POLYCHLORINATED NAPHTHALENE PROFILES IN HUMAN SERUM AND FLUE GAS FROM THE METROPOLITAN AREA

Park H, Chang Y-S

School of Environmental Science & Engineering, Pohang University of Science and Technology (POSTECH), San 31, Hyojadong, Namgu, Pohang, Kyungbuk, 790-784, Korea

Abstract
Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs) have been studied extensively; however, polychlorinated naphthalenes (PCNs) have been studied less widely. The concentrations of PCNs in the serum samples of 61 healthy human volunteers and in 10 stack gas samples of municipal solid waste incinerators (MSWIs) were measured by gas chromatography/high-resolution mass spectrometry (GC/HRMS). The mean concentration of PCNs in human serum was 2170 pg/g lipid, and the most predominant individual congener was hepta-CN-73. The overall serum PCN homologue profiles of all subjects were dominated by tetra- and penta-CN homologues. Whereas the total PCN concentrations in all stack gas samples varied between 0.07 and 1.51 ng/Nm^3, the average PCN homologue profile in the flue gas samples was dominated by the tetra- and hepta-CN homologues. Enrichment of hepta-CN-73 in the human serum samples might be due to contributors from combustion sources.

Introduction
Polychlorinated naphthalenes (PCNs) are primarily industrial chemicals consisting of 75 congeners that incorporate 1–8 chlorine atoms per naphthalene molecule. The physical and chemical properties of PCNs are similar to those of polychlorinated biphenyls (PCBs); PCNs have high thermal stability and chemical inertness, which favor their application in the electrical industry as cable insulators and as dielectric fluids in transformers and capacitors. PCNs have also been used as wood preservatives, carriers in dye production, machine oil additives, and rubber product additives[1,2]. Besides being industrially produced, PCNs are also released into the environment as byproducts of PCB-containing commercial mixtures[3,4]. PCNs are also formed in various incineration processes[1]. They persist in the environment due to lipophilic and bioaccumulative properties[5,6]. While polychlorinated-*p*-dibenzodioxin/dibenzofurans (PCDD/Fs) and PCBs have been studied for more than 2 decades, only a few reports on PCNs are available. Moreover, no information exists on the occurrence of PCN among people from countries such as Korea that do not import or use technical PCN formulations. In such countries, the primary sources of PCNs might be thermal and other processes that are conducted in the presence of chlorine, *de novo* PCN synthesis, and emissions from municipal waste incinerators.

Materials and Methods
Municipal Solid Waste Incinerator: Four municipal solid waste incinerators (MSWIs), namely, I_a, I_b, I_c, and I_d, were selected in the Seoul Nation Capital Area, Korea; these MSWIs have been operational since 1996, 1995, 1999, and 2001, respectively. All are stoker type incinerators that process primarily food waste and paper.

Sample Collection: Sixty one human serum samples consisted of 30 males and 31 females were obtained in 2007 from volunteer MSWI workers (n=14), nearby residents (n=36), and referential inhabitants (n=11) in Korea. Information such as age, smoking, dietary habit, body weight and height etc. was obtained from a questionnaire survey. All samples were kept frozen at –20℃ until analysis. Ten stack samples were collected from the 4 MSWIs, and the protocol followed for sample collection was the Korean Standard method, a modified version of US EPA method 23[7].

Chemical Analysis: Approximately 30 g of serum was added to a 500-mL separating funnel and spiked with a set of $^{13}C_{10}$-labeled PCNs as the surrogate internal standard. The sample was subjected to liquid/liquid extraction with acetone and hexane (2:1) and was processed through 2 cleanup steps, i.e., silica chromatography followed by alumina chromatography. For the stack gas samples, the water/ethylene glycol and resin/filter samples were

spiked with a mixture of $^{13}C_{10}$-labeled PCNs before extraction with toluene and Soxhlet. One round of 20-g BioBead-SX3 gel permeation chromatography was performed in addition to 2 absorption chromatography cleanup steps. The cleaned extract was analyzed by high-resolution gas chromatography/high-resolution mass spectrometry (an HP 6890N gas chromatograph coupled with a JEOL 800D mass spectrometer) in the electron impact mode after addition of a $^{13}C_{10}$-labeled recovery standard.

