LEVELS OF PCDD/DFs IN FOODSTUFFS IN TAIWAN

M.S. Hsu[1], E. Ma[1], P.S. Cheng[1], U. Chou[1], S.Y. Chen[1], C.F. Chang[1], Shin-Shou Chou[2], Chiu-Chen Cheng[2], Chen-Yea Yu[2], Chun-Heng Liao[2], Y.C. Ling[1]

[1]Department of Chemistry, National Tsing Hua University, Hsinchu 300, Taiwan, ROC
[2]National Laboratories of Foods and Drugs, Department of Health, Executive Yuan, Taipei 115 Taiwan, ROC

Introduction

PolyChlorinated Dibenzo-*p*-Dioxins (PCDDs) and PolyChlorinated Dibenzo-*p*-Furans (PCDFs) are persistent organic pollutants. Food is the major route of human intake of toxic dioxin compounds. Approximately 95 % of human dioxin exposure derives from food, with nearly 80 % coming from food of animal origin. The dioxin levels in foodstuffs and the consumption rate of foodstuffs are essential to evaluate health risk posed to humans. The lack of dioxin levels in foodstuffs increases the dioxin exposure probability of the population. It also makes the evaluation of the progress of improving dioxin pollution sources. To overcome these problems, the preliminary total diet study of PCDD/DFs levels in foodstuffs in Taiwan is, therefore, implemented for the first time.

Materials and Methods

The survey of PCDD/DFs levels in eight categories of foodstuffs was carried out from April to October in 2001. Foods were purchased from both supermarkets and traditional markets in eleven Taiwanese cities. Roughly 143 compound food samples were obtained by assembling from 906 individual food samples. A total of 21 pork samples, 21 chicken samples, 9 beef samples, 30 fish samples, 9 shrimp samples, 9 shellfish samples, 22 milk samples (cow milk and goat milk) and 22 milk powder samples were investigated in this study. Sample preparation and extraction were accordingly adjusted, depending on matrix type. The edible portions of all samples, except dairy products, were homogenized with a mechanical blender. About 20 to 50 grams test portions (depending on the lipid content) were mixed with 50 ml acetone and 100 ml n-hexane and shredded finely using a homogenizer. The sample was then dehydrated using anhydrous sodium sulfate, followed by column extraction using 50:50 dichloromethane/hexane[1]. The dairy products were extracted using a modified AOAC extraction procedure[2] (sodium oxalate, acetone and n-hexane). Aliquots of the sample were fortified with 15 $^{13}C_{12}$ labeled PCDD/DFs congeners as internal standards and $^{37}Cl_4$-TeCDD as the clean-up standard. The lipid contents were measured by gravimetric weighting. An activated carbon column (containing 50 mg AX-21) was used for fat removal. The fat-free extract was cleaned with a sulfuric acid-impregnated silica gel column, followed with another neutral alumina column. $^{13}C_{12}$-1,2,3,4-TeCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD were spiked into the clean extract as recovery standards. Samples were analyzed for the 17 2,3,7,8-substituted PCDD/DFs. The spiked concentrates were analyzed using a HP-5890GC/Fisson Autospec Ultima HRMS equipped with a J&W DB-5ms fused-silica capillary column (60 m × 0.25 mm i.d. × 0.25 mm film). A minimum dynamic mass resolution of 10000 (10% valley definition) was maintained. The recoveries of the internal standards were all within the quality control limits. The toxic equivalents (TEQ) were calculated using both WHO-TEF (1998)[3] and I-TEF(1988)[4] system. The concentrations of the not detected congeners were calculated with zero (lowerbound concentration), half the limit of determination (LOD) and the LOD (upperbound concentration), respectively.

