

POLYCHLORINATED NAFTALENES AND DLPCBs

DETERMINATION OF POLYCHLORINATED NAPHTHALENES IN VARIETY OF SAMPLES FROM JAPAN BY HRGC/HRMS A CASE STUDY

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Introduction

The Polychlorinated Naphthalenes (PCNs) have been recognized as persistent, ubiquitous environmental pollutants. Their presence in the environment is largely the result of the use of technical products, such as the Halowax series, as flame retardants and dielectric fluids¹. Particularly the industrial products of Halowax were described as follows;

N0471, Halowax 1001, 5000 mg/ml in MeOH

N0471, Halowax 1099, 5000 mg/ml in MeOH (These and the remaining Halowax 1000, and 1051 are being prepared as standard solutions at 10 mg/ml in methanol).

Emissions of trace levels of polychlorinated aromatic compounds as products of incomplete combustion from waste incinerators cause great environmental concern. Some of these compounds are highly toxic and pose significant ecological and health effects. PCNs are often formed during incineration together with polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs). Some of the PCN isomers have been determined to have toxicity comparable to those of PCDDs and PCDFs. However, most of the studies on the formation of toxic by-products from combustion have been conducted on PCDDs and PCDFs; very little work has been reported for PCNs in air samples in variety of conditions.

In order to clarify the formation for PCNs from various industrial applications, we determined mono-through octachloro naphthalenes from flue gas samples collected from thermal process steady operation, start and shut down, EP ash steady operation, start and shut down then original fly ash and dechlorinated flyash. In addition, levels of PCNs in winter and summer air collected in the year 1992 was also used. Furthermore, PCDD/DFs also analyzed and evaluated in this study.

Materials and Methods

Sample collection

The air samples were collected using high volume air-sampler that consisted of polyurethane foam and glass fiber filter. Besides, the low volume sampler consisted of impinger and XAD-2 that collected the thermal process gas samples at different stages (mentioned in the objective of this study). Further the commercial PCNs from Halowax was also analyzed in order to understand the major congeners evolved during thermal process. In addition, air samples from winter (Sep.1992) and summer (Dec.1992) was collected at western part of Japan.

Analysis

The samples were extracted according to the method described for dioxin and PCBs³. The brief cleanup and separation conditions of air samples can be described as a multilayer silicagel column chromatography of extracted solvents (silica, 10 % AgNO₃/silica, silica, 22 % H₂SO₄/silica, 44 % H₂SO₄/silica, silica, 2 % KOH/silica, silica) using hexane as a mobile phase. The eluants were further

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separated using alumina column chromatography using 10 % dichloromethane/hexane (V/V) as a mobile phase. Further the alumina eluants were further subjected in to HPLC, Porous Graphitized Carbon Column (PGC) and elaute with hexane and in case of interference's the re-cleanup was conducted using toluene.

Quantification and Identification

HRGC-HRMS, Micromass Autospec Ultima with Hewlette Packard HP 6980 series was used with DB-5 MS (60 m, 0.32 mm, 0.25 mm) capillary column. The temperature conditions were programmed as 150 °C for 1-min. (20 °C/min.) to 185 °C (1-min.) to 3 °C/min to 245 °C (10 min.) to 6 °C/min to 290 °C for (14 minutes). The interface temperature was programmed as 5-10 °C higher than the maximum value of each temperature program. The carrier gas was helium with flow of 1.0 ml/min. and the electron impact ionization energy was 35-40eV. The MS was operated in selected ion monitoring for each congener group at a resolution >10,000. Two ions were monitored for each isomer and congener group. Identity of calibration standards for PCNs, 12 congeners of individual PCN and Halowax series 1000, 1001, 1013, 1014, 1031, 1051 and 1099 was used to calibrate against 11 ¹³C₁₂-PCB congeners in order to calculate Relative Response Factor (RRF). We also participate PCN interlaboratory comparison study and bring out excellent recoveries using well-advanced analytical procedure.

Results and Discussion

Mono-through heptachloronaphthalenes in low temperature thermal process and commercial Halowax PCN congeners were shown in Table 1. TeCN-2367, PeCN-12367 and HxCN-123567 were major congeners. These combinations were used to calibrate RRF values with two monitor ions to get scientifically acceptable RRFs for the efficient quantification of PCNs in environmental samples (PCN inter-laboratory comparison results).

