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A comprehensive assessment of human exposure to phthalates from environmental media and food in Tianjin, China

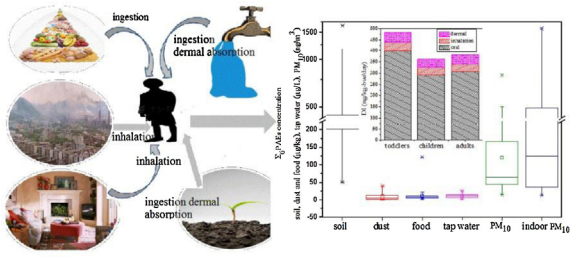
Yaqin Ji[a,b,*], Fumei Wang[a], Leibo Zhang[a,b], Chunyan Shan[a,b], Zhipeng Bai[c], Zengrong Sun[d,*], Lingling Liu[a], Boxiong Shen[a]

[a] College of Environmental Science and Engineering, Nankai University, Weijin Road 94, Tianjin 300071, China
[b] State Environmental Protection Key Laboratory of Urban Ambient Air Particulate Matter Pollution Prevention and Control, Weijin Road 94, Tianjin 300071, China
[c] Chinese Research Academy of Environmental Sciences, Beijing 100012, China
[d] School of Public Health, Tianjin Medical University, Qixiangtai Road 22, Tianjin 300070, China

HIGHLIGHTS

- PAEs levels in various environmental media and food were studied.
- PAEs daily intake was estimated via ingestion, inhalation and dermal absorption.
- DBP and DEHP were the most frequently detected PAEs.
- Contaminated air was another important exposure source except food and water.

GRAPHICAL ABSTRACT



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ABSTRACT

A total of 448 samples including foodstuffs (rice, steamed bun, vegetables, meat, poultry, fish, milk and fruits), ambient PM_{10}, drinking water, soil, indoor PM_{10} and indoor dust samples from Tianjin were obtained to determine the distribution of six priority phthalates (PAEs) and assess the human exposure to them. The results indicated that DBP and DEHP were the most frequently detected PAEs in these samples. The concentrations of PAEs in environmental media were higher than those in food. We estimated the daily intake (DI) of PAEs via ingestion, inhalation and dermal absorption from five sources (food, water, air, dust and soil). Dietary intake was the main exposure source to DEP, BBP, DEHP and DOP, whereas water ingestion/absorption was the major source of exposure to DBP, DEHP and DOP. Although food and water were the overwhelmingly predominant sources of PAEs intake by Tianjin population, contaminated air was another important source of DMP, DEP and DBP contributing to up to 45% of the exposure. The results of this study will help in understanding the major pathways of human exposure to PAEs. These findings also suggest that human exposure to phthalate esters via the environment should not be overlooked.

1. Introduction

Phthalates (phthalate esters, PAEs) are a group of plasticizers or softening agents that have been widely used in numerous consumer products and building materials [1,2]. They are also a class of endocrine-disrupting chemicals (EDCs) that can affect the reproductive system in laboratory animals [3–5]. For instance, Hauser et al. [6] and Duty et al. [7] found an association between DNA

* Corresponding author at: Corresponding authors at: Nankai University, College of Environmental Science and Engineering, Weijin Road 94, Tianjin, Tianjin 300071, China. Tel.: +86 22 23503397; fax: +86 22 23503397.
E-mail address: jiyaqin@nankai.edu.cn (Y. Ji).

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damage in sperm and environmental exposure to phthalates. Epidemiological studies also reported a relationship between high phthalate exposure and effects on the human endocrine or reproductive systems [2,8–10] and children's intelligence or behavior [11–14]. Furthermore, asthma and allergies were reported to be associated with di(2-ethylhexyl)-phthalate (DEHP) and butyl benzyl phthalate (BBP) exposure, respectively [1,15].

Phthalates, which are not chemically bound to the polymer, can be released easily from production into the environment and food. There is a wealth of data on phthalate distribution in various media. In China, phthalate levels in water samples have been monitored in several cities [16–19]. Wang et al. [20] determined the atmospheric levels of phthalate in total suspended particles (TSP) and gas phases in the atmosphere of Nanjing City, and Zeng et al. [21] detected PAEs in atmospheric deposition in Guangzhou City. Other studies analyzed phthalates in soil [22–24]. Data on phthalates in all types of diet have also been reported in the literature [25–27]. Guo et al. [28] and Kang et al. [29] conducted a study of phthalates in dust. The above-mentioned studies indicated widespread pollution of phthalates in the environment and universal exposure of humans to phthalates in China.

