb. The correlation coefficients were all above 0.99, which showed the good linearity of the relationship between the integral areas of peaks and the corresponding concentrations (Wei et al., 2014). A gas chromatograph–flame ionization detector (GC–FID) (GC5000, AMA Inc., Germany) was applied to further quantify ethane, ethylene, propane, and ethyne,

and more detailed description of this analysis method can be found in Liu et al. (2008b). Finally, 56 VOC concentrations were determined in total, and the species are listed in Table 2.

2. Results and discussion

2.1. HC and NO_x emission factors

HC and NO_x emission factors of LDDVs under different standards in this study are demonstrated in Fig. 2. The LDDV emission factors of HC and NO_x were 0.90 ± 0.40 and 1.05 ± 0.62 g/km, respectively by calculating the average value from Stage I to Stage IV vehicles. With the improvement of fuel quality, emission control technologies, and the implementation of stringent vehicle emission standards over the past few years in China, an appreciable reduction of HC and NO_x emission factors was observed. For instance, Stage I LDDVs had a relatively higher HC emission factor compared with other standards; HC emission factors of Stage I vehicles were approximately 1.2, 1.8, and 3.2 times higher than those of Stage II, Stage III, and Stage IV vehicles, respectively. Like HC emission factors, the NO_x emission factors were also obviously reduced and were related to implementation of emission control technologies. For instance, Stage I vehicles had higher NO_x emission, and the emission factors were approximately 1.5, 2.3, and 4.9 times higher than those of Stage II, and Stage III, Stage IV vehicles, respectively. This illustrated that the effect of the implementation of the standards for HC and NO_x emissions reduction was obvious. The variation tendency of HC emission factor obtained from this study was basically consistent with the measured values derived from Huo et al. (2012b) and Liu et al. (2009) using the on-board emission test system, which further proves the effectiveness of our experiment.

2.2. HC and NO_x emission factors under different speeds

LDDV emission characteristics are a complicated dynamic process, and closely related to the traveling speed (Chen et al., 2007). Due to the poor operating conditions and heavy traffic in the actual driving of China, vehicles would undergo frequent changes in motion and fuel consumption would increase during the period of “stop-and-go”. Therefore, the influence of emission factors under different running speeds was conducted in this study. Stage I and Stage III LDDVs were selected as an example and ran based on speeds of 20, 40 and 60 km/hr to investigate the relationships between emission and speed.

The emission factors of HC and NO_x at various speeds are presented in Fig. 3. The results demonstrated that the vehicle speed had an important influence on emissions. Both HC and NO_x emission factors decreased with the rise of vehicle speed. For Stage I diesel vehicles, the decrease rate of the NO_x emission factor was 9.5% and 24.1% as the speed increased from 20 to 40 and 60 km/hr, respectively due to the deterioration of combustion conditions. Similarly, for Stage III diesel vehicles, the NO_x emission factors also decreased by 28.1% and 36.5% when the speed rose from 20 to 40 and 60 km/hr, respectively. Additionally, as described above, the NO_x emission

Table 2 – Photochemical assessment monitoring stations (PAMS) hydrocarbons detected in this study.

