Reducing of polychlorinated naphthalenes (PCNs) emission from municipal waste incinerator

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Introduction

Polychlorinated naphthalenes (PCNs) are a group of compounds composed of two fused benzene rings with one to eight chlorines substitution. PCNs have total 75 congeners and have been listed as new POPs under Stockholm Convention in May, 2015. Thermal processes are reported as the most important PCN sources, accounting for over 80% PCN emissions[1]. Several thermal processes have been identified as major sources of PCNs, including waste incineration[2], nonferrous smelting processes[3], steel production, coking industries[4] and chloroalkali industries[5]. Municipal waste incinerators (MWIs) are major potential sources of PCNs in Taiwan where incineration is the mainstream approach for treating municipal wastes and 24 large-scale MWIs are in operation throughout the country. The removal efficiencies of PCNs achieved with existing air pollution control devices (APCDs) and variations of PCN characteristics (including concentration and distribution) in gas stream before and after APCDs are rarely reported. In this study, flue gas samples are collected at the inlet and outlet of ESP, wet scrubber (WS), selective catalyst reduction (SCR) and stack to investigate the removal efficiencies of PCNs achieved with existing APCDs.

Materials and methods

Two flue gas samples are simultaneously collected at inlet and outlet of ESP, SCR and stack, one flue gas sample is collected before and after ESP at the same time using automatic isokinetic sampling systems. Briefly, the sampling train consists of a heated probe, a filter box with a quartz-fiber filter, and a water-cooled XAD-2 adsorbent trap. The quartz-fiber filter is used to collect particulate-bound pollutants while the XAD-2 adsorbent resin is applied to trap vapor-phase contaminants. Boiler ash, fly ash and scrubbing water are collected from furnace, ESP and wet scrubber, respectively, as presented in Figure 1.

Samples collected were spiked with a known amount of $^{13}C_{10}$-PCN internal standards and Soxhlet-extracted for 24 h. The extracts were then concentrated by a rotary evaporation and subjected to cleanup using a multilayer column coupled with a carbon column. Finally, the eluted fractions were reduced to about 20 µL and $^{13}C_{10}$-PCN recovery standard was added before analysis. PCNs (MonoCN – OctaCN) analysis was carried out with GC/MS using a fused silica capillary column DB-5 MS (60 m × 0.25 mm × 0.25 µm) under positive EI condition, and all data were obtained with the selected ion monitoring (SIM) mode.

Results and discussions

The average concentrations of PCNs collected at inlet of ESP, outlet of ESP, inlet of SCR and stack are 69.0, 70.2, 123.2 and 2.65 ng/Nm^3, respectively. The average emission factor is 1328.6 ng/ton in term of mass concentration, while the TEQ emission factor is 6.7 pg TEQ/ton. The emission factor of PCNs obtained in this study is significantly lower than that reported in China[6].

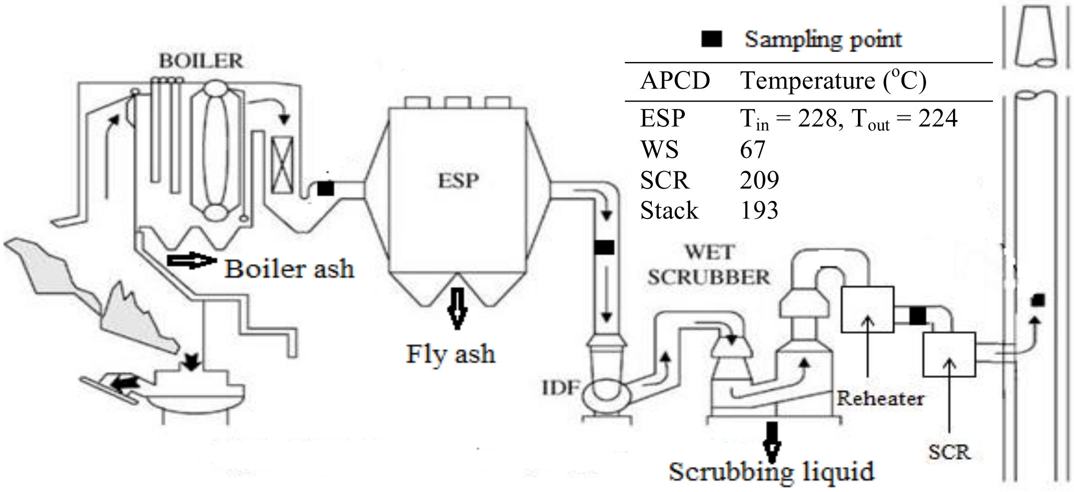

Figure 1. Flow diagram and sampling points of the MSWI investigated.

