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Toxaphene levels in retail food from the Pearl River Delta area of South China and an assessment of dietary intake

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HIGHLIGHTS

- Levels of toxaphene decrease in the order fish, poultry, livestock, egg, vegetable.
- Estimated daily intake for adults was 35.6 pg/kg bw/day with 62% from fish.
- Toxaphene levels and EDI are far lower than the EU MRLs and published data.
- This study provides first and valuable data of toxaphene levels in Chinese food.

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ABSTRACT

Limited literature exists on toxaphene contamination in food worldwide, particularly in mainland China. In this study, three toxaphene congeners, Parlar 26 (B8-1413), Parlar 50 (B9-1679) and Parlar 62 (B9-1025), were analyzed in five different food categories from the Pearl River Delta Area in China using isotope dilution high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS), and toxaphene levels in food were reported and toxaphene dietary intake by local residents estimated. The results showed that fish contained the highest toxaphene level with a median of 12.87 pg/g wet weight (ww), followed by poultry meat, egg products, livestock meat and vegetable, which had median levels of 5.8, 2.2, 1.89 and 0.67 pg/g ww, respectively. Parlar 50 and Parlar 26 were the predominant characteristic congeners in fish, and Parlar 26 was the predominant congener not only in poultry products and eggs, but also in livestock and vegetable. The estimated average daily intake found by local residents was 35.57 pg/kg body weight/day. Overall toxaphene levels and estimated dietary intake in the Pearl River Delta Area of South China are far lower than the European Maximum Residue Limits (EU MRLs), the German MRL for fish, and other international literature data. Therefore, the risk of adverse health effects from dietary intakes of toxaphene for the local residents is not considerable at the current time, but follow-ups are warranted to study dynamic changes of toxaphene in food in this area.

1. Introduction

Persistent organic pollutants (POPs) are important environment chemical pollutants (United Nations, 2009). Toxaphene is one of the 12 initial POPs that have been recognized to cause adverse health effects on human and animals under the Stockholm Convention in 2001 due to its persistence, bioaccumulation and toxicity (Alder et al., 1997; De Geus et al., 1999; Buranatrevedh, 2004). Toxaphene is a mixture consisting of several hundreds of congeners, mainly polychlorinated bornane and camphene congeners, and has an average chlorine content of 67–69% (Buranatrevedh, 2004). These mixtures were massively used as the insecticide in agriculture in the early 1970s to replace dichlorodiphenyltrichloroethane (DDT) in the United States and Europe for three decades. Moreover,

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toxaphene has the property of bioaccumulation in lipid-rich animal tissues, and then can enter human body through the food chain especially from animal-originated food (De Geus et al., 1999; Buranatrevedh, 2004). Since toxaphene is highly toxic to animals and is a potential human carcinogen (De Geus et al., 1999; Buranatrevedh, 2004), it has been banned in Europe since the early 1980s and in the USA in 1990.

Among the congeners of toxaphene, Parlar 26 (B8-1413), Parlar 50 (B9-1679) and Parlar 62 (B9-1025) account for about 50% of the total concentration (EFSA, 2005). The levels of the three individual congeners and their sum are often chosen as indicators, representing overall toxaphene contamination in environment and food (Alder and Vieth, 1996; Alder et al., 1997; Byard et al., 2015). These three congeners, as the predominant congeners, can enter the environment and biota where they remain stable and cann't be easily biodegraded. Thus, their adverse effects can be bio-magnified via the food chain (EFSA, 2005; Champoux et al., 2010). The Pearl River Delta Area is located in the southeast Guangdong province of China, and is close to Hong Kong and Macau. This area is highly industrialized and developed, and its economy ranks the top in China. Since this area is at the downstream of the Pearl River, all toxic inputs from various sources over its 2214-km course are accumulated there. Thus, the pollution status of the Pearl River Delta is becoming a growing worldwide concern. There have been some investigations reporting the contamination levels of DDTs (Kong et al., 2005; Guo et al., 2008 a), PCBs (Wei et al., 2011; Zhang et al., 2008), PCDDs and PCDFs (Zhang et al., 2007, 2008; Wei et al., 2011) as well as PBDEs (Guo et al., 2008b) in the Pearl River Delta Area. However, no data is available on toxaphene levels in that environment, particularly in food. Not only is there limited literature available on toxaphene contamination in food (mainly due to difficulties in its detection), but the different contamination status of toxaphene in varieties of food has not been investigated in China either. Thus, toxaphene exposures continue to remain a concern in mainland China.