| No. | Hydrocarbons | No. | Hydrocarbons | No. | Hydrocarbons | No. | Hydrocarbons |
|-----|--------------|-----|---------------------|-----|------------------------|-----|------------------------|
| 1 | Ethane | 15 | t-2-Pentene | 29 | 2,3-Dimethylpentane | 43 | n-Nonane |
| 2 | Ethene | 16 | c-2-Pentene | 30 | 3-Methylhexane | 44 | Isopropylbenzene |
| 3 | Acetylene | 17 | 2,2-Dimethylbutane | 31 | 2,2,4-Trimethylpentane | 45 | n-Propylbenzene |
| 4 | n-Propane | 18 | Cyclopentane | 32 | n-Heptane | 46 | m-Ethyltoluene |
| 5 | Propene | 19 | 2,3-Dimethylbutane | 33 | Methylcyclohexane | 47 | p-Ethyltoluene |
| 6 | Isobutane | 20 | 2-Methylpentane | 34 | 2,3,4-Trimethylpentane | 48 | 1,3,5-Trimethylbenzene |
| 7 | 1-Butene | 21 | 3-Methylpentane | 35 | Toluene | 49 | o-Ethyltoluene |
| 8 | n-Butane | 22 | 1-Hexene | 36 | 2-Methylheptane | 50 | 1,2,4-Trimethylbenzene |
| 9 | t-2-Butene | 23 | n-Hexane | 37 | 3-Methylheptane | 51 | n-Decane |
| 10 | c-2-Butene | 24 | Methylcyclopentane | 38 | n-Octane | 52 | 1,2,3-Trimethylbenzene |
| 11 | Isopentane | 25 | 2,4-Dimethylpentane | 39 | Ethylbenzene | 53 | m-Diethylbenzene |
| 12 | 1-Pentene | 26 | Benzene | 40 | m,p-Xylene | 54 | p-Diethylbenzene |
| 13 | n-Pentane | 27 | Cyclohexane | 41 | Styrene | 55 | n-Undecane |
| 14 | Isoprene | 28 | 2-Methylhexane | 42 | o-Xylene | 56 | n-Dodecane |

factors of Stage III diesel vehicles were 56.9%, 97.5%, and 87.4% lower than those of Stage I diesel vehicles at running speeds of 20, 40, and 60 km/hr, respectively.

The causes of this phenomenon have the following several aspects. Firstly, the formation of NO_x is mainly due to the presence of sufficient oxygen and the right temperature inside the cylinder. Fuel combustion of diesel vehicles would be supported by oxygen from the atmosphere. The percentage of O_2 was higher at low speed, thus NO_x was more easily produced. Secondly, the vehicle engine load increased as the speed increased. The increase of rotation speed was also beneficial to boost the homogeneity of fresh air and fuel in the cylinder. The temperature inside the cylinder was enhanced with the level of combustion. In return, high temperature could accelerate the evaporation of fuel, so that the air and fuel mixed more evenly. The fuel consumption rates at high speed were evidently lower than that at low speed (Yao et al., 2007). Therefore, NO_x emissions decreased with the increase of vehicle speed.

According to the results of sampling data, the exhaust concentrations of NO_x could be up to 1200 ppm. Also, the

exhausts were all vented to atmosphere directly after combustion. Thus it can be seen that the amount of NO_x emissions would be considerable for a city with hundreds of thousands of vehicles operating every day. Although China had made a certain amount of progress in air pollution control, the control technologies on diesel engines are still in a relatively backward position. Therefore, more stringent emission control standards for NO_x need to be enforced, and the NO_x emission reduction of diesel vehicles appears particularly important.

Similar to the emission characteristics of NO_x , HC emission factors decreased with rising vehicle speeds. For instance, HC emission factors decreased by 71.1% and 62.6% as the vehicle speed increased from 20 to 60 km/hr for Stage I and Stage III diesel vehicles, respectively. This might mainly be because HC are products of incomplete combustion. What's more, fuel combustion was not efficient owing to the lower temperature and speed, which resulted in relatively higher HC emission factors. Secondly, the increased vehicle speeds enhanced the air to flow into the cylinder, making the fuel and air mix more evenly. The improved combustion conditions also decreased the concentrations of HC. Thirdly, the vehicle engine load became larger with increasing speed and high load would achieve high temperature inside the cylinder. Moreover, part of HC would be transformed to other carbonaceous oxides at high temperature, which would play an important role in promoting the oxidation of HC. Additionally, the increase of cylinder temperature resulted in the rise of the cylinder wall temperature. High cylinder wall temperature would shorten the quenching distance, to alleviate the formation of HC (Wang et al., 2013).

