Aerosol and Air Quality Research, 15: 915–925, 2015

ISSN: 1680-8584 print / 2071-1409 online
doi: 10.4209/aaqr.2014.10.0261

On-Road Emission Characteristics of Carbonyl Compounds for Heavy-Duty Diesel Trucks

Zhiliang Yao[1*], Xi Jiang[1], Xianbao Shen[2], Yu Ye[1], Xinyue Cao[1], Yingzhi Zhang[2], Kebin He[2]

[1] *School of Food and Chemical Engineering, Beijing Technology and Business University, Beijing 100048, China*
[2] *State Key Joint Laboratory of Environment Simulation and Pollution Control, State Environmental Protection Key Laboratory of Sources and Control of Air Pollution Complex, School of Environment, Tsinghua University, Beijing 100084, China*

ABSTRACT

To study the emission characteristics of carbonyl compounds for in-use diesel vehicles on real roads, nine in-use heavy-duty diesel trucks (HDDTs) representing different emission standards from China 0 to China 3 were tested on roads in Xiamen using an on-board carbonyl compound sampling system with a 2,4-DNPH cartridge. High-performance liquid chromatography (HPLC) was used to quantify the carbonyl compound emission factors. In total, 10 carbonyl compounds were detected for all the tested vehicles in this work. Formaldehyde, acetaldehyde and propanal were the three largest contributors of carbonyl emissions, accounting for 47.9%, 21.0% and 9.9% of the total carbonyls, respectively. The emission standards had a significant effect on the emission factors and profiles of the carbonyl compounds from the test vehicles. The total emissions of carbonyls from the test vehicles with China 0, China 1, China 2 and China 3 emission standards were 318.4, 232.8, 108.1 and 88.8 mg/km, respectively. The relative contribution of formaldehyde to the total carbonyl emissions increased with increasing stringency of the emission standards. Driving patterns also affected the vehicular carbonyl emissions. The total carbonyl emissions under highway driving cycles were lower than those under non-highway driving cycles. In addition, the ozone-formation potential of the carbonyls from the tested diesel vehicles was analyzed. This work represents a preliminary step in measuring carbonyl emission characteristics using portable emission measurement systems (PEMS). More attention should be paid to carbonyl emissions from HDDTs.

Keywords: Heavy-duty diesel vehicles; Carbonyl compounds; PEMS; Emission characteristics; Xiamen.

INTRODUCTION

Carbonyl compounds are a class of organic compounds whose structures contain a carbon-oxygen double bond. These compounds mainly include aldehydes, ketones and carboxylic acids. Some carbonyls, such as formaldehyde, acetaldehyde, acrolein and methyl ethyl ketone, are toxic, mutagenic and even carcinogenic to the human body (Carlier *et al.*, 1986). Carbonyl compounds are highly reactive, making them important components in atmospheric photochemical reactions, and are sources of oxidative free radicals. Carbonyl compounds are also important precursors of photochemically formed secondary pollutants, such as ozone and peroxyacylnitrates (PAN) (Carter, 1995; Gaffney *et al.*, 1997).

Motor vehicles are a major source of atmospheric carbonyls, especially in urban areas (Grosjean *et al.*, 2001; Xu *et al.*, 2010). In the last several decades, many studies have focused on carbonyl emissions from motor vehicles (Siegl *et al.*, 1999; Caplain *et al.*, 2006; Jakober *et al.*, 2006; Pang *et al.*, 2006; He *et al.*, 2009; Song *et al.*, 2010; Zhao *et al.*, 2011; Wang *et al.*, 2013). Although diesel engines contribute very little to hydrocarbon emissions, the carbonyl emission rates per distance traveled from diesel engines have been found to be higher than those from gasoline engines (Schmid *et al.*, 1997; Grosjean *et al.*, 2001; Kristensson *et al.*, 2004; Ho *et al.*, 2007; Legreid *et al.*, 2007; Dong *et al.*, 2014). According to a 2006 emission inventory in California, diesel engines were the largest direct source of formaldehyde and acetaldehyde, accounting for 50 and 57% of total anthropogenic emissions, respectively (Ban-Weiss *et al.*, 2007). Thus, it is very important to understand the carbonyl emissions from diesel vehicles.

In previous studies, dynamometer testing and tunnel studies were the main methods used to measure the carbonyl emissions from motor vehicles. However, dynamometer testing does not represent real driving cycles on roads and is limited by the total weight of the tested vehicles. In

[*] Corresponding author.
Tel./Fax: +86 10 6898 4852
E-mail address: yaozhl@th.btbu.edu.cn

addition, tunnel studies only reflect the average emissions of a vehicle fleet. In the past several years, on-road testing based on portable emission-measurement systems (PEMS) has been widely used to study the emission characteristics of vehicles because this method accurately reflects the real emission profiles of individual vehicles on the road (Wang *et al.*, 2005; Yao *et al.*, 2007; Liu *et al.*, 2009; Wang *et al.*, 2011; Yao *et al.*, 2011; Hu *et al.*, 2012; Huo *et al.*, 2012). However, most of the studies based on PEMS focused only on the total hydrocarbons and other pollutants, and few studies have focused on vehicular carbonyl emissions.

The main aim of this study was to understand the real emission levels and emission characteristics of carbonyls from heavy-duty diesel trucks (HDDTs) in China. In this work, nine in-use HDDTs that met different emission standards were tested using PEMS on roads in Xiamen, China. The carbonyl compounds in the exhausts of the tested vehicles were sampled with 2,4-DNPH cartridges and were quantified by high-performance liquid chromatography (HPLC). The carbonyl emission characteristics of HDDTs were analyzed based on the test data. In addition, the ozone-formation potential of the carbonyls from the tested diesel vehicles was calculated. The results of this study will be helpful to understand and control the emissions of carbonyls from HDDTs in China.

METHODS

Test System

In this study, a combined portable emission-measurement system (PEMS) was used to sample the carbonyl emissions from vehicle exhaust, as shown in Fig. 1. This PEMS mainly comprised a SEMTECH-DS device (Sensors Inc., USA), an exhaust-flow meter (EFM), a micro-proportional sample system (MPS), a carbonyl-sampling unit and a data collection unit. The SEMTECH-DS was used to measure the CO_2, CO, NO_x and THC at one-second resolution. A GPS was included to measure the instantaneous speed and altitude. A 4-inch EFM tube was used to measure the exhaust mass flow of the vehicular exhaust. MPS was used to dilute the exhaust sample before carbonyl compound sampling. The carbonyl-sampling unit included a potassium iodide (KI) silicone tube, a two-stage 2,4-dinitrophenylhydrazine (DNPH) absorption cartridge, a flow meter and a Gast sampling pump. More detailed information on the equipment can be found in our previous studies (Yao *et al.*, 2007; Liu *et al.*, 2009; Yao *et al.*, 2011; Huo *et al.*, 2012; Zhang *et al.*, 2013).

