

# Polycyclic Aromatic Hydrocarbons and Phthalic Acid Esters in Vegetables from Nine Farms of the Pearl River Delta, South China

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**Abstract** This study investigated the occurrence of 16 polycyclic aromatic hydrocarbons (PAHs) and 6 phthalic acid esters (PAEs) in 11 vegetable species collected from nine farms of the Pearl River Delta, South China. Twelve PAH compounds and all PAE compounds were detected by gas chromatography coupled with mass spectrometry (GC-MS) in vegetables. The total concentrations of PAHs ( $\Sigma_{\text{PAHs}}$ ) and PAEs ( $\Sigma_{\text{PAEs}}$ ) ranged from 7.0 to 5353  $\mu\text{g kg}^{-1}$  dry weight (d.w.), with a mean value of 1173  $\mu\text{g kg}^{-1}$  d.w., and from 0.073 to 11.2  $\text{mg kg}^{-1}$  d.w., with a mean value of 3.2  $\text{mg kg}^{-1}$  (d.w.), respectively. The highest levels of  $\Sigma_{\text{PAHs}}$  and  $\Sigma_{\text{PAEs}}$  were found in *Brassica juncea* and *Brassica parachinensis*, respectively. For the same vegetable, the bioconcentration factors (BCFs; the ratio of contaminant concentration in plant tissue to the soil concentration) of PAHs (between 0.0037 and 5.5) are generally higher than those of PAEs (between <0.0001 and 0.61). It was also noted that there were great variations of organic contaminant levels, BCFs, and benzo[a]pyrene equivalent concentrations, which depend on the various contaminants,

sampling locations, and vegetable species. The occurrences of PAHs and PAEs in this study are compared with those in other studies and their sources are discussed.

Polycyclic aromatic hydrocarbons (PAHs) and phthalic acid esters (PAEs) are two large groups of organic contaminants with a relatively low solubility in water and a high lipophilicity. Because of their toxic, mutagenic, and/or carcinogenic properties, 16 PAHs and 6 PAEs were classed as priority pollutants by both the Chinese Environmental Agency and the United States Environmental Protection Agency (USEPA). Both classes of organic compounds are of worldwide concern due to their hazards and global distribution (Thomas et al. 1986; Ma et al. 2003).

A lot of work has been conducted on the occurrences of PAHs and PAEs in soils and different food categories such as vegetables outside China (Voutsas and Samara 1998; Kipopoulou et al. 1999; Kazerouni et al. 2001; Wennrich et al. 2002; Camargo and Toledo 2003; Nadal et al. 2004; Bishnoi et al. 2006; Zohair et al. 2006). It was found that the levels of PAHs and PAEs were dependent on vegetable species as well as sampling sites, exhibiting a site-specific or species-specific feature. Vegetables taken from highly industrialized areas or roadsides or contaminated areas showed higher concentrations of contaminants than those from rural areas in general (Kipopoulou et al. 1999). So-called organically farmed vegetables were frequently found to accumulate organic contaminants, such as PAHs, polychlorinated biphenyls, and organochlorine pesticides (Zohair et al. 2006). Some work has been conducted within China focusing on the occurrences of PAHs and PAEs in soils and different food categories such as vegetables

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(Yin and Su 1996; Ma et al. 2003; Tao et al. 2004; Zhang et al. 2004; Maskaoui et al. 2006; Shen and Zhu 2007; Li et al. 2008). However, all this work was conducted in comparatively underdeveloped areas, which might be less disturbed by anthropogenic activities. More attention needs to be paid on economically developed areas in China to better understand the occurrence of PAHs and PAEs in vegetables, to evaluate their accumulation, distribution, and possible sources, and to assess their potential risk to human health.

The Pearl River Delta (PRD) region is one of the most important and financially developed regions in China, covering southern Guangdong Province (Canton), Hong Kong, and Macao. The natural conditions of sunshine and heat enable the PRD to be an important production base of vegetables aiming at supply to North China, Hong Kong, and Southeast Asia. Nevertheless, rapid industrialization, urbanization, growing agricultural activities, and increasing usage of chemicals during the last two decades have severely deteriorated the environmental quality of this region. One of the indicators for deteriorating environments is the elevated concentrations of organic contaminants identified in the environments (Fu et al. 2003; Cai et al. 2005, 2007a, 2008a; Li et al. 2006). Although there are a few data sets in the literature concerning the occurrence of organic contaminants in vegetables of China (Tao et al. 2004; Zhang et al. 2004; Maskaoui et al. 2006; Shen and Zhu 2007; Li et al. 2008), more work needs to be done in this area, especially on the vegetables from various farms, since vegetables are considered to be basic foods in the Chinese diet, accounting for 27%–45% of the total dietary fiber (Zhong-Guang Web 2008). Such information could be helpful for elucidating the health risk of exposure to PAHs and PAEs.