The percentage of O_2 also dropped with the increase of speeds (Fig. 4). The O_2 percentage decreased by 17.9% and 14.3% as the speed increased from 20 to 60 km/hr for Stage I and Stage III, respectively. That might be because the vehicle exhausts passed through purification devices (e.g., ternary catalytic converters), leading to catalytic oxidation and oxygen consumption. On the other hand, the diesel engine was generally in the lean combustion state during the process of operation with increasing speed. The fuel was prone to weak oxidation and would produce more oxygenated volatile organic compounds, causing O_2 to be reduced (Qiao, 2011). Conversely, the percentage of CO_2 was increased with the increase of the speed (Fig. 4).

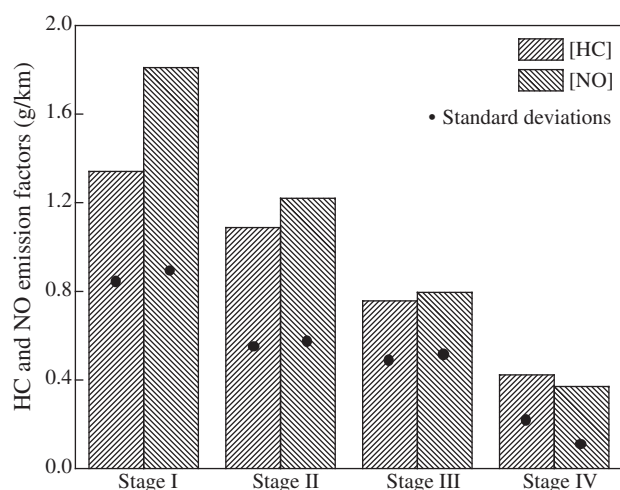


Fig. 2 – HC and NO emission factors of light-duty diesel vehicles (LDDVs) under different standards. Stages I, II, III, and IV refer to Section 1.2.

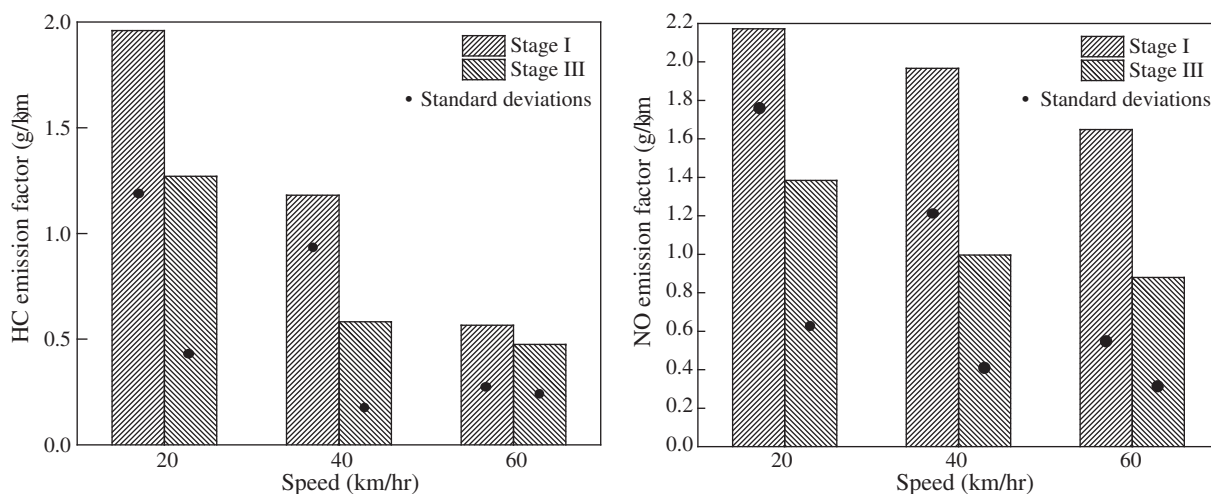


Fig. 3 – Emission factors of HC and NO at various speeds.

