

Polycyclic aromatic hydrocarbons (PAHs) in atmospheric dustfall from the industrial corridor in Hubei Province, Central China

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Abstract Thirty atmospheric dustfall samples collected from an industrial corridor in Hubei Province, central China, were analyzed for 16 USEPA priority polycyclic aromatic hydrocarbons (PAHs) to investigate their concentrations, spatial distributions, sources, and health risks. Total PAH concentrations (Σ PAHs) ranged from 1.72 to 13.17 $\mu\text{g/g}$ and averaged 4.91 $\mu\text{g/g}$. High molecular weight (4–5 rings) PAHs averaged 59.67 % of the Σ PAHs. Individual PAH concentrations were not significantly correlated with total organic carbon, possibly due to the semi-continuous inputs from anthropogenic sources. Source identification studies suggest that the PAHs were mainly from motor vehicles and biomass/coal combustion. The incremental lifetime cancer risks associated with exposure to PAHs in the dustfall ranged from 10^{-4} to

10^{-6} ; these indicate potentially serious carcinogenic risks for exposed populations in the industrial corridor.

Keywords Polycyclic aromatic hydrocarbons (PAHs) · Dustfall · Industrial corridor · Source apportionment · Health risk assessment

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are neutral, nonpolar, organic compounds composed of two or more fused aromatic rings, and 16 PAHs have been placed on a priority control list by the US Environmental Protection Agency (US-EPA) because of their carcinogenic and mutagenic properties (Yang et al. 2013; Kwon and Choi 2014). PAHs in the environment mainly originate from anthropogenic activities, especially the burning of organic materials (e.g., fossil fuels, wood, and straw), many industrial processes

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(Peng et al. 2011), and motor vehicle emissions (Lee and Dong 2010) although smaller amounts are produced by forest fires and volcanic eruptions (Ravindra et al. 2008).

Polycyclic aromatic hydrocarbons are ubiquitous environmental contaminants, and they have been found in a variety of media, including, soils, sediments, and surface dust (Khairy and Lohmann 2013; Xing et al. 2011; Wang et al. 2011). Atmospheric processes are largely responsible for the transport and deposition of PAHs (Fang et al. 2004), and these aromatic hydrocarbons adhere to both atmospheric aerosols and dustfall. Indeed, dustfall has been regarded as an important carrier of PAHs (Lian et al. 2008; Wu et al. 2005), and the deposition of airborne particulate matter leads to the transfer of PAHs from the air to the earth's surface. In urban and industrial areas, some toxic compounds carried by dustfall can be transferred to surface structures including buildings and streets, and this poses a threat to human health (Lian et al. 2008).

With the rapid development of industrialization and urbanization in China, the problems of environmental pollution caused by PAHs have become increasingly serious, and the high concentrations of these substances have serious implications for human health, ecological systems, and the environment (Yang et al. 2013; Xing et al. 2011; Peng et al. 2011). Hubei Province, located in central China, is an important base for traffic, agriculture, and industry. The area we studied is mainly composed of three small- to medium-scale industrial cities (Ezhou, Huangshi, and Daye) which form a metal-working corridor in the southeastern part of the province that exacerbates the problems associated with environmental pollution. Studies of PAHs in the industrial corridor will make it possible to evaluate the contributions of the heavy industries and transportation to the atmospheric burdens of PAHs. Furthermore, it is equally important to evaluate the human health risks associated with exposure to PAHs in the region. Therefore, the objectives of the present study were as follows: (a) to investigate the concentrations and distribution of 16 priority PAHs in atmospheric dustfall from the industrial corridor; (b) to determine the potential sources for the PAHs; and (c) to evaluate the potential cancer risks of PAHs using the incremental lifetime cancer risk approach.

Methodology

Sampling

The locations of the sampling stations for the study are shown in Fig. 1. Thirty atmospheric dustfall samples were collected from the famous industrial corridor of Hubei Province during May 2012. The dustfall samples were collected 1.2–1.5 m above the floor from various surfaces (shelves, window sills, etc.), using a brush and a dust pan on sunny, windless days. Samples were put into small sealable plastic bags and later air-dried in the laboratory. They were then processed with a 100- μm sieve to remove coarse debris and small stones.

Analysis of PAHs

The compounds measured were 16 USEPA priority PAHs: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenzo[a,h]anthracene (DBA), and benzo[g,h,i]perylene (BghiP).

After sieving, 10 g of each soil sample was spiked with 5 μL (200 $\mu\text{g}/\text{mL}$) mixed-recovery surrogates (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12), and the spiked sample was then extracted with dichloromethane (DCM) using soxhlet apparatus for 24 h. Elemental sulfur was removed by adding activated copper granules to the collection flasks. The sample extract was concentrated and the solvent exchanged with hexane and further reduced to 2–3 mL with the use of a rotary evaporator (Heidolph4000, Germany). A 1:2 (v/v) alumina/silica gel column (48-h extraction with DCM, then 180 and 240 $^{\circ}\text{C}$ muffle drying for 12 h, both deactivated 3 % with H_2O before use) was used to clean-up the extract; then the PAHs were eluted with 30 mL of DCM/hexane (2:3). The eluate was concentrated to 0.2 mL under a gentle nitrogen stream. Prior to analysis, a known quantity (1,000 ng) of hexamethylbenzene was added to the eluates as an internal standard.

PAHs were analyzed with the use of a gas chromatograph-mass spectrometer (GC-MS, 7890A/

