Effects of Retarding Fuel Injection Timing on Toxic Organic Pollutant Emissions from Diesel Engines

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ABSTRACT

Retarding the fuel injection timing is an effective strategy for controlling NO_x emissions from diesel engines. However, the influence of retarding the fuel injection timing on polycyclic aromatic hydrocarbon (PAH) and persistent organic pollutant (POP) emissions has not yet been investigated. In this study, the diesel engine was tested using four of the existing thirteen European steady state cycle (ESC) modes. The fuel injection timing was retarded from –8° to –6° and the diesel exhaust gas samples were analyzed for PAH and POP emissions. The NO_x emission factor reduced by ~25% when the fuel injection timing was retarded. However, the strategy had a negative effect on combustion efficiency. The carbon monoxide (CO) and particulate matter (PM) emissions were 1.4 and 1.2 times higher for the –6° scenario, respectively. The emission factors of all the toxic organic pollutants increased drastically when the fuel injection timing was retarded. For instance, the emission factors of PAH and polychlorinated dibenzo-*p*-dioxin/dibenzofuran (PCDD/F) for the –6° scenario, based on BaPeq and WHO-TEQ, were 22 and 10 times higher than for the –8° scenario. The retardation had more influence on these pollutants in the particle-phase than in gas-phase. The resultant negative impact on combustion increased the emissions of products of incomplete combustion, enhancing the potential of POP formation via de novo synthesis. The study concludes that although retarding the fuel injection timing leads to a decrease in NO_x emissions from diesel engines, it also results in an increase in PAH and POP emissions.

Keywords: Diesel engine; Retarding injection timing; PAHs; POPs.

INTRODUCTION

Diesel internal combustion engines are widely used in light and heavy transport, agricultural machinery, as well as industrial use due to their high power output coupled with high fuel efficiency and subsequently lower CO_2 emissions (Alriksson and Denbratt, 2006; Dober *et al.*, 2008). Despite these advantages, emissions from diesel engines are significant sources of nitrogen oxides (NO_x) and particulate matter (PM). Besides acting as precursors for PM and ground level O_3, NO_x from a diesel engine are believed to cause adverse effects to human health (Bell *et al.*, 2004; Khaniabadi *et al.*, 2017). In addition to the conventional air

pollutants, diesel engines also emit toxic and carcinogenic polycyclic aromatic hydrocarbons (PAHs) and persistent organic pollutants (POPs) including; polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs), polybrominated biphenyls (PBBs), and polybrominated diphenyl ethers (PBDEs) (McDonald *et al.*, 2011; Chang *et al.*, 2014b; Mwangi *et al.*, 2015; Cheruiyot *et al.*, 2016; Chen *et al.*, 2017c; Lai *et al.*, 2017).

Stricter emission standards on the conventional pollutants like NO_x and PM has led to the adoption of aftertreatment technologies over the years. The technologies and strategies employed to reduce NO_x emissions from diesel engines accomplish this fete through either one or more of these means; reducing the peak temperature, reducing the residence time of combustion products in high temperature zones and reducing the Air-to-fuel (A/F) ratio (Sindhu *et al.*, 2018). Some of the aftertreatment technologies and strategies employed include NO_x traps, exhaust gas recirculation (EGR), selective catalytic reduction (SCR) and retarding fuel

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injection timing (Koebel *et al.*, 2000; Kouremenos *et al.*, 2001; Agarwal *et al.*, 2011; Diao *et al.*, 2018; Chen *et al.*, 2019).

Retarding the fuel injection timing reduces NO_x formation in diesel engines by shifting the combustion event so that the peak pressures occur when the piston is well beyond the top-dead-center (TDC) resulting in lower pressure and temperature (Sayin and Canakci, 2009; Sindhu *et al.*, 2018). At constant engine load, Sayin and Canakci (2009) reported a ~30% decrease in NO_x emissions when the injection time was retarded by 5°. Mani and Nagarajan (2009) also reported a decrease in NO_x emissions with the retardation of the injection timing from the standard 23° to 14° before TDC. Specifically, they ranged from 8.9 g kW-h^{-1} to 16.35 g kW-h^{-1} for standard injection and from 8.56 g kW-h^{-1} to 14.63 g kW-h^{-1} for retarded injection at 100% to 0% engine loads, respectively. In an investigation carried out using different biodiesel blends, maximum NO_x emissions observed for B20 at 21° BTDC were lower than those observes at 24° BTDC. Overall, for all loads ranging between 100% to 0%, NO_x emission factors varied as follows; 27° BTDC > 24° BTDC > 21° BTDC (Gnanasekaran *et al.*, 2016).

