

# Identification of polycyclic aromatic hydrocarbons in soils in Taizhou, East China

Guanjiu Hu · Sulan Chen · Wei Shi ·  
Beibei Zhang · Yong Zhang · Juan Huang ·  
Jun Chen · John P. Giesy · Hongxia Yu

Received: 15 July 2014 / Accepted: 9 November 2014 / Published online: 22 November 2014  
© Springer Science+Business Media Dordrecht 2014

**Abstract** Polycyclic aromatic hydrocarbons (PAHs) and their hazards in surface soil ( $n = 92$ ) were investigated in Taizhou, China, which is an area in East China famous for production and exporting of rice. Total concentrations of PAHs in soils ranged from  $2.3 \times 10^1$  to  $7.6 \times 10^2$  with a mean of  $1.8 \times 10^2$   $\mu\text{g}/\text{kg}$  (dry mass; dm). Concentrations of 16 PAHs reported here were less than those observed in most previous studies in China and other countries. Concentrations of individual PAH in fluvo-aquic soils were greater than those in paddy soils except

naphthalene. Fluoranthene and pyrene were dominant PAHs, which accounted for 19.7 and 13.3 % of the total mass of PAHs, respectively. Based on ratios of low molecular weight PAHs to high molecular weight PAHs, diagnostic ratios and principal component analysis, the predominant source of PAHs was combustion and pyrolysis, especially coal, natural gas, gasoline and diesel emissions from traffic, as well as burning of straw. Carcinogenic potencies of 13 samples were 1.1- to 2.9-fold greater than the target values promulgated by the Netherlands, indicating increased carcinogenic risks of soils from these sites. However, risks of cancer via accidental ingestion, dermal absorption and inhalation to humans posed by PAHs in soil were relatively small.

**Electronic supplementary material** The online version of this article (doi:[10.1007/s10653-014-9656-x](https://doi.org/10.1007/s10653-014-9656-x)) contains supplementary material, which is available to authorized users.

G. Hu · S. Chen · B. Zhang · Y. Zhang ·  
J. Huang · J. P. Giesy (✉)  
State Environmental Protection Key Laboratory of  
Monitoring and Analysis for Organic Pollutants in Surface  
Water, Jiangsu Environmental Monitoring Center, 241  
Fenghuang West Street, Nanjing 210036, People's  
Republic of China  
e-mail: jgiesy@aol.com

W. Shi · J. P. Giesy · H. Yu (✉)  
The State Key Laboratory of Pollution Control and  
Resource Reuse, School of the Environment, Nanjing  
University, Nanjing 210093, People's Republic of China  
e-mail: yuhx@nju.edu.cn

J. Chen  
Taizhou Environmental Monitoring Station, 31 Renmin  
East Road, Taizhou 225300, People's Republic of China

J. P. Giesy  
Department of Veterinary Biomedical Sciences and  
Toxicology Centre, University of Saskatchewan,  
Saskatoon, SK, Canada

J. P. Giesy  
Department of Biology and Chemistry and State Key  
Laboratory in Marine Pollution, City University of Hong  
Kong, Kowloon, Hong Kong, SAR, People's Republic of  
China

J. P. Giesy  
School of Biological Sciences, University of Hong Kong,  
Hong Kong, SAR, People's Republic of China

**Keywords** Taizhou · Benzo[a]pyrene equivalents · Carcinogenic potency · PAHs · Soil

## Introduction

Taizhou city, which is located on the northern bank of the Yangtze River in Jiangsu Province in East China, covers an area of 5,790 km<sup>2</sup> (city area covers 428 km<sup>2</sup>) and according to the 2010 census has 5,046,500 inhabitants (Chen et al. 2002; Fu et al. 2008). The region around Taizhou is an important producer of rice, peanuts and vegetables, which are commonly transported to other areas of China and exported to foreign countries. All of the agricultural soil is irrigated with river water, which could result in contamination. During the past two decades, agriculture supported most of the gross domestic product (GDP) in Taizhou with an average annual increase of approximately 7 %. During this time, the population of the region has nearly doubled. In addition, rapid urbanization and industrialization during these years has resulted in pressures on and effects to the environment (Long and Ng 2001). Previous studies have reported relatively large concentrations of organic contaminants, especially polycyclic aromatic hydrocarbons (PAHs), in surface waters in the vicinity of Taizhou, especially water used for drinking (Shi et al. 2011). Previous studies have demonstrated that concentrations of PAHs in soil increase with the degree of human activities (Wilcke 2000). Rapid industrial development and urbanization in and around Taizhou might result in significant concentrations of PAHs. However, little information about absolute or relative concentrations of PAHs in soils of the Taizhou region was available. Generally, there are two types of soil in Taizhou: one is fluvo-aquic soil which is found along the banks of south side of the New Tongyang Canal and the other is paddy soil on the north bank of the Canal.

