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Rice ingestion is a major pathway for human exposure to organophosphate flame retardants (OPFRs) in China

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HIGHLIGHTS

- Six typical OPFRs are widely present in Chinese foods;.
- Rice contains the highest concentration of OPFRs, which were mainly in rice proteins;.
- Rice consumption is a major pathway for human exposure to OPFRs;.
- The contribution of meats and dairy products to the OPFRs intake was lowest;.
- OPFRs ranged from 1.67 to 49.0 ng/g with a median value of 12.4 ng/g in human hair.

GRAPHICAL ABSTRACT

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ABSTRACT

Although organophosphate flame retardants (OPFRs) have been shown to accumulate in abiotic and biotic environmental compartments, data about OPFRs concentrations in various foods are limited and are none in humans through diets. In this work, the concentrations of 6 typical OPFRs were investigated in 50 rice samples, 75 commonly consumed foods and 45 human hair samples from China. The dietary intakes of OPFRs for adult people via food ingestion were estimated. The concentrations of ΣOPFRs in foods ranged from 0.004 ng/g to 287 ng/g. OPFRs were detected in 53.3% of the human hair samples. The highest OPFRs concentrations were found in rice and vegetables. Tri(2-chloroethyl)phosphate(TCEP), tris(2-chloroisopropyl)phosphate(TCIPP), and tri(2-ethyltexyl)phosphate(TEHP) were predominant in all food samples. OPFRs concentrations in foods were not significantly affected by the packaging materials. The mean dietary intakes of ΣOPFRs for adult males and females were 539 and 601 ng/kg body weight/day, respectively. The greatest contribution to these values is from rice, accounting for approximately 60% of the total intake, particularly from rice protein. Rice ingestion was considered a potential major pathway for human exposure to OPFRs, and regional differences in the levels of OPFRs in foods and dietary differences should be given more attention in the future.

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1. Introduction

Organophosphate flame retardants (OPFRs) are widely used as flame retardants, plasticizers, and antifoaming agents in various commercial products [1–6]. Previous studies have demonstrated that OPFRs have toxic effects (e.g., endocrine disruption, reproductive/developmental toxicity, neurotoxicity, and carcinogenicity) on living organisms [7–12] and that some OPFRs are associated with atopic dermatitis, asthma and allergic rhinitis in human beings and alter hormone levels and decrease semen quality in humans [13,14]. Therefore, assessing human exposure to OPFRs is necessary and urgent.

In most applications, OPFRs are added to products rather than being chemically bonded to them, and thus, they can easily diffuse into their surrounding environments. OPFRs can enter the human body via ingestion, inhalation, and dermal absorption through various sources and accumulate in milk and urine [15–17]. Although OPFRs have been detected in various environmental compartments, such as indoor air, dust, atmospheric particles [18–20], water [21–23], soil and sediment [24,25], rain and snow [23,26], fish and biota [27–29] worldwide, a broad survey of OPFRs in foods has not been conducted.

Rice is an economic, nutritious staple food consumed by millions of people around the world. In China, rice is a source of arsenic in diets and is the major pathway for methylmercury exposure [30,31]. Similarly, rice may absorb and accumulate OPFRs from the soil or atmosphere, which can subsequently enter the human body. Starches and proteins are the main components of rice, and these components are used extensively in the food and medicine industries. Therefore, the distributions of OPFRs in starches and proteins are also critical for the corresponding assessment of human exposure. Commonly consumed foods such as vegetables, meats, grains, fruits and beverages are an indispensable part of human nutritional health. The concentrations of OPFRs in these common foods may contribute to human exposure to OPFRs. These foods are stored using different types of packaging materials, which may affect OPFRs concentration in food. Hair is a good indicator of exposure to heavy metals, drugs, and organic pollutants [32,33]. Compared to human urine, hair has numerous advantages for human biomonitoring, such as easy collection, low cost, and easy transport and storage [32]. Previous studies showed that hair could be used as an indicator of human exposure to OPFRs [34,35]. Therefore, in the present work, the concentrations of OPFRs in hair are used as an indicator of human exposure to OPFRs.

