Journal of Hazardous Materials 261 (2013) 753–762

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Size fraction effect on phthalate esters accumulation, bioaccessibility and *in vitro* cytotoxicity of indoor/outdoor dust, and risk assessment of human exposure

Wei Wang, Fu-Yong Wu, Min-Juan Huang, Yuan Kang, Kwai Chung Cheung, Ming Hung Wong*

State Key Laboratory in Marine Pollution – Croucher Institute for Environmental Sciences, Hong Kong Baptist University and City University of Hong Kong, Kowloon Tong, Hong Kong, PR China

HIGHLIGHTS

- The highest accumulation effect of phthalate in dust was found in <63 μm.
- Bioaccessibility of phthalates in dust varied with particle size.
- *In vitro* cytotoxic effect of dust extract decreased with particle size.
- Indoor dust ingestion accounted for the major source for DEHP exposure.
- DEHP *via* home dust resulted in high daily exposure and cancer risk (10^{-5}–10^{-4}).

ARTICLE INFO

Article history:
Received 20 September 2012
Received in revised form 22 April 2013
Accepted 24 April 2013
Available online 2 May 2013

Keywords:
Phthalate esters
Size fraction effect
Cytotoxicity
Bioaccessibility
Risk assessment
Dust

ABSTRACT

Indoor and outdoor dusts from two urban centers in the Pearl River Delta, China, were analyzed and phthalate esters varied from 4.95 to 2220 μg g^{-1} in indoor dust, significantly higher than outdoor dust (1.70–869 μg g^{-1}). Di-2-ethylhexyl phthalate (DEHP) was the dominant phthalate found and the highest distribution factor (DF) (1.56 ± 0.41) was noted in the <63 μm fraction ($p < 0.05$). *In vitro* cytotoxicity of dust extract on human T cell lymphoblast leukemic cell line (CCRF-CEM) indicated by Lethal Concentration 50 (LC_{50}) decreased with particle size. The power model was found as a better fit for explaining the relationship between LC_{50} and phthalates ($R^2 = 0.46$, $p < 0.01$). Bioaccessibility of phthalates in dust varied with different particle sizes, with the greatest bioaccessible fraction (2.49–38.6%) obtained in <63 μm. Risk assessment indicated that indoor dust ingestion accounted for the major source for DEHP exposure (81.4–96.4% of non-dietary exposure and 36.5% of total exposure), especially for toddlers. The cancer risks associated with DEHP *via* home dust were high (10^{-6}–10^{-4}), with 10% of houses estimated with unacceptable risks (>10^{-4}). After corrected with the bioaccessibility of phthalates, the cancer risks of dust exposure were moderate (10^{-7}–10^{-5}).

1. Introduction

Phthalate esters occur ubiquitously in the indoor environment and in food, as they are used as plasticizers in consumer products and building materials. Several million tons of phthalates are produced worldwide each year for the production of soft polyvinyl chlorine (PVC) and other plasticizers [1]. Inhalation, dermal absorption, and dietary intake are three major pathways for human exposure to phthalates esters. Indoor phthalate is found to positively correlate to asthma and allergic symptoms in human, and negatively correlate with the intelligence in children behavior [2,3]. House dust serves as a reservoir of many semi- and nonvolatile substances, contributing to the high concentration of phthalate esters. Consequently, non-dietary intake of indoor dust is a significant exposure pathway for human [4]. However, phthalate data on residential dust, especially in the Pearl River Delta (PRD) of south China, is limited. Outdoor dust is an important indicator of air deposition, which may impose adverse health effects on children [5,6]. Besides, size fractionation into particulate matter with diameter smaller than 2.5 μm and 10 μm ($PM_{2.5}$, PM_{10}) and total suspended particle (TSP) *via* vehicle and human activities are of concern [7]. In addition, pollutants in different size fractions of dust may also be transferred into the human body *via* oral ingestion and dermal contact. This study is also the first attempt to

* Corresponding author at: Croucher Institute for Environmental Sciences, and Department of Biology, Hong Kong Baptist University, Kowloon Tong, Hong Kong, P.R. China. Tel.: +852 34 117746; fax: +852 34 117743.
E-mail address: mhwong@hkbu.edu.hk (M.H. Wong).

0304-3894/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jhazmat.2013.04.039

report the effects of particle size on phthalates accumulation in dust.

Previous studies revealed that the sources of human exposure to phthalates vary, depending on the geographic area, phthalates types and the exposure models used [1]. Recently, it has been noted that the use of "bioaccessibility" based on *in vitro* digestion model would provide more accurate assessment on contaminant. The bioaccessible fraction has been recognized as the bioavailable portion of the tested contaminant, which is usually significantly lower than the solvent extractable portion [8,9]. Several studies have investigated the bioaccessibility of persistent organic pollutants (POPs), such as polycyclic aromatic hydrocarbons (PAHs) [8] in fish muscle, polybrominated diphenyl ethers (PBDEs) [10] in dust and (organochlorine pesticides) OCPs in soil [11]. While only one study related to the phthalates in indoor dust and revealed that oral bioaccessibility for phthalates of indoor dust ranged from 10.2% (DEHP) to 32% (DMP) and decreased with the K_{ow} value [12]. Tang et al. [13] and Wang et al. [8] found that the bioaccessibility of PAHs and OCPs in soil and fish muscle was negatively correlated with the K_{ow} values of congeners. However, there currently is no information related to the size fraction effects on the bioaccessibility of phthalates in dust or soil, and it is hoped that this study will generate some relevant data.

