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Persistent Organic Pollutant Reductions from a Diesel Engine Generator Fueled with Waste Cooking Oil-based Biodiesel Blended with Butanol and Acetone

Jen-Hsiung Tsai[1], Sheng-Lun Lin[2,3], Shui-Jen Chen[1*], Guo-Ping Chang-Chien[3,4], Bo-Cheng Jheng[1], Kuo-Lin Huang[1], Chih-Chung Lin[1], Juei-Yu Chiu[1]

[1] *Department of Environmental Science and Engineering, National Pingtung University of Science and Technology, Pingtung 91201, Taiwan*
[2] *Department of Civil Engineering and Geomatics, Cheng Shiu University, Kaohsiung 83347, Taiwan*
[3] *Super Micro Mass Research and Technology Center, Cheng Shiu University, Kaohsiung 83347, Taiwan*
[4] *Department of Cosmetics and Fashion Styling, Cheng Shiu University, Kaohsiung 83347, Taiwan*

ABSTRACT

This investigation focuses on the effects on emissions of persistent organic pollutants (POPs) (polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) and polybrominated diphenyl ethers (PBDEs)) from a diesel engine fuelled by 20 vol% waste cooking oil-based biodiesel (W20) blended with various fractions of dehydrate/hydrous butanol (B/B′) and acetone (A/A′). The emission concentrations of the POPs were in the order PBDE ≫ PBDD/F > PCB > PCDD/F, regardless of the blending fuel or engine load. The POP with highest concentration was PBDE, being 2–3 times that of the others. Conversely, the magnitude of emitted toxicity followed the order PCDD/F > PCB ≈ PBDD/F, while PCDD/F emissions had about 10 times the toxicity concentrations of PCBs and PBDD/Fs. Among the dioxin compounds, the emissions of PCDDs represented 46–73% (average 57%) and 50–72% (average 59%) of total PCDD/F mass and toxicity concentrations, respectively, and were which and were thus significantly higher than those of PCDFs. The non-*ortho*-PCB contributed almost all toxicity (~100%) of 14 dioxin-like-PCBs, even though its contribution in mass was only 9–32% (average 16%) among the congeners. Similarly, PBDFs accounted for ~100% of toxicity of PBDD/Fs. Additionally, *deca*-BDEs contributed to most of the mass emissions of PBDEs (47.0–90.5%, 82.4% in average), while *nona*-BDEs and *tri*- to *octa*-BDEs only contributed 10% and 8%, respectively. The reductions of the absolute mass concentrations of POPs from W20 were in the order PBDEs >> PBDD/Fs > PCDD/Fs ≈ PCBs for all multi-component diesel blends. The reduction fractions of POPs were in the order PCDD/F > PCB ≈ PBDD/F > PBDE, and those of TEQ were PCDD/F > PCB > PBDD/F. Thus, the addition of butanol and acetone, whether pure or hydrous, could further lower the POP emissions from W20.

Keywords: Generator engine; Waste cooking oil-based biodiesel; Butanol; Acetone; Persistent organic pollutants.

INTRODUCTION

Diesel engine exhausts (DEEs) may cause adverse health effects due to their varied chemical compositions, which include carbonaceous matter (Cheng *et al.*, 2015), trace metals (Lin *et al.*, 2005; Lin *et al.*, 2008), polycyclic aromatic hydrocarbons (PAHs) (Lin *et al.*, 2012; Lin *et al.*, 2017) and even persistent organic pollutants (POPs) (Gullett and Ryan, 2002; Chang *et al.*, 2014a; Chen *et al.*, 2017). In urban areas, the emissions emitted from diesel engines contain pollutants harmful to human health, such as carcinogens (Attfield *et al.*, 2012; IARC, 2012). In addition, several works have indicated that emissions of chlorine or bromine substituted pollutants, such as polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyl (PCBs), polybrominated dibenzo-*p*-dioxins and polybrominated dibenzofurans (PBDD/Fs) and polybrominated diphenyl ethers (PBDEs), are emitted not only from incinerators (Wei *et al.*, 2016), electric arc furnaces and secondary aluminum smelters (Wang *et al.*, 2015), but also from diesel engines (Laroo *et al.*, 2011; Laroo *et al.*, 2012; Cheruiyot *et al.*, 2016).

Diesel engine generators, which form one category of off-road diesel engines, are widely adopted and rapidly developed. The supply of electrical power has not kept up with the increasing demand in some applications, including crowded open-air bazaars, mine shafts, construction sites, and ship holds (Idjdarene *et al.*, 2008; USEPA, 2012). The

* Corresponding author.
Tel.: +886-8-7740263; Fax: +886-8-7740256
E-mail address: chensj@mail.npust.edu.tw

necessarily short wires or cables linked to diesel engine generators might cause health hazards to people close to the emitted exhausts. Lewne *et al.* (2007) reported that tunnel construction workers had diesel engine exhaust exposure levels one order of magnitude higher than above-ground workers in Stockholm. Nevertheless, few studies have investigated the emissions of persistent organic pollutants (POPs) from off-road diesel engines.

Biodiesel, as an alternative to diesel fuel, is considered one of sustainable ways to lower the impact of POPs. Transforming non-edible oil (i.e., waste cooking oil and microalgae oil) into biodiesel is attractive owing to the crude shortage and the competition between food and energy (Mwangi *et al.*, 2015b; Tsai *et al.*, 2015a). However, blends with an excessive percentage (> 50%) of biodiesel, which has a higher viscosity and cetane number than conventional fossil diesel, would negatively affect fuel atomization and increase emissions (Tsai *et al.*, 2010; Lin *et al.*, 2012; Wu *et al.*, 2016). Some researchers have reported that adding ethanol, which has less viscosity, to biodiesel blended fuel could balance the high viscosity of the biodiesel, improve fuel combustion efficiency and decrease PM emission (Shi *et al.*, 2005; Kwanchareon *et al.*, 2007; Tang *et al.*, 2016; Saxena and Maurya, 2016).

