CONSUMER EXPOSURE TO CHLORINATED AND BROMINATED DIOXINS AND BIPHENYLS AND POLYBROMINATED DIPHENYL ETHERS: NEW UK TOTAL DIET STUDY

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Introduction

Total diet studies (TDS) are a means of assessing consumer exposure to chemicals, including contaminants, in food. The outcomes can be used to prioritize contaminants for further investigation, establish a baseline level of exposure for emerging contaminants prior to any reduction initiatives and to measure the lowering of exposure resulting from such initiatives. Previous TDSs have been carried out in the UK for dioxins in 2001 and for brominated compounds in 2003[1,2]. For this investigation, as well as repeating these studies to determine any trends over the past decade, mixed halogenated dioxins and biphenyls have been included for the first time.

Table 1. Food Group Compositions

Food Group	No. of sub samples	% Fat content
Bread	29	4.14
Cereals	40	9.42
Carcass Meat	51	14.41
Offal	85	9.92
Meat Products	123	14.86
Poultry	51	7.32
Fish	140	9.31
Fats & Oils	84	73.80
Eggs	34	9.55
Sugar & Preserves	30	6.05
Green Vegetables	23	0.29
Potatoes	23	5.19
Other Vegetables	40	5.46
Canned Vegetables	15	0.53
Fresh Fruit	23	0.21
Fruit Products	15	0.42
Milk	44	1.97
Milk & Dairy Products	102	23.31
Nuts	34	41.84

Materials and methods

The Total Diet Study was conducted by measuring a range of contaminants in composites representing 19 food groups (a twentieth group, beverages, was excluded as it was considered of low importance with regard to lipophilic POPs). Between November 2011 and March 2012, a total of 986 retail food samples were purchased by Ventress Technical Ltd from a range of national supermarkets (50%), symbol retailers (25%) and independent retailers (25%) in twelve locations around the UK. Bigger ranges of samples were obtained for the animal product food groups, which are the more important sources of POPs in the diet. Table 1 shows the sample numbers for each group. Each individual sample was prepared as though for consumption, including different methods of cooking where appropriate. Samples were homogenized, put into their respective food groups in equal quantities and thoroughly re-homogenized. Aliquots were freeze dried prior to analysis. The method used for the preparation, extraction and analysis of samples for PCDD/Fs, PCBs, PBBs and PBDEs, which comprises part of CEN method EN16215:2012, is reported elsewhere[3]. For the mixed halogenated dioxins and biphenyls (PXDD/F/PXBs), the method was modified to include an additional activated carbon elution stage before quantification. This has been reported previously[4].

Exposure assessments were carried out using the Intake Programme, bespoke software developed for the Food Standards Agency. Total consumption for each food group was derived from food diaries kept by approximately 2,000 participants in an annual National Data and Nutrition Survey. From the distribution of calculated exposures across all participants, dietary exposures for average and high-level (97.5th percentile) consumers were estimated.

Results and discussion

Table 2 lists the levels of dioxins, furans and biphenyls found in each food group as the WHO-2005 TEQs, applying the TEFs for chlorinated compounds to their brominated and mixed halogenated analogues. Although the emphasis of this paper is on brominated chemicals, the results for chlorinated dioxins are included for contextual purposes. The brominated dioxins/furans only comprised nine congeners although these were mainly those with the higher TEFs (tetra/penta/hexa). For these, when compared with levels reported in food groups from 2003, the lower bound results have generally increased whilst the upper bound levels have generally decreased, although the changes are relatively small in absolute terms. Rather than a temporal effect, this is likely to be a reflection of improvements to the sensitivity of the analysis, meaning that there are fewer non-detects with upper bound estimates based on lower limits of quantification. This leads to a convergence of the upper and lower bound estimates. Table 3 lists the mixed halogenated congeners that were measured (mono-brominated analogues of PCBs 105, 118 and 156 were also measured but their contribution to the TEQ was negligible). Due to the very limited availability of standards, only two out of five possible TCDD analogues were quantified, two out of eight TCDF analogues, five out of 90 penta-substituted congeners and three out of 18 PCB 126 analogues. There was strong evidence for the presence of other congeners. Thus, whilst mixed halogenated compounds contributed about 3% (lower bound) or 8% (upper bound) to the total TEQ, only around 10% of the key congeners containing halogen substituents at the 2,3,7,8-positions were measured, and the actual contribution to the total TEQ for each food group may be between 20 and 50%, making the mixed halogenated congeners almost as significant as chlorinated. There is supporting scientific evidence that relative Ah-receptor binding potencies of brominated and mixed halogenated congeners are similar to their chlorinated analogues[9].

