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Science of the Total Environment

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https://doi.org/10.1016/j.scitotenv.2021.146281

Science of the Total Environment 778 (2021) 146281

Contents lists available at ScienceDirect

Science of the Total Environment

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

Contamination and human health risks of phthalate esters in vegetable and crop soils from the Huang-Huai-Hai region of China

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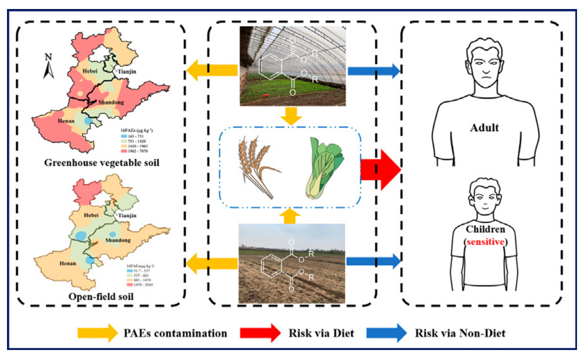
HIGHLIGHTS

- PAEs pollution in farmland of Huang-Huai-Hai region exhibited regional differences.
- The health risk of PAEs in crop soils require equal attention as vegetable soils.
- Type and concentration of PAEs and diet structure determined the degree of risk.
- The main non-carcinogenic and carcinogenic risk of PAEs in soils came from DEHP.
- Carcinogenic risk generated by DEHP is low in both dietary and non-dietary routes.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 19 November 2020
Received in revised form 17 January 2021
Accepted 28 February 2021
Available online 8 March 2021

Editor: Fang Wang

Keywords:
Bis(2-ethylhexyl) phthalate
Dibutyl phthalate
Noncarcinogenic risk
Carcinogenic risk
Agriculture soil

ABSTRACT

The widespread presence of phthalate esters (PAEs) in a variety of agricultural inputs has led to PAE contamination in soils and farm products. The endocrine disruption and carcinogenicity of PAEs have attracted much attention. Our research investigated the characteristics of PAE pollution in the soils of vegetable fields and adjacent stable crop fields in four provinces/municipalities across a major agricultural production area in China. We found that the concentrations of PAEs in vegetable soils were not significantly higher than those in stable crop soils. The noncarcinogenic and carcinogenic risks from bis (2-ethylhexyl) phthalate (DEHP) and dibutyl phthalate (DBP) to humans were calculated to represent the risk posed by PAEs. The results showed that diet was the main route for noncarcinogenic risks from PAEs in crop soil and vegetable soils. Because of the combined effect of the population dietary structure and the concentration of PAEs in soils, the noncarcinogenic risks from PAEs in crop soils were similar to or higher than those in vegetable soils. The same pattern was also applicable to the carcinogenic risk from DEHP. Low noncarcinogenic and carcinogenic risks posed by DEHP and DBP indicated that the current level of PAEs in soils did not decrease the safety of agricultural products in the Huang-Huai-Hai region. Stable crop soil, as a non-negligibly phthalate-polluted area, is worthy of as much attention as vegetable soil. This study provides scientific support for food safety risk assessment and control of PAE pollution in the main agricultural production areas in China.

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https://doi.org/10.1016/j.scitotenv.2021.146281

1. Introduction

Phthalate esters (PAEs) are utilized widely in polymeric materials as plasticizers to improve softness and flexibility (Li et al., 2016a). As PAEs are not chemically bound to plastic products, they can be easily released to the environment and are ubiquitous in various environmental compartments, including air, water, soil, and biota (Wang et al., 2013; Wang et al., 2018; Zhang et al., 2018b; Abtahi et al., 2019; He et al., 2019; Lee et al., 2019). Some PAEs, such as bis (2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), benzyl butyl phthalate (BBP) and diethyl phthalate (DEP), have endocrine disrupting effects based on many epidemiological and toxicological studies (Niu et al., 2014). Increasing evidence shows that PAEs have adverse effects on human reproductive and metabolic systems and may even cause cancer (Sayyad et al., 2017; Meeker et al., 2009; Mu et al., 2015; Du et al., 2016).

Because of the strict restrictions on the production and use of PAEs in the European Union and the United States, the majority of PAEs have been produced and consumed by developing countries such as Brazil, China, and India in recent years (Das et al., 2021). Many studies have reported the detection of PAEs in agricultural soils of different regions in China, with residual concentrations usually reaching the level of mg kg^{-1} in many areas (Lü et al., 2018; Zhou et al., 2020; Liu et al., 2019; Kong et al., 2012). Through reviewing 15 years of literature (2003–2018) on soil PAE contamination, Lü et al. (2018) pointed out that the levels of PAEs in soils in China were generally at the high point in the world, and their human health risk through soil ingestion and dietary intake should be taken seriously. Zhang et al. (2018a) found that the levels of human exposure to DEHP and DBP through the intake of vegetables planted in plastic greenhouses in China were considerably higher than those in western countries (4–17 times higher than those in the European Union, for example). Human exposure to PAEs via greenhouse vegetables in China has been widely studied by researchers, and vegetables are commonly identified as the main route of human exposure to PAEs (Lü et al., 2018; Wei et al., 2020; Yang et al., 2018). However, recent studies indicated that the total concentrations of six PAEs in wheat field soils (1.8–3.5 mg kg^{-1}) (Shi et al., 2019) were even higher than those in vegetable soils (from 5.42 μg kg^{-1} to 1.58 mg kg^{-1}) (Wei et al., 2020), indicating that the risk of PAEs through ingestion of cereal crops also needs considerable attention. Unfortunately, very little data comparing the contamination and human health risks of PAEs in vegetable and crop soils are available. Related research on vegetables is only related to greenhouse vegetables, and research on open-field vegetables is scarce.

