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The bioaccessibility of polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins/furans (PCDD/Fs) in cooked plant and animal origin foods

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ABSTRACT

In this study, we compared the effect of boiling and frying food preparation methods in determining the bioaccessibility of polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins/furans (PCDD/Fs) in rice, cabbage, milk powder, eggs, beef, and fresh water fish. We then used these data to calculate a toxic equivalent (TEQ) for risk assessment and compared it to published values that did not account for bioaccessibility.

When the foods were prepared by boiling, the mean bioaccessibility (%) in rice (PCBs: 16.5 ± 1.0, PCDD/Fs: 4.9 ± 0.3) and cabbage (PCBs: 4.2 ± 0.9, PCDD/Fs: 1.9 ± 0.7) were lower than in animal origin foods (beef, PCBs: 49.0 ± 3.3, PCDD/Fs: 7.8 ± 0.9; egg, PCBs: 29.7 ± 3.1, PCDD/Fs: 8.6 ± 1.3; fish, PCBs: 26.9 ± 2.5, PCDD/Fs: 7.9 ± 1.3; milk powder, PCBs: 72.3 ± 1.6, PCDD/Fs: 28.4 ± 1.2).

When fried in cooking oil, the bioaccessibilities of all analytes in all foods increased, but the increase in plant based foods (rice, PCBs: 3.4×, PCDD/Fs: 3.6×; cabbage, PCBs: 10.3×, PCDD/Fs: 7.9×) was greater than that of animal origin foods (beef, PCBs: 1.6×, PCDD/Fs: 3.4×; egg, PCBs: 2.1×, PCDD/Fs: 1.8×; fish, PCBs: 2.8, PCDD/Fs: 3.2×).

Comparison of PCBs/PCDD/Fs bioaccessibility in rice and cabbage showed that bioaccessibility was greater in the low fat, high carbohydrate/protein content food (rice) than in the low carbohydrate/protein, low fat content food (cabbage), regardless of the method used to prepare the food.

Adjusting for bioaccessibility reduced the gross estimated daily intake (EDI) of 112 pg WHO-TEQ/day, by 88% and 63% respectively for foods prepared by boiling and frying.

Our results indicate that: 1) The method used for cooking is an important determinant of PCBs/PCDD/Fs bioaccessibility, especially for plant origin foods, 2) there might be a joint fat, carbohydrate and protein effect that influences the bioaccessibilities of PCBs/PCDD/Fs in foods, and 3) use of bioaccessibility estimates would reduce the uncertainty in TEQ calculations.

1. Introduction

Polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins/furans (PCDD/Fs, also called dioxins) are lipophilic persistent organic pollutants (POPs). These contaminants persist in the environment where they can bioaccumulate through the food chain and cause adverse effects to human health, such as lesions, chloracne, and developmental defects (Kim et al., 2014; Lyche et al., 2015; Masuda, 2001).

For the general human population, intake of PCBs/PCDD/Fs sorbed to foodstuffs is regarded as the main route of exposure and it has been reported that approximately 90% of the human exposure to PCBs/PCDD/Fs originates from foods, especially those of animal origin (e.g. meat, egg, milk and their products) (Zhang et al., 2013). Recent reports using historical data found no significant contribution of residential soil/dust concentrations to serum lipid PCDD/Fs in Michigan adults (Paustenbach and Kerger, 2013) and that the contribution of PCDD/Fs in contaminated soils to human body burden was negligible (<1%) (Kimbrough et al., 2010).

The extent to which compounds desorb from a matrix and become accessible for uptake by other organisms has been termed bioaccessibility. For sorbed compounds post ingestion bioaccessibility has been defined

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as "the maximal amount of contaminants released from the test matrix in a synthetic gastrointestinal system" (Collins et al., 2015). When quantifying human exposure to POPs for risk assessment calculations, it is conservatively assumed that POPs sorbed to foods completely desorb in the gastrointestinal tract and are therefore 100% bioaccessible (Rostami and Juhasz, 2011). However, only a fraction of these chemicals is actually soluble in the digestive juice (bioaccessible) and therefore, total exposure/dose estimates likely overestimate the POPs bioaccessibility (Rostami and Juhasz, 2011). To make a more accurate exposure assessment, bioaccessibility of contaminants in matrices, especially in foods, is critical.

