RESIDUAL PATTERN RELATIONSHIP OF PCDD/Fs IN BEEF AND RAW MILK

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Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) are found in a variety of foods. Residual patterns of PCDD/Fs in food can probably reflect the sources of contaminants although animal metabolism and environmental fate are involved. The sources of PCDDs and PCDFs are distinguishable. PCDDs are usually from sources of anthropogenic, mineral, and chemical impurities. PCDFs are more often from hospital and industrial waste incineration. Animal feeds are a major source of PCDD/Fs contamination in food. These environmental contaminants directly affect animal and agriculture and the foodstuffs of animal origin and crops used as animal feed. Pork and chicken have shorter lifetimes than cattle before slaughter, so cattle have more time to accumulate PCDD/Fs in their bodies. Residual patterns of PCDD/Fs in beef and milk might help interpretation of their sources. This paper presents the residual pattern relationship of PCDD/Fs in beef and raw milk in order to investigate the sources of the contaminant throughout the food chain.

Materials and Methods

Beef samples were collected from February to October 2004 from sixty cattle at inspected slaughter facilities. Raw milk samples were collected in April 2005 from sixty farms. Each farm provided a sample of mixed raw milk from several dairy cows. Numbers of samples from each region decided depended upon the production rates. The samples of beef and raw milk were not related to each other. Fat was extracted from the beef samples in the oven under 80^{o}C before analysis. PCDD/Fs in beef fat were extracted with hexane. Extraction of PCDD/Fs from raw milk was carried out with methanol with sodium oxalate and ethyl ether/petroleum ether (1:1, v/v). An isotope dilution method was used for the analysis of PCDD/Fs based on U.S EPA Method 1613B. Clean-up was performed by silica, alumina, and carbon columns using a Power-Prep^{TM} (FMS Inc., U.S) automated column clean-up system. The extract was analyzed by HR-GC/MS (Autospec Ultima, Micromass Co., U.K) equipped with a DB5MS capillary column (50 m x 0.25 mm I.D., 0.25 μ m film thickness, J&W Scientific, U.S). A single analysis of each sample was made.

Results and Discussion

Congener profiles of PCDD/Fs in beef and in raw milk from each region are shown in Fig. 1 and Fig. 2, respectively. The nine regions expressed by alphabet A to I and the same alphabet represents the same region between beef and raw milk. The number of beef samples from the region A, B, C, D, E, F, G, H, and I were 6, 10, 9, 7, 9, 5, 2, 7, and 5, respectively. The number of raw milk samples from the region A, B, C, D, E, F, G, H, and I were 4, 20, 5, 5, 5, 5, 2, 10, and 4, respectively. WHO-TEQ concentrations were averaged from the regional samples. The regional mean concentrations of PCDD/Fs in beef were 0.39, 0.84, 0.55, 0.63, 0.94, 1.42, 0.02, 0.77, and 1.26 pg TEQ/g fat from A to I, respectively. The regional mean concentrations of PCDD/Fs in raw milk were 0.32, 0.90, 0.36, 0.70, 0.62, 0.63, 0.12, 0.50, and 0.70 pg TEQ/g fat from A to I, respectively. The congener profiles were very similar between beef and raw milk. 2,3,4,7,8-PeCDF was the most highly concentrated in almost all samples of beef and raw milk. 1,2,3,7,8-PeCDD was the most concentrated from beef collected from region F. PCDFs were more highly concentrated than PCDDs in TEQ level in all the regions for beef and raw milk. From a toxicological point of view, 2,3,7,8-TCDF and OCDF were found in few of the 60 samples of beef, 1,2,3,4,7,8-HxCDD, OCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 1,2,3,7,8,9-HxCDF, 1,2,3,4,7,8,9-HpCDF, and OCDF were found in few of the 60 samples of raw milk. The contributions of penta- and hexa-CDFs in congener profile were 83% in beef and 93% in raw milk. The total TEQ concentrations were 0.80 pg/g fat in beef and 0.65 pg/g fat in raw milk. The total TEQ level of PCDFs in beef was 5 times higher than and in raw milk 15 times higher than that of PCDDs. The samples containing 2,3,7,8-TCDD and /or 1,2,3,7,8-PeCDD showed the highest TEQ levels. PCDDs only were detected within 3% of the total samples and PCDFs only

were detected within 20% of the total samples.

