CONGENER-SPECIFIC ANALYSIS OF POLYCHLORINATED NAPHTHALENES (PCNs) IN INSULATING OIL FROM CHINESE ELECTRICAL CAPACITOR

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Introduction

Polychlorinated naphthalenes (PCNs) have been nominated by European Union (EU) in 2011 to be listed into the Stockholm Convention. Therefore PCNs are currently evaluated by the POPs Reviewing Committee (POPRC) which decided at a recent meeting (10/2012) that PCNs meet the screening criteria of Annex D of the Convention. Currently a draft risk profile is prepared for PCN which is the last stage before a chemical can be listed by the next Conference of Parties. Therefore it is necessary to investigate potential emission sources of PCNs for the purpose of establishing global inventories for emission control.

Small amount of PCNs as impurities in technical PCBs has received researchers' concerns since 1990s. These PCN contaminations were identified as one of three known main sources of PCNs in the environment. Other main sources are the technical PCN formulations (the major source) and other industrial processes using elemental chlorine (e.g. chloro-alkali industry)[1]. Therefore several studies have focused on the analysis of PCNs in various PCB formulations. For example, Yamashita et al. reported absolute and relative concentrations of individual PCN congeners in eighteen technical PCB preparations including Aroclors (USA), Kanechlors (Japan), Clophens (Germany), Phenoclors (France), Chlorofen (Poland), and Sovol (former USSR)[2]. However, there's no data about the PCNs in Chinese major technical PCB preparation PCB3 (also called #1 PCB), which in the history has been largely produced and mainly used as insulating oil in electrical capacitors. The present study aims to the accurate congener-specific analysis of PCNs in PCB3-based insulating oils from stored Chinese electrical capacitor and compare the data with PCB preparations from other countries.

Materials and methods

Two insulating oil samples were investigated in this study. One was taken from a domestic electrical capacitor excavated from a temporary storage of PCBs equipments site in Zhejiang Province. According to its label the capacitor has been produced by Xi'an Electrical Capacitor Plant (Sample #1). For comparison purpose, another sample of dielectric oil (ASKAREL Nr 1740) was taken from an imported transformer in China, which was currently offline and stored at State Engineering Center of Hazardous Waste Disposal in Shenyang (Sample #2).

The standard solution of native PCNs (PCN-MXB) was purchased from the Wellington Laboratories Inc. (Ontario, Canada), which contains 16 congeners (i.e. 1,5-Di-CN, 2,7-Di-CN, 1,2,3-Tri-CN, 1,2,3,5-Tetra-CN, 1,2,3,8-Tetra-CN, 1,4,5,8-Tetra-CN, 2,3,6,7-Tetra-CN, 1,2,3,4,5-Penta-CN, 1,2,3,4,6-Penta-CN, 1,2,3,5,7-Penta-CN, 1,2,3,5,8-Penta-CN, 1,2,3,4,6,7-Hexa-CN, 1,2,3,5,7,8-Hexa-CN, 1,2,4,5,7,8-Hexa-CN, 1,2,3,4,5,6,7-Hepta-CN, and Octa-CN). Isotopically labeled $^{13}C_{12}$ PCNs standards of 1,3,5,7-Tetra-CN, 1,2,3,4-Tetra-CN, 1,2,3,5,7-Penta-CN, 1,2,3,5,6,7-Hexa-CN, 1,2,3,4,5,7-Hexa-CN, 1,2,3,4,5,6,7-Hepta-CN, 1,2,3,4,5,6,7,8-Octa-CN and another deuterated standard of 2-Chloronaphtalene-d7 were purchased from the Cambridge Isotope Laboratories Inc. (USA). All organic solvents used for extraction and cleanup were of pesticide residue analysis grade and dioxin analysis grade, and provided by Kanto Chemicals Co., Inc. (Tokyo, Japan) and Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

