Estimates of Dietary Intake of Polychlorinated Dioxins, Furans, and Biphenyls from Chinese Total Dietary Study

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Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) are ubiquitous, persistent, lipophilic pollutants in food. Ingestion of contaminated food is the principal way of human exposure to these compounds[1], Most data about human exposure to PCDD/Fs and dioxin-like PCBs were available from the industrialized countries [2] while the data from developing countries were very scarce. To get the contamination level of 17 2,3,7,8-substituted PCDD/Fs and 12 dioxin-like PCBs in food and estimate of dietary intake in china, the samples from Chinese Total Diet Study (TDS) in 2000 was analyzed for PCDD/Fs and dioxin-like PCBs. With the consumption values for the foods in the market baskets surveyed in 2000, the dietary intake of PCDD/F and dioxin-like PCBs from foods in China was estimated and evaluated firstly.

Materials and Methods

Sampling and food consumption survey. The Chinese TDS was carried out in 2000. The overall study design and experimental methods were similar to carried out in 1990[3]. In brief, the food composite approach was used to study the total diet in four regional market baskets. Each region comprised of 3 provinces, i.e., North 1 comprised of Heilongjian province, Liaoning province and Hebei province; North 2 comprised of Henan province, Shanxi province and Ningxia province; South 3 comprised of Jiangxi province, Fujian province and Shanghai city; South 4 comprised of Hubei province, Sichuan province and Guangxi province. One city location and two rural locations (30 families for each location) were selected for consumption survey in each province. The food composition pattern and consumption date of a standard man (18-45 years old, 60kg body weight) in each of 1080 families was determined by a 3-day household dietary survey. Food samples were collected and prepared (cooked) in each place according to the local food habits. Twelve food groups composites were made for each province; the same food composites from each of the 3 provinces were combined to formulate regional market baskets. Due to foods from animal origin being the predominant sources of dioxin, four food groups of meats, eggs, aquatic foods, and milk were subjected to PCDD/Fs and dioxin-like PCBs analysis.

Sample preparation. All samples were dried by freezing drier. After spiking with known amounts of surrogates: 15 congeners of $^{13}C_{12}$-labeled PCDD/Fs and 12 congeners of $^{13}C_{12}$-labeled-dioxin-like PCBs (Wellington Laboratories, Guelph, ON, Canada), samples were soxhlet extracted with a mixture n-hexane/methylene chloride (1:1, v/v). Lipid removal was achieved by shaking with acid modified silica gel and further cleanup were achieved by using a Power Prep instrument (Fluid Management System, Waltham, MA) automatically with standard ABN silica gel column, basic alumina column, and carbon column. Two fractions were eluted containing PCDD/Fs and dioxin-like PCBs congeners respectively. After concentration to 10-20ul, the $^{13}C_{12}$-labeled injection standard for PCDD/Fs and dioxin-like PCBs (Wellington Laboratories) were added into the final extract.

Analysis. The analysis of 17 congeners of 2,3,7,8-substituted PCDD/Fs congeners and 12 congeners of dioxin-like PCBs were performed by GC-HRMS/ EI (+)- SIM on a GC (Trace GC Ultral, Thermo) with DB5 capillary column (60m*0.25mm*0.25um) coupled a HRMS (MAT95XP, Thermo) equipped with autosampler (AS2000, Thermo) at 10000 resolution (10% valley definition) using isotopic dilution method for quantification.

QA/QC. To ensure the quality of analysis, blank samples covering the whole analytical procedure were performed every eighth sample and certified reference material of fish (WMF-01,Wellington Laboratories) and reference material of powder milk (RM532, 533 and 534, BCR) were analyzed as quality control sample in the laboratory. The recoveries of all of $^{13}C_{12}$-labeled surrogates were between 37% and 112 %, which were in the acceptable range established by the USEPA. Our laboratory has successfully participated

in interlaboratory comparison study of PCDD/Fs and dioxin-like PCBs in different food matrices（fish, deer and fish oil）organized by the Norway Institute of Public Health (Norway, 2005).

Results and Discussion

The levels of PCDD/Fs and dioxin-like PCBs. WHO-TEQ, as pg/g fresh weight (fw), of PCDD/Fs and dioxin-like PCBs in selected food groups of each market basket are shown in the table 1. When calculating the TEQs of samples the concentrations of the congeners that non-detected were set equal to their reporting limit (LOD).