Food consumption is by far the main exposure route to PAHs and PAEs for the population (Phillips 1999; Falcó et al. 2005), and vegetables seem to be one of the main contributors to the total dietary intake of these pollutants except where there is high consumption of meat cooked over an open flame (Phillips 1999). This study investigated the occurrence of PAHs and PAEs in vegetables collected from nine representative farms within the PRD, evaluated their accumulation, distribution, and possible sources in vegetables, and assessed the toxicity of PAHs in vegetables based on benzo[*a*]pyrene equivalent concentration.

## Materials and Methods

### Chemicals

A composite stock standard solution (1000  $\mu\text{g mL}^{-1}$  in dichloromethane; 99.8% purity) was used, containing 16

USEPA PAHs and 6 USEPA PAEs, namely, naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo[*a*]anthracene (BaA), chrysene (Chr), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), dibenzo[*a,h*]anthracene (DahA), indeno[1,2,3-*cd*]pyrene (InP), benzo[*ghi*]perylene (BghiP), dimethyl phthalate (DMP), diethyl phthalate (DEP), di-*n*-butyl phthalate (DBP), butylbenzyl phthalate (BBP), di-*n*-octyl phthalate (DOP), and di(2-ethylhexyl) phthalate (DEHP). Working standard solutions in dichloromethane were prepared by diluting appropriate volumes of the stock standard solution. Surrogate standard mixture contained [ $^2\text{H}_8$ ]naphthalene (naphthalene- $\text{d}_8$ ), [ $^2\text{H}_{10}$ ]acenaphthylene (acenaphthylene- $\text{d}_{10}$ ), [ $^2\text{H}_{10}$ ]phenanthrene (phenanthrene- $\text{d}_{10}$ ), [ $^2\text{H}_{12}$ ]chrysene (chrysene- $\text{d}_{12}$ ), and [ $^2\text{H}_{12}$ ]perylene (perylene- $\text{d}_{12}$ ) in a mixture solution of 4000  $\mu\text{g mL}^{-1}$ . These standards were purchased from Ultra Scientific (North Kingstown, RI, US).

Analytical-grade dichloromethane (DCM) and ether were redistilled before use. Silica gel (80–200 mesh) and neutral alumina (80–100 mesh) were Soxhlet-extracted with DCM and *n*-hexane for 24 h, respectively, activated at 180° and 250°C, respectively, for 12 h, deactivated with 3% redistilled water, and kept in *n*-hexane prior to use. Anhydrous sodium sulfate was dried at 450°C for 6 h and stored in a sealed desiccator. These materials were purchased from Guangzhou Chemical Reagent Co., China. Special precautions were taken to avoid contamination as described by Cai et al. (2007b) during sampling and further processing of the samples. Briefly, detergents were not used during sample processing. No plastic equipment was used during sampling and processing. All glass apparatus was washed with a  $\text{K}_2\text{CrO}_4\text{-H}_2\text{SO}_4$  solution, with tap water and redistilled water, and then dried at 120°C. Glassware was furnace at 300°C for 4 h before use.

### Sampling Locality, Description of Area, and Vegetable Sampling

Nine representative farms located in different cities including Guangzhou and Shenzhen within the PRD were selected according to their geographic location, cultivated areas, history and model of operation, and environment. A detailed description of the PRD and representative farms and sampling locations has been presented elsewhere (Cai et al. 2007a; also presented in Supplementary Fig. 1S). A description of the vegetable sampling sites and numbers of samples are reported in Table 1.

Eleven vegetable species (including 18 varieties and 45 samples; Table 2) were collected from nine farms. The vegetable sample was randomly collected from five

**Table 1** Description of vegetable sampling sites and numbers of samples

Site	Location	Cultivated area (ha)	Vegetable species	No. of samples <sup>a</sup>
GZ01	Guangzhou, suburban	31	3	4
GZ02	Guangzhou, suburban	45	7	11
ZC01	Zengcheng, rural	145	3	6
HD01	Huadu, rural	23	3	4
HD02	Huadu, rural	114	4	4
HD03	Huadu, rural	75	1	2
SZ01	Shenzhen, rural	68	4	5
SZ02	Shenzhen, suburban	96	5	5
SZ03	Shenzhen, suburban	84	3	4

<sup>a</sup> Including the number of different cultivars

different sites on the same farm, then homogenized, and 2 kg fresh weight taken as a sample. Vegetable samples were carefully washed with tap water to remove any attached soil particles, then rinsed twice with redistilled water. The samples were dried, ground in a solvent-cleaned stainless-steel mill, and refrigerated until analysis.

#### Analytical Methods

Sample extraction and cleanup were performed according to USEPA methods 3550B and 3630C with modification, respectively. Twenty grams of dry samples spiked with surrogate standards was extracted in triplicate with 60 mL ether in a sonicator (SK5200H; China) for 30 min. The extracts were concentrated, cleaned up, and further processed as described in detail by Cai et al. (2007a, b).

