Technical Note

Emission Characteristics of Regulated and Unregulated Air Pollutants from Heavy Duty Diesel Trucks and Buses

Sungwoon Jung¹, Sunhee Mun¹, Taekho Chung¹, Sunmoon Kim¹, Seokjun Seo¹, Ingu Kim¹, Heekyoung Hong^{1*}, Hwansoo Chong¹, Kijae Sung², Jounghwa Kim¹, Youdeog Hong¹

¹ Transportation Pollution Research Center, National Institute of Environmental Research, Incheon 22689, Korea

² HORIBA Korea Ltd., Seoul 06259, Korea

ABSTRACT

Due to the common stop-and-go driving style, the low temperature of vehicular exhaust gas in the urban driving cycle is a major cause of air pollution in the Seoul Metropolitan Area. We herein investigate the characteristics of regulated (NO_x , PM, CO, and non-methane hydrocarbons (NMHC)) and unregulated (volatile organic compounds (VOCs), aldehydes, and polycyclic aromatic hydrocarbons (PAHs)) air pollutants emitted from heavy duty diesel trucks and buses equipped with different after-treatment systems (diesel particulate filter (DPF) + exhaust gas recirculation (EGR) and selective catalytic reduction (SCR) in urban conditions. NO_x emissions depended on the combustion and working temperature of the SCR catalysts, and PM emissions were low. Alkanes dominated the non-methane volatile organic compound (NMVOC) emissions, 43–59% of which resulted from the low efficiency of the oxidation catalyst for alkane. The after-treatment system and the engine start conditions influenced the chemical components of the NMVOC emissions due to incomplete combustion and the evaporation of liquid fuel. Formaldehyde comprised the largest portion of the aldehydes, whereas PAH emissions remained largely undetected. Furthermore, formaldehyde was the largest contributor to the NMHCs, forming 14–29%. The results of this study will aid in establishing a system for calculating hazardous air pollutants emitted by vehicles in Korea.

Keywords: Volatile organic compounds; Aldehydes; Polycyclic aromatic hydrocarbons; Heavy duty diesel trucks and buses; After-treatment systems.

INTRODUCTION

Since 1990, the major pollutants (carbon monoxide (CO), hydrocarbons (HC), nitrogen oxides (NO_x), and particulate matter (PM)) emitted from vehicles in Korea have been systematically regulated with stringent emission standards and inventories. However, to date, the characterization and monitoring of unregulated air pollutants (volatile organic compounds (VOCs), aldehydes, polycyclic aromatic hydrocarbons (PAHs)) has been unsatisfactory. Furthermore, no emission standards currently exist for the control of such emissions from automobile sources.

The Seoul Metropolitan Area, which includes Seoul, Incheon, and other regions of the Gyeonggi Province, has low air quality as a result of pollution emitted from road vehicles. In 2016, the total number of road vehicles was

approximately 10 million (MLTMA, 2017) due to the dense population of this area. Chen *et al.* (2009) noted that the number of vehicles has increased sharply in recent years, causing traffic congestion, low vehicle speeds, longer travel length and increased air pollution. Among the various road vehicles in Seoul Metropolitan Area, trucks contribute 49.7 and 60.0% of the NO_x and $\text{PM}_{2.5}$ emissions, respectively, while buses are responsible for 32.6% of the VOC emissions (NIER, 2016). As high emitters of pollution in the area of interest, the emission characteristics of heavy duty diesel trucks and buses therefore require investigation. Moreover, driving patterns, such as frequent stop-and-go driving, high traffic volumes, and growing congestion in the Seoul Metropolitan Area lead to middle and low vehicle speeds, which maintain low exhaust gas temperature.

Automobile-related NO_x , unburned HC, CO and PM emissions are major pollutants significantly impacting the urban environment (Keogh *et al.*, 2009), and vehicle emissions are main sources of gaseous and particulate matter pollution in urban atmosphere (Jung *et al.*, 2017). It has also been reported that the primary precursors of photochemical smog are formed by gaseous emissions

* Corresponding author.

Tel.: 82-32-560-7649; Fax: 82-32-561-7013

E-mail address: hong4590@korea.kr

under specific conditions in the presence of sunlight (Finlayson-Pitts and Pitts, 1997). However, Jiang *et al.* (2018) reported that NO_x emissions vary with driving cycle and the PM, HC, and CO emissions from heavy duty diesel trucks have been found to be low under the majority of test conditions, as these vehicles are equipped with diesel particulate filters (DPFs) and selective catalytic reduction (SCR) systems for PM and NO_x reduction. VOCs are important because they contribute to pollution through harmful photochemical processes (Streit, 2013), and VOCs have been classified as unregulated air pollutants due to their range of harmful effects on human health (Chang *et al.*, 2001; Ho *et al.*, 2002; Yang *et al.*, 2007). According to a report by the U.S. EPA (2002), investigations into VOCs rather than that of total HCs are of particular importance in the context of health effects and environmental impacts.

In addition, George *et al.* (2014) reported that carbonyls, formaldehyde, and acetaldehyde, are the major VOCs from heavy duty trucks equipped with the latest after-treatment systems, comprising 72% of the total VOC emissions. Furthermore, Nelson *et al.* (2008) reported that the VOC emissions from heavy duty diesel trucks and buses were 29.8 mg km⁻¹ of formaldehyde, 13.2 mg km⁻¹ of acetaldehyde, 6.1 mg km⁻¹ of benzene and 3.4 mg km⁻¹ of toluene. Moreover, Hu *et al.* (2013) indicated that gaseous PAHs comprised a large portion of the total PAHs emitted from heavy duty diesel vehicles without DPF, and revealed that this was not linked to the PM remaining in the exhaust line after DPF system.

