Comparison Study of Human Exposure Assessment for PCDD/DFs and Dioxin-like PCBs between Koreans and Americans, Using Hair as an indicator

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1. Introduction

The Stockholm convention is a global treaty that was signed in order to protect the human health and the environment from the persistent organic pollutants (POPs). The convention addresses 12 POPs as "Dirty Dozen".[1)] Particularly, Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (DL-PCBs) are known as UPOPs, a chemical substance which unintentionally created from anthropogenic sources. PCDD/DFs and DL-PCBs are contaminants widely distributed in environments and that can be accumulated in organisms through the foodchains.[2, 3)] Also, the dietary intake is noted as a main pathway of the Human exposure to PCDD/DFs and DL-PCBs .[4, 5)]

There have been many studies conducted in order to monitor the human exposure using samples such as the serum of human, human adipose tissue, breast milk from human and etc. However, these samples are hard to obtain in sufficient amounts that could be used for the analysis and evaluation of human exposure. For an example, in order to analyze the blood samples, 100 ml or more of blood is required. Also, in case of analyzing breast milk of human, there is a limit in age range that sample (breast milk) can be collected from. Unlike these samples, human hair can be easily collected from people in wide ranges of age, sex, residential area, eating habits and working environments.[6)]

In this study, human hair samples were used as an indicator of human exposure to PCDD/DFs and DL-PCBs. Also, the trend and range of exposure to PCDD/DFs and DL-PCBs were compared between Korean and American, and Man and Woman.

2 . Materials and Methods

i) Extraction:

The washed and naturally dried hair samples were cut to 0.5 cm to 1cm size. The hair sample was extracted by using the Soxhlet extraction. Before the extraction, spiking was held using $^{13}C_{12}$-labeled-PCDD/DFs and DL-

PCBs Congener as internal standards. The solvents used in the extractions were n-Hexane and dichloromethane. Solvents were mixed to 350mL by 1:1 ratio. The extract samples were concentrated by the Rotary Vacuum Evaporator.

ii) Clean Up of PCDD/DFs and DL-PCBs

PCDD/DFs were cleaned up by using multi layer silica gel column, which contained anhydrous Na_2SO_4, 1g of 10% of $AgNO_3$, 0.2g of silica gel, 1g of 22% H_2SO_4-silica gel, 1g of 44% H_2SO_4-silica gel. The elution was held with 100mL of n-Hexane and was concentrated to 10ml.

The eluted fractions were cleaned-up on an activated neutral alumina (70–230 mesh, Neutral, Merck) column with successive portions of 3% methylene chloride (Dioxin analysis grade, Wako, Japan) in *n*-hexane and 50% methylene chloride in *n*-hexane. The second fraction was concentrated to less than 1 ml, and left at room temperature for one or two days to evaporate to dryness. The residue was dissolved with 30 µl of *n*-nonane (Pesticide residue analysis, Fluka, Switzerland) and determined for PCDD/Fs. Clean-up of the DL-PCBs was performed using only the multi-layer silica gel column, as was used for the pre-cleaning of the PCDD/Fs.[7)8)]

iii) GC-MS Chromatography of PCDD/DFs and DL-PCBs:

High resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) analyses were performed using a HP 6890 gas chromatograph coupled to a JMS 700D mass spectrometer at a resolution of 10 000 in the selected ion monitoring (SIM) mode. An SP 2331 (60 m × 0.25 mm ID × 0.25 µm d.f., Supelco) and a DB-5MS (30 m × 0.25 mm ID × 0.25 µm d.f., J & W Scientific) were used for separation of PCDD/Fs. An HT-8 (50 m × 0.22 mm ID × 0.25 µm d.f., SGE) was used for DL-PCBs analysis.

3. Result and Discussion

The total homologue concentration of 4-8 PCDD/DFs from Korean male sample ranged from 0.87 pg/g to 43.40pg/g with the average concentration of 8.74pg/g. A total concentration of Korean female samples ranged from 9.75pg/g to 32.38pg/g with the average of 20.57pg/g, while the total concentration of American female sample ranged from 11.48 to 213.60pg/g with the average concentration of 75.56pg/g.

The Figure 1 shows the comparison of WHO-TEQ concentration level among male Korean hair, female Korean hair and Female American Hair. The concentration of WHO-TEQ was highest in Female American Hair with the average concentration of 0.16pg WHO-TEQ/g. The second highest was Female Korean hair with the average concentration of 0.07pg WHO-TEQ/g. Finally, the concentration of WHO-TEQ in Male Korean hair had the lowest measure with the average of 0.03pg WHO-TEQ/g. It is considered these differences in results are due to the divergence in dietary intake and the environmental contamination that hair donors are exposed to.

As it is shown in Figure 2, in all three sample categories, there was no pattern discovered in Homologue concentration. In all samples, 4~6PCDDs was not detected but 7-8PCDD/DFs was detected. This result suggests that high chlorinated compounds with high persistency cause great influence in human exposure and body

burden. Figure 3 shows the comparison of the concentration of DL-PCBs in three sample categories. Like PCDD/DFs, the concentration of DL-PCBs in Female American Hair had the highest measure with the average of 1.69 pg WHO-TEQ/g. The concentration of DL-PCBs in Female Korean Hair was the second highest with the average concentration of 0.81 pg WHO-TEQ/g. Finally, Korean Male Hair samples had the lowest concentration of DL-PCBs with the average of 0.58pg WHO-TEQ/g. A congener profile at Figure 3 clearly shows that in all sample categories, the congener 3,3',4,4',5-PCB was the congener with highest concentration and the congener 3,3',4,4',5,5'-PCB had the second highest concentration. However, in case of sample from Korean female, there was no 3,3',4,4',5,5'-PCB.

