



Characteristics of Persistent Organic Pollutant Emissions from a Diesel-Engine Generator Fueled Using Blends of Waste Cooking Oil-Based Biodiesel and Fossil Diesel

Jen-Hsiung Tsai¹, Shui-Jen Chen^{1*}, Kuo-Lin Huang¹, Guo-Ping Chang-Chien^{2,3},
Wen-Yinn Lin⁴, Chien-Wei Feng¹, Jin-Yuan Syu⁴, Ho-Tsang Huang¹

¹ Department of Environmental Science and Engineering, National Pingtung University of Science and Technology, Pingtung County 91201, Taiwan

² Supermicro Mass Research and Technology Center, Cheng Shiu University, Kaohsiung City 83347, Taiwan

³ Department of Cosmetics and Fashion Styling, Cheng Shiu University, Kaohsiung City 83347, Taiwan

⁴ Institute of Environmental Engineering and Management, National Taipei University of Technology, Taipei City 10608, Taiwan

ABSTRACT

This study elucidates the characteristics of persistent organic pollutants (POPs), including 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), that are emitted from a generator (non-road diesel engine) that is fueled with a blend of waste cooking oil biodiesels (WCO-biodiesels). Experimental results reveal that the mass concentrations of PCDD/Fs, PCBs, PBDD/Fs and PBDEs from the diesel generator that is fueled with petroleum diesel (D100) under loads of 1.5 kW and 3.0 kW were 583–875 pg Nm⁻³, 580–810 pg Nm⁻³, 982–1408 pg Nm⁻³, and 134–216 ng Nm⁻³, respectively, while the toxicity concentrations of PCDD/Fs, PCBs, and PBDD/Fs were 33.2–58.6, 2.72–3.11, and 1.54–2.30 pg WHO₂₀₀₅-TEQ Nm⁻³, respectively. W20 and W40 emitted 15–65% and 23–85% less of these POPs by mass (and 25–47% and 46–91% by toxicity), respectively. Among the tested fuel blends, the W40 exhibited the greatest emission factor reductions of mass and toxicity of these four POPs, despite of the load. Therefore, WCO-biodiesels can feasibly be used as an alternative generator fuel, favoring the recycling/reuse of waste oils and mitigating hazards to human health and environment.

Keywords: Persistent organic pollutant; PCDD/F; PBDE; Waste cooking oil; Biodiesel.

INTRODUCTION

In June 2012, the International Agency for Research on Cancer (IARC, WHO) officially recognized diesel engine exhaust as a human carcinogen (Group 1) (IARC, 2012), and diesel engine exhaust has for many years been a global concern owing to its adverse health effects. Epidemiological studies have shown that exposure to diesel exhaust pollutants, especially polycyclic aromatic hydrocarbons (PAHs), is an environmental factor (Cheruiyot *et al.*, 2015) that may be associated with lung adenocarcinoma in Taiwan (Huang *et al.*, 2010; Chio *et al.*, 2014). Diesel engines are known to emit hydrocarbons, including PAHs, nitro-*p* PAHs, and

particulate matter (PM) with a significant proportion of elemental carbon (Kittelson, 1998; Kleeman *et al.*, 2000), as well as various volatile organic compounds (VOCs) (Alves *et al.*, 2015) and carbonyl compounds (i.e., formaldehyde, acetaldehyde) (Yao *et al.*, 2015). In combustion systems, PCDD/Fs can be generated by the formation and oxidation of carbon in the following two-stage process; (1) carbon formation: carbon particles that comprise degenerated graphitic structures are formed in the combustion zone; (2) carbon oxidation: the unburned carbon particles continue to be oxidized in the low-temperature post combustion zone and PCDD/Fs are formed as by-products of the oxidative degradation of the graphitic structure of the carbon particles (Huang and Buekens, 1995). However, the amounts of PAHs and carbon particles in the exhaust of diesel engines may drive the formation of the other toxic organic pollutants, such as PCDD/Fs, PCBs, and PBDEs, by either precursor or *de novo* synthesis routes (Dyke *et al.*, 2007; Wenger *et al.*, 2008; Wang *et al.*, 2010c; Laroo *et al.*, 2011). Therefore,

* Corresponding author.

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

strategies and technologies for controlling the emissions from diesel engines must be developed.

Many studies have focused on the emissions of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) from various stationary sources, such as municipal solid waste incinerators (MSWIs) and metallurgical activities (Li *et al.*, 2007; Wang *et al.*, 2010a). However, PCDD/F emissions from mobile sources are also an important issue. For example, diesel vehicles rank third (10%) for total PCDD/F emissions in the Lombardy Region (a highly industrialized area) in Italy, following MSWIs (32%) and electric arc furnaces (EAFs, 26%) (Caserini and Monguzzi, 2002). Some studies have demonstrated that the concentrations of PCDD/Fs, PCBs, and PBDEs that are emitted from diesel engines are in the ranges of 7.11–13.57 pg I-TEQ L⁻¹, 12–260 pg WHO-TEQ L⁻¹, and 8.46 ng L⁻¹, respectively (Dyke *et al.*, 2007; Wang *et al.*, 2010b; Laroo *et al.*, 2011). Chang *et al.* (2014) described that the emission factors of PAHs, PCDD/Fs, PCBs, PBDD/Fs, and PBDEs from the diesel engine fueled with B2 (98% diesel + 2% WCO-based biodiesel) were 2.15 µg BaP_{eq} L⁻¹, 30.5 pg I-TEQ L⁻¹, 3.61 pg WHO₂₀₀₅-TEQ L⁻¹, 7.50 pg TEQ L⁻¹ and 129 ng L⁻¹, respectively. Chuang *et al.* (2010) indicated that the particulate-phase PCDD/Fs were responsible for 78.0, 90.3, and 71.1% of total-PCDD/Fs from sport utility vehicles (SUVs), diesel passenger vehicles (DPVs) and heavy duty diesel vehicles (HDDV), respectively, and suggested that the control of PM was more critical than the control of gaseous pollutants in reducing PCDD/Fs emissions from automobiles.