As the largest developing country and agricultural power, China produces nearly a quarter of the world's agricultural products. According to the National Statistical Yearbook of China, China's cereal output in 2019 was 613 million tons, of which 2.75 million tons of cereals and 9.79 million tons of vegetables were exported (National Bureau of Statistics of China, 2020). The Huang-Huai-Hai region is located from 113°00′ E to the eastern coastline, between 32°00′ N and 40°30′ N (Li et al., 2011), and is rated as a first-class agricultural zone in China (Li et al., 2018). The top three provinces in terms of vegetable production in China in 2016 were: Shandong, Hebei, and Henan, all of which are located in the Huang-Huai-Hai region (Yu and Mu, 2019). Several studies have shown that PAEs are widely detected in agricultural soils of the Huang-Huai-Hai region (Zhou et al., 2020; Li et al., 2016b; Kong et al., 2012). It is of vital importance and representative to compare the pollution characteristics of PAEs and the associated human health risks in greenhouse/open-field vegetable soils and nearby crop soils of the Huang-Huai-Hai region, and to provide support for the pollution management and risk control of PAEs in agricultural soils.

On the other hand, PAEs as endocrine disrupting chemicals (EDCs) have raised much concern regarding their impact on human health (Gao et al., 2019; Shi et al., 2019; Feng et al., 2020; Li et al., 2020). Some PAEs have been proven to be carcinogenic (Caldwell, 2012). Wei et al. (2020) assessed the health risks of PAEs including DEP, DBP, DEHP and BBP in vegetables consumed via a dietary route in the Yangtze River Delta of China, and found that DEHP and DBP posed carcinogenic and noncarcinogenic risks, while the risks posed by DEP and BBP were negligible. Shi et al. (2019) assessed the health risks of six PAEs in wheat, and showed that DEHP and DBP were the main types of PAEs that posed risks, and children were the sensitive resident group.

Therefore, in the present study, residual concentrations of 16 PAEs were measured in 136 agricultural soil samples collected from four provinces/municipalities located in the Huang-Huai-Hai region (1) to investigate pollution characteristics of PAEs in vegetable and nearby crop soils, (2) to assess the carcinogenic and noncarcinogenic risks to local residents caused by PAEs via non-dietary and dietary routes, and (3) to reveal the main routes of exposure relevant to PAE effects on human health.

2. Materials and methods

2.1. Soil sampling

Soil samples were collected from the countrysides of fourteen cities in Hebei Province (HB), Shandong Province (SD), Henan Province (HN) and Tianjin municipality (TJ) in China (details are shown in Table S1). Sixty-nine vegetable soils (including 54 greenhouse soils and 15 open-field soils) and 67 open-field maize or wheat soils were selected in total, and the geographical locations were marked by GPS. Soil sampling was conducted in April 2019. Fig. 1 shows the layout of the sample plots at the site. Sampling methods and sample storage were the same as in our previous research (Zhou et al., 2020). For each field, three topsoil (0–20 cm) samples were collected across the field with precleaned stainless-steel shovels and these soils were mixed to form a composite sample. Samples were uniformly wrapped in tin foil bags to avoid contact with plastics. In the laboratory, the soil samples were sorted to remove stones and residual roots manually; then, the soils were packed in aluminium boxes, covered with tin foil, freeze-dried, ground in a porcelain mortar, homogenized by sieving through a stainless-steel sieve (60-mesh), and sealed in kraft envelopes. All the samples were stored at −20 °C prior to analysis.

2.2. Sample extraction and clean-up

The sixteen PAEs investigated in the present study were dimethyl phthalate (DMP), DEP, di-isobutyl phthalate (DiBP), DBP, bis (2-methoxyethyl) phthalate (DMEP), bis (4-methyl-2-pentyl) phthalate (BMPP), bis (2-ethoxyethyl) phthalate (DEEP), diamyl phthalate (DPP), di-n-hexyl phthalate (DHXP), BBP, bis (2-n-butoxyethyl) phthalate (DBEP), dicyclohexyl phthalate (DCHP), DEHP, dipentyl phthalate (DPhP), di-n-octyl phthalate (DNOP), and di-nonyl phthalate (DNP).

The procedure for the extraction of PAEs in soil is the same as the previous method used in our research (Zhou et al., 2020). In brief, 30 mL of extraction solvent (acetone: hexane = 1:1, v/v) was added to 10 g of soil in a glass centrifuge tube. All organic solvents used in the extraction process had been redistilled to minimize the background concentration of PAEs. Tin foil and polypropylene caps were used to seal each centrifuge tube. After vortexing for 1 min and being left overnight, the samples were extracted ultrasonically for 30 min, followed by centrifugation at 2000 rpm for 5 min. The residue was subsequently extracted with 20 mL of the extraction solvent twice. The above supernatants were combined in a spinner flask and concentrated with a rotary evaporator to 1–2 mL. The rotary evaporator had been precleaned with hexane for 20 min. Five milliliters of hexane was then added to exchange with the acetone, and the extract was concentrated to approximately 1 mL for subsequent clean-up steps.

The extracts required additional clean-up steps: A glass column (22.7 cm × 10 mm id) containing 2 g of Na_2SO_4 and 5 g of neutral silica gel was used to clean the extracts. The column was prewashed with 2 mL of hexanefour times. The extracts were eluted with 2 mL of the

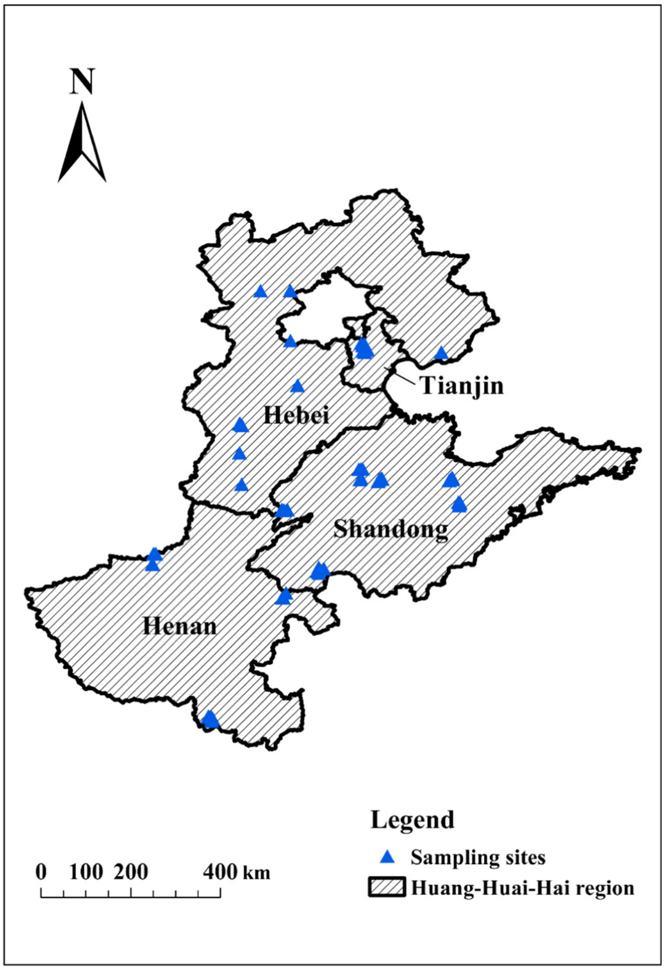

Fig. 1. Sample sites in the Huang-Huai-Hai region, China.

