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RESEARCH ARTICLE

Uptake of PAHs by cabbage root and leaf in vegetable plots near a large coking manufacturer and associations with PAHs in cabbage core

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Abstract Samples of ambient air (including gaseous and particulate phases), dust fall, surface soil, rhizosphere soil, core (edible part), outer leaf, and root of cabbage from eight vegetable plots near a large coking manufacturer were collected during the harvest period. Concentrations, compositions, and distributions of parent PAHs in different samples were determined. Our results indicated that most of the parent PAHs in air occurred in the gaseous phase, dominated by low molecular weight (LMW) species with two to three rings. Specific isomeric ratios and principal component analysis were employed to preliminarily identify the local sources of parent PAHs emitted. The main emission sources of parent PAHs could be apportioned as a mixture of coal combustion, coking production, and traffic tailing gas. PAH components with two to four rings were prevailing in dust fall, surface soil, and rhizosphere soil. Concentrations of PAHs in surface soil exhibited a significant positive correlation with topsoil TOC fractions. Compositional profiles in outer leaf and core of cabbage, dominated by LMW species, were similar to those in the local air. Overall, the order of parent PAH concentration in cabbage was outer leaf > root > core. Partial correlation analysis and multivariate linear stepwise regression revealed that PAH concentrations in cabbage core were closely associated with PAHs present both in root and in outer leaf, namely, affected by adsorption, then absorption, and translocation of PAHs from rhizosphere soil and ambient air, respectively.

Keywords PAHs · Coking industry · Air · Rhizosphere soil · Cabbage · Absorption

Highlights
- Dominant LMW and MMW components present in environmental media and different tissues of cabbage
- Substantial correlation of PAHs in rhizosphere soil with those in cabbage root
- Significant correlation of PAHs in outer leaf and core of cabbage with those in gaseous phase of ambient air
- Parent PAHs in cabbage tissues exhibited a concentration sequence of outer leaf > root > core.
- Close associations of PAHs in both ambient air and rhizosphere soil with those in cabbage core were presented.

Capsule PAHs in the edible core of local cabbage were closely associated with those in ambient air and in rhizosphere soil.

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Introduction

Sixteen parent polycyclic aromatic hydrocarbons (PAHs) that occur extensively in multiple environments are among the causes responsible for inducing mutagenesis, carcinogenesis, and teratogenesis (Srogi 2007; Zhan et al. 2013a) and have been placed on the list of pollutants with priority by the USEPA since the 1970s. With large-scale industrial development and the rapid growth of populations and motor vehicles in recent years, pollution by PAHs has become increasingly severe in many developing countries, especially China. In particular, some studies have detected different crops contaminated by PAHs in various regions (Ashraf and Salam 2012; Waqas et al. 2014). Because ordinary diet is the main exposure pathway of PAHs to human beings (Phillips 1999), the

presence of PAHs in crops may directly exert adverse impacts on the quality and safety of agricultural products and result in potential risks to human health. Some studies have investigated the associations between PAH contamination and crop safety. For example, PAHs present in different types of vegetables harvested from the wastewater irrigated suburbs of Beijing and Tianjin were harmful to the local people (Wang et al. 2011b). The estimated total daily dietary intake (TDI) of the benzo[a]pyrene (BaP)-equivalent PAHs in various vegetables collected near an e-waste incineration site in southern China indicated a potential health risk by ingestion (Wang et al. 2012). In addition, another recent report suggested that consumption of *Brassica chinensis* from the local farmlands in northwest China would lead to an average carcinogenic risk at the level of 1.66×10^{-4}, exceeding the international guideline (1.0×10^{-4}) on excessive lifetime risk of carcinogens (Zhang et al. 2015).

The natural background of PAHs synthetized in vegetables usually falls between 10 and 20 ng/g. The majority of PAHs that originate from anthropogenic sources can enter plants (such as vegetables) via different pathways (Edwards 1983), and then a chain of internal procedures can occur in different parts of plants, e.g., translocation, (bio)degradation, and accumulation (Trapp and Matthies 1995; Wild et al. 2007). Overall, two major routes are responsible for access of exogenic PAHs to vegetables: adsorption and absorption by the root system in the rhizosphere and by cuticles and stoma on leaves and then translocation towards other inner tissues (Wild et al. 2004; Wieczorek and Wieczorek 2007; Khan et al. 2008). Moreover, uptakes by roots and foliage exhibit different compositional profiles and contributions to the total amount of PAHs. For example, low molecular weight (LMW) species, with stronger volatility and bioavailability, are easily enriched in the gaseous phase, then are deposited and penetrate the foliar surface into inner tissues (Lv et al. 2014). Meanwhile, they are readily absorbed by the root surface in the rhizosphere. By contrast, high molecular weight (HMW) components, mainly adsorbed on particulate phase, are often washed off from leaf surface to the ground soil (Kipopoulou et al. 1999). HMW components were reported to pass into vegetables mainly through root uptake, while for LMW species, foliar absorption was as significant as root uptake (Fismes et al. 2002). A series of studies investigated PAHs in different tissues of rice in different growth stages and demonstrated that component profiles of individual PAHs in rice organs were similar to those in ambient air, rather than to those in surface soil (Tao et al. 2006a), and ambient air was seen as an important source of PAHs accumulated by maize plants (Lin et al. 2007). Furthermore, airborne particulate and gaseous PAHs may be the origins of PAHs in leaf cuticles and inner tissues of different trees, respectively, while hard migration of HMW species to inner tissues was an additional source (Wang et al. 2008). In contrast, median molecular weight (MMW) PAHs with four rings were reported to possess a larger potential to be taken up by the wheat root system (Tao et al. 2009b). A substantial portion of ^{14}C-labeled fluoranthene was detected in roots of *Pisum sativum* by root exposure regardless of upward transport, and notable labeled activity was observed in the apical parts of stem and root after foliar uptake (Zezulka et al. 2014). Other studies indicated that the proportions of LMW PAHs with two to three rings were greater in roots, shoots, and leaves, and absorption by the foliar surface via ambient air was the dominant pathway for plants to accumulate PAHs (Li et al. 2010a; Wang et al. 2011b). In addition, prediction models were established for different vegetables to assess the potential health risk, based on PAH concentrations in plant tissue and in soil (Empereur-Bissonnet et al. 2013). Another multiple linear regression model was also developed to simulate the correlations between root morphology and tissue composition for PAHs uptake (Zhan et al. 2013b). In particular, a multivariate linear regression model for predicting cabbage uptake of PAHs based on gaseous and particulate phase PAH concentrations at two sites in Tianjin, in northern China, indicated that the contribution of surface soil to accumulation of PAHs in the aerial part of cabbage may be insignificant (Tao et al. 2006b).

Due to significant discrepancies in socioeconomic levels, pollution characteristics, and crop species in different areas, current studies on the relationship and transport of individual PAH components in multiple surroundings and on the association of PAHs pollution with agricultural product safety and human health are still inadequate and have yielded a few conflicting or discordant interpretations. In this study, some vegetable plots near a large-scale coking industry base located in Shanxi Province in northern China were selected, and various field samples of ambient air (including gaseous phase and particulate phase), dust fall, surface soil, rhizosphere soil, and different parts of the cabbage plant (*Brassica oleracea Linnaeus* var. *capitata Linnaeus*, as one of the local popular vegetables with large yields) were collected to determine the concentration range and compositional profile of the parent PAHs. Furthermore, specific ratios of paired isomeric species combined with multivariate statistical analysis were employed for preliminary identification of the local emission sources of PAHs. Finally, associations between PAH concentrations in different media and those in various parts of cabbage (particularly in edible core) were explored.

Materials and methods

Sample collection

Based on the local prevailing wind direction and planting conditions, eight villages with different distances (0.6, 4.2, 7.1, 7.5, 9.7, 10.3, 12.7, and 21.1 km) from the coking base

and different sizes of cabbage plot were selected for sampling, as illustrated in Fig. S1. During the local harvest time (i.e., full mature stage), surface soil, rhizosphere soil, ambient air (including gaseous phase and particulate phase), dust fall, and cabbage plants (including outer leaf, root and core) were collected from the cabbage plots of the eight villages. In each sampling plot, 12 or 13 sites were assigned, and totally 100 surface soil (0~5 cm depth) samples were gathered in the form of composite samples including five sub-samples for each. In common practice, the outer leaves and roots of cabbages were discarded during harvest, while only the cores were considered the edible part.

