Environmental Pollution 241 (2018) 750–758

Contents lists available at ScienceDirect

Environmental Pollution

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

Characterization of polycyclic aromatic hydrocarbons (PAHs) in vegetables near industrial areas of Shanghai, China: Sources, exposure, and cancer risk

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ARTICLE INFO

Article history:
Received 2 March 2018
Received in revised form
22 May 2018
Accepted 1 June 2018
Available online 15 June 2018

Keywords:
PAHs
Dietary exposure
Cancer risk
Vegetable contamination
Industrial areas

ABSTRACT

Dietary consumption of contaminated vegetables may contribute to polycyclic aromatic hydrocarbon (PAH) exposure in humans; however, this exposure pathway has not been examined thoroughly. This study aims to characterize the concentrations of PAHs in six types of vegetables grown near industrial facilities in Shanghai, China. We analyzed 16 individual PAHs on the US EPA priority list, and the total concentration in vegetables ranged from 65.7 to 458.0 ng g^{-1} in the following order: leafy vegetables (romaine lettuce, Chinese cabbage and Shanghai green cabbage) > stem vegetables (lettuce) > seed and pod vegetables (broad bean) > rhizome vegetables (daikon). Vegetable species, wind direction, and local anthropogenic emissions were determinants of PAH concentrations in the edible part of the vegetable. Using isomer ratios and principal component analysis, PAHs in the vegetables were determined to be mainly from coal and wood combustion. The sources of PAHs in the six types of vegetables varied. Daily ingestion of PAHs due to dietary consumption of these vegetables ranged from 0.71 to 14.06 ng d^{-1} kg^{-1}, with contributions from Chinese cabbage > broad bean > romaine > Shanghai green cabbage > lettuce > daikon. The daily intake doses adjusted by body weight in children were higher than those in teenagers and adults. Moreover, in adults, higher concentrations of PAHs were found in females than in males. For individuals of different age and gender, the incremental lifetime cancer risks (ILCRs) from consuming these six vegetables ranged from 4.47×10^{-7} to 6.39×10^{-5}. Most were higher than the acceptable risk level of 1×10^{-6}. Our findings demonstrate that planting vegetables near industrial facilities may pose potential cancer risks to those who consume the vegetables.

1. Introduction

PAHs are generated during incomplete combustion of carbon-containing substances, such as wood, coal, gasoline, and diesel (Peng et al., 2011; Shen et al., 2011). The carcinogenicity of PAHs is now well established (Boström et al., 2002; Menzie et al., 1992). PAHs are widely distributed in various environmental media, including the atmosphere, water, sediment, and soil. They are taken up by plants due to their lipophilic and hydrophobic properties. Dietary consumption is a major route of exposure for PAHs, which can account for >70% of total exposure in non-smoking individuals (Khillare et al., 2012; Martorell et al., 2011; Wang et al., 2018). Vegetables are an important part of the human diet and important sources of nutrients and vitamins (Camargo and Toledo, 2003; Wang et al., 2018). Vegetables can be contaminated with PAHs through atmospheric deposition, irrigation, and soil uptake.

Numerous studies have characterized PAHs in the atmosphere and soil and have associated PAHs with health risks (Niu et al., 2017; Shi and Zhao, 2014; Zhang et al., 2008). However, few studies have considered the exposure pathway of vegetable consumption, despite the fact that PAHs in atmosphere and soil can accumulate in vegetables. Therefore, it is important to assess the health risk of PAHs in vegetables exposed to air and soil that may be

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https://doi.org/10.1016/j.envpol.2018.06.002
0269-7491/

polluted by PAHs, such as vegetables grown near industrial areas. Fismes et al. (2002) studied the migration and transformation of PAHs from the soil to vegetable roots and found that the concentrations of PAHs in vegetables increased with increasing soil PAH concentrations. Atmospheric absorption is another reported source of PAHs in vegetables. Kipopoulou et al. (1999) found that the concentrations of PAHs in the above ground parts of plants were greater than those of the underground parts. Wang et al. (2011) also found that lower molecular weight PAHs were found in higher proportions in the roots and shoots of vegetables than higher molecular weight PAHs, and atmospheric absorption was the main accumulation route.

In this study, we examined PAHs in vegetables grown near industrial facilities in suburban areas of Shanghai. Shanghai is one of the most highly developed and densely populated cities in China. Specifically, our study had the following objectives: (1) measure PAH concentrations in a variety of vegetables growing on farmland near industrial areas; (2) explore the factors that could affect the accumulation of PAHs in vegetables; (3) identify the possible sources of PAHs in different vegetables; and (4) evaluate the potential risk to human health through the dietary intake of vegetables growing in polluted areas. The results indicate PAH contamination in vegetables is a serious concern for consumers, and efforts should be made to improve urban land resources, food security and human health related to vegetable cultivation near industrial facilities.

2. Materials and methods

2.1. Study area

There were 3.15×10^5 ha (ha) of agricultural land in Shanghai suburbs, which covered 37.7% of the total land area of Shanghai (Shanghai Municipal Planning and Land & Resources Administration). Local residents often grow vegetables on agricultural land near industrial areas, making the consumption of locally grown vegetables a potential exposure route for PAHs. We selected seven agricultural sites near the Wujing chemical industry area, Shanghai Baoshan Iron and Steel Plant, Yuqiao Municipal Waste Incineration Power Plant and highways. Detailed information regarding the sampling is described by Bi et al. (2018). In brief, sites MH-1, MH-2, MH3 and MH4 are located southeast, west and south of Wujing chemical industry area, respectively. Site BS is located to the west of Shanghai Baoshan Iron and Steel Plant and adjoins a trunk route. Site PD is located to the south of Yuqiao Municipal Waste Incineration Power Plant. Site FX adjoins the Hujin highway. Site QP is relatively far from any large industrial facilities and is mainly used to grow strawberries and vegetables in a suburban area of west Shanghai. Therefore, we used this site as a control (Fig. 1).