This study therefore aimed to investigate the emission characteristics of regulated (NO_x, PM, CO, and NMHC) and unregulated (VOCs, aldehydes, and PAHs) air pollutants from heavy duty diesel trucks and buses under urban driving conditions in the Seoul Metropolitan Area. In addition, a

comparison of emission characteristics and the NMHC speciation for unregulated air pollutants was carried out with respect to the different after-treatment systems (DPF + exhaust gas recirculation (EGR) and SCR).

EXPERIMENTAL METHODS

Test Vehicles and Fuel

Four heavy duty diesel trucks and buses, which represent the majority of in-use trucks and buses in Korea, were selected for investigation of their emission characteristics. The tested vehicles were model year 2011–2013, all of which met the Euro 5 emission standards. These vehicles were equipped with two different after-treatment systems (DPF + EGR and SCR). The specifications of the test vehicles are shown in Table 1. The test fuel satisfied the diesel quality standards based on the Korean air quality conservation laws given in Table 2.

Test Cycles

The heavy duty diesel trucks and buses were tested on a chassis dynamometer (AVL Zöllner) following the National Institute of Environment Research (NIER)-9 mode according to vehicle type and considering the operating speed for heavy duty trucks and buses in the study area. The NIER-9 mode (average speed: 34–35 km h⁻¹) is one of the 15 driving cycles developed by the NIER to simulate actual vehicle operating conditions on various urban roads in Korea. The effects of cold and hot start conditions were also investigated in the test cycles considering a 50% load. The specifications of the driving cycles are given in Table 3.

Test Equipment and Emission Analysis

A chassis dynamometer system, a constant volume

Table 1. Specifications of vehicles tested

Vehicle ID	After-treatment system	Engine displacement (cc)	Max power (ps/rpm)	Model year	Emission standards
DT1	DPF ^a , EGR ^b	5,899	260/2500	2011	Euro 5
DT2	SCR ^c	5,880	250/2500	2013	Euro 5
DB1	DPF, EGR	12,742	425/1800	2012	Euro 5
DB2	SCR	10,964	425/1800	2013	Euro 5

^a Diesel particulate filter (Diesel oxidation catalyst is added as a part of DPF).

^b Exhaust gas recirculation.

^c Selective Catalyst Reduction.

Table 2. Properties of the tested diesel

Properties	Result	Standards ^b
Residual carbon content/10% residual oil (wt %)	0.01	≤ 0.15
Density (15°C, kg m ⁻³)	822	815–835
Sulfur content (ppm)	7	≤ 10
PAHs ^a (wt %)	2	≤ 5
Lubrication (μm)	291	≤ 400
Aromatic compounds (wt %)	22	≤ 30
Cetane index (or Cetane number)	55	≥ 52

^a Polycyclic aromatic hydrocarbons.

^b Korea Ministry of Environment, Air quality conservation law (KME, 2017).

Table 3. Specifications of driving cycles.

Driving cycle	Vehicle type	Driving time (sec)	Driving distance (km)	Average speed (km h ⁻¹)	Maximum speed (km h ⁻¹)
NIER-9	Truck	851	8.13	34.39	68.95
	Bus	905	8.88	35.32	73.60

sampler (CVS-7400T, Horiba), a dilution tunnel, and an exhaust gas analyzer were used for the purpose of this study. The heavy duty diesel vehicle chassis dynamometer had a maximum power, a total inertia weight, a maximum velocity, and a roller diameter of 10,096 N, 454–5443 kg, 200 km h⁻¹, and 1219.2 mm, respectively. The exhaust gas was analyzed with diluted ambient air in the CVS. Table 4 shows the specifications of the exhaust gas analyzer (MEXA-7200D, Horiba), and Fig. 1 shows a schematic representation of the vehicle emission test system. PM was collected in quartz filters using a PM sampling holder connected to the CVS. The quartz filters were weighed at the proper temperature ($20 \pm 5^\circ\text{C}$) and humidity ($47 \pm 5\%$) to obtain the PM mass data.

Following analysis of the regulated pollutants, the exhaust gas was collected in a 5 L Tedlar bag. The sampled gas was transferred to the automatic sampler at low temperature using a thermal desorber (Unity 2, Markes Int.). After passing the sampled gas through a purge and trap at -15°C , the VOCs were condensed, and moisture was removed using a Nafion dryer. Gas chromatography/mass spectrometry (GC/MS) was used to analyze sampled gas (see Table 5 for details regarding the pretreatment and analytical conditions). VOCs standard gas (56 Component VOC Mix, Supelco Inc.) was analyzed to calibrate the sampled gas.

The 2,4-dinitrophenylhydrazine (DNPH) method was used to analyze all aldehyde components. After passing the diluted exhaust gas through the DNPH cartridge (Waters), ultra-performance liquid chromatography (UPLC) was used to analyze the concentrated acetonitrile-containing solution (for analytical conditions, see Table 6). Aldehyde standard solution consisting of 13 components (Carbonyl-DNPH Mix 1, Supelco Inc.) was analyzed to calibrate the concentrated sample.

The PAHs were collected in quartz filters that had been placed in an 11 mL extraction cell of the accelerated solvent extractor. The accelerated solvent extractor was then extracted using 20 mL dichloromethane for 15 min at a pressure of 13,789.5 kPa and temperature of 100°C . GC/MS was used to analyze the PAHs (for analytical conditions,

see Table 7) according to the 16 EPA PAH compounds present in the 16 component PAH mixture (PAHs Mix, Supelco Inc.).