The corresponding samples of cabbages and rhizosphere soils were collected at the same sampling sites as the topsoil. After careful removal of nonrhizosphere soil, we used a stainless-steel knife to remove the rhizosphere soil (approximately 0~5 mm away from root surface) from the root system. Each whole cabbage sample was further separated into outer leaves, edible cores, and roots. In total, 101 rhizosphere soil samples, 103 outer-wrapping leaf samples, 101 core samples, and 101 root samples were obtained. For simplicity, the outer-wrapping leaf is hereinafter referred to as outer leaf or leaf.

Triplicate passive air samplers developed by Tao et al. (2009a) were mounted in different locations of each sampling village. Gaseous phase and particulate phase PAHs were collected by polyurethane foam (PUF) and glass fiber filter (GFF), respectively. Passive air sampling for 30 days included the whole sampling period for topsoil, rhizosphere soil, and cabbage. In addition, active air samples were collected in four villages selected from the eight sampling villages to calibrate the results of passive air samples, as in some previous studies (Tao et al. 2006b). The active samples were gathered by the active air samplers (QCD-3000, Tianyue Instrument Ltd. Company, Yancheng, China) at a low flow volume of 1.5 L/min at the beginning, at the middle, and at the end of the passive sampling period, and each sampling period lasted for 24 h. The active air sampler was equipped with a sampling tube, including a top GFF to collect particulate phase PAHs and a bottom PUF plug (22 mm × 76 m, Supelco Company, USA) to collect gaseous phase PAHs. Before sampling, all the PUFs were Soxhlet extracted for 8 h using 150 mL acetone, 150 mL dichloromethane and 150 mL *n*-hexane successively. The GFFs were roasted for 6 h in a muffle furnace at 450 °C, equilibrated in a desiccator (25 °C) for 24 h, and then weighed both before and after sampling. A total of 24 passive air samples and 12 active air samples were obtained.

The stainless-steel cylinders, each 33 cm in diameter and 28 cm high, were used to collect dust fall samples. The locations and sampling time intervals of these cylinders were the same as for the passive air samplers. After removal of impurities (such as leaves and insects) and cleaning with deionized water, we employed a filtering device to gather the dust fall samples, and all the filters were sealed immediately and kept at −15 °C until further pretreatment. A total of 21 dust fall samples were collected, due to an unexpected loss of three cylinders.

Sample pretreatment

All the soil samples (including surface soil and rhizosphere soil) were air-dried at room temperature. After removal of detritus and plant residues, 8 g of each sample was ground to pass a 70-mesh sieve, and then transferred into a microwave tube with a 20-mL mixture of *n*-hexane and acetone (*v*/*v* = 1:1) for microwave extraction (MARS2Xpress, CEM, USA). The programmed temperature conditions were set as follows: the microwave tubes were heated to 110 °C at 10 °C/min and held for 10 min, and then cooled back down to room temperature in 30 min. After filter pressing, each extract was concentrated to approximately 1 mL in a water bath at 37 °C by a vacuum rotary evaporator (R-201, Shensheng Sci. & Technol. Ltd., Shanghai, China). The concentrate was then purified through an alumina-silica gel column (Yang et al. 2014); the corresponding details will be described later. Another sub-sample of 1 g was further ground to pass a 200-mesh sieve for determining the TOC fraction (TOC-5000A, SSM-5000, Shimadzu Corporation, Japan).

Different parts of the cabbage samples were cleaned, freeze-dried, and ground into power. One gram (dry weight, d.w.) of each sample was transferred into the microwave tube with 20 mL acetonitrile. The microwave extraction conditions were the same as those for the soil samples. After filter pressing, the extract was moved into a 120-mL separating funnel containing 100 mL of a 4% solution of sodium sulfate. The mixture was extracted twice using 30 mL *n*-hexane each time. The extract in the organic phase was rotary evaporated to approximately 1 mL before the subsequent purification with a florisil-silica gel column.

All the PUF disks were Soxhlet extracted for 8 h in a water bath at 65 °C using a 125-mL mixture of *n*-hexane and acetone (*v*/*v* = 1:1) and then concentrated into approximately 1 mL by rotary evaporation and purified by the alumina-silica gel column. The GFFs used were weighed, cut into pieces, and moved into microwave tubes with a 25-mL mixture of *n*-hexane and acetone (*v*/*v* = 1:1) for each sample. After filter pressing, the extracts were concentrated into 1 mL for purification with the alumina-silica gel columns (Yang et al. 2014).

The dust fall samples were freeze-dried and weighed carefully. A stainless-steel knife was used to carefully scrape the dust off the filters, and the subsequent procedures of pretreatment and determination were identical with those for the soil samples.

Each chromatographic column for cleanup (10 mm i.d. × 350 mm length) was packed by the wet method with 12 cm neutral alumina, and 12 cm neutral silica gel, or with 12 cm neutral silica gel and 12 cm neutral florisil in sequence, and then 1 cm of anhydrous sodium sulfate was added to the top of each column. The concentrated extract was transferred

into the column with 2 mL of *n*-hexane added twice. Ten milliliters of *n*-hexane was employed to rinse the column at first and discarded, then a 50-mL mixture of *n*-hexane and acetone (*v*/*v* = 1:1) was added to rinse. The eluent was rotary evaporated into 1 mL, then 5 mL *n*-hexane was added and the extract was concentrated into 1 mL again. The concentrate was spiked with a mixture of internal standard substances including 200-ng of naphthalene (NAP)-d_8, acenaphthene (ACE)-d_{10}, anthracene (ANT)-d_{10}, chrysene (CHR)-d_{12}, and perelyne-d_{12} each (AccuStandard, USA), and kept sealed at −4 °C (Li et al. 2014).

All the reagents used in this study were of chromatographic purity (Fisher Scientific, USA). The glass fiber filters for filter pressing were roasted for 4 h at 450 °C. Alumina and silica gels (100~200 mesh, Sino-Pharm Chemical Reagent Co. Ltd., China) were baked for 6 h at 450 °C, and florisil (J&K Scientific Ltd., Germany) was roasted for 4 h at 650 °C. Afterwards, the calcined alumina, silica gel, and florisil were reactivated for 16 h at 130 °C, then 3% deionized water was added for 4 h, and finally *n*-hexane was added for equilibrium overnight. The anhydrous sodium sulfate (analytical grade, Sino-pharm. Chemical Reagent Co. Ltd., China) was roasted for 10 h at 650 °C.

PAHs quantification

Sixteen parent PAHs were determined in the research using a GC/MS (Agilent GC6890/5973 MSD, Agilent Technology, USA). The chromatographic column was a capillary column with film thickness HP-5 MS (30 m × 0.25 mm × 0.25 μm, Agilent Technology, USA). Helium was used as carrier gas at a flow rate of 1.0 mL/min. The inlet pressure was set at 30 kPa and the injection volume was 1 μL. The temperature of the column was programmed from 60 to 280 °C at 5 °C/min. The final isothermal stage was held for 20 min until the detected sample flowed out completely. The detector was set in electron mode at 70 eV, mass range from 45 to 600 amu, and multiplier pressure at 1288 V. The ion source temperature was 230 °C. Selected ion monitoring (SIM) mode was chosen.

The 16 components detected in this study included the following: NAP, acenaphthylene (ACY), ACE, fluorene (FLO), phenanthrene (PHE), ANT, fluoranthene (FLA), pyrene (PYR), benz(a)anthracene (BaA), CHR, benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[l,2,3-cd]pyrene (IcdP), dibenz[a,h]anthracene (DahA), and benzo[g,h,i]perylene (BghiP).

Quality assurance and quality control

Half of all the studied samples were randomly chosen and spiked with 2-floruo-1,1′-biphenyl and *p*-terphenyl-D14 (AccuStandard, USA), as the recovery rate indicators. The recoveries of the indicators were 50~98% and 89~150%, respectively. The method recoveries of the 16 PAHs in different sampling media ranged from 70 to 130%. The detection limits of different PAH components were from 0.01 to 0.64 ng/mL. The procedural blanks were examined for all types of samples to eliminate possible external contamination during the whole pretreatment procedures. In this study, NAP was excluded from the final results of total PAHs (hereafter termed as PAH15), due to its relatively high concentrations in the blanks and lower recovery rate. The PAH standard was examined for every 20 measured samples to monitor the retention times of the target components in GC and variations of MS response values. The corresponding results of the freeze-dried vegetable samples and the surface and rhizosphere soil samples were based on dry weight (d.w.). The initial concentrations of the studied PAHs in the particulate phase and gaseous phase of the passive air samples used the weights of the compounds bound to the particles on GFF and adsorbed on PUF per unit volume, respectively. Subsequently, they were calibrated using the active sampling results based on the established regression models (Tao et al. 2009a), as provided in the "Results and discussion" section.

Data analysis

The statistical analyses were implemented by SPSS version 20.0 (IBM, USA). The processes included principal component analysis (PCA), multiple linear regression (MLR), nonparametric Spearman correlation analysis, and partial correlation analysis.

