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Characteristics of $PM_{2.5}$-bound PCDD/Fs, PCBs, PBDD/Fs and PBDEs from a Diesel Generator Using Waste Cooking Oil-based Biodiesel Blends

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ABSTRACT

This study investigates fine particulate matter ($PM_{2.5}$) bound persistent organic pollutants (POPs) emitted from a diesel generator fueled with three waste cooking oil-based biodiesel (WCO-biodiesel) blends (W0 (pure diesel), W20 (WCO-biodiesel/diesel = 20%/80% (v/v)), and W40). These POPs are polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyl (PCBs), polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) and polybrominated diphenyl ethers (PBDEs). Experimental results indicate that the mass concentrations of $PM_{2.5}$-bound PCDD/Fs, PCBs, PBDD/Fs and PBDEs in the engine exhaust are 2.15–3.65, 16.7–35.4, 25.8–46.5 and 303–440 pg Nm^{-3}, respectively, at 1.5–3.0 kW loads for using W0, while the corresponding toxic equivalent (TEQ) concentrations of the above $PM_{2.5}$-bound pollutants are 0.282–0.527, 0.038–0.051 and 0.064–0.093 pg WHO_{2005}-TEQ Nm^{-3}, respectively (excluding PBDEs, which still have no toxic equivalency factors (TEFs) for TEQ calculation). Using W20 and W40 reduced the mass and TEQ emission concentrations of $PM_{2.5}$-bound PCDD/Fs, PCBs, PBDD/Fs and PBDEs in comparison with W0. The reductions of mass concentrations in exhausted $PM_{2.5}$ were in the order PBDEs >> PBDD/Fs > PCBs > PCDD/Fs, while the decrease in toxic concentration followed the order PCDD/Fs > PBDD/Fs > PCBs. Thus, adding WCO-biodiesel to the fuel mixture in generator engines lowers the adverse effects of $PM_{2.5}$ emissions on the environment and human health.

Keywords: $PM_{2.5}$; Biodiesel; PCDD/Fs; PCBs; PBDD/Fs; PBDEs.

INTRODUCTION

Air pollution from internal combustion engines is a major concern in many countries, and is one of the main causes of poor air quality in metropolitan areas (Lin *et al.*, 2005, 2008; Lee *et al.*, 2017). Gasoline and diesel engines generally emit a large number of nuclear-modes (aerodynamic particle size 0.005–0.05 μm) and accumulation-mode (aerodynamic particle size 0.05–1.0 μm) particles from the exhausts (Kittelson *et al.*, 2006). Particles emitted by diesel and gasoline engines have peaks for soot particles at around 40 nm and 80 nm, respectively (Baldauf *et al.*, 2016). These tiny particles can easily invade the depths of human lungs through respiration. *In-vitro* cytotoxicity studies have indicated that ultrafine particles from traffic sources result in large oxidative stress in human tissues, and even damage DNA (Bräuner *et al.*, 2007; Møller *et al.*, 2008). Therefore, many countries are concerned about the characteristics and reduction of fine aerosols in vehicle exhaust.

Although the development of science and technology has improved human life in the past century, it has also unconsciously created many harmful substances, such as persistent organic pollutants (POPs). The Stockholm Convention was established in 2001 with the aim of regulating or banning POPs. The total POP emissions have been significantly reduced through public effort, changing the ranking of the contribution of POPs from various pollution sources. According to the US EPA report (USEPA, 2005), PCDD/Fs emitted by mobile sources ranked 9th (0.27%) in terms of total PCDD/Fs emissions in the United States in 1987, rising to 8th (1.02%) in 1995. In 2000, the ranking of PCDD/Fs emissions from diesel truck (65.40

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g I-TEQ year^{-1}) rose to 7th, with an amount similar to that of PCDD/Fs emissions from municipal waste incinerators (78.90 g I-TEQ year^{-1}, ranked 3rd). In Taiwan, the PCDD/Fs emissions from vehicles in 2004, 2005, 2006 and 2007 were 2.317, 2.296, 2.269 and 2.308 g I-TEQ year^{-1}, respectively. The annual total PCDD/Fs emissions were 14.53, 102.616, 88.872 and 74.763 g I-TEQ year^{-1}, respectively. The proportion of PCDD/Fs from vehicles from 2004 to 2007 (1.57%, 2.24%, 2.55% and 3.09%, respectively) rose year by year, and by 2007 had risen to about twice that of 2004 (Taiwan EPA, 2008). Consequently, mobile vehicle exhausts have become one of biggest sources of POPs over the world.

