

CONTAMINATION OF U.S. BUTTER AND UPDATED ESTIMATE OF PBDE DIETARY INTAKE

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Introduction

The objective of this paper is to report for analytic techniques which assisted in analytic procedures which helped document the first time an incident of high level contamination of a U.S. food, butter, with the persistent organic pollutant (POP) polybrominated diphenyl ether or PBDE. Previous studies by our group and other researchers have documented polybrominated diphenyl ether (PBDE) levels in food from the United States and elsewhere.^{1,2,3,4} In the course of a 2008-09 market basket survey of U.S. meat, fish, dairy, fruit and vegetables, it was noted that one of the ten butter samples collected from Dallas, Texas supermarkets had elevation of certain PBDE congeners.^{5,6,7} This butter sample, produced by a large and widely known butter manufacturer, had markedly higher levels of Deca congeners, BDEs 206, 207, and 209, than did the other nine butter samples. The paper wrapping of this stick of butter was also analyzed and found to have even higher levels of PBDEs. We report from the analysis of individual butter samples rather than previously reported findings from the analysis of one pool of butter. Further, an updated estimation of daily adult dietary intake is presented.

Materials and Methods

Sample Collection

As part of an ongoing series of market basket surveys of U.S. food purchased from supermarkets or fast food franchises in Dallas, Texas and elsewhere in the U.S.A. ten butter samples were collected from Dallas supermarkets in December 2008 and January 2009.^{5,6,7} The ten samples were initially pooled into one composite sample and analyzed for the presence of brominated flame retardants including PBDEs. High levels of Nona and Deca congeners were detected in the analysis of the pooled sample. Another series of analyses of the butter was conducted for each of the ten individual butter samples. One sample was found highly contaminated with the Deca congeners, which accounted for the elevated level found in the pooled sample. The paper wrapping of the contaminated butter sample was then analyzed to determine if the origin of contamination. The manufacturer of the butter was notified and an investigation undertaken to determine how this paper was contaminated.

Analytic Methods

Quantification of PBDE levels in food has been described previously.^{3,8} A modification was employed using a shorter 12 m column and negative ion methodology for improved octa- through deca-BDE measurements. Cleanup of all lipid extracts was performed by acid treated alumina oxide columns. The final extract was reduced to a volume of 50 µl by a stream of nitrogen containing ¹³C₁₂ - labeled BDE 138 for recovery standard. Measurements were performed using GC/MS with negative chemical ionization (NCI) mode and DB 5 (15 m, 0.25 mm ID, 0.1µm film) column for gas chromatographic separation.

Results and Discussion

Table 1 presents the congener specific data for each of the 10 butter samples and also the wrapping paper which surrounded the one highly contaminated stick of butter. The highly contaminated butter sample had total PBDEs of 42,253 pg/g whole weight (ww). The levels of BDE 206, 207, and 209 were 2,000, 2,900, and 37,600 pg/g ww, respectively. The level of total PBDEs in the wrapping paper was 804,751, and the levels of BDE 206, 207, and 209 were 51,000, 117,000, 614,000 pg/g, respectively. The levels of total PBDEs in the remaining 9 butter samples varied from 181 to 1,213 with a geometric mean of 483 and median of 284 pg/g. The relative amounts of BDE 209, 207, 206, and the Octa congeners suggest contamination with the Deca commercial mixture.⁹ No PBDE congeners with less than seven bromines on the molecule were detected in butter sample 10's packaging.

This updates our most recent estimate of total PBDE daily dietary intake of 50,386 pg/day to the new lower level shown in Figure 1 of 22,764 pg/day. Figures 2 and 3 compare the percent of daily PBDE dietary intake by food type reported in our most recent PBDE levels in food paper to the newer percents calculated here by omitting the one

dairy PBDE outlier.⁶ The updated total PBDE dietary intake from meat, fish, dairy and eggs, and vegetable products was 9,099, 1,595, 11,027, and 1,043 pg/day, respectively. Therefore, the updated percent of dietary intake of PBDEs in meat, fish, dairy and eggs, and vegetable products excluding the outlier changed from 18% to 40%, 3% to 7%, 77% to 48% and 2% to 5%, respectively.

In discussions with representatives of the butter company they mentioned that it was possible an electrical incident at the factory could have released Deca congeners contaminating the paper, or the paper was contaminated prior to reaching the butter facility. The company has investigated the source but has not shared its findings with the authors to date. The results from this study underscore the potential for chemical contamination of the U.S. food supply. Studies such as this one point to the importance of federal monitoring of the US food supply, however, the FDA does not currently have tolerances, guidance levels, or action levels established for PBDEs.