Table 1 PCDD/Fs and dioxin-like PCBs WHO-TEQs in food (pg/g fw)

	Egg		Meat		Aquatic food		Milk	
	PCDD/Fs	PCBs	PCDD/Fs	PCBs	PCDD/Fs	PCBs	PCDD/Fs	PCBs
North 1	0.089	0.05	0.211	0.05	0.183	0.24	0.026	0.012
North 2	0.031	0.04	0.062	0.04	0.101	0.17	0.023	0.008
South 1	0.054	0.07	0.123	0.07	0.276	0.16	0.041	0.015
South 2	0.118	0.07	0.066	0.04	0.138	0.09	0.044	0.016

The concentration values were set to LOD for the congeners with ND

The total TEQ of all sample ranged 0.031-0.436pg TEQ/g. In general the total TEQ of all food groups in North 1 and South 1 were more than that in North 2 and South 2. The total TEQ of aquatic food was highest in each market basket followed by meat (except for South 2 in which total TEQ of egg was more than meat) and the TEQ of milk was lowest in each market basket, which was similar to the situation of PCDD/Fs. From the average value of all market baskets, the PCDD/Fs contributed to total TEQ more than PCBs in each food groups, especially in milk (77.3%) and meat (69.9%). In other two groups the average contribution of PCBs to total TEQ（45.1% for egg and 47.9% for aquatic food respectively） were close to that of PCDD/Fs.

Estimated dietary intake. Daily intakes of PCDD/Fs and PCBs were estimated by multiplying the measured TEQ concentrations of PCDD/Fs and dioxin-like PCBs by the average daily consumption data from the survey mentioned above. Table 2 showed the estimated daily intake of PCDD/Fs and dioxin-like PCBs from four selected food groups and whole animal origin in each market basket. The maximum value of daily intake was found in South 1 (57.1 pg TEQ/day) followed by North 1 (38.19pg TEQ /day), South 2 (21.56pg TEQ /day) and North 2 (9.06pg TEQ /day). In each market basket, the contribution of PCDD/Fs to intake of total TEQ was more than that of dioxin-like PCBs and was similar to each other with 65.2% for North1, 57.2% for North 2, 61.6% for South 1 and 62.4% for South 2, respectively. The contributions from four food groups were different in different market baskets. The meat groups made the most contribution to daily intake in North 1, North 2 and South 2 with 44.3%, 43.6% and 48.4%, respectively. The group with most contribution to daily intake was aquatic food (48.7%) in South 1. Although levels of contamination in aquatic food were higher, the contribution to daily intake from milk (23.5%) in North 2 and egg (25.4%) in South 2 were more than that from aquatic food (18 % in North 2 and 22.5% in South 2, respectively) because of more milk consumption in those market baskets. Generally, in china meat and fish account for major fraction of daily intake as studies of other countries. But the contribution from milk was lower than some western countries[2,4-6]. The difference consumption habits for milk and milk product was one of the possible reasons for that.

It is difficult to compare the results of intake estimations reported in the literatures from different countries duo to the various factors of methodologies used for their calculation. In these studies there were great difference in the sampling strategy (coverage of food type and region), the value for congeners (0, 1/2LOD or LOD) that were non-detected, the kind of TEQ used (I-TEQ or WHO-TEQ) and the means to study food consumption. Table3 showed an overview of estimated daily intake, as pg WHO-TEQ/kg body weight (bw) from China and a number of other countries or region reported recently. The value of daily intake of Japan [7] and Finland [8] were from all food items including beverages. Only food of animal origin

was involved in the daily intake of China, Korea[9], Chinese Taiwan[10], Belgium [5] and Spain (the city of Huelva) [11]. Besides food of animal origin, vegetable groups were included in study of US[4] and Netherlands[12]. Although the daily intake from this study was upper bound value, the daily intake of each market basket of China was lower than all other countries and regions except for Korea. The daily intake in North 2 of China was lowest among these studies. The results from a number of studies showed large effect of cooking and washing processes on levels of PCDD/Fs and dioxin-like PCBs, most of which showed reduction effect [13-15]. So the values from cooked foods were closer to real status. Because only the data of this study and Japan were from the foods analyzed after cooking, a deduction was made that the real daily intakes of other countries and regions were lower than the value reported in the literatures . All daily intakes of total TEQs for comparing in table 3 were lower than the Tolerable Daily Intake (TDI), 1-4 pg TEQ/kg bw , recommended by WHO.

