CONTAMINATION LEVELS OF POLYCHLORINATED/BROMINATED COPLANAR BIPHENYLS (Co-PXBs) IN THE MARKET FOODS AND MOTHER'S MILK OF JAPAN

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Abstract

It was firstly investigated the contamination of polychlorinated/brominated coplanar biphenyls (Co-PXBs) in the market foods and mother's milk of Japan. It could detect the Co-PXBs for all samples analyzed, their TEQ levels is fairly equal to the TEQ level of Co-PCBs. Therefore, we concluded that further study with Co-PXBs contamination needs to elucidate their human exposure.

Introduction

Similar to PCDDs/DFs, polybrominated dioxins and benzofuran (PBDDs/DFs) and polychlorinated/brominated dioxins and benzofuran (PXDDs/DFs) are not intentionally produced but are generated as undesired by-products in various processes. They also can be formed by *de novo synthesis* from precursors like BFRs. many researchers has been also reported the presence of PBDD/Fs and PXDD/Fs derived from BFRs in fly ash and/or flue gas of various waste incinerators [1, 2]. As a result, such dioxins have also found throughout the environment. And the intake of these contaminants from food, air and water is the primary route of human exposure. Finally, it was estimated such contamination give rise to adverse effect for human health. By such deep concern, it has been compared some toxicities indicating by PCDD/Fs, PBDD/Fs and PXDD/Fs. *In vitro* ED_{50} values for AHH induction and toxic effect of several PCDDs, PBDDs and PXDDs in the rat were studied [3]. The activities for *in vitro* hepatic AHH induction differed by seven orders of magnitude among the congeners tested, the most active being 2,3-DiBr-7,8-DiCl-DD and the least 1,3,7,8-TeCDD. Similar results were observed for *in vivo* EC_{50} study [4]. Therefore, by measuring only seventeen congeners of PCDD/Fs and twelve congeners of Co-PCBs, it has considered questionable whether safety of human health can find. Thus, current monitoring for twenty-nine of dioxins congeners is sufficient for the evaluation of human health or not? The daily dietary intake level was presently below the tolerable daily intake (TDI) of 4 pg toxic equivalency (TEQ) kg b.w. /day for PCDD/Fs and dioxin-like PCBs (Co-PCBs) in Japan set by the Environmental Agency and Ministry of Health and Welfare of Japan [5]. Also, this dietary intake level was within the TDI range 1-4 pg TEQ/kg/b.w./day recommended by WHO, and it should be noted that the upper range of the TDI of 4pg TEQ/kg b.w. /day should be considered as the maximal tolerable intake on a provisional basis and that the ultimate goal is to reduce human intake levels below 1 pg TEQ/kg b.w. /day. However, if other dioxin congeners like PBDD/Fs, PXDD/Fs Co-PBBs and Co-PXBs include for such calculation, it is very doubtful whether we can keep the above TDI value for the intake of human or not.

By the way, there are also many reports with PCBs and PBBs [6-8], but not with coplanar polychlorinated/brominated biphenyls (Co-PXBs) until present. Because lack of Co-PXBs standard, we have not

been able to investigate its contamination study. However, as mentioned the above, it was estimated that the incineration of consumer products containing such flame-retardant chemicals results in the formation of Co-PXBs. These new contaminants, as well as other dioxins, have high possibility to find in many samples of environmental and biota samples.

In the present study, we aimed to design five Co-PXBs standards having high toxicity estimated, and to investigate its contamination level in the mother's milk of Japan by using their new standards. In addition, as their primary route of human exposure by Co-PXBs, it was also investigated the contamination level in the samples of market food.

Materials and Methods

1) Samples

The samples of mother's milk were collected from three primiparae (age; 21-31 years old, sample A ~ C) and four multiparae (age; 22~33 years old, sample a ~ d) at one week and one month after delivery during 2006. After health conditions, clinical history, dietary and smoking habit etc. among the women were ascertained using the brief questionnaire method, and then selected the above seven healthy women at the beginning of this investigation. Food samples like meat, fish and vegetable were purchased from three markets in Hirakata and Osaka city of Osaka prefecture of Japan in 2006.