acetone: hexane (1:1 v/v) mixture five times. The eluate was concentrated to <1 mL and diluted to 1 mL using hexane for GC–MS analysis.

2.3. GC–MS analysis

Samples were analyzed on an Agilent 7890B gas chromatography-7000C triple quadrupole mass spectrometry (GC–MS) system (Agilent, USA) possessing a HP-5MS capillary column. The following oven temperatures were used: held for 1 min at 60 °C; increased to 220 °C at a rate of 20 °C per min and held for 1 min; increased to 280 °C at 5 °C per min and held for 1 min. Helium was used as the carrier gas (purity >99.999%), and the flow rate was 1.5 mL min^{-1}. The temperatures of the injection port, ion source and quadrupole mass spectrometer were set to 280 °C, 300 °C and 150 °C, respectively. The electron impact energy was 70 eV. One microlitre of extract was injected using splitless mode. We performed all analyses in selected ion monitoring (SIM) mode.

2.4. Health risk assessment

The noncarcinogenic and carcinogenic risks posed by PAEs were estimated according to the methods recommended by the US EPA (U.S. Environmental Protection Agency, 2013). It was assumed that the local residents consume food produced locally, and risks via non-dietary and dietary pathways were both assessed. Among the individual PAE congeners studied, DBP was recognized as a noncarcinogenic compound with respect to human health, while DEHP presented carcinogenic risk (Niu et al., 2014). In the noncarcinogenic risk assessments of DBP and DEHP, their average daily doses (ADDs, mg kg^{-1} day^{-1}) via dietary (only considering food grown in soils) and non-dietary (soil ingestion, dermal contact and inhalation) routes were calculated. A detailed description of the calculation methods is given in the Supporting Information. The parameters used for calculating the noncarcinogenic and carcinogenic risks are shown in Table S2.

2.5. Quality control and quality assurance

Quality control and quality assurance have been described in a previous study (Zhou et al., 2020). In brief, both solvent blanks and procedural blanks were analyzed for each batch of 10 samples to monitor potential background contamination. The extraction solvents (acetone and hexane) used to extract soil samples were redistilled on the same day and stored in a ground glass stoppered flask. After redistillation, the concentrations of PAEs in the extractants were all below the limits of detection. The data used in this article are the calibration data with the procedural blank value subtracted for each sample. We measured the recoveries and relative standard deviations (RSDs) of each PAE in spiked samples at 1 mg kg^{-1}. The average recoveries for PAEs varied from 75.6 to 117%, where the RSD for triplicate spiked samples was lower than 15.0% (Table S3). The limits of detection (LODs) were estimated as 3 times the signal to noise ratio. The LODs of all PAEs are shown in Table S4.

2.6. Data analysis

Origin 9 (OriginLab Inc., USA) was used to draw box plots. ArcGIS 10.2 was used to draw a map of sampling sites. Significance analysis for the difference between vegetable soils and crop soils (ANOVA, Duncan's test) was conducted by R 4.01 (R package *agricolae*).

3. Results and discussion

3.1. Overall characteristics of PAE contamination in the Huang-Huai-Hai region

Based on the analysis of 136 topsoil samples (0–20 cm), the descriptive statistics for PAE monomers and the total PAE concentrations in the surface soils of farmland in the Huang-Huai-Hai region are shown in Table 1. Among the 16 PAEs, DBP, DEHP, DiBP, DMEP, DMP, DEP, DBEP, DNOP and BBP were ranked according to their detection frequencies, which were 89.0%, 82.4%, 68.4%, 58.8%, 48.5%, 40.4%, 39.7%, 38.2% and 30.1% respectively. The concentrations of BMPP, DEEP, DPP, DHXP, DCHP, DPhP and DNP were all lower than their detection limits and are not discussed further. The total concentrations of the 16 PAEs in soil were 51.7–3569 μg kg^{-1}, and the mean value was 903 μg kg^{-1}, with a detection frequency of 100%. The total concentrations of six priority-controlled PAEs (DMP, DEP, DBP, DNOP, DEHP and BBP) recommended by the US EPA were 46.0–3423 μg kg^{-1}, with a mean value of 658 μg kg^{-1}, and the detection frequency was 100%. The concentrations of PAEs detected in this study were comparable to those reported in previous studies (Huang et al., 2013; Zhang et al., 2014; Chen et al., 2017; Gao et al., 2018). Chen et al. (2017) investigated 10 cities from the north to the south of China in 2015 and found that the concentrations of 5 PAEs in soil were 0.26–2.53 mg kg^{-1}. Wei et al.'s (2020) investigation on the Yangtze River Delta in 2019 found that the concentrations of 6 PAEs ranged from 5.42 to 1580 μg kg^{-1}. These results indicated that the residual levels of PAEs in soil were on the same order of magnitude in different regions of China, with little difference between years and regions. The concentrations of PAEs in this study were higher than those in the above two surveys, which may be related to the higher planting intensity in the Huang-Huai-Hai region as the main agricultural production area and a representative region for intensive agriculture. The amount of agricultural inputs used during agricultural production is large, especially for greenhouse vegetable soils. Due to the use of a

Table 1
Descriptive statistical summary of concentrations of individual PAEs (μg kg^{-1}) in agricultural soils across the Huang-Huai-Hai region in China (n = 136).