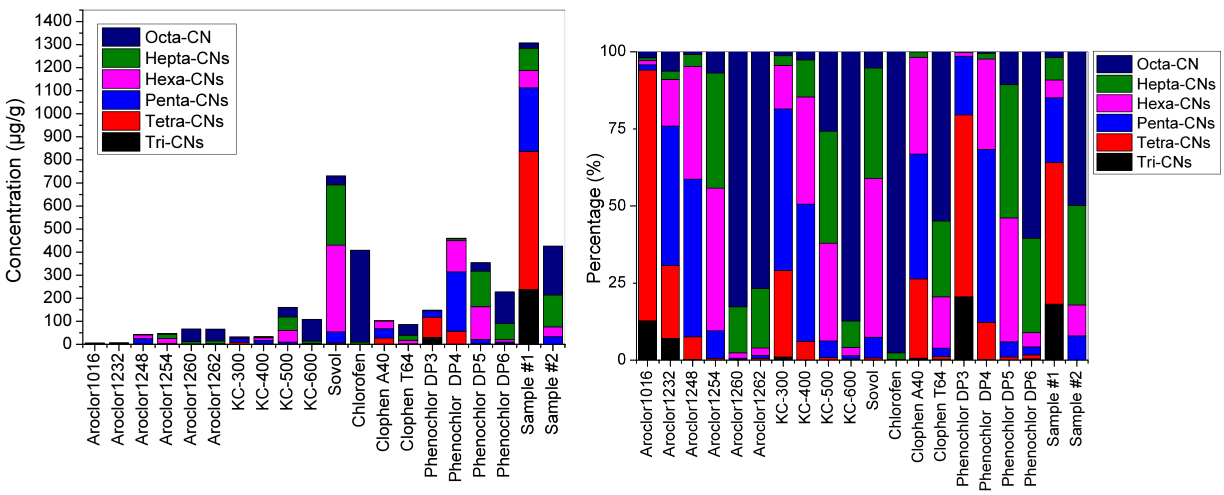
The testing of samples was performed in a qualified laboratory at the Institute of Environmental Innovation of IDEA Inc. in Shizuoka, Japan. For the measurements 80 mg of each oil sample was dissolved in 100 mL of decane in a volumetric flask. Such original stock solution with the concentration of 0.8 g/L was further sequentially diluted in decane by 100 times. An aliquot of 10 μL such solution was added with 10 μL $^{13}C_{12}$-labeled standard solution (50 pg/μL), and ready for instrumental analysis.

The quantification and identification of PCNs congeners were conducted on a Hewlett Packard 6890 series high resolution gas chromatography coupled to a Micromass AutoSpec high resolution mass spectrometer (HRGC/HRMS). BPX-DXN (60 m × 250 µm i.d., SGE, Australia) was used for the separation of target chemicals, and high-purity helium (99.999%) was used as the carrier gas. Splitless mode at 300 °C was adopted, with the injection volume of 1.5 µL. The oven temperature program was: 100°C for 1 min, 20°C/min to 180°C, 3°C/min to 240°C, 10°C/min to 330°C and hold. The mass spectrometer source temperature was set at 320 °C, with the interface line at 300 °C. The mass spectrometer was operated at an electron impact (EI) energy of 30-50 eV. CN congeners were determined by selected ion monitoring (SIM) at the two most intensive ions of each homologue. In this study, peaks were identified on the basis of retention time by comparing with internal standards and considering the elution order on the GC column[3].

Results and discussion

Total content and homologue profiles of PCNs in the samples

The detected PCN concentration and the homologue compositions of the Chinese PCN sample #1 and #2, as well as the comparison with the PCB formulations from other countries are shown in Figure 1(a). The total concentration of PCNs in sample #1 was considerably higher than those reported in technical PCBs formulations from other countries[2], as well as that in the transformer oil (ASKAREL Nr 1740) tested in the present study.



(a) (b)

Figure 1 Comparison of homologue profiles among tested samples and other formulations

Compared with the homologue compositions of PCNs of 18 PCBs formulations from other countries[1], what's the same is that neither mono-CNs nor di-CNs was detected in two samples. However, big difference can be found between Chinese PCBs formulation (sample #1) and PCBs formulations from other countries, as shown in Figure 1(b). In terms of the composition contributions of homologues, the situation in Chinese PCB3 (sample #1) was quite similar to those in Aroclor 1232, where the contributions from tri- to penta- CNs were predominant and accounted for similar proportions. Unlike PCB3, the situation in ASKAREL Nr 1740 is more similar to Aroclor 1260/1262 and KC-500/600, where the predominant homologues were octa-CN and hepta-CNs which account for about 90% of the total PCNs detected.

