

Distribution, transfer, and health risks of polycyclic aromatic hydrocarbons (PAHs) in soil-wheat systems of Henan Province, a typical agriculture province of China

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Abstract In order to investigate the distribution, transfer, and human health risks of polycyclic aromatic hydrocarbons (PAHs) in the soil-wheat systems, soil samples from 20 farmlands and corresponding wheat tissues were collected from selected regions of Henan Province in June 2013 and were analyzed to estimate the concentration of PAHs. The total concentrations of 15 PAHs ($\sum_{15}PAHs$) in soils from Henan Province varied from 6.91 to 72.4 ng/g. Moreover, two-ring to three-ring PAHs (1.59–29.1 ng/g) were the major species in soils, occupying 56.2% of total PAHs. Principal component analysis (PCA)-multiple linear regression (MLR) revealed that fossil fuel burning dominated the input of PAHs in agricultural soils of Henan Province. The range of $\sum_{15}PAHs$ concentrations in wheat tissues was 13.9–50.9 ng/g, which decreased along the root-straw-grain. Positive correlation among PAHs of soil and wheat tissues showed that PAHs in wheat mainly came from soil and then migrated along root-straw-grain. Moreover, PAHs were accumulated highest in root and

lowest in grain. Two-ring to three-ring PAHs were easier to transfer from soil to wheat than five-ring to six-ring PAHs. Consumption of wheat grain created potential risk of cancer in Henan Province.

Keywords Polycyclic aromatic hydrocarbons · Soil-wheat · Health risk · Transfer · Henan Province

Introduction

Polycyclic aromatic hydrocarbons (PAHs), composed of two or more condensed benzene rings, generate mainly from anthropogenic activities (e.g., industrial processes, incomplete combustion of fossil fuels, and coke production) and natural processes (e.g., volcanic activities and forest fires) (Huang et al. 2013a; Wei et al. 2014). The former generally plays a larger role in PAH pollution (Ravindra et al. 2008). Due to their toxicity, carcinogenicity, and ubiquitous presence in various environment media, a few PAHs are identified as the priority contaminants by both US Environmental Protection Agency (USEPA) and China. Published researches reveal that China is suffering from serious PAH contamination as a result of fossil fuel combustion and biomass burning (Wang et al. 2010). The PAH emission in China is up to 114,000 t/year and taking up more than 20% of the global PAH emission (Zhang and Tao 2009). Soil media is the primary environmental reservoir of PAHs in the terrestrial environment due to its tremendous capacity for retaining these chemicals (Wang et al. 2010). The continuous accumulation of PAHs in farmland soils as a consequence of the various human activities poses potential negative risks not only for the agricultural ecosystem but also for the human through food chain bioaccumulation (Agarwal et al. 2009; Duan et al. 2015). To assess such

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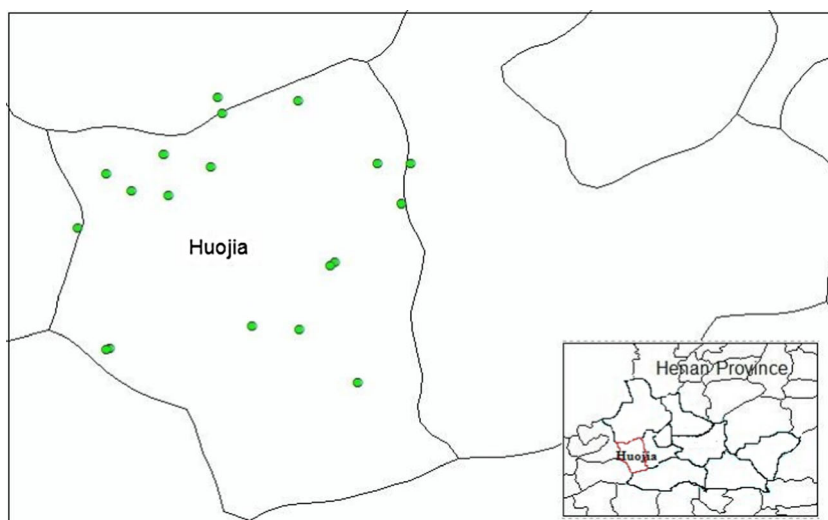
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Fig. 1 The sampling sites in the studied area



risks, it is imperative to investigate the concentrations and profiles of PAHs both in soils and in crops.

