Levels of Polybrominated Diphenyl Ethers (PBDEs) in Fish, Beef, and Fowl Purchased in Food Markets in Northern California USA

William J. Luksemburg[1], Richard J. Wenning[2], Andrew Patterson[1], and Martha Maier[1]
[1] Alta Analytical Laboratories, El Dorado Hills, CA 95630 USA
[2] ENVIRON International Corporation, Emeryville, CA 94608 USA

Introduction

Recent studies of human milk, blood, and adipose tissues demonstrate exposure to polybrominated diphenyl ethers (PBDEs) in the U.S. population [1,2,3]. Exposure modeling performed using the limited available environmental data suggests that one of the main routes of human exposure to PBDEs is likely through the consumption of food products such as eggs, meats, fish, and dairy products [4]. The contamination of Belgium store-bought chicken products in 1999 and, more recently, concerns regarding farm-raised fish products in the U.S., Ireland, and elsewhere by polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) and biphenyls (PCBs) has heightened concerns about the occurrence of other persistent organic pollutants (POPs), including PBDEs, in consumer food products [5,6]. In the U.S., for example, recent studies have shown the edible portions of farm-raised fish containing higher levels of PCDD/Fs, PCBs, and PBDEs than in wild fish [7,8,9].

In this study, fillets from several species of freshwater and ocean fish (both farm-raised and wild), as well as ground beef, ground deer, and meat from several species of fowl (chicken, turkey, duck, goose, and pheasant) were purchased from food markets in the cities of Sacramento and El Dorado Hills, California USA. The purpose of the study was to understand further the occurrence and potential for exposures in the general U.S. population to PBDEs through the consumption of store-bought consumer food products.

Methods

Sample Preparation & Analysis

Fish, meat, and fowl meat products were collected in December 2003 and February 2004 from 3 different food markets located in the cities of Sacramento and El Dorado Hills in northern California USA. Fish included 6 species of wild, ocean fish and one species of bivalve (swordfish, pacific salmon, coho salmon, tuna, petrale sole, tilapia and sea scallops) and 2 species of farm-raised fish (atlantic salmon and catfish fillets and nuggets). Meat products included ground beef from cows raised on grain-fed and free-range diets, and ground deer meat from animals caught in California. Fowl products included breast meat from wild or naturally raised duck, goose, and pheasant, ground meat from free-range chicken and turkey, and the thigh meat from free-range chickens. The term free–range diet refers to the farming method whereby animals are allowed to

roam and feed freely within a relatively large, but confined, area with (or without) supplementing the diet with manufactured or natural feed products.

The edible portions of each meat product were homogenized and a representative sub-sample was soxhlet extracted with 1:1 methylene chloride/hexane and analyzed for 31 individual PBDE congeners and total mono-through-deca-PBDE homologue groups using USEPA draft Method 1614. The cleanup procedures included columns containing silica gel and activated carbon. The quantification of PBDEs was performed by selective ion recording using an AutoSpec Ultima high resolution gas chromatograph/high resolution mass spectrometer (HRGC/HRMS). A laboratory method blank and ongoing precision and recovery sample were extracted and analyzed with the food samples. With the exception of three internal standards (C^{13}BDE-3, -207, and –209), the recoveries of internal standards were greater than approximately 85%. Limits of quantitation (LOQs) varied from 10.0 to 250 pg/g (parts per trillion; ppt) wet weight (ww) for all congeners.

Screening-Level Exposure Assessment

The theoretical daily intake of PBDEs was calculated using a screening-level USEPA dietary exposure model and default assumptions of the likely average daily intake of different meat products by adults and children in the U.S [10,11]. The oral absorption factor for all PBDEs was assumed to be 90%, which is the high end of the range of bioavailability factors reported in animal studies for different congener groups [3]. The model included fish ingestion rates for children aged <1 to 18 years (1 to 11.5 g/day) and adults (20 g/day) and meat and fowl ingestion rates for children aged <1 to 18 years (54 to 318 g/day) and adults (400 g/day) representing the upper-end of the range of values reported by USEPA for different ages and ethnic groups in the U.S. population.

