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Bioaccumulation and human health risks of OCPs and PCBs in freshwater products of Northeast China☆

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ABSTRACT

The levels and spatial distribution of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in freshwater products from Northeast China were investigated by gas chromatography coupled to isotope dilution high-resolution mass spectrometry. All samples were on-spot sampled from main production regions of freshwater products in Northeast China, and these samples were used to systematically assess the potential health risks of OCPs and PCBs associated with consumption of these fishery products. Dichlorodiphenyltrichloroethanes (DDTs), hexachlorocyclohexane (HCHs), hexachlorobenzene (HCB) and PCBs were the major pollutants with 100% detection rates, and their levels ranged from 0.086 to 58, 0.038–3.3, 0.093–4.5 and 0.032–1.4 ng g^{-1} wet weight, respectively. The estimated dietary intakes of these contaminants were all below their corresponding acceptable daily intakes. Significant regional differences in the levels of OCPs and PCBs ($P \leqq 0.001$) were found in samples from Liaoning and Inner Mongolia. The results showed that the concentrations of targeted contaminants in aquatic products had species-specific characteristics, and the levels of targeted pollutants in *Oncorhynchus mykiss* and *Eriocheir sienesis* were significantly higher than those in other aquatic product species. Advisories on ten species of aquatic products suggested that consumption of *Eriocheir sinensis, Oncorhynchus mykiss* and *Cyprinus carpio* at a rate exceeding 15 meals per month would pose a cancer risk. A health risk assessment indicated that exposure to these pollutants through freshwater products consumption would cause a non-ignorable potential carcinogenic risk to humans.

1. Introduction

Polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) are listed in the Stockholm Convention under the category of persistent organic pollutants (POPs) of the United Nations Environment Program because of their high persistence, toxicity and bioaccumulation for humans and wildlife (The United Nations Environment Programme, 2005). Historical industrial and agricultural activities have resulted in environmental pollution such that OCPs and PCBs are frequently detected in soil, air, water and wildlife (Robinson et al., 2016; Salamova et al., 2013; Wu et al., 2016). Exposure to OCPs and PCBs has been associated with a variety of health hazards in humans, such as carcinogenic, reproductive, neurological, immunological and other adverse effects (Rizzi et al., 2017; Wang et al., 2010, 2011). Diet has been proven to be one of the major sources of human exposure to OCPs and PCBs, especially aquatic product consumption (Robinson et al., 2016; Su et al., 2012). Due to the high nutritional value and delicious taste, aquatic products are increasingly popular among the public. In fact, the consumption of aquatic products in China has grown impressively from 23.10 kg per capita in 1996 to 49.11 kg in 2015 (National Bureau of Statistics of China, 2015a). At the same time, it could also pose a health risk to consumers because aquatic products are generally contaminated by OCPs and PCBs (Meng et al., 2007). Northeast China, including Inner Mongolia Autonomous Region and Liaoning, Jilin and Heilongjiang provinces, accounts for approximately 20% of China's total area. The output of aquatic products by Northeast China accounted for

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approximately 19% of the total production of China in 2015 (National Bureau of Statistics of China, 2015b). Non-negligible concentrations of OCPs and PCBs were detected in the soil and water systems of Northeast China, and these contaminants readily accumulated in the fatty tissues of aquatic organisms through bioaccumulation and biomagnification processes (Chen et al., 2015; Ke et al., 2015; Sharma et al., 2009; Zhang et al., 2009). What is worse, these POPs have potential health effects on humans via the consumption of aquatic products from polluted water system (Nakata et al., 2002; Shi et al., 2013; Yang et al., 2006). Some researchers have investigated the concentrations and health risks of organochlorines in fish collected from local markets in 11 coastal cities of Guangdong Province, a local market in coastal Zhoushan City (Shi et al., 2013), and the Pearl River Delta in China (Guo et al., 2008). However, studies on OCPs and PCBs in the freshwater products of Northeast China are rarely reported, and a human health risk assessment of the aquatic products of Northeast China has not been systematically conducted.

Northeast China is a main production region of agricultural products and an old industrial base in China, and these agricultural and industrial activities have resulted in larger amounts of OCPs and PCBs releasing into the environment (Zhang et al., 2016; Jia et al., 2010). Therefore, the aquatic products of Northeast China might be exposed to relatively high levels of OCPs and PCBs. Environmental and ecological conditions, including temperature and climate, vary both spatially and temporally. The variation of these conditions inevitably influences the spatial distribution of OCPs and PCBs and their bioaccumulation by aquatic products. Northeast China is the highest latitude region in China and the winter is very cold (average −25 °C). It has a typical humid temperate, semi-humid continental monsoon climate with the yearly average temperature below 10 °C. Due to its unique geographical location and development history, Northeast China is quite different from the other parts of China. However, no systematic information is available on the levels, regional distributions and health risks of OCPs and PCBs in freshwater products from Northeast China. This study fills the gap regarding the contamination status of OCPs and PCBs in freshwater products from the targeted region. The concentration of 23 OCPs and 18 PCBs in freshwater products from Northeast China were measured using developed isotope dilution/high resolution gas chromatography/high-resolution mass spectrometry (ID/HRGC/HRMS). This study aimed to investigate the level, regional distributions and species-specific differences of OCPs and PCBs in freshwater products from Northeast China. On the basis of a carcinogenic and noncarcinogenic risk assessment of daily exposure of humans to these pollutants via aquatic products consumption, the potential health risk and preliminary consumption advisories of freshwater products was proposed.

