

Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/jes

JES
JOURNAL OF
ENVIRONMENTAL
SCIENCES
www.jesc.ac.cn

Polycyclic aromatic hydrocarbons in ambient air, surface soil and wheat grain near a large steel-smelting manufacturer in northern China

Weijian Liu, Yilong Wang, Yuanchen Chen, Shu Tao, Wenxin Liu*

Laboratory for Earth Surface Processes, College of Urban and Environmental Sciences, Peking University, Beijing 100871, China. E-mail: wjliu0817@gmail.com

ARTICLE INFO

Article history:

Received 7 July 2016

Revised 5 October 2016

Accepted 27 October 2016

Available online 13 December 2016

Keywords:

PAHs

Ambient air

Surface soil

Wheat grain

Steel-smelting activity

ABSTRACT

The total concentrations and component profiles of polycyclic aromatic hydrocarbons (PAHs) in ambient air, surface soil and wheat grain collected from wheat fields near a large steel-smelting manufacturer in Northern China were determined. Based on the specific isomeric ratios of paired species in ambient air, principle component analysis and multivariate linear regression, the main emission source of local PAHs was identified as a mixture of industrial and domestic coal combustion, biomass burning and traffic exhaust. The total organic carbon (TOC) fraction was considerably correlated with the total and individual PAH concentrations in surface soil. The total concentrations of PAHs in wheat grain were relatively low, with dominant low molecular weight constituents, and the compositional profile was more similar to that in ambient air than in topsoil. Combined with more significant results from partial correlation and linear regression models, the contribution from air PAHs to grain PAHs may be greater than that from soil PAHs.

© 2016 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences.

Published by Elsevier B.V.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are worldwide persistent organic pollutants (POPs) that usually enter plants through: (1) root adsorption, absorption and upward transport and (2) foliage stomata and waxy cuticle after dry and wet deposition of fine particle or aerosol adhered PAHs (CCME, 2008). To date, limited absorption and transport of PAHs via plant roots has been confirmed in the literature, especially for high molecular weight (HMW) species, although a few papers reported a different phenomenon (Fismes et al., 2002). For example, some studies observed that PAHs in different parts of crops were considerably correlated with gaseous and particulate PAHs in air, and thus, ambient air was likely an

important source of the PAHs accumulated by crops (Lin et al., 2007; Tao et al., 2006). Many factors may affect the partitioning processes of PAHs between air and plants, such as the octanol-air partitioning coefficient (K_{OA}) and physiological properties of foliage (Kipopoulou et al., 1999; Lin et al., 2007).

In China, pollution characteristics and crop types are quite variable, and hazardous accidents of agricultural products (e.g., cereals and vegetables) frequently occur and have grown worse in recent years (Si et al., 2015; Xing et al., 2016). In China, systematic monitoring data in representative areas accounting for relationships between environmental pollution and crop safety are insufficient and mainly focused on heavy metals, but rarely on POPs (L. Shen et al., 2013). Handan in Hebei Province, located in the western watershed of the Bohai

* Corresponding author. E-mail: wxliu@urban.pku.edu.cn (Wenxin Liu).

Sea, is one of the main producing areas of spring wheat (*Triticum aestivum*) in North China (approximately 2 million tons/year). Meanwhile, Handan is an important base of raw coal (over 20 million tons/year) in the coking industry (approximately 5 million tons/year) and steel products (over 13 million tons/year); as a result, Handan has suffered severe air and soil pollution. For instance, a published report estimated that the local annual amount of emitted PAHs was up to 878.48 tons, with an emission density at 72.68 kg/km², 27 times higher than the national average (Zhang et al., 2007). The severity of the problem has generated a great deal attention from the local government and the public, particularly for resident morbidity from lung cancer (Zhang et al., 2009) and crop safety. However, corresponding studies on the spatial distribution, emission sources, and potential dietary exposure to PAHs via the local staple crops are fairly inadequate.

The objectives of the current study are to ascertain the following aspects: (1) the total concentration and component profile of PAHs in ambient air, surface soil and wheat grain in the vicinity of the local largest steelwork (Handan Steel-Smelting Manufacturer); and (2) the source apportionment of PAHs emitted and a comparison of the contribution to PAHs in wheat grain between ambient air and surface soil. Briefly, based on actual measurements from multimedia samples (ambient air, surface soil and wheat grain), the main emission sources of PAHs were identified by the specific isomeric ratios of paired components in ambient air as well as by principal component analysis (PCA) and multivariate linear regression (MLR). Further, the contribution to individual PAH species in wheat grain was compared between PAHs in ambient air and in surface soil using partial correlation analyses and multivariate linear regression models.

1. Materials and methods

1.1. Multimedia sampling

Based on a preliminary survey of surface soils and the local dominant wind direction, we selected 8 villages (assigned as S1–S8, respectively) with wide wheat fields in the vicinity of the large scale Handan Steel-Smelting Manufacturer as sampling areas near the local harvest time of spring wheat. The locations of sampling sites in 8 villages can be found in Fig. S1 of the Supplementary materials. Two neighboring wheat fields (S8–1 and S8–2, which are separated by a distance of 1 km) located the farthest distance from Handan Steelworks were considered to represent the local background field. All of the sampling fields chosen were far from the main road to avoid the possible influence of local traffic.

A total of 239 surface (0–5 cm in depth) soil samples were collected from wheat fields in 8 villages. The same number of wheat grain samples were simultaneously gathered, sealed, and quickly stored in a freezer at –15°C. Two improved passive air samplers (Tao et al., 2009) equipped with polyurethane foam (PUF) plugs and glass fiber filter (GFF) were deployed in each sampling village (on a roof or in open space near the wheat fields) to sample gas and particulate phase

PAHs for approximately 33 to 34 days. Before setup, PUF disks were extracted by a Soxhlet device containing 100 mL of acetone, 100 mL of dichloromethane and 100 mL of *n*-hexane over 8 hr, respectively. GFFs were preconditioned by roasting in a muffle furnace at 450°C over 6 hr. After air sampling, all of the sampling media (PUF and GFF) were removed, sealed and stored at –18°C. GFFs were equilibrated in desiccators (25°C) for 24 hr and weighed before and after sampling.

Meanwhile, active air samplers with a small flow volume (XQC-15E, Tianyue Instrument Ltd. Company, Yancheng, China) were installed in the selected 4 villages to calibrate the aforementioned passive sampling. In each sampler, the pretreated PUF tube (22-mm diameter × 76 mm length, Supelco) and GFF mounted inside the tube were employed to collect both gas and particulate PAHs. The sampling rate was set at 1.5 L/min, and the process continued for 24 hr. Due to local limitations and unexpected reasons, a total of 15 passive air samples and 4 active air samples were finally obtained.

1.2. Sample pretreatment and determination

1.2.1. Ambient air samples

Using the Soxhlet device, PUF disks were extracted with a 100-mL mixture of *n*-hexane and acetone (V:V = 1:1) at 70°C for 8 hr. The extract was then concentrated to a final volume of 1 mL using a vacuum rotary evaporator (R-201, Shensheng Sci. & Technol. Ltd., Shanghai, China) in a water bath at 37°C. GFFs were subjected to microwave extraction (MARS2Xpress, CEM, USA) with a 20-mL mixture of *n*-hexane and acetone (V:V = 1:1). The microwave tubes were heated to 100°C at a rate of 10°C/min, held for 10 min, and finally cooled for 30 min. After filter pressing, the extract was concentrated using a procedure similar to that of the PUF extraction and were then transferred into an alumina–silica gel column for purification. The eluent was first concentrated in a water bath at 37°C and then diluted with *n*-hexane up to 1.0 mL. The samples were then sealed in vials and stored at –4°C.