However, retarding the injection time leads to significant trade-offs between NO_x and particulate matter (PM), as well as the fuel consumption because the lower temperatures result in incomplete combustion of the fuel (Kouremenos *et al.*, 2001; Zeng *et al.*, 2006; Sayin and Canakci, 2009; Agarwal *et al.*, 2014). Several studies reported increase on emissions of products of incomplete combustion (PIC) including soot, carbon monoxide and hydrocarbon during fuel timing retardation (Kouremenos *et al.*, 2001; Sayin and Canakci, 2009; Liu *et al.*, 2014). This impact on combustion quality might also influence POP emissions from diesel engines since some of these PICs have been shown to act as precursors for the formation of POPs (Addink and Altwicker, 2004). However, to the best of our knowledge, this relationship between injection timing and POP emissions

has not yet been investigated.

Therefore, the objective of this research is to study the effect of retarding the fuel injection timings on PAH and POP emissions from a heavy-duty diesel engine (HDDE). The concentrations, congener profiles, and emission factors of PAHs, PCDD/Fs, PCBs, PBDD/Fs and PBDEs from the HDDE exhaust at −8° and −6° injection timings were collected and compared. The results from this research would shade light into the effects of conventional pollutant treatment technologies and strategies on PAH and POP emissions from diesel engines.

METHODS AND MATERIALS

Diesel Engine and Test Fuel

This experiment was performed using a Hino W06E, which is a heavy-duty diesel engine with a direct fuel injection system. Details of the specifications for the diesel engine are given in Table 1, including engine configuration, fuel injection system, compression ratio, injection timing and working boundary conditions. The torque and speed of the engine were monitored using the Schenck W230 engine dynamometer. The engine was tested using four of the existing thirteen European steady state cycle (ESC) modes: mode 1 (750 rpm, 0% load, 0 Nm), mode 2 (1650 rpm, 100% load, 360 Nm), mode 7 (1650 rpm, 25% load, 90 Nm) and mode 11 (1925 rpm, 25% load, 96.2 Nm). A commercial fuel blend of 98% fossil diesel and 2% biodiesel (B2) was used as the test fuel for this investigation.

Test Methods and Sampling Procedures

In order to carry out the tests on the exhaust gases, samples were collected at two different injection timings, at −8° and −6°, which represent the default engine setting and the retarded injection timing, respectively. Before each sampling, the engine was preheated for 30 minutes and for at least 3 minutes between the different test modes. During the entire testing cycle, samples of the exhaust gases from

Table 1. Properties of the diesel engine under investigation.

Item	Hino W06E
Configuration	In-line 6-cylinder
Stroke	118 mm
Bore	104 mm
Air intake	Naturally aspirated
Compression ratio	17.9
Type of fuel injection system	Bosch A type
Injection type	Direct injection
Fuel injection pressure	21560 kPa
Injection timing	15° Before top dead center
Displacement	6.0 L
Max torque	412 Nm @ 1800 rpm
Max power	121 kW @ 3000 rpm
EGR	No
Boundary condition	
Ambient air temperature	30–40°C
Ambient air pressure	Approximate 101 kPa (1 atm)
Ambient air humidity	60–70%

the diesel engine were collected directly at a constant velocity. The components of the sampling system included a glass fiber filter, flow meter, condenser, two-stage glass cartridges, and a pump. The glass fiber filter was applied for the collection of particulate phase pollutants. A set of cooling devices positioned immediately before the two-stage glass cartridges was used to lower the exhaust gas temperature to below 5°C and remove moisture from the exhaust gas. The toxic pollutants in their gaseous phase were collected through the two-stage glass cartridges. Structurally, the cartridges were composed of 5.0 cm (about 20 g) of XAD-2 resin packed inside a tube and held in place by two 2.5 cm polyurethane foam plugs.

