Newly Global Pollution by Coplanar Polychlorinated/brominated Biphenyls (CO-PXBs) Suggested from Contamination Study in Japanese Food Samples

Souichi Ohta, Hidekazu Tokusawa, Hirotoshi Magota, Teruyuki Nakao, Osamu Aozasa, and Hideaki Miyata

Faculty of Pharmaceutical Sciences, Setsunan University, 45-1 Nagaotoge-cho, Hirakata, Osaka 573-0101, Japan

Introduction

As is generally known, there has been extremely homologue/isomer of numbers in so-called "chlorinated dioxins". In fact, there are 75 isomers as dibenzo-p-dioxins, 135 isomers as dibenzofurans in polychlorinated dioxins (PCDDs/DFs), while are 209 isomers as biphenyls in polychlorinated biphenyls (PCBs). A number of studies have documented all over the world; it becomes general that PCDDs/DFs and Co-PCBs is easily formed by chemical, photochemical, or thermal reactions and so-called *de novo synthesis*[1,2].

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. As well as the case of Dioxin analogues, many researcher have been reported the presence of PBDDs/DFs and PXDDs/DFs in fly ash and/or flue gas of various waste incinerators [3,4]. As a result, these contaminants have been found to occur throughout the environment. And the intake of these contaminants from food, air and water is suspected to be the primary route of human. We also investigated the levels of PCDDs/DFs, PXDDs/DFs and PBDDs/DFs in human milk of nursing women in Japan (Ohta et al. 2004). The contribution ratio for daily intake of new-born baby as current total TEQ (34pg/kg/day) by each congener was in order, Σ PCDDs/DFs (81%) > Σ PXDDs/DFs (17%) > Σ PBDDs/DFs (2%), and the value of Σ PXDDs/DFs was not negligible level[5]. However, we could not investigate the contamination by coplanar polychlorinated/brominated biphenyls (Co-PXBs) until present. In general, Co-PCBs show high concentration in biota sample. Similar trend will be estimated for the contamination by Co-PXBs.

In this study, we firstly report the contamination of PXDDs/DFs and Co-PXBs in the food of Japanese market.

Materials and Methods

1) Samples

Samples of fish, shellfish, meat, vegetables were purchased from two Japanese food markets in Hirakata and Osaka city of Osaka prefecture of Japan in 2006.

2) Analytical method

As shown in Fig. 1, we used special 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).

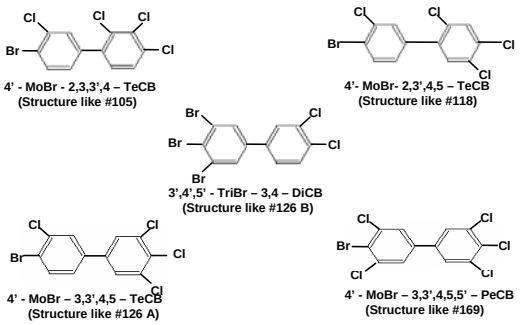

Fig.1 Chemical structure of Co-PXBs used for this study

The extraction of Co-PXBs congeners was 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 dispersed silica-gel column with eluent of n-hexane, CH_2Cl_2: n-hexane (1:3). 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[7].

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). Other detail methods should be referred to our paper[1-3].

Results and Discussion

From many results of the past Co-PCBs pollution in biological specimen[8-10], we selected and

investigated to the above five Co-PXBs, having high frequency observed in biota samples and high TEF. As shown in Figure 2, it was compared the TEQ levels by Co-PXBs and Co-PCBs in the imported fishes. Remarkable phenomenon was observed; Co-PXBs were detected in all samples, showing the highest concentration (21 pg TEQ/g fat wt) in Mink Whale from Antarctic Ocean. TEQ level of seven fish samples except Atlantic salmon and Mackerel were higher than that of Co-PCBs. Further, 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 fish (marine) samples. This data of Co-PXBs is our first observation.

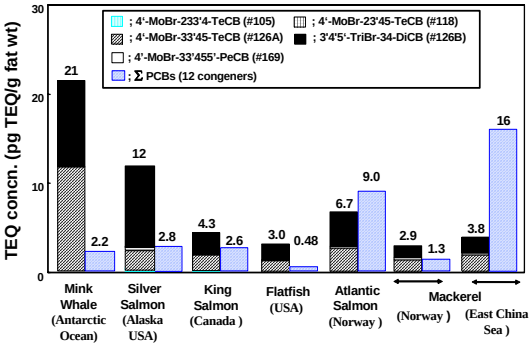

Fig.2 Comparison on TEQ levels of Co-PXBs and Co-PCBs in the imported fishes of Japanese food market

Figure 3 shows SIM chromatogram of the family peak of Co-PXBs by HRGC/HRMS observed in fish sample. As an interesting observation, we could recognize other family peaks like Co-PXBs, except five Co-PXBs studied. Therefore, if we prepare these standards and measure food samples, it will be estimated the TEQ level in food samples will be higher.

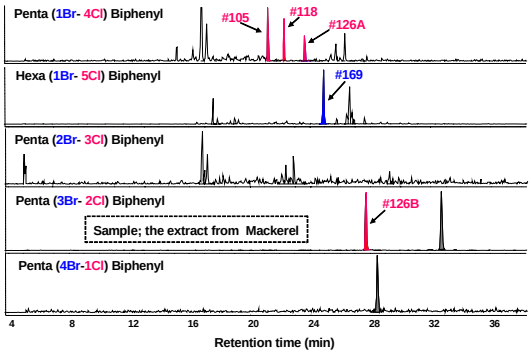

Fig. 3 SIM chromatogram of Co-PXBs in fish sample

Figure 4 summarized TEQ levels of Co-PXBs and Co-PCBs in fish, meat and vegetable. The most high levels of Co-PXBs is fish, and in order, meat and vegetable. Focused on fish data, it was ranged from 0.1 to 1.3 TEQ pg per gram wet weight for domestic products,

1) Contamination level: Fish > Meat > Vegetable

2) 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,

3) 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

4) Vegetable (pg TEQ/g) :

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

Fig.4 TEQ levels of Co-PXBs and Co-PCBs in fish, meat and vegetable of Japanese food market

While, ranged from 0.1 to 0.9 TEQ pg for imported products. With respect to TEQ level in vegetable, it was negligible level. From this all data, we have finally estimated this marine pollution by Co-PXBs is worldwide contamination or global pollution. However, the sources of Co-PXBs are presently unclear.

Additional investigations of Co-PXBs in fish and in various food products and total diet study by PCDDs/DFs, PXDDs/DFs, Co-PXBs and Co-PXBs contamination are warranted to better understand the nature and extent of Co-PXBs contamination of the Japanese food supply. Further study is needed to clarify the pollution sources and human contamination by Co-PXBs.

Acknowledgements

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