Our earlier studies investigated the characteristics of PCDD/Fs, PCBs, PBDD/Fs and PBDEs that were emitted from a generator fuelled with D100 (pure diesel), W20 (20 vol% waste cooking oil-based biodiesel + 80 vol% petrodiesel) and W40 under loads of 1.5kW and 3.0kW (Tsai *et al.*, 2016). Experimental results indicated that W20 and W40 emitted less POP than D100, (15–65% and 23–85% by mass (25–47% and 46–91% by toxicity), respectively). Furthermore, W40 exhibited the (greatest OR highest) reductions of mass and toxicity concentrations of these POPs at two loads, while W20 had the lowest PM concentrations. This study further explores the effect of adding pure or water-containing butanol and acetone to W20 on the POP emission from a diesel generator fuelled with different fuel blends.

MATERIALS AND METHODS

Sampling Procedures

The tested fuels with different biodiesel and solvent addition percentages were B30 (20% waste cooking oil-based biodiesel + 30% butanol + 50% diesel), B′30 (20% waste cooking oil-based biodiesel + 30% water-containing butanol + 50% diesel), A3 (20% waste cooking oil-based biodiesel + 3% acetone + 1% IPA + 79% diesel), A′3 (20% waste cooking oil-based biodiesel + 3% water-containing acetone + 1% IPA + 79% diesel), B30A3 (20% waste cooking oil-based biodiesel + 30% butanol + 3% acetone + 1% IPA + 46% diesel), and B′30A′3 (20% waste cooking oil-based biodiesel + 30% water-containing butanol + 3% water-containing acetone + 1% IPA + 46% diesel). These different blended fuels were tested in a generator at a stable energy output (110V/60 Hz, 1800 rpm) under loads of 1.5 kW and 3.0 kW. A water-cooled, natural-intake four-stroke diesel engine (TF110E; YANMAR, Japan) with a single fuel-injection cylinder (Bore × Stroke: 88 mm × 96 mm) was applied. The power generator (YSG-5SEN; YANMAR, Japan) had a 100/110 V (50/60 Hz) AC output (single-phase, two-wire type), with a maximum output of 4 kW at 1,800 rpm. 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.

An auto-detector flow sampling system equipped with quartz fiber filters (2500 QAT-UP, 47 mm; Pall Corporation, New York, USA) was installed on the downstream side of the tailpipe of the diesel generator to identify the particle-phase samples in the exhaust. Gas-phase samples were obtained using two-stage glass cartridges (filled with XAD-2 resins). The quartz filters were pretreated before being sampled by heating them in a muffle furnace in air for 2.5h at 900°C. 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 measure the collection efficiency of the sampling train. The recovery levels of the PCDD/Fs surrogate standards were 87–113%, which met the specified range of 70–130%. The experiments were performed three times (each sampling time = 30 min) for each combination of parameters. Sampling data were accumulated after the engine had been run for at least 30 min. The extraction of POPs was generally completed within one week after 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 filter and two-stage glass cartridges from each exhaust sample were combined to represent the entire exhaust sample. Each exhaust sample 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 them using ultra-pure nitrogen, and cleaned by a silica gel column. The extracts were treated with concentrated sulfuric acid in the first cleanup stage following extraction. Extract samples that were dissolved in 5 mL of hexane were then added to an acid silica gel column with two extra 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 third step involved an alumina column. The concentrated eluate was then transferred from the acid silica gel column to the top of the 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 5mL 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 to identify seventeen 2,3,7,8-substituted PCDD/F, twelve dioxin-like PCB, twelve 2,3,7,8-substituted PBDD/F and fourteen PBDE congeners using a high-resolution gas chromatograph/high-resolution mass spectrometer (HRGC/HRMS). The HRGC (Hewlett-Packard 6970 Series gas, CA) was equipped with a silica capillary column (J&W Scientific, CA) and a splitless injector, and the HRMS (Micromass Autospec Ultima, Manchester, UK) was used 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 35eV and 250°C, respectively. The analytical procedures and parameters for the instrumental analysis of POPs are described in detail in our earlier work (Wang *et al.*, 2010).

The toxic equivalency (TEQ) values of PCDD/Fs and PCBs were calculated using the World Health Organization's 2005 toxic equivalent factors (TEF) (Van den Berg *et al.*, 2006). Since the TEFs have not been determined for PBDD/Fs, the TEF values of PCDD/Fs were used as trial TEFs for PBDD/Fs to evaluate their toxicity concentrations.