Because diesel oil is cheaper than gasoline, and has more fuel-efficient engines, several major automakers have committed to the promotion of research and development of diesel vehicles, resulting in a surge in the number of diesel vehicles worldwide in the past decade. Recent works have indicated that most emissions of chlorine or bromine substituted pollutants are from diesel engines (Chang *et al.*, 2014b; Mwangi *et al.*, 2015; Chen *et al.*, 2017a). Besides the halogen content of fossil fuels affecting the characteristics of POPs in vehicle exhaust, the engine may also produce other toxic organic compounds (such as PCDD/Fs, PCBs, and PBDEs) in burning oil (precursor or *de novo* reaction). (Pekárek *et al.*, 2001; Dyke *et al.*, 2007; Wang *et al.*, 2010a; Chang *et al.*, 2014a; Cheruiyot *et al.*, 2016; Redfern *et al.*, 2017). Consequently, to reduce emissions of PCDD/Fs from engines, the Italian government banned the addition of chlorinated scavengers to fuel in 2002. However, Turrio-Baldassarri *et al.* (2005) noted that from a health point of view, any reduction due to limiting chlorine contents in fuel does significantly influence the total PCDD/Fs I-TEQ concentrations in exhaust.

In contrast with on-road diesel engines, persistent contaminants in off-road diesel engine exhausts are seldom explored. Therefore, the characteristics of POP emissions from $PM_{2.5}$ in off-road diesel engine exhausts need to be examined. Moreover, exhaust from off-road diesel engines (such as stacker, tractor, generator and boat engines) is closer to the human body or operator than that from on-road diesel engines, so has a greater effect on human health (Chung *et al.*, 2008). Our earlier works suggested that adding higher oxygen content additives (*i.e.*, butanol, acetone and waste cooking oil based biodiesel (WCO-biodiesel)) to petrochemical diesel could reduce the mass and toxicity concentrations of POPs (gas phase + particulate phase) in diesel generator exhaust (Tsai *et al.*, 2016; Chen *et al.*, 2017b; Tsai *et al.*, 2017). This study further explores the characteristics of $PM_{2.5}$ and the emission of $PM_{2.5}$-bound POPs, including PCDD/Fs, PCBs, PBDD/Fs and PBDEs, from a diesel generator fuelled with WCO-biodiesel blends.

MATERIALS AND METHODS

Sampling Procedures

This study tested fuels with different WCO-biodiesel blends, namely W0 (pure diesel), W20 (20 vol% WCO-biodiesel + 80 vol% diesel) and W40. The three blended fuels were tested on a small generator with a stable energy output (110V/60 Hz, 1800 rpm) under loads of 1.5 kW and 3.0 kW. The diesel-engine generator was a four-stroke, water-cooled, single fuel-injection cylinder (bore: 88.0 mm, stroke: 96.0 mm), manufactured by YANMAR Ltd., Japan (Model: TF110E&YSG-5SEN). The generator had one phase/two wires, an output frequency of 50/60 Hz and a maximum output power of 4 kW. The premium diesel fuel was obtained from the Chinese Petroleum Corporation, Taiwan, and the pure WCO-biodiesel was manufactured by Chant Oil Co. Ltd., Taiwan. Table 1 lists the properties of the tested fuels.

The samples of $PM_{2.5}$ and $PM_{2.5}$-bound POPs were accumulated from the generator exhaust by using $PM_{2.5}$ cyclones equipped with 47mm quartz fiber filters (2500 QAT-UP; Pall Corp., USA) to separate aerodynamic particle sizes $\leq$ 2.5 μm from the larger particles in the tailpipe stream according to Method 201A (USEPA). The quartz filters were pretreated before being sampled by heating them in a muffle furnace in air for 2.5 h at 900°C. Before and after field sampling, the quartz filters were dried for 24 h in a desiccator at 25 ± 3°C and a relative humidity of 40 ± 5%; they were then weighed on an electronic balance (Mettler Toledo UXM2) with a precision of 0.1 μg to determine the mass concentration. After that, the $PM_{2.5}$ mass concentration of particles was determined by dividing the particle mass by the sampled air volume.

Before sampling, known amounts of surrogate standards pre-labeled with isotopes (such as $^{37}Cl_4$-2,3,7,8-TeCDD, $^{13}C_{12}$-2,3,4,7,8-PeCDF, $^{13}C_{12}$-1,2,3,4,7,8-HxCDD, $^{13}C_{12}$-1,2,3,4,7,8-HxCDF and $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF) were spiked to evaluate the collection efficiency of the sampling train. The recoveries of precision and recovery (PAR), surrogate, and internal standards of toxic organic pollutants all met the relevant standards (see the Tables S1 and S2 of supplementary data). The recovery levels of the PCDD/Fs

Table 1. Specification of tested fuels.

