ACCUMULATION LEVELS OF DIOXINS, FURANS, AND POLYCHLORINATED BIPHENYLS IN FOODSTUFFS FROM CHINAESE MARKETS: ESTIMATION OF HUMAN DIETARY INTAKES

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Introduction

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) are two groups of widely-known environmental pollutants that have been added to the initial list of the Stockholm Convention on Persistent Organic Pollutants (POPs). Their accumulation in vivo could induce cancers and other potential adverse effects on reproduction, development, immune and nervous systems[1-4]. It is estimated that more than 90% of the PCDD/Fs and PCBs non-occupational exposures are due to the dietary intake[5]. Therefore, the dietary exposure to PCDD/Fs and PCBs has been widely monitored in many developed countries and regions [6-10.]

To estimate the dietary exposure of WHO toxic equivalents (WHO-TEQs) through food consumption, the concentrations of PCDD/Fs and PCBs in pooled samples of marketed food items have been periodically measured on the Chinese mainland using the Total Diet Study (TDS)[11-13]. Notably, except for the congeners with toxic equivalency factors (TEFs), the other PCDD/F and PCB congeners, such as tri-chlorinated PCDD/Fs (TriCDD/Fs) and indicator PCBs, also pose a considerable threat to human health[14-16]. Until now, the data on the total contents of PCDD/Fs and PCBs in representative food items have been less documented. In the present study, 11 types of representative animal-origin foodstuffs and 9 types of representative plant-origin foodstuffs marketed across five regions in China were randomly collected. The concentrations of the total tri- to octa-CDD/Fs (∑PCDD/Fs) and tri- to deca-CBs (∑PCBs) in these collected food samples were determined. The aims of this study are to conduct a comprehensive and detailed investigation of the total concentrations of PCDD/Fs and PCBs in main categories of foodstuffs in Chinese markets and further to reveal the difference in dietary intakes of WHO-TEQs in the different surveyed regions.

Materials and methods

Food sampling

Considering the great diversity of human demographic characteristics, dietary habits, and geographic factors, five sampling regions were established on the Chinese mainland, i.e., North Coast (NC), South Coast (SC), Northwest (NW), Midland (M), and Northeast (NE) regions (Figure 1). A total of 714 food samples (360 animal foods and 354 plant foods) were randomly acquired from local markets and supermarkets from January 2018 to November 2019. The animal-origin food samples were classified into 11 pools consisting of pork, beef, mutton, poultry meat, chicken eggs, pure milk, animal fat, fish, shrimp, shellfish, and cephalopods. The collected plant food samples were classified into nine pools consisting of cereals, beans, potatoes, leafy vegetables, root and stem vegetables, melon vegetables, legume vegetables, edible fungi, and mixed vegetable oil. Most of the terrestrial animal origin and plant origin samples were produced locally. All of the collected samples were frozen and maintained at a temperature less than 4°C in ice boxes, sealed and transported to the laboratory immediately and stored in a refrigerator at −20°C in the dark until analysis.

Figure 1. Classification of the five surveyed regions and the locations of sampling sites.

Sample preparation and instrumental analysis

Except for the mixed animal fat and vegetable oil samples, all of the pooled samples were homogenized and freeze-dried. The extraction and analysis of PCDD/Fs and PCBs were conducted according to the US EPA method

1613 and the US EPA method 1668C with a minor modification. Briefly, a food sample was spiked with 20 µL of $^{13}C_{12}$-labeled PCDD/Fs and PCBs extraction standard solution prior to being extracted with a mixture of dichloromethane and n-hexane (1:1, v/v) for approximately 20 h. The extraction standard solution contained 21 types of mono- to octa-CDD/F congeners and 18 types of tri- to hepta-CB congeners. In the case of the mixed animal fat and vegetable oil samples, 4 g of the homogenized sample was dissolved in 10 mL of n-hexane, spiked with the extraction standards, and then treated for purification procedure. The purification procedure was achieved using a combination of multi-layer silica gel column and alumina column. Finally, the elute was concentrated to near dryness and re-dissolved in 5 µL of internal standard solution for instrumental analysis. The quantitative analysis of PCDD/Fs and PCBs was performed using HRGC-HRMS (EI mode) on the selected ion monitoring mode at a resolution of >10000. Gas chromatographic separation of PCDD/Fs and PCBs was conducted on a DB-5MS capillary column (60 m × 0.25 mm × 0.25 µm, Restek, U.S.A.) and DB-XLB capillary column (30 m × 0.25 mm × 0.25 µm, Agilent J&W Scientific, U.S.A.), respectively.