CO₂ percentage increased by 17.9% and 14.3% as the speed increased from 20 to 60 km/hr in Stage I and in Stage III, respectively. This might be because HC consumed O₂ and was converted to carbonaceous oxides. Under the catalytic oxidative condition, more CO₂ would be produced, which would lead to the increase of CO₂ percentage.

2.3. Chemical profiles of VOCs emitted from LDDVs

As important components of HC vehicle exhaust pollution, 56 VOC (C₂–C₁₂) chemical species were measured in all samples collected from the on-board emission measurement system, including 29 alkanes, 10 alkenes, 16 aromatic hydrocarbons, and acetylene. The average percentages of detected VOC species calculated based on µg/m³ units for different vehicle types from Stage I to Stage IV vehicles are summarized in Table 3. It was found that the abundance of alkanes was significantly higher in

diesel vehicle emissions, approximately accounting for 41.1%–45.2% of the detected compounds, followed by aromatics (27.4%–34.9%) and alkenes (19.5%–28.7%).

The most abundant species in alkanes were *n*-decane (6.6%–8.3%), *n*-undecane (6.3%–8.6%), *n*-dodecane (6.1%–8.4%), and other straight-chain alkanes, which were mainly unburned components. The dynamometer data from Liu et al. (2008c) also supported this result. Propene (9.0%–10.8%), ethene (7.3%–10.7%) and other short chain hydrocarbons had greater abundance in the alkenes, which might be related to the high thermal efficiency in the engine and efficient burning. For aromatics, benzene (4.4%–5.6%), 1,2,4-trimethylbenzene (4.3%–6.7%), and toluene (3.1%–4.3%) were the most abundant species. This clearly showed that there were no obvious differences in the constituent contents for different vehicles, and the types of fuel might be the key factors influencing the composition of the VOC spectrum.

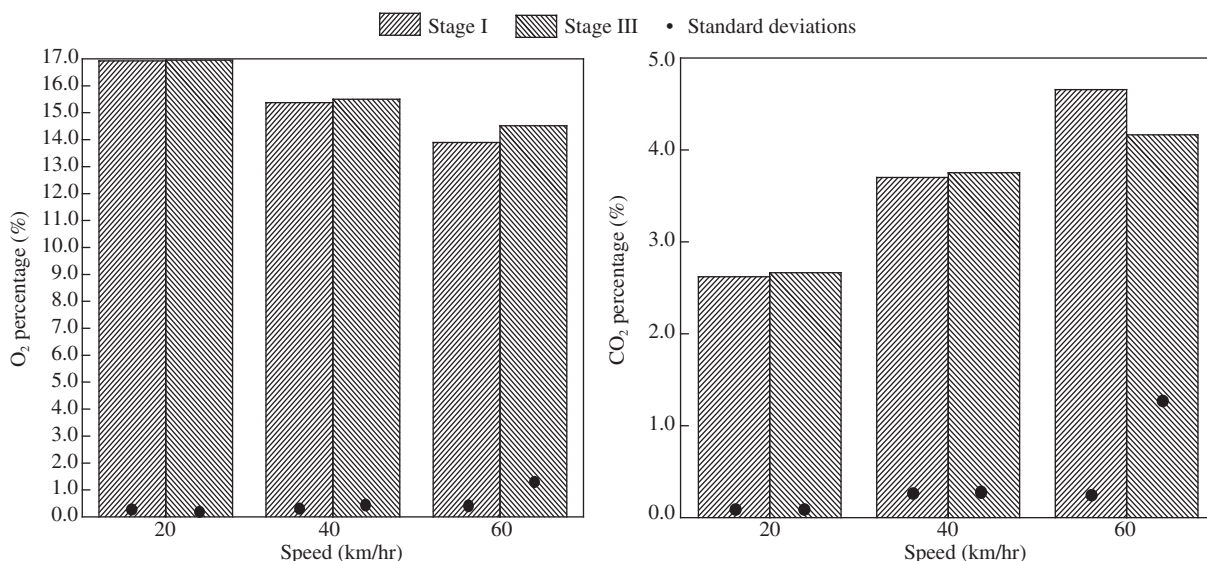


Fig. 4 – Percentage of O₂ and CO₂ under different speeds for Stage I and Stage III.

