DIOXIN CONTAMINATION OF CHILEAN PORK FROM ZINC OXIDE IN FEED

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Introduction

Dioxin (polychlorinated dibenzo-*p*-dioxins, PCDDs and dibenzofurans, PCDFs) are continually found in a variety of foods. Animal feed and feed additives are the major sources of dioxin contamination in a food chain. Recently, the Chilean government found zinc oxide as a source of dioxin contamination in pork meat that was exported to South Korea, Japan and to other countries. The National Veterinary Research and Quarantine Service (NVRQS), South Korea found dioxin over the Korean maximum residue limit in pork (MRL=2 pg TEQ/g fat) imported from Chile in June 2008. The Chilean government performed dioxin tests for variable matrixes based on Korean notification. Korea and Chile collaborated and analyzed to find out the sources of contamination. With the fast tracing and sincere efforts of the Chilean government, one of the contamination sources of dioxin was found in the premix ingredients. Contaminated zinc oxide from a smelting process was the primary source of dioxin. Zinc oxide is used as a mineral supplement in feed. In 2003, the U.S FDA also found dioxin contamination of zinc oxide from mineral mixes and mineral premixes for use in animal feed[1]. This paper presents the residual patterns of PCDD/Fs in pork meat and the contamination sources. The Chilean government carried out a surveillance program for dioxins and dioxin like PCBs in order to guarantee food safety in porcine meat after the crisis.

Materials and Methods

Chilean pork samples were randomly selected from the Korean Automated Import Information System (AIIS) in June 2008. The samples were treated either using extracted fat in a conventional oven under 80℃ or using Soxhlet extraction with hexane. An isotope dilution method was used for the analysis of PCDD/Fs based on U.S EPA Method 1613B[2]. Clean-up was performed with silica, alumina, and carbon columns using a Power-Prep™ (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 μm film thickness, J&W Scientific, U.S). Samples collected by the Chilean government were analyzed by the Research Productivity Council (RPC) in Canada. RPC also used the isotope dilution method based on U.S EPA Method 1613B.

Results and Discussion

PCDD/Fs were found from 2.3 to 15 pg/g fat from imported Chilean pork in NVRQS laboratories in South Korea. Table 1 presents the congener patterns of the lowest (Pork 1) and highest (Pork 2) concentration determined over the Korean MRL. Pork 3 (the lowest concentration) and Pork 4 (the highest concentration) on Table 1 were analyzed by RPC laboratory from the collected samples after Korea informed dioxin determination to Chile. The congener patterns were very similar not only in the samples shown on Table 1 but also in the others that were analyzed by both laboratories although the farms and periods of sampling were different. World Health Organization established toxic equivalency factors (TEFs, 1998) were used for both calculations by institutes. 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, and 2,3,4,6,7,8-HxCDF were found as the major congeners in pork meat samples analyzed. 2,3,4,7,8-PeCDF showed the highest concentration and contributed about 30% among the seventeen congeners in most of the dioxin contaminated samples. The 'nd' as a not detected was treated equal to zero in pork 1 and pork 2 analyzed by NVRQS and treated equal to the limit of detection (LOD) in pork 3 and pork 4 analyzed by RPC. 2,3,7,8-TCDD, 1,2,3,7,8,9-HxCDD, OCDD, 2,3,7,8-

TCDF, 1,2,3,7,8-PeCDF, 1,2,3,7,8,9-HxCDF, and OCDF were not detected or exist as background levels in the relatively lower contaminated samples. 1,2,3,7,8-PeCDD in pork 4 showed a little higher level compared to the other samples. The Chilean government carried out samplings from the production lines of feed and pork meat from the many farms and the environment in order to find the contamination source.

Table 1. Concentrations (pg TEQ/g fat) of PCDD/Fs in Chilean pork samples

PCDD/F	Pork 1*	Pork 2*	Pork 3**	Pork 4**
2,3,7,8-TCDD	nd***	nd	0.05	0.65
1,2,3,7,8-PeCDD	nd	nd	0.05	2.28
1,2,3,4,7,8-HxCDD	nd	0.24	0.07	0.65
1,2,3,6,7,8-HxCDD	0.03	0.23	0.04	0.59
1,2,3,7,8,9-HxCDD	nd	nd	0.007	0.13
1,2,3,4,6,7,8-HpCDD	0.02	0.14	0.03	0.28
OCDD	0.001	0.003	nd	0.005
ΣPCDDs	**0.05**	**0.61**	**0.25**	**4.59**
2,3,7,8-TCDF	nd	nd	0.005	0.14
1,2,3,7,8-PeCDF	nd	nd	0.003	0.18
2,3,4,7,8-PeCDF	0.83	4.97	0.62	12.35
1,2,3,4,7,8-HxCDF	0.55	4.89	0.59	9.91
1,2,3,6,7,8-HxCDF	0.30	2.10	0.26	4.18
2,3,4,6,7,8-HxCDF	0.38	1.25	0.18	2.61
1,2,3,7,8,9-HxCDF	nd	nd	0.04	0.08
1,2,3,4,6,7,8-HpCDF	0.19	1.03	0.20	2.38
1,2,3,4,7,8,9-HpCDF	0.01	0.14	0.02	0.30
OCDF	nd	0.003	nd	0.005
ΣPCDFs	**2.26**	**14.38**	**1.92**	**32.14**
ΣPCDD/Fs	**2.31**	**15.0**	**2.17**	**36.72**

