BROMINATED ORGANIC MICRO-POLLUTANTS IN THE UNITED KINGDOM DIET – RESULTS OF THE 2003 TOTAL DIET STUDY

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Introduction

There is strong evidence that many non-reactive brominated flame retardants (BFRs) are widely present in almost all compartments of the environment and in humans.[1] These compounds include recently restricted polybrominated diphenyl ethers (PBDEs) and banned polybrominated biphenyls (PBBs). Furthermore, some studies have also reported the presence of polybrominated dibenzo-p-dioxins and dibenzofurans, which are thermolytic breakdown products of BFRs, in the environment[2] and humans.[3] There is increasing concern over the toxicity of these three groups of brominated contaminants, among others, which have been shown to be persistent, bioaccumulative and have a range of toxic effects in animals with varying degrees of potency.[1]

Dietary intake is widely acknowledged as a primary vector for human exposure to most POPs. Therefore, it is important to accurately determine the extent of human exposure to PBBs, PBDEs and PBDD/Fs in order to quantify their associated risk. In general, a total diet study provides a good estimate of dietary contaminant intake for a country as a whole.

The modern United Kingdom Total Diet Study (TDS) is a model of the typical UK diet. The TDS is based on an analysis of retail foods prepared as if for consumption and combined into composite samples representative of a defined food group in amounts reflecting their relative importance in the typical UK diet. Foods that are eaten in large quantities, e.g. bread, milk and potatoes, are kept separate, as are foods that are susceptible to contamination, e.g. offals and fish. The 19 food groups studied here were bread, cereals, carcase meats, offal, meat products, poultry, fish, oils and fats, eggs, sugars and preserves, green vegetables, potatoes, canned vegetables, other vegetables, fresh fruit, fruit products, milk, dairy products and nuts. Beverages were omitted from this survey. Within these food groups foods are purchased in proportions representative of the UK diet, based on the National Food Survey or the Expenditure on Food Survey (2002-2004)[7].

The aim of this project was to analyse TDS composite samples from 2003 in order to assess average dietary exposure in the United Kingdom to PBBs, PBDEs and PBDD/Fs. Exposure estimates and temporal trends are presented.

Materials and Methods

The analytical method used has been described in detail elsewhere.[4,5] The method is accredited (ISO 17025) for each of the reported analytes, except BDE-209 and BB-209.

Briefly the method comprised: freeze dried samples were fortified with $^{13}C_{12}$ mass labelled PBDEs 15, 28, 47, 99, 153, 154, 183, 209; $^{13}C_{12}$ PBBs 52, 77, 126, 153 and 169; and 7 laterally substituted $^{13}C_{12}$ tri- to hexbromo-dioxins and furans. The samples were extracted using hexane with high speed blending followed by open column chromatography on acid modified and base modified silica gel. Further purification was carried out using acid and base modified silica followed by alumina chromatography. Determination was by high resolution gas chromatography - high resolution mass spectrometry (HRGC-HRMS, Autospec Ultima, Micromass). The instrument was operated in selected ion monitoring mode, two ions monitored for each analyte, mass resolution typically 10,000 at 10% peak height. Extracts were separated on a 60m DB5-MS column. A cryogenically cooled programmed temperature vaporisation (PTV) injector was used (Gerstel CIS4), injection volumes typically 10µl. Acceptance criteria followed were analogous to those used for the analysis of chlorinated dioxins and furans.

Table 1. Average UK consumption

Group		Consumption (g/day)#
1	Bread	105
2	Miscellaneous cereals	116.6
3	Carcase meat	20.4
4	Offal	0.7
5	Meat products	51.8
6	Poultry	19.3
7	Fish	13.7
8	Oils and Fats	21
9	Eggs	13
10	Sugar and preserves	57
11	Green vegetables	31.5
12	Potatoes	108.8
13	Other vegetables	85.0
14	Canned vegetables	32.0
15	Fresh fruit	78.8
16	Fruit products	52
18	Milk	258
19	Milk products	68
20	Nuts	2

Data derived from 2002-2004 EFS[7]

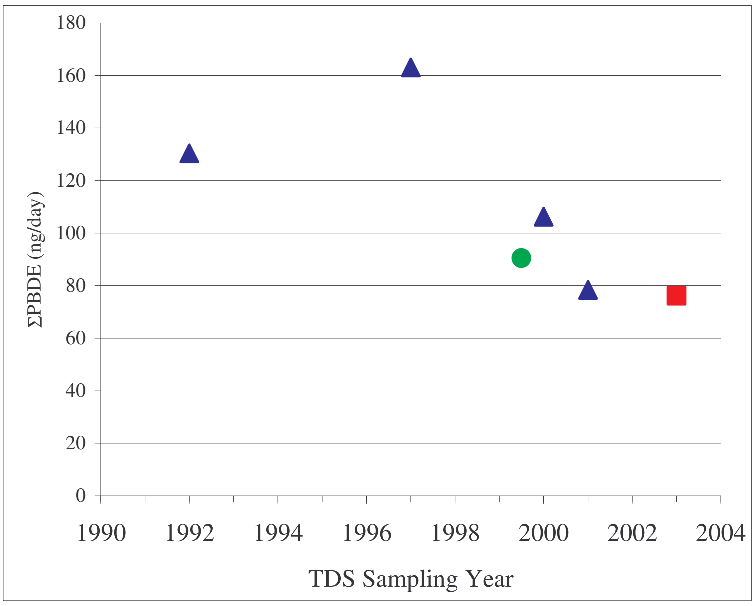
The TDS was made up of 119 categories of foods purchased from 24 locations throughout the UK during the year (total of 480 samples). The samples were combined into 20 groups of similar foods, Table 1. Group 17, beverages, was omitted. Shoppers were asked to select and purchase a single product from each food category in each location without reference to products purchased in other locations. Foods were prepared according to normal domestic practice. For each food group the foods from the 24 locations were combined and thoroughly homogenised. Sample procurement and preparation was conducted by the Laboratory of the Government Chemist (Teddington, UK).