PAEs	Minmum	Maxmum	Median	Mean	SD[a]	CV[b]	Percentiles		DF[d]
							25th	75th	
DMP	nd[c]	116	23.5	30.1	22.2	0.74	15.6	36.2	48.5%
DEP	nd	622	35.9	119	153	1.28	15.5	220	40.4%
DBP	nd	1413	214	287	284	0.99	80.4	414	89.0%
BBP	nd	688	98.2	159	164	1.03	42.2	217	30.1%
DEHP	nd	2314	373	414	356	0.86	182	568	82.4%
DNOP	nd	606	85.5	152	155	1.02	22.7	248	38.2%
DiBP	nd	724	81.2	113	103	0.91	45.2	156	68.4%
DMEP	nd	817	48.2	86.4	116	1.35	18.3	121	58.8%
DBEP	nd	221	21.5	35.0	36.1	1.03	15.4	42.0	39.7%
BMPP	nd	nd	nd	nd	–	–	nd	nd	0.0%
DEEP	nd	nd	nd	nd	–	–	nd	nd	0.0%
DPP	nd	nd	nd	nd	–	–	nd	nd	0.0%
DXHP	nd	nd	nd	nd	–	–	nd	nd	0.0%
DCHP	nd	nd	nd	nd	–	–	nd	nd	0.0%
DPhP	nd	nd	nd	nd	–	–	nd	nd	0.0%
DNP	nd	nd	nd	nd	–	–	nd	nd	0.0%
6PAEs	46.0	3423	658	776	551	0.71	402	1030	100%[e]
16PAEs	51.7	3569	778	903	629	0.70	443	1197	100%[e]

Note.
[a] SD, Standard deviation.
[b] CV, Coefficient of variation.
[c] nd, Below detection level, see Table S3.
[d] DF, Detective frequency.
[e] 100% of samples had at least one of either 6 or 16 PAEs detectable.

large amount of agricultural film, greenhouse vegetable soil has become a key area of PAE pollution, and it has also become a pollution source of PAEs.

In the case of monomeric PAEs, the mean concentration of DEHP was 414 μg kg^{-1}, with a concentration range was <LOD to 2314 μg kg^{-1}; and the mean concentration of DBP was 287 μg kg^{-1}, with a range from <LOD to 1413 μg kg^{-1}. It can be concluded that DEHP and DBP were the main phthalate residues in the farmland soils of the Huang-Huai-Hai region. According to the soil control standard recommended by the United States (Table S4) (Department of Environmental Conservation, 1994), DBP had the highest overlimit ratio, with 67.6% of the samples exceeding the soil control standard, followed by DMP and DEP, with 30.1% and 16.2% of the samples exceeding the standard respectively. DEHP, BBP and DNOP did not exceed the standard. However, the residual levels of the six PAEs did not reach the soil treatment standards (Table S4). In addition to the six PAEs regulated by the EPA, DiBP, as an isomer of DBP, is also worthy of attention in this study. DiBP is a PAE monomer, in addition to DEHP and DBP, with a high average and maximum concentration, and high detection frequency. Other studies on farmland soils in China also detected high concentrations of DiBP, which showed that DiBP is a specific PAE pollutant in China and should be included in the formulation of a control list (Li et al., 2016b; Niu et al., 2014). Furthermore, DiBP is not included in the US EPA priority control list, and its basic toxicological data, metabolic pathways and possible effects on crops and humans have rarely been studied or reported, which could be a new research direction of PAEs.

3.2. Regional differences in PAE contamination in the Huang-Huai-Hai region

Because the source of PAEs is closely related to the cultivation mode and agricultural inputs, the PAE pollution characteristics are regional (Zhou et al., 2020). Therefore, the data were further analyzed to reveal the pollution characteristics of PAEs in different provinces and municipalities. As shown in Table 2, in general, the total amount of the 16 PAEs in the vegetable soils was highest in Tianjin, reaching 1151 ± 616 μg kg^{-1}, followed by Shandong Province (1130 ± 805 μg kg^{-1}), Henan Province (965 ± 753 μg kg^{-1}), and Hebei Province (910 ± 545 μg kg^{-1}). The pollution level in crop soil was highest in Hebei, with the mean value of 842 ± 714 μg kg^{-1}, followed by Shandong, Henan and Tianjin, with the mean concentrations of 782 ± 502, 760 ± 457 and 717 ± 335 μg kg^{-1}, respectively. The mean pollution degree of total PAEs in vegetable soils was higher than that in crop soils.

From the perspective of phthalate monomers, the situation in each province showed obvious differences (Table 2). In general, DEHP and DBP were the main phthalate pollutants in all four provinces, but their concentration levels were different. The level of DEHP in vegetable soils was highest in Tianjin municipality, followed by Shandong Province (Table 2). In terms of the average agricultural plastic film usage, Tianjin also has the highest of the four provinces, followed by Shandong Province (National Bureau of Statistics of China, 2019). DEHP, one of the main plasticizers used in polyvinyl chloride (PVC) materials and other products (Muchangos et al., 2019), enters the soil with heavy use of agricultural shed film. The length of the alkyl chain and the K_{ow} are important factors affecting the degradation rate and corresponding half-life of PAE (Staples et al., 1997; Cai et al., 2008). PAEs with longer alkyl chains were degraded more slowly (Wang et al., 2004). This supports the observation that the concentrations of DEHP were higher than those of other PAEs in the present study. The level of DBP in vegetable soils was highest in Henan Province, followed by Tianjin municipality (Table 2). Plastic film mulching was deemed to be a significant source of PAEs in the Huang-Huai-Hai region, which may be responsible for the higher DBP concentration there. DBP is the most used PVC plasticizer. In addition, its volatility and water-extractable properties result in poor durability and make it easier to release into the environment (Daniels, 2009). PAE contamination may also be caused by agricultural nonpoint source pollution, including that from fertilizers, pesticides, and livestock raising (Wei et al., 2020). The mean concentration of DBP reached 1967 μg kg^{-1}, five times higher than the concentrations of other PAEs in organic fertilizers (Mo et al., 2008). The dose of fertilizers in Henan Province was highest in the Huang-Huai-Hai region (National Bureau of Statistics of China, 2019), possibly leading to higher DBP concentrations in the soils of Henan Province than in those of the other provinces in this region. Organic matter introduced by fertilizers can also affect the fate of PAEs. At the initial stage, PAEs may be incorporated into soil humic substances (sequestration or bound residue formation), and their loss may be delayed (Cai et al., 2008).

