Field Survey of Newly Dioxin Related Compounds (Polybrominated/chlorinated Biphenyls) in Various Environmental Samples and Estimation of their Contamination Sources

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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). 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. In recent years, we determined PXDDs/DFs, PBDDs/DFs and co-planar polybrominated/chlorinated biphenyls (Co-PXBs) in human milk and foods. In fact, we cleared contamination levels of PCDDs/DFs, PXDDs/DFs, PBDDs/DFs and Co-PCBs/PXBs 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. However, with respect to the environmental pollution by these compounds (PXDDs/DFs, PBDDs/DFs and Co-PXBs), only few reports is presently known. Further, the pollution sources of their compounds and the formation routes of Co-PXBs as emerging POPs are unknown. As a little information, Nakano et al proposed the formation of Co-PXBs during the manufacturing process of $FeCl_3$ under the treatment with substrate etching[2)].

In this paper, we tried to environmental pollution (flue gas, ambient air and sediment) research of PCDDs/DFs, PXDDs/DFs, PBDDs/DFs, Co-PCBs and Co-PXBs. Moreover, we investigated to estimate for PXB (except for six PXB isomers) generation by pyrolysis and photolysis of deca-BDE as BFRs.

Materials and Methods

1) Samples

The flue gas samples (n=20) were collected according to the JIS Z 8808. The burning contents were

municipal solid waste, industrial waste, sewage sludge, respectively. Each sample was extracted based on the JIS K 0311. The ambient air (n=21) samples were collected from various regions in Japan. The ambient air samples were treated with "manual for determination of dioxin related compounds in atmospheric environment". The sediment samples (n=14) were collected from Osaka Bay Areas and Seto Inland Sea. The sediment samples were treated with "manual for determination of dioxin related compounds in sediment".

2) Experimental method

The extracts of environmental specimen were spiked ^{13}C-labelled compounds (PCDDs/DFs, PXDDs/DFs, PBDDs/DFs, Co-PCBs, Co-PXBs). Then, these extracts were treated with sulfuric acid, and cleaned up on a multi-layer column containing Na_2SO_4, 10%(w/w) $AgNO_3$-silica, 22%(w/w) H_2SO_4-silica, 44%(w/w) H_2SO_4-silica, 2%(w/w) KOH-silica and silica with an eluent of 20% methylene chloride in n-hexane. The eluate was concentrated to 0.1 ml, and separated into two fractions with successive eluents of 50 ml of n-hexane, 300 ml of toluene on an activated carbon-blended silica gel (1 g, Wako Pure Chemical Industries, Ltd) column. Second eluate containing PCDDs/DFs, PXDDs/DFs, PBDDs/DFs, Co-PCBs and Co-PXBs was concentrated. The concentrate was left for complete evaporation of toluene in room temperature and then adjusted to a volume of 50 µl with n-nonane. Finally, purified sample was used for analysis of high-resolution gas chromatograph (GC) - high resolution mass spectrometer (MS).

Results and Discussion

Table 1 shows the TEQ concentrations of PCDDs/DFs, Co-PCBs and Co-PXBs in various samples (Flue gas, ambient air and sediment). As the evaluation of toxicity (TEQ concentration) 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; the total average TEQ concentrations were 1.57 ng-TEQ/m^3 (flue gas), 0.028 pg-TEQ/m^3 (ambient air) and 36.7 pg-TEQ/g (sediment), respectively. Co-PXBs were detected with all samples, but the ratio of TEQ concentration was less than 10%. Especially, that ratio of sediment sample was very low (less than 1%).