The total global production has been estimated to be $0.45–1.33 \times 10^6$ tons (Voldner and Li 1993), of which 2.0×10^4 tons were produced in China (Ministry of Environmental Protection of PRC, 2011; Hu et al., 2008). Thus, estimated cumulative usage of 1.3 million tons of toxaphene has been applied throughout the world. Top 10 countries and regions using toxaphene between 1947 and 2000 ranked descending as the USA (490 kiloton (kt)), the former Soviet Union (254 kt), then Europe, and Central and South America. Total global toxaphene emissions are around 407 kt from 1947 to 2000 (Li and Li, 2004). Furthermore, the amount of toxaphene usage in eastern Asia region is low, and the literature is also scarce. In addition, the production of toxaphene started in 1973 and ceased in 1985 in China (Hu et al., 2008), no published data are available on the amount of toxahphene usage in China thus far.

To elucidate the toxaphene contamination levels in food and assess the risk of toxaphene dietary exposure for the residents living in the Pearl River Delta area, this study analyzed the levels of the three toxaphene congeners (Parlar 26, Parlar 50 and Parlar 62) in five different categories of foods (these most commonly consumed by local residents) from the area. A newly developed and validated method by isotope dilution high-resolution gas chromatography/high-resolution magnet mass spectrometry was used (Liu et al., 2014). The aims of the study are to provide baseline data of toxaphene contaminations levels in fish, poultry meat, egg products, livestock meat and vegetables, and assess the dietary intake of toxaphene for local residents.

2. Materials and methods

2.1. Sample collection

Food sample selection was based on the most common known food consumed by the local residents. Samples were collected between October 2010 and June 2011 from major supermarkets and farm markets in four cities in the Pearl River Delta area: Guangzhou, Jiangmen, Dongguan, and Huizhou (Fig. 1). The five categories of food that were sampled consisted of fish (freshwater and saltwater fish), livestock meat (pork, beef, and mutton), poultry (chicken and duck), eggs (chicken eggs), and vegetables. Only the edible parts were analyzed excluding the viscera for animal origin food, and chicken, duck and fish samples were analyzed with the skin since it is commonly eaten. Detailed information on sampling quantity is shown in Table 1. Age and sex information on the collected samples were not available.

A total of 91 individual food samples were collected. Of these, 17 were freshwater fish (2 cyprinoid, 2 bighead carp, 4 *Carassius auratus*, 6 grass carp, 1 bian fish, 1 wuchang fish, and 1 *Cirrhinus molitorella*), 11 saltwater fish (3 sequoia fish, 4 ribbon fish, 2 pomfret fish, and 2 weever), 25 livestock samples (13 beef, 9 pork and 3 mutton), 19 poultry meat samples (9 chicken and 10 duck), 11 egg samples, and 8 samples of Chinese broccoli.

2.2. Chemicals and reagents

The three indicative congeners Parlar 26, Parlar 50 and Parlar 62 ($^{13}C_{10}$-Parlar 26, $^{13}C_{10}$-Parlar 50 and $^{13}C_{10}$-Parlar 62) for the toxaphene standard solution and $^{13}C_{12}$-PCB 114 were purchased from Cambridge Isotopic Laboratory (Andover, MA, USA) with a purity > 98%. Hexane, dichloromethane, methanol, dehydrated sodium sulfate and silica gel were obtained from Merck Inc. (Darmstadt, Germany). Acetone was purchased from J.T. Baker (Avantor Performance Materials, Center Valley, USA) and the alkaline aluminum oxide was from Sigma–Aldrich Inc. (St Louis, MO).

2.3. Sample preparation

Details of the method used for this study have been previously published (Liu et al., 2014). In brief, approximately 5–10 g food samples were homogenously grounded into powder after freeze-drying, then were spiked with internal standards $^{13}C_{10}$-Parlar 26, $^{13}C_{10}$-Parlar 50 and $^{13}C_{10}$-Parlar 62 and extracted with Soxtec extraction system (Foss, Germany) with 1:1 (v/v) acetone:hexane. Lipid contents were determined using the gravimetric method. Extracts were purified with a column filled with acid silica gel (30% sulphuric acid) and followed by further cleanup with alumina oxide column. Twenty mL dichloromethane was used to elute the target congeners from the column, and the eluant was then evaporated by a rotary evaporator to about 1 mL and further concentrated to 100 μL with high purity nitrogen. $^{13}C_{12}$-PCB 114 was added as the recovery standard.

2.4. Sample analysis

The concentrated eluants previously mentioned were analyzed by an isotope dilution high-resolution gas chromatography/high-resolution mass spectrometry (DFS, Thermo Fisher Inc., San Jose, CA, USA). Briefly, 1 μL of concentrated eluants were injected into the injector port (280 °C) in splitless mode; DB-5MS (J & W Scientific, USA) fused silica capillary column (15 m × 0.25 mm x 0.1 μm) was used for separation. The column temperature was programmed at 90 °C and held for 2 min then increased to 160 °C at 15°C/min. Oven temperature was then raised to 210 °C at the rate of 6°C/min and