The values of repeatability, linearity, zero drift and span drift for the exhaust gas analyzer were 0.1, 1.8, 0, and 2% for CO; 0.1, 1.5, 0, and 0.3% for CO₂; 0.2, -1.4 , 0%, and 0.1% for THC; and 0.3, -1.7 , 0, and 0.3% for NO_x, respectively. VOC, aldehyde (Carbonyl-DNPH), and PAHs standards were used for calibration, and the calibration curves were calculated for a minimum of five standard concentrations. The blanks values were subtracted from the sample values with respect to the VOCs, aldehydes and PAHs. Linearity was confirmed by R² values of 0.993–0.998 for the calibration curves. In addition, the method detection limit (MDL), precision and accuracy were within the ranges of 0.06–0.65 ppb, 1.0–13.4%, and 77.4–101.8% for the VOCs; 25.8–60.1 ppb, 4.1–17.7%, and 75.4–113.9% for the aldehydes; and 7.2–61.7 ppb, 2.4–16.5%, and 94.0–119.0% for the PAHs, respectively. These results were within the accepted ranges of the Korean quality control standards.

RESULTS AND DISCUSSION

Emission Characteristics of Regulated Air Pollutants

Emission characterization was initially performed to measure the quantities of regulated air pollutants emitted from the heavy duty diesel trucks and buses equipped with different after-treatment systems. Thus, the NO_x, PM CO and NMHC emissions from the test trucks and buses subjected to the NIER-9 mode test driving cycle with different start conditions of cold or hot engine temperatures are represented in the units of “mass emitted per kilometer” i.e., g km⁻¹ as shown in Fig. 2. More specifically, Fig. 2(a) indicates that the NO_x emissions from trucks equipped with two different after-treatment systems were relatively similar in the driving cycle with the cold temperature engine start, 5.63 ± 0.40 g km⁻¹ for the DPF + EGR system and 5.50 ± 0.26 g km⁻¹ for the SCR system. For the hot start condition, the SCR-equipped truck had noticeably lower NO_x emissions (4.27 ± 0.45 g km⁻¹) than the DPF + EGR

Table 4. Specifications of exhaust gas analyzer.

Species	CO	CO ₂	THC ^a	NO _x
Principle	NDIR ^b	NDIR ^b	HFID ^c	CLD ^d
Concentration range	50, 100, 300, 3000 ppm	1, 2, 3, 6%	20, 50, 100, 1000 ppmC	20, 50, 100, 250, 1000, 2500 ppm
Repeatability, Zero drift, Span drift	With $\pm 1\%$ of fuel scale per 8 hours (at ambient temperature difference of 5°C)			

^a Total hydrocarbons.

^b Non Dispersive Infrared.

^c Heated Flame Ionization Detector.

^d Chemiluminescence Detector.

Fig. 1. Schematic diagram of vehicle emission test system.

Table 5. Analytical conditions of TD and GC/MS.

Method		EPA TO-14A			
Thermal desorber	Model	Markes International / Unity2			
	Purge	Prepurge time (mL min ⁻¹)	1		
		Trap prepurge time (mL min ⁻¹)	1		
	Sample	Sampling time (min)	10		
		Sample flow rate (mL min ⁻¹)	20		
	Trap desorber	Trap low temp. (°C)	-15		
		Trap high temp. (°C)	300		
		Trap hold time (min)	5		
		Split flow (mL min ⁻¹)	30		
GC/MS	Model	Agilent 7890B / Almsco BenchTOF-Select			
	Column	DB-1 (60 m × 0.32 mm × 3.00 μm)			
	Column temp.	Temp. (°C)	Rate (°C min ⁻¹)	Hold time (min)	Total time (min)
		30	0.0	30.00	30.00
		150	5.0	10.00	64.00
		200	15.0	10.00	77.33
	Transfer line temp.	200			
	Ion source temp.	200			
	Electron energy	70 eV			
	Ionization mode	EI			
MS scan range	35–350 amu				

equipped truck did ($4.86 \pm 0.06 \text{ g km}^{-1}$). In general, SCR catalysts are expected to chemically react at temperatures of $\geq 200^\circ\text{C}$, where NO_x conversion efficiencies reduce the quantities of NO_x emissions in the exhaust tailpipe (Misra et al., 2013). In the case of NO_x measurement, similar values were obtained for the two different after-treatment systems, likely due to the low exhaust gas temperature, under

which the required chemical reaction could not efficiently occur to reduce the NO_x emissions in the SCR system. The findings of Jiang et al. (2018) support this, as they observed that NO_x emissions for SCR-equipped vehicles were strongly correlated with the SCR temperature.

In contrast, the buses examined herein were found to have higher NO_x emissions relative to the trucks due to

Table 6. Analytical conditions of UPLC.

Method	EPA TO-11A			
Model	Waters US / ACQUITY UPLC			
Detector	TUV, 360 nm			
Column	ACQUITY UPLC™ BEH C ₁₈ 1.7 µm, 2.1 × 100 mm			
Mobile phase	Solvent A: 90% Water + 10% TetraHydro Furan (THF) Solvent B: 100% Acetonitrile (ACN)			
Gradient	Time (min)	Flow (mL min ⁻¹)	A (%)	B (%)
	Initial	0.3	60	40
	5.0	0.3	60	40
	10.0	0.3	0	100
	12.0	0.3	60	40
	15.0	0.3	60	40
Flow rate	0.3 mL min ⁻¹			
Injection volume	2 µL			

Table 7. Analytical conditions of GC/MS.