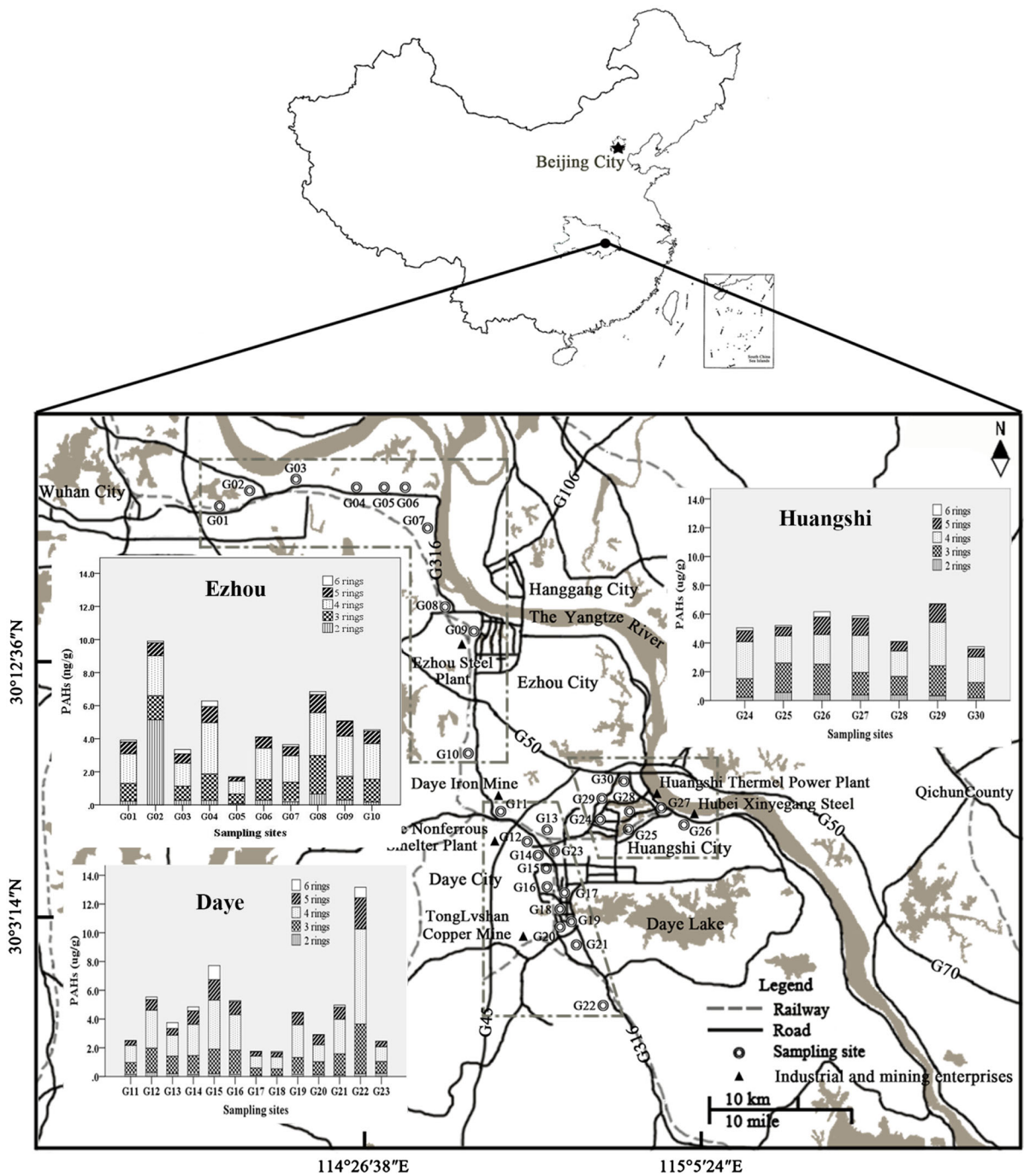


Fig. 1 Sampling sites for the atmospheric dustfall samples

5975MSD, Agilent Technologies, Santa Clara, CA, USA) equipped with a DB-5 capillary column (30 m × 0.25 mm i.d × 0.25 μm film thickness). The instrument was operated using electron impact

(EI) ionization at 70 Ev and in the selected ion monitoring (SIM) mode. The chromatographic conditions were as follows: injector temperature 270 °C and detector temperature 280 °C. The oven

temperature program was kept at 60 °C for 5 min and increased to 290 °C at a rate of 5 °C/min and kept at 290 °C for 20 min. The high-purity He carrier gas was delivered at a constant flow rate of 1.0 mL/min.

Quality assurance and quality control

Procedural blanks, spiked blanks, and sample duplicates (analyzed at a rate of 20 % of the total samples) were analyzed to evaluate the precision of the analyses. The PAHs found in the field blanks were generally below the limits of detection (LOD), which were defined as the amount of an analyte that would generate a signal-to-noise ratio of 3:1. No target PAHs were detected in any of the procedural blanks. The variations in PAH concentrations in duplicate samples

tweezers for CHN analysis (ELEMENTAR Vario EL Hanau, Germany). Samples were analyzed in duplicate, and the average percentages of total organic carbon (TOC) were calculated.

Risk assessment

Incremental lifetime cancer risks (ILCR) were calculated as a means of quantitatively evaluating the integrated lifetime risks of exposure to PAHs in atmospheric dustfall from the industrial corridor. The ILCRs for exposure by ingestion, dermal contact, and inhalation were calculated as probabilities from the following equations, which were adapted from the USEPA standard models (Peng et al. 2011; Chen and Liao 2006; USEPA 1991):

$$\text{ILCR}_{\text{Ingestion}} = \frac{\text{CS} \times (\text{CSF}_{\text{Ingestion}} \times \sqrt[3]{(\text{BW}/70)}) \times \text{IR}_{\text{Ingestion}} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT} \times 10^6} \quad (1)$$

$$\text{ILCR}_{\text{Dermal}} = \frac{\text{CS} \times (\text{CSF}_{\text{Dermal}} \times \sqrt[3]{(\text{BW}/70)}) \times \text{SA} \times \text{AF} \times \text{ABS} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT} \times 10^6} \quad (2)$$

$$\text{ILCR}_{\text{Inhalation}} = \frac{\text{CS} \times (\text{CSF}_{\text{Inhalation}} \times \sqrt[3]{(\text{BW}/70)}) \times \text{IR}_{\text{Inhalation}} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT} \times \text{PEF}} \quad (3)$$

were <15 %. Minimum detection limits (MDLs) for the 16 PAHs were in the range of 0.27–0.78 ng/g dry weight. Representative average percentage recoveries (arithmetic mean \pm SD) were 58 ± 6 , 82 ± 9 , 108 ± 10 , 112 ± 13 , and 118 ± 11 % for naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12, respectively.

Determination of total organic carbon

The samples were pretreated with 10 % HCl to remove carbonates. After each acid-pretreatment step, the residues were centrifuged and rinsed with deionized water. The retentates from the final pre-treatment step were dried in an oven at 50 °C for 6 h for total carbon analysis. A 5 mg subsample was placed into a tin capsule, which was folded and compressed with

In these equations, CS is the sum of BaP equivalent concentration (BaP_{eq} in $\mu\text{g}/\text{kg}$), BaP_{eq} is the product of the concentration of individual PAH compound and its corresponding toxic equivalence factor (TEF) (Table 1); CSF is the carcinogenic slope factor ($1/(\text{mg}/\text{kg}/\text{day})$); BW is the average body weight (kg); AT is the average life span (days); EF is the exposure frequency (days/year); ED is the exposure duration (year); $\text{IR}_{\text{Ingestion}}$ is the ingestion rate of soil (mg/day); $\text{IR}_{\text{Inhalation}}$ is the inhalation rate (m^3/day); SA is the surface area of the skin that contacts the soil (cm^2/day); AF is the skin adherence factor for soil (mg/cm^2); ABS is the dermal absorption factor (chemical specific); and PEF is the particle emission factor (m^3/kg).