Properties	Regular Diesel (D100)	WCO-biodiesel (W100)
Chemical formula	$C_{14}H_{28.33}$	$C_{19.54}H_{38.37}O_2$
Cetane number	50	56
Density at 15°C (g cm^{-3})	0.8405	0.8811
Kinematic viscosity at 40°C (cSt)	3.057	4.204
C (wt%)	86.30	75.64
H (wt%)	13.35	12.34
O (wt%)	–	12.34
Cl^- (ppm)	30.4	42.5

surrogate standards were 87–113%, which met the specified range of 70–130%. The experiments were performed 20 times (each sampling time = 60 min) for each combination of parameters, and the 20 samples were combined into one sample for POP analysis to satisfy the detection limits of the instrument. Sampling data were accumulated after the engine had been run for at least 30 min. The extraction of POPs was completed within one week of sampling. The POP extraction solutions were either immediately analyzed, or stored at –20°C for less than two weeks before analysis.

POPs Analysis

The quartz fiber filters from each exhaust sample were combined to represent the whole exhaust sample. Each exhaust sample (obtained by 20 quartz fiber filters) was extracted in a Soxhlet extractor with a mixed solvent (*n*-hexane and dichloromethane; vol/vol, 1:1; 250 mL each) for 24 h. The extracts were then concentrated by gently purging by ultra-pure nitrogen, and cleaned using a silica gel column. The extracts were treated with concentrated sulfuric acid in the first cleanup stage after extraction. Extract samples that were dissolved in 5 mL of hexane were then added to an acid silica gel column with two additional 5 mL rinses. The column was then eluted with an additional 20 mL of hexane. All of the eluate was retained and concentrated by rotary evaporation to approximately 1 mL. The concentrated eluate was then transferred from an acid silica gel column to the top of an alumina column, which was then eluted with hexane (10 mL). The hexane eluate was then discarded. The column was eluted again with 25 mL of hexane, followed by 15 mL of dichloromethane (DCM)/hexane (4/96, v/v). The eluate was collected and concentrated to near dryness using N_2 gas, and non-planar fractions of PCB congeners were thus obtained for further analysis.

The column was then eluted again using 25 mL of DCM/hexane (40/60, v/v), and then transferred to an active carbon column to separate PBDD/Fs and PBDEs. The extracts were eluted with 5 mL of toluene/methanol/ethyl acetate/hexane (5/5/10/80, v/v/v/v) for PBDEs and planar PCBs, followed by 40 mL toluene extraction for PBDD/Fs. The final extracts were then concentrated using N_2 gas before analysis. The solutions in the vials were then analyzed using a high-resolution gas chromatograph/high-resolution mass spectrometer (HRGC/HRMS) to identify seventeen 2,3,7,8-substituted PCDD/F, twelve dioxin-like PCB, twelve 2,3,7,8-substituted PBDD/F congeners and fourteen PBDE congeners.

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 installed with a positive electron impact (EI+) source. The SIM mode was used with a resolving power of 10,000. The electron energy and source temperature were set to 35 eV and 250°C, respectively. Our earlier work describes in detail the analytical procedures and parameters for the instrumental analysis of POPs (Wang *et al.*, 2010b).

The toxic equivalency (TEQ) values of PCDD/Fs and PCBs were computed with the World Health Organization's 2005 toxic equivalent factors (WHO_{2005}-TEF) (Van den Berg *et al.*, 2006). Since the TEFs have not been determined for PBDD/Fs, the WHO_{2005}-TEF of PCDD/Fs were adopted as trial TEFs for PBDD/Fs to assess their toxicity concentrations.

RESULTS AND DISCUSSION

W0, W20 and W40 were tested with the diesel engine generator at 1.5 kW and 3.0 kW loads to investigate their emissions of $PM_{2.5}$ and $PM_{2.5}$-bound PCDD/Fs, PCBs, PBDD/Fs and PBDEs. Table 2 and Fig. 1 show the mass and toxicity concentrations of target POPs.

$PM_{2.5}$ Concentrations in Exhaust Gases

The $PM_{2.5}$ concentrations in engine exhaust at 1.5 kW were in the ranges 10.8–21.9, 11.4–16.3, and 12.0–18.8 mg Nm^{-3} (16.5 ± 1.99, 14.1 ± 1.75, and 14.2 ± 2.21 mg Nm^{-3} in average) using W0, W20 and W40, respectively (as shown in Table 2). Conversely, the $PM_{2.5}$ levels at 3.0 kW load were higher at 20.9–47.2, 19.0–26.8, and 20.1–31.0 mg Nm^{-3} (30.7 ± 6.51, 23.9 ± 2.42, and 24.7 ± 3.21 mg Nm^{-3} in average), respectively. Based on the above results, the $PM_{2.5}$ reductions using W20 and W40 were 14.5% and 14.0%, respectively, at 1.5 kW, and 22.1% and 20.3%, respectively, at 3.0 kW. Additionally, the mass of $PM_{2.5}$ contributed about 25% of total PM mass using W0, W20 and W40 in the tested diesel engine, derived as the ratio

Table 2. Emissions of $PM_{2.5}$ and $PM_{2.5}$-bound POPs emitted from diesel engine generator.

