LEVELS AND DISTRIBUTIONS OF PBDEs AND PCDD/Fs IN BEEF

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Abstract

Levels of polybrominated diphenyl ethers (PBDEs) are increasing in food depending on the environmental levels of PBDEs which have been continuously increasing. PCDD/Fs are known as one of the most toxic compounds. They are in decreasing trend in many countries however, concerning levels are still found in food and animal feedingstuffs. Concentrations and distributions of BDE-28, 47, 99, 100, 153, 154, and 183 and PCDD/Fs were presented in this study. Ninety-six samples were collected from slaughterhouses from nine regions in South Korea. Fifty samples from four countries were collected by a randomly selected importing system. The sum of seven PBDEs ranged from 0.038 to 7.724 ng/g fat. Congener profiles of PBDEs in beef from the mean value showed that BDE-47 and BDE-99 were dominant. There was no difference between regions and detected concentration and pattern of samples. This was an indication that source of PBDEs contamination was similar. From a toxicological point of view, the mean concentration of PCDD/Fs from the one hundred forty six beef samples was 0.13 pg TEQ/g fat. The mean concentrations of PCDDs and PCDFs in beef were 0.04 pg TEQ/g fat and 0.09 pg TEQ/g fat, respectively. The congener-specific highest concentrations were found from 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDF.

Introduction

The environmental polybrominated diphenyl ethers (PBDEs) were first placed on the market in the 1960s as flame retardants and are still used to improve fire safety of consumer and industrial products. The environmental problems related to brominated flame retardants (BFRs) and dioxins (PCDDs/PCDFs) have raised great concern. BFRs are used in electrical supplies, computers, and furniture. However, dioxins are unintentional byproducts from chemical industries and combustion processes. Dioxins contained in the emissions from incineration plants have contaminated both crops and soil thus giving rise to a background level of dioxin in animal feeds.[1] Dioxins have been shown to cause risk of cancer, immune deficiency, and reproductive and developmental abnormalities.[2] PBDEs are known to affect thyroid hormones and to cause neurodevelopmental toxicity. Penta-BDEs are known to cause toxic effects although the dose is low.[3] Relatively high levels of PBDEs have been found in marine mammals, fish, and food of animal origin. PBDEs are persistent in the environment and bioaccumulate with their lipophilicity as dioxins. Ingestion of PBDEs and PCDD/Fs by humans occurs mainly through the food chain and especially through foods of fish and other animal origin.[4] Cattle is being relatively longer life time before slaughtering and beef is one of the common dietary item. A survey has been conducted to assess the safety of beef from PBDEs and dioxins in Korea.

Materials and Methods

Labeled standard solutions of PBDEs were purchased from Cambridge Isotope Laboratories Inc. PCDD/Fs and ^{13}C-labeled standards were purchased from Wellington Laboratories Inc. Both solutions were diluted with nonane to appropriate concentrations. Beef samples were collected from slaughterhouses and imported products. One hundred forty six samples were analyzed for BDE-28, 47, 99, 100, 153,154, 183 and seventeen 2,3,7,8-substituted PCDD/Fs. Fat was melted from the beef samples in an 80 ^{o}C oven before analysis.[5] The 5 g fat samples were solubilized in 10 mL ~ 50 mL of hexane and were spiked with a known amount of ^{13}C-labeled standards. US EPA Method 1614 for PBDEs and Method 1613B for PCDD/Fs were referenced. Clean-up was performed by Jumbo silica, silica, alumina, and carbon columns using a Power-Prep^{TM}. The sample was purified by elution from the silica and alumina columns with 90 mL of hexane and 60 mL of 2% methylene chloride/hexane followed by elution from the silica, alumina and carbon columns with 120 mL of 50% methylene chloride/hexane. PCDD/Fs were in toluene and PBDEs were in 50% methylene chloride/hexane at the last purification. The extract was analyzed by HR-GC/MS (Autospec Ultima, Micromass Co., U.K) equipped

with a DB5MS capillary column (60 m x 0.25 mm I.D., 0.25 μm film thickness, J&W Scientific, U.S). Two of the most abundant ions were measured. Recoveries of the internal standards were 65% ~ 134%. The results were calculated using zero for non-detects.