The PAHs are ubiquitous in soils, water, sediments, aerosols, sewage sludge and plants (White et al. 1998; Chen et al. 2004). Both activities of humans and natural sources contribute to concentrations of PAHs in soils (Yunker et al. 2002). Petrogenic sources of PAHs include unburnt petroleum and its products, including gasoline, kerosene, diesel and lubricating oil. Pyrogenic sources include high-temperature combustion products, such as incomplete combustion of organic materials, including combustion of fossil fuel,

vehicular engine combustion, smelting and waste incinerators (Banger et al. 2010). It has been reported that 90 % of PAHs are strongly fixed and stored in soils (Wild and Jones 1995), and soils are the principal source of PAHs, which enter other matrices, such as air where to global distillation and differential removal, atmospheric transport can result in contamination of remote areas (Wania and Mackay 1996; von Waldow et al. 2010).

The US Environmental Protection Agency (EPA) has identified the 16 most frequently occurring and/or dangerous PAHs as priority pollutants and has divided them into carcinogenic and non-carcinogenic groups (USEPA 2002b). The probable human carcinogens include chrysene (Chr), benzo(a)anthracene (Baa), benzo(a)pyrene (BaP), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), dibenzo(ah)anthracene (Dba) and indeno(123cd)pyrene (Inp) (USEPA 2002b). Therefore, contamination of soils with PAHs is an issue of concern (Subramanyam et al. 1994), particularly in China. Contamination of agricultural soil by PAHs can result in accumulation by crops and might affect human health (Gao and Zhu 2004). Identification and quantification of PAHs in soils is essential for characterizing their fate and transport in the environment and might affect strategies to prevent and/or remediate adverse effects (Agarwal et al. 2009; Banger et al. 2010). Biological sources of low molecular weight PAHs (LMWPAHs) play an important role in soils, and guidelines for protection of humans have been promulgated by a number of jurisdictions (Musa Bandowe et al. 2009; Cabrerizo et al. 2011).

Until this study, contaminants in soils of Taizhou had not been characterized. Thus, the main objective of the present study was to investigate the occurrence of 16 PAHs in soils of agricultural fields in the vicinity of Taizhou. Another related objective was to determine risks of cancer posed by PAHs to residents or farmers, and determine sources so that strategies for control of further contamination can be developed and implemented.

## Materials and methods

### Chemicals and materials

The following PAHs were quantified: acenaphthene (Ace), anthracene (Ant), acenaphthylene (Acy),

**Table 1** Concentrations (µg/kg dry mass) of individual PAHs in soils of Taizhou

Compound	Min	Max	Mean	SD	Detection frequency (%)	
Acenaphthene (Ace)	<2	2.6	0.1	0.4	2.2	
Acenaphthylene (Acy)	<2	6.6	0.8	1.5	24	
Fluorene (Fle)	<2	7.2	1.1	1.6	37	
Naphthalene (Nap)	<2	20.0	8.4	4.3	96	
Anthracene (Ant)	<2	16.9	2.1	3.5	39	
Fluoranthene (Fla)	4.5	153.1	35.2	24.0	100	
Phenanthrene (Phe)	<2	65.5	17.9	10.7	96	
<sup>a</sup> ∑16-PAHs means	Benzo(a)anthracene (Baa)	<2	50.3	9.7	9.8	88
concentration of 16 kinds of target PAHs	Benzo(b)fluoranthene (BbF)	<2	69.4	16.2	12.2	99
<sup>b</sup> ∑Car-PAHs means	Benzo(k)fluoranthene (BkF)	<2	46.2	10.5	8.2	99
concentrations of carcinogenic PAHs, including	Chrysene (Chr)	<2	61.3	14.5	10.5	100
Benzo(a)anthracene, chrysene,	Pyrene (Pyr)	3.2	102.4	23.9	17.5	100
benzo(b)fluoranthene, benzo(k)fluoranthene,	Benzo(a)pyrene (BaP)	<2	62.1	12.4	11.8	97
benzo(a)pyrene,	Dibenz(ah)anthracene (Dba)	<2	12.3	1.6	2.6	38
indeno(123cd)pyrene and dibenzo(ah)anthracene	Indeno(123_cd)pyrene (Inp)	<2	62.2	11.3	10.4	92
	Benzo(ghi)perylene (Bpe)	<2	67.2	13.5	12.4	98
	∑16-PAHs <sup>a</sup>	22.6	757.6	179.1	129.1	100
	∑Car-PAHs <sup>b</sup>	4.9	355.2	75.1	65.3	100