Results and discussion

Concentration range in environmental media

Ambient air and dust fall

The results of passive air sampling were calibrated by the data from corresponding active air sampling (Tao et al. 2009a), where two regression models were derived as follows to correct PAH concentrations in the particulate phase and gaseous phase.

Particulate phase (*subscript* P) : $lgPAH_P(A) = 0.919 + lgPAH_P(P)/e^{(-0.985+0.005\times MWt)}$, $r^2 = 0.80$

Gaseous phase (*subscript* G) : $lgPAH_G(A) = 1.061 \times lgPAH_G(P) - 3.274 \times MW_t^{0.122} + 6.576, r^2 = 0.91$

where PAH(A) is the average concentration of PAHs (ng/m^3) after calibration by active air sampling. PAH(P) represents the average concentration of PAHs obtained by passive air sampling (ng/device/day), and MWt denotes the molecular weight for each PAH species. The satisfactory accuracies of the calibration models are shown in Fig. S2.

The calibrated total concentrations of PAH15 in ambient air, including gaseous phase and particulate phase, as well as the compositional profiles in eight sampling villages, are illustrated in Fig. 1. No significant difference in total air concentrations of PAHs could be observed, while the concentrations of PAHs in the gaseous phase were obviously much greater than those in the particulate phase in all sampling villages, and LMW species with two to three rings were predominant in the atmosphere of all the studied villages.

The total PAH concentrations in dust fall ranged from 4.6 to 34.2 μg/g, with an average of 16.1 μg/g. Based on the opening area of each cylinder, the concentrations in dust fall, and the sampling interval, the deposition fluxes of local PAHs in different sampling villages were calculated and are shown in Fig. 1 and ranged from 1.5 to 6.1 μg/day/m^2 with a mean value of 3.6 μg/day/m^2.

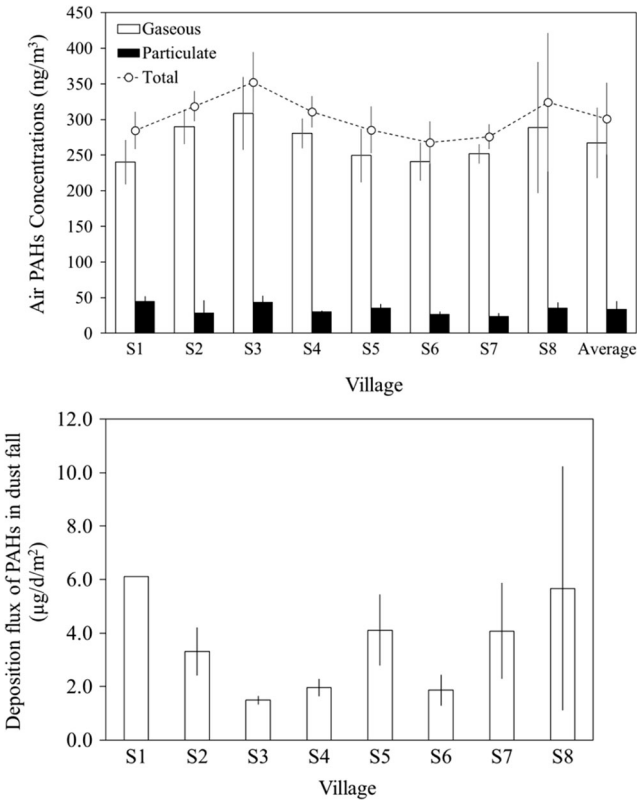

Fig. 1 Atmospheric concentrations (ng/m^3) of PAHs in total, gaseous phase, and particulate phase (*upper panel*), as well as deposition fluxes (μg/day/m^2) of PAHs in dust fall in vegetable plots from eight sampled villages (*lower panel*)

Surface soil and rhizosphere soil

Figure S3 shows the statistical results of PAHs in surface soils from the sampling villages. The concentrations of PAH15 ranged from 130 to 703 ng/g with a median value of 236 ng/g. The whole condition was designated as weakly contaminated, according to the European soil quality criteria (200~600 ng/g) issued in 1996 (Maliszewska-kordybach 1996). The Spearman correlation coefficients accounted for the relationships of single species and the summed concentrations with TOC fraction in surface soils are listed in Table S1. Concentrations both of the individual species and the total PAH15 exhibited a significant positive association with the topsoil TOC fraction, in agreement with many other studies (Chen et al. 2005a; Jiang et al. 2011, 2016).

The concentration of PAH15 in rhizosphere soils from sampling plots ranged from 93 to 623 ng/g with a median of 179 ng/g, as plotted in Fig. S4. The average concentrations of different components and the total amount in rhizosphere soil were somewhat lower than those in surface soil, as shown in Fig. 2. Rhizosphere is generally quite different from bulk soil in terms of physicochemical properties (such as pH and redox conditions) and microbial characteristics (e.g., population abundance, community diversity, biodegradation, and transformation activity to pollutants). For instance, an in situ increasing gradient of PAHs in different rhizosphere layers of *Trifolium pratense* L. and *Hyssopus officinalis* L. was in the order rhizoplane soil < strongly adhering soil < loosely adhering soil < bulk soil (Ling et al. 2013). Due to stronger microbial activity, parent PAH concentrations in rhizosphere soil revealed relatively lower level with respect to topsoil in this study.

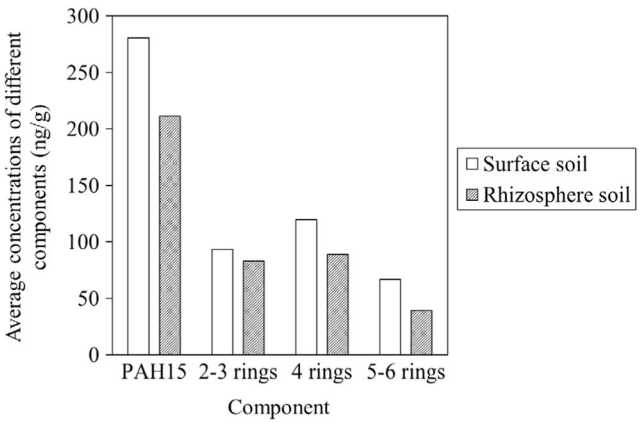

Fig. 2 Comparison of average concentrations of total PAHs and components with different rings in surface soils and rhizosphere soils (ng/g)

Component profile in environmental media

Based on the average concentrations in the eight sampling villages, Fig. 3 reveals the individual contributions of components with different rings to the total and different phases of air PAHs. The LMW species (two to three rings) were clearly predominant in all the sampling villages, contributing over 90% of the total PAHs, while the portion of species with five to six rings was negligible in the gaseous phase samples. By contrast, the proportions of MMW and HMW components with four to six rings increased markedly in the particulate phase samples. LMW and HMW PAHs appeared primarily in the gaseous and particulate phases, respectively. This difference is probably due to their differences in volatility and hydrophobicity, and our results were in accord with those from other studies (Li et al. 2010b; Hong et al. 2015; Masala et al. 2016).

For comparison, the component profiles of PAHs in atmospheric particulate phase, dust fall, surface soil, and rhizosphere soil are described in Fig. 4. Due to mutual collisions, heavier components in the dust fall, commonly with larger particle sizes relative to atmospheric suspended particles, were readily deposited from the air to the ground (surface soil). In contrast to the compositional spectra of total PAHs in ambient air (see upper panel in Fig. 3), portions of MMW and HMW species in the dust fall clearly increased, while contribution of LMW species decreased accordingly. However, except for a slight reduction in lighter species and a small increase in heavier ones in dust fall from most sampling villages, the overall component profiles of dust fall were quite similar to those of the particulate phase in air. The corresponding compositional profile indicated that PAH components with two to four rings (i.e., LMW and MMW species) were prevailing in rhizosphere soils and similar to those in surface soils, while a slight decrease in the fraction of HMW species occurred in rhizosphere soils with respect to surface soils (in other words, bulk soils), possibly because of stronger microbial biodegradation and transformation in the rhizosphere.

