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Article

Emission characteristics of hazardous air pollutants from medium-duty diesel trucks based on driving cycles

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Abstract: Studies on the characteristics of hazardous air pollutants (HAPs) in the emissions of medium-duty diesel trucks are significantly insufficient compared to that on heavy-duty trucks. This study investigates the characteristics of regulated pollutants and HAPs such as volatile organic compounds (VOCs), aldehydes, and polycyclic aromatic hydrocarbons (PAHs), and estimates non-methane hydrocarbon (NMHC) speciation in the emissions of medium-duty diesel trucks. Ten medium-duty diesel trucks conforming to Euros 5 and 6 were tested for worldwide harmonized light duty driving test cycle (WLTC), new European driving cycle (NEDC), constant volume sampler (CVS)-75, and National Institute of Environmental Research (NIER)-9 using a chassis dynamometer. CO and NMHC emissions were the highest in the NEDC because of its longer low-speed driving time. NOx emissions were the highest in WLTC owing to the influence of thermal NOx in the high-speed phase. Alkanes dominated non-methane volatile compound (NMVOC) emissions owing to the low reaction of the diesel oxidation catalyst. After-treatment system, driving, and engine conditions influenced the individual components of NMVOC emissions. Formaldehyde emissions were the highest among aldehydes irrespective of driving cycles. By sampling the particle-phase of PAHs, we detected benzo(k)fluoranthene and benzo(a)pyrene and estimated the concentrations of the gas-phase PAHs with models to obtain the total PAH concentrations. The toxic equivalency quantities of benzo(k)fluoranthene and benzo(a)pyrene from NIER-9 (cold) for both Euro 5 and Euro 6 vehicles were more than five times higher than that of NIER (hot) and NEDC. In the case of NMHC speciation, formaldehyde emissions were the highest in all the driving cycles. Formaldehyde and benzene must be controlled in the emissions of medium-duty diesel trucks to reduce their health threats. The results of this study will aid in establishing a national emission inventory system for HAPs of mobile sources in Korea.

Keywords: Hazardous air pollutants, Medium-duty diesel trucks, Driving cycles, Non-methane volatile compound, Aldehydes, Polycyclic aromatic hydrocarbons

1. Introduction

Air pollution caused by various transportation sources poses a serious threat to human health. The Seoul Metropolitan Area (SMA) is significantly affected by mobile sources of pollution as the number of registered vehicles in the region is more than ten million as of 2019 [1]. Therefore, the management of automobile emissions is required in areas of high population density. The SMA is a metropolitan area composed of Seoul in its center, the Gyeonggi Province, and Incheon, and the contribution of automobiles to air pollution is high in this region. According to the national air pollutant emissions [2] data for 2017, medium-duty trucks are a major source of emissions as they contribute high proportions of CO (37.4%), NOx (25.1%), and $PM_{2.5}$ (19.9%) in the SMA. Even though many studies on emissions from heavy-duty trucks have been conducted, domestic and overseas studies on emissions from medium-duty trucks are insufficient.

Regulated pollutants (e.g., CO, NOx, HC, and particulate matter (PM)) from mobile sources, such as trucks, have been systematically managed in South Korea by establishing emission standards and inventories. Recently, the importance of managing hazardous air pollutants (HAPs) including volatile organic compounds (VOCs), aldehydes, and polycyclic aromatic hydrocarbons (PAHs) is gradually increasing with the growing interest in health risks associated with them. HAPs emanating from diesel engines, which are mainly used in trucks, are known to have high health risks associated with long-term exposure because of their carcinogenicity, toxicity, and bioaccumulation properties despite their trace concentrations [3]. It is difficult to manage HAPs in emissions from mobile sources, such as trucks, owing to the absence of regulatory standards.

These HAPs are classified into gaseous and particulate matter. Mobile sources are the main contributors of gaseous and particulate matter pollutants in urban air [4]. Gaseous matter includes VOCs composed of aromatic hydrocarbons, such as benzene and toluene, and their derivatives, as well as aldehydes that have a unique odor. VOCs easily evaporate into the atmosphere because of their high saturation vapor pressures and are known as the precursors of photochemical smog that contribute to secondary ozone generation through photolysis reactions with NOx in the atmosphere. Benzene has been reported to cause leukemia, myeloma, and lymphoma [5-6]. Aldehydes are organic compounds with the carbonyl group of -(CH)=O [5], and are formed by the incomplete combustion of hydrocarbons [7]. Among aldehydes, exposure to formaldehyde is known to cause emotional instability, memory loss, and difficulty in concentration [8]. Particulate matter (PM) includes PAHs, which are known to cause bronchitis, lung cancer, dermatitis, and conjunctivitis [9-11], and carcinogenic substances, such as heavy metals. PAHs are present in large quantities in the PM of diesel engine emissions, and are highly likely to be generated by the incomplete combustion of fuel. In addition, the higher loading of a diesel engine has a significant relationship with endocrine disruption [12] due to their emission of polycyclic aromatic compounds (PAHs). Many studies [13-17] have explored the characterization of PAHs in particles from diesel vehicles. A recent study reported that the PAH concentration in terms of toxic equivalency quantity (TEQ) associated with benzene ring number demonstrated two peak concentrations with respect to smaller ultrafine (> 66 nm) and quasi-accumulation (170–330 nm) size ranges [18]. Therefore, various domestic and overseas studies have been conducted on the toxicity, generation mechanisms, and occurrence paths of HAPs.

According to Dong et al. (2014) [19], the quantity of carbonyls emitted from a medium-duty diesel truck was 67.1 ± 49.3 mg/km, and in that, formaldehyde was the highest, followed by acetaldehyde. According to George et al. (2014) [20], carbonyls, such as formaldehyde and acetaldehyde account for more than 72% of the VOCs of diesel trucks equipped with after-treatment technologies such as diesel particulate filter (DPF), selective catalytic reduction (SCR), and diesel oxidation catalysts (DOC). Nelson et al. (2008) [21] reported that formaldehyde (1.1–160 mg/km) exhibited the highest proportion among the VOCs emitted from diesel trucks and buses, followed by acetaldehyde (1.3–69 mg/km), benzene (2.1–11 mg/km), and toluene (1.1–7.2 mg/km). In addition, Jung et al. (2019) found high proportions of formaldehyde (14–29.9%) and acetaldehyde (5.7–12.4%) among the non-methane hydrocarbon (NMHC) emissions of heavy-duty diesel trucks equipped with a reduction device (DPF + exhaust gas recirculation (EGR) or SCR). According to Hu et al. (2013) [22], PAHs emitted from heavy-duty diesel vehicles fitted with DPFs reduced by more than 90%. They also reported that the proportion of gaseous PAHs among the total PAHs was high in the emissions of heavy-duty diesel vehicles without DPF. Domestic and overseas studies on the characteristics of emissions from medium-duty diesel trucks and on the speciation of HAPs in their emissions are significantly insufficient compared to those on heavy-duty trucks.

