



Status of phthalate esters contamination in agricultural soils across China and associated health risks



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ABSTRACT

The extensive utilization of phthalate-containing products has led to ubiquitous contamination of phthalate esters (PAEs) in various matrices. However, comprehensive knowledge of their pollution in Chinese farmland and associated risks is still limited. In this study, 15 PAEs were determined in soils from agricultural fields throughout the Mainland China. The concentrations of $\Sigma 15$ PAEs were in the range of 75.0–6369 $\mu\text{g kg}^{-1}$. Three provinces (i.e., Fujian, Guangdong and Xinjiang, China) showed the highest loadings of PAEs. Bis(2-Ethylhexyl) phthalate (DEHP) was found as the most abundant component and contributed 71.5% to the $\Sigma 15$ PAEs. The major source of PAEs in arable soils was associated with the application of agricultural plastic films, followed by the activities for soil fertility. Furthermore, the non-cancer and carcinogenic risks of target PAEs were estimated. The hazard indexes (HIs) of PAEs in all samples were below 1 and the carcinogenic risk levels were all within 10^{-4} . Results from this study will provide valuable information for Chinese agricultural soil management and risk avoidance.

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1. Introduction

Soil is an important environmental medium and a major reservoir for a diverse range of pollutants. With the rampant development of agriculture and industry, the soil environment has been extensively deteriorated. Many toxic pollutants have been introduced and remain in soils, such as organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), heavy metals and phthalate esters (PAEs) (Cai et al., 2008; Niu et al., 2013a, b). Among these persistent toxic substances (PTSs), PAEs have been demonstrated to be the most abundant organic contaminant in soils (Cai et al., 2008). Phthalate esters, a group of flexible, pliable and elastic chemicals, are widely used in plastic products, pesticides, cosmetics and personal care products (Gomez-Hens and Aguilar-Caballeros, 2003; Hu et al., 2003). It has been estimated that the global production and consumption of PAEs is approximately 6.0 million tons·year⁻¹ (Arbeitsgemeinschaft PVC and Umwelt e. V., 2006). Because of the widespread usage of phthalate-containing products, the residues of PAEs have been routinely detected in various matrices, such as soil,

water, air and sediments (Cai et al., 2008; Wang et al., 2012; Sun et al., 2013; Liu et al., 2014).

The application of agricultural plastic films is one of the important sources of PAEs in farmland soils. In 2011, the amount of plastic films applied agriculturally in China was approximately 2.29 million tons and the mulching area reached 19.8 million hectares (Department of Rural Survey National Bureau of Statistics of China, 2012). Another significant source of PAEs in farmland soil is associated with agricultural practices such as the application of sewage sludge, fertilizers, biosolids and irrigation wastewater, among others (Cai et al., 2007; Mo et al., 2008). In addition, the concentrations of PAEs in soils can also be influenced by atmospheric deposition, soil communities and meteorological conditions (Zeng et al., 2008, 2010).

Although PAEs are not as toxic as persistent organic pollutants (POPs), their ubiquitous existence poses great threats to humans. A phthalate incident that happened in Taiwan in 2011 aroused strong public concerns on the adverse effects of PAEs on human health (Li and Ko, 2012). Many epidemiology and toxicology studies have demonstrated that some PAEs, such as bis(2-Ethylhexyl) phthalate (DEHP), dibutyl phthalate (DnBP), benzyl butyl phthalate (BBP), diethyl phthalate (DEP) and dihexyl phthalate (DHP), are endocrine disrupting compounds (Gomez-Hens and Aguilar-Caballeros, 2003). Moreover, dimethyl phthalate (DMP), DEP, DnBP, BBP, DEHP and di-

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n-octyl phthalate (DnOP) have been classified as priority environmental pollutants by the U.S. Environmental Protection Agency (U.S. EPA) (Keith and Telliard, 1979). Therefore, numerous studies have addressed the potential risks, occurrence and sources of PAEs in diverse media (Hu et al., 2003; Zeng et al., 2008; Wang et al., 2013; Kranich et al., 2014). However, previous studies have largely focused on a regional scale. Although a national investigation was carried out in 2003, the information is still not sufficient for well understanding the PAE pollution in Chinese arable soils due to the limited number of sites and PAE species analyzed in that study (Hu et al., 2003). In addition, the potential risks of PAEs to human health via multiple pathways have been infrequently estimated. Therefore, a full-scale study on the status of PAE pollution in farmland soils at the national scale and associated health risks are of considerable significance for setting strategies to minimize their pollution and exposure risks.

