POLYBROMINATED DIPHENYL ETHERS IN MEAT SAMPLES COLLECTED FROM SUPERMARKETS ACROSS THE US

Janice Huwe

USDA, ARS, Biosciences Research Laboratory, PO Box 5674 University Station, Fargo, ND, 58105, USA

Introduction

Polybrominated diphenyl ethers (PBDEs) are common additive flame-retardants used in high impact polystyrene, polyurethane foam, and textile coatings. Over the past 10-20 years, environmental levels and human levels of PBDEs appear to be increasing.[1,2] Because PBDEs are lipophilic and structurally similar to other environmentally persistent aromatics, i.e. dioxins, PCBs, and furans, it seems plausible that human exposure to PBDEs may occur by the same route as exposure to these other persistent pollutants, namely through the food chain. A number of studies have shown the presence of PBDEs in food samples and estimated that fish and animal products provide the largest amount of dietary exposure.[1,3,4,5] Fish accounted for the majority of the European dietary intake (30-75%); however, a Canadian study showed meat products contributed 75% to the daily Canadian intake. We have seen no reports of PBDE levels in US food commodities. Because the typical US diet contains much higher amounts of meat than fish, we have begun to study PBDE levels in typical US foods by analyzing meat and poultry samples purchased at supermarkets across the US.

Materials and Methods

Meat and poultry samples were purchased at large supermarkets in nine cities across the US and shipped frozen to the USDA-ARS laboratory in Fargo, ND, for analysis. All samples were collected in 2001 and included bacon, whole chickens, sirloin steaks, and pork chops from each location. The bacon was analyzed whole; for the chickens, steaks, and chops, fat was trimmed and analyzed for PBDEs. Seven ^{13}C-labeled surrogates (BDEs-28, 47, 99, 153, 154, 183, and 209) (Wellington, Laboratories, Guelph, ON) were spiked into a 5 g sample and homogenized in methylene chloride. After drying with sodium sulfate, an aliquot was removed for gravimetric lipid determination. The sample was exchanged into hexane and applied to a Power Prep instrument (FMS) incorporating a jumbo and regular triphasic silica cartridge and a basic alumina cartridge. PBDEs were eluted from the silica cartridges with hexane onto the alumina column. The alumina column was rinsed with 2% methylene chloride in hexane, and then PBDEs were eluted with 50% methylene chloride in hexane. The final fraction was concentrated into 20uL of dodecane containing the internal standards (^{13}C-labeled BDE-77 and 139). A 2 uL aliquot was analyzed by high resolution GC/MS, as previously described.[6]

A method blank or a method spike containing 42 native PBDEs were run with each set of four samples. Because method blanks contained detectable levels of the major PBDEs, the sample data were blank-subtracted. Limits of detection were calculated as 3x standard deviations of the blanks (Table 1). Values below the detection limit were treated as non-detects and either set equal to zero or ½ the limit of detection.

Results and Discussion

Spiked samples showed that the major PBDE congeners reported in this study could be quantitated at the 50-250 part per trillion level (ppt) with better than 20% accuracy and precision by the method used. Recoveries of ^{13}C-surrogates averaged 71–102%. Table 1 shows the results for the analysis of 48 bacon and meat trimming samples on a whole-weight basis and the sum of tri- through hepta-congeners on a whole-weight and lipid-weight basis. Aside from the nine reported congeners, no other PBDEs were consistently found in the samples. The presence of BDE-209 is uncertain in many cases due to the large amounts found in the blanks.

Of the four types of meat included in the study, beef appeared to have the lowest amounts of PBDEs, while chicken and pork had the highest. This is opposite to results of recent dioxin analyses in US meats and poultry which showed beef animals with the highest dioxin levels compared to chickens and hogs (unpublished results). Two explanations for this difference are that the source of PBDE exposure for livestock is different than the source of dioxin exposure, which is generally thought to be from forages, or that ruminants such as cattle are better able to metabolize and excrete PBDEs than other livestock species resulting in lower body burdens. The PBDE data also suggested that the pork trimmings were higher than the bacon samples on a whole-weight or lipid-weight basis. This may be an anomaly due to the relatively small sampling size of the study, or, if real, may indicate that a step in the processing or handling of bacon can attenuate levels of PBDEs.