2.2. Sampling and preparation

According to the growth characteristics of different vegetables, six categories of commonly grown and consumed vegetables were selected. Leafy vegetables, including Chinese cabbage (*Brassica rapa* var.), Shanghai green cabbage (*Brassica chinensis* var.), romaine (*Spinacia oleracea* var.) and rhizome vegetables, such as daikon (*Raphanus sativus* L.), were collected in January 2014. The broad bean (*Vicia faba* L.), which belongs to seed and pod vegetables and lettuce (*Lactvca saiva* L.), belonging to stem vegetables, were collected in May 2014. Composite samples were generated from 3 to 5 plants of each species. The fresh vegetable samples were washed with tap water and rinsed with deionized water. The fresh weight was recorded after air-drying. After being dried at −54 °C in a lyophilizer (Christ, Germany), the samples were ground using a mortar and filtered through a 250 μm mesh sieve. The resulting particles were refrigerated at −18 °C until analysis.

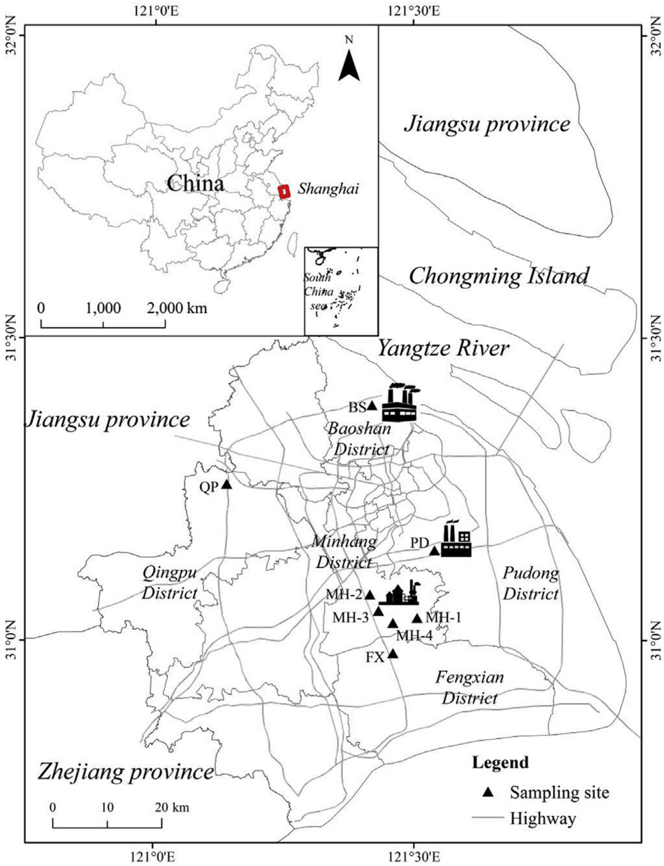

Fig. 1. Sampling sites of vegetables in Shanghai.

Pesticide grade reagents (dichloromethane, acetone and *n*-hexane) were obtained from Merck (Germany). Neutral aluminum oxide, granular anhydrous sodium sulfate and quartz sands were obtained from Sinopharm Chemical Reagent Co., Ltd (SCRC). Decachlorobiphenyl and deuterated PAHs (naphthalene-d8, acenaphthene-d10, phenantrene-d10, chrysene-d12, and perylene-d12) were purchased from Dr. Ehrenstorfer (Germany). After ultrasonic cleaning, all glassware was dried at 450 °C for 4 h. Silica gel (100–140 mesh) was activated at 130 °C for 16 h and other reagents, including glass wool (CNW, USA), alumina and quartz sands were heated at 450 °C for 4 h.

2.3. Sample analysis

Samples were extracted using accelerated solvent extraction (ASE300, Dionex, USA). Extractions were performed under 1500 psi and 120 °C for a 6 min static cycle. The extraction was purified using a silica-aluminum column. The eluate was concentrated by DryVap automatic concentrator (Horizon, USA). The PAH concentrations in the samples were analyzed by a gas chromatograph coupled with mass spectrometry (GC/MS) (7890A/5975C, Agilent Technology, USA) and equipped with a HP-5MS capillary column (30.0 m × 0.25 mm × 0.25 μm). The concentrations of sixteen PAHs were determined: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorine (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benz[*a*]anthracene (BaA), chrysene (Chr), benzo[*k*]fluoranthene (BkF), benzo[*b*]fluoranthene (BbF), benzo[*a*]pyrene (Bap), indeno[123cd]pyrene (Icdp), dibenz

[*ah*]anthracene (DahA) and benzo[*ghi*]perylene (BghiP). The detailed experimental process can be found in a previous study (Jia et al., 2017).

2.4. Quality control

Deuterated-PAHs (naphthalene-d8, acenaphthene-d10, phenantrene-d10, chrysene-d12, and perylene-d12) were spiked onto the samples as internal standards. In addition, blank samples and parallel samples were routinely analyzed every ten samples. No target compounds were detected in the blanks. The method detection limits (MDL, S/N = 3) ranged from 0.01 to 0.23 ng g^{-1}. The recoveries of deuterated PAHs ranged from 71.2% to 85.0%.

2.5. Estimation of dietary exposure and cancer risk for PAHs

The total B[a]P equivalent concentration was estimated using the following equation (Liao and Chiang, 2006):

$$BEC = \sum_{i=1}^{n} c_i \times TEF_i, \tag{1}$$

where *BEC* is the total B[a]P equivalent concentration in a vegetable sample (ng g^{-1} dry weight); C_i is the concentration of PAH congener *i* in the vegetable sample (ng g^{-1}, dry weight); and TEF_i is the corresponding toxic equivalence factor.