RESULTS AND DISCUSSION

Engine Performance and PM Emissions

Engine performance was the first priority for consideration in this study, since the diesel engines and their related apparatus were not temporarily modified along with fuels. Therefore, this investigation reported the fuel consumption rate (FCR) and brake specific fuel consumption (BSFC). The FCRs were measured by a scaled cylinder, and evaluated using the process described in the experimental section. The FCRs were 1.08–1.50, 1.22–1.71, 1.22–1.74, 1.16–1.61, 1.20–1.64, 1.26–1.73, and 1.22–1.78 L h^{-1} using W20, B30, B′30, A3, A′3, B30A3 and B′30A′3, respectively, at both engine loads (as shown in Table 1). Addition of 3% acetone caused FCR to rise by 7.3–7.4%, possibly owing to the low heating value resulting from solvent addition. By adding more solvent, the FCR increased by 13.0–14.0% and 15.3–16.7% when using B30 and B30A3, respectively. The replacement of dehydrate by hydrous solvent also slightly increased the FCR due to their lower heating values. To eliminate the effect of unstable electricity generation among the tests of various fuel blends, the BSFCs (L kWh^{-1}) were then computed with the following equation.

$$BSFC\left(\mathrm{L\ kWh^{-1}}\right)=\frac{FCR}{P_e} \tag{1}$$

where FCR stands for the fuel consumption rate (L h^{-1}), and P_e stands for the averaging electricity power output (kW) during each sampling period.

The BSFCs using W20, B30, B′30, A3, A′3, B30A3, and B′30A′3 were 0.50–0.73, 0.57–0.81, 0.58–0.81, 0.54–0.77, 0.55–0.80, 0.58–0.84 and 0.59–0.81 L kWh^{-1}, respectively, at both engine loads (as listed in Table 1). Adding 3% acetone

Table 1. Engine performance and PM emissions (n = 3) using WCO-based biodiesel-alcohol blends at various loads.

Fuels			W20[a]	B30		B′30		A3		A′3		B30A3		B′30A′3	
			Abs[b]	Abs	Inc[c], %	Abs	Inc, %	Abs	Inc, %	Abs	Inc, %	Abs	Inc, %	Abs	Inc, %
FCR *L h*$^{-1}$	1.5 kW	**Mean**	**1.08**	**1.22**	**13.0%**	**1.22**	**13.0%**	**1.16**	**7.4%**	**1.20**	**11.1%**	**1.26**	**16.7%**	**1.22**	**13.0%**
		SD	0.01	0.03	–	0.07	–	0.03	–	0.00	–	0.00	–	0.03	–
	3.0 kW	**Mean**	**1.50**	**1.71**	**14.0%**	**1.74**	**16.0%**	**1.61**	**7.3%**	**1.64**	**9.3%**	**1.73**	**15.3%**	**1.78**	**18.7%**
		SD	0.02	0.08	–	0.00	–	0.01	–	0.00	–	0.02	–	0.02	–
BSFC *L kWh*$^{-1}$	1.5 kW	**Mean**	**0.73**	**0.81**	**11.0%**	**0.81**	**11.0%**	**0.77**	**5.5%**	**0.80**	**9.6%**	**0.84**	**15.1%**	**0.81**	**11.0%**
		SD	0.01	0.02	–	0.05	–	0.02	–	0.00	–	0.00	–	0.02	–
	3.0 kW	**Mean**	**0.50**	**0.57**	**14.0%**	**0.58**	**16.0%**	**0.54**	**8.0%**	**0.55**	**10.0%**	**0.58**	**16.0%**	**0.59**	**18.0%**
		SD	0.01	0.03	–	0.00	–	0.00	–	0.00	–	0.01	–	0.01	–
PM *mg Nm*$^{-3}$	1.5 kW	**Mean**	**52.26**	**33.91**	**–35.1%**	**28.84**	**–44.8%**	**40.63**	**–22.3%**	**35.15**	**–32.7%**	**30.88**	**–40.9%**	**30.24**	**–42.1%**
		SD	2.66	4.00	–	1.83	–	2.97	–	2.35	–	5.16	–	4.33	–
	3.0 kW	**Mean**	**94.65**	**58.70**	**–38.0%**	**53.93**	**–43.0%**	**76.32**	**–19.4%**	**70.20**	**–25.8%**	**50.75**	**–46.4%**	**49.47**	**–47.7%**
		SD	9.17	3.28	–	1.69	–	6.94	–	2.57	–	3.88	–	2.76	–

[a] Cited from Tsai *et al.* (2016); [b] absolute values; [c] increases in comparison to W20 in percentage (%).

increased the BSFC by 5.5–8.0%, probably resulting from the lower heating values provided by additives. The BSFC were further increased to 11.0–14.0% and 11.0–18.0% by adding more solvent when using B30 and B30A3, respectively. Replacing of anhydrous with hydrous solvents also slightly increased the BSFC levels due to the lower heating values of hydrous solvents.

Some previous studies indicated that the oxygenated additives in diesel can improve the thermal efficiency of engine and reduce the BSFC (Yoshimoto *et al.*, 1999; Lin *et al.*, 2006; Lin *et al.*, 2010; Mwangi *et al.*, 2015a; Tsai *et al.*, 2015b). However, the alternative ratios in the current study were too high to overcome the loss of heating values. Therefore, this work did not obtain lower FCR or BSFC values. Fortunately, the various diesel blends had no more than 18% higher overall energy performances than W20. The emissions of regulated and toxic pollutants then became the major factor when considering alternative fuels. The PM emitted by W20 were 52.3 mg Nm^{-3} and 94.7 mg Nm^{-3} at 1.5 kW and 3.0 kW, respectively, and significantly reduced by 19.4–32.7% by using extra 3% dehydrate or hydrous acetone additives. The oxygen content in acetone effectively improved the oxidation of hydrocarbons, and lowered the PM emissions. Adding higher fractions of hydrous solvent additives increased this phenomenon was more significant, leading to PM reductions of up to 42.1–47.7% by using B30′A′3.

