



## Effects of Selective Catalytic Reduction on the Emissions of Persistent Organic Pollutants from a Heavy-Duty Diesel Engine

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### ABSTRACT

The emissions of persistent organic pollutants (POPs) from diesel engines is becoming more important due to their proximity to human beings compared to stationary sources whose emission have been well controlled over the years. The selective catalytic reduction (SCR) have been adopted in the heavy-duty diesel engine (HDDE) to reduce the nitrogen oxide (NO<sub>x</sub>). SCR has also been reported to reduce the polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), and polychlorinated biphenyls (PCBs). However, the memory effect and reformation of persistent organic pollutants (POPs) during SCR operation are not well understood. This study investigated the effect of Copper-zeolite SCR (CuZ SCR) on PCDD/F, PCB, polybrominated dibenzo-*p*-dioxin and dibenzofuran (PBDD/F), and polybrominated biphenyl (PBB) emissions from a HDDE at 50% and 75% engine load. Notably, PCDD/F and PCB toxicity emissions increased by 78.4% and 201%, respectively. The dominant PCDD/F congeners were OCDD, OCDF, 1,2,3,4,6,7,8-HpCDD, and 1,2,3,4,6,7,8-HpCDF and PCB-105, PCB-118 and PCB-77 for PCBs. More PCDFs were formed compared to PCDDs and lower chlorinated congeners increased more than the higher chlorinated ones. There was also an increase of PBDD/F concentrations from undetectable levels (ND) to 0.247 pg TEQ Nm<sup>-3</sup> (4.00 pg TEQ L<sup>-1</sup>) after the SCR. However, only 1,2,3,4,6,7,8-HpBDF and OBDF contributed to the concentrations. PBBs was the only compound measured that reduced after the SCR. The only congener detected before and after the SCR was PBB 15. Consequently, the CuZ SCR could be a source of POPs under mid and high engine loads in this study. Further detail research is required to focus on the formation of POPs on the catalyst surfaces and structures.

**Keywords:** Selective catalytic reduction; Persistent organic pollutants; Engine load; Heavy-duty diesel engine.

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### INTRODUCTION

The International Agency for Research on Cancer (IARC) classifies diesel engine exhaust as a Group 1 human carcinogen that causes lung cancer (Silverman *et al.*, 2012). They are also significant NO<sub>x</sub> and particulate matter (PM) sources (Herner *et al.*, 2009; Ramadhas *et al.*, 2016). The health risks of diesel particulate matter is associated with its chemical composition which includes heavy metals and toxic organic compounds e.g., PAHs (Jin *et al.*, 2017). Stiffer

regulations on traditional pollutants i.e., NO<sub>x</sub>, CO and hydrocarbons (HC) over the years has led to increased research and installation of air pollution control devices and employment of control strategies in the diesel engines. For example, exhaust gas recirculation (EGR), selective catalytic reduction (SCR) and retarding of the fuel injection time have been employed extensively in controlling NO<sub>x</sub> formation while diesel particulate filters (DPFs) with diesel oxidation catalysts (DOCs) have been used to reduce PM in heavy duty diesel engines (HDDEs) (Koebel *et al.*, 2000; Zheng *et al.*, 2004). DPFs can reduce PM mass by over 95% and will also reduce CO, HC and PAHs (Biswas *et al.*, 2009; Hu *et al.*, 2013). However, they can also be sources for persistent organic pollutants (POPs) emissions, especially when they have an accumulation of organic particulates, which could provide the necessary precursors or carbon matrix for their formation (Heeb *et al.*, 2013; Chen *et al.*, 2017). EGR technology reduces the amount of NO<sub>x</sub> emitted by reducing the oxygen concentration in the

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intake manifold and the combustion temperature. In turn, it causes incomplete combustion which increases the amount of unburnt carbon species in the emissions. Therefore, there is a trade-off between NO<sub>x</sub> and PM especially during high loads (Abd-Alla, 2002; Zheng *et al.*, 2004). In addition, since EGR is often scaled in proportion to engine load, the recirculation is completely disabled during idle conditions. Also, retardation of fuel injection reduces the combustion temperature and thereby increasing the amount of unburnt carbon (Sayin *et al.*, 2009). This unburnt carbon could later be a precursor or the carbon matrix for POPs to form either heterogeneously or homogeneously depending on the compositions of the unburnt products.