This result shows that Korean female are less exposed to the environmental pollution than Korean and American male hair donors. The profile patter of PCDD/DFs and DL-PCBs in this study was very similar to the result of previous study conducted by T.Nakao et al. However, the concentration level of PCDD/DFs and DL-PCBs were distinctively different. The concentration level of PCDD/DFs of Korean and American male and female samples was lower than the concentration level of Japanese sample used in T.Nakao et al.'s study. But in case of the concentration level of DL-PCBs, Korean female samples were twice higher and American female samples were three times higher than the Japanese sample [6].

Overall, in comparison of male and female, female samples had higher concentration of PCDD/DFs and DL-PCBs than male samples. However, in order to clearly distinguish the concentration level pattern between male and female, it is necessary to do farther studies on environmental factors, the accumulation ability of male and female, the influence of hormones and metabolism.

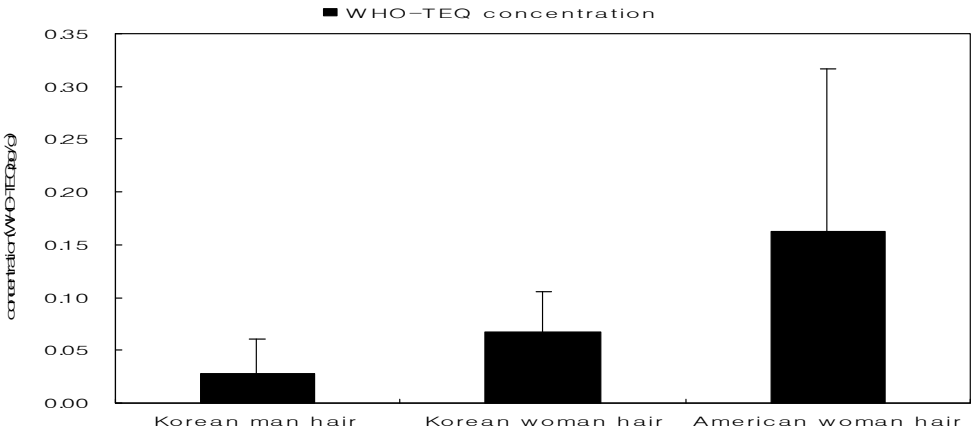

Figure 1. Concentration level (WHO-TEQ) of PCDD/DFs

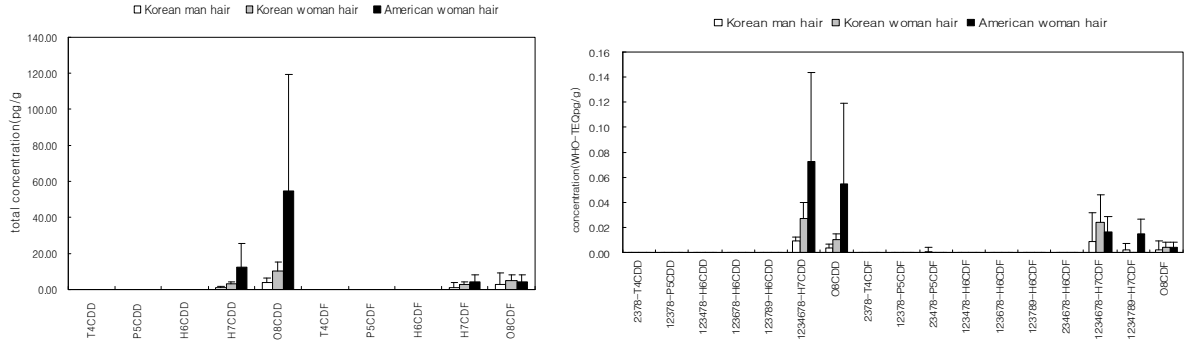

Figure 2. Profile of PCDDs and PCDFs in human hair of Korean man, Korean woman and American woman

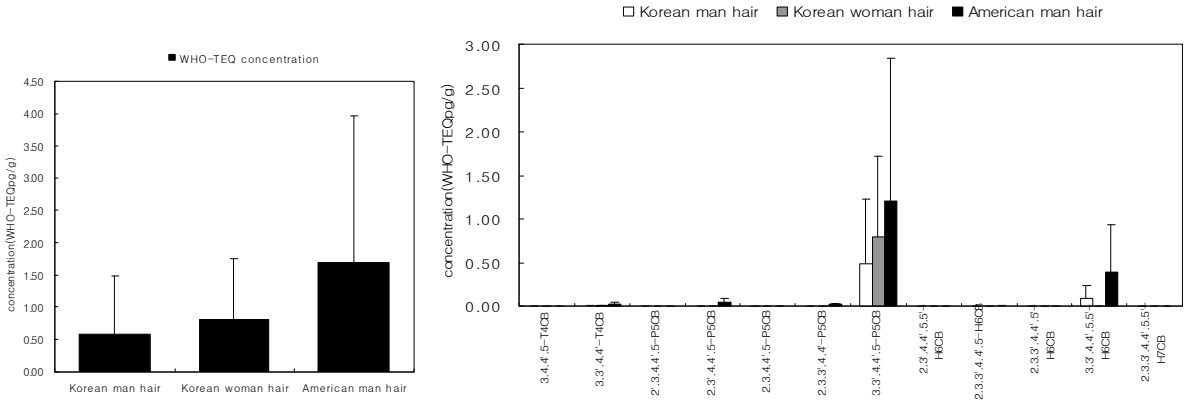

Figure 3. Comparison of concentration level (WHO-TEQ) of DL-PCBs and congeners profile of DL-PCBs in human hair of Korean man, Korean woman and American woman

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