Recent studies have established that the use of biodiesel as an alternative fuel for diesel engines can significantly reduce the amounts of PM in the exhaust (Lin *et al.*, 2007; Tsai *et al.*, 2010, 2014b). To prevent the conflictive competition between food and bioenergy, converting non-edible greases into biofuels is highly encouraged. The conversion of recycled WCO into biodiesels is a common and feasible technology. The estimated amounts of WCO that are collected in the USA, the UK and EU countries generate approximately 1.4 × 10⁶, 2 × 10⁵ and 0.7–1.0 × 10⁶ tons of WCO per year, respectively (Arjun *et al.*, 2008; Chhetri *et al.*, 2008). In Taiwan, the annual WCO production is 7.7–9.4 × 10⁴ tons (Taiwan EAP, 2007), of which only approximately 4% is retained for industrial use and this fact has important environmental consequences. However, the use of saucers with high salt content may lead to the presence of chloride in the recycled WCO converted biodiesel and increase the emissions of chlorine-substituted pollutants, including PCDD/Fs, PCBs, PBDD/Fs and PBDEs, in diesel-engine exhausts.

As we know, most of the large biodiesel plants use wet purification consisting of two consecutive liquid–liquid extraction stages (commonly named washings) in order to recover fatty acid and purify biodiesel products (Mendow *et al.*, 2012). In an ideal situation, this can effectively remove the water-soluble chlorine content in the biodiesels. However, the oils cooked or fried at high temperature may lead to the conversion of soluble chlorine from saucers to insoluble chlorine. For this reason, when using waste cooking oil (WCO) as raw materials for biodiesels, the insoluble

chlorine of WCO-biodiesel cannot be easily removed by washings. Although the content of insoluble chlorine in WCO-biodiesel is small, a research shows less dioxin output in gaseous emissions with lower chlorine input during the combustion of newspaper with PVC or sodium chloride (Katami *et al.*, 2000). Thus, it is necessary to clarify the emission characteristics of POPs when using WCO-biodiesels.

Most studies of biodiesels as alternative fuels for diesel engines focus on reducing the emissions of traditional gaseous pollutants (such as HC, NO_x and CO), PM, carbon species and PAHs (Lin *et al.*, 2012; Tsai *et al.*, 2014a, b; Cheng *et al.*, 2015). For example, Mwangi *et al.* (2015) tested a diesel engine using microalgae oil-based biodiesel and reported low emissions in the exhaust when using the fuel blends – B2 (2% microalgae biodiesel + 98% conventional diesel), B2-But20 (B2 + 20% Butanol) and B2-But20-W0.5 (B2-But20 + 0.5% water) showed a reduction of 22.0%, 57.2%, and 59.5% in PM emissions, and a decrease of 17.7%, 31.4% and 40.7% in BaP_{eq} emissions. Little attention has been paid to the emissions of persistent organic pollutants (POPs) from engines. In our earlier works, we investigated the characteristics of total PM, particle-bound carbons (EC and OC), and total PAHs that were emitted from a generator under 3 kW load by using biodieselholts which comprise pure/water-containing acetone, pure/water-containing butanol, waste-edible-oil-biodiesel (WEO-biodiesel), and fossil diesel. In addition, the human male monocyte cell line (U937) and MTT (3-(4,5-dimethyl-thiazol-2-yl)-2,5-diphenyltetrazolium bromide) assay were adopted to conduct cell toxicity tests for the organic-solvent extraction. It was found that water-containing and -free butanol-added WEO-biodiesel yielded 21.7–56.3% less PM, 28.7–63.8% less PM-EC, 11.8–48.7% less PM-OC, 23.5–59.2% less total-PAHs, and 37.0–55.3% less total-BaP_{eq} than fossil diesel (Tsai *et al.*, 2015a). And the cytotoxicity tests revealed that adding 1–3% acetone/water-containing acetone to bio-dieselholts reduced the mortality of U937 that were exposed to exhaust emissions organic-solvent extraction of to U937 when the generator was loaded at 3 kW (Tsai *et al.*, 2015b). To study further the influence of adding biodiesel to traditional petro-diesel (as D100) on the emission factors (EFs) of POPs (PCDD/Fs, PCBs, PBDD/Fs, and PBDEs) from a diesel-generator that was fuelled with different fuel blends were explored; in this investigation, D100 is blended with 20 and 40 vol% WOC-biodiesel (W20 and W40) to form alternative fuels for use in diesel engine generators.

MATERIALS AND METHODS

Sampling Procedures and Test Fuel

This study uses three biodiesel-diesel blends with different mixing ratios of WCO-biodiesel to premium diesel, which are premium diesel fuel (D100), W20 (20 vol% WCO-biodiesel + 80 vol% D100), and W40. Different blended fuels were tested in a generator at a stable energy output (110 V/60 Hz, 1800 rpm) under loads of 1.5 and 3.0 kW. The diesel engine was a water-cooled, natural intake, and four-stroke diesel engine (TF110E; YANMAR, Japan) with a single fuel-injection cylinder (Bore × Stroke: 88 mm × 96 mm). With a maximum

output of 4 kW at 1,800 rpm, the power generator (YSG-5SEN; YANMAR, Japan) had a 100/110 V (50/60 Hz) AC output (single-phase, two-wire type). The premium diesel fuel used herein 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.

An auto-detector flow sampling system that was 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 exhaust. Gas-phase samples were collected using two-stage glass cartridges (filled with XAD-2 resins). The quartz filters were pretreated before they were sampled by heating them in a muffle furnace in air for 2.5 h at 900°C. Before sampling, known amounts of surrogate standards that were pre-labeled with isotopes (such as $^{37}\text{C}_{14}$ -2,3,7,8-TeCDD, $^{13}\text{C}_{12}$ -2,3,4,7,8-PeCDF, $^{13}\text{C}_{12}$ -1,2,3,4,7,8-HxCDD, $^{13}\text{C}_{12}$ -1,2,3,4,7,8-HxCDF, and $^{13}\text{C}_{12}$ -1,2,3,4,7,8,9-HpCDF) were spiked to evaluate the collection efficiency of the sampling train. The recoveries of PCDD/Fs surrogate standards were 87–113% which met the criteria within 70–130%. For each combination of parameters, the experiments were performed three times (each sampling time = 30 min). Sampling data were collected after the engine had been run for at least 30 min. Generally, the extraction of POPs were completed within one week after sampling; additionally, the POPs 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 sampling were combined to represent the whole 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 using a silica gel column. Following extraction, the extracts were treated with concentrated sulfuric acid in the first cleanup stage. Then, extract samples that were dissolved in 5 mL of hexane were 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 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), before the hexane eluate was 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.

