



Phthalate esters contamination in vegetable–soil system of facility greenhouses in Jingmen, central China and the assessment of health risk

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Abstract Residual levels of six priority phthalate esters (PAEs) compounds in top soils and vegetables of 40 selected greenhouses in two typical facility vegetable greenhouse production areas of Jingmen (Hubei, central China) were determined. Total concentrations of six target PAEs ($\Sigma 6$ PAEs) in 72 vegetable and 40 soil samples ranged from 862 ± 209 to $4260 \pm 385 \mu\text{g kg}^{-1}$ (dry weight, DW), and from 1122 ± 156 to $4134 \pm 272 \mu\text{g kg}^{-1}$ (DW), respectively. Di-*n*-butyl phthalate and di-(2-ethylhexyl) phthalate (DEHP) are the two most frequently and massively detected in all samples. The highest $\Sigma 6$ PAEs appeared in leaf samples of Tuanlin, vegetable fruits of Zhongxiang and soils of

Tuanlin. No carcinogenic risk was posed based on the results of health risk assessment, but non-carcinogenic risk of DEHP to children less than 6 years old in Tuanlin (all 24 sampling sites) and Zhongxiang (4/16 sampling sites) and people older than 6 years old in Tuanlin (19/24 sampling sites) were achieved from hazard quotient values. The contamination risk problem of PAEs in Tuanlin deserves greatest concern in Jingmen. Combined with the results of our former study, the health risks of target pollutants were clarified and the lack of survey data on PAE concentrations in facility vegetable greenhouses of central China was filled in. Due to high residuals and significant non-carcinogenic risk values, DEHP should be nominated as priority PAEs in China. Our study suggested better regulation for PAEs control in intensively managed greenhouses and references for revision of Chinese environmental standards.

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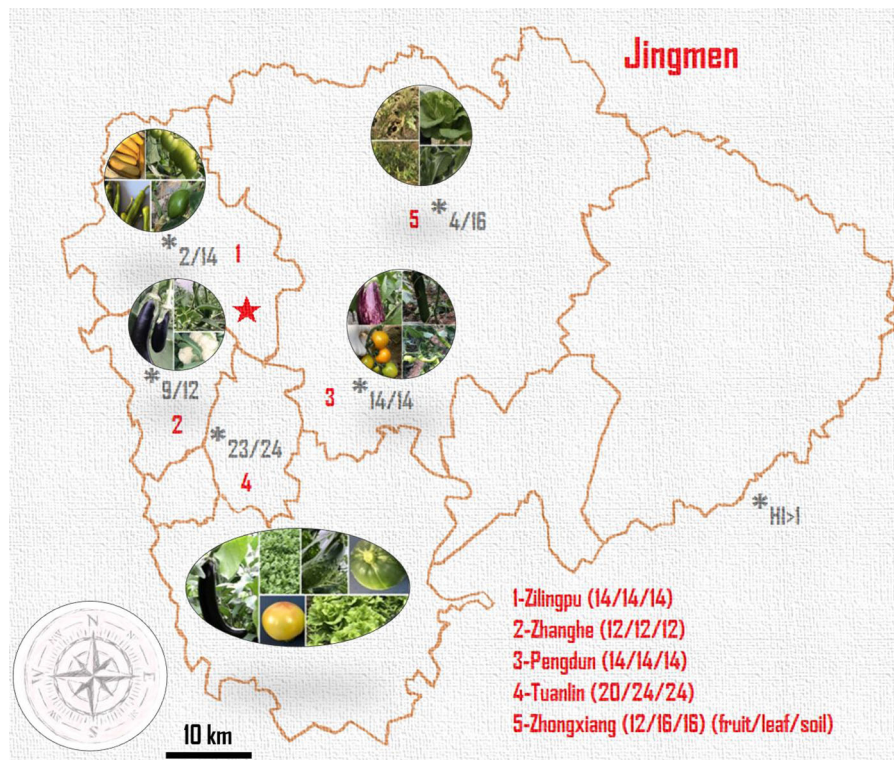
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Graphic abstract



Keywords 3D PCA · Central China · Health risks · Heatmap · Greenhouse vegetables

Introduction

China makes up over 90% of the greenhouse vegetable production operations worldwide due to market demands and financial motives, and in 2016, the total area has reached 39,000 km² (CCTV News 2017). At the current growth rate of about 1.25% each year, the total area of intensive vegetable production will stretch over 41,333 km² by 2021. Consisting of Hubei, Hunan and Henan provinces (from north to south), central China belongs to the seven major geographical regions of China. Central China encompasses about 560,000 km², covering 5.9% total area of Chinese land, with permanent residents of about 223 million people by the end of 2017. As the key development area for vegetable industry in inland China, Hubei province occupies a total of 185,900 km², that is 1.94% of China's total land area, but it feeds 4.3% of

the total population of China (Hubei Data 2017). In 2012, the total area of facility vegetable greenhouse production in Hubei province reached 1980 km² with a harvesting yield of 4.6 million tonnes (HDAR 2017). Nominated as the critical representative region for facility greenhouse production in central China and prestigious for “Chinese agricultural valley,” the facility agricultural area and vegetable yields in Jingmen rank the first in Hubei province. As an agrarian center and vegetable supply base to people not only in Hubei province, the contamination level and consumption safety of vegetables produced in greenhouses of Jingmen affects the health risk of a huge number of people and deserves more attention.

Agricultural films can be divided into shed films and mulching films. The commonly used agricultural films are made from polyethylene, polyvinyl chloride and other polymer compounds that not easy to degrade (Liu 2014). Film mulching is popularized to keep soil moisture from evaporation, raise soil temperature, and control salt and grass, in stabilizing agricultural production of crops and increase economic benefits, especially for vegetables in both open fields and

greenhouses (Wu et al., 2017). China produces the largest amount of commercial agricultural plastic films all over the world, and the coverage area of agricultural film in China, over 253,333 km², is also number one in the world, which is 1.6 times that of all other countries (GNEO 2016).

Wide distribution of phthalate esters (PAEs), a group of ubiquitous plasticizers largely added in agricultural films was mainly attributed to the extensively use and discard of plastic products in different environmental matrix (Acharee et al. 2018). Consistently used plasticizers in the manufacture of plastic-based products to improve flexibility and resilience, the concentrations in plastic mulching films could be up to 60% (Yu et al. 2011; Abdeldaiem et al. 2012). But PAE compounds could be easily released and accumulated in different environmental media during the process of manufacture, use, disposal and decomposition of plastic products since PAEs are not covalently bonded to the polymeric matrix (Bouhamidi et al. 2017). PAEs are endocrine disrupting compounds, with adverse effects on metabolism, reproduction (altered semen quality, shortened gestation, fertility, testicular dysgenesis), birth defects, negative effects on neurodevelopment and growth in children, cancer and so on (Li and Ko 2012; Selvaraj et al. 2015; Chen et al. 2019; Rashtian et al. 2019). The US Environmental Protection Agency (USEPA) has identified six congeners, including dimethyl phthalate (DMP), diethyl phthalate (DEP), di-*n*-butyl phthalate (DBP), butylbenzyl phthalate (BBP), di-(2-ethylhexyl) phthalate (DEHP) and dioctyl phthalate (DOP) as priority pollutants (USEPA 1996). DMP, DBP and DOP are listed as priority pollutants by the China State Environmental Protection Agency. So that the accumulation of PAEs could cause not only gradual deterioration of different environmental media, including the air, water and soil, slow the growth of plants, decrease in vegetable yield but also exhibit negative impacts on food safety and human health (Zhang et al. 2017; Gao et al. 2018; Lee et al. 2019). Establishing critical threshold concentrations for PAE pollutants in different environment mediums to protect human health and ecological safety has been taken as the main direction in the control and management of pollutants for the last two decades (VROM 2000).

On a national scale of China, the highest $\Sigma 6$ PAEs level in soils was up to 55 mg kg⁻¹, which is about 200 times higher than the reference values of $\Sigma 6$ PAEs in other countries like Demark (Guo and Wu 2011; Gao et al. 2018). Greenhouse soil PAE levels over 36 mg kg⁻¹ were detected (Ma et al. 2015), and clear link between PAEs contamination in vegetable soils and the consumption of plastic films was achieved (Gao et al. 2018). For central China, the concentrations of PAEs in farmland of Xiangyang were 23.99 ± 26.16 mg kg⁻¹, and in arable soils of Wuhan, Changsha and Luoyang were between 0.89 and 2.25 mg kg⁻¹ (Hu et al. 2003; Wu et al. 2015; Sun et al. 2017). However, basic research data on contamination of six priority PAEs nominated by USEPA in facility greenhouse areas and the corresponding environmental risks in densely populated middle China are scarce. On the other hand, the soil environmental standards in China for PAEs are still rough since set in 2008.

