CONCENTRATIONS AND TOXIC-CONGENER PATTERNS OF PCNs, PCDD/Fs, PCBs IN KOREAN HUMAN SERUM

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Abstract
Concentrations of Polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), naphthalenes (PCNs), and biphenyls (PCBs) in human serum samples were measured in 27 healthy volunteers. The mean concentrations of PCNs, PCDDs, PCDFs, and PCBs were 1913.27 pg/g lipid, 652.99 pg/g lipid, 135.08 pg/g lipid, and 199.87 ng/g lipid, respectively. The mean TEQs contributed by PCNs, PCDDs, PCDFs and PCBs in human serum samples were 1.92, 3.53, 6.09, 4.74 pg/g lipid, respectively. Contribution of PCNs to TEQs was 11.8 % of the total TEQs. 23478-PeCDF, PCB126 and PCN73 accounted for 50.9 % of total TEQs in human serum samples. PCN73 was the most predominant congener which contributed 22.7% of total PCN human serum concentrations. PCN66/67 and PCN33/34/37 accounted for more than 10% of the total PCN concentrations, respectively.

Introduction
Polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), naphthalenes (PCNs), and biphenyls (PCBs) are ubiquitous environmental contaminants and well-known byproducts formed in thermal processes. [1] They are chemically and environmentally stable, semi-volatile and bioaccumulable. While PCDDs, PCDFs, and PCBs have been studied for more than two decades, only few reports have been available for PCNs. Moreover, studies about PCNs in human samples are limited. Several PCN congeners have dioxin-like toxicity[2,3], even though they did not assign TEF. In this study, the TEQs calculated for PCNs were compared with those estimated PCDDs, PCDFs, and PCBs to evaluate the relative importance of these contaminants in serum samples from inhabitants around MSWIs. And total concentrations of PCDDs, PCDFs, PCBs, and PCNs in human sera were investigated.

Materials and Methods
Sampling & Storage: Twenty seven human serum samples were obtained in 2003 from volunteer workers (n=9) and residents (n=18) 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.

Sample analysis: Approximately 40 g was analyzed for congener-specific PCDD/Fs, PCBs and PCNs, as well as lipid content. Unfrozen serum samples were spiked with a mixture of $^{13}C_{12}$-labeled PCDD/Fs, PCBs, PCNs as internal standards. They were mixed with Sodium oxalate saturated water. The solution was extracted 3 times using 200 ml of 2:1 acetone/hexane for each extraction. The resultant organic layer was filtered and evaporated to dryness in order to evaluate the lipid content in the samples. Lipid content was determined by gravimetric. Dried samples were resuspended in hexane and subjected to further cleanup via multilayer-silica, alumina column. Identification and quantification of each congener was performed on HP 6890N gas chromatograph coupled to a JEOL JMS-800D high-resolution mass spectrometer.

Data analysis: *t*-test was used to determine whether mean changes in PCDDs, PCDFs, PCBs and PCNs concentrations were significantly different for categorical variables such as occupation and gender. The correlation between variable (age, percent body fat, body burden) and blood concentrations of the congeners was examined by the Spearman rank correlation coefficients and regression.

Results and Discussion

Concentrations
Total PCN concentrations in human serum samples were 1913 pg/g lipid. The workers contained slightly higher

concentrations (2192 pg/g lipid) than those of the residents (1773 pg/g lipid), although the difference was not statistically significant between the two groups ($p>0.05$). Concentrations of PCDDs and PCDFs were 3 and 14 times, respectively, less than those of PCNs. The workers showed slightly higher levels of PCDDs and PCDFs than the residents even though no statistically significance. Concentrations of PCBs in serum samples were 2 orders of magnitude greater than those of PCBs. There was no significant difference between workers and residents for PCBs concentrations (Table 1). Additionally we compared between concentrations of the males and those of the females (data not shown). There were also no remarkable differences for all homologues between gender groups. OCDD, H7CDFs, T4CNs, H6CBs were the most predominant homologue in PCDDs, PCDFs, PCNs, and PCBs, respectively.

