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Assessment of dietary intake of polychlorinated dibenzo-*p*-dioxins and dibenzofurans and dioxin-like polychlorinated biphenyls from the Chinese Total Diet Study in 2011

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HIGHLIGHTS

- Dietary intake for adults was below the PTMI indicating low health risk in China.
- Large variations of dioxin level and dietary intake were found among regions.
- Increasing exposure was found in some regions partly due to rising contamination.

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ABSTRACT

The concentrations of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) as well as dioxin-like polychlorinated biphenyls (dl-PCBs) were measured in food samples from the fifth Chinese Total Diet Study (TDS) performed in 2011. A total of 152 composite samples from various food groups were analyzed by high resolution gas chromatography–high resolution mass spectrometer (HRGC–HRMS). The dietary intakes of PCDD/Fs and dl-PCBs were subsequently estimated for the adult from various regions in China. The mean dietary intake of PCDD/Fs and dl-PCBs was 20.1 pg TEQ kg^{-1} bw $month^{-1}$ (WHO-TEF of 1998) within a range of 4.2 pg TEQ kg^{-1} bw $month^{-1}$ to 53.7 pg TEQ kg^{-1} bw $month^{-1}$ which were all much lower than the provisional tolerable monthly intake (PTMI) established by Joint FAO/WHO Expert Committee on Food Additives (JECFA). By comparing with results from previous Chinese TDS, a decline of the average dietary intake was observed from 2000 to 2011, but a notable elevation was observed in some regions partly stem from increasing contamination levels in certain foods.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) are ubiquitous and persistent environmental pollutants. PCDD/Fs are produced unintentionally derived from incomplete combustion process as well as manufacture of certain chemicals (Zheng et al., 2008a). In turn, PCBs had been largely produced and widely employed in industry as heat exchange fluid, insulating oil and so on until the ban of production and usage in 1980s (Scippo et al., 2008). Among these chemicals, 17 congeners of PCDD/Fs and 12 congeners of PCBs known as dioxin-like PCBs (dl-PCBs) are of great toxicological concern (Van den Berg et al., 1998). Some experimental studies and human epidemiology studies have suggested neurodevelopmental toxicity, immunotoxicity, reproductive effects and endocrine disturbing effects of PCDD/Fs and dl-PCBs indicating that they could have strictly adverse effect on human health (Scippo et al., 2008; De Coster and van Larebeke, 2012). The human exposure to PCDD/Fs and dl-PCBs as well as potential health risk has been therefore a matter of great concern in the world.

Due to their persistence and high lipophilicity, PCDD/Fs and dl-PCBs tend to bioaccumulate through the food chain, and the exposure of general population (non-occupational) to these pollutants is almost exclusively via diet (more than 90%), especially foods of animal origin (WHO, 1998; Liem et al., 2000; Malisch and Kotz, 2014). Therefore, dietary intake estimations are

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appropriate tools for the estimation of the exposure to PCDD/Fs and PCBs and the evaluation of the potential health risk in a population. Many studies have been conducted to investigate PCDD/Fs and dl-PCBs contamination in food to estimate human exposure via diet with various methodologies, and a notable decline of contamination level and dietary intake as well as human body burden has been observed in some developed countries due to global effort and strict regulation on emission (Perelló et al., 2010; Windal et al., 2010; Törnkvist et al., 2011; Sirot et al., 2012; Fång et al., 2013; Malisch and Kotz, 2014; Ryan and Rawn, 2014).

In China, the Total Diet Studies (TDS) recommended by WHO have been performed since 1990 aiming at providing contamination data for food prepared as consumed by population and dietary intake data to help the authority make public health decisions (Chen and Gao, 1993; WHO, 2006). In our previous studies, dietary intake of PCDD/Fs and dl-PCBs of the Chinese population was estimated from Chinese TDS in 2000 and again in 2007 showing a slightly increasing temporal trend (Li et al., 2007; Zhang et al., 2013a). The aim of the present study is to present the contamination levels of PCDD/Fs and dl-PCBs in main Chinese foodstuffs from the latest Chinese TDS in 2011 and assess the dietary intake as well as health risk.

2. Methods and materials

2.1. Food consumption and sampling

The Chinese TDS is a continually national study on monitoring the levels of various chemical pollutants in foods and estimating the dietary intake of these chemicals of general population, non-occupationally exposed population, in China, which has been detailed elsewhere (Wu et al., 2012; Zhang et al., 2013b). The food consumption survey was conducted in 19 provinces in 2011, including Heilongjiang, Liaoning, Hebei, Shanxi, Ningxia, Henan, Shanghai, Fujian, Jiangxi, Guangxi, Sichuan, Beijing, Jilin, Neimenggu, Qinghai, Jiangsu, Zhejiang, Hunan, and Guangdong (see Fig. 1). In each province, three sampling sites including 1 urban site and 2 rural sites were randomly selected. 30 households were randomly sampled from each site to conduct the food consumption survey by 24-h dietary recall over 3 day for each householder, enabling recording of individual food consumption data. In each province, all food items were aggregated into various food groups, then, the average food consumption was calculated to present the pattern of food consumption of a standard Chinese male adult (18–45y, 63 kg body weight). Food samples were collected from local food markets, grocery stores or rural households in each sampling site, and then prepared using local practice. The composite of each food group was made by blending the prepared food with weights proportional to the average daily consumption in each province. These provincial composites were shipped to the China National Center for Food Safety Risk Assessment and frozen at −20 °C until analysis.