Method	EPA TO-13A			
Model	Agilent 7890A / Almsco Bench TOF-dx			
Column	HP-5MS (30 m × 0.25 mm × 0.25 µm)			
Column temp.	Temp (°C)	Rate (°C min ⁻¹)	Hold time (min)	Total time (min)
	50		1	1
	180	8	0	17.25
	240	5	0	29.25
	300	10	10	45.25
Column flow	1 mL min ⁻¹			
Inlet heater	300°C			
Split ratio	10:1			
Injection volume	1 µL			
Transfer line	300°C			
Ion source	250°C			
MS scan range	100–300 amu			

their higher engine power and larger engine displacement. In addition, NO_x emissions under the cold start condition ($14.24 \pm 0.38 \text{ g km}^{-1}$) for the DPF + EGR system were similar to that of the SCR system ($14.76 \pm 0.32 \text{ g km}^{-1}$), while the SCR-equipped bus showed slightly higher NO_x emissions relative to the DPF + EGR-equipped buses under hot start conditions (13.85 ± 0.46 and $11.40 \pm 0.57 \text{ g km}^{-1}$, respectively). Although the NO_x emissions of heavy duty diesel trucks with similar engine displacement and power have generally received little attention, Jiang *et al.* (2018) showed a wide variation in the reported NO_x emissions from diesel buses complying with the Euro 5 standard, $0.41\text{--}13.98 \text{ g km}^{-1}$ under the idle, creep, transient, and cruise phases. Upon comparison of the data for the two different after-treatment systems, it was apparent that relatively low combustion temperatures during operation of the EGR system resulted in lower NO_x emissions than from the SCR-system. Indeed, previous studies (Zeldovich *et al.*, 1985; Gallus *et al.*, 2017; Ramos *et al.*, 2018) have indicated that NO_x tends to form in the high temperature combustion region, and that it is highly dependent on the EGR mass flow rate with respect to EGR valve operation. Accordingly, the EGR operation may lower the NO_x emissions from DPF + EGR-equipped bus compared to

SCR-equipped bus. Furthermore, for these cases, there were noticeable differences in the NO_x emissions between the two start conditions. These differences can be attributed to the EGR and the chemical reaction in the SCR system. For the hot start condition, it is important to note the difference in NO_x emissions between the DPF + EGR and SCR systems.

The overall PM emission results are presented in Fig. 2(b). For the trucks, the test values ranged $0.0022\text{--}0.0023 \text{ g km}^{-1}$ for the cold start condition and $0\text{--}0.0005 \text{ g km}^{-1}$ for the hot start condition. For the buses, PM emissions of close to zero were recorded for the DPF + EGR system, while these emissions ranged $0.0001\text{--}0.0006 \text{ g km}^{-1}$ for the SCR system. These results suggest that identification of the differences in PM emissions between the after-treatment systems is difficult due to the low PM emission levels in both the trucks and the buses. It is also important to compare our results with those reported in the literature. More specifically, Jiang *et al.* (2018) reported PM emissions of $0.0006\text{--}0.002 \text{ g km}^{-1}$ from experiments on a diesel bus with a similar displacement and power, while Quiros *et al.* (2018) reported PM emissions of 0.003 and 0.011 g km^{-1} for heavy duty diesel vehicles equipped with DPF and DPF + SCR systems, respectively. In addition, PM emissions from the

Fig. 2. Emission characteristics of (a) NO_x, (b) PM, (c) CO, and (d) NMHC according to vehicle type for cold and hot start conditions.

DPF + EGR-equipped diesel truck decreased with higher start temperatures, whereas similar values were recorded for the cold and hot start conditions in the SCR-equipped case. In theory, PM emissions depend on the flame temperature and the local flame equivalence ratio in the combustion chamber, and so the engine produces higher PM emissions at low flame temperatures and at high flame equivalence ratios. Furthermore, Ramos *et al.* (2018) reported that the quantity of PM can increase upon increasing the EGR mass flow rate. Accordingly, higher PM emissions in the DPF + EGR case can be attributed to low combustion temperature and air deficiency due to EGR valve opening. Moreover, PM filtration in the DPF also reduced PM emissions.

The CO and NMHC emissions for the diesel trucks and buses equipped with the two different after-treatment systems are depicted in Figs. 2(c) and 2(d), respectively. In the case of the trucks, CO emissions were 0.94–2.51 g km⁻¹ under the cold start condition and 0.71–2.01 g km⁻¹ under the hot start condition, while NMHC emissions were 0.06–0.23 g km⁻¹ under the cold start condition and 0.04–0.25 g km⁻¹ under the hot start condition. For the buses, CO emissions were 0.94–1.03 and 0.71–0.84 g km⁻¹ under the cold and hot start conditions, respectively, while NMHC emissions were 0.07–0.11 and 0.06–0.16 g km⁻¹, respectively. This result reveals that both the start conditions and the after-treatment systems can influence the CO and NMHC emissions. In addition, Jiang *et al.* (2018) reported that CO and NMHC emissions were lower in cruise mode than in creep mode, reporting CO emissions of 0.04 and 3.13 g km⁻¹, respectively, in addition to NMHC emissions of 0.006 and 0.28 g km⁻¹, respectively. Furthermore, Alves *et al.* (2015) noted that CO and HC emissions under cold start conditions were higher than those under hot start condition for in-use vehicles on chassis dynamometer urban cycles. The literature further reveals that CO forms due to incomplete combustion, and that NMHC is formed due to the evaporation of fuel and the chemical reaction of unburned HCs in the exhaust (Heywood, 1988; Kennedy *et al.*, 2015). In particular,

Mollenhauer *et al.* (2007) reported that NMHC forms in the zone of lean air-fuel mixture and excess fuel under over-fueling by late injection, while the high CO concentration can be attributed to the rich air-fuel mixture where incomplete conversion of the HCs to CO₂ takes place due to air deficiency. In addition, compared to the SCR-equipped vehicle, the DPF + EGR-equipped vehicles exhibited higher CO emissions, and the increased NMHC formation can be attributed to the EGR operation and excess fuel due to over-fueling by late injection for DPF regeneration. These results indicate that DPF had a significant effect on the reduction of CO, while the hot combustion temperature influenced the NMHC reduction. Furthermore, the cold start condition resulted in higher CO emissions than the hot start condition. In contrast, the NMHC emissions from the DPF + EGR-equipped truck and bus under the hot start condition were higher than those under the cold start condition, whereas the NMHC emissions from the SCR-equipped truck and bus under the cold start condition were higher than those recorded under the hot start condition. These findings can be attributed to lack of heat from the cylinder walls under the cold condition, as this heat is required to evaporate the fuel and the fuel-rich mixtures.