Considering the necessity of health risk assessments on PAEs based on vegetable consuming and the detailed data shortage on PAE contamination of facility greenhouses in central China, the present investigation has been conducted as a supplement of our former study. In our former study in two large-scale vegetable production facilities areas, Zilingpu, Zhanghe and Pengdun of Jingmen city, the total concentrations of PAEs in 40 soil samples and 80 vegetable samples were determined, and the carcinogenic risk and non-carcinogenic health risk were evaluated (Ma et al. 2019).

In this study, PAE residual concentrations from 40 typical production greenhouses in 40 collected soils and 72 vegetables (40 vegetable leaves and 32 vegetable fruits) from two large-scale vegetable production facilities areas at Tuanlin and Zhongxiang were determined. Evaluation of carcinogenic and non-carcinogenic health risk was assessed based on the contamination results of the six target PAE compounds in different collected samples. The summarized results of the five study areas could clarify the overall PAEs pollution status and health risks in the most typical facility greenhouses.

Materials and methods

Study area

As a representative facility greenhouse vegetable (pollution-free vegetables) production base, Jingmen has a total area of 12,400 km², locating in the middle and lower reaches of the Hanjiang River, 96 m above the mean sea level. By the year of 2015, the total greenhouse vegetable production area reached 400 km², which is still in the trend of growing (PGJM 2017). Other detailed geographical and facility production information could be referred to Ma et al. (2019).

In the overall plan of Jingmen City (2011–2015) to establish a national modern agricultural demonstration zone (PGJM 2017), five distinctive large-scaled facility greenhouse areas were screened, including (1) Luoyuan Vegetable Professional Cooperative (Zilingpu town, Dongbao district); (2) Shuangfu Ecological Agriculture Development Co. Ltd. (Zhanghe new district); (3) Pengdun Wisdom Farm (Shipai town, Zhongxiang city); (4) Circular Agriculture Demonstration Site (Tuanlin town, Duodao district) and (5) Jinghe Vegetable Planting Specialty Cooperative, a New Rural Construction Industry Support Demonstration Site (Phosphate rock town, Zhongxiang city). At the end of the year 2018, the investigations in No. 1 area Zilingpu, No. 2 area Zhanghe and No. 3 area Pengdun have been accomplished. Aiming at complete, the overall investigations in Jingmen city, No. 4 and No. 5 areas have been carried out in the present study.

Relying on the support from Hubei Institute of Vegetable Science about agriculture science and technology, the construction of plastic sunlight greenhouses, greenhouse intelligent, automation management, industrialized seedling production, soilless cultivations are popularized in No. 4 area, entitled Tuanlin because it is located in Tuanlin town. No. 5 area, entitled Zhongxiang, lies in Phosphorite Town, Zhongxiang, mainly engaged in vegetable cultivation and sales. The geography position and general vegetable production details of the two sampling locations are shown in Fig. 1 and Table S1.

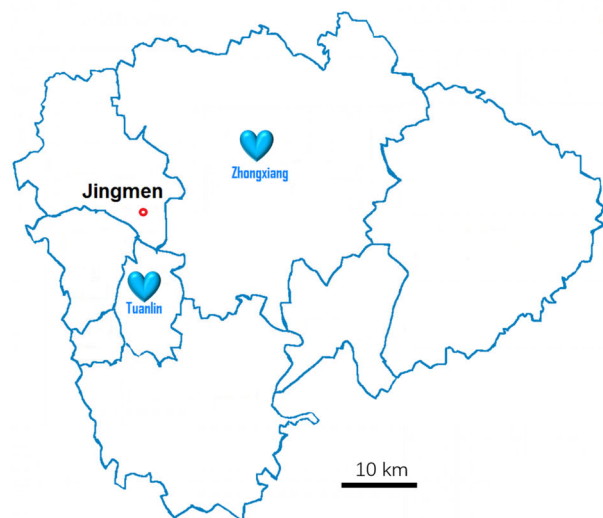
Chemicals and reagents

Standard solution mixture (1 mg mL⁻¹) of the six PAE compounds nominated by USEPA as priority pollutants dissolved in hexane and the internal standard dry powder of benzyl benzoate (BB) (100 mg, purity 98.7%) were purchased from AccuStandard Incorporation (New Haven, CT). The certified reference material 136-100 (BNAs-Clay 1) was obtained from RT Corporation (Laramie, WY). Acetone and hexane of HPLC-grade were from Tedia Company (Fairfield, OH). The packing materials, reagent grade of anhydrous sodium sulfate and neutral alumina (400 mesh), and neutral silica gel particle (200 mesh) were purchased from Yongda Chemical Reagent Co. LTD (Tianjin, China). The packing materials were separately baked for 4–6 h in a muffle furnace at 400 °C and kept in the desiccators away from damp (Ma et al. 2013).

Sampling

Forty soil samples and 72 vegetable samples were collected from 40 out of 220 greenhouses in Tuanlin and Zhongxiang in January 2019, giving a total of 112 samples (Fig. 1 and Table S1). Each sample was the mean values of five randomly picking samples in the same greenhouse from the 40 selected greenhouses in a quincunx pattern in the non-marginal region, so that a total of 560 samples were determined. Soil samples were collected from the top layer of 0–15 cm with a soil corer. The vegetable leaf and fruit samples were randomly screened and cut down from non-adjacent and non-marginal plants and analyzed separately in triplicate. Vegetable samples were firstly washed with the tap water, then rinsed with distilled water and wiped dry with paper tissue before freeze-dried in a Free Zone 2.5-Liter Freeze Dry System (Labconco Corp., Kansas City, MO). Soil samples were freeze-dried directly to anhydrous state before analysis after stored in linen sampling bags and taken back to the laboratory. The soil pH condition, organic matter content (SOM), electrical conductivity (EC) and mechanical composition from two study areas were determined (Lu 1999) and listed in Table S2.

Fig. 1 Geographical locations of sampling sites, Tuanlin and Zhongxiang in Jingmen, Hubei province, China



Sample determination and quality assurance

Prior to the analysis procedure, all the glassware was strictly washed following the methods of Ma et al. (2013). Dried samples were ground in liquid nitrogen to prevent the loss of the target pollutants and sieved (60 mesh for soil, 100 mesh for vegetable) for each replication before stored in the refrigerator at $-20\text{ }^{\circ}\text{C}$ for further analysis.

The extraction of target PAEs in 10 g of soil (dry weight, DW) or 2 g (DW) of frozen-dried vegetable sample was conducted with acetone/hexane (1:1 v/v) for three times (30 mL, 20 mL and 20 mL, respectively) in a $25\text{ }^{\circ}\text{C}$ water bath. The extractions were condensed by rotary evaporation to less than 2 mL in $40\text{ }^{\circ}\text{C}$ water bath (350 mbar, 80 rpm) after centrifugation (1500 rpm). Column chromatography was performed in a glass column ($1 \times 26\text{ cm}$) for purification of the concentrated solution with the three packing materials following the description of Ma et al. (2013). The elutions were collected and concentrated to less than 1 mL by rotary evaporation as described above.

Instrumental analysis performed with a Model 7890BGC-5977A MSD (Agilent Technologies, Santa Clara, CA) with a DB-5 fused silica capillary column (30-m length, 0.25 mm ID, 0.25 μm film thickness) under selected ion monitoring mode was used with programmed oven temperature. The transfer line and detector temperatures were $280\text{ }^{\circ}\text{C}$ and $290\text{ }^{\circ}\text{C}$, respectively. The programmed GC oven temperature was as follows: initial temperature of $50\text{ }^{\circ}\text{C}$ was held for 1 min, increased at a rate of $15\text{ }^{\circ}\text{C min}^{-1}$ to $200\text{ }^{\circ}\text{C}$, then held for 1 min, and then increased at a rate of $8\text{ }^{\circ}\text{C min}^{-1}$ to $280\text{ }^{\circ}\text{C}$, then held for 3 min. Post-run temperature was at $285\text{ }^{\circ}\text{C}$ for 2 min. Carrier gas (N_2 purity $> 99.999\%$) flow was 1.2 mL min^{-1} in splitless mode with a volume of $1\text{ }\mu\text{L}$ non-pulse injection at $250\text{ }^{\circ}\text{C}$. Three whole procedure blanks and one certified reference material were proceeded in every 40 samples during analysis for quality control (Ma et al. 2013). Limits of detection (LOD) of target PAE compounds calculated as three times the sample concentrations multiply by the noise-to-signal ratio of the instrument were between 0.10 and $0.35\text{ }\mu\text{g L}^{-1}$. Standard solutions of seven different concentrations (including 20, 50, 100, 200, 500, 1000 and $2000\text{ }\mu\text{g L}^{-1}$) were used to build calibration curve with the help of the response factor of the internal

standard. Newly built calibration curves were used to analyze newly prepared standard solutions with known concentration, and the difference between the real value and the detected value should be less than 20%. Limits of quantification (LOQ) of the spiked soil calculated as the standard deviation (SD) of the seven spiked matrices at the concentration of fivefold LODs multiply by $t_{(n-1,0.99)}$ were between 50 and $120\text{ }\mu\text{g kg}^{-1}$, where $n - 1$ is the degrees of freedom and 0.99 refers to the confidence interval of 99%.

