LEVELS OF POLYBROMINATED DIPHENYL ETHERS IN SWISS AND IRISH COW'S MILK

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Introduction

Brominated Flame Retardants (BFRs), e.g. PolyBrominated Diphenyl Ethers (PBDEs), TetraBromoBisphenol A (TBBPA) and HexaBromoCyloDodecane (HBCD) belong to a group of high-volume chemicals with a global production of over 310,000 t/a. PBDEs are typically produced with three different average degrees of bromination (Penta-BDE, Octa-BDE and Deca-BDE). In 1999 more than 67,000 t/a were used worldwide especially in plastics and textile coatings.[1] The use of certain PBDE formulations (Penta- and Octa-BDE mixtures) has been banned in the EU with adoption of the Hazardous Substances Directive which will come into force in July 2006.[2] The continued use of Deca-BDE products is a subject of ongoing debate.

Because of the production processes, use and disposal, BFRs are widespread in the environment and residues are found mainly in water, marine and freshwater sediments and soil. The PBDE levels in human tissue have increased significantly over the last three decades. Exponentially increasing PBDE levels have been observed in Swedish mother's milk from 1972 to 1997 and according to Hites, samples of blood and fat from North Americans contain levels of PBDEs which are on average ten times higher than those from Europeans[3,4]. The main source of human exposure to PBDEs is through food consumption; highest PBDE levels have been found in fatty foods. In recent market basket surveys in Ireland, the Netherlands and Sweden, PBDE levels have been investigated in samples of fish, meat, milk products, eggs, fats and oils.[5,6,7] Highest PBDE levels were found in fishery produce, hence a large contribution to dietary exposure of humans from fish consumption can be assumed. The levels in different dairy products were considerably lower.

Research in recent years mainly focused on three types of PBDE congeners: 47, 99 and 100. It appears that BDE-47 and BDE-99 are the main contributors to PBDE contamination of the food chain. However, only few estimates of human dietary PBDE exposure are available and little is known about other forms of human exposure (e.g. inhalation, skin contact).

According to a recently issued opinion of the scientific panel of the European Food Safety Authority, the inclusion of PBDEs (28, 47, 99, 100, 153, 154, 183 and 209), HBCD and the PBB congener 153 in European monitoring programmes on feed and food is recommended.[8] In this study, we present residue levels of Tri- to HeptaBDE congeners found in a number of cow's milk samples from Switzerland and from the Irish market. These investigations also included analyses for dioxins, furans (PCDD/Fs), polychlorinated biphenyls (PCBs) and hexabromocyclododecane (HBCD) which was only analysed in the samples from the Irish market.

Material and Methods

For the Swiss survey 55 individual raw farm milk samples were collected in autumn 2004. Each Swiss canton was represented with at least one sample, the remaining number of samples were attributed to individual cantons according to the importance of production. Two-thirds of the samples (37) were collected from conventional dairy-farms, and one-third (18) from organic dairy-farms. All the milk samples were shipped deep-frozen to eurofins / GfA in October 2005. Three additional pooled samples are not included in this survey. One of these showed atypically high levels warranting further confirmation/investigation.
The Irish survey, amongst other matrices included 16 dairy samples of which 12 are reported here. Samples were provided by the Food Safety Authority of Ireland (FSAI) and sent deep-frozen to eurofins / GfA in August 2005. The samples comprised two retail samples, 5 individual farm milk samples, 2 pooled samples from impact herds close to industrial activities and 3 pooled samples from control herds.