Emissions of PCDD/Fs

The mass concentrations of PCDD/Fs from the diesel engine generator were 44.5 ± 9.97, 32.1 ± 2.65, 51.5 ± 9.75, 37.3 ± 4.98, 43.8 ± 3.90 and 36.5 ± 2.79 pg Nm^{-3} by feeding B30, B′30, A3, A′3, B30A3, and B′30A′3, respectively, at 1.5 kW (as shown in Table 2). Meanwhile, the TEQ concentrations were 2.00 ± 0.39, 1.24 ± 0.28, 2.71 ± 0.22, 1.82 ± 0.18, 0.62 ± 0.17 and 0.58 ± 0.32 pg WHO_{2005}-TEQ Nm^{-3}. With the 3.0 kW engine, the mass concentration of PCDD/Fs were 113 ± 28.1, 61.1 ± 2.52, 123 ± 2.93, 76.6 ± 10.5, 106 ± 6.48 and 75.3 ± 1.27 pg Nm^{-3}, while the TEQ concentrations were 3.37 ± 0.30, 2.40 ± 0.18, 4.95 ± 1.6, 2.60 ± 0.23, 1.11 ± 0.63 and 0.98 ± 0.64 pg WHO_{2005}-TEQ Nm^{-3}. PCDD/Fs can form from homogeneous processes in the presence of precursors, such as chlorobenzenes (CBs), chlorophenols (CPs) and surface-associate chlorophenoxyl, under high temperature during combustion (Liu *et al.*, 2013b). The pyrolysis, elimination, and dechlorination of polychlorinated diphenyl ethers (PCDEs) and polycyclic aromatic hydrocarbons (PAHs) (Lindahl *et al.*, 1980; Nito *et al.*, 1997), as well as the condensations and recombination of fragments (PCDEs, CBs, and CPs) (Weber and Hagenmaier, 1999) have been reported as the major transformation mechanisms of these POPs in the gaseous phase. Nevertheless, *de novo* synthesis is the dominant heterogeneous reaction to form PCDFs (Stieglitz *et al.*, 1990; Huang and Buekens, 1995). Weber and Kuch (2003) and Liu *et al.* (2013b) indicated that the precursor reaction processes dominated over *de novo* synthesis for PCDD/F formation during combustion.

Previous studies reported that butanol has similar physical and chemical properties to the normal diesel fuel, and that butanol and acetone are highly soluble in diesel to improve combustion efficiency. Therefore, butanol was also tested as a diesel additive or alternative content (Yao *et al.*, 2010; Rakopoulos *et al.*, 2011; Campos-Fernandez *et al.*, 2012; Lin *et al.*, 2012; Liu *et al.*, 2013a). Adding hydrous/dehydrate butanol or acetone to W20 to form B30, B′30, A3, A′3, B30A3, and B′30A′3 reduced both mass and TEQ concentrations of PCDD/F. The reductions in mass concentration and TEQ reductions were higher in PCDDs than in PCDFs, as shown in Fig. 1. Specifically, the reductions of PCDD and PCDF levels using B30 and B′30 in comparison to using W20 were 47–53% (average 50%) and 28–39% (average 34%), respectively, for mass concentrations, and 67–77% (average 72%) and 15–23% (average 19%), respectively, for TEQ concentrations (as shown in Fig. 2). Similarly, A3 and A′3 achieved reductions in PCDD and PCDF mass concentrations of 47–50% (average 48%) and 26–38% (average 33%), respectively, and in TEQ emissions of 64–77% (average 71%) and 13–21% (average 18%), respectively, compared with W20. The diesel blends containing butanol-acetone (B30A3 and B′30A′3) had PCDD mass concentration 3% lower than those with single butanol or acetone (B30, B′30, A3 or A′3) but PCDF mass concentration increased by 2–8%, and TEQ concentrations of PCDDs and PCDFs increased by 2–8% and 2–5%, respectively.

Hydrous butanol and acetone blended fuels (B′30 and A′3) reduced both PCDD and PCDF mass concentrations from the exhaust by a further 1–7% (average 3%) from dehydrate-butanol- and dehydrate-acetone-diesel blends (B30 and A3), and reduced TEQ concentrations of PCDDs and PCDFs by 1–4% (average 3%) and 1–3% (2% in average), respectively. The finding is attributed to the micro-explosion for enhancing the secondary atomization of fuel spray and improving the combustion, when the small amount of water was stably present in the B′30 and A′3 (Garo *et al.*, 2004; Chang *et al.*, 2013; Tsai *et al.*, 2014).

Emissions of PCBs

Table 2 shows the PCB emissions from the diesel engine generator by feeding six different multi-component diesel blends with 1.5 kW and 3.0 kW electricity output power. At 1.5 kW load, the PCB mass concentrations were 227 ± 32.6, 186 ± 6.27, 272 ± 20.2, 238 ± 8.25, 209 ± 14.1, and 173 ± 9.64 pg Nm^{-3} by using B30, B′30, A3, A′3, B30A3, and B′30A′3, respectively; and the corresponding TEQ values were 0.39 ± 0.13, 0.14 ± 0.14, 0.36 ± 0.21, 0.13 ± 0.08, 0.26 ± 0.08 and 0.16 ± 0.09 pg WHO_{2005}-TEQ Nm^{-3}, respectively. At 3.0 kW, the mass concentrations were 289 ± 11.6, 211 ± 12.1, 356 ± 23.3, 305 ± 33.6, 245 ± 42.6, and 200 ± 25.8 pg Nm^{-3}, respectively, while the TEQ concentrations were 0.32 ± 0.21, 0.14 ± 0.10, 0.35 ± 0.20, 0.17 ± 0.09, 0.21 ± 0.05, and 0.17 ± 0.10 pg WHO_{2005}-TEQ Nm^{-3}, respectively.