This study investigates the characteristics of regulated pollutants and HAPs in the emissions of medium-duty diesel trucks using various test modes. This study presents measurement-based characteristics of regulated pollutants and speciation of HAPs that reflect the domestic situation in Seoul and identifies pollutants for priority management.

2. Materials and Methods

2.1. Test vehicle and fuel

In this study, a total of ten medium-duty diesel trucks, five each conforming to Euro 6 and Euro 5, were selected based on data of their market share derived from the statistics of registered vehicles obtained from the Korea Automobile Manufacturers Association [23] to investigate the characteristics of their emissions in terms of regulated pollutants and HAPs. Table 1 lists the specifications of the test vehicles. The fuel used for testing satisfies the diesel emission standards of the Clean Air Conservation Act of Korea, and its properties are listed in Table 2.

Table 1: Specifications of test vehicles.

Vehicle type	Fuel type	Maker	Displacement (cc)	GVW (kg)	Max power	After-treatment system^a	Emission standards

					(ps/rpm)		
Medium-duty truck	Diesel	Hyundai	2,497	2,975	133 3600^{-1}	DPF+LNT	Euro 6
		Hyundai	2,497	2,915	133 3800^{-1}		
		Hyundai	2,497	2,945	133 3600^{-1}		
		Hyundai	2,497	3,200	133 3800^{-1}		
		KIA	2,497	2,985	133 3600^{-1}		
		Hyundai	2,497	3,200	133 3800^{-1}	DPF	Euro 5
		KIA	2,497	2,895	133 3800^{-1}		
		KIA	2,497	2,985	133 3600^{-1}		
		SSangyong	1,998	2,720	155 4000^{-1}		
		SSangyong	1,998	2,720	155 4000^{-1}		

[a] DPF(Diesel Particulate Filte), LNT(Lean NOx Trap)

Table 2

Properties of diesel used for testing.

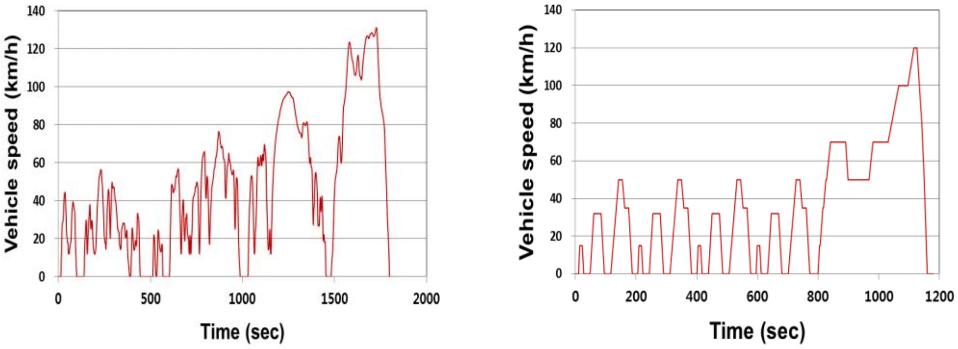
Properties	Result	Standards[b]
Residual carbon content/10 % residual oil (wt %)	0.01	≤ 0.15
Density (15°C, kg/m^3)	824	815 - 835
Sulfur content (ppm)	7	≤ 10
PAHs[a] (wt%)	2	≤ 5
Lubrication (μm)	292	≤ 400
Aromatic compounds (wt %)	21	≤ 30
Cetane index (or Cetane number)	55	≥ 52

[a] Polycyclic aromatic hydrocarbons.

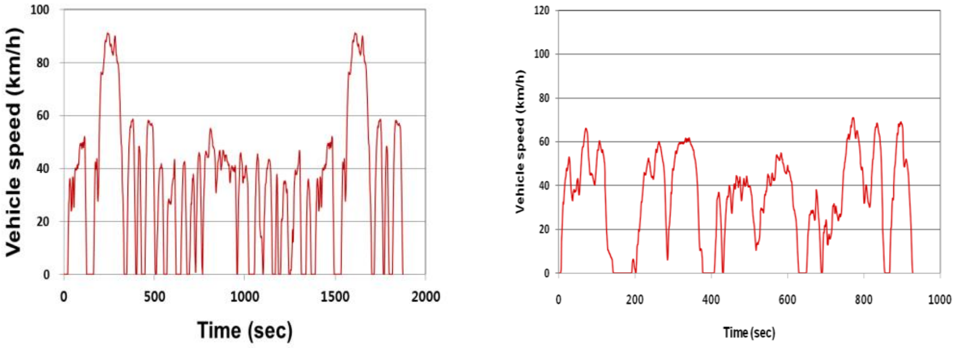
[b] Korea Ministry of Environment, Air Quality Conservation Law (KME, 2020).

2.2. Test cycles

To investigate the characteristics of air pollutants from emissions of medium-duty diesel trucks, test cycles were classified based on vehicle speed and by simulating the driving characteristics on major arterial roads, including those in Seoul. The National Institute of Environment Research (NIER)-9 driving cycle, with an average speed of 34–35 km/h, is one of the 15 driving cycles developed by the NIER to simulate real driving conditions on various urban roads in Korea. Apart from NIER-9, various certification cycles including worldwide harmonized light duty test cycle (WLTC), new European driving cycle (NEDC), and constant volume sampler (CVS)-75 were used. In addition, 50% of the maximum load was reflected in the test vehicles, and the test was conducted three times or more. Table 3 lists the specifications of the test cycles. The driving patterns of the considered driving cycles are shown in Figure 1.



(a) WLTC (b) NEDC



(c) CVS-75 (d) NIER-9

Fig. 1. Driving pattern of in (a) WLTC, (b) NEDC, (c) CVS-75 and (d) NIER-9 cycles.

Table 3

Specifications of driving cycles used for testing.

Driving cycle	Driving time (sec)	Driving distance (km)	Average speed (km/h)	Maximum speed (km/h)
WLTC	1800	23.25	46.4	131.3
NEDC	1180	10.93	33.4	120.0
CVS-75	1874	17.77	36.1	91.2
NIER-9	926	8.76	34.1	70.9

2.3. *Measuring instruments and test method*

2.3.1. Chassis dynamometer emission measurement system

As shown in Figure 2, the concentrations of pollutants were measured using a chassis dynamometer emission measurement system. The measurement system consists of a chassis dynamometer, an auxiliary operation device, a dilution tunnel, a constant volume sampler, and an exhaust gas analyzer. In the chassis dynamometer, set mechanical loads were applied to reflect the driving conditions of the vehicles, such as acceleration, deceleration, and constant speed. According to the set driving cycle, the gas emitted from the exhaust pipe during vehicle driving was mixed with air in the dilution tunnel and allowed to flow into the constant-volume sampler. The mixed gas was collected in a sample collection bag in the constant volume sampler for analysis using an exhaust gas analyzer. The quantity of emission was calculated by converting into weight unit per traveled distance (g/km). Among the emissions, CO and CO_2 were analyzed using nondispersive infrared (NDIR) spectroscopy, and total hydrocarbons (THC) and CH_4 were analyzed using a heated flame ionization detector (HFID). The NOx was analyzed using a chemiluminescence detector (CLD). Table 4 lists the specifications of the exhaust gas analyzer.

