ANALYSIS OF TRI- TO DECA-BROMINATED DIPHENYL ETHERS IN SPANISH COMMERCIAL FOODSTUFFS

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Introduction

Brominated flame retardants (BFRs), especially polybrominated diphenyl ethers (BDEs), have recently been found to be increasing in human tissues over the world [1, 2]. It is mainly due to both, their production and uses have undergone a dramatic increase starting in the 1980s [3] and their persistence and lipophilic character which tend to concentrate in the food chain, and thus accumulate in the human body [4].

Data on the levels of these environmental pollutants in food are only relatively abundant in fish [5, 6]. However, much less is known on BDE concentrations in other major food groups. The majority of data are focused on tetra- to hexa-BDE congeners while little information is available on BDEs 183 and 209 (the major components of the commercial flame retardant mixture octa-BDE and deca-BDE, respectively). On the other hand, any data of BDEs 184, 191, 196, and 197 (impurities of commercial deca-, octa- and/or penta- preparations, and degradation compounds of BDE 209 [7, 8]), are available up to now.

We present here the results of the first monitoring program of the presence and congener distribution of 15 BDE congeners, including tri- to deca-BDEs in fish, shellfish, dairy products, oil, egg and meat foodstuffs commercially available in Spanish markets from 2003 to 2005. The results were compared with those found in other surveys conducted in Spain and other countries.

Material and Methods

A total of 104 food samples were randomly acquired from several supermarkets all over Spain from 2003 to 2005. The study involved 21 types of food samples combined into 6 groups of similar items as follows: milk and dairy products (commercial pasteurized cow's whole milk, cream, butter, and cheese), chicken eggs, sea fish (salmon, fatty fish: tuna fish and sardine, lean fish: bogue, mackerel, gilthead and little sole), meat and meat products (pork, chicken, processed cold pork meat, and cured ham), vegetable oil (olive and sunflower oils), and shellfish (oyster, clam, and mussel).

Once at the laboratory, the non-edible part of the food products was removed and the edible part, skin excluded, was stored in stable conditions, either freeze-dried or frozen at –20ºC, until analysis. All samples, except oil and butter were extracted by matrix solid phase dispersion (MSPD) as previously described in detail elsewhere [9]. The extraction of BDEs from butter and oil samples was carried out by dialysis in hexane using a semi permeable membrane of polypropylene bag. Further clean-up and lipid removal was achieved by using acid and basic impregnated silica gel multilayer columns. Hexane was used as elution solvent. The lipid content was determined following the Smedes method [10].

BDEs 17, 28, 47, 66, 85, 99, 100, 153, and 154 were analyzed following the isotope dilution technique by GC-LRMS/MS(ITD) method, previously developed [11]. BDEs 183, 184, 191, 196, 197, and 209 were analyzed by GC-ECD, and confirmed by GC-LRMS(SIM). Samples were spiked with three $^{13}C_{12}$- labeled standards; BDEs 47, 99, and 153. Two more $^{13}C_{12}$- labeled standards; BDEs 100 and 139 were used as recoveries standards in the isotope dilution technique (GC-LRMS/MS(ITD)). $^{13}C_{12}$-BDE-139 was used as internal standard in the GC-ECD method. All standard were purchased from Wellington Laboratories (Ontario, Canada).

Results and Discussions

Levels: BDEs 47, 99, 183, 197, and 196 were detected in more than 90 % of the samples; while BDEs 66, 100, 153, 154, 184, 191, and 209 were detected in more than 40 % of the samples. BDEs 17, 28 and 85 were frequently below or close to the limit of detection (LOD).

Fish samples exhibited the highest values (median of 189, range of 24-880 pg/g fresh weight, f.w.), followed by oils (median of 119, range of 14.8-2958 pg/g f.w.), meats (median of 75.9, range of 6.82-2517 pg/g f.w.), shellfish (median of 75.7, range of 3.29-677 pg/g f.w.), eggs (median of 73.5, range of 12.8-557 pg/g f.w.), and dairy products (median of 66.1, range of 3.24-1588 pg/g f.w.).
The total BDE values found in this study are in most of the cases within the range of those recently reported by other European and Japanese studies and below those conducted in USA [12-15]. This fact is related with the total amount of BDEs as flame retardant used in each country, which is much higher in USA than in Europe [16].

The contribution of higher brominated BDEs (hepta- to deca-BDEs) with regard to the total BDE concentration values are shown in Figure 1. For egg samples a clearly contribution of higher brominated BDEs (55%) to the total BDEs was found. For oils, the contribution was also high representing more than 30 % to the total content. For dairy product, meat and shellfish samples similar contribution was found (between 22 and 23 %), whereas for fish sample the contribution was only 4 %.