Concentrations		1.5 kW			3.0 kW		
		W0	W20	W40	W0	W20	W40
$PM_{2.5}$ (N = 20)	Mass (mg Nm^{-3})	16.5 (±1.99)	14.1 (±1.75)	14.2 (±2.21)	30.7 (±6.51)	23.9 (±2.42)	24.7 (±3.21)
PCDD/Fs (N = 1)	Mass (pg Nm^{-3})	2.15	1.50	1.64	3.65	2.49	3.45
	WHO-TEQ (pg WHO_{2005}-TEQ Nm^{-3})	0.282	0.172	0.209	0.527	0.266	0.425
PCBs (N = 1)	Mass (pg Nm^{-3})	16.7	13.1	13.9	35.4	24.2	26.7
	WHO-TEQ (pg WHO_{2005}-TEQ Nm^{-3})	0.038	0.021	0.027	0.051	0.034	0.039
PBDD/Fs (N = 1)	Mass (pg Nm^{-3})	25.8	16.1	17.0	46.5	30.6	43.4
	WHO-TEQ (pg WHO_{2005}-TEQ Nm^{-3})	0.064	0.033	0.034	0.093	0.045	0.063
PBDEs (N = 1)	Mass (pg Nm^{-3})	303	247	228	440	355	324
	WHO-TEQ (pg WHO_{2005}-TEQ Nm^{-3})	–	–	–	–	–	–