Table 3 – Chemical profiles of volatile organic compounds (VOCs) emitted from light-duty diesel vehicles (LDDVs).

| Species | | State I | | State II | | State III | | State IV | | |
|------------------------|-----------------|------------------------|-----------|----------|-----------|-----------|-----------|----------|-----------|-------|
| | | Average | Deviation | Average | Deviation | Average | Deviation | Average | Deviation | |
| Alkanes | n-Undecane | 8.66% | 5.30% | 8.00% | 3.57% | 7.51% | 6.53% | 6.32% | 2.43% | |
| | n-Dodecane | 8.41% | 5.15% | 7.97% | 3.46% | 7.29% | 6.35% | 6.11% | 2.36% | |
| | n-Decane | 6.89% | 4.00% | 8.31% | 6.16% | 7.36% | 5.80% | 6.64% | 2.35% | |
| | n-Nonane | 3.93% | 0.30% | 2.63% | 0.53% | 4.13% | 1.99% | 3.36% | 0.52% | |
| | Ethane | 2.05% | 0.68% | 1.16% | 0.15% | 2.13% | 1.65% | 2.02% | 1.29% | |
| | n-Butane | 1.43% | 0.92% | 1.32% | 0.44% | 0.87% | 0.84% | 1.85% | 3.02% | |
| | Isopentane | 1.42% | 1.81% | 0.45% | 0.09% | 1.99% | 2.97% | 0.17% | 1.90% | |
| | n-Propane | 1.35% | 0.76% | 0.67% | 0.20% | 1.41% | 1.73% | 0.69% | 0.91% | |
| | n-Octane | 1.14% | 0.21% | 0.97% | 0.14% | 1.12% | 0.45% | 1.39% | 0.41% | |
| | 2-Methylpentane | 1.06% | 0.66% | 1.66% | 0.32% | 0.58% | 0.80% | 1.44% | 0.47% | |
| | Isobutane | 0.98% | 0.44% | 0.98% | 0.30% | 0.77% | 0.56% | 1.45% | 3.29% | |
| | n-Pentane | 0.96% | 0.76% | 1.16% | 0.30% | 1.58% | 1.47% | 2.16% | 1.88% | |
| | Other Alkanes | 6.91% | 3.52% | 6.23% | 0.80% | 4.39% | 3.76% | 11.31% | 2.52% | |
| | Total Alkanes | 45.17% | 8.77% | 41.50% | 1.86% | 41.12% | 6.34% | 44.91% | 5.15% | |
| Alkenes | Propene | 10.00% | 1.35% | 8.95% | 2.75% | 10.82% | 4.09% | 9.13% | 5.53% | |
| | Ethene | 7.78% | 6.04% | 7.67% | 5.04% | 10.71% | 9.80% | 7.31% | 3.02% | |
| | 1-Butene | 3.59% | 0.49% | 2.70% | 0.85% | 3.49% | 1.37% | 1.04% | 0.42% | |
| | 1-Hexene | 1.90% | 0.17% | 1.44% | 1.15% | 1.25% | 0.54% | 0.23% | 0.04% | |
| | 1-Pentene | 1.69% | 0.15% | 1.33% | 0.21% | 1.40% | 0.63% | 0.64% | 0.04% | |
| | Other alkenes | 1.39% | 0.73% | 1.62% | 0.16% | 1.03% | 0.79% | 1.11% | 0.54% | |
| | Total alkenes | 26.34% | 7.23% | 23.72% | 7.39% | 28.71% | 12.70% | 19.46% | 4.73% | |
| | Aromatics | Benzene | 5.31% | 0.31% | 4.37% | 0.09% | 4.91% | 1.22% | 5.57% | 1.92% |
| | | 1,2,4-Trimethylbenzene | 4.32% | 2.21% | 6.66% | 3.38% | 4.51% | 2.18% | 6.13% | 1.41% |
| | | Toluene | 3.08% | 1.81% | 4.00% | 1.19% | 3.47% | 1.08% | 4.28% | 2.84% |
| m-Ethyltoluene | | 2.94% | 0.71% | 3.25% | 1.01% | 2.22% | 0.92% | 4.26% | 1.00% | |
| m,p-Xylene | | 1.94% | 0.58% | 3.01% | 1.04% | 2.84% | 1.23% | 4.66% | 2.55% | |
| 1,2,3-Trimethylbenzene | | 1.90% | 0.64% | 1.95% | 0.91% | 1.97% | 1.13% | 1.19% | 0.53% | |
| o-Xylene | | 1.37% | 0.62% | 2.44% | 0.82% | 1.77% | 0.49% | 2.83% | 0.97% | |
| Other aromatics | | 6.50% | 3.83% | 7.87% | 2.38% | 7.07% | 2.09% | 5.94% | 1.79% | |
| Total aromatics | | 27.38% | 8.03% | 33.53% | 9.63% | 28.75% | 9.50% | 34.86% | 5.03% | |
| Alkynes | | Acetylene | 1.11% | 2.27% | 1.25% | 1.19% | 1.43% | 1.03% | 0.77% | 0.22% |

