Levels of Non-ortho- and Mono-ortho-substituted Polychlorinated Biphenyls in Human Serum Near to Waste Incinerator from Korea

Kyoung-Sim Kim[1], Kim Jong-Guk[1], Kim Yeon-Je [2]

[1]Dept. of Environmental Engineering, Chonbuk National University, Jeonju
[2]Doping Control Center, Korea Institute of Science and Technology, Seoul

Introduction

Dioxins and PCBs are the most important persistent organic compounds found in the environment, which are toxic to human and other living organisms. Now a days, environmental contamination by dioxin is mainly from the waste incinerator emissions and also from other sources. Hence, the control and monitoring of dioxins are having much important role in developed countries when the environmental management is concerned. These chemicals are ubiquitous in the environment and, therefore, it can be also found in adipose tissues, human milk, blood plasma, and serum of the human.

Community exposure to PCBs occurs primarily through the dietary intake of foods which are contaminated with PCBs1. Biological concentrations of PCBs can be significantly influenced by serum lipid content; therefore, PCB values should be assessed in lipid content in order to compare between the populations. Most of the human health effects associated with PCBs were from the occupational exposures and were related to total PCBs2. Especially, coplanar PCBs (Co-PCBs) are considered as the most toxic congeners because of their TCDD like characteristics. The literature indicates that Co-PCBs, 3,3',4,4'-tetrachlorobiphenyl (PCB 77), 3,3',4,4',5-pentachlorobiphenyl (PCB 126), and 3,3',4,4',5,5'-hexachlorobipheny (PCB 169), produce a number of health effects in some species of animals. These health effects include body weight loss, thymic atrophy, dermal disorder, hepatic damage, tetratogenicity, reproductive toxicity and immunotoxicity3.

The previous reports from USA and Europe showed that the milk and beef were of good indicators for the evaluation of the environmental impacts due to incinerators. In Japan, the shellfishes and fishes contaminated with PCDDs

contribute significant amount to human. Though there are many studies related to human exposure, toxicity and health effects due to PCDD/Fs, there are only few reports are available in Korea. In this study, we provide specific-congener data of Co-PCBs in serum of the residents living near to the waste incinerator.

Materials and Methods

Study Area and Sampling Sites: The industrial waste incinerator located in Pyoungtak, the rural area in Korea and was started its operation in the year of 1988 and the stopped its operation in the year of 2001. The incinerator was operated to process about an average of 0.8 tons/hr. According to the measurements conducted during 2000 and 2001, the average concentration of PCBs in the stack samples was 10.4 ng I-TEQ/Nm^3.

The surrounding land was used mainly for the cultivation of rice and vegetables. And also number of small-scale factories are scattered over the area. According to the nature of activities, there were no significant emissions of PCDD/Fs around 5 km from the incinerator. Three small-scale waste incinerators were identified within 5 km around the target incinerator. However, from the stack gas measurements, the total PCDD/Fs emissions from these incinerators were found to have little influence to the study area[4].

The blood samples were collected from the residents as follows; 20 samples from the 'near-site zone' peoples and 10 samples from the 'far-site zone' peoples (about 12 km from the incinerator). All the residents were above the age of 20 and have lived there for more than five years. The information about each participant was also obtained which included data about age, gender, occupation, smoking history, diet, and length of the residence period etc., in order to know the association of this factors with Co-PCBs level in blood.

Analytical Methods: Human serum samples were analyzed for the Co-PCBs using numbering system of Ballschmiter and Zell(1980), four non-ortho PCB congeners(#77, #81, #126, #169) and eight mono-ortho PCBs congeners (#105, #114, #118, #123, #156, #157, #167, #189) were determined.

The serum was separated from the blood by centrifugation (HA-1000-3, Han Il Co., Korea). Then it was kept frozen at -25°C until analysis. C^{13}-labeled Co-PCB compounds were used as internal standards (Wellington Laboratories) and were spiked into the homogenized serum samples (30 g). The extraction of PCBs from the serum as follows; which involves the addition of 30ml aqueous saturated ammonium sulfate solution, shaking for 30min, addition of 50ml of 2N-KOH/EtOH, shaking for 30min, and three-fold extraction with 50 ml n-hexane

with liquid-liquid extraction. The extracted hexane layer was passed through anhydrous sodium sulfate column to remove water, and evaporated at 40°C. And then the lipid content in serum sample was measured. The extract was thoroughly washed with concentrated sulfuric acid until the color was disappeared.

