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## CHARACTERIZATION OF PCDD/Fs AND PCBs EMITTED FROM TWO WOODCHIP BOILERS IN TAIWAN

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### Introduction

Combustion of biofuels offers a number of economic and environmental benefits in reduction of CO<sub>2</sub> emissions and minimization of waste disposal. However, their combustion can result in the release of toxic compounds including PCDD/Fs and PCBs. These toxic compounds are environmentally persistent and are bio-accumulative. In USA, more than 15% of the atmospheric emissions of PCDD/Fs are derived from wood combustion (Dwyer et al., 2015).

The use of recycled woodchips has been increasing for heat and steam generation in Taiwan. Combustion of woodchips in Taiwan is mainly accomplished by using small-scale boilers. Woodchips boilers emit significant amounts of toxic compounds due to non-continuous and unstable operation. Lundin et al. (2014) indicate that demolition waste wood contains elevated levels of chlorine and metals. If the compositions of the woodchips used are relatively complex (demolition waste wood as an example), toxic compounds may be formed in substantially greater quantities than the case of combusting virgin biofuels. Previous study shows that the emission factor of wood boiler is 17.1 µg I-TEQ/ton (Lavric et al., 2004). The main objectives of this study are to investigate the formation and removal of PCDD/Fs and PCBs in two woodchips boilers during different operating periods.

### Materials and methods

Two woodchips boilers (referred to as Plant A and Plant B) investigated in this study are located in northern Taiwan to produce steam for use. The fuels used are mixtures of bark, demolition waste wood (DWW) and waste furniture.

The Plant A, with a capacity of 240 ton/day, is equipped with a cyclone (CY) and bag filters (BF) for controlling particulate emissions. Additionally, Ca(OH)<sub>2</sub> and activated carbon are injected to remove acid gases and dioxin with the injection rates of 3.1 kg/hr and 4.5 kg/hr, respectively. Intensive sampling program was conducted at two sampling positions (APCDs inlet and stack) during different operating stages including start-up, normal operation and shut-down periods.

The Plant B is with a capacity of 224 tons per day and the combustion chamber is operated at 850°C. The APCDs consist of activated carbon injection (ACI) and bag filters (BF). The injection rate of activated carbon is controlled at 2 kg/hr. The sampling points are selected at APCDs inlet and stack, respectively. For flue gas sampling, vapor-phase sample was collected by XAD-2 resin while the solid-phase portion was collected with a fiber glass filter and by rinsing of the sampling probe thereafter. Further, the solid- and gas-phase samples of flue gas and the fly ash collected were spiked with Method 23 internal standard and Method 1613 labeled standards, respectively. Thereafter, the XAD-2 and filter samples are extracted for 24 h by Soxhlet extraction with toluene. Then, these samples were treated with series of clean-up columns and the cleaned-up solutions were spiked with recovery standard solution as described in Chi et al. (2006). Finally, 17 2,3,7,8-substituted PCDD/F congeners and 12 toxic PCB congeners were analyzed by high-resolution gas chromatography/high resolution mass spectrometer (HRGC/HRMS) (JEOL JMS 700D), equipped with a DB5-MS capillary column (60 m×0.25 mm×0.25 µm film thickness).

### Results and discussion

At APCDs inlet of the Plant A, PCDD/F and PCB concentrations in flue gas during the start-up period were much higher than those measured during normal operation and shut-down periods. PCDD/Fs composed 85% of the total concentrations in flue gas during different operating periods. Moreover, the solid-phase PCDD/F concentration is higher than that of gas-phase PCDD/F concentration at APCDs inlet, except during shut-down period. The results show that combustion condition remarkably affected PCDD/F and PCB formation within the woodchip combustion process. Combustion condition during start-up stage is unstable, resulting in high concentrations of the products of incomplete combustion (PICs) like soot, hydrocarbons and PCDD/Fs (Blumenstock et al., 2000). PCDD/F and PCB

concentrations measured at APCDs inlet during the shut-down period was even lower than that measured during the normal operating period. It is attributed to the fact that woodchips were not fed into the boiler during the shut-down period. Additionally, HCl concentration measured at APCDs inlet was 68 ppm during normal operation stage and decreased to 4 ppm during the shut-down period.