Health risk assessment

Health exposure risk assessment connects the levels of contaminants in the environment with a probability of toxic effects for a human population (Liu et al. 2019). Based on the risk assessment guidelines recommended by USEPA (2013), the carcinogenic and non-carcinogenic risks of the six PAE compounds were assessed. Daily oral exposure by eating vegetable and different absorption pathways from soils, including dermal and inhalation contact and soil ingestion, are mainly considered during potential risk evaluations (Ma et al. 2015). Dietary intake data recommended by the Environment Agency and Department of Environment, Food and Rural Affairs, Danish Nationwide Dietary Survey, CLEA, London, were considered with slight modification in the vegetable consumption estimates (Ma et al. 2015). Non-carcinogenic risk assessment was quantified by hazard quotient (HQ) values of the six target compounds calculated as follows (Wang et al. 2017a).

$$\text{ADD}_{\text{intake}} = \frac{C_{\text{fruit}} \times \text{IRF} \times \text{EF} \times \text{ED} \times \text{CF}}{\text{BW} \times \text{AT}}$$

$$\text{ADD}_{\text{ingestion}} = \frac{C_{\text{soil}} \times \text{IRS} \times \text{EF} \times \text{ED} \times \text{CF}}{\text{BW} \times \text{AT}}$$

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

$$\text{ADD}_{\text{inhale}} = \frac{C_{\text{soil}} \times \text{EF} \times \text{ED} \times 1000}{\text{PEF} \times \text{AT}}$$

$$\begin{aligned} \text{HI} &= \sum_{i=6} \text{HQ} \\ &= \sum_{i=6} \frac{\text{ADD}_{\text{intake}} + \text{ADD}_{\text{ingestion}} + \text{ADD}_{\text{dermal}} + \text{ADD}_{\text{inhale}}}{\text{RfD}} \end{aligned}$$

where ADD, average daily dosage ($\text{mg kg}^{-1} \text{d}^{-1}$); C_{fruit} , PAE concentration in edible vegetable parts ($\text{mg kg}^{-1} \text{DW}$); IRF, daily vegetable intake; EF, exposure frequency (days y^{-1}); ED, exposure duration (production duration of different plastic greenhouses); BW, body weight; AT, average time, ($365 \times \text{ED}$ for HQ calculation; 25,550 days for lifetime) for carcinogenic risk assessment); CF, conversion factor ($10^{-6} \text{kg mg}^{-1}$); C_{soil} , PAE concentration in soil samples ($\text{mg kg}^{-1} \text{DW}$); IRS, soil ingestion rate; SA, soil surface area; AF, soil adherence factor; ABS, fraction of contaminant absorbed dermally from the soil; PEF, particle emission factor; and RfD, reference dose ($\text{mg kg}^{-1} \text{d}^{-1}$).

The hazard index (HI) is the summed HQ values of different PAEs. When the HI value is less than 1, there are no non-carcinogenic effects to target population, but when the HI is higher than 1, non-carcinogenic effects are considered (USEPA 2001).

For risk assessment of the carcinogenic, carcinogenic risk (CR, unitless) less than 10^{-4} suggested the cancer risk is acceptable.

$$\text{CR}_j = \text{ADD}_j \times \text{SFO}$$

where SFO, slope factor of the carcinogen of oral exposure ($(\text{mg kg}^{-1} \text{d}^{-1})^{-1}$). Detailed of all the parameters used for the assessment of health risks are presented in Table S3.

Statistical analysis

PAE concentrations are listed as the average values (quintuplicate in each greenhouse) \pm the standard deviations (SD) of quintuplicates in this greenhouse. Microsoft Excel 2013 and the Origin 2017 software package were used for data processing. Differences were assessed by one-way analysis of variance followed by least significance difference test at $p < 0.05$ for comparison. 3D principal component analysis (PCA) of PAEs in different vegetable edible parts from the two study areas, and the heatmap of HQs were plotted with Origin 2017. Pearson correlation was analyzed at $p < 0.05$ and $p < 0.01$ with two-tailed test of significance to compare between different target PAEs in all the sampled greenhouses.

Results and discussion

Contamination level of six PAE compounds in soils

The $\Sigma 6\text{PAEs}$ in the surface soils ranged from 2032 ± 125 to $4134 \pm 272 \mu\text{g kg}^{-1} \text{DW}$ in Tuanlin, and 1122 ± 156 to $2824 \pm 698 \mu\text{g kg}^{-1} \text{DW}$ in Zhongxiang (Table S4 and Fig. 2). And in our former study, the $\Sigma 6\text{PAEs}$ in the surface soils ranged from 1699 ± 314 to $7015 \pm 475 \mu\text{g kg}^{-1} \text{DW}$ in Zilingpu, 919 ± 135 to $4435 \pm 522 \mu\text{g kg}^{-1} \text{DW}$ in Zhanghe and 1867 ± 281 to $4655 \pm 1091 \mu\text{g kg}^{-1} \text{DW}$ in Pengdun (Ma et al. 2019). The total concentrations in the five study areas were all below the less stringent grade II limits for $\Sigma 6\text{PAEs}$ (10mg kg^{-1}) in arable soils listed in the Environmental Quality Standard for Soil of China (GB-15618-2008) (CNEPA 2008). Omitting the outlier values in each sample type from different areas, the concentration ranges of the six PAE compounds in five study areas followed the order of: Zhanghe ($n = 12$) > Zilingpu ($n = 14$) > Pengdun ($n = 14$) > Tuanlin ($n = 24$) > Zhongxiang ($n = 16$). DBP, DEHP and DOP were the major soil congeners in all the sampled plastic greenhouse in Tuanlin, with slightly amount of BBP detected. DMP and DEP concentrations in soils were all relatively low, $< 70 \mu\text{g kg}^{-1} \text{DW}$ soils. The determined concentrations of target PAEs varied so much that even in greenhouses planting the same vegetable types, especially for DBP, DEHP and DOP (Table S4). Total PAEs average concentrations in soils of six vegetables followed the sequence order: lettuce > cucumber > garland chrysanthemum > pumpkin > eggplant > tomato. Quite different patterns were observed in six PAEs of Tuanlin and Zhongxiang (Table S4). DBP and DEHP were also the major soil congeners in all the samples collected from Zhongxiang, without much DMP and BBP detected. The average levels of soil total PAEs followed the sequence: chili > Chinese cabbage > cauliflower > asparagus lettuce (Table S4).