The silica gel chromatography (Wakogel S-1, Wako Pure Chemical Industries, Ltd), basic alumina (Activity I, E. Merck) and activated carbon columns (Wako Pure Chemical Industries, Ltd.) were used to clean the extract. An activated carbon-impregnated silica gel column was first eluted with 20 ml of n-hexane containing 25% dichloromethane and the elute was added to the initial fraction of alumina column chromatography for collecting mono-/di-, ortho- and normal PCBs. After that, 200 ml toluene was used to elute PCDD/Fs, ortho and non ortho -PCBs.

HRGC/HRMS analysis: Co-PCBs were analyzed by HRGC (HP6890, Hewlett Packard)/HRMS (AutoSpec, Micromass). The DB-5 (60m, 0.25mm i.d., 0.25μm film thickness, J&W Scientific) column was used to separate Co-PCB congeners. The temperature programs were as follows: 120 °C for 1 min, 40 °C/min to 200 °C, hold for 2 min, 6 °C/min to 320 °C, hold for 5 min (for non-ortho-PCBs); 70 °C for 1 min, 40 °C/min to 190 °C, 1 °C/min to 240 °C, 10 °C/min to 310 °C, hold for 9 min (for mono-/di-, ortho-PCBs). The carrier gas was helium and the electron impact ionization energy was 40 eV. The selected ion monitoring (SIM) mode was used and the resolution was kept higher than 10,000 (5% valley). 12 Co-PCBs were analyzed for congener-specific and the toxic equivalent (TEQ) levels were calculated based on the toxic equivalency factors (TEFs) for human and mammals established by the WHO[5].

Results and Discussion

The levels of non-ortho and mono-ortho PCBs in human serum samples were summarized in Table 1. There is no prominent difference in total levels of Co-PCB between near-site (7.512 pg WHO-TEQ/g,lipid) and far-site (6.205 pg WHO-TEQ/g,lipid) population. In general, the highest level of Co-PCB was 3,3',4,4',5-PeCB(IUPAC No.126) which contributed above 60% of the total coplanar PCB TEQ. On the other hand, the non-ortho PCBs such as 3,3',4,4'-TeCB (IUPAC No.77) and 3,4,4',5-TeCB(IUPAC No.81) were measured below the detection limit (very lower levels). The levels of total PCDD/Fs were ranged from 4.803 to 30.185 pg WHO-TEQ/g,lipid in the near-site, and 6.232 to 22.447 pg WHO-

TEQ/g,lipid in the far-site. The estimated total coplanar PCBs were about half of PCDD/Fs levels.

Table 1. The levels of coplanar PCBs (WHO-TEQ) in the human serum.

(Unit: pg WHO-TEQ/g,lipid)

PCB	Congener	IUPAC No	Near site (n=20)		Far site (n=10)		WHO-TEF
			Mean	Range (Min~Max)	*Mean*	Range (Min~Max)	
Non-ortho CBs	33'44'-TeCB	#77	-	N.D.~0.003	-	N.D.~0.001	0.0001
	344'5-TeCB	#81	-	N.D.~0.001	*N.D.*	N.D	0.0001
	33'44'5-PeCB	#126	*4.985*	1.200~11.000	*3.290*	1.200~6.400	0.1
	33'44'55'-HxCB	#169	*0.351*	N.D.~0.570	*0.273*	0.100~0.710	0.01
Mono-ortho CBs	233'44'-PeCB	#105	*0.142*	0.032~0.380	*0.132*	0.053~0.460	0.0001
	2344'5-PeCB	#114	*0.128*	0.027~0.315	*0.159*	0.036~0.650	0.0005
	23'44'5-PeCB	#118	*0.670*	0.160~1.700	*0.658*	0.270~2.400	0.0001
	2'344'5-PeCB	#123	*0.012*	0.003~0.027	*0.009*	0.004~0.029	0.0001
	233'44'5-HxCB	#156	*0.960*	0.195~2.250	*1.290*	0.250~4.550	0.0005
	233'44'5'-HxCB	#157	*0.262*	0.055~0.500	*0.353*	0.070~1.200	0.0005
	23'44'55'-HxCB	#167	*0.008*	0.002~0.016	*0.009*	0.003~0.028	0.00001
	233'44'55'-HpCB	#189	*0.028*	0.005~0.066	*0.032*	0.008~0.100	0.0001
Total Non-ortho PCB (WHO-TEQ)			***5.302***	**1.200~11.541**	***3.563***	**1.460~3.563**	
Total Mono-ortho PCB (WHO-TEQ)			***2.210***	**0.478~4.753**	***2.641***	**0.706~2.641**	
Total Coplanar PCB (WHO-TEQ)			***7.512***	**1.678~15.168**	***6.205***	**3.021~16.106**	

