BROMINATED DIOXINS AND PBDES: OCCURRENCE TREND IN UK FOOD

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Introduction

One of the primary pathways of human exposure to a number of persistent organic pollutants (POPs) such as brominated dioxins (PBDD/Fs) and polybrominated diphenylethers (PBDEs) is through dietary intake. In recent years there have been reports on declining levels of PBDEs in some foods, such as domestic meat and poultry in the US[1]. The ban on the production and use of commercial PBDE mixtures (since 2004) is likely to have contributed to the reported decline in environmental and biotic media over the last few years.

The corresponding situation with respect to PBDD/Fs is not known. Despite awareness of the toxicity of these compounds, that is similar to their chlorinated counterparts, the pool of available data on food occurrence is small. It is clear that humans are exposed to these contaminants, as evidenced by the reports on occurrence in human milk and adipose tissue[2,3]. PBDD/Fs occur in the environment through formation pathways that are associated with combustion processes such as incineration. However they can also occur as trace contaminants in brominated flame retardants (BFRs) such as PBDEs, and studies on formation chemistry show that the incineration of products containing BFRs as well as thermolysis of BFR material such as PBDEs is an important source of PBDD/F emissions. Although the ban on the use of PBDEs and other BFRs such as HBCD has been in place for some years, the global use of bromine, in particular for the production of organic bromine compounds (e.g. other BFRs), and the gradual disposal of older products containing BFRs, ensure a significant source of these contaminants for future years.

The occurrence of PBDEs and PBDD/Fs in food, is examined here, using data from 3 studies, representing foods collected in 2003, 2007 and 2012. The first and last of these are total diet studies (TDS) and the other is an investigation into the occurrence of these contaminants in commonly consumed foods.

Materials and methods

The food samples for studies 1 (2003) and 3 (2012) were collected as per usual practice for total diet studies. The protocol for these, is well characterised and has been published before[4]. All food groups were analysed apart from beverages, which have negligible fat content. Study 2 involved the measurement of just over 100 samples of individual foods consisting of meat, meat products, eggs, milk and dairy products, fish, poultry, offal, potatoes, green vegetables and other vegetables. Apart from the fact that these were individual samples rather than pools, there are many similarities with the TDS food group samples collected for studies 1 and 3. The analytes included the following PBDEs - IUPAC numbers 17, **28, 47**, 49, 66, 71, 77, 85, **99**, 100, 119, 126, 138, **153, 154**, **183** and **209,** and 12 tri-hepta substituted PBDD/Fs - 2,3,7-triBDD, 2,3,8-triBDF, 2,3,7,8-Br substituted tetra- to hexa- PBDD/Fs (note that this includes only one hexa-bromo substituted furan as no standards were available for the other three congeners). Analytes for which ^{13}Carbon labeled standards were used as internal or sensitivity standards are shown in bold type and these also included six PBDD/F congeners.
The samples for all studies were analysed at the same laboratory using the same accredited (IS17025) methodology[5,6] which uses ^{13}C-labelled internal standardization throughout, followed by high resolution GC-high resolution mass spectrometry measurement. Confidence in the data quality is enhanced by successful participation in available PT schemes.

Results and discussion

The volume of data generated from these three studies is considerable, and was therefore condensed for presentation. For PBDEs, the upper-bound (non-detected congeners are included at the limit of detection) sum of the 17 measured PBDEs was used; for PBDD/Fs, the upper and lower-bound (non-detected congeners not included) TEQ was computed using analogous chlorinated dioxin TEFs$_{(1998)}$. The data is presented in Table 1 on a fat weight basis; the included fat content allows conversion to whole weight basis if required for comparative purposes. In order to facilitate comparison between the three studies, 10 food groups that were common to all three studies (as described in materials and methods) were used to estimate trends. For the second study (2007), the mean value of the individual concentrations within a particular food group has been used.

Table 1: Summed PBDE and PBDD/F TEQ* concentrations in food groups.

Food group	Carcase meat	Offal	Meat products	Poultry	Fish	Eggs	Green vegetables	Potatoes	Other vegetables	Dairy products
% lipid 2003	12.0	6.2	18.0	6.9	8.4	8.7	0.4	2.4	2.8	17.4
% lipid 2007	9.1	7.6	17.1	10.2	11.3	11.2	0.3	11.6	0.4	22.1
% lipid 2012	14.4	9.9	14.9	7.3	9.3	9.6	0.3	5.2	5.5	23.3
PBDE concentrations µg/kg										
2003	2.72	1.59	21.65	5.49	6.98	1.73	7.71	1.35	7.89	1.6
2007	1.16	2.05	1.95	1.83	24.60	2.65	9.83	3.51	10.14	0.85
2012	0.56	0.40	0.50	0.48	3.44	0.57	1.62	0.31	0.44	0.31
PBDD/F TEQ concentrations ng/kg										
2003 TEQ lower	0.11	0.43	0.07	0.04	0.05	0.02	0.31	0.01	0.01	0.05
2003 TEQ upper	0.27	0.89	0.18	0.37	0.46	0.38	0.66	0.39	0.30	0.25
2007 TEQ lower	0.05	0.33	0.03	0.06	0.02	0.03	0.48	0.04	0.21	0.03
2007 TEQ upper	0.23	0.54	0.20	0.23	0.32	0.31	1.70	1.01	1.97	0.18
2012 TEQ lower	0.21	0.40	0.08	0.04	0.11	0.09	1.25	0.18	0.08	0.09
2012 TEQ upper	0.25	0.44	0.11	0.12	0.17	0.17	2.03	0.24	0.18	0.12