Emission Characteristics of Unregulated Air Pollutants

The NMVOC emissions from the DPF + EGR-equipped vehicles were composed of 11.2–14.2 mg km⁻¹ of alkanes, 3.2–11.8 mg km⁻¹ of alkenes, 5.3–9.1 mg km⁻¹ of aromatics, and 0.7–1.0 mg km⁻¹ of cycloalkanes, whereas those from the SCR-equipped vehicles were 4.5–12.7 mg km⁻¹ of alkanes, 3.0–8.5 mg km⁻¹ of alkenes, 2.0–9.6 mg km⁻¹ of aromatics, and 0.6–2.2 mg km⁻¹ of cycloalkanes. Fig. 3 shows the compositions of the NMVOCs emitted from the trucks and buses subjected to different driving cycles under the cold or hot start temperatures. Among the various NMVOCs, alkanes were the most abundant, accounting for 44.5–52.0% of the total for the trucks and 42.6–59.4% for the buses. In addition, for both trucks and buses, higher quantities of alkenes were detected from the SCR-equipped

Fig. 3. NMVOCs composition according to vehicle type for cold and hot start conditions.

vehicles, while those equipped with the DPF + EGR system emitted higher quantities of aromatics. The emission trends of the cycloalkanes were similar to those of the alkenes. The above results therefore indicate that alkane emissions were higher than those of alkenes, cycloalkanes, and aromatics, likely due to the efficiency of oxidation catalysts toward alkanes being lower than for the other components. Similar results have also been reported in the literature, with alkane, aromatic, and alkene emissions of 46.1–48.5, 24.2–25.8, and 22.3–25.1%, respectively, being reported from heavy duty diesel trucks and buses (NIER, 2017). In addition, Knafl *et al.* (2006) reported that the VOCs gave different conversion efficiencies through diesel oxidation catalysts, corresponding to 63–80, 74–83, and 92–99%, for alkanes, aromatics, and alkenes, respectively.

Table 8 summarizes the five major chemical components in the NMVOC emissions from the heavy duty diesel trucks and buses. For the diesel truck equipped with the DPF + EGR systems, the major components were 4.79–5.44 mg km⁻¹ of propylene and 4.26–4.45 mg km⁻¹ 1-butene, although *n*-nonane, *n*-decane, dodecane, and benzene were also detected. In contrast, the NMVOCs from the SCR-equipped diesel truck comprised mainly 1.59–1.84 mg km⁻¹ of benzene, 1.39–1.63 mg km⁻¹ of propylene, and 1.49–1.62 mg km⁻¹ of 1-butene, although *n*-heptane, *n*-decane, dodecane, and *n*-octane were also present. In the case of the buses, 3.91–4.73 mg km⁻¹ of *n*-nonane, 3.1 mg km⁻¹ of dodecane, and 1.7–2.27 mg km⁻¹ of *n*-decane were the major components obtained from the DPF + EGR system, while 5.78–6.66 mg km⁻¹ of propylene and 2.93–3.4 mg km⁻¹ of benzene were the main constituents in the SCR system. These results indicate that the chemical components of the NMVOC emissions were strongly dependent on the after-treatment system employed, the engine start conditions, and the vehicle type, as these types of emissions are produced upon the incomplete combustion of diesel fuels or lubricating oils. We also note that Hong *et al.* (2018) reported that the main components of NMVOCs from heavy duty diesel trucks

equipped with after-treatment systems were 11.3–16.1% of propylene, 15.5% of benzene, and 10.3–11.3% of 1-butene.

The aldehyde emissions from the trucks and buses subjected to different driving cycles with cold and hot start conditions are outlined in Fig. 4. For the trucks, the formaldehyde, acetaldehyde, and acrolein emissions for the SCR-equipped and DPF + EGR systems were 5.12 and 9.08–10.62, 2.17 and 3.39, and 0 and 2.75–4.81 mg km⁻¹, respectively. For the buses, the corresponding values were 8.67–14.61, 3.66–5.09, and 1.50–2.46 mg km⁻¹, respectively. Similar results were also previously reported, in that the most dominant carbonyl compounds from medium-duty diesel trucks were formaldehyde (9.2 mg km⁻¹) and acetaldehyde (3.5 mg km⁻¹) (Siegl *et al.*, 1999). In addition, Nelson *et al.* (2008) noted formaldehyde and acetaldehyde emissions of 29.8 and 13.2 mg km⁻¹, respectively, from diesel vehicles, while Yao *et al.* (2015) reported that formaldehyde and acetaldehyde comprised 47.9 and 21.0% of the carbonyl emissions from heavy duty diesel trucks.