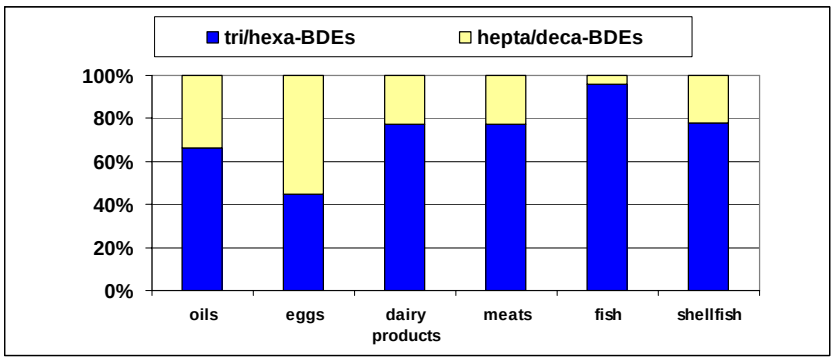

Figure 1. Contribution of higher (hepta- to deca-) and lower (tri- to hexa-) brominated BDEs to the total BDE concentration in Spanish foodstuffs.

Profiles: In fish and shellfish, BDE 47 was the predominant congener accounting for 36 % of total BDEs measured in the case of shellfish and ranging from 59 to 63 % in the case of fish samples. BDE 100 was the second predominant congener in the case of lean and fatty fish, followed by BDE 99. For salmon samples BDE 99 was the second predominant congener, followed by BDE 100. In the case of shellfish samples the second predominant congener was BDE 209, followed by BDE 99. BDE 183, the main component of octa-BDE formulations, was detected in almost all fish and shellfish samples, but with very low contribution to the total BDE concentrations (Figure 2 a).

BDE 99 dominated the profile in pork and transformed meat samples, with a contribution of 26 and 33 % to the total BDE, respectively, followed by BDEs 47, 209, and 153. In chicken samples, BDE 47 dominates the profile (27 % of total BDEs) followed by BDEs 209, 99, 153, and 183. The BDEs 209 and 183, which are predominant in deca- and octa- formulations, respectively, were detected in more than 90 % of the meat samples. These results agreed with other findings in the recent literature. Thus, BDE 209 was the dominant BDE congener in calf and chicken liver from supermarkets chain in Dallas (USA) [2], and was the third BDE predominant congener in some chicken fat from Arkansas, USA [15]. In this last study, BDE 183 was detected in all chicken samples and three unknown BDEs (one octa- and two nona-BDEs) were detected in some of them. The two hepta-BDEs 184 and 191, and the two octa-BDE congeners 196 and 197, either minor components of the octa- formulations and products of the BDE 209 enzymatic degradation in biota [17, 18], were also detected in more than 80 % of the meats, although their contribution to the total BDE were very low (between 0.04 and 2.1 %).

Butter BDE profile is completely different from the rest of dairy products studied. (Figure 2 c). BDEs 196 and 209 were the major contributing congeners, each accounting for more than 40 % of the total BDEs (between 40 and 44 %), followed by BDEs 47, 183, and 99. BDEs 47 and 99 seemed to be the most

important among BDE in cow's milk, cream and cheese samples (Figure 2 c), with a contribution ranging from 39 to 41 % in the case of BDE 47 and from 22 to 30 % in the case of BDE 99. The third predominant congener was BDE 100 (8 %), BDE 209 (7 %) and BDE 153 (10 %) for cow's milk, cream and cheese samples, respectively. On the other hand, BDEs 184, 191, 196, and 197, detected in the majority of the dairy samples contributed with a very low percentage to the total BDEs. Although higher brominated (hepta- to deca-) BDEs are not usually analysed in similar surveys, some authors have also found BDE 209 congener as the predominant in some dairy products [14].

In oil and egg samples, BDE 209 was the dominant congener (with a contribution ranging from 40 to 50 %, respectively), followed by BDEs 47 and 99 (Figure 2 d). BDEs 183, 197, and 196 are present at detectable levels in almost all the individual oil and egg samples.

In the majority of foodstuffs samples, BDE 47 dominates the BDE congener profiles, mainly in fish and shellfish samples. But in the studies where the BDE 209 was included, its contribution to the total BDEs was important and, in some cases was the dominant congener. So, it is interesting to note that BDE 209 was the predominant congener in some meats, butter and cheese samples from USA [14, 15, 18]. Because BDEs 184, 191, 196 and 197 were not analysed in any foodstuffs samples, it is not possible to compare our findings with other studies in the related literature.