SCR injects a nitrogen based fluid-reductant agent, usually urea, to reduce NO<sub>x</sub> into mostly diatomic nitrogen, water and CO<sub>2</sub> (Liu and Woo, 2006). It can achieve NO<sub>x</sub> reduction greater than 75% during cruise and transient modes (Herner *et al.*, 2009). However, the technology has some demerits which include stoichiometric imbalance of urea consumption, deactivation of catalyst caused by deposition, cost and the emission of NH<sub>2</sub> radicals (Fang and DaCosta, 2003; Liu and Woo, 2006). SCR works well at high engine load when the exhaust temperature are high enough, but some latest study also indicated lower-temperature reduction of PCDD/Fs is possible (Yu *et al.*, 2016). Some studies have reported that SCR can reduce polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) from stationary sources (Chang *et al.*, 2007; Liu *et al.*, 2015).

POPs such as PCDD/Fs, polychlorinated biphenyls (PCBs), and their brominated counterparts are semi-volatile organic compounds (SVOCs) that have been linked to health risks to human beings and the environment (Tsai *et al.*, 2001; Bernard *et al.*, 2002; Birnbaum *et al.*, 2003; Nadal *et al.*, 2004; Xia *et al.*, 2010). There has been growing concern on the POP emissions from mobile sources due to their proximity to human beings and their increasing contribution to the total anthropogenic POP emissions which is driven by significant reduction from major stationary sources e.g., municipal solid waste incinerators (U.S.EPA, 2006; Cheruiyot *et al.*, 2015). However, there are still no regulations on POP emissions from mobile sources (Cheruiyot *et al.*, 2016). Several studies have studied ways to reduce these POP emissions e.g., by testing biofuels and biofuels-diesel blends and water containing alcohol blends with positive results in terms of POP emission reduction (Mwangi *et al.*, 2015a, b; Tsai *et al.*, 2015, 2016).

Laroo *et al.* (2011) studied the PCDD/F and PCB emissions under steady state and found the emission factors of CuZ-SCR HT, CuZ-SCR LT (A 20 Hp difference in power between HT and LT), and FeZ-SCR to be 1.6 pg I-TEQ L<sup>-1</sup> and 0.1 pg WHO-TEQ L<sup>-1</sup>, 2.55 pg I-TEQ L<sup>-1</sup> and 15.21 pg WHO-TEQ L<sup>-1</sup>, and 2.78 pg I-TEQ L<sup>-1</sup> and 0.04 pg WHO-TEQ L<sup>-1</sup>, respectively. They also concluded that PAH, PCDD/F and PCB emissions from modern HDDEs equipped with DOCs, DPFs and SCRs are significantly lower compared to legacy HDDEs. Furthermore, the presence of copper in Copper based zeolite SCRs had no adverse effects PCDD/Fs. However, it is quite unclear the contribution these air pollution control devices (APCDs) have on the POP

emissions compared to the better engine technologies over the years.

In this research, we characterized and compared the emissions of PCDD/Fs, PCBs, PBDD/Fs and PBBs from a heavy duty engine before and after an SCR treatment. The aim of the paper was to study in detail the differences in emission characteristics from these operations and compare with previous studies. The heavy-duty diesel engines was studied under the European Stationary Cycle (ECS) mode 5, 6, and 13 on an engine dynamometer. The engine load for both mode 5 and 13 was 50% engine load and 75% for mode 6. Each mode was run for 20 minutes and the temperature of the engine, engine intake flow volume for the different modes were monitored.

## METHODS AND MATERIALS

### *Test Fuel, Diesel Engine and Test Cycles*

The commercial diesel produced by CPC Corporation and certified by the diesel regulation in Chinese National Standards (CNS) was the base fuel used in the study. The experiments were carried out with a six-cylinder, 6 L, naturally aspirated, water-cooled, direct-injection heavy-duty diesel engine (Hino W06E). The engine specifications and the operating boundary conditions are listed in Table 1. An engine dynamometer (Schenck W230) was used to control the engine torque and speed. European Stationary Cycle (ESC) modes 5, 6, and 13 were used to measure the emissions from the engine. The modes represent 50%, 75%, and 50% load, respectively, representing medium and high engine loads. The exhaust samples for analysis were simultaneously collected in both the upstream and downstream of the CuZ SCR and are denoted in this study as before and after SCR, respectively.