1.2.2. Surface soil samples

After the removal of detritus and plant residues, each soil sample was air-dried at room temperature and ground to pass through a 2-mm sieve. A subsample of 2.0 g of soil was further ground to pass a 70-mesh sieve and then transferred into a tube with a 20-mL mixture of *n*-hexane and acetone (V:V = 1:1) for microwave extraction like that for GFFs. Based on filter pressing, the extract was concentrated using the vacuum rotary evaporator to a volume of approximately 1.0 mL for clean-up in the aforementioned alumina–silica gel column.

1.2.3. Wheat grain samples

The wheat grains were air-dried at room temperature for over 7 days, ground to remove husks, and then stored at –18°C. A 10-g portion of the ground sample was transferred to a tube for microwave extraction using 20 mL of acetonitrile. After extraction and filter pressing, the extract was transferred into a 250-mL separating funnel, combined with 100 mL of deionized water containing 4% sodium sulfate, and then extracted twice using 30 mL of *n*-hexane. The extracted organic phase was shifted to a flask and then concentrated by rotary evaporation to a volume of 1.0 mL for the subsequent column purification step.

1.2.4. Column purification

The alumina and silica gels (100–200 mesh) were baked at 450°C in a muffle furnace for 6 hr. and then reactivated at 130°C for 16 hr and kept in a sealed desiccator. Before being packed into the clean-up column, the gels were equilibrated in sequence with deionized water for 4 hr with *n*-hexane overnight. The glass column (10 mm i.d. × 350 mm length) was packed with 12-cm height alumina, 12-cm height silica gel and 2-cm height anhydrous sodium sulfate (baked at 650°C for 10 hr in advance). The concentrated extract was moved into the clean-up column using *n*-hexane (2 × 2 mL) and rinsed with 10 mL of *n*-hexane followed by 50 mL of a mixture (V:V = 1:1) of *n*-hexane and dichloromethane at a rate of 2 mL/min. The collected eluent was concentrated by rotary evaporation to approximately 1.0 mL in the water bath at 37°C. After being spiked with 50 µL of a mixed internal standard solution (containing NAP-d₈, ACE-d₁₀, ANT-d₁₀, CHR-d₁₂ and Perelyne-d₁₂), the eluent was sealed in a vial and stored at −4°C before quantitative analysis. All of the solvents used were of analytical or better grade and were further purified by distillation before use.

1.2.5. Quantification

Quantitative analyses were conducted using a gas chromatograph/mass spectrometer (GC/MS), equipped with a HP-5 MS (0.25 mm i.d. × 30 m length × 0.25 µm film thickness) capillary column (Agilent GC6890/5973 MSD). The GC temperature was ramped from an initial 60°C up to 280°C at 5°C/min and maintained at 280°C for 20 min. Helium was used as the carrier gas. A 1.0-µL aliquot of extract was injected in splitless mode at a flow rate of 1.0 mL/min, and the column head pressure was 30 kPa. MSD was operated in selective ion monitoring (SIM) mode with an electron impact ionization of 70 eV, and the mass range fell within 45–600 AMU. The electron multiplier voltage was 1288 V, and the ionic source temperature was 230°C. The working linear range for the internal standard method was 1–800 ng/mL. Sixteen parent PAHs on the USEPA priority list were included as follows: naphthalene (NAP), acenaphthene (ACE), acenaphthylene (ACY), fluorene (FLO), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benz(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenz[a,h]anthracene (DahA), indeno(1,2,3-cd)pyrene (IcdP), and benzo(g,h,i)perylene (BghiP). The concentration data on surface soil and wheat grain were shown on the basis of dry weight (d.w.).

1.3. Quality assurance and quality control

1.3.1. Surrogate recovery

Prior to extraction, a 50-µL mixture of deuterated PAHs (2-fluoro-1,1'-biphenyl and p-terphenyl-D14) was spiked to 20% of the total samples in each batch to monitor the extraction and clean-up procedures. The corresponding recoveries were 53%–98% and 75%–140%, respectively.

1.3.2. Method recovery

By spiking the sample matrices (PUF, GFF, soil and grain) with a mixed stock standard for 16 parent PAHs, we detected the sample blanks and standard spiked samples simultaneously using the extraction procedures mentioned before. Table S1

shows the calculated recoveries of 15 PAHs (excluding NAP), which ranged from 70% to 120%.

1.3.3. Detection limit

The detection limits were determined by sequentially determining 6 standard solutions with known concentrations close to five times the instrument background noise and calculating 3.36 times their standard deviation. The detection limits ranged from 0.85 to 7.00 ng/mL for the different PAH species in this study, as shown in Table S1.

1.3.4. Laboratory blanks

Blanks for ambient air samples were prepared using the baked blank GFFs and Soxhlet extracted PUF with the identical preparation steps (extraction, purification and quantification) as the actual samples. Both blanks for surface soil and wheat grain samples (with pure solvents only) were prepared using the solvent and procedural blanks; while the actual samples were pretreated according to the same extraction and purification procedures as before. All of the final results were corrected by lab blanks and recovery rates. Of 16 parent PAHs, NAP was excluded in this study due to its high volatility and low recovery rate in real analyses, and all the other 15 species were denoted as PAH15. After measuring every 20 samples, a PAHs standard was examined to confirm the GC peak retention time and MSD response values.

1.3.5. Calibration of passive air sampling

Based on the particulate phase concentrations of PAHs [PAH_P(P), ng/device/d] passively collected by GFF and using the molecular weights of the compounds studied, the bulk concentrations (ng/m³) in the particulate phase were calculated using the regression Eq. (1) (Tao et al., 2009). Moreover, with the aid of the log-transformed gas phase concentrations of PAHs (log₁₀PAH_G(P), log₁₀(ng/device/d)) passively sampled by PUF and using the molecular weights (MW_i) of the compounds studied, the log-transformed bulk concentrations of gas PAHs (log₁₀PAH_G(A), log₁₀(ng/m³)) were computed using the regression Eq. (2) below. The relevant details on 15 individual species of 15 passive air samples are described in Fig. S2, which indicate that the calculations for the bulk concentrations of PAHs with the corrected data are satisfactory.

Particulate phase:

$$\text{PAH}_P(A) = \text{PAH}_P(P) / e^{(-2.1383 - 3.3257 \times \text{MW}_i / 10000)}, r^2 = 0.71 \quad (1)$$

Gas phase

$$\log_{10} \text{PAH}_G(A) = 0.4599 \times \log_{10} \text{PAH}_G(P) - 49.95 \times \text{MW}_i^{0.05235} + 65.88, r^2 = 0.87 \quad (2)$$

1.4. Data statistics

To date, a number of methods for the source apportionment of PAHs have been developed, such as the chemical mass balance (CMB, Li et al., 2003), compound-specific isotopes (Bosch et al., 2015), diagnostic ratio of paired isomeric components (Katsoyiannis et al., 2011; Tobiszewski and Namiesnik, 2012; Yunker et al., 2002), multivariate statistical analysis (Mari et al., 2010; Yang et al., 2013), and multimedia fate fugacity

model (Wang et al., 2013; Zhang et al., 2005). Considering the limitations of the available data in this study, the specific isomeric ratios, principal component analysis and multivariate linear regression were applied to preliminarily identify the local emission sources, mainly for PAHs in ambient air.