Test Vehicles and Routes

In total, nine heavy-duty diesel trucks (HDDTs) were selected to measure the carbonyl emissions in Xiamen in this study. All of the tested vehicles were rented from private owners and were used under normal operation conditions. The model years of the tested vehicles spanned from 1999 to 2011. No exhaust after-treatment equipment was installed in the tested vehicles. More detailed information on the tested vehicles is listed in Table 1.

The China 4 vehicular emission standards for the compressive ignition engines used for heavy-duty diesel vehicles were implemented in 2013 in Xiamen, China. Because China 4 had not yet been implemented during the period of our tests, the tested HDDTs in this work included only technologies that met China 0 to China 3. In addition, it was very difficult to find China 0 and China 1 HDDTs in

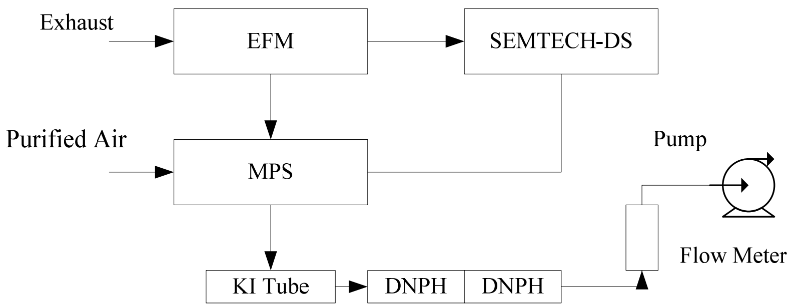


Fig. 1. PEMS for measuring carbonyl compounds in motor-vehicle exhaust.

Table 1. Characteristics of the tested diesel trucks.

Test No.	Vehicle Model	Model Year	Total Mass (kg)	Engine Capacity (L)	Odometer (km)	Emission Standard
XM01	Dongfeng EQ1141G7D3	1999	14900	5.9	602208	China 0
XM02	Hanyang HY5140XXY	2003	17100	6.5	701040	China 1
XM03	Dadi RX5200XXY	2006	20495	7.3	600105	China 2
XM04	XingguangCAH5200XYPIK2L11T	2007	20010	7.3	360312	China 2
XM05	Jiefang CA1241PK2L11T4A95	2006	24375	7.1	300050	China 2
XM06	Dongfeng EQ5161XXY2E1	2008	16010	7.3	172958	China 2
XM07	Jiefang CA5283XXYP7K2L11	2009	28010	7.7	236902	China 3
XM08	Dongfeng DFL5311XXBA8	2010	31000	8.9	144507	China 3
XM09	Jiefang CA1250PK217T3EA	2011	25000	7.1	39912	China 3

Xiamen. Thus, in this study, only one China 0 and one China 1 HDDT were tested. The fuel used by the tested vehicles in this study was commercial 0# diesel, which conforms to the third-phase fuel-quality standard in China.

In this study, a fixed route method following the traffic on the roads was used to measure the emissions of the tested vehicles in Xiamen (Yao *et al.*, 2007; Huo *et al.*, 2012). A typical test route included different types of roads in the Jimei District of Xiamen. The total length of the test route was approximately 32.9 km, including 21.7 km of non-highways and 11.2 km of highways. The testing was conducted in March 2012. The ambient temperature on the test days was approximately 20°C. For all the tested vehicles, the engines were under hot stabilized conditions.

Sampling and Quantification Analysis of Carbonyls

The carbonyl emissions were sampled while the tested vehicle was driven on the pre-designed test routes using the combined sampling system described in the above section. For each vehicle, the carbonyls were separately sampled on highways and non-highways of the test route and were tested twice.

Aldehydes and ketones were trapped on a two-stage DNPH absorption cartridge followed by the extraction of derivatized compounds and HPLC analysis. A KI tube was used to remove the influence of O_3 before the sample passed through the DNPH cartridge. The DNPH and KI tubes were produced by Agela Technologies Inc. in Tianjin, China. The sampling flow rate was controlled at a rate of 1.2 L/min.

HPLC (Agilent1200) was used to quantify the carbonyl emissions. The separation column was an Agilent C-18 column (4.6 × 250 mm I.D., 5 µm), and the mobile phase was acetonitrile (HP) and high-purity water. The column temperature was controlled at 25°C, the flow rate was set at 1.0 mL/min, and the injection volume was 50 µL. An ultraviolet detector was used, and the detection wavelength was 360 nm.

A standard solution of a mixture of 15 carbonyl-DNPH derivatives (TO-11; Supelco Inc., Bellefonte, PA, USA) was used to determine the aldehyde and ketone concentrations. More detailed information about the sampling and analysis of carbonyls can be found in our previous study (Zhang *et al.*, 2013).

RESULTS AND DISCUSSION

Carbonyl Components and Emissions from the HDDTs

From the nine tested heavy-duty diesel trucks (HDDTs), a total of 10 carbonyl compounds were detected. For almost all the tested vehicles, eight carbonyl compounds were found, including formaldehyde, acetaldehyde, acraldehyde, acetone, propanal, butyraldehyde, crotonaldehyde and benzaldehyde. Valeraldehyde and methyl benzaldehyde were found in the exhaust of several of the tested vehicles.

Table 2 lists the minimum, maximum and average values of the emission factors and the percentage composition of carbonyls for the tested vehicles. From Table 2, the emission of total carbonyls from the tested vehicles varied from 83.1 to 318.4 mg/km, and the average value was 138.9 mg/km. There was an approximately 3.8-fold difference between the maximum and minimum emission factors due to the emission standards used. The maximum and minimum carbonyl emissions were from the XM 01 and XM 08 test vehicles, respectively, which conformed to the China 0 and China 3 emission standards, respectively. Further discussion of the impacts of emission standards on carbonyl emissions is provided in the following section.

Regarding the compositions of the carbonyl emission species, we can observe in Table 2 that low molecular weight aldehydes and ketones composed the majority of the carbonyl-emission factors from the tested vehicles. The average percentage distribution of the carbonyls for all the tested vehicles showed that formaldehyde, acetaldehyde and propanal were the top three emission components and contributed approximately 47.9%, 21.0% and 9.9%, respectively. The three most-abundant compounds comprised approximately 80% of the total emissions. Other studies have also observed that low molecular weight aldehydes and ketones are the main vehicular carbonyl emissions (Sawant *et al.*, 2007; Dong *et al.*, 2014). Based on real-world testing of nine Class 8 HDD tractors operated on the ARB 4-Mode heavy HDDT driving cycle, Sawant *et al.* (2007) found that formaldehyde and acetaldehyde were the two largest contributors to the total carbonyl emissions, with median

Table 2. Carbonyl emission factors and component distributions for the tested vehicles.

