



# Organophosphate esters and phthalate esters in human hair from rural and urban areas, Chongqing, China: Concentrations, composition profiles and sources in comparison to street dust<sup>☆</sup>

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## ABSTRACT

Human hair and street dust from rural and urban areas in Chongqing were collected to analyze Organophosphate esters (OPEs) and phthalate esters (PAEs). Concentrations of OPEs in urban hair were significantly higher than those in rural hair, whereas PAEs concentrations in rural hair were significantly higher than those in urban hair. Different composition patterns of OPEs were observed in rural and urban hair, where tris (2-chloroisopropyl) phosphate (TCIPP), tris (butyl) phosphate (TNBP) and triphenyl phosphate (TPHP) were the dominating analogues in rural hair, accounting for 62.1% of the OPEs burden, and tris (methylphenyl) phosphate (TMPP) exhibited a high contribution in urban hair, responsible for 51.3% of total OPEs, which differed from the composition profiles in corresponding street dust. Analogous composition patterns of PAEs were found in hair of both areas. Di-(2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DNBP), diisobutyl phthalate (DIBP) and diethyl phthalate (DEP) were the most abundant analogues in hair samples, while DEHP was the predominant analogue in dust samples. No clear tendency was obtained between the increasing ages and the concentrations of both compounds. Most OPEs and PAEs congeners showed significantly positive correlation with one another in rural hair. On the contrary, different correlation patterns were observed in urban hair for OPEs and PAEs, indicating multiple or additional sources existed in urban areas. Significant correlations of OPEs and PAEs were found between hair and corresponding street dust samples, but poor correlations of OPEs and PAEs were observed between rural hair and rural indoor dust, suggesting that street dust may be a predominant exogenous source for human exposure to OPEs and PAEs in this area.

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## 1. Introduction

A variety of chemical additives is commonly utilized in numerous consumer products to enhance the ideal physical properties. Organophosphate esters and phthalate esters may constitute the dominating part of plastic additives in our daily life (Luongo and Östman, 2016), and both compounds are widely used as flame retardants and plasticizers in an extensive range of household products such as upholstery materials, polyvinyl chloride (PVC) resins, polyurethane foam (PUF) furniture as well as personal care products (Net et al., 2015; Wei et al., 2015). Due to the global

restriction of some polybrominated diphenyl ethers (PBDEs) congeners (Stockholm Convention, 2009), the consumption of OPEs as the alternatives of PBDEs has been increasing sharply in the world (Wei et al., 2015). The estimated market demands for OPEs were reported to be 620 kilotons in 2013, accounting for 30% of the flame retardants globally (Sühring et al., 2016), and were expected to reach 680 kilotons in 2015 (Ou, 2011; Van der Veen and de Boer, 2012). In China, the production of OPEs in 2001 was estimated to be 100 kilotons, and the demands for OPEs were expected to rise by 15% annually (Ou, 2011). Furthermore, the global production of plasticizers was reported to be approximately 3.5 million tons annually, with more than 80% of the plasticizers constituted by PAEs (Kubwabo et al., 2013).

Only physically rather than chemically bound to the polymeric matrix, OPEs and PAEs can be easily released into the environment directly and/or indirectly, during manufacture, use, or disposal (Xie

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et al., 2007). To date, OPEs and PAEs are ubiquitous in the environment, including atmospheric aerosols, air, sludge, waters, dust, sediments, and biota, which has been well documented in some recent reviews (Net et al., 2015; Wei et al., 2015). Meanwhile, considerable attention has been attracted to their environmental behavior due to their potential adverse impact on ecosystem as well as on human health. Some PAEs were proved to be endocrine disrupting chemicals, and consequently United States Environmental Protection Agency (U.S. EPA, 2014) and the European Union (EU) (Net et al., 2015) have placed six PAEs congeners in the priority pollutants list. So far, extensive reports have also argued the adverse health issues associated with OPEs mostly including mutagenic, carcinogenic, and neurotoxic effect on human and biota (Meeker et al., 2013; Van der Veen and de Boer, 2012). For instance, TCIPP, tris (1,3-dichloro-2-propyl) phosphate (TDCIPP) and tris (2-butoxyethyl) phosphate (TBOEP) have been suspected to cause cancer (Van der Veen and de Boer, 2012), whereas neurotoxic effects have been observed for tris (2-chloroethyl) phosphate (TCEP), TNBP and TPHP (Wei et al., 2015). Additionally, hormone levels and semen quality in men can be affected through exposure to TPHP and TDCIPP in house dust (Zhao et al., 2016).