Table 1. Predominant PCN congeners in thermal processes and commercial Halowax mixture, respectively.

Homologue	Thermal Processes*	Commercial PCN (Halowax)
MoCN	1	1
DiCN	14/16, 26/17, 12, 23, 18 (13)	14/16>>15/27 26/17
TriCN	123, 124, 128, 145, 146, 127, 167/236 (136), (138)	146>>145 124
TeCN	1 1 3 6 / 1 2 4 5 2367 1238 1278 (1368/1256)	1257/1246/1247 1258/1268>1235/1358 1248 1458
PeCN	12357/12467 12356 12367 12346 12345 12378	
HxCN	123467/ 123567 123457/123568 123578 123456 123678	124568/124578>>123578 123457/123568 123456
HpCN	1234567	1234568

*Municipal solid waste incinerator flue gas and flyash with low temperature; the bold figures denotes toxic congeners.

In Figure 1, we showed the congener pattern of PCNs in Halowax and with comparison to the flue gas at steady operation of incinerator. Among mono- CNs, there was not much difference. Whereas, Di-14/16CN, tri-146CN was greatly reduced. However, other isomers have formed considerably in tri-through hepta-CNs. Particularly, congeners like Pe-12357/12467CN, 123467/123567CN and Hp-1234567CN was greatly increased in steady operation conditions. We also conducted analysis of PCNs is gas samples when start the incinerator and also during shutdown conditions (the results not presented here). There was not considerable variation in either conditions excluding slight increase of 136, 1368, isomers. Furthermore, flyash samples at start; shutdown and stability operation conditions were collected and found there was no pronounced isomer/congener-specific modifications (the results not shown). However, there was a slight modification in isomer/congener profiles in start and shutdown stages.

There was a significant result of homologue profiles in between steady operation condition and start/shut-down condition gas samples. Particularly lower chlorinated PCNs were greatly increased

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during shutdown followed by start up. While, there was not considerable effect in steady state. In case of ash samples, the PCNs was slightly influenced even in steady operation conditions with slight fluctuation of homologues.

More interestingly, we also determined the PCN congener pattern in original flyash and thermal dechlorinated flyash under nitrogen stream to see any specific modification (Figure 2). Each homologue from mono- through heptachlorinated naphthalenes was adjusted to 100%. The dechlorination effect was greatly pronounced the formation of 12357/12467-PeCNs rather than rest of isomers/congeners. However, reductions for congeners such as 123467/123567 HxCN and 1234567-HpCN were noticed when compare to original flyash (Figure 2). Altogether, dechlorination effect was greatly affected the homologues of di- through octachlorinated naphthalenes as for as concentration is concern. When the results were transferred to a percentage, dechlorinated ash greatly elevated mono-chloronaphthalenes and penta-chlorinated naphthalenes (results not shown).

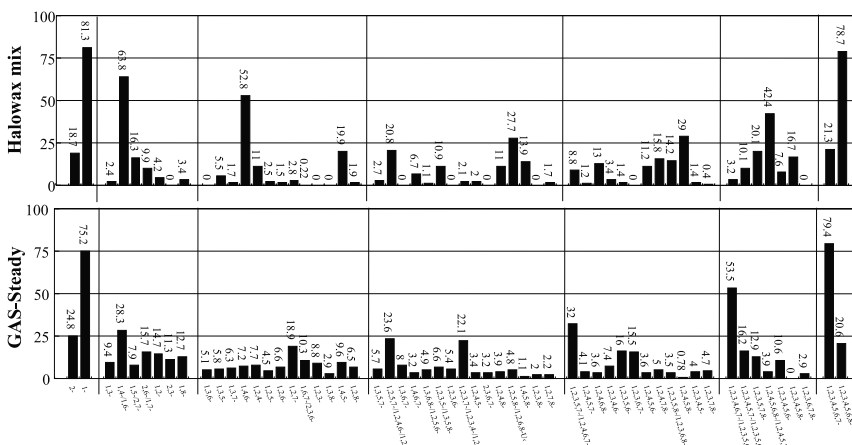


Figure 1. PCN Isomer/congener profiles in Halowax and in gas of steady operation condition.