Component	Emission factor (mg/km)			Percentage (%)		
	Min	Max	Avg	Min	Max	Avg
Formaldehyde (C1)	41.04	104.30	61.75	32.8	60.6	47.9
Acetaldehyde (C2)	14.15	63.36	28.70	14.9	26.5	21.0
Acraldehyde (C3)	1.86	22.86	7.51	1.9	8.1	4.7
Acetone (C3)	ND[a]	25.62	7.70	ND	8.7	4.6
Propanal (C3)	ND	26.50	13.51	ND	17.7	9.9
Crotonaldehyde (C4)	1.90	33.04	9.05	2.0	11.2	5.4
Butyraldehyde (C4)	ND	21.32	4.78	ND	9.2	3.1
Benzaldehyde (C7)	0.83	22.25	5.38	1.0	7.0	2.8
Valeraldehyde (C5)	ND	1.26	0.14	ND	1.3	0.1
Methyl-Benzaldehyde (C8)	ND	2.28	0.38	ND	2.3	0.4
Total	83.1	318.4	138.9			

[a] not detected.

Table 3. Comparison of the carbonyl emission factors in this study with those in the references.

	Emission factor (mg/km)		
	Formaldehyde	Acetaldehyde	Total carbonyls
Average for HDDTs (this study)	61.8	28.7	138.9
HDDVs under VECC driving cycle (Dong *et al.*, 2014)	19.81	11.41	109.1
HDDVs under C-WTVC driving cycle (Dong *et al.*, 2014)	8.45	5.18	69.6
HDVs in Tuscarora Mountain Tunnel, 1999 (Grosjean *et al.*, 2001)	6.73	3.95	26.1
MDDTs under FTP test cycle (Schauer *et al.*, 1999)	22.3	41.8	169
HDVs in the Tuscarora Mountain Tunnel, 1992 (Pierson *et al.*, 1996)	32.7	20.0	

relative contributions of 53.7% and 18.4%, respectively, similar to the results in this study. Dong *et al.* (2014) found that acetaldehyde, acetone and propionaldehyde were the most abundant species in the emissions from heavy-duty diesel vehicles tested on a chassis dynamometer using typical heavy-duty driving cycles and fuel economy cycles.

Table 3 compares the carbonyl emission factors in this study with those reported in other studies. The average emission of total carbonyls (138.9 mg/km) for the HDDTs tested in this study was comparable to the results for heavy-duty diesel vehicles (26.1–169 mg/km) reported in other studies (Pierson *et al.*, 1996; Schauer *et al.*, 1999; Grosjean *et al.*, 2001; Dong *et al.*, 2014). The average emission of formaldehyde (61.8 mg/km) was higher than that reported in the references (6.73–32.7 mg/km). The average emission of acetaldehyde in this study was 28.7 mg/km, while in other studies, the results ranged from 3.95–41.8 mg/km. However, it should be noted that there were large differences among the carbonyl emissions in the different studies. This pattern was mainly due to the differences in the test conditions in different studies (Table 3). The average speed of the test driving cycle in this study was 38.4 km/hr, which was higher than that of the VECC driving cycle used by Dong *et al.* (2014) (15.1 km/hr) and the FTP test cycle used by Schauer *et al.* (1999) (34.1 km/hr) and lower than that of the C-WTVC driving cycle used by Dong *et al.* (2014) (41.0 km/hr. This difference would lead to the varying carbonyl emissions results. The effect of the driving cycles on carbonyl emissions will be discussed further in the following section. In addition, the differences in vehicle engine type, exhaust control technology, fuel composition and so on were important factors. This finding also demonstrates the need to establish local emission profiles of carbonyls from motor vehicles (Ho *et al.*, 2007).

Influence of Emission-Control Level on Carbonyl Emissions for HDDTs

As described in the previous section, emission standards have an important influence on the carbonyl emissions from HDDTs. Fig. 2 presents the emissions of formaldehyde, acetaldehyde and total carbonyls per distance traveled for all the tested vehicles in this study. The total carbonyl emissions for the test vehicles with China 0, China 1, China 2 and China 3 emission standards were 318.4, 232.8, 108.1 and 88.8 mg/km, respectively; for formaldehyde, the emissions were 104.3, 96.4, 53.9 and 46.5 mg/km, respectively; and for acetaldehyde, the emissions were 63.4, 46.4, 22.5 and 19.5 mg/km, respectively. It is obvious that the emissions of formaldehyde, acetaldehyde and total carbonyls for the China 0 and China 1 tested HDDTs were significantly higher than those of all the other tested HDDTs. Compared to the China 2 tested vehicles, the emissions of formaldehyde, acetaldehyde and total carbonyls from the China 3 tested vehicles were reduced by 13.7%, 13.2% and 17.9%, respectively.

As listed in Table 1, the total masses and the engine capacity of the tested vehicles varied. In addition, although the test routes for all the tested vehicles were the same, there were small differences between the driving cycles of the tested vehicles. These factors would weaken the basis of the comparison of emission factors of carbonyls. To alleviate the impact of vehicle weight and driving cycle, we calculated the carbonyl emissions based on the CO_2 emissions of the tested HDDTs, as shown in Fig. 3. The total carbonyl emissions based on the CO_2 emissions of the test vehicles with China 0, China 1, China 2 and China 3 emission standards were 0.42, 0.30, 0.17 and 0.11 mg/g CO_2, respectively. The average total carbonyl emissions from the China 3 tested HDDTs were 38.8% lower than those of the China 2 HDDTs. Similar trends were observed for formaldehyde and acetaldehyde. The emission factors of these compounds for the China 3 tested vehicles decreased by 37.0% and 35.4% compared with those for the China 2 vehicles.

At present, there are no specific carbonyl-emission standards for vehicles within the Chinese vehicular-emission standards. The existing standards only focus on the emission of hydrocarbons (HC). Regarding HDDTs, China enforced the China 1, 2 and 3 regulations for compressive ignition engines in the years 2001, 2005 and 2008, respectively, with corresponding HC emission limits of 1.1, 1.1 and 0.66 g/kWh. The China 3 limit was 29% lower than the China 2 limit. As described in the above section, the carbonyl emissions decreased by 38.8% from the China 2 vehicles to the China 3 HDDTs in this study. Therefore, more stringent vehicular-emission standards have important effects on the reduction of carbonyl emissions for HDDTs in China.

In addition, compared with the results based on distance traveled, the changes of formaldehyde, acetaldehyde and total carbonyl emissions based on CO_2 emissions from China 2 to China 3 were different. This pattern may be due to the differences in the total weight and driving cycles among the tested vehicles. The influence of the driving cycle on the carbonyl emissions of the HDDTs will be discussed in the following section. To address the impact of vehicle weight on carbonyl emissions, more studies should be carried out in the future.