Results & Discussion

Results are summarized in Table 1. Seven congeners (BDE-1, -2, -3, -10, -77, -116, and -156) were not detected in samples and are excluded from further discussion. Total PBDE levels were higher in fish (ranging from 208 – 4,955 pg/g ww) and fowl (ranging from 196 – 2,516 pg/g ww) than in beef and deer meat products (ranging from 164 – 379 pg/g ww). In contrast to fish and fowl products, the hepta- and higher brominated congeners were generally absent from wild fish fillets and ground grain-fed beef and deer meat. With the exception of farm-raised fish, mono- and di- (and in some cases tri-) brominated congeners were absent in wild fish fillets, ground beef and deer meat, and fowl meat products. The highest concentrations of PBDEs detected in all samples of fish and beef, deer, and fowl meat products were BDE-47, BDE-99, and BDE-100. This is consistent with the results of market basket testing reported in other countries for a range of food products [3,6].

With the exception of swordfish, total PBDE levels were generally higher in fish products from farm-raised species than in wild-caught species; in the case of salmon, total PBDE concentrations in farm-raised fish were 5- to 6-fold higher than in wild fish. The high

levels in swordfish are likely due to the age of the fish when harvested; however, the comparable high concentrations measured in farm-raised salmon and catfish fillets may be explained by contamination of manufactured feed and/or by various environmental factors related to their enclosures (e.g., location of fish pens, runoff, sediment quality).

The theoretical daily intakes of total PBDEs by adults and children through the consumption of fish, meat, and fowl products were calculated assuming that the concentrations reported in this study were representative of the levels in fish and meat products potentially consumed by adults and children in the U.S. Assuming the highest and lowest concentrations measured in wild or farm-raised fish, theoretical average daily intakes of PBDEs through fish ingestion ranged between 6×10^{-8} and 1×10^{-6} mg/kg/day in children aged <1-18 years and between 8×10^{-8} and 1×10^{-6} mg/kg/day in adults. Assuming the highest and lowest concentrations measured in beef and chicken products, theoretical average daily intakes of PBDEs through ingestion ranged between 1×10^{-6} and 4×10^{-6} mg/kg/day in children aged <1-18 years and between 8×10^{-7} and 3×10^{-6} mg/kg/day in adults. The consumption of deer meat and fowl other than chicken (i.e., duck, goose, turkey, and pheasant) was assumed to represent a negligible proportion of the typical American diet and was not included in this screening-level analysis.

Assuming that total exposure to PBDEs by a child or adult was through the consumption of fish, meat, and fowl products at the levels found in meats purchased in 3 northern California food markets, the results of the screening exposure model were well below health effects benchmark values identified in ENVIRON (2003) [12] to evaluate the potential for thyroid effects based on the incidence of thyroid hyperplasia (0.04 mg/kg/day) and the potential for developmental effects based on changes in T4 levels in the fetus or neonate exposed in utero (0.07 mg/kg/day).

References

[1] Hooper, K, and She, J, *Environ Health Perspect. 111(1)*, 109-114 (2003).
[2] Schecter, A, Pauvak, M, et al., *Environ Health Perspect. 111(1)*, 1723-1729 (2003).
[3] Hites, R, *Environ Sci Technol. 38(4)*, 945-56 (2004).
[4] Wenning, RJ, *Chemosphere 46(5)* 779-96 (2002).
[5] McHugh, B, McGovern, E, Duffy, C, *et al., Organohalogen Compounds 62*, 89-92 (2003).
[6] Ferrario, J and Byrne, C, *Chemosphere 40*, 221-224 (2000).
[7] Hites, RA, Foran, JA, Carpenter, DO, *et al., Science 303*, 226-229 (2004).
[8] Luksemburg, W, Maier, M, Patterson, A, USEPA National Forum on Contaminants in Fish, San Diego, CA USA (2004).
[9] Brown, F, Winkler, J, Visita, P, *et al., Organohalogen Compounds 62*, 1-4 (2003).
[10] U.S. Environmental Protection Agency, Dietary Exposure Potential Model, v. 5, April. (2003).
[11] U.S. Environmental Protection Agency, Exposure Factors Handbook, (1997).
[12] ENVIRON, Tier 1 Assessment of the Potential Health Risks to Children Associated With Exposure to the Commercial Pentabromodiphenyl Ether Product (2003).