The daily dietary PAH exposure dose (E_D) for each group (children: 1–11 years old; teenagers: 12–17 years old; adults: 18–70 years old) was calculated as follows (Liao and Chiang, 2006):

$$E_D = \frac{BEC \times IR \times (1 - W)}{BW}, \tag{2}$$

where *IR* is amount of the vegetable ingested per day (g d^{-1}) (shown in supporting information Table S2); *W* is the water content of the vegetable (the average water content of Shanghai green cabbage, Chinese cabbage, romaine, broad bean, lettuce and daikon is 92.64%, 88.25%, 94.82%, 78.33%, 93.97% and 96.61%, respectively); *BW* is the body weight of local people (Table S1).

The incremental lifetime cancer risk via consuming contaminated vegetables was calculated as follows (Liao and Chiang, 2006; Wang et al., 2017):

$$ILCR = \frac{E_D \times EF \times ED \times SF \times CF}{AT}, \tag{3}$$

where *ILCR* is the incremental lifetime cancer risk of dietary exposure. The *ILCR* calculated in this study represents the risk of each life stage, rather than the sum of *ILCR* of each stage; *EF* is the exposure frequency (365 d yr^{-1}); *ED* is the exposure duration (yr) (for childhood: *ED* = 11; for adolescence: *ED* = 6; for adulthood: *ED* = 53); *SF* is the oral cancer slope factor of B[a]P (1 (mg kg^{-1} $day^{-1})^{-1}$) (USEPA, 2013), *CF* is a conversion factor (10^{-6} mg ng^{-1}) and *AT* is the average lifespan (70 yr i.e. 25,550 day). As children are more sensitive to PAH exposure than teenagers and adults, USEPA recommends an age dependent adjustment factor (ADAF = 3) to calculate exposures to children (USEPA, 2005).

3. Results

3.1. Concentrations of PAHs in different vegetables

The total concentrations of 16 PAHs in vegetables grown near industrial areas of Shanghai ranged from 65.7 to 458.0 ng g^{-1} (dry weight) (Table 1), with the highest concentrations in romaine (223.3–458.0 ng g^{-1}), followed by Chinese cabbage (206.0–348.1 ng g^{-1}), Shanghai green cabbage (206.4–284.7 ng g^{-1}), lettuce (132.0–319.2 ng g^{-1}), broad bean (77.9–197.1 ng g^{-1}) and finally daikon (65.7–92.4 ng g^{-1}), successively. The 16 PAHs showed the highest concentrations in leafy vegetables (romaine, Chinese cabbage and Shanghai green cabbage), followed by stem vegetables (lettuce), seed and pod vegetables and rhizome vegetables (daikon) (Fig. 2).

Almost all 16 PAH congeners were detected in Shanghai green cabbage and Chinese cabbage. Because of their greater water solubility, volatility and bioavailability (Wild and Jones, 1992), the lower molecular weight (LMW) PAH compounds (≤4 rings) were predominant in all 6 types of vegetables (Fig. S1). Phe, Ant, Fla and Pyr had the highest concentrations. These lower molecular PAHs accounted for 47.8%–54.9% of the total 16 PAHs in different vegetables, whereas the high molecular weight (HMW) compounds (>4 rings) accounted for 19.9%–31.4% of the total 16 PAHs. This was consistent with the results of previous studies (Ding et al., 2013; Wang et al., 2017; Waqas et al., 2014).

3.2. Spatial distribution of PAHs in different vegetables

Since romaine and daikon were not collected from all sampling areas, only the spatial distribution of average PAH concentrations in the other four vegetables are given in Fig. 3. Among the four sampling sites (MH-1, MH-2, MH-3 and MH-4) around the Wujing chemical industry area, MH-4 and MH-1 had higher PAHs concentrations. According to local meteorological data (http://lishi.tianqi.com/minhang/index.html), northwestern and northern winds prevailed during the growth periods of the vegetables in the present study. MH-1 and MH-4 are located south and southeast of the Wujing chemical industry area, respectively, and could be significantly affected by atmospheric PAH pollution. Wind direction could affect the spread of contaminants and, thus, influence the accumulation of PAHs in vegetables. Iron and steel smelting and solid waste incineration processes produce large amounts of PAHs and pollute the surrounding environment (Yang et al., 2002). Therefore, the concentrations of PAHs in vegetables were slightly higher at sites BS and PD. As expected, the lowest concentration of PAHs in the four species of vegetables was found at site QP, since the sampling area was far from the urban areas and other sources of PAH pollution. Our previous study on the characteristics of PAHs in soils and road dusts at the same eight sampling sites also produced similar spatial distribution patterns (Jia et al., 2017). This finding confirms that PAH concentrations in vegetables can reflect the degree of PAH contamination in the local environment where vegetables are grown.

In the present study, the concentrations of PAHs in vegetables were significantly and positively correlated with PAH concentrations in soils ($r = 0.78$, $p < 0.05$) (see Fig. S2), indicating that PAH absorption through roots from contaminated soil is an important pathway for PAH accumulation in vegetables (Samsøe-Petersen et al., 2002; Waqas et al., 2014). Affected by local pollutant emissions and prevailing winds, the concentrations of PAHs in the atmosphere and in the soil were higher at corresponding sites. In addition to soil, some previous studies found that PAHs are absorbed by vegetable foliage (Kipopoulou et al., 1999; Wang et al., 2011).

