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Levels, congener profiles, and dietary intake assessment of polychlorinated dibenzo-*p*-dioxins/dibenzofurans and dioxin-like polychlorinated biphenyls in beef, freshwater fish, and pork marketed in Guangdong Province, China

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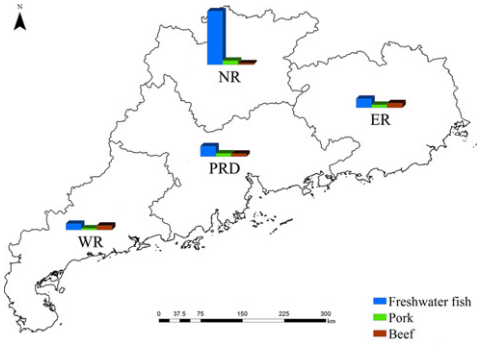
HIGHLIGHTS

- The general levels of PCDD/Fs and DL-PCBs in three food groups marketed around Guangdong Province were first reported.
- Different congener profiles were found in three food groups from four different regions.
- Freshwater fish from north region of Guangdong Province were more prone to accumulate PCDD/Fs rather than DL-PCBs.
- Dietary exposure of PCDD/Fs and DL-PCBs had a low contribution to PTMI.

GRAPHICAL ABSTRACT



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ABSTRACT

Persistent organic pollutants such as polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and dioxin-like polychlorinated biphenyls (DL-PCBs) consisting of non-*ortho* and mono-*ortho* PCBs are suggested to be very hazardous and have adverse effects on human health. However, their levels and congener profiles in retail foods marketed in Guangdong Province of China have not been elucidated thus far. Thus, in this study, 226 individual samples of beef, freshwater fish, and pork marketed across four regions of Guangdong Province were randomly collected during 2013–2015 to determine their levels of PCDD/Fs and DL-PCBs. The results showed that the total toxic equivalency quantities (TEQs) of most samples were below the maximum limits except for the 26 samples collected from the vicinities of pollution areas. The median total TEQs of these three categories were 0.174, 0.488, and 0.113 pg TEQ/g fw, respectively, which indicated that the contamination status of the studied foods was not serious. For congener profiles, significantly different patterns were observed in three food groups, but with the same major

Abbreviation: PCDDs, polychlorinated dibenzo-*p*-dioxins; PCDFs, polychlorinated dibenzofurans; DL-PCBs, dioxin-like polychlorinated biphenyls; TEF, toxic equivalency factors; TEQ, toxic equivalency quantity; POPs, persistent organic pollutants; JECFA, Joint FAO/WHO Expert Committee on Food Additives; TDS, total dietary survey; HA, *n*-hexane; DCM, dichloromethane; HRGC/HRMS, high-resolution gas chromatography-high resolution mass spectrometer; SIM, selected ion monitoring; LOD, limit of detection.

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Foodstuff
Congener profile
Dietary intake

TEQ contributors being 2,3,4,7,8-PeCDF in beef, freshwater fish, and pork. Regional differences of congener profiles in each food group were also found in this study, which might be attributed to the regionally different distributions of PCDD/Fs and DL-PCBs in environment media.
The dietary exposures of four population subgroups (girls, boys, male adults, and female adults) to PCDD/Fs and DL-PCBs via three food groups were estimated to assessed the potential risks. They were all lower than the provisional tolerable monthly intake (PTMI, 70 pg TEQ/kg bw/month) established by Joint FAO/WHO Expert Committee on Food Additive. In these food categories, the exposure to PCDD/Fs and DL-PCBs via freshwater fish was the highest one, which accounted for about 20% of PTMI, indicating that it was the major route to expose dioxin compounds.

1. Introduction

Persistent organic pollutants (POPs) are toxic organic chemicals that are resistant to environmental degradation via mechanisms such as photolysis, chemical or biological actions (Eduljee, 2001). Owing to their unique characteristics including extensive release in environmental media, high environmental stability, and severe adverse effects on biota and human health, the emissions of POPs need to be reduced and their production prohibited (Chen et al., 2008; G. Zhang et al., 2007a; J.Q. Zhang et al., 2007b). Among POPs, three closely related families of polyhalogenated aromatic hydrocarbons referred to as dioxins, comprising polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and dioxin-like polychlorinated biphenyls (DL-PCBs), are regarded as the most hazardous ones and put into the initial list of Stockholm Convention. Thus, they have received great attention in the recent decades. PCDDs and PCDFs occur naturally and as the unintentional by-products of incomplete combustion and various industrial processes, in contrast, DL-PCBs mainly result from the wide production and a variety of commercial uses of PCBs before the applications have been banned by most countries since 1970s. These environmental toxicants can bioaccumulate easily through the food chain and ultimately show similar spectrum of adverse biological effects and responses in wild life and humans that include dermal toxicity, reproductive and developmental effects, neurological effects, immunomodulatory, and carcinogenic effects (Chan and Wong, 2013; Costopoulou et al., 2016; Marin et al., 2011; Zhang et al., 2012).

