LEVELS OF DIOXIN-LIKE COMPOUNDS IN TAIWAN FOODSTUFFS

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Introduction

Food is the major route of human intake of toxic dioxin-like compounds (DLCs), which include PolyChlorinated Dibenzo-*p*-Dioxins (PCDDs), PolyChlorinated DibenzoFurans (PCDFs), and WHO PolyChlorinated Biphenyls (PCBs). Approximately 95% of human DLCs exposure derives from food, with nearly 80% coming from food of animal origin. The DLCs levels in foodstuffs and the consumption rate of foodstuffs are essential to evaluate health risk posing to humans. The lack of DLCs levels in foodstuffs increases the population risk to DLCs exposure. The Department of Health, Taiwan has entrusted us to conduct a comprehensive monitoring program on PCDD/Fs levels in Taiwan foodstuffs in 2001[1] and 2002. In 2003, the program has extended the analytes to include 12 WHO-PCBs[2]. The DLCs levels in Taiwan foodstuffs is, therefore, being surveyed for the first time.

Materials and Methods

Sample selection & preparation: The survey of DLCs levels in 12 categories of foodstuffs was carried out from May to September in 2003. Foodstuffs were purchased from supermarkets and traditional markets all over Taiwan. A total of 125 compound food samples were prepared by assembling from 1803 individual food samples. A total of 18 pork samples, 12 beef samples, 4 mutton samples, 12 chicken samples, 4 duck samples, 2 goose samples, 24 fish samples, 4 shellfish samples, 19 milk samples, 12 dairy product samples, 8 fat and oil samples, 6 egg 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 2 to 100 grams test portions (depending on the lipid content) were used. The samples were pre-treated and analyzed using the Chinese National Standard (CNS) method of test for residual dioxins and dioxin-like PCBs in foods (CNS 14758)[3].

Instrumental analysis: Samples were analyzed for the seventeen 2,3,7,8-substituted PCDD/Fs and twelve WHO-PCBs. The spiked concentrates were analyzed using an Agilent 6890N high resolution gas chromatograph coupled with a Micromass AutoSpec Ultima high resolution mass spectrometer (HRGC/HRMS). The analysis of seventeen PCDD/Fs congeners and twelve WHO-PCBs was performed separately with a DB-5MS capillary column (60 m × 0.25 mm i.d. × 0.25μm film thickness), dynamic mass resolution greater than 10000 was reached, and isotope dilution method was used for quantification. The LOD for tetra~penta-chlorinated PCDD/Fs, hexa~hepta-chlorinated PCDD/Fs, octa-chlorinated PCDD/Fs, and WHO-PCBs were 01. pg, 0.2 pg, 0.5 pg, and 0.2 pg, respectively. The toxic equivalents (TEQ) were calculated using WHO-TEF system[2]. The concentrations of the non-detected congeners were calculated with zero (lower-bound concentration), half the limit of determination (LOD) and the LOD (upper-bound concentration), respectively. The TEQs were reported on both fresh weight and lipid weight basis

