JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

ARTICLE

pubs.acs.org/JAFC

Polybrominated Diphenyl Ethers in U.S. Meat and Poultry from Two Statistically Designed Surveys Showing Trends and Levels from 2002 to 2008

Janice K. Huwe*,† and Mark West‡

†Biosciences Research Laboratory, Agricultural Research Service, U.S. Department of Agriculture, 1605 Albrecht Boulevard, Fargo, North Dakota 58102, United States

‡Northern Plains Area, Agricultural Research Service, U.S. Department of Agriculture, Fort Collins, Colorado 80526, United States

Supporting Information

ABSTRACT: Polybrominated diphenyl ether (PBDE) body burdens in the general U.S. population have been linked to the consumption of red meat and poultry. Exposure estimates have also indicated that meat products are a major contributor to PBDE dietary intake. To establish solid estimates of PBDE concentrations in domestic meat and poultry, samples from two statistically designed surveys of U.S. meat and poultry were analyzed for PBDEs. The two surveys were conducted in 2002−2003 and 2007−2008, between which times the manufacturing of penta-BDE and octa-BDE formulations had ceased in the United States (December 2004). Thus, the data provided an opportunity to observe prevalence and concentration trends that may have occurred during this time frame and to compare the mean PBDE levels among the meat and poultry industries. On the basis of composite samples, the average sum of the seven most prevalent PBDEs (BDE-28, -47, -99, -100, -153, -154, and -183) decreased by >60% from 1.95 ng/g lipid in 2002−2003 to 0.72 ng/g lipid in 2007−2008 for meat and poultry. PBDEs measured in individual samples in 2008 showed that beef samples had the lowest PBDE levels followed by hogs and chickens and then by turkeys. The PBDE congener pattern was the same for both surveys and resembled the penta-BDE formulation with BDE-47 and -99 accounting for 30 and 40% of the total, respectively. On the basis of the data from the two surveys, it appears that PBDE levels in U.S. meat and poultry have declined since manufacturing ceased; however, exposure pathways of PBDEs to livestock are still not known.

KEYWORDS: polybrominated diphenyl ethers, food, survey, temporal trend

INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are a class of flame retardant chemicals that have become ubiquitous in the environment and biota. Due to their persistent, bioaccumulative, translocational, and toxicological properties, tetra- through hepta-BDEs have recently been included on the list of persistent organic pollutants scheduled to be eliminated from production and use.[1] The PBDE congeners listed are found in commercial penta- and octa-BDE formulations and include BDE-47, -99, -100, -153, and -154 in the penta-formulations and BDE-153, -154, and -183 in the octa-formulations (Figure 1).

Historically, most of the penta-BDE formulation has been used in the Americas, where demand was 97% of the worldwide market in 1999 and 95% in 2001 or 8290 and 7100 t, respectively.[2] The octa-BDE formulation is a minor product, and 35−40% of its total demand was in the Americas (1500 t in 2001). Due to the higher usage in North America, several studies have noted elevated PBDE levels in North Americans compared to European or Japanese populations,[3−5] specifically >20-fold higher levels of the tetra- to hexa-BDE congeners in North Americans.

To account for the high PBDE levels found in Americans, two major sources have been suggested: dietary input and indoor dust exposure.[6] Two recent studies estimated that absorption and ingestion of indoor dust accounted for 60−80% of the typical U.S. exposure,[7,8] whereas diet accounted for the remainder. Within the diet, meat and poultry products accounted for 30−84% of the intake;[7,8] however, these results were based on measurements from a relatively few localized samples, 62 food samples from Texas[9] and 88 fish from coastal Florida.[10]

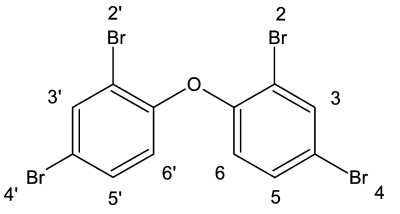

Figure 1. Structure and numbering of BDE-47 (2,2′,4,4′-tetraBDE). Other PBDEs (IUPAC naming) include BDE-99 (2,2′,4,4′,5-pentaBDE), BDE-100 (2,2′,4,4′,6-pentaBDE), BDE-153 (2,2′,4,4′,5,5′-hexaBDE), BDE-154 (2,2′,4,4′,5,6′-hexaBDE), and BDE-183 (2,2′,3,4,4′,5′,6-heptaBDE).

Other studies have shown that PBDE body burdens are significantly related to house dust levels and meat and dairy intake.[11,12] In particular, Fraser et al.[11] noted a significant dietary

Received: January 27, 2011
Revised: April 12, 2011
Received: April 14, 2011
Published: April 14, 2011

contribution from poultry and red meat consumption. Given that meat and poultry appear to be major dietary sources of PBDEs, a more thorough sampling of these domestic products is warranted to better characterize their contribution to human exposure.