In humans, exposure routes of PCDD/Fs and DL-PCBs from contaminated matters include ingestion, inhalation, and dermal contact (Chan et al., 2013). Dietary intake is regarded as the main pathway of exposure to dioxins, because food ingestion is known to account for >90% of total human exposure (Bocio et al., 2007; Fernandes et al., 2010; Grassi et al., 2010; Li et al., 2007; Wang et al., 2015). Due to their ubiquitous nature, persistence, and lipophilicity, dioxins can easily accumulate at high levels in food of animal origin with high fat content, especially meat and dairy products (Chan et al., 2013). Thus, in many countries and regions, the contamination levels of PCDD/Fs and DL-PCBs in foodstuffs have been extensively investigated, particularly in livestock and poultry products (Fernandes et al., 2010; Hoogenboom et al., 2016; Huwe and Larsen, 2005; Kim et al., 2007; Squadrone et al., 2015), dairy products (Durand et al., 2008; Esposito et al., 2009; Schmid et al., 2003), and aquatic products (Han et al., 2007; Moon and Ok, 2006; Munschy et al., 2008; Sakuraia et al., 2000; C.F. Shen et al., 2009a; H.T. Shen et al., 2009b). These studies showed that the toxic equivalency quantity (TEQ) levels, which are used to estimate the harmful effects of these hazardous chemicals, of certain animal-origin food exceeded the limits set by EU Regulation 1259/2011, indicating that intake of such highly contaminated food may pose hazardous effects for residents. In China, the standard of determination method for PCDD/Fs and DL-PCBs in foodstuffs was implemented in 2007 and revised in 2013, but the limits of PCDD/Fs and DL-PCBs still not set by the relevant department. Therefore, the limits for foodstuffs set by EU were recommended as reference in researches and risk assessments.

In order to estimate the dietary exposure of PCDD/Fs and DL-PCBs through food to reveal the extent of chronic intake, total dietary survey (TDS) has been performed in numerous developed and developing countries in recent years (De Mul et al., 2008; Rauscher-Gabernig et al., 2013; Sasamoto et al., 2006; Sirot et al., 2012; Taioli et al., 2005; Wang et al., 2009; Windal et al., 2010; Zhang et al., 2013; Zhang et al., 2015). The results from the latest Chinese TDS show that a relatively higher exposure is observed in some developed regions such as Zhejiang Province, Guangdong Province, and Shanghai City, suggesting that foods polluted by dioxins may cause by a high environmental burden and pose a threat to the health of local residents (Zhang et al., 2015). Therefore, it is necessary to conduct an in-depth survey to give researchers integral insights on the levels of PCDD/Fs and DL-PCBs in foods marketed in these Chinese developed regions.

The occurrences and concentrations of PCDD/Fs and DL-PCBs in food of animal and plant origin marketed in Shenzhen City, one of the developed cities of Guangdong Province, were determined recently by J.Q. Zhang et al. (2007b, 2008). However, their general levels in retail foods available in Guangdong Province have not been reported thus far. Accordingly, one of the objectives of this study was to carry out the first investigation with wide coverage on the general levels and congener profiles of PCDD/Fs and DL-PCBs in three main categories of food including beef, freshwater fish, and pork, sampled from Guangdong Province. Further, we estimated the dietary intakes of PCDD/Fs and DL-PCBs by employing deterministic assessment and evaluated the risk to the health of general and special populations.

2. Materials and methods

2.1. Chemical reagents and standards

The column packing materials including Silica gel 60 (63–200 μm), Bio-Beads™ S-X3 support (38–75 μm), and Florisil (149–250 μm, pesticide grade) used for column purification were purchased from Merck (Darmstadt, Germany), Bio-Rad Laboratories (Hercules, CA, USA), and Supelco (Bellefonte, PA, USA), respectively. Organic solvents of pesticide grade applied for extraction, elution, and dissolution including *n*-hexane (HA), acetonitrile, acetone, *n*-nonane were obtained from Honeywell Burdick & Jackson (Ulsan, Korea), and dichloromethane (DCM) from Merck Chemicals Co., Ltd. (Shanghai, China). Other chemicals used in the process of pretreatment are anhydrous sodium sulfate, sodium hydroxide, and sulfuric acid. The quantification standard solutions, internal standards, spiking solutions, and injection standards of PCDD/Fs and DL-PCBs were all purchased from Cambridge Isotope Laboratories Co. (Andover, MA, USA).

2.2. Sample collection and preparation

2.2.1. Sampling

A total of 226 individual food samples were purchased from local food markets and supermarkets during 2013–2015. These samples were classified into three categories of beef ($n = 71$), freshwater fish ($n = 76$), and pork ($n = 79$). As part of the annual national food contaminants survey in China, 17 sampling sites covering most of the 22 prefectures of Guangdong Province were investigated according to population and economic status, which respectively located in Eastern