QA/QC: Procedural blanks were analyzed with every 9 samples as a check for interferences and/or contamination from solvent and glassware. The limit of detection (LOD) for each PCN congener was estimated as 2.5 times the S/N value found for procedural blanks; this LOD was in the range of 1 - 2 pg/g lipid for human serum sample and <1 pg/m^3 for stack gas sample. Quality control standards for PCNs were analyzed after every 10 samples, to monitor for instrument stability. Recoveries of $^{13}C_{10}$-labeled PCNs spiked into each sample were 95±21% for 1,3,5,7-TetraCN, 90±18% for 1,2,3,4-TetraCN, 104±22% for 1,2,3,5,7-PentaCN, 76±11% for 1,2,3,5,6,7-HexaCN, 79±23% for 1,2,3,4,5,6,7-HeptaCN, and 82±32% for OctaCN.

Results and Discussion

PCN Levels in Human Serum

The overall serum PCN profiles of all subjects were dominated by the tetra- and penta-CN homologues; the actual concentrations measured were 1020 and 419 pg/g lipid, respectively. The hepta-CN congener (PCN73) was the most predominant congener and contributed 17.5% of the total PCN detected in the serum samples. Tetra-CN-38/40 and tetra-CN-33/34/37 accounted for approximately 11% of the total serum PCN concentration, and hexa-CN-66/67 accounted for 9.3%. Together, these congeners comprised approximately 50% of the total serum PCN concentration. Penta-CN-52/60 showed a relatively high contribution of approximately 5% to the total serum PCN concentration (Table 1).

Table 1. Each PCN congener concentration (pg/g lipid) in human serum

		Mean	Min	Max			Mean	Min	Max
T4CN					**P5CN**				
	PCN42	48.6	12.4	172		**PCN52/60**	95.5	ND	431
	PCN33/34/37	245	93.2	556		**PCN58**	1.6	ND	19.6
	PCN44	37.5	ND	134		**PCN61**	11.0	ND	61.2
	PCN47	35.6	ND	125		**PCN50**	76.1	ND	314
	PCN36/45	58.1	ND	160		**PCN51**	191	21.5	714
	PCN28/43	97.4	31.8	239		**PCN54**	6.2	ND	38.5
	PCN29	13.7	ND	42.6		**PCN57**	6.5	ND	38.5
	PCN30/27	20.2	ND	86.0		**PCN62**	7.4	ND	91.9
	PCN39	15.9	ND	48.0		**PCN53/55**	6.3	ND	60.5
	PCN32	17.7	ND	67.4		**PCN59**	17.4	ND	145
	PCN48/35	61.2	ND	162		**PCN49**	ND	ND	ND
	PCN38/40	248	77.0	629		**PCN56**	ND	ND	ND
	PCN46	105	ND	285	**H7CN**				
	PCN31	4.0	ND	64.4		**PCN73**	379	160	1020
	PCN41	9.3	ND	40.1		**PCN74**	21.9	ND	608
H6CN					**OCN**				
	PCN66/67	202	92.4	744		**PCN75**	75.3	ND	224
	PCN64/68	47.0	ND	634					
	PCN69	2.7	ND	92.4					
	PCN71/72	1.8	ND	80.6					
	PCN63	ND	ND	3.29					
	PCN65	ND	ND	11.4					

*ND; no detection

More than half of serum PCN was composed of only a few congeners; hence, we investigated the correlation

between the serum concentrations of PCN and each of the congeners. Tetra-CN-28/43 showed the highest correlation coefficient value (r = 0.90); on the other hand, the most predominant congener, hepta-CN-73, had a correlation coefficient value of only 0.66.

PCNs Distribution in MSWI Stack Gas

At all MSWIs, the average PCN homologue profile in the flue gas samples was dominated by the tetra- and penta-CN homologues. In the I_a and I_c samples, the tetra- and penta-CN homologues were most prevalent; in the I_b and I_d samples, the tetra- and hepta-CN homologues were most prevalent. The PCN congener pattern also showed variability for each stack sample (Figure 1). Tetra-CN-33/34/37, hepta-CN-73, tetra-CN38/40, hexa-CN-66/67, tetra-CN-28/43, and tetra-CN-48/35 were the predominant congeners and accounted for approximately 58% of PCNs in all stack gas samples. The tetra-CN homologue contribution to the total PCNs ranged from 36.3 to 80.9% with a mean of 63%. The total PCN concentrations in all stack gas samples varied between 0.07 and 1.51 ng/Nm^3. This level was similar to the findings of the report of Abad *et al.*[8] who found that in MWI flue gases, the total PCN concentration ranged between 0.33 and 5.72 ng/Nm^3, and the TEQ ranged from 0.0002 to 0.002 ng/Nm^3.