### *Sampling Procedures, Sample Preparation and Analysis*

The engine was warmed up for 30-min and for a minimum of 3 min in-between test modes before each sampling procedure. The exhaust of the diesel engine was sampled directly and isokinetically during the entire testing cycle by a sampling system. The system consisted of a glass fiber filter, a flow meter, a condenser, two-stage glass cartridges and a pump. The particulate phase pollutants were collected by the glass fiber filter while the gaseous phase ones were collected by the two-stage glass cartridges. A condenser located before the two-stage glass cartridges lowered the exhaust temperature to less than 5°C and removed moisture from the exhaust. The glass cartridges were packed with 5.0 cm of XAD-2 resin sandwiched between two 2.5 cm polyurethane foam (PUF) plugs. The samplings from the three ESC modes were combined into one exhaust to ensure that the pollutants contents were higher than the detection limit. The total sampling time was approximately 60 min. The exhaust samples were then normalized to 760 mmHg and 273 K. The sample mixture was extracted in a Soxhlet extractor with toluene for 24 hours.

The extracts were sequentially concentrated, treated with concentrated sulfuric acid, and then underwent a series of sample cleanup and fractionation procedures, including the

**Table 1.** Specification of the tested engine.

Item	Hino W06E
<i>Engine Specifics</i>	
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 (BTDC)
Displacement	6.0 Liters
Max torque	412 Nm @ 1800 rpm
Max power	121 kW @ 3000 rpm
<i>Operation conditions</i>	
Ambient air temperature	30–40°C
Ambient air pressure	Approximately 101 kPa
Ambient air humidity	60–70%

use of a multi-layered silica column, alumina column and activated carbon column. The compounds of biphenyls, such as non-planar PCBs and PBBs, were eluted with 15 mL hexane during the alumina column cleanup. The activated carbon column was used for the further cleanup procedure. After the elution of 25 mL DCM/hexane (1/24, v/v), the activated carbon column was sequentially eluted with 5 mL toluene/methanol/ethyl acetate/hexane (1/1/2/16, v/v) for planar PCBs and PBBs, which was followed by 40 mL of toluene for PCDD/Fs and PBDD/Fs. Before instrument analyses, the planar and nonplanar PCBs/PBBs eluates were mixed together, representing the PCB and PBB samples. Seventeen 2,3,7,8-substituted PCDD/F, twelve dioxin-like PCB, twelve 2,3,7,8-substituted PBDD/F, and five PBBs congeners were analyzed by a high-resolution gas chromatograph/high-resolution mass spectrometer (HRGC/HRMS). The detailed POPs analytical procedures are given in more detail in previous works (Wang *et al.*, 2007, 2009).

#### **Quality Assurance and Quality Control (QA/QC)**

Before sampling, the glass fiber filters were placed in an oven at 450°C for 8 h to burn off any organic pollutants present. Field and laboratory blank samples were also used in the study. The POPs in these blank samples were all lesser than 0.5% of total POPs in the real samples. Before the extraction, the samples were spiked with <sup>13</sup>C<sub>12</sub>-labeled internal standards (as shown in Table S1), which were useful in quantifying the samples and monitoring recoveries during extraction process. Then also prior to instrumental analysis, the recovery standard solution was added to the samples to ensure recovery during analysis. The recoveries of the precision and recovery (PAR), the surrogate, internal and recovery standards of POPs all met the relevant standards as shown in Table S2. The limit of detection (LOD) in this study was defined as a signal-to-noise (S/N) greater than 3, whereas the limit of quantification (LOQ) was defined as an S/N greater than 10.

## **RESULTS AND DISCUSSION**

The POP emission concentrations and factors from the engine are presented in Tables 2, 3, 4 and 5. The general trend in the mass concentration of the POPs before the SCR was PCBs > PCDD/Fs > PBBs > PBDD/Fs while after the SCR, the trend was PBDD/Fs > PCBs > PCDD/Fs > PBBs. Discussions of each POP emission characteristics from the engine follows.