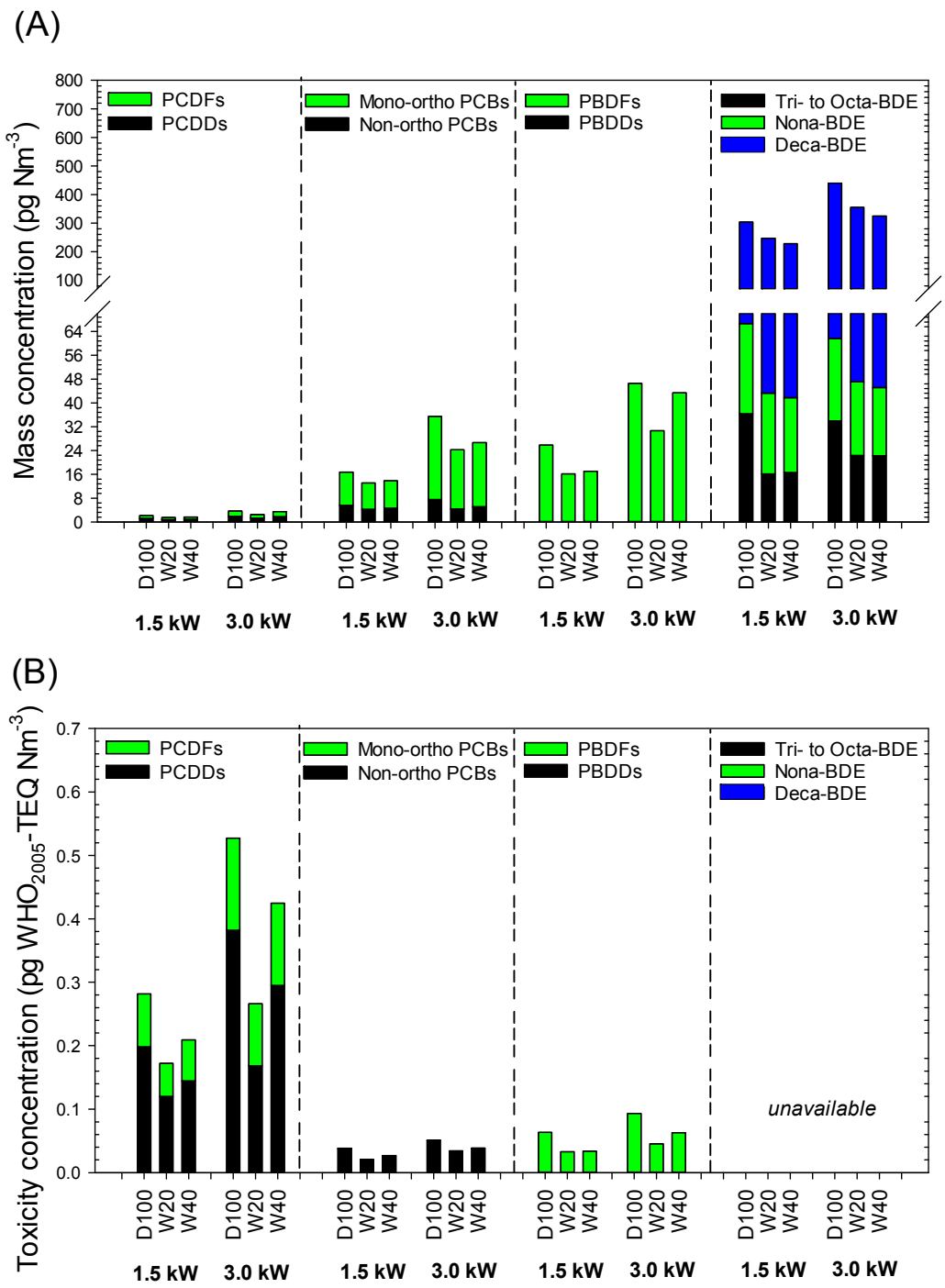

Fig. 1. (A) Mass and (B) TEQ concentrations of POPs on $PM_{2.5}$ from diesel engine generator.

of the current measured $PM_{2.5}$ and PM levels (52.3–129 mg Nm^{-3}) recorded in our previous study that adopted the same engine and testing condition (Tsai *et al.*, 2016).

In comparison with W0, the significant reductions of $PM_{2.5}$ mass in the exhaust gases using W20 and W40 resulted from their greater oxygen contents (~12.0 wt.%) and cetane numbers (Chhetri *et al.*, 2008; Tsai *et al.*, 2015), which improved the combustion reaction, and reduced the level of incomplete combustion products. However, the higher additive fraction of WCO-based biodiesel did not always reduce the engine emission, while the emission of $PM_{2.5}$ became higher using W40 than using W20. This finding is attributed to the high viscosity of WCO-base biodiesel, which affecs the primary breakdown of fuel droplets in spray (Zareh *et al.*, 2017) and unwinds the benefit of increasing fuel oxygen, leading to higher $PM_{2.5}$ emission when using W40.

Mass and TEQ Concentrations of $PM_{2.5}$-bound POPs in Exhaust Gases

Table 1 lists the mass concentrations of each of tested POP at 1.5 kW using W0, W20, and W40 were as follows:

PCDD/F 2.15 pg Nm^{-3}, 1.50 pg Nm^{-3} and 1.64 pg Nm^{-3}, respectively; PCBs 16.7 pg Nm^{-3}, 13.1 pg Nm^{-3} and 13.9 pg Nm^{-3}, respectively; PBDD/Fs 25.8 pg Nm^{-3}, 16.1 pg Nm^{-3}, and 17.0 pg Nm^{-3}, respectively, and PBDEs 303 pg Nm^{-3}, 247 pg Nm^{-3}, and 228 pg Nm^{-3}, respectively. The corresponding total TEQ concentrations at 1.5 kW were: PCDD/Fs 0.282 pg WHO_{2005}-TEQ Nm^{-3}, 0.172 pg WHO_{2005}-TEQ Nm^{-3}, and 0.209 pg WHO_{2005}-TEQ Nm^{-3}, respectively; PCBs 0.038 pg WHO_{2005}-TEQ Nm^{-3}, 0.021 pg WHO_{2005}-TEQ Nm^{-3} and 0.027 pg WHO_{2005}-TEQ Nm^{-3}, respectively, and PBDD/Fs 0.064 pg WHO_{2005}-TEQ Nm^{-3}, 0.033 pg WHO_{2005}-TEQ Nm^{-3}, and 0.034 pg WHO_{2005}-TEQ Nm^{-3}, respectively. The mass concentrations at 3.0 kW using W0, W20 and W40 were: PCDD/F 3.65 pg Nm^{-3}, 2.49 pg Nm^{-3}, and 3.45 pg Nm^{-3}, respectively; PCBs 35.4 pg Nm^{-3}, 24.2 pg Nm^{-3} and 26.7 pg Nm^{-3}; PBDD/Fs 46.5 pg Nm^{-3}, 30.6 pg Nm^{-3} and 43.4 pg Nm^{-3}, respectively, and PBDEs 440 pg Nm^{-3}, 355 pg Nm^{-3} and 324 pg Nm^{-3}, respectively. The TEQ concentrations using W0, W20 and W40 and were: PCDD/Fs 0.527 pg WHO_{2005}-TEQ Nm^{-3}, 0.266 pg WHO_{2005}-TEQ Nm^{-3} and 0.425 pg WHO_{2005}-TEQ Nm^{-3}, respectively; PCBs 0.051 pg WHO_{2005}-TEQ Nm^{-3}, 0.034 pg WHO_{2005}-TEQ Nm^{-3} and 0.039 pg WHO_{2005}-TEQ Nm^{-3}, and PBDD/Fs 0.093 pg WHO_{2005}-TEQ Nm^{-3}, 0.045 pg WHO_{2005}-TEQ Nm^{-3} and 0.063 pg WHO_{2005}-TEQ Nm^{-3}, respectively.