Table 2. Dioxins/furans/biphenyls, (pg WHO-2005 TEQ /kg whole weight)

Group	Chlorinated		Brominated		Mixed	
	lower	*upper*	*lower*	*upper*	*lower*	*upper*
Bread	7.0	11.5	8.2	20.7	1.2	4.0
Cereals	5.0	12.6	23.1	34.4	3.5	5.8
Carcase meat	76.7	76.9	29.8	37.0	2.0	4.5
Offal	191	191	42.0	45.9	3.4	5.0
Meat products	29.9	30.2	12.0	16.0	1.9	4.4
Poultry	10.0	10.8	3.0	9.1	0.4	2.1
Fish	326	326	10.5	16.4	4.5	5.1
Fats & oils	70.8	91.5	0	79.0	1.2	19.5
Eggs	43.9	44.2	8.4	16.8	0.5	2.6
Sugar and preserves	55.5	55.6	94.9	102	2.2	4.9
Green vegetables	4.5	4.6	3.6	6.0	0.5	1.1
Potatoes	8.1	9.7	9.1	12.6	0.2	2.9
Other vegetables	52.6	52.7	4.6	10.1	1.9	2.6
Canned vegetables	1.0	2.1	0.6	3.4	0	1.4
Fresh fruit	1.4	3.2	4.0	7.3	0	1.2
Fruit products	6.3	7.5	12.2	16.9	0	2.5
Milk	8.2	8.3	3.5	5.1	0.1	0.8
Milk & dairy	105	105	21.7	28.2	1.4	5.9
Nuts	5.0	18.8	3.3	34.7	1.0	13.7

Dietary exposure estimates are shown in table 3. The chlorinated congeners show only small falls of around 5-10% since the last UK TDS in 2001[1]. High consuming toddlers and young children continue to exceed the Tolerable Daily Intake of 2.0 pg/kg bodyweight. The differences between upper and lower bound estimates for both average and high consumers are relatively small for all age groups, reflecting the reliability of the analysis. In the case of brominated analogues, there appears to have been little change since 2003. The lower bound exposure estimates have increased two to threefold whilst the upper bound estimates have fallen by around 20-30%, probably as a result of the improved analytical performance noted earlier. The contribution to the total TEQ from the brominated component is consistently around 30% for all age groups and for average and high consumers, whether based on upper or lower bound data. This shows the importance of the forthcoming WHO review of evidence to support the use of chlorinated dioxin TEFs for the brominated analogues. The contribution from the mixed halogenated components to the total TEQ is much lower at 3-6%. However, as noted above only a small minority of potentially active congeners could be quantified. It is likely that the contribution to overall dietary exposure is significantly higher and it is therefore important that more reference standards are made available and that more analytical laboratories familiarize themselves with this difficult analysis. The time and resource currently put into reducing dietary exposure to chlorinated dioxins may be wasted if other significant *contributors to the dioxin TEQ are overlooked.*

Table 3. Dietary exposure estimates for all age groups (pg WHO-2005 TEQ/kg BW d^{-1}).

Age Group	Total PCDD/F/PCB TEQ				Total PBDD/F/PBB TEQ				Total PXDD/F/PXB TEQ			
	Mean LB	Mean UB	P97.5 LB	P97.5 UB	Mean LB	Mean UB	P97.5 LB	P97.5 UB	Mean LB	Mean UB	P97.5 LB	P97.5 UB
Toddlers(1.5 - 4.5 y.o.)	1.42	1.5	3.24	3.33	0.19	0.95	0.35	1.64	0.05	0.15	0.09	0.27
Children (4-6 y.o.)	1.81	1.27	2.35	2.46	0.58	0.84	0.94	1.29	0.05	0.14	0.08	0.21
Children (7-10 y.o.)	0.88	0.95	1.58	1.71	0.46	0.67	0.76	1.05	0.04	0.11	0.07	0.17
Children (11-14 y.o.)	0.59	0.64	1.16	1.21	0.33	0.47	0.61	0.83	0.03	0.08	0.04	0.13
Youths (15-18 y.o.)	0.47	0.51	0.88	0.94	0.24	0.35	0.48	0.67	0.02	0.06	0.04	0.10
Adults (19-64 y.o.)	0.49	0.52	1.04	1.08	0.19	0.29	0.35	0.51	0.02	0.05	0.04	0.09
Elderly (>65 y.o.), home	0.52	0.55	0.99	1.02	0.19	0.29	0.36	0.51	0.02	0.05	0.03	0.09
Elderly (>65 y.o.), inst	0.66	0.7	1.1	1.15	0.28	0.41	0.47	0.66	0.03	0.07	0.04	0.10