Due to the pervasive use of phthalates, individuals are unavoidably regularly exposed to phthalates via multiple sources and pathways, such as ingestion via food, drinking water, dust and soil; inhalation of air (outdoors and indoors); and dermal absorption from dust, soil, water and consumer products [6,15]. The European Food Safety Authority (EFSA) specified tolerable daily intakes (TDI) of 0.01 mg/kg-bw for DBP and 0.05 mg/kg-bw for DEHP. The Scientific Committee on Toxicity, Eco-toxicity and the Environment (CSTEE) formulated TDI limits for the exposure of infants and young children to some phthalates migrating from toys, and the TDI limits set down were as follows (in μg/kg/day): 37 for DEHP, 200 for BBP and 100 for DBP. The issue of phthalate pollution was also assessed by the U.S. Environmental Protection Agency (USEPA) which suggested reference doses (RfD) for the daily intake of phthalates of 800, 100, 200 and 20 μg/kg-bw/day for diethyl phthalate (DEP), DBP, butyl benzyl phthalate (BBP) and DEHP, respectively. The estimated intake of DEHP via dust ingestion has been reported in Denmark [30] and the USA [28]. In the USA [31], the DI values of DEHP, DBP, DEP, and BBP were estimated to be 0.60, 1.56, 12.34 and 0.73 μg/kg-bw/day, respectively. In Germany, Koch et al. [32] determined a median intake of 13.8 μg/kg-bw/day for DEHP via urine analysis. In China, the DIs of phthalates in children were estimated by detecting urinary phthalate metabolites, which were 285 μg/day for DEP, 580 μg/day for DBP and 182 μg/day for DEHP [33]. Zhang et al. [34] estimated that DBP exposure for Chinese infants due to indoor air inhalation was 664.332 ng/kg-bw/day.

In China, PAEs account for 90% of the plasticizer usage in PVC production. Tianjin, the largest harbor in Northern China, is a fast-growing and economically developed city. A comprehensive industrial system has been built including integrated machinery, electronics, petroleum and chemicals, metallurgy, textiles and vehicles. The PAE concentrations in air, soil, water and blood have been reported in Tianjin [35,36]. However, to date, no data on human exposure to PAEs from these pollution sources are available in Tianjin.

In this study, we conducted a comprehensive investigation of phthalate exposure in Tianjin. We investigated the concentrations of six ubiquitous phthalates [dimethyl phthalate (DMP), DEP, DBP, BBP, DEHP, and di-*n*-octyl phthalate (DOP)] in ambient air, drinking water (tap water), soil, indoor air and dust, and food samples collected in Tianjin. Furthermore, using the evaluation models of phthalate exposure sources, we estimated exposure doses of phthalates in humans by determining daily intake (DI) through various sources and pathways in Tianjin. The ratio of each source/pathway to phthalates exposure for various age groups was also calculated. The study of phthalate exposure is particularly significant in China, where environmental PAEs are widespread and there are few regulations restricting the production and usage of PAEs.

2. Materials and methods

2.1. Samples

2.1.1. Collection and preparation

2.1.1.1. Ambient PM_{10}, soil, indoor PM_{10} and dust. A total of 105 ambient PM_{10}, 84 soil, 82 indoor PM_{10} and 26 dust samples were collected in Tianjin. Specific details on sampling and sampling sites can be found in our previous studies [34–36].

2.1.1.2. Drinking water (tap water). A total of 92 Tap water samples were collected from residents' homes located in six districts in Tianjin City during the dry season (in June, 2010) and the wet season (in July, 2010), respectively. The water samples were placed in 1 L solvent-cleaned brown glass bottles at ambient temperature and 0.5 g sodium thiosulfate was added to eliminate residual chlorine and 1.25 g sodium chloride to adjust the salinity. These samples were analyzed within 24 h. Prior to extraction, the pH of the samples was adjusted to 2 with 1 N HCl solution.

2.1.1.3. Foodstuffs. During October and November 2010, daily foods consumed by Tianjin residents were randomly purchased from grocery stores or markets. The food samples included meat, poultry, fish, vegetables, fruit, milk, and staple food samples (Supplementary materials (SM) Table SM-1). The food samples were analyzed in the raw state with the exception of the steamed rice and bun. They were stored at −4 °C (for no more than one day) on a fresh weight basis until analysis.

A questionnaire was used to record sociodemographic characteristics of the participants, living conditions, building characteristics and age, possible sources of contaminants, cleaning habits and dietary habits.

2.2. Chemical extraction

Details of the reagents, analytical instruments and extraction methods used are provided in the supporting material. Briefly, whole PM_{10}, soil and dust samples were extracted using a KQ-300DE ultrasonic extractor (Shumei, Co., Ltd. Kunshan, China), as described previously [34–36]. Drinking water samples were extracted using a solid phase extraction (SPE) technique with a low carbon-C18 column at a flow rate of approximately 4 mL/min. Food samples were extracted using a Scientz-IID ultrasonic homogenizer instrument (Scietz Biotechnology CO., Ltd, Ningbo, China). All extracts were concentrated under a gentle nitrogen stream to a final volume of 2 mL by dichloromethane after known quantities of internal standard were spiked. The extracts were finally transferred into auto-injection vials and stored at −4 °C.

2.3. Instrumental analysis

Determination of phthalates was carried out by gas chromatography (Agilent Technologies 7890 N) equipped with a mass spectrometer (Agilent Technologies 5975) in the selective ion-monitoring (SIM) mode. The details of this method are described by Kong et al. [36]. DMP, DEP, benzyl benzoate (internal standard), DBP, BBP, DEHP and DOP were eluted at 8.590, 10.608, 12.982, 15.399, 19.741, 21.648 and 23.362 min, respectively, and the total run time was 26 min.