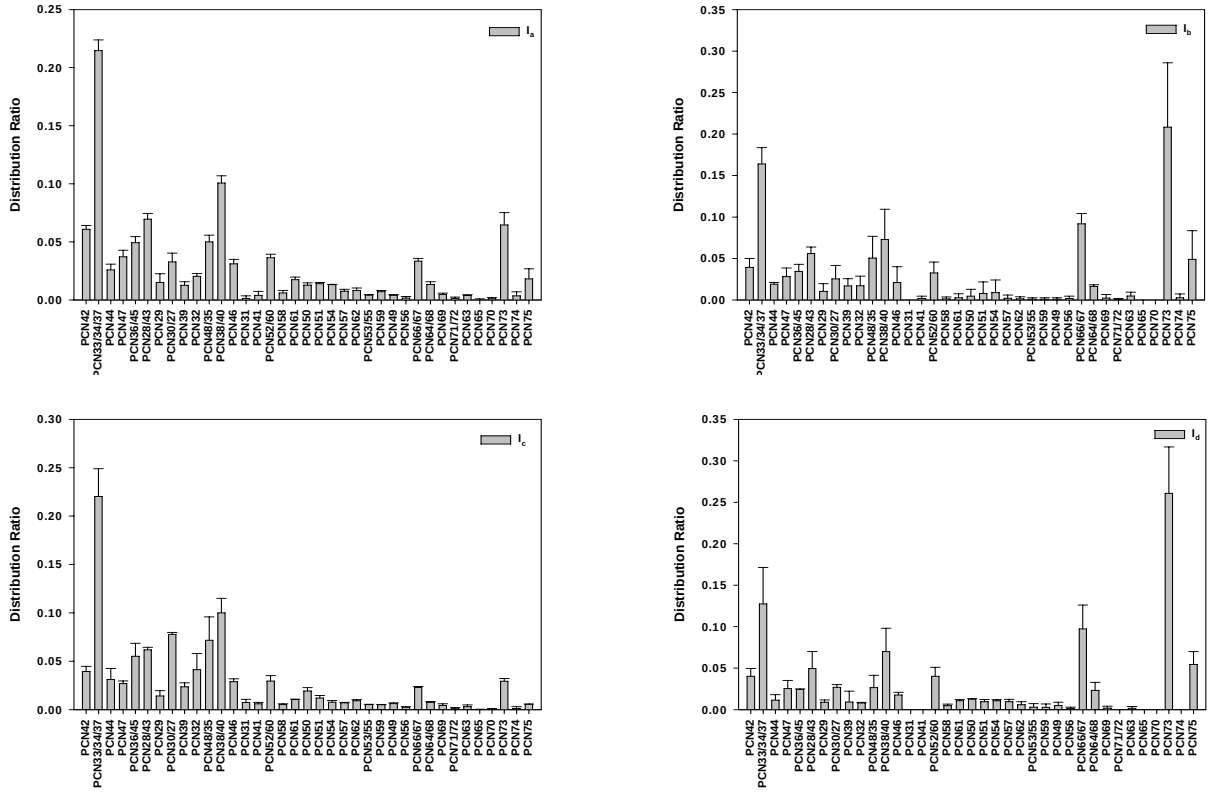

Figure 1. PCNs profiles in MSWI stack gas

Combustion Congener

Hexa-CN-66/67 and hepta-CN-73 could be labeled as combustion markers[1,3]. Thus, the relative enrichment of these congeners as compared to the Halowax series can be explained by contributors from combustion sources.

Due to their high octanol-water partition coefficients and NVC-Cl structure, these congeners are more likely to bioaccumulate[1]. Additionally, tetra-CN congeners have $\log K_{ow}$ values of approximately 6, and there is only one NVC-Cl CN, namely, tetra-CN-42. Therefore, most tetra-CN congeners are relatively easier to metabolize than the more chlorinated compounds. The hepta-CN-73/total PCN percentage was 19.6%, 18.3%, and 15.8% in the workers, nearby residents, and referential inhabitants, respectively. These data showed a clear enrichment of hepta-CN-73 in the serum samples of the workers and nearby residents as compared to hepta-CN-73 in the serum samples of the inhabitants residing >10 km away from the MSWI.

In summary, the tetra-, penta-, and hepta-CN homologues were dominant and contributed approximately 84% of the total detected human serum PCN concentration. Moreover, the most predominant congener, i.e., hepta-CN-73, was not detected in the technical mixtures, which might be explained by the underlying combustion processes. Further long-term monitoring of PCN levels in rural areas would be useful to understand the effect of incineration on PCN distribution in humans.

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