Characterized by the primary contributions of the LMW and MMW species, there was an overall resemblance among the distribution patterns of PAH components in solid particles from the various media (see Fig. 4), which implied their source homology. Some studies indicated a larger percentage of HMW PAHs present in surface soils (Cui et al. 2015), while others reported a dominant contribution of LMW PAHs (Okedeyi et al. 2013). The compositional differences would be affected by the differences in type of emission source, dispersion distance, (bio)degradation, and transformation of

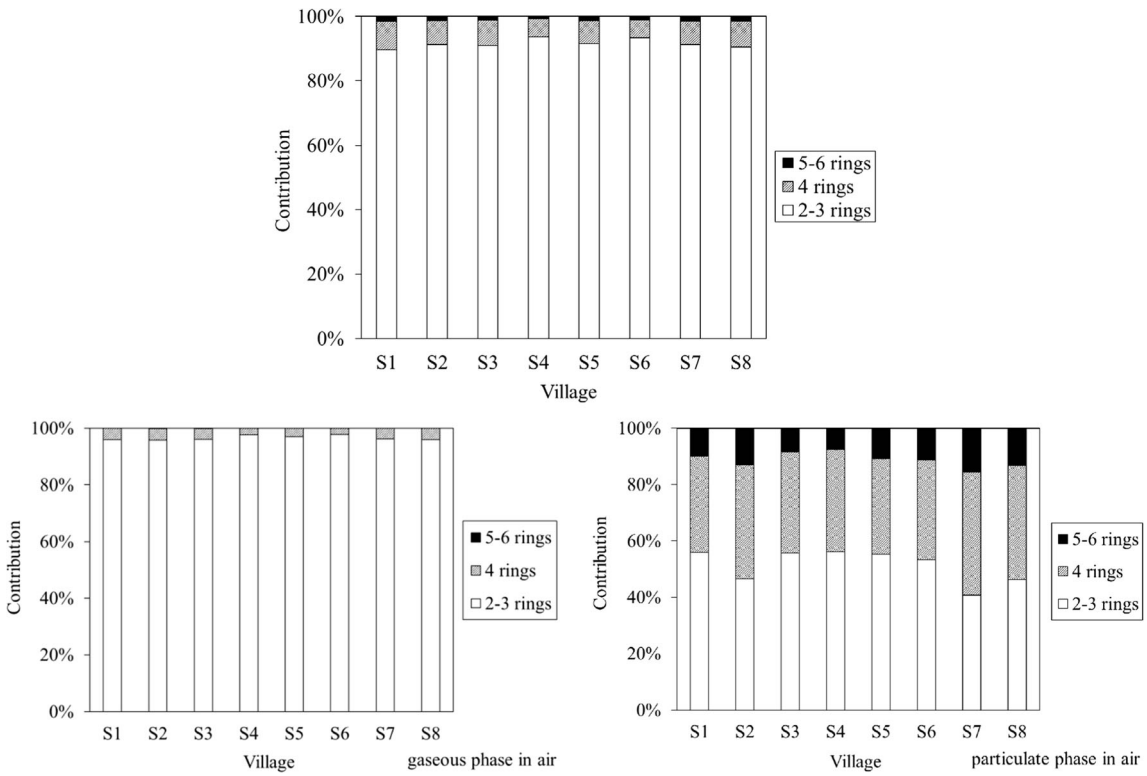

Fig. 3 *Upper panel*: Component profiles (%) of atmospheric PAHs (gaseous phase plus particulate phase) in vegetable plots of sampled villages. *Lower panel*: Contributions of individual PAH components with different rings to gaseous phase PAHs (*left*) and to particulate phase PAHs (*right*) in each sampled village

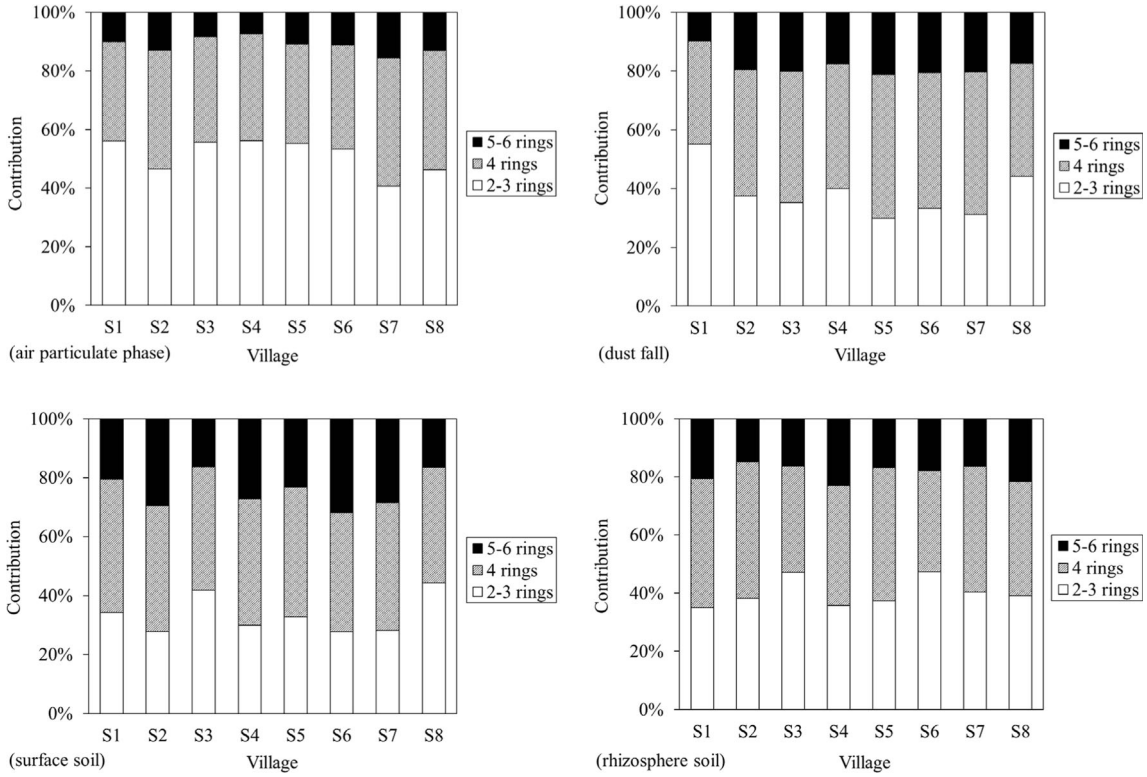

Fig. 4 Compositional profiles of parent PAHs in atmospheric particulate phase, dust fall, surface soil, and rhizosphere soil samples collected from the sampled vegetable fields

parent PAHs within or between different environmental media (Cao et al. 2013).

Preliminary source apportionment

A number of methods to identify emission sources of parent PAHs have been developed, such as a chemical mass balance model (Li et al. 2003); specific ratio of paired isomers (Yunker et al. 2002; Tobiszewski and Namiesnik 2012); multivariate statistical analysis (Golobočanin et al. 2004); isotopic technique of $\Delta^{13}C$, $\Delta^{14}C$, and $\Delta^{2}H$ (Bosch et al. 2015); and a multimedia fate fugacity model (Mackay and Hickie 2000; Zhang et al. 2005). The simple method of paired isomeric ratios has some limitations, e.g., differences in (bio)degradation behaviors, and there is a resultant risk of misjudgment. Considering the limited conditions and gaps of available data in the present study, calibration by multimedia fate modeling (Zhang et al. 2005) was not implemented and the simple isomeric ratio was employed instead. Two specific ratios of FLA/(FLA + PYR) and IcdP/(IcdP + BghiP), as relatively stable MMW and HMW species, were utilized (Tobiszewski and Namiesnik 2012) and are depicted in Fig. 5. All the ratios of FLA/(FLA + PYR) were greater than 0.5 in the local ambient air, which meant that the emission sources were from biomass and coal combustion. Meanwhile, all the values of IcdP/(IcdP + BghiP) fell between 0.2 and 0.5, indicating a dominant contribution from petroleum combustion (namely, tailing gas emitted by motor vehicles; Tobiszewski and Namiesnik 2012). On the whole, a mixed emission source from biomass and coal burning and traffic exhaust for the parent PAHs in local air could be apportioned.

