Polybrominated diphenylethers (PBDE) in German meat

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Abstract

Polybrominated diphenylethers (PBDE) are an important class in the group of flame retardants. Due to their persistence PBDE accumulate in environment, food chain and finally in food products, especially in those of animal origin which are the main source of contamination for humans. This group of contaminants represents a risk for man, which can only be reduced by minimisation of uptake. For this purpose an analytical method for the selective and sensitive determination of PBDE-congeners in food was developed and evaluated. With this method 103 samples of various types of animal food products originating from a pool which is representative for the German consumer were checked for PBDE-contents and -patterns. The median values of total PBDE-content (sum of BDE 28, 47, 99, 100, 153, 154 and 183) were 0.36 µg/kg for pork/cattle meat and 0.25 µg/kg for chicken/turkey meat, respectively, related to fat content. The main congeners were BDE 47 and 99, respectively. Results indicated that PBDE-contents of pork, cattle, chicken and turkey meat seem to be less influenced by animal species, but rather by factors of animal husbandry like feed and environment. It is intended to integrate the presented results as a German contribution to a planned EU-monitoring project.

Introduction

There exist strict regulations concerning fire protection for many articles of the daily use, e.g. the requirement of treatment with flame retardants. An important class in the group of flame retardants are the polybrominated diphenylethers (PBDE) [1]. In the course of production, processing and use of consumer goods – e.g. computers, TV-sets, furniture and textiles – PBDE are transferred into the environment and afterwards to the food chain where they accumulate due to their persistence and high fat solubility. As a consequence contamination of food products can appear.

PBDE are effective neurotoxic agents and interact with the hormones of the thyroid gland which was shown by animal studies [2]. Furthermore mutagenic and cancerogenic effects have to be assumed. This type of contaminant represents therefore a risk for man, which only can be reduced by minimisation of uptake. The main contamination source for humans is food, especially food products of animal origin [3]. It is therefore absolutely necessary to get an overview on PBDE-contents of food products of animal origin. In this study a screening of PBDE-contents in German food originating from animals was made.

Although there are 209 congeners of PBDE in total only 8 are most important in respect of toxicity and presence in environment. These are BDE 28, 47, 99, 100, 153, 154, 183 and 209. A planned EU-monitoring project will also focus on these congeners [4]. For the determination of PBDE an adequate analytical method has been developed and evaluated which was applied to 103 food samples of animal origin from a sample pool representative for the German consumer. The presented study focused on pork, cattle, chicken and turkey meat. The analytical method as well as PBDE-contents and -congener distributions for the mentioned types of meat are presented.

Materials and methods

Meat samples originated from a sample pool representative for the German consumer. This sample pool was generated in the scope of a research project – starting in 2004 and supported by the Federal Ministery of Food, Agriculture and Consumer Protection – for monitoring contamination levels of dioxins and PCB in animal food. The project was coordinated by MRI, Analysis Division, Kulmbach.

Analytical method. The homogenized meat samples were lyophilised and afterwards extracted by Accelerated Solvent Extraction (ASE). Extraction cells were filled with lyophilisate, sea sand and drying material, furthermore labelled ^{13}C-standards were added. The extraction was performed with n-hexane at 100°C and 100 bar. The solvent of the extraction procedure was removed by nitrogen flushing. The residue of ASE extraction was dissolved in cyclohexane/ethyl acetate and transferred to a glass column filled with Bio-beads. Elution has been carried out with cyclohexane/ethyl acetate. Before rotary evaporation 1 ml of toluene was added to the collected fraction. The evaporated eluate of the GPC-procedure was transferred into a SPE column filled with deactivated florisil. Elution was performed with toluene. The eluate was evaporated

and transferred into a brown vial, concentrated in a nitrogen stream and a labelled recovery standard was added. This solution was applied to GC/HRMS analysis.