In 2004, the manufacture of penta-BDE and octa-BDE voluntarily ceased in the United States. As observed for another class of persistent organic compounds, namely, polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs), once emissions were controlled, levels in the environment and the food supply declined within a few years.[13] To determine if a similar trend occurred for PBDEs following the removal of penta-BDE and octa-BDE from production, we have used two sets of domestic meat and poultry samples collected by the U.S. Department of Agriculture (USDA) in 2002−2003 and 2007−2008. These two sample sets were collected as part of the periodic surveillance of PCDD/Fs and coplanar polychlorinated biphenyls (co-PCBs) in foods conducted by the USDA.[14,15] The surveys were statistically designed to represent 90% of the meat and poultry consumed in the United States and so should provide both a solid estimate of PBDE levels in these U.S. foods and evidence of any trends that may be occurring.

MATERIALS AND METHODS

Adipose tissue samples collected during two USDA surveys of PCDD/Fs and co-PCBs in domestic meat and poultry[14,15] were analyzed for PBDEs. Details of the surveys' sampling design have been published previously and are summarized here. Adipose tissue samples were collected weekly at slaughtering establishments chosen using a probability-proportional-to-size design, where slaughter totals were used as the size variable. Under this design, establishments were scheduled to collect approximately the same percentage of samples in a product class as the percentage of national slaughter that they performed. All active slaughtering establishments were eligible for random selection; however, many (80%) of the establishments were the same in the two surveys. The sample collections were conducted from May 2002 to May 2003 (2002 survey) and again from September 2007 to September 2008 (2008 survey). The four slaughter classes included in the surveys were steers and heifers (beef), market hogs (pork), young chickens, and young turkeys, which together account for 90% of the domestic meat and poultry production. In each survey, 139 beef, 136 pork, 151 chicken, and 84 turkey samples were collected for a total of 510 samples.

Because these samples were collected at meat-producing facilities for surveys of PCDD/Fs and co-PCBs, the analysis of samples for compounds other than those of which the industry had been notified was not authorized by the USDA. Therefore, individual samples were pooled to form regional composites (Table 1) for PBDE analysis, both to provide anonymity for producers and to reduce costs. Composites were formed by aggregating individual samples over the state in which they were raised or by grouping several states in a region that had similar production. Most composites consisted of between 10 and 30 individual samples. Use of composite samples was identified as problematic for comparing mean PBDE levels among meat industries because these could not be viewed as sampling units. Midway through the 2008 survey, notification was given to the industries, thus allowing PBDEs to be measured in individual samples and used for identifying differences in mean PBDE levels among the meat industry classes (i.e., beef, pork, chicken, and turkey). In the end, PBDEs were measured in 26 composites from the 2002 survey, 26 similar composites from the 2008 survey, 189 individual samples from the 2008 survey, and 5 individual turkey samples from California from each of the two surveys. Eight samples from the 2002 survey and one sample from the 2008 survey were lost or completely used during previous analyses and so could not be included. A comparison of the results for three composites to the mean of the individual samples in those composites showed variations of 1−20% for detected congeners, an acceptable sample-to-sample variation.

Pooled composites (150 g) were made by combining equal weights (generally 5−10 g) of individual samples and grinding three times until homogeneous. All samples were stored at −20 °C to prevent degradation until analysis by a high-resolution GC/high-resolution MS isotope-dilution method based on EPA Method 1614 (brominated diphenyl ethers in water, soil, sediment, and tissue by HRGC/HRMS) and described previously.[16,17] Briefly, a 2 or 5 g subsample of adipose tissue was spiked with 10 ^{13}C-labeled PBDEs (nos. 28, 47, 99, 100, 153, 154, 183, 197, 207, and 209), dissolved in organic solvent, and purified on a Power Prep unit (Fluid Management Systems, Waltham, MA) for automated chromatographic cleanup using jumbo acid silica, triphasic silica, and basic alumina cartridges. The silica cartridges were eluted with hexane onto the alumina cartridge, which was subsequently eluted with 2% methylene chloride in hexane (v/v) and then 50% methylene chloride in hexane (v/v). The PBDEs were recovered in the 50% methylene chloride fraction, which was concentrated, spiked with three internal standards (^{13}C-BDE-77, -139, and -205), and quantitated for 16 native PBDEs (nos. 28, 47, 66, 85, 99, 100,153, 154, 183, 196, 197, 201, 203, 206, 207, and 209). Lipid content was determined gravimetrically prior to sample cleanup and averaged 82 ± 8% in the 2002 survey and 79 ± 9% in the 2008 survey. An alternative to the jumbo acid silica cartridge was stirring with 40% sulfuric acid silica (w/w) in hexane to digest the lipids prior to placing on the Power Prep unit; this method proved more cost-effective for the 2 g samples, where the full capacity of the jumbo cartridges was not needed. All concentrations are reported on a lipid weight (lw) basis. Feed samples (50 g) were extracted by sonication in toluene/acetone (70:30, v/v) and then purified as described above.

Method blanks were run in each set of 10 samples, and known spiked samples were run on a routine basis to validate the method's precision, accuracy, and limits of quantitation. Because certain PBDEs were detected in the method blanks, all data were blank-subtracted. Limits of detection (LOD) were calculated as three standard deviations of the method blanks and ranged from 0.5 to 29 pg for tri- to octa-BDEs, from 65 to 80 pg for nona-BDEs, and 1900 pg for BDE-209. Weighted mean PBDE concentrations (ng/g lipid) from the composite samples were computed and then compared between years for each meat industry using a procedure called npar.t.test available in R.[18,19] The npar.t.test is a statistical function that performs a Wilcoxon test on equality of distributions of values between two independent samples. It is also a nonparametric test for the relative effect of two independent samples or the tendency of values to be smaller in one sample than another. The individual samples collected from the California turkey producers in 2002 and 2008 were also compared between years using the npar.t.test procedure.