PCA, combined with MLR, was applied to assist in diagnosing the emission sources of parent PAHs (Golobočanin et al. 2004; Manoli et al. 2004). As summarized in Table S2, three factors (principal components) could be extracted by a varimax rotation with the accumulative variance up to 88%. Based on previous investigations, the coking industry was responsible for ACE, FLO, and PHE (Khalili et al. 1995);

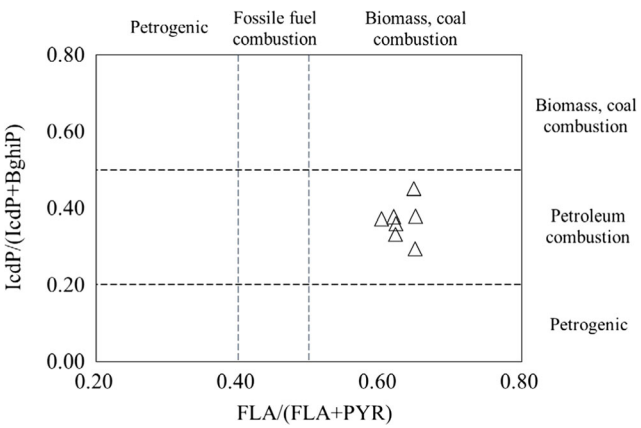

Fig. 5 Specific isomeric ratios of paired PAH species in ambient air from the sampled vegetable plots. Note: a ratio value for one of the sampled village was discarded due to error in determination

while FLA, PYR, and BaA were indicators of coal combustion (Simcik et al. 1999; Ravindra et al. 2006). CHR, BbF, and BkF were emitted mainly from industrial coal burning (Chen et al. 2005b; Brown and Brown 2012). BaP and IcdP are often considered as the typical products of vehicular exhaust (Miguel et al. 1998; Simcik et al. 1999; Ravindra et al. 2006). Accordingly, F_1 accounted for the influence of coal combustion, while F_2 and F_3 were associated with emission from coking production and traffic exhaust. The contributions of different emission sources were calculated by MLR using the standardized scores of total concentrations of air PAHs from the eight sampling villages as the dependent variable and the factor scores of three principal components as the independent variables. The corresponding model equation is shown below, where F_3 was excluded due to low statistical significance ($p > 0.05$).

$$\Sigma\text{PAH15} = 0.705 \times F_1 + 0.647 \times F_2 \quad r^2 = 0.86, p = 0.01$$

Based on the regression coefficients of F_1 and F_2, PAHs released from coal combustion contributed 52% of the total air concentration, while emissions from the coking industry and vehicular exhaust were responsible for the other 48%. The results correspond to those by diagnostic ratios mentioned above.

Shen et al. estimated the global emission inventory corresponding to the 16 atmospheric parent PAHs in 2008 (Shen et al. 2013), and the extracted results, shown in Fig. S5, indicate that PAHs emitted from domestic coal combustion played a dominant role (up to 52.5%) in the local total amount. In addition, indoor biomass (crop residue plus firewood) burning (20.4% + 9.4%) and traffic fuel oil (vehicular exhaust, 9.6%) were also important emission sources of air PAHs, in agreement with the source apportionment results above. The air sampling period in this study covered only the harvest season of local cabbages (summer), rather than the whole growth cycle. However, the PAH emissions in winter are usually much greater than those in summer in northern China (Liu et al. 2008), especially the emissions from biomass burning and coal combustion for residential cooking and heating.

Concentration range and component profile in cabbage

Figures S6–S8 illustrate the statistical results of PAH15 in cabbage leaf, core, and root gathered from eight sampling villages, respectively. The dry-weight based distribution ranges of total PAHs in leaf, core, and root fell between 52 and 269 ng/g, between 0.9 and 47.6 ng/g, and between 14 to 199 ng/g, and the corresponding median values were 174, 12.9, and 93 ng/g, respectively. As a result, a decreasing trend was seen in the order outer leaf > root > core for the average concentrations of total PAH15 and individual components with different rings (see Fig. 6). The phenomenon may be

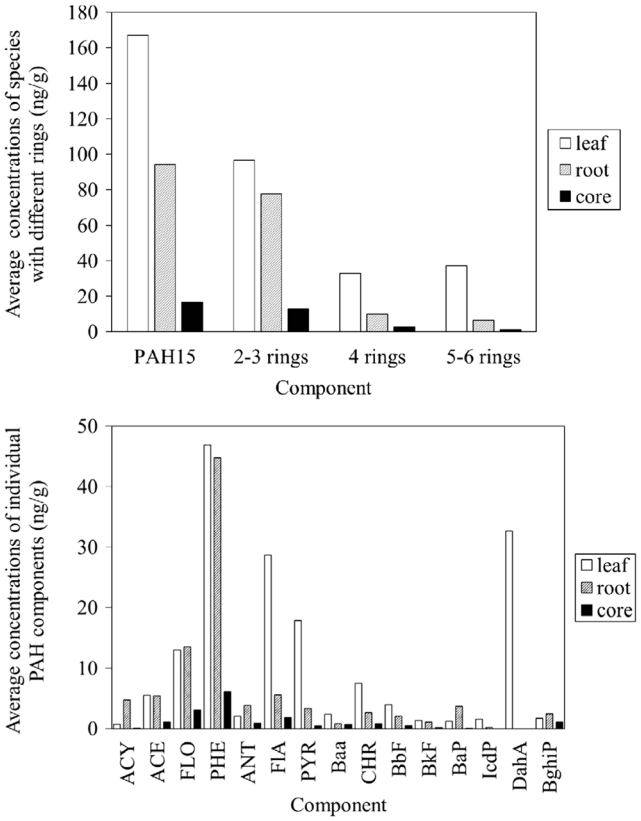

Fig. 6 Average concentrations of total PAHs, components with different rings (*upper panel*), and individual species (*lower panel*) in cabbage leaf, root, and core (ng/g)

ascribed to larger foliar area and higher planting density of local cabbage, which enhanced absorption of atmospheric PAHs by foliar surfaces and to some extent hindered the deposition of PAHs on the surface soil. In view of the total amount of PAHs in the edible part (cabbage core), the health risk by exposure from ingestion of local cabbage is relatively low. Considering the individual species, all the corresponding concentrations in cabbage core were much lower than those in leaf and root. The differences in concentrations between leaf and root mainly occurred for the FLA, PYR, and CHR in the MMW species and for DahA in the HMW species. On the whole, the distribution features of total PAHs and individual components in different tissues of cabbage were similar to those observed in earlier studies (Li et al. 2010a; Wang et al. 2011b), such as greater concentrations of LMW species in root, core and leaf, except for DahA in leaf.

Comparison of PAH component profiles between different parts of the cabbage plant (leaf, core, and root) is plotted in Fig. 7. PAH species with two to four rings (LMW + MMW) were dominant in the cabbage core and root (exceeding 80%), especially the LMW species, while the contribution of the HMW species increased notably in the outer leaf samples collected from some vegetable plots (S3, S4, S6, and S8),

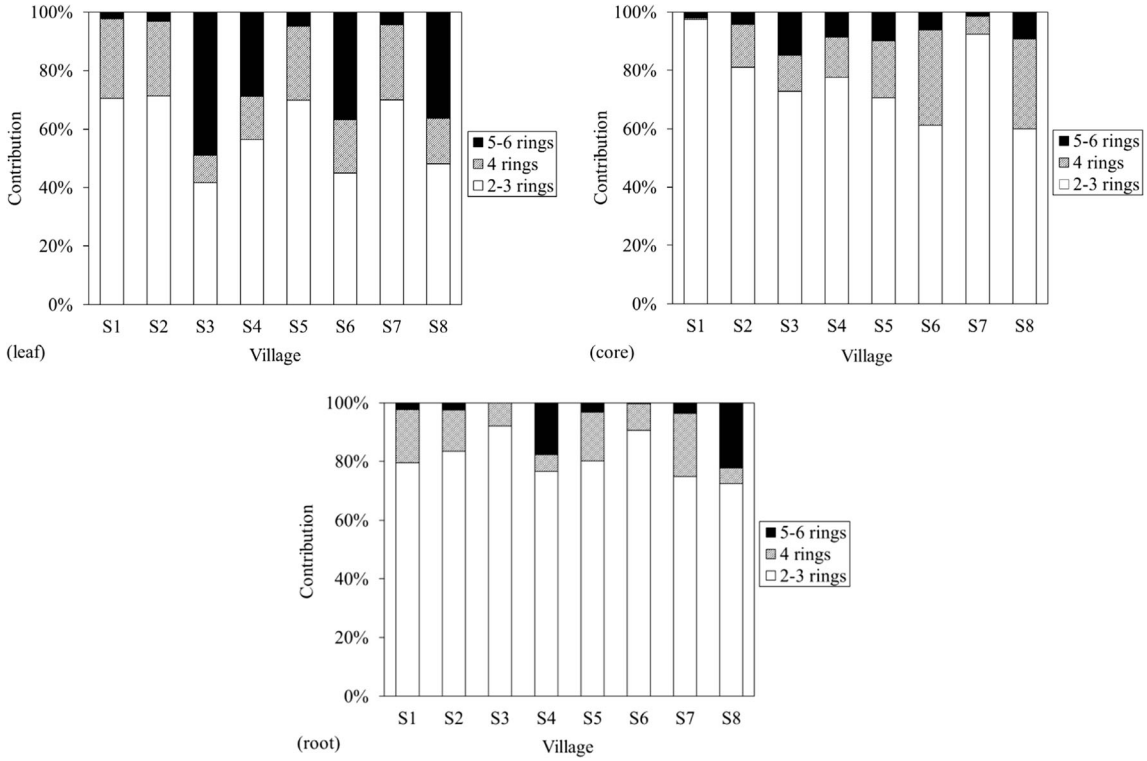

Fig. 7 Compositional profiles of PAHs in cabbage leaf, core, and root samples collected from the sampled vegetable fields

though LMW components were still predominant in most sampling villages. Overall, the distribution patterns of PAH components in the edible part of cabbage (i.e., core) in this study, characterized by the prevailing LMW and MMW species, seemed to be more associated with those in the particulate phase of ambient air (see lower panel in Fig. 3) than with those in the solid particles from dust fall, rhizosphere soil, and surface soil (Fig. 4), in accord with other studies (Waqas et al. 2014).