Table 1. Concentrations of PCDDs, PCDFs, PCNs and PCBs in human serum samples

	Total (n=27)		Resident (n=18)		Worker (n=9)		*p*-value
	Mean	**Median**	**Mean**	**Median**	**Mean**	**Median**	
T4CDD*	24.32	13.02	16.10	8.03	40.77	13.02	0.35
P5CDD*	2.54	0.00	0.50	0.00	6.62	0.00	0.71
H6CDD*	114.59	109.89	71.40	21.75	200.98	158.90	0.08
H7CDD*	161.18	80.25	110.56	52.82	262.43	124.23	0.29
OCDD*	350.35	221.20	312.13	212.70	426.79	224.42	0.46
T4CDF*	10.13	0.00	6.31	0.00	17.78	12.31	0.06
P5CDF*	18.84	13.91	12.98	10.45	30.56	14.80	0.22
H6CDF*	26.83	20.81	28.11	27.15	24.25	18.01	0.70
H7CDF*	60.26	27.76	65.21	23.17	50.36	28.38	0.66
OCDF*	19.02	0.00	11.67	0.00	33.71	0.00	0.98
T4CN*	717.92	629.05	641.04	597.77	871.69	663.42	0.23
P5CN*	337.38	318.95	327.25	329.49	357.66	318.95	0.68
H6CN*	318.31	227.43	290.76	205.05	373.41	387.87	0.44
H7CN*	463.58	326.26	449.07	319.29	492.60	432.84	0.71
O8CN*	76.27	64.42	65.30	62.42	98.21	99.52	0.30
T4CB**	61.16	46.20	58.27	42.08	66.95	66.51	0.57
P5CB**	36.49	28.83	36.11	28.44	37.26	30.33	0.90
H6CB**	66.76	57.75	63.20	58.94	73.88	40.05	0.66
H7CB**	35.45	27.73	32.29	32.83	41.78	20.62	0.56
$\sum Cl_{4\text{-}8}DD$*	652.99	426.19	510.69	330.59	937.58	554.47	0.23
$\sum Cl_{4\text{-}8}DF$*	135.08	73.29	124.29	58.13	156.66	95.72	0.62
$\sum Cl_{4\text{-}8}CN$*	1913.47	1703.34	1773.42	1641.05	2193.56	1812.00	0.29
$\sum Cl_{4\text{-}7}CB$**	199.87	157.37	189.87	162.89	219.86	155.61	0.61

* unit: pg/g lipid, ** unit: ng/g lipid

TEQs

Toxic equivalency factors (TEF) or relative potencies have been reported for several PCN congeners based on *in vitro* bioassays using H4IIE rat hepatoma cells.[2,3,4] We could estimate TEQs for PCNs by summing the product of concentrations and their corresponding TEFs. Therefore we compared TEQs contributed by PCNs, PCDDs, PCDFs and PCBs. The mean TEQs contributed by PCNs, PCDDs, PCDFs and PCBs in human serum samples

were 1.92, 3.53, 6.09, 4.74 pg/g lipid, respectively. Contribution of PCNs to TEQs was 11.8 % of the total TEQs, which is the least among PCNs, PCDDs, PCDFs and PCBs (Figure 1). The TEQ levels of PCDDs, PCDFs and PCNs in the workers showed slightly higher than those of the residents, although there was not significant.
PCN73 accounted for 65.8 % of the PCN-TEQs in human serum samples. 123678-HxCDD and 1234678-HpCDD were the predominant congeners for the PCDD-TEQs, those accounted for 24.6 % and 23.5 %, respectively. 23478-PeCDF was a major contributor (57.7%) to the PCDF-TEQs. PCB126 accounted for 74.0 % of the PCB-TEQs in human serum samples.