After the above stage, the column was 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 to identify 17 2,3,7,8-substituted PCDD/F, 12 dioxin-like PCB, twelve 2,3,7,8-substituted PBDD/F, and 30 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 35 eV and 250°C , respectively. Further details of the analytical procedures and parameters for the instrumental analysis of POPs can be found in our earlier work (Wang et al., 2010d).

RESULTS AND DISCUSSION

Impact of WCO-biodiesel on POPs Emissions

The mean mass and toxicity concentration of PCDD/Fs, PCBs, PBDD/Fs and PBDEs in the exhaust of the diesel generator fueled with D100, W20, and W40 at 1.5 kW and 3.0 kW loads are shown in Table 2 and Figs. 1–2, while the reduction rate (compared with D100) of POP congeners of each test fuel are listed in Figs. 3–4. The mass concentrations of POPs followed the order PBDEs \gg PBDD/Fs $>$ PCBs $>$ PCDD/Fs. However, the toxicity concentrations of the pollutants with dioxin-like toxicity were in the order PCDD/Fs $>$ PCBs $>$ PBDD/Fs. PBDEs (89.1 ng Nm^{-3} on average) dominated (more than 95%) these POPs, and their concentrations were approximately two orders of magnitude higher than those of the other POPs (660 pg Nm^{-3} on average). Of these POPs, PCDD/Fs (26.2 pg WHO₂₀₀₅-TEQ Nm^{-3} on average) had the highest toxicity concentrations, which

Table 1. Specification of tested fuels.

Properties	Regular Diesel (D100)	WCO-biodiesel (W100)
Chemical formula	$\text{C}_{14}\text{H}_{28.33}$	$\text{C}_{19.54}\text{H}_{38.37}\text{O}_2$
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

Table 2. Concentrations of the POPs from the diesel-engine generator fueled with WCO-biodiesel blends.

Concentrations	1.5 kW load			3.0 kW load		
	D100	W20	W40	D100	W20	W40
PM						
Mass (mg Nm ⁻³)	64.9 ± 4.47	52.3 ± 2.66	60.7 ± 2.21	129 ± 4.52	94.7 ± 9.17	104 ± 6.40
PCDD/Fs						
Mass (pg Nm ⁻³)	583 ± 106	278 ± 42.9	258 ± 88.1	875 ± 29.5	457 ± 72.9	310 ± 16.7
TEQ ^a (pg WHO ₂₀₀₅ -TEQ Nm ⁻³)	33.2 ± 9.90	17.5 ± 2.99	6.24 ± 2.54	58.6 ± 7.79	36.5 ± 13.6	5.18 ± 0.944
PCBs						
Mass (pg Nm ⁻³)	580 ± 141	419 ± 60.0	359 ± 50.1	810 ± 46.6	489 ± 84.5	455 ± 123
TEQ ^a (pg WHO ₂₀₀₅ -TEQ Nm ⁻³)	2.72 ± 1.16	1.43 ± 0.517	1.46 ± 0.150	3.11 ± 0.342	1.60 ± 0.662	1.62 ± 0.398
PBDD/Fs						
Mass (pg Nm ⁻³)	982 ± 38.9	801 ± 355	759 ± 28.4	1408 ± 38.9	1202 ± 135	854 ± 28.4
TEQ ^b (pg WHO ₂₀₀₅ -TEQ Nm ⁻³)	1.54 ± 0.24	1.16 ± 0.415	0.702 ± 0.023	2.30 ± 0.571	1.66 ± 0.298	0.927 ± 0.140
PBDEs						
Mass (ng Nm ⁻³)	134 ± 7.58	50.4 ± 1.73	24.7 ± 2.10	216 ± 9.94	76.6 ± 3.09	32.1 ± 2.87
TEQ	—	—	—	—	—	—

^a TEF from WHO₂₀₀₅-TEFs (2005).

^b A tentative TEFs from WHO₂₀₀₅-TEFs of PCDD/Fs (WHO, 2005).

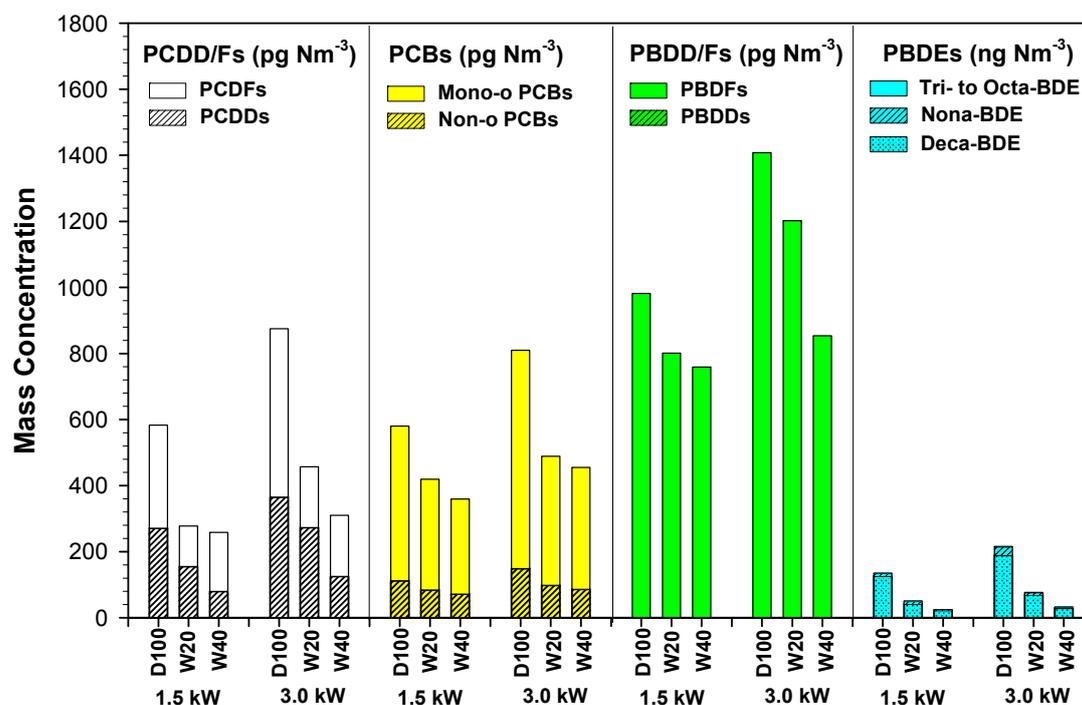


Fig. 1. The mean mass concentrations of the POPs.