The TEQ levels of $PM_{2.5}$-bound PCDD/Fs (0.266–0.527 pg WHO_{2005}-TEQ Nm^{-3}) in the exhaust gases at 3.0kW engine load in this investigation were only 0.5–10.1% of the total PCDD/F TEQ concentration (5.18–58.6 pg WHO_{2005}-TEQ Nm^{-3}) found by our previous work (Tsai *et al.*, 2016), and about 1.8–8.2% of 6.4–14.5 pg I-TEQ Nm^{-3} and 2.7–31.7% of 1.66–9.72 pg I-TEQ Nm^{-3} reported by Kim *et al.* (2003) and Chang *et al.* (2014a), respectively. The TEQ emissions of PCDD/Fs in this study were 1.3–22.0% of those measured from the flue gases of a power plant (2.4–20.3 pg I-TEQ Nm^{-3} (Hutson *et al.*, 2009)). Nevertheless, those TEQ emission concentrations were about 36 times that measured in the ambient air around the engine (0.0113 pg WHO_{2005}-TEQ Nm^{-3} (Chao *et al.*, 2014)). The TEQ levels of $PM_{2.5}$-bound PCBs at 3.0 kW engine load were 0.034–0.051 pg WHO_{2005}-TEQ Nm^{-3}, approximately 1.1–3.2% and 3.0–24.1% of those from our previous study (1.60–3.11 pg WHO_{2005}-TEQ Nm^{-3} (Tsai *et al.*, 2016)) and from another study (0.212–1.15 pg WHO_{2005}-TEQ Nm^{-3} (Chang *et al.*, 2014a)), respectively. Additionally, the TEQ emissions of PCBs from diesel engine were about 32 times that of PCB in the nearby ambient air (0.00122 pg WHO_{2005}-TEQ Nm^{-3} (Chao *et al.*, 2014)).

The TEQ concentrations of PBDD/Fs emitted from diesel engine at 3.0 kW load were 0.045–0.093 pg WHO_{2005}-TEQ Nm^{-3}, which were 2.0–10.0% and 1.9–10.4% of those found in our previous work (0.927–2.30 pg WHO_{2005}-TEQ Nm^{-3} (Tsai *et al.*, 2016) and another study (0.892–2.40 pg WHO_{2005}-TEQ Nm^{-3} (Chang *et al.*, 2014a)), respectively. Notably, the TEQ emission concentrations of PBDD/Fs from diesel engine were about 52 times that of PCB in the nearby ambient air (0.00122 pg WHO_{2005}-TEQ Nm^{-3} (Chao *et al.*, 2014)).

The emission mass concentrations of all four $PM_{2.5}$-bound POPs were in the order PBDEs >> PBDD/Fs > PCBs > PCDD/Fs at both 1.5 kW and 3.0 kW engine loads (Fig. 1). The PBDE had the significantly highest emission mass concentrations, at 10 times that of PCB and PBDD/F and more than 100 times that of PCDD/F. Dissimilarly, the emission TEQ concentrations of $PM_{2.5}$-bound POPs followed the order PCDD/Fs > PBDD/Fs > PCBs. The emission TEQ concentrations of PCDD/Fs were 7.2–10.9 times (8.7 times on average) and 4.4–6.7 times (5.6 times on average) those of PCBs and PBDD/Fs. Although the non-ortho PCBs contributed only 18.2–33.6% (26.2% on average) of total PCB mass concentration, they dominated in the total TEQ emission of PCBs (98.3–99.1% (98.6% in average)). For PBDD/Fs, all the TEQ concentrations were provided by PBDFs (100%). The total PBDD/F mass was dominated by the OctBDF at 95% (ranging 93.3–96.5%) of, while the remainder was dominated by 1,2,3,4,6,7,8-HpBDF (3.7%) and 1,2,3,4,7,8-HxBDF (1.3%) within 12 PBDD/F congeners. However, the TEQ concentration of PBDD/Fs resulted mainly from the higher 1,2,3,4,7,8-HxBDF TEQ concentration (61.7–68.4% (65.2% on average)). Additionally, most of the PBDE mass concentration was from BDE-209, which supplied 78.0–86.7% (83.5 in average) of total PBDEs.