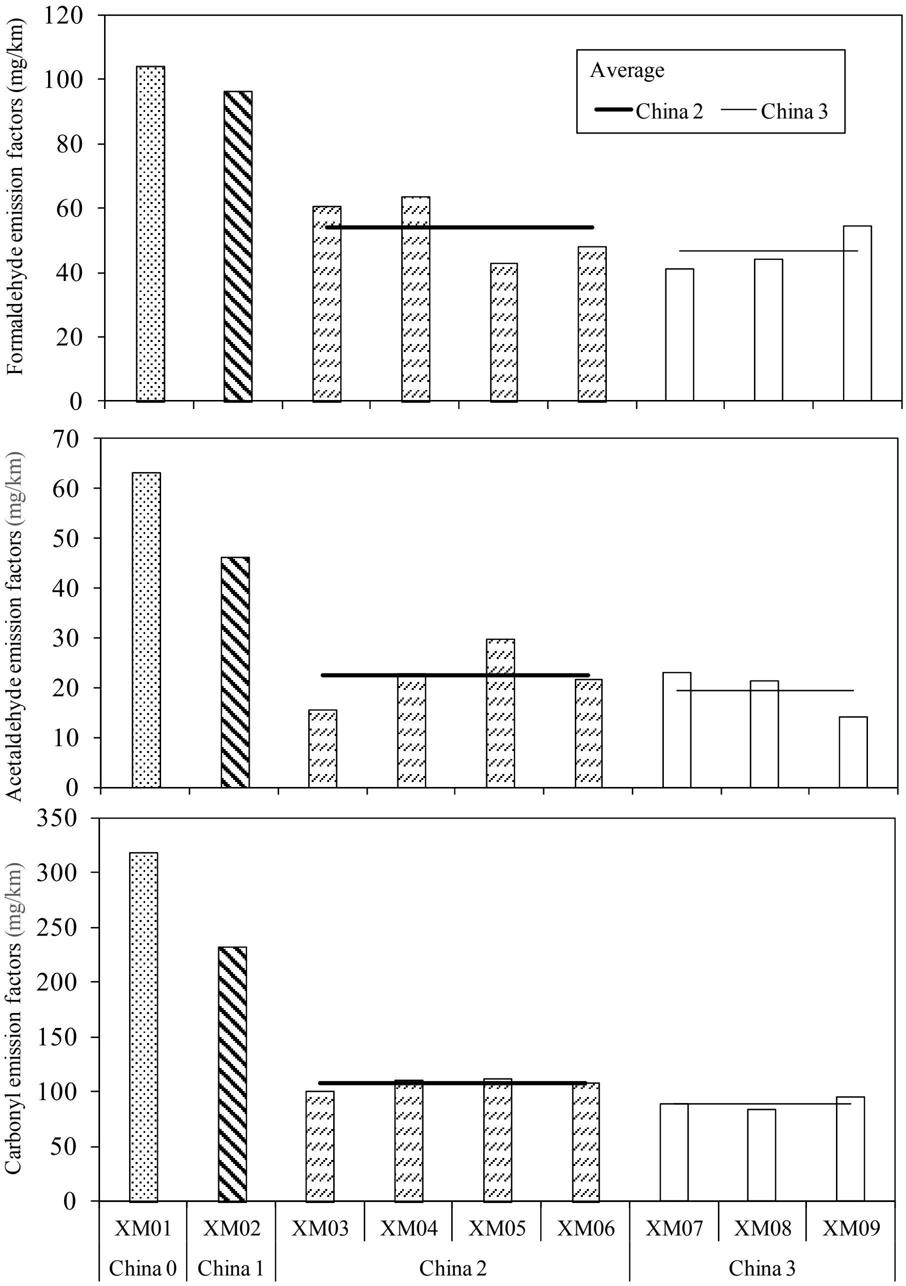


Fig. 2. Emissions of formaldehyde, acetaldehyde and total carbonyls based on mileage traveled for all the tested vehicles.

The emission standards also had significant impacts on the compositions of the carbonyl emissions from the tested HDDTs. As shown in Fig. 4, we plotted the composition distribution of the carbonyls on the basis of carbon numbers against the emission standards. The share rates of C1 (formaldehyde) for the total carbonyl emissions of the tested vehicles increased from China 0 to China 3. However, there was a decrease in the proportion of C > 3 compounds with the tightening of emission standards. Combined with the above conclusion, we can see that the emission standards had different effects on the individual carbonyl emissions. The proportion of carbonyls with relatively fewer carbons and lower molecular weights increased with tightening emission standards.

Influence of Driving Cycles on Carbonyl Emissions from the HDDTs

It is well known that the driving cycles of vehicles have important impacts on vehicular emissions. We calculated the average speed of the vehicles tested on the non-highway and highway test routes individually, as shown in Fig. 5. The average speeds of the nine tested HDDTs on the non-highway test route varied from 27.3 to 46.0 km/hr, and the average speed was 33.2 km/hr; the average speeds of the nine tested HDDTs on the highway test route were between 41.7 and 55.8 km/hr, and the mean speed was 48.4 km/hr. There was a significant difference between the speeds of the driving cycles on the non-highway and highway test routes. As a result, the carbonyl emissions varied under the