were approximately one order of magnitude higher than those of the PCBs and PBDD/Fs (1.99 and 1.38 pg WHO₂₀₀₅-TEQ Nm⁻³ on average, respectively). The mass and toxicity concentrations of the POPs that were emitted in the exhaust decreased as a percentage of added WCO-biodiesel increased from 0 vol% to 40 vol%, regardless of the loading, except for the toxicity concentration of W40. The reductions of the mass concentrations of the four POPs followed the order PBDEs >> PCDD/Fs > PCBs ≈ PBDD/Fs, and the reduction rates followed the order PBDEs > PCDD/Fs > PCBs > PBDD/Fs. However, the toxicity concentrations of those POPs followed the order PCDD/Fs

> PCBs > PBDD/Fs, independently of the reduction of toxicity concentration and the rate thereof. This phenomenon was probably resulted from the addition of biodiesel in pure petroleum diesel (e.g., the W20 and W40 cases) to increase oxygen content of the fuel blends, enhance the combustion efficiency of the engine, and reduce pollutant emissions (Tsai et al., 2010; Mwangi et al., 2015). Besides, it is also possibly related to the fact that the amounts of PCDD/Fs precursors (such as aromatic compounds and C₂ radical) of biodiesel were few, and thus the *de novo* synthesis of POPs were inhibited (Weber and Kuch, 2003).

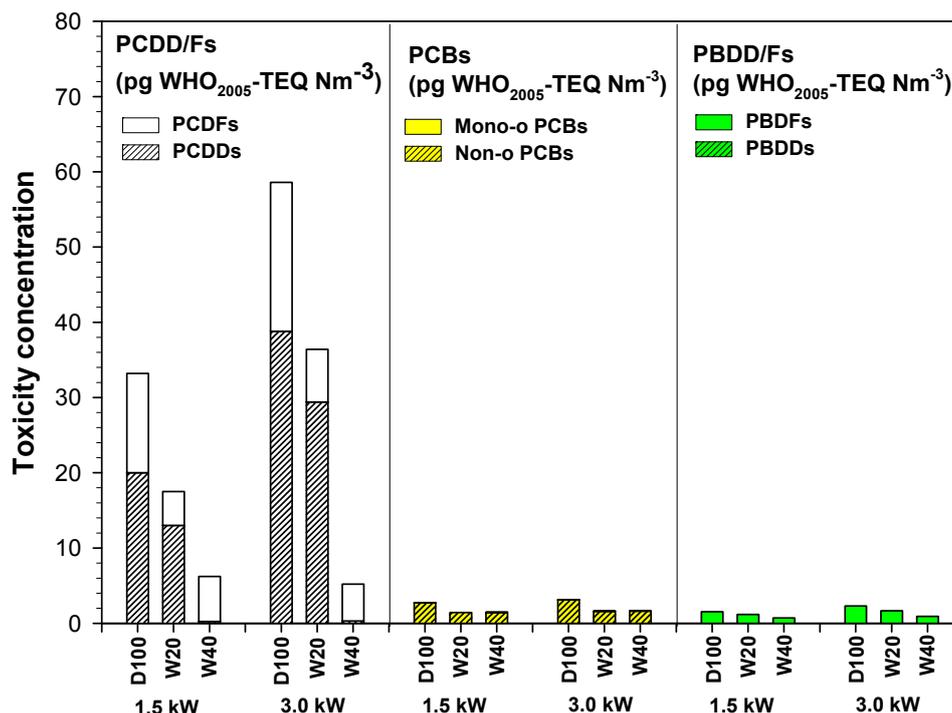


Fig. 2. The mean toxicity concentrations of the POPs.

As presented in Table 3, the EFs of the PCDD/Fs, PCBs, PBDD/Fs and PBDEs, based on mass and toxicity, were calculated in terms of fuel consumption (FC) and power output (PO). Regardless of generator loading, the EFs of each POP decreased as the addition of WCO-biodiesel increased; furthermore, the EFs of each POP at 1.5 kW load were higher than those at 3.0 kW. Compared with D100, the reductions of mass EFs of PCDD/Fs, PCBs, PBDD/Fs, and PBDEs for using W40 (based on FC: 63.9%, 48.4%, 40.1%, and 85.6%, respectively; based on PO: 64.6%, 49.0%, 41.5%, and 85.9%, respectively) were greater than for using W20 (based on FC: 48.7%, 32.8%, 15.4%, and 62.9%, respectively; based on PO: 51.8%, 37.0%, 20.7%, and 65.4%, respectively) under all tested loads. A similar trend was also observed for the reductions of toxicity EFs of those POPs.

Table 4 lists the POP emission factors in the exhausts of various emission sources. The toxicity EFs of PCDD/Fs under all tested settings in this study (1.95–20.7 pg WHO₂₀₀₅-TEQ L⁻¹) were close to those (5.20–30.5 pg I-TEQ L⁻¹ for a heavy-duty diesel engine (HDDE), 7.15–20.9 pg I-TEQ L⁻¹ for a diesel passenger car, and 7.11–21.60 pg I-TEQ L⁻¹ for a 2-stroke DI-diesel engine, respectively) reported by Chang *et al.* (2014), Rey *et al.* (2014), and Laroo *et al.* (2012), but lower than those for a 4-stroke DI-diesel engine (13.57–44.25 pg I-TEQ L⁻¹) by Laroo *et al.* (2012). For the PCB EFs, our data (0.65–1.89 pg WHO₂₀₀₅-TEQ L⁻¹) were close to those for a HDDE (0.664–3.61 pg I-TEQ L⁻¹) by Chang *et al.* (2014), but around one order lower than those for a 2-stroke DI-diesel engine (8.5–41.4 pg TEQ Nm⁻³) by Laroo *et al.* (2012) and a diesel engine equipped with catalyzed emission control systems (48.9 pg WHO₂₀₀₅-TEQ L⁻¹) by Laroo *et al.* (2011). However, the PBDD/F EFs obtained in

this study (0.37–1.06 pg WHO₂₀₀₅-TEQ L⁻¹) were about one-tenth of those for a HDDE (2.79–7.50 pg I-TEQ L⁻¹) by Chang *et al.* (2014). Nevertheless, our data (6.47–69.4 ng L⁻¹) were also similar to those from HDDE measurements (34.8–129 ng L⁻¹) (Chang *et al.*, 2014) and those from diesel-fuelled passenger car measurements (8.46 ng L⁻¹) (Wang *et al.*, 2010c).

