


RESEARCH ARTICLE

Distribution, sources, and potential risk of polycyclic aromatic hydrocarbons in soils from an industrial district in Shanxi, China

Haihua Jiao^{1,2} · Gaopeng Bian¹ · Xi Chen² · Suiliang Wang¹ · Xuliang Zhuang^{2,3} · Zhihui Bai^{2,3} 

Received: 28 August 2016 / Accepted: 2 February 2017 / Published online: 29 March 2017
© Springer-Verlag Berlin Heidelberg 2017

Abstract Concentration, composition profile, orientation distribution, sources, and potential risks of 16 polycyclic aromatic hydrocarbons (PAHs) were analyzed in 76 surface (0–25 cm) soil samples collected from the Changzhi industrial district in July 2014 using a gas chromatography mass spectrometer (GC-MS QP2010 Ultra) system. The composition patterns of the PAHs were dominated by the presence of four-ring PAHs (average 42.9%), followed by three-ring (average 25.9%), five-ring PAHs (average 25.6%), two-ring PAHs (average 5.03%), and lastly, six-ring PAHs (average 0.641%). Source apportionment of the soil PAHs was also performed by the diagnostic ratios, principal component analysis (PCA), and coefficient of divergence (CD) analysis indicated signatures of PAHs sources (including incineration, coal/wood combustion, and vehicular exhaust emission). The total concentration of 16 PAHs ($\sum 16\text{PAHs}$) found in the roadsides soils (RS) ranged from 2197 to 25,041 $\mu\text{g kg}^{-1}$, with an arithmetic mean value of 12,245 $\mu\text{g kg}^{-1}$; followed by the village soils (VS), which ranged from 2059 to 21,240 $\mu\text{g kg}^{-1}$, with a mean of 8976 $\mu\text{g kg}^{-1}$; and lastly, the agricultural soils (AS), which ranged from 794 to

16,858 $\mu\text{g kg}^{-1}$, with a mean of 3456 $\mu\text{g kg}^{-1}$. According to the numerical effect-based soils quality guidelines of Maliszewska-Kordybach, the levels of PAHs in the sampled industrial areas range from high to heavy contamination. The values of total benzo[a]pyrene toxicity equivalent values ($\sum \text{Bapeq}16\text{PAHs}$) in the sample areas ranged from 0.087 to 3611 $\mu\text{g kg}^{-1}$ with an average of 969 $\mu\text{g kg}^{-1}$. According to the soil quality guidelines of Canada, values found in the highest range (100 $\mu\text{g kg}^{-1}$), which are equal to those of $\sum \text{Bapeq}16\text{PAHs}$ found in the industrial area samples, will exert adverse biological effects. The results of this research could potentially be useful for local governments to control toxicity exposure, promote actions to alleviate PAHs contamination, and to manage human health at both work and industrial areas.

Keywords PAHs · Contamination · Benzo[a]pyrene · Potential risk · Soil

Responsible editor: Hongwen Sun

Gaopeng Bian, Xi Chen, and Suiliang Wang contributed equally to this work.

✉ Zhihui Bai
zhbai@rcees.ac.cn

¹ Department of Biological Sciences and Technology, Changzhi University, Changzhi 046011, China

² Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

³ College of Resources and Environment, University of Chinese Academy of Sciences, Beijing 100190, China

Abbreviations

RS	Soil samples collected from soil within 0–5 m from the roadside around the industrial district
AS	Soil samples collected from croplands and vegetable field soils, which are approximately 1–2 km away from the industrial district
VS	Soil samples collected from parks, the greenbelt, public squares, and residential areas of the villages nearby the industrial district
IARC	International agency for research on cancer
MW	Molecular weight
PAHs	Polycyclic aromatic hydrocarbons
US	United States Environmental Protection
EPA	Agency

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a sort of organic compounds with similar structure of two or more fused aromatic rings, which are considered to be environmental recalcitrant toxic pollutants (Crampon et al. 2014). Sixteen PAHs has been listed as priority control pollutants by the US Environmental Protection Agency (USEPA), including naphthalene (Nap), acenaphthene (Ace), acenaphthylene (Acel), fluorene (Flu), 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 (Daa), indeno[1,2,3-cd]pyrene (Ind), and benzo[g,h,i]perylene (Bghip) (16 USEPA). Eight PAHs has been classified with respect to their carcinogenicity to humans by the International Agency for Research on Cancer (IARC) as follows: Bap (group 1 toxic, carcinogenic); Daa (group 2A, probably carcinogenic); Baa, Bbf, Bkf, Chr, Ind, and Nap (group 2B toxic, possibly carcinogenic to humans) and all other PAHs compounds (group 3, carcinogenicity not classifiable). Eight PAH species have been defined as probably (2A) or possibly (2B) carcinogenic to humans according to the literature (Callén et al. 2008; Cancer and Organization 1983; Humans et al. 1991; Humans et al. 2004; LYON 2014; Organization and Humans 1994).

PAHs have ubiquitously contaminated industrial environments (Hussar et al. 2012; Lundstedt et al. 2007). Generally, point sources of PAHs are from industrial waste residues and wastewaters, transportation exhaust, as well as accidental fuel spills (Johansson and van Bavel 2003). PAHs have the properties of high hydrophobicity, which can attach on the atmospheric particles and float for long distances, becoming sources of diffuse pollution (Ravindra et al. 2008; Wilcke 2007).

Most PAHs released into the environment will eventually enter into the soil ecosystem, becoming restricted to the top layer of the soil; therefore, the soil system is considered to be one of the principal reservoirs for PAHs and is also regarded as a steady indicator of the degree of environmental contamination (Liu et al. 2001; Mueller et al. 2006; Wang et al. 2012b; Wild and Jones 1995), attracting considerable attention (Bourotte et al. 2005; Callén et al. 2011).

Recently, soil contamination of industrialized areas has received worldwide attention (Gaga et al. 2012; Luo et al. 2009; Wang et al. 2010). Industrial processes are the major source of PAHs found in the contaminated soils (Finkelman et al. 2002; Wang et al. 2003). It has been considered in areas where large-scale coking production and consumption occur, soils have been severely contaminated by PAHs (Wang et al. 2012a). Studies (Haugland et al. 2008; Jiao et al. 2009b) show that PAHs in soils from Tianjin, China and Bergen, Norway were observed to have much higher concentrations of PAHs from

their industrial region than other regions. The PAHs existed in polluted areas not only influence soil physicochemical characteristics, but also harm the environment and the people living in the actual region (Blake et al. 2007; Mostert et al. 2012). Thus, it is critical to remove PAHs in the soils of polluted areas.

The industrial district, located in the Southeast of Shanxi, includes coke, coal chemical, iron and steel, and thermal power plants, and is one pillar industry of the national economy system occupies an important position in the local economy. A large amount of fly ash, coal gangue, ash, peat, wastewater, and hot exhaust gas (water vapor) are produced annually as by-products. Due to these by-products being poorly managed for a long time, the industrial areas are now faced with serious environmental problems. The soil found at many of these industrial enterprise sites has been contaminated and is considered a hazard to plant and human health. More so, many crops would not be able to tolerate these contaminated soils. To our knowledge, there is a lack of data on the characterization of these compounds from these industrial areas. Therefore, the objectives of this study are the following: to determine the occurrence and levels of PAHs in soil samples collected in agricultural districts, roadside green belts, and village soils in Changzhi; to assess source contributions to the soil PAHs burden; and finally, to evaluate the potential human health risk. This study may be meaningful to control the pollution from PAHs and alleviate the hazard to human beings.

Materials and methods

Chemicals and materials

A composite standard solution of 16 PAHs, including Nap, Ace, Acel, Flu, Phe, Ant, Fla, Pyr, Baa, Chr, Bbf, Bkf, Bap, Ind, Daa, and Bghip, each at a concentration of 2000 $\mu\text{g mL}^{-1}$, were purchased from Supelco (Bellefonte, PA, USA). A work standard solution containing 16 PAHs was prepared in hexane before use. Silicagel column (15 cm length \times 10 mm id) and granular anhydrous sodium sulfate were baked at 100 °C for 16 h prior to use. All solvents and chemicals were analytically graded.

Study area

Changzhi lies between 35° 49' 0" N and 37° 8' 0" N latitude and between 111° 58' 3" E and 112° 44' 4" E longitude, covering an area of 13,896 km². It shares its boundaries with Taiyue Mountain in the west and Taihang Mountain in the eastern. Changzhi comes under the Loess Plateau and has an average elevation of 696 m, among which elevation is higher in southeast than northwest, and exhibits climate transitional

between a typical temperate and semi-arid continental climate with four clearly distinct seasons and continental monsoon is strong lasting. The annual average temperature is 9.1 °C. The annual average rainfall is 618.9 mm year⁻¹. The rainfall capacity vary from 62.7% of the total annual rainfall during summer to as low as 2.6% during winter season. The annual average evaporation capacity is 1740.1 mm year⁻¹. The average wind speed is 2.3 m s⁻¹ during all year, and the dominant wind direction is southeast, follow is northwest.

Soil sampling

The industrial area, from where the samples were collected, is located in Changzhi. The district houses an iron and steel factory, two power plants, and a coke plant. There are several villages and roads around the traditional industrial area. In this study, regions have been classified into three different functional areas represented by the main roadside, country district, and agricultural area. Furthermore, the sampled areas have been categorized in directional relation to the industrial areas. Roadside soil samples (RS) were collected from soil within 0–5 m from the roadside. Village soil samples (VS) were collected from parks, the greenbelt, public squares, and residential areas of the villages. Agricultural soil samples (AS) were collected from croplands and vegetable field soils, which are approximately 1–2 km away from the industrial areas. A total of 76 surface soil samples were collected from areas surrounding the industrial district in Changzhi (Fig. 1) in July 2014. Among the 76 soil samples, 36 were from roadside soils (RS_i, *i* represent the number of sample sites, follows same as), 30 from agricultural soils (AS_i), and 10 from village soils (VS_i). For each soil sample, 40 subsamples were taken from the same functional region (at a depth of 0–25 cm in a 300 m² area) and mixed thoroughly to form one composite sample. All of the samples were air-dried at room temperature and sieved through a 1-mm mesh screen after removing stones and residual plants and then stored in the dark at 4 °C prior to analysis.

Extraction, purification, and analysis

Soil samples were extracted by ultrasonic agitation, a method developed and recommended by various authors (Agarwal et al. 2006; Jiao et al. 2015; Ray et al. 2008). The 10-g soil sample was extracted thrice and washed in 30-mL mixture solvents (acetone/dichloromethane = 1:1) for 15 min with ultrasonic agitation (ultrasonic agitation–SB 5200 DT, Ningbo Xingzhi Biological Technology Co. Ltd., Ningbo, China) at a frequency of 40 kHz in a water bath (15–25 °C). Following that, samples were filtered through a silica gel column filled with 10-cm dried anhydrous sodium sulfate to remove particles. The extracts were mixed together, concentrated to 1 mL using a gentle stream of nitrogen, cleaned by a 0.2-μm organic

phase membrane filter, and calibrated to 1.5 mL with *n*-hexane (chromatographically pure) in a vial.

The samples were then analyzed by a gas chromatography mass spectrometer (GC-MS) system (GC-MS QP2010 Ultra, 30 m length × 0.25 mm i.d. × 0.25 μm film thickness, HP-5 MS capillary column, Shimadzu enterprise management (China) Co. Ltd.) with helium as the carrier gas. The injection volume was 1 μL in splitless mode. The oven temperature program was as follows: start at 50 °C hold for 1 min, 200 °C at 20 °C min⁻¹ hold for 1 min, 260 °C at 6 °C min⁻¹ hold for 1 min, and 290 °C at 20 °C min⁻¹ hold for 10 min. An aliquot sample (1 μL) was injected in the splitless mode, and helium was used as the carrier gas (1.0 mL min⁻¹). The mass spectrometer was operated in the selective ion monitoring (SIM) mode using positive ion electron impact ionization (EI).

The identification of individual compounds was achieved by comparing GC retention time and ion abundance ratio of two exacts (M/M-1) with the corresponding retention time of an authentic standard and the acquired ion abundance ratio of the two exacts (M/M-1), the ions followed for each PAH, such as Nap(127/129), Ace(150/151), Ace(152/154), Flu(163/165), Phe(176/179), Ant(176/179), Fla(200/203), Pyr(200/201), Baa(226/229), Chr(226/229), Bbf(250/253), Bkf(250/253), Bap(250/253), Ind(138/274), Daa(276/279), and Bghip(137/138). Quantification of individual compounds was based on the comparison of peak areas. The 16 PAHs were quantified using the response factors related to the respective external standards based on a 7-point (0.1, 1.0, 5.0, 50.0, 100, 200, 500 μg kg⁻¹) calibration curve for individual compounds with a linear relationship $R^2 > 0.9997$. Results presented for soil samples were not corrected according to the spike recoveries.

Quality control

Solvent blanks, checking standards, and sample duplicates were analyzed for every set of samples. Variation in PAH concentrations of the replicated samples was less than 10% ($n = 3$); the procedural blank values are always smaller than the detection limit; the linearity of the method was evaluated in the range of 0.1–500 μg kg⁻¹. The calibration curve showed an $R^2 > 0.99$. The repeatability of the method was assessed by analyses of six soil samples that had previously been extracted with the extraction mixture, supplemented at 100 μg kg⁻¹ with a standard mixture (USEPA PAH standard mixture at 2000 μg mL⁻¹ in methanol; Supelco, PA, USA). Matrix spike experiment recoveries of certified reference materials ranged from (87 ± 3%, Ace) to (98 ± 4%, Phe) for the 16 PAHs. The limits of detection, which were defined as the standard deviation from solvent blanks ($n = 7$), ranged from 0.002 (Bghip) to 0.005 (Ind) μg kg⁻¹ for individual PAHs.