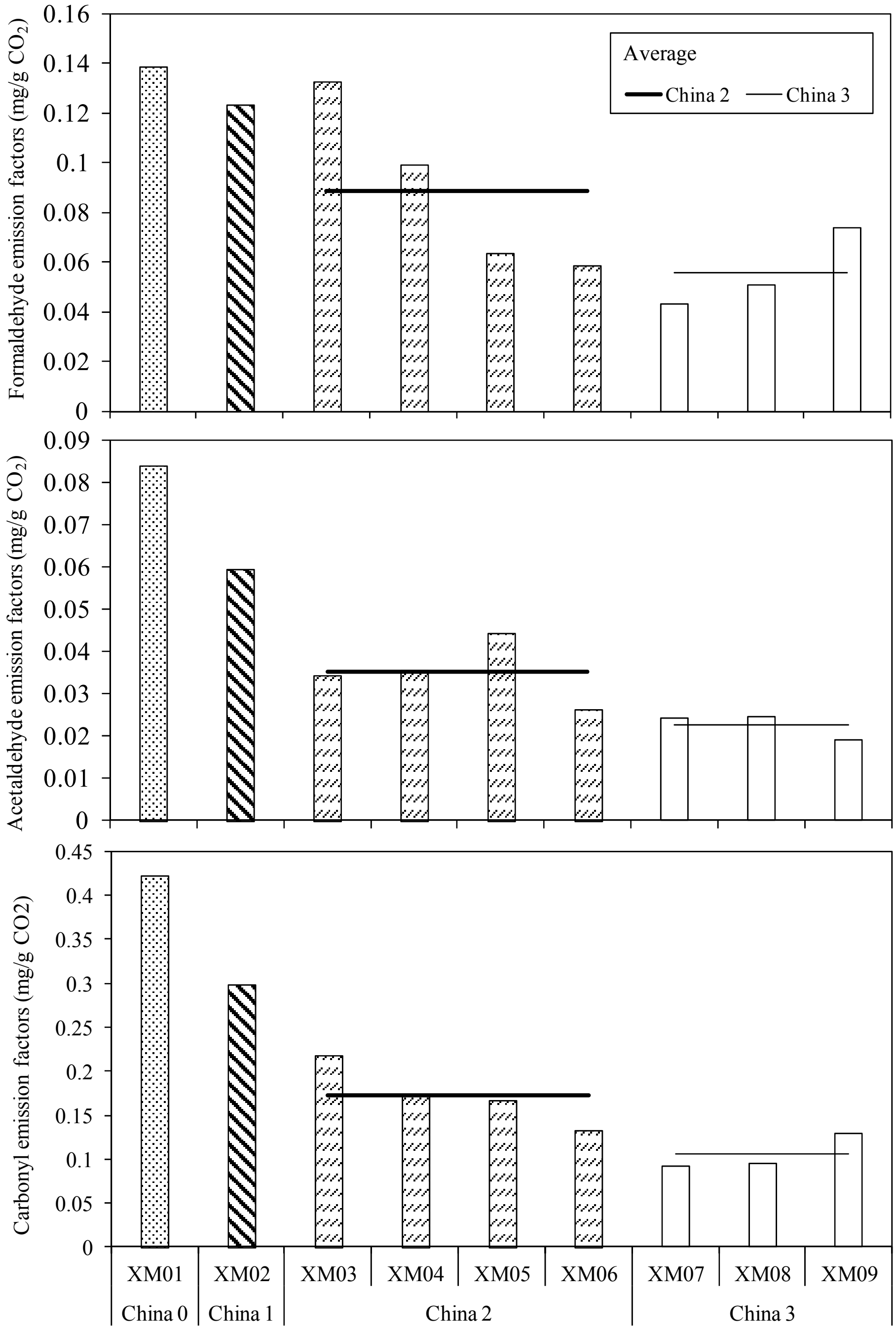


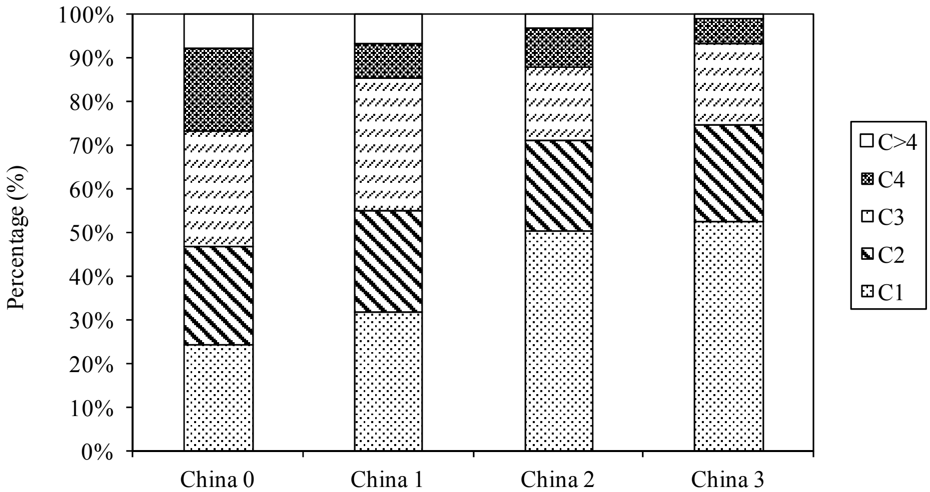
Fig. 3. Emissions of formaldehyde, acetaldehyde and total carbonyls based on CO_2 emissions for all the tested vehicles.

non-highway and highway driving cycles.

Fig. 6 presents the emissions of formaldehyde, acetaldehyde and total carbonyls under the non-highway and highway test routes relative to distance traveled for all the tested vehicles in this study. The average emissions of formaldehyde, acetaldehyde and total carbonyls for the test vehicles under the non-highway driving cycle were 66.3, 32.1 and 156.3 mg/km, respectively, which were 1.3, 1.4 and 1.5 times higher than those under the highway driving cycle, respectively.

Considering the slight differences in the total weights and driving speeds among the test vehicles, we also calculated the carbonyl-emission factors under non-highway and highway test routes based on CO_2 emissions, as shown in Fig. 7. The average emissions of formaldehyde, acetaldehyde and total carbonyls for the test vehicles under the non-highway driving cycle were 0.09, 0.04 and 0.21 mg/g CO_2, respectively, representing increases of 1.2-, 1.3- and 1.4-fold, respectively, relative to the highway driving cycle.

The effect of speed on carbonyl emissions has also been observed in other studies. For example, Dong *et al.* (2014) reported that the carbonyl emissions from heavy-duty diesel vehicles at low speeds (15.1 km/hr) were 60% greater than those at high speeds (41.0 km/hr). Tsai *et al.* (2012) found



Note: C1, formaldehyde; C2, acetaldehyde; C3, acraldehyde, acetone, propanal; C4, butyraldehyde, crotonaldehyde, C > 4, other carbonyls

Fig. 4. Influence of emission-control standards on composition distributions of carbonyl emissions for tested HDDTs.

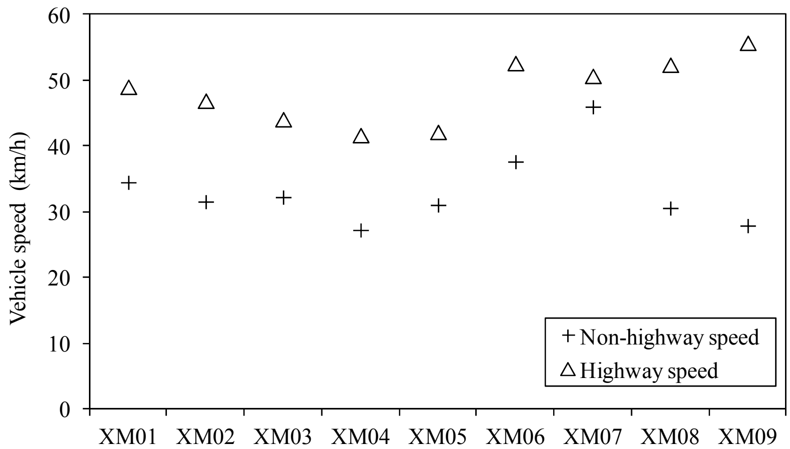


Fig. 5. Average speeds of the tested vehicles on non-highway and highway test routes.

that the carbonyl emissions from light-duty diesel vehicles were 24.6 and 11.8 mg/km under an FTP cycle (average speed 34.1 km/hr) and a highway cycle (average speed 77.7 km/hr), respectively. This pattern primarily occurs because more fuel is needed for acceleration and speed maintenance under low-speed driving cycles, and thus, incomplete combustion leads to high carbonyl emissions due to the oxygen-enriched combustion conditions in the diesel engine (Dong *et al.*, 2014).

Ozone-Formation Potential

In this study, we used the ozone-formation potential (OFP) calculated by the Carter method (Carter, 1994) to assess the contribution of the tested vehicles' exhaust to photochemical ozone production. This method was based on a model scenario in which VOCs yield a maximum ozone formation, represented by a maximum incremental reactivity (MIR, g O_3/g VOC) (Carter, 1994). The OFPs calculated for the nine tested HDDTs are presented in Fig. 8. From the figure, the OFPs of the XM01 and XM02 test vehicles were 1769.9 and 1341.2 mg O_3/km, respectively, values that were significantly higher than those of the China 2 and China 3 test vehicles. The average OFPs of the China 2 and China 3 test HDDTs were 667.9 and 573.3 mg O_3/g VOC. Compared to the China 2 test HDDTs, the OFP of the China 3 test HDDTs was lower by 14.2%. With increasing strictness of emission standards, the OPFs of the HDDTs decreased, following the same trend as that of the carbonyl emissions. Regarding the contribution of the carbonyl-emissions profile for ozone formation, formaldehyde, acetaldehyde and propanal were the top three species. Similar results can also be found in other studies (Dong *et al.*, 2014). Dong *et al.* (2014) obtained an OFP from carbonyls of tested heavy-duty diesel vehicle exhaust of 537 mg O_3/km, and formaldehyde, acetaldehyde and methylglyoxal revealed high ozone-formation potential.