Results and Discussion

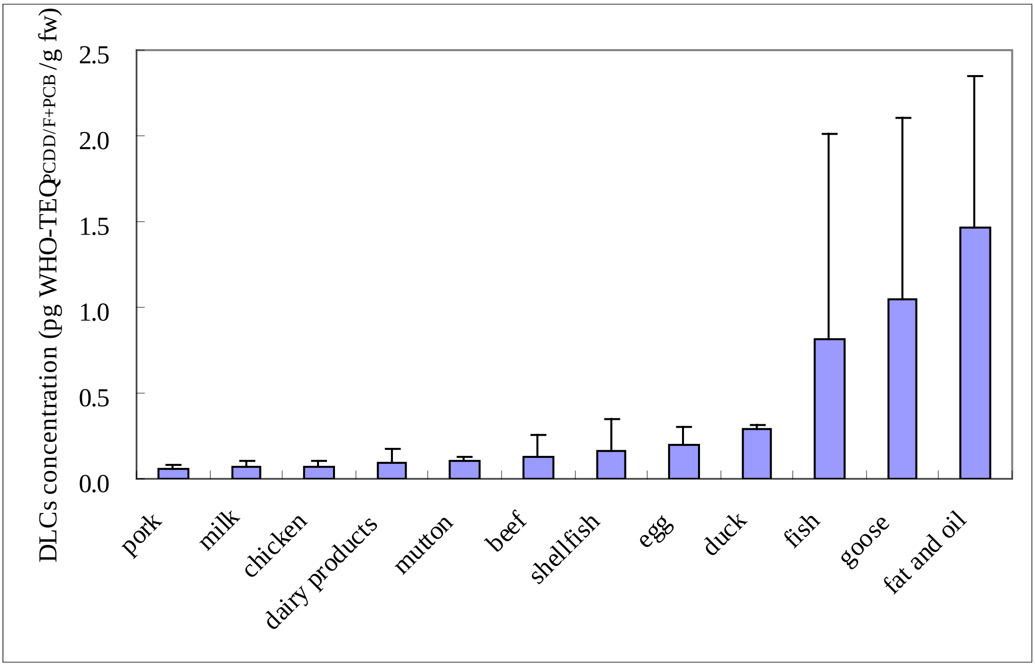
DLCs levels: The DLCs concentrations on fresh weight and lipid basis in Taiwan foodstuffs are listed in Table 1 and Table 2, respectively. The TEQ values do not differ much between the ND=0, ND=½LOD, and ND=LOD values for most samples, indicating the use of larger amount of sample size and fine tune of the HRMS would lower the detection limits. This is beneficial when analyzing food samples which are generally low in DLCs. The uncertainty caused by the magnifying effect when using LOD to replace the concentrations of non-detected congeners could be reduced. The data fulfills the QA/QC requirements by the CNS method 14758. In addition, we have used the method to participate 2003 Inter-laboratory Comparison on Dioxins in Food. The Z-scores of 17 PCDD/Fs are all smaller than 1. The results for PCB-77, PCB-81, PCB-126, and PCB-169 are all being accepted (except PCB-81 in salmon).

The DLCs levels expressed in pg WHO-$TEQ_{PCDD/F+PCB}$/g fw from high to low are: fat and oil (1.41) > goose (1.05) > fish (0.811) > duck (0.291) > egg (0.202) > shellfish (0.160) > beef (0.132) > mutton (0.101) > dairy products (0.093) > chicken (0.075) > milk (0.066) > pork (0.058). The ranking of DLCs levels in various food categories on fresh weight basis is illustrated in Fig. 1. The high TEQ of fat and oil is attributed partially to the near 100% lipid content in animal fat. The unexpectedly high TEQ of goose is attributed to the inadequate sampling. Two samples alone are not representative of the goose population. In addition, the two geese are of different race and grown by different means, which might explain the significant difference in TEQ. The associated SD is just the percent difference between two measurements. Considering the high consumption rate of fishery products in Taiwan, fish appears to be the main exposure route of DLCs.

Table 1: DLCs levels in Taiwan foodstuffs on fresh weight basis

Category	DLCs Mean±SD (pg WHO-TEQ/g fw)		
	ND=0	ND=½ LOD	ND=LOD
Pork (n=18)	0.057 ± 0.020	0.058 ± 0.020	0.058 ± 0.020
Beef (n=12)	0.132 ± 0.120	0.132 ± 0.120	0.132 ± 0.120
Mutton (n=4)	0.101 ± 0.031	0.101 ± 0.031	0.101 ± 0.031
Chicken (n=12)	0.073 ± 0.034	0.074 ± 0.033	0.075 ± 0.033
Duck (n=4)	0.291 ± 0.020	0.291 ± 0.019	0.291 ± 0.018
Goose (n=2)	1.05 ± 1.06	1.05 ± 1.06	1.05 ± 1.06
Fish (n=24)	0.811 ± 1.20	0.812 ± 1.20	0.812 ± 1.20
Shellfish (n=4)	0.144 ± 0.155	0.152 ± 0.170	0.160 ± 0.184
Milk (n=19)	0.066 ± 0.039	0.066 ± 0.039	0.066 ± 0.039
Dairy products (n=12)	0.089 ± 0.082	0.091 ± 0.082	0.093 ± 0.082
Fat and oil (n=8)	1.41 ± 0.873	1.44 ± 0.878	1.46 ± 0.885
Egg (n=6)	0.200 ± 0.106	0.201 ± 0.106	0.202 ± 0.106

