Science of the Total Environment 616–617 (2018) 288–295

Contents lists available at ScienceDirect

Science of the Total Environment

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

Halogenated and parent polycyclic aromatic hydrocarbons in vegetables: Levels, dietary intakes, and health risk assessments

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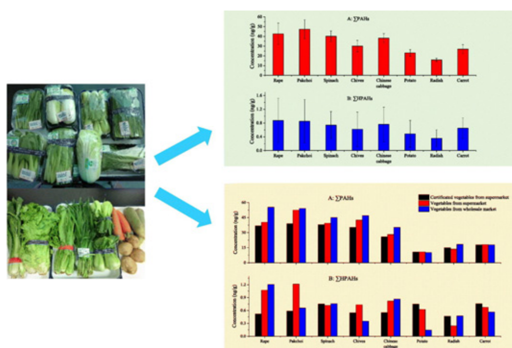
HIGHLIGHTS

- ∑HPAHs concentrations in leafy vegetables were higher than those in root vegetables.
- 2-BrFle and 9-ClFle were the predominant HPAHs in vegetables.
- Trace concentrations of HPAHs and PAHs were found in certificated vegetables.
- Males were in a slightly higher exposure dose to HPAHs and PAHs than females.
- Children faced the highest cancer risk, followed by adolescents, adults and seniors.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 20 July 2017
Received in revised form 22 September 2017
Accepted 31 October 2017
Available online 6 November 2017

Editor: Yolanda Picó

Keywords:
Halogenated polycyclic aromatic hydrocarbons
Polycyclic aromatic hydrocarbons
Vegetables
Dietary intake
Risk assessment

ABSTRACT

Halogenated polycyclic aromatic hydrocarbons (HPAHs) are attracting increasing concern because of their greater toxicity than their corresponding parent PAHs. However, human exposure to HPAHs via food consumption is not fully understood. In this study, daily intake via vegetable ingestion of 11 HPAHs and 16 PAHs and subsequent cancer risk were assessed for population in Beijing. A total of 80 vegetable samples were purchased from markets, including five leafy vegetables and three root vegetables. The concentrations of total HPAHs (∑HPAHs) were 0.357–0.874 ng/g in all vegetables, lower than that of total PAHs (∑PAHs, 10.6–47.4 ng/g). ∑HPAHs and ∑PAHs concentrations in leafy vegetables were higher than those in root vegetables, suggesting that the atmospheric deposition might be the dominant source of PAHs and HPAHs in leafy vegetables. Among the HPAH congeners, 2-BrFle and 9-ClFle were the predominant compounds and frequently detected in the vegetable samples. HPAHs and PAHs were also found in certificated vegetables at the concentrations of 0.466–0.751 ng/g and 10.6–38.9 ng/g, respectively, which were lower than those in non-certificated vegetables except for spinach. For leafy vegetables from local farms, the ∑PAHs and ∑HPAHs levels in the rape and Chinese cabbage samples significantly decreased with increasing the distance away from the incineration plant. The incremental lifetime cancer risks of HPAHs were below the acceptable risk level (10^{-6}), suggesting that there might be little or no risk to consumers from these compounds in vegetables. For all population groups, children were the most sensitive population to PAHs and HPAHs, and their health issues should be paid more attention.

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https://doi.org/10.1016/j.scitotenv.2017.10.336
0048-9697/

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a large group of ubiquitous environmental contaminants containing two or more fused aromatic rings. Both natural and anthropogenic activities such as incomplete combustion of carbon containing fuels, transportation emissions, sludge application, irrigation with domestic or industrial effluent, and mining activities contribute to the release of PAHs to the environment (Cai et al., 2012; Freddo et al., 2012; Gan et al., 2009; Qin et al., 2013; Zheng et al., 2014). PAHs have been attracting widespread attention because of their adverse human health effects, such as carcinogenicity and mutagenicity (Alshaarawy et al., 2016; Kim et al., 2013; Pieterse et al., 2013; White et al., 2016). Halogenated PAHs (HPAHs) are derivatives of PAHs with one or more halogen atom substituent attached to the aromatic rings of corresponding parent PAHs, including chlorinated PAHs (ClPAHs) and brominated PAHs (BrPAHs) (Sun et al., 2013). Toxicological studies have shown that certain HPAHs have greater toxicity than their corresponding parent PAHs (Kitazawa et al., 2006; Ohura, 2007; Ohura et al., 2009). The human exposure to these contaminants was of great concerned because of the ubiquity and toxicity of PAHs and HPAHs in the environment.

Many studies have demonstrated that food stuffs are the predominant source of PAHs exposure (>70%) for nonsmokers and non-occupationally (Alomirah et al., 2011; Fontcuberta et al., 2006; Menzie et al., 1992; Ohura et al., 2007; Ohura et al., 2009; Vyskocil et al., 2000). Vegetables are one of the most consumable food items in human diet especially in Asia area, and the occurrence of PAHs in vegetables have been highlighted due to their high consumption (Camargo and Toledo, 2003; Tao et al., 2004a; Zhong and Wang, 2002). In 2011, European Food Safety Authority suggested that the PAHs in vegetables should be further monitored (EU835/2011). Several studies have investigated the uptake of PAHs by plants, and the results have shown that the main pathway for the accumulation of PAHs in vegetables is the gaseous deposition (Kipopoulou et al., 1999; Tao et al., 2004b; Voutsa and Samara, 1998; Wild et al., 2004; Wild et al., 1992). In some cases, plants can also accumulate PAHs from contaminated soil through active or passive uptake by plant root (Inam et al., 2016; Khan et al., 2008; Khan and Cao, 2011; Khan et al., 2015; Qamar et al., 2017; Waqas et al., 2014b; Zheng et al., 2014). Wang et al. (2011) reported that root and air uptake pathways are the dominant pathways, and the dominance of one pathway over the other depends on the vegetable, contaminant, and local conditions. Up to date, numerous studies have been reported about PAHs in vegetables (Camargo and Toledo, 2003; Jánská et al., 2006; Wang et al., 2017; Zhao et al., 2009; Zhong and Wang, 2002). However, very limited information is available on the HPAHs in diet or food, let alone in the vegetables. To our best knowledge, the investigations on HPAHs were only reported in rice and seafood in China by Ni and Guo (2013) and Ding et al. (2012, 2013).