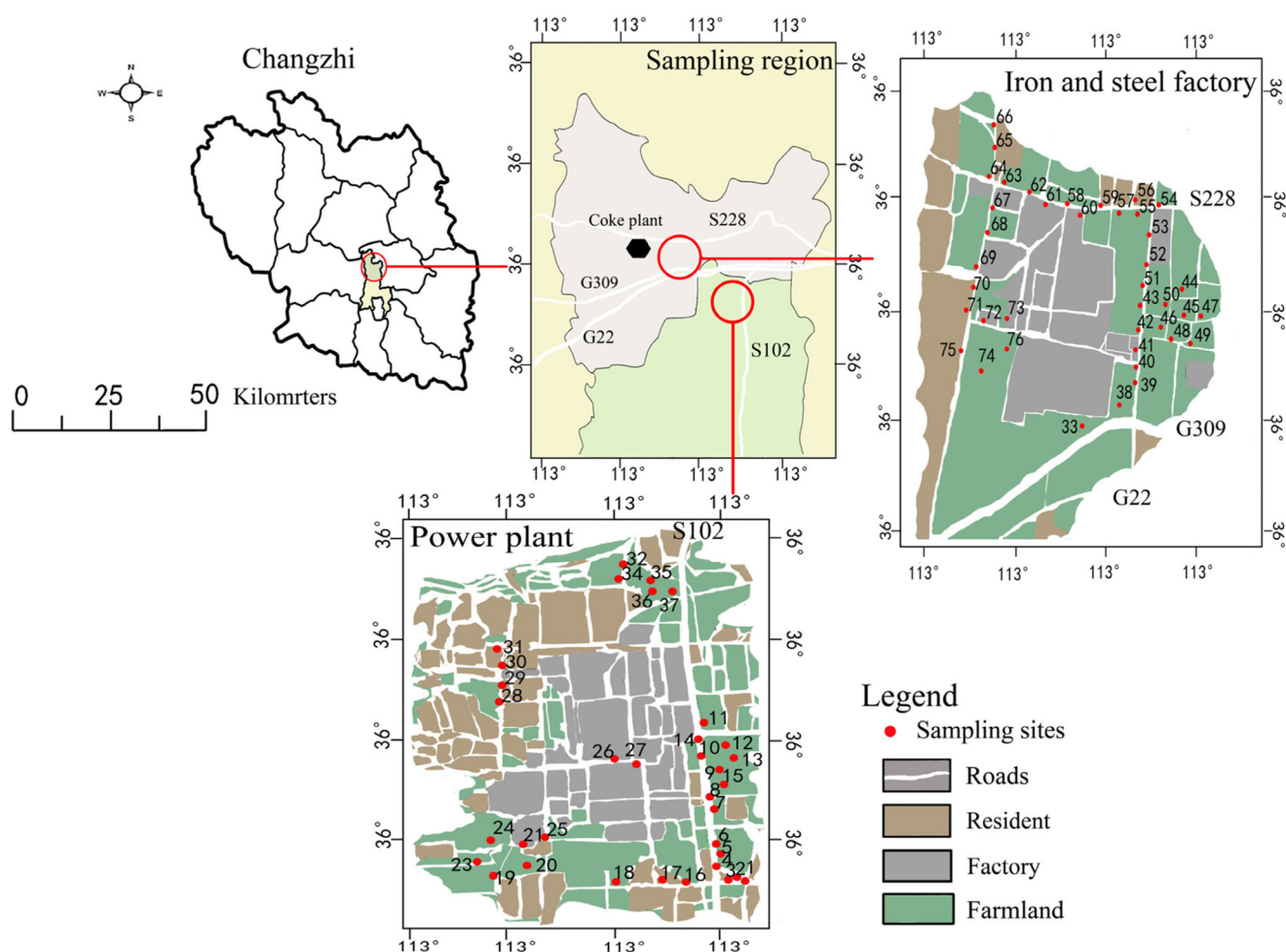


Fig. 1 Geographical locations of the sampling sites in Changzhi, Shanxi province (China)

Data processing and statistical analysis

All statistical analyses employed the Statistical Analysis Systems (SPSS Statistics Data Editor, Version 17.0). Arc GIS 9.0 was used to draw the map of the sampling sites. All data was processed by Microsoft Excel and all diagrams were drawn using Origin 8.0.

Molecular diagnostic ratios

Due to formation routes of various PAHs under different combustion conditions, the ratios of different PAHs are expected to vary with different sources. Thus, diagnostic ratios of PAHs were commonly used to qualitatively investigate the source contribution. The most frequently used PAH isomer ratios in some other publications included low/high molecular weight (LMW/HMW) (Aichner et al. 2007; Chen et al. 2005), Phe/Ant (Ünlü and Alpar 2009), Ant/(Ant + Phe), Fla/(Fla + Pyr) (Khairy and Lohmann 2012), Baa/(Baa + Chr) (Katsoyiannis and Breivik 2014; Yunker et al. 2002), and Bap/(Bap + Chr) (Akyüz

and Çabuk 2008). Many studies (Galarneau 2008) suggested that the use of isomer ratios in PAH source apportionment should be done cautiously as they might be similar among different sources, moreover for the same source type, the ratios could vary dramatically depending on fuel properties and burning conditions. In addition, once emitted into the environment, the ratio would change, causing difficulty in and uncertainty of their use. Although the use of diagnostic ratios has known uncertainties, the method is probably more pronounced at special locations, such as areas close to the point sources, and the sources of PAHs in the soil around the industrial district can be distinguished using the ratios of diversity PAHs (Christensen and Bzdusek 2005); thus, it was used in the present paper only as an indicative way to provide insight into the sources.

Coefficient of divergence

The coefficient of divergence (CD) was used to identify the similarities between the profiles of PAHs at different sites

(e.g., AS-RS comparison). The generic formula used for CD calculation is as follows:

$$CD_{ij} = \sqrt{\frac{1}{p} \sum_{i=1}^p \left(\frac{X_{ij} - X_{ik}}{X_{ij} + X_{ik}} \right)^2} \quad (1)$$

where X_{ij} represents the average concentration for a PAH component i at site j , j and k represent two sampling sites, and p is the number of PAH components. If the two sampling sites are similar, the CD approaches zero. If the two sampling sites are very different, the CD approaches one. By using the CD, PAHs in the soil can be compared even if the number of PAH components measured for each site is different, provided that the same set of chemical components is used in each case (Wongphatarakul et al. 1998).

Nemerow composite index

The Nemerow composite index (P value) was used to assess soil environmental risks based on the Chinese environmental quality standards of the GB 15618-2008 (China 2008), which provide the maximum permissible concentrations of 16 PAHs for soil. These limits are as follows: Nap ($100 \mu\text{g kg}^{-1}$), Ace ($500 \mu\text{g kg}^{-1}$), Acel ($500 \mu\text{g kg}^{-1}$), Flu ($500 \mu\text{g kg}^{-1}$), Phe ($500 \mu\text{g kg}^{-1}$), Ant ($500 \mu\text{g kg}^{-1}$), Fla ($500 \mu\text{g kg}^{-1}$), Pyr ($500 \mu\text{g kg}^{-1}$), Baa ($100 \mu\text{g kg}^{-1}$), Chr ($100 \mu\text{g kg}^{-1}$), Bbf ($100 \mu\text{g kg}^{-1}$), Bkf ($200 \mu\text{g kg}^{-1}$), Bap ($100 \mu\text{g kg}^{-1}$), Daa ($100 \mu\text{g kg}^{-1}$), Ind ($100 \mu\text{g kg}^{-1}$), and Bghip ($500 \mu\text{g kg}^{-1}$) (GB 15618-2008, 2008 discussion draft). These were then calculated using the following formula:

$$P_i = \text{Soil}_{\text{PAH}_i} / \text{Standard}_{\text{PAH}_i} \quad (2)$$

$$P = \sqrt{\frac{(P_{i_{\text{av}}})^2 + (P_{i_{\text{max}}})^2}{2}} \quad (3)$$

$$P_{i_{\text{av}}} = \frac{1}{n} \sum_{i=1}^n P_i \quad (4)$$

where $\text{Soil}_{\text{PAH}_i}$ is the concentration of PAH_i in the soil sample and $\text{Standard}_{\text{PAH}_i}$ is the GB 15618-2008 soil standard of PAH_i . Where, $P_{i_{\text{av}}}$ is the average value of the individual pollutant index, and $P_{i_{\text{max}}}$ is the maximum value of the individual pollutant index.

Toxic equivalent concentrations

As PAHs seldom occur as individual chemicals in the environment, there has been much discussion as to the most appropriate way of assessing the risk to human health following exposure to PAH mixtures. One method of risk-assessing PAHs would be to assume that the toxicity of all PAHs is equivalent to that of Bap (Bull and Collins 2013). Since Bap was one of the PAHs with

sufficient toxicological data to derive a carcinogenic potency factor proven in animal tests, and according to cultures is mutagenic for human cells, it is regarded as one of the most carcinogenic of all the PAHs (Lim et al. 2007). The USEPA supplied a first approach to the toxicity of the PAHs referring it to that presented for Bap. The toxic equivalent factor (TEF) for Bap is 1.0. Because toxicity criteria are not available for all PAHs, various TEFs have been proposed in order to relate the potencies of these compounds, and in addition, several agencies and scientists have tried to establish the real value of every single PAH TEF (Muller et al. 1997; Kumar et al. 2013; Nisbet and LaGoy 1992). The TEF has been devised as a method to compare the carcinogenicity of individual PAHs to the carcinogenicity of Bap. The carcinogenic potency of every collected soil sample was determined relative to its toxic equivalent concentrations (Bapeq), which estimates the health risk from exposure to the PAHs in the soil. The Bapeq for a given PAH compound was calculated as the product of its TEF and its concentration (Chen and Liao 2006):

$$\text{Bapeq} = \sum_{i=1}^n (\text{Soil}_{\text{PAH}_i} \times \text{TEF}_i) \quad (5)$$

where Bapeq is the total toxic equivalent concentration for all aim PAHs, $\text{Soil}_{\text{PAH}_i}$ represents the concentration of one individual PAH in the soil samples, and TEF_i is the toxic equivalent factor for the corresponding individual PAH. These TEFs are as follows: Nap (0.001), Ace (0.001), Acel (0.001), Flu (0.001), Phe (0.001), Ant (0.01), Fla (0.001), Pyr (0.001), Baa (0.1), Chr (0.01), Bbf (0.1), Bkf (0.1), Bap (1.0), Daa (0.1), Ind (1.0), and Bghip (0.01) in the study.

Results and discussion

Distribution

Distribution characteristics of PAHs in three functional soils

All of the 16 individual USEPA priority PAHs were identified in the soil samples collected from the industrial district (Fig. 2). The concentrations of $\Sigma 16\text{PAHs}$ found in the 76 samples ranged from 794 (AS19) to 25,041 $\mu\text{g kg}^{-1}$ (RS52), with an average value of 8346 $\mu\text{g kg}^{-1}$. The geometric mean value was found to be very high when compared with typical values for $\Sigma 16\text{PAHs}$ in the following countries: South Korea (220–190 $\mu\text{g kg}^{-1}$, mean 390 $\mu\text{g kg}^{-1}$) (Kwon and Choi 2014), Poland (280–2450 $\mu\text{g kg}^{-1}$) (Maliszewska-Kordybach 1996; Oleszczuk and Pranagal 2007), Germany (100–775 $\mu\text{g kg}^{-1}$), and Switzerland (145–593 $\mu\text{g kg}^{-1}$) (Desaules et al. 2008). Furthermore, the contents of the $\Sigma 16\text{PAHs}$ varied and clearly depended on the sampled soil functions (Fig. 2a). The lowest level of $\Sigma 16\text{PAHs}$ is observed in AS sample sites, ranging