Associations of PAHs in root and leaf with those in core

In general, some complex interactions existed between different environment media. For instance, interactions of PAHs in air, soil, litter, and different tissues of trees were confirmed by significant correlations between the studied compartments (Odabasi et al. 2015). Similarly, we employed partial correlation analysis to explore the correlations between two specific media and the associations between different tissues of cabbage, after eliminating other related influences. Table S3 tabulates the partial correlation results of average PAH concentrations in surface soil, rhizosphere soil, ambient air (including total, gaseous phase and particulate phase), and dust fall. It is well known that air-soil exchange (dry and wet deposition from atmosphere vs. reemission from topsoil) is one of the most important processes affecting the local distribution of PAHs between the two media. In this study, after eliminating the influences of PAHs in both ambient air and dust fall, concentrations of total PAH15 and components with different rings in surface soil were significantly associated with those in rhizosphere soil. Furthermore, much closer relations were observed between total and different species concentrations in surface soil and those in dust fall than in ambient air, after the individual impacts of PAHs in ambient air or in dust fall were removed, suggesting the influences of air-soil exchange (Tao et al. 2008; Liu et al. 2011; Wang et al. 2011a, 2015a). Likewise, the correlation of total PAH15 in dust fall with the atmospheric particulate phase was much stronger than that with the gaseous phase, as indicated by the partial correlation coefficients r (D-P, G) and r (D-G, P) in Table S3.

Table S4 summarizes the results of partial correlation analysis for the different cabbage tissues. After excluding the associations with root, ambient air (including gaseous and particulate phases), and dust fall, the LMW and MMW species concentrations in cabbage cores showed significant partial correlations with the PAHs in cabbage leaves input via foliar absorption. Similarly, based on removing the associations with atmospheric gaseous phase and rhizosphere soil, the LMW and MMW species concentrations in cabbage cores revealed significant partial correlations with the PAHs in cabbage roots taken up from rhizosphere soil. These relations indicated that LMW and MMW PAHs present in cabbages were correlated with both exposure pathways (foliar uptake and root absorption), consistent with the previous study (Lin et al. 2007). However, the HMW species concentrations both in leaves and in roots were not partially correlated with those

in the cores (see Fig. 6), possibly because most HMW PAHs were not detected in cores. A recent report showed that only LMW and MMW PAHs had the potential to be transported from root system to shoot tissues (Alagić et al. 2015). As for total PAH15 in cabbages, after the contributions of other factors were eliminated, the partial correlation coefficient of PAH15 concentrations between cores and outer leaves, r (C-L, R + A + D) = 0.18, $p < 0.01$, was greater than that between cores and roots, r (C-R, G + RS) = 0.04, $p > 0.05$. Accordingly, compared with roots, there may be a closer correlation between cores and outer leaves in terms of total PAH15 amount.

Many previous studies have described the correlations between pollutant concentrations in plant organs and in surrounding media. For example, PAHs in leaves of some evergreens were found to be closely related to concentration and composition of particulate matters (Librando et al. 2002), and a positive correlation among the PAH concentrations in honey, blossom, and soil was also observed (Ciemniak et al. 2013). Since the local cabbage core (edible part) is usually wrapped by outer leaves until harvest time, atmospheric particles and dust fall are unlikely to directly bypass the outer leaf into the cabbage core. Thus, in this study, we inferred that a minority of the PAHs in cabbage core may originate from diffusion of gaseous phase PAHs in air. However, the outer leaves are exposed to ambient air for a relatively long period, and PAHs both in the atmosphere (including gaseous and particulate phases) and in dust fall would affect those in the cabbage outer leaf. Generally, the cabbage root system contacts the rhizosphere soil directly, and most, if not all, the PAHs in the root system come from adsorption and then absorption in the root hair zone. Table 1 demonstrates the results of partial correlation of PAHs between different cabbage organs and different environment media. After eliminating the associations with ambient air and cabbage roots, LMW and MMW species concentrations in cabbage leaves revealed a significant partial correlation with those in dust fall by r (L-D, A + R). Similarly, based on removing the associations with dust fall and cabbage roots, LMW and MMW species concentrations in cabbage leaves also displayed a significant partial correlation with those in ambient air by r (L-A, D + R). Furthermore, PAHs in the atmospheric gaseous phase showed a stronger partial correlation with those in cabbage leaves, compared to PAHs in the atmospheric particulate phase. Meanwhile, PAH concentrations in cabbage roots were significantly associated with those in rhizosphere soil after the correlations with surface soil were excluded. Additionally, LMW components in cabbage cores were significantly related to those in the atmospheric gaseous phase, based on removing the correlations with cabbage leaves and roots.

For the purpose of further exploring the correlations between concentrations of parent PAHs in various environment media and the edible part (core) of cabbage, after the normality tests, the natural-logarithm mean concentrations of PAHs in ambient air (gas plus particle), rhizosphere soil, and dust fall were considered as three independent variables, and the natural-logarithm average concentration of PAHs in cabbage core as one dependent variable. Then, a multivariate linear regression model (MLR), with stepwise selection of all the independent variables aforementioned, was developed as follows, and the corresponding details are provided in Table S5.

$$\ln C = 0.417 \times \ln A + 0.289 \times \ln RS - 1.840 \quad r^2 = 0.35, p < 0.01$$

where C, A, and RS denote the concentrations of PAHs in cabbage core, ambient air, and rhizosphere soil, respectively. The good fitting of the regression model manifested parent PAHs in cabbage cores was closely associated with those in ambient air and in rhizosphere soil, and statistical exclusion of the influences from PAHs in dust fall on PAHs in cabbage core. In another previous report, no specific gradient trends of PAHs along the root, stem, ear axe, and grain of rice were observed, which suggested systematic translocation among the rice organs was unlikely (Tao et al. 2006a). However, a clear sequence of PAH concentration distribution, including total PAH15 and individual species with different rings, was observed in the current research, namely, outer leaf > root > core, as shown in Fig. 6. Furthermore, the related multivariate linear regression models indicated that the contribution of

Table 1 Partial correlation of PAHs between different cabbage organs and different environmental media in sampled vegetable plots

Component	r (L-P, D + G + R)	r (L-G, D + P + R)	r (L-D, A + R)	r (L-A, D + R)	r (R-RS, SS)	r (C-G, L + R)
2~3 rings	0.49**	0.59**	0.60**	0.58**	0.28**	0.28**
4 rings	0.09	0.44**	0.35**	0.59**	0.27**	−0.07
5~6 rings	0.02	0.12	0.11	−0.21	0.04	−0.37*
ΣPAH15	0.60**	0.73**	0.40**	0.69**	0.21**	−0.11**

r (X-Y, Z1 + Z2 + Z3) represents the correlation coefficient of the PAH concentrations between X and Y after eliminating the contribution of Z1 + Z2 + Z3. *SS* surface soil, *RS* rhizosphere soil, *A* ambient air, *G* gaseous phase, *P* particulate phase, *D* dust fall, *C* cabbage core, *L* cabbage leaf, *R* cabbage root
*$p < 0.05$; **$p < 0.01$

PAHs in surface soil to the accumulation of PAHs in the aerial part of the cabbage plant (Tao et al. 2006b) or in the wheat grain (Liu et al. 2017) was insignificant or negligible, whereas rhizosphere soil, rather than surface soil (i.e., bulk soil), plays an important role in occurrence of PAHs in cabbage core (edible part) and root in this study.

A few deficiencies are noted in the current study, which can be improved in the future. For example, the multimedia samples were only collected during the local harvest time; however, concentrations of parent PAHs in vegetables may change in different growth stages. Some similar investigations indicated that PAH concentrations and profiles varied in soil, water, and different rice tissues at different growth stages (Wang et al. 2015b). The appearance and structure of crops at different growth times would also affect the air-soil exchange significantly (Wang et al. 2015c). Therefore, if the sampling period could cover the whole growth cycle of the local vegetables, the resulting assessment of root uptake and foliar absorption would be more accurate with more available data. Additionally, for continuous monitoring of long-term changes in PAH concentrations inside the crops (including different tissues or organs), applications of some novel or modified devices are required as well (Wang et al. 2015a).