Individual samples from the 2008 survey were used to compare PDBE levels among meat industries using a nonparametric multiple-comparison procedure called nparcomp available in R.[18,19] The nparcomp procedure in R computes simultaneous Tukey confidence intervals for the relative effects for each pair of samples (beef, pork, chicken, turkey) in the study and the overall nonparametric comparison of the four samples.

RESULTS

Table 1 summarizes the data for the composite samples showing the similar regional distribution of the composites and the concentration of PBDEs in each composite from both surveys. Because nona- and deca-BDEs were not detected in >95% of the composites and octa-BDEs were detected in >80% of the composites, the sum of PBDEs in this paper is limited to the seven major congeners, BDE-28, -47, -99, -100, -153, -154, and -183. These seven congeners accounted for >90% of the total PBDEs detected, and five congeners (BDE-47, -99, -100,-153, and -154) were detected in every composite.

Table 1. Concentrations of the Sum of PBDEs (ng/g Lipid) in Meat and Poultry Composites from Two Surveys Grouped by Slaughter Class and Geographical Area and the Percent Change from 2002 to 2008

	2002−2003 survey			2007−2008 survey			
	states[a]	N[b]	sum PBDEs[c]	states	N	sum PBDEs	% change
beef	KS	28	0.34	KS	30	0.21	−38.6
	TX	24	0.46	TX	30	0.10	−78.1
	NE	24	5.91	NE	22	0.58	−90.2
	ND, MN, SD, IA	19	1.28	ND, MN, SD, IA	27	0.17	−86.7
	OK, CO	19	0.67	OK, CO	9	0.24	−64.0
	WA, OR, ID, NV	13	0.53	WA, AB, WY, AZ	8	0.55	+3.8
	ME, KY, IN, IL, OH, WI, ON	11	0.44	MI, IL, OH, WI	7	0.32	−27.1
				CA	6	1.10	
	weighted mean	**151**	**1.53**		**150**	**0.30**	**−80.2**
	SEM[d]		**0.83**			**0.09**	
pork	IA	34	0.71	IA	47	0.41	−42.3
	MN, SD, MB, ND, WI	26	1.18	MN, SD, MB, WI	22	0.26	−78.0
	NC	25	1.96	NC, MD, VA	19	0.74	−62.2
	IN, IL, MI, PA, OH	21	1.97	IN, IL, MI, PA, OH	21	0.78	−60.4
	MT, MO, NE, KY	18	0.60	CO, MO, NE, AR	18	0.39	−35.3
	TX, OK, UT, AZ	11	0.30	TX, OK, AZ	9	0.80	+166
	weighted mean	**138**	**1.18**		**139**	**0.51**	**−56.6**
	SEM		**0.27**			**0.09**	
chicken	AL, FL, GA	38	2.47	AL, GA	40	0.72	−70.8
	AR	23	1.89	AR	19	0.56	−70.3
	SC, NC, TN	20	2.17	NC, TN	16	0.77	−64.5
	VA, DE, MD, PA	18	0.90	VA, DE, MD, PA, WV, IN	22	0.47	−47.8
	LA, MS	18	3.07	LA, MS	18	0.38	−87.6
	TX, OK	17	1.78	TX, OK	17	1.96	+10.2
	MO, MN, KY	9	1.36	MO, KY	13	0.61	−55.1
	CA	5	5.97	CA, WA, OR	5	0.82	−86.3
	miscellaneous[e]	3	1.26				
	weighted mean	**135**	**2.17**		**136**	**0.76**	**−64.9**
	SEM		**0.35**			**0.17**	
turkey	WI, MN, IA	23	2.56	WI, MN, IA	23	2.10	−18.0
	AR, MO, TX	20	3.81	AR, MO, TX, KS, NE, CO	21	1.26	−66.9
	SC, NC	19	3.80	SC, NC	16	1.27	−66.6
	MI, IN, PA, OH, VA	16	2.47	MI, IN, PA, IL, VA, WV	18	2.13	−13.8
	CA	6	9.82	CA	5	2.47	−74.8
	weighted mean	**84**	**3.64**		**83**	**1.76**	**−51.7**
	SEM		**0.91**			**0.22**	
overall	**weighted mean**	**508**	**1.95**		**508**	**0.72**	**−63.2**

[a] Abbreviations are states of the United States (AL, Alabama; AR, Arkansas; AZ, Arizona; CA, California; CO, Colorado; DE, Delaware; FL, Florida; GA, Georgia; IA, Iowa; ID, Idaho; IL, Illinois; IN, Indiana; KS, Kansas; KY, Kentucky; LA, Louisiana; MD, Maryland; ME, Maine; MI, Michigan; MN, Minnesota; MO, Missouri; MS, Mississippi; MT, Montana; NC, North Carolina; ND, North Dakota; NE, Nebraska; NV, Nevada; OH, Ohio; OK, Oklahoma; OR, Oregon; PA, Pennsylvania; SC, South Carolina; SD, South Dakota; TN, Tennessee; TX, Texas; UT, Utah; VA, Virginia; WA, Washington; WI, Wisconsin; WV, West Virginia; WY, Wyoming); and three Canadian provinces (AB, Alberta; ON, Ontario; MB, Manitoba). [b] *N*, number of individual samples in composite. [c] Sum of BDE-28, -47, -99, -100, -153, -154, and -183 expressed as ng/g lipid. [d] SEM, standard error of the mean. [e] One sample each from TX, DE, and AL.