Results and Discussion

One hundred forty six samples of beef were analyzed for PBDEs and PCDD/Fs. Ninety six of domestically produced beef were collected from nine regions. Fifty samples of imported beef from four countries were collected. Mean concentrations, minimum levels, maximum levels and detected frequencies of seven PBDEs for the one hundred forty six samples were presented in Table 1. The sum of seven PBDEs ranged from 0.038 to 7.724 ng/g fat. Overall, the mean concentration of PBDEs was 0.451 ng/g fat. The mean concentration of domestic beef and imported beef were 0.50 ng/g fat and 0.39 ng/g fat, respectively. The distributions of concentrations were similar between domestic and imported beef when two of unusually high concentrations (7.627 and 7.724 ng/g fat) from domestic beef were excluded. 5% of domestic beef samples and 10% of imported beef samples were over 1 ng/g fat. BDE-47 was found as the highest concentration and 100% of detected frequency from the one hundred forty six samples. Both of BDE-99 and BDE-100 were found 99.3% from the samples and the concentration of BDE-99 was 4.6 times higher than BDE-100. BDE-28, BDE-154, and BDE-153 were found from more than 50% of samples. BDE-183 was found to have the least concentration and detected frequency (1.4%). This suggested that BDE-183 is low level in the environment or the rate of accumulation is poor. It might be related to a lesser bioavailability or a short half-life compared to other PBDEs. Minimum concentrations were below the limit of detection except BDE-47 from all the samples. The minimum concentration of BDE-47 from the total one hundred forty six samples was 0.018 ng/g fat. Tri-BDE, tetra-BDE and penta-BDE were the major compounds of contribution in beef. From tetra- to hepta-BDE, the detected frequency decreases with increasing bromine substitutions.

Figure 1 shows the relative % distributions of seven PBDEs in beef. The distributions of BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, and BDE-28 were 53, 31, 7, 4, 3, and 2%, respectively. BDE-183 was a very small portion unable to measure in percent. The amount of distribution is probably related to the composition of brominated flame retardant in commercial products. The changes in contribution with the biological metabolism in cattle were also involved. There was no difference between origin of samples and detected concentrations. This suggested that the sources of PBDEs contamination were similar.

Figure 2 showed the congener distributions of PBDEs in domestic beef. The congener specific distributions were very similar. BDE-47 in samples from region E showed relatively high concentration. The sum of PBDEs in those samples was the highest level. The reason could not be found. The bar on the very right is the mean of total distributions. Concentration of BDE-99 was also high except the sample from region H. Only BDE-47 showed high concentration in samples from region H. The distribution profiles of imported beef were not different. Concentration of BDE-47 was the highest in almost all imported samples. It is indicated that the composition of commercial products of BFRs were similar.

Table 2 presented the concentrations and detected frequencies of PCDD/Fs in beef. From a toxicological point of view, the mean concentration of PCDD/Fs from the one hundred forty six samples was 0.13 pg TEQ/g fat which was similar to the result (0.17 pg TEQ/g fat) in the monitoring conducted in 2001-2002.[6] The mean concentrations of PCDDs and PCDFs from the one hundred forty six samples were 0.04 pg TEQ/g fat and 0.09 pg TEQ/g fat, respectively. The congener-specific highest concentrations were found from 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDF. OCDD, 1,2,3,7,8,9-HxCDF, 1,2,3,4,7,8,9-HpCDF, and OCDF showed not detected (nd) in TEQ calculations. However, 60%, 5%, and 15% of samples were detected for OCDD, OCDF, and 1,2,3,4,7,8,9-HpCDF, respectively. 1,2,3,7,8,9-HxCDF was not detected from all of the one hundred forty six samples. The concentration of beef from domestically produced and imported products were 0.14 and 0.11 pg TEQ/g fat, respectively. The concentrations by weight were reverse between domestic beef (2.79 pg/g fat) and imported beef (3.26 pg/g fat). The detected weight concentrations of OCDD and 1,2,3,4,6,7,8-HpCDD in imported beef were almost twice as high as domestic beef. The detected frequency of 1,2,3,7,8-PeCDD was only 5% and that of 2,3,4,7,8-PeCDF was 23%. From penta- to hepta CDFs were frequently detected however, the level of PCDDs by weight was 3 times higher than PCDFs because of OCDD contribution.

In comparison to PBDEs and PCDD/Fs, tri- to hexa-BDEs and penta- to hepta-PCDD/Fs were dominant residuals in beef. The residual levels of PBDEs were more than 150 times higher than PCDD/Fs. It is difficult to make a direct comparison because there are no toxic equivalencies for PBDEs. There was no relationship found between concentrations of PBDEs and PCDD/Fs in the samples. However, the relatively high mean value of PBDEs from a certain province showed the high levels of PCDD/Fs although the contamination sources are different.