Henan Province is an important crop-producing area, which is located in Central China. Previous research highlights the enormity of PAH contamination in Huanghuai Plain, which covers the eastern part of Henan Province (Yang et al. 2012). The agricultural soil in Henan Province is mainly used for wheat production and making up 27% of total wheat production in China (Zheng et al. 2011). Because diet is supposed to be the primary way of human exposure to PAHs (Phillips 1999) and wheat is the basic food in Chinese dietary structure, it is necessitated to understand how and to what extent of PAHs are accumulated in the wheat and agricultural soils from Henan Province. This urgently needs a thorough study on their distribution, transfer, and human health risks of PAHs in soil and wheat tissues.

The present research was carried out to survey the concentrations, profiles, and potential sources of PAHs in agricultural soils from Henan Province. In addition, concentration and composition of PAHs in different tissues of wheat were determined. The uptake and transfer of PAHs from soil to wheat were determined as well. Finally, dietary exposures to PAHs and potential carcinogenic risks associated with the ingestion of wheat grains for population were estimated.

Materials and methods

Sample collection

As illustrated in Fig. 1, the sampling area is located in Huojia, northwest of Henan Province, Central China, where winter wheat–summer maize rotation is the main two-crop-per-year cropping system. In today's farming system, winter wheat is sown in October after tillage by tractor and harvested in June

of the following year. Farmers irrigate by water pump according to weather conditions. The fertilization goes through the stages of sowing and elongation. Moreover, it is now a universal phenomenon that straw is burned in fields after harvesting, even which has become a significant seasonal source of air pollution (Huang et al. 2013b). A total of 20 composite soil samples were collected in June 2013 at various locations in Huojia during full maturation of wheat. When sampling, surface layer soil of 0–15 cm in depth where wheat grew was collected. For each sampling site, five sub-samples were taken from the same area (100 m²) and bulked together to form one composite sample, which were wrapped with precleaned aluminum foil and then placed into polyethylene Ziplock bags. After transported to the laboratory, soil samples were freeze-dried, sieved through a 70-mesh sieve after removing stones, and stored at −18 °C prior to analysis.

Table 1 The targeted PAHs and their toxic equivalence factor

PAHs	Abbreviations	Toxic equivalence factor
Naphthalene	Nap	0.001
Acenaphthylene	Acy	0.001
Fluorene	Flu	0.001
Phenanthrene	Phe	0.001
Anthracene	Ant	0.01
Fluoranthene	Flua	0.001
Pyrene	Pyr	0.001
Benz(a)anthracene	BaA	0.1
Chrysene	Chr	0.01
Benzo(b)fluoranthene	BbF	0.1
Benzo(k)fluoranthene	BkF	0.1
Benzo(a)pyrene	BaP	1.0
Dibenz(ah)anthracene	DBA	1.0
Benzo(ghi)perylene	BghiP	0.01
Indeno(123-cd)pyrene	InP	0.1

Table 2 Concentrations of PAHs in soils and in different wheat tissues (ng/g)

PAHs	Soil Range/mean ± standard error of mean	Root Range/mean ± standard error of mean	Straw Range/mean ± standard error of mean	Grain Range/mean ± standard error of mean
Nap	1.78–6.83/2.69 ± 0.34	1.02–25.8/7.65 ± 1.82	0.76–18.0/6.64 ± 1.61	0.26–4.58/1.80 ± 0.35
Acy	0.95–17.7/7.09 ± 1.72	1.07–19.3/7.64 ± 1.76	0.94–19.9/8.44 ± 1.92	0.43–0.89/2.36 ± 0.67
Flu	0.37–3.17/0.94 ± 0.18	0.93–7.53/2.54 ± 0.48	0.93–5.19/2.46 ± 0.54	0.90–4.98/1.93 ± 0.42
Phe	n.d.–8.77/2.66 ± 0.58	0.98–10.9/3.61 ± 0.65	1.34–28.3/5.68 ± 1.02	0.94–3.63/2.05 ± 0.58
Ant	0.24–0.97/0.35 ± 0.05	0.12–3.91/1.08 ± 0.26	0.11–1.54/0.84 ± 0.22	0.11–0.59/0.48 ± 0.11
Flua	0.25–19.3/2.48 ± 0.95	0.66–25.4/5.64 ± 1.54	1.22–20.6/4.18 ± 1.09	0.11–6.58/0.81 ± 0.13
Pyr	0.29–4.69/1.24 ± 0.24	0.50–21.2/4.78 ± 1.49	0.57–7.10/2.12 ± 0.37	0.32–3.44/1.19 ± 0.25
BaA	0.21–6.36/1.65 ± 0.42	0.25–13.1/3.10 ± 1.11	0.91–5.32/1.95 ± 0.31	0.46–4.37/1.50 ± 0.28
Chr	0.10–0.79/0.37 ± 0.06	0.59–15.0/3.65 ± 1.32	0.44–5.12/1.61 ± 0.41	0.46–2.29/0.99 ± 0.23
BbF	n.d.–3.61/0.84 ± 0.20	0.42–9.56/2.43 ± 0.67	0.44–2.40/1.11 ± 0.20	n.d.–0.56/0.18 ± 0.04
BkF	n.d.–1.76/0.41 ± 0.09	0.11–4.69/1.29 ± 0.33	0.25–1.28/0.67 ± 0.11	n.d.–0.19/0.12 ± 0.02
BaP	0.20–3.65/0.82 ± 0.18	0.42–7.51/2.19 ± 0.59	0.48–1.46/0.93 ± 0.15	n.d.–0.42/0.25 ± 0.03
DBA	n.d.–5.58/1.67 ± 0.29	n.d.–6.58/3.15 ± 1.07	n.d.–2.71/1.49 ± 0.24	n.d.–0.84/0.17 ± 0.02
BghiP	n.d.–1.23/0.58 ± 0.10	n.d.–3.48/1.07 ± 0.31	n.d.–2.60/0.34 ± 0.06	n.d.
InP	n.d.–2.81/0.64 ± 0.16	n.d.–1.98/1.07 ± 0.42	n.d.–1.86/0.43 ± 0.08	n.d.
Σ ₁₅ PAHs	6.91–72.4/24.4 ± 4.07	26.7–174/50.9 ± 8.33	15.4–79.5/38.9 ± 5.85	4.43–30.7/13.9 ± 3.67