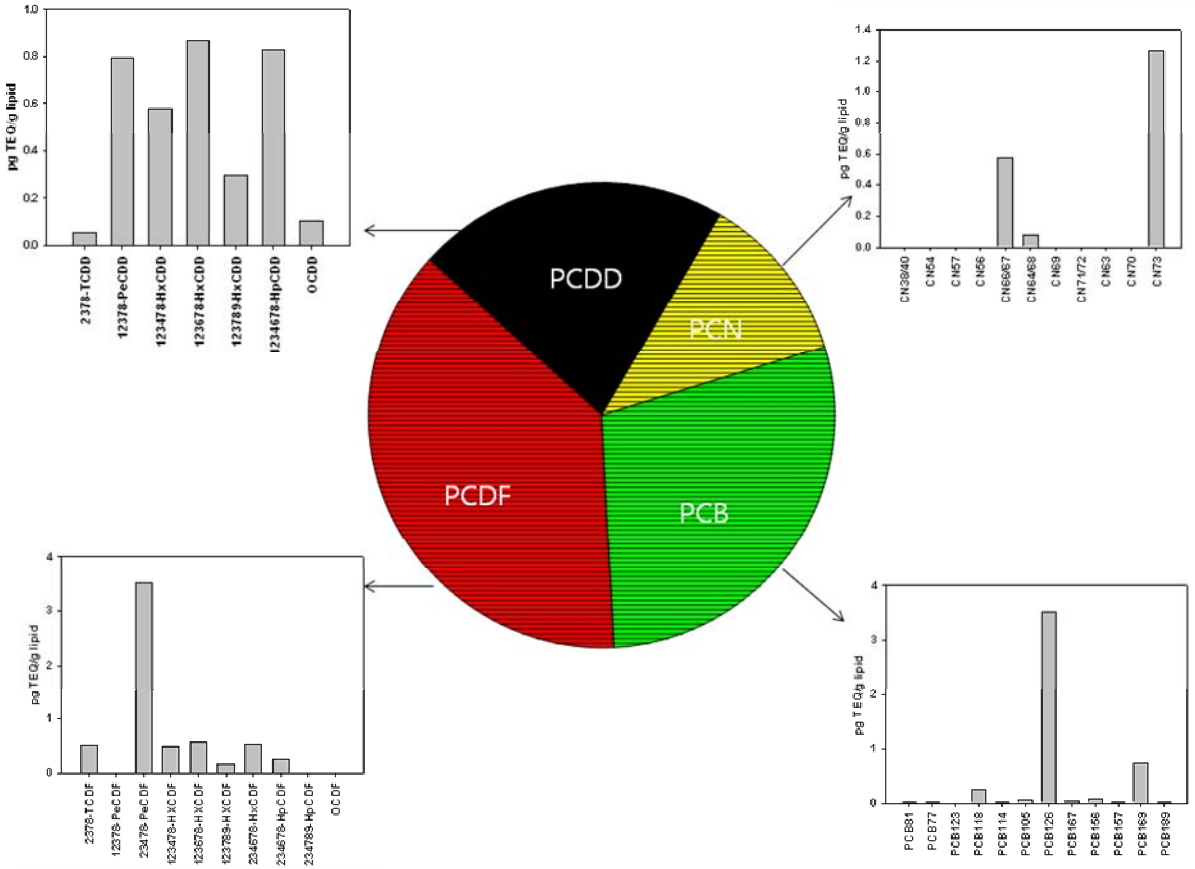

Figure 1. Contribution of TEQs of PCNs, PCDDs, PCDFs, and PCBs in human serum samples

PCN congeners
Tetra- and heptachloronaphthalenes accounted for 61.7% of the total PCN concentrations in human serum samples. HpCN congener 123467 (PCN73) was the most predominant congener which contributed 22.7% of total PCN concentrations. PCN66/67 (123467/123567) and PCN33/34/37 (1246/1247/1257) accounted for more than 10% of the total PCN concentrations, respectively. PCN 38/40 was also a major contributor (8.2%). Some PCN congeners, such as PCN48 (2367), PCN66/67 can serve as combustion marker congeners because of their formation during thermal process.[5,6] The mean levels of PCN48 and PCN66/67 in human serum samples were 9.62 and 229.65 pg/g lipid, respectively. However, we could not find any significant difference although the workers showed slightly higher levels.

In this study, we evaluated TEQs and concentrations of PCNs, PCDDs, PCDFs and PCBs in human serum samples. The mean TEQ concentration was 16.38 pg TEQ/g lipid, PCBs contributed more than 98% of total

concentration. Although there was no report about the employment of technical PCN mixtures in Korea, PCN concentrations were 3 times higher than PCDD/Fs. The concentrations of PCNs, PCDD/Fs in the workers' sera showed slightly higher than the residents' although there was no significant difference. These finding suggest that PCNs, PCDD/Fs and PCBs from MSWI emissions is not much enough to affect the human body burden.

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