The overall PAH emission results are presented in Fig. 5. As shown in this figure, the naphthalene and phenanthrene emissions were 1.13–1.72 and 0.91–1.31 µg km⁻¹ under the cold and hot start conditions in the trucks, and 0–1.57 and 0–1.19 µg km⁻¹ under identical conditions in the buses, respectively. It was also reported that the main PAH components emitted from heavy duty diesel vehicles were naphthalene (25.2 ± 20.8%), pyrene (24.5 ± 11.7%), and phenanthrene (16.3 ± 7.4%) (Shah *et al.*, 2005). In addition, the amounts of naphthalene and phenanthrene from the DPF + EGR-equipped truck decreased with higher start temperatures, whereas the SCR-equipped vehicles showed similar values under both the cold and hot start conditions. In the case of the buses, the emission of naphthalene and phenanthrene also decreased with higher start temperatures, with virtually no naphthalene being detected under hot start conditions. Furthermore, phenanthrene was barely detected under either start condition. According to Nelson *et al.* (2008), naphthalene and phenanthrene emissions of

Table 8. Comparison of the 5 major chemical components in NMVOCs emissions from the heavy duty diesel trucks and buses subjected to different driving conditions with (a) cold and (b) hot temperature start

unit: mg km ⁻¹								
(a) Cold start condition								
Rank	DT1(DPF + EGR)		DT2(SCR)		DB1(DPF + EGR)		DB2(SCR)	
	Compounds	Emissions	Compounds	Emissions	Compounds	Emissions	Compounds	Emissions
1	Propylene	5.44	Benzene	1.84	n-Nonane	3.91	Propylene	6.66
2	1-Butene	4.45	Propylene	1.63	Dodecane	3.10	Benzene	3.46
3	n-Nonane	3.56	1-Butene	1.62	n-Decane	1.70	n-Nonane	1.98
4	n-Decane	2.43	n-Heptane	0.93	Propylene	1.54	Undecane	1.66
5	Dodecane	2.07	n-Decane	0.80	1-Butene	1.53	n-Decane	1.60

unit: mg km ⁻¹								
(b) Hot start condition								
Rank	DT1(DPF + EGR)		DT2(SCR)		DB1(DPF + EGR)		DB2(SCR)	
	Compounds	Emissions	Compounds	Emissions	Compounds	Emissions	Compounds	Emissions
1	Propylene	4.79	Benzene	1.59	n-Nonane	4.73	Propylene	5.78
2	1-Butene	4.26	1-Butene	1.49	n-Decane	2.27	Benzene	2.93
3	Dodecane	2.22	Propylene	1.39	Undecane	1.63	n-Nonane	1.97
4	n-Nonane	1.90	Dodecane	0.96	n-Octane	1.55	1,2,4-trimethylbenzene	1.71
5	Benzene	1.59	n-Octane	0.60	1-Butene	1.51	n-Decane	1.66

Fig. 4. Emission characteristics of aldehydes according to vehicle type for (a) cold and (b) hot start conditions.

Fig. 5. Emission characteristics of PAHs according to vehicle type for (a) cold and (b) hot start conditions.

2605 and 215 $\mu\text{g km}^{-1}$ were recorded from diesel vehicles without after-treatment systems, whereas Hu *et al.* (2013) reported that the after-treatment systems in heavy duty diesel vehicles efficiently abated more than 90% of the total PAHs. Furthermore, Nelson *et al.* (2008) showed that PAH emissions were lowered where high-quality fuels were employed. It was therefore apparent that the fuels employed in this study satisfied the high-quality diesel fuel standards in terms of the ultra-low sulfur, PAHs, lubrication, and aromatic compounds, as listed in Table 2.

Table 9 summarizes the 10 major chemical components present in the NMHC emissions from the heavy duty diesel

trucks and buses. The portions of the chemical components present in the unregulated pollutants were calculated from the NMVOCs and the aldehydes based on the NMHC emissions. Regardless of the driving conditions employed, formaldehyde was the most abundant component in both trucks and buses (14.0–29.9%), while for the DPF + EGR-equipped truck, the major component was acetaldehyde (7.7–7.9%), and for the SCR-equipped truck, acetaldehyde (12.4%) and benzene (11.0%) were dominant. Similarly, *n*-nonane (12.3–12.5%) was the main component in the case of the DPF + EGR-equipped bus, whereas propylene (15.5–15.7%) was dominant for the SCR-equipped bus. In a

Table 9. Comparison of the 10 major chemical components in NMHC emissions from the heavy duty diesel trucks and buses subjected to different driving conditions with (a) cold and (b) hot temperature start

(a) Cold start condition									unit: %
Rank	DT1(DPF+EGR)		DT2(SCR)		DB1(DPF+EGR)		DB2(SCR)		
	Compounds	Speciation	Compounds	Speciation	Compounds	Speciation	Compounds	Speciation	
1	Formaldehyde	21.0	Formaldehyde	14.0	Formaldehyde	15.5	Formaldehyde	20.8	
2	Acetaldehyde	7.9	Benzene	11.0	n-Nonane	12.3	Propylene	15.7	
3	Acrolein	7.2	1-Butene	9.8	Dodecane	10.6	Benzene	8.2	
4	Propylene	6.9	Propylene	9.8	Acetaldehyde	6.2	Acetaldehyde	7.5	
5	1-Butene	6.7	n-Heptane	5.7	n-Decane	5.4	n-Nonane	5.0	
6	n-Nonane	4.8	Acetaldehyde	5.7	1-Butene	4.9	Acrolein	3.7	
7	n-Decane	4.7	n-Octane	4.5	Propylene	4.9	n-Decane	3.7	
8	Dodecane	3.9	n-Decane	4.5	m,p-Xylene	4.5	Methylcyclohexane	3.4	
9	Benzene	3.8	n-Nonane	4.4	n-Octane	4.2	Undecane	3.4	
10	Undecane	3.6	Undecane	3.6	Undecane	3.4	1-Butene	3.3	