Samples from four runs were combined into one to ensure the pollutant concentrations were above the detection limit. The total sampling time was ~80 minutes with each ESC mode requiring about ~20 minutes each. The sample volumes were normalized to standard temperature and pressure (273 K and 760 mmHg, respectively) and denoted as Nm^{-3}.

Analytical Procedures

To determine the mass of particulate matter in the respective samples, a Precisa XR 205SM-DR balance with a sensitivity of 0.01 mg was applied for weighing the filters. The concentration of NO_x in the exhaust gas was determined using a Rosemount Model 951A NO/NO_x analyzer (Chang *et al.*, 2014b).

Each POP sample was extracted by a Soxhlet extractor using a mixed solvent (n-hexane and dichloromethane; vol/vol, 1:1; 250 mL each) for 24 hours. Internal standards of PAHs, PCDD/Fs, PCBs, PBDD/Fs, and PBDEs were spiked into the extract to monitor the sample recoveries. The extracts were concentrated by gently purging a stream of ultra-pure nitrogen and then cleaned up by passing through a silica gel column. The effluents were re-concentrated to exactly 1 mL. PAH contents were detected with gas chromatography/mass spectrometry (GC/MS). The detailed PAH analytical procedures are given in our previous works (Wang *et al.*, 2007, 2009)

After the GC/MS analysis, the solutions in the vials were then analyzed for seventeen 2,3,7,8-substituted PCDD/Fs, twelve dioxin-like PCBs, twelve 2,3,7,8-substituted PBDD/Fs and fourteen PBDE congeners. In brief, the sample solution was treated with concentrated sulfuric acid, followed by a series of sample cleanup and fractionation procedures, including a multi-layered silica column, alumina column, and an activated carbon column. During the alumina-column cleanup, non-planar PCBs were first eluted with 25 mL hexane and then with 15 mL DCM/hexane (4/96, v/v) prior to their trapping by activated carbon. The activated carbon column was sequentially eluted with 25 mL dichloromethane/hexane (40/60, v/v) for extracting PBDEs and planar PCBs, which was followed by 40 mL of toluene for extracting PCDD/Fs and PBDD/Fs. Before instrumental analyses, the planar and non-planar PCB eluates were mixed together. The detailed analytical procedures are described in more detail in previous works (Chang *et al.*, 2014a; Wu *et al.*, 2014).

Instrumental Analysis

The GC/MS (Agilent 5890A and Agilent 5975) for PAH measurement was equipped with a capillary column (HP Ultra 2 - 50 m × 0.32 mm × 0.17 µm). The operating conditions were an injection volume of 1 µL; splitless injection at 300°C; ion source temperature at 310°C; oven temperature held at 45°C for 1 min, ramped from 45 to 100°C in 5 min, ramped from 100 to 320°C at 8 °C min^{-1} and held at 320°C for 15 min. The masses of the primary and secondary PAH ions were determined by using the scan mode for pure PAH standards. The PAHs were qualified by using the selected ion monitoring (SIM) mode.

A high-resolution gas chromatography/high-resolution mass spectrometer (HRGC/HRMS) was used for the POP analyses. The HRGC (Hewlett-Packard 6970 Series gas, CA) was equipped with a silica capillary column (J&W Scientific, CA) and a splitless injector, while the HRMS (Micromass Autospec Ultima, Manchester, UK) was equipped with a positive electron impact (EI+) source. The SIM mode was used with a resolving power of 10,000. The electron energy and the source temperature were specified at 35 eV and 250°C, respectively. Each analyte requires an individual injection, i.e., one exhaust sample needs six injections for the analyses of PCDD/Fs, PCBs, PCDEs, PBDD/Fs, PBBs and PBDEs. The detailed instrumental analysis parameters are given in previous works (Wang *et al.*, 2003; Chang *et al.*, 2013; Wu *et al.*, 2014).

Quality Assurance and Quality Control (QA/QC)

Prior to samplings, the glass fiber filters were placed in an oven at 450°C for 8 h to burn off all organic pollutants. Field and laboratory blank controls were incorporated into this study. Compared with the corresponding exhaust samples, the POPs in these blank samples were all lesser than 0.5% of total POPs in the real samples, except for PBDEs, which were < 2% of real samples. All these blank samples were negligible compared with the corresponding exhaust samples.