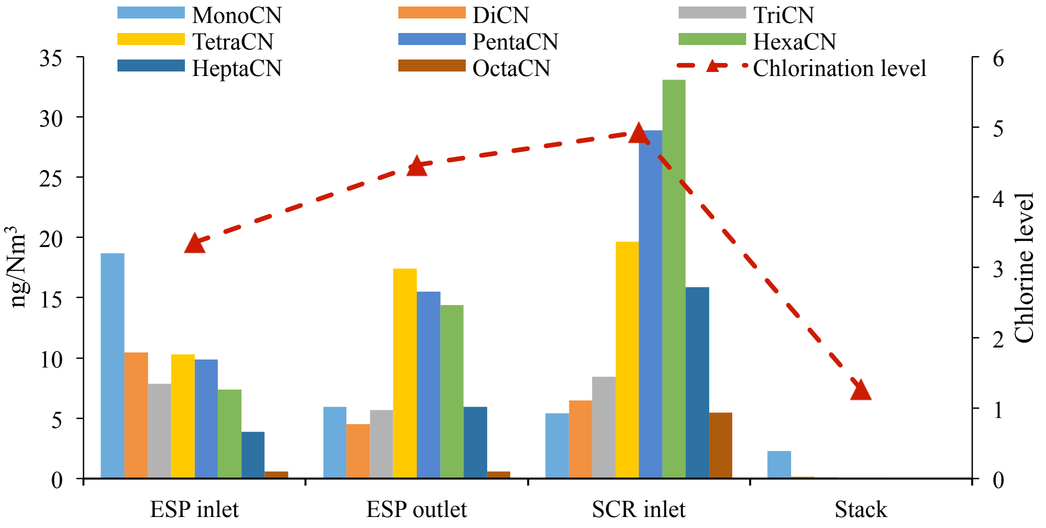

Figure 2. Average concentrations of PCN homologues and chlorine content

The average concentrations of PCN homologues (gas + particulate phases) measured at ESP inlet and outlet, SCR inlet and stack are presented in Figure 2. Low chlorinated PCNs (MonoCN and DiCN) dominate in the inlet of ESP, accounting for 40% of total PCNs. TetraCN and PentaCN dominate in ESP outlet (accounting for 47% of total PCNs), whereas, PentaCN and HexaCN are dominant in SCR outlet, accounting for 49% of total PCNs. The chlorination level increases from 3.36 to 4.46 and from 4.46 to 4.92 as the flue gas passes through the ESP and WS, respectively, indicating the chlorination of PCNs in ESP and WS.

The removal efficiencies of PCN homologues achieved with different APCDs and overall efficiency are presented in Figure 3. The removal efficiencies of PCNs achieved with ESP and ESP+WS decrease with the increase of chlorination level. Low chlorinated homologues (Mono- to Tri-CN) are removed by ESP and ESP+WS with the efficiencies decreasing from 68% for MonoCN to 4% for Tri-CN. The removal efficiencies of highly chlorinated homologues (Tetra- to Octa-CN) achieved with ESP and ESP+WS are negative. The removal efficiencies of Tetra- to Octa-CNs achieved with ESP and ESP+WS are in the ranges of -37 to -268% and -115 to -506%, respectively. The results indicate significant formation of these homologues in ESP and WS. There is no report for the removal of PCNs achieved with existing APCDs, however, some studies indicate that the removal efficiencies of PCDD/Fs achieved with ESP and WS are in the ranges of -44 to -113% and -24.7 to -5730% achieved with ESP and WS, respectively[7]. The increments of PCDD/Fs in ESP and WS may be attributed to De-novo formation of PCDD/Fs on fly ash and the memory effect as reported by various studies[8,9]. Interestingly, the trend of PCN removal achieved with ESP+WS in this study is consistent with the removal of PCDD/Fs reported previously for the same MWI[10], which confirms similar formation mechanism of PCNs and PCDD/Fs in ESP+WS. As presented in Figure 3, the removal efficiencies of highly chlorinated homologues achieved with ESP are higher than those achieved with ESP+WS (except for heptaCN), indicating formation of PCNs is more severe in WS if compared with that in ESP.