#### **PCDD/F Concentrations, Congener Profiles and Emission Factors**

The PCDD/F TEQ concentration in the exhaust of the engine before SCR was 1.53 pg WHO-TEQ Nm<sup>-3</sup>. This was less than 2.73 pg WHO-TEQ Nm<sup>-3</sup> in those after the SCR as it can be seen in Table 4. Fig. 1 represents the mass concentration and the congener profile of PCDD/Fs. It can be observed that more lower chlorinated PCDD/Fs were produced after the SCR. Although SCR has a tendency to reduce higher chlorinated PCDD/F to lower chlorinated congeners (Wang *et al.*, 2003; Chang *et al.*, 2007), there was only a slight decrease of OCDD and a significant increase in lower chlorinated PCDD/Fs after exhaust passed through SCR. Therefore, the dechlorination of the higher PCDD/Fs was unlikely the reason for the observed trend. The possible reason for the increase in this study could be formation of PCDD/Fs via *de novo* synthesis which resulted from an accumulation of soot on the inner surface of SCR and its operating temperature which were within PCDD/Fs formation window (200–450°C). This formation mechanism is characterized by a larger PCDFs/PCDDs ratio (Altarawneh *et al.*, 2009). When the two results were compared, the PCDFs/PCDD ratio of the after SCR was larger implying that more PCDFs were formed as shown in Table 2. However, our results were contrary to previous studies which have reported a reduction of PCDD/Fs after the engine was retrofitted with a SCR (Hovemann *et al.*, 2010; Laroo *et al.*, 2011).

**Table 2.** PCDD/F congener concentrations before and after the SCR.

PCDD/F congeners	Before SCR (pg Nm <sup>-3</sup> )	After SCR (pg Nm <sup>-3</sup> )	Increases (%)
2,3,7,8-TeCDD	0.847	1.31	+54.7
1,2,3,7,8-PeCDD	0.392	0.473	+20.7
1,2,3,4,7,8-HxCDD	ND	ND	-
1,2,3,6,7,8-HxCDD	ND	0.382	-
1,2,3,7,8,9-HxCDD	0.647	0.920	+ 42.2
1,2,3,4,6,7,8-HpCDD	1.61	3.25	+102.2
OCDD	14.8	14.0	-5.4
2,3,7,8-TeCDF	0.261	1.59	+510.2
1,2,3,7,8-PeCDF	0.792	1.25	+57.4
2,3,4,7,8-PeCDF	0.287	0.992	+246.2
1,2,3,4,7,8-HxCDF	0.385	1.08	+180.7
1,2,3,6,7,8-HxCDF	0.163	0.571	+250.3
2,3,4,6,7,8-HxCDF	ND	0.927	-
1,2,3,7,8,9-HxCDF	ND	ND	-
1,2,3,4,6,7,8-HpCDF	1.19	2.40	+100.9
1,2,3,4,7,8,9-HpCDF	0.257	0.576	+123.8
OCDF	5.37	6.10	+14.0
PCDD	18.3	20.3	+11.1
PCDF	27.0	35.8	+32.7
PCDFs/PCDDs Ratio	0.476	0.762	-