benzo[a]anthracene (Baa), benzo[a]pyrene (BaP), benzo[b]fluoranthene (BbF), benzo[ghi]perylene (Bpe), benzo[k]fluoranthene (BkF), chrysene (Chr), dibenzo[ah]anthracene (Dba), fluoranthene (Fla), fluorene (Fle), indeno[123cd]pyrene (Inp), phenanthrene (Phe), pyrene (Pyr) and naphthalene (Nap) (Table 1). Chemicals dissolved in dichloromethane were purchased from Supelco (Bellefonte, PA, USA) with the purity of over 99 %. Phenanthrene-D<sub>10</sub>, 2-fluorobiphenyl, 2,4,6-triborophenol and terphenyl-d<sub>4</sub> were also from Supelco.

Anhydrous sodium sulfate was dried at 450 °C for 8 h and stored in a sealed desiccator before use. Sampling bottles were combusted at 450 °C for 4 h, and pre-cleaned sequentially by rinsing with high-purity *n*-hexane (Merck Darmstadt, Germany), dichloromethane (Tedia Co. Ltd, Fairfield, OH, USA), acetone (Tedia Co. Ltd, Fairfield, OH, USA) and methanol (Tedia Co. Ltd, Fairfield, OH, USA).

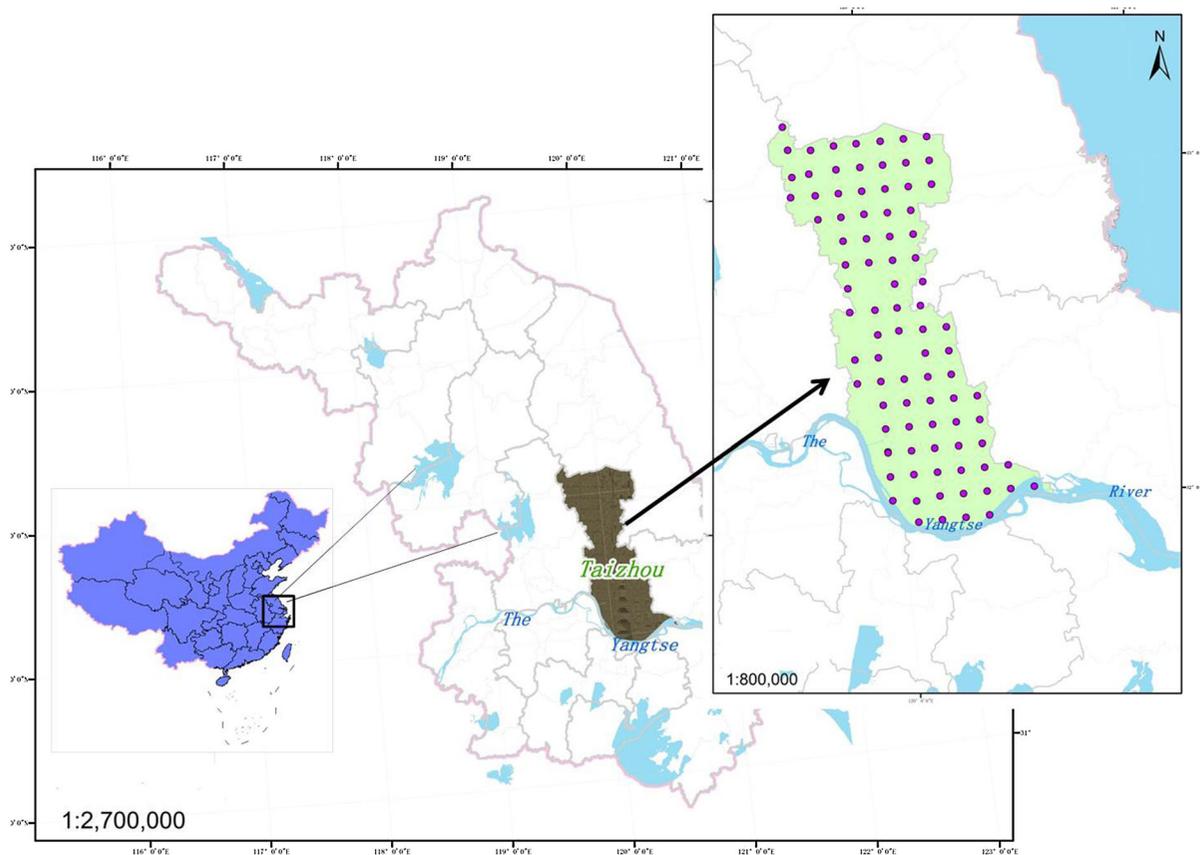
Study area and sampling

Samples were collected from 92 locations, distributed in different rural soil zones in the region in and around Taizhou, and were selected from 8 × 8 km grids (Fig. 1). Samples of soils were collected (depth 0–20 cm) with a spade, from November to December.

Each sample was a composite of eight subsamples. Samples of soils were stored in pre-cleaned aluminum containers for transportation. Among the soils, 24 samples were fluvo-aquic soil (Semi-Aquatic soils) and 68 samples were paddy soil.

Sample preparation and instrumental analysis

Ten-gram aliquants of soil sample (wet mass) were mixed with 10 g anhydrous sodium sulfate to remove water. Samples, spiked with surrogate standards (1.0 mL, 20 mg/L) containing 2-fluorobiphenyl, 2,4,6-triborophenol and terphenyl-d<sub>4</sub> were Soxhlet extracted with *n*-hexane/acetone (1:1) (v/v) for 16 h, following the criteria described in US EPA Method 3540C (USEPA 1996a). The obtained extract was concentrated by rotary vacuum evaporation to approximately 25 mL and solvent-exchanged to hexane. Extracts were purified by use of a Florisil column (LC-Florisil, 1 g, 6 mL, Sipelco, Bellefonte, PA, USA) which was pre-activated at 180 °C for 12 h, and the column was eluted with 10 mL *n*-hexane/acetone (9:1, v/v) to obtain the fraction containing PAHs. The eluate was concentrated under a steam of nitrogen to an exact volume of 1.0 mL in a 30 °C water bath. Extracts were spiked with 20 µg of phenanthrene-D<sub>10</sub> as the internal standard before instrumental analysis. Another wet aliquant of soil sample (10 g) was taken to



**Fig. 1** Locations of the sampling sites from Taizhou in Jiangsu Province, China

measure water content, and the final analysis results were calibrated and reported as dry mass.