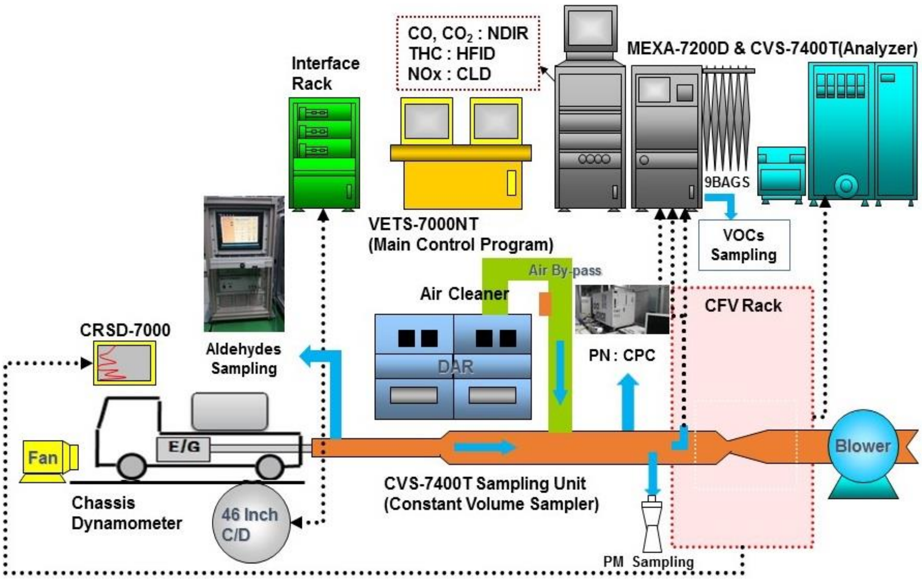


Table 4

Specifications of exhaust gas analyzer.

Pollutant	Measuring Method	Measuring Conc. range
CO	NDIR[b]	50, 100, 300, 3000 ppm
THC[a]	HFID[c]	20, 50, 100, 200 ppmC
NOx	CLD[d]	20, 50, 100, 1000 ppm
CO_2	NDIR[b]	1, 2, 3, 6 %
CH_4	HFID[c]	10, 20, 50 ppm

[a] Total hydrocarbons.

[b] Non Dispersive Infrared.

[c] Heated Flame Ionization Detector.

[d] Chemiluminescence Detector.

Fig. 2. Schematic diagram of exhaust emission test system.

PM was collected by diluting the exhaust gas with air at a certain ratio while driving using the chassis dynamometer. After collecting part of the exhaust gas and diluting it with external air in the dilution tunnel, the PM was collected using a quartz filter. A microbalance (CP2P-F, Sartorius) was used to measure the weight of the PM collected in the filter, and the measurement was performed in a weighing chamber at a temperature of 20 ± 5 °C and a relative humidity of 47 ± 5% for accurate measurement. PM measurements were performed in the following sequence: First, a filter the weight of which was measured at a constant temperature in a humidity chamber was installed in the filter holder of the PM sampler, and a PM sample was collected by suctioning the exhaust gas from the exhaust pipe at a constant flow rate and constant speed. During this process, the temperature of the exhaust gas that penetrates through the filter was maintained at 52 °C or less. The filter in which the PM was collected was stored in a Petri dish to ensure that it remained intact. The filter containing the PM sample remained in the weighing chamber at a temperature of 20 ± 5 °C and a relative humidity of 47 ± 5% for 24 ± 4 h, and the weight difference before and after the measurement was obtained. The number of particles was measured using a condensation particle counter (CPC, MEXA-2000 SPCS).

2.3.2. Analysis method for HAPs

For VOCs, a sample was collected in a 5-L Tedlar bag through a purge line after collecting diluted exhaust gas in a sample collection bag during the vehicle driving and analysis processes. VOCs were analyzed using the US EPA TO-14A [24] method. In the sample concentration and pretreatment process through a thermal desorption system, the moisture of the sample was removed using a Nafion dryer using the purge and trap technique, and VOCs were concentrated and adsorbed at a low temperature of −15 °C in the cold trap part. The concentrated sample was heated to 300 °C for desorption and injected into the gas chromatograph/mass spectrometer (GC/MS) for analysis. A 100-ppb standard gas containing a mixture of 56 materials, including ozone precursors, was used as the standard material. The calibration curve was confirmed at 2, 5, 10, 20, and 50 ppb, and the coefficient of determination (R^2) for the concentration and area was 0.998. Table 5 lists the analytical conditions used. Aldehydes were sampled by collecting the exhaust gas at a flow rate of 2 L/min through the dilution tunnel of the engine dynamometer and the pitot tube of the portable emission measurement system after connecting the Waters ozone scrubber and 2,4-dinitrophenylhydrazine cartridge to the front and rear ends. The sample was stored in a freezer at −4 °C or less before pretreatment. For the extraction solvent, acetonitrile was filtered with a GHP filter (47 mm and 0.2 µm) before use in the extraction of the cartridge. The extraction volume was set to 5 mL. The sample was placed in a dedicated 2-mL vial and analyzed using ultra-performance liquid chromatography (UPLC) based on the US EPA TO-11A [25] method. A 40 µg/mL standard solution from Supelco, a mixture of 13 materials, was mixed and diluted and used as the standard material, and the calibration curve was confirmed at concentrations of 100, 200, 500, 800, and 1000 ng/mL. The R^2 for the concentration and area was 0.997. Table 6 lists the analytical conditions used. The PM was collected in quartz filters for the analysis of PAHs. The front and rear filters that collected PM were placed in the 11 mL extraction cell of the accelerated solvent extractor. The empty space of the cell was filled with diatomite to prevent errors during extraction. The accelerated solvent extractor performed sample extraction at high temperature and pressure, and it extracted approximately 20 mL with dichloromethane for 15 min at a temperature of 100 °C and a pressure of 2,000 psi. For the analysis of PAHs, the standard material was analyzed using the US EPA TO-13A [26] method. A 100 µg/mL standard solution from Supelco, a mixture of 16 materials, was diluted and used as the standard material. The calibration curve was confirmed at 0.1, 0.25, 0.5, 1, and 2 µg/mL, and R^2 for the concentration and area was 0.995. Table 7 lists the analytical conditions used.