n.d. indicates that it is below the detection limit

Twenty composite samples of wheat were similarly collected by hand from all of the sampling sites. After the samples were transported to the laboratory, the wheat was carefully separated manually into three components of root, straw (stem/leaf), and grain. These different components of wheat were thoroughly washed with running water, then washed three times with deionized water and freeze-dried. Afterwards, they were ground to pass a 70-mesh sieve, mixed to homogenize, and stored at -18 °C until further analysis.

Chemicals

The 16 PAHs designated as the priority pollutants by the US Environmental Protection Agency were selected as the target pollutants (Table 1). The mixed standard solution containing 16 PAHs (each at 100 mg/L in acetonitrile) was purchased from Ultra Scientific Inc. (North Kingston, RI, USA). The stock solution containing 10 mg/L each of the 16 PAHs was prepared by diluting the purchased solution with methanol and stored in the dark at 4 °C. The working standard solutions of PAHs (2–500 µg/L) were obtained by diluting certain volume of stock solution with methanol. All solvents used during the entire experiment (methanol, acetone, dichloromethane, *n*-hexane) were HPLC grade and bought from Dikma (USA). Anhydrous sodium sulfate and silica gel (analytical grade, Beijing Chemical Reagent Co., China) were baked in a furnace oven at 450 °C for 6 h and were kept in a sealed desiccator prior to use. Water was produced from a Milli-

Q system (Millipore, Bedford, MA, USA). Glassware was cleaned in an ultrasonic cleaner (KQ-502B, Kunshan Ultrasonic Instruments, China) and rinsed with acetone first and then *n*-hexane.

Sample pretreatment

Soil samples (5 g) and wheat components (1 g) were extracted with 30 mL of mixed *n*-hexane/acetone (1:1, *v/v*) using the sonication extraction method (Feng et al. 2007). Following centrifugation at 4000 rpm for 20 min, the extracts were removed and concentrated to approximately 1.0 mL by a rotary evaporator (RV 05 basic, IKA, Germany). Afterwards, the extracts were cleaned by passing them through a glass column packed with 1 g of anhydrous sodium sulfate and 2 g of silica gel in sequence. PAHs were eluted with 10 mL of mixture of *n*-hexane and dichloromethane (1:1, *v/v*), and then, the eluent was concentrated to 1–2 mL, subjected to a solvent exchange to methanol, and concentrated to 1.0 mL using a rotary evaporator prior to HPLC analysis. In order to eliminate lipids, plant extracts were further purified using a gel permeation chromatography column (GPC, 2.0 cm i.d., 12 g of S-X3 Biobeads, Accustandard Co., USA). After extract loading, 80 mL of *n*-hexane and dichloromethane (1:1, *v/v*) was used to elute the GPC column. The first 35 mL of eluent was discarded, and the following 45 mL of eluent was concentrated to 1–2 mL, subjected to a solvent exchange to methanol, and concentrated to 1.0 mL prior to HPLC analysis.