Quantitative analysis of 16 PAHs in extracts of soils was conducted by gas chromatography (GC) with mass spectrometer detector following US EPA Method 8270D (USEPA 1996b). Identification and quantification of PAHs was performed on a Hewlett Packard (HP) 6890 GC with HP-5MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness), equipped with HP 5973 mass selective detector (MSD). Splitless injection of 1 μL of sample was conducted with a solvent delay of 5 min. Column temperature started at 50 °C (4 min hold), followed by an increase to 320 °C at 8 °C/min with a final holding time of 3 min. Helium was used as the carrier gas at a flow of 1 mL/min. Injector and interface temperatures were 230 and 250 °C, respectively. Quantification was performed using the internal calibration method based on five-point calibration curve for individual components.

#### Quality control

Method blanks, sample duplicates, matrix spikes and matrix spike duplicates were routinely analyzed with field samples. Each type of quality control sample consists of more than 10 % of the total samples. The relative deviation of the sample duplicates ranged from 0 to 39.1 %, the recovery of the matrix spikes ranged from 41.4 to 129.9 %, and the relative deviation of the matrix spike duplicates ranged from 0 to 28.2 %. Method detection limits (MDLs, S/N = 3) for the target PAHs were calculated based on the standard deviations of analytical results from seven parallel blank matrix samples spiked with small concentrations of target standards. The analytical procedure of MDLs was identical to that of sample analysis, including sample preparation. MDLs of the individual PAHs was 2.0 μg/kg, dm and recoveries of the surrogate were from 40.8 to 130 %, which were sufficient to meet the data quality requirements for this

study, and the measured concentrations were not corrected by the surrogate recovery data.

Assessment of hazard

The International Agency for Research on Cancer (IARC) has classified several PAHs into probable (2A) or possible (2B) human carcinogens (IARC 1987). The carcinogenic potency associated with exposure of a given PAH compound can be obtained by calculating its BaP equivalent concentration (BaP<sub>eq</sub>). The toxic equivalent factor (TEF) is used to calculate the BaP<sub>eq</sub> for each individual PAH. In order to compare the carcinogenic potencies associated with the total PAH concentrations at examined sites, the sum of each individual BaP<sub>eq</sub> (i.e., total BaP<sub>eq</sub>) was used as a surrogate indicator (Eq. 1).

$$\text{BaP}_{\text{eq}}(\mu\text{g}/\text{kg}) = \sum \text{TEF} \times \text{PAH}_i \tag{1}$$

where PAH<sub>*i*</sub> is the concentration (μg/kg, dm) of each individual PAH compound and TEF for each PAH has been previously described (Tsai et al. 2004).