Table 2 Estimated daily intake from food and contribution of each food group (pg TEQ/day)

	North 1			North 2			South 1			South2		
	PCDD/Fs	PCBs	Sum	PCDD/Fs	PCBs	Sum	PCDD/Fs	PCBs	Sum	PCDD/Fs	PCBs	Sum
egg	4.42	2.49	6.91	0.59	0.76	1.35	3.04	3.95	6.99	3.43	2.04	5.47
			(18.1%)			(14.9%)			(12.2%)			(25.4%)
aquatic	5.22	6.84	12.06	0.61	1.02	1.63	17.61	10.21	27.82	2.94	1.92	4.86
food			(31.6%)			(18%)			(48.7%)			(22.5%)
meat	13.67	3.24	16.91	2.4	1.55	3.95	12.12	6.89	19.01	6.49	3.94	10.43
			(44.3%)			(43.6%)			(33.3%)			(48.4%)
milk	1.58	0.73	2.31	1.58	0.55	2.13	2.40	0.88	3.28	0.59	0.21	0.80
			(6%)			(23.5%)			(5.7%)			(3.7%)
∑TEQ	24.89	13.3	38.19	5.18	3.88	9.06	35.17	21.93	57.10	13.45	8.11	21.56
	[65.2%]	[34.8%]		[57.2%]	[42.8%]		[61.6%]	[38.4%]		[62.4%]	[37.6%]	

Contribution (%) of different food to daily intake in parenthesis and contribution (%) of PCDD/Fs and PCBs to daily intake in brackets

Table 3 Comparison the estimated daily dietary in this study and other studies(pg TEQ /day kg bw)

Country or Region	Period	PCDD/Fs	PCBs	Sum-$_{PCDD/Fs+PCBs}$	Method for ND
Chinese North 1	2000	0.41	0.22	0.63	LOD
Chinese North 2	2000	0.09	0.06	0.15	LOD
Chinese South 1	2000	0.59	0.37	0.96	LOD
Chinese South 2	2000	0.22	0.14	0.36	LOD
Chinese Taiwan	2004			1.62	LOD
Korea	2004			0.195	0
Japan	2000	1.64	1.59	3.23	1/2 LOD
U S	1995	1.66	0.67	2.33	1/2 LOD
Netherlands	1999	0.65	0.58	1.23	0
Finland	1999	0.76	0.74	1.5	0
Spain(Huelva City)	2004	1.15	1.48	2.63	LOD
Belgium	2001	1.00	1.04	2.04	0

The data of this study suggested that generally there was no health risk of PCDD/Fs and dioxin-like in food in China so far. Although the estimated daily intake of China was lower than industrialized countries around 2000, there is potential possibility of higher level of contamination in China in the future. The continual monitoring of contamination of PCDD/Fs and dioxin-like PCBs, especially in food, is needed.

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References

1. Sweetman AJ, Alcock RE, Wittsiepe J, Jones KC.Environ. Int 2000; 26: 37.
2. Liem AKD, Furst P, Rappe C. Food Add. Contam 2000; 17: 241.
3. Chen JS, Gao JQ. J.AOAC Int 1993;76: 1193.
4. Schecter A, Cramer P, Boggess K, Stanley J, Papke O, Olson J, Silver A, Schmitz M. J. Toxicol. Environ. Health 2001; 63: 1.
5. Focant JF, Eppe G, Pirard C, Massart AC, Andre JE, de Pauw E. Chemosphere 2002; 48: 167.
6. Baars AJ, Bakker MI, Baumanna RA, Boonb PE, Freijer JI, Hoogenboomb LAP, Hoogerbrugge R, Klaveren JD, Liem AKD, Traag WA,de Vries J. Toxicol. Letters 2004; 151: 51
7. Tsutsumi T, Yanagi T, Nakamura M, Kono Y, Uchibe H, Iida T, Hori T, Nakagawa R, Tobiishi K, Matsuda R, Sasaki K, Toyoda M. Chemosphere 2001; 45: 1129.
8. Kiviranta H, Ovaskainen ML, Vartiainen T. Environ Intl 2004; 923
9. Suh J, Choi D, Lee E, Hong M. Organohalogen Comp 2004;: 2023
10. Hsu MS, Wang SM, Chou U, Huang NC, Liao GY, Yu TP, Ling YC. Organohalogen Comp2004; 66: 2143.
11. Bordajandi LR, Gomez G, Abad E, Rivera J, Fernandez-Baston MM, Blasco J, Gonzalez MJ. Food Chem 2004; 52: 992.
12. Freijer JI, Hoogerbrugge R, van Klaveren JD, Traag WA, Hoogenboom LAP, Liem AKD. RIVM report 639102022,2001, Bilthoven, The Netherlands.
13. Zabik ME, Zabik MJ, Booren AM, Nettles M, Song JH, Welch R, Humphrey HJ. Agric. Food Chem 1995; 43: 993.
14. Schecter A, Dellarco M, Papke O, Olson J. Chemosphere 1998; 37: 1723.
15. Petroske E, Zaylskie RG, Feil J J. Agric. Food Chem 1998; 46: 3280.