The concentrations of other PAEs other than the main pollutants (DBP and DEHP) were relatively low and varied greatly from province to province. It is worth noting that the DEP content in Shandong

Table 2
The average concentration of individual PAEs (μg kg^{-1}) in agricultural soils of different provinces across the Huang-Huai-Hai region ($n = 136$)*.

Province		DMP	DEP	DBP	BBP	DEHP	DNOP	DiBP	DMEP	DBEP	PAEs
Hebei	Vegetable soil	7.60 ± 9.77a	4.12 ± 6.21a	190 ± 272a	102 ± 181a	363 ± 335a	117 ± 177a	72.1 ± 71.2a	40.2 ± 57.4a	14.9 ± 14.9a	910 ± 545a
	Crop soil	7.92 ± 9.58a	16.1 ± 51.0a	250 ± 285a	36.0 ± 58.8a	335 ± 241a	74.5 ± 123a	118 ± 169a	75.1 ± 192a	12.5 ± 17.5a	842 ± 714a
Henan	Vegetable soil	11.8 ± 9.84a	6.96 ± 7.6a	456 ± 449a	35.2 ± 80.0a	318 ± 249a	24.7 ± 46.8a	83.6 ± 122a	24.9 ± 29.6a	5.94 ± 9.12a	965 ± 753a
	Crop soil	6.15 ± 8.18a	4.58 ± 5.54a	295 ± 307a	3.56 ± 5.75a	353 ± 242a	2.66 ± 4.35a	60.9 ± 50.0a	32.6 ± 49.2a	3.02 ± 4.44a	760 ± 457a
Shandong	Vegetable soil	22.5 ± 20.0a	106 ± 157a	282 ± 269a	69.3 ± 147a	428 ± 576a	70.9 ± 142a	64.7 ± 77.5a	66.7 ± 91.1a	22.6 ± 32.5a	1130 ± 805a
	Crop soil	24.3 ± 30.4a	95.9 ± 151a	174 ± 174a	42.9 ± 97.4a	240 ± 241a	59.1 ± 106a	55.6 ± 82.7a	68.6 ± 94.2a	21.1 ± 41.4a	782 ± 502a
Tianjin	Vegetable soil	33.9 ± 31.1a	19.1 ± 18.4a	309 ± 187a	–	578 ± 339a	19.7 ± 48.2a	174 ± 105a	2.00 ± 4.91a	15.0 ± 36.7a	1151 ± 616a
	Crop soil	21.0 ± 22.9a	15.0 ± 13.3a	170 ± 165a	–	409 ± 107a	2.03 ± 4.97a	94.7 ± 77.2a	–	4.90 ± 7.65a	717 ± 335a

* ANOVA, Duncan's test; different letters indicate $p < 0.05$.

Province was much higher than that in the other provinces. As a phthalate with high water solubility and low K_{ow} ($lgK_{ow} = 2.42$), DEP has a faster degradation rate and is not tightly bound to soil organic matter (Wang et al., 2004). The high DEP concentration in Shandong should be related to a large and more recent input. The distribution of PAEs such as BBP and DNOP, which have obvious regional characteristics, may be related to regionally differentiated agricultural inputs. Except in Tianjin, where BBP was not detected, the BBP in vegetable soils was much higher than that in crop soils. The detection rate of BBP in agricultural film is as high as 96%, and the highest concentration is 220 μg kg^{-1} (Li et al., 2016b). According to our survey, most mulch film is composed of polyethylene; thus, BBP, as one of the major plasticizers in polyethylene, may be derived from mulching film (Zhang and Choudhury, 2017). The concentrations of various PAEs, except for DMP and DMEP, in Shandong Province were generally high, and the concentration differences among PAE monomers were small. In Tianjin, although the total amount of PAEs was the highest, with the concentration of DEHP being much higher than that in other provinces, the concentrations of other PAEs were very low, and some PAEs were not detectd. We suppose that it is inadequate to consider the concentration of PAEs alone, and the composition and concentration range of PAEs should be considered simultaneously to obtain a comprehensive understanding of the extent of pollution in regions.

3.3. Comparison of PAE pollution in vegetable and crop soils in the Huang-Huai-Hai region

In this study, 69 vegetable soil samples and 67 crop soil samples from the Huang-Huai-Hai region were analyzed. The results are shown in Fig. 2. The concentrations of the 9 PAEs analyzed in crop soils were comparable to those in vegetable soils. The main pollutants were DEHP and DBP in the vegetable soils (276 ± 372 μg kg^{-1} and 255 ± 264 μg kg^{-1}, respectively) and in the crop soils (257 ± 222 μg kg^{-1} and 218 ± 217 μg kg^{-1}, respectively). These two PAEs are also major pollutants in other regions of China (Chen et al., 2017; Gao et al., 2018). Therefore, monitoring these two PAEs is the primary task of pollution investigations in agricultural soils. However, the maximum value of DEHP in the vegetable soils (2314 μg kg^{-1}) was nearly three times that in the crop soils (812 μg kg^{-1}). Li et al. (2016b) found that DEHP, DiBP and DBP were the main species detected in plastic film, and the highest contents were 15.9, 16.7, 11.2 mg kg^{-1}, respectively. The aging of plastic film, as well as the evaporation of gas and the leaching of water vapor in vegetable soils, leads to a higher level of PAE pollution (Ma et al., 2015). Because of the migration of PAEs, the differences among the types of PAEs in different planting patterns was relatively small. Therefore, as endocrine disruptors, the human health risks posed by PAE contamination in both vegetable and crop soils are worth of considering.