When compared to data from other countries, total PBDEs in US beef were similar on a lipid-weight basis to meat products analyzed in Sweden (360 ppt)[1] and beef in Spain (290 ppt).[3] The average lipid-weight total in bacon was also similar to levels in pork and pork products from Spain (597 ppt);[3] however, trimmings from pork chops in the US averaged four times this value. Total PBDEs in US chickens averaged 100-times higher than chicken from Spain (247 pg/g lipid).[3] The PBDE content of chickens in this study was in the same range as nine samples analyzed in a previous study with chickens collected from US slaughtering facilities in 1997 but lower than four highly contaminated chickens found in that study (high range 23–43 ppb).[6]

The average PBDE pattern in each meat type is shown in Figure 1. BDE-47 and 99 were the largest contributors to the total PBDE sum. The ratio of 47/99 was generally less than unity, and for individual samples varied from 0.3 to 1.3. A similar congener pattern is seen in other animal products from Canada,[5] Japan,[4] Spain,[3] and the US.[6] In contrast, the congener patterns in fish and seafood[3,4] and human samples,[4,5,7,8,9] generally show a ratio

of 47/99 greater than 2. For populations who are not largely fish eaters, this implies that sources other than diet may be contributing to the PBDE body burdens or that congener pattern changes occur in humans via selective uptake or metabolic routes.

Conclusions

While meat products from supermarkets in the US had similar congener patterns to foods analyzed in other countries, the levels of PBDEs in pork and chicken were much higher. The congener pattern strongly resembles the penta-BDE formulations used commercially in North America which has a BDE-47/99 ratio of 0.5. Higher levels of PBDEs in US foods may reflect the larger amount of penta-BDE used in North America.[10] How these contaminants enter the food chain is unknown, but may include animal feeds (eg. fish meal), environmental inputs (housing or litter), or even food packaging materials. The contribution of food products to human exposure is also not well understood at this time.

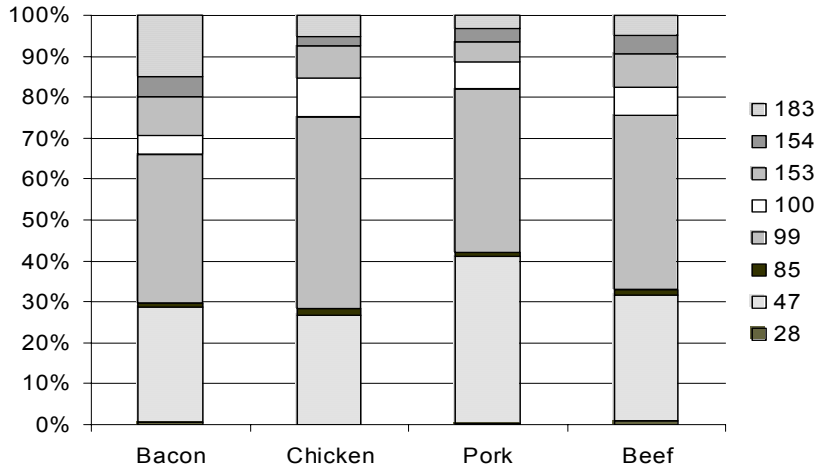

Figure 1. Contribution of individual PBDE averages to the total sum. Values are from lipid-adjusted concentrations with non-detects set to DL/2.