The weighted means for PBDE concentrations in the composites decreased by >50% from 2002 to 2008 in all four slaughter classes; however, only the decreases in mean levels for chickens and turkeys were statistically significant (p = 0.0039 and 0.0160, respectively). Only 3 of the 26 regional composites showed increased mean PBDE concentrations over time. Chickens from

Table 2. Concentrations of the Sum of PBDEs in Individual Poultry Samples from California (CA) and the Weighted Mean of Poultry from the Rest of the United States (U.S.) Collected in 2002−2003 and 2007−2008

			sum PBDEs[a]	
		N^b	mean ± SD	range
2002−2003	CA turkeys	5 ind	9.27 ± 5.85	3.10−17.53
	rest of the U.S.	4 comp	3.16 ± 0.75	2.47−3.81
2007−2008	CA turkeys	5 ind	2.45 ± 2.14	0.90−6.20
	rest of the U.S.	4 comp	1.69 ± 0.49	1.26−2.13
	rest of the U.S.	30 ind	2.34 ± 4.10	0.43−23.2
2007−2008	CA chickens	3 ind	0.73 ± 0.25	0.61−1.02
	rest of the U.S.	7 comp	0.80 ± 0.53	0.38−1.96
	rest of the U.S.	55 ind	0.55 ± 0.47	0.12−2.19

[a] Sum of BDE-28, -47, -99, -100, -153, -154, and -183 expressed as ng/g lipid. [b] *N*, number of individual (ind) or composite (comp) samples.

Texas (TX) and Oklahoma (OK) increased from 1.78 to 1.96 ppb lw (10%), pork from this same region (TX, OK, UT, and AZ) increased from 0.3 to 0.8 ppb lw (166%), and beef from the northwestern/western United States (WA, OR, ID, NV, WY, and AZ) and Alberta, Canada (AB), increased from 0.53 to 0.55 ppb lw (3.8%). PBDE concentrations in all other composites decreased from 2002 to 2008 with absolute deceases of 0.13−7.35 ppb lw or relative decreases of 14−90%. The regional composites with the numerically highest PBDE concentrations (>5.9 ppb lw) were turkey and chicken from California (CA) and beef from Nebraska (NE), all collected in 2002−2003. These same composites showed the largest declines in 2008 with absolute decreases of 7.35, 5.15, and 5.33 ppb lw, respectively.

Unfortunately, most individual samples from the 2002 survey were either discarded or used up after making the composites, preventing further investigation of the high values from the California chicken or Nebraska beef in more detail. However, individual turkey samples from California from both surveys were available and, therefore, were analyzed separately. The results are given in Table 2 along with results from the 2008 California chickens and composite, and individual samples from the rest of the U.S. PBDE concentrations in turkeys raised in California averaged almost 3 times higher than turkeys raised in the rest of the United States in 2002−2003 and almost 4 times higher than turkeys from California collected in 2007−2008. The mean concentration difference between California turkeys from the 2002 and 2008 surveys was statistically significant ($p = 0.0037$). In 2008, turkeys and chickens raised in California had PBDE levels similar ($p > 0.05$) to those of poultry raised in other parts of the United States.

PBDE levels for California turkeys showed a wide range of concentrations, a characteristic that was also observed in each animal class when 189 individual samples from the 2008 survey were analyzed. Figure 2 summarizes the data for the individual samples showing median values for each animal class and concentrations that range over 3 orders of magnitude. The mean PBDE levels in this subset of samples were 0.18 ± 0.23, 0.41 ± 0.39, 0.55 ± 0.47, and 2.44 ± 4.03 ppb lw for beef, pork, chicken, and turkey, respectively. Simultaneous comparisons of PBDE levels among beef, pork, chicken, and turkeys using nparcomp

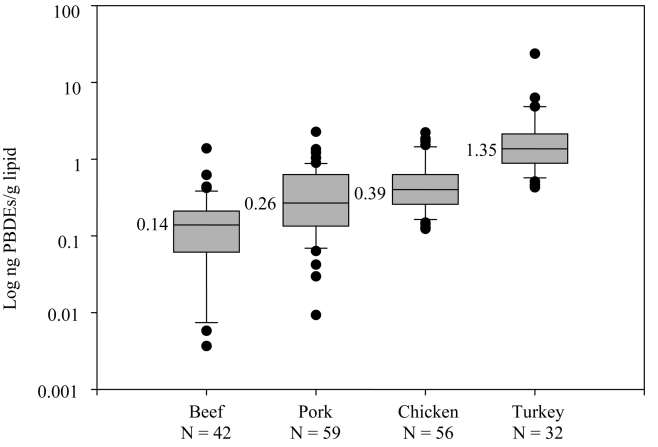

Figure 2. Summed concentrations of seven PBDEs (ng/g lipid) in individual samples from the 2008 survey by animal class. Horizontal lines indicate the 5th, 25th, 50th (median), 75th, and 95th percentiles; the median values are listed. Dots represent individual sample points outside the 5th and 95th percentiles.