**Table 3.** PCB congener concentrations before and after the SCR.

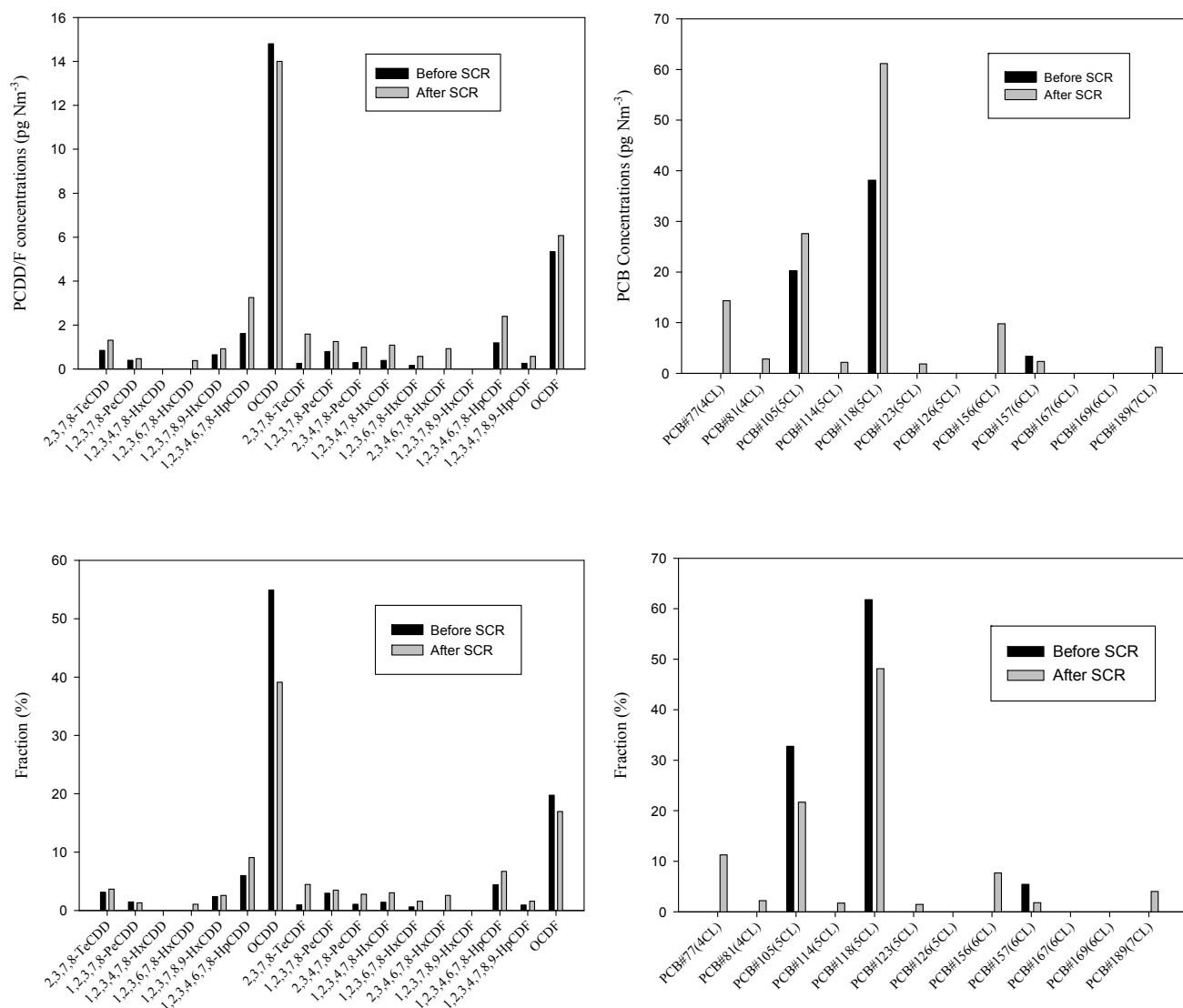
PCB congeners	Before SCR (pg Nm <sup>-3</sup> )	After SCR (pg Nm <sup>-3</sup> )	Increases (%)
PCB77(4CL)	ND	14.3	-
PCB81(4CL)	ND	2.81	-
PCB105(5CL)	20.2	27.6	+36.3
PCB114(5CL)	ND	2.16	-
PCB118(5CL)	38.1	61.2	+60.4
PCB123(5CL)	ND	1.84	-
PCB126(5CL)	ND	ND	-
PCB156(6CL)	ND	9.77	-
PCB157(6CL)	3.36	2.31	-31.2
PCB167(6CL)	ND	ND	-
PCB169(6CL)	ND	ND	-
PCB189(7CL)	ND	5.13	-