Results for individual PBDE congeners are shown in Table 4. In general, levels appear to have fallen since 2003, which may be a reflection of the reduction in use of commercial penta- and octa-BDE mixtures since their phasing out in the mid-2000s. BDE 47 is, as expected, the most abundant congener, followed by BDE 99. Together with BDE 153 and BDE 209 ('deca'), these are the congeners for which the European Food Safety Authority was able to identify enough toxicological data to calculate margins of exposure, although not Health Based Guidance Values.[6] BDE 209 levels have also fallen in the majority of food groups, although several, including some of the fish and non animal product food groups, have risen. Exposure estimates are shown in table 5. They are consistently lower, by 50% or more, than the exposures estimated in 2003. They are also approximately half to one order of magnitude lower than the estimated intakes reported in the EFSA opinion on PBDEs, although the latter contained a number of estimates with significant variation. Eveb based on the intakes used by EFSA, the margins of exposure (MoE) to BDEs 47, 153 and 209 did not raise any toxicological concerns. In the case of BDE 99, EFSA did identify a potential health concern in highly exposed toddlers, whilst acknowledging that the exposure may have been an over-estimate. In any event, the MoE based on the current results is about ten times greater and would not be of concern with regard to neurodevelopment. This is consistent with the earlier conclusions of the UK's independent expert Committee on Toxicity of Chemicals in Food, Consumer Products and the Environment (COT) that dietary exposure to PBDEs did not to raise any toxicological

Table 4. PBDE and α-HBCDD congener levels, µg/kg whole weight

Group	**BDE 47**		**BDE 99**		**BDE 153**		**BDE 209**	
	2003	*2012*	*2003*	*2012*	*2003*	*2012*	*2003*	*2012*
Bread	0.013	0.005	0.010	0.006	0.002	0.002	0.057	<0.2
Cereals	0.013	0.006	0.010	0.008	0.001	0.002	0.043	<0.19
Carcase meat	0.022	0.018	0.020	0.022	0.007	0.007	0.256	<0.13
Offal	0.019	0.007	0.016	0.009	0.007	0.003	0.039	<0.12
Meat products	0.081	0.018	0.092	0.019	0.023	0.004	3.638	<0.14
Poultry	0.049	0.005	0.080	0.006	0.014	0.001	0.208	0.22
Fish	0.256	0.134	0.059	0.023	0.009	0.007	0.087	0.17
Fats & oils	0.077	0.037	0.084	0.035	0.023	0.008	0.291	<0.39
Eggs	0.017	0.013	0.024	0.016	0.007	0.005	0.084	0.09
Sugar and preserves	0.062	0.121	0.051	0.062	0.008	0.007	0.393	1.95
Green vegetables	0.002	0.002	0.002	0.001	0.000	0.0002	0.026	0.05
Potatoes	0.004	0.005	0.004	0.005	0.001	0.001	0.020	0.05
Other vegetables	0.029	0.005	0.059	0.008	0.011	0.001	0.078	0.05
Canned vegetables	0.003	0.001	0.003	0.000	0.001	<0.001	<0.009	0.02
Fresh fruit	0.002	0.001	0.002	0.001	0.000	0.0002	0.024	0.14
Fruit products	0.013	0.001	0.010	0.001	0.002	0.0004	0.039	0.03
Milk	0.007	0.002	0.008	0.002	0.002	0.0005	0.021	0.12
Milk & dairy	0.057	0.023	0.068	0.025	0.016	0.006	0.106	0.02
Nuts	<0.019	0.006	<0.014	0.005	<0.005	0.001	0.110	0.1

concerns.[2] Nevertheless, EFSA did note that other PBDE sources, such as in houses and cars, may also be an important route of exposure, although with the comment that this was still not of concern in the case of BDE 209.

Table 5. Upper bound exposures to PBDEs (ng/kg BWd^{-1})

	BDE-47		**BDE-99**		**BDE-153**		**BDE-209**	
Age Group	Mean	P97.5	Mean	P97.5	Mean	P97.5	Mean	P97.5
Toddlers (1.5 - 4.5 y.o.)	0.61	1.22	0.48	0.91	0.10	0.20	9.21	16.21
Children (4-6 y.o.)	0.55	1.02	0.41	0.67	0.09	0.15	7.81	14.00
Children (7-10 y.o.)	0.43	0.77	0.32	0.54	0.07	0.11	6.12	11.30
Children (11-14 y.o.)	0.30	0.70	0.23	0.43	0.05	0.08	4.36	9.10
Youths (15-18 y.o.)	0.22	0.46	0.17	0.30	0.04	0.06	3.18	7.05
Adults (19-64 y.o.)	0.20	0.41	0.14	0.25	0.03	0.06	2.56	5.03
Elderly (>65 y.o.), home	0.21	0.41	0.15	0.25	0.03	0.06	2.53	4.96
Elderly (>65 y.o.), inst.	0.28	0.49	0.21	0.34	0.04	0.07	3.67	6.89

In conclusion, brominated and probably also mixed halogenated dioxins, furans and biphenyls may make a significant contribution to dietary exposure to dioxin-like compounds. One of their main sources is likely to be combustion of materials and items containing a high level of bromine and there is a need to better understand their relationship with the use of brominated flame retardants. Dietary exposure to PBDEs, on the other hand, does not raise any health concerns and may be a lower priority for further investigation, although it will be important to put this into context with regard to other routes of exposure.

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