GC/HRMS measurements were carried out with a Thermo Electron DFS-high resolution mass spectrometer connected to a Trace-GC 2000. For separation a low bleed GC capillary column DB5-MS (30 m x 0,25 mm i.d. x 0,1 µm film thickness) from J&W Scientific was applied. The initial oven temperature of 70°C was kept for 2.0 min prior to an increase of 20°C/min to 230°C. The oven temperature was afterwards increased at a rate of 6°C/min to 330°C and finally kept for 25 min. Helium was used as the carrier gas at a constant flow rate of 1.0 ml/min. Transfer line temperature was set at 280°C. The GC/HRMS system was operated in the positive electron impact ionization mode at a resolution of 10 000 (10 % valley). Calibration and reference gas was perfluorokerosene and it was held at a temperature of 150°C. The source temperature was kept at 280°C and electron energy at 45 eV. 1 µl was injected in the splitless mode with a splitless time of 2.0 min. Identification and quantification of PBDE-congeners occurred by GC retention time and specific masses.

Method evaluation took place by checking corresponding analytical parameters, by analysis of reference materials and by participation on interlaboratory comparison.

Results and discussion

Total PBDE-contents (sum of BDE 28, 47, 99, 100, 153, 154 and 183) of the analysed pork and cattle meat samples varied from 0.05 to 1.12 µg/kg fat (fig. 1A), those of the chicken and turkey meat samples from 0.06 to 1.86 µg/kg fat (fig. 1B).

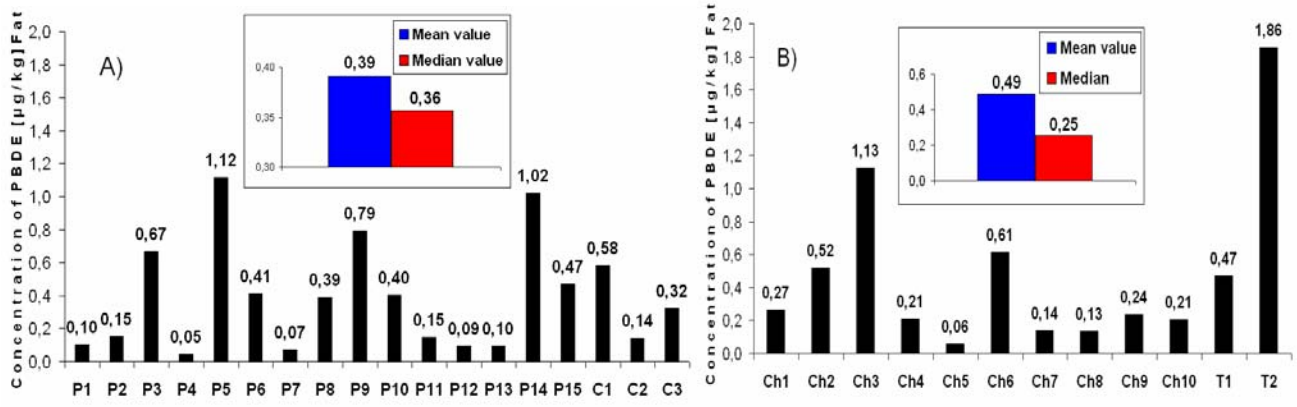

Figure 1. Total PBDE-contents (∑BDE 28 – 183) of pork and cattle meat samples (A) as well as of chicken and turkey meat samples (B) and corresponding mean and medium values, respectively, related to the fat content (P=pork meat, C=cattle meat, Ch=chicken meat, T=turkey meat).

Median values for pork/cattle and chicken/turkey meat were 0.36 and 0.25 µg/kg fat, respectively, the corresponding mean values were 0.39 and 0.49 µg/kg fat, respectively. Median and mean values, respectively, as well as the ranges of contamination levels were similar for all of the four animal species. Although the numbers of analysed samples for cattle as well as for turkey meat were only low results indicate that animal species seems to be no main factor taking influence on PBDE-content and -congener distribution which deviates from results for fish (not presented here). It is likely that other, species independent factors, will have effects on the PBDE-content. This assumption was confirmed by the congener distributions of pork/cattle and chicken/turkey meat samples presented in figures 2A and B, respectively. BDE 28 was not taken into consideration in the diagrams, because this congener was below the limit of quantitation (LOQ) for all meat samples.

