CONTAMINATION LEVELS OF ORGANIC BROMINE COMPOUNDS (BFRs, DIOXINs) IN MOTHER'S MILK AND DAILY MILK PRODUCTS

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Introduction

Polybrominated diphenyl ethers (PBDEs) and Tribromophenol (TBP) are used in large quantities for many applications such as television sets, computers, paints, and textiles etc. In Japan, the annual consumption of DecaBDE and TBP in 2003 was 2,200 and 4,150 tons, respectively. As a result, there is growing evidence that the large amounts of PBDEs or TBP in the environment are due to released during the manufacturing of these chemicals or consumer products containing these chemicals[1-3]. In addition, there is sufficient evidence that the incineration of consumer products containing such flame-retardant chemicals results in the formation of polybrominated/chlorinated dibenzo-p-dioxins (PXDDs) and –furans (PXDFs), polybrominated dibenzo-p-dioxins (PBDDs) and –furans (PBDFs)[4-6]. These chemicals, as well as the BFRs, 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. In humans, it was reported in 1990 on high concentration of PBDEs in adipose tissue[7]. Since that time, several studies in Sweden, Canada and the USA have reported human contamination in adipose tissue, serum blood lipid, and breast milk by PBDEs[8,9]. Therefore, because PBDEs are extremely lipophilic and stable substances in vivo, there has been much concern about future adverse effects on human health in these countries and elsewhere.

At present, little is known about human pollution of the above brominated compounds in Japan[10,11] . In this study, in order to generally evaluate Japanese body burden and future adverse effects of newborn infant by PBDEs, PCDDs/DFs, PXDDs/DFs and PBDDs/DFs, we investigated the pollution levels of above contaminants in Japanese breast milk and powdered milk. As similar purpose, it was also investigated their contamination levels in some dairy milk products like cow's milk, cheese, butter and margarine.

Materials and Methods

1) Samples

The samples of mother's milk were collected from sixteen primiparae and twenty multiparae at one month after delivery in 2002[6]. Samples of cow's milk and powdered milk for newborn baby were purchased from four markets in Hirakata and Osaka city of Osaka prefecture of Japan in 2004. With respect to the daily milk products like cheese, butter and margarine, they were purchased from a market in Hirakata city of Japan and Berlin city of Germany in 2004, respectively. Each sample was used for this study.

2) Analytical method

For the analysis of PBDEs, the quantification of PBDE congeners was performed according to our previous paper[10]. With respect to the quantification of seventeen PCDDs/DFs (seven PCDD isomers and ten PBDF isomers), five PBDDs (2,3,7,8-TeBDD, 1,2,3,7,8-PeBDD, 1,2,3,4,7,8-HxBDD, 1,2,3,6,7,8-HxBDD and 1,2,3,7,8,9-HxBDD), five PBDFs (2,3,7,8-TeBDF, 1,2,3,7,8-PeBDF, 2,3,4,7,8-PeBDF, 1,2,3,4,7,8-HxBDF and 1,2,3,4,6,7,8-HpBDF), six PXDDs (2-Br-3,7,8-TriCl-DD, 2,3-DiBr-7,8- DiCl-DD, 1-Br-2,3,7,8-TeCl-DD, 2-Br-3,6,7,8,9-PeCl-DD, 1-Br-2,3,6,7,8,9-HxCl-DD and 1-Br-2,3,6,7,8,9-HxCl-DD) and two PXDFs (3-Br-2,7,8-TriCl-DF and 1-Br-2,3,7,8-TeCl-DF) congeners, the purified method was multi-layer silica-gel column chromatography, with an eluent of n-hexane and CH_2Cl_2:n-hexane (1:4). 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) and toluene. 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[6]. As the

evaluation method of toxicity or body burden for PXDDs/DFs and PBDDs/DFs, It was assumed that the toxicity of same congener of PBDDs/DFs or PXDDs/DFs is nearly equal to that of PCDDs/DFs. On the basis of this assumption, the contribution ratio to total TEQ by PCDDs/DFs, PBDDs/DFs and PXDDs/DFs was calculated by using 2,3,7,8-TCDD equivalent factors (WHO-TEF).

