

# Phthalate esters contamination in soils and vegetables of plastic film greenhouses of suburb Nanjing, China and the potential human health risk

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**Abstract** The contamination of phthalate esters (PAEs) has become a potential threat to the environment and human health because they could be easily released as plasticizers from the daily supply products, especially in polyethylene films. Concentration levels of total six PAEs, nominated as priority pollutants by the US Environmental Protection Agency (USEPA), were investigated in soils and vegetables from four greenhouse areas in suburbs of Nanjing, East China. Total PAEs concentration ranged from  $930 \pm 840$  to  $2\,450 \pm 710$   $\mu\text{g kg}^{-1}$  (dry weight (DW)) in soil and from  $790 \pm 630$  to  $3\,010 \pm 130$   $\mu\text{g kg}^{-1}$  in vegetables. Higher concentrations of PAEs were found in soils except in Suo Shi (SS) area and in vegetables, especially in potherb mustard and purple tsai-tai samples. Risk assessment mainly based on the exposures of soil ingestion

and daily vegetable intake indicated that bis(2-ethylhexyl) phthalate (DEHP) in the samples from Gu Li (GL) and Hu Shu (HS) exhibited the highest hazard to children less than 6-year old. Therefore, the human health risk of the PAEs contamination in soils and vegetables should greatly be of a concern, especially for their environmental estrogen analog effects.

**Keywords** Phthalate esters · Ambient pollution · Soil ingestion · Vegetable intake · Health risk assessment

## Abbreviations

Al <sub>2</sub> O <sub>3</sub>	Alumina
BB	Benzyl benzoate
BBP	Butyl benzyl phthalate
CLEA	The Contaminated Land Exposure Assessment
DEHP	Bis(2-ethylhexyl) phthalate
DEP	Diethyl phthalate
DMP	Dimethyl phthalate
DnBP	Di- <i>n</i> -butyl phthalate
DnOP	Di- <i>n</i> -octyl phthalate
DW	Dry weight
H <sub>2</sub> SO <sub>4</sub>	Sulphuric acid
IR	Index of risk
LOD	Limit of detection
MCRA	Monte Carlo Risk Assessment
Na <sub>2</sub> SO <sub>4</sub>	Anhydrous sodium sulfate
ND	Not detected
PAEs	Phthalate esters
RfD	Oral reference dose
TDI	Total daily intake
USEPA	US Environmental Protection Agency

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## Introduction

The reality of large human population and a relatively small arable land resulted in the convert of over 3.33 million ha of farmland to highly profitable greenhouse vegetable area in China (CNWest, 2012a). Aiming at improving the daily diet quantity and quality, more than 38 thousand ha arable land has been turned to poly-tunnel greenhouses for vegetable growing and over 1.88 million tonnes of agricultural film has been used annually in Nanjing, capital of Jiangsu Province (CEC-CEDA information, 2012b).

Depending on plastic composition, the amount of phthalate esters (PAEs) as plasticizers in polyvinyl chloride (PVC) can be up to 50 %, which has led to potential environmental contamination in facility agriculture due to the large application of plastic film (Bergé et al. 2013). These compounds were found to be characteristics of endocrine disruptors, carcinogens, teratogens, and mutagens (Liu et al. 2012a; Shi et al. 2012; Balbuena et al. 2013) and occurred ubiquitously in the environment recently (Cecinato et al. 2012; Liu et al. 2012b, 2014; Zhang et al. 2012; Masood and Malik 2013; Xu et al. 2014). Dimethyl phthalate (DMP), diethyl phthalate (DEP), and di-*n*-octyl phthalate (DnOP) have been proposed as priority pollutants by the Chinese government because of their pronounced tendency to accumulate in biological systems and their potential damage to the human body through contamination of the food chain (Environmental Monitoring Center of China 1992). Soils can be contaminated with PAE compounds by atmospheric precipitation, water irrigation, and fertilizer application (Zhang et al. 2012). However, particle precipitation after volatilization from and direct release of PAEs from plastic film are supposed to be the main sources in soils in poly-tunnel greenhouses (Wang et al. 2007). PAE contamination in vegetables such as rape in Nanjing and toxicity effects on the physiology and ultrastructure of cucumber seedling roots have been recorded (Cai et al. 2008; Chai et al. 2008; Zhang et al. 2014); however, contamination of soils and vegetables in poly-tunnel greenhouse has not been studied in detail.

PAEs is one type of emerging contaminants (Ni and Ou 2000; Chen et al. 2011; Tai et al. 2011) which has been less of a concern than pesticides and heavy metals such as chromium, copper, cadmium, and lead in the production of greenhouse vegetables (He 2004; Wu et al. 2009; Li et al. 2010a). However, evidences have been provided that PAE compounds with  $\log K_{ow}=2\sim7$  and  $\log K_{oa}>6$  could be accumulated or magnified in terrestrial organisms and human body, which also highlights the importance of their health risk assessments (Fierens et al. 2012; Teil et al. 2012).

In the present study, our objectives were to clarify the accumulation of PAEs in vegetable edible parts and the potential risk to human health via soil ingestion and vegetable intake; the concentrations of six target PAEs in soils and vegetables in typical greenhouse areas were investigated. Therefore, soil and vegetable samples were collected from four representative

poly-tunnel greenhouses in suburban of Nanjing city for PAEs analysis.