CONCLUSIONS

In this study, nine heavy-duty diesel trucks (HDDTs) in

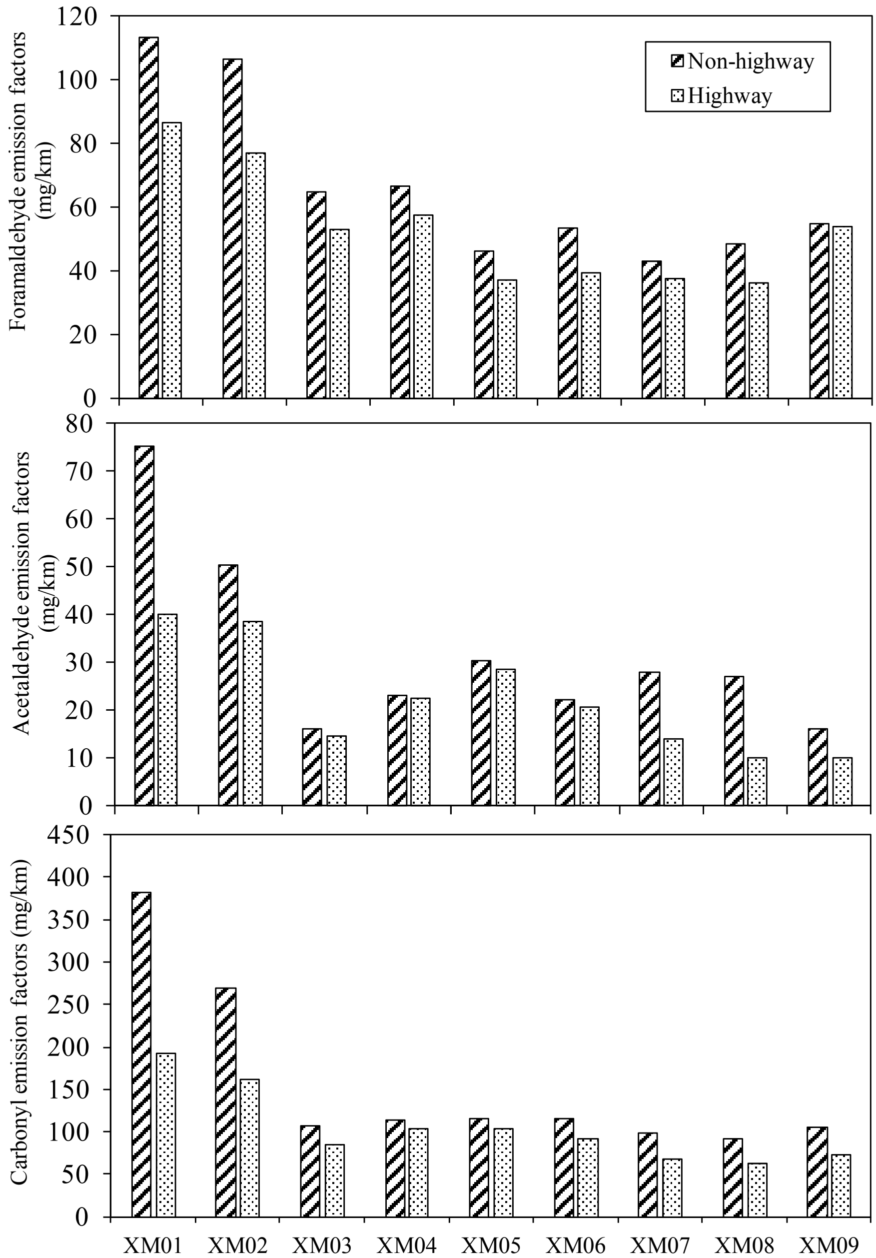


Fig. 6. Emissions of formaldehyde, acetaldehyde and total carbonyls based on mileage traveled under non-highway and highway driving cycles for all the tested vehicles.

Xiamen were tested in the real world with on-board emission measurements, and the carbonyl emissions were sampled and quantified.

Based on the nine tested HDDTs, 10 carbonyl compounds were detected in this work, including formaldehyde, acetaldehyde, acraldehyde, acetone, propanal, butyraldehyde, crotonaldehyde, benzaldehyde, valeraldehyde and methyl benzaldehyde. Among the species in the carbonyl emissions, formaldehyde, acetaldehyde and propanal were the three most-abundant compounds; together, these three compounds accounted for approximately 80% of the emissions. Carbonyls of lower molecular weight were the main pollutants in the vehicular carbonyl emissions. The carbonyl emissions from the nine tested vehicles ranged from 83.1 to 318.4 mg/km, and the average value was 138.9 mg/km. The results of this study were comparable to the test results of other studies. However, there were large differences among the carbonyl emissions from different studies due to differences in the vehicle engine, exhaust-control technology, driving cycle, fuel composition and so on. It is therefore necessary to establish local emission profiles of carbonyls for motor vehicles in China.

Emission standards had a very important influence on the carbonyl emissions from the tested HDDTs. The average carbonyl emissions from the tested China 2 and China 3 HDDTs were higher than those from the China 0 and China 1 HDDTs. Compared to the China 2 tested vehicles, the emissions of formaldehyde, acetaldehyde and total