Table 5

Analytical conditions for thermal desorber and GC/MS.

Method	**EPA TO-14A**		
Thermal desorber	Model	Markes International / Unity2	
	Purge	Prepurge time (mℓ/min)	1
		Trap prepurge time (mℓ/min)	1
	Sample	Sampling time (min)	10
		Sample flow rate (mℓ/min)	20
	Trap desorber	Trap low temp. (°C)	-15

	Trap high temp. (°C)	300			
	Trap hold time (min)	5			
	Split flow (㎖/min)	30			
GC/MS	Model	Agilent 7890B / Almsco BenchTOF-Select			
	Column	DB-1 (60 m × 0.32 ㎜ × 3.00 ㎛)			
	Column temp.	Temp. (°C)	Rate (°C /min)	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			

Table 6

Analytical conditions of UPLC.

Method	**EPA TO-11A**			
Model	Waters US / ACOUITY UPLC			
Detector	TUV, 360 ㎚			
Column	ACQUITY UPLC™ BEH C18 1.7 ㎛ 2.1 × 100 ㎜			
Mobile phase	Solvent A : 90% Water + 10% TetraHydro Furan (THF) Solvent B : 100% Acetonitrile (ACN)			
Gradient	Time (min)	Flow (㎖/min)	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 ㎖/min			
Injection volume	2 ㎕			

Table 7

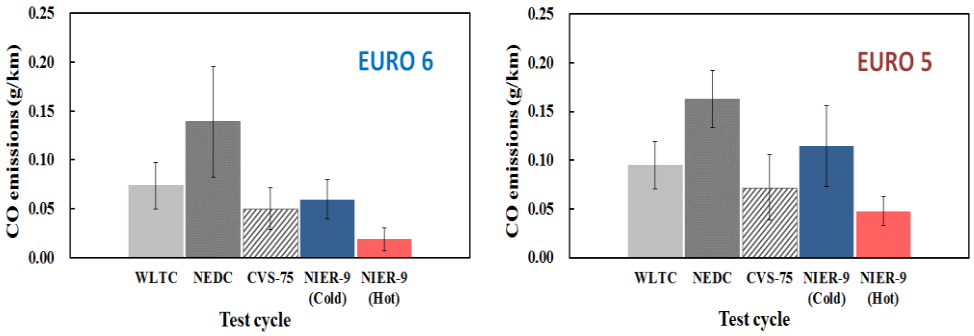
Analytical conditions of GC/MS.

Method	**EPA TO-13A**			
Model	Agilent 7890A / Almsco Bench TOF-dx			
Column	HP-5MS (30 m × 0.25 ㎜ × 0.25 ㎛)			
Column temp.	Temp (°C)	Rate (°C/min)	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 ㎖/min			
Inlet heater	300 °C			
Split ratio	10:1			
Injection volume	1 ㎕			
Transfer line	300 °C			
Ion source	250 °C			
MS san range	100-300 amu			

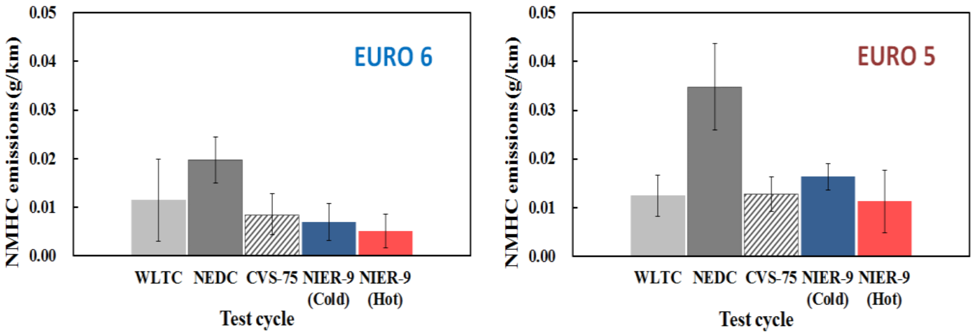
3. Results

3.1. Emission characteristics of regulated pollutants

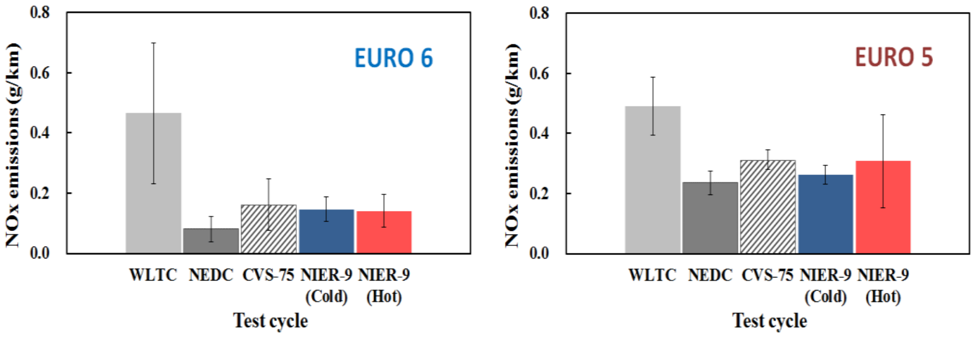
The results of the tests conducted in various test cycles (WLTC, NEDC, CVS-75, and NIER-9) using a chassis dynamometer for medium-duty diesel trucks are presented in Figure 3. As shown in Figure 3, as the regulatory standard for diesel vehicles is strengthened from Euro 5 to Euro 6, CO (0.021–0.55 g/km (15–61%)), NMHC (0.001–0.015 g/km (8–64%), and NOx (0.02–0.17 g/km (5–54%)) showed a tendency to decrease. CO and NMHC emissions were the highest in the NEDC. This appears to be because the acceleration and deceleration rates of the engine speed were higher, and the low-speed driving time was longer than that of the other modes. In the NIER-9, CO emissions were 2.4–3.2 times higher and NMHC emissions were 1.4–1.5 times higher because the cold start condition had a higher combustion instability and a lower catalytic activity than that of the hot start condition [6, 16, 27, 28]. In the WLTC, NOx emissions were 1.5–5.8 times higher than those in the other cycles. This appears to be due to the influence of thermal NOx caused by the high-speed section [15-16]. Euro 6 showed a 43% reduction in NOx emissions compared to Euro 5 owing to the lean NOx trap (LNT). As shown in Figure 4, the PM emissions of medium-duty diesel trucks were less than 0.001 g/km. It appears that the PM emissions were significantly low owing to the installation of the DPF in the test vehicles. Particle numbers (PN) in the emissions from the Euro 6 vehicles ranged from 8.2 × 1010 to 1.2 × 1011 #/km, which were lower than those from the Euro 5 vehicles (1.0 × 1011 to 1.3 × 1011 #/km).