Effect of Using WCO-biodiesel on $PM_{2.5}$-bound POP Emissions

At 1.5 kW engine load, using W20 reduced the mass concentrations of $PM_{2.5}$-bound PCDDs and PCDFs by 31.5% and 29.5%, respectively, from those using W0. The corresponding reductions of WHO_{2005}-TEQ were 39.5% and 37.3%, respectively. The reductions from W0 of $PM_{2.5}$-bound PCDD and PCDF emissions when using W40 under the same engine operation condition were lower (mass reduced by 25.0% and 22.5%, respectively, and WHO_{2005}-TEQ by 27.1% and 22.6%, respectively) (Fig. 2(A)). The reductions of $PM_{2.5}$-bound PCDD and PCDF emissions at 3.0 kW load were close to 33.5% and 30.0%, respectively by using W20, and their corresponding reductions of WHO_{2005}-TEQ were 56.0 and 32.6%, respectively. However, W40 had significantly smaller reductions of $PM_{2.5}$-bound PCDD and PCDF (6.75% and 3.76%, respectively, in mass, and 22.9% and 10.4%, respectively, in WHO_{2005}-TEQ (Fig. 2(B)). The above result indicates that using WCO-based biodiesel reduces mass and WHO-TEQ concentrations of both PCDDs and PCDFs, with greater reductions for PCDDs than for PCDFs.

The mass and TEQ emissions of $PM_{2.5}$-bound non-ortho PCBs were reduced by 16.3–41.4% (28.6% on average) and 24.4–46.6% (33.5% on average), respectively for W40 compared to W0, while those of mono-ortho PCBs were slightly lower (17.7–29% (22.4% on average) and 17.7–29.0% (22.4% in average), respectively).

At 1.5 kW engine load, the dominated $PM_{2.5}$-bound PBDFs were reduced by 37.5% and 34.1% in mass when using W20 and W40, respectively, and the reduction in TEQ was greater at 48.4% and 46.7%, respectively. At 3.0 kW, the reductions of $PM_{2.5}$-bound PBDFs from W0 when using W20 and W40 were 34.2% and 6.78% , respectively, in mass, and 51.5% and 32.6%, respectively, in TEQ.