**Table 4.** Summary of the results of before and after the SCR.

Pollutants		Before SCR	After SCR	Increases (%)
PCDD/Fs	Mass (pg Nm <sup>-3</sup> )	27	35.8	+32.6
	WHO-TEQ (pg WHO-TEQ Nm <sup>-3</sup> )	1.53	2.73	+78.4
	Emission Factor (pg L <sup>-1</sup> )	437	580	+32.7
	Emission Factor (pg WHO-TEQ L <sup>-1</sup> )	24.8	42.2	+70.2
PCBs	Mass (pg Nm <sup>-3</sup> )	61.7	127	+106
	WHO-TEQ (pg WHO-TEQ Nm <sup>-3</sup> )	0.00185	0.00557	+201
	Emission Factor (pg L <sup>-1</sup> )	1000	2060	+106
	Emission Factor (pg WHO-TEQ L <sup>-1</sup> )	0.03	0.0904	+201
PBBD/Fs	Mass (pg Nm <sup>-3</sup> )	ND	126	Formation
	WHO-TEQ (pg WHO-TEQ Nm <sup>-3</sup> )	ND	0.247	
	Emission factor (pg L <sup>-1</sup> )	ND	2045	Formation
	Emission Factor (pg WHO-TEQ L <sup>-1</sup> )	ND	4.00	
PBBs	Mass (pg Nm <sup>-3</sup> )	5.36	4.61	-14.0
	Emission factor (pg L <sup>-1</sup> )	86.9	74.7	-14.0

**Table 5.** Comparison of emission factors from previous paper.

Type of SCR	Test cycle	Emission factors		References
		PCDD/Fs	PCBs	
CuZ	Steady state	42.4 pg WHO-TEQ L <sup>-1</sup>	0.0904 pg WHO-TEQ L <sup>-1</sup>	This study (Laroo <i>et al.</i> , 2011)
CuZ	Steady state	1.60 pg I-TEQ L <sup>-1</sup>	0.1 pg WHO-TEQ L <sup>-1</sup>	
CuZ	Steady state	2.55 pg I-TEQ L <sup>-1</sup>	15.21 ± 12.37 pg WHO-TEQ L <sup>-1</sup>	(Laroo <i>et al.</i> , 2013)
FeZ	Steady state	2.78 pg I-TEQ L <sup>-1</sup>	0.04 pg WHO-TEQ L <sup>-1</sup>	
DOC + CuZ SCRF	Steady state	0.14 I-TEQ L <sup>-1</sup>	0.038 pg WHO-TEQ L <sup>-1</sup>	(Laroo <i>et al.</i> , 2013)
DOC + FeZ SCRF	Steady state	0.16 I-TEQ L <sup>-1</sup>	0.071 pg WHO-TEQ L <sup>-1</sup>	

**Fig. 1.** PCDD/Fs and PCBs concentration and congener profiles before and after the SCR.

Although the performance of SCR, which depends on its type, surface properties and exhaust residence time (Liu *et al.*, 2011), may be one of the reasons, we speculated that the particulate matters and precursors of POPs emitted from diesel engine play an important role on the formation/destruction of POPs when exhaust passes through SCR. That is because the heavy diesel engine, a 2008 MY 6.7 L Cummins ISB, used in Laroo *et al.* (2011) is more modern than the engine used in our study, and its PCDD/F emission

factor (1.89 pg I-TEQ L<sup>-1</sup>) was significantly lower than that (24.8 pg WHO-TEQ L<sup>-1</sup>) in this study as shown in Table 5. Also, different test cycles and/or modes, load, mileage and composition of the SCR contribute to the differences in the emissions from these engines (Cheruiyot *et al.*, 2016).

As shown in Table 2, PCDFs were more predominant than PCDDs in both engines. This was similar to results from diesel engines from other studies (Ryan and Gullett, 2000; Kim *et al.*, 2003). The congeners that had the highest

percentage increase were 2,3,7,8-TeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF and 1,2,3,6,7,8-HxCDF. The general increase of lower chlorinated PCDF was the reason for the increase in toxic concentration to 2.73 pg WHO-TEQ Nm<sup>-3</sup>. Some congeners e.g., 1,2,3,6,7,8-HxCDD and 2,3,4,6,7,8-HxCDF were below the detection limit in the before SCR samples but were detected in the after SCR ones. OCDD was the only congener that was reduced. This compound can undergo dechlorination reactions and produce lesser chlorinated PCDDs. For both before and after SCR, OCDD, OCDF, 1,2,3,4,6,7,8-HpCDD, and 1,2,3,4,6,7,8-HpCDF were the most dominant congener as shown in Fig. 1. This is similar to other reported results from previous studies (Laroo *et al.*, 2011; Liu *et al.*, 2011; Laroo *et al.*, 2013).