PAH analysis

Quantification of PAHs was performed on a liquid chromatography (HPLC) coupled with a fluorescence detector (FLD) (Waters, USA). Separation of PAHs was carried out using a ChromSep guard column (10 mm × 4.6 mm, particle size 5 μm, Agilent, USA) followed by an Eclipse PAH column (250 mm × 4.6 mm, particle size 5 μm, Agilent, USA). Methanol-water was used as mobile phase, operating at a flow rate of 1 mL/min under a gradient elution program. The wavelength program of FLD for detected PAHs was described in detail in the literature (Feng et al. 2007). The injection volume was 20 μL. Identification of targeted PAHs was conducted using the retention time of the corresponding ones in the standard solution. Quantification of each PAHs was performed based on six-point calibration curves. However, acenaphthene cannot be detected using FLD due to lack of fluorescence. Therefore, acenaphthene was excluded in the target list.

QA/QC

Strict quality control was performed during the entire procedure. For example, solvent blanks, spiked blanks, and spiked matrix were analyzed during the treatment and analysis procedure. Solvent blanks were used to determine any background contamination, which showed no detectable PAHs. The spiked recoveries of 15 PAHs in soil and wheat tissues were set in a range of 80.5–119.8%, and the method detection limits (MDLs) of them ranged from 0.04 to 1.08 ng/g.

Risk assessment

In this study, health risks of PAHs from wheat grains are evaluated using the classical method of toxic equivalents, based on a set of toxicity equivalency factors (TEFs) proposed by Tsai et al. (2004). In this TEF system, BaP, the most toxic PAH, is recognized as the reference chemical and is assigned a value of 1 (Pufulete et al. 2004). Other PAHs have their TEF values based on their carcinogenic level compared to BaP (Table 1). The BaP equivalent concentration (C_{eq}) is calculated by multiplying PAH concentration with the corresponding TEF (Eq. (1)). The BaP equivalent concentration of total PAHs (TEC) is obtained by summing BaP equivalent concentrations (C_{eq}) of targeted PAHs according to Eq. (2):

$$C_{eq,i} = C_i \times TEF_i \quad (1)$$

$$TEC = \sum C_{eq,i} \quad (2)$$

where C_i is the concentration of PAH species i in wheat grains in ng/g dw. TEF_i is the toxic equivalency factor of a given PAH relative to BaP.

The daily dietary exposure level (D_{inh}) of PAHs through the intake of wheat grains is calculated using Eq. (3):

$$D_{inh} = TEC \times IR \quad (3)$$

where IR is the daily dietary intake of wheat grains by Chinese residents (143 g/day, according to the Chinese Statistics Press 2014).

The incremental lifetime cancer risk (ILCR, is the average annual excess risk of cancer for an individual, dimensionless) (Li and Ma 2016) resulted from PAH exposure through the wheat grain consumption is evaluated as

$$ILCR = \frac{D_{inh} \times ED \times EF \times SF \times 10^{-6}}{BW \times AT} \quad (4)$$

where ED is the exposure duration (70 years), EF is the exposure frequency (365 days/year), SF is the oral cancer slope factor of BaP (geometric mean, $7.27 \text{ (mg/kg/day)}^{-1}$) (USEPA 1997), BW is the body weight for an adult (70 kg), and AT is the average lifespan (70 years, i.e., 25,550 days).

Statistical analysis

All the statistical analysis is performed using SPSS software version 13.0 (SPSS Inc., Chicago, USA). Principal component analysis (PCA)-multiple linear regression (MLR) is used to quantitatively identify the potential sources of PAHs in the agricultural soils (Shi et al. 2012; Feng et al. 2014). The measured PAHs are regarded as variables, and all of the samples are treated as cases. Each PAH lower than the MDLs is set at one half of MDLs. The eigenvectors are normal varimax rotated to facilitate the explanation of the obtained results. One-way analysis of variance (ANOVA) is used for statistical comparisons (a value of $p < 0.05$ is considered to be statistically significant), and Pearson coefficient is used for correlation analysis.