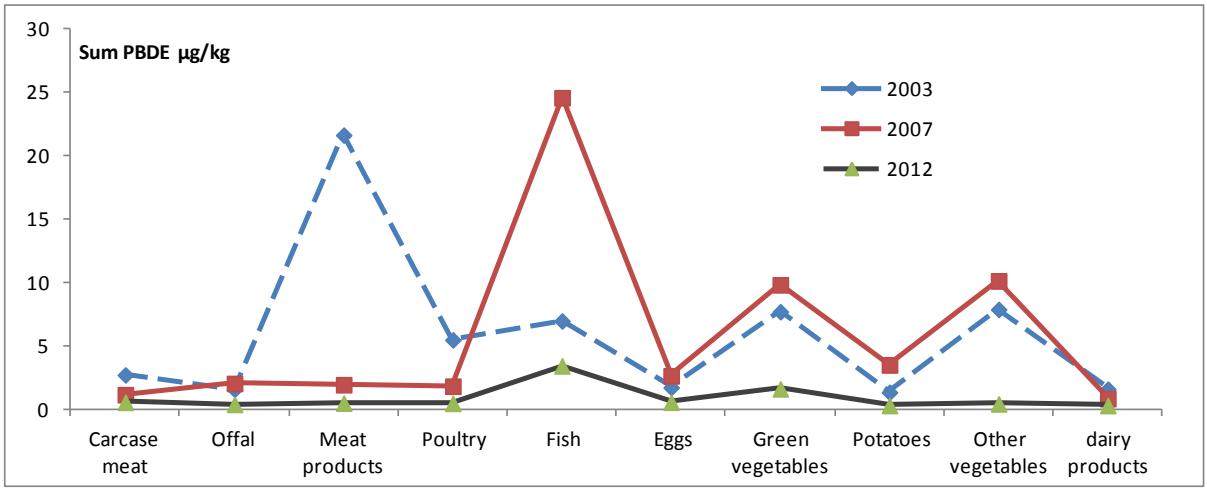
*Teqs computed using PCDD/F TEF$_{(1998)}$

Although 17 PBDEs including BDE-209 were measured, the majority of the contribution to the summed PBDE total can be attributed to the widely measured congeners – BDE 28, 47, 99, 100, 153, 154 and 209. There is poor correlation between the occurrence of BDE 209 and the sum of the other congeners, which probably reflects the historical use of the different commercial mixtures. Figure 1 plots the concentrations of the food groups over time. A number of observations are evident from this plot. The most obvious of these is the maxima for meat products in 2003, and for fish in 2007. It is noteworthy that the ban on the commercial PBDE mixture –Penta came into force in 2004, whereas that for Deca was later during the decade. The maxima for fish in 2007 is more difficult to explain – the group consisted of both oily and non-oily species (n=38), but did not include shellfish, which do form a part of the TDS fish group. However shellfish harvested in the UK are reported to show relatively high PBDE concentrations[7]. The other major observation is the decline in concentrations over time, as observed by the data for 2012, and may be a measure of the efficacy of the regulations regarding the ban and use of commercial PBDE mixtures.

The occurrence of PBDD/Fs in the majority of foods is characterised by a more frequent detections of PBDFs, and in particular, the tri-, tetra, 23478-penta, and the hepta-brominated furan. PBDDs were less frequently observed, and in most cases were limited to the tri- and tetra brominated congeners. This lower frequency of PBDD detection, when coupled with the condensation of the congener data to TEQs, may result in conventionally reported upper-bound TEQ values containing a number of "less than" or non-detected values.

This is compounded by the higher TEF values for PBDDs, in particular the penta-BDD which was rarely detected. The use of the analogous chlorinated TEFs for PBDD/Fs is debateable, but has been used in the absence of a full set of TEFs derived for PBDD/Fs.