The most remarkable of this study was the high contribution of the most brominated BDE (hepta- to deca-BDE), mainly the BDE 209, to the total BDE concentration found in Spanish foods, except fish and shellfish, and the presence of BDEs 184, 191, 196, and 197 in almost all samples.

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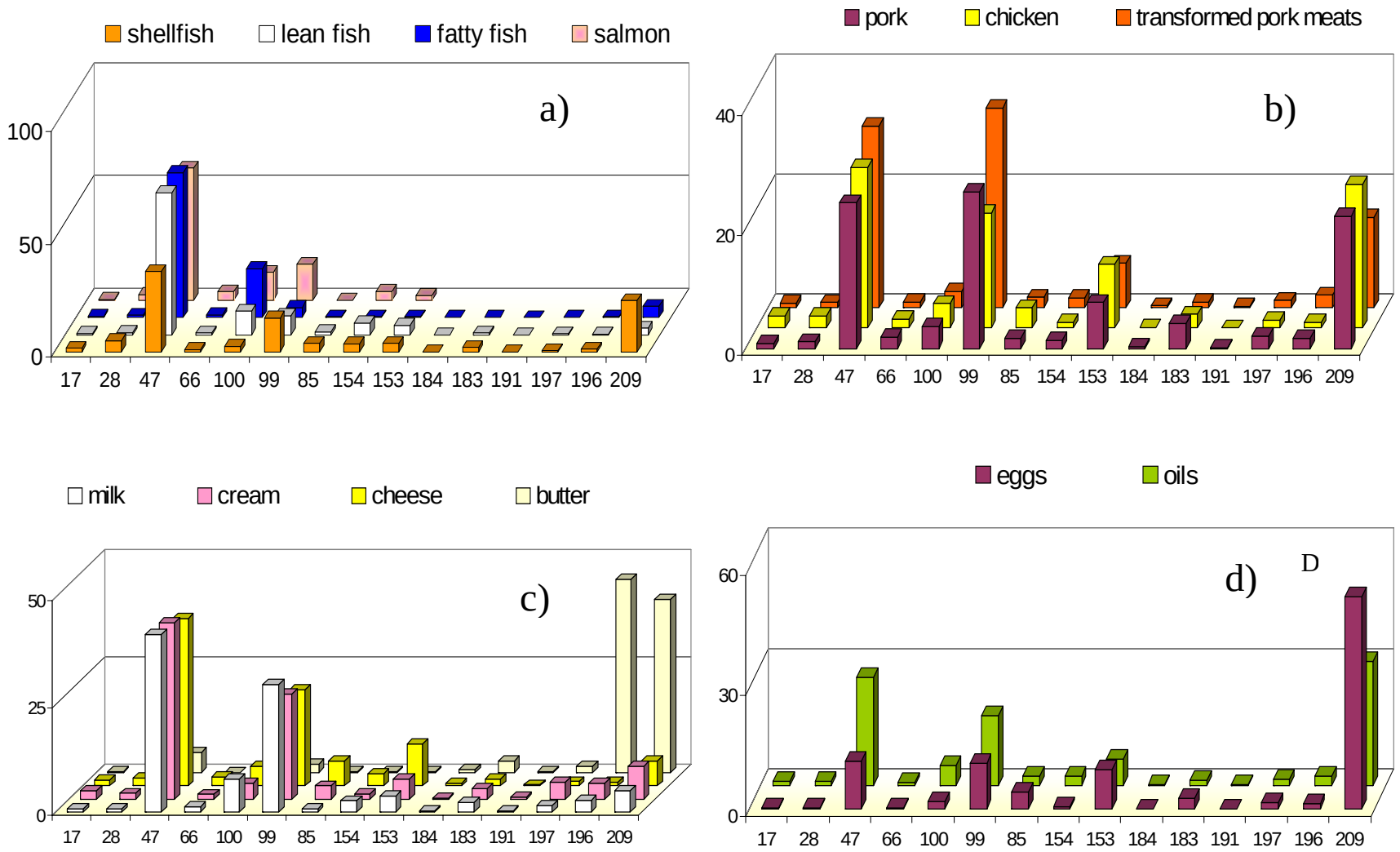

Figure 2. Profiles of BDEs (in percentages of total BDEs) found in Spanish foods. Fish and shellfish (a), meats (b), dairy products (c), oils and eggs (d).