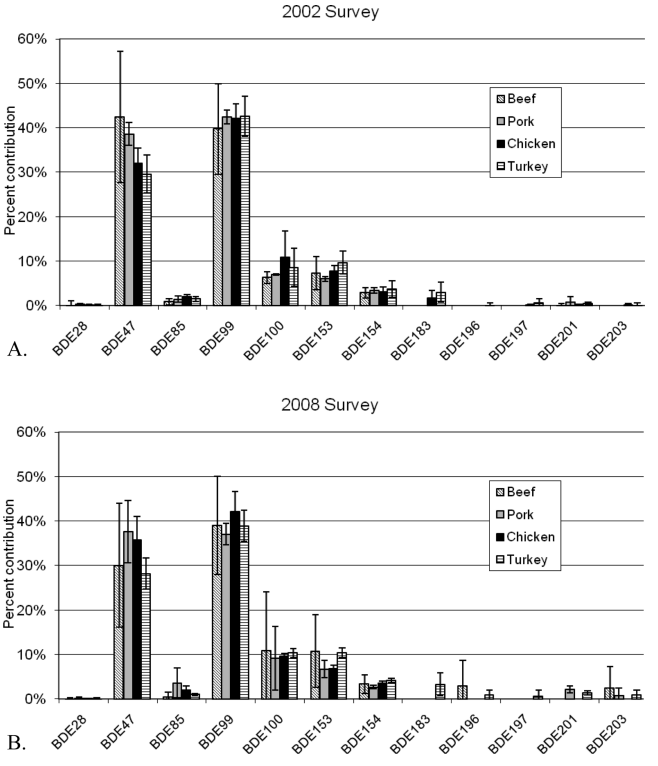

Figure 3. Relative contribution of individual PBDE congeners to total tri- to octa-BDE sums in each animal class for the 2002 and 2008 surveys.

procedures in R indicated that beef was lower than chicken and pork and that turkey was higher than the other classes ($p < 0.001$). The three highest samples were turkeys from Minnesota, California, and West Virginia with PBDE concentrations equal to 23.2, 6.2, and 4.77 ppb lw, respectively.

In addition to comparison of the mean PBDE levels of the 2002 and 2008 surveys, the average congener patterns were compared (Figure 3). Little variation was seen between animal classes or surveys. BDE-99 accounted for 40% of the total, BDE-47 for

30−40%, BDE-100 and -153 for 6−10% each, and BDE-154 for 4%. Other congeners were generally <1% of the total content. The concentration of individual congeners in the composite samples is summarized in the Supporting Information (Tables S1 and S2).

DISCUSSION

This study used a relatively large set of samples (1016) from two statistically designed surveys to measure PBDEs and thus gives the most extensive data set on the levels of these contaminants in U.S. meat and poultry to date. Because lipophilic persistent organic pollutants such as PCDD/Fs and PCBs are generally reported on a lipid weight basis in animal products,[20] the USDA collected trimmed fat for analysis of these pollutants in the surveys. As with PCDD/Fs and PCBs, the adipose tissue samples should provide an adequate measure for most PBDEs in edible muscle on a lipid weight basis because the persistent PBDEs (tri- to hexa-congeners) have been shown to distribute equally to adipose and carcass muscle lipids in numerous species, including cattle,[21] birds,[22] and rats.[23] For other congeners (hepta- to deca-BDEs), the use of adipose tissue as a surrogate for edible muscle will not be as accurate because these congeners do not readily partition into fat.[23,24] To apply any lipid-weight food concentrations to dietary intake estimates, the typical lipid composition of food items is required which, in many cases, can be found in databases such as the USDA National Nutrient Database for Standard Reference.[25]

Our data show a strong decreasing temporal trend for PBDEs in domestic food animals with a significant decrease in the overall mean of tri- to hepta-BDEs (63%) across species. The large distribution range and the use of a limited number of composites rather than individual samples most likely overshadowed the significance of declines for beef and pork; however, PBDE concentrations in both chickens and turkeys were statistically lower in the 2008 survey compared to the 2002 survey, despite these limitations. The analysis of 189 individual samples from the 2008 survey showed that the data were not normally distributed (data not shown); therefore, a simple comparison of composite means may not be the most appropriate assessment of trends. Nonetheless, most regional composites showed decreases of >40% between 2002 and 2008.

Notably, the California poultry composites had the highest PBDE levels relative to other regions. California is known to have one of the strictest furniture flammability codes in the United States, which has been suggested as a contributory factor to the higher levels of PBDEs measured in Californians and California house dust compared to other U.S. regions.[26] Although it is not expected that poultry would have direct access to flame-retarded furniture, indirect exposure may be through sewage sludge application to fields where crops are raised, contamination of water supplies by leaching from discarded products, the use of flame-retarded materials in poultry housing, or the inadvertent incorporation of fire-retarded material into bedding or feed ingredients. Alternatively, the small number of individual samples from California may not reflect the true status of poultry contamination in that state. The individual California poultry concentrations ranged from 0.57 to 17.53 ppb lw, which is within the range measured in all poultry samples from the two surveys (0.12−23.2 ppb lw).