2. Materials and methods

2.1. Chemicals and reagents

^{13}C-labeled stock solutions of OCPs were purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA), and ^{13}C-labeled stock solutions of PCBs were obtained from Wellington Laboratories, Inc. (Ontario, Canada). The detailed information on the ^{13}C-labeled stock solutions (surrogate standard and injection internal standard for OCPs and PCBs) is found in the supporting materials (Table S1). Hexane (Honeywell, New Jersey, USA) and dichloromethane (Honeywell, New Jersey, USA) used for sample preparation were of pesticide analysis grade. Florisil packing (60–100 meshes from LGC, UK) was baked in a muffle furnace at 650 °C for 4–5 h. Analytical grade anhydrous sodium sulfate (Da Mao, Tianjin, China) was ultrasonically cleaned in hexane solution before use.

2.2. Survey region and sample collection of aquatic products

The sampling of ten species of aquatic products was conducted in representative freshwater farms of Liaoning Province and Inner Mongolia Autonomous Region in 2015. Liaoning Province (148000 km^2 in area) and Inner Mongolia Autonomous Region (1183000 km^2 in area) were chosen as representative regions of Northeast China, as the economy of Liaoning Province is typically based on heavy industry and crop farming, whereas animal husbandry is dominant in the Inner Mongolia Autonomous Region. Therefore, aquatic products sampled from these two regions are sufficiently representative of the overall aquatic products in Northeast China.

Sample collection were conducted at main production regions of freshwater products of Northeast China, according to the Chinese sampling regulation for contaminant monitoring in fishery products (Ministry of Agriculture of China, 2004). The detailed information on sampling sites is shown in Fig. 1. To make the sample sufficiently representative, each sample for analysis is a mixture muscle from three aquatic products of the same species collected from the same sampling site. A total of 57 representative samples were made from 171 aquatic product samples that were on-spot sampled with the help of fishermen. These samples were applied to systematically assess the potential health risks of PCBs and OCPs associated with aquatic product consumption in Northeast China. Ten common aquatic product species (fish and crabs) were sampled, namely, *Oncorhynchus mykiss*, *Hypophthalmichthys molitrix*, *Eriocheir sinensis*, *Cyprinus carpio*, *Ophiocephalus argus cantor*, *Hypophthalmichthys nobilis*, *Ctenopharyngodon idellus*, *Carassius auratus*, *Megalobrama amblycephala* and *Chanodichthys erythropterus*. These species of aquatic products were favored by the residents of Northeast China, and their output accounted for most of the total production of aquatic products in Northeast China. Samples were placed in aluminized paper and then stored in polythene self-sealing bag under −10 °C. Before the samples were freeze-dried, their wet weight was obtained to calculate the water contents. The feeding habits, fat content (%) and sample numbers of the investigated species are shown in Table S2 of the supporting information.

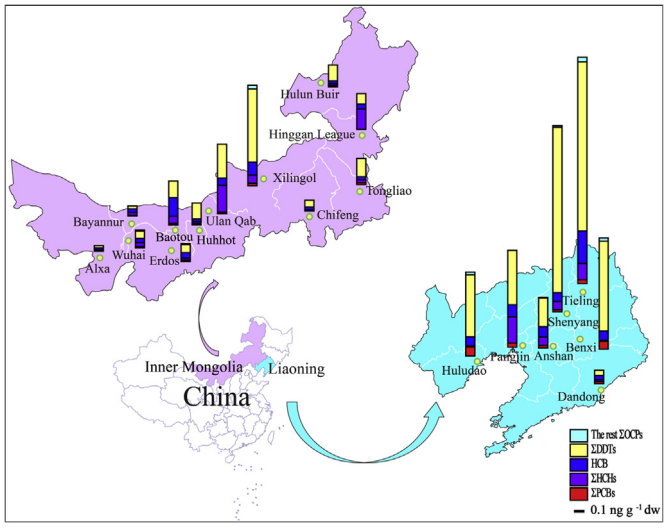

Fig. 1. Sampling locations of aquatic products and the corresponding concentration levels of OCPs and PCBs in aquatic products from Northeast China.