Because part of the measured data could not satisfy the normal or logarithm-normal distribution, nonparametric statistical methods were employed to test the related hypotheses. Regarding the exchanging procedures of PAHs between ambient air and surface soil, together with absorption and transport via leaf surfaces and root systems as the main possible introduction routes of PAHs into crops, partial correlation analysis was applied to explore the correlation of PAHs in wheat grain with PAHs in ambient air or in surface soil. Due to a lack of measures for statistical significance testing in the nonparametric Kendall rank partial correlation, only correlation coefficients were provided without a corresponding significance level.

2. Results and discussion

2.1. Ambient air PAHs

2.1.1. Concentration and profile

Fig. 1 shows the total concentration distribution of atmospheric PAH15 in 8 sampling villages during the maturity time for local wheat (at the beginning of June). The mean air concentration of total PAH15 (excluding NAP) in summer was 132 ng/m^3 (Fig. 1). The two sampling villages located closer to Handan Steelworks (S1 and S2) possessed relatively higher concentrations. As for BaP, which had an average concentration at 2.6 ng/m^3 , it exceeded the national ambient air quality standard (1.0 ng/m^3 , GB 3095-2012) that was recently implemented.

A previous investigation of atmospheric PAHs indicated that the local energy structure, characterized by the substantial consumption of raw coal led to a heavy coal-burning pollution in Handan, and the large amount of PAHs emitted by Handan Steelworks in manufacturing processes for steel and coke products had adverse impacts on neighboring ambient air (Dong, 2008). In this study, the total PAH concentrations in the ambient air of the 8 sampling villages and the reciprocals of the distance to Handan Steelworks revealed a significant correlation ($r = 0.75$, $p = 0.02$; see Fig. S3), which further confirmed the influence of the diffusion of PAHs emitted from the local steel-smelting manufacturer.

From Fig. 1, low molecular weight (LMW) species were, on the whole, dominant in local ambient air, especially PHE, which is consistent with the literatures' reports (Lang et al., 2007; Lin et al., 2015; Liu et al., 2008). In addition, the profile patterns among different sampling villages were similar, i.e., LMW and median molecular weight (MMW) components played a primary role (close to or over 80%) in the total amount. And in view of partitioning phases (Fig. S4), LMW components were chief in gaseous phase, while MMW and HMW species prevailed in particulate phase.

2.1.2. Emission source diagnostics

We employed two pairs of relatively conservative isomeric ratios of FLA / (FLA + PYR) and IcdP / (IcdP + BghiP), like

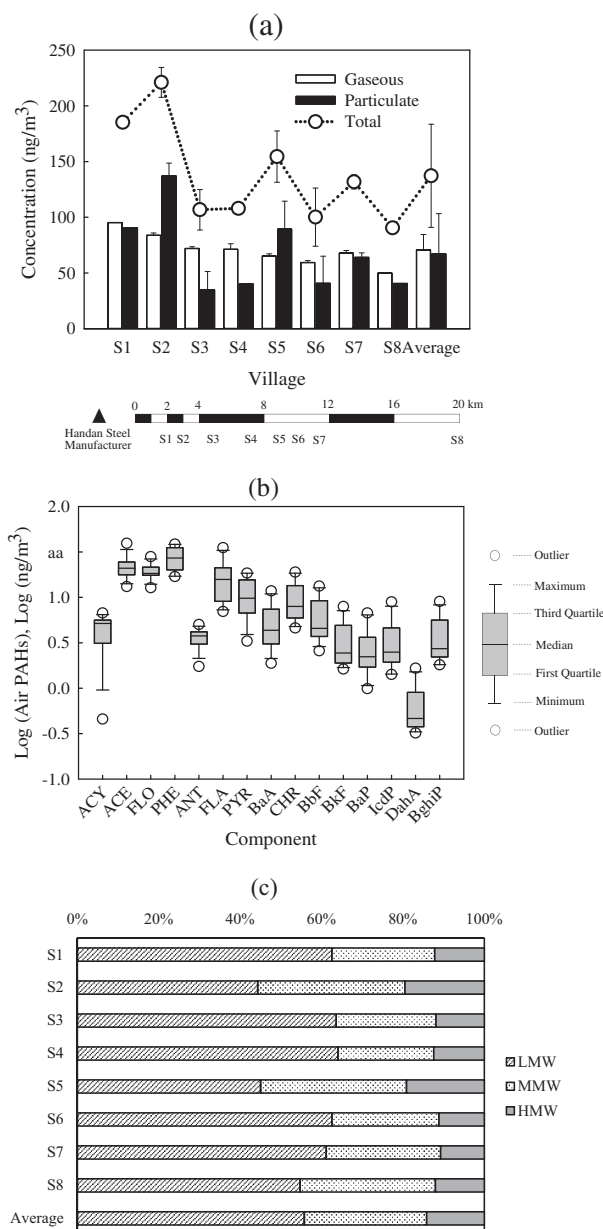


Fig. 1 – Total PAH concentrations (a), log-transformed concentrations (b) and component profile (c) of individual components in ambient air from different sampling villages LMW (ACY, ACE, FLO, PHE and ANT), MMW (FLA, PYR, BaA and CHR) and HMW (BbF, BkF, BaP, IcdP, DahA, and BghiP) fractions.

numerous relevant studies (Tobiszewski and Namiesnik, 2012), to preliminarily identify the local emission sources of PAHs in Handan. Based on the ratio of FLA / (FLA + PYR) in Fig. 2, coal (involving domestic coal and industrial coal) and biomass (such as straw and firewood) combustion appeared to be the two predominant emission sources. Meanwhile, most of the IcdP / (IcdP + BghiP) values suggested an important contribution from vehicular exhaust. In comparison with other cities in China (some are shown in Fig. 2), a typical feature of multiple emission sources for PAHs generally existed, especially in Northern China (Zhang et al., 2008).

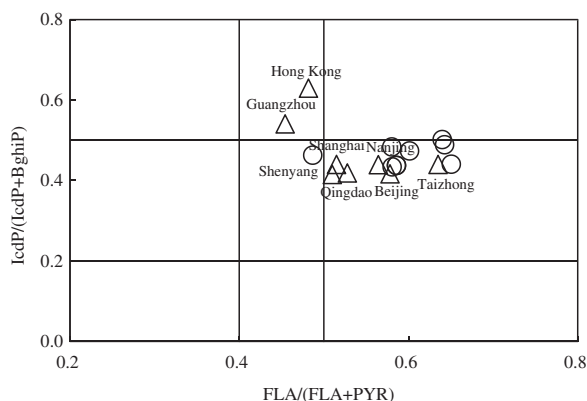


Fig. 2 – Specific ratios of paired isomeric components in ambient air from different sampling villages Open circles denote measured data in Handan, open triangles represent literature data in other cities of China. The data sources in the figure are as follows: Beijing (Okuda et al., 2006), Guangzhou (Tan et al., 2011), Nanjing (Wang et al., 2007), Qingdao (Z.G. Guo et al., 2003), Shanghai (Feng et al., 2006), Shenyang (Tang et al., 2005), Taizhong (Fang et al., 2005), and Hong Kong (H. Guo et al., 2003).

