



Relative importance of polychlorinated naphthalenes compared to dioxins, and polychlorinated biphenyls in human serum from Korea: Contribution to TEQs and potential sources

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Hepta-CN-73 from combustion sources was the predominant and major toxic congener in human serum.

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ABSTRACT

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs) in human have been studied extensively; however, polychlorinated naphthalenes (PCNs) have been studied less widely. The mean concentrations of PCNs, PCDDs, PCDFs, and PCBs in 61 healthy human volunteers were 2170 pg/g lipid, 452 pg/g lipid, 116 pg/g lipid, and 120 ng/g lipid respectively, and the mean toxic equivalents (TEQs) contributed by PCNs, PCDDs, PCDFs, and PCBs were 5.88, 5.22, 5.48, and 5.33 pg/g lipid, respectively. PCNs contributed to 26.8% of the total TEQs. 1,2,3,7,8-PeCDD, 2,3,4,7,8-PeCDF, PCB126, and hepta-CN-73 accounted for >62% of the total TEQs in the human serum samples. The overall serum PCN homologue profiles of all subjects were dominated by tetra- and penta-CN homologues, and the most predominant individual congener was hepta-CN-73, which contributed 17.5% of the total serum PCN concentration. Enrichment of hepta-CN-73 in the human serum samples might be due to contributors from combustion sources.

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1. 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 (Falandysz, 1998, 2003). Besides being industrially produced, PCNs are also released into the environment as byproducts of PCB-containing commercial mixtures (Haglund et al., 1993; Järnberg et al., 1997). PCNs are also formed in various incineration processes (Crookes and Howe, 1993; Falandysz, 1998) and in industrial processes such as the production of magnesium (Ofstad et al., 1978), copper (Theisen et al., 1993), and chloroalkalis (Järnberg et al., 1993; Kannan et al., 1998). The production and use of PCNs has been banned in the US and Europe since the 1980s; however, they persist in the environment due to their lipophilic and

bioaccumulative properties (Corsolini et al., 2002; Falandysz, 1998, 2003; Schuhmacher et al., 2004; Sum et al., 2007).

The toxicity of PCNs is similar to those of polychlorinated-*p*-dibenzodioxin/dibenzofurans (PCDD/Fs) and PCBs, with measured relative potencies (REPs) and proposed toxic equivalency factors (TEFs) (Blankenship et al., 2000; Puzyn et al., 2007; Villeneuve et al., 2000). While PCDD/Fs and PCBs have been studied for more than 2 decades, relatively a small number of reports on PCNs are available. Although studies on a few PCN congeners in human samples have been performed using adipose tissue, breast milk, liver, and blood samples, the number of samples has been small (Haglund et al., 1995; Hayward et al., 1989; Kunisue et al., 2009; Norén and Meironyté, 2000; Ryan and Masuda, 1994; Weistrand and Norén, 1998; Weistrand et al., 1997; Williams et al., 1993; Witt and Niessen, 2000). 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.

In this study, we quantified the PCN profiles of individuals working in municipal solid waste incinerators (MSWIs), residents staying near the MSWIs, and the general population living in large cities. The total PCN concentrations as well as the concentration of

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each PCN congener in the serum samples was measured, and the TEQs calculated for PCNs were compared with those estimated for PCDDs, PCDFs, and PCBs in order to evaluate the relative importance of these contaminants. Additionally, we also identified the PCN patterns in the stack emission gas samples. Using these results, we evaluated the potential exposure of MSWI workers and residents living near the MSWIs to PCNs and also investigated for the plausible compounds that determine the effects of exposure on the total serum PCN concentrations in humans.

2. Materials and methods

2.1. Blood and flue gas sampling

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 (see [Supplementary information](#)). Fifty blood samples were obtained from worker volunteers at I_a ($n = 14$, designated as W) and from the nearby residents living within 0.3 km of the facility ($n = 36$, designated as R) in 2007. Additionally, 11 samples were obtained from the inhabitants (designated as B) living >10 km away from the MSWI. Information on the age, smoking habits, diet, occupational history, and medical history was obtained from a questionnaire, and the body weight and height of each subject was measured during the survey. Approximately 100 mL of blood (without anticoagulant) was collected from each of the volunteers who had been instructed not to eat breakfast on the day of sample collection. Each sample was separated into serum and cruent and filled manually into 50-mL contamination-free (sterile) Pyrex bottles with Teflon-coated tops. All samples were kept frozen at -20°C until analysis. Along with blood collection, we also collected and analyzed representative stack gas samples from the 4 MSWI facilities. The stack gas samples were collected 3 times from I_a and I_b and twice from I_c and I_d. The protocol followed for sample collection was the Korean Standard Method, a modified version of US EPA method 23 (Oh et al., 1999).

2.2. Chemical analysis

Approximately 30 g of serum was added to a 500-mL separating funnel and spiked with a set of ^{13}C -labeled PCDDs, PCDFs, PCBs, and PCNs as the surrogate internal standard. The sample was subjected to liquid/liquid extraction with 200 mL of acetone and hexane (2:1) and was processed through 2 cleanup steps, i.e., multilayer silica chromatography (2 g of silica, 8 g of 44% sulfuric acid-silica, 2 g of silica, 4 g of 30% NaOH-silica, and 2 g of silica) followed by alumina chromatography (10 g of acidic alumina). For the stack gas samples, the water/ethylene glycol and resin/filter samples were spiked with a mixture of ^{13}C -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 -labeled recovery standard. The details of chemical analysis and quality assurance/quality control (QA/QC) of PCNs have been included under [Supplementary information](#). The PCNs were analyzed using a DB5-MS column. The PCDDs, PCDFs, PCBs, and analytical procedures used in this study have been previously described in detail (Ikonomou et al., 2001; Park et al., 2007).