For the composition patterns of target PAEs in soils (Fig. S1a), DBP, DEHP and DOP accounted for over 95% of the total six PAE concentrations in samples collected from Tuanlin. The proportions of DBP are between 17 and 43%, and that of DEHP and DOP from

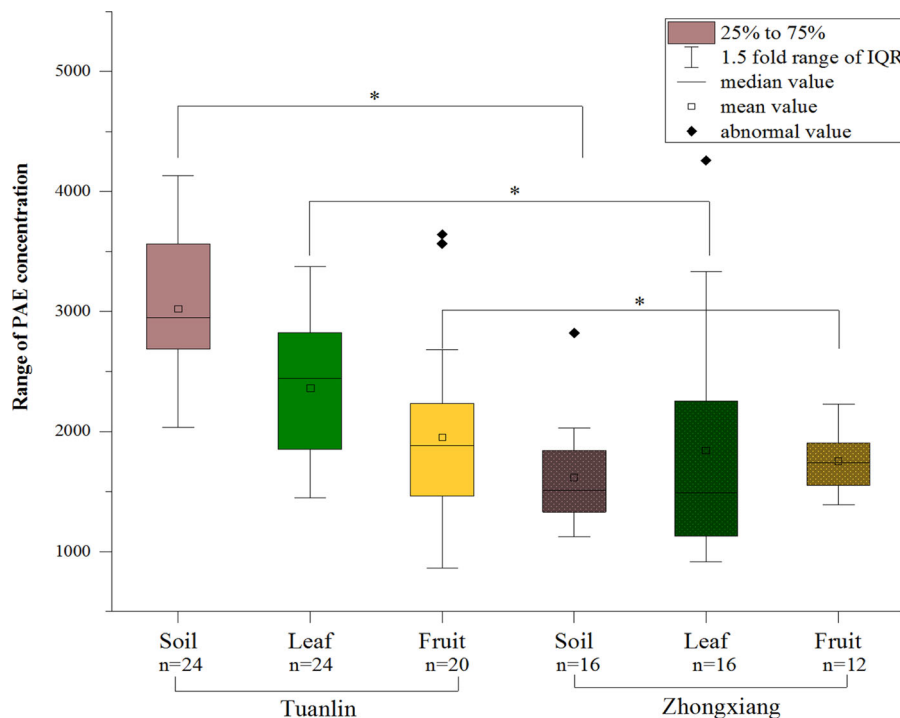


Fig. 2 PAE concentration ranges of 112 samples from the two study areas. *Significant difference at $p < 0.05$ compared with the same sampling group

25 to 68% and from 8 to 45%. At Zhongxiang, the sum percentage of DBP and DEHP was almost over 95% (Fig. S1b), ranging from 13 to 76% (DBP) and 19 to 83% (DEHP). However, in the other study areas of our former study, DBP and DEHP were the major soil congeners in Zilingpu and Zhanghe (Ma et al. 2019).

Due to the high cropping index, large agricultural inputs and closed environment in the greenhouses, the accumulation of various pollutants can lead to high health risks, and this is not consistent with the sustainable development of production (Hu et al. 2017). Environmental degradation over the past 30 years has encouraged numerous investigations on the distribution of soil PAEs and their risk assessment in China (Lv et al. 2018). The residual concentrations of PAEs in the soils of China are on the high side of the global scale and some exceeded the Grade II limits of the Environmental Quality Standard for soils in China, 10 mg total PAEs kg^{-1} soil DW (Lv et al. 2018), although the limitation standards are many times higher than that in the UK, Denmark and other European countries (Vikelsøe et al. 2002; Gibson et al. 2005; Peijnenburg and Struijs 2006). Higher total soil

concentrations of PAEs have been found in greenhouses in north China in recent years, for example in northeast China ($\Sigma 15\text{PAE}$ 4.90 mg kg^{-1} DW), Shandong province, 25.2 mg kg^{-1} DW in Tai'an and $\Sigma 16\text{PAE}$ 9.786 mg kg^{-1} DW in Shouguang (the most famous and large-scale greenhouse vegetable production area in China) (Wang 2007; Zhang et al. 2015; Li et al. 2016a). Intensive greenhouse vegetable production in north and northeast China developed firstly and draw more attention because of the relatively cold weather and short growing season in the field. However, in central China (Hubei, Hunan and Henan provinces), where intensive greenhouse production using plastic greenhouse has also greatly developed did not capture the attention of researchers for a long time. The present study results provide important supplement to the research data in central China area.

Contamination level of six PAE compounds in vegetables

The selections of vegetable types were based on the types of locally grown ones in the two study areas.

Total PAE concentrations in foliar and vegetable fruits of the two study areas were determined, respectively (Table S4 and Fig. 2). Total average PAE concentrations in vegetable leaves were between 1450 ± 99 and $3372 \pm 254 \mu\text{g kg}^{-1}$ DW following the order: pumpkin > cucumber > eggplant > garland chrysanthemum > tomato > lettuce at Tuanlin (Table S4), and 1388 ± 109 to $2229 \pm 138 \mu\text{g kg}^{-1}$ DW following the sequence: asparagus lettuce > cauliflower > chili > Chinese cabbage at Zhongxiang (Table S4). In our former study in Zilingpu, Zhanghe and Pengdun, the foliar $\Sigma 6\text{PAEs}$ ranged from 1432 ± 763 to $4290 \pm 607 \mu\text{g kg}^{-1}$ DW, 1222 ± 276 to $11,683 \pm 1313 \mu\text{g kg}^{-1}$ DW and 1238 ± 56 to $3091 \pm 805 \mu\text{g kg}^{-1}$ DW, respectively (Ma et al. 2019). However, pollutants in vegetable fruits are the most possible to be transferred to human body via the food chain. For vegetables of the same species, the total concentrations of the six target PAEs in vegetable edible parts were between 862 ± 209 and $3641 \pm 203 \mu\text{g kg}^{-1}$ DW following the order: tomato > cucumber > eggplant > garland chrysanthemum > pumpkin at Tuanlin (Table S4), and 911 ± 44 to $4260 \pm 385 \mu\text{g kg}^{-1}$ DW following the sequence: cauliflower > chili > asparagus lettuce in Zhongxiang (Table S4). The $\Sigma 6\text{PAEs}$ in Zilingpu, Zhanghe and Pengdun ranged from 1377 ± 99 to $9216 \pm 632 \mu\text{g kg}^{-1}$ DW, 642 ± 46 to $3392 \pm 396 \mu\text{g kg}^{-1}$ DW and 387 ± 63 to $5506 \pm 3330 \mu\text{g kg}^{-1}$ DW, respectively (Ma et al. 2019). Leave the outlier samples alone, the mean concentration ranges of total PAEs in leaves and fruits from different areas were in the sequence of: Zhanghe ($n = 12$) > Zilingpu ($n = 14$) > Pengdun ($n = 14$) Tuanlin ($n = 24$) > Zhongxiang ($n = 16$) and Zilingpu ($n = 14$) > Pengdun ($n = 14$) > Zhanghe ($n = 12$) > Tuanlin ($n = 24$) > Zhongxiang ($n = 16$), respectively (Fig. 2) (Ma et al. 2019). DBP, DEHP and DOP were the largest proportion components detected in both the vegetable leaves and fruits of Tuanlin, but the concentrations of BBP were very little ($< 1 \mu\text{g kg}^{-1}$ DW) almost the same as it is in Zhongxiang (Table S4) and the other three study areas of our former study (Ma et al. 2019). The other two congeners DMP and DEP were less than $350 \mu\text{g kg}^{-1}$ DW (Table S4).

The contamination levels of DBP and DEHP changed heavily in greenhouses planting the same vegetable types. The proportion of six target PAEs

(Fig. S1a) exhibited that DBP, DEHP and DOP made up over 95% of the total concentrations in both foliar and edible parts collected in Tuanlin. The proportions of DBP were between 32 and 72% in foliar, and between 13 and 53% in vegetable fruits, and that of DEHP and DOP were between 8 and 30% and between 8 and 46% in foliar, and that of DEHP and DOP were between 6 and 46% and between 9 and 53% in vegetable fruits, respectively. The proportions of DOP in samples of Tuanlin were higher than other samples from other greenhouses of other areas, even higher than that of DEHP of some foliar and vegetable edible parts determined. The proportion of DMP and DEP in almost all determined soils was lower than that in vegetables at Tuanlin. DEP in all foliar samples of non-leafy vegetable was higher than 3%, so much higher than that in soil samples at Zhongxiang. The total proportions of DBP, DEHP and DOP were > 80%, especially in leafy vegetable, Chinese cabbage, samples (Fig. S1b), ranging between 30 and 62% and between 29 and 65% (DBP), between 16 and 54% and between 17 and 72% (DEHP) and from no more than 3% to 19% and less than 3% to 11% (DOP) in foliar and vegetable fruits, respectively.