(b) Hot start condition									unit: %
Rank	DT1(DPF+EGR)		DT2(SCR)		DB1(DPF+EGR)		DB2(SCR)		
	Compounds	Speciation	Compounds	Speciation	Compounds	Speciation	Compounds	Speciation	
1	Formaldehyde	20.7	Formaldehyde	29.9	Formaldehyde	23.2	Formaldehyde	21.5	
2	Acetaldehyde	7.7	Acetaldehyde	12.4	n-Nonane	12.5	Propylene	15.5	
3	Acrolein	6.3	Benzene	9.3	Acetaldehyde	9.9	Benzene	8.0	
4	1-Butene	6.1	1-Butene	8.4	n-Decane	5.7	Acetaldehyde	7.5	
5	n-Decane	5.8	Propylene	8.1	Acrolein	5.6	n-Nonane	5.0	
6	Propylene	5.7	Dodecane	5.1	Undecane	4.7	n-Decane	4.3	
7	n-Nonane	5.4	n-Octane	3.5	1-Butene	4.3	Methylcyclohexane	4.0	
8	Undecane	4.3	n-Heptane	3.2	n-Octane	4.2	n-Octane	3.6	
9	Dodecane	4.1	Methylcyclohexane	2.2	m,p-Xylene	3.7	Undecane	3.3	
10	n-Octane	3.6	n-Nonane	2.2	Propylene	3.4	n-Heptane	2.9	

previous study by the EEA (2016), the aldehyde components of the NMVOCs were found to consist of 8.4% formaldehyde and 4.6% acetaldehyde for heavy duty vehicles. In addition, the NIER (2017) noted that for heavy duty diesel trucks and buses, the NMHCs were composed of 22.3% formaldehyde, 8.9% acetaldehyde, and 8.7% propylene. Overall, we found that the composition ratios of the various unregulated pollutants exhibited differences with respect to the vehicle type, the engine start conditions, and the after-treatment system. This was supported by the HEI (1995), who reported that the composition of diesel emissions differed significantly based on the vehicle type, driving conditions, fuel type, lubricant, and after-treatment system employed.

CONCLUSIONS

Objective data and detailed information on the emissions released during real urban driving cycles is necessary for developing effective policies on the reduction of air pollutants from heavy duty diesel vehicles in the Seoul Metropolitan Area. In contrast to previous studies, we reported the emission characteristics and speciation of unregulated air pollutants from heavy duty diesel vehicles while also considering different vehicle types (trucks and buses), engine start conditions (cold and hot temperatures), and after-treatment systems (DPF + EGR and SCR). Additionally, we characterized both the regulated and unregulated emissions of Euro 5-compliant diesel trucks

and buses that were equipped with different after-treatment systems (DPF + EGR or SCR). Using identical heavy duty diesel vehicles, differences between the emissions from two driving cycles under cold and hot start conditions were assessed. We found that NO_x emissions were similar for vehicles equipped with either after-treatment system due to the low temperature of the exhaust gas. Moreover, PM emissions from trucks and buses were close to zero under both cold and hot start conditions. For NMVOCs, alkane emissions were higher than alkene, cycloalkane, and aromatic emissions for both vehicle types because of the low efficiency of the oxidation catalysts with regard to alkane. Furthermore, the individual components of the NMVOC emissions were affected by both the after-treatment system and the engine start conditions due to incomplete combustion and the evaporation of liquid fuel. Formaldehyde was the most abundant aldehyde as well as the most abundant NMHC, and no PAHs, with the exception of naphthalene and phenanthrene, were detected. These results can be attributed to the differences in vehicle type, engine start condition, and after-treatment system. In the Seoul Metropolitan Area, the low temperature of vehicular exhaust gas during the urban driving cycle leads to heavy air pollution due to the common stop-and-go driving pattern. We therefore expect that our speciation of NMHCs produced by heavy duty diesel trucks and buses will assist in the establishment of a Korean emissions system for hazardous air pollutants from vehicular sources.

ACKNOWLEDGMENTS

This work was supported by a grant from the National Institute of Environmental Research (NIER), funded by the Ministry of Environment (MOE) of the Republic of Korea (ex: NIER-2017-01-01-078).