Analysis of individual PAHs and PAEs was performed using gas chromatography coupled with mass spectrometry (GC-MS) by a modification of USEPA method 8270C. The temperature program for GC-MS analysis, the quantification method, and the details of quality assurance/quality control (QA/QC) have been presented elsewhere (Cai et al. 2007a). Briefly, analysis of PAHs and PAEs employed a Thermo Finnigan TRACE gas chromatograph, equipped with a Thermo Finnigan TRACE MS<sup>plus</sup> and HP-5 silica fused capillary column (30 m × 0.25-mm i.d., with 0.25-μm membrane thickness; Agilent Technology). Splitless surge injection of 1 μL of extract was conducted manually. Column temperature was programmed from 45°C (held for 1 min) to 110°C at 35 deg min<sup>-1</sup>, followed by an increase to 275°C at 15 deg min<sup>-1</sup>, then increased to 280°C at 25.0 deg min<sup>-1</sup> (held for 5 min). The injection port and the interface line temperature were maintained at 230° and 250°C, respectively. Helium was used as the carrier gas, with split flow 50 mL min<sup>-1</sup> for 2 min, surge pressure 300 kPa for 2 min, and gas saver flow 20 mL min<sup>-1</sup> for 2 min. Column pressure was programmed from 80 to 120 kPa at 8 kPa min<sup>-1</sup>, followed by an increase to 150 kPa at 60 kPa min<sup>-1</sup> and a hold for 5 min at 150 kPa.

Mass spectra were acquired in the electron ionization (EI) mode. Identification of PAH and PAE components was based on comparison of retention time data between samples and the standard solution containing 16 PAHs and 6 PAEs. The external calibration method was applied based on a five-point calibration curve for individual components (1–10 μg L<sup>-1</sup>). The concentration of each PAH or PAE was determined by an individual calibration database set up from the certified standards. The detection limits of individual PAHs and PAEs ranged from 0.20 μg kg<sup>-1</sup> (for Ace) to 1.4 μg kg<sup>-1</sup> (for Pyr) and from 0.39 μg kg<sup>-1</sup> (for BBP) to 1.4 μg kg<sup>-1</sup> (for DMP), respectively.

#### Results

##### Polycyclic Aromatic Hydrocarbons

The occurrence of PAHs in vegetable samples is reported in Table 2 (all results of this study are expressed on a dry weight basis). Twelve PAH compounds of interest were detected, and other PAHs including BkF, BaP, InP, and BghiP were below the detection limits. The total concentrations ( $\Sigma_{\text{PAHs}}$ ) ranged from 7.0 μg kg<sup>-1</sup> (*Ipomoea aquatica*) to 5353 μg kg<sup>-1</sup> (*Brassica juncea*), with an average value of 1173 μg kg<sup>-1</sup> ( $n = 45$ ). The  $\Sigma_{\text{PAHs}}$  were >1000 and <100 μg kg<sup>-1</sup> in 36.7% and 26.5% of samples, respectively. The  $\Sigma_{\text{PAHs}}$  in *Brassica juncea* was about 790 times higher than that in *Ipomoea aquatica*, indicating large variations for  $\Sigma_{\text{PAHs}}$  in various plant species.

Comparable  $\Sigma_{\text{PAHs}}$  in vegetables collected within China were found in the literature. Tao et al. (2004) reported  $\Sigma_{\text{PAHs}}$  in vegetables collected from Tianjin, northern China, ranging from 280 to 690 μg kg<sup>-1</sup>. Vegetables grown near an iron and steel industrial area of Hangzhou, Zhejiang Province, had  $\Sigma_{\text{PAHs}}$  of 227 to 1533 μg kg<sup>-1</sup> (Shen and Zhu 2007). Even higher  $\Sigma_{\text{PAHs}}$  were found in vegetables collected from Minjiang River Estuary (8600–111,000 μg kg<sup>-1</sup>) (Zhang et al. 2004) and from some