References

1. Darnerud, P .O., Eriksen, G. S., Jóhannesson, T., Larsen, P. B., and Viluksela, M. Environ. Health Perspec. (2001) 109, 49-68 and references therein
2. de Wit, C. Chemosphere (2002) 46, 583-624 and references therein
3. Bocio, A., Llobet, J. M., Domingo, J. L., Corbella, J., Teixidó, A., and Casas, C. J. Agric. & Food Chem. (2003) 51, 3191-3195
4. Ohta, S., Ishizuka, D., Nishimura, H., Nakao, T., Aozasa, O., Shimidzu, Y., Ochiai, F., Kida, T., Nishi, M., Miyata, H. Chemosphere (2002) 46, 689-696
5. Ryan, J. J. and Patry, B. Organohalogen Cpds (2001) 51, 226-229
6. Huwe, J. K., Lorentzsen, M., Thuresson, K., and Bergman,Å. Chemosphere (2002) 46, 635-640
7. Meneses, M., Wingfors, H., Schuhmacher, M., Domingo, J. L., Lindström, G., van Bavel, B. Chemosphere (1999) 39, 2271-2278
8. Meironyté, D., Norén, K., and Bergman, Å. J. Toxicol. Environ. Health, Part A, (1999) 58, 329-341
9. She, J., Petreas, M., Winkler, J., Visita, P., McKinney, M., Kopec, D. Chemosphere (2002) 46, 697-707
10. www.bsef.com

Table 1. Concentrations of major PBDEs in blanks, bacon, and meat trimmings on a pg/g sample basis. Sample data are blank-subtracted. Individual values below the detection limit (DL=3x standard deviation of the blanks) were considered non-detects (nd) and set to either DL/2 or zero (in parentheses) before averages were calculated.

	Blanks, n=7		Bacon, n=11		Chicken fat, n=17		Pork fat, n=11		Beef fat, n=9	
PBDE#	**Average**	**DL (3xSD)**	**Average**	**Range**	**Average**	**Range**	**Average**	**Range**	**Average**	**Range**
tri-28/33	1.5	2.6	1.7 (0.7)	nd–4.6	1.7 (0.5)	nd–6	3.3 (2.1)	nd–23	1.3 (0)	nd
tetra-47	31.8	56.9	83.0 (62.3)	nd–454	424.0 (419)	nd–2764	518.0 (513)	nd–3897	50.4 (28)	nd–178
penta-85	1.7	4.2	3.3 (1.4)	nd–15	22.9 (22.4)	nd–182	13.2 (12.2)	nd–66	2.5 (0.6)	nd–5.3
penta-99	31.2	52.5	104.9 (88.2)	nd–624	742.7 (742)	60–4447	510.0 (508)	nd–2972	70.6 (53)	nd–279
penta-100	4.4	5.9	14.0 (12.7)	nd–85	151.8 (151)	10–859	85.7 (85.7)	9–559	11.4 (9.8)	nd–48
hexa-153	2.6	7.3	27.4 (26.4)	nd–140	126.1 (126)	17–576	61.6 (61.6)	8–178	13.9 (13)	nd–42
hexa-154	2.4	5.6	14.8 (13.5)	nd–85	38.9 (37.9)	nd–126	43.2 (43.0)	nd–137	7.5 (6.3)	nd–24
hepta-183	3.1	14.7	46.9 (42.9)	nd–135	84.9 (82.7)	nd–469	46.8 (43.5)	nd–134	7.3 (0)	nd
deca-209	914.0	3385.4	1693 (0)	nd	1845 (251)	nd–4275	1913 (374)	nd–4120	1693 (0)	nd
Σ tri-hepta			296 (248)	nd–7831	1593 (1582)	86–8965	1282 (1269)	17–7831	165(111)	nd–586
Σ lipid wt			818 (634)	nd–4642	2508 (2412)	124–15,139	2603 (2488)	35–16,329	251 (178)	nd–835
% lipid			39.1165(111)	30.7–46.3	65.6	56.0–71.6	51.0	37.2–71.6	62.3	45.2–73.4