In this study, 15 PAEs were measured in agricultural soils collected from 123 regions throughout China. Our aims were to characterize the spatial distribution features and congener profiles of PAEs, as well as to discern their possible sources. In addition, the non-cancer and carcinogenic risks of toxic PAEs in soils were also estimated for local residents via dietary and non-dietary routes. These results will provide baseline information for soil quality assessments and rational farming practices, thus protecting human health.

2. Materials and methods

2.1. Sample collection

In total, 123 soil samples were collected from agricultural fields in 31 provinces, municipalities or autonomous regions across China in April and May of 2013. The sampling sites were chosen according to the distribution of farmland soils in China (National Bureau of Statistics of China, 2013) and located by GPS (Fig. S1 in Supporting Information, SI). Before collection, overlying vegetation was thoroughly excluded. At each sampling site, five agricultural soil sub-samples (0–20 cm) were collected with a pre-cleaned stainless steel scoop and mixed to form a composite sample in a pre-cleaned aluminum foil bag. Then, the soil samples were immediately transported to the laboratory and stored at -20°C until analysis. Soils for pH measurement were freeze-dried, ground and passed through a stainless steel sieve (2 mm). Then, the remaining soils were further sieved through a 0.154 mm sieve for the analysis of PAEs and soil organic matter (SOM).

2.2. Sample extraction and analysis

A standard mixture of 15 PAEs, including DMP, DEP, diisobutyl phthalate (DiBP), DnBP, bis(2-Methoxyethyl) phthalate (DMGP), bis(4-Methyl-2-pentyl) phthalate (DMPP), bis(2-Ethoxyethyl) phthalate (DEEP), dipentyl phthalate (DnAP), DHP, BBP, bis(2-n-butoxyethyl) phthalate (DBEP), dicyclohexyl phthalate (DCHP), DEHP, DnOP and dinonyl phthalate (DNP) and a surrogate standard mixture, including dibenzyl phthalate, diphenyl isophthalate and diphenyl phthalate, were purchased from AccuStandard, Inc. (New Haven, CT, US). A solid internal standard of benzyl benzoate (99.5% purity) was acquired from Dr. Ehrenstorfer (Augsburg, Germany). Other solvents and reagents of residue analysis grade were obtained from J&K Chemical Ltd. (Beijing, China). Neutral silica gel, aluminum, florisil and anhydrous granular sodium sulfate (Na_2SO_4) were activated prior to use.

After being spiked with surrogate standards of ibenzyl phthalate, diphenyl isophthalate and diphenyl phthalate, the soil samples containing activated copper granules were extracted with dichloromethane (DCM) using a Soxhlet apparatus. The extract was then solvent-exchanged into hexane and cleaned on a column filled with Na_2SO_4 , florisil, neutral silica gel, neutral aluminum and Na_2SO_4 (from bottom to top). The column was first eluted with 20 mL of hexane and 70 mL of hexane/DCM (7/3, v/v). Then, the target analytes were recovered in the final eluate with 40 mL of hexane/acetone (4:1, v/v). After being concentrated and reduced to 0.5 mL, the extracts were spiked with the internal standard before instrumental analysis.

The quantitative analysis of PAEs was carried out on an Agilent 7890 GC coupled to an Agilent 5975C MS (Agilent Technologies, Avondale, PA, USA). An HP-5MS capillary column (30 m \times 320 μm \times 0.25 μm film thickness, Agilent Technologies Inc., Santa Clara, CA) was used for separation. The selective ion monitoring mode and electron impact were employed and the temperature of the transfer line and the ion source were 280 $^{\circ}\text{C}$ and 230 $^{\circ}\text{C}$, respectively. The gas chromatography temperature programs were as follows: initial temperature 80 $^{\circ}\text{C}$ for 1.0 min, increase at a rate of 10 $^{\circ}\text{C min}^{-1}$ to 180 $^{\circ}\text{C}$ (hold for 1.0 min), ramp at 2 $^{\circ}\text{C min}^{-1}$ to 260 $^{\circ}\text{C}$ (hold for 1.0 min) and finally ramp to 300 $^{\circ}\text{C}$ at 2 $^{\circ}\text{C min}^{-1}$ (hold for 5 min). The carrier helium gas was kept at a rate of 0.8 mL min^{-1} . A five-point calibration curve was made for

individual PAEs to quantify the amounts of analytes in samples using the internal calibration method.