Impact of WCO-biodiesel on PCDD/Fs Emission

As shown in Figs. 1–2, the generator that was fueled with W40 the mass and toxicity concentrations of PCDD/Fs that were emitted from had the lowest values at all evaluated loadings. Independently of the loading of the generator, when W40 was used, the mass and toxicity concentrations of PCDD/Fs (average mass: 284 pg Nm⁻³; average toxicity: 5.71 pg WHO₂₀₀₅-TEQ Nm⁻³) were 39% and 12% of those obtained when D100 was used (average mass: 729 pg Nm⁻³; average toxicity: 45.9 pg WHO₂₀₀₅-TEQ Nm⁻³), respectively. The use of W20 reduced the mass concentrations of PCDF (32% and 37%, respectively) more than those of PCDDs (20% and 10.5%, respectively), relative to the use of D100, at engine loads of 1.5 and 3.0 kW (Fig. 3). Using W40 further reduced the mass concentration of PCDDs by a further 75.6 and 148 pg Nm⁻³ at 1.5 kW and 3.0 kW, respectively, but left the mass concentrations of PCDFs almost unchanged (1.5 kW: increased 56 pg Nm⁻³; 3.0 kW: almost no change) (Fig. 1). This result may follow from the fact that the WCO-biodiesel contained fewer PCDD/Fs precursors, aromatic contents, disfavoring the formation of dioxin emissions (Chang *et al.*, 2014).

The obtained PCDF/PCDD mass concentration ratios when D100, W20 and W40 were used were 1.15, 0.80 and 2.25, respectively, at a load of 1.5 kW, and 1.40, 0.68 and

Table 3. Emission factors of the POPs from the diesel-engine generator fueled with WCO-biodiesel blends.

Emission factors		1.5 kW			3.0 kW		
		D100	W20	W40	D100	W20	W40
<i>Based on fuel consumptions</i>							
PCDD/Fs	Mass (pg L ⁻¹)	371 ± 63.7	185 ± 34.9	136 ± 50.0	337 ± 2.80	178 ± 14.3	119 ± 9.31
	TEQ ^a (pg WHO ₂₀₀₅ -TEQ L ⁻¹)	20.0 ± 6.27	10.7 ± 2.37	2.10 ± 1.43	20.7 ± 2.55	10.7 ± 4.78	1.95 ± 0.41
PCBs	Mass (pg L ⁻¹)	398 ± 110	292 ± 48.6	199 ± 28.6	340 ± 18.2	208 ± 24.3	181 ± 52.4
	TEQ ^a (pg WHO ₂₀₀₅ -TEQ L ⁻¹)	1.89 ± 0.90	1.00 ± 0.38	0.81 ± 0.08	1.31 ± 0.10	0.68 ± 0.24	0.65 ± 0.17
PBDD/Fs	Mass (pg L ⁻¹)	672 ± 82.6	552 ± 231	420 ± 9.05	590 ± 83.4	514 ± 41.3	338 ± 25.9
	TEQ ^b (pg WHO ₂₀₀₅ -TEQ L ⁻¹)	1.06 ± 0.25	0.80 ± 0.27	0.39 ± 0.01	0.97 ± 0.24	0.70 ± 0.08	0.37 ± 0.06
PBDEs	Mass (ng L ⁻¹)	91.8 ± 9.49	35.0 ± 2.08	13.7 ± 1.15	90.9 ± 6.84	32.8 ± 2.71	12.7 ± 0.84
<i>Based on power generation</i>							
PCDD/Fs	Mass (pg kWh ⁻¹)	280 ± 29.4	127 ± 22.8	96.0 ± 35.3	167 ± 5.29	85.4 ± 12.7	60.9 ± 4.66
	TEQ ^a (pg WHO ₂₀₀₅ -TEQ kWh ⁻¹)	14.9 ± 3.59	7.38 ± 1.56	1.48 ± 1.01	10.3 ± 1.47	5.17 ± 2.64	0.99 ± 0.21
PCBs	Mass (pg kWh ⁻¹)	297 ± 54.2	197 ± 29.3	140 ± 20.4	168 ± 6.60	100 ± 14.5	92.1 ± 26.4
	TEQ ^a (pg WHO ₂₀₀₅ -TEQ kWh ⁻¹)	1.39 ± 0.59	0.67 ± 0.24	0.57 ± 0.06	0.65 ± 0.06	0.33 ± 0.13	0.33 ± 0.09
PBDD/Fs	Mass (pg kWh ⁻¹)	509 ± 58.3	376 ± 166	296 ± 6.47	292 ± 40.9	248 ± 20.8	172 ± 12.2
	TEQ ^b (pg WHO ₂₀₀₅ -TEQ kWh ⁻¹)	0.80 ± 0.16	0.54 ± 0.20	0.27 ± 0.01	0.48 ± 0.11	0.34 ± 0.06	0.19 ± 0.03
PBDEs	Mass (ng kWh ⁻¹)	69.4 ± 3.13	23.6 ± 0.85	9.62 ± 0.83	45.0 ± 2.17	15.8 ± 1.05	6.47 ± 0.44

^a TEF from WHO₂₀₀₅-TEFs (2005).

^b A tentative TEFs from WHO₂₀₀₅-TEFs of PCDD/Fs (WHO, 2005).

Table 4. Emission factors of POPs in the exhausts of different emission sources.