Aliquots of the milk samples were freeze-dried and six $^{13}C_{12}$-labelled PBDE congeners ($^{13}C_{12}$-BDE-28, 47, 99, 153, 183, 209) were added to a homogenised fraction of the dried sample material. A fat extraction in a Soxleth apparatus was done by means of a hexane/acetone mixture and the fat fraction was determined gravimetrically after evaporation of the solvents. The extract aliquots were treated with sulfuric acid and further cleaned-up by liquid/solid chromatography. $^{13}C_{12}$-PCB 141 was added as recovery standard prior to instrumental analysis using HRGC (HP Agilent 6890) coupled with a low-resolution GC/MS system (HP Agilent MSD 5973). The gas-chromatographic separation was performed on a 30 m non-polar HP-5 column with 0.25 mm inner diameter and 0.10 µm film thickness. The native PBDE congeners were quantified via the $^{13}C_{12}$-labelled PBDE congeners. Relative response factors of native to isotope labelled PBDEs were determined by means of calibration mixtures analysed within each analytical sequence. The limits of quantification were in the range of 5 ng/kg fat for the Tri- to HexaBDEs and 10 ng/kg for the HeptaBDEs.

Within this study the recoveries of the internal $^{13}C_{12}$-labelled PBDE standards were in general in the range of 60 to 120 %, demonstrating the appropriateness of the applied method for the analysis of PBDEs in fatty matrices. The differences of PBDE concentrations determined in several duplicate analyses were below 10 %, which is well within the expected range.
The accuracy of the method was verified by analysing a certified fish reference material (CIL EDF-2525). The relative deviation of the determined compared to the assigned values ranged from 2.8 and 15.6 % for the Tetra- to HeptaBDEs. Furthermore, a great number of method blanks was performed and no relevant blanks were found for the Tri- to HeptaBDEs.

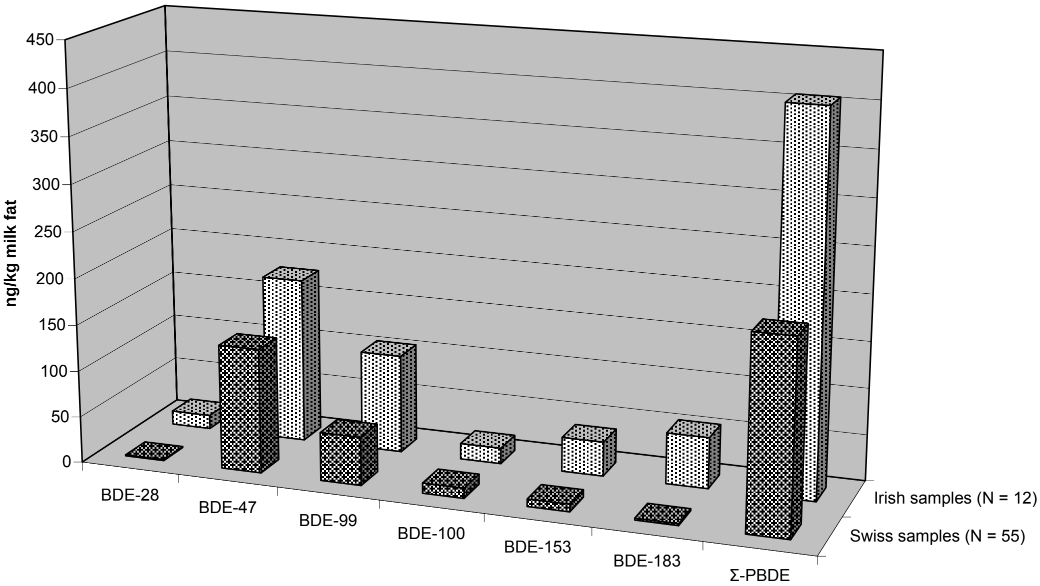
Results and Discussion

Figure 1 provides an overview of the mean lower-bound concentrations of the most abundant PBDE congeners BDE-28, 47, 99, 100, 153 and 183 and the mean value of the sum of all detected Tri- to HeptaBDE congeners (Σ–PBDE). The results of the cow's milk samples from Switzerland and Ireland are shown separately.