Figure 1: PBDE concentrations in food groups



In order to allow a meaningful comparison of the data and any trends, another relevant observation must be made. Since the measurement of the first data set (2003 TDS), there have been advances in measurement techniques which have allowed improvements in the method detection limits. This has resulted in a greater degree of convergence of the upper and lower bound TEQs in the most recent data (2012 TDS). In order to minimise the effects of this artefact, both upper and lower bound TEQ data is presented for the PBDD/Fs in Figures 2 and 3, and show differing trends for PBDD/F concentrations (the maxima for vegetables is simply a result of the low fat content of this food group). The biggest difference between upper and lower bound is that whilst the upper bound data shows an apparent decline over time, the lower bound data does not – it is difficult to discern any trend from the lower bound data which may suggest that PBDD/F concentrations are steady over time, with some apparent marginal increase over time for some food groups. The decline in concentrations over time, observed for the upper bound data may simply be a measure of the improvement in measurement sensitivity.

In terms of concentrations, both, individual congener levels as well as TEQ are significantly lower for the PBDD/Fs in comparison to the PCDD/Fs.

Figure 2: PBDD/F TEQ concentrations in food groups – upper bound data

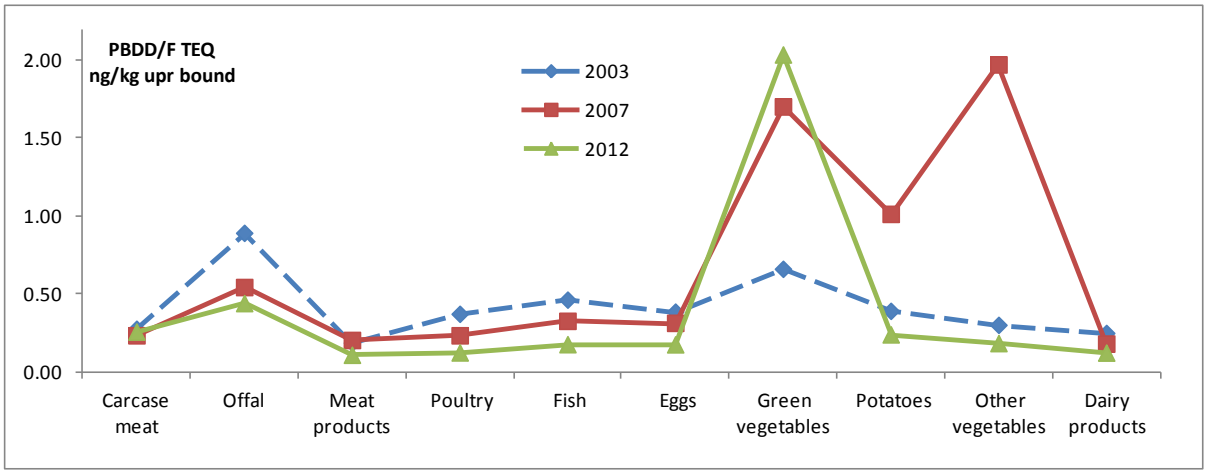
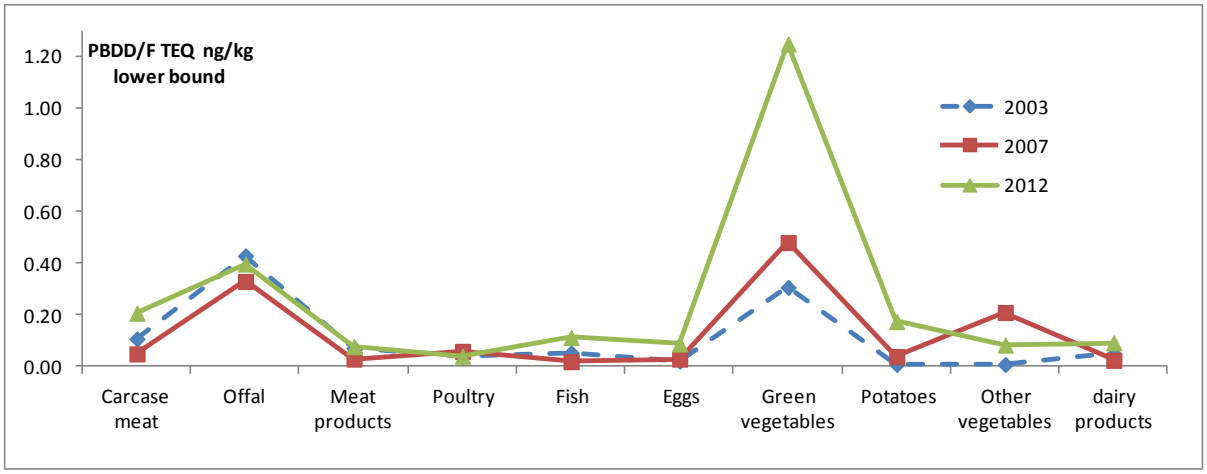


Figure 3: PBDD/F TEQ concentrations in food groups – lower bound data



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