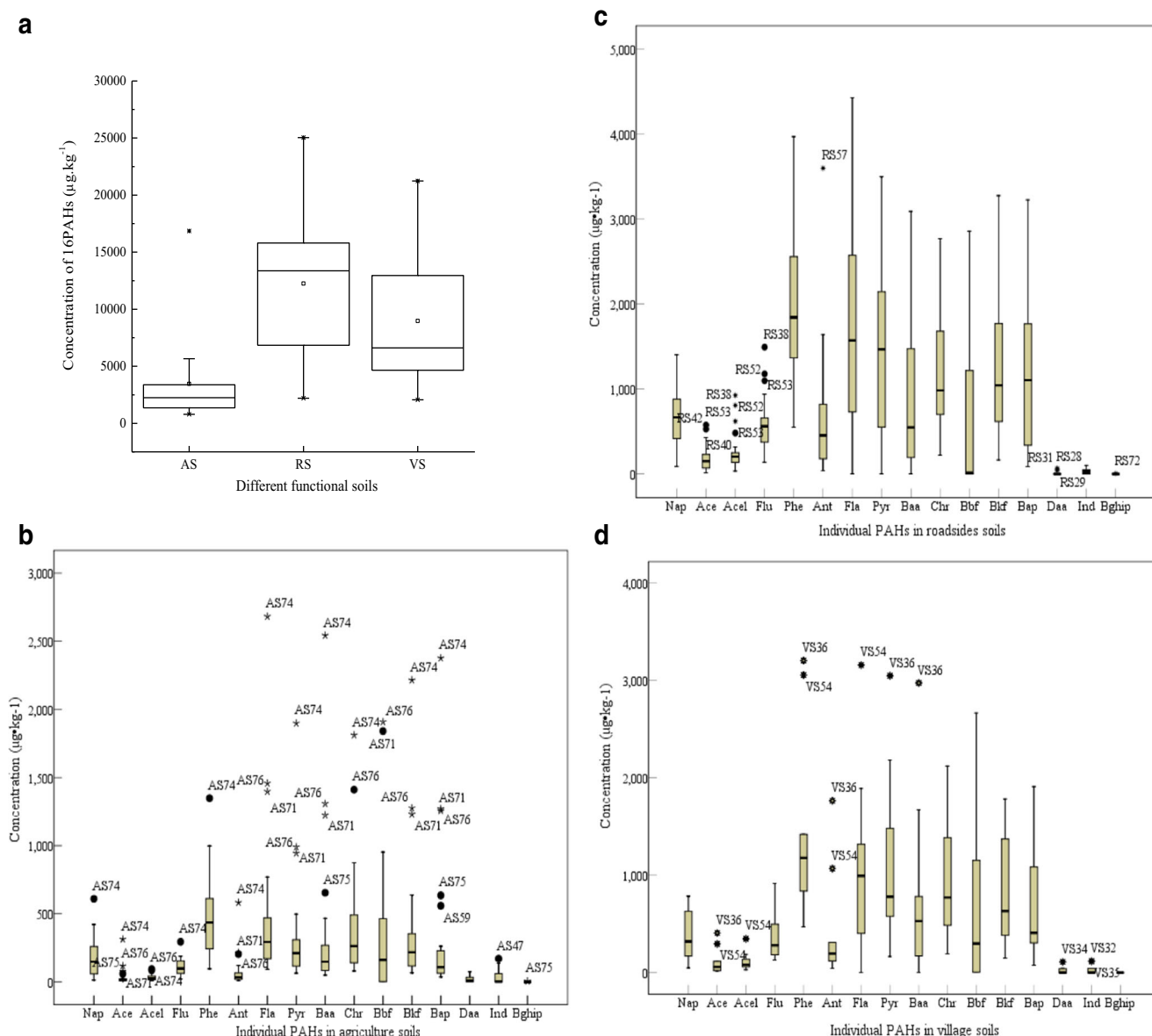


Fig. 2 a Total PAHs concentrations. b–d Concentrations of individual PAHs in different soil samples from agriculture soils (AS), roadside soils (RS), and village soils (VS), respectively. The boxes are of interquartile

range, with the *line inside the box* as the median, whiskers are 95% of data, and outlier values are indicated by an asterisk, dot, and triangle

from 794 to 16,858 $\mu\text{g kg}^{-1}$, with an average value of 3456 $\mu\text{g kg}^{-1}$, and a median value of 2287 $\mu\text{g kg}^{-1}$. The modest level of $\Sigma 16\text{PAHs}$ is observed in VS sample sites ranging from 2059 to 21,240 $\mu\text{g kg}^{-1}$, with an average value of 8976 $\mu\text{g kg}^{-1}$, and a median value of 7711 $\mu\text{g kg}^{-1}$. A particularly high level of the compounds was noted from RS sample sites, ranging from 2197 to 25,041 $\mu\text{g kg}^{-1}$, with an average value of 12,245 $\mu\text{g kg}^{-1}$, and a median value of 13,414 $\mu\text{g kg}^{-1}$. The RS values are almost 3.54 and 1.36 times higher than those found at the AS and VS sample sites (Fig. 2a) and could be a result of heavy traffic and inhabitant and industry activities. The concentration of $\Sigma 16\text{PAHs}$ in the RS sample sites were higher than that found in urban dust samples

of Bangkok (1100 $\mu\text{g kg}^{-1}$) (Boonyatumanond et al. 2007), Dalian (1890–17,100 $\mu\text{g kg}^{-1}$) (Wan et al. 2006), and Guangzhou (840–12,300 $\mu\text{g kg}^{-1}$) (Wang et al. 2011), and were comparable to those found in Northeast England (6000–46,000 $\mu\text{g kg}^{-1}$) (Lorenzi et al. 2011). In AS samples, the values of $\Sigma 16\text{PAHs}$ were also higher than those found in the Dongjiang River Basin (24.0–231 $\mu\text{g kg}^{-1}$) (Zhang and Tao 2009; Zheng et al. 2014), Hong Kong (7.00–200 $\mu\text{g kg}^{-1}$) (Zhang et al. 2006), South Korea (23.0–2830 $\mu\text{g kg}^{-1}$) (Nam et al. 2003), Nanjing (21.0–533 $\mu\text{g kg}^{-1}$) (Yin et al. 2008), and Shantou (22.0–1260 $\mu\text{g kg}^{-1}$) (Rong et al. 2007). The VS sample values were also higher than those typically found in Guanting Res (62.0–4210 $\mu\text{g kg}^{-1}$) (Jiao et al. 2009c).

The contribution of the individual PAHs was analyzed in detail, which indicates that four-ring compounds were dominant in most of the soil samples (Fig. 2b–d). The most abundant PAHs found in the AS samples were Phe, Fla, Chr, and Bkf. The concentrations of individual PAHs in the AS were ranged from not detected (ND) (Bghip) to $2682 \mu\text{g kg}^{-1}$ (Fla) with 100% detection frequencies (except Bhigp, 90%), and have a higher levels found specifically in the AS74, AS76, AS71, and AS75 sites (Fig. 2b). The most abundant PAHs found in the RS samples were Fla, Phe, Pyr, Bkf, Bap, Bbf, Baa, and Chr. The concentrations of individual PAHs in the RS were ranged from ND (Bghip) to $4431 \mu\text{g kg}^{-1}$ (Fla) with 69.4–100% detection frequencies (Fig. 2c). The most abundant PAHs found in the VS samples were Phe, Pyr, Fla, Baa, Bbf, Bkf, and Bap. The concentrations of individual PAHs in the VS were ranged from ND (Bghip) to $3206 \mu\text{g kg}^{-1}$ (Phe) with 90.0–100% detection frequencies; higher values were specifically found in the VS36 and VS54 sites (Fig. 2d). The results indicate that these compounds are ubiquitous in the soil environments of surrounding industrial areas.

Distribution characteristics of PAHs in four directional soils

Figure 3 shows that the AS sample sites located in the east (direction in relation to the industrial district) had a $\Sigma 16\text{PAHs}$ average concentration of $1834 \mu\text{g kg}^{-1}$; in the west, it was $1454 \mu\text{g kg}^{-1}$, south $8379 \mu\text{g kg}^{-1}$, and north $3839 \mu\text{g kg}^{-1}$. Moreover, the concentration levels of a total probably or possibly carcinogenic PAHs ($\Sigma 8\text{BPAHs}$) were 930, 713, 5061, and $2197 \mu\text{g kg}^{-1}$ for the AS sample sites located in the east,

west, south, and north, respectively. Levels of $\Sigma 16\text{PAHs}$ and $\Sigma 8\text{BPAHs}$ in the AS sample sites significantly declined as south > north > east > west. As indicated by Fig. 4, the average values of $\Sigma 16\text{PAHs}$ in the RS sample sites were 14,213; 8436; 9337; and $14,179 \mu\text{g kg}^{-1}$, and the average values of $\Sigma 8\text{BPAHs}$ were 6493, 3837, 4928, and $6329 \mu\text{g kg}^{-1}$ for the RS sample sites located in the east, west, south, and north (direction in relation to the industrial district), respectively. Levels of $\Sigma 16\text{PAHs}$ and $\Sigma 8\text{BPAHs}$ in the RS sample sites significantly declined as east > north > south > west. Compared to AS sample sites, the average value of $\Sigma 16\text{PAHs}$ in RS sample sites is higher by 1.98 times and the average $\Sigma 8\text{BPAHs}$ value is higher by 1.43 times.

Regarding the specific profile of PAHs concentrations, the major contribution to the total amount of $\Sigma 16\text{PAHs}$, was composed of compounds with four aromatic rings (Fla, Pyr, Baa, and Chr); the second most dominant group of PAHs was composed of those with five aromatic rings (Bbf, Bkf, Bap), followed by those with three aromatic rings (Phe). The highest value of the average level of individual PAHs in the AS sample sites was found south of the industrial district. The distribution showed orientation makes a significant difference ($p < 0.01$), as a consequence of some areas being exposed to coal and coke used as fuel in industrial activities. For the RS sample sites, the highest value was found to the east, with less diversity ($p < 0.05$), indicating the impacts from the provincial road (S228) and national road (G22), which provides easy access into the area. In the monitored areas, the north direction prevails, indicating the impact of the steel plant, power plants, and vehicular emissions.

Fig. 3 Concentration of individual, total 16 PAHs ($\Sigma 16\text{PAHs}$) and total carcinogenic PAHs ($\Sigma 8\text{BPAHs}$) in agriculture soils (AS) found in different directions surrounding the industrial district

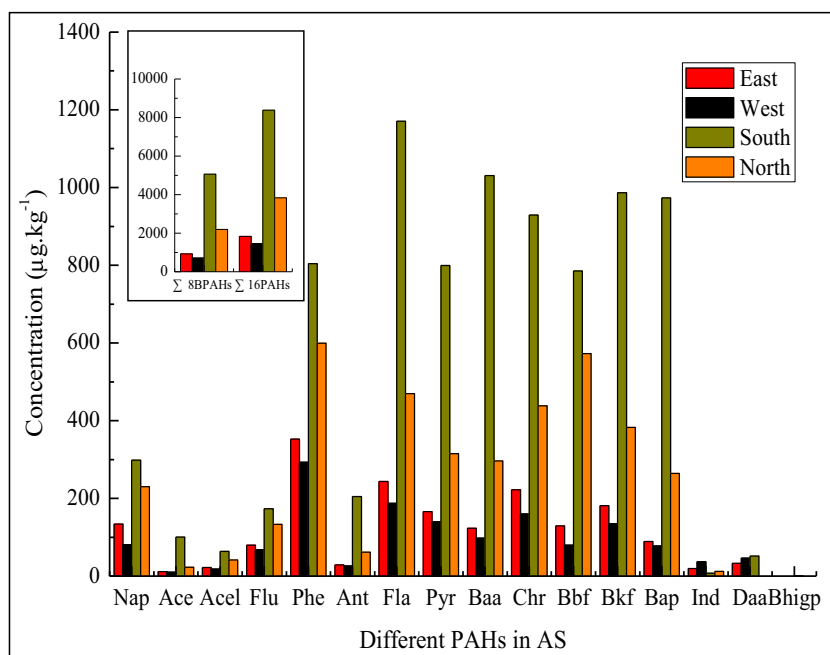
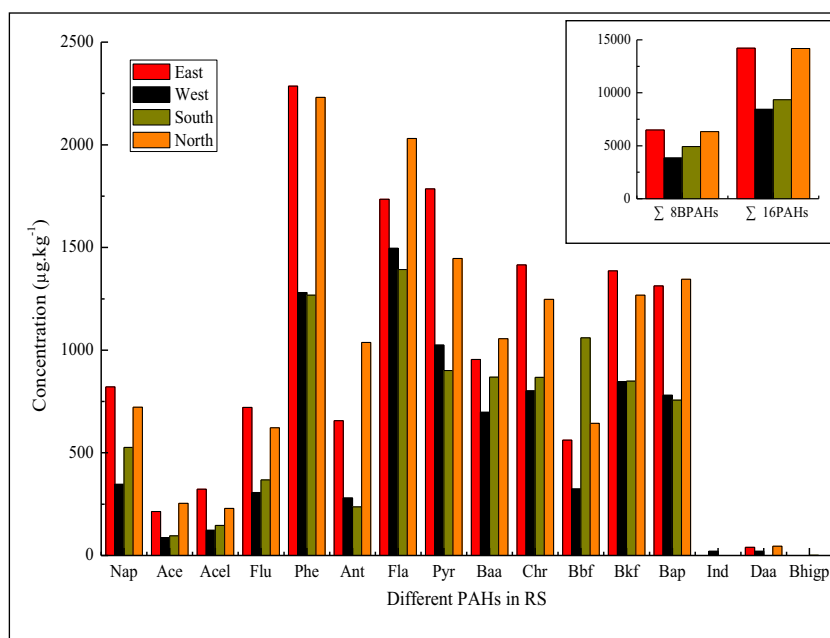


Fig. 4 Concentration of individual, total 16 PAHs ($\Sigma 16\text{PAHs}$) and total carcinogenic PAHs ($\Sigma 8\text{BPAHs}$) in roadside soils (RS) found in different directions surrounding the industrial district



The distribution of PAHs in the AS sample soils pointed to the south and north as dominant directions. Both directions were probably affected by steel plant activity and the potential contribution of power stations sited in the southeast of the steel plants. This includes the use of coke as heating fuel in the steelworks and the thermal power stations sited in the southeast using coal for power production. In addition, the distribution of PAHs also reflected the influence of the roads: S228 located in the north (direction towards the steel plant), S102 located in the southeast (direction towards the industrial district), and G22 and G309 located between the steel and power plants. Some roads leading to the monitored areas were not named but they located in the east and north and are highly used for transportation of raw materials and products.