Table 1. The concentrations of PBDEs (pg/g wet weight) in beef, fish, and fowl meat products purchased in three food markets in northern California USA.

	WILD FISH PRODUCTS								FARM-RAISED FISH PRODUCTS					MEAT PRODUCTS			FOWL PRODUCTS					
	SWORD FISH	SWORD FISH	SALMON	COHO SALMON	TILAPIA	SCALLOP	CAN TUNA	PETRALE SOLE	SALMON	SALMON	CATFISH FILLET	CATFISH FILLET	CATFISH NUGGET	GROUND BEEF (grain-fed)	GROUND BEEF (free-range)	GROUND DEER	CHICKEN THIGHS	CHICKEN THIGHS (free-range)	DUCK	GOOSE	GROUND TURKEY	PHEASANT
Total Mono-BDE	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**
BDE-7	ND	ND	ND	ND	ND	ND	ND	ND	0.77	0.57	2.65	0.50	2.7	ND	ND	ND	ND	ND	ND	ND	ND	ND
BDE-13	ND	ND	ND	ND	ND	ND	ND	ND	0.88	0.25	0.22	0.19	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BDE-15	ND	0.53	ND	ND	ND	ND	ND	0.12	1.7	1.4	2.1	1.4	0.76	ND	ND	ND	ND	ND	0.60	ND	ND	ND
Total Di-BDE	**ND**	**0.53**	**ND**	**ND**	**ND**	**ND**	**ND**	**0.12**	**4.3**	**2.0**	**5.0**	**2.1**	**3.5**	**ND**	**ND**	**ND**	**ND**	**ND**	**0.60**	**ND**	**ND**	**ND**
BDE-17	0.97	5.9	ND	ND	ND	ND	ND	ND	9.7	17	3.7	1.8	3.1	ND	ND	ND	ND	ND	1.3	ND	ND	ND
BDE-25	ND	12	ND	ND	ND	ND	ND	1.8	16	9.8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BDE-28	3.3	99	3.1	3.6	ND	ND	ND	6.0	60	42	4.4	2.5	3.8	ND	0.36	ND	ND	ND	4.2	0.40	0.36	0.55
BDE-35	ND	ND	ND	ND	ND	ND	ND	0.62	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Total Tri-BDE	**4.2**	**117**	**3.1**	**3.6**	**ND**	**ND**	**ND**	**7.8**	**100**	**73**	**9.7**	**4.3**	**8.7**	**ND**	**0.36**	**ND**	**ND**	**ND**	**5.4**	**0.40**	**0.36**	**0.55**
BDE-47	58	3240	17	35	11	5.5	8.1	187	1310	727	218	78	124	45	10	120	37	12	187	20	77	26
BDE-49	15	193	3.4	1.5	ND	ND	ND	31	276	147	8.1	4.9	10	ND	0.61	ND	ND	ND	7.3	ND	1.7	0.75
BDE-66	3.5	68	1.5	2.0	ND	ND	ND	4.9	68	15	5.2	2.3	3.4	ND	0.45	ND	ND	ND	2.8	ND	ND	ND
BDE-75	2.0	12	ND	0.49	ND	ND	ND	1.5	2.1	12	1.5	0.82	1.3	ND	ND	ND	ND	ND	ND	ND	ND	ND
Total Tetra-BDE	**79**	**3520**	**24**	**39**	**11**	**5.5**	**8.1**	**225**	**1740**	**915**	**240**	**87**	**144**	**45**	**11**	**120**	**37**	**12**	**195**	**20**	**79**	**26**
BDE-85	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	13	4.1	5.0	ND	ND	6.5	1.3	ND	ND	1.3	2.9	1.2