2.4. Analysis of VOC ozone formation potential

It is well known that VOCs are important precursors of O₃ formation, and OFP is connected with VOC concentration and reactivity. In order to analyze the OFP of individual compounds from LDDVs, maximum incremental reactivity (MIR), a widely used method in OFP analysis, was adopted in this study (Duan et al., 2008). It can also be used to identify the high reactivity materials. More details of this method can be found in Li et al. (2014). The OFP can be calculated as follows (Liu et al., 2008b):

$$\text{OFP}_i = \text{VOC}_i \times \text{MIR}_i \quad (2)$$

where, VOC_i represents the percentage of a certain VOC species i, and MIR_i (g O₃/g VOCs) is the maximum incremental reactivity of VOC species i which can be found in Carter (1994).

According to the content of VOC components in LDDVs, the OFP analysis results are depicted in Fig. 5. It can be observed that the majority of these VOC components were alkenes and aromatics. The sum of OFP from alkenes and aromatics approximately accounted for 87.7%–91.5% of the total OFP. The OFP of acetylene was less than 1%, and was omitted. As discussed above, although the percentage of alkanes from diesel exhaust was the highest (Table 3), the OFP of alkenes were much higher and they had better reactivity in the process of atmospheric photochemical smog formation due to the higher MIR values. For instance, the O₃ formation was

dominated by alkenes, which accounted for over 43% of the total OFP, although they only accounted for about 20% of VOC concentrations. Therefore, priority measures should be taken to reduce alkene emissions to control the generation of O₃ contributed by diesel exhaust.

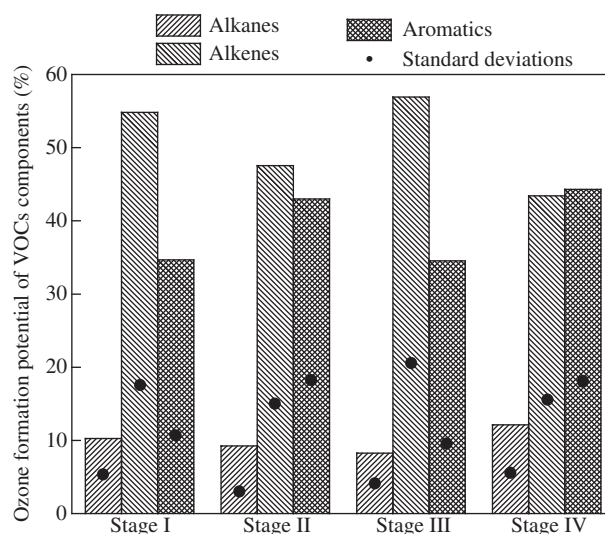


Fig. 5 – Ozone formation potential of volatile organic compound (VOC) components from diesel vehicles.