Total PAEs concentrations between 0.9 and 8.607 mg kg^{-1} DW have been reported in vegetables of other study areas in China (Ma et al. 2015; Wang et al. 2015; Li et al. 2016a; Chen et al. 2017; Zhang et al. 2019). Compared with the results in soils, DEHP, DBP and DOP are also the major congeners, accounting for over 90% of PAE sum values, especially in line with results of Tuanlin. Total PAE concentrations were usually the highest in leafy vegetable than other vegetables (Zhang et al. 2019). In leafy vegetables, contaminants transported from the roots exist only in the blade and are not be shared with vegetable fruits any more, even depending more on differences in transport capacity, i.e., bio-accumulation factor, between plants. However, in leafy vegetables of these two study areas, lettuce and Chinese cabbage did not show higher contamination compared with other vegetables. Although the contamination level of lettuce in Tuanlin is the lowest in all foliar samples, the habit of eating raw can pose more risks compared with other vegetables. PAE contamination could deteriorate the quality of cultivated vegetables and weaken the resistance of vegetables to environmental stress especially for winter melon, cucumber and chili (Yin et al. 2002; Zhang and

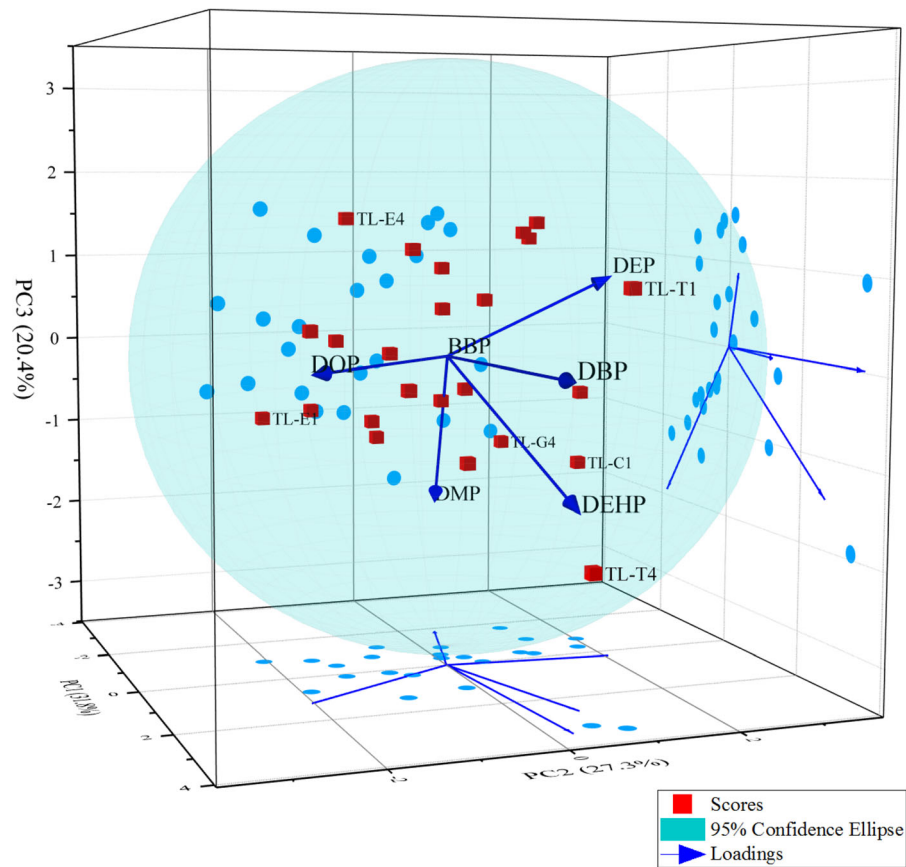


Fig. 3 Principal component analysis (PCA) of six PAEs in vegetable fruits collected from Tuanlin. 3D PCA biplot (loading plot and score plot) results of all determined vegetables. Sample number TL-T1 is the first sampled tomato greenhouse in Tuanlin; TL-P1 is the first sampled pumpkin greenhouse in Tuanlin; TL-C1 is the first sampled cucumber greenhouse in Tuanlin; TL-G1 is the first sampled garland chrysanthemum

greenhouse in Tuanlin; TL-E1 is the first sampled eggplant greenhouse in Tuanlin; TL-L1 is the first sampled lettuce greenhouse in Tuanlin; ZX-C1 is the first sampled cauliflower greenhouse in Zhongxiang; ZX-A1 is the first sampled asparagus lettuce greenhouse in Zhongxiang; ZX-CH1 is the first sampled chili greenhouse in Zhongxiang; and ZX-CC1 is the first sampled Chinese cabbage greenhouse in Zhongxiang

Ouyang 2017). PAE contamination control and future remediation with the help of various ways deserves attention.

PCA results of vegetable edible parts from individual study areas and all the vegetable edible parts are shown in Figs. 3, 4, 5, S2 and S3, Tables 1 and S5. For vegetables collected from Tuanlin, the eigenvalues and contribution rates of the PCA results are listed in Table 1. In Table 1, the contribution of the first principle component (PC1) was 26.48%, and the characteristics of factor variables values in DBP, DEHP, DOP and DEP were all in positive load; the contribution of the second principle component (PC2) was 22.76%, and the characteristics of factor variables values in DEP, DEHP, DMP and DBP were all in

positive load; the contribution of the third principle component (PC3) was 17.03%, and the characteristics of factor variables values in DMP, DEHP and DOP were all in positive load (Table 1). The determined values of BBP are zero, so that the total cumulative contribution rate of all eigenvalues should be $100\% \times 5/6 = 83.33\%$. So, the cumulative contribution rate of PC1, PC2 and PC3 could explain the pollution characteristics of target pollutants well, which is 66.27% , equivalent to the original value. 79.53% . The positive load of target PAEs indicated that DBP and DEHP in PC1, DEP in PC2, and DMP and DEHP in PC3 are the characteristic pollutants. From Figs. 3, S2a and S2b, the positions of samples projected to the positive direction of abscissa axis