Figure 1. Updated Estimation of Daily PBDE Dietary Intake (pg/day)

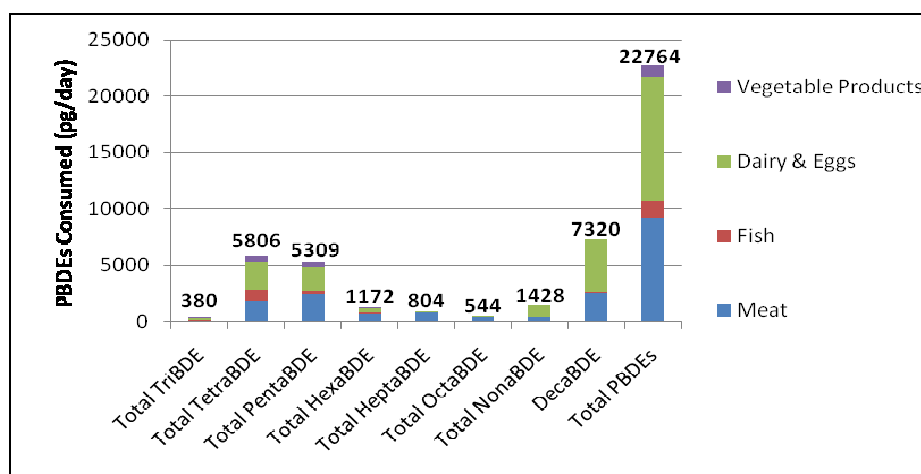


Figure 2. Food Type Contribution to Daily PBDE Intake (With Outlier)

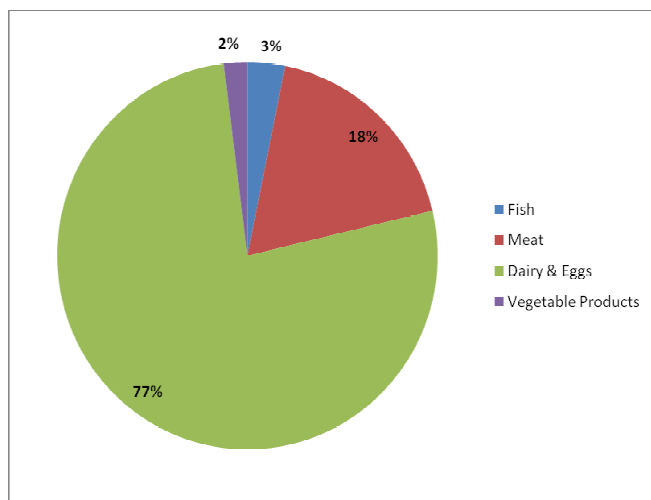
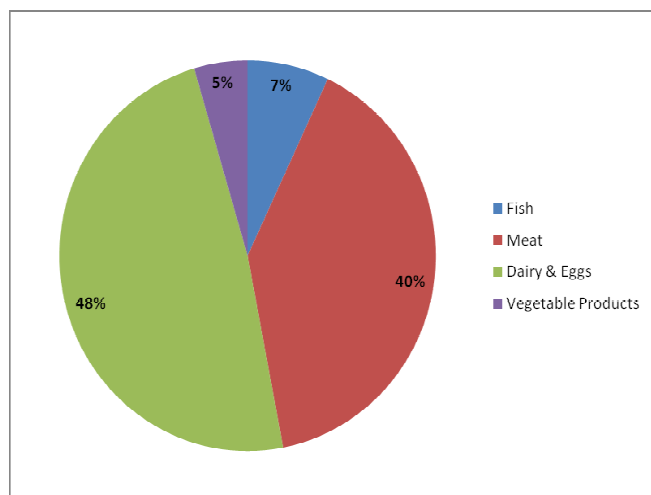


Figure 3. Food Type Contribution to Daily Total PBDE Intake (Without Outlier)



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Table 1. PBDE concentrations measured in 10 butter samples and one butter wrapper (pg/g wet weight/original weight)