Aside from California poultry, no particular region in the United States showed a strong spatial trend (Figure S1 of the Supporting Information). For example, in 2008 beef from Texas had the lowest level (0.10 ppb), whereas pork and chicken from Texas and surrounding states had the highest levels (0.80 and 1.96 ppb, respectively) in each slaughter class. Probably the most important reason that regional trends are not seen is because livestock are raised in fairly localized areas of the United States and, therefore, not all regions will be represented in a statistical survey. Most pork is raised in Iowa (>25% of the pork in the survey), and most beef is raised in the Great Plains states (Kansas, Texas, and Nebraska accounted for >55% of the beef in the survey).

Because PBDE manufacturing voluntarily ceased in the United States in 2004, the declining PBDE levels in domestic meat and poultry suggest a direct association with this action. One explanation may be the removal of certain point sources that affected local animal feeding operations and, thereby, elevated the average concentrations of PBDEs in composites. Similar sharp declines in environmental and biota samples were observed after controls and bans on PCDD/Fs and PCB were imposed in the late 1970s to early 1980s.[13] In particular, PCDD/Fs and PCBs in meat, milk, and dairy products declined by 54−78% from 1982 to 1992 according to U.K. food surveillance information.[27] More recently, declines in PCDD/Fs and PCBs in foods have slowed but are still observed.[15,28] A similar slowing of PBDE declines may be expected as time goes on, and the exposure pathway for food animals may become dominated by reservoir sources.

Three smaller market basket studies have reported PBDE concentrations in U.S. meat and poultry samples collected in the early 2000s and in 2009.[9,16,29] On a lipid weight basis, these studies found PBDE levels ranging from not detected to 16.6 ppb and means equal to 1.74 ± 3.37 ppb (65 samples collected in 2001),[16] 1.43 ± 1.80 ppb (18 samples collected in 2003),[9] and 0.42 ± 0.26 ppb (7 samples collected in 2009).[29] These results are similar to the weighted means found in the 2002 and 2008 surveys. To compare our survey data to European studies, mean PBDE concentrations can be converted to a whole weight basis by using the following estimated factors for lipid content: 17% (beef), 19% (pork), and 9% (poultry).[30] Using these estimates, the overall weighted means were 0.20 ppb whole weight in 2002 and 0.09 ppb whole weight in 2008. The 2008 survey mean is at the high end of the means summarized by Frederiksen et al.[31] for meats in Europe (not detected−0.102 ppb) and Japan (0.006−0.064 ppb). Although PBDE levels may still be somewhat higher in U.S. meat and poultry, they appear to be approaching those of Europe and Japan after manufacturing of penta-BDE and octa-BDE formulations has ceased.

The congener patterns from both the 2002 and 2008 surveys show a typical "penta-BDE" pattern with BDE-47 and -99 dominating (Figure 3). This is not surprising because the penta-BDE formulation was heavily used in North America and the major congeners are highly accumulative in fat tissues. The use of adipose tissues for analyses in these USDA surveys favors the detection of these lipid-accumulating congeners compared to octa- to deca-BDEs, which are not as readily partitioned into adipose.[23,24] One shortcoming of the survey data is that nothing can be said about the levels of BDE-209, which may be present in U.S. meat and poultry. Likewise, the octa- and nona-BDEs quantitated in these surveys (BDE-196, -197, -201, -203, -206, and -207) were not detected in 82−100% of the samples with the exception of BDE-201, which was detected in 60% of the samples in both surveys.

When individual samples were analyzed from the four slaughter classes, a large concentration range was observed. Beef appeared

to have the lowest levels, whereas turkeys had the highest (Figure 2). The low levels in beef are opposite to the trends seen for PCDD/Fs and co-PCBs in U.S. meats, where beef generally has the highest levels and pork the lowest. This implies that, unlike PCDD/Fs and co-PCBs, the source of PBDE exposure for livestock at this time is not dominated by deposition onto lands or fields where cattle graze. Instead, livestock typically raised indoors appeared to have the higher residue levels, pointing to sources such as housing materials, bedding, or specific feed ingredients as the source of PBDEs.

In one instance, we were able to obtain two feed samples from a farm where a turkey with a high PBDE level (4.77 ppb lw) was raised. These feed samples had concentrations equal to 0.15 and 0.17 ppb wet weight for the sum of the seven major congeners. Because no data have been published on PBDEs in poultry feed, it is not known whether these are typical or elevated levels. Two chicken feeds that our laboratory had on hand from another study were analyzed and found to have levels of 0.04 and 0.08 ppb wet weight. These values are 2−3 times lower than the turkey feeds. Bioconcentration factors (ppb in fat/ppb in feed) for persistent PCDD/Fs, furans, and PCBs can be calculated from published studies in broilers[32,33] and are on the order of 5−10. In rats, bioconcentration factors into adipose tissue for most tri- to hexa-BDEs were found to be 8−15.[17] If a bioconcentration factor of 10 is assumed for all of the tri- to hepta-BDEs, the turkey feeds would predict fat concentrations of 1.5 and 1.8 ppb, one-third the observed value. These results suggest that the turkey feed may not be the only contributor to PBDE levels in these birds. However, it should be noted that the feed samples were collected several months after the bird sample and, therefore, may not reflect the actual feed source.