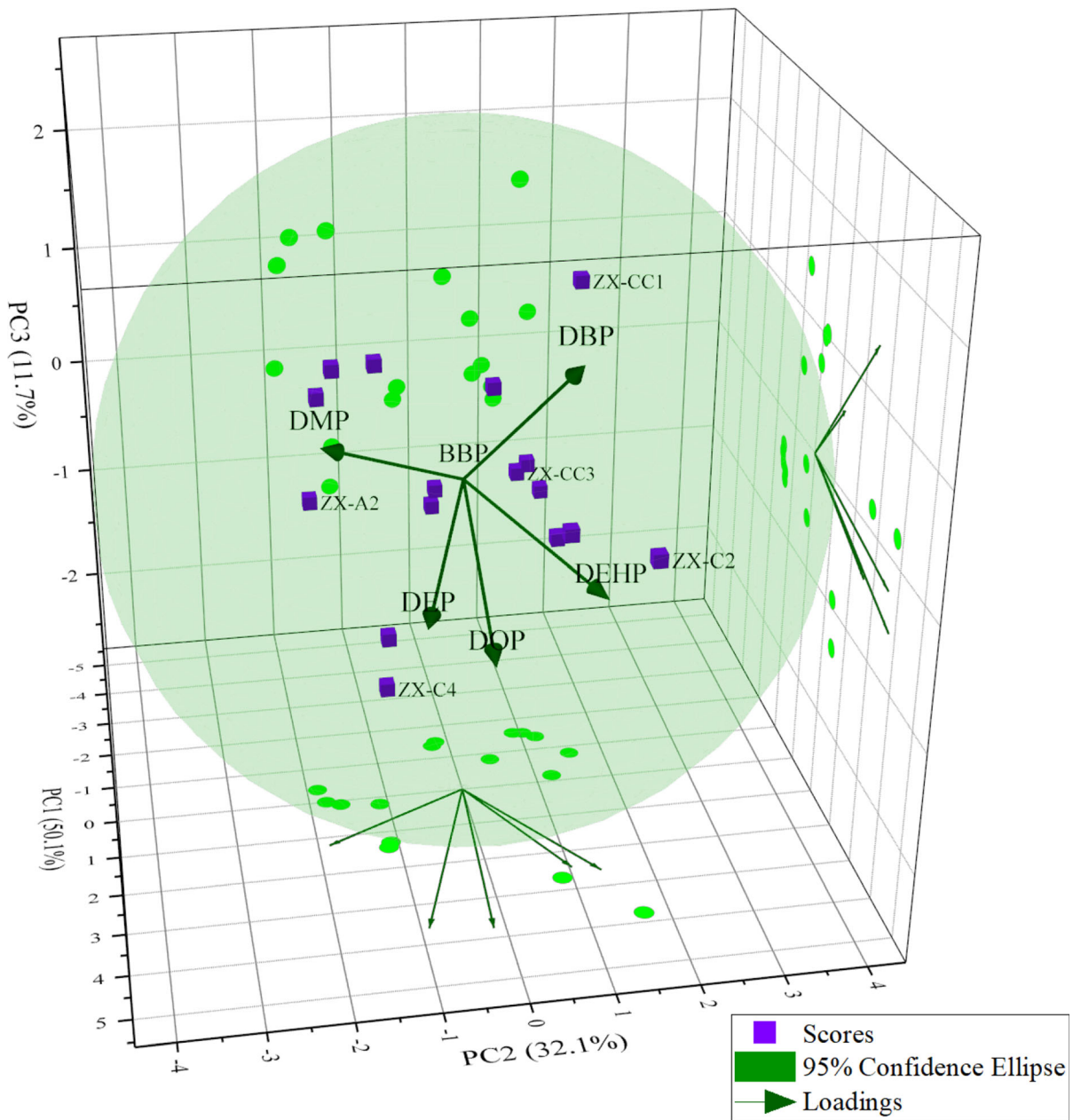
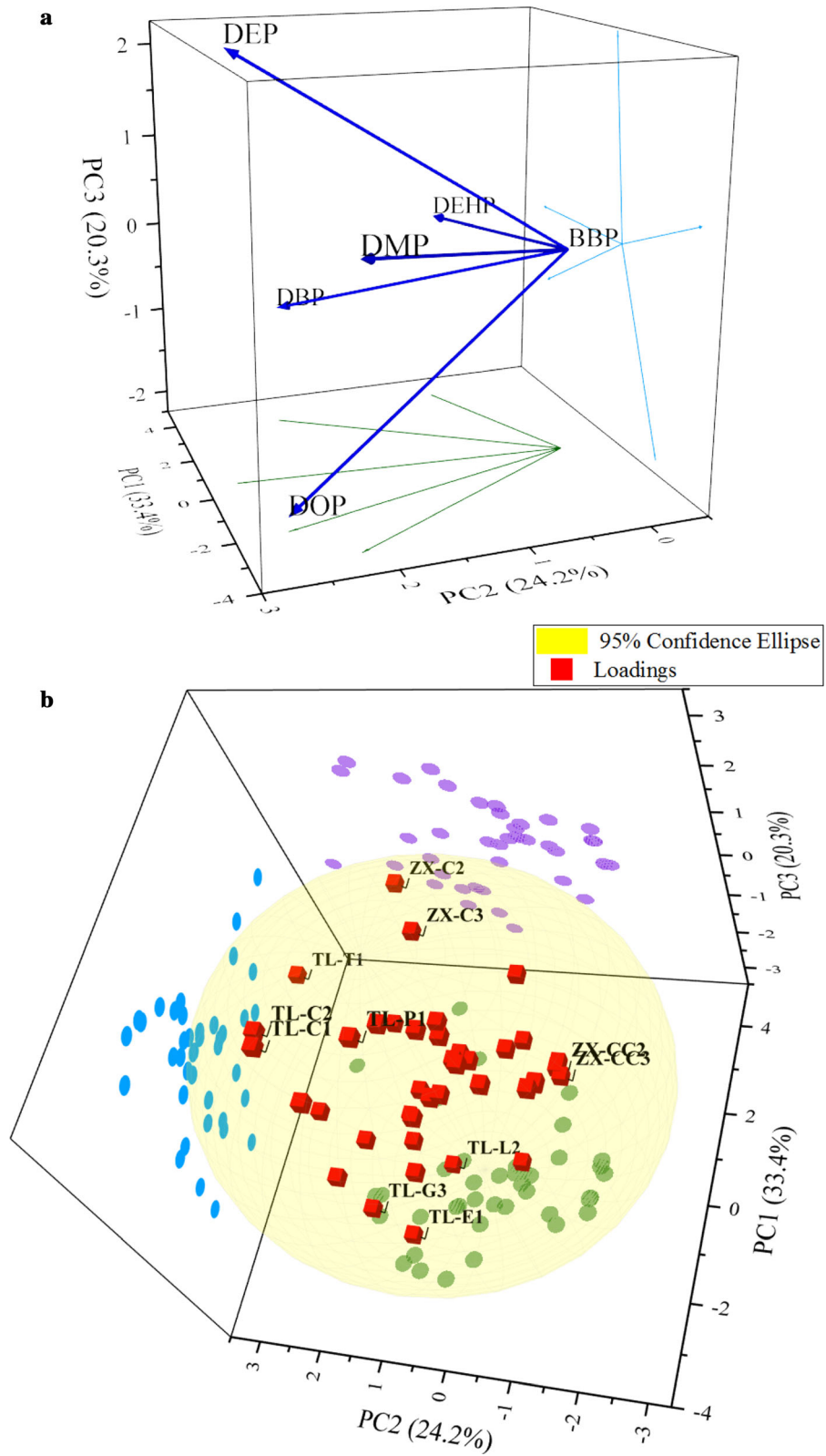


Fig. 4 PCA of six PAEs in vegetable fruits collected from Zhongxiang. 3D PCA biplot (loading plot and score plot) results of all determined vegetables. Refer the denotes to Fig. 3

(PC1) suggest tomatoes in Tuanlin are mainly contaminated by DBP, DEHP and DOP, especially tomato 1 and 4. From Figs. 3, S2a, S2b and S2c, the position of cucumber 1 projected to the positive direction of abscissa axis (PC2 and PC3) suggests that it is contaminated mostly by DMP and DEHP. For garland chrysanthemum 4, the position projected to the

positive direction of abscissa axis (PC2 and PC3) and the negative direction of abscissa axis (PC1) indicated that the characteristic pollutant is DMP (Figs. 3, S2a, S2b and S2c). The sample of eggplant 1 presented negative relationship with PC2 and positive relationship with PC3, and the sample of eggplant 4 revealed negative relationship with PC3, indicating



◀ **Fig. 5** PCA of six PAEs in vegetable fruits collected from two study areas. a) 3D PCA of all determined vegetables (loading plot) and b) 3D PCA of all determined vegetables (score plot). Refer the denotes to Fig. 3

that the characteristic pollutants of them are DEP, DBP and DOP.

For vegetables collected from Zhongxiang, the eigenvalues and contribution rates of the PCA results are listed in Table 1. In Table 1, the contribution of PC1 was 41.71%, and the characteristics of the factor variables values in all the nonzero PAE components were all in positive load; the contribution of PC2 was 26.78%, and the characteristics of the factor variables values in DMP, DEP and DOP were all in positive load; the contribution of PC3 was 9.79%, and characteristics of the factor variables values in DMP and DBP were all in positive load (Table 1). The total cumulative contribution rate of PC1, PC2 and PC3 is equal to the original value of 93.94%, which could well explain the characteristics of target pollutants in Zhongxiang. The positive load of target PAEs indicated that DEP and DOP in PC1, DMP in PC2 and DBP in PC3 are the characteristic pollutants. From Figs. 4, S3a, S3b and S3c, the positions of sample cauliflower 2 projected to the positive direction of abscissa axis (PC1 and PC3) and the negative direction of abscissa axis (PC2) but that of cauliflower 4 projected to the positive direction of abscissa axis (PC1 and PC2) and the negative direction of abscissa axis (PC3) suggested that cauliflowers are mainly contaminated by DEHP and DOP. From Figs. 4, S3a and S3c, the position of asparagus lettuce 2 projected

to the negative direction of abscissa axis (PC1 and PC3) and the positive direction of abscissa axis (PC2) suggests that it is contaminated mostly by DMP. For Chinese cabbage 1, the position projected to the positive direction of abscissa axis (PC3) and the negative direction of abscissa axis (PC1 and PC2) (Figs. 4, S3a, S3b and S3c), but for Chinese cabbage 3 the position projected to the negative direction of abscissa axis (PC1, PC2 and PC3), (Figs. 4, S3a and S3b), indicating that the characteristic pollutants of them are DOP and DEP.

In the PCA results of vegetables collected from two study areas (Fig. 5a, b, Table S5), the contribution of PC1 was 33.39%, and the characteristics of the factor variables values in DEP, DBP and DEHP were all in positive load; the contribution of PC2 was 24.21%, the characteristics of the factor variables values in all the nonzero PAE components were all in positive load; the contribution of PC3 was 20.32%, and the characteristics of the factor variables values in DMP and DBP were all in positive load (Table S5). The total cumulative contribution rate of PC1, PC2 and PC3 is equal to the original value of 93.52%, which could well explain the characteristics of target pollutants in the two study areas. The positive load of target PAEs indicated that DBP, DEHP and DEP in PC1, DMP, DEP, DBP, DEHP and DOP in PC2, and DEP and DMP in PC3 are the characteristic pollutants.