Table 1 Concentrations of TEQ levels of PCDDs/DFs, Co-PCBs and Co-PXBs in various samples

Samples	Range of total TEQ		Average TEQ concentration			
	Min.	Max.	PCDDs/DFs	Co-PCBs	Co-PXBs	Total
Flue gas (n=20) [ng-TEQ/m^3]	0.01	6.79	1.39	0.13	0.05	1.57
Ambient air (n=21) [pg-TEQ/ m^3]	0.002	0.145	0.021	0.005	0.002	0.028
Sediment (n=14) [pg-TEQ/g dry wt.]	9.98	109	30.6	5.96	0.132	36.5

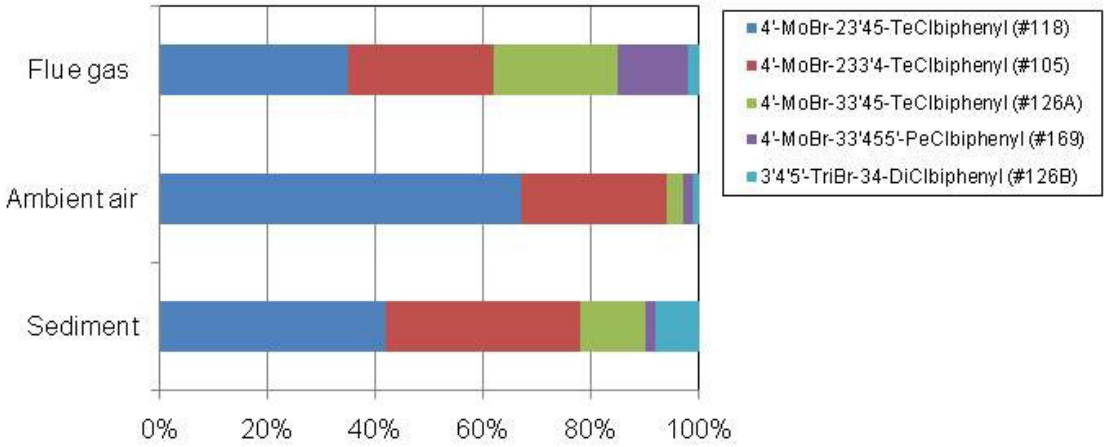


Fig. 1 Contribution ratio (%) for actual concentration by five congeners of Co-PXBs

As shown in Figure 1, it was compared the average contribution ratio for actual concentration by five Co-PXB congeners in various environmental samples. As results, Co-PXBs #118, #105 and #126A indicated highly contribution, and their pattern was comparatively similar to flue gas and marine sediment samples. However, in regard to ambient air samples, 4'-MoBr-2,3',4,5-TeCl biphenyl (#118) accounted for equal to or more than 50%. As the reason why similar contribution pattern was not observed between flue gas and ambient air, it was estimated the existence of other contamination sources, affecting the flue gas from other chemical factory or indoor gas from human living house.

There are several routes of formation for PXBs. Nakano et al.[2)] reported formation of Co-PXBs during the manufacturing process of $FeCl_3$. Figure 2 showed the possible pathway of Co-PXBs and PXDFs from PBDEs in the presence of HCl, $FeCl_2$ and $CuCl_2$ under pyrolysis or photolysis. It was estimated that PBDEs decompose and become to bromophenol etc., and also resynthesized to PXDFs or Co-PXBs. Therefore, we tried to demonstrate this pathway by using of deca-BDE under the above experimental conditions. Figures 3 and 4 showed that EI-SIM chromatogram of PXBs and PXDFs generate from deca-BDE with pyrolysis and photolysis. In pyrolysis (Fig. 3), there are some peaks at monobromo-polychlorinated and dibromo-polychlorinated

