# NEWLY FINDING OF COPLANAR POLYCHLORINATED/BROMINATED BIPHENYLS (CO-PXBs) IN THE MARKET FISH OF JAPAN

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## Introduction

As is generally known, there has been extremely homologue/isomer of numbers in so-called "dioxins", which has consisted of halogenated compounds having chemical structure of dibenzo-p-dioxins, dibenzofurans and biphenyls. 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). To evaluate their toxicity, it is present situation that 29 dioxin congener are measured. On the other hand, with respect to polybrominated/chlorinated dibenzo-p-dioxins (PXDDs) and –furans (PXDFs) having the above similar bone structures, there are theoretically about 4600 homologue/isomer, and 2,3,7,8- congeners exist over 900 among them.

We investigated the TEQ levels of PCDDs/DFs (17 congeners), PXDDs/DFs (8 isomer) and PBDDs/DFs (9 congeners) in thirty six samples of mother's milk[1)]. The contribution ratio of PCDDs/DFs, PXDDs/DFs (8 congeners) and PBDDs/DFs (9 congeners) for total TEQ level was 67-93, 11-31 and 0.6-3.1%, respectively. In results, it was observed that such ratio of PXDDs/DFs for human pollution was unexpectedly high, and that of PBDDs/DFs can be ignored. Similar results can refer to human pollution by coplanar polychlorinated/brominated biphenyls (Co-PXBs). However, there is no report with human contamination by Co-PXBs.

In this paper, by using our specially ordered four kinds of Co-PXBs, we investigated PXBs contamination in foods of Japan.

## 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, four $^{13}C_{12}$-labelled and four unlabelled Co-PXBs were used 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 (like PCB #126) and 3',4', 5'-TriBr-3,4-DiCB (like PCB #126) purchased from Cambridge Isotope Laboratories (MA, USA).

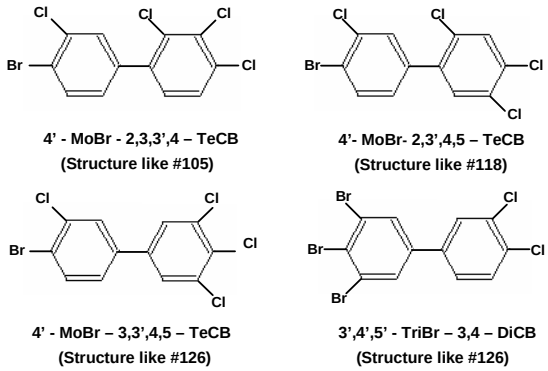


**Fig.1 Newly investigated Co-PXBs structure in this study**

The extraction of Co-PXBs congeners was performed according to our previous paper[2].

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[3].

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[4-6], we selected and investigated to the above four Co-PXBs. The TEQ concentrations of Co-PXBs in edible filet tissue of three species of fish purchased from two Japanese food markets are presented in Table 1. ∑Co-PXBs concentration in fish tissue ranged between 3.6 to 47 pg/g fresh weight. As its detail, it was determined that Co-PXBs and the concentration certain congeners were lowest in sardine (2.8% lipid content), and increased in mackerel (9.3%), followed by natural young yellowtail (3.5%) and were highest in cultured young yellowtail (6.1%). Therefore, it is presently unknown that the species-specific differences observed in the data are likely

more due to differences in lipid content between species than their aquatic exposure.

Next, focus on each Co-PXBs congener, a very interesting phenomenon was observed. Thus, we firstly estimated a high concentration by Co-PXBs which only one substituted bromine atom for in halogenations position of Co-PCBs like 4'-MoBr-2,3,3',4-TeCB or 4'-MoBr-2, 3',4,5-TeCB, but it was unexpectedly detected high concentration of 3',4', 5'-TriBr-3,4-DiCB which three bromine atoms substituted for it in fish samples. This observation suggested the possibility of another pollution sources except the incinerator facilities.

**Table 1. Comparison of TEQ level of Co-PXBs in the market fish of Japan**

| Species | Mackerel [1] | | Sardine [2] | | Young yellowtail [3] | | | |
|---|---|---|---|---|---|---|---|---|
| | natural | | natural | | natural | | cultured | |
| Co-PXBs | A | B | A | B | A | B | A | B |
| 4'-Br-233'4-Cl-B (Structure like #105) | 0.0028 | 0.00022 | 0.090 | 0.0025 | 0.139 | 0.0048 | 0.17 | 0.010 |
| 4'-Br-23'45-Cl-B (Structure like #118) | 0.021 | 0.0017 | 0.48 | 0.014 | 0.017 | 0.00059 | 0.022 | 0.0014 |
| 4'-Br-33'45-Cl-B (Structure like #126) | 0.6 | 0.047 | 0.21 | 0.0058 | 13 | 0.44 | 15 | 0.90 |
| 3'4'5'-Br-34-Cl-B (Structure like #126) | 20 | 1.6 | 2.8 | 0.078 | 24 | 1.6 | 32 | 1.9 |
| Total | 21 | 1.6 | 3.6 | 0.10 | 37 | 1.3 | 47 | 2.8 |

1): lipid content; 9.3%, 2); 2.8%, 3); natural 3.5%, cultured 6.1%, A: pg/g lipid, B: pg/g w.w.

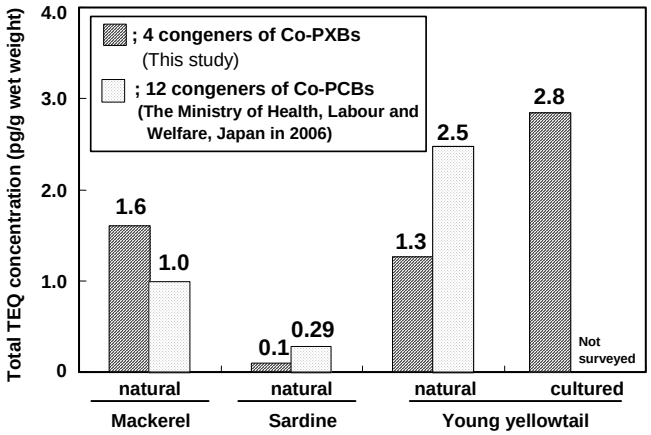


**Fig. 2 Comparison of total TEQ concentrations by Co-PXBs and Co-PCBs in the market fish of Japan**

Fig. 2 compared total TEQ concentrations (pg/g wet weight) by Co-PXBs and the Co-PCBs previously reported by the Ministry of Health, Labour and Welfare, Japan[7] in mackerel, sardine and young yellowtail. It has not yet determined Co-PCBs concentration in three fish samples of this study, however, it has recognized that total TEQ concentrations from only four kinds of Co-PXB congener were higher than that from twelve kinds of Co-PCB congener in the samples of mackerel and young yellowtail. Therefore, by measuring only seventeen congeners of PCDDs/DFs and twelve congeners of Co-PXBs, it has considered questionable whether safety of food can

find. Thus, can we keep the TDI value as below 4pg/kg/day?
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.

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