2.3. Quality control and quality assurance

During the analytical procedures, all data were subjected to strict quality control and quality assurance measures. Blank samples were included with every 15 field samples to check for the interference and contamination. Only small levels of DnBP, DiBP and DEHP were detected in procedural blank and ranged from 0.996 to 3.20 $\mu\text{g kg}^{-1}$. Then the concentrations of PAEs in soil samples were all blank corrected. All samples were spiked with surrogate standards to monitor the recovery, which ranged from 80.7 to 99.9%. The recoveries of the 15 PAEs in the spiked blank and spiked matrix samples ranged from 76.7 to 105.1 and 75.2 to 101.9%, respectively. PAE calibration standards of were employed to calibrate the instrument every day. The limits of detection (LOD) of individual PAEs were calculated as three times the signal-to-noise ratio and fell in the range of 0.008–0.295 $\mu\text{g kg}^{-1}$.

2.4. Analyses of soil organic matter and pH

A pH electrode was used to determine soil pH with a soil/water (CO_2 -freed deionized) ratio of 1:2.5 (w/v). The soil organic matter content was measured by dichromate digestion at 180 $^{\circ}\text{C}$ according to Lu (2000).

2.5. Health risk assessment

The non-cancer and carcinogenic risks of PAEs were estimated according to the methods recommended by the U.S. EPA (2013). Because the local residents eat their own self-produced food, risks via non-dietary and dietary pathways were all involved. Among the individual PAE congeners studied, DEP, DnBP and DnOP were recognized as non-cancer compounds with respect to human health, while DEHP did present carcinogenic risk. In the non-cancer risk assessments of DEP, DnBP, DEHP and DnOP, their average daily doses (ADDs, $\text{mg kg}^{-1} \text{day}^{-1}$) via dietary (only considering food grown in soils) and non-dietary (soil ingestion, dermal contact and inhalation) routes were calculated as follows.

$$\text{ADD}_{\text{intake}} = \frac{C_{\text{soil}} \times \text{BAF} \times \text{IRF} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \times \text{CF} \quad (1)$$

where C_{soil} is the concentration of target chemical in farmland soil (mg kg^{-1}); BAF is the bioaccumulation factor of individual PAEs from soil to foodstuff (vegetables and grains); IRF is the daily intake rate of food by inhabitants (mg/day), where the IRF for children is supposed to be 1/3 of that for adults; EF is the exposure frequency (days yr^{-1}); ED is the exposure duration (yr); BW is the body weight (kg); AT is the average lifetime (days); and CF is the conversion factor (kg mg^{-1}).

$$\text{ADD}_{\text{ingest}} = \frac{C_{\text{soil}} \times \text{IRS} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \times \text{CF} \quad (2)$$

where IRS is the soil ingestion rate (mg day^{-1});

$$\text{ADD}_{\text{dermal}} = \frac{C_{\text{soil}} \times \text{SA} \times \text{AF} \times \text{ABS} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \times \text{CF} \quad (3)$$

where SA is the soil surface area ($\text{cm}^2 \text{day}^{-1}$); AF is the soil adherence factor (mg cm^{-2}); and ABS is the fraction of contaminant absorbed dermally from the soil (unitless).

$$\text{ADD}_{\text{inhal}} = \frac{C_{\text{soil}} \times \text{EF} \times \text{ED}}{\text{PEF} \times \text{AT}} \times 10^3 \quad (4)$$

where PEF is the particulate emission factor ($\text{m}^3 \text{kg}^{-1}$) and a default PEF equal to $1.36 \times 10^9 \text{ m}^3 \text{kg}^{-1}$ was used.

The hazard index (HI), which represents the total risks of a certain PAE in soil to human health through multiple exposure pathways, was calculated with the following equations.

$$\text{HQ} = \frac{\text{ADD}}{\text{RfD}} \quad (5)$$

$$\text{HI} = \sum \text{HQ}_i \quad (6)$$

where HQ is the hazard quotient; i represents the different exposure pathways; RfD ($\text{mg kg}^{-1} \text{day}^{-1}$) is defined as the daily maximum permissible level of contaminants, including the reference dose for ingestion and intake of contaminated food (RfD_o, $\text{mg kg}^{-1} \text{day}^{-1}$), the reference dose for dermal contact ($\text{RfD}_{\text{ABS}} = \text{RfD}_o \times \text{ABS}_{\text{CI}}$, $\text{mg kg}^{-1} \text{day}^{-1}$) and the reference dose of inhalation (RfD_i, mg m^{-3}); ABS_{CI} is the fraction of pollutant absorbed in the gastrointestinal tract (unitless).

The local inhabitants are considered to be exposed to non-cancer risks if the value of HI is greater than 1.

The ADD of DEHP via dietary pathways for carcinogenic risk assessment was calculated using Eq. (1) and these via non-dietary pathways were calculated based on the following.

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