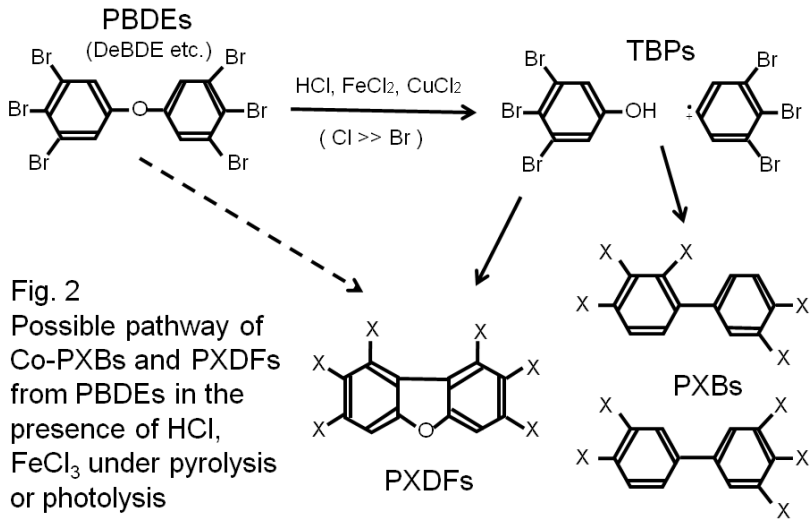


Fig. 2
Possible pathway of Co-PXBs and PXDFs from PBDEs in the presence of HCl, $FeCl_3$ under pyrolysis or photolysis

congeners under the existence of 1% $FeCl_2$ or $CuCl_2$. On the other hand, there are polybromo-pentachloro congeners in photolysis. It could find and identified many peaks of Co-PXBs as expected on SIM-chromatogram by the pyrolysis of deca-BDEs. Especially, by the pyrolysis experiment in the existence of $CuCl_2$, we certainly could recognize Co-PXBs #77 and #126B using their standard. Further study is needed to search other Co-PXBs family congeners in the pyrolysis or photolysis samples of deca-BDE or flue gas from incinerator, showing high concentration, by using HRGC/HRMS scanning method. Then, it needs to evaluate their toxicity of Co-PXBs congeners as newly contaminants.

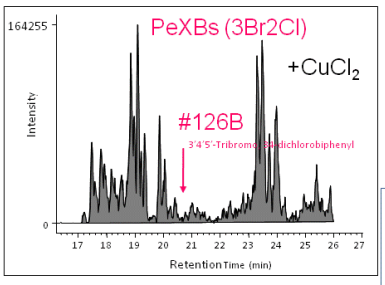


Fig. 3
EI-SIM chromatogram of Co-PXBs congeners observed in the presence of $CuCl_2$ & $FeCl_2$ under pyrolysis for DeBDEs

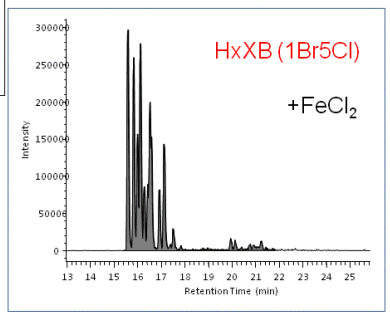
Pyrolysis for DeBDE

Experimental conditions

(1) In enclosed glass tube

(2) Heating time : 90 min

(3) Heating temperature : 400ºC



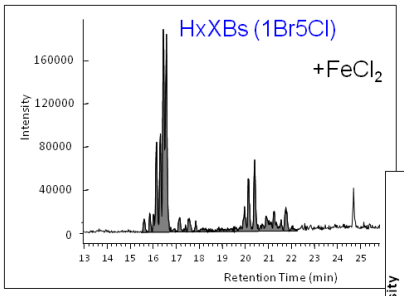


Fig. 4
EI-SIM chromatogram of Co-PXBs and PXDFs congeners observed in the presence of $FeCl_2$ under photolysis for DeBDEs

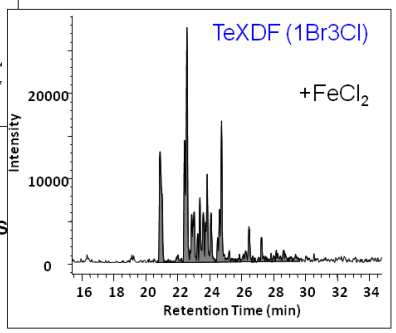
Photolysis for DeBDE

Experimental conditions

(1) In quartz tube

(2) Irradiation time : 60 min

(3) Irradiation : UV (254 nm, 120 IX)



Acknowledgements

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