The PCDD/F emission factors before and after SCR in the study were 24.8 and 42.2 pg WHO-TEQ L<sup>-1</sup>, respectively. This values are higher than other reported values as shown in Table 5.

### **PCB Concentrations, Congener Profiles and Emission Factors**

Like PCDD/Fs results in this study, PCB concentrations from the before SCR were lower than the after SCR, 0.00185 and 0.00557 pg WHO-TEQ Nm<sup>-3</sup>, respectively. The emission factors of the engine before and after SCR were 0.03 and 0.0904 pg WHO-TEQ L<sup>-1</sup>, respectively. From Table 3, it can be seen that only 3 of the 12 PCB congeners measured, PCB 105, PCB 118 and PCB 157, were detected in the engine samples before SCR while after SCR, all measured PCB congeners were detected except for PCB 126, PCB 167 and PCB 169. Therefore, PCB 77, PCB 118, PCB 156, PCB 105, and PCB189 significantly increased after the SCR. This caused the increase in the overall toxic concentration of the sample. PCB 157 which decreased by 31.2% might be considered one of the sources for the lower chlorinated PCBs since it may undergo dechlorination reactions on the surface of the SCR. The dominant congeners for the after SCR were PCB 118, PCB 105 and PCB 77. This was similar with Laroo *et al.* (2011) results for CuZ SCR HT engine but different to CuZ SCR LT which had PCB 126 and PCB 169 and that were below detection limits in our study.

### **PBDD/F Concentrations**

The concentration of PBDD/Fs were also studied in this paper. We found that PBDD/F were not detected in the engine samples before SCR samples but were present after the SCR. The mass and toxic concentrations were 126 pg Nm<sup>-3</sup> and 0.247 pg TEQ Nm<sup>-3</sup>. Only 1,2,3,4,6,7,8-HpBDF and OBDF were detected in the samples. This congener profile is similar to the results from Chang *et al.* (2014a) who found 1,2,3,4,7,8-HxBDF, 1,2,3,4,6,7,8-HpBDF and OBDF were the only detectable congeners. The PBDD/Fs have similar heterogeneous formation mechanism through *de novo* synthesis as PCDD/Fs, which may have led to the increase in the exhaust after SCR treatment. Additionally, the PBDEs have been reported to form PBDD/Fs either via *de novo* synthesis or the more likely elimination, debromination, condensation and/or recombination reactions (Ebert and

Bahadir, 2003; Weber and Kuch, 2003; Altarawneh and Dlugogorski, 2013). Though it was not measured in our study, PBDEs easily occur in diesel engine combustion as found in previous research (Chang *et al.*, 2014a, b; Mwangi *et al.*, 2015a; Chen *et al.*, 2017; Redfern *et al.*, 2017). The concentration of PBDEs from the same engine and with similar fuel was reported to be 39.4 ng Nm<sup>-3</sup> (Chang *et al.*, 2014b). Therefore, PBDD/Fs could be the potential pollutants form after SCR unit in the diesel engine operation.

### **PBB Concentrations**

Unlike the other compounds studied, the PBB concentrations reduced after the SCR from 5.36 to 4.61 pg Nm<sup>-3</sup>. The contribution was entirely from PBB 15, while other congeners were not detected. Chang *et al.* (2014b) also reported only PBB 15 was detected but their concentration was much higher at 9.66 pg Nm<sup>-3</sup>. To the best of our knowledge, this is the second time PBB data from a diesel engine has been published and the reasons as to why only this particular PBB congener is detected is not quite understood.

## **CONCLUSIONS**

We can conclude that SCR can significantly increase several POP emissions, including PCDD/Fs, PCBs, and PBDD/Fs from heavy duty engines at mid and high loads except PBBs. The congener profiles of these compounds were also different between the two tests. For the test with SCR, more PCDFs were formed compared to PCDDs and with a preference for formation of lower chlorinated than higher chlorinated compounds, which could be attributed to the reformation of PCDD/Fs. The reformation trends could also be found in PCB and PBDD/F emissions. The increases of POP emissions in this research provide another academic aspect of treating the diesel engine exhaust by SCR. Further investigations need to be carried to understand the possible formation mechanisms of these POPs on the surfaces of the SCR.

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## **SUPPLEMENTARY MATERIAL**

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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