The results agree with that DBP and DEHP are the priority pollutants among the six target PAEs achieved from the concentration levels of different PAE compounds in vegetable samples. DBP and DEHP are always the most frequently detected PAE compounds as well as the highest levels (Zhang et al. 2019).

Table 1 Eigenvalues and contribution rates of PCA

Sampling site	Principal component	Eigenvalue	Contribution rate (%)	Cumulative contribution rate (%)
Tuanlin	1	1.58867	26.48	26.48
	2	1.3658	22.76	49.24
	3	1.02191	17.03	66.27
Zhongxiang	1	2.50287	41.71	41.71
	2	1.60651	26.78	68.49
	3	0.58727	9.79	78.28
All together	1	1.66971	33.39	33.39
	2	1.21064	24.21	57.61
	3	1.01593	20.32	77.93

Higher concentrations or proportions of DBP and DEHP are directly related to human health risks. The exposure to PAEs by the way of daily consuming of vegetables is considered to take up over 45.5% of the total exposure channels, especially by eating vegetables including bean, eggplant, luffa, tomato, cucumber, melon, Chinese cabbage, radish, celery, leek and cauliflower (Yang et al. 2018). Eggplant, tomato, cucumber, Chinese cabbage and cauliflower were all investigated in this study, indicating the underlying crying needs for health risk assessment they might cause.

Variation of PAEs in different sampling types

The total PAE values in soil, vegetable foliar and fruits of each study area were combined for Pearson correlation analysis (Table S6). At Tuanlin, the correlations between DMP and DEHP (0.05), DMP and DOP (0.05), and DEHP and DOP (0.05) were significant. At Zhongxiang, the correlations between DMP and DEHP (0.05), DEP and DEHP (0.05), DBP and DEHP (0.05), and DEP and DOP (0.01) were significant. Significant correlations indicate similar environmental sources or environmental behavior between pollutants. DMP and DEP are usually added as solvents in insecticide sprays, but they are easily degraded for the low molecule weights. DEHP and DOP are solvent additions of high molecular weights hard to degrade. However, more profound interrelationships need further investigation to fully elucidate the relationships between PAE congeners and pesticides.

Determined PAEs values of utilized materials in greenhouses of the two study areas are listed in Table S7. In all the tested materials, DEHP is always the one with the highest concentrations, followed by DBP and DOP. Concentrations of the other three PAE compounds were relatively low, especially BBP, which is almost not detected. Polyethylene (PE) membrane contains higher PAEs than polyolefin (PO) membrane. Total PAE concentrations in colorless mulching films is twofold high than that of the black mulching films, but still higher than that in colored weeding mulching films. Both Tuanlin and Zhongxiang used commercial organic fertilizers in greenhouse production, ordered by the local agricultural materials company from Wuhan city and Hunan

province, respectively. The total PAE level was higher in fertilizers used in Tuanlin.

DBP and DEHP are the most frequently detected PAEs in soils, dusts, sediments and different plants (Li et al. 2016b; Lv et al. 2018). And in 241 surface soil samples from 0 to 15 cm depth of different farmlands areas of the Yangtze River Delta, the detection rates of DBP, DEHP and DOP were all 99%, much higher than the other 12 PAE congeners (Sun et al. 2016). According to Wang et al. (2016), PAE levels are affected by the color of plastic films and the amount of residue. In the current study, higher concentrations of DOP in black mulching films used in Tuanlin proved the leading roles of used materials in PAEs residual levels (Figs. 3, 4, 5, S2 and S3, Table S7). Results of the determined PAEs levels in different commercial organic fertilizers supported the practically determined higher levels of PAEs in soils of Tuanlin than Zhongxiang. On the other hand, wastewater irrigation and pesticides could be the other important PAEs sources in contaminated soils (Chen et al. 2017), which has not been analyzed in the present study.

The order in respects of the sum concentrations of six target PAEs was Tuanlin ($n = 24$) > Zhongxiang ($n = 16$) in the integral level of sampled soils, leaves and the vegetable fruits with significant differences ($p < 0.05$), indicating differences in contamination level between two study areas. The planting duration of study areas in Tuanlin and Zhongxiang was 10 and 4 years, respectively, and the cultivated areas, consumption of plastic membranes and mulching film types were largely different. The total planting cycle of greenhouses has serious time-dependent impact on the total PAEs residue levels (Chen et al. 2012), so that the concentrations of target PAEs are supposed to be at a higher level in Tuanlin. However, high-quality plastic films for greenhouses or mulching films tend to be more durable, reducing the frequency of replacement and also releasing smaller quantities of PAEs, a major aim in developing substitute materials to replace PAEs and plastic films. At Tuanlin and Zhongxiang, mainly applied as greenhouse shed films, PE and PO films have been recognized as the source of soil microplastics worldwide. About 63–430 and 44–300 thousand tonnes of microplastics may be accumulated to agricultural land every year in Europe and North America, respectively (Nizzetto et al. 2016; Rillig, et al. 2017). PE films are globally and widely used polymer materials for lightness, damp-proof, acid- and

alkali-resistance, and it is safe to be used for food packing, but PE has poor aging and heating resistance, which is also the merit of PO films. In full compliance with FDA and USDA standards as excellent hot packaging materials, PO films are more environmentally friendly. PO films are the best choice in reducing pests and diseases and improving the quality of crops. That explains in Zhongxiang where PO membranes have been used, the spray of pesticides was greatly reduced. Plus, the determined PAEs level of PE and PO also proved the worth spreading of PO membranes.

Large differences in cropping management have also resulted in a wide range of total PAE levels in all the soil, foliar and vegetable fruit samples at the two study areas (Fig. 2). Although as a privately run company, the plastic greenhouse production at Zhongxiang compared to Tuanlin has led to better plastic films for greenhouse and mulching, for longer cycle of use for plastic films in the long term. And aiming at producing healthier vegetables, very little pesticides were sprayed at Zhongxiang. Highly intensive pesticide spraying has resulted in the highest foliar contamination with PAEs, and this might be one explanation for the higher contamination and health risks than at Tuanlin. Differences in dominant congeners may also be greatly affected by soil texture (Wang et al. 2018) in addition to pesticide spraying variety.

BBP is used primarily in flexible polyvinyl chloride (PVC) products and food packaging materials (IARC 1984; IPCS 1999). Very little BBP was detected in the three types of sample from the two study areas in the current study. There were no major sources of BBP in the sampled greenhouses because BBP concentrations in the tested materials, irrespective of the color of mulching films or the types of plastic films (shed film or mulching film), were very low (Table S7).

Exposure health risks of target PAE compounds

In Fig. 6, only DEHP was present at adequate concentrations to represent non-carcinogenic risk, but not to people of all ages. Although in the other three study areas of our former study, both DBP and DEHP represent non-carcinogenic risk, the risks of DEHP to people of all ages in some areas of Pengdun and Zhanghe deserved special attention compared with DBP (Ma et al. 2019). In this study, rather than the common found non-carcinogenic risk to young

children, the potential of non-carcinogenic risk caused by only DEHP to adults was predicted in 19 of the 40 greenhouses sampled, which were all from greenhouses at Tuanlin. All sampling sites at Tuanlin exhibited non-carcinogenic risk to children aged < 6 years old. A quarter of sampling sites in Zhongxiang showed similar risk to young children less than 6 years old. From the results of this study, the weight of ingestion and dermal absorption in the contribution of non-carcinogenic risks are the largest compared with intakes from vegetable edible parts and inhalation from the soil, which agrees with the results of street dust (Wang et al. 2017b). Other studies emphasized contributions of dietary daily intake (Cheng et al. 2016), although it is not the revealed most important factor in our current study. The non-carcinogenic risk here due more to DEHP than other PAEs, and the risk to young children was higher than that to older children and adults, which is similar with the conclusions of Wang et al. (2017b). However, Chen et al. (2017) found that vegetable intake showed higher PAEs exposure risk than the total exposure from other foodstuffs, inhalation or dermal absorption. The non-carcinogenic risks for young child should not be neglected because PAEs may be related with premature breast development for girls, a decline in sperm quality and reduction in the anogenital distance of male infants, anti-androgen effects, speeding up and delay of growth and puberty in girls and boys, respectively, poor attentional performance, and childhood obesity, and increase the risk for hypertension (Wang et al. 2020). All pathways of PAE transfer to the human body and causing health risks along the food chain and greenhouse PAEs control in soils and vegetables require further investigation.