For POPs, the surrogate standards were spiked into the cartridges and their recoveries were used to analyze the breakthroughs of POPs in the samples. The sampling probe and other components of the sample train were rinsed after each sampling. The nozzle, probe and probe lines were rinsed three times with methylene chloride and then three times with toluene. The rinsate were collected and included for POPs analyses. For each diesel engine test, a prior leak check was carried out between the inlet of the filter holder and the outlet of the flow meter. During the pretreatment procedures of sample analyses, both the internal and recovery standards were added to the sample. The recoveries of precision and recovery (PAR), surrogate, and internal labeled standards of POPs all met the respective standards.

RESULTS AND DISCUSSION

Emission Factors of Conventional Pollutants

Table 2 presents the emission factors of CO, PM and NO_x from the diesel engine at the two different fuel

injection timings. As expected, retarding the fuel injection timing resulted in lower NO_x emissions. The emission factor of NO_x was 24.8% lower for –6° injection timing when compared to –8° scenario. Similar decreases have been reported in previous studies (Agarwal *et al.*, 2013; Gnanasekaran *et al.*, 2016). However, since retarding the fuel injection timing has a negative impact on combustion, the emission factors of CO and PM, which are indicators of combustion efficiency, were 1.4 and 1.2 times higher for –6° than for –8° fuel injection timing, respectively.

PAH and POP Concentrations and Gas- and Particle-phase Partitioning

Sampling artifacts can result in over- or underestimation of semi-volatile organic compounds because of their wide range of gas- and particle-phase partitioning (Cheruiyot *et al.*, 2015; Melymuk *et al.*, 2016). Table 3 presents the PAH and POP contents in the particles collected by the sampling filters and from the inner surface of the exhaust duct. The contents in the particles collected by the sampling filter were generally higher than those from particles collected from the inner surface of the duct. For instance, the PAH mass contents in the particulates collected by sampling filter were ~3 and 5 times higher than those in the inner surface of the duct for –8° and –6° fuel injection timings, respectively. For PCDD/F toxicity, the difference was even increase to ~13 times during the –8° scenario. This observed difference could be because the gas-phase congeners were adsorbed on to the particulates collected by the filter and on the filter itself. Therefore, to eliminate the bias caused by the sampling artifacts, the PAH and POP concentrations were corrected using a similar method discussed in our previous studies (Kuo *et al.*, 2012; Chen *et al.*, 2017c).

The corrected gas- and particle-phase PAH and POP concentrations are presented in Table 4. The gas-phase

PAHs and POPs were found to dominate diesel engine exhaust during both fuel injection timings. That is because the high exhaust temperature and the formation of POPs were through homogenous gas-phase pathway (Chen *et al.*, 2017c).

The concentrations during the –6° injection timing were drastically higher for all toxic organic pollutants than during –8°. For instance, the mass concentrations of PAHs and POPs during the –6° were 1.1–63 times higher than those during –8° injection timing. Retarding the injection time reduces the combustion temperature which leads to incomplete combustion. This assertion is supported by the increased emission of CO and PM in our study. The lower combustion efficiency results in a generation of products of incomplete combustion including these toxic compounds and their precursors. Therefore, it can be concluded that retarding the fuel injection timing results in an increase in PAH and POP concentrations from diesel engines.

Comparing the –6°/–8° ratios of particle-phase with those of gas-phase, we found that retarding the injection timing had more influence on these toxic pollutants in particle-phase, except for PCBs. For instance, –6°/–8° ratios of the gas- and particle-phase PCDD/F were 1.0 and 3.3 while those of PBDD/Fs were 1.7 and 28, respectively. That is because the negative effect on combustion that resulted from the injection timing retardation led to an increase in PM and other products of incomplete combustion including soot. Thereby, providing the necessary carbon matrix for POP formation via de novo synthesis.

PAH and POP Emission Factors

The emission factors of the diesel engine during the two injection timings were calculated and are presented in Table 5. Retarding the injection timing lead to a dramatic increase in PAH and POP emission factors. For instance, the mass emission factors of PAHs, PCDD/Fs, PCBs, PBDD/Fs,

Table 2. Emission factors of CO, PM and NO_x from the diesel engine.