**Table 2** Occurrence of PAHs in vegetables from the nine farms of the PRD ( $\mu\text{g kg}^{-1}$  dry weight)

Vegetable species		Nap	Acy	Ace	Fl	Phe	Ant	Fla	Pyr	BaA <sup>a</sup>	Chr <sup>a</sup>	BbF <sup>a</sup>	DahA <sup>a</sup>	$\Sigma_{\text{PAHs}}^{\text{carc}^b}$	$\Sigma_{\text{PAHs}}$
<i>Brassica parachinensis</i> Bailly; flowering Chinese cabbage ( $n = 9$ )	Min	11	ND <sup>c</sup>	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0	20
	Max	237	429	ND	23	209	ND	260	317	ND	138	ND	ND	138	867
	Mean	90	63	ND	7.0	55	ND	152	56	ND	15	ND	ND	15	438
<i>Brassica chinensis</i> Linn; paitai ( $n = 6$ )	Min	6.9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0	72
	Max	115	ND	ND	7.8	108	ND	2819	101	ND	172	ND	ND	172	2910
	Mean	40	ND	ND	2.4	41	ND	948	17	ND	29	ND	ND	29	950
<i>Ipomoea aquatica</i> ; water spinach ( $n = 8$ )	Min	6.3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0	7
	Max	159	14	ND	26	74	145	3258	1896	105	201	ND	ND	306	3612
	Mean	41	1.8	ND	4.0	9.2	22	746	256	13	45	ND	ND	58	1139
<i>Amaranthus tricolor</i> Linn; edible amaranth ( $n = 4$ )	Min	5.6	ND	ND	ND	57	ND	ND	ND	ND	ND	ND	ND	0	65
	Max	334	540	ND	20	114	ND	ND	1217	ND	94	ND	ND	94	2017
	Mean	178	135	ND	8.4	81	ND	ND	557	ND	23	ND	ND	23	982
<i>Brassica juncea</i> Linn; mustard ( $n = 5$ )	Min	7.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0	12
	Max	51	108	ND	2.1	94	28	2085	377	ND	ND	2361	ND	2361	5353
	Mean	25	30	ND	1.0	29	6.0	661	93	ND	ND	472	ND	472	1790
<i>Loctuca satira</i> Linn; lettuce ( $n = 6$ )	Min	17	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0	46
	Max	115	ND	ND	18	155	99	3091	55	176	ND	ND	417	593	3272
	Mean	54	ND	ND	4	45	48	967	15	35	ND	ND	83	119	1253
<i>Vigna sesquipedalis</i> Fruvvirth; asparagus bean ( $n = 3$ )	Min	14	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0	874
	Max	41	114	ND	3.7	76	ND	2914	ND	ND	860	ND	ND	860	2930
	Mean	24	38	ND	1.2	25	ND	1261	ND	ND	287	ND	ND	287	1598
<i>Allium ascalonicum</i> Linn; shallot		245	ND	68	ND	ND	ND	ND	ND	ND	ND	ND	ND	0	313
<i>Allium tuberosum</i> Rottler; Chinese chive		11	ND	ND	ND	59	67	ND	ND	ND	ND	ND	ND	0	137
<i>Momordica charantia</i> Linn; balpear		739	ND	ND	22	75	68	1562	ND	ND	ND	ND	ND	0	2467
<i>Cucumis sativus</i> Linn; cucumber		264	ND	ND	20	164	ND	ND	1108	ND	ND	ND	ND	0	1556
Mean		82	43	1.0	5.2	46	15	692	174	9.2	53	79	14	155	1173
Toxic equivalent factor (TEF)		0.001	0.001	0.001	0.001	0.001	0.01	0.001	0.001	0.1	0.01	0.1	1.0		

Note. Scientific name of vegetable given first; common name, second

<sup>a</sup> Carcinogenic PAH

<sup>b</sup> Sum concentrations of carcinogenic PAHs

<sup>c</sup> ND, not detectable. BaP, BkF, InP, and BghiP were below the detection limits, and their TEFs were 1.0, 0.1, 0.1, and 0.01, respectively

locations in Xiamen ( $8236\text{--}58873 \mu\text{g kg}^{-1}$ ), Fujian Province (Maskaoui et al. 2006). However, comparatively low  $\Sigma_{\text{PAHs}}$  were reported for vegetables collected in other countries, e.g., Greece ( $25\text{--}294 \mu\text{g kg}^{-1}$ ) (Voutsas and Samara 1998; Kipopoulou et al. 1999), Germany ( $1\text{--}120 \mu\text{g kg}^{-1}$ ) (Wennrich et al. 2002), Brazilian ( $4.4\text{--}48 \mu\text{g kg}^{-1}$ ) (Camargo and Toledo 2003), India ( $60$  to  $194 \mu\text{g kg}^{-1}$ ) (Bishnoi et al. 2006), and England (from  $8.4 \pm 0.9$  to  $40.1 \pm 4.9 \mu\text{g kg}^{-1}$ ) (Zohair et al. 2006). The remarkably higher  $\Sigma_{\text{PAHs}}$  in vegetables from China than in those from other countries might suggest heavier contamination by PAHs than in the other, aforementioned countries. Further investigation of PAH levels in vegetables from different regions is necessary in the future.

Great variations were observed not only in different vegetable species, but also in different vegetable cultivars or growth periods (Voutsas and Samara 1998; Zohair et al. 2006). For example, white *Vigna sesquipedalis* Fruvvirth and *Vigna sesquipedalis* Fruvvirth both were collected from the same farm, but they showed big differences in  $\Sigma_{\text{PAHs}}$  values ( $2930$  vs  $990 \mu\text{g kg}^{-1}$ ; data not shown). Similarly, filiform-leaf *Ipomoea aquatica* and Ensiform green *Ipomoea aquatica* had  $\Sigma_{\text{PAHs}}$  of  $3610$  and  $1039 \mu\text{g kg}^{-1}$ , respectively (data not shown). Shen and Zhu (2007) reported the highest  $\Sigma_{\text{PAHs}}$  in leafy vegetables, while Wennrich et al. (2002) found the highest one in parsley and kale. The present study did not find such a big difference of  $\Sigma_{\text{PAHs}}$  in different vegetable species.