2) Analytical method

As shown in Fig. 1, we designed and specially ordered five $^{13}C_{12}$-labelled and four unlabelled Co-PXBs in this study; 4'-MoBr-2,3,3',4-TeCB (structure like PCB #105), 4'-MoBr-2, 3',4,5-TeCB (like PCB #118), 4'-MoBr-3,3',4,5-TeCB (#126A; like PCB #126), 3',4', 5'-TriBr-3,4-DiCB (#126B; like PCB #126) and 4'-MoBr-3,3',4,5,5'-PeCB (like PCB #169) purchased from Cambridge Isotope Laboratories (MA, USA).

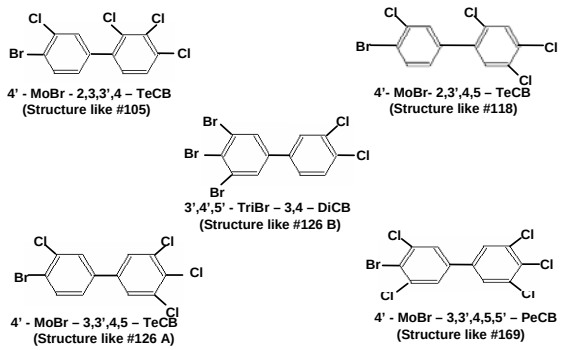

Fig.1 Chemical structure of Co-PXBs used for this study

Each 50 g of mother's milk and food were used for this study. The extractions of Co-PXBs congeners in these samples were performed according to our previous paper[6]. For the analysis of Co-PXBs, the purified method was multi-layer silica-gel column chromatography, with an eluent of n-hexane. The eluate was concentrated and purified by an active carbon mixed silica-gel column with eluent of 25% CH_2Cl_2 in n-hexane (#105, #118) and toluene(#169, #126A&B). All purified sample was analyzed by the use of HP6890 GC-JEOL JMS700 MS (HRGC-HRMS) at high-resolution condition (R=10,000) in EI-SIM mode.

As the evaluation method of toxicity (TEQ level) for Co-PXBs and PXDDs/DFs, It was assumed that the toxicity of same congener of Co-PXBs or PXDDs/DFs is nearly equal to that of Co-PCBs and PCDDs/DFs. On the basis of this assumption, each contribution ratio to total TEQ by PCDDs/DFs, Co-PXBs, PXDDs/DFs and Co-PXBs was calculated by using 2, 3, 7, 8-TCDD equivalent factors (WHO-TEF, 2005). Other detail methods should be referred to our paper[9].

Results and Discussion

From many results of the past Co-PCBs pollution in biological specimen, we selected and investigated to the above five Co-PXBs, having high frequency and high TEF. As shown in Figure 2, it was compared the TEQ

levels by Co-PXBs and Co-PCBs in the market fishes. Co-PXBs were detected in all samples, showing the highest concentration (1.24 pg TEQ/g fresh wt) in young yellow-tail cultured by the coastal area of western Japan, and the concentration of Co-PXBs ranged between 0.13 and 1.24 pg TEQ/g fresh wt. In addition, when the contribution ratio of each congener for total TEQ concentration was calculated, two Co-PXB congeners as #126 type were dominated; 3',4', 5'-TriBr-3,4-DiCB (#126B) detected only in the samples. This data of Co-PXBs is our first observation. On the other hand, the concentration of Co-PCBs ranged between 0.01 and 6.4 pg TEQ/g fresh wt. and high concentrations were observed in two mackerel and Japanese Spanish mackerel, which were captured in East China Sea and Japan Sea. Contamination level by total Co-PXBs (TEQ) from five congeners is fairly equal to that by total Co-PCBs from twelve congeners