(a) CO

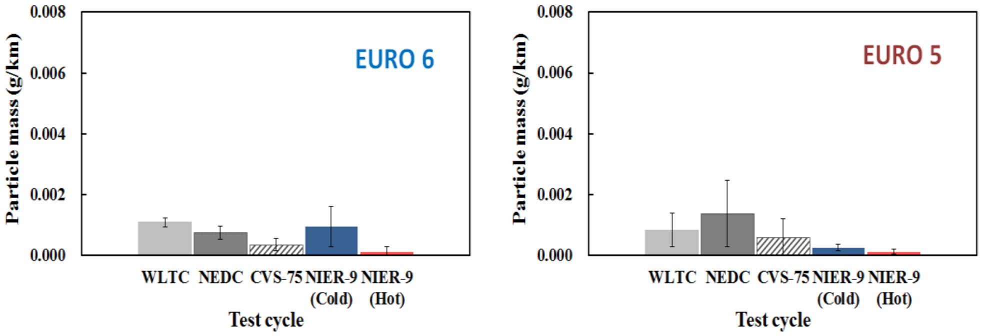


(b) NMHC

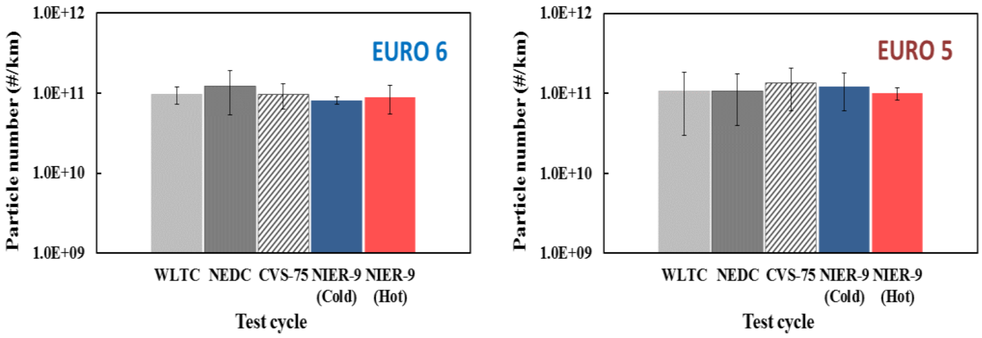


(c) NOx

Fig. 3. Emission characteristics of (a) CO, (b) NMHC, (c) NOx, and (d) PM from medium-duty diesel trucks according to driving cycles



(a) PM



(b) PN

Fig. 4. Emission characteristics of (a) PM and (b) PN from medium-duty diesel trucks according to driving cycles.

3.2. Emission characteristics of HAPs

As for the components of non-methane volatile organic compounds (NMVOCs), alkanes exhibited the highest proportion (36.5–37.5%) in all the test modes of the Euro 6 and Euro 5 vehicles, followed by aromatics (14.4–40.1%), alkenes (8.0–34.9), and cycloalkanes (1.7–12.7%) as shown in Figure 5. Alkanes showed the highest proportion because they have lower reactivity in the DOC than in the other components [29-30].

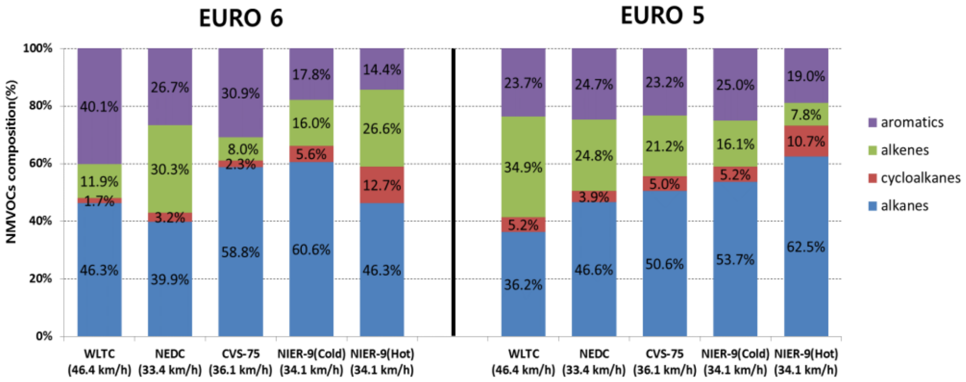


Fig. 5. NMVOC composition of medium-duty diesel trucks according to driving cycles.

Table 8 shows the five major chemical components in the NMVOC emissions for each regulatory standard and test mode. For Euro 6, benzene emissions (0.19–1.01 mg/km) were the highest in the WLTC, NEDC, CVS-75, and NIER-9 (hot) cycles, and dodecane emissions (1.72 mg/km) were the highest in the NIER-9 (cold). For Euro 5, the highest emissions were benzene (0.38 mg/km) in the WLTC, propylene (0.91 mg/km) in the NEDC, and dodecane (0.41–1.91 mg/km) in the CVS-75 and NIER-9 (cold and hot) cycles. The rankings of chemical components of the emissions varied based on the regulatory standard and test mode, and they are known to be influenced by emission reduction devices, driving conditions, and engine start conditions [15-16].

Table 8

Comparison of the five major chemical components of NMVOC emissions from diesel medium-duty trucks for driving cycles.

(a) Euro 6 (unit : mg/km)

No.	WLTC		NEDC		CVS-75		NIER-9(Cold)		NIER-9(Hot)	
1	Benzene	0.51	Benzene	0.91	Benzene	0.19	Dodecane	1.72	Benzene	1.01
2	Dodecane	0.24	Propylene	0.35	Undecane	0.18	Undecane	1.70	Dodecane	0.67
3	Undecane	0.23	Undecane	0.16	Dodecane	0.16	n-Heptane	1.18	Undecane	0.52
4	Propylene	0.13	Dodecane	0.13	1,2,4-T.M.B.[a]	0.11	n-Decane	1.02	Propylene	0.43
5	n-Decane	0.12	1-Butene	0.12	n-Decane	0.09	1,2,4-T.M.B.[*]	0.84	n-Decane	0.29