2.3. Data analysis

Descriptive statistics were used to characterize the level of the congeners in the serum and stack gas samples. One-way analysis of variance (ANOVA) was used for normally distributed variables and Kruskal–Wallis test, for the remaining variables. The correlation between the variables (age, proportional body fat, body burden, etc.) and serum concentrations of the congeners was examined using Spearman correlation coefficients. Multivariate analysis of the results was performed to elucidate the differences in PCDD/F, PCB, and PCN congener patterns between the sources and those detected in human serum. Data matrices were evaluated by principal component analysis (PCA). Hierarchical cluster analysis (HCA) was used according to the average linkage between the groups on a square Euclidian distance matrix derived from the PCA scores in order to identify the homogeneous groups. The level of each congener below the limit of detection (LOD) assigned to a value of zero. All statistical analyses were carried out using SPSS 12.0. A significance level of 0.05 was used for all tests.

3. Results and discussion

3.1. PCNs in human serum

The overall serum PCN profiles of all subjects were dominated by the tetra- and penta-CN homologues; the actual mean

concentrations measured were 1020 and 419 pg/g lipid, respectively. In the R and B groups, the tetra- and penta-CN homologues were most prevalent; however, in the W group, the tetra- and hepta-CN homologues were the primary contributors. The total PCN concentrations and those of the individual homologues in the sera from the R, W, and B groups were similar, and there was no significant difference among the 3 groups ([Table 1](#)). To our knowledge, the only available study on the effect of possible occupational exposure on plasma PCN levels failed to demonstrate a significant difference in the plasma PCN levels between the exposed workers (cable incineration and installation and reparation of electronic items) and unexposed controls (Weistrand et al., 1997). However, that study was conducted on only 5 workers and 6 controls, and the sum of the concentrations of the 6 congeners ranged from 152 to 677 pg/g lipid. Individuals from the Yu-Cheng incident showed extraordinarily high blood PCN concentrations, i.e., up to 30 400 pg of PCN66/67 per g of lipid (Ryan and Masuda, 1994).

The mean serum concentration of $\sum\text{Cl}_{4-8}\text{CN}$ among the participants, estimated to be 5 and 19 times that of the serum concentrations of $\sum\text{Cl}_{4-8}\text{DD}$ and $\sum\text{Cl}_{4-8}\text{DF}$, respectively, was 2170 pg/g lipid. The PCDD profile was dominated by the most chlorinated congener, i.e., OCDD, accounting for approximately 60.6% of serum $\sum\text{Cl}_{4-8}\text{DD}$. Comparison of the individual PCDF homologue concentrations suggested that the R and W group sera contained relatively higher levels of the hepta-CDF homologue as compared to the B group sera. Even if there was no significant difference among the 3 groups, elevated levels of the hepta-CDF homologue might be indicative of exposure to incineration (Park et al., 2009). The mean serum concentration of $\sum\text{Cl}_{4-7}\text{CB}$ was greater than that of $\sum\text{Cl}_{4-8}\text{CN}$ by 2 orders in magnitude. The hexa- and hepta-CB homologues accounted for >65% of serum $\sum\text{Cl}_{4-7}\text{CB}$ in all subjects. The PCB patterns observed in this study were very similar to those observed in previous studies that we had recently conducted on human serum samples (Park et al., 2009, 2007).

The PCN congener distribution pattern in the human serum samples did not differ significantly among the 3 groups ([Fig. 1](#)). 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. In previous studies, the dominant PCN congeners in human breast milk, plasma, liver, and adipose tissue samples were penta-CN-52/60 and hexa-CN-66/67; some tetra-CN congeners were also detected (Kunise et al., 2009; Lundén and Norén, 1998; Weistrand and Norén, 1998; Weistrand et al., 1997). In a study of the PCN concentration in adipose tissues from children in Germany, Russia, and Kazakhstan, tetra-chloronaphthalenes were the most prevalent, with concentrations ranging from 900 to 7000 ng/kg lipid (Witt and Niessen, 2000).

PCN congeners without adjacent carbons not substituted with chlorine (NVC-Cl) are resistant to metabolism and are hence more likely to bioaccumulate (Helm et al., 2008). Generally, congeners with $\log K_{ow} < 6$ are easily biodegraded or excreted by aquatic organisms, and those with $\log K_{ow} > 7$ have difficulty in accumulation due to their water solubility and steric reasons (Barron, 1990). Theoretically, bioaccumulation of PCNs with $\log K_{ow}$ values between 6 and 7 is rather easy. Although a few congeners were measured by a physical experiment, computational modeling could estimate the $\log K_{ow}$ of all PCN congeners. Tetra- to octa-CN congeners showed $\log K_{ow}$ values of approximately 6–7 (Puzyn and Falandysz, 2005, 2007).

According to the literature, the patterns of PCNs in air samples from urban areas were dominated by less chlorinated homologues,

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