Seventeen PBDEs, ten PBBs and eleven tri- to heptabromo dioxins and furans were determined in each composite sample. ΣPBDE levels quoted are the sum of 16 congeners except BDE-209. ΣPBB values are the sum of 6 PBBs excluding BB-209 and non-ortho PBBs 77, 126 and 166. Total PBB and PBDD/F ΣWHO-TEQ estimates were calculated using PBDD/F and PBB TEF values corresponding to the equivalent WHO PCDD/F or PCB TEF as an interim estimate[6], in the absence of any TEFs for these compounds. Exposure estimates for 2003 were generated using consumption statistics derived from the 2002-2004 Expenditure and Food Survey[7], Table 1.

Results and Discussion

This study builds on previously published results by D'Silva[4,8] for archived TDS samples and supplements the published data with results from recent diet samples. PBDEs were determined above the limits of quantitation in every composite sample tested, demonstrating the ubiquity of PBDEs in the diet. Lower bound dietary exposure to PBDEs (excluding BDE-209) was estimated at ΣPBDE 76.2 ng/day. This value is in agreement with previous studies[4,8,9]. When compared to previously published estimates for dietary exposure, the results presented here appear to supplement the hypothesis that dietary exposure to PBDEs appears to be falling, Figure 1.

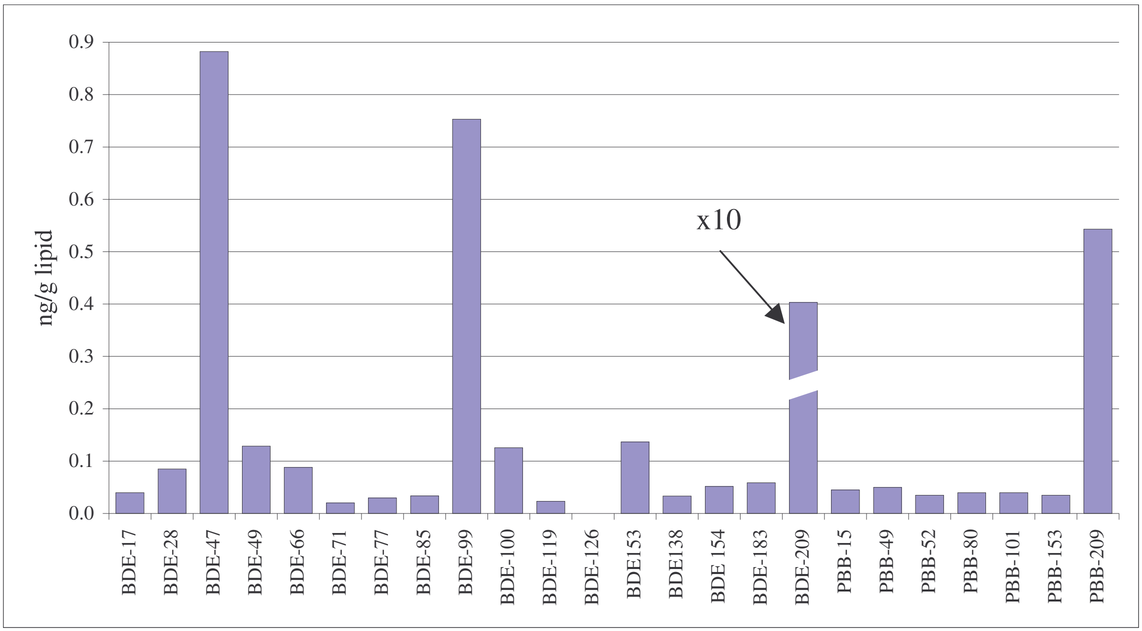
Figure 1. Average lower bound dietary exposure to PBDEs in UK (excluding BDE-209)