3.3. Source apportionment of PAHs in vegetables

PAH isomer ratios have been widely used as a tool for source identification in different environmental media (Lin et al., 2015; Tobiszewski and Namiesnik, 2012). In this study, the Ant/(Ant + Phe) ratios ranged from 0.1 to 0.6, and the Fla/(Fla + Pyr) ranged from 0.5 to 0.7 in most of vegetable samples, suggesting

Table 1
Concentrations of PAHs in different vegetables near the industrial areas of Shanghai (ng g^{-1} dw).

PAH	Detection limit (ng g^{-1})	Shanghai green cabbage (n = 8)		Chinese cabbage (n = 8)		Romaine (n = 5)		Broad bean (n = 8)		Lettuce (n = 8)		Daikon (n = 5)	
		Min-Max	Mean	Min-Max	Mean	Min-Max	Mean	Min-Max	Mean	Min-Max	Mean	Min-Max	Mean
Nap	8.3×10^{-1}	4.0–9.1	5.8	2.5–6.9	5.4	ND-41.1	13.9	ND-24.8	12.3	3.1–33.7	17.2	ND-4.4	2.3
Acy	1.2×10^{-2}	2.9–5.2	4.0	2.8–3.9	3.3	ND	ND	ND	ND	ND-3.4	1.1	ND-2.5	1.3
Ace	4.3×10^{-2}	2.6–4.0	3.2	2.7–3.3	3.0	ND	ND	ND	ND	ND-4.6	1.1	ND-1.8	1.0
Flu	1.4×10^{-2}	6.5–18.4	11.6	8.6–16.2	11.3	9.6–15.6	12.9	ND-4.6	1.1	ND-19.2	8.9	4.6–8.2	5.7
Phe	3.2×10^{-2}	33.9–70.6	51.6	30.4–84.3	61.4	47.5–70.6	59.0	14.1–38.8	24.7	15.5–59.2	34.9	10.3–21.1	14.7
Ant	3.6×10^{-2}	7.0–11.2	9.1	8.1–12.0	9.9	9.5–49.3	32.0	2.8–38.5	19.5	5.2–39.8	19.6	4.4–19.3	9.2
Fla	1.8×10^{-2}	22.6–50.1	34.6	11.6–56.2	36.6	29.4–73.7	50.1	8.4–18.9	12.8	7.9–30.2	19.2	6.8–11.4	8.6
Pyr	2.0×10^{-1}	13.5–23.9	18.9	14.4–35.7	23.8	23.5–54.5	35.2	5.4–12.3	8.2	8.1–33.0	15.7	58–10.3	8.0
BaA	1.9×10^{-2}	9.2–12.3	10.8	9.8–13.4	11.3	17.3–25.7	20.9	7.7–16.0	12.3	ND-28.6	13.4	ND-8.9	6.9
Chr	1.0×10^{-3}	10.6–17.6	14.4	9.1–20.0	13.7	13.8–37.8	24.6	6.2–9.7	7.9	ND-19.5	11.8	ND-8.3	5.6
BbF	2.4×10^{-2}	19.8–25.5	21.7	18.4–39.0	28.1	ND-54.4	18.3	ND-13.2	3.6	ND-28.4	12.6	ND	ND
BkF	3.0×10^{-3}	13.0–20.1	14.7	13.4–26.6	18.5	ND-44.0	14.8	ND-10.8	2.9	ND-22.8	11.4	ND-11.4	6.1
BaP	4.0×10^{-3}	ND-48.6	12.6	ND-8.7	4.3	15.1–30.8	21.1	ND	ND	ND-40.2	13.6	ND-10.0	5.5
IcdP	1.0×10^{-3}	10.1–13.9	12.3	11.5–16.2	13.3	6.82–19.6	10.9	1.8–10.7	7.4	ND-22.0	10.8	ND-4.3	1.5
DahA	1.0×10^{-3}	ND-9.6	5.7	ND-11.6	8.2	ND-20.6	7.0	ND-16.2	6.1	ND-28.2	7.1	ND	ND
BghiP	1.0×10^{-3}	7.4–9.4	8.2	7.2–10.7	8.6	ND	ND	ND-20.1	8.3	ND-13.5	6.2	ND-6.6	2.6
∑PAH		206.4–284.7	238.9	206.0–348.1	260.6	223.3–458.0	320.6	77.9–197.0	126.9	132.0–319.2	204.6	65.7–92.4	78.9

ND: Not determined.

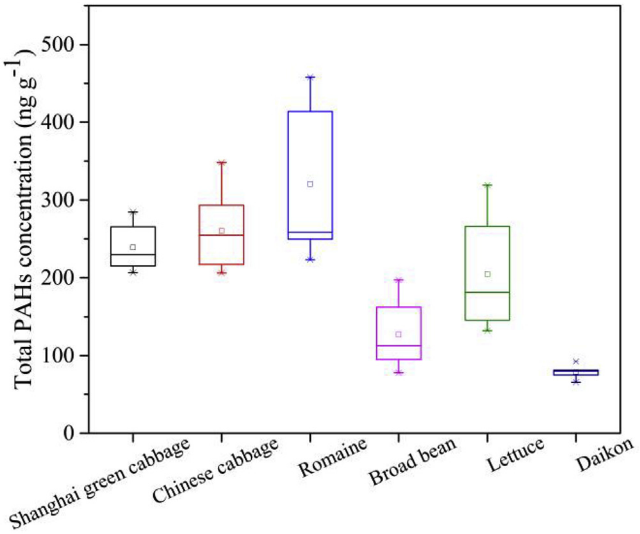

Fig. 2. Total PAHs concentration in different vegetables.