Figure 1: The ranking of DLCs levels in various food categories (fresh weight basis)

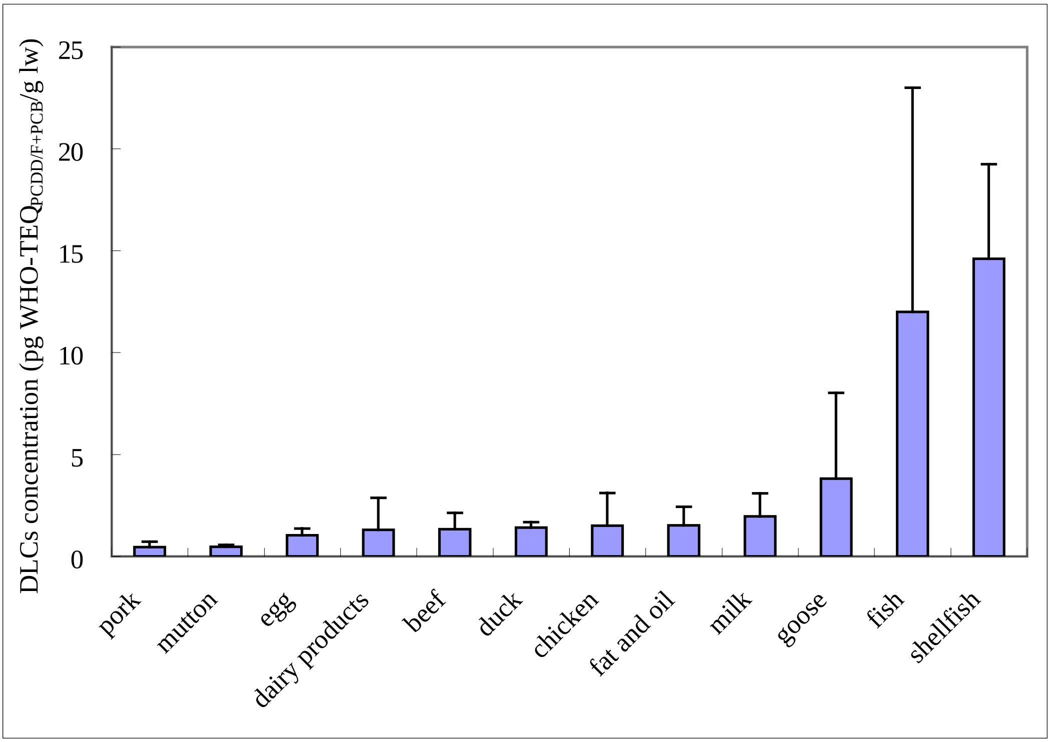


To facilitate the regulatory control of PCDD/Fs in foodstuffs, the EU regulatory limits of PCDD/Fs are mostly expressed on lipid basis, except fishery products. The DLCs levels expressed in pg WHO-$TEQ_{PCDD/F+PCB}$/g lw from high to low are: shellfish (14.0) > fish (12.0) > goose (3.82) > milk (1.95) > fat and oil (1.47) > chicken (1.46) > duck (1.42) > beef (1.32) > dairy products (1.27) > egg (1.03) > mutton (0.473) > pork (0.447). The ranking of DLCs levels in various food categories on lipid weight basis is illustrated in Fig. 2. The elevation for shellfish is attributed to the amplification effect caused by the low lipid content in shellfish. The high TEQ of milk, i.e., close to the EU action levels, similar to the 2001 survey results[4], warrants further investigation of the cause. Pork possesses the lowest TEQ and is the major meat for Taiwanese.