From the results, we can inference that the concentration of $\Sigma 16\text{PAHs}$ were higher in north samples, but were lower in west samples both in the AS and RS. The reason can fall into three categories: (1) wind direction, the year leading wind direction, prevailing southeasterly winds in the areas throughout the year, but winter prevailing northwest wind; (2) Topography, the elevation is higher in southeast than northwest direction, and the Taiyue Mountain location in the west, the Taihang Mountain in the east; and (3) traffic condition, the main roads such as S228, S102, G22, and G309 are located in the north and southeast. Moreover, because of the prevailing southeasterly winds, the concentration of PAHs is the highest in the AS sample located in the south, but as impacted on the traffic, the highest content of the soil PAHs is in the RS samples located in the east of the industrial areas.

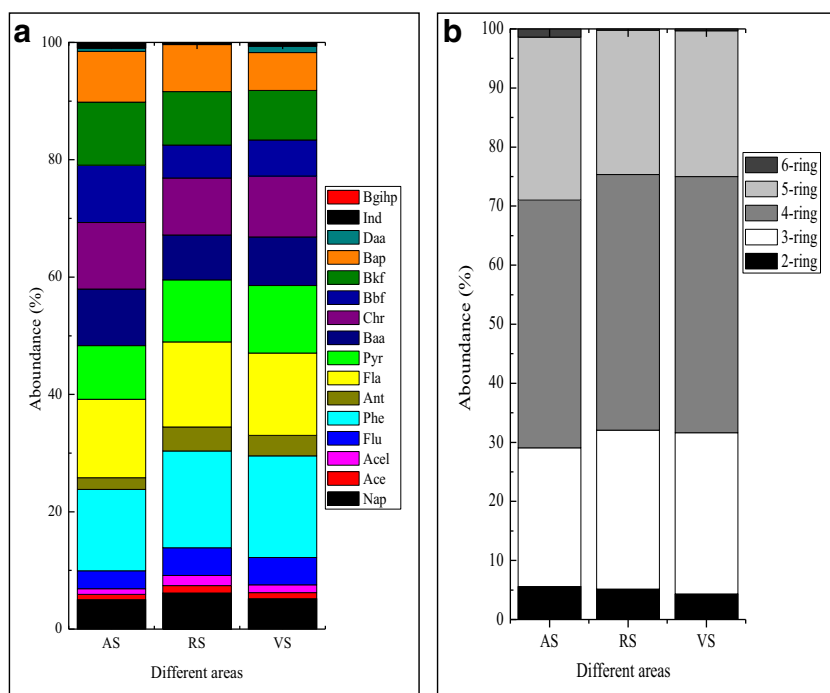
Source identification

Source identification by compositional profiles of PAHs

Generally, PAHs in the environment are originated principally from anthropogenic sources, such as combusted/pyrolyzed organic materials, including wood, coal, coke, fossil fuels, and petroleum products (Ravindra et al. 2008). Burning oil and operating vehicles releases more Fla, Pyr, Bghip, Bbf, Bkf, Bap, and Chr. Gas-powered vehicles release Fla, Pyr, and Bghip and diesel-powered vehicles release Bbf and Bkf (Miguel et al. 1998; Venkataraman et al. 1994). Furthermore, Bghip and Bap were found to be enriched in traffic tunnels (Robinson et al. 2006), and Fla, Chr, and Pyr are increased by diesel exhaust (Masclet et al. 1986). Combustion/incineration of coal, wood, and grass produces more Phe, Baa, Ant, Fla, Pyr, Bap, Bghip, and Chr. The literature describes combustion of wood, coal, or coke as releasing more Ant, Phe, Fla, Pyr, Baa, and Chr, and especially Pyr (Duval and Friedlander 1981). Petrogenic PAHs are normally abundant in lower molecular weight compounds (LMW, rings ≤ 3). While LMW PAHs can easily undergo weathering compared to those with greater molecular weight (HMW, rings ≥ 4) PAHs (Giger and Blumer 1974; Lee et al. 1977), and HMW PAHs are mainly in the particulate phase and easily collect in soil sediments (Harner and Bidleman 1998; Wang et al. 2013).

This study demonstrated that there were 16 PAHs in the soil samples with the normalized composition profile of these PAHs shown in Fig. 5a. The mean abundant compound at all sites are as follows: Phe (16.6%), Fla (13.6%), Pyr (10.2%), Chr (10.4%), Baa (7.85%), Bkf (9.07%), Bap (6.97%), Bbf (6.97%), Nap (5.71%), Flu (4.33%), Ant (3.08%), Acel

Fig. 5 Relative abundance of parent PAHs in samples of agricultural soils (AS), roadside soils (RS), and village soils (VS) surrounding the industrial district. **a** Relative abundance of different PAHs. **b** Relative abundance of PAHs with different numbers of rings



(1.38%), Ace (0.990%), Daa (0.970%), Ind (0.650%), and BghiP (0.002%). Therein, Phe, Chr, and Pyr were the three most abundant compounds. The 16 PAHs were divided into five clusters according to rings (Fig. 5b): 2-ring (Nap); 3-ring (Ace, Acel, Flu, Phe, and Ant); 4-ring (Fla, Pyr, Baa, and Chr); 5-ring (Bbf, Bkf, Bap, and Daa); and 6-ring (Ind and BghiP) hydrocarbons. For all sample soils (AS, RS, and VS), the 4-ring compounds were most abundant (42.0–43.4%, mean 42.9%), followed by 3-ring PAHs (23.5–27.3%, mean 25.9%), 5-ring PAHs (24.5–27.6%, mean 25.6%), 2-ring PAHs (mean 5.0%), and 6-ring PAHs (mean 0.6%). Apparently, the total PAHs were dominated by a greater molecular weight for the PAHs compounds (HMW PAHs ≥ 4 rings) in all AS, RS, and VS surface soil samples. Their presence was 2.24 times higher than that of low molecular weight PAHs compounds (LMW PAHs ≤ 3 rings). The study indicated that in comparison to LMW PAHs, compounds with HMW PAHs often show considerable tendency to accumulate in soil (Aichner et al. 2007). The presence of Ind and BghiP were a result of gasoline (Boonyatumanond et al. 2007) and diesel (Robinson et al. 2006) emissions. The results shown here can be explained by the huge abundance of HMW PAH compounds being released to the surroundings during daily transport and production processes of the local industries.

Source identification by PAHs isomer ratios

Many studies (Jiao et al. 2009a; Katsoyiannis and Breivik 2014; Yunker et al. 2002) reported that $Baa/(Baa + Chr)$ less than 0.20 indicates a petroleum origin, whereas $0.20 < Baa/(Baa + Chr) < 0.35$ is from either petroleum or combustion,

and $Baa/(Baa + Chr) > 0.35$ has a combustion origin alone. A ratio of $Fla/(Fla + Pyr) < 0.4$ implies a petroleum source, while a ratio of $0.4 < Fla/(Fla + Pyr) < 0.5$ indicates a fossil fuel combustion source, such as crude and vehicle oil combustion, and $Fla/(Fla + Pyr) > 0.5$ originates from coal or biomass burning (Opune et al. 2009). Plotted in Fig. 6a, 86.4% of all sample sites had $Baa/(Baa + Chr)$ ratio values of more than 0.35, and 93.4% of all sample sites had a $Fla/(Fla + Pyr) > 0.5$, in this study. The results show that the PAH sources in all soil samples come mainly from combustion (coal, biomass, or petroleum).

Researchers (Ünlü et al. 2009) believe that petroleum often contains more thermodynamically stable PAHs (e.g., Phe) than the less stable isomers (e.g. Ant); therefore, soils with $Phe/Ant > 10$ were mainly contaminated by petroleum, and those with $Phe/Ant < 10$ were typical of sediments impacted by combustion residues. In the present study, the $Phe/Ant > 10$ is recorded in 29.0% of the 76 soil samples (Fig. 6b), specifically, 63.3% of the AS samples had a Phe/Ant ratio > 10 , and 97.2% of RS samples and 90.0% of VS samples had a Phe/Ant ratio < 10 . According to these Phe/Ant ratios, it suggests that source of PAHs in the areas were combustion and petroleum, and the combustion is the main (71.0%) sources of the PAHs in all the samples, among which AS sample are mainly from petroleum, but more than 90% of the RS and VS sample that the ratio of Phe/Ant were below 10, and indicate combustion source. Tobiszewski (Tobiszewski and Namieśnik 2012) reported that the ratio of $Ant/(Ant + Phe) < 0.10$, indicating petroleum as a PAH source, while $Ant/(Ant + Phe) > 0.10$ suggests biomass combustion. In the study, for the $Ant/(Ant + Phe)$ ratio, 67.2% of sample site values were more than 0.10 which confirms a pyrolytic origin (Fig. 6b).

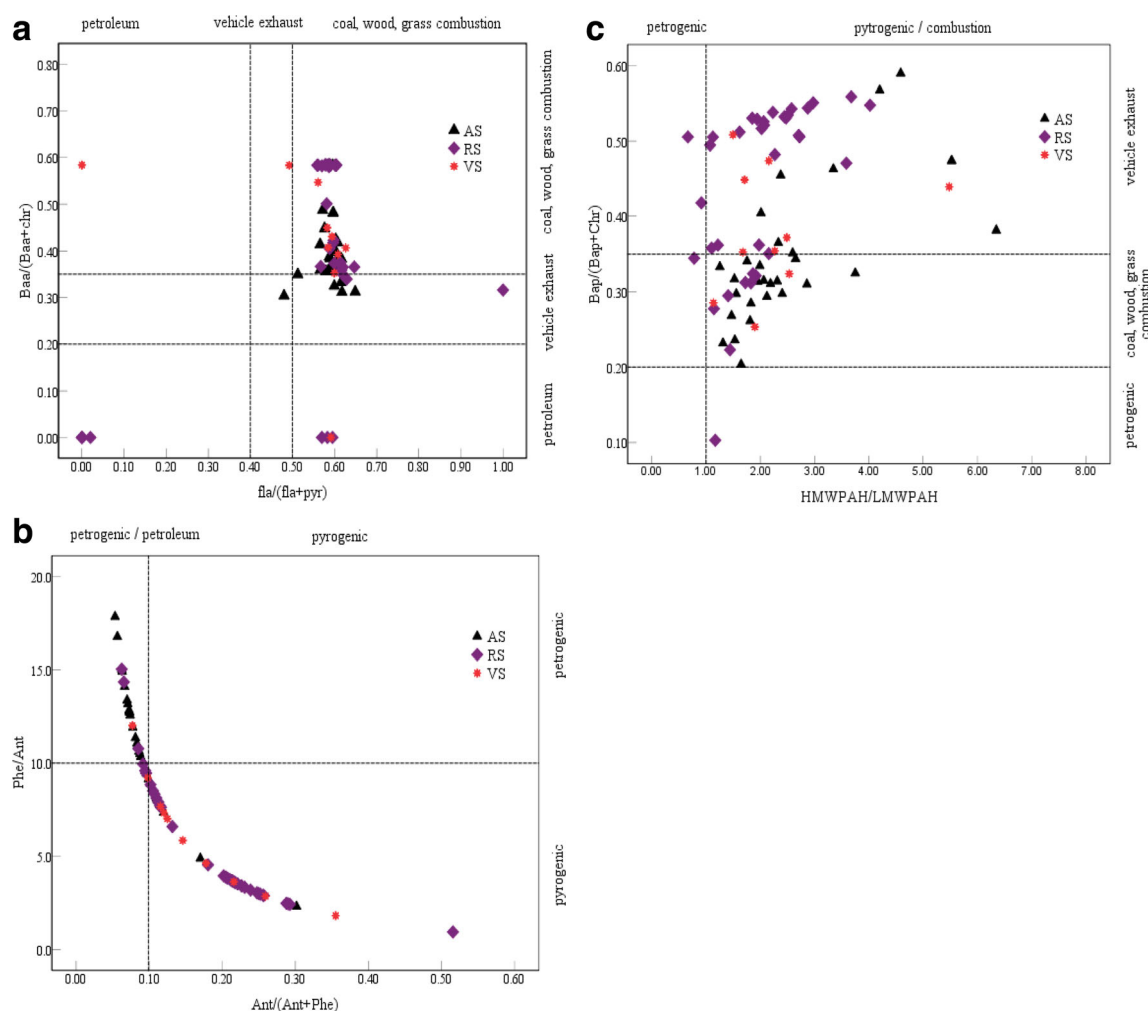


Fig. 6 **a** Diagnostic ratio charts for Baa/(Baa + Chr) and Fla/(Fla + Pyr) in soil samples. **b** Diagnostic ratio charts for Ant/(Phe + Ant) and Phe/Ant. **c** Diagnostic ratio charts for Bap/(Bap + Chr) and HMW/LMW in

soil samples. AS, RS, and VS represent sample sites located in the agricultural soils, roadside soils, and village soils, respectively

The literature (Oliveira et al. 2011) reports that an HMW/LMW PAH < 1.00 indicates PAHs in the soils, which probably originate from a petrogenic source, while an HMW/LMW PAH = 1 indicates a combustion origin, and an HMW/LMW PAH > 1.00 suggests a pyrogenic origin. For Bap/(Bap + Chr) < 0.20 suggests a petrogenic origin, while Bap/(Bap + Chr) > 0.35 indicates a vehicular and combustion source, and $0.20 < Bap/(Bap + Chr) < 0.35$ indicates PAHs in the soils with a probable source being coal, wood, and grass combustion (Akyüz and Çabuk 2008). In the present study, 96.1% of the sample sites have HMW/LMW > 1.00, 47.4% of the sample sites have Bap/(Bap + Chr) > 0.35, while 38.2% of the sample sites have $0.20 < Bap/(Bap + Chr) < 0.35$. These results indicate that the distribution of PAHs in the industrial district is mainly derived from combustion sources (coal, wood, and grass combustion and petroleum) (Fig. 6c).