Therefore, the main aim of this study was to investigate the occurrence of 11 HPAHs and 16 PAHs in 80 vegetable samples (including five leafy vegetable species, and three root vegetable species) from Beijing, China. Moreover, considering that certificated food (refers to the "controlled and limited use of synthesized fertilizer, pesticide, growth regulator, etc., and production area with high grade of atmospheric standards") are becoming attractive to many consumers (Liu et al., 2013; McCarthy et al., 2016; Revell, 2016), we also examined if the HPAHs and PAHs were present in certificated vegetables. The differences of these compounds between certificated and non-certificated vegetables were further evaluated to explore the potential sources, and the potential health risks were finally assessed.

2. Materials and methods

2.1. Sample collection and preparation

A total of 80 vegetable samples were purchased from local supermarkets and wholesale markets from May to July 2012 in Beijing, China. Five varieties of leafy vegetables included 14 samples of spinach (*Spinacia oleracea* L.), 12 samples of rape (*Brassica napus* L.), 15 samples of pakchoi (*Brassica campestris* L. ssp. *chinensis* Makino), 11 samples of Chinese cabbage (*Brassica rapa pekinensis*), and 10 samples of Chinese chives (*A. tuberosum Rottl. ex Spreng*). Six samples each of root vegetables included potato (*Solanum tuberosum* L.), carrot (*Daucus carota* L. var. sativa Hoffm.) and radish (*Raphanus sativus*). Twenty-three of the above samples were certificated vegetables. Besides, a total of 36 leafy vegetable samples including rape, Chinese cabbage and Chinese chives were collected from farms (about 12–14 km from the vicinity of an incineration plant) in September 2017, in Daxing District of Beijing, which is the capital's largest vegetable producing area. Each variety vegetable was collected at four sampling points and the sampling locations are shown in the Supporting Information (SI) Fig. S1. The points were numbered by increasing distance from the incineration plant, and three samples were collected at each sampling point. Only edible parts of each sample were used in the respective subsamples. All vegetables were removed surface dust with soft brushes, grounded, homogenized in a solvent-cleaned food processor with stainless steel cutter, and finally freeze-dried.

2.2. Sample extraction and cleanup

Procedures for sample extraction and cleanup were carried out according to our previous study (Wang et al., 2013). Briefly, approximately 1 g of freeze-dried vegetable was weighed and transferred into a 50-mL centrifuge tube. Then, the labeled internal standards of PAHs (naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12}) were added into the tube. The tube was vortexed for 1 min and allowed to settle for 1 h prior to the extraction step at room temperature, this step help to distribute the compounds evenly in the sample matrix. Next, 10 mL of *n*-hexane was added and the tube was vortexed intensively for 1 min, sonicated for 10 min, and then centrifuged for 5 min (10,000 rpm at 4 °C). Afterwards, 2 mL of the upper layer was transferred into a 10-mL centrifuge tube including an amount of different sorbent (C_{18} 150 mg and PSA 150 mg). The extract was again vortexed vigorously for 1 min to fully absorb impurities of extract by sorbents, and centrifuged for 5 min (10,000 rpm and 4 °C). Finally, the supernatant was filtered through a 0.22 μm membrane for gas chromatography-tandem mass spectrometry analysis (GC–MS/MS).

2.3. GC–MS/MS condition

The method used to analyze the HPAHs and PAHs in vegetable samples was based on the method we developed in a previous study (Wang et al., 2013). Briefly, PAHs and HPAHs (shown in SI Text S1 and SI Table S1) analyses were performed using a Varian 3800 gas chromatograph connected to a Varian 300 mass spectrometer. The mass spectrometer was operated in the electron impact ionization mode with an ionizing energy of 70 eV. The injector temperature was maintained at 280 °C. A VF-5 MS capillary column (30 m × 0.25 mm i.d. with a film thickness of 0.25 μm) was used. The temperature program began at 60 °C and then ramped at 12 °C/min to 200 °C, then increased to 214 °C at 2 °C/min, and finally, increased at 5 °C/min up to 290 °C and held for 1 min. The injection volume was 1 μL, and the splitless mode was used. Quantitative analysis was performed using the multiple-reaction monitoring (MRM) mode, and the fragment ions were selected according to the most abundant ions in each oligomer (as shown in SI Table S2).

2.4. Quality assurance and quality control

Procedural blank and spiked blank samples were processed with each batch of samples (10 samples). Procedural blank was determined by going through the extraction and cleanup procedures and analyzed with every batch of samples to monitor procedural contamination. The recoveries for 11 HPAHs and 16 PAHs ranged from 74.7% to 115.1% in these kinds of vegetables. The recoveries of the surrogate standards were 60.4–83.3% (naphthalene-d_8), 72.2–90.2% (acenaphthene-d_{10}),