Table 2 shows that the total concentrations of the seven carcinogenic PAHs ( $\Sigma_{\text{PAHs}}^{\text{carc}}$ ; BaA, Chr, BbF, BkF, BaP, InP, and DahA) in the investigated vegetables ranged from not detectable (ND) to  $2361 \mu\text{g kg}^{-1}$ , with an average value of  $155 \mu\text{g kg}^{-1}$ . These  $\Sigma_{\text{PAHs}}^{\text{carc}}$  values were comparable to or even higher than those in vegetables grown near an iron and steel industrial area of Hangzhou (ranging from 7.1 to  $231 \mu\text{g kg}^{-1}$ , with a mean value of  $71 \mu\text{g kg}^{-1}$ ) (Shen and Zhu 2007) but markedly higher than those reported in vegetables of Greece (Voutsas and Samara 1998; Kipopoulou et al. 1999).

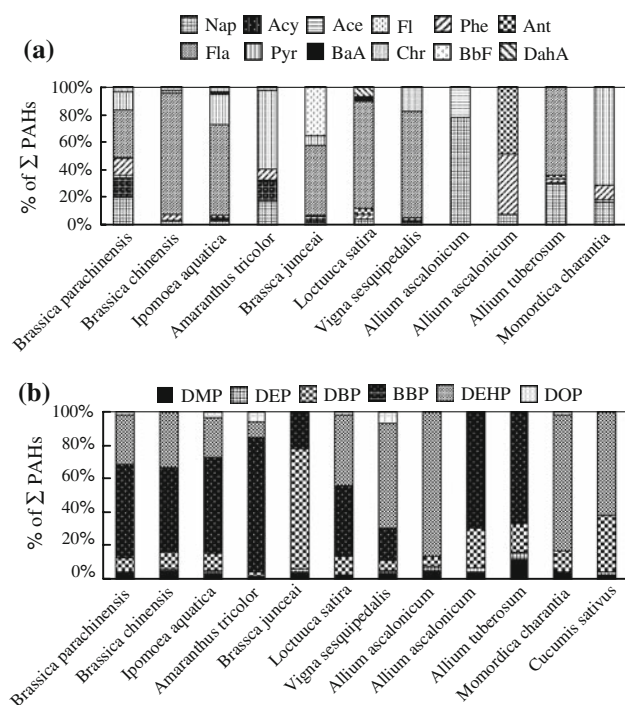
It is worth noting that the concentrations of individual PAHs in the vegetable samples, when detected, varied widely. Only Nap was detected in all samples, at concentrations ranging from  $5.6 \mu\text{g kg}^{-1}$  (*Amaranthus tricolor*) to  $739 \mu\text{g kg}^{-1}$  (*Momordica charantia*) and accounting for 1.4–78% of the  $\Sigma_{\text{PAHs}}$  (Fig. 1a). Fla was the most abundant among 12 detectable PAHs, accounting for 35–87% of the  $\Sigma_{\text{PAHs}}$  in seven vegetable species (*Brassica parachinensis*, *Brassica chinensis*, *Ipomoea aquatica*, *Brassica juncea*, *Loctuca satira*, *Vigna sesquipedalis*, *Momordica charantia*), while Pyr was the dominant compound, accounting for 57% and 71% of the  $\Sigma_{\text{PAHs}}$  in *Amaranthus tricolor* and *Cucumis sativus*, respectively. Phe and Ant were the predominant compounds, accounting for 92% of the  $\Sigma_{\text{PAHs}}$  only in *Allium ascalonicum*. Fla and BbF accounted for 37% and 27% of the  $\Sigma_{\text{PAHs}}$  in *Brassica juncea* (Fig. 1a). These results indicated the different distribution profiles of PAHs in various vegetables and implied different

accumulation of various PAH compounds in vegetables. Maskaoui et al. (2006) reported that InP was the most abundant (accounting for >80% of the  $\Sigma_{\text{PAHs}}$ ) in all vegetables in some locations in Xiamen, Fujian Province, which is different from the results of the present study. The concentrations of Ant, Fla, BaA, and BaP, when detected, were comparable to or higher than those in vegetables collected from northern Chinese wholesale markets (between 3.3 and  $6.5 \mu\text{g kg}^{-1}$  fresh weight) (Zhong et al. 2002). The concentrations of BaP in vegetable samples in this study were below the detection limit and also lower than the limit ( $1.0 \mu\text{g kg}^{-1}$ ) set for vegetable food in Germany (Wennrich et al. 2002).

### Phthalic Acid Esters

Descriptive statistics for PAEs are reported in Table 3. Six PAEs were detected in the investigated vegetable samples and their total concentrations ( $\Sigma_{\text{PAEs}}$ ) ranged from  $0.073 \text{ mg kg}^{-1}$  (*Ipomoea aquatica*) to  $11.2 \text{ mg kg}^{-1}$  (*Brassica parachinensis*), with an average value of  $3.2 \text{ mg kg}^{-1}$ . These values are quite high, even close to those observed in the radish (*Raphanus sativus*) planted in sewage sludge-amended soils (Cai et al. 2008b). The high concentrations of PAEs in the vegetables might result from extensive utilization of agricultural chemicals such as film and plastics in recent years (Agriculture Department of Guangdong Province 2005).