Principal Component Analysis

In order to further identify sources of PAHs in the industrial areas soil, principal component analysis (PCA) can be also used to conduct quantitative assessments. By utilizing the orthogonal transformation method to extract valuable information from multivariate, after varimax rotation, principle components (PCs) are extracted with individual factor loadings showing correlations of each variable value with each PC (Harrison et al. 1996; Larsen and Baker 2003). Each PC is further affirmed and evaluated by source markers. PCA was performed using SPSS17.0 software.

In this work, two PCs were extracted by PCA. The rotated factor loadings were listed in Fig. 7a. The PC1 is responsible for 73.2% of the total variance, and received high loading for Phe, Chr, Pyr, Bkf, Bap, and Ace. These species were associated with combustion and vehicle exhaust. According to the literature (Li and Kamens 1993; Miguel and Pereira 1989;

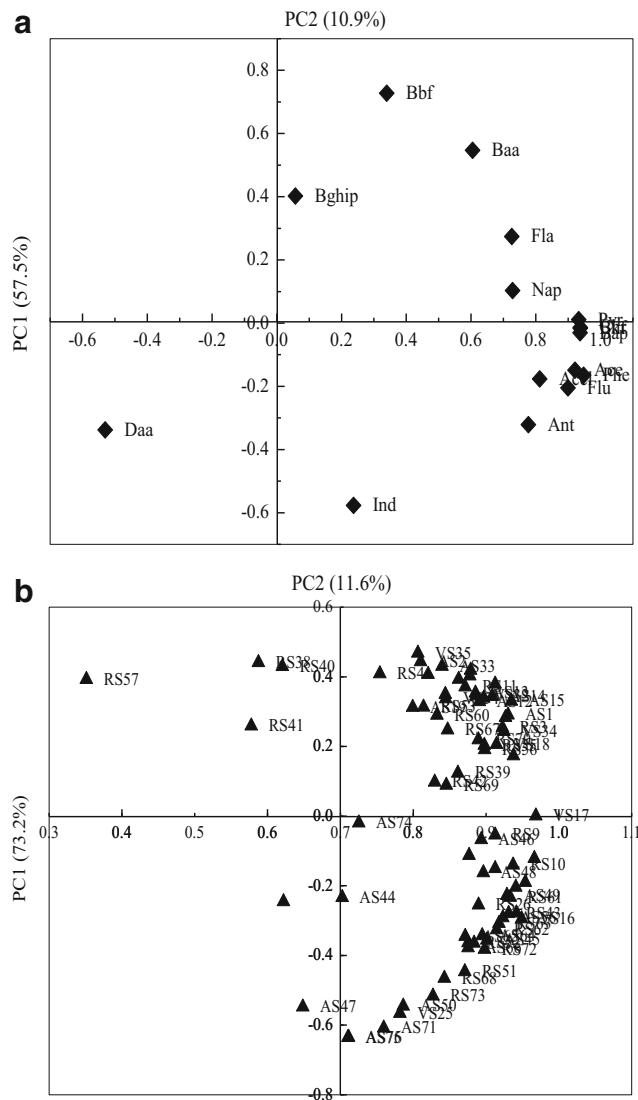


Fig. 7 **a** Principal component analysis loading plot for 16 individual PAHs. **b** Different sample sites. AS, RS, and VS represent sample sites located in the agricultural soils, roadside soils, and village soils, respectively

Tsai et al. 2007), Ace, Phe, Bkf, Bap, and Pyr are species associated with combustion and sintering process (coal, wood, and diesel), and Phe and Chr are markers for coal combustion (Duval and Friedlander 1981; Harrison et al. 1996; Larsen and Baker 2003). So, this factor might be in the pyrogenic origin categories. PC2 is responsible for 11.6% of the total variance. This factor got high loading for Phe, Baa, Ind, Bghip, Ant, Fla, Flu, and Daa (Fig. 7a). These species were also associated with combustion and auto emissions and coke ovens. According to the literature (Fraser et al. 1997; Venkataraman et al. 2002), Bghip, Bbf, and Ind are species associated with auto emissions, while Phe, Flu, Ant, and Fla are the predominant PAHs emitted from coke ovens (Knafla et al. 2006). The factor received medium loading for Flu, Ace, Ant, Fla, Nap, Baa, and Daa. These

species were associated with vehicle exhaust. Simcik et al. (1999) report that Ace, Flu, Ant, Fla, and Nap have been used as tracers for vehicles. So, this factor might be in the mixed combustion and auto emissions source categories.

The high score was observed at sampling locations RS38, RS39, RS40, RS41, RS42, RS51, RS52, RS53, RS55, RS57, RS60, RS67, RS72, VS36, and VS54 (Fig. 7b), which are located near the S102 and S228 roadsides of high traffic densities. The medium score was found at the most sampling sites, which suggested PAHs in the soil around the industrial areas originated from similar sources (Fig. 7b).

Many studies have demonstrated that the sintering process exists in several industries, such as coking plants and steel and iron industries. These mainly produce PAHs that are emitted via unsealed oven doors during charging, pushing, and cooling processes (Mastral et al. 1996). The high score was observed at sampling locations which are located near the roadsides of high traffic densities around the industrial areas. The medium score was found at the most sampling sites; moreover, the periphery between the AS and RS cleared relatively, but not clear between the VS and AS or RS. Therefore, it suggested PAHs in the soil around the industrial areas originated from similar sources, but have also a little distinction and the sources of PAHs included coal and coke combustion, sintering processes, and vehicle exhaust; the latter, however, contributed the least to the industrial area soils contamination. The result is according to the source identification by PAHs isomer ratios and compositional profiles of PAHs.

Coefficient of divergence analysis

In this study, the CD of total and individual PAHs among the three different functional soils is calculated as Eq. (1) and listed in Table 1. The values of the 16 individual PAHs is $CD > 0.290$ (with the exception of Baa, Bkf, Bbf, Chr, Ind, and Bghip) between the AS and RS; between the AS and VS is $CD < 0.290$ (with the exception of Ace, Flu, Ant, Pyr, and Bghip); between the RS and VS is $CD < 0.12$ (with the exception of Daa and Bghip). The average value of CD (Ave-CD) of the PAHs in the different functional soils is 0.319, 0.253, and 0.120 for the AS-RS, AS-VS, and RS-VS, respectively. The CD was applied to analyze the similarities of the sources between the soil samples collected from two areas (such as AS-RS). Generally, it is supposed that the CD value approaching zero illustrates a similar source, while based on the literature (Wongphatarakul et al. 1998), the CD value ≥ 0.269 may be a symbol of the divergence between sample soils from two different points. According to the standard values, the results concluded that possible PAHs sources of the RS and VS samples have the least divergence (Ave-CD = 0.120), the different PAHs were Daa

Table 1 The coefficient of divergence (CD) of total and individual PAHs among the three different functional soils (AS agriculture soils, RS roadside soils, VS village soils)

PAH	AS-RS (CD)	AS-VS (CD)	RS-VS (CD)
Nap	0.338	0.146	0.066
Ace	0.493	0.316	0.054
Acel	0.566	0.290	0.129
Flu	0.465	0.326	0.033
Phe	0.359	0.246	0.022
Ant	0.621	0.510	0.028
Fla	0.327	0.166	0.046
Pyr	0.406	0.310	0.016
Baa	0.213	0.165	0.005
Chr	0.248	0.155	0.017
Bbf	0.076	0.143	0.013
Bkf	0.268	0.122	0.042
Bap	0.337	0.149	0.063
Daa	0.384	0	0.387
Ind	0.001	0.004	0.001
Bghip	0.001	1.000	1.000
Ave-CD	0.319	0.253	0.120

(markers of coal combustion) and Bghip (markers of auto emissions). The AS and RS samples have the largest divergence (Ave-CD = 0.319), with differing PAHs being Baa, Bkf, Chr (markers of coal combustion and sintering), Bghip, Bbf, and Ind (markers of vehicular emissions). Lastly, between the AS and VS samples,

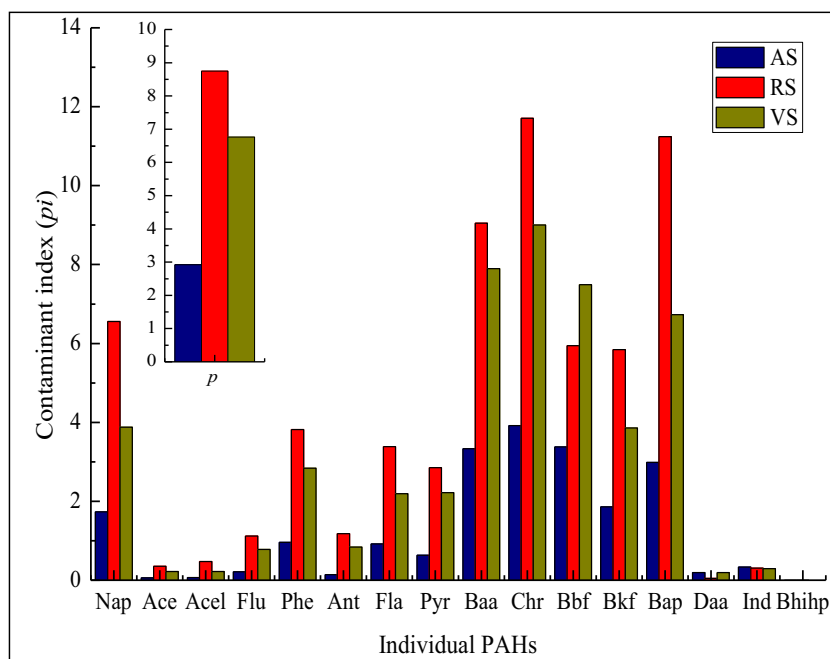
there is a moderate diversity in sources (Ave-CD = 0.253), with the differing PAHs being Ace, Flu, Ant, Pyr, and Bghip (markers of vehicles emissions and combustion). The results indicated that the sources of PAHs in the three function soils mainly included coal combustion, sintering, and vehicular emissions, but in RS main from vehicular emissions, AS main from combustion, sintering, and VS has a least difference to AS or RS, included coal combustion, sintering and vehicular emissions, and according with the source identification by PAHs isomer ratios.

Thus, as evidenced by the calculated CD values, PCA, and the compositional profiles of PAHs, the PAH isomer ration in all sample sites are affected in particular by combustion, incineration, and vehicular exhaust. The majority of the PAH mass was associated with pyrogenic origin, from which the authors conclude that industrial activity is responsible for the major source of PAHs found in the soil environment of the industrial district of Changzhi.

Potential risk assessment

Risk assessment by contaminant indexes

The single-factor and Nemerow composite indexes were adopted to assess the quality of the soil of the industrial area with the USEPA 16 PAHs in accordance of the environmental standards of the GB 15618-2008 (China 2008). Applying formulas (2), (3), and (4), the mean values of the

Fig. 8 Single factor of individual PAHs(P_i) and the Nemerow composite index (P) in different functional soils: agriculture soil (AS), roadside soil (RS), and village soil (VS)

single factor contaminant index (P_i) of individual PAHs and the Nemerow composite index (P) of the total PAHs in the different functional soils are shown in Fig. 8. This figure shows the following concentration indexes: Ace (P_{Ace}), Acel (P_{Acel}), Flu (P_{Flu}), Ant (P_{Ant}), Pyr (P_{Pyr}), Daa (P_{Daa}), Ind (P_{Ind}), and Bhig (P_{Bhig}) are below 0.70; $0.70 \leq Phe$ (P_{Phe}), Fla (P_{Fla}) ≤ 1.00 ; $1.00 \leq Nap$ (P_{Nap}), Bkf (P_{Bkf}) ≤ 2.00 ; $2.00 \leq Bap$ (P_{Bap}) ≤ 3.00 ; and the Baa (P_{Baa}) = 3.33, Bbf (P_{Bbf}) = 3.38, and Chr (P_{Chr}) = 3.92 in the AS samples. In the RS samples, the P_{Ace} , P_{Acel} , P_{Daa} , P_{Ind} , P_{Bhig} ≤ 0.70 ; $1.0 \leq P_{Flu}$, P_{Ant} ≤ 2.00 ; $2.00 \leq P_{Pyr}$ ≤ 3.00 ; $3.38 \leq P_{Fla}$, P_{Phe} , P_{Nap} , P_{Bkf} , P_{Bbf} , P_{Baa} , P_{Bap} , and P_{Chr} ≤ 11.7 . And in VS sample soils, the P_{Ace} , P_{Acel} , P_{Daa} , P_{Ind} , and P_{Bhig} ≤ 0.7 ; $0.7 \leq P_{Flu}$, P_{Ant} ≤ 1.00 ; $2.00 \leq P_{Phe}$, P_{Fla} , P_{Pyr} ≤ 3.00 ; $3.88 \leq P_{Nap}$, P_{Bkf} , P_{Bbf} , P_{Baa} , and P_{Chr} ≤ 9.00 . The results indicate that the P_{Chr} was the highest ($3.92 \leq P_{Chr} \leq 11.7$), followed by Bap ($2.98 \leq P_{Bap} \leq 11.2$), Baa ($3.33 \leq P_{Baa} \leq 9.05$), and Bbf ($3.38 \leq P_{Bbf} \leq 7.49$). Using the same formulas, the Nemerow composite index (P) values of the 16 PAHs in AS, RS, and VS samples were 2.92, 8.75, and 6.77, respectively. Based on the P_i of individual PAHs or the P value (P_i or P), the environmental quality can be classified within five pollution levels such as: clean (safe) (P_i or $P \leq 0.7$), warning value ($0.7 < P_i$ or $P \leq 1.0$), light pollution ($1.0 < P_i$ or $P \leq 2.0$), and middle-high pollution ($2.0 < P_i$ or $P \leq 3.0$) and heavy pollution (P_i or $P > 3.0$) (Ribeiro et al. 2005).