## Materials and methods

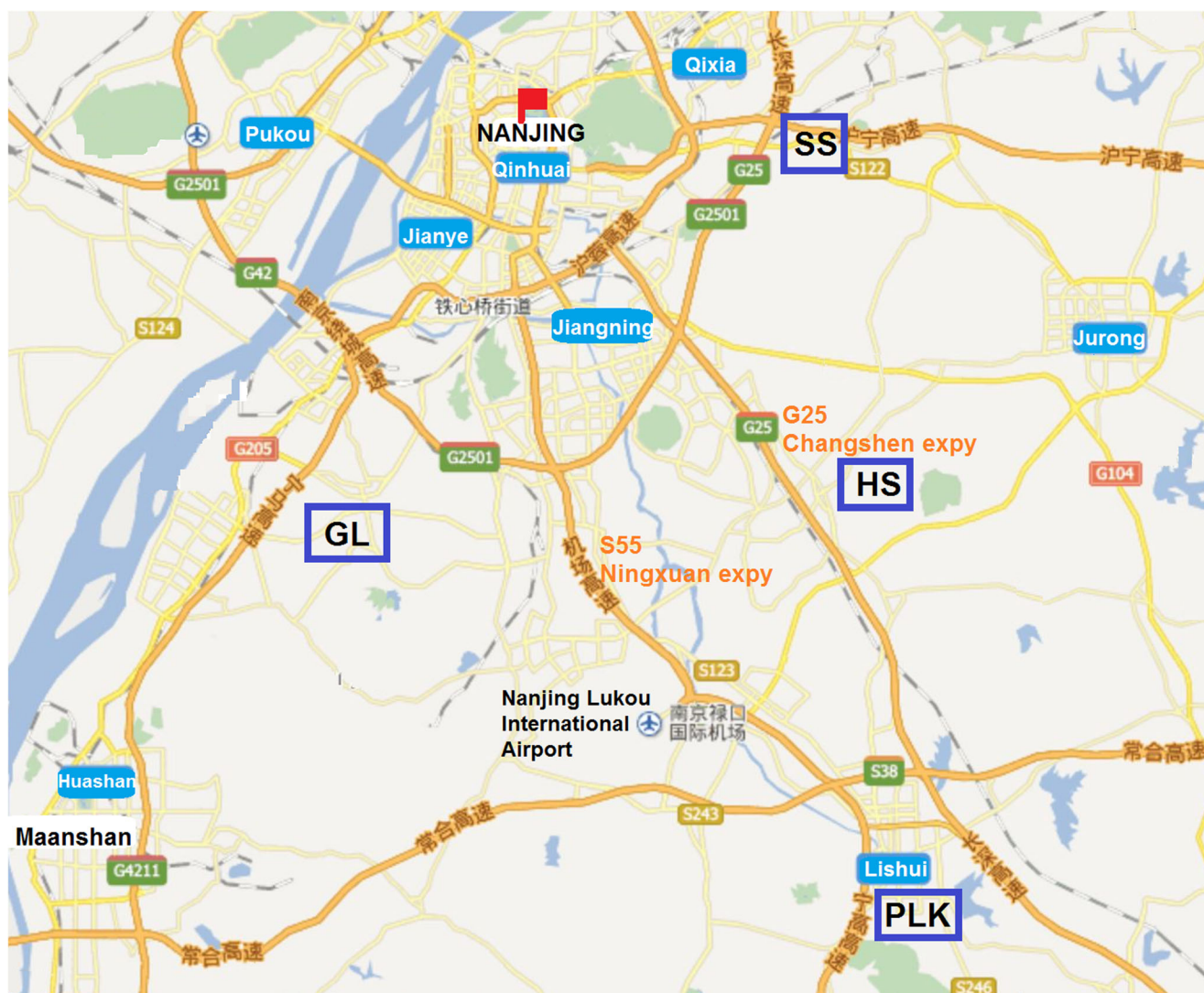
### Chemicals

A mixed standard solution ( $10^3 \mu\text{g mL}^{-1}$ ) of six target pollutants and the internal standard benzyl benzoate (BB) solution ( $5\times10^3 \mu\text{g mL}^{-1}$ ) were all obtained from AccuStandard Incorporation (New Haven, Connecticut, USA), which were applied throughout this experiment as total PAEs, including DMP, DEP, butyl benzyl phthalate (BBP), di-*n*-butyl phthalate (DnBP), bis(2-ethylhexyl) phthalate (DEHP), and DnOP, in the list of priority pollutants by US Environmental Protection Agency (USEPA). Certified reference material CRM 136-100 (BNAs-Clay 1) was purchased from RT Corporation (Laramie, Wyoming, USA), one of the original proficiency test providers recognized by USEPA and utilized in the analysis procedure for reliable testing of the analytical method.

Analytical-grade solvents (acetone and hexane) obtained from chemical reagent companies in Nanjing were re-distilled in an all-glass system to remove trace impurities before use. HPLC-grade hexane was purchased from Tedia Company Incorporation (Fairfield, San Francisco and Oakland Helicopter Airlines, USA).  $\text{Na}_2\text{SO}_4$  (reagent grade), neutral  $\text{Al}_2\text{O}_3$  (400 mesh and reagent grade), neutral silica gel (100~200 mesh), and  $\text{H}_2\text{SO}_4$  (guaranteed reagent) were obtained from the National Pharmaceutical Group Chemical Reagent Limited Corporation (Shanghai, China). Packing materials ( $\text{Na}_2\text{SO}_4$ , neutral  $\text{Al}_2\text{O}_3$ , and neutral silica gel) were dried in a muffle furnace at 400 °C for 6 h and stored in desiccators before use (Ma et al. 2013).