Table 1. PCDD/DFs levels in Taiwanese foodstuffs on total weight basis

Objects	PCDD/DFs Mean±SD (pg WHO-TEQ/g)		
	ND=0	ND=½ LOD	ND=LOD
Pork	0.036 ±0.071	0.059 ±0.070	0.083 ±0.071
Beef	0.113 ±0.088	0.122 ±0.088	0.131 ±0.088
Chicken	0.016 ±0.016	0.033 ±0.017	0.049 ±0.022
Fresh water fish	0.257 ±0.287	0.261 ±0.284	0.265 ±0.282
Saltwater fish	0.210 ±0.184	0.219 ±0.179	0.227 ±0.175
Shellfish	0.039 ±0.032	0.061 ±0.034	0.083 ±0.048
Milk	0.057 ±0.029	0.060 ±0.026	0.063 ±0.024
Milk powder	0.032 ±0.059	0.072 ±0.048	0.112 ±0.041

Table 2. PCDD/DFs levels in Taiwanese foodstuffs on lipid basis

Objects	PCDD/DFs Mean±SD (pg WHO-TEQ/g lipid)		
	ND=0	ND=½ LOD	ND=LOD
Pork	0.554 ±1.286	0.838 ±1.320	1.123 ±1.397
Beef	0.906 ±0.659	1.049 ±0.575	1.193 ±0.588
Chicken	0.278 ±0.365	0.668 ±0.530	1.057 ±0.890
Freshwater fish	4.009 ±4.635	4.072 ±4.597	4.136 ±4.559
Saltwater fish	2.900 ±2.418	3.017 ±2.346	3.134 ±2.283
Shellfish	3.537 ±3.420	5.621 ±3.046	7.705 ±3.910
Milk	1.652 ±0.909	1.744 ±0.832	1.837 ±0.759
Milk powder	0.127 ±0.213	0.298 ±0.183	0.471 ±0.192

Table 3. The % difference of PCDD/DFs TEQ in foods expressed with different TEF system (the value is from (WHO-TEQ – I-TEQ)×100% / (I-TEQ))

	ND=0	[a]ND=0	ND=1/2 LOD	[a]ND=1/2 LOD	ND=LOD	[a]ND=LOD
percentage difference	3.2 %	28.1 %	17.9 %	26.7 %	21.3 %	25.7 %

[a] Only 1,2,3,7,8-PeCDD detected in samples are calculated.

Results and Discussion

The dioxin concentrations on total weight basis in Taiwanese foodstuffs are listed in Table 1. The lowerbound concentrations range from 0.016 to 0.257 pg WHO-TEQ/g. The PCDD/DFs levels in fish and beef foods are apparently higher than those in other food categories. Considering the wide range of lipid contents in fat-containing foods, lipid basis TEQs shown in Table 2 are used to facilitate the uniform comparison of PCDD/DFs levels in different food. After the lipid normalization, lowerbound dioxin levels range from 0.127 to 4.01 pg WHO-TEQ/g lipid. Fish foods still posses the higher levels of PCDD/FS. However, the ranking of PCDD/DFs levels in shellfish dramatically arises from fifth on

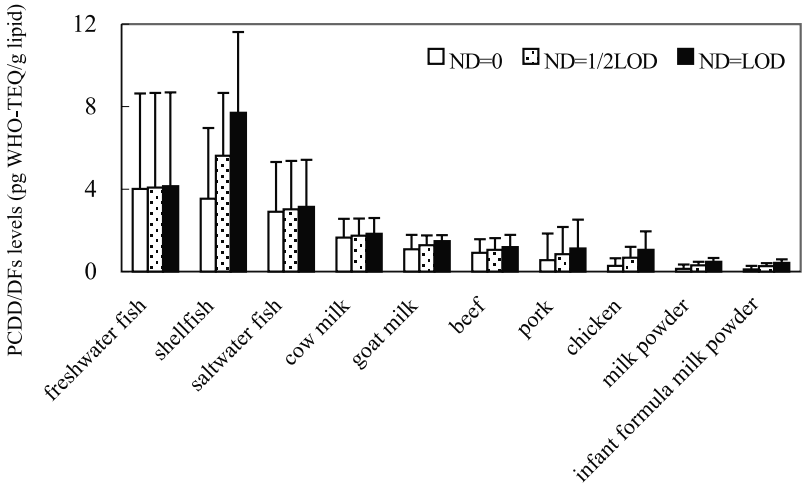

Figure 1. The ranking of PCDD/DFs levels in various food categories (lipid basis)

total weight basis to second place on lipid basis. Figure 1 illustrates the ranking of PCDD/DFs levels in the 10 categories of foods on lipid basis. The elevation for shellfish is attributed to the amplification gain effect caused by the low lipid content in shellfish. The average lipid content is 1.1 % in shellfish.

