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# Contamination of Phthalate Esters in Vegetable Agriculture and Human Cumulative Risk Assessment

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## ABSTRACT

Phthalate esters (PAEs), which can disturb human endocrine system, have been widely detected in vegetable greenhouse agriculture in China. To investigate the effects of environmental factors on PAEs in soils, pollution sources were identified, and the cumulative risks of PAEs to humans through vegetables in the diet were evaluated in this study. Ninety-eight vegetable samples were collected from 10 markets along with 128 vegetable and 111 soil samples from agricultural greenhouses and open field. All soil and vegetable samples were contaminated with PAEs, and the total concentrations of the 5 PAEs, including dimethyl phthalate (DMP), diethyl phthalate (DEP), di-iso-butyl phthalate (DiBP), di-*n*-butyl phthalate (DnBP), and di-2-ethylhexyl phthalate (DEHP), were in the ranges of 0.26–2.53 mg kg$^{-1}$ for soils and 0.95–8.09 mg kg$^{-1}$ for vegetables. Three components extracted from principle component analysis could explain 51.2%, 19.8%, and 15.3% of the total variance of the 5 PAEs in soils, which may represent three major sources of PAEs, *i.e.*, wastewater irrigation, application of fertilizers and pesticides, and plastic film. Long-term greenhouse cultivation could accumulate DEHP in soils, and a higher soil $FeO_x$ content reduced the DnBP concentration. Based on a survey of vegetables in the diet, the hazard index of PAEs was $< 0.15$ for individuals in different cities. The exposure of PAEs through vegetable intake was higher than the total exposure from other food stuffs, inhalation, and dermal absorption. More attention should be given to controlling PAEs in greenhouse vegetables.

*Key Words*: average daily intake, dietary survey, environmental factors, greenhouse agriculture, hazard index

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## INTRODUCTION

Phthalate esters (PAEs) are a group of 1,2-benzene dicarboxylate esters that are widely applied in commercial products, including foods, cosmetics, cleaning products, building materials, polyvinyl chloride plastics, and toys (Rudel and Perovich, 2009; Wittassek *et al*., 2011; Dodson *et al*., 2012). Since no covalent bond exists between PAEs and the surrounding matrix, these compounds easily leach into the environment and have been ubiquitously detected (Tropea *et al*., 2010; Guo and Wu, 2011; Guo *et al*., 2011).

It has been proven that PAEs are endocrine disrupters, which can interrupt reproductive system development (Mylchreest *et al*., 1999; Wang *et al*., 2012). Based on animal studies, di-*n*-butyl phthalate (DnBP) can interfere with androgen levels in rats during the period of reproduction gestation (Mylchreest *et al*., 1999). A study by Wang *et al*. (2012) reported that di-2-ethylhexyl phthalate (DEHP) could cause malfunction in the antral follicles of mouse ovaries. Thus, PAEs have been banned for use in toys and children clothes by the Council of the European Union (ECHA, 2016) and the U.S. Consumer Product Safety Commission (CPSC, 2008).

Greenhouse agriculture in China began in the 1960s and grew vigorously since the 1970s–1980s all over the country, with 1 000 ha greenhouse area for agriculture purpose in 2007 (He and Ma, 2007). The temperature and humidity inside greenhouses are higher than those outside, especially in winter and spring, and vegetables inside can grow faster and have higher yields. The reported data showed that the total concentration of PAEs in agricultural soils was in the range of 0.51–7.16 mg kg$^{-1}$, including dimethyl phthalate (DMP), diethyl phthalate (DEP), di-iso-butyl phthalate (DiBP), Dn-

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BP, DEHP, and benzyl butyl phthalate (BBP), among which DnBP and DEHP were the two most abundant PAEs detected in the soils (Ma *et al.*, 2015). Vegetables grown in greenhouses can take up PAEs from soil through their roots and from the atmosphere through their leaves. Xiao *et al.* (2012) showed that the total concentration of PAEs in the vegetables from typical greenhouse agriculture was 0.46–12.0 mg kg$^{-1}$.