	Butter Sample 1	Butter Sample 2	Butter Sample 3	Butter Sample 4	Butter Sample 5	Butter Sample 6	Butter Sample 7	Butter Sample 8	Butter Sample 9	Butter Sample 10	Sample 10 Wrapper	Butter Samples Geo. Mean	Butter Samples Median
BDE-17	(5.80)	(1.45)	(0.80)	(6.30)	(0.90)	(0.60)	(0.70)	(0.50)	(1.50)	(1.50)	(50)	0.7	0.6
BDE-28	(5.10)	7.60	15.30	(5.50)	(0.80)	2.80	(1.40)	2.10	(2.40)	(2.40)	(50)	2.1	2.3
BDE-47	62.00	472.00	151.00	136.00	79.20	55.20	88.80	138.00	104.00	101.00	(100)	113	102.5
BDE-49	(1.80)	(2.30)	(1.50)	(3.10)	(1.60)	(1.60)	(1.40)	(1.20)	(1.90)	(2.70)	(100)	0.9	0.9
BDE-66	(1.90)	(2.40)	(1.60)	(3.30)	(1.60)	(1.70)	(1.40)	(1.30)	(1.90)	(2.70)	(100)	0.9	0.9
BDE-71	(1.80)	(2.40)	(1.60)	(3.20)	(1.60)	(1.70)	(1.40)	(1.30)	(1.80)	(2.70)	(100)	0.9	0.9
BDE-77	(1.10)	(1.40)	(0.90)	(1.80)	(0.90)	(0.90)	(0.80)	(0.70)	(1.00)	(1.40)	(100)	0.5	0.5
BDE-85	(1.40)	(5.40)	(3.40)	(8.40)	(2.60)	(2.20)	(1.70)	(1.70)	(4.90)	(4.50)	(100)	1.5	1.5
BDE-99	41.20	489.0	84.00	56.30	47.80	40.00	76.10	107.00	75.00	67.20	(100)	77.2	71.1
BDE-100	8.60	83.80	22.00	13.70	9.50	6.70	14.40	22.20	17.60	12.00	(100)	15.7	14.1
BDE-119	(1.50)	(5.70)	(3.60)	(9.00)	(2.80)	(2.40)	(1.80)	(1.80)	(5.30)	(4.90)	(100)	1.7	1.6
BDE-126	(0.90)	(3.40)	(2.20)	(5.40)	(1.70)	(1.40)	(1.10)	(1.10)	(3.10)	(2.90)	(100)	1	1
BDE-138	(4.50)	(5.20)	(6.60)	(13.70)	(3.60)	(2.00)	(4.80)	(4.20)	(4.30)	(4.40)	(200)	2.4	2.2
BDE-153	10.20	72.00	18.10	(14.00)	11.20	6.50	13.10	17.10	11.70	8.80	(200)	13.2	11.5
BDE-154	(3.50)	24.40	(5.20)	(10.70)	4.50	(1.50)	(3.80)	7.20	(3.60)	(3.70)	(200)	3.1	2.3
BDE-156	(5.40)	(6.30)	(8.00)	(16.60)	(4.40)	(2.40)	(5.80)	(5.00)	(5.10)	(5.30)	(200)	2.9	2.7
BDE-183	(5.70)	(7.70)	(9.40)	(3.30)	(3.80)	(2.70)	(3.10)	(4.90)	(6.20)	(4.70)	900	2.4	2.4
BDE-184	(5.30)	(7.20)	(8.80)	(3.10)	(3.60)	(2.60)	(2.90)	(4.60)	(4.60)	(4.40)	(300)	2.2	2.3
BDE-191	(4.00)	(5.40)	(6.60)	(2.30)	(2.70)	(1.90)	(2.20)	(3.40)	(3.20)	(3.30)	(300)	1.6	1.6
BDE-196	(9.20)	(9.60)	(9.20)	(8.10)	(6.20)	(7.10)	(4.80)	(6.80)	(8.30)	101.0	11900	5.2	4.1
BDE-197	(9.50)	(9.90)	(9.50)	(8.30)	(6.40)	(7.30)	(5.00)	(7.00)	(8.60)	47.10	9950	5	4.2
BDE-206	(9.90)	(7.20)	(6.60)	(7.50)	(10.30)	(4.90)	(8.40)	(7.30)	(8.00)	2000	51000	7.1	3.9
BDE-207	(7.40)	(5.40)	(13.20)	(5.60)	(7.70)	(3.60)	(6.30)	(5.50)	(10.80)	2290	117000	6.5	3.4
BDE-209	(31.50)	(39.80)	(32.20)	(30.40)	(43.70)	(32.90)	(37.80)	(48.70)	(51.60)	37600	614000	40.6	19.4
Total BDE	181	1213	356	291	206	152	241	347	277	42253	804751	483	284
Samples below the limit of detection denoted with the detection limit in parentheses.													