When using various WCO-based-solvent-containing diesel blends at two engine loads, *mono-ortho* PCBs dominated the mass concentration (84%) of dioxin-like PCBs (*dl*-PCBs), while the *non-ortho* PCBs were predominant in TEQ emission (97%) (Fig. 1). In comparison with W20, the

Table 2. Mass and TEQ concentrations of POPs emitted from diesel engine generator.

	Concentrations of POPs (n = 3)						
	W20[a]	B30	B'30	A3	A'3	B30A3	B'30A'3
1.5 kW							
PCDD/Fs							
mass (pg Nm^{-3})	**278** ± 42.9	**44.5** ± 9.97	**32.1** ± 2.65	**51.5** ± 9.75	**37.3** ± 4.98	**43.8** ± 3.90	**36.5** ± 2.79
TEQ (pg WHO_{2005}-TEQ Nm^{-3})	**17.5** ± 3.0	**2.00** ± 0.39	**1.24** ± 0.28	**2.71** ± 0.22	**1.82** ± 0.18	**0.62** ± 0.17	**0.58** ± 0.32
PCBs							
mass (pg Nm^{-3})	**419** ± 60.0	**227** ± 32.6	**186** ± 6.27	**272** ± 20.2	**238** ± 8.25	**209** ± 14.1	**173** ± 9.64
TEQ (pg WHO_{2005}-TEQ Nm^{-3})	**1.4** ± 0.52	**0.39** ± 0.13	**0.14** ± 0.14	**0.36** ± 0.21	**0.13** ± 0.08	**0.26** ± 0.08	**0.16** ± 0.09
PBDD/Fs							
mass (pg Nm^{-3})	**801** ± 354	**444** ± 18.2	**328** ± 23.6	**523** ± 15.8	**460** ± 160	**500** ± 55.0	**401** ± 186
TEQ (pg WHO_{2005}-TEQ Nm^{-3})	**1.2** ± 0.42	**0.79** ± 0.12	**0.42** ± 0.05	**0.93** ± 0.18	**0.59** ± 0.41	**0.68** ± 0.21	**0.65** ± 0.27
PBDEs							
mass (ng Nm^{-3})	**47.8** ± 1.92	**31.7** ± 4.93	**29.6** ± 6.72	**43.4** ± 8.05	**35.1** ± 3.51	**29.7** ± 3.43	**27.9** ± 2.60
3.0 kW							
PCDD/Fs							
mass (pg Nm^{-3})	**457** ± 72.9	**113** ± 28.1	**61.1** ± 2.52	**123** ± 2.93	**76.6** ± 10.5	**106** ± 6.48	**75.3** ± 1.27
TEQ (pg WHO_{2005}-TEQ Nm^{-3})	**36.5** ± 13.5	**3.37** ± 0.30	**2.40** ± 0.18	**4.95** ± 1.63	**2.60** ± 0.23	**1.11** ± 0.63	**0.98** ± 0.64
PCBs							
mass (pg Nm^{-3})	**489** ± 84.5	**289** ± 11.6	**211** ± 12.1	**356** ± 23.3	**305** ± 33.6	**245** ± 42.6	**200** ± 25.8
TEQ (pg WHO_{2005}-TEQ Nm^{-3})	**1.61** ± 0.66	**0.32** ± 0.21	**0.14** ± 0.10	**0.35** ± 0.20	**0.17** ± 0.09	**0.21** ± 0.05	**0.17** ± 0.10
PBDD/Fs							
mass (pg Nm^{-3})	**1202** ± 135	**656** ± 54.5	**476** ± 33.8	**714** ± 107	**559** ± 17.5	**673** ± 32.0	**506** ± 30.4
TEQ (pg WHO_{2005}-TEQ Nm^{-3})	**1.66** ± 0.30	**0.99** ± 0.13	**0.76** ± 0.03	**1.26** ± 0.20	**0.96** ± 0.38	**1.08** ± 0.25	**0.95** ± 0.21
PBDEs							
mass (ng Nm^{-3})	**76.6** ± 3.09	**45.4** ± 5.33	**41.2** ± 4.03	**71.7** ± 9.75	**62.0** ± 4.01	**41.5** ± 2.49	**39.8** ± 0.78

[a] Cited from Tsai *et al.* (2016).

reductions of 12 *dl*-PCB mass concentrations ranged 27–59% by using B30, B′30, A3, A′3, B30A3 and B′30A′3, contributed mainly by *mono-ortho* PCBs (19–50%) and less by *non-ortho* PCBs (5.8–15%). However, the TEQ reductions had an opposite result, as the *non-ortho* PCBs had much higher contribution (72–91%) than *mono-ortho* PCBs (0.2–0.4%) to the overall *dl*-PCB reductions (78–91%) when using the six fuels blended with additives in comparison to using W20 (Fig. 2). However, our WCO-based hydrous butanol-diesel blend, B′30, had 4–12 times TEQ emission (0.14 pg WHO-TEQ Nm^{-3}) of *dl*-PCB at both engine loads than Chang *et al.* (2014b) (0.0117–0.0361 pg WHO-TEQ Nm^{-3}), using 2% biodiesel mixed with 10–20% hydrous butanol as alternative diesel fuel blends. This result is attributable to the difference in fuel properties, such as viscosity, chlorine/sulfur/oxygen content, flash point, fatty acid structures and cetane numbers of WCOs. Therefore, the stability of WCO must be considered when adjusting the compositions of fuel blends.