POPs	Sources	Emission factors	References
PCDD/Fs	Heavy-duty diesel engine	5.20–30.5 pg I-TEQ L ⁻¹	(Chang et al., 2014)
	Diesel-fuelled passenger vehicle	7.15–20.9 pg I-TEQ L ⁻¹	(Rey et al., 2014)
	2-stroke DI-diesel engine	7.11–21.60 pg I-TEQ L ⁻¹	(Laroo et al., 2012)
	4-stroke DI-diesel engine	13.57–44.25 pg I-TEQ L ⁻¹	(Laroo et al., 2012)
PCBs	Heavy-duty diesel engine	0.664–3.61 pg I-TEQ L ⁻¹	(Chang et al., 2014)
	2-stroke DI-diesel engine	1.39–91.51 pg WHO ₂₀₀₅ -TEQ L ⁻¹	(Laroo et al., 2012)
	Diesel engine (with diesel oxidation catalyst)	48.9 pg WHO ₂₀₀₅ -TEQ L ⁻¹	(Laroo et al., 2011)
PBDD/Fs	Heavy-duty diesel engine	2.79–7.50 pg I-TEQ L ⁻¹	(Chang et al., 2014)
PBDEs	Heavy-duty diesel engine	34.8–129 ng L ⁻¹	(Chang et al., 2014)
	Diesel-fuelled passenger vehicle	8.46 ng L ⁻¹	(Wang et al., 2010c)

1.49, respectively, at a load of 3.0 kW (Fig. 1). This result reveals that using W20 limits the formation of furans (such that the PCDFs/PCDDs ratio is less than one) by inhibiting their *de novo* synthesis (Huang and Buekens, 1995), which is associated with more complete combustion and the formation of less soot upon the addition of a moderate amount of WCO-biodiesel (Tsai et al., 2012; Chang et al., 2014). Nevertheless, when the WCO-biodiesel addition rose from 20% to 40%, the PCDFs/PCDDs ratio increased from less than one to more than one (average 1.5 kW for 2.25 and 3.0 kW for 1.49) (Fig. 1) perhaps because of the increase in PM emission concentrations from 60.7 to 104 mg Nm⁻³ respectively, when W40 is used at all evaluated loadings; these values exceed the corresponding values that were obtained using W20 (52.3 and 94.7 mg Nm⁻³, respectively) (Table 2). The temperature of the combustion chamber of the generator when W40 was used exceeded that by when W20 was used, and carbon accounted for approximately 80% of all diesel engine particles (DEPs) (Chung et al., 2008; Tsai et al., 2010; 2015), so the PCDD/Fs that were emitted using W40 contained more furan that was formed by *de novo* synthesis, yielding PCDFs/PCDDs > 1. The

high PM with a high proportion of soot particles and *de novo* synthesis of furan occurs favorably on the small soot particles (Stieglitz et al., 1990). Hell et al. (2000) claimed that at low trichlorophenol concentrations, PCDFs were formed mostly by *de novo* synthesis from the residual carbon of fly ash; moreover, as the trichlorophenol concentrations increased, the condensation reaction of 2,4,6-Cl₃Ph to PCDD proceeded increasingly more strongly than the *de novo* reaction. The trichlorophenol might have blocked catalytic sites for the formation of PCDF from carbon.

A comparison of the toxicity of dioxins (Fig. 4) with that of D100 (average of 1.5 kW: 33.2 pg WHO₂₀₀₅-TEQ Nm⁻³; 3.0 kW: 58.6 pg WHO₂₀₀₅-TEQ Nm⁻³) show that the reductions of PCDF toxicity concentrations that were achieved using W20 at 1.5 and 3.0 kW (average of 26.2% and 21.8%, respectively) slightly exceeded the reductions of PCDDs toxicity concentrations (average of 21.2% and 16.0%, respectively). Conversely, the reductions of the PCDD toxicity concentrations (average of 59.7% and 65.7%, respectively) significantly exceeded those of PCDFs (average of 21.5% and 25.2%, respectively) when W40 was used under all tested loads. However, compared with W20, the

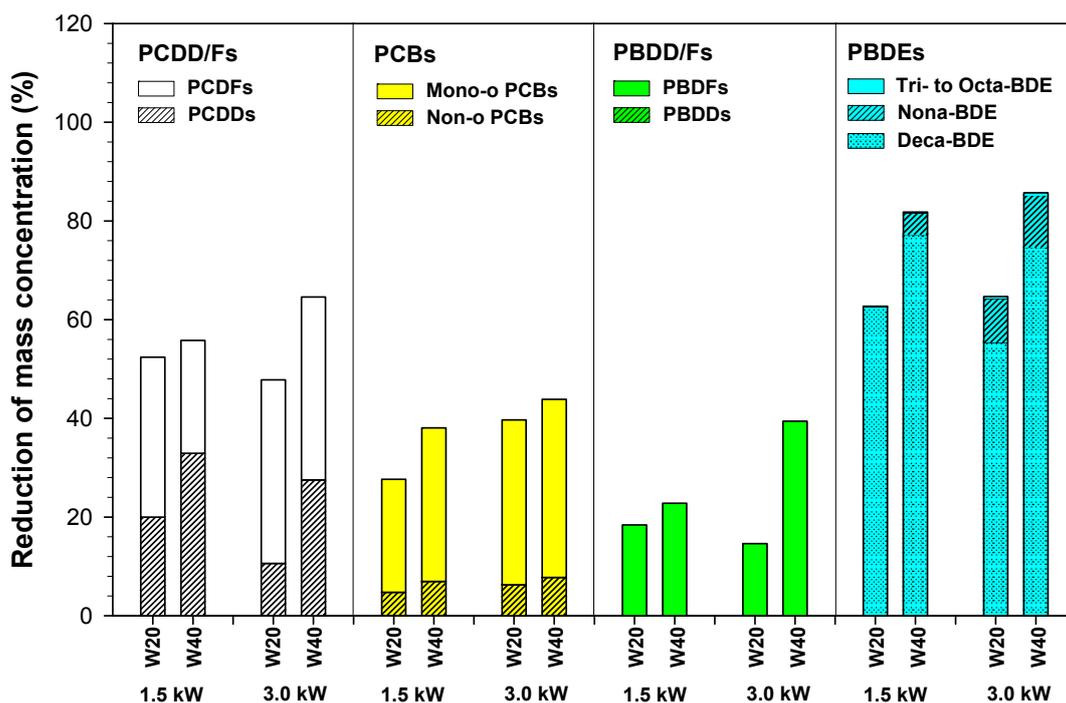


Fig. 3. Reduction rates of the mass concentrations of the POPs (compared with D100).