Estimation of dietary intakes

The WHO-TEFs proposed in 2005 was adopted to calculate WHO-TEQs[17]. The analytical results of 2,3,7,8-chlorine substituted PCDD/Fs, dioxin-like PCBs (dl-PCBs), and indicator PCBs were expressed as upperbound levels[18]. The estimated dietary intakes (EDIs) of PCDD/Fs and PCBs were calculated using the following equation:

$EDI = \sum(C_i \times CA_j) / bw$ (1)

where C_i represents the concentration (pg WHO-TEQ/g fw) of congener i in food group j; CA_j represents the food consumption amount (g/week) of group j; bw is estimated to be 60 kg for a standard adult. The data of food consumption amounts were gained from the China's State Statistical Bureau (SSB).

Results and discussion

Concentrations of PCDD/Fs and PCBs

Animal-origin foods. The concentrations of ∑PCDD/Fs, ∑PCBs, and WHO-TEQs were calculated based on the lipid weight (lw). As shown in Figure 2, the observed levels of PCDD/Fs and PCBs in animal foods from two coastal regions (North and South Coast regions) were significantly higher than those from three inland regions (Northwest, Midland, and Northeast regions) (Mann-Whitney U test, $P < 0.01$), especially in shellfish and fish. The aquatic animal food groups from coastal regions primarily consisted of sea species, which typically accumulate more PCDD/Fs and PCBs due to pollution in coastal waters[19]. The elevated levels of PCDD/Fs and PCBs in the terrestrial animal foods from coastal regions likely results from rapid industrialization and urbanization in coastal regions[20]. ∑PCDD/Fs in the collected animal foods were measured to be in the ranges of 4.9–978.1 pg/g lw. The concentrations of ∑PCDD/Fs in the aquatic animal foods were significantly higher than those in the terrestrial animal foods (Mann-Whitney U test, $P < 0.01$). ∑PCBs in the collected animal foods were measured to be in the ranges of 0.3–189.9 ng/g lw. Aquatic animal foods are also prone to accumulate more PCBs compared with terrestrial animal foods. The WHO-TEQs of PCDD/Fs and PCBs were calculated to be in the ranges of 0.13–17.5 pg/g lw (Figure 2). The measured WHO-TEQs were below the maximum levels promulgated by the EU[18]. The highest WHO-TEQ was observed in shellfish from South Coast region. In the terrestrial animal foods, PCDD/Fs accounted for 60–94% of the WHO-TEQs. In the aquatic animal foods, except cephalopods, PCDD/Fs also accounted for more than 50% of the WHO-TEQs.

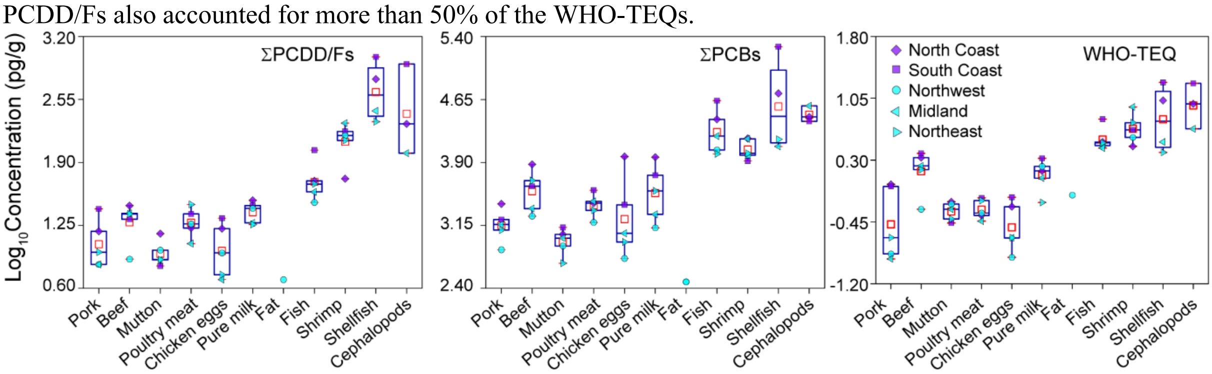

Figure 2. Levels of ∑PCDD/Fs, ∑PCBs, and WHO-TEQs in animal food samples from five surveyed regions.