Carcinogenic slope factors (SCF) based on the cancer-causing ability of BaP were parameterized as

Table 1 PAHs concentrations ($\mu\text{g/g}$) in atmospheric dustfall from the industrial corridor of Hubei Province

Compound	Abbreviation	Aromatic rings	TEF	Minimum	Maximum	Mean	Median	SD	
Naphthalene	Nap	2	0.001	0.07	5.14	0.41	0.21	0.90	
Acenaphthylene	Acy	3	0.001	0.02	0.52	0.09	0.08	0.09	
Acenaphthene	Ace	3	0.001	0.01	0.15	0.04	0.03	0.03	
Fluorene	Flu	3	0.001	0.04	0.32	0.14	0.13	0.07	
Phenanthrene	Phe	3	0.001	0.32	2.44	1.03	0.97	0.44	
Anthracene	Ant	3	0.01	0.02	0.17	0.08	0.07	0.04	
Fluoranthene	Fla	4	0.001	0.35	3.11	1.04	0.99	0.53	
Pyrene	Pyr	4	0.001	0.02	2.20	0.64	0.57	0.39	
Benzo[a]anthracene	BaA	4	0.1	0.04	0.65	0.21	0.20	0.12	
Chrysene	Chr	4	0.01	0.09	0.65	0.25	0.22	0.14	
Benzo[b]fluoranthene	BbF	5	0.1	0.08	0.86	0.31	0.29	0.18	
Benzo[k]fluoranthene	BkF	5	0.1	0.06	0.58	0.20	0.19	0.10	
Benzo[a]pyrene	BaP	5	1	0.08	0.69	0.26	0.24	0.13	
Indeno[1,2,3-cd]pyrene	IcdP	6	0.1	0.01	0.53	0.09	0.04	0.12	
Dibenzo[a,h]anthracene	DBA	5	1	N.D. ^a	0.17	0.02	0.01	0.03	
Benzo[g,h,i]perylene	BghiP	6	0.01	N.D.	0.49	0.09	0.05	0.13	
				LMW PAHs ^b	0.52	6.60	1.80	1.54	1.14
				HMW PAHs ^c	1.00	8.78	2.93	3.01	1.47
				Σ PAHs ^d	1.72	13.17	4.91	4.69	2.41

^a N.D. stands for not detected

^b Low molecular weight 2–3 ring PAHs

^c High molecular weight 4–5 ring PAHs

^d Total concentrations of 16 individual PAHs

7.3, 25, and 3.85 (1/(mg/kg/day)) for ingestion, dermal contact, and inhalation, respectively (Peng et al. 2011). Cancer risks were estimated for three age groups: childhood (0–10 years), adolescence (11–18 years), and adulthood (19–70 years). Moreover, the cancer risks for males and females were calculated separately. Details of the values of the exposure parameters used to derive the ILCRs are shown in Table 2. Total risks were estimated as the sum of the individual risks for the three exposure routes.

Statistical analysis

Correlation analyses, principal component analyses (PCA), and other statistical procedures were applied to the geochemical data using SPSS 18.0 and Origin 8.0. The correlation analyses were used investigate relationships between individual PAHs and between the

PAHs and TOC. The PCA analyses were used to identify presumptive sources for the PAHs.

Results and discussion

Concentrations of PAHs

The statistical data for the individual PAHs and total PAHs in atmospheric dustfall from the industrial corridor are summarized in Table 1. The total concentrations of 16 individual PAHs (Σ PAHs) exhibited a rather moderate level of variability, ranging over roughly one order-of-magnitude from 1.72 (at G05) to 13.17 $\mu\text{g/g}$ (at G22) with an arithmetic mean of 4.91 $\mu\text{g/g}$. The mean concentrations ($\mu\text{g/g}$) of individual PAHs increased in the following order: DBA (0.02) < Ace (0.04) < Ant (0.08) < IcdP (0.09) < Acy (0.09) < BghiP (0.09) < Flu (0.14) < BkF (0.20) < BaA (0.21) < Chr (0.25) < BaP

Table 2 Parameters used for the estimation of the incremental lifetime cancer risks (ILCRs)

Exposure parameters	Unit	Childhood		Adolescence		Adulthood		References
		Male	Female	Male	Female	Male	Female	
Body weight (BW) ^a	kg	14.3	13.6	48.1	45.4	62.8	54.7	MHC (2007)
Ingestion rate (IR _{ingestion})	mg/day	200	200	100	100	100	100	USDOE (2011)
Exposure frequency (EF)	days/year	350	350	350	350	350	350	USDOE (2011)
Exposure duration (ED)	years	6	6	14	14	30	30	Wang (2007)
Average life span (AT)	days	LT × 365	LT × 365	LT × 365	LT × 365	LT × 365	LT × 365	USDOE (2011)
Lifetime (LT)	years	72	72	72	72	72	72	WHO (2006)
Surface area (SA)	cm ² /day	2,800	2,800	2,800	2,800	5,700	5,700	USDOE (2011)
Dermal surface factor (AF)	mg/cm	0.2	0.2	0.2	0.2	0.07	0.07	USDOE (2011)
Dermal absorption factor (ABS)	unitless	0.13	0.13	0.13	0.13	0.13	0.13	USEPA (2002)
Inhalation rate (IR _{Inhalation})	m ³ /day	10.9	10.9	17.7	17.7	17.5	17.5	Wang (2007)
Particle emission factor (PET)	m ³ /kg	1.36 × 10 ⁹	1.36 × 10 ⁹	1.36 × 10 ⁹	1.36 × 10 ⁹	1.36 × 10 ⁹	1.36 × 10 ⁹	USDOE (2011)

^a Values based on the 2002 National nutrition and health survey

(0.26) < BbF (0.31) < Nap (0.41) < Pyr (0.64) < Phe (1.03) < Fla (1.04). The three most abundant PAHs, Fla, Phe, and Pyr, accounted for 21.18, 20.98, and 13.03 % of the ΣPAHs, respectively, on average. With reference to the number of aromatic rings, 2-, 3-, 4-, 5-, and 6-ring PAHs contributed averages of 8.27, 28.30, 43.62, 16.10, and 3.70 % to the ΣPAHs, respectively.

