# Hair as an Indicator of Dietary Exposure to Polycyclic Aromatic Hydrocarbons (PAHs) and Polybrominated Diphenyl Ethers (PBDEs)

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***Introduction***

Polycyclic Aromatic Hydrocarbons (PAHs) are the group of organic compounds with two or more fused aromatic rings. PAHs are mostly produced by the incomplete combustion of organic materials. Polybrominated Diphenyl Ethers(PBDEs) are another kind of Persistent Organic Pollutants (POPs) that has long-range transport in atmosphere and bio accumulative in many specious. PBDEs are chemical commonly used as an additive flame retardant that are mainly found in plastic, textiles, electronic devices, furniture and paint. PBDEs are also known to have low vapor pressure and with high log $K_{ow}$. Both PAHs and PBDEs have very solubility to water but highly soluble to lipids. Humans are exposed to PAHs through many routes such as inhalation, dermal, and dietary. The inhalation of air is one was that humans can be exposed to PAHs. Certain amount of PAHs that enters human body is metabolized while some remains accumulated in human body. It is important to assess the human exposure to PAHs and PBDEs through diet because the consuming of the food is the most influential route of exposure to PAHs [1,2,5,6]. Additionally, since PBDEs produced from industry remains in the food chain, PBDEs can cause the dietary exposure.[3]

In this study, hair was used as an indicator of dietary exposure. In many studies hair has been used to assess the drug abuse, medicines and environmental pollutants [4]. Especially, in the past, Persistent Organic Pollutants like dioxins and PCBs were measured using hair as an indicator. The purpose of study is to assess the human's dietary exposure to PAHs and PBDEs, and discover how one's diet habits (vegetarian and non vegetarian) influences the bioaccumulation of PAHs and PBDEs

*Methods and Materials*

**i) Questionnaire and Sample collection**

The hair samples were obtained from all age groups of female. In order to discover the relationship between one's dietary habits and accumulation of PAHs and PBDEs, twelve or more samples were collected from vegetarians. Also, twelve or more samples from non-vegetarians who preferred meat and twelve or more samples from non-vegetarians who preferred sea food were collected. Furthermore in this study, in order to hold the ethnic comparison, Korean hair samples were also collected. Unlike American samples, Korean samples were categorized into two categories: non-vegetarians who prefer meat and non-vegetarians who prefer sea food. For the hair donors, the envelope with number coded zip lock bag, letter to the participants, human subject form and questionnaire was provided. The questionnaire mainly asked participants' dietary habits and living environment.

**ii) 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-BDE 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. The concentrated extract samples were placed in the dry thermo bath where the conversion of solvent occurred. By adding $N_2$, n-hexane and dichloromethane was removed and only Hexane with PAHs or PBDEs was remained in the tube.

**iii) Clean Up of PAHs and PBDEs:**

In the process of Clean up, 130 ° C 16 hour activated silica gel column was used. n-Hexane with dissolved PAHs was passed through the silica gel column. Afterward, the 100mL solution with 10% dichloromethane and 90% hexane was eluted from the silica gel column. The eluted materials were concentrated to approximately 200uL in the room temperature. PBDEs 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 100mL of 10% dichloromethane. The eluants were concentrated to 200uL.

**iv) GC-MS Chromatography of PAHs and PBDEs:**

Instrumental analysis of PAHs was held by using High Resolution Gas Chromatography and Low Resolution Mass Spectrometry (HRGC/LRMS; HP6890/HP5973). The Capillary column used was DB-5 MS (30m x 0.25mm x 0.25um). For PBDEs chromatography instrumental analysis, High Resolution Gas Chromatography/ High Resolution Mass Spectrometry (HRGC, HP6890/HRMS, JMS 700D) were used. The Capillary Column used was DB-5 MS (30m x 0.25mm x 0.25um).

**Result and Discussion**

**i) Concentration levels of PAHs and PBDEs**

The concentration of sum of ∑PAHs16 (sum of 16 PAH compounds) from 18 female American hair ranged from 66.0965ng/g to 769.734ng/g. ∑PAHs16 from 15 female Korean hair ranged from 20.00649ng/g to 401.9172ng/g. The total carcinogenic PAHs from American samples ranged from 7.03ng/g to 69.96ng/g while total carcinogenic PAHs of Korean samples ranged from 0.87ng/g to 11.30ng/g.