Following the literature data (Ribeiro et al. 2005), we deduced that the following PAHs exceeded critical levels of “heavy pollution: Baa, Bbf, and Chr in the AS samples; Fla, Phe, Nap, Bkf, Bbf, Baa, Bap, and Chr in RS; Nap, and Bkf, Bbf, Baa, and Chr in VS. Furthermore, 56.3, 75.0, and 68.8% of 16 PAHs P_i exceeded the level of light pollution in our study’s samples ($P_i > 1.0$); 25.0, 50.0, and 43.8% of 16 PAHs P_i exceeded the level of heavy pollution ($P_i > 3.00$) in our samples. Based on the value of P , we can regard the AS samples ($P = 2.92$) as being moderately polluted ($2.0 < P \leq 3.0$) and RS ($P = 8.75$) and VS ($P = 6.77$) samples as being heavily polluted ($P > 3.00$).

Risk assessment by concentrations of total PAHs

The limit concentrations of $\Sigma 16$ PAHs in soils are regulated in a few countries; Maliszewska-Kordybach (1996) suggests a soil pollution classification system based on the total 16 USEPA priority control PAH concentrations, namely, unpolluted soil ($\Sigma 16$ PAHs $\leq 200 \mu\text{g kg}^{-1}$), weakly polluted soil ($200 < \Sigma 16$ PAHs $\leq 600 \mu\text{g kg}^{-1}$), polluted soil ($600 < \Sigma 16$ PAHs $\leq 1000 \mu\text{g kg}^{-1}$), and heavily polluted soil ($\Sigma 16$ PAHs $> 1000 \mu\text{g kg}^{-1}$). The system was used as a standard to assess soil environmental risk. In the present study, by the classification system, only two sampling sites belong to

weakly contaminated, i.e., AS44 ($848 \mu\text{g kg}^{-1}$), AS19 ($794 \mu\text{g kg}^{-1}$), and all others were categorized as severely polluted ($\Sigma 16$ PAHs $> 1000 \mu\text{g kg}^{-1}$). This illustrates the gravity of PAHs pollution continuing to exist in the soils surrounding industrial districts. Strategies are needed to prevent the soils themselves from becoming sources, which would transfer PAHs into the air or groundwater of these areas.

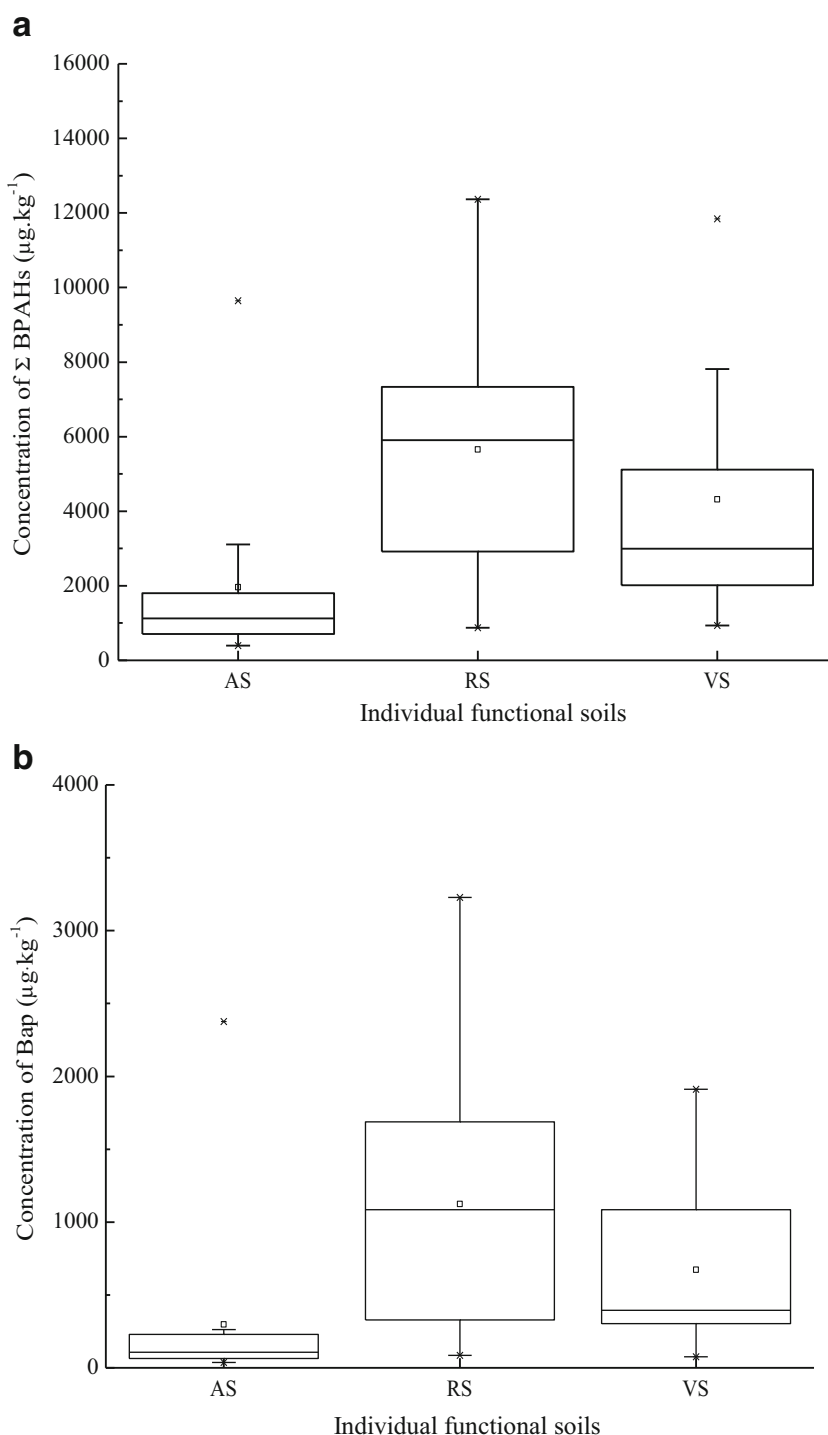
Risk assessment by concentrations of carcinogenic PAHs

The total concentrations ($\Sigma 8$ BPAHs) of the eight varieties of PAHs have been considered probably or possibly carcinogenic (i.e., Nap, Baa, Chr, Bbf, Bkf, Bap, Inp, Daa), with Bap, one of the most potent carcinogenic PAHs, being found in all three of the functional soils sampled from areas surrounding the industrial district, as shown in Fig. 9.

As seen in Fig. 9a, the value of total carcinogenic PAH ($\Sigma 8$ BPAHs) concentrations in the AS samples ranged from 398 to $9646 \mu\text{g kg}^{-1}$ with an average value of $1959 \mu\text{g kg}^{-1}$; RS samples ranged from 871 to $12,366 \mu\text{g kg}^{-1}$ with an average value of $5654 \mu\text{g kg}^{-1}$; and VS samples ranged from 934 to $11,842 \mu\text{g kg}^{-1}$ with an average value of $4320 \mu\text{g kg}^{-1}$. The median concentration was lower for the AS samples ($1151 \mu\text{g kg}^{-1}$) than the RS and VS samples (approximately 5944 and $3469 \mu\text{g kg}^{-1}$, respectively), and the range of the 25th and 75th percentiles was wider for the RS samples. Comparing the functional regions, the highest concentrations of $\Sigma 8$ BPAHs were discovered in the roadside soils, followed by the village soils, then the agricultural soils. According to a number of investigations about $\Sigma 8$ BPAH distribution in soils, the concentrations of $\Sigma 8$ BPAHs are much higher than those found in urban and agricultural soils. For example, they are higher than oilfield soils (1090 – $4560 \mu\text{g kg}^{-1}$), soils surrounding the Tiefa coalmine district (3200 – $2460 \mu\text{g kg}^{-1}$) (Liu et al. 2012b; Wang et al. 2015b; Weiss et al. 1994); however, they are below Texas oil exploration area soil (3100 – $86,400 \mu\text{g kg}^{-1}$) (Bojes and Pope 2007; Kuang et al. 2011).

At present, only a few studies focused on Bap contamination in the soils near the industrial areas. Figure 9b shows that the concentrations of Bap in the AS samples ranged from 36.5 to $2377 \mu\text{g kg}^{-1}$ with a mean value of $298 \mu\text{g kg}^{-1}$; in RS, it ranged from 86.1 to $3228 \mu\text{g kg}^{-1}$ with a mean value of $1124 \mu\text{g kg}^{-1}$; and in VS, it ranged from 76.3 to $1911 \mu\text{g kg}^{-1}$ with a mean value of $673 \mu\text{g kg}^{-1}$. Soil concentrations of Bap from this study’s industrial district were higher than those found in roadside soils of Chiang-Mai, Thailand ($22.0 \mu\text{g kg}^{-1}$) (Amagai et al. 1999), urban soils of Beijing (5 – $270 \mu\text{g kg}^{-1}$) (Hung et al. 2005; Ma et al. 2005), Hangzhou urban soils (9.18 – $117 \mu\text{g kg}^{-1}$, mean $27.0 \mu\text{g kg}^{-1}$) (Yu et al. 2014), Tiefa coalmine soils (mean value of $99.9 \mu\text{g kg}^{-1}$) (Liu et al. 2012a), and Shanghai urban soils (24.4 – $824 \mu\text{g kg}^{-1}$). Concentrations of Bap in soil found in this study, just, were lower than those found in the soil surrounding a ferroalloy

Fig. 9 Box plot of total carcinogenic PAHs ($\Sigma 8\text{BPAHs}$) (a) and Bap concentrations (b) sampling data in agriculture soils (AS), roadside soils (RS), and village soils (VS). The boxes are interquartile range, with the line inside box as the median, the circle is the mean, whiskers are 95% of data, and outlier values are indicated by asterisk



production plant run by the Sino-steel Corporation in Jilin ($5690 \mu\text{g kg}^{-1}$) (Jiang et al. 2009). But the concentrations were higher 2.98–11.2 times than the environmental quality standard value ($100 \mu\text{g kg}^{-1}$) of the GB 15618-2008 (China 2008). This might illustrate that the high concentrations of $\Sigma 8\text{BPAHs}$ and Bap in village and agricultural soils of the industrial district may lead to high carcinogenic potential in the human being here.

Risk assessment by Bap equivalent concentrations (Bapeq)

In this study, the carcinogenic potency of every sample is calculated using Bap equivalent concentrations (Bapeq) as seen in Eq. (5). Based on the Bapeq, human health risks were assessed. The TEFs provided by Nisbet and LaGoy (1992) for the 16 USEPA priority control PAHs (0.001 for Nap, Ace, Acel, Flu, Phe, Fla, and Pyr; 0.01 for Ant, Chr, and Bghip;

Table 2 Concentrations and Bap equivalent concentrations of PAHs in agriculture soil (AS), roadside soils (RS), and village soils (VS) samples

Name	PAHs ($\mu\text{g kg}^{-1}$)				Bapeq ($\mu\text{g kg}^{-1}$)			
	AS	RS	VS	Average value	AS	RS	VS	Average value
Nap	174	656	388	406	0.174	0.656	0.388	0.406
Ace	31.1	178	111	106	0.031	0.178	0.111	0.106
Acel	33.3	236	111	127	0.033	0.236	0.111	0.127
Flu	106	561	388	352	0.106	0.561	0.388	0.352
Phe	478	1910	1421	1270	0.478	1.91	1.42	1.27
Ant	69.8	588	419	359	0.698	5.88	4.19	3.59
Fla	461	1692	1096	1083	0.461	1.69	1.10	1.08
Pyr	316	1427	1110	951	0.316	1.43	1.11	0.951
Baa	333	905	789	676	33.3	90.5	78.9	67.6
Chr	392	1171	900	821	3.92	11.7	9.00	8.21
Bbf	338	594	749	560	33.8	59.4	74.9	56.0
Bkf	372	1168	772	771	37.2	117	77.2	77.1
Bap	298	1124	673	698	298	1124	673	698
Ind	20.0	5.00	19.7	14.6	19.5	4.58	19.7	14.6
Daa	33.1	31.0	29.0	31.0	3.31	3.10	2.90	3.10
Bhigp	0.169	0.158	ND	0.109	0.002	0.002	ND	0.001
$\sum 16\text{PAHs}/\sum \text{Bapeq}16\text{PAHs}$	3455	12,245	8975	8346	432	1423	944	933
$\sum \text{BPAHs}/\sum \text{BapeqBPAHs}$	1959	5654	4320	3977	430	1411	936	925

0.1 for Baa, Bbf, Bkf, and Ind; and 1 for Bap and Daa) were used to assess the health hazard of PAH pollution in the industrial district's soils.

The toxic values of individual PAHs (Bapeq_i), total toxic values of 16 PAHs ($\sum \text{Bapeq}16\text{PAHs}$) and 8 carcinogenic PAHs ($\sum \text{BapeqBPAHs}$) in the AS, RS, and VS samples are listed in Table 2.