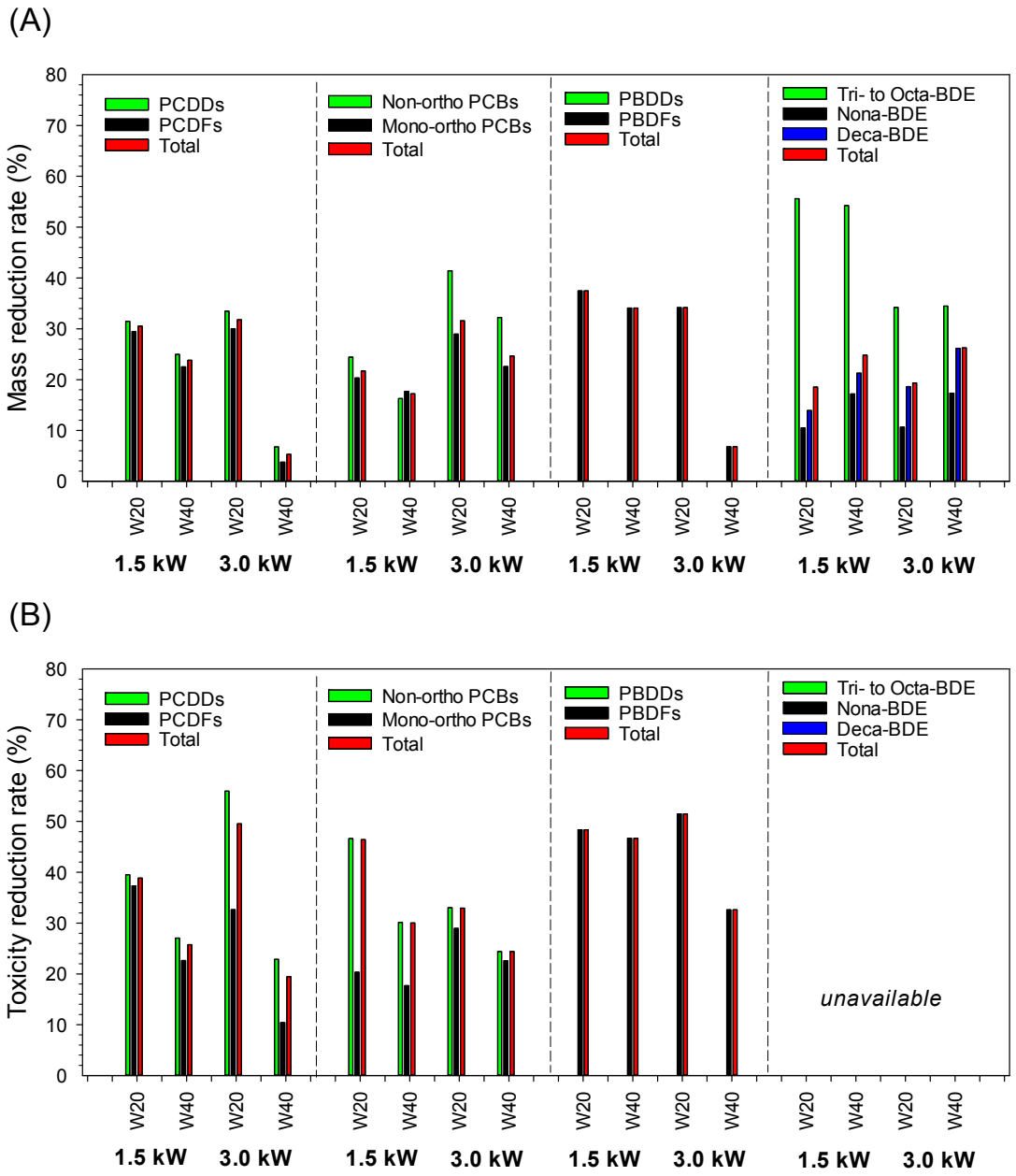

Fig. 2. Reduction rates of (A) mass and (B) TEQ concentrations of POPs on $PM_{2.5}$ from the diesel engine generator (compared with W0).

The reductions of PBDE mass concentration with various numbers of bromine substitutions were significantly different by using WCO-based biodiesels. At both 1.5 kW and 3.0 kW engine loads, using W20 and W40 achieved higher reduction rates for 3- to 8-Br PBDEs (34.2–55.6% (44.6% in average)) than for 10-Br PBDEs (13.9–26.2% reduction; 20.0% on average) and 9-Br PBDEs, including BDE-206, -207, and -208 (10.5–17.3%; 14.0% on average).

The mass and toxicity emissons of $PM_{2.5}$-bound PCDD/Fs, PCBs, PBDD/Fs and PBDEs were reduced by using W20 and W40 when compared by using W0. The mass reductions (absolute value) were in the order PBDEs >> PBDD/Fs > PCBs > PCDD/Fs (Fig. 1(A)), while the reduction ratios (%) followed the order PBDEs > PCDD/Fs ≈ PCBs > PBDD/Fs (Fig. 2(A)). Additionally, the orders of TEQ reduction (absolute value) and reductions ratios (%) were PCDD/Fs > PBDD/Fs > PCBs (Fig. 1(B)) and PCDD/Fs > PCBs > PBDD/Fs (Fig. 2(B)), respectively.

Accordingly, when replacing W0 with W20 and W40, the mass emission reductions of $PM_{2.5}$-bound PCDD/Fs were 31.0% and 14.6%, respectively, with corresponding 44.3% and 22.6% reductions in WHO_{2005}-TEQ, respectively. The corresponding data for PCBs were 26.6% and 20.7%, respectively, in mass, and 39.0% and 26.2%, respectively, in TEQ. For PBDD/Fs, they were 35.9% and 20.4%, respectively, in mass, and 50.0% and 39.6%, respectively, in TEQ, while the mass emission reductions of PBDEs were 18.9% and 25.6% using W20 and W40, respectively.

These significant reductions for the emissions of POPs could be attributed to the higher fuel-containing oxygen, lower aromatic compounds, and more short-chain and saturated hydrocarbons (Schönborn *et al.*, 2009; Pham *et al.*, 2013; Chen *et al.*, 2017b), which led to more complete combustion of hydrocarbon, reduced the soot emisison, and futher prevented the formation of brominated/chlorinated dioxins and furans by *de novo* syntheses (Weber and Kuch, 2003; Le *et al.*, 2016).

CONCLUSIONS

Four POPs were measured in a heavy-duty diesel engnine fueled with W0, W20 and W40, operating at 1.5 kW and 3.0 kW output power loads. The mass emissions of these POPs were in the order PBDEs >> PBDD/Fs > PCBs > PCDD/Fs, while the corresponding toxicity equivalent concentrations followed the order PCDD/Fs > PBDD/Fs > PCBs. The emisison of $PM_{2.5}$ was 20% lower using WCO-biodiesel than using W0. Additionally, the $PM_{2.5}$-bound PCDD/Fs were redued by 14.6–31.0% in mass and 22.6–44.3% in WHO_{2005}-TEQ. Nevertheless, the mass emission reductions of PCBs, PBDD/Fs and PBDEs were 20.7–26.6%, 20.4–35.9%, and 18.9–25.6%, respectively, while the toxicity equivalent concentrations of PCB and PBDD/Fs were reduced by 26.2–39.0% and 39.6–50.0%, respectively. Consequently, the recycling WCO-based biodiesel blends are more environmentally friendly fuels for off-road, heavy-duty and high-emission diesel fueled facilities.

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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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