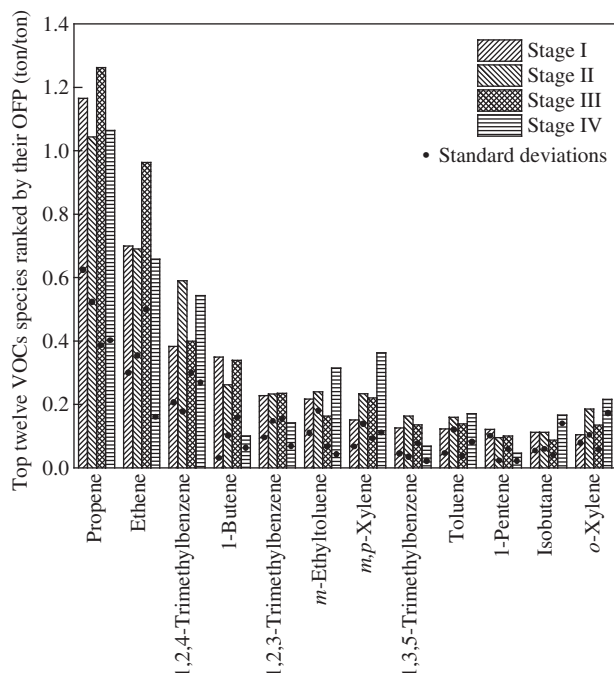


Fig. 6 – Top twelve VOC species ranked by their ozone formation potential (OFP).

The top twelve VOC species ranked by their OFP are presented in Fig. 6. The results demonstrate that the contributions of these substances accounted for 81.8%–84.7% of the total measured reactivity. Propene, ethene, 1,2,4-trimethylbenzene, 1-butene, and 1,2,3-trimethylbenzene were the largest contributors to O_3 production, accounting for 54.0%–64.8% (Qiao et al., 2012). It can also be found that the contributions to O_3 production of propene were 1.17 ton O_3 /ton VOCs, 1.04 ton O_3 /ton VOCs, 1.26 ton O_3 /ton VOCs and 1.06 ton O_3 /ton VOCs for Stage I, Stage II, Stage III and Stage IV diesel vehicles, respectively. Integrating the total VOC species, the contributors to O_3 production from Stage I, Stage II, Stage III and Stage IV were 3.78 ton O_3 /ton VOCs,

4.01 ton O_3 /ton VOCs, 4.18 ton O_3 /ton VOCs, and 3.86 ton O_3 /ton VOCs, respectively.

2.5. Stench index of VOCs

A stench is a smell that excites the olfactory senses by certain chemicals that could damage the living environment and cause displeasure to human beings. Stench pollution has often been caused by VOCs (Chen et al., 2000). VOCs with stench could lead to various diseases, such as those affecting the breathing and nervous system, even resulting in death (Sheridan et al., 2003). Odor thresholds refer to the lowest quantity of an odorous material that could be detected or the lowest concentration people could perceive. Odorant substances could be perceived when their concentrations were higher than the corresponding odor thresholds. The threshold dilution factor was applied in this study to represent the possibility of stench pollution by VOC components. The threshold dilution factor can be estimated as follows:

$$M_i = \frac{C_i}{u_i} \quad (3)$$

where, M_i represents the dilution factor of component i , C_i ($\mu\text{g}/\text{m}^3$) and u_i ($\mu\text{g}/\text{m}^3$) represent the mass concentration and odor threshold (Nagata, 2003) of component i , respectively.

