POLYBROMINATED DIPHENYL ETHERS (PBDE) AND POLYCHLORINATED DIBENZO-P-DIOXINS (PCDD/F) AND BIPHENYLS (PCB) IN FISH, BEEF, AND FOWL PURCHASED IN FOOD MARKETS IN NORTHERN CALIFORNIA USA

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Introduction

Food basket surveys and exposure studies conducted over the past decade suggest that one of the main routes of human exposure to polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) and biphenyls (PCBs) is likely through the consumption of food products such as eggs, meats, fish, and dairy products [1]. More recently, studies of human milk, blood, and adipose tissues also demonstrate human exposure to polybrominated diphenyl ethers (PBDEs) [2,3,4]. 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 PCDD/Fs and 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. Foods were tested for PCDD/Fs, PCBs, and PBDEs and the results used to evaluate human exposure through the consumption of store-bought consumer food products.

Materials and Methods

Sample Preparation and Analysis

Fish, meat, and fowl products were purchased 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 8 species of wild, ocean fish (swordfish, ahi, pacific salmon, coho salmon, sockeye, halibut, tilapia, tuna, and petrale sole), and one species of bivalve (sea scallops), and 2 species of farm-raised fish (atlantic salmon and catfish). Meat products included ground beef

from cows raised on grain 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 chickens. The term "free-range diet" refers to the farming method whereby animals are allowed to roam and feed freely within a relatively large, yet 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 17 2,3,7,8-substituted PCDD/F congeners and 31 PBDE congeners and total mono-through-deca-BDE homologue groups using USEPA draft Method 1614. The 209 PCB congeners were quantified using USEPA Method 1668. The cleanup procedures included columns containing silica gel and activated carbon. The quantification of PCDD/Fs, PCBs, and PBDEs were performed by selective ion recording using an AutoSpec Ultima high resolution gas chromatograph / high resolution mass spectrometer. A laboratory method blank and ongoing precision and recovery sample were extracted and analyzed along with the food samples. With the exception of three internal PBDE standards (C^{13}BDE-3, -207, and -209), the recoveries of the internal standards were greater than approximately 85%.

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 various 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 and Discussion

PBDE results are summarized in Tables 1 and 2. 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 88 to 4,955 pg/g ww) and fowl (ranging from 85 to 2,516 pg/g ww) than in beef and deer meat products (ranging from 106 to 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 individual PBDE congeners 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. For example, 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).

PCB results are summarized in Table 3. PCDD/F results are not summarized because, with few exceptions, PCDD/Fs were generally non-detect in food products. The congener profile in two samples of farm-raised catfish had a PCDD pattern similar to that reported in ball clay, which historically has been used as an additive in fish feed. In general, farm-raised fish had higher levels of PCBs than wild fish, though the data are limited.

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 to 18 years and between 2×10^{-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 4×10^{-7} and 2×10^{-5} mg/kg/day in children aged <1 to 18 years and between 4×10^{-7} and 1×10^{-5} 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

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

Sample	Total Di-BDEs	Total Tri-BDEs	Total Tetra-BDEs	Total Penta-BDEs	Total Hexa-BDEs	Total Hepta-BDEs	Total Octa-BDEs	Total Nona-BDEs	Total Deca-BDE	Total PBDEs
Wild Fish Products										
Swordfish	ND	4	79	41	34	1.2	ND	15	800	974
Swordfish	0.5	117	3,520	871	242	6	3	7	189	4,955
Pacific Swordfish Steak	ND	7	152	74	48	2	ND	ND	ND	282
Yellowfin Tuna Ahi	ND	3	46	30	35	ND	ND	ND	39	153
Salmon	ND	3	24	11	3	2	ND	9	504	555
Coho Salmon	ND	4	38	28	6	9	3	ND	167	255
Wild Sockeye Fillet	0.4	8	51	27	16	ND	5	6	41	153
Alaskan Halibut Fillet	ND	49	2,820	520	99	4	ND	ND	37	3,528
Tilapia	ND	ND	11	11	2	15	ND	ND	328	367
Scallop	ND	ND	6	9	0.9	ND	ND	ND	220	235
Can Tuna	ND	ND	8	15	2	1	ND	ND	181	208
Can Tuna	ND	ND	14	21	2	4	ND	ND	46	88
Petrale Sole	0.1	8	225	85	14	7	4	6	123	472
Farm-Raised Fish Products										
Salmon	4	100	1,740	561	212	18	ND	17	411	3,063
Atlantic Salmon	2	73	915	209	82	19	16	12	265	1,593
Atlantic Salmon Fillet	0.9	67	1,160	347	158	10	ND	3	ND	1,746
Catfish Fillet	5	10	240	466	58	25	9	17	453	1,283
Catfish Fillet	2	4	87	128	23	3	2	7	249	506
Catfish Fillet	2	5	100	81	18	3	ND	ND	102	311
Catfish Nugget	4	9	144	191	42	15	10	3	214	631