		CO (g kW-h^{-1})	PM (g kW-h^{-1})	NO_x (g kW-h^{-1})
Injection Timing	–6°	4.69	0.62	4.44
	–8°	3.28	0.50	5.91

Table 3. PAH and POP contents in the particles collected by the sampling filters and collected from the inner surface of the duct.

		particle collected by the sampling filter		particle collected from inner surface of duct	
		–8°	–6°	–8°	–6°
PAHs	Mass (µg g^{-1})	174	92.3	52.4	18.6
	BaP$_{eq}$ (µg g^{-1})	11.7	73.8	0.0544	0.302
PCDD/Fs	Mass (pg g^{-1})	3746	369	126	90.3
	WHO-TEQ (pg WHO-TEQ g^{-1})	15.0	38.6	1.13	8.18
PCBs	Mass (pg g^{-1})	NA	55.3	23.5	13.5
	WHO-TEQ (pg WHO-TEQ g^{-1})	NA	3.96	0.00218	0.839
PBDD/Fs	Mass (pg g^{-1})	2497	1797	88.9	175
	WHO-TEQ (pg WHO-TEQ g^{-1})	6.09	18.0	0.453	4.75
PBBs	Mass (pg g^{-1})	122	NA	NA	NA
PBDEs	Mass (ng g^{-1})	139	1114	20.0	45.0

Table 4. Corrected concentrations of toxic organic pollutants in the exhaust gas.

Toxic organic pollutants		Gas-phase			Particle-phase			Total		
		$-8°$	$-6°$	$-6°/-8°$ Ratio	$-8°$	$-6°$	$-6°/-8°$ Ratio	$-8°$	$-6°$	$-6°/-8°$ Ratio
PAHs	Mass ($\mu g\ Nm^{-3}$)	23.9	34.5	1.4	0.182	0.341	1.9	24.1	34.8	1.4
	total BaPeq ($\mu g\ Nm^{-3}$)	0.0644	1.39	22	0.000189	0.00554	29	0.0646	1.4	22
PCDD/Fs	Mass ($pg\ Nm^{-3}$)	29.8	30.2	1	0.501	1.65	3.3	30.3	31.8	1.1
	WHO-TEQ ($pg\ WHO\text{-}TEQ\ Nm^{-3}$)	0.144	2.75	19	0.0323	0.15	4.6	0.294	2.9	9.9
PCBs	Mass ($pg\ Nm^{-3}$)	5.27	51.8	9.8	0.0815	0.248	3	5.35	52	9.7
	WHO-TEQ ($pg\ WHO\text{-}TEQ\ Nm^{-3}$)	0.205	0.419	2	N.D.	N.D.	-	0.205	0.419	2
PBDD/Fs	mass ($pg\ Nm^{-3}$)	20.4	34.1	1.7	0.308	8.72	28	20.7	42.8	2.1
	WHO-TEQ ($pg\ WHO\text{-}TEQ\ Nm^{-3}$)	0.0579	0.341	5.9	0.00157	0.0872	56	0.0595	0.428	7.2
PBBs	Mass ($pg\ Nm^{-3}$)	1.09	68.2	63	N.D.	N.D.	-	1.09	68.2	63
PBDEs	Mass ($ng\ Nm^{-3}$)	3.72	26.6	7.2	0.069	0.824	11.9	3.79	27.4	7.2

Table 5. Emission factors for the toxic organic pollutants in the diesel engine exhaust gas.

		Injection timing		
		$-8°$	$-6°$	$-6°/-8°$ ratio
PAHs	Mass ($g\ kW\text{-}h^{-1}$)	252	361	1.4
	Total-BaPeq ($\mu g\ kW\text{-}h^{-1}$)	0.676	14.5	22
PCDD/Fs	Mass ($pg\ kW\text{-}h^{-1}$)	318	330	1
	Total TEQ ($pg\ WHO\text{-}TEQ\ kW\text{-}h^{-1}$)	3.05	30.1	9.9
PCBs	Mass ($pg\ kW\text{-}h^{-1}$)	56	539	9.6
	Total TEQ ($pg\ WHO\text{-}TEQ\ kW\text{-}h^{-1}$)	2.15	4.34	2
PBDD/Fs	Mass ($pg\ kW\text{-}h^{-1}$)	218	444	2
	Total TEQ ($pg\ WHO\text{-}TEQ\ kW\text{-}h^{-1}$)	0.623	4.44	7.1
PBBs	Mass ($pg\ kW\text{-}h^{-1}$)	11.4	707	62
PBDEs	Mass ($ng\ kW\text{-}h^{-1}$)	39.7	284	7.2