*Samples collected in Korea. Analyzed by NVRQS, Korea.
**Samples collected in Chile. Analyzed by RPC, Canada.
***nd: not detected. nd=0 in pork 1 and pork 2. nd=LOD in pork 3 and pork 4.

Table 2 shows the concentration of PCDD/Fs in premix ingredients related with zinc oxide. Remarkably high concentrations of PCDD/Fs were found from the sample of zinc oxide, zinc oxide based premix and the crust in a mixing chamber of feed. All of seventeen congeners were found, however, a few congeners including 2,3,7,8-TCDD and 2,3,4,7,8-PeCDF were not quantified due to interferences. Congener patterns were similar between samples based on zinc oxide. PCDD/Fs of 17147, 6673, and 800 pg TEQ/g (normalized weight based on 12% moisture content) were found in pure zinc oxide from a supplier, in premix and in crust residue in a mixing chamber of a feed mill, respectively. Samples of two different feed from a farm were analyzed and averaged the determined concentrations of PCDD/Fs. The percent contributions of congeners were very close to the samples based zinc oxide. The contributions of PCDFs from the four samples in Table 2 were 82~83% although several

congeners could not be quantified due to interferences in the sample of zinc oxide.

Table 2. Concentrations (pg TEQ/g nw*) of PCDD/Fs in premix ingredients

PCDD/F	ZnO	Premix (ZnO Based)	Mix residue (ZnO Based)	Feed
2,3,7,8-TCDD	NDI**	90.4	21.3	0.18
1,2,3,7,8-PeCDD	NDI	718	81.3	1.44
1,2,3,4,7,8-HxCDD	386	57.9	4.98	0.11
1,2,3,6,7,8-HxCDD	1060	117	9.94	0.22
1,2,3,7,8,9-HxCDD	656	89.4	8.74	0.18
1,2,3,4,6,7,8-HpCDD	899	139	9.89	0.25
OCDD	18.6	2.99	0.22	0.006
ΣPCDDs	**3020**	**1215**	**136**	**2.4**
2,3,7,8-TCDF	NDI	178	40.1	0.40
1,2,3,7,8-PeCDF	NDI	164	34.9	0.37
2,3,4,7,8-PeCDF	NDI	2255	219	4.27
1,2,3,4,7,8-HxCDF	3460	648	120	1.48
1,2,3,6,7,8-HxCDF	3860	696	83.7	1.30
2,3,4,6,7,8-HxCDF	6170	1090	105	2.25
1,2,3,7,8,9-HxCDF	236	58.7	9.83	0.15
1,2,3,4,6,7,8-HpCDF	NDI	296	40.8	0.86
1,2,3,4,7,8,9-HpCDF	364	66.3	9.65	0.14
OCDF	37.7	6.56	0.846	0.01
ΣPCDFs	**14128**	**5459**	**664**	**11.2**
ΣPCDD/Fs	**17148**	**6674**	**800**	**13.6**

*Normalized weight (based on 12% moisture content)
**NDI: Not determined due to interference.

The characteristics of the congeners of positive samples from the meat and supplies associated premix 1 were presented in Figure 1 and from the meat and associated premix 2 were presented in Figure 2. Premix 1 and associated meat showed a similar congener pattern to the contaminated zinc oxide. However, the premix 2 association included more PCDDs especially 2,3,7,8-TCDD and 1,2,3,7,8-TCDD that were from vegetable fatty acid and/or animal fatty acid. It is supposed that a secondary source of contamination may exist in addition to the zinc oxide. The congener pattern of each meat sample was reflected by the pattern of the associated premix. Background level or less than 1.06 pg/g levels of PCDD/Fs were found from the sample of sodium acid pyrophosphate, calcium carbonate, copper sulphate, antioxidant, threonine, fitasa, and celite that are not shown here. The congener distributions of these ingredients were also similar to the pattern of samples based on zinc oxide. It probably reflects the cross contamination of PCDD/Fs from the mixing process of zinc oxide. After many analytical results, the Chilean government concluded that zinc oxide was the major source for the dioxin contamination in this case.