It is obvious that more data are needed on the sources of PBDEs to livestock including the levels in animal feeds, feed ingredients, litters, and local surroundings. Studies that measure bioconcentration of these contaminants into animal tissues are also needed to help predict their transfer from the environment into the food supply. Although we found turkeys to have higher concentrations of PBDEs in their fat compared to other animal classes, it is important to remember that turkey meat, especially skinless breast meat which is most often consumed, has the lowest lipid content of most meat and poultry products (<1%). Because most PBDEs are lipophilic and tend to concentrate in the lipids, human dietary exposure can be reduced by selecting lean cuts of meat, trimming fat, and skinning poultry. At present there are no recommended or regulatory limits for PBDEs in foods, but reducing the levels of unnecessary, persistent, toxic compounds in food and our diet is certainly desirable.

■ ASSOCIATED CONTENT

Supporting Information. Tables S1 and S2 contain congener specific concentrations, limits of detection, GC retention times, and percentage not detected for composite samples in the two surveys. Figure S1 presents a geographical representation of the PBDE levels. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: janice.huwe@ars.usda.gov. Phone: (701) 239-1288. Fax: (701) 239-1430.

■ DISCLOSURE

Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture.

■ ACKNOWLEDGMENT

We acknowledge Mary Hallgren, Kristin McDonald, Jean Picard, and Tyler Carlsen for technical assistance with sample purification and Margaret Lorentzsen for mass spectral analyses.

■ REFERENCES

(1) Stockholm Convention, http://chm.pops.int/ (accessed Aug 25, 2010).

(2) Bromine Science and Environmental Forum website, www.bsef.com (accessed April 25, 2005, and Aug 23, 2010).

(3) Hites, R. A. Polybrominated diphenyl ethers in the environment and in people: a meta-analysis of concentrations. *Environ. Sci. Technol.* **2004**, *38*, 945–956.

(4) Schecter, A.; Pavuk, M. P.; Päpke, O.; Ryan, J. J.; Birnbaum, L.; Rosen, R. Polybrominated diphenyl ethers (PBDEs) in US mothers' milk. *Environ. Health Perspect.* **2003**, *111*, 1723–1729.

(5) Sjödin, A.; Wong, L.-Y.; Jones, R. S.; Park, A.; Zhang, Y.; Hodge, C.; Dipietro, E.; McClure, C.; Turner, W.; Needham, L. L.; Patterson, D. G., Jr. Serum concentrations of polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyl (PBB) in the United States population: 2003−2004. *Environ. Sci. Technol.* **2008**, *42*, 1377–1384.

(6) Jones-Otazo, H. A.; Clarke, J. P.; Diamond, M. L.; Archbold, J. A.; Ferguson, G.; Harner, T.; Richardson, G. M.; Ryan, J. J.; Wilford, B. Is house dust the missing exposure pathway for PBDEs? An analysis of the urban fate and human exposure to PBDEs. *Environ. Sci. Technol.* **2005**, *39*, 5121–5130.

(7) Lorber, M. Exposure of Americans to polybrominated diphenyl ethers. *J. Exp. Sci. Environ. Epidemiol.* **2008**, *18*, 2–19.

(8) Johnson-Restrepo, B.; Kannan, K. An assessment of sources and pathways of human exposure to polybrominated diphenyl ethers in the United States. *Chemosphere* **2009**, *76*, 542–548.

(9) Schecter, A.; Päpke, O.; Harris, R. T.; Tung, K. C.; Musumba, A.; Olson, J.; Birnbaum, L. Polybrominated diphenyl ether (PBDE) levels in an expanded market basket survey of United States (US) food and estimated PBDE dietary intake by age and gender. *Environ. Health Perspect.* **2006**, *114*, 1515–1520.

(10) Johnson-Restrepo, B.; Kannan, K.; Addink, R.; Adams, D. H. Polybrominated diphenyl ethers and polychlorinated biphenyls in a marine foodweb of coastal Florida. *Environ. Sci. Technol.* **2005**, *39*, 8243–8250.

(11) Fraser, A. J.; Webster, T. F.; McClean, M. D. Diet contributes significantly to the body burden of PBDEs in the general U.S. population. *Environ. Health Perspect.* **2009**, *117*, 1520–1525.

(12) Wu, N.; Herrman, T.; Paepke, O.; Tickner, J.; Hale, R.; Harvey, E.; La Guardia, M.; McClean, M. D.; Webster, T. F. Human exposure to PBDEs: associations of PBDE body burdens with food consumption and house dust concentrations. *Environ. Sci. Technol.* **2007**, *41*, 1584–1589.

(13) Alcock, R. E.; Jones, K. C. Dioxins in the environment: a review of trend data. *Environ. Sci. Technol.* **1996**, *30*, 3133–3143.

(14) Hoffman, M. K.; Huwe, J.; Deyrup, C.; Lorentzsen, M.; Zaylskie, R.; Clinch, N.; Saunders, P.; Sutton, W. Statistically designed survey of polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, and co-planar polychlorinated biphenyls in U.S. meat and poultry, 2002−2003: results, trends, and implications. *Environ. Sci. Technol.* **2006**, *40*, 5340–5346.