PCDD/F and PCB concentrations in flue gas at APCDs inlet of the Plant A and B are 22.91 and 15.96 ng WHO-TEQ/Nm<sup>3</sup>, respectively. Concentrations of PCDD/Fs and PCBs of Plant A are higher than that of the Plant B. This is attributed to the higher combustion temperature of the Plant B (850 °C) compared to the Plant A (650 °C), resulting in significantly lower PCDD/F and PCB formation in Plant B. Concentrations of PCDD/Fs and PCBs measured at the stack of Plants A and B during normal operating stage are 1.47 and 0.11 ng WHO-TEQ/Nm<sup>3</sup>, respectively. PCDD/Fs and PCBs formation potential of the Plants A and B are 291.2 and 220.9 µg WHO-TEQ/ton, respectively. On the other hand, PCDD/Fs and PCBs emission factors of Plants A and B are 18.7 and 1.5 µg WHO-TEQ/ton, respectively.

Removal efficiencies of PCDD/F and PCB congeners achieved with APCDs of Plants A and B during normal operating period are evaluated (Fig. 2). The results show that removal efficiencies of PCDD/Fs and PCBs of Plant A are lower than that of Plant B. Removal efficiencies of solid-phase and gas-phase PCDD/Fs and PCBs of Plant A are 96% and 84%, respectively. For the Plant B, removal efficiencies of solid-phase and gas-phase PCDD/Fs and PCBs are 99% and 95%, respectively. At the stack of Plant A, solid-phase PCDD/F concentration is higher than gas-phase PCDD/Fs. On the contrary, gas-phase PCDD/F concentration at the stack of the Plant B is higher than solid-phase PCDD/Fs.

Major PCDD/F congeners at APCDs inlet of Plant A include O8-CDD, 1,2,3,4,6,7,8-H7-CDF and 1,2,3,4,6,7,8-H7CDD, being similar to Plant B. Removal efficiencies of PCDD/F congeners of both plants increase with increasing Cl-substituted level. Highly chlorinated PCDD/F congeners have higher tendency to adhere to the particles due to their lower vapor pressures and are further removed by BF. Major PCDD/F congeners in the stack flue gas of Plants A and B include O8CDD, 1,2,3,4,6,7,8-H7CDD and 1,2,3,4,6,7,8-H7CDF.

Major PCB congeners at APCDs inlet of Plants A and B include TeCB-77, PeCB-126 and PeCB-118. PCB congener distribution is similar to that reported by Lundin et al. (2014). Moreover, major PCB congeners in the stack flue gas of Plants A and B include TeCB-77, PeCB-105 and PeCB-118. However, the removal efficiencies of PCB congeners achieved with the APCDs of Plants A and B are different. For Plant A, the congener with the highest removal efficiency is PeCB-114 (94%), follow by TeCB-77 (90%). However, both PeCB-126 and HpCB-189 are effectively removed with efficiencies of 99% in Plant B. Concentrations of PCDD/Fs and PCBs in the BF ash of Plants A and B are measured as 1,064 and 420 ng/g, respectively. Concentration of dioxin-like compounds in the fly ash of Plant A is much higher than that of Plant B. It is attributed to the fact that formation of PCDD/Fs and PCBs at APCDs inlet of Plant A is much higher than that of Plant B. Major PCDD/F congeners in the BF ash of Plants A and B include 1,2,3,4,6,7,8-H7CDF, 1,2,3,4,6,7,8-H7CDD and O8CDD. Highly chlorinated PCDD/F congeners dominate in the BF ash. Major PCB congeners in the BF ash of Plants A and B include TeCB-77, PeCB-126 and PeCB-169. The results are similar to that reported by Wu et al. (2016).