### Sampling

Soil and vegetable samples were collected from 61 out of approximately 500 plastic film greenhouses for vegetable production in the four suburban areas Gu Li village (GL), Hu Shu village (HS), Planck farm (PLK), and Suo Shi village (SS) in December 2011 (Fig. 1; Table 1). The environmental status contour in terms of the distribution of agriculture and industry, hydrogeological conditions of nearby rivers, and features of greenhouses (age and species of vegetables) were all considered during sampling. From the selected 61 greenhouses, a total of 305 surface (0~15 cm) soil and vegetable paired samples (using quincunx sampling method in each greenhouse) were collected. The soil samples were collected by using a soil corer, while the plant samples were selected randomly for five fruit and compared after one quarter of each fruit was cut, mixed, and analyzed with three replicates. The fresh edible parts of each vegetable sample were collected and brought to the laboratory, washed with tap water, rinsed with distilled water, and wiped dry with paper tissue. Both vegetables and soils



**Fig. 1** The distribution maps of four investigated protected agricultural areas in suburb Nanjing

were then freeze dried in a Free Zone 2.5-Liter Freeze Dry System (Labconco Corp., Kansas City, MO). The average pH value of the soils was 7.4, mean organic carbon content was  $14.6 \text{ g kg}^{-1}$ , and available nitrogen, phosphorus, and potassium were 9.68, 1.44, and  $10.28 \text{ g kg}^{-1}$ , respectively (Lu 1999). Ten grams of dried soils was ground and sieved (60 mesh), and 2 g of vegetable sample was homogenized for each replication in liquid nitrogen prior to storage at  $-20^\circ \text{C}$  for subsequent analysis.

### Sample processing

Glassware was washed by strictly following the procedure described by Ma et al. (2013) prior to analysis. Sample processing procedure was conducted following the description of Ma et al. (2013) for soils and Ma et al. (2012a) for vegetables.  $10 \mu\text{L}$  of internal standard (BB) was added before hexane (HPLC grade) was added to bring the final volume to 1 mL.

**Table 1** Related information of four selected protected agricultural areas

Sampling position	Mode of business operation	Planting age (year)	Quality of mulch plastic film	Melt index of plastic film
GL	Corporation and peasant cooperate	4~6	Non-age-resistant, thinner than 0.012 mm	5.5 g/10 min
HS	Corporation and peasant cooperate	1~4	Non-age-resistant, thinner than 0.010 mm	7 g/10 min
PLK	Corporation operate	7~10	Age-resistant, thicker than 0.015 mm	2.8 g/10 min
SS	Peasant operate	Over 10	Age-resistant, thicker than 0.015 mm	3.0 g/10 min

Samples were transferred to brown sample bottles and stored at  $-20^{\circ}\text{C}$  before further analysis.

### Instrumental analysis, quality assurance and quality control

Analysis of individual PAEs in samples was performed exactly following the description of Ma et al. (2012a) modified from USEPA method 8270C with an Agilent 7890GC-5975 MSD. Quality assurance and quality control results showed the high accuracy and sensitivity of this method and the reliability of the results (2012a). For every 16 samples, two whole procedure blanks, two soil matrix blanks, and one CRM 136-100 were analyzed to ensure the analysis reliability.

### Health risk assessment

The main intake source of PAEs was assumed to be soil ingestion and daily vegetable eating in this assessment. In this study, soil ingestion and daily vegetable eating were assumed to be the major intake sources of PAEs. PAE concentrations in soils were used to estimate the soil ingestion exposure and characterize the risk of local people that in vegetables were for intake exposure assessment. The consumption estimates of vegetables were based on dietary intake data published by the Environment Agency and Department of Environment, Food and Rural Affairs Danish Nationwide Dietary Survey in CLEA of London with slight modification and divided into age groups of 0~6 (refer to the data of 1~4 of CLEA) and 7~70 (Table 2).

Soil ingestion amount of PAE intake can be calculated as:

$$\text{Insoil} = \frac{\text{EF} \times \text{ED} \times \text{IR}_{\text{soil}} \times C_s \times \text{CF}}{\text{BW} \times \text{AT} \times 365} \quad (\mu\text{g} \quad (\text{kg BW day})^{-1}) \quad (1)$$

Where, EF is exposure frequency ( $\text{day year}^{-1}$ ); ED is exposure cycle (year);  $\text{IR}_{\text{soil}}$  is intake rate of soil ( $10^3 \mu\text{g day}^{-1}$ );  $C_s$  is the concentration of individual PAE compounds in the soil ( $\mu\text{g kg}^{-1}$ ); CF is a conversion factor ( $10^{-6} \text{ g } \mu\text{g}^{-1}$ ); BW is body weight (kg); and AT is average time (year).

Food consumption amount of PAE intake can be calculated as:

$$\text{Infood} = \text{daily vegetable intake} \times R_v \times C_f \quad (\mu\text{g} \quad (\text{kg BW day})^{-1}) \quad (2)$$

**Table 2** Summary consumption rates of vegetables used in CLEA according to age class

Age (year)	Daily vegetable intake ( $\text{g (DW kg-BW day)}^{-1}$ )		
	Salad leafy vegetables	Carrot	Wild cabbage
0~6	0.037	0.125	0.051
7~70	0.019	0.054	0.035

Where, daily vegetable intake ( $\text{g (fw kg BW day)}^{-1}$ ) is as shown in Table 2;  $R_v$  is the ratio of fresh and dry vegetables; and  $C_f$  is the concentration of individual PAE compounds in the food which is mainly vegetables ( $\mu\text{g kg}^{-1}$ ).

IR is the sum of multi-exposure to pollutants, can be calculated as:

$$\text{IR}_j = \sum \text{IR}_i \quad (i = 1, 2, 3, \dots) \quad (3)$$

$$\text{HQ} = \frac{\text{Intake}}{\text{RfD}}$$

Where, HQ is the hazard quotient, which is defined as the relation between the predicted exposure and the RfD. Intake is the exposure amount, and RfD is the reference amount of each individual pollutant ( $10^3 \mu\text{g (kg day)}^{-1}$ ). The values of RfD and TDI are listed in Table 3 (USEPA 1996; CSTEE 1998; NMED 2009).

### Statistics analysis

All data were processed with Microsoft Excel 2003 and the SPSS v.14.0 software package. Chemical concentrations under the limit of detection (LOD) were assumed to be equal to one third of that value (not detected (ND),  $-1/3 \text{ LOD}$ ). The data were analyzed for significant differences from the control treatment or between treatments using one-way analysis of variance. The level of significance was set at  $p < 0.05$ .