The concentrations of low-molecular weight PAHs (LMW PAHs: those with two or three aromatic rings) in the dustfall samples varied from 0.52 to 6.60 µg/g and had a mean of 1.80 µg/g. In comparison, the concentrations of high molecular weight PAHs (HMW PAHs: those with four or five aromatic rings) varied from 1.00 to 8.78 µg/g with a mean of 2.93 µg/g. In general, the HMW PAHs made greater contributions to the total PAH concentrations than the LMW PAHs; indeed, the HMW PAHs contributed an average of 59.67 % to the ΣPAHs. The LMW PAHs are more volatile than the HMW PAHs (Agarwal et al. 2009), and losses from the particles may have decreased the LMW PAH concentrations in the dustfall samples. In addition, the HMW PAHs have more emission sources compared with the LMW PAHs; these include domestic heating, industrial emissions, and agriculture-related activities (Xing et al. 2011). Therefore, our observations concerning the relative abundances

of LMW and HMW PAHs may be explained by the differences between the two groups in terms of their physicochemical properties and the emission sources.

Spatial distributions

To investigate the patterns in the spatial distributions of PAHs in the dustfall samples, the study area was separated into three regions: Ezhou, Daye, and Huangshi. The sampling sites G11 to G15 and G23, which are actually in the city of Huangshi, were assigned to Daye because they located along the No. 316 national highway. This highway (shown in Fig. 1) is an important transportation route, and it passes through the central urban regions of Ezhou and Daye.

The mean concentrations of ΣPAHs in Ezhou were similar to those in Daye, and these two regions both had lower PAH concentrations than Huangshi. Compared with Huangshi, stronger gradients in PAH concentrations were observed in the dustfall samples from Daye and Ezhou. The strengths of the gradients are manifest in the coefficients of variation for the PAHs, which followed the order Daye (65.36 %) > Ezhou (46.08 %) > Huangshi (20.59 %). Industrial and vehicle emissions increase the concentrations of ΣPAHs in urban surface dust (Wang et al. 2011), and therefore,

Table 3 Correlation coefficient matrix for individual PAHs and total organic carbon (TOC)

PAH	Nap	Acy	Ace	Flu	Phe	Ant	Fla	Pyr	BaA	Chr
Nap	1									
Acy	0.35	1								
Ace	0.75**	0.62**	1							
Flu	0.80**	0.66**	0.91**	1						
Phe	0.52**	0.67**	0.67**	0.79**	1					
Ant	0.72**	0.69**	0.88**	0.93**	0.66**	1				
Fla	0.38*	0.71**	0.55**	0.65**	0.91**	0.54**	1			
Pyr	0.29	0.58**	0.47**	0.54**	0.79**	0.45*	0.90**	1		
BaA	0.50**	0.75**	0.73**	0.77**	0.68**	0.86**	0.69**	0.64**	1	
Chr	0.47**	0.35	0.58**	0.49**	0.29	0.56**	0.31	0.35	0.49**	1
BbF	0.27	0.81**	0.49**	0.58**	0.83**	0.57**	0.86**	0.79**	0.72**	0.33
BkF	0.49**	0.66**	0.59**	0.61**	0.55**	0.64**	0.64**	0.50**	0.72**	0.58**
BaP	0.38*	0.79**	0.59**	0.65**	0.75**	0.69**	0.83**	0.74**	0.86**	0.32
IcdP	-0.04	0.18	-0.02	0.12	0.43*	0.08	0.47**	0.39*	0.19	-0.05
DBA	0.10	0.52**	0.19	0.27	0.47**	0.31	0.51**	0.39*	0.46*	0.09
BghiP	0.20	0.01	0.15	0.23	0.49**	0.11	0.42*	0.45*	0.23	0.11
LMW PAHs	0.72**	0.72**	0.80**	0.91**	0.91**	0.78**	0.83**	0.72**	0.75**	0.44*
HMW PAHs	0.47**	0.71**	0.63**	0.71**	0.86**	0.65**	0.94**	0.91**	0.79**	0.47**
ΣPAHs	0.61**	0.73**	0.71**	0.82**	0.91**	0.72**	0.92**	0.84**	0.81**	0.45*
TOC	0.41*	0.13	0.31	0.26	0.20	0.21	0.07	-0.11	0.05	0.23

PAH	BbF	BkF	BaP	IcdP	DBA	BghiP	LMW PAHs	HMW PAHs	ΣPAHs
Nap									
Acy									
Ace									
Flu									
Phe									
Ant									
Fla									
Pyr									
BaA									
Chr									
BbF	1								
BkF	0.58**	1							
BaP	0.84**	0.79**	1						
IcdP	0.44*	0.27	0.34	1					
DBA	0.62**	0.43*	0.55**	0.58**	1				
BghiP	0.31	0.30	0.31	0.55**	0.43*	1			
LMW PAHs	0.73**	0.64**	0.73**	0.23	0.44*	0.41*	1		
HMW PAHs	0.88**	0.71**	0.89**	0.41*	0.49**	0.43*	0.83**	1	
ΣPAHs	0.83**	0.71**	0.85**	0.34	0.51**	0.47**	0.95**	0.94**	1
TOC	0.11	0.19	0.04	-0.26	-0.25	-0.24	0.20	0.08	0.12

* Correlation is significant at the 0.05 level (two-tailed); ** Correlation is significant at the 0.01 level (two-tailed)

the heavy traffic in Ezhou and Daye presumably contributed to their greater variability in PAHs.

The levels of PAHs in atmospheric dustfall varied greatly between the different sampling sites in the three regions. As shown in Fig. 1. The highest concentration of Σ PAHs was measured at G20 in Daye City. That site is located in an industrial area surrounded by a small smelter and an ore dressing plant where the high Σ PAHs concentrations presumably combined with PAHs from industrial releases and motor vehicle emissions. In contrast to the essentially uncontrolled emissions from these sources, a large factory in the region has established a systematic program for controlling and monitoring production activities. The sites near this large factory (G09, G11, G12, and G20) did not exhibit the same high levels of PAHs seen at G20.