Currently the mechanism of PCNs formation during PCB production is not fully inderstood. It is suspected that a certain amount of naphthalene has been contained in the respective raw biphenyl mixtures and that these were chlorinated simultaneously with the chlorination of biphenyl. The average degree of chlorination of PCNs is higher than the corresponding chlorination of the PCBs. This can be explained by the higher reactivity of naphthalenes than biphenyls, caused by the greater mean electron localization energy reactivity[4].

Estimation of PCNs production in Chinese PCBs formulation

As recorded in China's National Implementation Plan (NIP) for the Stockholm Convention on Persistent Organic Pollutants published in April 2007, about 6000 tons of PCB3 have been produced and used as insulating oil for electrical capacitor in China. Nowadays most of PCB3 containing electrical capacitors have been offline and stored all over the country.. Using the tested concentration (1300 μg/g) in sample #1, the total PCNs contained in the PCB3 based insulating oil in Chinese electrical capacitors can be estimated to be 7.8 tons. This is only about 0.0052% of the total global production of PCNs of 150,000 tons estimated by Falandysz[1]. On the other hand, such amount is larger than the production of PCNs from technical PCB mixtures estimated by Yamashita et al.[2], such as Kanechlor (Japan) and Aroclor (UK), as shown in Figure 2. In general, the estimated PCNs production in Chinese PCB3 is comparable with those in Aroclor (US or UK), Kanechlors (Japan), Chlophens (Germany), but much lower than those in Phenochlors (France) and Sovol (former USSR). Therefore, PCBs-based insulating oil should receive sufficient concerns as an important source of PCNs.

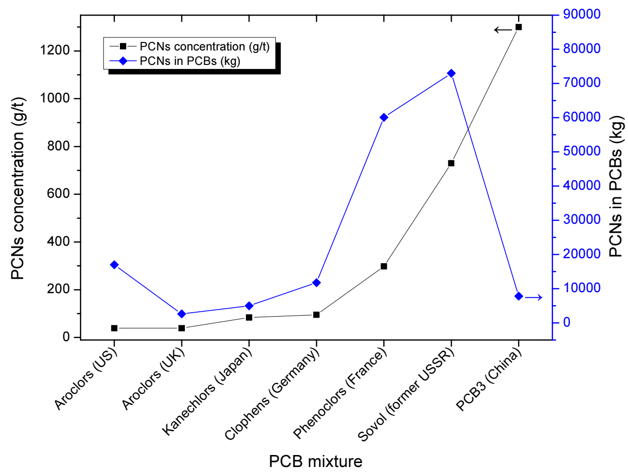


Figure 2 Concentrations and total amounts of PCNs in various PCBs mixtures

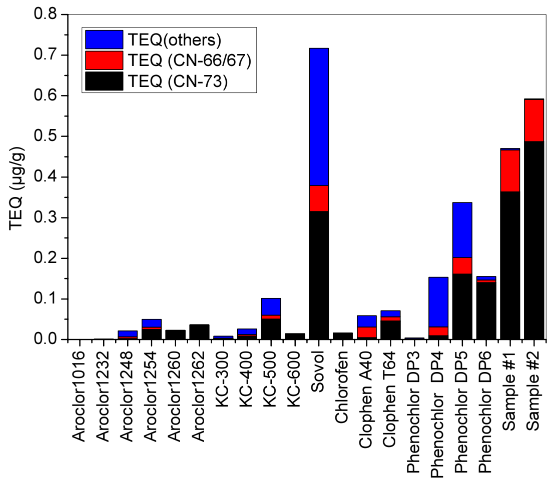


Figure 3 Comparison of TEQ caused by dioxin-like PCN congeners among tested samples and other formulations

Dioxin-like toxicity of PCNs in the two samples

Some studies have investigated the dioxin-like toxicity of PCNs, evaluating ethoxyresolfin-O-deethylase (EROD) activities or arylhydrocarbon- (Ah-) receptor-mediated effects via in vitro bioassays to determine potencies of specific PCN congeners relative to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TeCDD), and relative potency factors (RPFs) have been estimated.