## Results and discussion

### Target PAE compounds level in soil samples of four investigated areas

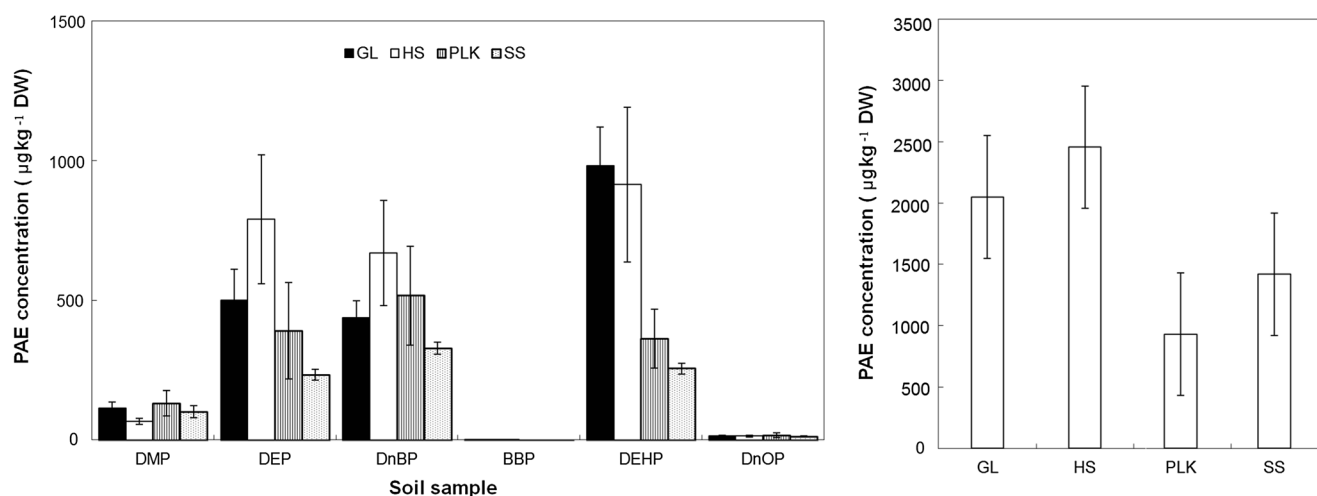
The concentrations of total PAEs in soils of the four investigated protected agricultural areas of suburb Nanjing, GL, HS, PLK, and SS are shown in the order of  $\text{HS} > \text{GL} > \text{PLK} > \text{SS}$  in Fig. 2. Individual concentrations of the PAE compounds were all less than  $981 \pm 140 \mu\text{g kg}^{-1} \text{ DW}$ , showing an order of  $\text{DEHP} > \text{DnBP} > \text{DEP} > \text{DMP} > \text{DnOP} > \text{BBP}$ . However, the molecular signatures of PAEs were not equal in the four areas studied; in fact, the first three dominant compounds were shown in the following orders in each study area:  $\text{DEHP} > \text{DEP} > \text{DnBP}$  in HS,  $\text{DEHP} > \text{DEP} > \text{DnBP}$  in GL,  $\text{DnBP} > \text{DEHP} > \text{DEP}$  in SS, and  $\text{DnBP} > \text{DEP} > \text{DEHP}$  in PLK.

**Table 3** Referred values of six PAE target pollutants for people of all ages ( $10^3 \mu\text{g (kg day)}^{-1}$ )

	DMP	DEP	DnBP	BBP	DEHP	DnOP
RfD (NMED)	10	0.8	0.1	0.2	0.02	0.04
RfD (USEPA)	<sup>a</sup>	<sup>a</sup>	0.1	0.2	0.02	<sup>a</sup>
TDI (EU)	<sup>a</sup>	<sup>a</sup>	0.1	0.2	0.037	0.37

<sup>a</sup> Without relative reference RfD criteria values





**Fig. 2** Phthalate ester concentrations in soils of four investigated protected agricultural areas GL, HS, PLK, and SS of suburb Nanjing ( $\mu\text{g kg}^{-1}$  DW). Each point is the mean of three replicates  $\pm$  standard deviation (SD)

In GL, the total PAEs concentration in the soil was  $2\,050 \pm 330 \mu\text{g kg}^{-1}$  DW (Fig. 2); in particular, DEHP reached  $980 \pm 140 \mu\text{g kg}^{-1}$ , DEP  $500 \pm 110 \mu\text{g kg}^{-1}$  DW, DnBP  $440 \pm 60 \mu\text{g kg}^{-1}$  DW, and DMP  $130 \pm 20 \mu\text{g kg}^{-1}$  DW (Fig. 2; Table 4), which cumulatively accounted for over 99 % of the total PAE concentration. The PAE concentrations in GL soils were generally lower than HS which is as high as  $2\,450 \pm 710 \mu\text{g kg}^{-1}$  DW although the planting time (4–6 y) of GL greenhouse was longer than HS and agricultural films of poor quality were used. The reasons were assumed to be the effective field managements such as periodical uncovering of agricultural films for better venting to cut down plant diseases and insects growth and to accelerate the PAE removing from soils by chemical degradation and biodegradation (Pradeep and Benjamin 2012). Such a management pattern could also increase the transfer of PAEs from inside to outside the greenhouse, which further reduced the chance of PAE accumulation in soils.

Similarly to GL, the total PAE concentrations was  $2\,450 \pm 710 \mu\text{g kg}^{-1}$  DW (Fig. 2); in particular, DEHP reached  $910 \pm 280 \mu\text{g kg}^{-1}$ , DEP  $790 \pm 230 \mu\text{g kg}^{-1}$  DW, and DnBP  $700 \pm 190 \mu\text{g kg}^{-1}$  DW, which cumulatively account for over 96 % of the total PAE compounds in HS soils (Fig. 2; Table S1). Soils showed a great variety in both total concentration and individual concentration (Table S1). Actually, poor-quality agricultural film with shorter application cycle and higher aging rate require more frequent replacements, which perhaps result in more expense. In addition, the aging of agricultural film is a main source of PAE compounds release to the soil, which is highly in accordance with PAE tested concentrations in soils in this area.