Correlations between individual PAHs and between PAHs and TOC

Correlations between the individual PAHs were calculated and examined as a means of assessing whether specific compounds were likely to have originated from the same sources (Yang et al. 2012). A matrix of correlation coefficients among the individual PAHs (Table 3) showed that most of the compounds, especially the LMW PAHs, were significantly positively correlated with one another. In contrast, some of the HMW PAHs, including IcdP, DBA, and BghiP, were not significantly correlated with these compounds or with other members of the HMW group. This is an indication that these two groups of PAHs originated from the different sources. The vapor pressures of semi-volatile organic compounds, including organochlorine pesticides (OCPs) and PAHs, are critical determinants of their vapor-particle partitioning. This means that vapor pressure will affect the propensity for these compounds to be mobilized by long-range atmospheric transport and eventually to be transferred to soils, both directly and indirectly (Agarwal et al. 2009). As LMW PAHs exhibit higher vapor pressures and hence greater atmospheric mobility than the heavier compounds, they are more easily distributed by atmospheric transportation processes (Chung et al. 2007).

TOC has been shown to be important for the sorption, sequestration, and fate of PAHs (Jiang et al.

2009; Agarwal et al. 2009). The TOC concentrations in our study varied between 1.97 and 14.77 %, with a mean value of 5.64 %. As shown in Table 3, no significant correlations were found between the individual PAHs and TOC, except for a relatively weak correlation (correlation coefficient, $r = 0.41$) between TOC and Nap. Some researchers have previously reported that no significant correlations were observed between TOC and PAHs in soil and dustfall samples (Wang et al. 2013; Jiang et al. 2009; Zhang et al. 2006; Wu et al. 2005). The lack of correlation between TOC and PAHs might be a result of non-steady state partitioning (Wang et al. 2013; Jiang et al. 2009); that is, a semi-continuous input of fresh contaminants would prevent sorption–desorption processes from reaching a steady state (Katsoyiannis 2006). In summary, the lack of correlations in our study suggests that the dustfall samplers were greatly affected by the inputs of anthropogenic PAHs, especially those from traffic emissions and biomass/coal combustion, and that steady state partitioning was not reached.

Source identification

We used compositional pattern analysis, molecular composition analysis, and principal component analysis to identify the possible source for PAHs in atmospheric dustfall of the study area. The identification of likely sources for PAHs is important not only for understanding the patterns in the data from this study but also for developing scenarios of what might be expected as emissions change in the future.

Composition pattern analysis

Two of the main anthropogenic sources of PAHs are combustion processes and the incomplete combustion of petroleum products (Xing et al. 2011). Of the PAHs released by combustion, LMW PAHs are produced primarily at low to moderate temperatures, while HMW PAHs are generated at higher temperatures (Wang et al. 2006). Therefore, large relative abundances of LHM PAHs indicate that more of the PAHs originated from petrogenic sources while in contrast, high relative abundances of HMW PAHs can be explained by greater impacts from pyrogenic sources. In our study, the average LHM/HMW PAH ratios at all sites (except G02 and G25) were above unity,

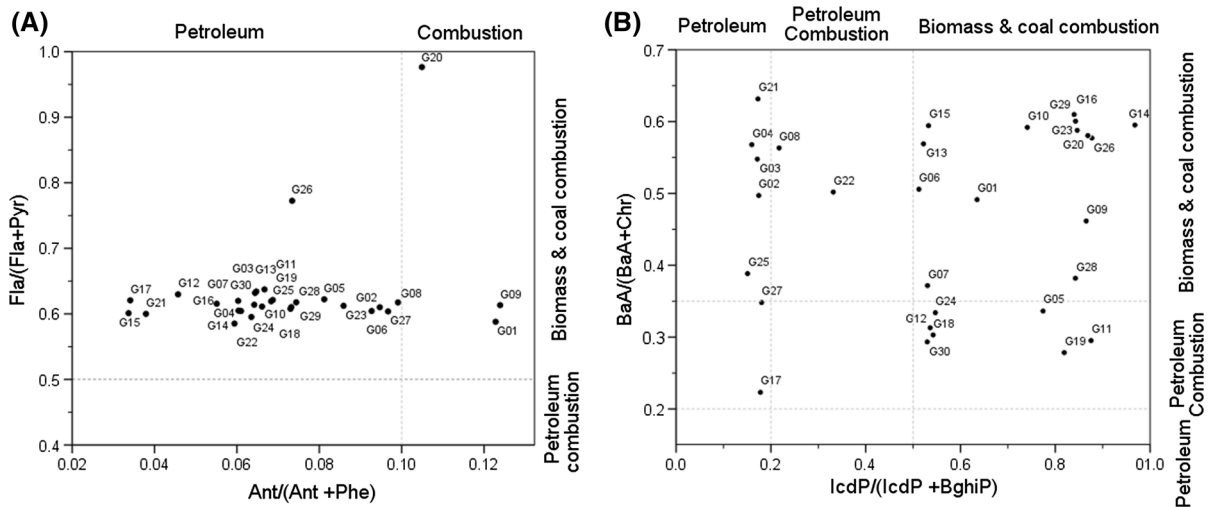


Fig. 2 Scatterplot of molecular indices used to identify PAH sources: **a** Fla/(Fla + Pyr) versus Ant/(Ant + Phe) and **b** BaA/(BaA + Chr) versus IcdP/(IcdP + BghiP)

suggesting that combustion was a greater influence on the PAH contaminants than petrogenic emissions.

Molecular composition analysis

Molecular indices based on ratios of individual PAH congeners have been used to discriminate between petrogenic and pyrolytic sources. In particular, the ratios of Ant/(Ant + Phe), Fla/(Fla + Pyr), IcdP/(IcdP + BghiP), and BaA/(BaA + Chr) have been used for this purpose (Kwon and Choi 2014; Yang et al. 2012; Xing et al. 2011; Wang et al. 2011). Scatterplots of the ratios of selected PAH congeners were drawn based on the principle of molecular indices (Xing et al. 2011; Wang et al. 2011), and these PAH congener-pair relationships were employed to evaluate the PAH sources.