Results and discussion

Concentrations and composition profiles of PAHs in agricultural soils from Henan Province

Concentrations of 15 targeted PAHs in agricultural soil samples from Henan Province are presented in Table 2. As shown in Table 2, the sum concentrations of 15 PAHs ($\sum_{15}PAHs$) in the studied area range from 6.91 to 72.4 ng/g with a mean concentration of 24.2 ng/g, which fall within the concentration range of PAHs in agricultural soils from the Huanghuai Plain (15.7–1247.6 ng/g) (Yang et al. 2012). In comparison to the published data, the $\sum_{15}PAHs$ levels in agricultural soil from Henan Province are lower than those from Shunde (188 ng/g)

(Li et al. 2008), from Shantou (318.2 ng/g) (Hao et al. 2007), from Beijing/Tianjin (336.4 ng/g) (Wang et al. 2010), from Chengdu (3234 ng/g) (Xing et al. 2011), and from the Yangtze River Delta (397 ng/g) (Ping et al. 2007). Moreover, $\sum_{15}PAHs$ concentrations in soils from this study are lower than those from Seoul (236 ng/g) (Nam et al. 2003), from Japan (320 ng/g) (Honda et al. 2007), from Poland (616 ng/g) (Maliszewska-Kordybach et al. 2008), and from Delhi (1906 ng/g) (Agarwal et al. 2009). Based on the classification system proposed by Maliszewska-Kordybach (1996), all of the soil samples in the present study are not polluted by PAHs (<200 ng/g). However, $\sum_{15}PAHs$ levels exceed that of the endogenous source (1–10 ng/g), which result from natural fires and plant synthesis (Wilcke 2000). This suggests that anthropogenic activities are responsible for PAHs occurring in agricultural soils from Henan Province.

In terms of compositional characteristics of PAHs in soil samples, the three-ring and four-ring PAHs are dominated at 39.2 and 23.5%, respectively. The percentage follows by two-ring PAHs (17.0%) and five-ring PAHs (15.4%). The six-ring PAHs make the least contribution to $\sum_{15}PAHs$, which are only accounted for 4.94%. In comparison to high molecular weight (four to six rings) PAHs (43.8%), low molecular weight (two to three rings) PAHs occupy a higher proportion of $\sum_{15}PAHs$ (56.2%). In addition, the relative abundance of individual PAH in the present study varies significantly. Acy is the most predominant species with a mean concentration of 7.10 ng/g and a relative abundance of 29.1%, which suggests that biomass burning could be a primary source of PAHs in the studied area (Feng et al. 2014). Phe, Nap, and Flua have the similar values of the relative composition, which are responsible for 11.0, 10.9, and 10.1% of $\sum_{15}PAHs$, respectively.

Source identification and contribution of PAHs in agricultural soils

In the present study, based on 15 detected PAHs in 20 agricultural soil samples from Henan Province, three factors are extracted with the eigenvalues >1, which is accounted for 78.0% of the total variance in the original data set (Table 3).

Factor 1, accounting for 52.4% of the total variance, is characterized by BaP, BkF, DBA, Pyr, BbF, Flua, BaA, BghiP, and InP with high loading. BaP, Flua, and Pyr are the species related with coal combustion (Larsen and Baker 2003), while BghiP and InP are typical markers for gasoline engine emissions (Kavouras et al. 2001). In addition, BaA, DBA, and BkF are usually derived from the traffic emission of diesel vehicle (Khalili et al. 1995). Consequently, factor 1 reflects that fossil fuel combustion is the primary origin of PAHs in the studied area, which might be closely associated with utilizing coal as the primary energy, and increasing vehicles brought about a large amount of petroleum and diesel

Table 3 Principal component analysis after varimax rotation for the detected PAHs in agricultural soils from Henan Province

PAHs	Component		
	Factor 1	Factor 2	Factor 3
Nap			0.683
Acy		0.881	
Flu		0.945	
Phe	0.640	0.555	
Ant	0.526	0.696	
Flua	0.807		0.223
Pyr	0.848		
BaA	0.757		
Chr		0.867	
BbF	0.835		
BkF	0.922		
BaP	0.930		
DBA	0.864		
BghiP	0.715		0.282
InP	0.683		0.366
Variance	52.4%	16.0%	9.60%
Sources	Fossil fuel combustion	Biomass burning	Coke oven

consumption. Factor 2, responsible for 16.0% of the total variance, is dominated by high loadings of Flu and Acy and moderate loadings of Ant and Phe. Acy is the predominant PAH released from biomass burning (Feng et al. 2014). In addition, Flu, Phe, and Ant are also originated from the low-temperature pyrogenic processes, with an example of straw and firewood burning (Jenkins et al. 1996). Therefore, factor 2 is used to indicate biomass burning origin. This is underscored by the fact that straw burning during the harvest is universal in the studied area. Moreover, combustion of firewood is common practice for cooking and heating in the rural study area. In the case of factor 3, contributing 9.60% to the total variance is predominantly weighed in Nap, with a moderate influence from Flua, InP, and BghiP. These compounds are recognized as markers of coke production (Wang et al. 2013; Yang et al. 2013). There are coking plants in the region, and during production and transportation, coke oven gas and fly ash are taken to non-industrial areas. Therefore, factor 3 is identified as coke oven emissions.