Emissions of PBDD/Fs

Table 2 presents the emissions of PBDD/Fs from the diesel engine generator fuelled with B30, B′30, A3, A′3, B30A3, and B′30A′3 and operated at 1.5 kW and 3.0 kW loads. The PBDD/F mass concentrations were 444 ± 18.2, 328 ± 23.6, 523 ± 15.8, 460 ± 160, 500 ± 55.0, and 401 ± 186 pg Nm^{-3} at 1.5 kW by using B30, B′30, A3, A′3, B30A3, and B′30A′3, respectively, and the corresponding TEQ values were 0.79 ± 0.12, 0.42 ± 0.05, 0.93 ± 0.18, 0.59 ± 0.41, 0.68 ± 0.21 and 0.65 ± 0.27 pg WHO_{2005}-TEQ Nm^{-3}, respectively. At 3.0kW, the mass concentration data were 656.4 ± 54.5, 476 ± 33.8, 714 ± 107, 560 ± 17.5, 673 ± 32 and 506 ± 30.4 pg Nm^{-3}, and the TEQ values were 0.99 ± 0.13, 0.76 ± 0.03, 1.26 ± 0.20, 0.96 ± 0.38, 1.08 ± 0.25, and 0.95 ± 0.21 pg WHO_{2005}-TEQ Nm^{-3}, respectively.

The mass and TEQ concentrations of PBDD/Fs were both provided by PBDFs (100%), because the PBDDs were non-detectable in the engine exhaust from all fuel blends (Figs. 1 and 2). The reductions of PBDD/F mass and TEQ concentrations when using B30, B′30, A3, A′3, B30A3 and B′30A′3 as alternative fuels in comparison with using W20 were 35–60% (48% in average) and 20–64% (40% in average), respectively, provided entirely by PBDFs (Fig. 2). Specifically, the reductions of PCDD/F mass concentrations and TEQ levels by using anhydrous diesel blends (B30, A3 and B30A3) were 35–45% (average 41%) and 20–41% (average 32%), respectively,. The hydrous diesel blends (B′30, A′3 and B′30A′3) reduced TEQ concentrations by 42–60% (average 54%) mass and 42–64% (average 49%) when compared with W20, representing further reductions of 7–15% (13% in average) mass and 3–32% (17% in average) TEQ from dehydrate-solvent-additive blends (B30, A3 and B30A3).

Emissions of PBDEs

From Table 2, the mass concentrations of PBDEs emitted from the diesel engine generator for using B30, B′30, A3, A′3, B30A3 and B′30A′3 were 31.7 ± 4.9, 29.6 ± 6.7, 43.4

± 8.0, 35.1 ± 3.5, 29.7 ± 3.4 and 27.9 ± 2.6 ng Nm^{-3}, respectively, at 1.5 kW, and 45.4 ± 5.3, 41.2 ± 4.0, 71.7 ± 9.8, 62.0 ± 4.0, 41.5 ± 2.5 and 39.8 ± 0.8 ng Nm^{-3}, respectively, at 3.0 kW.