The stench index of the primary VOC species emitted from vehicle exhaust is depicted in Table 4. It can be observed that odor pollution existed in the vehicle exhaust, and that the majority of stench components were aromatics, which might have a definite influence on the surrounding environment. The stench indexes of *p*-diethylbenzene, propylbenzene, *m*-ethyltoluene, and *p*-ethyltoluene were the highest, and great attention needs to be given to the stench pollution of vehicle exhaust.

3. Conclusions

The main finding from this work was that the emission factors of HC and NO_x were 0.90 ± 0.40 and 1.05 ± 0.62 g/km,

Table 4 – Stench index of VOCs species emitted from vehicle exhaust.

| | Species | Odor threshold | Stage I | Stage II | Stage III | Stage IV |
|-----------|--------------------------|----------------|---------|----------|-----------|----------|
| Alkanes | <i>n</i> -Dodecane | 834.8 | 0.9 | 0.3 | 0.7 | 0.3 |
| | <i>n</i> -Decane | 3930.4 | 0.2 | 0.1 | 0.1 | 0.1 |
| | <i>n</i> -Undecane | 6058.9 | 0.1 | 0.0 | 0.1 | 0.0 |
| | Total alkanes | – | 1.7 | 0.5 | 1.1 | 0.6 |
| Alkenes | 1-Pentene | 312.5 | 0.6 | 0.1 | 0.3 | 0.1 |
| | 1-Butene | 900.0 | 0.4 | 0.1 | 0.3 | 0.0 |
| | 1-Hexene | 525.0 | 0.4 | 0.1 | 0.2 | 0.0 |
| | Total alkenes | – | 1.4 | 0.4 | 0.9 | 0.2 |
| Aromatics | <i>p</i> -Diethylbenzene | 2.3 | 11.7 | 2.9 | 9.0 | 1.8 |
| | Propylbenzene | 20.4 | 3.7 | 1.0 | 2.6 | 0.6 |
| | <i>m</i> -Ethyltoluene | 96.4 | 3.2 | 1.1 | 1.8 | 1.7 |
| | <i>p</i> -Ethyltoluene | 44.5 | 2.2 | 0.9 | 1.7 | 1.1 |
| | <i>m,p</i> -Xylene | 234.2 | 0.9 | 0.4 | 0.9 | 0.8 |
| | Isopropylbenzene | 45.0 | 0.7 | 0.4 | 0.7 | 0.1 |
| | 1,2,4-Trimethylbenzene | 642.9 | 0.7 | 0.3 | 0.5 | 0.4 |
| | Total aromatics | – | 24.5 | 7.6 | 18.4 | 6.9 |

“–” represent data missing.

respectively, and that emission reductions of HC and NO_x have been achieved as the control technology has become more rigorous from Stage I to Stage IV. It was also found that HC and NO_x emissions and the percentage of O₂ dropped with the increase of speed, while the percentage of CO₂ was increased. The abundance of alkanes was significantly higher in diesel vehicle emissions, approximately accounting for 41.1%–45.2%, followed by aromatics and alkenes. The most abundant species were propene, ethane, *n*-decane, *n*-undecane, and *n*-dodecane. The MIR method was applied to analyze the OFP. The results indicated that the majority of VOC species were alkenes and aromatics, and the sum of OFP could account for 87.7%–91.5% of the total OFP. Propene, ethene, 1,2,4-trimethylbenzene, 1-butene, and 1,2,3-trimethylbenzene were the top five VOC species based on their OFP, and they accounted for 54.0%–64.8% of the total OFP. The threshold dilution factor was applied to represent the probability of VOC stench pollution. It was illustrated that aromatics made up the majority of stench components, especially *p*-diethylbenzene, propylbenzene, *m*-ethyltoluene, and *p*-ethyltoluene.

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