The results of principal component analysis (PCA) for PAHs in local ambient air are tabulated in Table S2. PC1 indicated influence coming from MMW and HMW PAHs, while PC2 represented the contribution of LMW species. ACY was considered to be an emission indicator for biomass (e.g., straw and firewood) burning (Gupta et al., 2011); FLO and PHE represented emissions from the coking industry (mainly as coking coal, Ciaparra et al., 2009); BbF, BkF and CHR were identified as the emitted products of industrial coal combustion (Brown and Brown, 2012; Chen et al., 2005); and IcdP and BghiP were regarded as the typical products of traffic exhaust or vehicular fuel oil (Larsen and Baker, 2003). Consequently, PC1 and PC2 may reflect the local emission contributions from industrial coal combustion and traffic exhaust (or vehicular fuel oil), and from biomass burning and coking industry (mainly as coking coal), respectively. In addition, multivariate linear regression (MLR) was performed in the form of the normalized fraction of the total PAH15 concentration in each village as the dependent variable and respective scores of two factors as the independent variables:

$$\Sigma\text{PAH15} = 0.791 \times \text{PC1} + 0.608 \times \text{PC2}$$

The regression coefficients of PC1 and PC2 demonstrated that industrial coal combustion and traffic exhaust contributed 57% of total PAHs in ambient air; while biomass (e.g., straw and firewood) burning and coking industry contributed the remaining 43%, both of which were generally in accordance with the results of the specific isomeric ratios mentioned before.

In one of our former studies, based on a statistical survey performed in 2003, on natural conditions, socioeconomic development, and energy structure and consumption, predictive models were employed to estimate emission amount,

spatial distribution and composition profile of PAHs according to emission factors (EFs), and then, a steady-state Level III fate model was used to simulate the distribution and processes of PAHs in multimedia environments in the whole western watershed of the Bohai Sea in Northern China (Zuo, 2007). Similar to this study, a combination of PCA, MLR and the specific isomeric ratio was applied to source diagnostics for local PAHs. In another study, using specific ratios of paired PAH isomers in ambient air and the positive matrix factorization (PMF) model, the local emission inventory of PAHs and source apportionment were further supplied and compared in the same western watershed (Liu, 2008). All of these data are summarized in Table 1. In Handan, an updated emission inventory of PAHs was generated in 2011 from a high spatial resolution fuel combustion inventory (H.Z. Shen et al., 2013) that mainly contained biomass burning, covered indoor and outdoor straw and firewood, domestic coal combustion, traffic fuel oil, coking coal and non-traffic fuel oil, as also listed in Table 1.

In emission inventory, domestic coal combustion, biomass (including straw and firewood) burning are the primary contributors according to these statistical data, and the majority of which is consistent with the results aforementioned. On the other hand, in the whole western watershed of Bohai Sea, the contribution of industrial coal and traffic fuel oil to total PAHs emission in spring and summer (covering the growth and harvest periods of spring wheat) increased, as compared to the annual average (Table 1, Liu, 2008); meanwhile the fraction of domestic coal combustion decreased. The seasonal variations in emission inventory caused some uncertainties and deviations in source diagnostics. It should be clarified that either the specific isomeric ratio or the principal component analysis in the current study provided a relatively rough identification of the main PAHs emission sources, due partly to the limited number and period of atmospheric sampling. Accordingly, the source apportionment here only reflected the contributions of the different sources, rather than an indicator to accurately quantify the influence of the local emission sources, such as Handan Steelworks.

2.2. Surface soil PAHs

2.2.1. Concentration and profile

Similar to those for ambient air, the statistics of the total PAH15 concentration in surface soils from different sampling villages are illustrated in Fig. 3, with an average value of 689.6 ng/g.

Due to the lack of a formal domestic quality standard, an alternative quality standard (1000 ng/g for total PAHs) based on ecological risk recommended by Denmark (Danish Environmental Protection Agency, 2002) was adopted to roughly evaluate the current state of surface soil in local wheat fields. The concentrations of PAH15 in 44 soil samples (18% of the total) exceeded the risk threshold, and most of them were situated in the S1 and S2 villages. Consistent with the conditions of local ambient air, the two sampling villages (S1 and S2) closest to the Handan Steelwork revealed the highest mean concentrations, and the average concentrations of PAH15 in surface soil were also in proportion to the

Table 1 – Simplified emission inventory of PAHs in local areas.

Studying area	Category	Annual fraction			Subtotal
Western watershed of Bohai Sea ^a , 2003	Domestic coal	34.7%			52.2%
	Straw	26.5%			
	Firewood	25.7%			
	Coking	10.7%			
	Industrial coal	1.0%			
	Industrial fuel oil	0.8%			
	Traffic fuel oil	0.3%			
	Electrolytic aluminum	0.3%			
Handan, Hebei Province ^a , 2003	Domestic coal	61.4%			
	Coking	30.6%			
	Biomass (firewood + straw)	5.8%			
	Industrial coal/traffic fuel oil	2.2%			

Studying area	Category	Seasonal variations in fraction (%) of PAHs emission sources				
		Annual	Spring	Summer	Autumn	Winter
Western watershed of Bohai Sea ^b , 2003	Firewood/coking	41%	42%	45%	42%	40%
	Domestic coal	24%	13%	8%	16%	32%
	Straw	18%	8%	9%	17%	22%
	Industrial coal/traffic fuel oil	17%	37%	38%	25%	6%

Studying area	Category	Annual fraction
Handan, Hebei Province ^c , 2011	Biomass (firewood + straw)	43.8%
	Domestic coal	43.3%
	Traffic fuel oil	7.5%
	Coking	2.2%
	Non-traffic fuel oil	2.0%
	Electrolytic aluminum	0.7%
	Industrial coal	0.4%

^a Zuo, Q., 2007. PAHs in surface soils from the western watershed of Bohai Sea, China. Doctoral Dissertation, Peking University, China.

^b Liu, S. Ze. 2008. Atmospheric PAH Contamination in the Western Watershed of Bohai Sea, China. Doctoral Dissertation, Peking University, China.

^c Shen et al., 2013b. Global Atmospheric Emissions of Polycyclic Aromatic Hydrocarbons from 1960 to 2008 and Future Predictions. Environmental Science & Technology, 47, 6415–6424.

reciprocal of the distance to Handan Steelworks ($r = 0.740$, $p = 0.023$, see Fig. S5). Previous studies indicated that PAHs in ambient air may enter surface soil by multiple processes, such as diffusion and dry and wet deposition (Mostert et al., 2010; Wang et al., 2014; Wania and Mackay, 1995). Still, all of the studied villages used underground water as the irrigation water source, while the contribution of irrigation water to PAHs in surface soil is usually negligible compared to atmospheric deposition (Tao et al., 2006), which suggests that atmospheric deposition is the main input source of PAHs in surface soil (Mostert et al., 2010; Wania and Mackay, 1995). On the other hand, air-soil exchange (e.g., reemission of PAHs from surface soil), similar to that of organochlorine pesticides (Tao et al., 2008), affected the local distribution of PAHs in ambient air (Kaya et al., 2012; Wang et al., 2013, 2015a). Therefore, PAHs in ambient air and in surface soil are usually correlated, reinforced by a significant positive correlation in our study (Fig. S6, $r = 0.921$, $p < 0.001$).

The PAH component concentrations with a logarithm scale and the compositional profiles in surface soils from sampling villages are depicted in Fig. 3 as well. In contrast to those in ambient air, the contribution of HMW species increased, while the fraction of LMW components

substantially decreased, although PHE presented the highest mean concentration. By the aid of similar calculations in a multimedia fate model (Wang et al., 2013) with the corresponding parameters adapted for Handan, the local transmission fluxes of individual components between surface soil and ambient air near the harvest time of spring wheat (at the beginning of June) could be achieved using the average data for the 8 sampling villages, and plotted in Fig. S7. Obviously, the LMW species mainly transferred from surface soil to ambient air, while the MMW and HMW components predominantly deposited from ambient to surface soil, which were consistent with the profile characteristics presented in Figs. 1 and 3.