Published bioaccessibility data for POPs in foods are very limited. Wang et al. (2011) reported that the average bioaccessibilities for DDT in market fish were 5.48% and 17.6% in the gastric and intestinal compartments, respectively. Xing et al. (2008) reported that the bioaccessibility of PCBs in freshwater fish (3%) was much lower than that in leafy vegetables (25%), concluding that the high lipid content of fish resulted in lower bioaccessibility. In contrast, Yu et al. (2011) reported a positive correlation ($P < 0.001$) between the bioaccessibility of polybrominated diphenyl ethers (PBDEs) and fat content of 299 food items, including both vegetables and animal-based foods. Generally, more observations are needed to resolve this discrepancy.

The effect of food preparation on the bioaccessibility of POPs is unknown and differences in preparation techniques might also play an important role in the bioaccessibility of sorbed PCBs/PCDD/Fs because they can change the structure and composition of food. Previous bioaccessibility studies of food-sorbed organics have used freeze-drying of raw materials to prepare the samples for in vitro testing (Wang et al., 2011; Yu et al., 2012; Zheng et al., 2013). However, foods are more frequently cooked prior to consumption. Although the culinary process might vary due to regional, cultural, or personal preferences, preparation methods like boiling in water or frying in cooking oil are universal processes which may influence the physical-chemical behavior of sorbed pollutants. For example, boiling significantly decreased the bioaccessibility of cadmium and lead in vegetables (Fu and Cui, 2013), but increased that of arsenic in rice (Moreda-Piñeiro et al., 2011).

The purpose of this study was to: 1) determine the bioaccessibility of PCBs and PCDD/Fs in boiled and fried foods, 2) discuss possible influencing factors therein, and 3) calculate the estimated daily intake (EDI) of selected PCBs/PCDD/Fs toxic equivalent (TEQ) from foods on a bioaccessibility-corrected basis, and compare these results with published data from the total dietary study (TDS) conducted by the Chinese government (Li et al., 2007; Zhang et al., 2013).

2. Materials and methods

2.1. Standard solutions and chemical reagents

In this study, bioaccessibilities were determined for 17 toxic PCDD/F congeners and 12 dioxin-like PCB congeners (mono-ortho and non-ortho) that were added to each of six food types (rice, cabbage, milk powder, eggs, beef, and fresh water fish), and either boiled or fried in cooking oil. The bioaccessibility of six indicator PCB congeners, which do not have toxic equivalency factors but are relatively abundant in the environment, were calculated using the amounts pre-existing in each food type. A complete list of all PCBs/PCDD/Fs used for this research (including surrogate and internal standards) is located in Table S1.

Native PCDD/Fs (EDF-5008), used for fortification of the foods, and $^{13}C_{12}$-labeled PCDD/F compounds, used as surrogates (EDF-8999) and internal standards (EDF-5999) for the PCDD/Fs were purchased from Cambridge Isotope Laboratories (Tewksbury, MA, USA). The dioxin-like (mono-ortho native PCBs, EC-4987, and non-ortho native PCB solutions, EC-4986) PCBs used to fortify the foods were also purchased from Cambridge Isotope Laboratories while labeled mixtures used as surrogates ($^{13}C_{12}$-dioxin-like PCBs, WP-LCS, and $^{13}C_{12}$-indicator PCBs, EC-9605 SS) and internal standards (EC-9605 RS) were obtained from Wellington Laboratories (Guelph, ON, Canada). Pre-mixed calibration standards were purchased from Cambridge Isotope Laboratories and Wellington Laboratories.