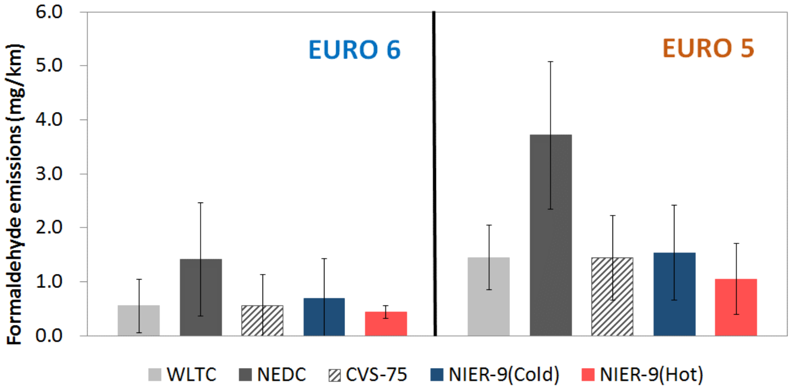
[a] 1,2,4-trimethylbenzene

(b) Euro 5 (unit : mg/km)

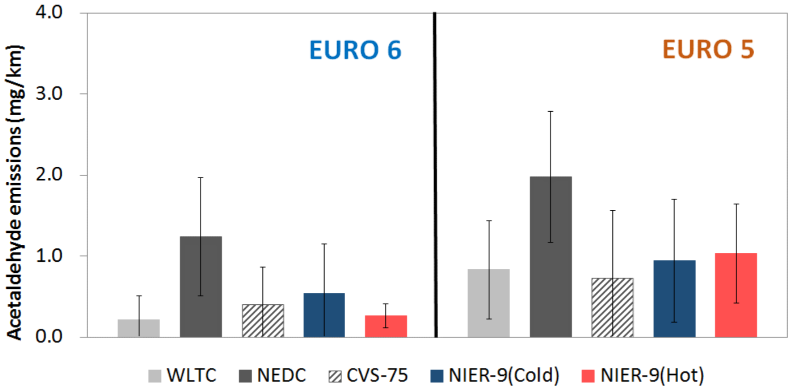
No.	WLTC		NEDC		CVS-75		NIER-9(Cold)		NIER-9(Hot)	
1	Benzene	0.38	Propylene	0.91	Dodecane	0.41	Dodecane	1.91	Dodecane	0.63
2	Propylene	0.36	Dodecane	0.39	Toluene	0.19	Toluene	1.18	n-Nonane	0.43
3	Dodecane	0.16	n-Nonane	0.36	Undecane	0.16	m,p-Xylene	0.78	n-Octane	0.41
4	n-Nonane	0.14	Benzene	0.31	n-Decane	0.14	n-Nonane	0.76	Methyl C.H.[a]	0.32
5	m,p-Xylene	0.13	n-Decane	0.28	n-Nonane	0.14	Isobutane	0.73	Isobutane	0.28

[a] Methylcyclohexane

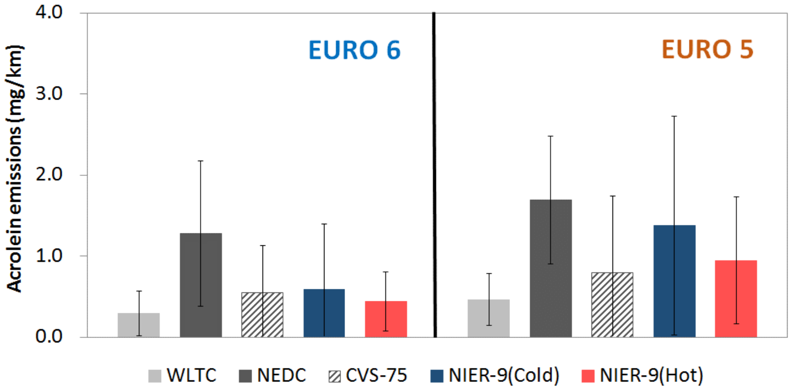
As for aldehyde emissions, formaldehyde emissions (0.44–3.71 mg/km) were the highest for all regulatory standards and test modes, followed by acetaldehyde (0.22–1.97 mg/km) and acrolein (0.29–1.69 mg/km) emissions as shown in Figure 6. Formaldehyde (34.6–52.8%) and acetaldehyde (20.5–34.1%) were present in high proportions. Formaldehyde emissions are known to be the highest from diesel trucks, followed by acetaldehyde emissions among the aldehydes [7, 22]. A similar tendency (formaldehyde 48% and acetaldehyde 21%) was observed in heavy-duty diesel trucks [31]. In the NEDC, the aldehyde emissions were the highest. In the case of the NIER-9, they were 1.0–1.9 times higher under the cold start condition compared to the hot start condition.



(a) Formaldehyde



(b) Acetaldehyde



(c) Acrolein

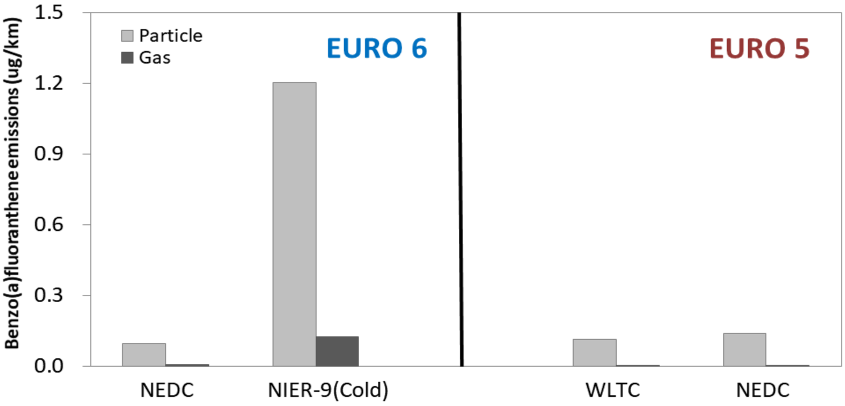
Fig. 6. Emission characteristics of (a) formaldehyde, (b) acetaldehyde, and (c) acrolein from medium-duty diesel trucks according to driving cycles.

In this study, 16 particle-phase PAHs in PM were analyzed, while gas-phase PAHs were not sampled. In the atmosphere, PAHs are present as semi-volatile compounds in both the gas and particle phases [32]. For total PAH concentrations, gas-phase PAHs were estimated using the gas–particle partition coefficient (K_P) calculated for five low molecular weight PAH compounds [32] based on previously established models [33-36] using the following equation:

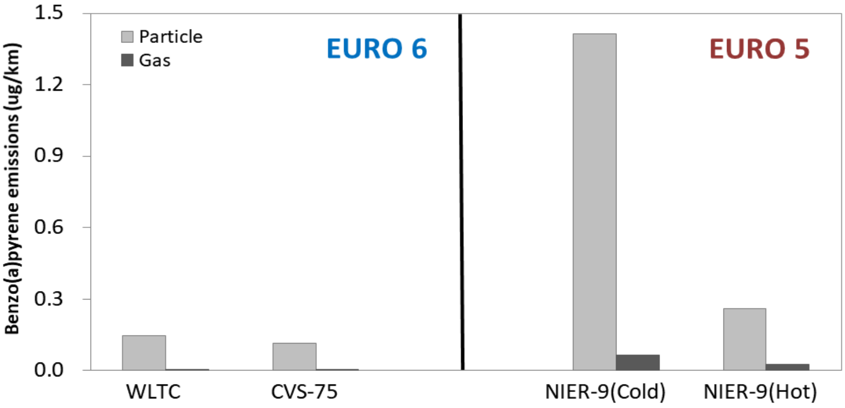
$$K_P = (F/TSP) / A \tag{1}$$

Where, K_P is the gas–particle partition coefficient (μg/m^3), TSP is the concentration of total suspended particulate material (μg/m^3), F is the particle phase concentration of PAHs (μg/m^3), and A is the gaseous phase concentration of PAHs (μg/m^3).