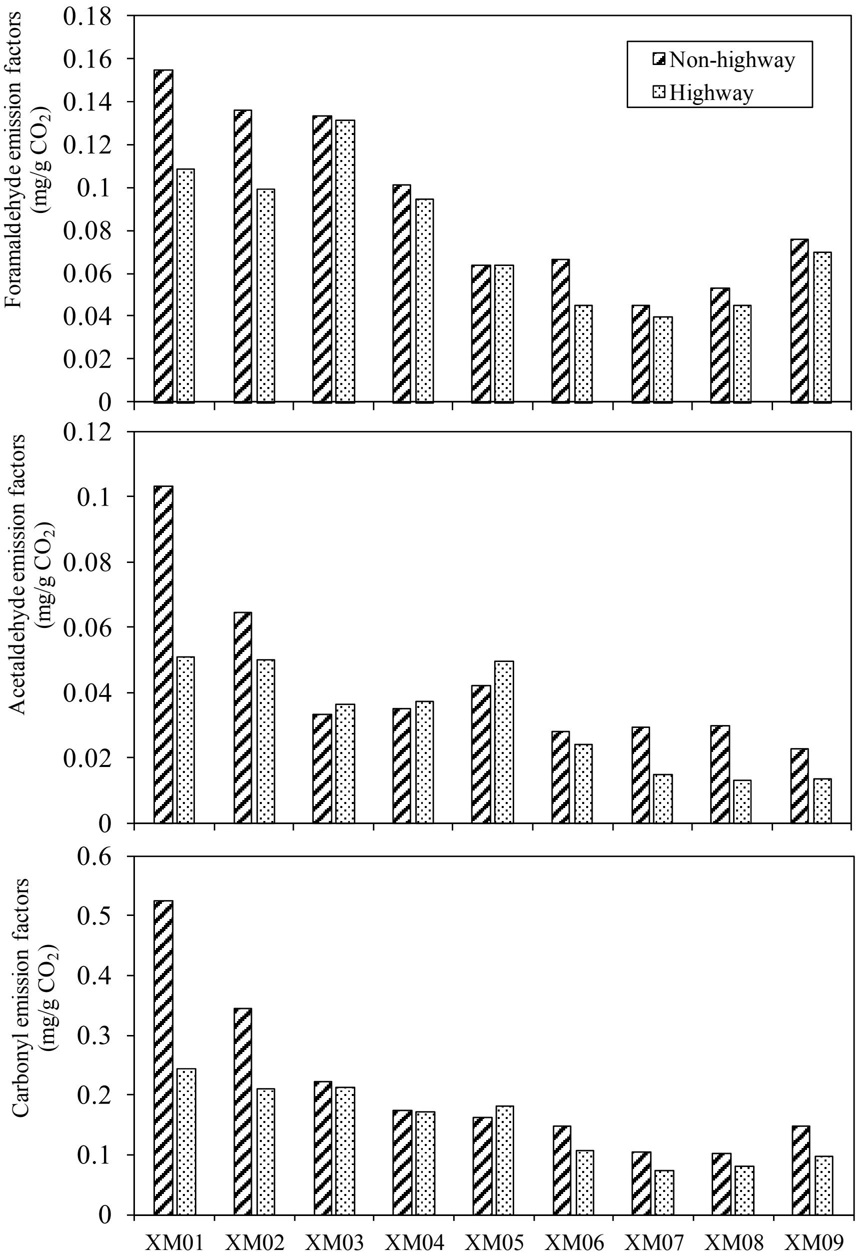


Fig. 7. Emissions of formaldehyde, acetaldehyde and total carbonyls based on CO_2 emissions for all the tested vehicles.

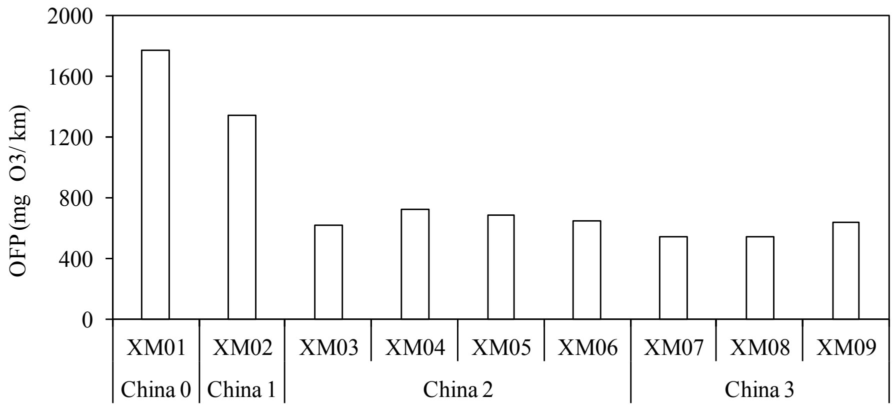


Fig. 8. Ozone-formation potential for all the tested vehicles.

carbonyls from the China 3 tested vehicles decreased by 13.7%, 13.2% and 17.9%, respectively. As a result, the OPF produced by the HDDTs conforming to the new emission standards had a lower value. In addition, the emissions of carbonyl species also decreased with the tightening of vehicular-emission standards. The emission standards had different effects on individual carbonyl emissions. There was a smaller reduction in the carbonyls with fewer carbons compared with the reductions observed for longer-chain carbons along with increasing strictness in the emission standards. Although there is no regulation of carbonyl emissions for vehicles in China, the strictness of emission-control standards for heavy-duty diesel engines focused on HC also had an important effect on the carbonyl emissions from HDDTs.

The driving cycle also had an important impact on the carbonyl emissions from the HDDTs. The average emissions of formaldehyde, acetaldehyde and total carbonyls for the test vehicles under the non-highway driving cycle were 0.09, 0.04 and 0.21 mg/g CO_2, respectively, which were 1.2, 1.3 and 1.4 times higher than those under the highway driving cycle. Low-speed driving cycles produced more carbonyl emissions from the HDDTs. From this conclusion, we note that the emission factors determined using the lab dynamometer method may create uncertainty due to the unrealistic driving cycles used.

This study represents preliminary research on the carbonyl emissions of HDDTs on real roads using the PEMS method, although only some of the important factors were considered. There remains considerable work to be done to better understand vehicle emissions in China. In the future, additional factors such as the vehicle sample, cold-start driving pattern, vehicle type, engine capacity, tailpipe control method, vehicle condition, load, fuel composition and temperature should be considered.

ACKNOWLEDGEMENTS

The authors thank the National Science Foundation of China (41275124, 41005068) and the Beijing Municipal Natural Science Foundation (8142011).

REFERENCES

Ban-Weiss, G.A., McLaughlin, J.P., Harley, R.A., Kean, A.J., Grosjean, E. and Grosjean, D. (2008). Carbonyl and Nitrogen Dioxide Emissions from Gasoline- and Diesel-Powered Motor Vehicles. *Environ. Sci. Technol.* 42: 3944–3950.

Caplain, I., Cazier, F., Nouali, H., Mercier, A., Déchaux, J., Nollet, V., Joumard, R., André, J. and Vidon, R. (2006). Emissions of Unregulated Pollutants from European Gasoline and Diesel Passenger Cars. *Atmos. Environ.* 40: 5954–5966.

Carlier, P., Hannachi, H. and Mouvier, G. (1986). The Chemistry of Carbonyls in the Atmosphere—A Review. *Atmos. Environ.* 20: 2079–2099.

Carter, W.P.L. (1994). Development of Ozone Reactivity Scales for Volatile Organic-Compounds. *J. Air Waste Manage. Assoc.* 44: 881–899.

Dong, D., Shao, M., Li, Y., Lu, S., Wang, Y., Ji, Z. and Tang, D. (2014). Carbonyl Emissions from Heavy-duty Diesel Vehicle Exhaust in China and the Contribution to Ozone Formation Potential. *J. Environ. Sci.* 26: 122–128.

Gaffney, J.S., Marley, N.A., Martin, R.S., Dixon, R.W., Reyes, L.G. and Popp, C.J. (1997). Potential Air Quality Effects of Using Ethanol–Gasoline Fuel Blends: A field Study in Albuquerque, New Mexico. *Environ. Sci. Technol.* 31: 3053–3061.