Plant-origin foods. The concentrations of ∑PCDD/Fs, ∑PCBs, and WHO-TEQs in the plant foods with low lipid contents were calculated on a fresh weight basis (fw). As shown in Table 1, the concentrations of ∑PCDDs, ∑PCDFs, and ∑PCBs in the fresh plant food pools were measured to be in the ranges of 6.1–217.2 pg/kg fw, 32.7–1201.8 pg/kg fw, and 5316.4–100790.7 pg/kg fw, respectively. The concentrations of ∑PCDD/Fs, ∑PCBs, and WHO-TEQs in the cereal and bean sample pools were significantly higher than those in the sample pools of potato, vegetable, and edible fungus (Mann-Whitney U test, $P < 0.01$) (Table 1). Additionally, the concentrations of ∑PCDD/Fs in the leafy vegetables were significantly higher than those of the other vegetable and edible fungus species (Mann-Whitney U test, $P < 0.05$) (Table 1). It is not surprising since the leafy vegetables have a large surface area that can easily adsorb contaminants via air deposition[21]. The WHO-TEQs in the fresh plant food pools were in the range of 0.9–14.5 pg/kg fw (Table 1). The measured WHO-TEQs in the cereals, beans, potatoes, vegetables, and edible fungi (range: 0.9–14.5 pg/kg fw) were much lower than the action levels (cereals: 0.85 pg/g fw; vegetables: 0.40 pg/g fw) recommended by the EU commission[22]. The measured WHO-TEQs in the mixed vegetable oil (129.4 pg/kg lw) was also much lower than the maximum limits (1.25 pg/g lw) promulgated by the EU commission[18]. The contributions of 2,3,7,8-chlorine substituted PCDD/Fs to the WHO-TEQs (range: 61.1–97.7%, average: 89.7%) were obviously higher than those of the dl-PCBs in the test fresh plant food pools. However, dl-PCBs accounted for 80.0% of the WHO-TEQ in the mixed vegetable oil.

Table 1. Concentrations of ∑PCDDs, ∑PCDFs, and ∑PCBs in plant food samples.

Sample	Sampling region	Sample numbers	Concentration			
Fresh plant pool			∑PCDDs (pg/kg fw)	∑PCDFs (pg/kg fw)	∑PCBs (pg/kg fw)	WHO-TEQ (pg/kg fw)
Cereals	NC, SC, NW, M, NE	60	18.8–46.4 (29.5)	160.9–1201.8 (632.6)	30678.3–46095.0 (37244.2)	9.0–12.1 (10.2)
Beans	NC, SC, NW, M, NE	40	30.5–45.8 (35.0)	557.2–1006.3 (845.5)	35654.1–100790.7 (66266.0)	10.4–14.5 (12.4)
Potatoes	NC, SC, NW, M, NE	36	6.1–72.3 (22.6)	44.5–159.1 (99.0)	5316.4–17605.6 (10597.6)	2.0–8.4 (4.4)
Vegetables and edible fungi	NW, M, NE	105	25.6–36.6 (29.8)	156.7–185.0 (172.3)	12134.4–15403.8 (13814.9)	1.0–2.1 (1.4)
Leafy vegetables	NC, SC	28	163.5–217.2 (190.4)	461.2–599.8 (530.5)	26675.7–48451.2 (37563.4)	7.3–7.7 (7.5)
Root and stem vegetables	NC, SC	20	15.6–41.5 (28.6)	62.8–119.7 (91.3)	19137.3–33388.2 (26262.7)	1.0–2.3 (1.7)
Melon vegetables	NC, SC	32	15.0–24.2 (19.6)	81.9–179.2 (130.5)	5788.5–10312.2 (8050.4)	0.9–1.9 (1.4)
Legume vegetables	NC, SC	12	20.1–97.4 (58.8)	75.9–142.4 (109.2)	17947.4–18777.0 (18362.2)	1.0–1.4 (1.2)
Edible fungi	NC, SC	13	13.1–67.4 (40.3)	32.7–172.3 (102.5)	9154.0–10503.3 (9828.7)	1.1–1.7 (1.4)
Plant oil			∑PCDDs (pg/kg lw)	∑PCDFs (pg/kg lw)	∑PCBs (pg/kg lw)	WHO-TEQ (pg/kg lw)
Mixed vegetable oil	NC	8	166.5	79.7	196047.3	129.4

Note: The range of values are given with the mean values in parentheses.