PBBs and PBDEs during $-6°$ injection timing were 1.4, 1, 10, 2, 62, and 7 times higher than those of $-8°$ injection timing, respectively. The total toxic (PCDD/Fs + PCBs + PBDD/Fs) emission factors during the $-8°$ and $-6°$ injection timing were 6 pg WHO-TEQ kW-h^{-1} and 39 pg WHO-TEQ kW-h^{-1}, respectively. The results show that there is a similar trade-off relationship between the toxic organic pollutants and NO$_x$ as the PM and NO$_x$ emissions during NO$_x$ treatment strategies. NO$_x$ reduction requiring lower combustion temperature in turn causes incomplete combustion which resulted in higher emissions of PM and toxic organic pollutants.

PAH and POP Congener Profiles

The PAH and POP mass congener profiles of the two different injection timings are shown in Fig. 1. The predominant PAH for the two scenarios was Nap which is similar to published results on diesel exhaust emissions (He *et al.*, 2010; Chang *et al.*, 2014b; Chen *et al.*, 2017a, c). Nap, PA and Pyr accounted for ~92% and ~90% of the total congeners for the $-6°$ and $-8°$ fuel injection timing, respectively. The total mass fraction of the six most toxic PAH congeners with TEF values of 0.1 and 1 were 2.7% and 2.0% for the $-6°$ and $-8°$ scenarios, respectively. This resulted in the higher BaP$_{eq}$ concentration observed during

the $-6°$ injection timing scenario.

OCDD, OCDF, 1,2,3,4,6,7,8-HpCDD/Fs, TeCDF, and PeCDFs were the predominant PCDD/Fs. This is similar to other HDDEs exhaust emissions (Laroo *et al.*, 2012; Chang *et al.*, 2014a; Cheruiyot *et al.*, 2017). The PCDD/F congener profile for the $-6°$ scenario was found to contain a higher fraction of lower chlorinated PCDFs, while the fractions of higher chlorinated congeners were lower than the $-8°$ scenario. For instance, for TeCDFs increased from 3.9% to 7.7% while PeCDFs from 10.8% to 12.8%. This increase of lower chlorinated PCDFs is an indication of POP formation via de novo synthesis (Iino *et al.*, 1999; Ni *et al.*, 2009). This led to the observed higher toxic concentrations observed during $-6°$ scenario.