Furthermore, cytotoxicity of the dust extract based on human cell line could be used as a bioassay to characterize the toxicity of contaminants contained in dust. Such combination of chemical analysis and bioassay using human cell comprehensively explain the potential contaminants in dust and health risk for human [12]. So far there is a lack of information on the particle fraction effect on the cytotoxicity of dust which indicates the toxic potential of different fractions of dust on human body. Human hepatocellular liver carcinoma cell line (HepG2) and human skin keratinocyte cell line (KERTr) have been applied to better understand oral ingestion [14] and dermal contact pathways accordingly [15]. However, considering the possibility of asthma and allergic symptoms may be related to phthalate in dust [2,16], and the use of human T cell lymphoblast leukemic cell line (CCRF-CEM) is therefore employed to indicate any effects on the immune system [17].

Thus, it is hypothesized that: (1) the size fraction of particles could affect phthalate accumulation in dust and its subsequent bioaccessibility and cytotoxicity of dust; and (2) indoor dust exposure would be another major contributor to phthalate exposure for residents of PRD. The objectives of this study were: (1) to determine the concentrations and profiles of phthalates in both indoor and outdoor dust in two populated urban centers of PRD; (2) to examine the effects of particle size fraction on phthalates accumulation; (3) to study the dust size fraction effect on the cytotoxicity of dust extract on human CCRF cell line; (4) to investigate the bioaccessibility of phthalate in dust and the size effect on bioavailability; and (5) to evaluate the daily intake (DI) of phthalates *via* indoor dust and assess the related health risks.

2. Materials and methods

2.1. Sampling

A total of 120 outdoor (90 in Guangzhou and 30 in Hong Kong) and 40 indoor (20 in Guangzhou and 20 in Hong Kong) dust samples were collected from 5 and 6 different urban districts from Guangzhou and Hong Kong, respectively, from August to October 2010. The sampling urban areas comprised of Tianhe, Liwan, Yuexiu, Haizhu and Panyu in Guangzhou and Ap Lei Chow, Shek Tong Tsui, Yau Ma Tei, Kwun Tong, Tuen Mun and Tin Shui Wai in Hong Kong. The collection locations of outdoor dust are indicated in Fig. S1 and the sampling details are described in our previous study [6]. Approximately 100 g of the outdoor dust particles accumulated on the impervious surfaces of the pavement and road within a 5-m radius circle were collected using plastic brushes and dustpans by gentle sweeping motion to collect fine particles. Before each sampling, brushes, dustpans and vacuum cleaners were cleaned. Thirty-two sampling locations in GZ were chosen to represent seven various functional classes designated to reveal the pollution impacts from various human activities: Traffic Area (TR), Central Business District (CB), Residential Area (RA), Mixed Residential and Commercial Area (MRC), Industrial Nearby (IN), Suburban Road (SB) and Park and Green Area (PG).

Indoor dust samples were collected in the same period of outdoor dust sampling in 2010. In the current work, indoor dusts for phthalate esters analyses were collected in the living room and bedrooms by vacuuming the floor, sofa, and electric appliances with a small vacuum cleaner. Vacuum cleaner bags from 40 households were located in Tianhe ($n=4$), Liwan ($n=4$), Yuexiu ($n=4$), Haizhu ($n=4$) and Panyu ($n=4$) for Guangzhou; while Ap Lei Chow ($n=3$), Shek Tong Tsui ($n=3$), Yau Ma Tei ($n=4$), Kwun Tong ($n=4$), Tuen Mun ($n=3$) and Tin Shui Wai ($n=4$) for Hong Kong of Pearl River Delta. Table S1 gives a descriptive profile of the sampling environments in details. Both indoor and outdoor dust samples were then placed in a dessicator to remove moisture, sieved (<0.1 mm), and homogenized using mortar and pestle. For phthalates fractionation analyses, the collected outdoor dust was size-fractioned by sieving using four stainless sieves (2000, 280, 100, 63 μm), resulting in the following fractions: <63, 63–100, 100–280 and 280–2000 μm.

2.2. Extraction and analysis of phthalates

Each dust sample (about 2 g) was extracted for 18 h with 100 mL acetone/dichloromethane/n-hexane (1:1:1, v/v/v) in a Soxhlet apparatus [18]. The concentrated extract was cleaned up using a florisil column according to the EPA Standard Method 3620B [19]. The concentrated dust extracts were evaporated to 500 μL by rotary evaporator (Buchi, Japan) and under a gentle N_2 stream. Deuterated PAHs (acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12}) were then added as internal standards for quantification. Phthalates were analyzed by Agilent Technologies 890A GC system and 5973 C inert Mass Selective Detector (GC-MS) EI with 30 m HP-5MS column (0.25 mm diameter and 0.25 μm film thickness). The following 13 phthalate esters investigated in this study were: dimthyl phthalate (DMP), diethyl phthalate (DEP), di-n-propyl phthalate (DPRP), diisobutyl phthalate (DiBP), di-n-butyl phthalate (DBP), bis (2-methoxyethyl) phthalate (DMEP), di-n-hexyl phthalate (DHP), butyl benzyl phthalate (BBP), di-2-ethylhexyl phthalate (DEHP), dicyclohexyl phthalate (DCHP), di-n-octyl phthalate (DnOP), dinonyl phthalate (DNP) and di-isodecyl phthalate (DiDP) in order of retention times. Phthalate esters were confirmed by three criteria: (1) GC retention times matched (±0.05 min) those of standard compounds; (2) qualifier to target ratios (±20%) matched those of standard compounds; and (3) signal to noise ratio was greater than 3.

2.3. Bioaccessibility and risk assessment

The physiologically based *in vitro* digestion test was performed according to the methods described in [8,9]. The digestible solution was concentrated to 200 μL for phthalate analyses. Deuterated PAHs (acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12}) were then added as internal standards for quantification. The bioaccessibility (%BA) of phthalate esters (gastric and intestine) were calculated as the ratio of the amount of phthalate in liquid phase to the total phthalates in dust [20]. The details of