Table 2. The concentrations of PBDEs (pg/g wet weight) in meat and fowl products purchased in three food markets in northern California USA.

Sample	Total Di-BDEs	Total Tri-BDEs	Total Tetra-BDEs	Total Penta-BDEs	Total Hexa-BDEs	Total Hepta-BDEs	Total Octa-BDEs	Total Nona-BDEs	Total Deca-BDE	Total PBDEs
Meat Products										
Ground Beef	ND	ND	45	95	ND	24	ND	ND	ND	164
Ground Beef	ND	ND	11	19	5	6	3	5	57	106
Ground Beef (free-range)	ND	0.4	11	20	5	5	7	15	113	177
Ground Beef (free-range)	ND	ND	12	18	3	4	3	ND	120	159
Ground Deer	ND	ND	120	218	41	ND	ND	ND	ND	379
Fowl Products										
Chicken (free-range)	ND	ND	14	27	6	2	ND	3	35	86
Chicken Thighs	ND	ND	37	68	41	112	46	30	284	618
Chicken Thighs	ND	ND	51	95	25	25	ND	ND	ND	196
Chicken Thighs (free-range)	ND	ND	12	26	5	5	ND	21	417	486
Duck	0.6	5	195	370	1,440	174	110	33	188	2,516
Goose	ND	0.4	20	36	7	2	2	6	123	196
Ground Turkey	ND	0.4	79	216	66	71	45	32	147	656
Ground Turkey	ND	ND	118	258	82	21	23	48	197	747
Ground Turkey (free-range)	ND	ND	10	23	5	2	2	2	41	85
Pheasant	ND	0.5	26	42	9	3	6	14	106	207

Table 3. Concentrations (pg/g wet weight) of coplanar/mono-ortho substituted and mono through deca chlorinated PCBs in farm-raised and wild fish purchased in three northern California USA food markets.

Congener	Wild Fish				Farm-Raised Fish		
PCB-77	4.09	ND	0.197	0.271	21.2	2.31	0.93
PCB-81	4.30	ND	ND	ND	18.9	ND	ND
PCB-105	78.7	19.2	0.185	0.544	438	6.71	9.63
PCB-114	6.65	2.39	ND	ND	27	ND	0.617
PCB-118/106	312	80.3	2.53	1.53	1590	17	35.9
PCB 123	7.53	1.85	ND	ND	18.7	ND	0.707
PCB 126	5.57	1.08	ND	ND	9.46	ND	0.29
PCB-156	57.3	4.07	0.29	ND	151	ND	3.49
PCB-157	11.9	1.99	ND	ND	41.8	ND	1.09
PCB-167	52.5	3.45	0.22	ND	110	1.29	2.53
PCB-169	6.15	ND	0.151	0.177	ND	ND	ND
PCB-189	5.75	ND	ND	ND	16.7	ND	0.535
Total Mono-PCB	ND	6.03	0.597	0.165	ND	ND	0.968
Total Di-PCB	ND	ND	2.18	3.02	ND	ND	4.19
Total Tri-PCB	39.6	261	4.26	5.05	1,210	93.3	43.1
Total Tetra-PCB	861	1,310	7.96	8.84	10,300	318	145
Total Penta-PCB	1,680	700	13.2	8.73	8,720	104	251
Total Hexa-PCB	3,250	473	18.3	7.37	12,000	92.8	302
Total Hepta-PCB	1,520	106	7.69	1.51	3,760	244	123
Total Octa-PCB	260	11.5	1.86	0.319	554	2.44	33.2
Total Nona-PCB	36.5	0.739	0.169	ND	68.3	3.37	9.46
Total Deca-PCB	14	1.28	0.114	ND	31.7	0.948	4.61
Total PCB	7,660	2,870	56	35	36,600	639	917
PCB TEQs	0.698	0.122	0.002	0.002	1.26	0.002	0.036