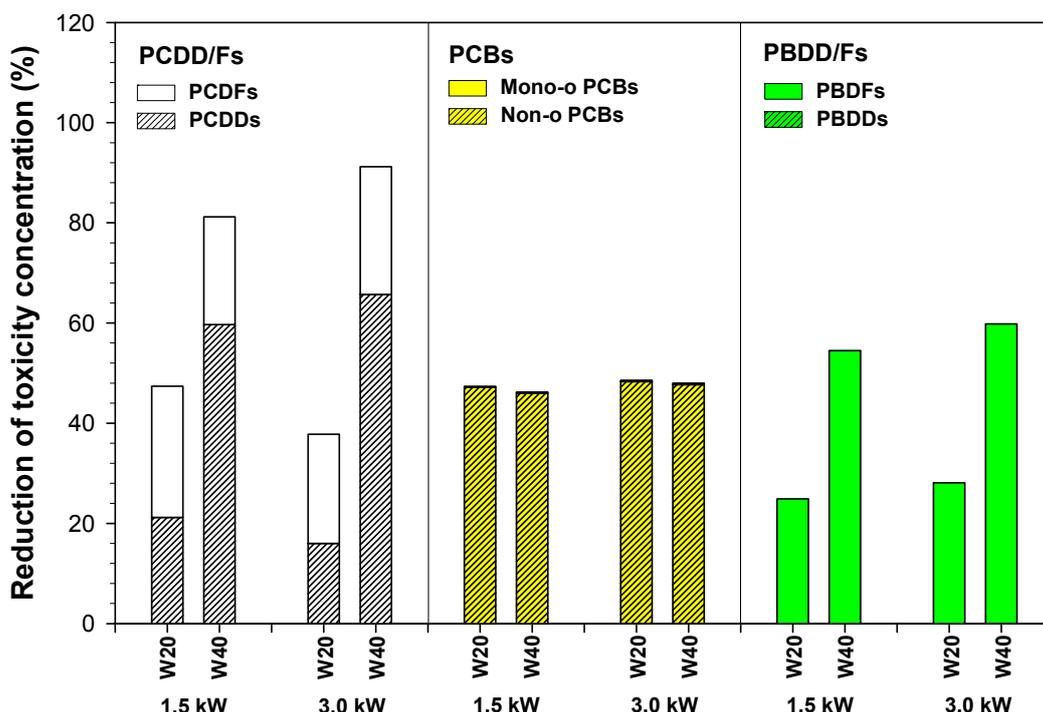


Fig. 4. Reduction rates of the toxicity concentrations of the POPs (compared with D100).

reductions of PCDD toxicity concentrations achieved using W40 exceeded 70% (1.5 kW: 73.1%; 3.0 kW: 79.9%) independently of the generator load; therefore, only low PCDD toxicity concentrations were observed (1.5 kW: 0.23 pg WHO₂₀₀₅-TEQ Nm⁻³; 3.0 kW: 0.29 pg WHO₂₀₀₅-TEQ Nm⁻³). Although the reduction of the toxicity concentration of PCDFs was only 2.15 pg WHO₂₀₀₅-TEQ Nm⁻³ under a

3.0 kW load, it was 1.54 pg WHO₂₀₀₅-TEQ Nm⁻³ at 1.5 kW. This result shows that more than 95% of the toxicity of PCDD/Fs arose from PCDFs when W40 was used as fuel, and about 75% of the toxicity of PCDD/Fs arose from PCDDs when W20 was used. The observation that the WCO-biodiesel that was used in this study generated less PCDD/Fs is explained by the more complete combustion

and the inhibition of *de novo* synthesis. Chang *et al.* (2014) made a similar observation when a HDDE fueled with biodiesel blends. Some factors such as the age of the lubricating oil, the presence of carbon deposits, and engine wear may also affect the emission of pollutants from diesel engines (Andrew *et al.*, 1999; Kim *et al.*, 1998; Sappok and Wong; 2008).

Under a 3.0 kW load, the toxicity concentrations of PCDD/Fs were 5.18–58.6 pg WHO₂₀₀₅-TEQ Nm⁻³, close to those observed by Kim *et al.* (2003) for a diesel engine under loads of 25%, 50%, and 75% at 2400 rpm that were measured using a dynamometer (6.4–14.5 pg I-TEQ Nm⁻³). The data were similar to those obtained from measurements made of HDDEs (1.66–9.72 pg I-TEQ Nm⁻³) (Chang *et al.*, 2014) and those made at coal-fired power plants (2.4–20.3 pg I-TEQ Nm⁻³) (Hutson *et al.*, 2009). The data in this work were lower than those for sintering plants (0.995–2.06 ng I-TEQ Nm⁻³) (Wang *et al.*, 2003) and municipal solid waste incinerators (MSWIs) (72.5–118 pg I-TEQ Nm⁻³) (Wang *et al.*, 2010c) by two and one orders of magnitude, respectively, but they were two to three orders of magnitude higher than the ambient values (0.0113 pg WHO₂₀₀₅-TEQ m⁻³) that were measured by Chao *et al.* (2014) at a location close to that where measurements were made in this study.

Impact of WCO-biodiesel on PCB Emissions

As presented in Figs. 1–2, mono-ortho PCBs account for 80.6% of the mass concentration of dioxin-like PCB regardless of the generator load or fuel blend; however, non-ortho PCBs (99.4%) were responsible for most of the toxicity concentration of dioxin-like PCB. WCO-biodiesel blends generated an approximately 30% lower dioxin-like PCB mass concentration (W20: 27.7%; W40: 38.1%) than D100 under a 1.5 kW load, an approximately 40% lower concentration (W20: 39.7%; W40: 43.9%) under a 3.0 kW load (Fig. 3). Using W20 and W40 reduced the mass concentrations of mono-ortho PCBs (over 80%) more than those of other dioxin-like PCBs. Under all loadings, the reduction of the concentration of non-ortho PCBs was less than 20%. Using WCO-biodiesel (W20 and W40) as fuel reduced the PCB toxicity concentrations by about 45% on average (46.2–48.5%) below those obtained using D100, and almost all of the reduction of PCB toxicity was associated with non-ortho PCBs (99.5%), and the reduction of mono-ortho PCBs toxicity was negligible (0.1–0.3%) (Fig. 4).

