Characteristics of polychlorinated naphthalenes (PCNs) associated with ambient-air particles and fly ash collected from existing APCDs in Taiwan

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Introduction

As new POPs listed by Stockholm Convention in May, 2015, PCNs have been receiving much public attention due to their adverse effect on human health and environment. In this study, the characteristics of PCNs associated with ambient-air particles collected from different sites in winter and summer are compared with those in fly ash samples collected from air pollution control devices (APCDs) of municipal waste incinerators (MWIs) and electric arc furnace (EAF) in Taiwan. As reported in various studies, similar pathways for PCDD/Fs and PCNs formations on fly ash[1,2] are observed and fly ash is the main reservoir for PCDD/Fs released from sources. It is interesting to investigate the concentration, distribution of PCNs in fly ash and compare the characteristics of PCNs in fly ash with ambient-air particles. The comparison of characteristics of PCNs in ambient-air particle and fly ash sample is necessary for the evaluation of potential effect of PCNs on human health and environment.

Materials and methods

Fifteen samples of ambient-air particles were collected at three sites including rural, urban and industrial sites in Taoyuan City in winter and summer, 2017 as described in previous publication[3]. The fly ash samples were collected from some APCDs including ESP, cyclone, baghouse and economizer equipped in MWIs and baghouse of EAF. Detailed information on solid samples collected are given in Table 1.

Table 1. Description of solid samples collected

Designation	Description	Number of samples
RR_ _W	Particles collected at rural site in winter	2
RR_ _S	Particles collected at rural site in summer	3
UB_ _W	Particles collected at urban site in winter	2
UB_ _S	Particles collected at urban site in summer	3
ID_ _W	Particles collected at industrial site in winter	2
ID_ _S	Particles collected at industrial site in summer	3
FA-ESP	Fly ash collected from ESP of MWI	1

FA-Cy	Fly ash collected from cyclone of MWI	1
FA-BH1	Fly ash collected from baghouse of MWI, AC added	1
FA-BH2	Fly ash collected from baghouse of EAF, without AC	1
FA-Eco	Fly ash collected from economizer of MWI	1

Samples collected (filters of ambient-air particles or 10 g of fly ash) 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 clean up 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 (DiCN – OctaCN) analysis was carried out by 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 levels of total PCNs measured for various ambient-air particles and fly ash samples are presented in Figure 1. Generally, the levels of PCNs measured in ambient-air particles are significantly higher than those in fly ash samples in terms of both mass and TEQ concentrations. The average level of PCNs found in ambient-air particle is 50.4 ± 33.1 ng/g (27.2 ± 25.8 pgTEQ/g), while the average level of PCNs measured in fly ash is 7.20 ± 2.61 ng/g (5.3 ± 3.3 pgTEQ/g). Since PCNs are semi-volatile, the gas/particle distribution of PCNs depends on numerous factors such as temperature, size and compositions of particles. In general, as lower temperature and particle size decrease, higher association of PCNs with particles is observed[6]. Therefore, the higher levels of PCNs measured in ambient-air particles compared with those found in fly ash may be due to the lower temperatures (14-30^{o}C) and smaller particle size of air samples collected compared with those of fly ash samples collected by APCDs (at temperatures of 190-205^{o}C). The highest PCNs level is found at industrial site in summer, while the lowest level of PCNs is observed in fly ash collected from economizer of MWI. The levels of PCNs measured in fly ash collected in this study are in the range of PCN level found in cement kiln (1.1-84.7 ng/g)[4] and significantly lower than those reported for fly ash collected from copper smelting plant (708 ng/g)[5].

The homologue distributions of PCNs measured in ambient-air particles and fly ash samples are shown in Figure 2. OctaCN dominates in samples collected in rural and urban sites in both two seasons, accounting for 40 ± 10%. Similar homologue distribution of PCNs is found for ambient-air particle collected in industrial site and fly ash samples and they are the high contributions of Tetra- and Penta-CNs. The chlorination degrees of PCNs in particles collected at rural and urban sites are the highest (6.17±0.528), while the chlorination degrees of PCNs in particle collected at industrial site and fly ash samples are comparable (5.16 ± 0.214 and 4.87 ± 0.424, respectively). The results suggest that the source of particulate PCNs collected from industrial site may be related to similar sources of fly ash samples.

The distribution of PCNs measured in two fly ash samples collected from baghouse are quite different. Contributions of low chlorinated homologues (Di- to Tetra-CNs) are higher in fly ash collected from

MWI (63%) than that collected from EAF (51%). Injection of AC may influence the homologue composition of fly ash since AC may increase the level of low chlorinated PCNs due to adsorption.