Table 1 presents the mean concentration and percent frequency of determination for each congener in beef and raw milk. The mean concentration was calculated using 0 for non-detects. In samples of both beef and raw milk, OCDD, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 2,3,4,6,7,8-HxCDF, and 1,2,3,4,6,7,8-HpCDF were the major congeners of contribution to elevated residual concentration and frequency of determination. It is suggested that the sources of contamination were very similar for the samples and regions. The 50% of detects of 1,2,3,6,7,8-HxCDD in beef was contributed to 13% of the concentration of PCDDs. It was a significantly different pattern from raw milk which showed 2% of detects and 0.7% contribution to the concentration of PCDDs. It seems that 1,2,3,6,7,8-HxCDD has a greater affinity to lipid in cattle. 1,2,3,4,6,7,8-HpCDD was the only congener which showed higher concentrations and detected frequency in raw milk than in beef. The unique difference from the general trend between beef and raw milk suggests that the excretion rate of 1,2,3,4,6,7,8-HpCDD might be fast in cattle through feces and/or milk. The highest TEF compounds, 2,3,7,8-TCDD showed relatively low mean concentrations of 0.01 pg/g fat in beef and in raw milk and 3% of detects for both beef and raw milk. 1,2,3,7,8-PeCDD showed 0.06 pg/g fat in beef and 13% detects which were 3 to 4 times more frequent than in raw milk. 2,3,7,8-TCDF were not detected from the beef. 1,2,3,4,7,8-HxCDD, 2,3,7,8-TCDF, 1,2,3,7,8-TCDF, 1,2,3,7,8,9-HxCDF were not detected from the 60 samples of raw milk. Overall, the detected frequencies of PCDDs and PCDFs in beef and in raw milk were almost the same.

The residual patterns of PCDDs and PCDFs in our domestic beef and milk were very different from products in other countries. U.S beef reported by Ferrario et al. and ground beef and milk from southern Mississippi reported by Fiedler et al. showed similar congener profiles.[1,2] The total contributions of PCDDs were higher than PCDFs in U.S beef fat and milk. Pentachlorophenol treated wood was one of the sources of contamination. German dairy products and Belgium beef showed higher levels of PCDFs than PCDDs in line with our results.[2,3] We also had different congener-specific profiles between domestic beef and imported beef from 4 non-European countries that conducted studies in 2001-2002.[4] It indicated that the sources of PCDDs and PCD/Fs were different between our domestic products and others. However, the levels and detects for 1,2,3,6,7,8-HxCDD compared to other congeners showed similar profiles to that of the U.S beef fat. The age of cattle for our samples ranged from 2 years old to 7 years old. The body weights were about 410 kg to 850 kg. The age, body weight, and type of cattle were not related to the residual levels of PCDD/Fs.

The pathway of dioxin contamination was not clear, however the residual distributions of PCDD/Fs in beef and raw milk are similar to residual distributions in feed of animal origin, especially fish stuffs.[5] The cycle of food and feed are very complex. For example, PCDD/Fs enter the atmosphere from incinerators and settle down to the ground and crops by dry and wet deposition. Then, PCDD/Fs are directly transferred to the animal through inhalation and are indirectly transferred to the animal through crops as animal feeds. The by-products of animals that contained PCDD/Fs are used as feeds. During the cycle, a small amount of PCDD/Fs in one compartment will get together to make larger amount into an animal. Alternatively, large amounts of PCDD/Fs in one compartment will be diluted to small amounts with many ingredients in the production of animal feed. Therefore, it is difficult to investigate the sources of contamination. Based on this study, the residual distribution of PCDD/Fs in raw milk should represent the contamination rates to cattle although the congener profiles might change through the food chain. For the last few years, animal feed was the major contamination source of food of animal origin. Mineral origin or anthropogenic sources were major contributors of PCDD/Fs in accidental contamination of animal feed. However, accidents involving citrus pulp or PCBs with animal fat might have different origins from PCDD/Fs. The environment and feed for livestock will be affected to the residual patterns of PCDD/Fs in cattle. The contamination source of PCDD/Fs in our domestic food of animal origin was closer to incinerators based on the residual patterns analyzed. The food of animal origin from U.S and non-European countries related to contamination from mineral and anthropogenic sources. There needs to be more monitoring of different food categories and production areas to find the relationship between sources and contaminations.