(15) Huwe, J.; Pagan-Rodriguez, D.; Abdelmajid, N.; Clinch, N.; Gordon, D.; Holterman, J.; Zaki, E.; Lorentzsen, M.; Dearfield, K. A survey of polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans and co-planar polychlorinated biphenyls in U.S. meat and poultry, 2007−2008. *J. Agric. Food Chem.* **2009**, *57*, 11194–11200.

(16) Huwe, J.; Larsen, G. Polychlorinated dioxins, furans, and biphenyls, and polybrominated diphenyl ethers in a U.S. meat market basket and estimates of dietary intake. *Environ. Sci. Technol.* **2005**, *39*, 5606–5611.

(17) Huwe, J. K.; Hakk, H.; Smith, D. J.; Diliberto, J. J.; Richardson, V.; Stapleton, H. M.; Birnbaum, L. S. Comparative absorption and bioaccumulation of polybrominated diphenyl ethers following ingestion via dust and oil in male rats. *Environ. Sci. Technol.* **2008**, *42*, 2694–2700.

(18) Munzel, U.; Hothorn, L. A. A unified approach to simultaneous rank test procedures in the unbalance one-way layout. *Biometric J.* **2001**, *5*, 553–569.

(19) R Development Core Team. *R: A Language and Environment for Statistical Computing*; R Foundation for Statistical Computing: Vienna, Austria, 2009; ISBN 3-900051-07-0, URL http://www.R-project.org.

(20) European Food Safety Authority. Results of the monitoring of dioxin levels in food and feed. *EFSA J.* **2010**, *8*, 1385.

(21) Kierkegaard, A.; De Wit, C. A.; Asplund, L.; McLachlan, M. S.; Thomas, G. O.; Sweetman, A. J.; Jones, K. C. A mass balance of tri-hexabrominated diphenyl ethers in lactating cows. *Environ. Sci. Technol.* **2009**, *43*, 2602–2607.

(22) Voorspoels, S.; Covaci, A.; Lepom, P.; Jaspers, V. L. B.; Schepens, P. Levels and distribution of polybrominated diphenyl ethers in various tissues of birds of prey. *Environ. Pollut.* **2006**, *144*, 218–227.

(23) Huwe, J. K.; Hakk, H.; Birnbaum, L. S. Tissue distribution of polybrominated diphenyl ethers in male rats and implications for biomonitoring. *Environ. Sci. Technol.* **2008**, *42*, 7018–7024.

(24) Kierkegaard, A.; Asplund, L.; De Wit, C. A.; McLachlan, M. S.; Thomas, G. O.; Sweetman, A. J.; Jones, K. C. Fate of higher brominated PBDEs in lactating cows. *Environ. Sci. Technol.* **2007**, *41*, 417–423.

(25) http://www.ars.usda.gov/SP2UserFiles/Place/12354500/Data/SR23/nutrlist/sr23a204.pdf.

(26) Zota, A. R.; Rudel, R. A.; Morello-Frosch, R. A.; Brody, J. G. Elevated house dust and serum concentrations of PBDEs in California: unintended consequences of furniture flammability standards? *Environ. Sci. Technol.* **2008**, *42*, 8158–8164.

(27) U.K. Food Standard Agency (FSA). Dioxins and dioxin-like PCBs in the U.K. diet: 2001 total diet study samples, July 2003, http://food.gov.uk/science/surveillance/.

(28) De Mul, A.; Bakker, M. I.; Zeilmaker, M. J.; Traag, W. A.; van Leeuwen, S. P. J.; Hoogenboom, R. L. A. P.; Boon, P. E.; van Klaveren, J. D. Dietary exposure to dioxins and dioxin-like PBCs in The Netherlands anno 2004. *Regul. Toxicol. Phamacol.* **2008**, *51*, 278–287.

(29) Schecter, A.; Haffner, D.; Colacino, J.; Patel, K.; Päpke, O.; Opel, M.; Birnbaum, L. Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD) in composite U.S. food samples. *Environ. Health Perspect.* **2010**, *118*, 357–362.

(30) Lorber, M.; Patterson, D.; Huwe, J.; Kahn, H. Evaluation of background exposures of Americans to dioxin-like compounds in the 1990s and the 2000s. *Chemosphere* **2009**, *77*, 640–651.

(31) Frederiksen, M.; Vorkamp, K.; Thomsen, M.; Knudsen, L. E. Human internal and external exposure to PBDEs — a review of levels and sources. *Int. J. Hyg. Environ. Health* **2009**, *212*, 109–134.

(32) Iben, C.; Böhm, J.; Tausch, H.; Leibetseder, J.; Luf, W. Dioxin residues in the edible tissue of broiler chicken. *J. Anim. Physiol. Anim. Nutr.* **2003**, *87*, 142–148.

(33) Maervoet, J.; Chu, S. G.; De Vos, S.; Covaci, A.; Voorspoels, S.; De Schrijver, R.; Schepens, P. Accumulation and tissue distribution of selected polychlorinated biphenyl congeners in chickens. *Chemosphere* **2004**, *57*, 61–66.