The concentrations of individual PAEs varied, with different detection frequencies. DOP was detected only in 22%, DMP and BBP in 45%, and DBP and DEHP in 67 and 80% of the samples ( $n = 45$ ), respectively. DMP, DEP, and DOP had concentrations lower than  $1.0 \text{ mg kg}^{-1}$ , and DBP lower than  $3.0 \text{ mg kg}^{-1}$ . Concentrations of BBP and DEHP reached  $7.7$  and  $9.3 \text{ mg kg}^{-1}$ , respectively (Table 3). BBP and/or DEHP were the most abundant in most vegetable samples (except *Brassica juncea*), accounting for 67%–90% of the  $\Sigma_{\text{PAEs}}$  (Fig. 1b). The concentrations of DEHP, when detected, were remarkably higher than those in vegetables (with a geometric mean of  $41.8 \mu\text{g kg}^{-1}$ ) from the Netherlands (Peijnenburg and Struijs 2006) but far lower than those ( $2.6$ – $75.5 \text{ mg kg}^{-1}$  fresh weight) in the edible fruit flesh of *Benincasa hispida* (wax gourd) collected from southern and northern provinces in China (Du et al. 2006).



**Fig. 1** Percentage distribution of individual PAHs (a) and PAEs (b) in vegetables

## Discussion

### Bioconcentration Factors of PAHs and PAEs

Bioconcentration factors (BCFs) are expressed as the ratio of PAH (or PAE) concentration in the vegetable on a dry

**Table 3** Occurrence of PAEs in vegetables from the nine farms of the PRD (mg kg<sup>-1</sup> dry weight)

Vegetable species		DMP	DEP	DBP	BBP	DEHP	DOP	Σ <sub>PAEs</sub>
<i>Brassica parachinensis</i> Bailly ( <i>n</i> = 9)	Min	ND <sup>a</sup>	ND	ND	ND	ND	ND	0.15
	Max	0.69	0.084	2.03	9.7	9.3	0.47	11.2
	Mean	0.17	0.030	0.35	2.4	1.3	0.077	4.4
<i>Brassica chinensis</i> Linn ( <i>n</i> = 6)	Min	ND	ND	ND	ND	0.047	ND	0.95
	Max	0.71	0.048	1.2	6.1	2.6	ND	6.2
	Mean	0.17	0.031	0.34	1.7	1.1	ND	3.3
<i>Ipomoea aquatica</i> ( <i>n</i> = 8)	Min	ND	ND	ND	ND	ND	ND	0.073
	Max	0.24	0.10	0.40	8.10	2.4	0.33	8.4
	Mean	0.066	0.036	0.18	1.1	0.45	0.061	1.9
<i>Amaranthus tricolor</i> Linn ( <i>n</i> = 4)	Min	ND	ND	ND	0.029	0.071	ND	0.79
	Max	0.10	0.080	0.28	6.6	0.86	0.88	6.6
	Mean	0.020	0.034	0.080	2.5	0.30	0.18	3.1
<i>Brassica juncea</i> Linn ( <i>n</i> = 5)	Min	0.12	0.044	1.2	0.59	ND	ND	1.9
	Max	0.13	0.049	2.9	0.63	ND	ND	3.3
	Mean	0.13	0.047	2.0	0.61	ND	ND	2.8
<i>Loctuca satira</i> Linn ( <i>n</i> = 6)	Min	ND	ND	0.12	ND	0.34	ND	0.63
	Max	0.14	0.048	0.91	7.0	3.7	0.28	7.6
	Mean	0.065	0.023	0.48	1.8	1.7	0.070	4.1
<i>Vigna sesquipedalis</i> Fruvvirth ( <i>n</i> = 3)	Min	ND	0.044	ND	ND	ND	ND	1.0
	Max	0.14	0.051	0.23	1.2	4.2	0.29	5.9
	Mean	0.090	0.048	0.15	0.51	1.7	0.18	2.7
<i>Allium ascalonicum</i> Linn		0.16	0.065	0.81	2.4	ND	ND	3.4
<i>Allium tuberosum</i> Rottler		0.14	0.049	0.20	0.79	ND	ND	1.2
<i>Momordica charantia</i> Linn		0.29	0.040	0.92	ND	5.9	0.12	7.2
<i>Cucumis sativus</i> Linn		0.15	0.061	1.7	ND	3.2	ND	5.2

<sup>a</sup> Not detectable

weight basis to the respective concentration in the soils. The concentrations of PAHs and PAEs in the corresponding soils have been presented in detail elsewhere (Cai et al. 2005, 2007a; also presented in Supplementary Tables 1S and 2S). From those values as well as Tables 2 and 3 here, the BCFs are calculated and presented in Table 4. Because the concentrations of some individual PAHs or PAEs in some vegetable samples were not detectable in the present study, BCFs are reported in Table 3 only for Σ<sub>PAHs</sub>, Σ<sub>PAEs</sub>, and three typical PAE compounds.