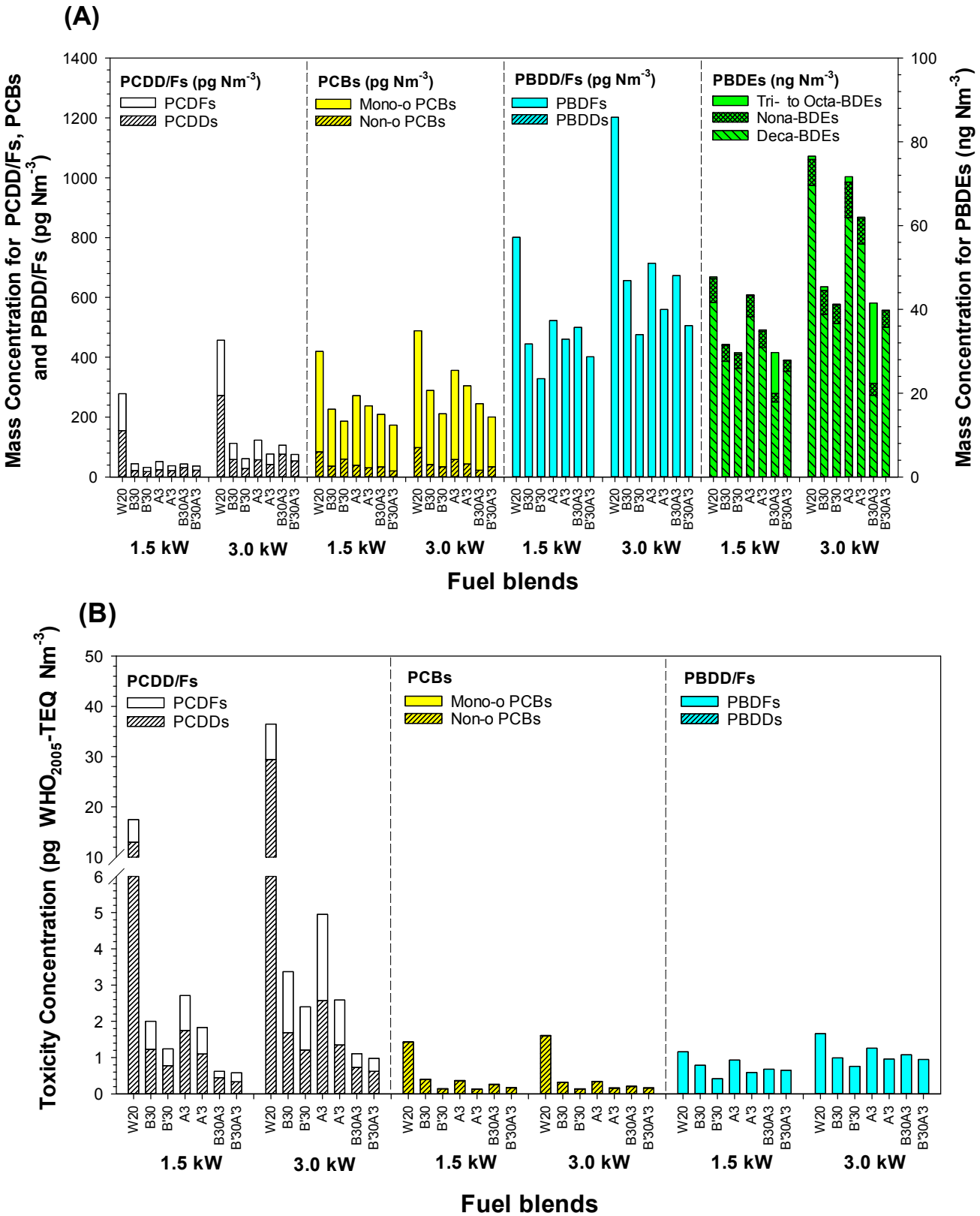

Fig. 1. Mass (A) and TEQ (B) concentrations of POPs from diesel engine generator fueled by W20 and various solvent-containing diesel blends.

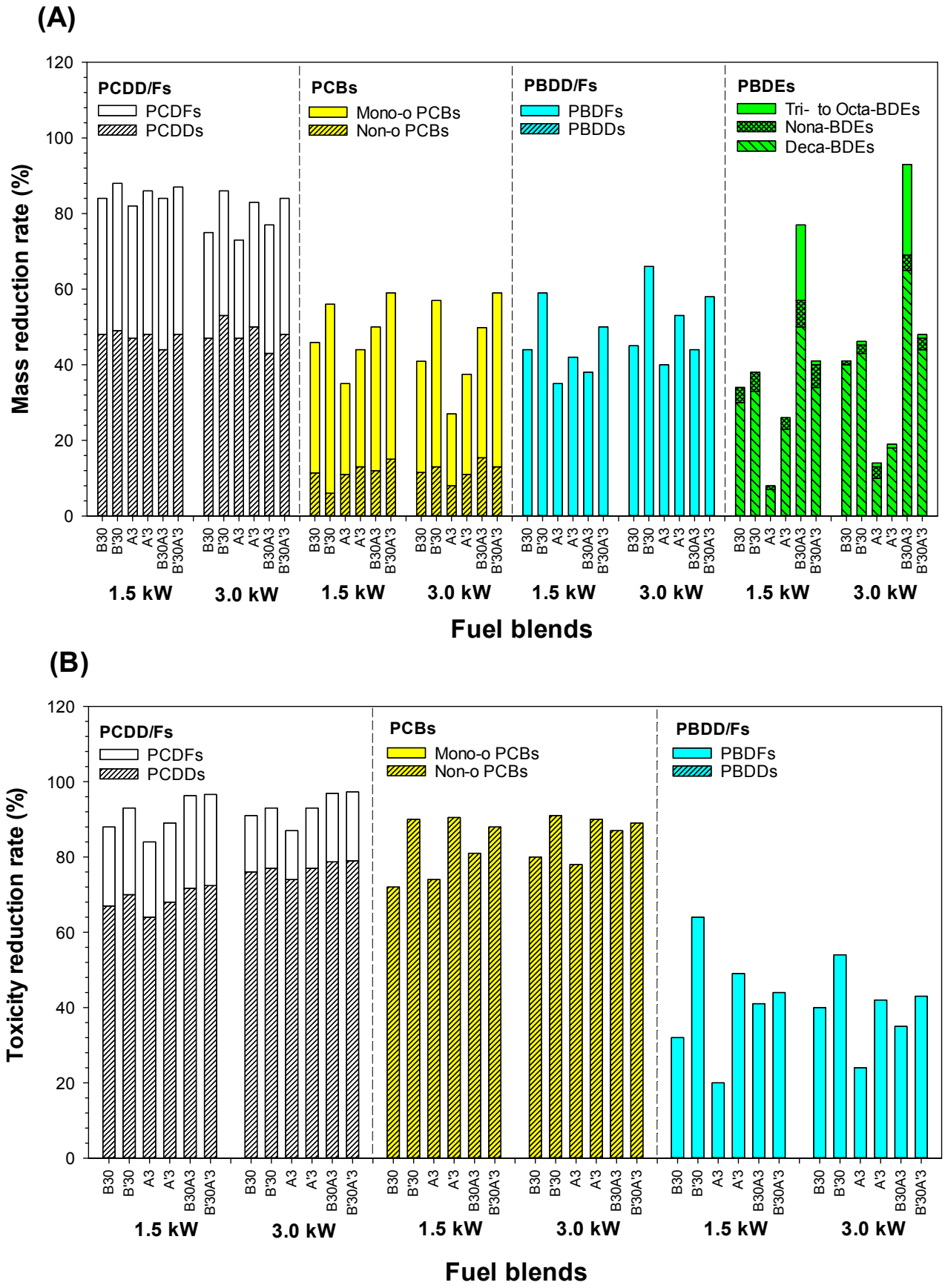

Fig. 2. Reduction rates of (A) mass and (B) TEQ concentrations of POPs from using various solvent-containing diesel blends in comparison to using W20.