Conclusions

In the local air, most of the atmospheric parent PAHs occurred in the gaseous phase with dominant contribution by the LMW PAH species. Source apportionment results indicated the local PAH emission sources were a mixture of coal combustion, coking activity, and traffic exhaust. Concentrations of 15 parent PAHs in rhizosphere soils from the sampled cabbage plots were slightly lower than those in surface soils. In comparison with cabbage cores and roots, parent PAHs accumulated more readily in cabbage leaves, and PAH species with two to four rings were prevailing in different tissues of local cabbages.

Based on the similarity in component profiles and partial correlation statistics, PAHs in cabbage cores originated mainly from uptake by foliage and root and subsequent inner translocation. In addition, after eliminating the corresponding associations with the other media studied, parent PAH concentrations in cabbage roots exhibited a significant partial correlation with those in rhizosphere soils. Meanwhile, parent PAH concentrations in both cabbage leaves and cabbage cores had significant partial correlations with those in the atmospheric gaseous phase.

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References

Alagić SC, Maluckov BS, Radojicic VB (2015) How can plants manage polycyclic aromatic hydrocarbons? May these effects represent a useful tool for an effective soil remediation? A review. Clean Techn Environ Policy 17(3):597–614

Ashraf MW, Salam A (2012) Polycyclic aromatic hydrocarbons (PAHs) in vegetables and fruits produced in Saudi Arabia. Bull Environ Contam Toxicol 88(4):543–547

Bosch C, Andersson A, Krusa M, Bandh C, Hovorkova I, Klanova J, Knowles TDJ, Pancost RD, Evershed RP, Gustafsson O (2015) Source apportionment of polycyclic aromatic hydrocarbons in central European soils with compound-specific triple isotopes (ΔC-13, ΔC-14, and ΔH-2). Environ Sci Technol 49(13):7657–7665

Brown AS, Brown RJC (2012) Correlations in polycyclic aromatic hydrocarbon (PAH) concentrations in UK ambient air and implications for source apportionment. J Environ Monit 14(8):2072–2082

Cao X, Liu M, Song Y, Ackland ML (2013) Composition, sources, and potential toxicology of polycyclic aromatic hydrocarbons (PAHs) in agricultural soils in Liaoning, People's Republic of China. Environ Monit Assess 185(3):2231–2241

Chen L, Ran Y, Xing B, Mai B, He J, Wei X, Fu J, Sheng G (2005a) Contents and sources of polycyclic aromatic hydrocarbons and organochlorine pesticides in vegetable soils of Guangzhou, China. Chemosphere 60(7):879–890

Chen Y, Sheng G, Bi X, Feng Y, Mai B, Fu J (2005b) Emission factors for carbonaceous particles and polycyclic aromatic hydrocarbons from residential coal combustion in China. Environ Sci Technol 39(6): 1861–1867

Ciemniak A, Witczak A, Mocek K (2013) Assessment of honey contamination with polycyclic aromatic hydrocarbons. J Environ Sci Health B 48(11):993–998

Cui Y, Guo L, Zhang G, Li H, He Q (2015) Human health risks of PAHs in soils and agricultural products in coking areas, Shanxi Province, China. J Agro-Environ Sci 34(1):72–79 **(in Chinese)**

Edwards NT (1983) Polycyclic aromatic-hydrocarbons (PAHs) in the terrestrial environment—a review. J Environ Qual 12(4):427–441

Empereur-Bissonnet P, Asselineau J, Bernillon P, Daniau C, Fismes J, Morel JL, Cabanes PA (2013) Modeling polycyclic aromatic hydrocarbon uptake in common vegetables grown in aged polluted soils. Environ Risqué Santé 12(1):29–40

Fismes J, Perrin-Ganier C, Empereur-Bissonnet P, Morel JL (2002) Soil-to-root transfer and translocation of polycyclic aromatic hydrocarbons by vegetables grown on industrial contaminated soils. J Environ Qual 31(5):1649–1656

Golobočanin DD, Skrbic BD, Miljevic NR (2004) Principal component analysis for soil contamination with PAHs. Chemom Intell Lab Syst 72(2):219–223

Hong Y, Chen J, Zhang F, Zhang H, Xu L, Yin L, Chen Y (2015) Effects of urbanization on gaseous and particulate polycyclic aromatic hydrocarbons and polychlorinated biphenyls in a coastal city, China: levels, sources, and health risks. Environ Sci Pollut Res 22(19): 14919–14931

Jiang Y, Wang X, Wu M, Sheng G, Fu J (2011) Contamination, source identification, and risk assessment of polycyclic aromatic hydrocarbons in agricultural soil of Shanghai, China. Environ Monit Assess 183(1–4):139–150

Jiang Y, Yves UJ, Sun H, Hu X, Zhan H, Wu Y (2016) Distribution, compositional pattern and sources of polycyclic aromatic hydrocarbons in urban soils of an industrial city, Lanzhou, China. Ecotoxicol Environ Saf 126(1):54–62

Khalili NR, Scheff PA, Holsen TM (1995) PAH source fingerprints for coke ovens, diesel and gasoline-engines, highway tunnels, and wood combustion emissions. Atmos Environ 29(4):533–542

Khan S, Lin AJ, Zhang S, Hu Q, Zhu Y (2008) Accumulation of polycyclic aromatic hydrocarbons and heavy metals in lettuce grown in the soils contaminated with long-term wastewater irrigation. J Hazard Mater 152(2):506–515

Kipopoulou AM, Manoli E, Samara C (1999) Bioconcentration of polycyclic aromatic hydrocarbons in vegetables grown in an industrial area. Environ Pollut 106(3):369–380

Li A, Jang JK, Scheff PA (2003) Application of EPA CMB8.2 model for source apportionment of sediment PAHs in Lake Calumet, Chicago. Environ Sci Technol 37(13):2958–2965

Li J, Shang X, Zhao Z, Tanguay RL, Dong Q, Huang C (2010a) Polycyclic aromatic hydrocarbons in water, sediment, soil, and plants of the Oujiang River waterway in Wenzhou, China. J Hazard Mater 173(1–3):75–81

Li W, Zhang C, Ma W, Zhou B, Liu Y, Jiang J, Li Y (2010b) Pollution characterizations and source apportionment of polycyclic aromatic hydrocarbons in air during domestic heating season of Xi'an. Environ Sci 31(7):1432–1437 **(in Chinese)**

Li T, Li Y, Yuan C, Tao S (2014) Distribution of polycyclic aromatic hydrocarbons in surface soils of Yinchuan plain and surrounding areas. J Agro-Environ Sci 33(11):2136–2142 **(in Chinese)**

Librando V, Perrini G, Tomasello M (2002) Biomonitoring of atmospheric PAHs by evergreen plants: correlations and applicability. Polycycl Aromat Compd 22(3–4):549–559

Lin H, Tao S, Zuo Q, Coveney RM (2007) Uptake of polycyclic aromatic hydrocarbons by maize plants. Environ Pollut 148(2):614–619

Ling W, Dang H, Liu J (2013) In situ gradient distribution of polycyclic aromatic hydrocarbons (PAHs) in contaminated rhizosphere soil: a field study. J Soils Sediments 13(4):677–685

Liu S, Tao S, Liu W, Dou H, Liu Y, Zhao J, Mark GL, Tian Z, Wang J, Wang L, Gao Y (2008) Seasonal and spatial occurrence and distribution of atmospheric polycyclic aromatic hydrocarbons (PAHs) in rural and urban areas of the North Chinese Plain. Environ Pollut 156(3):651–656

Liu G, Yu L, Li J, Liu X, Zhang G (2011) PAHs in soils and estimated air soil exchange in the Pearl River Delta, South China. Environ Monit Assess 173(1–4):861–870

Liu WJ, Wang YL, Chen YC, Tao S, Liu WX (2017) Polycyclic aromatic hydrocarbons in ambient air, surface soil and wheat grain near a large steel-smelting manufacturer in northern China. J Environ Sci. doi:10.1016/j.jes.2016.10.016

Lv H, Cai Q, Jones KC, Zeng Q, Katsoyiannis A (2014) Levels of organic pollutants in vegetables and human exposure through diet: a review. Crit Rev Environ Sci Technol 44(1):1–33

Mackay D, Hickie B (2000) Mass balance model of source apportionment, transport and fate of PAHs in Lac Saint Louis, Quebec. Chemosphere 41(5):681–692

Maliszewska-kordybach B (1996) Polycyclic aromatic hydrocarbons in agricultural soils in Poland: preliminary proposals for criteria to evaluate the level of soil contamination. Appl Geochem 11(1–2): 121–127