The present carcinogenic risks were due largely to the contamination of DEHP (Fig. 7), but the sum values of different target PAEs were still not close to the threshold (10^{-4}), the same for Zilingpu, Zhanghe and Pengdun, indicating that the cancer risks were acceptable. Similar with conclusions of the present study, no non-cancer and cancer risks caused by PAEs through the ingestion absorption and dermal absorption were observed in health risk assessment along with Beiji River (Tang et al. 2017). However, in the other studies, although the non-carcinogenic risk could be neglected, the carcinogenic risk of target DEHP is not acceptable (Wang et al. 2017a), implying

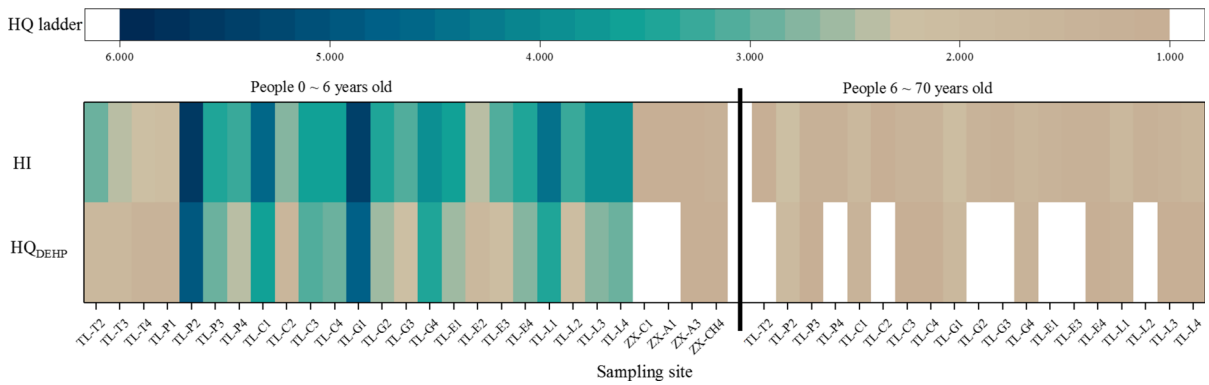


Fig. 6 Heatmap of all the calculated HQs from collected samples in two study areas. Refer the denotes to Fig. 3

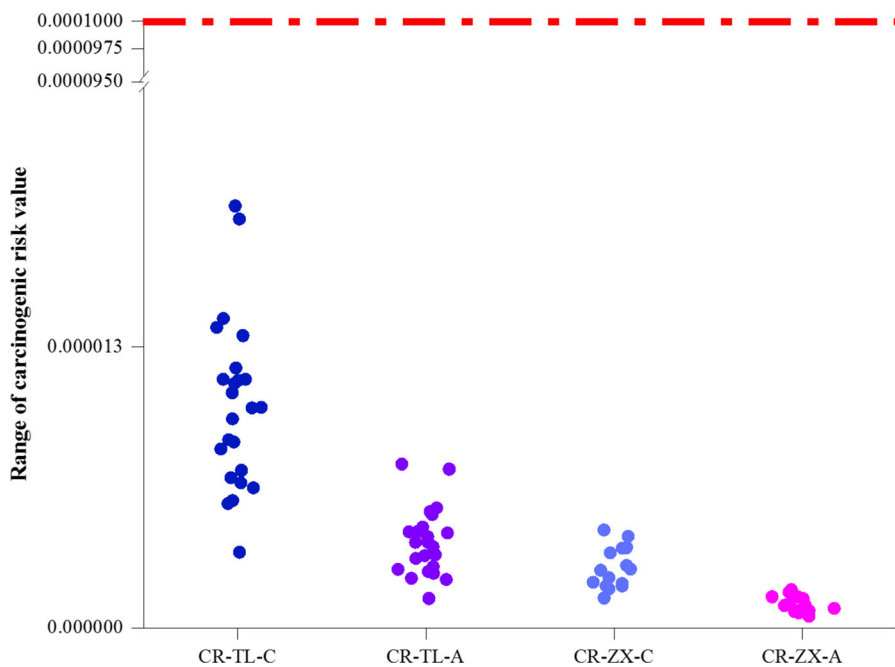


Fig. 7 Carcinogenic risks in different sampling sites of Tuanlin and Zhongxiang. CR-TL-C, carcinogenic risk to children less than six years old in Tuanlin, CR-TL-A, carcinogenic risk to children older than 6 years old and adults in Tuanlin, CR-ZX-C,

carcinogenic risk to children less than 6 years old in Zhongxiang, CR-ZX-A, carcinogenic risk to children older than 6 years old and adults in Zhongxiang

the risk of DEHP worth more close attention than usual.

Although the RfD of DEHP used in this study was $20 \mu\text{g kg}^{-1} \text{bw day}^{-1}$, the current regulatory limit for DEHP is the tolerable daily intake (TDI) of $50 \mu\text{g kg}^{-1} \text{bw day}^{-1}$ recommended by the European Food Safety Authority and endorsed by the French Agency for Food, Environmental and Occupational Health and Scientific Committee on Emerging and Newly Identified Health Risks of the European

Commission (Chen et al. 2019). But based on the current epidemiological investigations, the recommended RfD and TDI values are not reasonable enough to protect public health (Chen et al. 2019). Therefore, not only the recommended reference levels of DEHP should be refreshed, the list of priority control pollutants in China should be updated by adding DEHP.

Summary of five typical facility agricultural areas in Jingmen

The five selected typical facility greenhouse vegetable production areas are the largest scaled ones in Jingmen (Graphical abstract), and the PAEs contamination concentration levels and health risk results could represent the whole situation of Jingmen city. In the total of 80 soils and 152 vegetables, the Σ 6PAEs ranged from 919 ± 134 to $7015 \pm 475 \mu\text{g kg}^{-1}$ (DW), and from 387 ± 63 to $11,683 \pm 1313 \mu\text{g kg}^{-1}$ (DW), respectively. The result indicated that the contamination level of six target PAEs in Tuanlin and Zhongxiang is in the middle of these five areas. The most frequently and abundantly detected PAEs in Zilingpu, Zhanghe and Tuanlin are DBP and DEHP, but DBP, DEHP and DOP in Pengdun and Zhongxiang. The contamination level of different samples from different areas was Zhongxiang < Pengdun < Zilingpu < Tuanlin < Zhanghe for soils; Zhongxiang < Tuanlin < Pengdun < Zilingpu < Zhanghe for foliar samples and Zhongxiang < Tuanlin < Zhanghe < Pengdun < Zilingpu for vegetable fruits. Study areas No. 5 Zhongxiang and No. 3 Pengdun are all located in the big region of Zhongxiang City; the similar source of agricultural materials and similar longer operating duration (10 and 8 years, respectively) might have contributed to the similar major pollutants. The highest concentration of total six PAEs appeared in leaf sample of Zhanghe, and the lowest in leaf sample of Zhongxiang. Non-carcinogenic risk rates for children less than 6 years old from different study areas were 2/14 in Zilingpu, 24/24 in Tuanlin, 9/12 in Zhanghe, 4/16 in Zhongxiang and 14/14 in Pengdun. And for older children and adults, the non-carcinogenic risk rates were 0/14 in Zilingpu, 19/24 in Tuanlin, 3/12 in Zhanghe, 0/16 in Zhongxiang and 2/14 in Pengdun. The target PAEs health risks from vegetable consuming in Tuanlin and Pengdun, geographically close to each other, deserve more attention.

Conclusion

The concentrations of the total six PAEs in soil and vegetable samples suggested the impact of different management systems and planting years on the contamination levels. From the perspective of the

whole Jingmen area, the major PAE pollutants in Zilingpu, Zhanghe and Tuanlin are DBP and DEHP, but in Pengdun and Zhongxiang they are DBP, DEHP and DOP. Carcinogenic risks were not observed in all the five study areas. Non-carcinogenic risks to people should be noticed, especially in Tuanlin where the risk for young children (no more than 6 years old) is 23/24 and even for older children and adults is 19/24. The situation for Pengdun also deserves attention because the non-carcinogenic risk to young children is 14/14. DEHP should be classified as a new priority PAEs in the future modified list of China based on the contribution to the total HI values. PE membranes and colored weeding mulching films should be popularized in facility greenhouse production areas to lower the contamination of DEHP as well as reduce the health risk caused by DEHP. The present study mainly contributed as a guidance for reference of PAEs contamination and health risks in central China, the selection of greenhouse production materials and the management of environmental pollution.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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