Based on the above results, combustion of fossil fuel, biomass burning, and coke oven are the major sources of PAHs in agricultural soils from Henan Province, which is basically consistent with the results from Huanghuai Plain (Yang et al. 2012) and middle and lower reaches of the Yellow River (Feng et al. 2014). In addition, as shown in Fig. 3 from MLR, combustion of fossil fuel is the most significant contributor of PAHs (45.3%), followed by biomass burning (32.9%) and coke oven (21.8%).

Table 4 Correlation coefficient of Σ PAH concentrations between soil and wheat tissues

	Root	Straw	Grain	Soil
Root	1	0.887**	0.703**	0.788**
Straw		1	0.828**	0.897**
Grain			1	0.675**
Soil				1

**Extremely significant correlation ($p < 0.01$)

Concentrations and compositions of PAHs in the wheat tissues

Concentrations of PAHs in different wheat plant tissues are presented in Table 2. As seen from Table 2, 15 PAHs designated as priority pollutants are detected in the wheat tissues. The concentrations of Σ_{15} PAHs range from 26.7 to 174 ng/g for roots, from 15.4 to 79.5 ng/g for straws, and from 4.43 to 30.7 ng/g for grains, respectively. Based on one-way ANOVA, significant differences ($p < 0.05$) are observed among various plant tissues, which show the pronounced decline trend of Σ_{15} PAHs concentrations along the root-straw-grain. In comparison to the corresponding concentration of PAHs in soils (24.4 ng/g), PAHs in roots (50.9 ng/g) and straws (38.9 ng/g) are relatively high, while those in grains (13.9 ng/g) are insignificantly low ($p < 0.05$). Organic pollutants are introduced into wheat tissues mainly through two ways: from the air through respiration or from soil via transpiration (Lin et al. 2006). The positive correlation between PAH concentrations in wheat tissues and those in the cultured soils (Table 4) indicates that the PAHs in the wheat roots are derived from root-soil uptake and the transfer of PAHs from roots-straws-grains is significant (Wild and Jones 1992; Tao et al. 2004).

The PAH profiles in the different wheat tissues from different sites resemble each other (Fig. 2) but slightly differ from those in the soil even where the wheat sample is sampled. The mild disparity for wheat uptake individual PAH may be ascribed to properties of PAHs. It is recorded

that Nap, Acy, Phe, and Flua are dominant species in wheat tissues and their concentrations are in the range of 0.26–26.8 ng/g for Nap, 0.43–19.9 ng/g for Acy, 0.94–28.3 ng/g for Phe, and 0.11–20.6 ng/g for Flua. In terms of ring-wise distributions of PAHs in wheat tissues (Fig. 2), three-ring (33.7–49.1%) and four-ring (25.3–32.3%) PAHs are the dominant congeners in roots, straws, and grains. The translocation of two-ring to four-ring PAHs in wheat tissues is easier due to their greater volatility, water solubility, and bioavailability (Wild and Jones 1994; Voutsas and Samara 1998). On the contrary, the proportions of five-ring to six-ring PAHs contributed to Σ_{15} PAHs in wheat tissues become less and less compared with those in soil, indicating that high molecular weight (HMW) PAHs are more difficult to uptake and transfer by wheat tissues due to their hydrophobicity and strong affinity with soil particles. These results also reveal that uptake of PAHs by wheat is selective, which is in accordance with the dissimilar compositional characteristics in other plant and vegetable species (Wang et al. 2012).

Bioconcentration and translocation factors

Root concentration factors (RCFs), defined as the ratio of PAH concentrations in wheat roots to those in cultured soils on a dry weight basis, are calculated and listed in Table 5. As illustrated in Table 5, RCFs of PAHs in the present study range from 1.04 to 3.76. The variation of RCFs along with the ring-wise of PAHs is plotted in Fig. 3, which indicates that four-ring and three-ring PAHs have relatively high RCF values, especially in the case where Pyr exhibits the highest RCF value among the detected 15 PAHs. The similar conclusion is also concluded from the other researches made by Tao et al. (2009) and Li and Ma (2016). The highest RCF value of Pyr is 3.76, which is comparable to the RCF of Pyr, as published by Li and Ma (2016). The RCF values of four-ring to six-ring PAHs are comparable or slightly higher than those reported by Li and Ma (2016). However, for two-ring to three-ring PAHs, RCFs in the present study are lower than those reported in literature (Li and Ma 2016). The difference in RCFs is