2.2.2. Correlation with soil TOC fraction

Many studies observed that the distribution of POPs in soils was affected by natural organic matter (Mackay, 2001; Tao et al., 2003). After an angle transformation (Wang et al., 2012), i.e., $\arcsin[\sqrt{\text{TOC}\%}]$, TOC fractions of 75 randomly selected soil samples with even distribution satisfied the normal distribution test ($p = 0.348$), and were significantly correlated ($p < 0.001$, see Table S3) with total PAH15 and individual components.

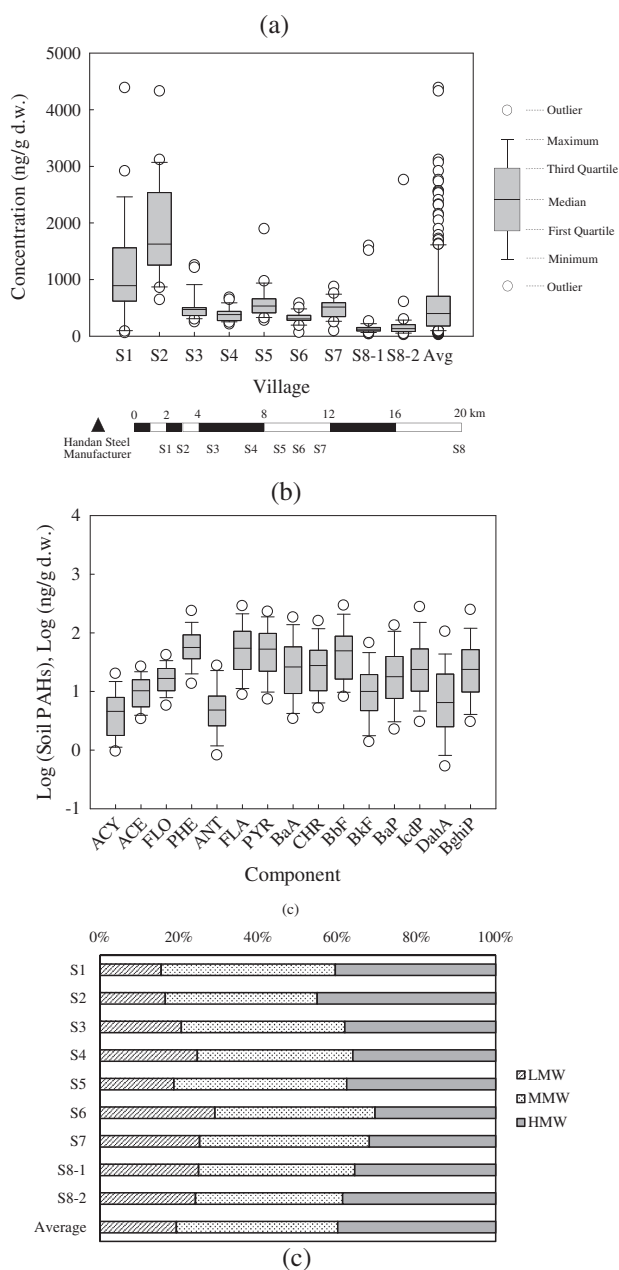


Fig. 3 – Total PAH concentrations (a), log-transformed concentrations (b) and component profiles (c) of individual components in surface soil from different sampling villages
 Annotation: Avg denotes an average of all of the villages studied; LMW (ACY, ACE, FLO, PHE and ANT), MMW (FLA, PYR, BaA and CHR) and HMW (BbF, BkF, BaP, IcdP, DahA and BghiP) fractions.

2.3. Wheat grain PAHs

2.3.1. Concentration and composition

Fig. 4 illustrates the statistics of 15 PAH compounds in wheat grains collected from 8 sampling villages. The lower average concentration of the total PAHs occurred in two local background villages (S8-1 and S8-2), while a relatively higher mean concentration appeared in the S4 village instead of S1

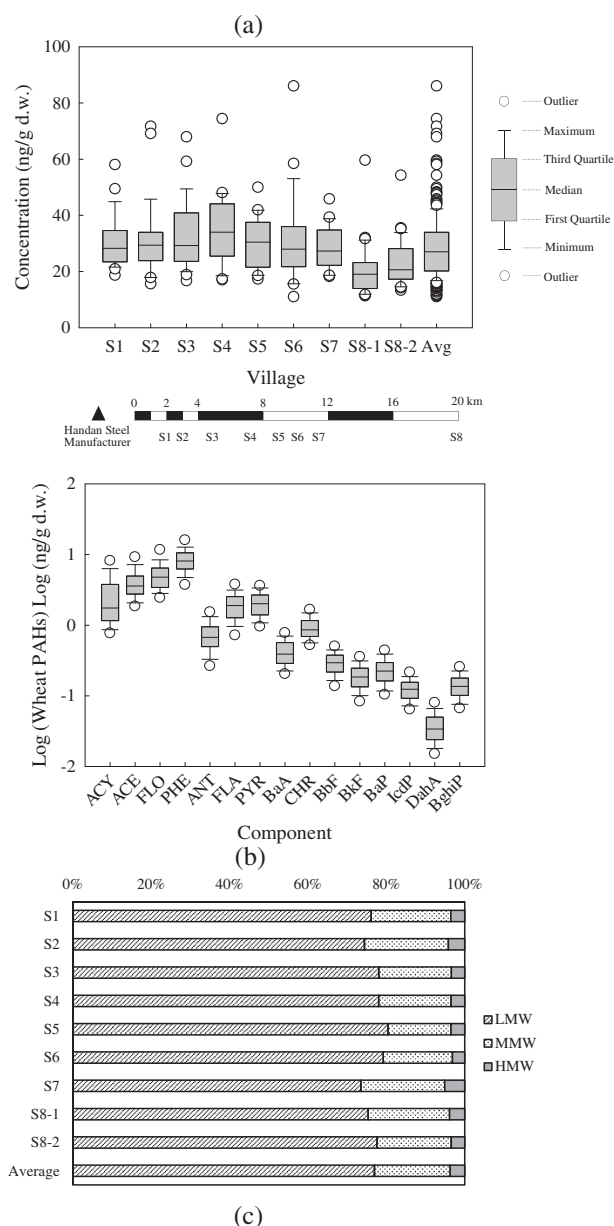


Fig. 4 – Total PAH concentrations (a), log-transformed concentrations (b) and component profiles (c) of individual components in wheat grains from different sampling villages
 Annotation: Avg denotes the average of all of the villages; LMW (ACY, ACE, FLO, PHE and ANT), MMW (FLA, PYR, BaA and CHR) and HMW (BbF, BkF, BaP, IcdP, DahA and BghiP) fractions.

and S2, which are much closer to Handan Steelworks; these results were different from those of ambient air and surface soil.

In comparison with the currently available quality standard of BaP in grain by the EU (1 ng/g, No. 1881/2006) or in food by China (5 ng/g, GB 7104-94), rare grain samples in Handan exceeded the critical values, which means that the PAH contamination in local wheat grains was low. In view of the concentrations and fractions of the individual components with different rings, the distribution pattern in wheat grain

(see Fig. 4) was more similar to that in ambient air compared with that in surface soil. Obviously, LWM compounds played a dominant role in local wheat grain, while HMW species only accounted for less than 5% of the total PAHs. These results were in accordance with those of another study on rice (Jiao et al., 2007).