In this study, the concentrations of six typical OPFRs in rice and other commonly consumed foods were analyzed using a gas chromatograph-triple quadrupole mass spectrometer (GC–MS/MS). The effects of the packaging materials on the OPFRs concentrations in food were preliminarily evaluated. Subsequently, human exposure to OPFRs was indicated by the concentrations of OPFRs in human hair. Finally, we assessed the health risks of OPFRs ingested through dietary sources to determine which foods significantly contributed to human exposure.

2. Materials and methods

2.1. Sample collection and preparation

Rice samples were collected from four representative areas in China (Hubei, Chongqing, Sichuan and Guangxi). The collected rice is representative, because these four areas are the key suppliers of rice in China. Hubei, Chongqing and Sichuan are located in southern China and are urban/industrial areas with large population densities. The main companies that manufacture or use OPFRs located in these areas are described in Fig. S1. Guangxi is a minority nationality region on the southern border of China. It is characterized as a rural and agricultural area with a small population density and with fewer anthropogenic sources of OPFRs pollution than the other three cities. Rice was picked in real areas of rice cultivation lands, as shown in Fig. S1. Each measurement was performed on mixtures of three rice samples from the same agricultural area. A total of 50 rice samples (18 of Sichuan, 18 of Chongqing, 7 of Hubei and 7 of Guangxi province) were analyzed. Prior to sample preparation, rice samples were ground into flours. To investigate OPFRs in starch or protein, rice samples (R1-R6) were prepared using an alkali method, as described in the Supplemental Material.

75 kinds of common food samples (information is provided in Tables S2 and S3), were obtained from supermarkets in Tianjin, China. These food samples were delivered from different areas of China and made from the dominate manufacturers in China. These food samples were grouped into six categories: beverages, dairy products, grains, vegetables, meats, and fresh fruits. The edible parts of the solid foods were freeze-dried and homogenized, and all samples were stored at −20 °C prior to analysis. Each measurement was performed on mixtures of three same food samples. Hair samples (45 samples, approximately 2 g per person) were collected from a subset of adult volunteers in Tianjin, China. Their ages ranged from 18 to 45. All participants provided permission for their participation, and were informed of the objectives of this research. The participants were all in good health and not engaged in work related to OPFRs. The hair was cut using stainless-steel scissors and subsequently stored in paper envelopes in the dark at 4 °C. After rinsing with ultrapure Milli-Q water, all hair samples were cut into small pieces (approximately 1 cm × 1 cm), and 1.0 g of hair sample was weighed to analyze OPFRs. All the samples were collected, shipped and stored according to strict quality assurance and quality control to avoid background contamination.

2.2. Analytical methods

The experimental procedures for sample preparation were described elsewhere [36–38] and were used with some modifications. The surrogate standard of dipentyl phthalate-3, 4, 5, 6-d4 (DPP-d4) was added to each sample prior to extraction. For solid foods, samples (1.0–10.0 g per sample) were extracted twice with microwave-assisted extraction for 30 min at 130 °C with acetone/hexane (1:1, v/v). For the beverages and dairy products, 50 mL of samples were extracted twice for 2 h with 100 mL of organic solvents (ethyl acetate for beverages and acetonitrile for dairy products) using ultrasonication. The extract combined was concentrated to approximately 2 mL on a vacuum rotary evaporator. A glass column, which was packed from bottom to top with 4 g of florisil, 4 g of neutral silica gel, and 2 g of anhydrous sodium sulfate, was used for sample purification. Prior to packing the column, the florisil, neutral silica gel, and anhydrous sodium sulfate were prewashed with dichloromethane and activated for 12 h at 130, 160 and 450 °C, respectively. The column was prewashed with methanol and *n*-hexane prior to loading the extract. Acetone: ethyl acetate (3:7, v/v) was used to elute the analytes. The analytes were passed through a disc filter (0.2 μm, Waters, Milford, MA, U.S.A.), dried using automated nitrogen evaporation, suspended in 200 μL of acetone, and subsequently analyzed using GC–MS/MS. Procedure blanks and the recovery rate of OPFRs were also simultaneously processed and analyzed to assure the quality of the analytical results. The information of chemicals and reagents, instrumental

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