REFERENCES

- Alves, C., Lopes, D.J., Calvo, A.I., Evtyugina, M., Rocha, S. and Nunes, T. (2015). Emissions from light-duty diesel and gasoline in-use vehicles measured on chassis dynamometer test cycles. *Aerosol Air Qual. Res.* 15: 99–116.
- Chang, C.C., Lo J.G. and Wang J.L. (2001). Assessment of reducing ozone forming potential for vehicles using liquefied petroleum gas as an alternative fuel. *Atmos. Environ.* 35: 6201–6211.
- Chen, J., Wang, W., Zhang, J., Liu, H., Ren, L., Liu, X., Zhang, W. and Wang, X. (2009). Characteristics of gaseous pollutants near a main traffic line in Beijing and its influence factors. *Atmos. Res.* 94: 470–480.
- European Environment Agency (EEA) (2016). *EMEP/EEA air pollutant emission inventory guidebook 2016*. European Environment Agency, European Union.
- Finlayson-Pitts, B.J. and Pitts, J.N. (1997). Tropospheric air pollution: Ozone, airborne toxics, polycyclic aromatic hydrocarbons, and particles. *Science* 276: 1045–1051.
- Gallus, J., Kirchner, U., Vogt, R. and Benter, T. (2017). Impact of driving style and road grade on gaseous exhaust emissions of passenger vehicles measured by a portable emission measurement system (PEMS). *Transp. Res. Part D* 52: 215–26.
- George, I.J., Hays, M.D., Snow, R., Faircloth, J., George, B.J., Long, T. and Baldauf, R.W. (2014). Cold temperature and biodiesel fuel emissions of volatile organic compounds from diesel trucks. *Environ. Sci. Technol.* 48: 14782–14789.
- Health Effects Institute (HEI) (1995). *A critical analysis of emissions, exposure and health effects*. Health Effects Institute, Cambridge, MA, USA.
- Heywood, J.B. (1988). *Internal combustion engine fundamentals*. McGraw-Hill Press, New York, USA.
- Ho, H.F., Lee, S.C. and Chiu, G.M.Y. (2002). Characterization of selected volatile organic compounds, polycyclic aromatic hydrocarbons and carbonyl compounds at a roadside monitoring station. *Atmos. Environ.* 36: 57–65.
- Hong, H., Mun, S., Seo, S., Kim, J., Jung, S., Chung, T., Hong, Y., Sung, K. and Kim, S. (2018). Emission characteristics of hazardous air pollutants from diesel heavy duty trucks for Euro 5. *J. Liq. Atomization Spray Sys. Korea* 23: 74–80.
- Hu, S., Herner, J.D., Robertson, W., Kobayashi, R., Chang, M.C., Huang, S., Zielinska, B., Kado, N., Collins, J.F., Rieger, P., Huai, T. and Ayala, A. (2013). Emissions of polycyclic aromatic hydrocarbons (PAHs) and nitro-PAHs from heavy-duty diesel vehicles with DPF with SCR. *J. Air Waste Manage. Assoc.* 63: 984–996.
- Jiang, Y., Yang, J., Cocker III, D., Karavalakis, G., Johnson, K.C. and Durbin, T.D. (2018). Characterizing emission rates of regulated pollutants from model year 2012+ heavy-duty diesel vehicles equipped with DPF and SCR system. *Sci. Total Environ.* 619–620: 765–771.
- Jung, S., Lim, J., Kwon, S., Jeon, S., Kim, J., Lee, J. and Kim, S. (2017). Characterization of particulate matter from diesel passenger cars tested on chassis dynamometers. *J. Environ. Sci.* 54: 21–32.
- Kennedy, J., Lee, W.J., Chang, Y.C., Chen, C.Y. and Wang, L.C. (2015). An overview: Energy saving and pollution reduction by using green fuel blends in diesel engines. *Appl. Energy* 159: 214–236.
- Keogh, D.C., Ferreira L. and Morawska, L. (2009). Development of a particle number and particle mass vehicle emissions inventory for an urban fleet. *Environ. Modell. Software* 24: 1323–1331.
- Knafl, A., Busch, S.B., Han, M., Bohac, S.V. and Assanis, D.N. (2006). Characterizing light-off behavior and species-resolved conversion efficiencies during in-situ diesel oxidation catalyst degreening. *SAE 2006-01-0209*.
- Ministry of Land, Transport, Maritime Affairs (MLTMA) (2017). *Automobile registration statistics (2016)*, Ministry of Land, Transport, Maritime Affairs, Sejong, Republic of Korea.
- Misra, C., Collins, J.F., Herner, J.D., Sax, T., Krishnamurthy, M., Sobieralski, W., Burmizki, M. and Chernich, D. (2013). In-use NO_x emissions from model year 2010 and 2011 heavy duty diesel engines equipped with aftertreatment devices. *Environ. Sci. Technol.* 47: 7892–7898.
- Mollenhauer, K., Tschöke, H., and Johnson, K.G.E. (2007). *Handbook of diesel engines*. Springer-Verlag Press, Berlin, Germany.
- National Institute of Environmental Research (NIER) (2016). *National air pollutants emission service (2014)*. National Institute of Environmental Research, Incheon, Republic of Korea.
- National Institute of Environmental Research (NIER) (2017). *The emission characteristics of mobile source air toxics and management strategy (IV)*. National Institute of Environmental Research, Incheon, Republic of Korea.
- Nelson, P.F., Tibbett, A.R. and Day, S.J. (2008). Effect of vehicle type and fuel quality on real world toxic emissions from diesel vehicles. *Atmos. Environ.* 42: 5291–5303.
- Quiros, D.C., Thiruvengadam, A., Pradhan, S., Besch, M., Thiruvengadam, P., Demirgok, B., Carder, D., Oshinuga, A., Huai, T. and Hu, S. (2016). Real-world emissions from modern heavy-duty diesel, natural gas, and hybrid diesel trucks operating along major California freight corridors. *Emission Control Sci. Technol.* 2: 156–172.
- Ramos, A., Munoz, J., Andres, F. and Armas, O. (2018). NO_x emissions from diesel light duty vehicle tested under NEDC and real-world driving conditions. *Transp. Res. Part D* 63: 37–48.
- Shah, S.D., Ogunyoku, T.A., Miller, J.W. and Cocker, D.R. (2005). On-road emission rates of PAH and *n*-alkane

- compounds from heavy-duty diesel vehicles. *Environ. Sci. Technol.* 39: 5276–5284.
- Siegl, W.O., Hammerle, R.H., Hermann, H.M., Wenclawiak, B.W. and Luers-Jongen, B. (1999). Organic emissions profile for a light-duty diesel vehicle. *Atmos. Environ.* 33: 797–805.
- Streit, H. (2013). *Investigation on emissions from buses with compressed natural gas and diesel engines*. Bachelor of Science Environmental Science, USA.
- U.S. Environmental Protection Agency (U.S. EPA) (2002). *A comprehensive analysis of biodiesel impacts on exhaust emissions-draft technical report*. Environmental Protection Agency, Washington DC, USA.
- Yang, H.H., Chien, S.M., Cheng, M.T. and Peng C.Y. (2007). Comparative study of regulated and unregulated air pollutant emissions before and after conversion of automobiles from gasoline power to liquefied petroleum gas/gasoline dual-fuel retrofits. *Environ. Sci. Technol.* 41: 8471–8476.
- Yao, Z., Jiang, X., Shen, X., Ye, Y., Cao, X., Zhang, Y. and He, K. (2015). On-road emission characteristics of carbonyl compounds for heavy-duty diesel trucks. *Aerosol Air Qual. Res.* 15: 915–925.
- Zeldovich, I., Barenblatt, G.I., Librovich, V.B. and Makhviladze, G.M. (1985). *Mathematical theory of combustion and explosions*. Springer Press, USA.

Received for review, June 25, 2018

Revised, October 10, 2018

Accepted, October 11, 2018