Although the paired isomeric ratios in some specific bio-indicators have been utilized for source identification, such as in pine needles (Ratola et al., 2010; Tomashuk et al., 2012), few applications have been found using crops. In addition to the various physicochemical properties of individual species, other influencing factors, for example, diverse pathways (root absorption and upward transport, and/or dry/wet deposition on foliage stomata and waxy cuticle) and various biochemical reactions inside plants, probably lead to some changes in diagnostic ratios, and therefore, the ratios may become invalid or cause large deviations for the source apportionment of PAHs.

2.3.2. Correlations of PAHs in wheat grain with surface soil and ambient air

To preliminarily distinguish the source contribution of ambient air and surface soil to individual PAH components in wheat grain, the results of multivariate correlation and partial correlation analyses are tabulated in Table 2. The nonparametric testing methods were employed because a portion of the measured data did not conform to a normal or log-normal distribution. Significant correlations of most PAH components in wheat grain with those in ambient air $r(W-A)$ and in surface soil $r(W-S)$ could be observed, and the correlation coefficients for ambient air were commonly higher than those for surface soil. In general, the exchange procedures of PAH species between ambient air and surface soil

occurred and resulted in their close correlation, as shown in Fig. S6 and $r(S-A)$ in Table 2.

To eliminate the interactions between ambient air and surface soil, partial correlation analysis was conducted. Due to the lack of a significance testing method for the Kendall rank partial correlation, the correlation coefficients $r(W-S, A)$ and $r(W-A, S)$ without significance levels are given in Table 2. Most of the partial correlation coefficients of the PAH components between wheat grain and ambient air $r(W-A, S)$ were superior to those between wheat grain and surface soil $r(W-S, A)$, from which we inferred that ambient air had a greater contribution than surface soil. Our findings are reinforced by other relevant studies (Lin et al., 2007; Tao et al., 2006).

Additionally, we employed the median concentrations of PAHs in different sampling media as linear regression model variables, including 3 independent variables (gas and particulate phase PAHs in ambient air, PAHs in surface soil) and 1 dependent variable (PAHs in wheat grain). Then, two linear regression models, with the constraint inclusion (Enter mode) of all of the previously mentioned independent variables and with stepwise variable selection (Stepwise mode), were established using SPSS. The results calculated by two models indicated statistical elimination of the influences from PAHs in surface soil on PAHs in wheat grain, and the corresponding details are offered in Table 3.

Last but not least, it should be noted that some limitations existed in the current study, for example, the local prevailing wind direction and other meteorological conditions at different seasons should be considered to obtain more accurate results of air PAHs, and the successively kinetic sampling of PAHs in ambient air, surface soil and spring wheat in different periods (i.e., different growth periods of spring wheat) should be also performed in future research for exploring the whole

Table 2 – Multivariate correlation and partial correlation analyses of PAH components in different media.

Component	$r(W-S)^a$	$r(W-A)^a$	$r(W-S, A)^b$	$r(W-A, S)^b$	$r(W-S)^b$	$r(S-A)^b$	$r(W-A)^b$
ACY	0.243*	0.310**	0.042	0.160	0.155**	0.559**	0.216**
ACE	0.033	0.101	-0.026	0.073	0.014	0.516**	0.070
FLO	0.085	0.175**	-0.014	0.113	0.054	0.529**	0.124**
PHE	0.238**	0.360**	0.018	0.206	0.157**	0.563**	0.253**
ANT	0.330**	0.331**	0.109	0.141	0.213**	0.536**	0.230**
FLA	0.293**	0.319**	0.072	0.135	0.198**	0.631**	0.227**
PYR	0.197**	0.240**	0.032	0.118	0.129**	0.609**	0.171**
BaA	0.147*	0.086	0.083	0.032	0.099*	0.329**	0.063
CHR	0.295**	0.112	0.197	0.027	0.205**	0.239**	0.075
BbF	0.390**	0.457**	0.070	0.223	0.272**	0.656**	0.337**
BkF	0.325**	0.396**	0.049	0.209	0.218**	0.618**	0.292**
BaP	0.179**	0.248**	0.051	0.136	0.125**	0.452**	0.176**
IcdP	0.322**	0.399**	0.066	0.216	0.222**	0.573**	0.296**
DahA	0.231**	0.282**	0.081	0.162	0.165**	0.433**	0.214**
BghiP	0.413**	0.492**	0.095	0.262	0.281**	0.572**	0.361**

* and **: statistical significance at the levels of $p < 0.05$ and $p < 0.01$ for the Spearman correlation test or Kendall rank correlation test, respectively.

$r(W-S)$ indicates the correlation coefficient between the PAHs concentration in wheat grain and that in surface soil; $r(W-A)$ denotes the correlation coefficient between the PAHs concentration in wheat grain and that in ambient air; $r(S-A)$ represents the correlation coefficient between the PAH concentration in surface soil and that in ambient air. $r(W-S, A)$ is the rank partial correlation coefficient between the PAHs concentration in wheat grain and that in surface soil after eliminating the influence of the PAHs concentration in ambient air; $r(W-A, S)$ shows the rank partial correlation coefficient between the PAHs concentration in wheat grain and that in ambient air after eliminating the influences of the PAHs concentration in surface soil.

^a Spearman correlation coefficient.

^b Kendall rank correlation coefficient.

Table 3 – Linear regression models for PAHs in ambient air (gas and particle), surface soil and wheat grain using SPSS.

Model I	Enter (criteria: $p_{in} = 0.05$, $p_{out} = 0.10$)		Coefficient		ANOVA		Sum
	Independent variable	Dependent variable	t value	Significance	F value	Significance	r^2
	Air–gas	Wheat grain	16.108	0.000	97.763	0.000	0.691
	Air–particle		4.585	0.000			
	Surface soil		-1.597	0.113			
Model II	Stepwise (criteria: $p_{in} = 0.05$, $p_{out} = 0.10$)		Coefficient		ANOVA		Sum
	Input variable	Dependent variable	t value	Significance	F value	Significance	r^2
Model II—a	Air–gas	Wheat grain	14.494	0.000	210.076	0.000	0.612
Model II—b	Air–gas		16.057	0.000	143.679	0.000	0.685
	Air–particle		5.529	0.000			
Model II	Eliminated variable	Dependent variable	t value	Significance	Partial correlation		
Model II—a	Surface soil	Wheat grain	3.290	0.001	0.275		–
	Air–particle		5.529	0.000	0.434		–
Model II—b	Surface soil		–1.597	0.113	–0.138		–
ANOVA: analysis of variance. SPSS: Statistical Package for Social Science.							

ANOVA: analysis of variance. SPSS: Statistical Package for Social Science.

fate behaviors and relationships of PAHs between different media (Wang et al., 2015b). Moreover, the risk assessment on the potential exposure of residents to wheat grain should be implemented as well.

3. Conclusions

LMW and MMW components were predominant in the PAH component profile in ambient air of Handan. Based on specific ratios of paired isomers and analyses by PCA and MLR, multiple emission sources of PAHs may be mainly attributed to local coal combustion, biomass burning and traffic exhaust.

A close correlation of the total PAHs between ambient air and surface soil largely occurred due to their exchanging procedures. The contribution of HMW species to the total concentration in surface soil was noticeably higher compared to that in ambient air. The TOC fraction in local surface soil was significantly correlated with the total and individual PAH concentrations.