Table 2: DLCs levels in Taiwan foodstuffs on lipid weight basis

Category	DLCs Mean±SD (pg WHO-TEQ/g lw)		
	ND=0	ND=½ LOD	ND=LOD
Pork (n=18)	0.447 ± 0.280	0.449 ± 0.279	0.451 ± 0.278
Beef (n=12)	1.32 ± 0.801	1.33 ± 0.802	1.33 ± 0.802
Mutton (n=4)	0.476 ± 0.094	0.476 ± 0.094	0.476 ± 0.094
Chicken (n=12)	1.46 ± 1.59	1.48 ± 1.60	1.50 ± 1.61
Duck (n=4)	1.42 ± 0.265	1.42 ± 0.258	1.42 ± 0.254
Goose (n=2)	3.82 ± 4.21	3.82 ± 4.21	3.82 ± 4.21
Fish (n=24)	12.0 ± 11.0	12.0 ± 11.0	12.0 ± 11.0
Shellfish (n=4)	14.0 ± 4.27	14.2 ± 4.40	14.6 ± 4.65
Milk (n=19)	1.95 ± 1.13	1.96 ± 1.13	1.96 ± 1.13
Dairy products (n=12)	1.27 ± 1.57	1.29 ± 1.57	1.30 ± 1.57
Fat and oil (n=8)	1.47 ± 0.895	1.49 ± 0.903	1.52 ± 0.912
Egg (n=6)	1.03 ± 0.325	1.04 ± 0.325	1.04 ± 0.324

Figure 2: The ranking of DLCs levels in various food categories (lipid weight basis)



Ratio of PCDD/Fs and PCBs in Taiwan foodstuffs: The TEQ contribution from the 12 WHO-PCBs to the DLCs in foodstuffs is of growing interest, partly due to the increasing understanding of their toxicity. The EU plans to re-evaluate the addition of TEQ from WHO-PCBs to its regulations by the end of 2004. The understanding of the relationship between the PCDD/Fs-TEQ and DLCs-TEQ is useful to convert the large amount of PCDD/Fs-TEQ currently available, gaining understanding of the true impact of past foodstuffs. Table 3 lists ratio of PCDD/Fs-TEQ and WHO-PCBs-TEQ in Taiwan foodstuffs. The ratio of DLCs-TEQ to PCDD/Fs-TEQ ranges from about 1 for eggs, about 1.5 for land animals and their products, and about 3 for aquaculture animals and their products. The amplification factor of 3 by the WHO-PCBs on current PCDD/Fs-TEQ warrants the study of dietary habits with high consumption of fish and fishery products.

Table 3: Ratio of PCDD/Fs-TEQ and WHO-PCBs-TEQ in Taiwan foodstuffs

Category	Upper bound TEQ		
	% PCDD/Fs	PCB / PCDD/Fs	DLCs / PCDD/Fs
Pork (n=18)	67.8%	0.47	1.47
Beef (n=12)	72.7%	0.38	1.38
Mutton (n=4)	60.5%	0.65	1.65
Chicken (n=12)	48.5%	1.06	2.06
Duck (n=4)	63.9%	0.56	1.56
Goose (n=2)	78.0%	0.28	1.28
Fish (n=24)	34.3%	1.92	2.92
Shellfish (n=4)	50.0%	1.00	2.00
Milk (n=19)	68.4%	0.46	1.46
Dairy products (n=12)	70.9%	0.41	1.41
Fat and oil (n=8)	61.6%	0.62	1.62
Egg (n=6)	87.4%	0.14	1.14

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