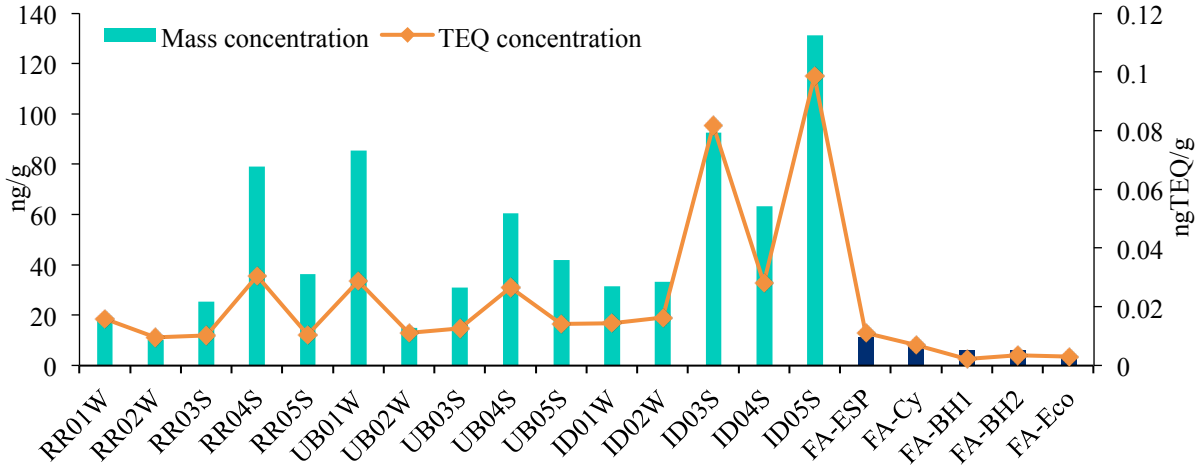

Figure 1. PCNs levels measured in various ambient-air particles and fly ash samples

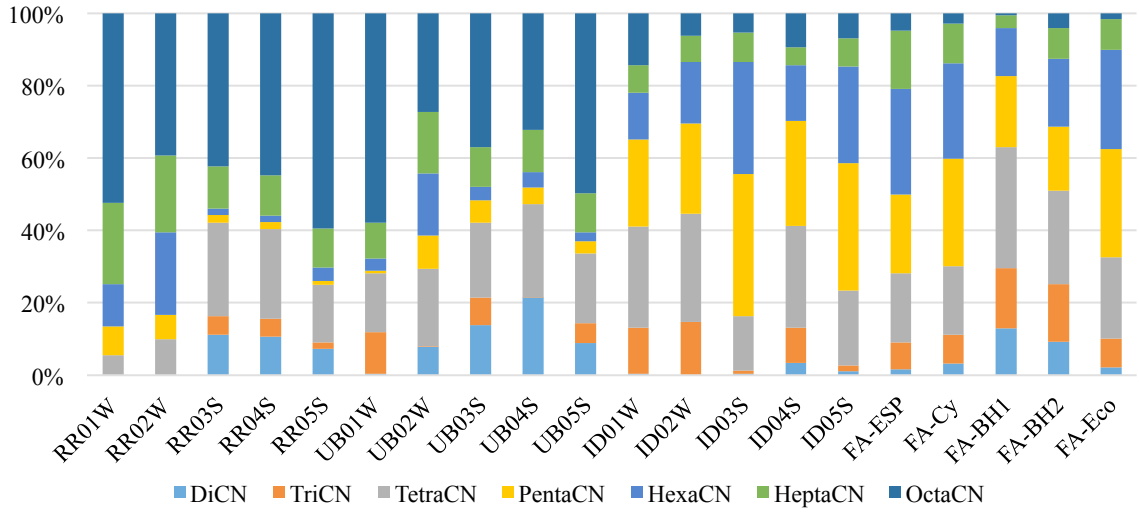

Figure 2. Homologue distribution of PCNs measured in various ambient-air particles and fly ash samples

The fraction of Σcombustion-related PCNs/ΣPCNs can serve as an indicator to distinguish evaporation sources (<0.11) from combustion emissions (>0.5)[3]. In this study, the ratio is used to evaluate the contribution of two source types to PCNs in particles. The results indicate that very low ratios are observed for ambient-air particles collected at rural and urban sites, with the average value of 0.106 ±

0.0482. On the other hand, significantly higher ratio is observed for industrial site with the average value of 0.517 ± 0.0402. The results indicate that the particles collected at industrial site are more likely from thermal processes.

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