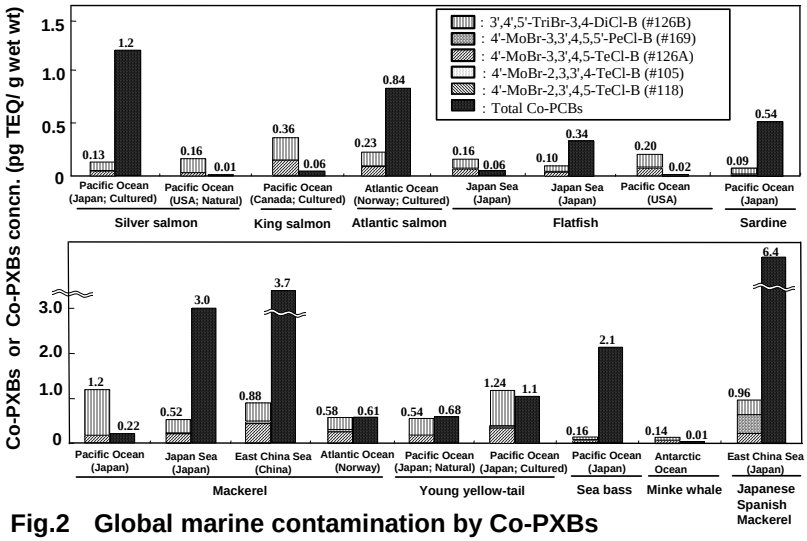

Fig.2 Global marine contamination by Co-PXBs and Co-PCBs observed in the market fishes

1) Contamination level: Fish > Meat > Vegetable

2) Interesting phenomenon: Co-PXBs #126B detect in only fish samples

3) Fish (pg TEQ/g) :

a) Domestic product

per wet wt ; Co-PXBs ; 0.1 ~ 1.3, per fat wt ; Co-PXBs ; 1.9 ~ 26,

b) Imported product

per wet wt ; Co-PXBs ; 0.1 ~ 0.9, per fat wt ; Co-PXBs ; 2.1 ~ 21,

4) Meat (pg TEQ/g) :

a) per wet wt ; Co-PXBs ; 0.0023 ~ 0.06, Co-PCBs ; 0.002 ~ 0.1

b) per fat wt ; Co-PXBs ; 0.03 ~ 0.2, Co-PCBs ; 0.02 ~ 0.3

5) Vegetable (pg TEQ/g) :

a) per wet wt ; Co-PXBs ; 0.0002 ~0.007, Co-PCBs ; 0.005 ~ 0.014

Fig.3 Contamination levels and its characterization of Co-PXBs and Co-PCBs in the food of Japanese market

Fig.3 summarized the contamination levels and its characterization of Co-PXBs and Co-PCBs in the food of Japanese market. As results, the contamination level is fish, meat and vegetable in order, and the level of vegetable was negligible, comparison with that of fish sample. Further, among all sample analyzed, 3',4', 5'-TriBr-3,4-DiCB (#126B) detected only in fish samples, and it was suggested that the contamination pattern by Co-PXBs is mainly diffused by way of water. However, the sources of contamination is presently unclear,

Next, in order to clear human exposure by Co-PXBs, it was investigated the Co-PXBs