BCFs for PAHs in different species varied from 0.0037 (*Ipomoea aquatica*) to 5.5 (*Loctuca satira* Linn); 68.2% and 25% of the investigated samples (*n* = 45) had BCFs lower than 1.0 and 0.1. *Loctuca satira* Linn showed a higher BCF, which is due to its large surface area in comparison to other vegetable species (Kipopoulou et al. 1999; Camargo et al. 2003), because atmospheric deposition is an important input of PAHs (Kipopoulou et al. 1999). BCFs in the present study were comparable to those recorded in Shunde, China (Li et al. 2008), and substantially higher than those reported in Tianjin, China (Tao

et al. 2004), England (Zohair et al. 2006), and Greece (Kipopoulou et al. 1999), but far lower than those in the Xiamen region and Minjiang River Estuary, when calculated using the values reported by Zhang et al. (2004) and Maskaoui et al. (2006).

As for the PAEs, the BCF values for DBP, DEHP, and the Σ<sub>PAEs</sub> were lower than 1.0 (except for the maximum value in *Brassica parachinensis*) (Table 4). Fifty percent of the samples had BCFs for the Σ<sub>PAEs</sub> lower than 0.1. The highest BCF value for the Σ<sub>PAEs</sub> was observed in *Ipomoea aquatica*. Our previous study showed that, after growth in sewage sludge-amended soil, *Ipomoea aquatica* accumulated PAEs with BCF values in the range of 0.09–0.34 (Cai et al. 2006).

It should be noted that the BCFs for Σ<sub>PAEs</sub> were generally lower than those for Σ<sub>PAHs</sub> in the same sample, despite most samples having higher Σ<sub>PAEs</sub> than Σ<sub>PAHs</sub>. This might be attributed to their concentrations in farm soils, their physicochemical properties, and uptake and translocation mechanism by vegetables. In the corresponding farm soils, the Σ<sub>PAEs</sub> (ranging from 3.0 to 46 mg kg<sup>-1</sup>) (Cai et al. 2005) were significantly higher than the Σ<sub>PAHs</sub> (ranging from 160 to 3700 μg kg<sup>-1</sup>) (Cai et al. 2007a). The accumulation of

**Table 4** Bioconcentration factors (BCFs) of PAHs and PAEs in vegetables from nine farms of the PRD

Vegetable species		BBP	DBP	DEHP	$\Sigma_{\text{PAEs}}$	$\Sigma_{\text{PAHs}}$
<i>Brassica parachinensis</i> Bailly ( $n = 9$ )	Min	<0.0001 <sup>a</sup>	<0.0001	<0.0001	0.0043	0.0083
	Max	42.3	0.47	1.1	0.59	1.4
	Mean	12.5	0.080	0.17	0.24	0.40
<i>Brassica chinensis</i> Linn ( $n = 6$ )	Min	<0.0001	<0.0001	0.003	0.046	0.10
	Max	16.1	0.32	0.37	0.44	1.7
	Mean	4.9	0.069	0.13	0.23	0.72
<i>Ipomoea aquatica</i> ( $n = 8$ )	Min	<0.0001	<0.0001	<0.0001	0.0032	<0.0001
	Max	2.0	0.11	0.22	0.61	3.6
	Mean	0.33	0.038	0.044	0.13	1.1
<i>Amaranthus tricolor</i> Linn ( $n = 4$ )	Min	<0.0001	0.016	0.031	0.035	0.026
	Max	31.8	0.18	0.40	0.36	3.1
	Mean	8.0	0.096	0.18	0.24	1.2
<i>Brassica juncea</i> Linn ( $n = 5$ )	Min	0.074	0.000	0.005	0.058	0.0088
	Max	16.8	0.029	0.098	0.44	4.8
	Mean	9.2	0.011	0.033	0.20	1.5
<i>Loctuca satira</i> Linn ( $n = 6$ )	Min	<0.0001	<0.0001	<0.0001	0.064	0.041
	Max	2.6	0.76	0.45	0.43	5.5
	Mean	1.6	0.18	0.092	0.20	1.29
<i>Vigna sesquipedalis</i> Fruvvirth ( $n = 3$ )	Min	<0.0001	<0.0001	0.009	<0.0001	0.76
	Max	<0.0001	0.016	0.15	0.10	2.3
	Mean	<0.0001	0.011	0.102	0.064	1.5
<i>Allium tuberosum</i> Rottler		<0.0001	0.17	0.39	0.33	0.12
<i>Allium ascalonicum</i> Linn		3.3	0.054	<0.0001	0.11	0.24
<i>Momordica charantia</i> Linn		<0.0001	0.40	0.35	0.38	1.9
<i>Cucumis sativus</i> Linn		–	0.075	<0.0001	0.12	0.86

<sup>a</sup> When calculating the BCF, “ND” in Table 2 was substituted by one-half the detection limit