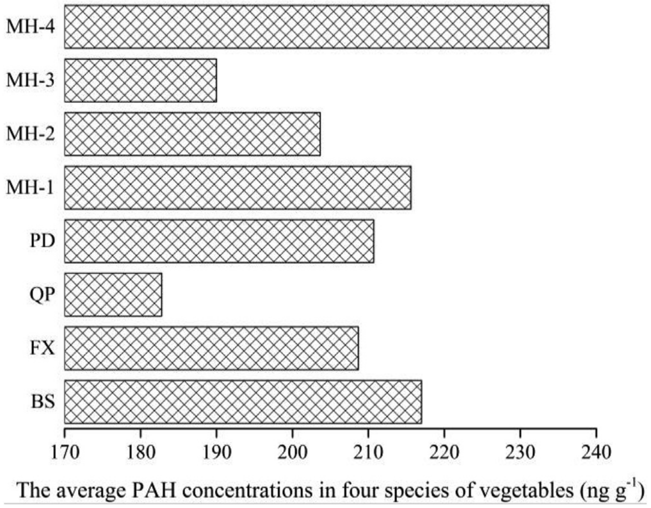

Fig. 3. PAH concentrations in vegetables from different sites.

grass, coal and petroleum combustion as the primary contributors (Fig. 4). The BaA/(BaA + Chr) ratios in most of the samples were higher than 0.35, and the IcdP/(IcdP + BghiP) ratios ranged from 0.5 to 1.0, which suggests the combustion of biomass and coal were the main sources of PAHs in most of the vegetable samples (Wang et al., 2017; Waqas et al., 2014). The source structure of PAHs in vegetables was similar to that of PAHs in soils and dusts (Jia et al., 2017). The Baogang thermal power plant and Wujing thermal power plant are located near the study areas. Therefore, the sampling sites were in close proximity to iron and steel plants, as well as coal-fired power plants (BS, MH-1, MH-2, MH-3 and MH-4). Coal and biomass combustion took place near the domestic solid waste incinerator (PD). The sampling sites (FX) near highways had PAHs generated from petroleum combustion.

For further investigations of possible sources of PAHs in the vegetable samples, principal component analysis (PCA) (SPSS 23.0 software) was used to identify factors based on the correlation matrix of the long-transformed PAH levels and eigenvalues. As presented in the supporting information (Table S3), 77.0% variance of the scaled data was explained by four factors (PC1, PC2, PC3 and PC4) for vegetables. PC1 was responsible for 39.54% and heavily weighted by Phe (0.85), Fla (0.81), Pyr (0.80), Chr (0.82), BbF (0.87), and BkF (0.83). Chr, BbF and BkF are indicators of coal combustion (Rogge et al., 1993), while Phe, Fla and Pyr are mainly produced from wood combustion (Duval and Friedlander, 1981; Jiang et al., 2014). Thus, PC1 reflected the source of coal and wood combustion. PC2 was dominated by Nap (0.63), Ant (0.71) and BaA (0.64). Nap could arise from unburned petroleum. BaA and Chr often result from the combustion of both diesel and natural gas (Rogge et al., 1993). Therefore, PC2 indicated petroleum leakage and combustion as the PAH sources. PC3 had high loadings of DahA (0.60) and BghiP (0.69), which represent vehicle emissions (Larsen and Baker, 2003). PC4 weighed in Ant (0.45) and BaA (0.49) in represent coal combustion (Duval and Friedlander, 1981). As illustrated in Fig. 5, PAHs in Shanghai green cabbage and Chinese cabbages mainly originated from the combustion of coal and wood. PAHs in romaine were mainly due to petroleum leakage and combustion as well as the combustion of coal and wood. The sources of PAHs in lettuce and broad bean were more complicated but were not affected by

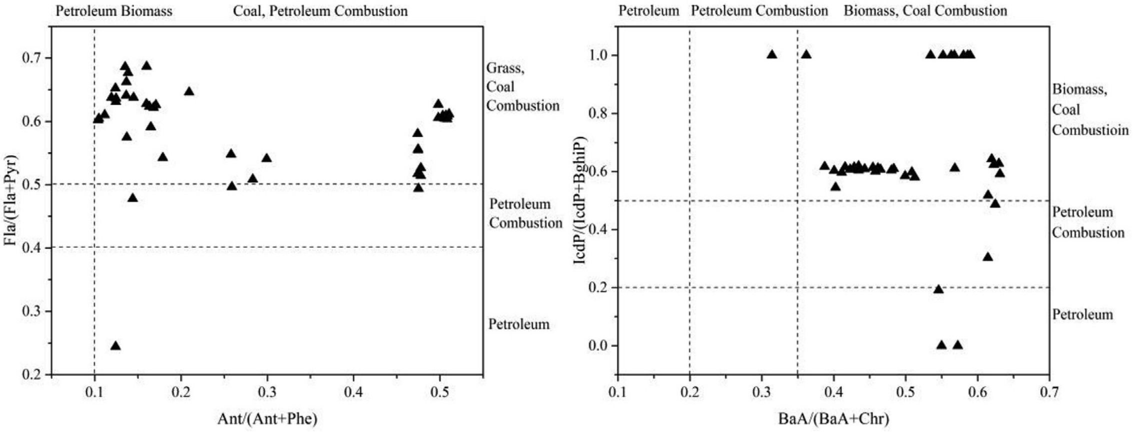

Fig. 4. PAH cross-plots for the ratio of Ant/(Ant + Phe) vs. Fla/(Fla + Pyr) and BaA/(BaA + Chr) vs. IcdP/(IcdP + BghiP).