Figure 7 shows the total PAH emissions (gas + particle phase) estimated in this study. For the benzo(k)fluoranthene, 0.14–1.33 μg/km for Euro 6 and 0.12–0.15 μg/km for Euro 5 were estimated. For the benzo(a)pyrene, 0.11–0.15 μg/km for Euro 6 and 0.21–0.28 μg/km for Euro 5 were estimated. The results show that 68.7–99.8% of benzo(k)fluoranthene and 90.7–98.1% benzo(a)pyrene were in the particle phase. According to Akyüz and Çabuk (2010), high molecular weight PAHs (4–5 rings) are mainly associated with the particle phase. When the KP·TSP is larger than 1, the compound partitions dominantly to the particle phase; a KP·TSP smaller than 1 indicates partitioning dominantly to the gaseous phase [37]. It appears that some PAHs were detected in trace amounts due to the high PM reduction rate as DPF was installed in all the test vehicles. Hu et al. (2013) [22] reported that vehicles with DPF can efficiently reduce emission of PAHs by more than 90%. In addition, standards for PAH emissions from high-quality diesel fuel have been made more stringent [21]. In this study, the tested diesel fuel satisfied the high-quality diesel fuel standard specified limits for sulfur, PAHs, lubrication, and aromatic compounds.



(a) Benzo(a)fluoranthene



(b) Benzo(a)pyrene

Fig. 7. Emission characteristics of (a) benzo(a)fluoranthene and (b) benzo(a)pyrene from medium-duty diesel trucks according to driving cycles. Particle data points represent an average of triplicate measurements with a standard deviation of (a) 0-0.32 μg/km for NEDC, 0.32-2.10 μg/km for NIER-9 (Cold), 0-0.37 μg/km for WLTC and 0-0.46 μg/km for NEDC, (b) 0-0.33 μg/km for WLTC, 0-0.24 μg/km for CVS-75, 0-2.99 μg/km for NIER-9 (Cold) and 0-0.84 μg/km for NIER-9 (Hot).

The toxicity equivalent factor (TEF) method is commonly used and is reliable for the evaluation of carcinogenicity of the identified PAHs. [14, 15, 18, 38, 39]. Since Nisbet and LaGoy (1992) put forward the concept of TEF based on the toxicity of PAHs (Table 9), benzo(a)pyrene is usually used as a reference compound to derive the TEQ of PAHs [14, 15, 18, 38, 39].

Table 9

Chemical parameters and toxic equivalent factors of PAHs.

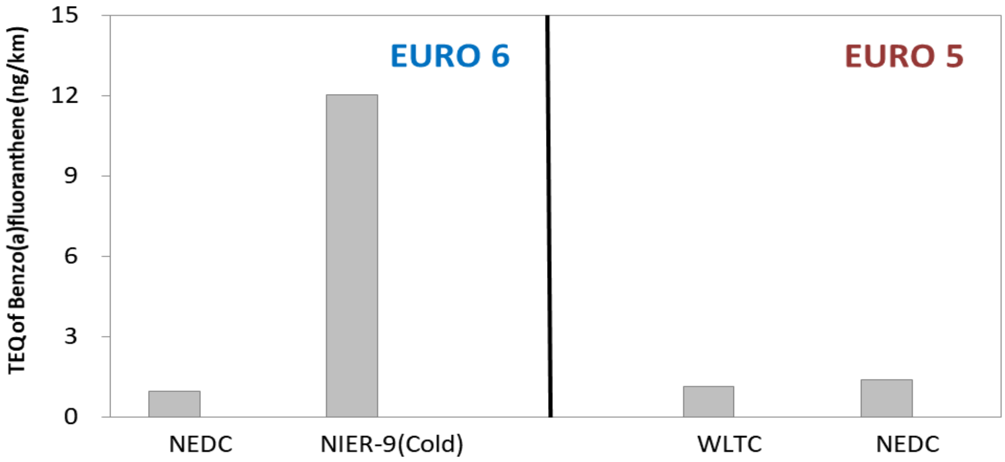
PAHs	Abbreviation	Rings	Mol. Weight	Toxic Equivalent Factors
Benzo(k)fluoranthene	BkFt	5	252	0.01
Benzo(a)pyrene	BaP	5	252	1.0

TEQ is a classic method to evaluate the toxicities of particles and it is calculated as follows:

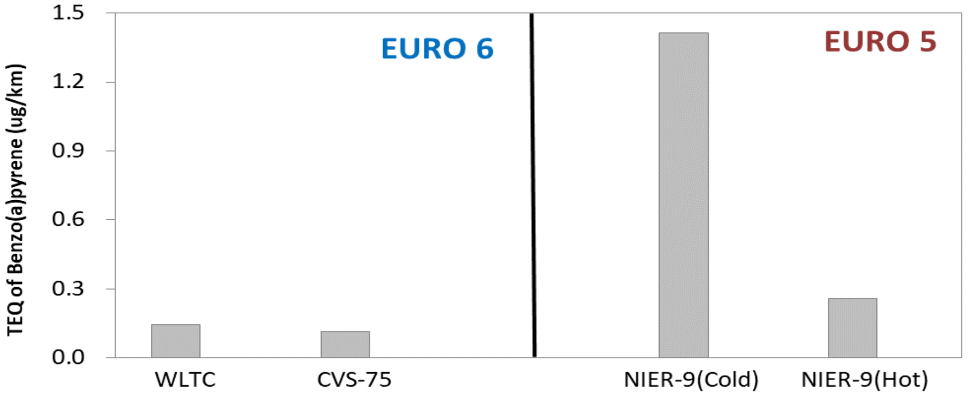
$$TEQ = \sum Ci \times TEFi \quad (1),$$

where, Ci denotes the concentration of an individual i PAH.