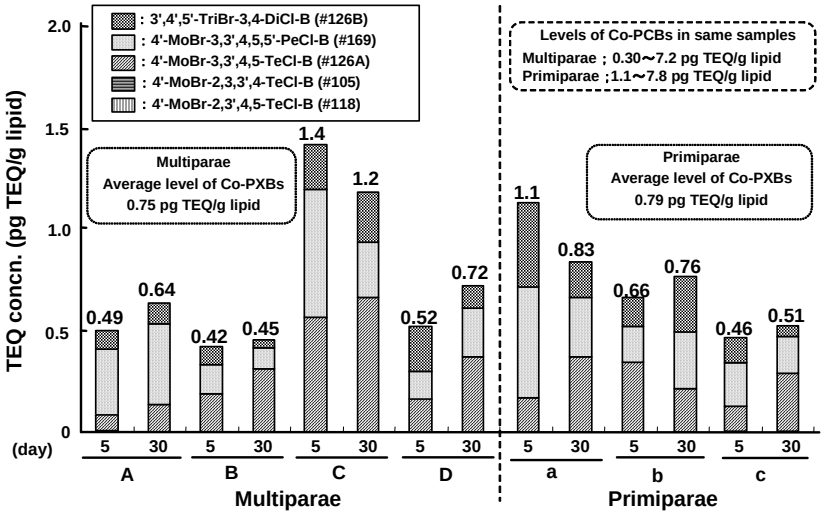

Fig. 4 Comparison of Co-PXBs concn. in the breast milk of Japanese multiparae and primiparae

concentration in the breast milk (sampling day; 5 and 30 days) of Japanese multiparae and primiparae (Figure 4). The concentration of Co-PXBs ranged between 0.42 and 1.41 pg TEQ/g lipid, and this observation is our first finding for human exposure by Co-PXBs. With respect the average TEQ level in mother's milk, there is no difference between of multiparae and primiparae, not in the case of CO-PCBs. Interestingly, when the level of Co-PCBs at 5 and 30 days of same woman was compared, that at 5 days-breast milk samples were higher than that at 30days-samples for almost sample analyzed. However, in the case of CO-PXBs, such tendency was not always observed. Then, the abundant congeners of Co-PXBs were #126A, #126 B and #169, and it was estimated that human exposure by this Co-PXBs #126B is derived from the eating of fish.

As shown in Fig. 5, it was compared the contribution ratio of four kinds of dioxin analogues for total TEQ concentration in mother's milk of Japan. Major analogues were PCDDs/DFs, Co-PCBs and Co-PXBs, and PXDDs/DFs were negligible level, showing unexpected high contribution ratio of Co-PXBs in the breast milk of multiparae. As there are theoretically more few hundreds congeners in the Co-PXBs group, and therefore it needs further detail survey of Co-PXBs contamination

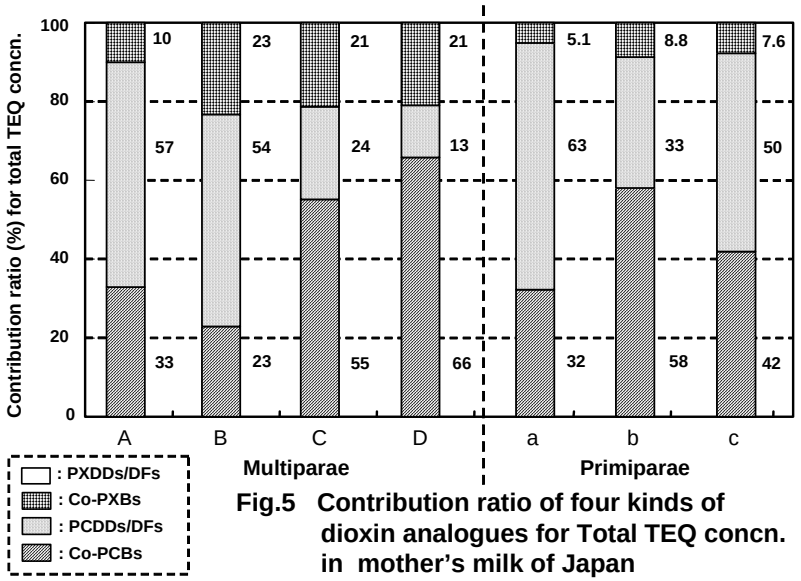

Fig.5 Contribution ratio of four kinds of dioxin analogues for Total TEQ concn. in mother's milk of Japan

Further study is warranted to evaluate whether Co-PXBs exposures to nursing infants pose a health risk. Additional investigations of Co-PXBss in the daily foods are warranted to better understand the nature and extent of Co-PXBs contamination of Japanese food supply.

Ackowlegements

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