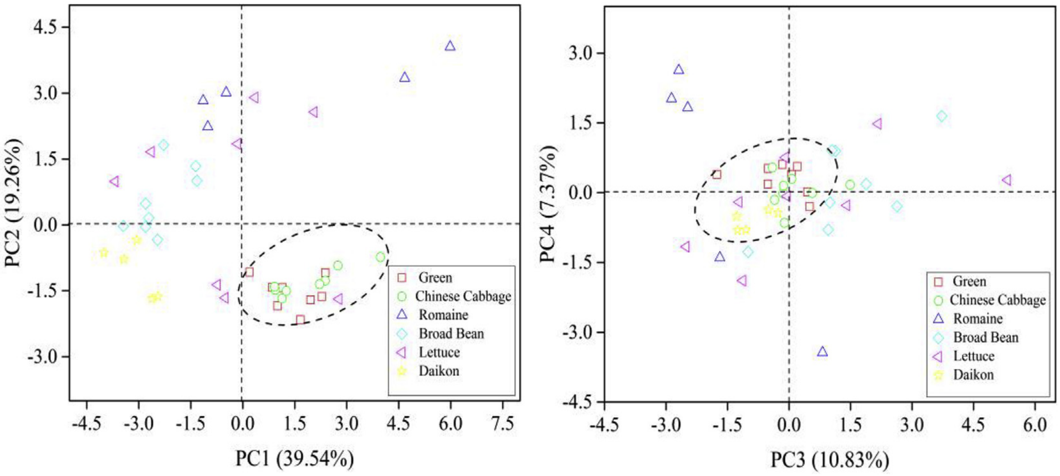

Fig. 5. Score plots of principal components analysis in different vegetables from industrial areas in Shanghai.

the combustion of coal and wood. Radish was not affected by any of the four sources of pollution.

3.4. Exposure and cancer risk assessments

Adjusted by body weight, the estimated daily dietary exposures of local residents to PAHs via vegetable consumption are shown in the supporting information (Table S4). The results showed that the potential intake dose ranged from 0.71 to 14.06 ng d^{-1} kg^{-1} for different age groups. Different vegetables had different contributions to PAH exposure, in which Chinese cabbages had the greatest contribution (6.97–14.06 ng d^{-1} kg^{-1}) for all groups, followed by broad beans (5.83–11.75 ng d^{-1} kg^{-1}), romaine (5.39–10.86 ng d^{-1} kg^{-1}), Shanghai green cabbage (5.35–10.79 ng d^{-1} kg^{-1}) and lettuce (4.62–9.31 ng d^{-1} kg^{-1}). Daikon (0.71–1.44 ng d^{-1} kg^{-1}) had the lowest contribution to PAH exposure. Although the concentration of PAHs in broad beans was lower than that in leafy vegetables, the E_D value was higher than some of the leafy vegetables. The reason may be due to the relatively low water content of broad beans, resulting in higher relative intake of PAHs. This is supported by our observation that daikon had the highest water content and lowest PAH concentration. Therefore, eating more root and stem vegetables with high water content may be associated with a lower dietary intake of PAHs.

In terms of gender and age groups, the daily intake of PAHs via vegetable consumption by females was higher than in males. This difference was mainly due to body weight and the intake amount of vegetables by different genders and age groups. In general, daily exposure was higher in children than in adults.

The ILCR was used to assess potential carcinogenic risk to residents exposed to PAHs via vegetable consumption. ILCRs lower than 10^{-6} are considered to be at a safe risk level. Those between 10^{-6} and 10^{-4} indicate a low health risk, while ILCRs more than 10^{-4} predict a serious potential health risk (Khillare et al., 2012; USEPA, 1996).

As shown in Table 2, the ILCRs values of all six vegetables for different groups were ranged from 4.47×10^{-7} to 6.39×10^{-5}, most of which were higher than the acceptable risk level (1×10^{-6}). Among the tested vegetables, the ILCRs values of Chinese cabbage were the highest, and daikon had the lowest. For different groups, adults had the highest carcinogenic risk from consuming PAH-contaminated vegetables, while teenagers had the lowest risk. In the three different age groups, females had higher cancer risk than males. The results suggest that female adults are more susceptible to carcinogenic PAHs in vegetables. Leafy vegetables and vegetables with low water content were more likely to accumulate PAHs under the same conditions. The minimum, average and maximum ILCR values for children, teenagers and adults in different industrial areas are presented in Fig. 6. For the various industrial sampling sites, vegetables harvested from MH-1, MH-3 and PD posed higher

Table 2
ILCR values for males and females in different vegetables.

Vegetable	Children (1–11 years old)		Teenagers (12–17 years old)		Adults (18–70 years old)	
	Male	Female	Male	Female	Male	Female
Shanghai Green cabbage	3.57×10^{-5}	3.71×10^{-5}	3.35×10^{-6}	4.49×10^{-6}	4.60×10^{-5}	4.90×10^{-5}
Chinese cabbage	4.66×10^{-5}	4.84×10^{-5}	4.36×10^{-6}	5.85×10^{-6}	6.00×10^{-5}	6.39×10^{-5}
Romaine	3.60×10^{-5}	3.74×10^{-5}	3.37×10^{-6}	4.52×10^{-6}	4.63×10^{-5}	4.94×10^{-5}
Broad bean	3.90×10^{-5}	4.04×10^{-5}	3.65×10^{-6}	4.89×10^{-6}	5.01×10^{-5}	5.34×10^{-5}
Lettuce	3.09×10^{-5}	3.20×10^{-5}	2.89×10^{-6}	3.88×10^{-6}	3.97×10^{-5}	4.23×10^{-5}
Daikon	4.78×10^{-6}	4.96×10^{-6}	4.47×10^{-7}	6.00×10^{-7}	6.14×10^{-6}	6.55×10^{-6}