Given the ubiquity of OPEs and PAEs in the environment, human exposure to these chemicals is inevitable, and an increasing number of studies have reported the occurrence of OPEs and PAEs in human body worldwide (Frederiksen et al., 2010; Kim et al., 2014; Koch et al., 2004; Silva et al., 2004; Sundkvist et al., 2010), but most of them have focused on milk, serum and urine. Milk collection is only available in lactating women, and it is somewhat invasive, whereas blood is regarded to be an ideal matrix to monitor human exposure because blood can contact with all body organs and tissues, leading to the equilibrium between these chemicals in blood and those in the organs (Liu et al., 2016). However, the blood samples collection is also invasive and may cause ethical and practical issues, and besides, blood and urine samples can only reflect recent exposure due to the rapid metabolism of some chemicals in human tissues. Thus, human hair is a good example of noninvasive matrices for human biomonitoring owing to its low cost, accessible, sample stability and simple transportation and storage. So far, numerous studies have used hair to assess human exposure to a variety of organic pollutants, including polycyclic aromatic hydrocarbons (PAHs) (Toriba et al., 2003), PBDEs (Zheng et al., 2014), polychlorinated biphenyls (PCBs) (Covaci et al., 2002), and Dechlorane Plus (DPs) (Zheng et al., 2010). Data on the presence of OPEs and PAEs in hair is limited. To the best of our knowledge, only a few studies reported on the analysis of OPEs in hair (Kucharska et al., 2014, 2015; Liu et al., 2016; Qiao et al., 2016), and there is only one study where five DEHP metabolites were explored as compounds which could truly reflect the level of DEHP exposure in hair (Chang et al., 2013).

For many years, hair samples have been considered to represent both endogenous exposure (through deposition from blood at the hair follicle/root) and exogenous (transportation from air and dust) (Zheng et al., 2011; Qiao et al., 2016). Recently, some studies tend to indicate that the exogenous exposure is the primary sources of some organic pollutants. Zheng et al. (2011) found significant correlations between the concentrations in hair and dust for two flame retardants but not for PBDEs, while He et al. (2017a) argued that the female hairs likely suffered from more exogenous exposure to DDTs from ambient environment, whereas Zheng et al. (2016) revealed that exogenous sources (air and indoor dust) accounted for approximately 73% of the PCBs in human hair. All of the above studies may highlight the significant role played by the external environment such as dust in the distribution of pollutants in human hair, but to date, reports on OPEs and PAEs in human hair associated with street dust were limited.

To fill the gap of this relevant field, the objectives of this study were to determine the concentrations of OPEs and PAEs in human hair from rural and urban areas and to compare these levels, composition profiles to those corresponding street dust samples. Furthermore, the influence of age in the distribution of OPEs and PAEs in hair was also investigated. Comparison of OPEs and PAEs congener patterns between hair and dust, as well as the correlation patterns may help to verify whether street dust was a primary exogenous exposure pathway for human exposure to these compounds.

## 2. Material and methods

### 2.1. Chemicals and materials

PAEs standard mixtures, including dimethyl phthalate (DMP), diethyl phthalate (DEP), butyl benzyl phthalate (BBP), dibutyl phthalate (DNBP), diisobutyl phthalate (DIBP), di-n-octyl phthalate (DNOP), and di-(2-ethylhexyl) phthalate (DEHP), at 1000 mg/L each were purchased from o2si smart solutions (Charleston, SC, USA). Individual standard of OPEs containing triethyl phosphate (TEP), tributyl phosphate (TNBP), tris(2-butoxyethyl) phosphate (TBOEP), tri(2-ethylhexyl) phosphate (TEHP), tris(methylphenyl) phosphate (TMPP), tripropyl phosphate (TPRP), triphenyl phosphate (TPHP), tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCIPP), and tris(1,3-dichloroisopropyl) phosphate (TDCIPP) were purchased from Accustandard (USA). As for internal standards, TNBP-*d*<sub>27</sub> and TPHP-*d*<sub>15</sub> were purchased from Toronto Research Chemicals (Canada) while DEP-*d*<sub>4</sub> and DMP-*d*<sub>6</sub> were from Dr. Ehrenstorfer GmbH (Germany). All the solvent used in this study was of HPLC-grade. Acetone, n-hexane, and ethyl acetate were purchased from J. T. Baker (USA). Dichloromethane was obtained from Adamas (China), while methanol and acetonitrile were purchased from Merck (Germany). The SPE column (Cleanert-Flo-risil, 6ml/1000 mg) was supplied by Agela technologies (China).

### 2.2. Sample collection

Based on the population density and the degree of the urbanization, hair samples were collected in rural and urban area of Chongqing (Fig. 1). Site Jiangbei (E:106.5707, N: 29.5995) was selected as the urban area due to its high population density (about 600,000 people), while Hechuan County (E:106.2204, N:30.0872) with a population of 54,000 was regarded as the rural area, where the largest vegetable production base in Chongqing locates. The distance between the two areas is approximately 80 km. Hair samples from urban (n = 43) and rural (n = 154) were collected using stainless steel scissors after the volunteer participants' permission during May 2014 to September 2014. All samples were cut on the posterior vertex as close to the scalp as possible, and the hair lengths were 0–5 cm from the hair root. It was ensured that the dyed or bleached hair samples were excluded. The information of age was recorded. Due to limited number of the female hair samples, gender differences were not discussed in this study. In either region, the participants who reside in the same community were chosen, which could guarantee the similar environmental exposure the residents were subjected to. The occupations of the volunteers in urban area included government officers, salesmen, students and retired people. Most of the participants in rural area engaged in agricultural activities.

A total of 12 composited street dust samples containing 6 samples in rural area and 6 samples in urban area were collected in Wuma Road (E:106.2324, N: 30.0919) and Haier Road (E:106.5730, N: 29.6013) respectively, within 5 km around the residents' house by plant fiber broom under a stable weather condition in July 2014

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