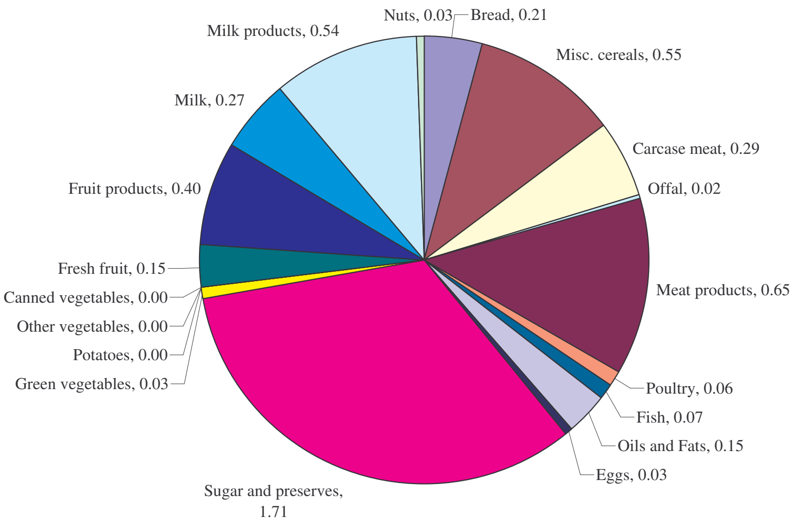


It has been reported that the lowest observed adverse effect level (LOAEL) value for PBDEs is 40 µg/kg/day based on the incidence of thyroid hyperplasia[10], although other studies have estimated the LOAEL values at approximately an order of magnitude higher. The current dietary exposure of ΣPBDE 76.2ng/day remains several orders of magnitude lower than any of the LOAEL estimates for PBDEs, and indicates a margin of exposure (MoE) significantly larger than the target MoE recommended by the Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment (COT)[12]. However, until the toxicology of PBDEs in humans is better defined it is not possible to say that there is no associated risk with the level of PBDEs in the UK diet.

In order that this data was comparable to earlier studies, BB-209 and BDE-209 results were omitted from the ΣPBDE and ΣPBB values. Dietary exposure to these congeners was estimated at 15.2 ng/day and 265.6 ng/day respectively. Dietary exposure to tetra-hexa PBBs was typically low, as reported in earlier studies, with ΣPBB at about 0.2 ng/day. The most dominant PBB congeners were BB-209 and BB-153.

Figure 2. Average PBB and PBDE congener profile in 2003 UK diet

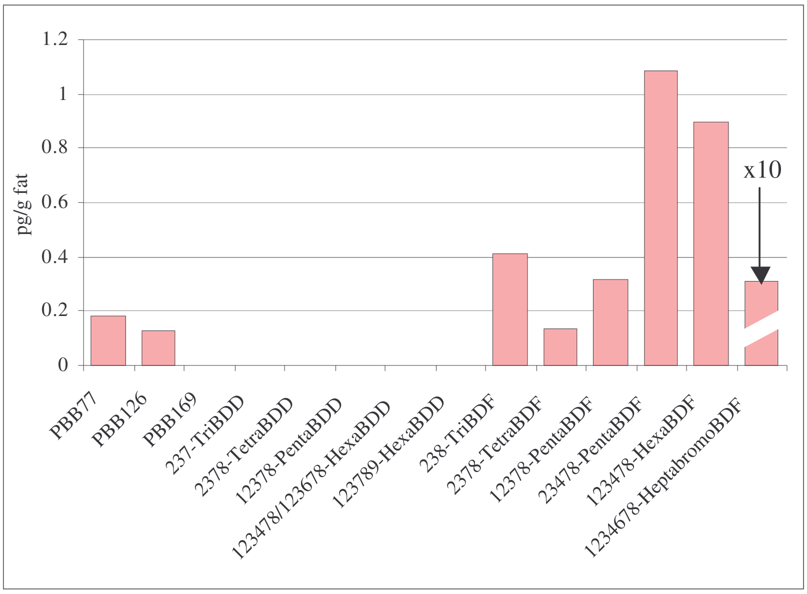




Dietary exposure to PBDD/Fs was dominated by lower brominated furans, Figure 4. Exposure to non-ortho brominated biphenyls and brominated dioxins and furans was principally from Sugars and Preserves, Figure 3. This is in agreement with earlier studies. Reasons for this remain unclear. It is possible that PBDD/Fs are introduced as process contaminants in the manufacture of these products.

Figure 3. Dietary exposure to PBDD/Fs and dioxin like PBBs (PBB PBDD/Fs ΣWHO-TEQ pg/day)

Figure 4. Average non-ortho PBB and PBDD/F congener profile in 2003 UK diet



Exposure to brominated dioxins and dioxin-like biphenyls was estimated to be in the range ΣWHO-TEQ 5.3-27.1 pg/day (Lower to Upper bound).

Whilst this level is low it is based on the assumption that TEFs are equivalent to chlorinated dioxins.

Several PBDD/Fs have been shown to have greater toxicity than their chlorinated analogues[11].

Moreover, the ΣWHO-TEQ model used here omits tribromo- dioxins and furans. These compounds were detected in several foodstuffs and have been demonstrated to have significant toxicty[11]. Consequently it is possible that the estimated total toxic equivalence is lower than the 'true' value.

Further work is required to quantify more recent dietary exposure and to assess the actual toxic equivalence factors of PBDD/Fs.

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