## References

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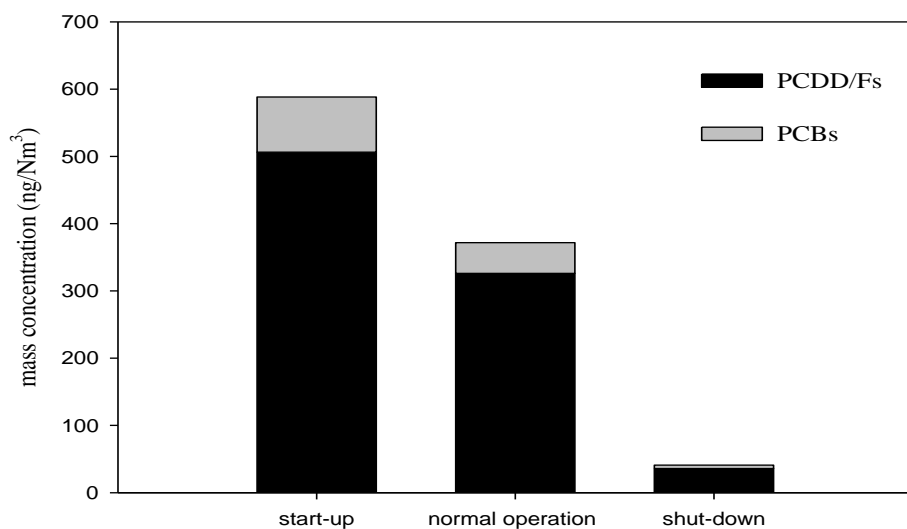


Fig. 1 PCDD/Fs and PCBs concentrations at APCDs inlet of the Plant A during different operating stages.

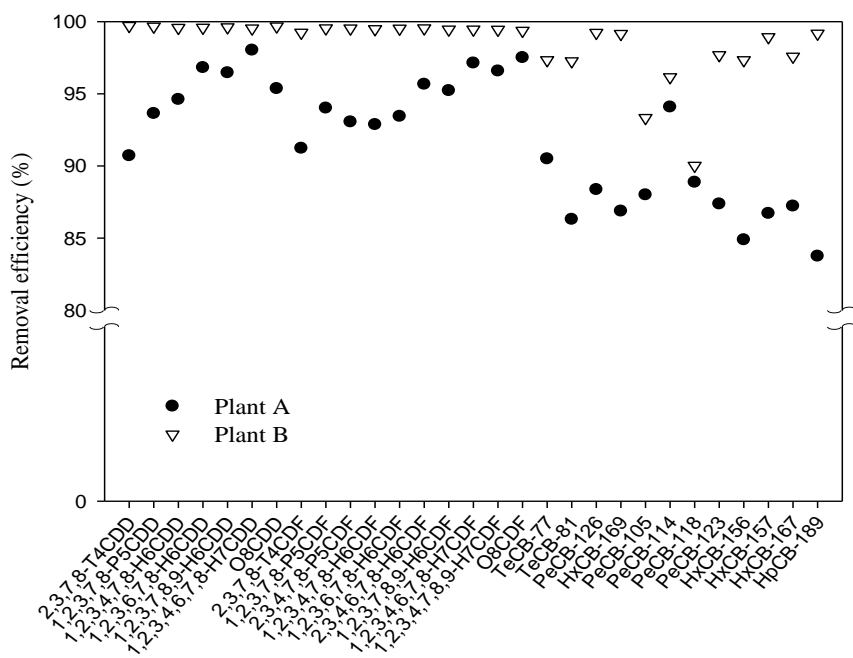


Fig. 2 Removal efficiencies of PCDD/F and PCB congeners achieved with the APCDs of Plant A and B, respectively, during normal operating period.