Figure 8 depicts the TEQ of the two identified PAHs based on driving conditions. The two identified PAHs had a 5-ring structure, but the TEQ of benzo(a)pyrene was 100 times higher than that of benzo(a)fluoranthene because of a more bay-region-like benzene ring structure, which could cause more mutagenicity and carcinogenicity compared to linear structured PAHs [40-42].



(a) TEQ of Benzo(a)fluoranthene



(b) TEQ of Benzo(a)pyrene

Fig. 8. Toxicity equivalent quantity (TEQ) of (a) benzo(a)fluoranthene and (b) benzo(a)pyrene from medium-duty diesel trucks according to driving cycles. All data points represent an average of triplicate measurements with a standard deviation of (a) 0-3.16 µg/km for NEDC, 3.16-20.96 µg/km for NIER-9 (Cold), 0-3.68 µg/km for WLTC and 0-4.56 µg/km for NEDC, (b) 0-0.33 µg/km for WLTC, 0-0.24 µg/km for CVS-75, 0-2.99 µg/km for NIER-9 (Cold) and 0-0.84 µg/km for NIER-9 (Hot).

Notably, the TEQs of benzo(a)pyrene and benzo(a)fluoranthene emitted from NIER-9 (cold) was more than 5 times and 12 times higher than that of NIER (hot) and NEDC for each Euro 5 and Euro 6 vehicles, respectively, implying that sufficient warm-up of vehicles could prevent the emission of carcinogenic aromatic compounds.

Moreover, only two 5-ring PAHs were identified because of the equipped after-treatment systems such as DPF and LNT, which reduce the particle phase emission of PAHs from the tested vehicles [43].

3.3. Speciation of HAPs and selection of priority management pollutants

In this study, HAPs speciation was derived based on the NMHC emissions of medium-duty diesel trucks measured in various test cycles. As shown in Table 10, formaldehyde tended to exhibit the highest proportion (9.8–44.6%) in terms of all the regulatory standards and test modes, and a tendency similar to that of European Environment Agency [44] was observed. The proportion of formaldehyde was relatively the highest in both Euro 6 and Euro 5. The proportion of benzene was higher for Euro 6 than for Euro 5. When the speciation was derived during various test cycles based on each relevant regulatory standard, there were differences in speciation between the overseas driving cycles and the domestic driving cycle, confirming that the consideration of the domestic situation is important. In addition, it is deemed necessary to consider formaldehyde and benzene, which are carcinogens, as priority management pollutants through continuous monitoring.

Table 10

Speciation of hazardous air pollutants from NMHC emissions of medium-duty diesel trucks (unit : %).

Compounds	This study										EEA
	Euro 6					Euro 5					
	WLTC	NEDC	CVS-75	NIER-9 (Cold)	NIER-9 (Hot)	WLTC	NEDC	CVS-75	NIER-9 (Cold)	NIER-9 (Hot)	
Benzene	16.02	10.46	6.32	2.92	4.89	2.92	2.13	1.54	3.45	1.88	1.98
Toluene	2.33	0.37	2.15	1.37	2.90	1.51	1.30	2.63	4.96	1.81	0.69
Ethylbenzene	1.02	0.16	0.87	0.83	0.22	0.62	0.48	0.86	2.58	1.16	0.29

Xylene	2.36	0.32	2.05	1.95	0.63	1.49	1.50	1.98	4.40	2.03	0.88
Formaldehyde	21.09	22.75	19.35	13.48	12.43	44.64	35.93	31.40	9.75	14.49	12.00
Acetaldehyde	16.02	22.30	13.68	10.97	14.92	14.08	16.49	17.63	4.63	14.01	6.47
Acrolein	8.24	23.43	18.18	13.16	27.99	8.18	12.93	11.91	5.88	14.01	3.58

4. Discussion

In this study, measurement-based speciation that reflects the domestic situation was derived and priority management pollutants were identified by investigating the emission characteristics of regulated pollutants and volatile organic compounds (VOCs), aldehydes, and polycyclic aromatic hydrocarbons (PAHs)) using various test modes for medium-duty diesel trucks. When the emission characteristics of the regulated pollutants from medium-duty diesel trucks were investigated, the CO and NMHC emissions were highest in the NEDC mode because its low-speed driving time was longer compared to the other modes. NOx emissions were 1.5–5.8 times higher in the WLTC than in the other cycles because of the influence of thermal NOx caused by the high-speed section. PM emissions were 0.001 g/km or less because of the influence of the installation of a diesel particulate filter (DPF) in the test vehicles, and they were lower for Euro 6 than for Euro 5.

When the emission characteristics of HAPs were investigated, alkanes exhibited the highest proportion (36.2–62.5%) among the components of non-methane volatile organic compounds (NMVOCs) because they have a lower reactivity in DOC than those of the other components. Among the components of NMVOCs, benzene, propylene, and dodecane exhibited the highest emissions. The rankings of the chemical components in terms of emissions differed based on the test mode because of the influence of emission reduction devices as well as the engine and driving conditions. As for aldehydes, formaldehyde emissions were the highest (34.6–52.8%) in all the regulatory standards and test modes followed by acetaldehyde and acrolein emissions.

For PAHs, only benzo(k)fluoranthene and benzo(a)pyrene were detected in trace amounts because PM emissions were low owing to the influence of the DPF installation. We detected benzo(k)fluranthene and benzo(a)pyrene in the particle-phase PAHs and estimated the concentrations of the gas-phase PAHs with models to obtain the total PAH concentrations. The TEQ of two identified PAHs (benzo(k)fluoranthene and benzo(a)pyrene) from NIER-9 (cold) for each Euro 5 and Euro 6 vehicles were more than five times and 12 times higher than NIER (hot) and NEDC, respectively.

When HAPs speciation was derived from particulate material based on the NMHC emission results of the medium-duty diesel trucks measured in various test cycles, formaldehyde exhibited the highest proportion in all regulatory standards and test cycles, and a tendency similar to that of the European Environmental Agency (EEA) was observed. Differences in speciation between the domestic and overseas test cycles indicated the importance of considering the domestic situation. The carcinogens, formaldehyde and benzene, were identified as priority management pollutants that require continuous monitoring. The HAP speciation from medium-duty diesel trucks and the priority management pollutants identified in this study are expected to form the basis for policy implementation that will ensure the reduction of HAPs from domestic mobile sources in the SMA, where automobiles have a significant influence on air pollution.

Author Contributions: For research articles with several authors, a short paragraph specifying their individual contributions S. Jung, S. Kim, T. Chung, H. Hong, S. Lee – Measurement and Analysis. S. Jung – Data analysis and modeling of gas-phase PAHs. J. Lim – Estimation of PAHs TEQ. S. Jung, J. Lim – Preparation of manuscript and finalization.

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Conflicts of Interest: The authors declare no conflict of interest.

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