The total PAEs concentration of soil in PLK was  $1\,420 \pm 510 \mu\text{g kg}^{-1}$  DW (Fig. 2), in particular, DnBP reached  $520 \pm 180 \mu\text{g kg}^{-1}$  DW, DEP  $390 \pm 170 \mu\text{g kg}^{-1}$ , DEHP  $360 \pm 100 \mu\text{g kg}^{-1}$  DW, and DMP  $130 \pm 50 \mu\text{g kg}^{-1}$  DW in PLK (Fig. 2; Table S2), which cumulatively account for over 98 % of the total PAE compounds in PLK soils. The PLK soil

showed the lowest total PAEs concentration due to the application of medium-quality agricultural films of under the corporate management for 7 to 10 years. This situation is similar to that of SS (Fig. 2). These two sites are characterized of organic vegetables growing; hence, the continuous high-intensity planting of different vegetable types might take away relatively more PAE compounds from soil than in other investigated areas.

The total PAE concentrations was  $930 \pm 840 \mu\text{g kg}^{-1}$  DW (Fig. 2); in particular, DnBP reached  $330 \pm 20 \mu\text{g kg}^{-1}$  DW, DEHP  $260 \pm 20 \mu\text{g kg}^{-1}$  DW, DEP  $23 \pm 20 \mu\text{g kg}^{-1}$  DW, and DMP  $100 \pm 20 \mu\text{g kg}^{-1}$  DW in SS (Fig. 2; Table S3), which cumulatively account for over 98 % of the total PAEs in SS soils. The total PAEs concentrations were distinctively lower than HS and GL (Fig. 2) due to the application of a better agricultural film under the management of independent farmer groups for more than 10 years. Although a long history of greenhouse planting and the application of greenhouses in a large scale and quantity could result in the accumulation of PAEs in soil (Chai et al. 2014), continuously planting of different vegetables all year round after building of greenhouses would remove the PAEs from soil by several ways, such as releasing of PAEs from agricultural film in each planting season, volatilization with vegetable transpiration and greenhouse venting by uncovering films, and degradation by direct episodic exposure to sunlight.

Compared with the soil cleanup objectives and cleanup levels issued by the New York Department of Environmental Conservation (1994), the concentrations of DnBP and DEP in all the soils have been over their relative cleanup objectives but less than their listed cleanup levels (Table S4). According to former investigation, gaseous evaporation and leaching of water vapor inside greenhouses are two major sources of PAEs (Wang et al. 2007) in addition to the factors such as quality of agricultural films, temperature inside the greenhouses, replacing and uncovering frequency of agricultural films, and the management methods of greenhouse quality (Ma 2012b). However, when it

**Table 4** PAE concentrations in test soil and vegetables of GL in suburb Nanjing ( $\mu\text{g kg}^{-1}$  DW)

Sample	Concentration in soils							Vegetable/classification		Concentration in vegetables						
	DMP	DEP	DnBP	BBP	DEHP	DnOP	PAEs			DMP	DEP	DnBP	BBP	DEHP	DnOP	PAEs
1	110±0	679±2	456±2	1±0	1213±4	12±0	2471±9		Chinese cabbage/leafy	ND	40±0	1403±6	20±0	1130±12	47±6	2640±23
2	089±0	532±2	514±2	1±0	954±3	15±0	2105±8		Garlic bolt/leafy	ND	10±0	877±15	30±6	607±15	387±25	1883±62
3	094±0	521±2	496±2	1±0	864±3	16±0	1992±7		Asparagus lettuce/stem	ND	30±0	1387±29	27±6	1893±57	803±20	4140±112
4	96±0	514±2	486±2	1±0	570±2	12±0	1679±6		Crowndaisy chrysanthemum/leafy	ND	47±6	1183±12	33±6	840±12	27±6	2130±40
5	132±1	546±2	420±2	1±0	871±3	15±0	1985±7		Pakchoi/leafy	27±0	30±0	210.8±10	ND	1857±71	403±45	2327±327
6	110±0	679±2	399±1	1±0	1353±5	12±0	2554±9		Bovine heart shaped cabbage/leafy	ND	20±0	277±0	ND	800±21	10±0	1107±21
7	110±0	631±2	329±1	1±0	1302±5	12±0	2385±8		Temip/root	150±0	20±0	140±21	30±6	473±30	683±71	1469±128
8	119±0	667±2	334±1	–	1026±4	12±0	2158±8		Pakchoi/leafy	ND	ND	573±12	ND	1120±6	590±29	2283±46
9	122±0	426±2	414±1	1±0	863±3	12±0	1838±6		Celery/leafy	ND	33±6	460±29	10±0	690±73	1020±44	2213±152
10	163±1	414±1	488±2	1±0	946±3	11±0	2023±7		Spinach/leafy	ND	20±10	537±6	3±0	1537±6	37±29	2134±50
11	152±1	442±2	496±2	–	925±3	13±0	2028±7		Asparagus lettuce/stem	ND	20±0	900±21	10±10	1697±72	1313±72	3940±176
12	116±0	463±2	436±2	1±0	998±4	13±0	2027±7		Cayenne/solanaceous	ND	13±6	527±0	ND	237±15	30±10	807±31
13	86±0	391±1	466±2	<sup>a</sup>	965±3	12±0	1920±7		Pakchoi/leafy	10±0	137±0	173±10	30±6	5817±21	617±6	6757±42
14	102±0	402±1	452±2	1±0	954±3	13±0	1924±7		Florists chrysanthemum leaf/leafy	30±0	33±15	630±31	30±10	5817±257	617±15	7157±328
15	110±0	357±1	524±2	1±0	964±3	15±0	1971±7		Pakchoi/leafy	30±0	20±0	553±23	30±6	1247±71	10±10	1863±110
16	89±0	523±2	543±2	1±0	965±3	17±0	2138±8		Chinese cabbage/leafy	ND	20±0	277±10	ND	637±25	790±40	1724±75
17	89±0	426±2	512±2	1±0	933±3	19±0	1980±7		Garlic bolt/leafy	ND	20±0	797±21	ND	3437±10	10±12	4264±42
18	99±0	512±2	494±2	<sup>a</sup>	914±3	19±0	2038±7		Chinese cabbage/leafy	ND	ND	53±10	23±0	757±6	7±42	840±57
19	141±12	390±32	463±38	<sup>a</sup>	1102±91	12±1	2108±174		Pakchoi/leafy	ND	ND	163±10	23±0	197±17	10±33	393±60