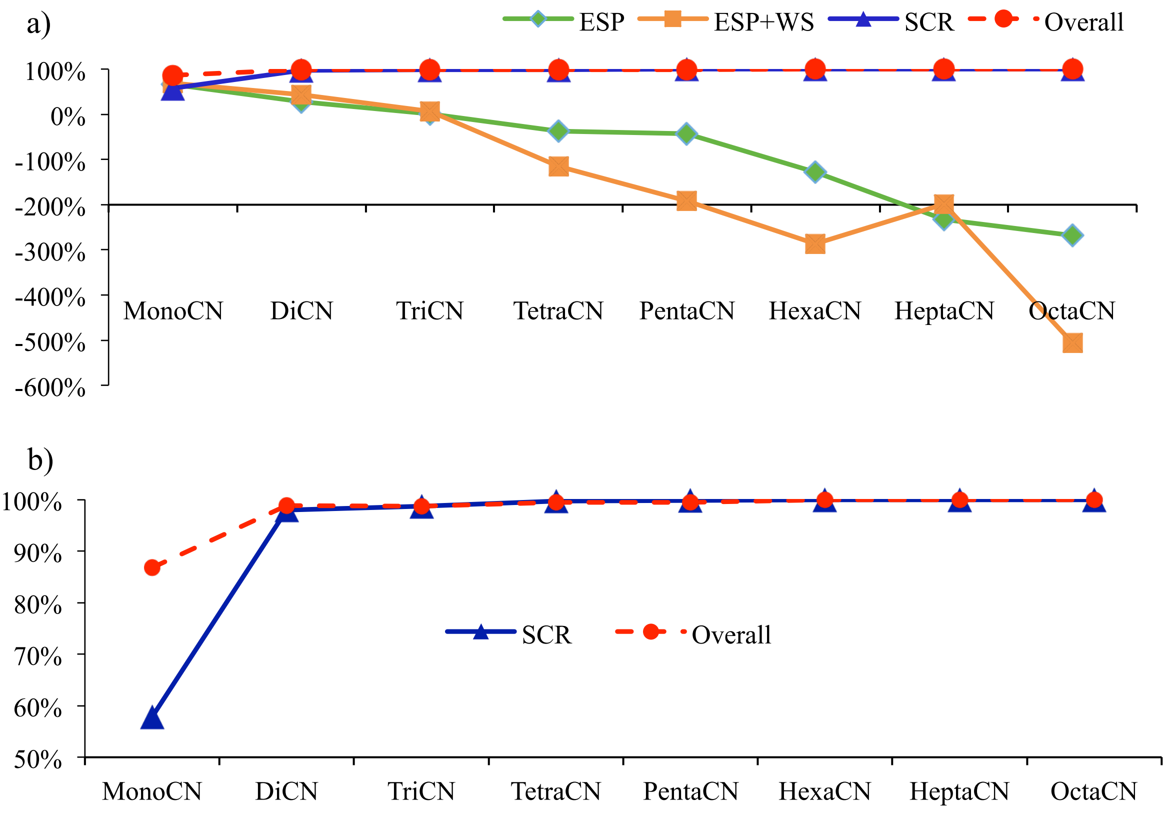

Figure 3. Removal efficiencies of PCN homologues achieved with existing APCDs

The overall removal efficiency and the efficiency achieved with SCR are presented in Figure (3b). Except for MonoCN, the removal efficiencies of other homologues achieved with ESP are consistently high (98-100%). On the other hand, the removal efficiency of MonoCN achieved with ESP is only 58%. Interestingly, the highest and lowest removal efficiencies for the removal of ESP+WS and SCR for MonoCN are observed, respectively. The high removal efficiencies of low chlorinated homologues (Mono- to Tri-CN) and the decrease of removal efficiencies with increasing chlorination level as observed in ESP and WS may be attributed to the chlorination mechanism, i.e., lower chlorinated PCNs are chlorinated to form higher chlorinated PCNs. High level of PCN with the dominance of highly chlorinated homologues (Tetra- and PentaCNs) is measured in fly ash collected from ESP, (as presented in Figure 4), which is in consistence with the assumption. On the other hand, low removal efficiency for MonoCN and significantly high removal efficiencies for higher chlorinated homologues achieved with SCR may be attributed to the dechlorination mechanism, i.e., the higher chlorinated PCNs are dechlorinated to form lower chlorinated homologues.

The removal efficiencies of low chlorinated homologues (Mono- to Tri-CNs) achieved with ESP+WS are consistently higher than those achieved with ESP. Furthermore, only low chlorinated homologues are found in scrubbing liquid collected from WS (Figure 4), which is in agreement with the high solubilities of low chlorinated homologues. These results indicate that low chlorinated PCNs are not only removed by dechlorination but also by scrubbing liquid in WS.

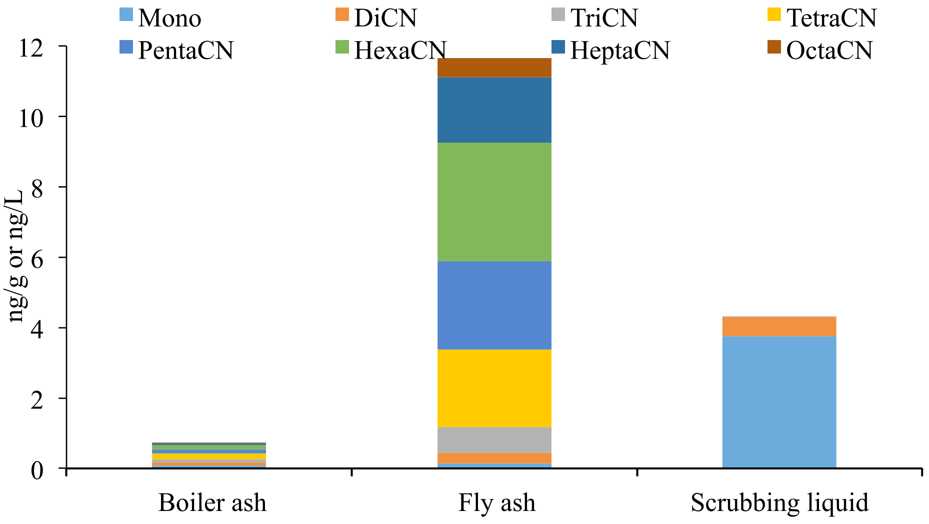

Figure 4. PCN contents in ashes and scrubbing liquid

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