Acknowledgement
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References
1. US FDA, Information for manufacturers of animal feed mineral mixes. CVM Update on March 12, 2003.
2. Kim, M, Kim S, Yun SJ, Kim D-G, Chung G-S. *Chemosphere* 2007; 39:479.

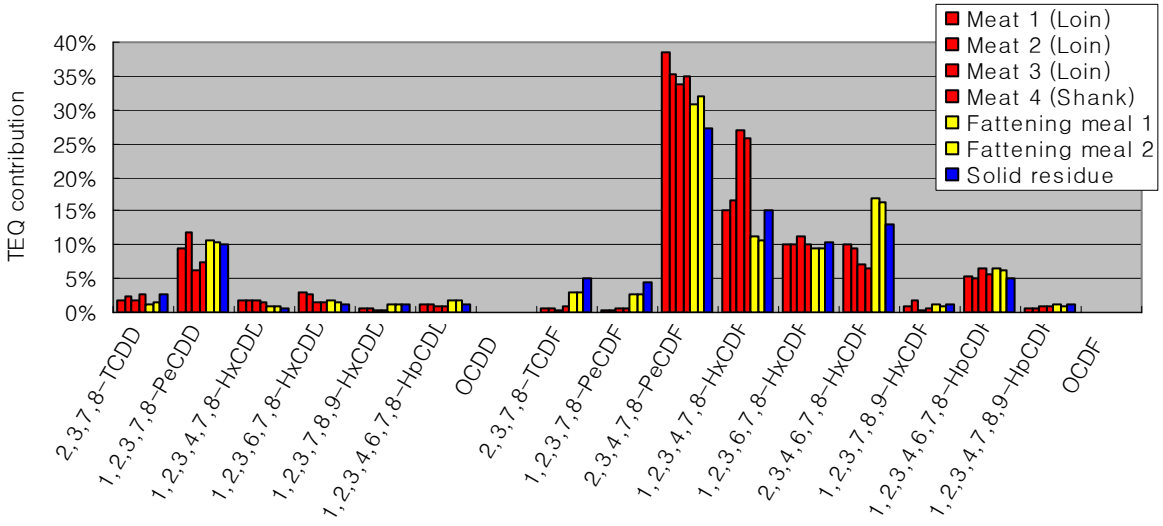

Figure 1. Characteristics of congeners of positive samples from meat and supplies associated with premix 1.

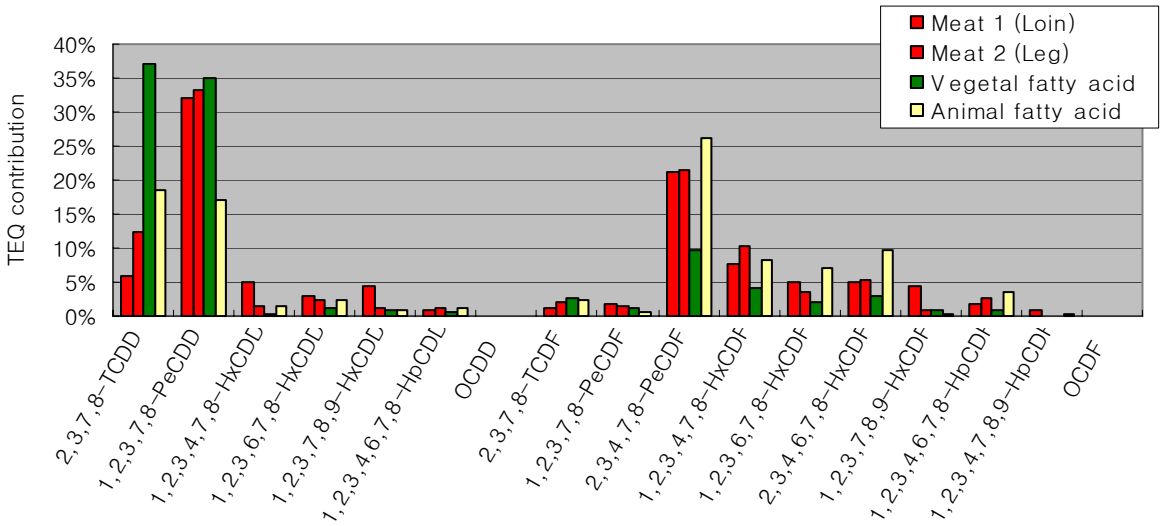

Figure 2. Characteristics of congeners of positive samples from meat and supplies associated with premix 2.