Each point is the mean of three replicates±SD. SD values less than 0.5 were unified written as 0

ND not detected

<sup>a</sup> The value is below 1

comes to the decreasing of PAE content, it has been concluded that both photodecomposition and hydrolysis of PAEs proceed very slowly and the key method to eliminate the pollutants is the biodegradation approach (Wolfe et al. 1980). Most PAEs are readily degraded under aerobic conditions but more slowly in anaerobic environments, especially DEHP and DnOP (Ziougou et al. 1989; Wu et al. 2010; Yuan et al. 2010).

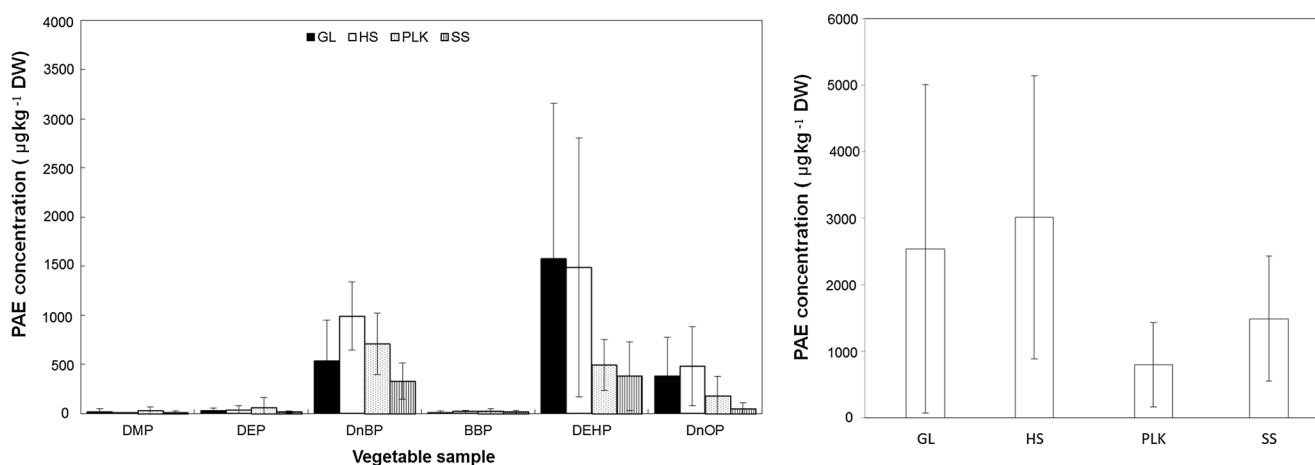
### Target PAE compounds in vegetable samples of four target investigated areas

The reported average levels of DnBP and DEHP in Chinese greenhouse-planted vegetables were approximately between 900 and 3 050  $\mu\text{g kg}^{-1}$  (Pang et al. 1995; Wang et al. 2007), which were very close to or even higher than food concentration limitations of the EU (300  $\mu\text{g kg}^{-1}$  for DnBP and 1 500  $\mu\text{g kg}^{-1}$  for DEHP) (Laturnus and Grøn 2007). The total PAEs concentration of the vegetables was between 790 $\pm$ 630 and 3 010 $\pm$ 2 130  $\mu\text{g kg}^{-1}$  DW in the four investigated areas and was in the order of HS>GL>SS>PLK, which was quite different from the order of soil concentrations in the four areas (Fig. 3). Concentrations of the individual PAE compounds were all lower than 1 580 $\pm$ 1 580  $\mu\text{g kg}^{-1}$  DW and were in the order of DEHP>DnBP>DnOP>DEP>DMP>BBP, and the increasing of DnOP showed notable difference. DEHP, DnBP, and DnOP were the three dominant compounds in all areas; however, the percentages of each PAE compound in the different areas were not in consistent (Fig. 3).

Total PAEs concentrations in vegetable edible parts were in the range of 1 070 and 6 340  $\mu\text{g kg}^{-1}$  DW with great variety in both total and individual concentrations; in particular, DEHP reached 1 490 $\pm$ 1 320  $\mu\text{g kg}^{-1}$  DW, DnBP 990 $\pm$ 350  $\mu\text{g kg}^{-1}$  DW, and DnOP 480 $\pm$ 400  $\mu\text{g kg}^{-1}$  DW over 98 % of the total PAEs in HS vegetables (Fig. 3; Table 4). Typical leafy vegetables, potherb mustard and celery, as well as solanberry (cayenne) from soil No. 1 showed higher PAEs concentration, which were

all over 5 000  $\mu\text{g kg}^{-1}$  DW (Table 4). Correspondingly, soil No. 1, 2, and 13 exhibited higher PAEs concentration (about 3 000  $\mu\text{g kg}^{-1}$  DW) than others, which implied PAEs concentrations in vegetables fit well with those in soils. Also same vegetables in different greenhouses showed positive correlations with the corresponding soil concentrations (see soils No. 1, 9, 10, 11, 13, and 15), especially in the case of DnBP accumulation (Table 4). The differed PAE soil/vegetable ratio for soils No. 5, 6, 8, and 14 was 1.28, 1.29, 1.57, and 0.74, respectively, which indicated that PAEs accumulation in the vegetable changed with pakchoi types. The PAEs accumulation followed in the order of cole, shanghai cole, Chinese cabbage, and asparagus lettuce.