PAEs in vegetables mainly resulted from soil-to-root transfer and subsequently root-to-shoot translocation, while that of PAHs mainly derived from atmospheric deposition or foliar uptake from the air (Kipopoulou et al. 1999; Tao et al. 2006). In Guangzhou the  $\Sigma_{\text{PAHs}}$  in the air (vapor + particulate phases) ranged from 60.9 to 602 ng m<sup>-3</sup> (mean, 337 ± 137 ng m<sup>-3</sup>) and were higher than in many urban areas in the world (Li et al. 2006). Simonich and Hites (1995) suggested that vapor-phase absorption and dry particle deposition are the two most important pathways of contribution to vegetation concentrations of PAHs. On the other hand, PAHs can also be taken up from the soil by the vegetable roots and then transported to the shoots (Zohair et al. 2006; Cai et al. 2008b). However, no obvious relationship ( $R^2 < 0.2$ ) was observed between BCF and  $\log K_{\text{ow}}$  (octanol-water partition coefficient) values of contaminants. This is likely attributable to the fact that their concentrations varied widely and even were not detectable, but it also implies that contaminant concentrations in vegetables might be influenced by processes (e.g. atmosphere deposition) other than uptake from the soil. The contribution of PAHs in the soil and atmospheric deposition to the vegetable PAHs in

the field/farm is unidentified. This emphasizes that further research is necessary.

#### Toxicity Based on BaP Equivalent Concentration

Since BaP is one of the most toxic compounds and the only PAH for which toxicological data are sufficient for derivation of a carcinogenic potency factor. The USEPA (1993) suggested a first way to determine the toxicity of seven carcinogenic PAHs referring to BaP toxicity, being similar to the toxic equivalents applied for assessment of the toxicity of polychlorinated dibenzo-*p*-dioxins and dibenzofurans. Other values of individual PAH toxic equivalence factor (TEF) were established, as compiled by Tsai and Shih (2004) (Table 2). In the present study, in order to estimate the carcinogenic potencies associated with the total PAH exposures via vegetables, the BaP equivalent concentration (BaP<sub>eq</sub>) for each PAH in vegetables is calculated by multiplying its concentration by the corresponding TEF (Table 2). When calculating the BaP<sub>eq</sub>, “ND” for individual PAHs was substituted by one-half of the detection limit.

**Table 5** Benzo[*a*]pyrene equivalent concentration ( $\mu\text{g}$  total BaP<sub>eq</sub> kg<sup>-1</sup>) of 16 PAHs for various vegetables from the PRD<sup>a</sup>

Vegetable species	Min	Max	Mean
<i>Brassica parachinensis</i> Bailly	0.73	2.68	1.29
<i>Brassica chinensis</i> Linn	0.82	3.62	2.04
<i>Ipomoea aquatica</i>	0.72	7.35	2.56
<i>Amaranthus tricolor</i> Linn	0.72	7.35	2.50
<i>Brassica juncea</i> Linn	0.72	25.0	6.33
<i>Loctuca satira</i> Linn	0.80	419	71.9
<i>Vigna sesquipedalis</i> Fruvvirth	1.82	9.32	4.93
<i>Allium ascalonicum</i> Linn			1.03
<i>Allium tuberosum</i> Rottler			1.45
<i>Momordica charantia</i> Linn			3.79
<i>Cucumis sativus</i> Linn			2.27
Mean			9.09

<sup>a</sup> When calculating the BaP<sub>eq</sub>, “ND” for individual PAHs was substituted by one-half the detection limit

The sum of each individual BaP<sub>eq</sub> (total BaP<sub>eq</sub>) in vegetables is presented in Table 5. Apparently, the total BaP<sub>eq</sub> varied greatly among different vegetable species, ranging from 0.72 to 419  $\mu\text{g}$  total BaP<sub>eq</sub> kg<sup>-1</sup>. The minimum total BaP<sub>eq</sub> values obtained for six vegetable species were similar. This is attributed to the comparatively high TEFs (=1.0) for BaP and DbahA, which have a concentration below the detection limits. Except for the maximum total BaP<sub>eq</sub> for *Brassica juncea* Linn and *Loctuca satira* Linn, all total BaP<sub>eq</sub> values were <10  $\mu\text{g}$  kg<sup>-1</sup>, and total VaP<sub>eq</sub> values were <1.0  $\mu\text{g}$  kg<sup>-1</sup> in 31.8% of samples ( $n = 45$ ). The total BaP<sub>eq</sub> values in vegetables from nine farms of PRD (except for the maximum value for *Loctuca satira* Linn) were noticeably lower than those for broiled vegetables ( $40 \pm 50 \mu\text{g}$  kg<sup>-1</sup>) (Kuo et al. 2006), but significantly higher than those for vegetables from Greece (Kipopoulou et al. 1999) and England (Zohair et al. 2006), when calculating their total BaP<sub>eq</sub> using the values reported.

## Conclusion

The detection frequencies and the total concentrations of PAHs in vegetables were both generally lower than those of PAEs, whereas the BCFs for  $\Sigma_{\text{PAHs}}$  were higher than those for  $\Sigma_{\text{PAEs}}$ . Large variations in PAH and PAE levels, BCFs, and total BaP<sub>eq</sub> values were observed among different farms as well as various vegetable species even within cultivars. Because there are seasonal changes of PAHs in the air (vapor and particulate) of Guangzhou, even the PRD, additional data are required to test seasonal variations of PAHs in vegetables as well as to test more classes of vegetables (e.g., root vegetables, tomato) and obtain more information.

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