For all of the four animal meat species BDE 47 and 99 were the main congeners – in mean BDE 47-percentage was higher than that of BDE 99 for pork/cattle meat (fig. 2A), whereas for chicken/turkey meat it was in the other way around (fig. 2B). But with regard to single samples of pork and chicken meat either BDE 47 or BDE 99 can be the dominant congener. These two congeners are the main compounds of the industrially applied "penta mixture". Furthermore these two congeners can also originate from the degradation of BDE 209 (deca-congener) which is currently the only PBDE-congener allowed for industrial application in the EU. For BDE 209 the developed method is up to now not very sensitive because of the high blank value (LOQ: 3 µg/kg fat) for this congener. In the case of the analysed meat samples no contents higher than 3 µg/kg fat were obeserved. Responsible for the slight variation of the proportion of the two main congeners BDE 47 and 99, respectively, in single samples could be the varying influences of the "penta

mixture" and BDE 209. Possibly metabolism of the animal will take additional influence. We have analysed several samples of animal feed where these two congeners were also the main compounds and the proportion of both showed a similar variation as for the meat samples.

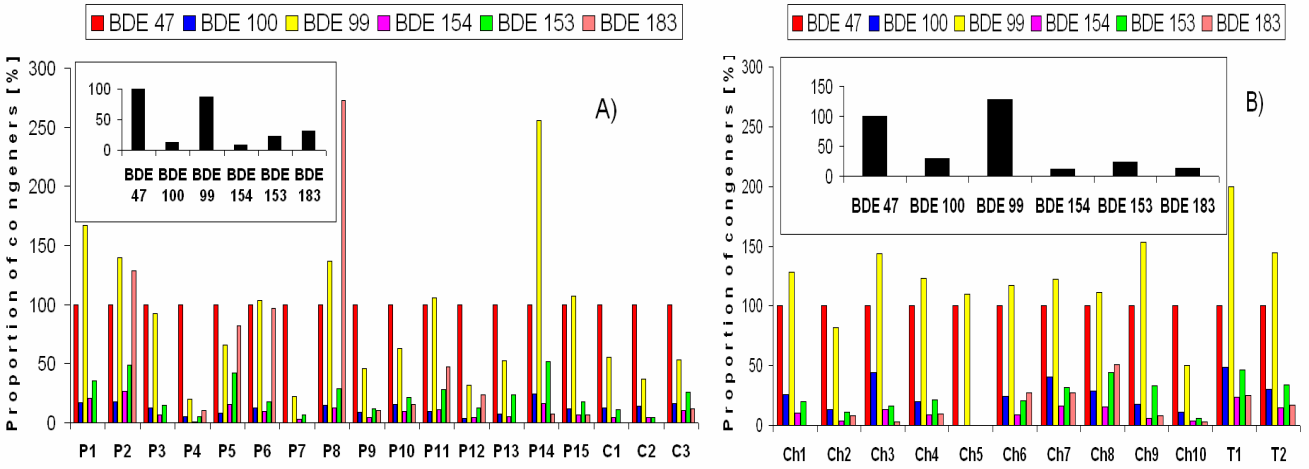

Figure 2. Distribution of single congeners in reference to BDE 47 (100 %) in pork and cattle meat samples (A) as well as in chicken and turkey meat samples (B) and corresponding mean distribution of congeners (small diagrams) (P=pork meat, C=cattle meat, Ch=chicken meat, T=turkey meat).

Another interesting congener is BDE 183, the main component of the industrially applied "octa mixture". In some pork meat samples this congener was a main compound (fig. 2A). BDE 183 showed the largest variations between the samples in pork/cattle meat and a large variation in chicken/turkey meat, too (fig. 2A and B). For chicken meat samples no information concerning the kind of husbandry was available. As analysed feed samples did not show high BDE 183-concentrations, the concentration of this congener in meat seems to be influenced to a higher degree by the environment of the animal.

Conclusions

Our results indicated that PBDE-content in meat was influenced by special factors of husbandry like environment and animal feed. Furthermore they demonstrated that there is a considerable variation of the PBDE-concentration within the single analysed meat samples. The PBDE-contents found in meat were significantly lower than in seafish. With this background it can be recommended to make a survey to increase the database, especially concerning processed meat products.

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