Grosjean, D., Grosjean, E. and Gertler, A.W. (2001). On-road Emissions of Carbonyls from Light-duty and Heavy-duty Vehicles. *Environ. Sci. Technol.* 35: 45–53.

He, C., Ge, Y., Tan, J., You, K., Han, X., Wang, J., You, Q. and Shah, A.N. (2009). Comparison of Carbonyl Compounds Emissions from Diesel Engine Fueled with Biodiesel and Diesel. *Atmos. Environ.* 43: 3657–3661.

Ho, K.F., Ho, S.S.H., Cheng, Y., Lee, S.C. and Yu, J.Z. (2007). Real-world Emission Factors of fifteen Carbonyl Compounds Measured in a Hong Kong Tunnel. *Atmos. Environ.* 41: 1747–1758.

Hu, J., Wu, Y., Wang, Z., Li, Z., Zhou, Y., Wang, H., Bao, X. and Hao, J. (2012). Real-world Fuel Efficiency and Exhaust Emissions of Light-duty Diesel Vehicles and Their Correlation with Road Conditions. *J. Environ. Sci.* 24: 865–874.

Huo, H., Yao, Z., Zhang, Y., Shen, X., Zhang, Q. and He, K. (2012). On-board Measurements of Emissions from Diesel Trucks in Five Cities in China. *Atmos. Environ.* 54: 159–167.

Jakober, C.A., Robert, M.A., Riddle, S.G., Destaillats, H., Charles, M.J., Green, P.G. and Kleeman, M. (2008). Carbonyl Emission from Gasoline and Diesel Motor Vehicles. *Environ. Sci. Technol.* 42: 4697–4703.

Kristensson, A., Johansson, C., Westerholm, R., Swietlicki, E., Gidhagen, L., Wideqvist, U. and Vesely, V. (2004). Real-world Traffic Emission Factors of Gases and Particles Measured in a Road Tunnel in Stockholm, Sweden. *Atmos. Environ.* 38: 657–673.

Legreid, G., Reimann, S., Steinbacher, M., Staehelin, J., Young, D. and Stemmler, K. (2007). Measurements of OVOCs and NMHCs in a Swiss Highway Tunnel for Estimation of Road Transport Emissions. *Environ. Sci. Technol.* 41: 7060–7066.

Liu, H., He, K., Lents, J., Wang, Q. and Tolvett, S. (2009). Characteristics of Diesel Truck Emission in China Based on Portable Emissions Measurement Systems. *Environ. Sci. Technol.* 43: 9507–9511.

Pang, X., Shi, X., Mu, Y., He, H., Shuai, S., Chen, H. and Li, R. (2006). Characteristics of Carbonyl Compounds Emission from a Diesel-engine Using Biodiesel-ethanol-diesel as Fuel. *Atmos. Environ.* 40: 7057–7065.

Pierson, W.R., Gertler, A.W., Robinson, N.F., Sagebiel, J.C., Zielinska, B., Bishop, G.A., Stedman, D.H., Zweidinger, R.B. and Ray, W.D. (1996). Real-world Automotive Emissions—Summary of Studies in the Fort McHenry and Tuscarora Mountain Tunnels. *Atmos. Environ.* 30: 2233–2256.

Sawant, A.A., Shah, S.D., Zhu, X., Miller, J.W. and

Cocker, D.R. (2007). Real-world Emissions of Carbonyl Compounds from In-use Heavy-duty Diesel Trucks and Diesel Back-Up Generators (BUGs). *Atmos. Environ.* 41: 4535–4547.

Schauer, J.J., Kleeman, M.J., Cass, G.R. and Simoneit, B.R.T. (1999). Measurement of Emissions from Air Pollution Sources. 2. C1 through C30 Organic Compounds from Medium Duty Diesel Trucks. *Environ. Sci. Technol.* 33: 1578–1587.

Schmid, H., Pucher, E., Ellinger, R., Biebl, P. and Puxbaum, H. (1997). Decadal Reductions of Traffic Emissions on a Transit Route in Austria—Results of the Tauern Tunnel Experiment 1997. *Atmos. Environ.* 35: 3585–3593.

Siegl, W.O., Hammerle, R.H., Herrmann, H.M., Wenclawiak, B.W. and Luers-Jongen, B. (1999). Organic Emissions Profile for a Light-duty Diesel Vehicles. *Atmos. Environ.* 33: 797–805.

Song, C., Zhao, Z., Lv, G., Song, J., Liu, L. and Zhao, R. (2010). Carbonyl Compound Emissions from a Heavy-duty Diesel Engine Fueled with Diesel Fuel and Ethanol-diesel Blend. *Chemosphere* 79: 1033–1039.

Tsai, J.H., Chang, S.Y. and Chiang, H.L. (2012). Volatile Organic Compounds from the Exhaust of Light-duty Diesel Vehicles. *Atmos. Environ.* 61: 499–506.

Wang, A., Ge, Y., Tan, T., Fu, M., Shah, A.N., Ding, Y., Zhao, H. and Liang, B. (2011). On-road Pollutant Emission and Fuel Consumption Characteristics of Buses in Beijing. *J. Environ. Sci*. 23: 419–426.

Wang, J., Jin, L., Gao, J., Shi, J., Zhao, Y., Liu, S., Jin, T., Bai, Z. and Wu, C. (2013). Investigation of Speciated VOC in Gasoline Vehicular Exhaust under ECE and EUDC Test Cycles. *Sci. Total Environ.* 445–446: 110–116.

Wang, Q., He, K., Huo, H. and Lents, J. (2005). Real-world Vehicle Emission Factors in Chinese Metropolis City – Beijing. *J. Environ. Sci.* 17: 319–326.

Xu, Z., Liu, J., Zhang, Y., Liang, P. and Mu, Y. (2010). Ambient Levels of Atmospheric Carbonyls in Beijing during the 2008 Olympic Games. *J. Environ. Sci.* 22: 1348–1356.

Yao, Z., Wang, Q., He, K., Huo, H., Ma, Y. and Zhang, Q. (2007). Characteristics of Real-world Vehicular Emissions in Chinese Cities. *J. Air Waste Manage. Assoc.* 57: 1379–1386.

Yao, Z., Huo, H., Zhang, Q., Streets, D.G. and He, K. (2011). Gaseous and Particulate Emissions from Rural Vehicles in China. *Atmos. Environ.* 45: 3055–3061.

Zhang, M., Yao, Z., Zhang, Y., Shen, X., Ye, Y., Yi, Y. and He, K. (2013). Study on Emission Characteristics of Carbonyl Compounds from Gasoline Vehicles. *Acta Sci. Circumst.* 33: 1376–1381 (in Chinese).

Zhao, H., Ge, Y., Tan, J., Yin, H., Guo, J., Zhao, W. and Dai, P. (2011). Effects in Different Mixing Ratios on Emissions from Passenger Cars Fueled with Methanol/ Gasoline Blends. *J. Environ. Sci.* 23: 1831–1838.

Received for review, November 6, 2014
Revised, December 27, 2014
Accepted, January 28, 2015