Similar to HS in GL, total PAEs concentrations in the vegetable was in the range of 390 to 7 150  $\mu\text{g kg}^{-1}$  DW; in particular, DEHP reached 1 580 $\pm$ 1 580  $\mu\text{g kg}^{-1}$  DW, DnBP 540 $\pm$ 410  $\mu\text{g kg}^{-1}$  DW, and DnOP 380 $\pm$ 400  $\mu\text{g kg}^{-1}$  DW in GL; thus, the three PAEs accounted for over 98 % of the total (Fig. 3). Pakchoi (soil No. 13), florists chrysanthemum leaf (soil No. 14), and garlic bolt (soil No. 17) accumulated more than 4 000  $\mu\text{g kg}^{-1}$  DW of the total PAE concentration, however, the corresponding concentration of PAEs in the soil samples was not as high as the vegetables (Table S1). Garlic bolt from soil No. 2 and 17 showed different compositions and concentrations of PAEs. A relatively higher concentration of DnOP occurred in the samples of soil No. 2, while higher concentration of DEHP occurred in garlic bolt samples of soil No. 17. Newly planted garlic bolt, soil No. 2, accumulated less DEHP because of the short growing period; less DnOP in the soil No. 17 could be explained by the reason of greenhouse opening before the sampling and the compound release into the atmosphere mostly. Different accumulated characteristics have been observed in different types of leafy vegetables more commonly planted in this area. Although (soil No. 4) crowndaisy chrysanthemum and (soil No. 10) spinach accumulated similar PAEs concentration, spinach showed a higher accumulation of PAE with respect to the different concentrations of soil PAEs concentrations.



**Fig. 3** Concentrations of total PAEs in vegetables of four investigated protected agricultural areas GL, HS, PLK, and SS of suburb Nanjing ( $\mu\text{g kg}^{-1}$  DW). Each point is the mean of three replicates $\pm$ SD

Total PAEs concentrations in the vegetable were in the range of  $780\sim 2\,710\ \mu\text{g kg}^{-1}\text{ DW}$ ; in particular, DnBP reached  $710\pm 310\ \mu\text{g kg}^{-1}\text{ DW}$ , DEHP  $490\pm 260\ \mu\text{g kg}^{-1}$ , and DnOP  $170\pm 200\ \mu\text{g kg}^{-1}\text{ DW}$  in SS; thus, the three PAEs cumulatively accounted for over 92 % of the total in vegetable samples (Fig. 3). The accumulation of total PAEs in edible parts of the vegetables was distinctively lower than that in the former two areas. Soil No. 9 (potherb mustard) in this area also showed its considerable ability to accumulate PAE target pollutants, similar with that in HS (Table S2).

Little variety existed in total and individual concentration of vegetable samples in PLK. PAEs in vegetable samples of PLK show less variety in component and total contents (Table S3). Total PAEs concentrations were about 370 to  $1\,990\ \mu\text{g kg}^{-1}\text{ DW}$ ; in particular, DEHP reached  $380\pm 350\ \mu\text{g kg}^{-1}\text{ DW}$ , DnBP  $330\pm 190\ \mu\text{g kg}^{-1}$ , DW and DnOP  $50\pm 60\ \mu\text{g kg}^{-1}\text{ DW}$  in PLK was over 75 % of the total PAE compounds in PLK vegetables or the second low in four investigated different protected houses (Fig. 3). Soil No. 4 cauliflower and soil No. 17 broccoli showed relative higher accumulation as well as soil No. 6 endive and soil No. 7 lettuces as raw eaten vegetables, which needs more attention in case of causing potential risk to human feeding on them.

According to the investigation of Zhang et al. (2013), both plastic materials and cosmetic and personal care products are important sources of DEHP and DnBP in urban settled house dust of Nanjing (Zhang et al. 2013). DEHP and DnBP were also the predominant compounds in freshwater fish and marine fish of Hong Kong market (Cheng et al. 2013). Total PAEs have been detected in vegetable samples of all nine farms located in the Pearl River of China, within which the maximum content reached  $11\,200\ \mu\text{g kg}^{-1}$  (Mo et al. 2009); in vegetable samples of a green and organic vegetable production base of Guangzhou, the highest concentration was found for DEHP, but the total PAEs in soil were no more than  $500\ \mu\text{g kg}^{-1}$  (Li et al. 2010b). Severe DEHP accumulation has also been found in potherb mustard, Chinese cabbage, celery, spinach, cabbage, lettuce, garlic, and amaranth of areas using different agricultural films (Fu and Du 2011). The PAE contamination levels in vegetables were similar to that in the other greenhouses, especially for DnBP and DEHP. Besides, most of them have been much higher than food concentration limitations of the EU but no higher than other reported areas. PAE accumulation in leafy plants such as potherb mustard was so serious that it deserves more attention.

The most common approaches for PAEs accumulation in vegetables were root absorption from the soil and shoot absorption from the air (Wang et al. 2007). The absorption and migration of PAE compounds in vegetables were in relation to the physicochemical properties of PAEs such as molecular weight, octanol–water partition coefficient ( $K_{ow}$ ), and volatility. Compared with DEHP, the lower molecular weight and  $K_{ow}$  of DnBP enabled its easy absorption and migration in the root of vegetables. It has even been studied that the net DnBP content absorbed in plants through the roots from the soil increased

with their concentrations in the soil (Chen et al. 1997). Overcash et al. (1982) proved that corn, soybean, wheat, and fescue could rarely absorb DEHP from their planting soil, which also truly occurred in the rape, spinach, lettuce, carrots, and peppers (Kato et al. 1981; Aranda et al. 1989). However, other studies show, DEHP can also be accumulated in high quantity, like barley applied sludge as fertilizer absorbed DEHP five times higher than without any fertilizer ones (Kirchman and Tengsred 1991). It is shocking that DEHP content in Chinese cabbage planted in soil covered with plastic films could reach  $3\,050\ \mu\text{g kg}^{-1}$  fresh weight (about  $25\,000\ \mu\text{g kg}^{-1}\text{ DW}$ ) (Pang et al. 1995). Compounds with higher vapor pressure are more prone to volatilization from plants to the atmosphere or to atmospheric absorption into the plant (Pang et al. 1995), which explain why the content of DnOP was so much higher in vegetables than that in soils. The severe and visible accumulation of PAE compounds in vegetables initiate us to pay more attention to the risk induced by daily eating vegetables on human health.