The PAE levels in soils are correlated to soil properties. It has been reported that soil organic matter (SOM) can sequestrate hydrophobic compounds during the course of aging, and that higher amounts of SOM sequestrate more organic pollutants (Nam *et al.*, 1998). The concentrations of dyes, pesticides, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons in soils have been reported to increase with higher SOM content (Chiou *et al.*, 1983; Sheng *et al.*, 2001; Chen *et al.*, 2003). The clay-silt content (particle size $< 50$ μm) is reported to play an important role in interacting with organic pollutants (Gillott, 1987; Wang *et al.*, 2011). In our previous research, DEP was shown to intercalate into the interlayer spacings of montmorillonite clay minerals (Wu *et al.*, 2015). The content of iron oxides ($FeO_x$) in soils has been defined as an index of soil activity (Patrick and Khalid, 1974; Waychunas *et al.*, 1993; Bowell, 1994), as $FeO_x$ can effectively react with organic pollutants in soils. Soil $FeO_x$ can facilitate adsorption, oxidation, heterogeneous photo-Fenton reactions, and microorganism metabolisms to degrade organic compounds (Beller *et al.*, 1992; Kwan and Voelker, 2002; Hug and Leupin, 2003; Barreiro *et al.*, 2007). However, correlations between organic pollutants and soil properties have been lightly investigated, and most of the studies only focused on the impact of SOM within small regions with a bivariate correlation (Chiou *et al.*, 1983; Sheng *et al.*, 2001; Chen *et al.*, 2003). To understand the impact of soil properties on organic pollutants, thorough and detailed analyses of a wide distribution of soil samples with varied properties are needed.

Previous research has reported the observation of PAEs and their metabolites in human urine (Koch *et al.*, 2007; Langer *et al.*, 2014; Wang *et al.*, 2015; Gao *et al.*, 2016), which indicates that the general population, especially children, are highly exposed to this group of compounds. Previous cumulative risk assessments of PAEs focused on exposure pathways of PAEs through air, dust, oil, beverages, and fish (Guo *et al.*, 2011, 2012; Schecter *et al.*, 2013). These studies found that dietary intake was the major exposure pathway (Schettler, 2006; Tropea *et al.*, 2010). However, limited attention has been given to vegetables, which have been contaminated with PAEs, but have not raised enough attention yet (Ma *et al.*, 2015). Vegetable dietary is an important part of our everyday diet; the average consumption of vegetables is 0.35 kg d$^{-1}$ for adults and 0.12 kg d$^{-1}$ for 6–11-year-old children (USEPA, 2011). Previous research has examined PAEs in vegetables and soils to estimate hazard index (HI) values (Niu *et al.*, 2014; Ma *et al.*, 2015); however, dietary habits and cooking styles (washing and stewing) were not included in the assessments, which could overestimate the average daily intake (ADI) of PAEs.

The objectives of this study were to (i) investigate PAE contamination levels in vegetables both sold on the market and grown in greenhouses; (ii) examine the effects of environmental factors on PAE levels in greenhouse soils with varied soil properties ($FeO_x$ content, clay-silt content, and SOM content) and greenhouse cultivation times in 10 cities in China; and (iii) conduct a human cumulative risk assessment of PAEs from vegetables on a group of 6–11-year-old children and a group of $>$ 11-year-old individuals based on a dietary survey. This research contributes to the understanding of PAE contamination in vegetable agriculture and provides a solid knowledge base for establishing PAE standards in greenhouse agriculture.

## MATERIALS AND METHODS

### *Chemicals*

Phthalate ester standards of DMP, DEP, DnBP, DiBP, and DEHP were obtained from Sigma-Aldrich, USA; neutral silica gel (100- to 200-mesh) and anhydrous sodium sulfate were obtained from Sinopharm Co. Ltd. (Shanghai, China); HPLC-grade acetone and *n*-hexane were purchased from Tedia Company Inc., USA. All chemicals and reagents were $>$ 99% pure and used without further purification. In this experiment, ultrapure water (18.2 MΩ cm$^{-1}$) from a Synergy UV ultrapure water system equipped with a Millipak-40 filter unit (Merck KGaA, Germany) was used to make the solutions. The physical and chemical properties of these 5 PAEs can be found in Table I.

### *Soil and vegetable samples from agricultural greenhouses*

In this study, 111 soil samples and 128 vegetable samples were collected during May–July in 2015 from greenhouses and open fields in 10 cities from north to south in China, including Shenyang, Beijing, Shouguang, Xianyang, Siyang, Haimen, Nanjing, Changshu, Fuzhou, and Kunming, where there was flourishing greenhouse agriculture in the suburban a-