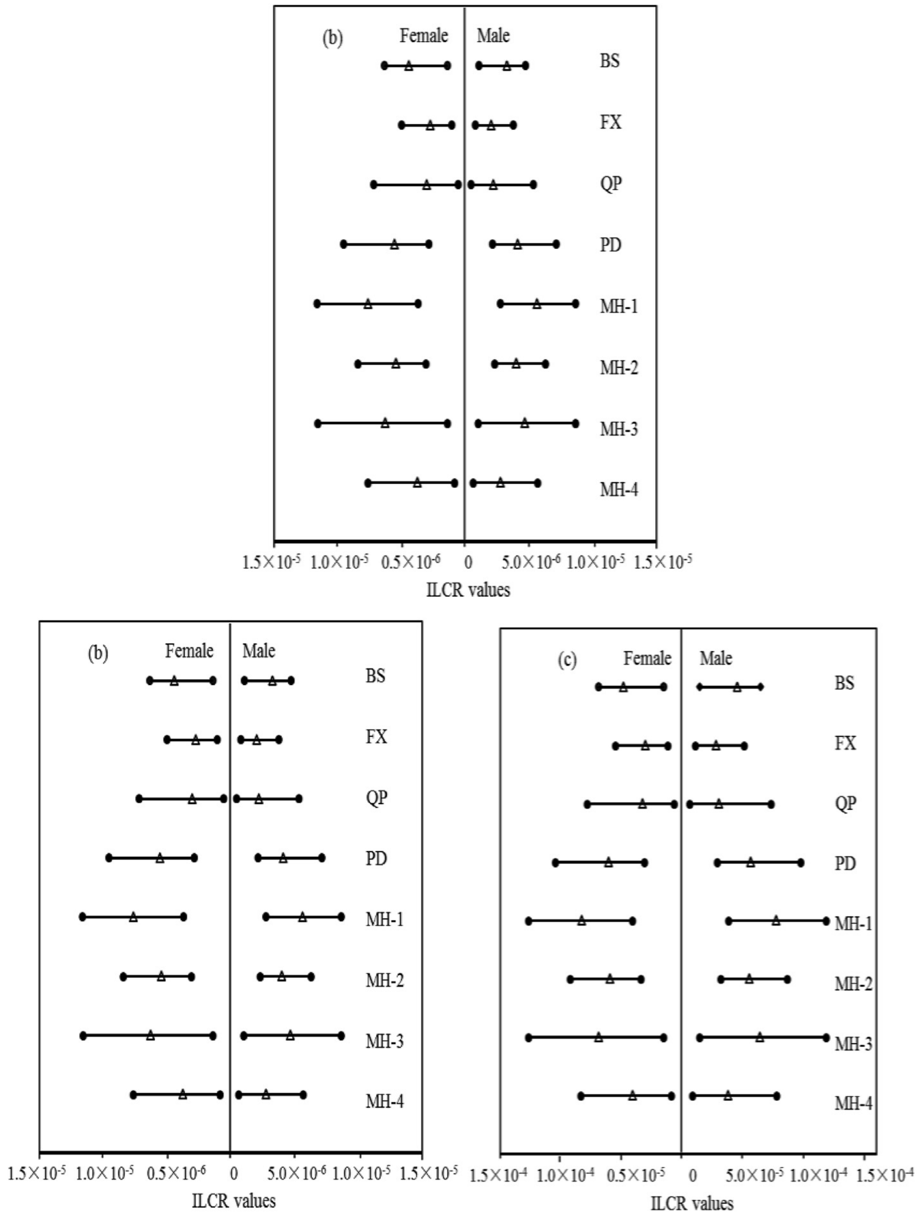

Fig. 6. ILCR values for children (a), teenagers (b) and adults (c) in different industrial areas.

cancer risk for children, teenagers and adults. Vegetables sampled from QP and FX exhibited the lowest cancer risk, which might be associated with the chemical structures and concentrations of PAHs in vegetables from these industrial areas.

4. Discussion

In this study, we quantified 16 PAHs in six types of vegetables grown near industrial areas. These six types of vegetables are commonly consumed by the local population in China. To provide a reference for source control, we investigated the main sources of PAHs in the edible parts of these vegetables. Our results showed that vegetable species, wind direction, and local anthropogenic emissions were determinants of PAH concentrations in the edible parts. PAHs in the vegetables were mainly from coal and wood combustion. The sources of PAH contamination in different vegetables varied. Different from previous studies, we estimated the daily ingestion of PAHs via consumption of these vegetables per unit of body weight, thereby reflecting PAH exposure in a more realistic fashion. We assessed the cancer risk from PAHs contained in these vegetables for individuals of both genders and different age groups. Compared to male adults and children, female adults had the highest risk associated with consuming PAH-contaminated vegetables.

Previous studies have found that foliar uptake is the principal transfer pathway of PAHs in the environment to vegetables (Kipopoulou et al., 1999; Tao et al., 2004). Considering the lipophilic and hydrophobic nature of PAHs, leafy vegetables have larger surface/mass ratio than other types of vegetables. This large surface/mass ratio facilitates the absorption and accumulation of PAHs in the edible parts of leafy vegetables. Besides vegetable species, wind direction, and local anthropogenic emission, future research may reveal other factors that influence PAH concentrations in vegetables, including precipitation, growth period and growth dilution.

On average, the six types of vegetables tested in our study had PAH concentrations substantially higher than vegetables purchased from grocery stores and wholesale markets in Beijing (10.6–47.4 ng g^{-1}) (Wang et al., 2018). The concentrations were slightly higher than garden vegetables grown in southern Jiangsu (11.62–129.54 ng g^{-1}) (Cao et al., 2015), similar to those (14.2–413.2 ng g^{-1}) collected from local markets in Shandong province (Li et al., 2018), and lower than vegetables collected from a more polluted area (340–850 ng g^{-1}) (Tao et al., 2004). Therefore, the cultivation of vegetables in soils near heavily contaminated areas should be discouraged through changes in policy. More importantly, regulations should limit industrial zoning in close vicinity to agricultural areas.