Fig. 2 The ring-wise distribution profiles of PAHs in soils and wheat tissues

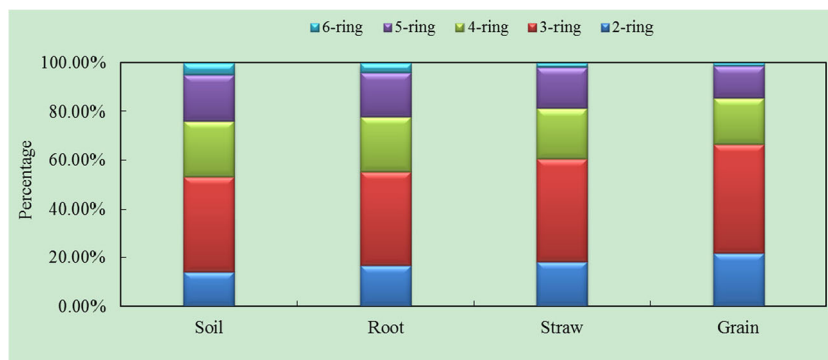


Table 5 Root concentration factors and transfer factors for PAHs

PAHs	RCF	RSF	GSF
Nap	2.71	0.91	0.26
Acy	1.04	1.14	0.28
Flu	2.69	0.97	0.76
Phe	1.59	1.35	0.36
Ant	3.22	0.75	0.54
Flua	2.12	0.8	0.18
Pyr	3.76	0.45	0.56
BaA	2.1	0.56	0.59
Chr	3.37	0.71	0.61
BbF	2.6	0.51	0.17
BkF	3.13	0.53	0.15
BaP	2.48	0.46	0.27
DBA	2.26	0.39	0.11
BghiP	1.94	0.3	0
InP	1.52	0.45	0

RCF root concentration factor, RSF root-to-straw translocation factor, GSF grain-to-straw translocation factor

primarily due to the disparity of PAH levels in soil samples. In addition, total organic carbon contents in soil, having considerable effect on bioavailability of PAHs, might be another reason for the difference in RCFs of PAHs (Tang et al. 2005; Agarwal et al. 2009). In the case of other properties of PAHs, a strong positive linear correlation between $\log K_{ow}$ and \log RCF was observed for the translocation of PAHs by tea cultivated in a hydroponic solution (Lin et al. 2006). However, in the soil-wheat systems, no such relationship is obtained, which the same results are concluded from Li and Ma (2016).

There is strong positive correlation between PAHs in the straws and in cultivated soils, delineating that PAHs in the straws mainly originated from root uptake and transferred

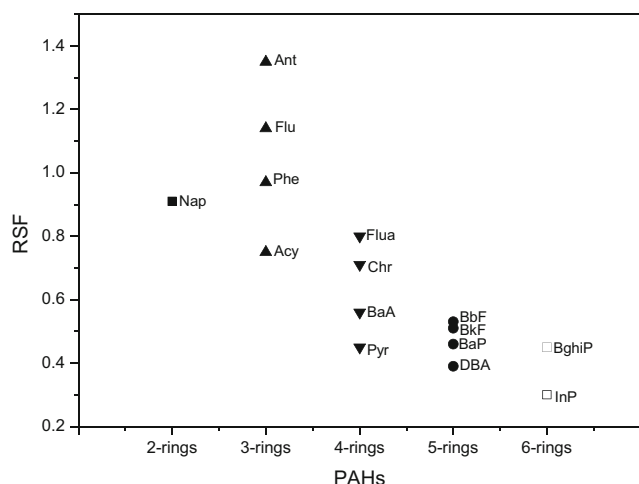


Fig. 4 Relationship between RSF and ring number of PAHs (RSF is defined as the ratio of the concentration in the straw (ng/g dw) to that in the root (ng/g dw))