Of all the PBDEs, the highest contribution was from *deca*-BDE (BDE-209) (88%), followed by *nona*-BDEs (11%, BDE-208, 207 and 206), and *tri*- to *octa*-BDEs (1%), except for B30A3. In comparison with W20, the reductions of PBDEs for using the six blends were mostly contributed by *deca*-BDE (7–47% reduction, average 28%), followed by *nona*-BDEs (6–12% reductions, 9% in average), although the reductions of *tri*- to *octa*-BDEs contributed only 1% to total BDE reductions. Restated, *nona*- and *deca*-BDEs provided most of the PBDE reductions (> 99%) from using B30, B′30, A3, A′3, B30A3 and B′30A′3 as alternatives to W20.

Comprehensive Discussion among Four POPs Emitted from Diesel Engine Generator

Fig. 1 illustrates the mass and TEQ concentrations of PCDD/Fs, PCBs, PBDD/Fs and PBDEs emitted from the diesel engine generator by using various WCO-based solvent-diesel blends. The emission concentrations of the four POPs were in the order PBDE ≫ PBDD/F > PCB > PCDD/F, for all blending fuel (B30, B′30, A3, A′3, B30A3 and B′30A′3) at both engine loads. Among the POPs, PBDE had the highest level, being equal to 2–3 times that of the others. Conversely, the corresponding emitted toxicity followed the order PCDD/F > PCB ≈ PBDD/F, while PCDD/Fs had about 10 times the toxicity concentrations those of PCBs and PBDD/Fs. In addition, the diesel engine generator using W20 blended with dehydrate/hydrous butanol and acetone had lower BSFC (Table 1) and POP emissions (Table 2) under 3.0 kW load than under 1.5 kW load. One possible reason for this phenomenon is that fewer precursors (e.g., PAHs) and high oxygen content in the mixed alcohol-biodiesel fuel blends resulted in the reduction of POPs formation during combustion.

Among the dioxin compounds, the emissions of PCDDs represented 46–73% (average 57%) and 50–72% (average 59%) of total PCDD/F mass and toxicity concentrations, respectively, and were significantly higher than those of PCDFs. The non-*ortho*-PCB contributed almost all toxicity (~100%) of 14 *dl*-PCBs, even though its contribution in mass was only 9–32% (average 16%) among the congeners. A similar case was found in PBDFs, which accounted for ~100% toxicity of PBDD/Fs. Additionally, the mass emissions of PBDEs were mostly provided by *deca*-BDEs (47.0–90.5%, average 82.4%), and *nona*-BDEs and *tri*- to *octa*-BDEs only contributed 10% and 8%, respectively.

The TEQ emission concentrations of PCDD/Fs, PCBs, and PBDD/Fs were 0.58–4.95, 0.13–0.40, and 0.42–1.26 pg WHO_{2005}-TEQ Nm^{-3}, respectively, which were 1–3 times those (0.0113, 0.00129, and 0.00129 pg WHO_{2005}-TEQ Nm^{-3}) measured in the atmospheric environment around the testing engine generator (Chao *et al.*, 2014). This finding indicates the heavy impact of a diesel engine emission on ambient air quality, and the importance of reducing POP emission by using alternative fuels.

The reductions in concentrations of the four POPs from using W20 were in the order PBDE ≫ PBDD/F > PCDD/F ≈ PCB for absolute mass concentrations, and PCDD/F > PCB ≈ PBDD/F > PBDE, and PCDD/F > PCB > PBDD/F for the TEQ reduction rates, for all multi-component diesel blends (B30, B′30, A3, A′3, B30A3 and B′30A′3) (Fig. 2). Consequently, the addition of butanol or acetone (pure and hydrous mixtures) into W20 could further reduce POP emissions.

Our previous work observed that the PM emission was mainly contributed by carbonaceous species (~80%) (Tsai *et al.*, 2010). Stieglitz *et al.* (1990) indicated that higher soot emission might lead to the formation of furans by *de novo* synthesis. Thus, the lower PM reflects fewer unburned carbon particles and lower PCDD/F formation in exhaust gas (Huang and Buekens, 1995). Tsai *et al.* (2016) reported that addition of 20% or 40% biodiesel to pure diesel (D100) could reduce PCDD/F, PCB, PBDD/F and PBDE emissions in the exhaust gas from the diesel engine generator. Chang *et al.* (2014a) also found that WCO-based biodiesel blends could reduce PAH, PCDD/F, PCB, PBDD/F and PBDE emissions from a diesel engine. These previous studies all support the findings of the current investigation.

CONCLUSIONS

The emission concentrations of four POPs were in the order PBDE ≫ PBDD/F > PCB > PCDD/F, despite using different blending fuels at both engine loads. PBDE had the highest level among the POPs, being equal to 2–3 times that of the others. In contrast, the emitted toxicity followed the order PCDD/F > PCB ≈ PBDD/F, and the emission toxicity concentrations of PCDD/Fs were about 10 times those of PCBs and PBDD/Fs. The reductions of the absolute mass concentrations of these POPs by using all multi-component diesel blends were in the order PBDE ≫ PBDD/F > PCDD/F ≈ PCB in comparison with using W20. Meanwhile, the reduction fractions of the POPs followed the order PCDD/F > PCB ≈ PBDD/F > PBDE, and PCDD/F > PCB > PBDD/F for the corresponding TEQ reductions. Consequently, the addition of butanol and acetone (pure and hydrous mixtures) into W20 could further decrease the POP emission.

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