In Shandong Province, 15 greenhouse vegetable soils, 15 open-field vegetable soils and 30 adjacent crop soil samples were collected to investigate the characteristics of PAE pollution in the three cropping systems. The results are shown in Table 3. The mean concentration of the sum of the 16 PAEs in the greenhouse vegetable soils was 1330 ± 946 μg kg^{-1}, which was more than twice of the mean concentration in the nearby crop soils (651 ± 123 μg kg^{-1}). However, the pollution degree in the open-field vegetable soils was similar to that in the adjacent crop soils, and the total concentrations of the 16 PAEs were 918 ± 604 μg kg^{-1} and 896 ± 466 μg kg^{-1}, respectively. The total concentration of the 16 PAEs followed the order of greenhouse vegetable soils > open-field vegetable soils ≈ crop soils near open-field vegetable soils > crop soils near greenhouse vegetable soils. For the PAE monomers, the DEHP pollution degree in the greenhouse vegetable soils was higher than that in the other soils. Chen's research also showed that DEHP tended to accumulate in greenhouse soils (Chen et al., 2017). For DBP, the pollution degree in the greenhouse and open-field vegetable soils was similar, and the pollution degree of in the crop

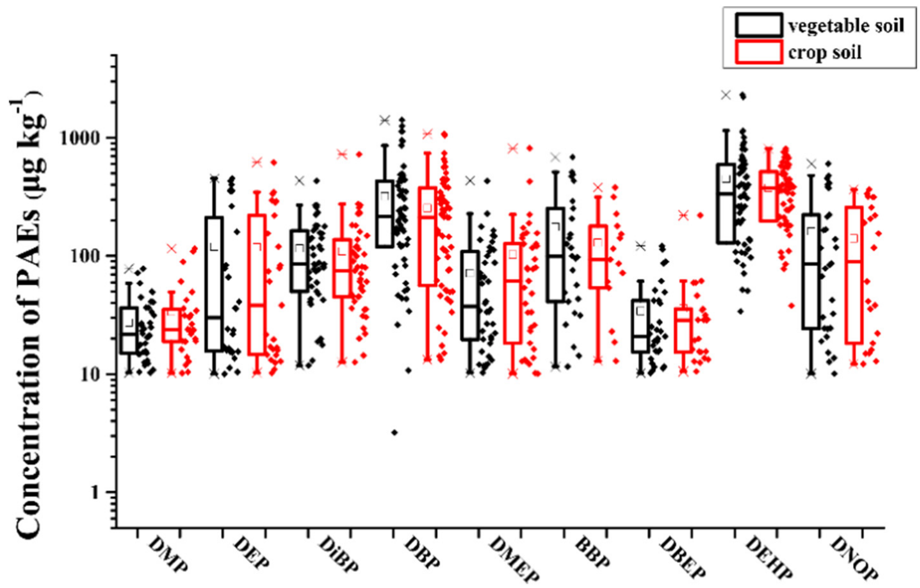

Fig. 2. Concentrations of PAEs detected in greenhouse and open-field soils in the Huang-Huai-Hai Region, China (The upper and lower bounds of the boxes indicate the 75th and 25th percentiles, respectively. The horizontal lines within the boxes indicate median values, and the square within the boxes indicate mean values. The upper and lower limits of the whiskers indicate 95% and 5% values, respectively, and forks above or below the whiskers indicate outlier values. Scattered points indicate the concentration of each sample. n = 136).

soils near the two types of vegetable fields was also similar. However, the concentration of DBP in the vegetable fields was higher than that in the crop soils. In contrast, the concentration of BBP in the greenhouse vegetable soils was the lowest, followed by that in the adjacent crop soils. In the open-field vegetable soils and adjacent crop soils, the concentration of BBP was relatively high. It has been explained above that the content of BBP is related to the use of agricultural film, especially mulching film (Zhang and Choudhury, 2017). In the region studied, open-field vegetable soils were sometimes also covered with mulching film to maintain the soil temperature and moisture. Unlike the relatively closed environment in a greenhouse (Wang et al., 2020), open fields are conducive to the migration of BBP, so the contaminated open-field vegetable soils also affected the adjacent crop fields as a source of PAE pollution.

3.4. Health risk assessment of PAEs in agricultural soils from the Huang-Huai-Hai region

Due to their endocrine-disrupting, teratogenic and carcinogenic effects, PAEs are of high concern in terms of their impact on human health (Gao et al., 2019; Shi et al., 2019; Feng et al., 2020; Li et al., 2020). Because of its characteristics, DEP is more easily absorbed by plants and more easily accumulates in the edible parts of crops than does DEHP (Wang et al., 2015b; Tan et al., 2018). However, the concentration of DEP in crops is still lower than that of DEHP, and the RfDo value of DEP is forty times that of DEHP (U.S. Environmental Protection Agency, 2013); thus, DEP would not pose a threat to the safety of agricultural products. Based on the results of Wei et al. (2020), the risks of DEHP and DBP are dominant. Our results show that the concentrations of DEHP and DBP are higher than those of other monomers. Therefore, DEHP and DBP were selected to assess noncarcinogenic risks and DEHP was used to evaluate carcinogenic risks.

The noncarcinogenic risks and carcinogenic risks in the Huang-Huai-Hai region are shown in Fig. 3. For non-carcinogenic risks of PAEs to adults and children via non-dietary routes (Fig. 3a), the value of the hazard index (HI) for all samples was no greater than 1, therefore, the noncarcinogenic risks posed by PAEs via non-dietary routes is limited for both adults and children. This indicates that non-dietary routes are not the main route by which PAEs threaten human health.. This indicates that non-dietary routes are not the main route by which that PAEs pose a threat to human health. This result agrees with previous studies and can be mutually corroborated (Niu et al., 2014; Wang et al., 2015b). Nevertheless, the noncarcinogenic risk via non-dietary routes in the Huang-Huai-Hai region is more serious for children than for adults, indicating that children are the sensitive group. Studies have indicated that chronic exposure to PAEs can disrupt endocrine activity, hamper reproduction, and cause atopic disorders and carcinoma in children (Huang et al., 2019; Arfaeinia et al., 2020).