In this study, 8 groups were selected for the determination of PCDD/Fs and dl-PCBs, including various foods of animal origin (aquatic foods, meat and meat products, egg and egg products, and milk and dairy products) and foods of plant origin (cereals, bean products, potatoes, and vegetables).

2.2. Analytical methods

Determination of PCDD/Fs and dl-PCBs in food samples were based on the US EPA method 1614 for PCDD/Fs, and the US EPA method 1668a for dl-PCBs, which with some modification has been detailed elsewhere (Zhang et al., 2013a). Briefly, after homogenization and lyophilization, $^{13}C_{12}$-labeled extraction standards were added to the sample to control the whole sample preparation process. Food samples were extracted using *n*-hexane/dichloromethane mixture (1:1, v/v) as solvent. The bulk lipid was removed by shaking with acid-modified silica-gel after solvent evaporation, and further cleanup was achieved using a Power Prep instrument (Fluid Management Systems, Waltham, MA, USA) with multiple commercial silica-gel columns, alumina columns and carbon columns. Two fractions containing PCDD/Fs and dl-PCBs were collected and concentrated to approximately 20 μL, respectively. After adding $^{13}C_{12}$-labeled injection standard, the final extract was analyzed by a high-resolution gas chromatography–high resolution mass spectrometer (HRGC–HRMS) on a Trace 1300 Gas Chromatography (Thermo Scientific, Italy) equipped with a DB-5MS capillary column (60 m × 0.25 mm i.d. × 0.25 μm) and coupled to a DFS High Resolution Mass Spectrometer (Thermo Scientific, Germany). The injector temperature was set at 270 °C, the interface temperature was 270 °C, and the injection volume was 1 μL. The temperature program for determination of PCDD/Fs was following: initial temperature was set at 120 °C hold for 1.5 min, and 43 °C/min to 220 °C hold for 15 min, then 2.3 °C/min to 250 °C, 1 °C/min to 260 °C, 20 °C/min to 310 °C hold for 11 min. For dl-PCBs, the temperature program was following: initial temperature was set at 110 °C hold for 1 min, and 15 °C/min to 180 °C hold for 1 min, then 3 °C/min to 300 °C hold for 2 min.

In this study, 17 congeners of 2,3,7,8-substituted PCDD/Fs and 12 congeners of dl-PCBs designated by WHO were quantified, and toxic equivalent quantity (TEQ) of the analyzed PCDD/Fs and dl-PCBs were calculated using the toxic equivalency factors (TEF) proposed by WHO in 1998 (Van den Berg et al., 1998) (TEF 1998) and in 2005 (Van den Berg et al., 2006) (TEF2005), respectively.

2.3. Dietary intake estimates

Total dietary intake of PCDD/Fs and dl-PCBs was calculated by summing the results of multiplying the concentration of PCDD/Fs and dl-PCBs (pg TEQ g^{-1} fresh weight, 'fw') in each food group by the amount consumed of that food. For calculations, when a concentration was under the limit of detection (LOD), the value was assumed to be equal to '0' (ND = 0) as lower bund (LB) estimation, and 'LOD' (ND = LOD) as upper bund (UB) estimation, respectively.

2.4. Quality assurance and quality control

One test of procedural blank was carried out for every eight samples. The recoveries of internal standards were all in the range of 40–110%. The laboratory performance was validated by successfully participating the Interlaboratory Comparison on Dioxins in Food organized by Norwegian Institute of Public Health in 2012–2014. Z-scores for total TEQ of PCDD/Fs and dl-PCBs were in the range of −0.60 to 0.54. We also attended the proficiency test on determination of PCDD/Fs and dl-PCBs in pork and lard 2012 (1201-PL) organized by European Union Reference Laboratory for Dioxin and PCBs in Feed and Food, and Z-scores for PCDD/Fs plus dl-PCBs in pork and lard was −1.1 and 0.6, respectively. All statistical analyses were performed with the SAS software package (version 8.2; SAS Institute Inc., Cary, NC). All *p* values are two-tailed, and α were set at a significance level of 0.05. The limit of detection of each congener of PCDD/Fs and dl-PCBs in each food group was listed in Supplementary Table 1.

3. Results and discussion

3.1. Occurrence of PCDD/Fs and dl-PCBs in food samples

Table 1 shows concentrations of PCDD/Fs and dl-PCBs with large variation in various food composite samples from Chinese