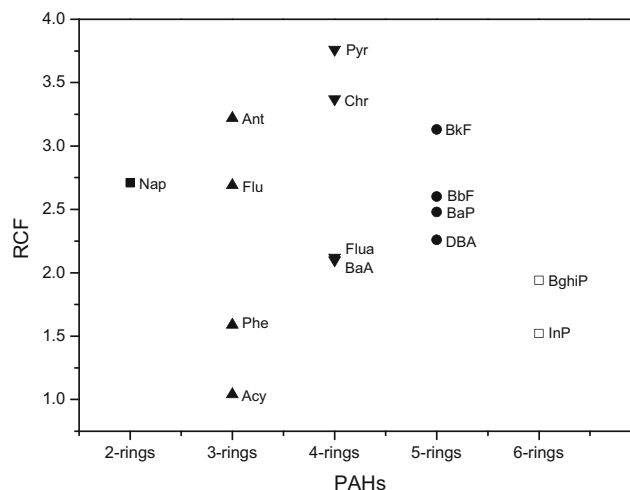


Fig. 3 Relationship between RCF and ring number of PAHs (RCF is defined as the ratio of the concentration in wheat root (ng/g dw) to that in the soil (ng/g dw))

from root to straw. Root-to-straw translocation factors (RSFs) are calculated and presented in Table 5. It is noticeable that the RSFs of NaP, Acy, Flu, and Phe for wheat tissues are close to 1 or greater than 1, indicating either that two-ring to three-ring PAHs are more easier to be transferred by xylem or that they are directly taken up by straws due to their high volatility. The relationship between RSF and the ring-wise of PAHs is shown in Fig. 4. It is observed that the RSFs

Table 6 Total BaP equivalent concentrations (TECs) in wheat grain, daily dietary intake (D_{inh}), and incremental lifetime cancer risks (ILCRs) of PAHs through wheat grain consumption

Sites	TEC (ng/g dw)	D_{inh} (ng/day)	ILCR
S1	0.36	51.8	5.38E-05
S2	0.51	73.2	7.60E-05
S3	0.41	59.3	6.16E-05
S4	0.44	62.9	6.53E-05
S5	0.36	51.9	5.39E-05
S6	0.36	51.0	5.29E-05
S7	0.40	57.4	5.96E-05
S8	0.32	45.8	4.75E-05
S9	0.35	49.8	5.17E-05
S10	0.12	17.4	1.80E-05
S11	0.41	58.7	6.09E-05
S12	0.40	57.3	5.95E-05
S13	0.38	55.0	5.71E-05
S14	0.40	57.2	5.94E-05
S15	0.53	75.8	7.87E-05
S16	0.55	79.3	8.23E-05
S17	0.45	64.4	6.68E-05
S18	0.46	66.4	6.89E-05
S19	0.30	42.8	4.44E-05
S20	0.44	63.3	6.57E-05

decrease along with the ring numbers of PAH increase. This is reasonable because more ring numbers mean higher molecular weight and greater hydrophobicity, therefore making PAHs more difficult to transfer by the plants (Li and Ma 2016).

Health risks of PAHs in wheat

The calculated TEC of PAHs in wheat grains from Henan Province is illustrated in Table 6. It can be seen from Table 6 that TEC of PAHs in wheat grains varies from 0.12 to 0.55 ng/g dw and the daily intake PAHs through wheat grain consumption ranges from 17.4 to 79.3 ng/day. Comparing with other studies, daily intake PAHs in the present study are far lower than those from intake of vegetables cultured in the vicinity of e-waste recycling sites in South China (Wang et al. 2012), but are above the doses from intake of vegetables cultured in wastewater-irrigated agricultural soils from North China (Khan et al. 2008a,b). In the case of ILCR, ILCRs of 10^{-6} or less denote virtual safety; ILCRs between 10^{-6} and 10^{-4} indicate potential risk, and ILCRs greater than 10^{-4} denote potentially high risk (Peng et al. 2011). The ILCR for dietary exposure to PAHs through wheat grain in this study ranges from 1.80×10^{-5} to 8.23×10^{-5} , with 100% values between 10^{-6} and 10^{-4} . Even under the worst-case scenario, no ILCR of the normal exposures exceeds 10^{-4} . However, the potential health risk cannot be ignored because they are above the “point of departure” (1×10^{-6}) for risk assessment.

Conclusions

The total concentrations of 15 PAHs in soil of Henan Provinces are lower than those in agricultural soils from other areas in China as well as some European countries. The dominating components in the soils from Henan Province are low molecular weight PAHs (two to three rings), which includes Acy, Phe, Nap, and Flua. Pyrogenic origins include coal combustion, traffic emissions, biomass burning, and coke oven that are the major sources of PAHs in collected soil. The PAHs in wheat mainly come from soil and then migrate along root-stem-grain, and its concentrations decrease along root-stem-grain. Moreover, wheat roots have the highest bioaccumulation ability, while grains have the lowest bioaccumulation. Two-ring to three-ring PAHs are easier to transfer from soil to wheat than five-ring to six-ring PAHs. Levels of PAHs present in wheat grains using ILCR may pose elevated cancer risks if consumed at high consumption rates over many years.

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