Estimation of dietary intakes

The estimated dietary intakes of WHO-TEQs via consumption of animal foods by a standard adult in South Coast, North Coast, Midland, North West, and North East regions were 19.63, 12.74, 4.06, 3.83, and 3.57 pg TEQ/kg bw/month, respectively, which were much less than the provisional tolerable monthly intake (PTMI, 70 pg WHO-TEQ/kg bw/month) proposed by JECFA at its fifty-seventh meeting in 2001[23]. This indicates that the consumption of animal foods marketed on the Chinese mainland should pose a lower risk for human health. However, in 2018, the EFSA Panel on Contaminants in the Food Chain decreased the tolerable weekly intake (TWI) from 14 to 2 pg WHO-TEQ/kg bw/week[5]. In this study, the estimated dietary intakes of WHO-TEQs via consumption of animal foods in South Coast, North Coast, Midland, North West, and North East regions were 4.58, 2.97, 0.95, 0.89, and 0.83 pg TEQ/kg bw/week, respectively. The estimated dietary intakes via consumption of animal foods in the two coastal regions were higher than the new criterion of the TWI. Considering the TWI was derived from long-term accumulation and protective toward all endpoints, exceeding the guideline value slightly does not necessarily mean that there would be an appropriate risk to the health of individuals[5].

The contributions of different animal food groups to the WHO-TEQs intakes of human body were further estimated. To simplify the results, the collected animal food samples were classified into five categories, i.e., pork category, beef and mutton category, other terrestrial animal food category (poultry meat, chicken eggs, and mixed animal fat), milk category, and aquatic animal food category. As shown in Figure 3, the consumption of aquatic animals and pork products contributed 48.3% and 28.4%, respectively, of the estimated WHO-TEQs intake in South Coast region, and the corresponding values were 26.8% and 41.0%, respectively, in North Coast region. In Northeast region, consumption of the aquatic animal food category also exhibited the largest contribution (44.9%) to the estimated WHO-TE intake. The consumption of beef, mutton, and milk made up the primary contribution to the estimated WHO-TEQs intake (61.7%) in Northwest region, while the consumption of the other terrestrial animal food category showed the largest contribution to the estimated WHO-TEQs intake (40.5%) in Midland region.

The estimated plant food-borne dietary intakes of WHO-TEQs by a standard adult were 0.97, 0.92, 0.90, 0.81, and 0.78 pg WHO-TEQ/kg bw/week in Northeast, Midland, Northwest, North Coast, and South Coast regions, respectively. Cereals and vegetable oil were the major contributors to the plant food-borne dietary intakes of WHO-TEQs by adults in all of the five surveyed regions. The average contributions of cereals and vegetable oil consumption to the plant food-borne dietary intakes of WHO-TEQs were 43.9% and 44.8%, respectively.

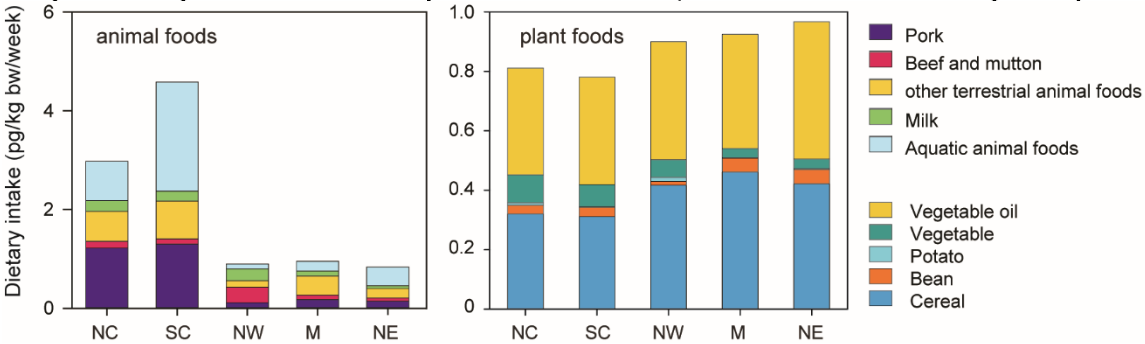

Figure 3. Estimated dietary intakes for adults via animal foods and plant foods consumption and contribution proportions of the different food groups in the five regions.

Conclusions

The levels of PCDD/Fs and PCBs in most of the animal-origin food samples from coastal regions were obviously higher than those from inland regions. Despite the higher contents of PCBs, PCDD/Fs were the predominant contributors to WHO-TEQs in both animal and plant food samples except for the mixed vegetable oil, in which the WHO-TEQs mainly derived from dl-PCBs. The dietary intakes of WHO-TEQ via consumption of animal foods in South Coast and North Coast regions were estimated to exceed the new TWI of 2 pg WHO-TEQ/kg bw/week, primarily because of the higher consumption of aquatic animal foods and pork. This result indicated that residents in coastal regions had a higher risk of exposure to PCDD/Fs and PCBs. Furthermore, in view of the high consumption amounts of the plant foods, the plant food-borne dietary intakes of PCDD/Fs and PCBs should not be neglected on the Chinese mainland.

Acknowledgements

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