The scatterplot for Ant/(Ant + Phe) and Fla/(Fla + Pyr) (Fig. 2a) shows that the data for twenty-seven of the sampling sites (all except G01, G09, and G20) were influenced by petroleum and coal/biomass combustion, and this finding suggests that the PAHs mainly originated from motor vehicular emissions and biomass/coal combustion. This result is in agreement with the conclusions from studies in Guangzhou and Shanghai that vehicular emissions and biomass/coal combustion were the main contributors to PAHs in urban surface dusts (Wang et al. 2011; Liu et al. 2007). The ratios of BaA/(BaA + Chr) in our study ranged from 0.22 to 0.65 (Fig. 2b), suggesting that the PAHs

were derived from the combustion of petroleum and biomass. However, the ratios of IcdP/(IcdP + BghiP) were concentrated in two areas of the plots, and this is consistent with mixtures of petrochemicals and coal/biomass burning products (Fig. 2b).

From the patterns in the congener-pair ratios, we can conclude that the PAHs in the dustfall were not dominated by a single source. Local human activities undoubtedly are the greatest influence on pollutant concentrations and overall a major influence on the environmental chemistry of the study area. For instance, several large factories, including the Ezhou Steel Plant and Daye Nonferrous Smelter Plant, consume large amounts of energy and release substantial levels of pollutants. In addition, the No. 316 national highway, as the lifeline of the industrial corridor, bears a heavy burden of transportation. Recent statistics reported by National Bureau of Statistics of China show that coal remains the predominant energy source, accounting for ~ 76.7 percent of China's energy consumption (NBSC 2009). In any case, the sources of PAHs clearly are complex and their concentrations are affected by many factors, including industrial activity, transportation, day-to-day human routines, and so on.

Principal component analysis

Three principal components (PC1, PC2, and PC3) with the eigenvalues >1 were extracted, and they collectively accounted for the majority (79.46 %) of the total

Table 4 Principal components for the individual PAHs (factor loadings greater than 0.5 are shown in bold)

Variable	Principal component		
	PC1	PC2	PC3
Nap	-0.07	0.42	-0.05
Acy	0.81	0.30	0.08
Ace	0.25	0.88	0.05
Flu	0.38	0.84	0.16
Phe	0.79	0.43	0.27
Ant	0.43	0.87	0.07
Fla	0.94	0.17	0.19
Pyr	0.96	0.09	0.01
BaA	0.78	0.57	-0.05
Chr	0.56	0.40	-0.41
BbF	0.84	0.17	0.23
BkF	0.79	0.41	0.10
BaP	0.87	0.33	0.22
IcdP	0.48	-0.26	0.73
DBA	0.13	0.26	0.82
BghiP	0.79	-0.17	0.17
Eigenvalue	7.35	3.68	1.68
% of variance	45.96	22.98	10.51
Cumulative %	45.96	68.95	79.46
Probable sources	Diesel and coal combustion	Low-temperature combustion	Traffic emission

variance in the Σ PAH concentration data (Table 4). PC1 explained 45.96 % of the total variance, and it had strong loadings of Acy, Phe, Fla, Pyr, BaA, BbF, BkF, BaP, and BghiP and moderate loadings of Chr. Of these Fla, Pyr, BaA, BaP, and Chr are the typical markers for coal combustion (Larsen and Baker 2003; Simcik et al. 1999), while BkF and BbF are components of fossil fuels and thus associated with their combustion products (Kavouras et al. 2001). BaA and Chr often originate from the combustion of both diesel fuels and natural gas (Khalili et al. 1995), and BghiP is associated with traffic emission (Fraser et al. 1997). Therefore, PC1 apparently represents mixed sources of petroleum and coal combustion.

PC2 accounted for 22.98 % of the total variance in the data: It was mainly loaded with Ace, Flu, and Ant, and had moderate loadings of Nap. Two of these PAHs, Flu and Ant, have been used as the indicators of

emissions from coke ovens (Yunker et al. 2002; Simcik et al. 1999). Furthermore, all four of these compounds are LMW PAHs, and so they presumably have significant contributions from low-temperature pyrogenic processes (Yang et al. 2012; Jenkins et al. 1996). Nap is one of the LMW PAHs that accounted for the majority of the PAH mass in a study conducted in Chicago, USA, of emissions from coke ovens, a highway tunnel, and gasoline engines (Khalili et al. 1995). Thus, PC2 apparently represents low-temperature combustion sources.

The last principal component extracted, PC3, accounted for 10.51 % of the total variance, and it had high loadings of IcdP and DBA. This factor probably represents road traffic because these two PAHs previously have been linked to motor vehicle emissions (Simcik et al. 1999; Fraser et al. 1997).

Health risk assessments

We calculated the incremental life cancer risks (ILCRs) associated with the contaminated dustfall with the aim of estimating the potential health risks to humans caused by PAH exposure through ingestion, dermal contact, and inhalation. The ILCRs calculated for the three exposures routes and the total ILCRs for each of the sampling sites are presented in Fig. 3. The cancer risks for PAHs for the different routes of exposure decreased in the following order: dermal contact > ingestion > inhalation (Fig. 3a). In fact, the cancer risks calculated for the inhalation of PAHs on resuspended particles ranged from 10^{-9} to 10^{-11} , approximately 10^{-3} – 10^{-6} times lower than those for ingestion or dermal contact. Therefore, the cancer risks calculated for the inhalation of resuspended particles contaminated with PAHs would be vanishingly small in comparison with those for the other exposure routes. The differences between the ILCRs stratified by gender for persons of the same age group were not significant. On the other hand, the ILCRs for children or adulthood were higher than for adolescence, suggesting that adolescents have the lowest health risks of three age groups. Hu et al. (2014) similarly observed that the cancer risk for youths exposed to OCP contaminated soils were less than for children or adults.

In terms of regulatory concerns, minimal risks are indicated by an ILCR of 10^{-6} or less, while an ILCR