The noncarcinogenic risks posed by DBP and DEHP to adults and children via the dietary route are shown in Fig. 3b. The joint risks posed by DBP and DEHP can represent the overall risk posed by PAEs and are worthy of attention and vigilance. The average ΣHI of the two PAEs in vegetable soils and crop soil samples in Hebei Province for adults was 0.400 and 0.456, respectively, while the average ΣHI for children was 0.623 and 0.709, respectively. For adults, only 10.0% of the vegetable soil samples had a ΣHI value greater than 1, but for children, 20.0% of the vegetable soil samples and 38.9% of the crop soil samples had a ΣHI value greater than 1. The average ΣHI in vegetable and crop soils in Henan Province was for adults 0.411 and 0.454, respectively, while the average ΣHI for children was 0.640 and 0.706, respectively. For adults, only 7.14% of the crop soil samples had a ΣHI value greater than 1, but for children, 21.4% of the vegetable soil samples and 21.4% of the crop soil samples had a ΣHI value greater than 1. The average ΣHI in vegetable and crop soils in Shandong Province for adults was 0.480 and 0.292, respectively, while the average ΣHI for children was 0.747 and 0.454, respectively. For adults, only 13.3% of the vegetable samples had a ΣHI value greater than 1, but for children, 16.7% of the vegetable samples and 16.7% of the crop soil samples had a ΣHI value greater than 1. The average ΣHI for adults in vegetable and crop soils in Tianjin was 0.500 and 0.503, respectively, while the average ΣHI for children was 0.778 and 0.782, respectively. For adults, only 6.25% of the vegetable samples had a ΣHI value greater than 1, but for children, 12.5% of the vegetable samples and 20.0% of the crop soil samples had a ΣHI value greater than 1. DEHP contributes more to the ΣHI than does DBP. Specifically, the contribution of DEHP to the ΣHI in vegetable soils was 61.4%–81.3%, and this rate was the highest in Hebei Province. In crop soils, DEHP contributed more than 96.8% to the ΣHI, and the highest contribution rate reached 98.2% in Tianjin municipality. Therefore, the main risk of PAEs in soils was posed by DEHP. The higher risk posed by DEHP than by DBP was due to the differences in the BAF and

Table 3
The concentrations ($\mu g\ kg^{-1}$) of detected 9 PAEs in soils of Shandong Province*.

Planting pattern		DMP	DEP	DBP	BBP	DEHP	DNOP	DiBP	DMEP	DBEP	PAEs
Greenhouse vegetable regions	Vegetable soil	34.9 ± 22.4a	258 ± 194a	301 ± 245a	93.1 ± 89.7a	631 ± 746a	180 ± 244a	116 ± 78.2a	95.8 ± 128a	51.3 ± 42.2a	1330 ± 946a
	Crop soil	41.0 ± 36.4a	159 ± 210a	219 ± 145a	153a	222 ± 198a	41.2a	109 ± 93.7a	116 ± 134a	30.5 ± 18.7a	651 ± 527a
Open-field vegetable regions	Vegetable soil	28.0 ± 11.2a	123 ± 138a	328 ± 301a	252 ± 243a	399 ± 281a	149 ± 150a	87 ± 58.9a	94.1 ± 60.1a	19.3 ± 15.1a	918 ± 604a
	Crop soil	35.4 ± 30.1a	143 ± 140a	200 ± 197a	185 ± 143a	433 ± 220a	153 ± 131a	116 ± 80.9a	81.8 ± 69.7a	56.2 ± 74.6a	896 ± 466a

* : ANOVA, Duncan's test; different letters indicate $p < 0.05$.

RfDo values of these two PAEs in addition to the differences in their concentrations. Compared with the results of other research, the human health risks via diet in the present study were at an intermediate level (Niu et al., 2014; Lü et al., 2018). In summary, the noncarcinogenic risk posed by DBP via the dietary route is higher in vegetable soils than in crop soils, while the trend is opposite for DEHP(except for children in Tianjin). The higher risk posed by the DBP in vegetables is caused by a higher concentration of DBP in vegetable soils than in crop soils. The reasons for the variations in the DEHP risk in different provinces were more complicated. The risk was greatly affected by both the concentration levels of DEHP in each cropping system and the diet structure of the population in the four provinces/municipalities. For regions with similar concentrations of DEHP in vegetable soils and crop soils, such as Hebei and Henan provinces, the diet structure of the population was the main determinant of the noncarcinogenic risk posed by DEHP. When there was a large difference in the concentration of DEHP, such as those in Shandong and Tianjin, the concentration of DEHP in soil was the main determinant of the noncarcinogenic risk from DEHP. Therefore, to assess the health risks posed by PAEs, it is necessary to comprehensively consider the type and concentration of PAEs and the diet structure of the population. Previous research (Niu et al., 2014; Wang et al., 2015a; Lü et al., 2018; Wang et al., 2018; Wei et al., 2020) showed that PAE pollution in vegetable soils was serious and that vegetables were the main carrier of PAEs through the dietary route (Yang et al., 2018). Our study suggests that the risks from PAE contamination in crop soils require attention equal to that received by PAE contamination in vegetable soils. In addition to the differences in the risks from different cropping systems, we found that the risks from PAEs for children are higher than those for adults. As endocrine disruptors, PAEs have a more serious impact on children.

Furthermore, chronic exposure to PAEs, such as DEHP, causes a variety of cancers, including breast cancer in women and prostate cancer in men (Arfaeinia et al., 2020). As shown in Fig. 3c, the estimated carcinogenic risk from only two vegetable soil samples in Shandong exceeded 10^{-6} among all the samples. A value of 10^{-6} means that the carcinogenic risk was "low". More than 99% of the samples posed a carcinogenic risk below 10^{-6}. This indicates that the carcinogenic risk due to DEHP was "very low". It is worth noting that the carcinogenic risk from crop soils was much higher than that from vegetable soils. Compared with other studies in which the carcinogenic risk for all population groups fell in the range of 10^{-5}–10^{-4} (Shi et al., 2019), and 10^{-7}–10^{-4} (Wei et al., 2020), our results show that the level of carcinogenic risk caused by DEHP is relatively low. These results indicate that the risk from PAEs for agricultural products in the Huang-Huai-Hai region is acceptable.

4. Conclusions and implications

The mean concentrations of total PAEs in vegetable soils were higher than those in crop soils; however, both the noncarcinogenic and carcinogenic risks from PAEs in crop soils were similar to or higher than those in vegetable soils. Crop soils, as nonnegligibly phthalate-polluted areas, deserve as much attention as vegetable soils receive. Diet is the main route of human exposure to PAE pollution, and children are the sensitive group. Risk is affected by a combination of population dietary structure and soil pollution levels. Overall, the human health risks from PAEs in agricultural soils in the Huang-Huai-Hai region in China are low. This study provides scientific support for food safety risk assessment and pollution control of PAEs in the main agricultural production areas in China.