The average concentration for Σ–PBDE was 203 ng/kg fat for the 55 Swiss samples and 407 ng/kg fat for the 12 samples from Ireland. The difference in the mean PBDE contamination in cow's milk from both countries is noteworthy. The values range from 70 to 1,040 ng/kg fat in the Swiss samples and from 221 to 723 ng/kg fat in the Irish samples. Especially the significantly high PBDE concentration in a few cow's milk samples from both countries is remarkable and may be due to environmental factors of the sampling locations or the sampling procedure itself.
In keeping with data reported in the literature, BDE-47 and 99 were found in all cow's milk samples. BDE-47 on average contributed to more than 50 % of the total sum of the Tri- to Hepta BDEs. For the Swiss samples the exact value was 64 % and for the Irish samples the contribution of BDE-47 was 44 %. The average contribution of BDE-99 to Σ–PBDE was 26 % for the Swiss and the Irish samples.
BDE-153 was determined in most of the Swiss samples (5 – 17 ng/kg fat) and in all Irish samples (18 - 75 ng/kg fat), whereas BDE-28 and BDE-154 were detected in small concentrations in four and three of the Swiss samples, respectively. BDE-28 was also present in more than half of the samples from Ireland in concentrations of 16 to 35 ng/kg fat and a further TriBDE (BDE-17) was detected in one sample. BDE-154 was present in three Irish milk samples in small concentrations. Only four milk samples from Switzerland contained BDE-183 (13 - 45 ng/kg fat), whereas it was detected in most of the investigated Irish milk samples at a concentration range of 31 to 98 ng/kg fat. Furthermore, most samples from Ireland contained BDE-66 in small concentrations, while this TetraBDE was not detected in any of the Swiss samples. BDE-85, 71, 77, 119, 126 and 138 were not detectable in any of the analysed milk samples from either country included in this study.

Figure 1 illustrates the differences in the contamination levels and the distribution of the Tri- to HeptaBDE congeners in Swiss versus Irish milk. The average Σ–PBDE data of the 12 Irish cow's milk samples were more than two times higher than the corresponding values of the 55 samples from Switzerland. The main contributors to total PBDE load were congeners BDE-47 and 99, contributing about 90 % to the Σ–PBDE in the Swiss samples and 70 % to the Σ–PBDE in the Irish samples. Considerable concentrations of BDE-153 and 183 were determined in most of the samples from Ireland, but hardly in any of the Swiss samples.

Figure 1: Mean concentration of the most abundant BDE congeners and the sum* of Tri- to HeptaBDEs in Swiss and Irish cow's milk samples (lower-bound values).



**Sum of BDE congeners 17, 28, 49, 71, 47, 66, 77, 100, 119, 99, 85, 126, 154, 153, 138, 183*

Compared to recently published data in milk and dairy produce from European countries, the PBDE levels presented in this study are in the lower range. A preceding survey on PBDE levels in Irish produce showed total PBDE levels from 850 to 1140 ng/kg fat (upper-bound values) for different dairy products. Only BDE-47 and 99 in nearly equal concentrations could be detected in most samples.[5] In 2004 the Institute of Food Safety of the Netherlands (RIKILT) reported an average concentration of 2000 ng/kg fat for BDE-47 in semi-skimmed milk samples, whereas no levels were detected above the LOQ for BDE 99, 100, 153, 154 and 183. Dairy products with higher fat contents (butter and cheese) showed significantly lower PBDE levels ranging from 250 and 500 ng/kg fat containing also detectable levels for BDE-99 and 100.[6] Levels in mixed dairy products from Swedish market basket samples from 1999 (sum of levels of BDE-47, 99, 100, 153 and 154) showed an average value of 360 ng/kg milk fat.[7] Milk samples and dairy products from supermarket stores in the United States showed a higher PBDE contamination. In general, the PBDE contamination in food and human tissues from the United States is higher than found in European countries and Japan.[9] Findings of this study indicate a wide variation in occurrence and occurrence patterns of Brominated flame retardant congeners in milk analysed in Europe and elsewhere.

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