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Dietary exposure to short- and medium-chain chlorinated paraffins in meat and meat products from 20 provinces of China☆

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ABSTRACT

Food intake is one of the main pathways of human exposure to chlorinated paraffins (CPs). This study assessed the dietary exposure for the general Chinese population to short-chain chlorinated paraffin (SCCPs) and medium-chain chlorinated paraffins (MCCPs) through meat and meat products. Twenty samples of meat and meat products from 20 Chinese provinces were collected in 2011. As the sampling sites covered about two-thirds of the Chinese population, the meat samples were considered to be representative of the true characteristics of CPs contamination in Chinese meat products. The concentrations of SCCPs and MCCPs in the meat samples were measured using the comprehensive two-dimensional gas chromatography electron capture negative ionization high-resolution time-of-flight mass spectrometry method. Forty-eight SCCP and MCCP homolog groups were detected in the meat samples. The mean SCCP and MCCP concentrations in all meat samples were 129 ± 4.1 ng g^{-1} wet weight and 5.7 ± 0.59 ng g^{-1} wet weight, respectively. The concentrations of SCCPs and MCCPs varied in samples from different provinces. The geographical distribution of CP concentrations was similar to the distribution of CPs manufacturing plants in China. The most abundant groups of SCCPs in all samples were $C_{10\text{-}11}$ $Cl_{6\text{-}7}$, and the most abundant groups of MCCPs in most samples were C_{14} $Cl_{7\text{-}8}$. The possible sources of SCCPs and MCCPs in meat and meat products might be CP-42 and CP-52. The 50th percentile estimated daily intakes of SCCPs and MCCPs through meat consumption for a "standard" Chinese adult male were 0.13 and 0.0047 μg kg^{-1} bw d^{-1}, respectively, both much lower than the tolerable daily intakes (TDIs) for SCCPs and MCCPs. This preliminary risk assessment has indicated that the indirect exposure of SCCPs and MCCPs through meat consumption does not pose significant risk to human health in China.

1. Introduction

Chlorinated paraffins ($C_nH_{2n+n\text{-}z}Cl_z$; CPs), also known as polychlorinated n-alkanes, are a class of highly complex chemical compounds. Based on their chain lengths, CPs are divided into short-chain ($C_{10\text{-}13}$), medium-chain ($C_{14\text{-}17}$), and long-chain chlorinated paraffins ($C_{18\text{-}30}$). They have a wide range of industrial applications, mainly as plasticizers, flame retardants in sealants and

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leather, cutting fluids for metal working, lubricants, and paint additives (Qiao et al., 2016). This wide industrial application means that, during production, service life, and disposal of CPs and CP-containing products, CPs have been released into different environmental matrices, such as air (Fridén et al., 2011), water (Zeng et al., 2012), soil (Wang et al., 2013), sediment (Gao et al., 2012), aquatic and terrestrial organisms (Luo et al., 2015; Basconcillo et al., 2015; Zeng et al., 2015), milk (Thomas et al., 2006), and even food (Iino et al., 2005). Owing to their persistent characteristics (Iozza et al., 2008), long-distance migration (Li et al., 2016; Tomy et al., 2000), bioaccumulation (Sun et al., 2017; Zeng et al., 2011), and toxicity (Cooley et al., 2001; Wyatt et al., 1993), SCCPs have recently been added to the list of the Stockholm Convention of the Persistent Organic Pollutants (POPs) which aims to limit their production and use (van Mourik et al., 2015).

Among the characteristics of SCCPs, toxicity is of great concern. Some previous studies have indicated that SCCPs can affect the thyroid, liver and kidneys, and in the long term could lead to carcinogenicity in these organs. Furthermore, SCCPs may cause cancer in humans and disrupt endocrine functions (UNEP, 2015). Recently, Geng et al. (2015) have found that exposure to SCCPs decreased viability and caused significant metabolic disruptions in human hepatoma HepG2 cells. Compared with the amount of research on SCCPs, that on MCCPs in the environment has been relatively little. This may because the toxicities of MCCPs are lower than those of SCCPs (Wyatt et al., 1993), because the toxicities of CPs generally decrease as the length of the carbon chain increases (de Boer, 2010). SCCPs and MCCPs have similar physico-chemical properties and toxicity profiles, so simultaneous exposure to them may increase the risk to humans through their dietary intake. MCCPs have also been shown to biomagnify between prey and predators from Lake Ontario and Lake Michigan (Houde et al., 2008). Therefore, both SCCPs and MCCPs should be paid more attention than previously.