Although the current risk is acceptable, we are still concerned about the potential risk from PAEs in soil due to the increasing use of agricultural plastic film with the intensification of agriculture. Therefore, we suggest that the Chinese government issue a restriction standard for PAEs suitable for its national conditions, including the types and thresholds of PAEs, especially DiBP, which is not on the US EPA recommended control list, in soil, and implement relevant bans on PAEs in plastic

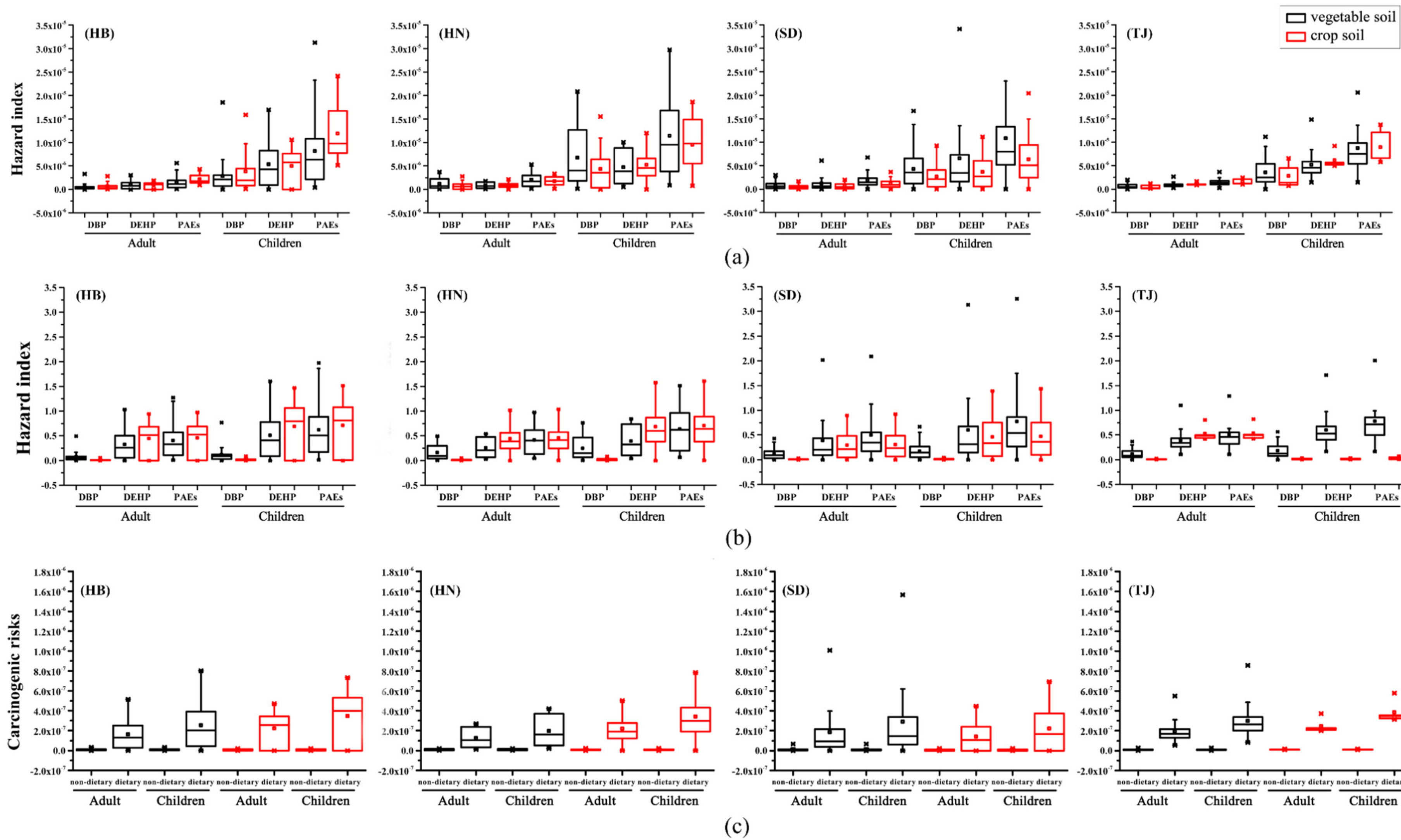

Fig. 3. Noncarcinogenic risks of PAEs to adults and children via non-dietary (a) and dietary routes (b), and carcinogenic risks of DEHP via non-dietary and dietary routes (c) in the Huang-Huai-Hai region, China. (The upper and lower bounds of the boxes indicate the 75th and 25th percentiles, respectively. The horizontal lines within the boxes indicate median values, and the square within the boxes indicate mean values. The upper and lower limits of the whiskers indicate 95% and 5% values, respectively, and forks above or below the whiskers indicate outlier values. n = 136).

products, especially for highly toxic phthalates such as DEHP. Second, we aimed to research the key limiting factors of PAE metabolism in soil, such as soil major elements and physicochemical properties, to clarify the degradation mechanism of PAEs. Third, biological fertilizers with PAE-degrading bacteria should be developed to promote the degradation of PAEs in soil and reduce the risk of ingesting PAEs that entered agricultural products.

CRediT authorship contribution statement

Bin Zhou: Investigation, Writing – original draft, Writing – review & editing. **Lixia Zhao:** Conceptualization, Writing – review & editing, Funding acquisition. **Yang Sun:** Writing – review & editing, Funding acquisition. **Xiaojing Li:** Writing – review & editing. **Liping Weng:** Writing – review & editing. **Yongtao Li:** Conceptualization, Writing – review & editing, Supervision, Project administration.

Declaration of competing interest

The authors declare no competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the National Key Research and Development Program of China (2016YFD0800201), Central Public-interest Scientific Institution Basal Research Fund and National Natural Science Foundation of China (41771517). We are grateful to Associate Prof. Chuanyu Shang and Dr. Yuebo Wang for their support and assistance with this work.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.146281.

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