Manoli E, Kouras A, Samara C (2004) Profile analysis of ambient and source emitted particle-bound polycyclic aromatic hydrocarbons from three sites in northern Greece. Chemosphere 56(9):867–878

Masala S, Lim H, Bergvall C, Johansson C, Westerholm R (2016) Determination of semi-volatile and particle-associated polycyclic aromatic hydrocarbons in Stockholm air with emphasis on the highly carcinogenic dibenzopyrene isomers. Atmos Environ 140:370–380

Miguel AH, Kirchstetter TW, Harley RA, Hering SV (1998) On-road emissions of particulate polycyclic aromatic hydrocarbons and black carbon from gasoline and diesel vehicles. Environ Sci Technol 32(4):450–455

Odabasi M, Falay EO, Tuna G, Altiok H, Kara M, Dumanoglu Y, Bayram A, Tolunay D, Elbir T (2015) Biomonitoring the spatial and historical variations of persistent organic pollutants (POPs) in an industrial region. Environ Sci Technol 49(4):2105–2114

Okedeyi OO, Nindi MM, Dube S, Awofolu OR (2013) Distribution and potential sources of polycyclic aromatic hydrocarbons in soils around coal-fired power plants in South Africa. Environ Monit Assess 185(3):2073–2082

Phillips DH (1999) Polycyclic aromatic hydrocarbons in the diet. Mutat Res-Genet Toxicol Environ Mutagen 443(1–2):139–147

Ravindra K, Bencs L, Wauters E, De Hoog J, Deutsch F, Roekens E, Bleux N, Berghmans P, Van Grieken R (2006) Seasonal and site-specific variation in vapor and aerosol phase PAHs over Flanders (Belgium) and their relation with anthropogenic activities. Atmos Environ 40(4):771–785

Shen H, Huang Y, Wang R, Zhu D, Li W, Shen G, Wang B, Zhang Y, Chen Y, Lu Y, Chen H, Li T, Sun K, Li B, Liu W, Liu J, Tao S (2013) Global atmospheric emissions of polycyclic aromatic hydrocarbons from 1960 to 2008 and future predictions. Environ Sci Technol 47(12):6415–6424

Simcik MF, Eisenreich SJ, Lioy PJ (1999) Source apportionment and source/sink relationships of PAHs in the coastal atmosphere of Chicago and Lake Michigan. Atmos Environ 33(30):5071–5079

Srogi K (2007) Monitoring of environmental exposure to polycyclic aromatic hydrocarbons: a review. Environ Chem Lett 5(4):169–195

Tao S, Jiao X, Chen S, Liu W, Coveney RM, Zhu L, Luo Y (2006a) Accumulation and distribution of polycyclic aromatic hydrocarbons in rice (*Oryza sativa*). Environ Pollut 140:406–415

Tao S, Jiao X, Chen S, Xu F, Li Y, Liu F (2006b) Uptake of vapor and particulate polycyclic aromatic hydrocarbons by cabbage. Environ Pollut 140(1):13–15

Tao S, Liu W, Li Y, Yang Y, Zuo Q, Li B, Cao J (2008) Organochlorine pesticides contaminated surface soil as reemission source in the Haihe Plain, China. Environ Sci Technol 42(22):8395–8400

Tao S, Cao J, Wang W, Zhao J, Wang W, Wang Z, Cao H, Xing B (2009a) A passive sampler with improved performance for collecting gaseous and particulate phase polycyclic aromatic hydrocarbons in air. Environ Sci Technol 43(11):4124–4129

Tao Y, Zhang S, Zhu Y, Christie P (2009b) Uptake and acropetal translocation of polycyclic aromatic hydrocarbons by wheat (*Triticum aestivum L.*) grown in field-contaminated soil. Environ Sci Technol 43(10):3556–3560

Tobiszewski M, Namiesnik J (2012) PAH diagnostic ratios for the identification of pollution emission sources. Environ Pollut 162:110–119

Trapp S, Matthies M (1995) Generic one-compartment model for uptake of organic-chemicals by foliar vegetation. Environ Sci Technol 29(9):2333–2338

Wang Y, Tao S, Jiao X, Coveney RM, Wu S, Xing B (2008) Polycyclic aromatic hydrocarbons in leaf cuticles and inner tissues of six species of trees in urban Beijing. Environ Pollut 151:158–164

Wang W, Simonich S, Giri B, Chang Y, Zhang Y, Jia Y, Tao S, Wang R, Wang B, Li W, Cao J, Lu X (2011a) Atmospheric concentrations and air-soil gas exchange of polycyclic aromatic hydrocarbons (PAHs) in remote, rural village and urban areas of Beijing-Tianjin region, North China. Sci Total Environ 409(15):2942–2950

Wang Y, Qiao M, Liu Y, Arp HPH, Zhu Y (2011b) Comparison of polycyclic aromatic hydrocarbon uptake pathways and risk assessment of vegetables from waste-water irrigated areas in northern China. J Environ Monit 13(2):433–439

Wang Y, Tian Z, Zhu H, Cheng Z, Kang M, Luo C, Li J, Zhang G (2012) Polycyclic aromatic hydrocarbons (PAHs) in soils and vegetation near an e-waste recycling site in south China: concentration,

distribution, source, and risk assessment. Sci Total Environ 439(22): 187–193

Wang Y, Luo C, Wang S, Liu J, Pan S, Li J, Ming L, Zhang G, Li X (2015a) Assessment of the air-soil partitioning of polycyclic aromatic hydrocarbons in a paddy field using a modified fugacity sampler. Environ Sci Technol 49(1):284–291

Wang Y, Wang S, Luo C, Xu Y, Pan S, Li J, Ming L, Zhang G, Li X (2015b) Influence of rice growth on the fate of polycyclic aromatic hydrocarbons in a subtropical paddy field: a life cycle study. Chemosphere 119(1):1233–1239

Wang Y, Wang S, Luo C, Li J, Ming L, Zhang G, Li X (2015c) The effects of rice canopy on the air-soil exchange of polycyclic aromatic hydrocarbons and organochlorine pesticides using paired passive air samplers. Environ Pollut 200(2):35–41

Waqas M, Khan S, Chao C, Shamshad I, Qamar Z, Khan K (2014) Quantification of PAHs and health risk via ingestion of vegetable in Khyber Pakhtunkhwa Province, Pakistan. Sci Total Environ 497-498:448–458

Wieczorek JK, Wieczorek ZJ (2007) Phytotoxicity and accumulation of anthracene applied to the foliage and sandy substrate in lettuce and radish plants. Ecotoxicol Environ Saf 66(3):369–377

Wild E, Dent J, Barber JL, Thomas GO, Jones KC (2004) A novel analytical approach for visualizing and tracking organic chemicals in plants. Environ Sci Technol 38(15):4195–4199

Wild E, Dent J, Thomas GO, Jones KC (2007) Use of two-photon excitation microscopy and autofluorescence for visualizing the fate and behavior of semivolatile organic chemicals within living vegetation. Environ Toxicol Chem 26(12):2486–2493

Yang C, Su Y, Chen Y, Huang Y, Liu W, Shen G, Duan Y, Liu W, Tao S (2014) Emission factors of particulate matter and polycyclic aromatic hydrocarbons for residential solid fuels. Asian J Ecotoxicol 9(3): 545–555 **(in Chinese)**

Yunker MB, Macdonald RW, Vingarzan R, Mitchell RH, Goyette D, Sylvestre S (2002) PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Org Geochem 33(4):489–515

Zezulka S, Klems M, Kummerova M (2014) Root and foliar uptake, translocation, and distribution of C-14 fluoranthene in pea plants (*Pisum sativum*). Environ Toxicol Chem 33(10):2308–2312

Zhan X, Liang X, Jiang T, Xu G (2013a) Interaction of phenanthrene and potassium uptake by wheat roots: a mechanistic model. BMC Plant Biol 13(1):1–9

Zhan X, Liang X, Xu G, Zhou L (2013b) Influence of plant root morphology and tissue composition on phenanthrene uptake: stepwise multiple linear regression analysis. Environ Pollut 179(8):294–300

Zhang X, Tao S, Liu W, Yang Y, Zuo Q, Liu S (2005) Source diagnostics of polycyclic aromatic hydrocarbons based on species ratios: a multimedia approach. Environ Sci Technol 39(23):9109–9114

Zhang J, Fan S, Du X, Yang J, Wang W, Hou H (2015) Accumulation, allocation, and risk assessment of polycyclic aromatic hydrocarbons (PAHs) in soil—*Brassica chinensis* system. PLoS One. doi:10.1371/journal.pone.0115863