The occurrence of dioxin-like PCNs (dl-PCNs) is as shown in Table 1, where the RPFs of PCN congeners summarized by in Noma et al.[5] and Guo et al.[6] have been adopted. The TEQ concentrations in two samples are 0.47 and 0.59 μg TEQ/g, respectively. And the dominant contributions come from CN-73 and CN-66/67.

Table 1 Concentration of dioxin-like PCN congeners in samples, μg/g

IUPAC No.	Congener	RPF	Sample #1		Sample #2	
			Content	TEQ	Content	TEQ
CN-1	1-	1.7×10^{-5}	ND	0	ND	0
CN-2	2-	1.8×10^{-5}	ND	0	ND	0
CN-4	1,3-	2.0×10^{-8}	ND	0	ND	0
CN-5/7	1,4- /1,6-	1.8×10^{-8}	ND	0	ND	0
CN-10	2,3-	2.7×10^{-5}	ND	0	ND	0

IUPAC No.	Congener	RPF	Sample #1		Sample #2	
			Content	TEQ	Content	TEQ
CN-38/40	1,2,5,8- / 1,2,6,8-	8.0×10^{-6}	130	1.3×10^{-3}	ND	0
CN-48/35	2,3,6,7- / 1,2,4,8-	2.1×10^{-5}	23	6.0×10^{-4}	ND	0
CN-50	1,2,3,4,6-	6.8×10^{-5}	17	1.5×10^{-3}	ND	0
CN-54	1,2,3,6,7-	1.7×10^{-4}	ND	0	ND	0
CN-56	1,2,3,7,8-	4.6×10^{-5}	ND	0	33	1.9×10^{-3}
CN-57	1,2,4,5,6-	1.6×10^{-6}	25	5.0×10^{-5}	ND	0
CN-63	1,2,3,4,5,6-	2.0×10^{-3}	ND	0	ND	0
CN-64/68	1,2,3,4,5,7- / 1,2,3,5,6,8-	1.0×10^{-3}	ND	0	ND	0
CN-66/67	1,2,3,4,6,7- / 1,2,3,5,6,7-	2.5×10^{-3}	33	1.0×10^{-1}	33	1.0×10^{-1}
CN-69	1,2,3,5,7,8-	2.0×10^{-3}	ND	0	ND	0
CN-70	1,2,3,6,7,8-	1.1×10^{-3}	ND	0	ND	0
CN-71/72	1,2,4,5,6,8- / 1,2,4,5,7,8-	3.5×10^{-6}	15	6.6×10^{-5}	ND	0
CN-73	1,2,3,4,5,6,7-	3.0×10^{-3}	97	3.6×10^{-1}	130	4.9×10^{-1}
	In total	**-**	**340**	**0.47**	**200**	**0.59**

When comparing with the situlations in other PCB formulations reported by Yamashita et al.[2], the detected TEQ levels in sample #1 and #2 are higher than those in most other PCB formulations excluding Sovol (Figure 3). In particular the PCN TEQ levels in Aroclors (more than 50% of global PCB production) are quite low.
According to Haglund et al.[4], naphathalene has higher reactivity than biphenyl due to the greater mean electron localisation energy reactivity. During the chlorination process, PCN congeners were formed along with the PCB congeners. Therefore one possible reason for higher TEQ level in Chinese PCBs formulation might be the higher content of naphathene in biphenyl as the raw materials for PCBs production. However due to the unavailability of the original biphenyl starting material, this can not be confirmed by actual measurements

As a conclusion, PCB insulating oil sample from a Chinese electrical capacitor was collected and analyzed using isotope dilution technique and HRGC/HRMS. The accurate congener specific analysis was conducted and provided the detailed homologue profile and congener pattern of PCNs as well as the concentration of dioxin-like PCN congeners. The results provided a supplement to the existing data about PCN in PCB formulations in other countries, and presented the new determination about the detailed PCNs pattern and concentration in PCBs based insulating oil for Chinese electrical capacitors which was the major use of Chinese PCBs.

Acknowledgements
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