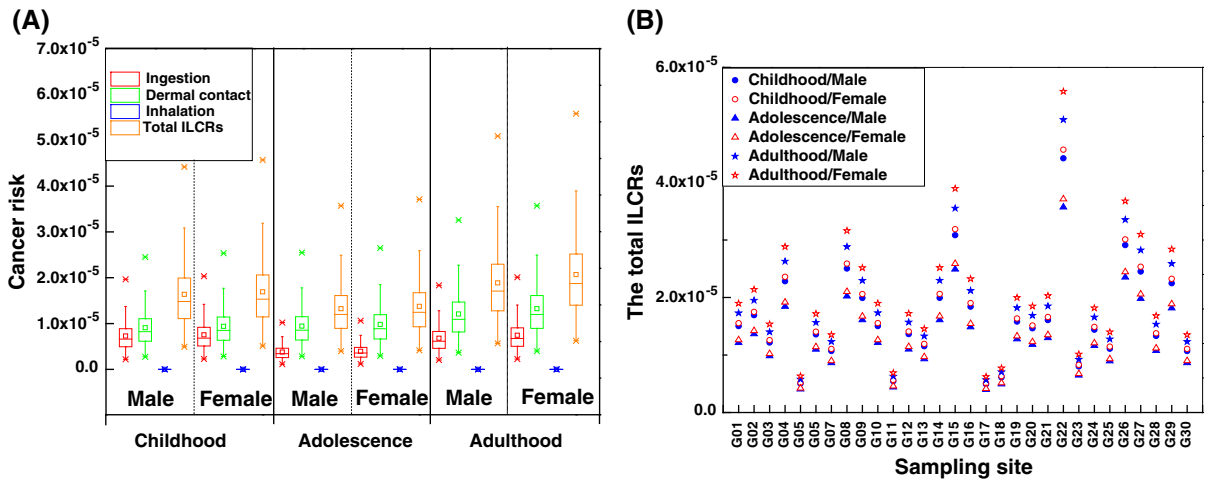


Fig. 3 Incremental lifetime cancer risks (ILCRs) calculated for atmospheric dustfall: **a** ILCRs for three exposures routes and **b** total ILCRs stratified by age group and gender at the sampling sites

between 10^{-6} and 10^{-4} signifies potential human health risks; higher risks have been connected to ILCRs larger than 10^{-4} (Chen and Liao 2006). In this study, the total ILCRs for the three age groups fluctuated from 10^{-6} to 10^{-4} , indicating a potential carcinogenic risk for the residents who are exposed to the atmospheric dustfall, especially by contact. As shown in Fig. 3b, the total ILCRs for the regions with the high PAH concentrations tend to have more serious cancer risks. Nonetheless, it is important to point out that the sampling site (G02) with the second-highest Σ PAH concentration did not have particularly high total ILCRs; this can be explained by the high proportion of LMW PAHs at the site, which tend to be less harmful. As to the toxicity of individual PAHs (BaPeq), BaP accounted for the largest fraction of the total PAH BaPeq (range 54.14–78.08 %; mean = 71.60 %), and therefore, BaP made the greatest contribution to the overall ILCRs. BaP has been used a tracer for vehicular emissions (Khairy and Lohmann 2013), and therefore, one can infer that PAHs emitted from motor vehicles play a significant role relative to cancer risks. This finding has important implications the formulation of effective environmental health protection policies.

Summary and conclusions

Sixteen priority PAHs in atmospheric dustfall from the industrial corridor of Hubei Province were analyzed to

investigate their spatial distributions, possible sources, and health risks. The total concentrations of 16 PAHs ranged from 1.72 to 13.17 $\mu\text{g/g}$ with a mean of 4.91 $\mu\text{g/g}$. The highest concentrations of PAHs were found in an industrial area surrounded by small smelter and ore dressing plant. However, other sites near the factory did not have especially high Σ PAH concentrations. The dustfall samples showed a common pattern in terms of PAH composition; that is, the HMW PAHs averaged 59.67 % of the Σ PAHs, and thus, heavier compounds were more abundant than the LMW PAHs.

Source identification studies indicated that motor vehicle emissions and biomass/coal combustion were the major sources for PAHs in dustfall from the industrial corridor. The individual PAH concentrations were not significantly correlated with TOC, and therefore, TOC cannot be used as an indicator of the levels of PAHs in the industrial corridor. Incremental life cancer risks (ILCRs) were calculated to evaluate the potential risks associated with exposure PAHs in dustfall from the area. The ILCRs fluctuated within the range of 10^{-6} – 10^{-4} , and this is strong evidence that there are potentially serious carcinogenic risks for exposed populations in the industrial corridor.

The ILCRs indicate that the exposure to PAHs from the inhalation of contaminated particles presented a much smaller risk than either ingestion of the PAHs or exposure through dermal contact, which had the highest ILCRs. It should be noted, however, that the ILCRs were calculated for only for the PAHs in

dustfall, and the risks from exposure to the vapor-phase fractions of the PAHs were not considered. The first implication of this limitation is that the combined cancer risks from exposure to the particle-bound and vapor-phase PAHs will be higher than those calculated here, and the second is that the relative risks of the three routes of exposure may change. The partitioning of PAHs between the particulate and vapor phases also will vary with temperature (Lang et al. 2007), and so in addition to seasonal changes in PAH sources and sinks, weather and climate also will play a role in exposure and the effects of PAHs on human health.