BDE-99	24	206	7.8	20	8.3	6.7	12	50	243	59	395	102	151	75	17	179	53	21	209	29	165	34
BDE-100	15	641	3.1	7.7	2.6	1.8	3.4	35	279	136	57	22	36	ND	3.4	33	13	5.2	144	5.4	47	7.3
BDE-126	ND	2.3	ND	ND	ND	ND	ND	ND	3.3	0.90	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Total Penta-BDE	**41**	**871**	**11**	**28**	**11**	**8.5**	**15**	**85**	**561**	**209**	**466**	**128**	**191**	**95**	**20**	**218**	**68**	**26**	**370**	**36**	**216**	**42**
BDE-138	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.7	1.2	2.0	ND	ND	ND	ND	ND	44	ND	2.3	ND
BDE-153	4.5	47	ND	2.6	1.6	ND	1.5	5.8	39	17	28	10	20	ND	2.8	27	33	3.4	1220	5.3	38	5.9
BDE-154	22	164	1.9	3.1	0.84	0.92	1.6	7.1	116	48	22	9.0	16	ND	1.2	14	7.8	1.9	170	1.9	21	2.9
BDE-155	7.6	31	0.80	0.56	ND	ND	0.61	1.1	47	15	ND	1.2	1.9	ND	ND	ND	ND	ND	ND	ND	1.3	ND
Total Hexa-BDE	**34**	**242**	**2.6**	**5.7**	**2.4**	**0.92**	**2.1**	**14**	**212**	**82**	**58**	**23**	**42**	**ND**	**4.8**	**41**	**41**	**5.3**	**1440**	**7.2**	**66**	**8.8**
BDE-181	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	11	ND	ND	ND
BDE-183	1.2	4.3	2.1	8.6	15	ND	1.5	7.4	1.5	13	25	3.3	15	14	5.1	ND	112	5.3	146	2.5	71	3.5
Total Hepta-BDE	**1.2**	**5.8**	**2.1**	**8.6**	**15**	**ND**	**1.5**	**7.4**	**18**	**19**	**25**	**3.3**	**15**	**24**	**5.1**	**ND**	**112**	**5.3**	**174**	**2.5**	**71**	**3.5**
BDE-197	ND	2.9	ND	3.3	ND	ND	ND	4.4	ND	10	8.8	2.1	5.8	ND	5.5	ND	35	ND	46	1.6	26	5.8
BDE-203	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.9	ND	1.5	ND	ND	ND	17	ND	9.0	ND
Total Octa-BDE	**ND**	**2.9**	**ND**	**3.3**	**ND**	**ND**	**ND**	**4.4**	**ND**	**16**	**8.8**	**2.1**	**9.6**	**ND**	**7.0**	**ND**	**46**	**ND**	**110**	**1.6**	**45**	**5.8**
BDE-207	15	6.6	8.6	ND	ND	ND	ND	5.9	12	12	17	7.3	ND	ND	11	ND	30	16	23	5.9	26	8.7
Total Nona-BDE	**15**	**6.6**	**8.6**	**ND**	**ND**	**ND**	**ND**	**5.9**	**17**	**12**	**17**	**7.3**	**3.1**	**ND**	**15**	**ND**	**30**	**21**	**33**	**5.9**	**32**	**14**
BDE-209	800	189	504	167	328	220	181	123	411	265	453	249	214	ND	113	ND	284	417	188	123	147	106
Total PBDEs	**974**	**4955**	**556**	**255**	**368**	**235**	**208**	**472**	**3063**	**1593**	**1283**	**506**	**631**	**164**	**177**	**379**	**618**	**486**	**2516**	**196**	**656**	**207**