Although the chlorine content of the WCO-biodiesel herein exceeded that of petroleum diesel, using WCO-biodiesel blends (W20 and W40) reduced the mass and toxicity concentrations of PCDD/Fs and dioxin-like PCBs that were emitted from the generator under loads of 1.5 and 3.0 kW, perhaps because the chlorine content in the WCO-biodiesel was below the threshold (0.8–1.1%) for PCDD/Fs formation (Wikström *et al.*, 1996; Chang *et al.*, 2014). The above results indicate that mono-ortho PCBs accounted for 80% of the mass concentration of emitted dioxin-like PCBs, while 99% of the corresponding toxicity concentration was associated with non-ortho PCBs, regardless of the loading and the fuel blend. Using WCO-biodiesel blends as fuels significantly reduced the mass concentration and toxicity of

dioxin-like PCBs that were emitted from the generator at all tested loads, relative to those obtained using D100. Mono-ortho PCBs were responsible for more than 80% of the reduction of the mass of all dioxin-like PCBs (28–44%) whereas non-ortho PCBs were responsible for 99.5% of all of the reduction of dioxin-like PCB toxicity (46–48%).

In this work, the toxicity concentrations of dioxin-like PCBs that were obtained using D100, W20 and W40 at 3.0 kW (1.60–3.11 pg WHO₂₀₀₅-TEQ Nm⁻³) were close to those measured in an HDDE (0.212–1.15 pg WHO₂₀₀₅-TEQ Nm⁻³) (Chang *et al.*, 2014); smaller than those for some stationary sources (secondary copper and aluminum smelters (19–23 pg WHO₂₀₀₅-TEQ Nm⁻³) (Ba *et al.*, 2009), MSWIs (22–61 pg WHO₁₉₉₈-TEQ Nm⁻³) (Kim *et al.*, 2004), and power plants (10–11 pg WHO₁₉₉₈-TEQ Nm⁻³) (Dyke *et al.*, 2003)), and greater than that measured in the ambient (0.00122 pg WHO₂₀₀₅-TEQ m⁻³) (Chao *et al.*, 2014).

Impact of WCO-biodiesel on PBDD/F and PBDE Emissions

PBDFs were responsible for most of the mass and toxicity of PBDD/Fs that were obtained using D100, W20 and W40 at loads of 1.5 and 3.0 kW (no PBDD was detected), and the PBDEs were mostly deca-BDEs (89%), nona-BDEs (10%), and tri- to octa-BDEs (1%) (Figs. 1–2). Additionally, the reduction in mass and toxicity concentrations of PBDD/Fs that were obtained using W20 and W40 rather than D100 under all tested conditions were all associated with PBDFs (Figs. 3–4). Therefore, at 1.5 and 3.0 kW, the toxicity reductions (25% and 28%, respectively, for W20; 54% and 60%, respectively, for W40) of PBDFs were greater than the mass reductions (18% and 15%, respectively, for W20; 23% and 39%, respectively, for W40). Most of the reductions of the PBDE mass concentrations (63 and 64% for W20, respectively, and 82 and 85% for W40, respectively) were associated with deca-BDEs (accounting for 86–100%, average = 92%).

The toxicity concentrations of PBDD/Fs under all test settings (0.927–2.30 pg WHO₂₀₀₅-TEQ Nm⁻³) were close to those that were obtained for an HDDE (0.892–2.40 pg WHO₂₀₀₅-TEQ Nm⁻³) by Chang *et al.* (2014) and those obtained in arc furnaces (EAFs) and sinter plants (1.88 and 4.16 pg WHO₂₀₀₅-TEQ Nm⁻³, respectively) by Wang *et al.* (2010c), but they were lower than those obtained for power plants (8.5–41.4 pg WHO₂₀₀₅-TEQ Nm⁻³) by Hutson *et al.* (2009) or for MSWIs (65.3–88.1 pg WHO₂₀₀₅-TEQ Nm⁻³) by Wang *et al.* (2010b). However, our data were around three orders of magnitude greater than the ambient value (0.00129 pg WHO₂₀₀₅-TEQ m⁻³) that was measured by Chao *et al.* (2014). In this study, the mass concentrations of PBDEs (24.7–216 ng Nm⁻³) were close to those obtained from diesel engines (NEDC test), MSWIs, sinter plants, EAFs, secondary aluminum smelters, power plants (29.1, 26.1–109, 22.2, 19.4, 33.5 and 29.1–46.7 ng Nm⁻³, respectively) (Wang *et al.*, 2011b, 2010c) and an HDDE (11.1–41.3 ng Nm⁻³) (Chang *et al.*, 2014), but approximately three orders of magnitude greater than the ambient value (15.9 pg m⁻³) (Chao *et al.*, 2014).

CONCLUSIONS

In this investigation, the mass concentrations of four POPs that were emitted from a generator that was fueled with D100, W20 and W40 under loads of 1.5 kW and 3.0 kW followed the order PBDEs >> PBDD/Fs > PCBs > PCDD/Fs. The mass concentrations of PBDEs were two orders of magnitude higher than those of the other POPs, but their corresponding toxicity concentrations varied in the order PCDD/Fs > PCBs > PBDD/Fs, although the toxicity concentrations of PCDD/Fs were approximately ten times those of PCBs and PBDD/Fs. Compared with D100, the mass and toxicity concentrations of PCDD/Fs, PCBs, PBDD/Fs and PBDE decreased as the ratio of WCO-biodiesel to petroleum diesel decreased, regardless of generator loading. The reductions of the mass concentrations of these four POPs followed the order PBDEs >> PCDD/Fs > PCBs = PBDD/Fs, the reduction rates of mass concentration, in order, were PBDEs > PCDD/Fs > PCBs > PBDD/Fs, and the reductions and reduction rates of toxicity concentration both followed the order PCDD/Fs > PCBs > PBDD/Fs. Compared with D100, the EF reductions of mass and toxicity of these four POPs for using W40 were greater than for using W20 under all tested loads. Accordingly, WCO-based biodiesel (W40) can be used as alternatives to petroleum diesel as a fuel to reduce POP emissions from generators and so can reduce the risk of cancer in humans that is associated with the POP emission.

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