Table 2 shows that the value of $\sum \text{Bapeq}16\text{PAHs}$ is 432, 1423, and 944 $\mu\text{g kg}^{-1}$ in AS, RS, and VS, respectively. Moreover, the concentrations of the $\sum \text{BapeqBPAHs}$ were also calculated; the value was 430 $\mu\text{g kg}^{-1}$ in AS, 1411 $\mu\text{g kg}^{-1}$ in RS, and 936 $\mu\text{g kg}^{-1}$ in VS. The $\sum \text{Bapeq}16\text{PAHs}$ levels in the industrial district's soils are higher than those from soils found surrounding a thermal desorption plant in Zhejiang (67.0–479 $\mu\text{g kg}^{-1}$) (Liu et al. 2015), and from oilfield soils in Daqing (113 $\mu\text{g kg}^{-1}$), Shengli (168 $\mu\text{g kg}^{-1}$), Xinjiang (94.0 $\mu\text{g kg}^{-1}$), Hebei (212 $\mu\text{g kg}^{-1}$) (Wang et al. 2015a). According to the Dutch government, uncontaminated soils that could be considered multi-usage soils should have a $\sum \text{Bapeq}16\text{PAH}$ level of less than 20.0–50.0 $\mu\text{g kg}^{-1}$ (Annokkee 1990). Canada has the highest set $\sum \text{Bapeq}16\text{PAH}$ value of 100 $\mu\text{g kg}^{-1}$ (Lu et al. 2008). The mean values of $\sum \text{Bapeq}16\text{PAH}$ (933 $\mu\text{g kg}^{-1}$) in the investigated soils were higher 9.3 times than the Canadian standard value. The $\sum \text{BapeqBPAHs}$ shows very high contribution rates on the $\sum \text{Bapeq}16\text{PAHs}$ concentrations (more than 99%), and the individual contribution rates of the eight carcinogenic PAHs on the $\sum \text{BapeqBPAHs}$ showed a decrease in the

following order: Bap (73.7%) > Bkf (8.40%) > Baa (7.54%) > Bbf (6.69%) > Ind (2.32%) > Chr (0.900%) > Daa (0.430%). Compared with the $\sum 16\text{PAHs}$, although the average concentration of $\sum 16\text{PAHs}$ in the monitored regions was not the highest, the $\sum \text{BapeqBPAHs}$ level was extremely high (430–1411 $\mu\text{g kg}^{-1}$, mean 925 $\mu\text{g kg}^{-1}$), specifically, the contribution rates of Bap at 73.7%. The $\sum \text{Bapeq}16\text{PAHs}$ values indicated that local residents' health could be put at risk by the existence of high concentrations of PAHs. Moreover, the high contribution rates of Bap on the $\sum \text{BapeqBPAHs}$ also suggest that the PAHs in the industrial district's soils may cause a high incidence of cancer among people living close to the industrial district. In addition, this might indicate that it is not sufficient to manage the risk of PAHs by just detecting the total concentrations of them in the traditional industry areas' soils. And more attention should be paid to the carcinogenic potential of Bap in the actual regions.

Conclusions

In this study, the levels of PAHs were detected in the soil samples shown an increased trend AS–VS–RS. The detected concentrations of PAHs in the samples were much higher than the limits permitted by many countries' standard. The result demonstrates that soils close to the industrial areas are polluted seriously (average = 8346 $\mu\text{g kg}^{-1}$). The overall profile based on molecular weight of PAHs was almost similar in soil

samples from AS, VS, and RS; the composition of PAHs was characterized by HMWPAHs (four to six rings) with an average ratios of 69.6% of HMWPAHs to total PAHs content in the all sample sites, therein, the 4-ring compounds were the most abundant (average = 42.9%). PCA and PAH isomeric ratios and the characteristics of the composition of the PAHs in sampling points indicated that PAHs mainly originated from pyrogenic origin, especially coal combustion and vehicle exhaust. And the distribution characteristics of soils PAHs have been impacted by the wind direction and topography of the areas. The high-level PAHs were in the soil samples both from RS and AS located in the east and north and the south and north of the industrial areas, respectively. According to the estimated values of Bapeqs of 16 PAH and 8 BPAHs (especially, Bap), the risk coming from contact with the polluted soils should be considerably very high. It should also be noted that, apart from the hazard, the presence of these PAHs pose to the ecosystem, there is a great health risk to humans in the regions. It is concluded, therefore, that the local environments surrounding industrial areas may pose a serious potential hazard to the health of humans living there.

Acknowledgments This work was supported by the ‘863’ Program of China (2013AA06A205), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB15010404), and the Science and Research Program of Changzhi university (JD201603).

References

- Agarwal T, Khillare PS, Shridhar V (2006) PAHs contamination in bank sediment of the Yamuna River, Delhi, India. *Environ Monit Assess* 123(1-3):151-166
- Aichner B, Glaser B, Zech W (2007) Polycyclic aromatic hydrocarbons and polychlorinated biphenyls in urban soils from Kathmandu, Nepal. *Org Geochem* 38:700-715
- Akyüz M, Çabuk H (2008) Particle-associated polycyclic aromatic hydrocarbons in the atmospheric environment of Zonguldak, Turkey. *Sci Total Environ* 405:62-70
- Amagai T, Takahashi Y, Matsushita H, Morknoy D, Sukasem P, Tabucanon M (1999) A survey on polycyclic aromatic hydrocarbon concentrations in soil in Chiang-Mai, Thailand. *Environ Int* 25:563-572
- Annokkee G (1990) MT-TNO Research into the biodegradation of soils and sediments contaminated with oils and polycyclic aromatic hydrocarbons (PAH's), Contaminated Soil' 90. Springer, pp. 941-945
- Blake WH, Walsh RP, Reed JM, Barnsley MJ, Smith J (2007) Impacts of landscape remediation on the heavy metal pollution dynamics of a lake surrounded by non-ferrous smelter waste. *Environ Pollut* 148:268-280
- Bojes HK, Pope PG (2007) Characterization of EPA's 16 priority pollutant polycyclic aromatic hydrocarbons (PAHs) in tank bottom solids and associated contaminated soils at oil exploration and production sites in Texas. *Regul Toxicol Pharmacol* 47:288-295
- Boonyatumanond R, Murakami M, Wattayakorn G, Togo A, Takada H (2007) Sources of polycyclic aromatic hydrocarbons (PAHs) in street dust in a tropical Asian mega-city, Bangkok, Thailand. *Sci Total Environ* 384:420-432
- Bourotte C, Forti M-C, Taniguchi S, Bicego MC, Lotufo PA (2005) A wintertime study of PAHs in fine and coarse aerosols in São Paulo city, Brazil. *Atmos Environ* 39:3799-3811
- Bull S, Collins C (2013) Promoting the use of BaP as a marker for PAH exposure in UK soils. *Environ Geochem Health* 35:101-109
- Callén M, De la Cruz M, López J, Murillo R, Navarro M, Mastral A (2008) Long-range atmospheric transport and local pollution sources on PAH concentrations in a South European urban area. Fulfilling of the European directive. *Water Air Soil Pollut* 190:271-285
- Callén M, De la Cruz M, López J, Mastral A (2011) PAH in airborne particulate matter: Carcinogenic character of PM10 samples and assessment of the energy generation impact. *Fuel Process Technol* 92:176-182
- Cancer IAFRo, Organization WH (1983) Polynuclear aromatic compounds, Part 1, chemical, environmental and experimental data. International Agency for Research on Cancer
- Chen L, Ran Y, Xing B, Mai B, He J, Wei X, Fu J, Sheng G (2005) Contents and sources of polycyclic aromatic hydrocarbons and organochlorine pesticides in vegetable soils of Guangzhou, China. *Chemosphere* 60:879-890
- Chen S-C, Liao C-M (2006) Health risk assessment on human exposed to environmental polycyclic aromatic hydrocarbons pollution sources. *Sci Total Environ* 366:112-123
- China E (2008) Environmental quality standard for soils (GB15618-2008)
- Christensen ER, Bzdusek PA (2005) PAHs in sediments of the Black River and the Ashtabula River, Ohio: source apportionment by factor analysis. *Water Res* 39:511-524
- Crampon M, Bureau F, Akpa-Vinceslas M, Bodilis J, Machour N, Le Derf F, Portet-Koltalo F (2014) Correlations between PAH bioavailability, degrading bacteria, and soil characteristics during PAH biodegradation in five diffusely contaminated dissimilar soils. *Environ Sci Pollut Res* 21:8133-8145
- Desaules A, Ammann S, Blum F, Brändli RC, Bucheli TD, Keller A (2008) PAH and PCB in soils of Switzerland—status and critical review. *J Environ Monit* 10:1265-1277
- Duval M, Friedlander S (1981) Source resolution of polycyclic aromatic hydrocarbons in the Los Angeles atmosphere application of a CMB with first-order decay. United States Environmental Protection Agency, Washington, DC
- Finkelmann RB, Orem W, Castranova V, Tatu CA, Belkin HE, Zheng B, Lerch HE, Maharaj SV, Bates AL (2002) Health impacts of coal and coal use: possible solutions. *Int J Coal Geol* 50:425-443
- Fraser MP, Cass GR, Simoneit BR, Rasmussen R (1997) Air quality model evaluation data for organics. 4. C2-C36 non-aromatic hydrocarbons. *Environmental science & technology* 31:2356-2367
- Gaga EO, Ari A, Döğeroğlu T, Çakırca EE, Machin NE (2012) Atmospheric polycyclic aromatic hydrocarbons in an industrialized city, Kocaeli, Turkey: study of seasonal variations, influence of meteorological parameters and health risk estimation. *J Environ Monit* 14:2219-2229
- Galarneau E (2008) Source specificity and atmospheric processing of airborne PAHs: implications for source apportionment. *Atmos Environ* 42:8139-8149
- Giger W, Blumer M (1974) Polycyclic aromatic hydrocarbons in the environment. Isolation and characterization by chromatography, visible, ultraviolet, and mass spectrometry. *Anal Chem* 46:1663-1671
- Harner T, Bidleman TF (1998) Octanol-air partition coefficient for describing particle/gas partitioning of aromatic compounds in urban air. *Environmental Science & Technology* 32:1494-1502
- Harrison RM, Smith D, Luhana L (1996) Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, UK. *Environmental Science & Technology* 30:825-832