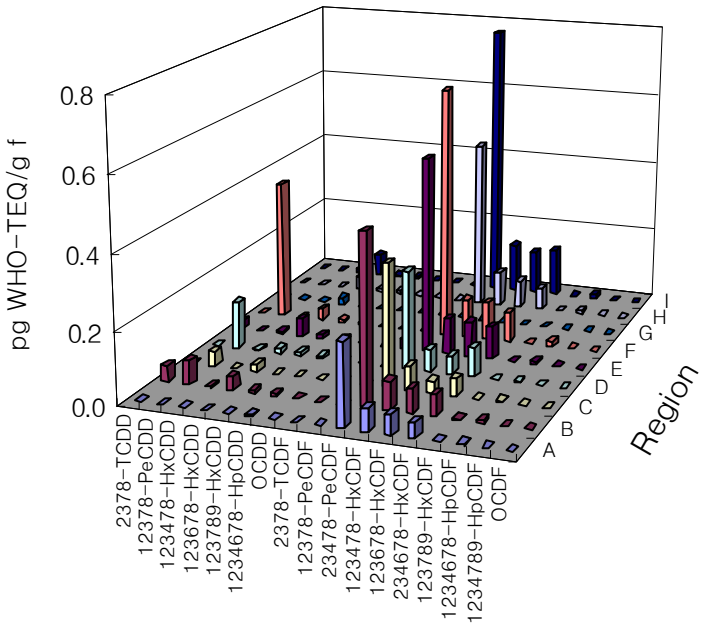

Fig. 1. Congener profiles of average level of PCDD/Fs in beef from each region. Number of samples from region A, B, C, D, E, F, G, H, and I were 6, 10, 9, 7, 9, 5, 2, 7, and 5, respectively.

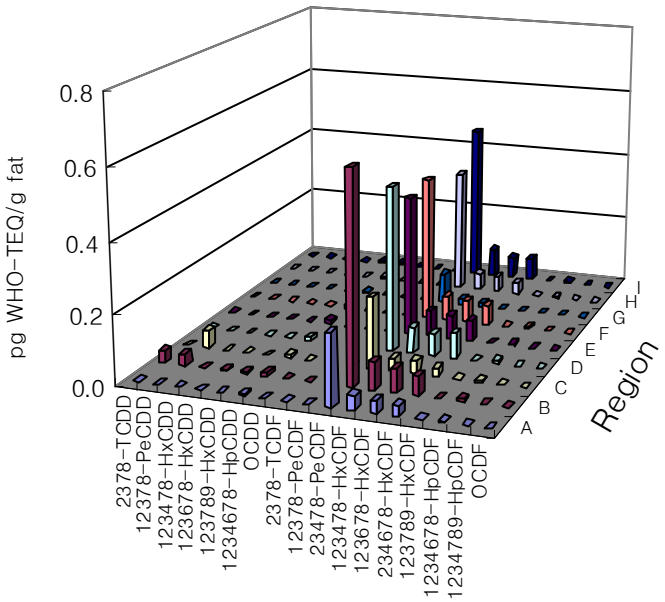

Fig. 2. Congener profiles of average level of PCDD/Fs in raw milk from each region. Number of samples from region A, B, C, D, E, F, G, H, and I were 4, 20, 5, 5, 5, 5, 2, 10, and 4, respectively.

Table 1. Concentrations and detected frequencies of PCDD/Fs in beef and raw milk

PCDD/Fs	Mean Concentration (pg /g fat)		Detected Frequency (%)	
	Beef (n=60)	Raw milk (n=60)	Beef (n=60)	Raw milk (n=60)
2,3,7,8-TCDD	0.01	0.01	3	3
1,2,3,7,8-PeCDD	0.06	0.02	13	3
1,2,3,4,7,8-HxCDD	0.03	0.00	10	0
1,2,3,6,7,8-HxCDD	0.31	0.01	50	2
1,2,3,7,8,9-HxCDD	0.06	0.02	18	5
1,2,3,4,6,7,8-HpCDD	0.05	0.10	58	85
OCDD	1.80	1.67	85	97
PCDDs	**2.32**	**1.83**		
TEQ(PCDDs)	**0.12**	**0.04**		
2,3,7,8-TCDF	0.00	0.00	0	0
1,2,3,7,8-PeCDF	0.07	0.00	2	0
2,3,4,7,8-PeCDF	0.88	0.86	88	90
1,2,3,4,7,8-HxCDF	0.82	0.65	88	78
1,2,3,6,7,8-HxCDF	0.70	0.57	82	78
2,3,4,6,7,8-HxCDF	0.69	0.49	87	70
1,2,3,7,8,9-HxCDF	0.004	0.00	3	0
1,2,3,4,6,7,8-HpCDF	0.62	0.57	75	83
1,2,3,4,7,8,9-HpCDF	0.01	0.006	2	3
OCDF	0.07	0.007	7	7
PCDFs	**3.86**	**3.15**		
TEQ(PCDFs)	**0.68**	**0.61**		
PCDDs+PCDFs	**6.18**	**4.98**		
TEQ(PCDDs+PCDFs)	**0.80**	**0.65**		

References

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