The pathways of human exposure to CPs are complicated and can include dietary intake, dust intake, inhalation uptake, and dermal absorption (Fridén et al., 2011). It is well-known that the exposure of the non-occupationally exposed population to polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (dl-PCBs) originates mainly from foods, especially those of animal origin (Zhang et al., 2015). Moreover, the Canadian authority on the environment (Environment Canada, 2008) has estimated the population indirectly exposed to SCCPs and MCCPs and found that, for all age groups, food was the major source, contributing 50%–100% to the total intake of SCCPs and 71%–100% to the total intake of MCCPs, from uptake via ambient air, indoor air, drinking water, food, and soil. Regarding human exposure through food consumption, data on the concentration of SCCPs and MCCPs are relatively abundant for fish, but much less information has been reported for other major food groups whose contribution to total dietary exposure should also be considered. Therefore, the contamination status of SCCPs and MCCPs in foods consumed in China and their potential health risks have become matters of great interest and concern.

In the present study, for the first time a nation-wide survey was carried out to investigate the levels and national geographical distribution of SCCPs and MCCPs in meat and meat products, to evaluate the dietary exposure of the Chinese general population, and to assess the potential risks to health posed by SCCPs and MCCPs. This will be achieved through using the comprehensive two-dimensional gas chromatography coupled to electron capture negative ionization high-resolution time-of-flight mass spectrometry method (GC × GC-ECNI-TOFMS).

2. Materials and methods

2.1. Meat sample collection

2.1.1. Food consumption survey

The food consumption data were collected by the Chinese Center for Disease Control and Prevention (Chinese CDC) in 2009 using the Total Diet Study (TDS) approach described previously (Gao et al., 2016; Zhou et al., 2012). The food samples in the 5th Chinese TDS in 2011 were collected from 20 Chinese provinces. The detailed sampling locations are shown in Fig. S1. The data collection for the food consumption survey was based on a 3-d household dietary survey and 24-h recalls. Three sampling sites (1 urban and 2 rural) were randomly selected in each of 20 provinces in China, and 30 households were randomly selected at each sampling site. The total dietary survey involved extensive regional coverage to provide a high coverage of the population. The average food consumption of a "standard" Chinese adult male (18–45 years old, 63 kg body weight, employed in light physical work) was used as the standard for food consumption for the province. The average values for the daily consumption of meat and meat products for adults from 20 provinces of China are shown in Table S1.

2.1.2. Food category

All the food consumed was classified into 12 categories, such as cereals and cereal products, meat and meat products. In the present study, the meat and meat products surveyed comprised pork, mutton, beef, chicken, duck, rabbit, pork liver, and swine blood.

2.1.3. Food sampling and preparation

Details on the sampling methodology of the 5th TDS in China are described elsewhere (Shi et al., 2016; Zhang et al., 2015). To conform to the usual pattern of food consumption, the samples were purchased from local markets, grocery stores, and rural households at each of the 3 survey sites in each province. The food was then prepared according to local cooking methods, steaming, frying, boiling, and pan-frying. The samples were prepared on the basis of food consumption data from each province. Finally, the samples were homogenized then frozen at −20 °C until analysis. In the present study, the data came from samples of meat and meat products collected from the 5th Chinese TDS in 2011 from 20 provinces in China which included approximately 70% of the Chinese population. Thus the meat samples were collected systematically to be representative of the Chinese population. The detailed information has been listed in the Supplementary Information.

2.2. Sample preparation

Briefly, approximately 30 g of the meat food sample was freeze-dried. After spiking with 2.5 ng of $^{13}C_{10}$-labeled *trans*-chlordane (Cambridge Isotope Laboratories, Andover, MA, USA), the samples were treated in an ASE 350 extraction apparatus (Dionex, Sunnyvale, CA, USA) with a mixture of n-hexane and dichloromethane (1:1, *v*/*v*). Extractions were performed by three cycles at 100 °C and 1.03×10^4 kPa, 5 min of heating, a 10-min static extraction, a flush volume of 60% and a N_2 purge time of 60 s. After the extract was evaporated to dryness, the lipid content was determined by gravimetric analysis. The extract was then redissolved in n-hexane/dichloromethane (1:1, *v*/*v*).

The extracts were first cleaned up with a sulfuric acid silica gel column to remove lipids. Then a gel permeation chromatography column was used to remove sulfur-containing compounds and lipids. Finally the extracts were cleaned by passing them through a multi-layer silica gel column packed with 3 g of florisil, 2 g of activated silica gel, 5 g of acidified silica gel (44% mass fraction