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References

- Agarwal, T., Khillare, P., Shridhar, V., & Ray, S. (2009). Pattern, sources and toxic potential of PAHs in the agricultural soils of Delhi, India. *Journal of Hazardous Materials*, *163*(2), 1033–1039.
- Chen, S. C., & Liao, C. M. (2006). Health risk assessment on human exposed to environmental polycyclic aromatic hydrocarbons pollution sources. *Science of the Total Environment*, *366*(1), 112–123.
- Chung, M., Hu, R., Cheung, K., & Wong, M. (2007). Pollutants in Hong Kong soils: Polycyclic aromatic hydrocarbons. *Chemosphere*, *67*(3), 464–473.
- Fang, G. C., Chang, C. N., Wu, Y. S., Fu, P. P. C., Yang, I. L., & Chen, M. H. (2004). Characterization, identification of ambient air and road dust polycyclic aromatic hydrocarbons in central Taiwan, Taichung. *Science of the Total Environment*, *327*(1), 135–146.
- Fraser, M. P., Cass, G. R., Simoneit, B. R., & Rasmussen, R. (1997). Air quality model evaluation data for organics. 4. C2-C36 non-aromatic hydrocarbons. *Environmental Science and Technology*, *31*(8), 2356–2367.
- Hu, W., Huang, B., Zhao, Y., Sun, W., & Gu, Z. (2014). Distribution, sources and potential risk of HCH and DDT in soils from a typical alluvial plain of the Yangtze River Delta region, China. *Environmental Geochemistry and Health*, *36*(3), 345–358.
- Jenkins, B. M., Jones, A. D., Turn, S. Q., & Williams, R. B. (1996). Emission factors for polycyclic aromatic hydrocarbons from biomass burning. *Environmental Science and Technology*, *30*(8), 2462–2469.
- Jiang, Y. F., Wang, X. T., Wang, F., Jia, Y., Wu, M. H., & Sheng, G. Y. (2009). Levels, composition profiles and sources of polycyclic aromatic hydrocarbons in urban soil of Shanghai, China. *Chemosphere*, *75*(8), 1112–1118.
- Katsoyiannis, A. (2006). Occurrence of polychlorinated biphenyls (PCBs) in the Soulou stream in the power generation area of Eordea, northwestern Greece. *Chemosphere*, *65*(9), 1551–1561.
- Kavouras, I. G., Koutrakis, P., Tsapakis, M., Lagoudaki, E., Stephanou, E. G., Von Baer, D., et al. (2001). Source apportionment of urban particulate aliphatic and polynuclear aromatic hydrocarbons (PAHs) using multivariate methods. *Environmental Science and Technology*, *35*(11), 2288–2294.
- Khairy, M. A., & Lohmann, R. (2013). Source apportionment and risk assessment of polycyclic aromatic hydrocarbons in the atmospheric environment of Alexandria, Egypt. *Chemosphere*, *91*(7), 895–903.
- Khalili, N. R., Scheff, P. A., & Holsen, T. M. (1995). PAH source fingerprints for coke ovens, diesel and gasoline engines, highway tunnels, and wood combustion emissions. *Atmospheric Environment*, *29*(4), 533–542.
- Kwon, H. O., & Choi, S. D. (2014). Polycyclic aromatic hydrocarbons (PAHs) in soils from a multi-industrial city, South Korea. *Science of the Total Environment*, *470–471*, 1494–1501.
- Lang, C., Tao, S., Wang, X., Zhang, G., Li, J., Jiamo, F., et al. (2007). Seasonal variation of polycyclic aromatic hydrocarbons (PAHs) in Pearl River Delta region, China. *Atmospheric Environment*, *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. *Environmental Science and Technology*, *37*(9), 1873–1881.
- Lee, B. K., & Dong, T. T. (2010). Effects of road characteristics on distribution and toxicity of polycyclic aromatic hydrocarbons in urban road dust of Ulsan, Korea. *Journal of Hazardous Materials*, *175*(1), 540–550.
- Lian, J. J., Ren, Y., Chen, J. M., Wang, T., & Cheng, T. T. (2008). Distribution and source of alkyl polycyclic aromatic hydrocarbons in dustfall in Shanghai, China: The effect on the coastal area. *Journal of Environmental Monitoring*, *11*(1), 187–192.
- Liu, M., Cheng, S., Ou, D., Hou, L., Gao, L., Wang, L., et al. (2007). Characterization, identification of road dust PAHs in central Shanghai areas, China. *Atmospheric Environment*, *41*(38), 8785–8795.
- MHC. (2007). Ministry of Health of China. Health Statistical Yearbook of China 2007.
- NBSC. (2009). National Bureau of Statistics of China. Statistical Yearbook of China 2009.
- Peng, C., Chen, W., Liao, X., Wang, M., Ouyang, Z., Jiao, W., et al. (2011). Polycyclic aromatic hydrocarbons in urban soils of Beijing: Status, sources, distribution and potential risk. *Environmental Pollution*, *159*(3), 802–808.
- Ravindra, K., Sokhi, R. S., & Van Grieken, R. (2008). Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. *Atmospheric Environment*, *43*(13), 2895–2921.
- Simcik, M. F., Eisenreich, S. J., & Liroy, P. J. (1999). Source apportionment and source/sink relationships of PAHs in

- the coastal atmosphere of Chicago and Lake Michigan. *Atmospheric Environment*, 33(30), 5071–5079.
- USDOE. (2011). U.S. Department of Energy's Oak Ridge Operations Office (ORO). The Risk Assessment Information System (RAIS).
- USEPA. (1991). Risk Assessment Guidance for Superfund, Volume 1, Human Health Evaluation Manual (Part B, Development of Risk-based Preliminary Remediation Goals). EPA/540/R-92/003 Publication 9285.7e01B.
- USEPA. (2002). US Environmental Protection Agency, Washington, DC, USA. Supplemental guidance for developing soil screening levels for superfund sites OSWER 9355.4-24.
- Wang, Z. (2007). *Regional study on soil polycyclic aromatic hydrocarbons in Liaoning: Patterns, sources and cancer risks*. Dalian: Dalian University of Technology.
- Wang, W., Huang, M. J., Kang, Y., Wang, H. S., Leung, A. O., Cheung, K. C., et al. (2011). Polycyclic aromatic hydrocarbons (PAHs) in urban surface dust of Guangzhou, China: Status, sources and human health risk assessment. *Science of the Total Environment*, 409(21), 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. *Science of the Total Environment*, 447, 80–89.
- Wang, X. P., Yao, T. D., Cong, Z. Y., Yan, X. L., Kang, S. C., & Zhang, Y. (2006). Gradient distribution of persistent organic contaminants along northern slope of central-Himalayas, China. *Science of the Total Environment*, 372(1), 193–202.
- WHO. (2006). World Health Organization. Working together for health (World Health Reports). <http://www.who.int/whr/2006/en/>.
- Wu, S., Tao, S., Xu, F., Dawson, R., Lan, T., Li, B., et al. (2005). Polycyclic aromatic hydrocarbons in dustfall in Tianjin, China. *Science of the Total Environment*, 345(1), 115–126.
- Xing, X. L., Qi, S., Zhang, J., Wu, C., Zhang, Y., Yang, D., et al. (2011). Spatial distribution and source diagnosis of polycyclic aromatic hydrocarbons in soils from Chengdu Economic Region, Sichuan Province, western China. *Journal of Geochemical Exploration*, 110(2), 146–154.
- Yang, D., Qi, S., Zhang, Y., Xing, X., Liu, H., Qu, C., et al. (2013). Levels, sources and potential risks of polycyclic aromatic hydrocarbons (PAHs) in multimedia environment along the Jinjiang River mainstream to Quanzhou Bay, China. *Marine Pollution Bulletin*, 76(1), 298–306.
- Yang, B., Xue, N., Zhou, L., Li, F., Cong, X., Han, B., et al. (2012). Risk assessment and sources of polycyclic aromatic hydrocarbons in agricultural soils of Huanghuai plain, China. *Ecotoxicology and Environmental Safety*, 84, 304–310.
- 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. *Organic Geochemistry*, 33(4), 489–515.
- Zhang, H., Luo, Y., Wong, M., Zhao, Q., & Zhang, G. (2006). Distributions and concentrations of PAHs in Hong Kong soils. *Environmental Pollution*, 141(1), 107–114.