Figure 1 clearly shows that there are 13 specimens had the value above 7.056 pg WHO-TEQ/g,lipid (mean value). Among these specimens, ten were from the ‘near-site group’ and only three were from the ‘far-site group’. It can not rule out the possibility that the incinerator substantially affected coplanar PCBs in the human blood.

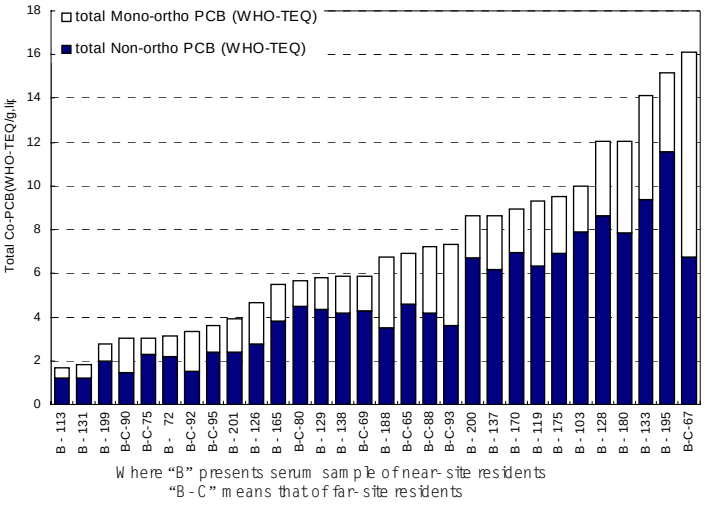

Figure 1. Rank analysis of Co-PCBs TEQ levels in serum sample

Figure 2 presents the total coplanar PCB-TEQ values versus age and gender of human. It is clear that the total coplanar PCBs were proportional to the age in case of female, where as male does not show any proportion with age.

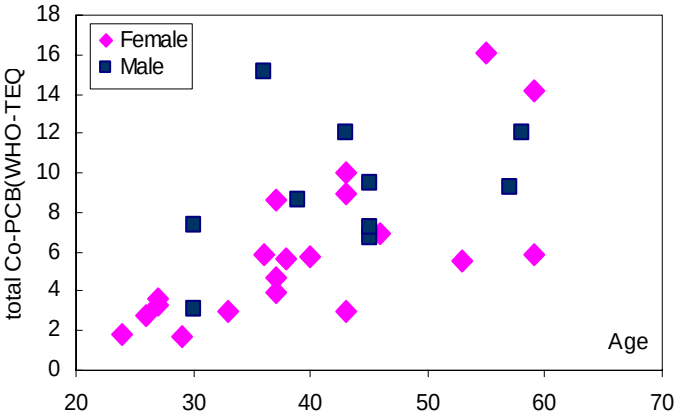

Figure 2. Scatterplot of total coplanar PCBs and age

In Korea, only limited data are available on the levels of PCDD/Fs and PCBs in human blood. According to Yoon-Hee Yang's study, the average TEQ concentration of PCBs in workers were 7.32 pg I-TEQ/g, lipid and for residents it was 7.20 pg I-TEQ/g lipid. This level was slightly higher than the present study,

which is about 7.056 pg-WHO-TEQ/g,lipid (n=30), and these levels were within the background concentrations compared to that of other countries.

This study has provided the data on PCBs, PCDDs and PCDFs in the human serum samples. This may be useful for inter-country comparisons, monitoring of temporal trends or for the assessment of exposure or potentially exposed subpopulations.

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