Due to the variety of vegetables and the complex growing conditions that may influence PAH accumulation in vegetables, existing studies mainly focused on the absorption, accumulation, migration and transformation of PAHs in a single type of vegetable (Kipopoulou et al., 1999; Wang et al., 2017). Few studies have attempted to identify the sources of PAH contamination in vegetables. In this study, isomer ratios were used to identify coal and wood combustion as the primary sources of PAH contamination in the vegetables. However, the predominant sources of PAH contamination in the six types of vegetables differed, as determined by principal component analysis. The above results were closely related to the physiological characteristics and different growth environments of vegetables. PAHs produced by the combustion of coal and wood were mainly transmitted via the atmosphere. Kipopoulou et al. (1999) found that gaseous deposition is the main pathway for the accumulation of PAHs in vegetables. The edible parts of leafy vegetables have a larger leaf surface area exposed to the atmosphere and tend to accumulate PAHs from the surrounding air. Daikon is a rhizome vegetable, and its edible part is below the soil surface. Therefore, it is less affected by the four sources of PAHs identified by PCA. Neither the lettuce nor the edible parts of broad beans were directly exposed to the atmosphere and were therefore not affected by the largest sources (coal and wood combustion). Therefore, the leafy vegetables can accumulate more PAHs than the root or seed and pod vegetables. This result is in agreement with a report by Wang et al. (2012). As the sources of PAHs contributed differently to PAH levels in different vegetables, it can be speculated that different plants may be sensitive to various pollution sources. Therefore, it may not be accurate to use a single plant species as an indicator of contamination in the environment, which is a standard practice.

Interestingly, PAH intake via ingestion may be higher than by inhalation. Xia et al. (2013) found inhalation exposures of ambient atmospheric PAHs in Taiyuan ranged from 103 to 347 ng d^{-1} for all population groups in rural and urban areas. These inhalation intakes were slightly lower than the daily dietary intake via vegetable consumption in Shanghai. Previous studies mainly focused on the health risks to humans under single exposure conditions, such as polluted outdoor and indoor air, road dust or contaminated water (Saeedi et al., 2012; Sarria-Villa et al., 2016; Shi and Zhao, 2014).

Daily dietary intake of PAHs by local residents ranged from 28.17 to 745.16 ng d^{-1}, which is lower than those estimated for people living in an industrial area in Greece (1600–4500 ng d^{-1}) and slightly higher than those in Shandong province (23–213 ng d^{-1}), Tianjin (145–345 ng d^{-1}) and Taiyuan (90–170 ng d^{-1}) (Li et al., 2018; Voutsa and Samara, 1998; Xia et al., 2010). In addition to vegetable PAH concentrations, daily consumption of vegetables greatly affected E_D values. With reference to Duan (2013), the daily intake of vegetables by Shanghai residents was higher than that of other provinces and municipalities in China, which led to a slightly higher daily exposure level in this study than other research areas in China. However, this does not mean that people need to limit their intake of vegetables in order to reduce PAH exposure. Our results suggest people need to avoid consuming vegetables grown near industrial facilities.

This study assessed PAH cancer risk associated with ingesting different PAH-contaminated vegetables for different gender and age groups. The population was divided into three groups: children, adolescents and adults to account for differences in body weight, daily food intake, and immunity at different ages. In addition, male and female subjects were examined separately in the risk assessment to account for these differences. Our results found that female adults had the highest cancer risk from consuming PAH-contaminated vegetables. This may be because female adults had the highest vegetable intake compared to other groups, and females had lower body weights than male adults.

However, there were some limitations in this study. Due to the variety of vegetables consumed by local residents and the diversification of vegetable sources, there was a certain degree of uncertainty in the risk assessment. If local air samples were collected, we could compare the relative contributions to cancer risk for local residents through a comparison of ingestion of PAH-contaminated vegetables with breathing PAH-polluted air. Future studies may be conducted to characterize contributions through different uptake pathways of PAHs in vegetables (e.g., from air to the shoot, from soil to the root and then to the shoot, and from both air and soil to the shoot.).

5. Conclusions

The concentrations of 16 PAHs in edible parts of a variety of commonly consumed vegetables ranged from 65.7 to 458.0 ng g^{-1}. In succession, the highest concentrations of PAHs were found in leafy vegetables, followed by stem vegetables, seed and pod vegetables and rhizome vegetables. It was found that vegetable species, wind direction, and local anthropogenic emissions were all determinants of PAH concentrations. This study of dietary consumption of contaminated vegetables found that it is necessary to reduce the cultivation of vegetables, especially leafy vegetables, in heavily polluted areas. Using isomer ratios and principal component analysis, the main sources of PAH contamination in the study areas were coal and biomass combustion, and they contributed differently to the PAH levels in different vegetables. The results suggest that different plant species may be used as contamination markers for different pollution sources in the environment. The assessment of incremental lifetime cancer risks indicates that lower consumption of leafy vegetables and vegetables with low water content would reduce the cancer risk. Female adults had the highest cancer risk from consumption of vegetables contaminated with PAHs compared with other groups. Moreover, vegetables grown near MH-1, MH-3 and PD posed higher cancer risks for children, teenagers and adults. Policies and regulations should be implemented to disallow or discourage farming or gardening of vegetables near industrial facilities.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (NSFC) (41271472), Natural science fund project of Shanghai (12ZR1409000), and Large Instruments and Equipment Open Fund Projects of East China Normal University. We would like to thank Dr. Xueping Wang and graduate student Xue Guo for their help in sample collection and analysis. At the same time, we would like to thank Dr. Xiaoxing Cui from Duke University for her detailed revisions of our manuscript.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2018.06.002.

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