### Health risk assessment of PAEs in four investigated areas exposed by soil ingestion and vegetable intake

It has been reported that higher concentrations of PAEs were in leafy vegetables rather than in gourd and fruit vegetables, and based on the same calculation method, high HQ values were directly related to the body weight of the target person, so that there would be higher risk to females than to males due to distinct mean body weight (Shen et al. 2013). Calculated HQ of the total PAEs in the four investigated areas (Table 5) indicated that there was no PAE exposure risk for local adults. However, DEHP was shown the highest potential health risk to local children aged between 0 and 6, followed by DnBP in HS. Total risk of PAE exposure was in the order of  $GL>HS>SS>PLK$  in the four investigated areas.

Numerous studies have indicated that for phthalates, the intake of contaminated foods is the most important exposure pathway for the general population (Sioen et al. 2012). However, it has been reported that cooking can eliminate most of the PAEs in vegetables (Mikula et al. 2005). Therefore, reference values were calculated by the adding a removal efficiency of 80 % of the measured concentration (Mikula et al. 2005). In this way, only DEHP in HS and GL had potential health risk to local children (Table 5). The results in Table 5 also raised the problem as the greater harm of soil ingestion in daily life (Sioen et al. 2012).

### Uncertainty analysis and suggestions

Except for daily human gastrointestinal digestion, milking process, the intake of phthalate containing feed by the cattle and contact pack major aging materials of milks were mainly contamination sources for phthalates in milk and dairy products (Cheng et al. 2013; Fierens et al. 2013). It has been



**Table 5** Calculated HQ of six PAE target pollutants in investigated areas

Sampling position	Age (year)	HQ values of different PAE compounds					Age (year)	HQ values of different PAE compounds					
		DMP	DEP	DnBP	BBP	DEHP		DnOP	DMP	DEP	DnBP	BBP	DEHP
HS	0~6	0.001	0.090	0.705	0.002	0.647~4.530	7~70	0	0.004	0.026	0	0.024~0.170	0~0.003
GL		0.001	0.052	0.455	0.001	0.684~4.790		0	0.002	0.017	0	0.025~0.175	0
PLK		0.001	0.036	0.382	0.001	0.249~1.740		0	0.002	0.015	0	0.010~0.070	0
SS		0.001	0.025	0.382	0.001	0.192~1.345		0	0.001	0.013	0	0.007~0.050	0~0.003

HQ values higher than 1 means the pollutant has healthy risk to humans in the investigated area

recorded that the indoor phthalates mainly accumulated in gaseous form in the air household, in which more plastic toys and furnishings were displayed; DEHP posed the greatest health risk to children aged 1~2, and the carcinogenic risk of DEHP was evaluated to be 39 times higher than the limit set by the USEPA (Pei et al. 2013). The use of personal care products and diet increase the danger of exposed to PAEs (Romero-Franco et al. 2011). In consideration of the special conditions for production in greenhouses, higher temperature and higher moisture, the volatilization of PAE pollutants and the afterwards PAEs inhalation could cause more and more serious health risk, especially for DEHP. So even without detailed data of total PAEs in the air, their health risk can be predicted to be greater than expected according to this study. Also, the risk caused by soil ingestion and inhalation, no other reduction method, may result in greater potential harm rather than other contamination approaches that could be removed by heating, or cooking.

To reduce of environmental risks caused by PAEs in this investigation, the decrement of working time, also avoiding of exposure time for children, in greenhouses would be the most important way. In addition, the introduction of more advanced production technology and equipment could lessen working time and improve production safety and stability. Urinary phthalate metabolites have been proven reliable as biomarkers of human exposures to PAEs (Guo et al. 2011), so in further assessment, urine of residents in survey area could be collected for more comprehensive and reliable risk analysis.

The utility of plastic sheeting with less PAE compounds or the employment of biodegradable plastic, plus scientific and reasonable recycling policy, would be referable in creating better agricultural production conditions and eliminating environmental risks. Transferring of environmental risk measures such as more ventilation in greenhouse, more frequent uncovering of plastic films, could accelerate the decomposition of toxic compounds inside the greenhouses or transfer the pollutants to outside by air circulation, which could also reduce the chance of some vegetable diseases.

## Conclusions

The concentration data of soil and vegetable of the four typical protected agriculture areas in suburb Nanjing, reveal the serious contamination of PAE contamination. As for soils, the PAE concentration exhibits a higher relationship with film quality, continuous planting, and greenhouse management mode. As for vegetables, PAEs accumulation depends mainly on the physical and chemical properties of these compounds in addition to the factors such as adsorption pathways, soil PAEs concentration, soil properties, growing period, plant concentrate capabilities, and so on. Root vegetables accumulated some PAH compounds by mainly direct contact with the

contaminated soil. Eating raw vegetables, without the elimination of PAEs by cooking or heating, might increase the PAE risk to human health. Based on the results of the investigation and risk assessment, DEHP presents the highest health risk, and risk caused by soil ingestion is relatively high and more difficult to avoid. Overall, PAEs contamination problem in vegetables produced in facility agricultural areas should be the focus of concern in the area of agricultural environmental pollution. Meanwhile, determination of soil and food standards for PAEs is urgently necessary for the human health in China.

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