Results and Discussion

As shown in Figure 1, the TEQ levels of PCDDs/DFs, PXDDs/DFs and PBDDs/DFs in the mixed breast milk, cow's milk and powdered milk were investigated. Average TEQ concentration (20.3 pg TEQ/g lipid) in breast samples from primiparae was over two-fold against that (10.8 pg TEQ/g lipid) from multiparae. On the other hand, low levels in cow's milk and powdered milk was detected, seeing as almost PCDDs/DFs. As an extremely interesting phenomenon, it was recognized that the ratio of PXDDs/DF for PCDDs/DFs calculated as TEQ concentration ranged between 4 and 46 %. This data suggested that both dioxin analogues were arised from same contamination sources like the incinerators. The TEQ level of PBDDs/DFs was low, however, actual concentration of PBDDs/DFs congener except 2,3,7,8 isomers was observed; TeBDDs was dominant (50 ~ 90%), especially observing as 1,3,6,8- and 1,3,7,9-TeBDD isomer (data not shown). From this observation, it was estimated that there are a large amount of TeBDDs in human bodies, which derived from the pyrolysis or photoysis of BFRs like bromophenol in the environment.

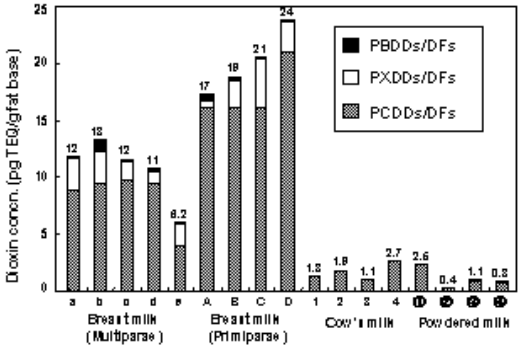

Fig.1 Levels of three kinds of dioxin concn. (TEQ) in mother's milk, cow's milk and powdered milk

Figure 2 shows the levels of PBDEs in Japanese powdered milk products for newborn babies. Its concentration ranged between 1.10 and 23.2 ng/g lipid. In addition, a remarkable contamination in the samples of a-1 and d-2 was notified, observing at 23.2 and 14.1 ng/g lipid, respectively. However, when the level of same products as different lot number was compared, their concentrations were low. With respect to the congener pattern of PBDEs, high contribution by DeBDE for total PBDEs concentration was observed in all sample analyzed. Further, there were a large amount of HepBDEs and OctaBDEs, which estimated to derive from the pyrolysis or photoysis of DeBDE in high concentration samples.

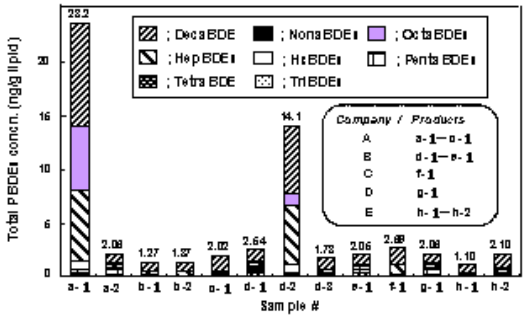

Fig.2 Levels of PBDEs in Japanese powdered milk products for newborn babies

As further survey, the levels of PBDEs in cheese, butter and margarine as daily milk products in Japan and Germany were surveyed (Fig. 3). Its concentration ranged between 723 and 1894 pg/g lipid. There was no significant difference between daily milk products of Japan and that of Germany. Interestingly, although it was observed that PeBDE (#99,100) was dominant for total PBDEs concentration, the reason is presently unclear.

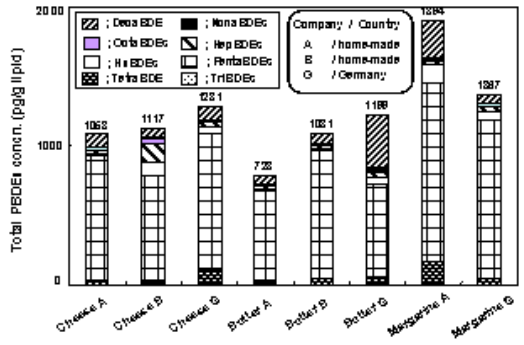

Fig.3 Levels of PBDEs in cheese, butter and margarine of Japan and Germany

Additional investigations by total diet study are warranted to better understand the nature and extent of PBDE contamination of the Japanese food supply.

Ackowlegements

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