- Haugland T, Ottesen RT, Volden T (2008) Lead and polycyclic aromatic hydrocarbons (PAHs) in surface soil from day care centres in the city of Bergen, Norway. *Environ Pollut* 153:266–272
- Humans IWGotEoCRt, Cancer IAfRo, Organization WH (1991) IARC monographs on the evaluation of carcinogenic risks to humans, 51. World Health Organization
- Humans IWGotEoCRt, Organization WH, Cancer IAfRo (2004) Tobacco smoke and involuntary smoking: this publication represents the views and expert opinions of an IARC working group on the evaluation of carcinogenic risks to humans, which Met in Lyon, 11–18 June 2002. Iarc
- Hung H, Blanchard P, Halsall CJ, Bidleman T, Stern G, Fellin P, Muir D, Barrie L, Jantunen L, Helm P (2005) Temporal and spatial variabilities of atmospheric polychlorinated biphenyls (PCBs), organochlorine (OC) pesticides and polycyclic aromatic hydrocarbons (PAHs) in the Canadian Arctic: Results from a decade of monitoring. *Sci Total Environ* 342:119–144
- Hussar E, Richards S, Lin Z-Q, Dixon RP, Johnson KA (2012) Human health risk assessment of 16 priority polycyclic aromatic hydrocarbons in soils of Chattanooga, Tennessee, USA. *Water Air Soil Pollut* 223:5535–5548
- Jiang Y-F, Wang X-T, Wang F, Jia Y, Wu M-H, Sheng G-Y, Fu J-M (2009) Levels, composition profiles and sources of polycyclic aromatic hydrocarbons in urban soil of Shanghai, China. *Chemosphere* 75:1112–1118
- Jiao L, Zheng GJ, Minh TB, Richardson B, Chen L, Zhang Y, Yeung LW, Lam JC, Yang X, Lam PK (2009a) Persistent toxic substances in remote lake and coastal sediments from Svalbard, Norwegian Arctic: levels, sources and fluxes. *Environ Pollut* 157:1342–1351
- Jiao W, Lu Y, Li J, Han J, Wang T, Luo W, Shi Y, Wang G (2009b) Identification of sources of elevated concentrations of polycyclic aromatic hydrocarbons in an industrial area in Tianjin, China. *Environ Monit Assess* 158:581–592
- Jiao W, Lu Y, Wang T, Li J, Han J, Wang G, Hu W (2009c) Polycyclic aromatic hydrocarbons in soils around Guanting Reservoir, Beijing, China. *Chem Ecol* 25:39–48
- Jiao HH, Rui XP, Wu SH, Bai ZH, Zhuang X L and Huang Z B (2015). Polycyclic aromatic hydrocarbons in the Dagang Oilfield (China): Distribution, sources, and risk assessment. *Int J Environ Res Public Health* 12: 5775–5791
- Johansson I, van Bavel B (2003) Levels and patterns of polycyclic aromatic hydrocarbons in incineration ashes. *Sci Total Environ* 311:221–231
- Katsoyiannis A, Breivik K (2014) Model-based evaluation of the use of polycyclic aromatic hydrocarbons molecular diagnostic ratios as a source identification tool. *Environ Pollut* 184:488–494
- Khairy MA, Lohmann R (2012) Field validation of polyethylene passive air samplers for parent and alkylated PAHs in Alexandria, Egypt. *Environmental science & technology* 46:3990–3998
- Knafla A, Philipps K, Brecher R, Petrovic S, Richardson M (2006) Development of a dermal cancer slope factor for benzo [a] pyrene. *Regul Toxicol Pharmacol* 45:159–168
- Kuang S, Wu Z, Zhao L (2011) Accumulation and risk assessment of polycyclic aromatic hydrocarbons (PAHs) in soils around oil sludge in Zhongyuan oil field, China. *Environmental Earth Sciences* 64: 1353–1362
- Kumar B, Gaur R, Kumar S, Sharma CS (2013) Environmental and human health risk assessment of Benzo (a) pyrene levels in agricultural soils from the National Capital Region, Delhi, India. *Human and Ecological Risk Assessment: An International Journal* 19:118–125
- Kwon H-O, Choi S-D (2014) Polycyclic aromatic hydrocarbons (PAHs) in soils from a multi-industrial city, South Korea. *Sci Total Environ* 470:1494–1501
- Larsen RK, Baker JE (2003) Source apportionment of polycyclic aromatic hydrocarbons in the urban atmosphere: a comparison of three methods. *Environmental Science & Technology* 37:1873–1881
- Lee M, Prado G, Howard J, Hites RA (1977) Source identification of urban airborne polycyclic aromatic hydrocarbons by gas chromatographic mass spectrometry and high resolution mass spectrometry. *Biological Mass Spectrometry* 4:182–186
- Li CK, Kamens RM (1993) The use of polycyclic aromatic hydrocarbons as source signatures in receptor modeling. *Atmospheric Environment. Part A. General Topics* 27:523–532
- Lim MC, Ayoko GA, Morawska L, Ristovski ZD, Jayaratne ER (2007) Influence of fuel composition on polycyclic aromatic hydrocarbon emissions from a fleet of in-service passenger cars. *Atmos Environ* 41:150–160
- Liu J, Li X, Chen T, Qi Z, Buekens A, Lu S, Yan J (2015) Polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins and dibenzofurans, and polycyclic aromatic hydrocarbons around a thermal desorption plant in China. *Environ Sci Pollut Res* 22:3926–3935
- Liu L-Y, Wang J-Z, Wei G-L, Guan Y-F, Zeng EY (2012a) Polycyclic aromatic hydrocarbons (PAHs) in continental shelf sediment of China: implications for anthropogenic influences on coastal marine environment. *Environ Pollut* 167:155–162
- Liu S-H, Lin Y-C, Hsu K-H (2012b) Emissions of regulated pollutants and PAHs from waste-cooking-oil biodiesel-fuelled heavy-duty diesel engine with catalyzer. *Aerosol Air Qual Res* 12
- Liu Y, Zhu L, Shen X (2001) Polycyclic aromatic hydrocarbons (PAHs) in indoor and outdoor air of Hangzhou, China. *Environmental science & technology* 35:840–844
- Lorenzi D, Entwistle JA, Cave M, Dean JR (2011) Determination of polycyclic aromatic hydrocarbons in urban street dust: implications for human health. *Chemosphere* 83:970–977
- Lu H, Zhu L, Chen S (2008) Pollution level, phase distribution and health risk of polycyclic aromatic hydrocarbons in indoor air at public places of Hangzhou, China. *Environ Pollut* 152:569–575
- Lundstedt S, White PA, Lemieux CL, Lynes KD, Lambert IB, Öberg L, Haglund P, Tysklind M (2007) Sources, fate, and toxic hazards of oxygenated polycyclic aromatic hydrocarbons (PAHs) at PAH-contaminated sites. *AMBIO: A Journal of the Human Environment* 36:475–485
- Luo Q, Catney P, Lerner D (2009) Risk-based management of contaminated land in the UK: Lessons for China? *J Environ Manag* 90: 1123–1134
- LYON F (2014) IARC monographs on the evaluation of carcinogenic risks to humans
- Ma L, Chu S, Wang X, Cheng H, Liu X, Xu X (2005) Polycyclic aromatic hydrocarbons in the surface soils from outskirts of Beijing, China. *Chemosphere* 58:1355–1363
- 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* 11:121–127
- Masclat P, Mouvier G, Nikolaou K (1986) Relative decay index and sources of polycyclic aromatic hydrocarbons. *Atmos Environ* (1967) 20:439–446
- Mastral AM, Callen M, Murillo R (1996) Assessment of PAH emissions as a function of coal combustion variables. *Fuel* 75:1533–1536
- Miguel AH, Pereira PA (1989) Benzo (k) fluoranthene, benzo (ghi) perylene, and indeno (1, 2, 3-cd) pyrene: new tracers of automotive emissions in receptor modeling. *Aerosol Sci Technol* 10:292–295
- 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. *Environmental Science & Technology* 32:450–455
- Mostert MM, Ayoko GA, Kokot S (2012) Multi-criteria ranking and source identification of metals in public playgrounds in Queensland, Australia. *Geoderma* 173:173–183
- Mueller KE, Mueller-Spitz SR, Henry HF, Vonderheide AP, Soman RS, Kinkle BK, Shann JR (2006) Fate of pentabrominated diphenyl ethers in soil: abiotic sorption, plant uptake, and the impact of

- interspecific plant interactions. *Environmental science & technology* 40:6662–6667
- Muller P, Leece B, Raha D (1997) Scientific criteria document for multimedia standards development: polycyclic aromatic hydrocarbons (PAH). Part 1, Hazard identification and dose-response assessment. Standards Development Branch, Ontario Ministry of Environment and Energy, Ontario
- Nam J, Song B, Eom K, Lee S, Smith A (2003) Distribution of polycyclic aromatic hydrocarbons in agricultural soils in South Korea. *Chemosphere* 50:1281–1289
- Nisbet IC, LaGoy PK (1992) Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). *Regul Toxicol Pharmacol* 16:290–300
- Oleszczuk P, Pranagal J (2007) Influence of agricultural land use and management on the contents of polycyclic aromatic hydrocarbons in selected silty soils. *Water Air Soil Pollut* 184:195–205
- Oliveira C, Martins N, Tavares J, Pio C, Cerqueira M, Matos M, Silva H, Oliveira C, Camões F (2011) Size distribution of polycyclic aromatic hydrocarbons in a roadway tunnel in Lisbon, Portugal. *Chemosphere* 83:1588–1596
- Opune K, Agbozu I, Adegboro O (2009) A critical appraisal of PAH indices as indicators of PAH source and composition in Elelenwo Creek, southern Nigeria. *Environmentalist* 29:47–55
- Organization WH, Humans IWGoEoCRt (1994) IARC monographs on the evaluation of carcinogenic risks to humans: schistosomes, liver flukes and *Helicobacter pylori*. International Agency for Research on Cancer
- Ravindra K, Sokhi R, Van Grieken R (2008) Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. *Atmos Environ* 42:2895–2921
- Ray S, Khillare P S, Agarwal T, & Shridhar V (2008). Assessment of PAHs in soil around the International Airport in Delhi, India. *J Hazard Mater* 156:9–16
- Ribeiro CO, Vollaie Y, Sanchez-Chardi A, Roche H (2005) Bioaccumulation and the effects of organochlorine pesticides, PAH and heavy metals in the eel (*Anguilla anguilla*) at the Camargue Nature Reserve, France. *Aquat Toxicol* 74:53–69
- Robinson AL, Subramanian R, Donahue NM, Bernardo-Bricke A, Rogge WF (2006) Source apportionment of molecular markers and organic aerosol 1. Polycyclic aromatic hydrocarbons and methodology for data visualization. *Environmental science & technology* 40:7803–7810
- Rong H, Hong-Fu W, Yan-Tun S, JIANG H, Shao-Lin P (2007) Polycyclic aromatic hydrocarbons in agricultural soils of the southern subtropics, China. *Pedosphere* 17:673–680
- Simcik MF, Eisenreich SJ, Liroy PJ (1999) Source apportionment and source/sink relationships of PAHs in the coastal atmosphere of Chicago and Lake Michigan. *Atmos Environ* 33:5071–5079
- Tobiszewski M, Namieśnik J (2012) PAH diagnostic ratios for the identification of pollution emission sources. *Environ Pollut* 162:110–119
- Tsai J-W, Bremner KH, Vallee RB (2007) Dual subcellular roles for LIS1 and dynein in radial neuronal migration in live brain tissue. *Nat Neurosci* 10:970–979
- Ünlü S, Alpar B (2009) Evolution of potential ecological impacts of the bottom sediment from the Gulf of Gemlik; Marmara Sea, Turkey. *Bull Environ Contam Toxicol* 83:903–906
- Ünlü S, Alpar B, Aydin S (2009) Spectrofluorometric characterization of aromatic hydrocarbon contamination in the sediment from the Zonguldak Industrial region, Black Sea, Turkey. *Fresenius Environ Bull* 18:474–480
- Venkataraman C, Lyons JM, Friedlander SK (1994) Size distributions of polycyclic aromatic hydrocarbons and elemental carbon. 1. Sampling, measurement methods, and source characterization. *Environmental science & technology* 28:555–562
- Venkataraman C, Negi G, Sardar SB, Rastogi R (2002) Size distributions of polycyclic aromatic hydrocarbons in aerosol emissions from bio-fuel combustion. *J Aerosol Sci* 33:503–518
- Wan X, Chen J, Tian F, Sun W, Yang F, Saiki K (2006) Source apportionment of PAHs in atmospheric particulates of Dalian: factor analysis with nonnegative constraints and emission inventory analysis. *Atmos Environ* 40:6666–6675
- Wang F, Xing S, Hou X (2012a) Study on the distribution pattern of PAHs in the coking dust from the coking environment. *Procedia Engineering* 45:959–961
- Wang J, Zhu L, Shen X (2003) PAHs pollution in air of coke plant and health risk assessment. *Huan jing ke xue = Huanjing kexue/[bian ji, Zhongguo ke xue yuan huan jing ke xue wei yuan hui" Huan jing ke xue" bian ji wei yuan hui]* 24:135–138
- Wang J, Zhan X, Zhou L, Lin Y (2010) Biological indicators capable of assessing thermal treatment efficiency of hydrocarbon mixture-contaminated soil. *Chemosphere* 80:837–844
- Wang J, Cao X, Liao J, Huang Y, Tang X (2015a) Carcinogenic potential of PAHs in oil-contaminated soils from the main oil fields across China. *Environ Sci Pollut Res* 22:10902–10909
- Wang N, Li H-B, Long J-L, Cai C, Dai J-L, Zhang J, Wang R-Q (2012b) Contamination, source, and input route of polycyclic aromatic hydrocarbons in historic wastewater-irrigated agricultural soils. *J Environ Monit* 14:3076–3085
- Wang W, M-j H, Kang Y, Wang H-s, Leung AO, Cheung KC, Wong MH (2011) Polycyclic aromatic hydrocarbons (PAHs) in urban surface dust of Guangzhou, China: status, sources and human health risk assessment. *Sci Total Environ* 409:4519–4527
- Wang X-T, Miao Y, Zhang Y, Li Y-C, Wu M-H, Yu G (2013) Polycyclic aromatic hydrocarbons (PAHs) in urban soils of the megacity Shanghai: occurrence, source apportionment and potential human health risk. *Sci Total Environ* 447:80–89
- Wang X-T, Chen L, Wang X-K, Lei B-L, Sun Y-F, Zhou J, Wu M-H (2015b) Occurrence, sources and health risk assessment of polycyclic aromatic hydrocarbons in urban (Pudong) and suburban soils from Shanghai in China. *Chemosphere* 119:1224–1232
- Weiss P, Riss A, Gschmeidler E, Schentz H (1994) Investigation of heavy metal, PAH, PCB patterns and PCDD/F profiles of soil samples from an industrialized urban area (Linz, Upper Austria) with multivariate statistical methods. *Chemosphere* 29:2223–2236
- Wilcke W (2007) Global patterns of polycyclic aromatic hydrocarbons (PAHs) in soil. *Geoderma* 141:157–166
- Wild SR, Jones KC (1995) Polynuclear aromatic hydrocarbons in the United Kingdom environment: a preliminary source inventory and budget. *Environ Pollut* 88:91–108
- Wongphatarakul V, Friedlander S, Pinto J (1998) A comparative study of PM_{2.5} ambient aerosol chemical databases. *Environmental Science & Technology* 32:3926–3934
- Yin C-Q, Jiang X, Yang X-L, Bian Y-R, Wang F (2008) Polycyclic aromatic hydrocarbons in soils in the vicinity of Nanjing, China. *Chemosphere* 73:389–394
- Yu G, Zhang Z, Yang G, Zheng W, Xu L, Cai Z (2014) Polycyclic aromatic hydrocarbons in urban soils of Hangzhou: status, distribution, sources, and potential risk. *Environ Monit Assess* 186:2775–2784
- 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* 33:489–515
- Zhang H, Luo Y, Wong M, Zhao Q, Zhang G (2006) Distributions and concentrations of PAHs in Hong Kong soils. *Environ Pollut* 141:107–114
- Zhang Y, Tao S (2009) Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs) for 2004. *Atmos Environ* 43:812–819
- Zheng T, Ran Y, Chen L (2014) Polycyclic aromatic hydrocarbons (PAHs) in rural soils of Dongjiang River Basin: occurrence, source apportionment, and potential human health risk. *J Soils Sediments* 14:110–120