In this study 39 Polybrominated compound from mono-BDE to Hepta-BDE was measured. The total concentration of PBDEs of American samples ranged from 6.16 ng/g to 253.93ng/g while the total concentration of PBDEs in Korean samples ranged from 0.155ng/g to 41.158ng/g. In both Korean and American samples, the isomer 2,2,4,4,5-pentaBDE(BDE99) and 2,2,4,4,-TetraBDE(BDE47) were two highest PBDEs measured from the hair samples. In Korean samples, the concentration of BDE 47 was little bit higher than BDE99 as BDE99 ranged 4.210ng/g and the BDE47 ranged 5.172ng/g. Unlike, Korean samples, American sample had higher concentration of BDE99 than BDE 47. The concentration of BDE 99 in American sample was 48.89ng/g and the concentration of BDE 47 was 48.05ng/g. In Korean sample, the concentration of BDE100 was 1.061ng/g while the American sample's BDE100 concentration was 9.76ng/g.

**ii) Evaluation of Dietary Exposure**

**a) PAHs;** In American samples, there were 3 vegetarian samples, 5 seafood samples, 8 non vegetarian (prefer meat) samples. The concentration from vegetarians ranged from 116.30ng/g to 222.49ng/g with the total average of 175.54 ng/g, sea food ranged from 124.90 ng/g to 769.73 ng/g with total average of 308.97ng/g and non-vegetarian who prefers meat ranged from 101.48ng/g to 391.94ng/g with total average of 29.10ng/g. Overall, in American samples the seafood had the highest concentration, non vegetarian was the second highest and the vegetarian diet had the lowest concentration.

The Korean samples were consisted of 9 non vegetarian samples and 4 seafood samples. The concentration of non vegetarian samples ranged from 20.01ng/g to 412.35ng/g with the total of 134.41ng/g. The seafood diet samples ranged from 71.22ng/g to 401.92ng/g with total range of 209.14ng/g.

In American vegetarian samples, the carcinogenic compounds with the highest concentration were benzo[b]fluranthene. In non vegetarian (who prefers meat) samples of Americans, the carcinogenic compounds with the highest concentration was benzo[b]fluoranthene (10.21ng/g

In Korean non-vegetarian samples, the carcinogenic compound with the highest concentration was benzo[g,h,i]perylene (3.09ng/g). The concentration of carcinogenic compound of Korean seafood diet samples was highest in benzo[g,h,i]perylene (13.81ng/g).

**b) PBDEs;** In this study, it was found that the concentrations of PBDEs were not related to the dietary habits. Observing two highest isomers BDE47 and BDE99, the vegetarian diet had the highest concentration of PBDEs

in American samples, and seafood diet and meat diet followed. In case of Korean sample, the seafood diet was higher than the meat diet for BDE 47, while meat diet ranged higher than the sea food diet in BDE99.

Unlike American samples, there was no category of vegetarian diet in Korean samples. However, it should be keep in mind that Korean people's daily diet is main consist of bowl of rice and the side dishes consist of vegetables, seafood and meat. The indication of one's diet was one's preferable or favorite type of food. On the other hand, American samples used in PBDE analysis were consists of 15 non vegetarians who prefers meat and three vegetarians. Overall, the ranges of total concentration of PBDEs from American samples were about five times higher than Korean samples.

**Conclusion**

The study showed that the human exposure to the PAHs is highly related to the one's dietary habits. As it was hypothesized, in both Korea and America the vegetarians were less exposed to carcinogenic and non carcinogenic PAHs than the non vegetarians who preferred seafood and meat. The fact that should be noted is that the seafood caused higher PAHs exposure than the meat. In case of PBDEs, the dietary trend was not found in this study. According to the result it could be concluded that the human exposure of PBDEs is more dependent on living environment rather than the dietary habits. Whether the person is exposed to more electric devices or fabric products which contains fire retardant chemicals determines one's exposure to PBDEs.

Also, one of the most important fact suggest in this study was the concentration difference of PAHs and PBDEs between American and Korean samples. Americans had significantly higher amount of concentration for both PAHs and PBDEs than Korean samples. Through out the history, Korean houses are made of heating system called "Ondol" which is a marble floor that uses natural sources to create heat. However, for a long time, Americans are exposed to the carpet flooring. The carpet is highly consisting of fire retardant chemicals. It is suggested that the great PBDEs concentration difference between American and Korean samples are due to the living environmental factors.

**References**


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