The total concentrations of PAH15 in collected wheat grain were generally lower than the corresponding quality standards. LMW species played a dominant role in the compositional profile. The distribution pattern of component profiles, multivariate correlation and partial correlation analyses suggested that in Handan, the contribution of PAHs in ambient air to PAHs in wheat grain was relatively greater than that in surface soil. In other words, air deposition was an important, if not a predominant, pathway for PAHs into wheat grain.

Acknowledgments

The present study was supported by the Natural Science Foundation Committee of China (No. 41390240), the National Basic Research Program of China (No. 2014CB441101), the Science & Technology Basic Special Fund of China (No.

2013FY111100-04), and “111” Project (No. B14001) of Peking University (PKU). Graduate students at PKU participated in the field sampling were appreciated. The authors were sincerely grateful to Huizhong Shen, Ye Huang, Han Chen, Tongchao Li, Shu Zhang, Siyu Cui, Ruixue Lei, and Baobao Ma for participating in multimedia sampling. All the authors were grateful to The Elsevier Language Editing Services for English expression polishing.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.jes.2016.10.016>.

REFERENCES

- Bosch, C., Andersson, A., Kruså, M., Bandh, C., Hovorková, I., Klánová, J., et al., 2015. Source apportionment of polycyclic aromatic hydrocarbons in central European soils with compound-specific triple isotopes ($\delta^{13}C$, $\Delta^{14}C$, and δ^2H). *Environ. Sci. Technol.* 49 (13), 7657–7665.
- Brown, A.S., Brown, R.J.C., 2012. Correlations in polycyclic aromatic hydrocarbon (PAH) concentrations in UK ambient air and implications for source apportionment. *J. Environ. Monit.* 14 (8), 2072–2082.
- CCME (Canadian Council of Ministers of the Environment), 2008. Canadian Soil Quality Guidelines for Carcinogenic and Other Polycyclic Aromatic Hydrocarbons (PAHs) (Environmental and Human Health Effects). Scientific Supporting Document PN1401 (Gatineau, Quebec).
- Chen, Y.J., Sheng, G.Y., Bi, X.H., Feng, Y.L., Mai, B.X., Fu, J.M., 2005. Emission factors for carbonaceous particles and polycyclic aromatic hydrocarbons from residential coal combustion in China. *Environ. Sci. Technol.* 39 (6), 1861–1867.
- Ciapparra, D., Aries, E., Booth, M.J., Anderson, D.R., Almeida, S.M., Harrad, S., 2009. Characterization of volatile organic compounds and polycyclic aromatic hydrocarbons in the ambient air of steelworks. *Atmos. Environ.* 43 (12), 2070–2079.

- Danish Environmental Protection Agency, 2002. Danish PAH Soil Quality Criteria (2002) - Sensitive Land Use (Available: http://www.mst.dk/udgiv/publications/2002/87-7972-280-6/html/kap06_eng.htm. Accessed October 5, 2016).
- Dong, H.L., 2008. Source Apportionment of Atmospheric Inhalable Particulate Matter and Polycyclic Aromatic Hydrocarbons in Handan City. (Master Thesis). Tianjin University, China.
- Fang, G.C., Wu, Y.S., Chen, J.C., Fu, P.P.C., Chang, C.N., Ho, T.T., et al., 2005. Characteristic study of polycyclic aromatic hydrocarbons for fine and coarse particulates at Pastureland near Industrial Park sampling site of central Taiwan. *Chemosphere* 60 (3), 427–433.
- Feng, J.L., Chan, C.K., Fang, M., Hu, M., He, L.Y., Tang, X.Y., 2006. Characteristics of organic matter in PM_{2.5} in Shanghai. *Chemosphere* 64 (8), 1393–1400.
- Fismes, J., Perrin-Ganier, C., Empereur-Bissonnet, P., Morel, J.L., 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.
- Guo, Z.G., Sheng, L.F., Feng, J.L., Fang, M., 2003a. Seasonal variation of solvent extractable organic compounds in the aerosols in Qingdao, China. *Atmos. Environ.* 37 (13), 1825–1834.
- Guo, H., Lee, S.C., Ho, K.F., Wang, X.M., Zou, S.C., 2003b. Particle-associated polycyclic aromatic hydrocarbons in urban air of Hong Kong. *Atmos. Environ.* 37 (38), 5307–5317.
- Gupta, S., Kumar, K., Srivastava, A., Srivastava, A., Jain, V.K., 2011. Size distribution and source apportionment of polycyclic aromatic hydrocarbons (PAHs) in aerosol particle samples from the atmospheric environment of Delhi, India. *Sci. Total Environ.* 409 (22), 4674–4680.
- Jiao, X.C., Xu, F.L., Dawson, R., Chen, S.H., Tao, S., 2007. Adsorption and absorption of polycyclic aromatic hydrocarbons to rice roots. *Environ. Pollut.* 148 (1), 230–235.
- Katsoyiannis, A., Sweetman, A.J., Jones, K.C., 2011. PAH molecular diagnostic ratios applied to atmospheric sources: a critical evaluation using two decades of source inventory and air concentration data from the UK. *Environ. Sci. Technol.* 45 (20), 8897–8906.
- Kaya, E., Dumanoglu, Y., Kara, M., Altioek, H., Bayram, A., Elbir, T., et al., 2012. Spatial and temporal variation and air-soil exchange of atmospheric PAHs and PCBs in an industrial region. *Atmos. Pollut. Res.* 3 (4), 435–449.
- Kipopoulou, A.M., Manoli, E., Samara, C., 1999. Bioconcentration of polycyclic aromatic hydrocarbons in vegetables grown in an industrial area. *Environ. Pollut.* 106 (3), 369–380.
- Lang, C., Tao, S., Wang, X., Zhang, G., Li, J., Fu, J., 2007. Seasonal variation of polycyclic aromatic hydrocarbons (PAHs) in Pearl River Delta region, China. *Atmos. Environ.* 41 (37), 8370–8379.
- Larsen, R.K., Baker, J.E., 2003. Source apportionment of polycyclic aromatic hydrocarbons in the urban atmosphere: a comparison of three methods. *Environ. Sci. Technol.* 37 (9), 1873–1881.
- Li, A., Jang, J.K., Scheff, P.A., 2003. Application of EPA CMB8.2 model for source apportionment of sediment PAHs in Lake Calumet, Chicago. *Environ. Sci. Technol.* 37 (13), 2958–2965.
- Lin, H., Tao, S., Zuo, Q., Coveney, R.M., 2007. Uptake of polycyclic aromatic hydrocarbons by maize plants. *Environ. Pollut.* 148 (2), 614–619.
- Lin, Y., Qiu, X.H., Ma, Y.Q., Ma, J., Zheng, M., Shao, M., 2015. Concentrations and spatial distribution of polycyclic aromatic hydrocarbons (PAHs) and nitrated PAHs (NPAHs) in the atmosphere of North China, and the transformation from PAHs to NPAHs. *Environ. Pollut.* 196, 164–170.
- Liu, S.Z., 2008. Atmospheric PAH Contamination in the Western Watershed of Bohai Sea, China. (Doctoral Dissertation). Peking University, China.
- Liu, S.Z., Tao, S., Liu, W.X., Dou, H., Liu, Y.N., Zhao, J.Y., et al., 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.
- Mackay, D., 2001. Multimedia Environmental Models: the Fugacity Approach. second ed. Lewis Publication, Boca Raton.
- Mari, M., Harrison, R.M., Schuhmacher, M., Domingo, J.L., Pongpiachan, S., 2010. Inferences over the sources and processes affecting polycyclic aromatic hydrocarbons in the atmosphere derived from measured data. *Sci. Total Environ.* 408 (11), 2387–2393.
- Mostert, M.M.R., Ayoko, G.A., Kokot, S., 2010. Application of chemometrics to analysis of soil pollutants. *TrAC Trend Anal. Chem.* 29 (5), 430–445.
- Okuda, T., Naoi, D., Tenmoku, M., Tanaka, S., He, K.B., Ma, Y.L., et al., 2006. Polycyclic aromatic hydrocarbons (PAHs) in the aerosol in Beijing, China, measured by aminopropylsilane chemically-bonded stationary-phase column chromatography and HPLC/fluorescence detection. *Chemosphere* 65 (3), 427–435.
- Ratola, N., Amigo, J.M., Alves, A., 2010. Comprehensive assessment of pine needles as bioindicators of PAHs using multivariate analysis. The importance of temporal trends. *Chemosphere* 81 (11), 1517–1525.
- Shen, L., Xia, B.C., Dai, X.K., 2013a. Residues of persistent organic pollutants in frequently-consumed vegetables and assessment of human health risk based on consumption of vegetables in Huizhou, South China. *Chemosphere* 93 (10), 2254–2263.
- Shen, H.Z., Huang, Y., Wang, R., Zhu, D., Li, W., Shen, G.F., et al., 2013b. Global atmospheric emissions of polycyclic aromatic hydrocarbons from 1960 to 2008 and future predictions. *Environ. Sci. Technol.* 47 (12), 6415–6424.
- Si, W.T., Liu, J.M., Cai, L., Jiang, H.M., Zheng, C.L., He, X.Y., et al., 2015. Health risks of metals in contaminated farmland soils and spring wheat irrigated with Yellow River water in Baotou, China. *Bull. Environ. Contam. Toxicol.* 94 (2), 214–219.
- Tan, J.H., Guo, S.J., Ma, Y.L., Duan, J.C., Cheng, Y., He, K.B., et al., 2011. Characteristics of particulate PAHs during a typical haze episode in Guangzhou, China. *Atmos. Res.* 102 (1–2), 91–98.
- Tang, N., Tetsuyuki, H., Rina, T., Kazuhiko, I., Yang, X.Y., Kenji, T., et al., 2005. Polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in urban air particulates and their relationship to emission sources in the Pan-Japan Sea countries. *Atmos. Environ.* 39 (32), 5817–5826.
- Tao, S., Cao, H.Y., Liu, W.X., Li, B.G., Cao, J., Xu, F.L., et al., 2003. Fate modeling of phenanthrene with regional variation in Tianjin, China. *Environ. Sci. Technol.* 37 (11), 2453–2459.
- Tao, S., Jiao, X.C., Chen, S.H., Xu, F.L., Li, Y.J., Liu, F.Z., 2006. Uptake of vapor and particulate polycyclic aromatic hydrocarbons by cabbage. *Environ. Pollut.* 140 (1), 13–15.
- Tao, S., Liu, W.X., Li, Y., Yang, Y., Zuo, Q., Li, B.G., et al., 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.T., Zhao, J.Y., Wang, W., Wang, Z.H., et al., 2009. A passive sampler with improved performance for collecting gaseous and particulate phase polycyclic aromatic hydrocarbons in air. *Environ. Sci. Technol.* 43 (11), 4124–4129.
- Tobiszewski, M., Namiesnik, J., 2012. PAH diagnostic ratios for the identification of pollution emission sources. *Environ. Pollut.* 162, 110–119.
- Tomashuk, T.A., Truong, T.M., Mantha, M., McGowin, A.E., 2012. Atmospheric polycyclic aromatic hydrocarbon profiles and sources in pine needles and particulate matter in Dayton, Ohio, USA. *Atmos. Environ.* 51, 196–202.
- Wang, G.H., Kawamura, K., Zhao, X., Li, Q.G., Dai, Z.X., Niu, H.Y., 2007. Identification, abundance and seasonal variation of anthropogenic organic aerosols from a mega-city in China. *Atmos. Environ.* 41 (2), 407–416.
- Wang, X.L., Zuo, Q., Duan, Y.H., Liu, W.X., Cao, J., Tao, S., 2012. Factors affecting spatial variation of polycyclic aromatic