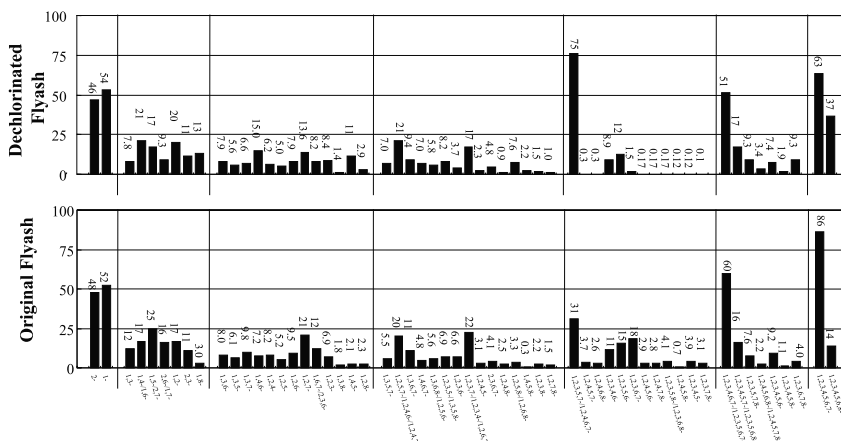


Figure 2. PCN Isomer/congener profiles in original flyash and dechlorinated flyash.

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The seasonal trend of PCDD/DF, PCBs and PCNs of air sample were shown in Figure 3. As for as PCDD/DF is concern, winter samples showed greater increase in concentrations on up to 20-50 pg/m^3 when compare to summer conditions. Similarly, PCNs showed the same trend as PCDD/DFs with the increase of 378 to 391 pg/m^3 in winter. Interestingly, only PCBs showed reverse pattern of decreasing concentrations in winter than summer from 2-3 magnitude. These observations are clearly reflects the cold condensation effect of PCBs rather than PCDD/DFs and PCNs.

We also calculated WHO-toxic equivalency (WHO-TEQ) levels based on the concentrations of PCDD/DFs (0.3-0.9 pg/m^3) and dioxin-like PCBs (0.029-0.31 pg/m^3) on seasonal basis (Figure 3). The TEQ by non-*ortho* PCBs increased slightly in winter. While, mono-*ortho* PCBs declined in the winter season with accordance to the concentrations. On the other hand, TEQ by PCDD/DF was increased in winter when compare to the summer. Particularly PCDFs were greatly contributed to the total concentrations as well as TEQs in both the seasons. It should be also mentioned that increase of some high toxic congener of PCDF is apparent due to greater increase of TEQs than concentrations.

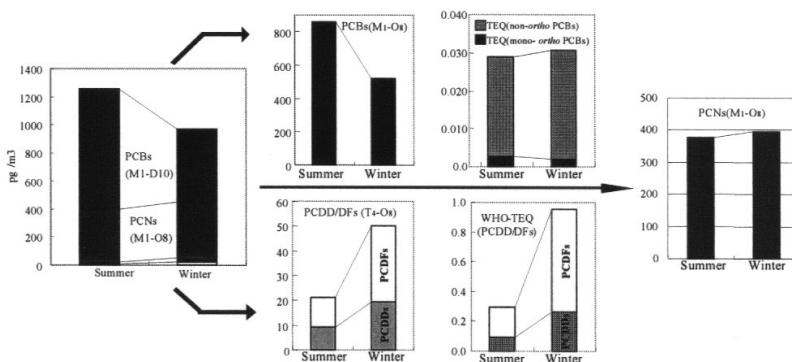


Figure 3. Seasonal concentrations and WHO-TEQ of PCDD/DFs, PCBs and PCNs from winter and summer air samples from Japan in 1992.

Not only polychlorinated aromatic compounds, we also measured organochlorine pesticides such as DDT (dichlorodiphenyltrichloroethane) and its metabolites, HCHs (hexachlorocyclohexane) and CHLs (chlordane isomers) on seasonal basis. Collectively, DDTs, HCHs and CHLs were greatly increased in summer than in winter (data not shown).

Our results highlighted that isomer/congener variation of PCNs during summer and winter samples. For example, in summer there was not much difference in between air samples and Halowax mixture. In contrast, some polychlorinated naphthalenes in air samples had considerable increase when compare to Halowax (Table 1). These results indicated that the thermal process in winter might have played possible role. Similarly, the concentrations and TEQ of PCBs had increased in winter, these observations are in contrast to PCDD/DFs and therefore, we can conclude that the other alien sources is the possible explanation of these differences. As for as our knowledge, this is first of its kind of work in Japan.

References

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