A significant difference between upperbound concentration and lowerbound concentration was observed in food categories, such as shellfish, pork, chicken and milk powder. The PCDD/DFs concentrations in these food categories are at ultra-trace levels. Only few higher chlorine substituted congeners were detected. We attribute this to the contribution from congeners with larger TEF value dominating the estimation of upperbound concentration. In this study, detection limit is *ca* 0.06 pg/g lipid for each individual congener. The determination limit is *ca.* 0.2 pg WHO-TEQ/g lipid from the summation of all 17 2,3,7,8-substituted PCDD/DFs. The major TEQ contributors are 1,2,3,7,8-PeCDD, 2,3,4,7,8-PeCDF and 2,3,7,8-TeCDD in our study. Furthermore, 10 % of total TEQs coming from 2,3,7,8-TeCDF was observed in foods of aquatic animal origin. To facilitate the comparison to literature data, the I-TEQs are calculated and compared to WHO-TEQs. Table 3 indicates the percentage difference of PCDD/DFs TEQs expressed in WHO-TEF system and I-TEF system. A smaller increase occurs when all congeners are taken into consideration when calculating the lowerbound concentration (ND=0). The decreasing TEF value of OCDD and OCDF, namely from 0.001 (I-TEF) to 0.0001 (WHO-TEF), offsets the increasing TEF value of 1,2,3,7,8-PeCDD. A large increase, *ca.* 20~25 %, was observed when only samples containing detectable 1,2,3,7,8-PeCDD were used for calculation. This result agrees with Malisch's work reported in 1998[5].

Using the upperbound levels to represent the PCDD/DFs levels in Taiwanese foodstuffs, the levels are below the maximum levels in the EC Regulation[6]. The PCDD/DFs levels in meat are similar to those found in Korea[7] (pork: 0.042 pg TEQ/g; chicken: 0.021 pg TEQ/g; beef: 0.132 pg WHO-TEQ/g), slightly higher than Belgian's pork and chicken, lower than its beef (pork: 0.22 pg WHO-TEQ/g lipid; chicken: 0.35 pg WHO-TEQ/g lipid; beef: 1.84 pg WHO-TEQ/g lipid)[8]. Kang *et al.*[9] reported the PCDD/DFs levels in Korean fish products ranging from 0.10 to 0.89 pg WHO-TEQ/g, covering the PCDD/DFs levels in Taiwanese fish. Hsu *et al.*[10] presented the PCDD/DFS levels in Taiwanese milk collected in April 2000 (1.9 pg WHO-TEQ/g lipid, ND=LOD). Almost the same levels were

determined in Taiwanese milk collected in 2001 (1.8 pg WHO-TEQ/g lipid, ND=LOD). The level is close to the action level of 2 WHO-TEQ/g lipid for milk suggested by the European Communities[11].

Acknowledgements

The authors are thankful to the National Laboratories of Foods and Drugs, Department of Health, of the Republic of China (9000238) and National Tsing Hua University for their financial support.

References

1. Laboratory Information Bulletin No. 4084 Dioxins, 1997.
2. AOAC Official Methods of analysis Vol. 2, 970.52L(c), 1990.
3. Assessment of the health risk of dioxins: re-evaluation of the Tolerable Daily Intake (TDI), WHO Consultation, WHO May 1998.
4. NATO/CCMS Report No. 176, 1988.
5. Malisch, R. (1998) Chemosphere, 37, 1687-1698.
6. Commission Regulation EC/466/2001.
7. Choi, D., Park, S., Jeong, J., Lee, L., Park, J. and Won, K. (2001) Organohalogen Compounds, 51, 384-387.
8. Focant, J.F., Massart, A.C., Eppe, G., Pirard, C., André, J.E., Xhrouet, C. and Pauw, E.D. (2001) Organohalogen Compounds, 51, 243-246.
9. Kang, Y.S., Choi, J.W., Na, T.H., Oh, C.H. and Park, J.S. (2001) Organohalogen Compounds, 51, 392-395.
10. Hsu, M.S., Chen, P. C., Ma, E., Chou, U., Liou, E.M.L. and Ling, Y. C. (2001) Organohalogen Compounds, 51, 255-258.
11. Commission Regulation 2002/201/EC.