Table 1. Concentrations and detected frequencies of PBDEs in beef

	Concentration (ng/g fat) (N = 146)			LOD (ng/g fat)
	Min.	Max.	Mean	
2,4,4'-TriBDE (BDE-28)	nd	0.070	0.010	0.020
2,2',4,4'-TetraBDE (BDE-47)	0.018	4.617	0.236	0.064
2,2',4,4',6-PentaBDE (BDE-100)	nd	0.266	0.030	0.027
2,2',4,4',5-PentaBDE (BDE-99)	nd	3.632	0.138	0.033
2,2',4,4',5,6'-HexaBDE (BDE-154)	nd	0.104	0.015	0.088
2,2',4,4',5,5'-HexaBDE (BDE-153)	nd	0.282	0.020	0.098
2,2',3,4,4',5',6-HeptaBDE (BDE-183)	nd	0.046	0.001	0.096
Sum of PBDEs			0.451	

nd: not detected

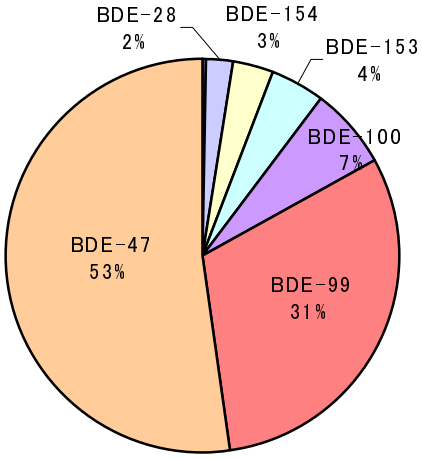

Fig. 1. Percent distributions of PBDEs in beef.

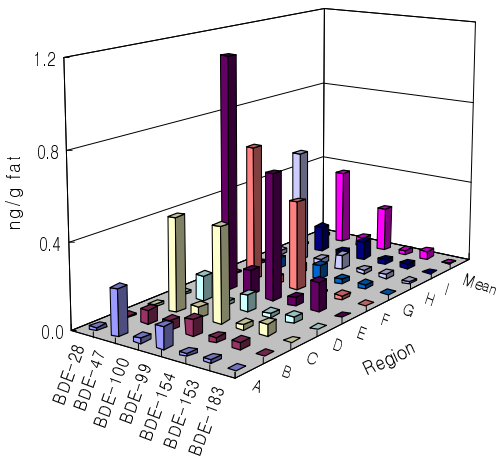

Fig. 2. Congener distributions of PBDEs in domestic beef.

Table 2. Concentrations and detected frequencies of PCDD/Fs in beef

PCDD/Fs	Concentration (N= 146) (pg TEQ/g fat)			LOD (pg/g fat)
	Min.	Max.	Mean	
2,3,7,8-TCDD	nd	0.68	0.01	0.040
1,2,3,7,8-PeCDD	nd	1.29	0.02	0.017
1,2,3,4,7,8-HxCDD	nd	0.02	0.0	0.041
1,2,3,6,7,8-HxCDD	nd	0.30	0.01	0.033
1,2,3,7,8,9-HxCDD	nd	0.17	0.0	0.034
1,2,3,4,6,7,8-HpCDD	nd	0.29	0.0	0.038
OCDD	nd	nd	0.0	0.041
2,3,7,8-TCDF	nd	0.45	0.0	0.019
1,2,3,7,8-PeCDF	nd	0.01	0.0	0.020
2,3,4,7,8-PeCDF	nd	1.27	0.05	0.016
1,2,3,4,7,8-HxCDF	nd	0.12	0.02	0.040
1,2,3,6,7,8-HxCDF	nd	0.09	0.01	0.036
2,3,4,6,7,8-HxCDF	nd	0.06	0.01	0.043
1,2,3,7,8,9-HxCDF	nd	nd	0.0	0.051
1,2,3,4,6,7,8-HpCDF	nd	0.01	0.0	0.019
1,2,3,4,7,8,9-HpCDF	nd	nd	0.0	0.032
OCDF	nd	nd	0.0	0.023
Sum of PCDDs			0.04	
Sum of PCDFs			0.09	
Sum of PCDD/Fs			0.13	

nd: not detected

References

1. Malisch, R. *Chemosphere* 2000;40:1041.
2. Schecter A, Birnbaum L, Ryan JJ, Constable JD. *Environ. Res*. 2006 ;101:419.
3. Darnerud PO. *Environ. Int*. 2003; 29:841.
4. Baars A.J, Bakker M.I, Baumann R.A, Boon P.E, Freijer J.I, Hoogenboom L.A.P, Hoogerbrugge R, van Klaveren J.D, Liem A.K.D, Traag W.A, de Vries J. *Toxicol. Lett.* 2004;151:51.
5. Covaci A, Ryan JJ, Schepens P. *Chemosphere* 2002; 47: 207.
6. Kim M, Kim S, Yun S, Cho B, Lee M, Son S, Park J. *Organohalogen Comp* 2003; 64:9.