Organic and inorganic chemicals used in digestive fluids were purchased from Sigma-Aldrich (Shanghai, China). The constituents of digestive fluids were similar to a previous study (Versantvoort et al., 2005) and are listed in Table S2. All solvents were distilled-in-glass grade and purchased from Caledon Laboratories Ltd. (Georgetown, ON, Canada). Prior to use, all solvents and reagents were screened to ensure they were free of PCBs and PCDD/Fs.

2.2. Fortified sample preparation

A brief experimental flowchart showing the sample preparation and processing steps is illustrated in Fig. 1. Six kinds of commonly consumed food, including rice, cabbage, milk powder, hen eggs, beef, and freshwater fish were purchased from the local market in Hangzhou, China. For each food type, 120 g samples were taken and homogenized using a high-speed blender (IKA, KG, Germany), then freeze-dried for 48 h, and pulverized. 100 g of these samples were homogenized and spiked with unlabeled PCDD/Fs (EDF-5008) and dioxin-like PCBs (EC-4987, EC4986) standards (100 pg/μL each analyte in nonane) to obtain fortified samples at concentrations of 2000 pg/g for PCDD/F (4 Cl and 5–7 Cl) and PCB, 4000 pg/g for PCDD/F (8 Cl)). The spiked samples were vortexed for 60 min to disperse the analytes, then sealed in glass bottles and heated at 40 °C for 6 h. After heating, the samples were cooled to room temperature, stored in the dark for one week. The remaining 20 g of each homogenized sample (unspiked) was used to determine background levels of PCBs/PCDD/Fs, and skipped these preparation steps.

2.3. Cooking procedure

Each of the six types of food samples was assigned to one of two groups, boiled or fried. Triplicates of each food type were prepared by boiling, and three by frying. For samples to be prepared by boiling; 1.5 g subsamples were spiked with 2000 pg of $^{13}C_{12}$-labeled PCDD/Fs (EDF-8999), dioxin-like (mono and non-ortho) PCBs (WP-LCS), and indicator PCBs (EC-9605 SS) to serve as surrogate standards (sample processing controls). The samples were then rehydrated with 4.5 mL ultrapure water. Following hydration 4.0 mL ultrapure water was added to the homogenate, and the samples were boiled at 100 °C on a hot plate for 5 min. The 1.5 g samples in the fried group were similarly spiked with 2000 pg of the surrogates for the PCBs and PCDD/Fs, then rehydrated with 4.5 mL ultrapure water. Following rehydration, the mixtures were fried in 1.0 g of a cooking oil made from corn and soybeans (negligible dioxin/PCB concentration as shown in Table S3) at 200–300 °C on a hot plate for 5 min. Flow charts see Fig. 1.

2.4. In vitro digestion procedure

The process for determining the bioaccessibility of PCDD/Fs and PCBs in foods was similar to the method developed by Oomen et al. (2003) which describes a three-step procedure simulating digestive processes in the mouth, stomach, and small intestine. A flow chart showing the steps used in our assay is provided in Fig. 1 and the constituents used for each digestive compartment are provided in Table S2. In brief, each cooked meal (with the cooking matrix, either water or oil) was transferred into a 50 mL centrifuge tube, to which 6 mL of simulated saliva was added and the samples were vortexed for 2 min. Then, 13 mL of synthetic gastric juice were added, the pH was adjusted to 1–2, and the tube was incubated in a reciprocating water bath for 2 h (37 °C, 60 rpm). In the next step, 12 mL of duodenal juice and 6 mL of bile juice were added and the pH was adjusted to 7.5–8.0 using 1 M $NaHCO_3$ and 1 M HCl. The tube was incubated in the water bath for another 2 h (37 °C, 60 rpm) then centrifuged for 5 min at 18,000 × *g*. The supernatant (chyme) was transferred into a separatory funnel containing 100 mL hexane to perform liquid-liquid separation.