- hydrocarbons in surface soils in North China Plain. *Environ. Toxicol. Chem.* 31 (10), 2246–2252.
- Wang, Y.L., Xia, Z.H., Liu, D., Qiu, W.X., Duan, X.L., Wang, R., et al., 2013. Multimedia fate and source apportionment of polycyclic aromatic hydrocarbons in a coking industry city in Northern China. *Environ. Pollut.* 181, 115–121.
- Wang, X.L., Liu, S.Z., Zhao, J.Y., Zuo, Q., Liu, W.X., Li, B.G., et al., 2014. Deposition flux of aerosol particles and 15 polycyclic aromatic hydrocarbons in the North China Plain. *Environ. Toxicol. Chem.* 33 (4), 753–760.
- Wang, Y., Luo, C.L., Wang, S.R., Liu, J.W., Pan, S.H., Li, J., et al., 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.R., Luo, C.L., Xu, Y., Pan, S.H., Li, J., et al., 2015b. Influence of rice growth on the fate of polycyclic aromatic hydrocarbons in a subtropical paddy field: a life cycle study. *Chemosphere* 119, 1233–1239.
- Wania, F., Mackay, D., 1995. A global distribution model for persistent organic-chemicals. *Sci. Total Environ.* 160–161, 211–232.
- Xing, W.Q., Zhang, H.Y., Scheckel, K.G., Li, L.P., 2016. Heavy metal and metalloid concentrations in components of 25 wheat (*Triticum aestivum*) varieties in the vicinity of lead smelters in Henan province, China. *Environ. Monit. Assess.* 188 (1), 23.
- Yang, B., Zhou, L.L., Xue, N.D., Li, F.S., Li, Y.W., Vogt, R.D., et al., 2013. Source apportionment of polycyclic aromatic hydrocarbons in soils of Huanghuai Plain, China: comparison of three receptor models. *Sci. Total Environ.* 443, 31–39.
- Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., 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.
- Zhang, X.L., Tao, S., Liu, W.X., Yang, Y., Zuo, Q., Liu, S.Z., 2005. Source diagnostics of polycyclic aromatic hydrocarbons based on species ratios: a multimedia approach. *Environ. Sci. Technol.* 39 (23), 9109–9114.
- Zhang, Y.X., Tao, S., Cao, J., Coveney, R.M., 2007. Emission of polycyclic aromatic hydrocarbons in China by county. *Environ. Sci. Technol.* 41 (3), 683–687.
- Zhang, Y.X., Dou, H., Chang, B., Wei, Z.C., Qiu, L., Tao, S., 2008. Emission of polycyclic aromatic hydrocarbons from indoor straw burning and emission inventory updating in China. *Ann. N.Y. Acad. Sci.* 1140, 218–227.
- Zhang, Y.X., Tao, S., Shen, H.Z., Ma, J.M., 2009. Inhalation exposure to ambient polycyclic aromatic hydrocarbons and lung cancer risk of Chinese population. *Proc. Natl. Acad. Sci. U.S.A.* 106 (50), 21063–21067.
- Zuo, Q., 2007. PAHs in Surface Soils From the Western Watershed of Bohai Sea, China. (Doctoral Dissertation). Peking University, China.