The predominant PCB congeners were PCB-118, PCB-77, and PCB 105, while 1,2,3,4,6,7,8-HpBDF, OBDF, PBB-15, and BDE-209 were the major brominated congeners. These congeners are also abundant in most combustion sources (Wang *et al.*, 2010a, b, 2011; Chang *et al.*, 2013; Chang *et al.*, 2014b; Kuo *et al.*, 2015; Chen *et al.*, 2017b, c; Redfern *et al.*, 2017a, b) and environmental media (Mwangi *et al.*, 2016). PCB-118 and PCB-77 contributed to 85% of the total congener for $-6°$ scenario and 49% for $-8°$ injection timing.
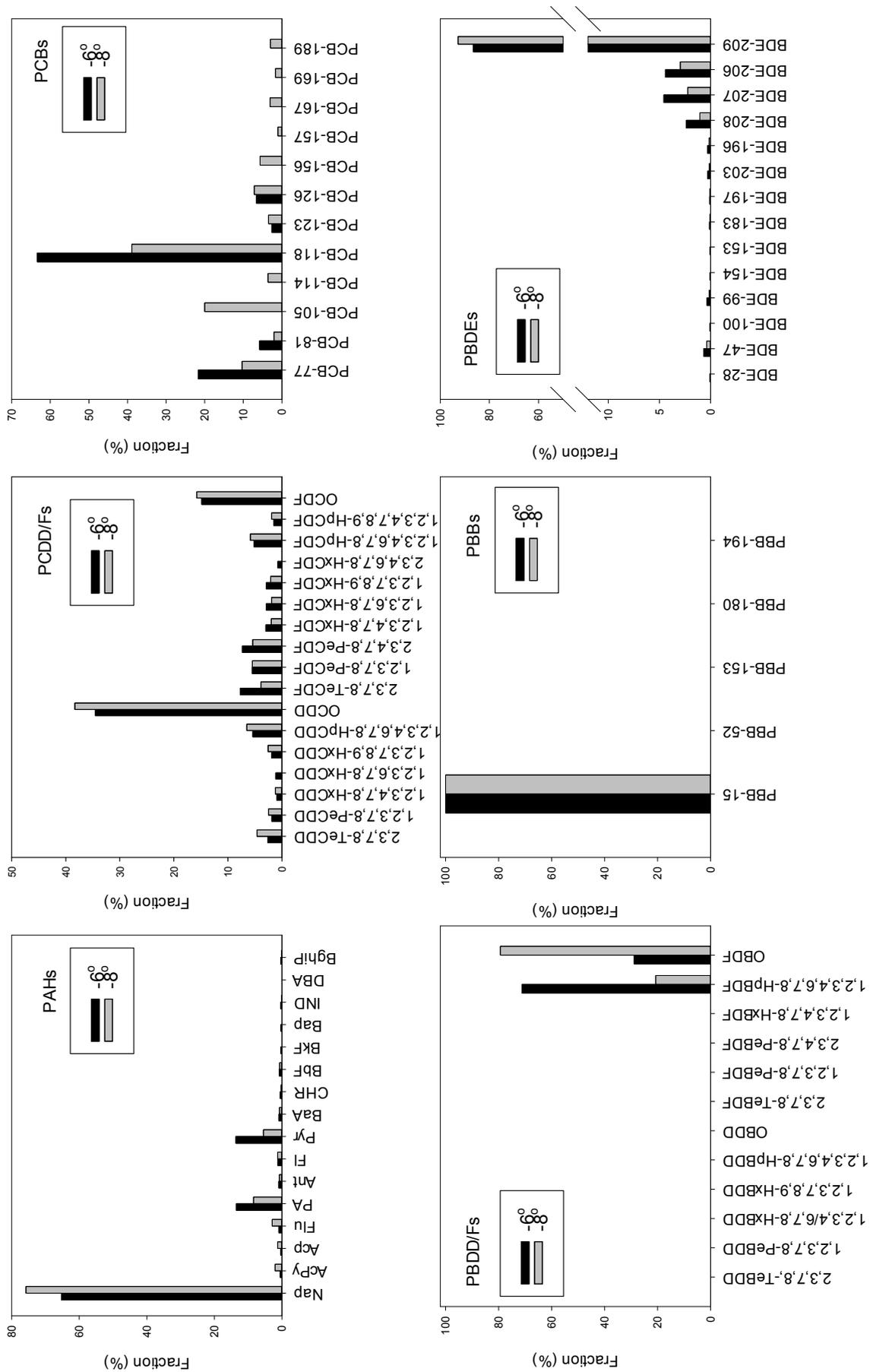
Fig. 1. PAH and POP congener profiles during –8° and –6° injection timing.

CONCLUSIONS

The toxic concentrations of PAHs and POPs during the −6° injection timing were 2–22 times higher than those in −8° scenario. The increases were due to the reduced combustion efficiency that occurred during the retardation. The reduced combustion efficiency assertion was supported by the higher CO and PM emissions during retardation, which were 1.4 and 1.2 times higher than in −8° injection timing. The retardation of the injection timing was also found to influence the gas- and particle-phase partitioning of the organic compounds. We found that the retardation had more influence on these pollutants in the particle-phase than in the gas-phase. The −6° injection timing had higher fractions of more toxic congeners than the −8° scenario, for example, the TeCDF mass fraction increased from 3.9% to 7.7%, while that of PeCDFs increased from 10.8% to 12.8%. This was the reason for the high BaPeq and WHO-TEQ concentrations measured during the −6° scenario. Therefore, it can be concluded that retarding the injection timing has a negative impact on PAH and POP emissions from diesel engines.

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