According to results of previous studies (Man et al. 2013), potential cancer risks of soils imposed on farmers or residences may occur through accidental ingestion of soil particles (Risk<sub>ingest</sub>), dermal absorption of pollutants via soil particle contact (Risk<sub>dermal</sub>) or inhalation of fugitive soil particle (Risk<sub>inhale</sub>). The risks posed by the three major exposure pathways were calculated (Eqs. 2–4).

$$\text{Risk}_{\text{ingest}} = \frac{\text{BaP}_{\text{eq}} \times \text{IR} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \times \text{SFO} \tag{2}$$

BaP<sub>eq</sub>, BaP equivalent concentration (mg/kg, dm soil); IR, the ingestion rate of soil (mg, dm/day); EF, the exposure frequency (day/year); ED, the exposure duration (year); BW, the average body mass (kg, bm); AT, the time period over which the dose is averaged (day); SFO, the oral slope factor (mg/kg, bm/day)<sup>-1</sup>.

$$\text{Risk}_{\text{dermal}} = \frac{\text{BaP}_{\text{eq}} \times \text{SA} \times \text{AF} \times \text{ABS} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \times \text{CF} \times \text{SFO} \times \text{GIABS} \tag{3}$$

SA, the surface area of the skin that contacts soil (cm<sup>2</sup>/day); AF, the skin adherence factor for soil (mg/cm<sup>2</sup>); ABS, the dermal absorption factor; GIABS, the gastrointestinal absorption factor.

$$\text{Risk}_{\text{inhale}} = \frac{\text{BaP}_{\text{eq}} \times \text{EF} \times \text{ET} \times \text{ED}}{\text{PET} \times \text{AT}} \times \text{IUR} \tag{4}$$

ET, exposure time (h/day); IUR, the inhalation unit risk (mg/m<sup>3</sup>)<sup>-1</sup>; AT, the averaging time (h); PEF, the particle emission factor = 1.36 × 10<sup>9</sup> m<sup>3</sup>/kg.

Parameter values selected based on former research studies on the local populations are given in Table 2.

Statistical analyses

Normality was confirmed by @Risk software (5.7 version, Palisade Corporation, Newfield, NY, USA), and homogeneity of variance was confirmed by use of Levine’s test. Data were tested by use of one-way analysis of variance (ANOVA) and Duncan’s multiple comparisons test using SPSS 11 (SPSS Inc., Chicago, IL, USA). Principal component analysis (PCA) was performed using Simca-P 11.5 software (Umetrics, Sweden).

Results and discussion

Presence of PAHs in soil

Frequencies of detection varied from 2.2 for Ace to 100 % for Fla, Pyr and Chr. Total concentrations of PAHs (∑PAHs) in soils of the Taizhou region ranged from 2.3 × 10<sup>1</sup> to 7.6 × 10<sup>2</sup> μg/kg, dm. Fla occurred at the greatest concentration (19.7 %), followed by

**Table 2** Parameters for the estimation of cancer risk

Exposure factors	Value
Ingestion rate, IngR (mg/day)	100
Exposed skin area, SA (cm <sup>2</sup> /day)	3,300
Skin adherence factor, AF <sub>soil</sub> (mg/cm <sup>2</sup> )	0.2
Exposure frequency, EF (days/year)	365
Exposure duration, ED (year)	25
Exposure time, ET (h/day)	8
Body mass, BM (kg)	60
Averaging time, AT (days) = (70 years × 365 days/year)	25,550
SFO (mg/kg day) <sup>-1</sup>	7.3
SFO × GIABS (mg/kg day) <sup>-1</sup>	7.3
IUR (mg/m <sup>3</sup> ) <sup>-1</sup>	1.1 × 10 <sup>-6</sup>
Dermal absorption factor (ABS) (chemical-specific)	0.13

**Table 3** Concentrations of PAHs in soils from different locations

Location	Soil type	Number of samples	PAHs Concentration ( $\mu\text{g}/\text{kg}$ , dm)			References
			Range	Median	Mean	
China						
Taizhou	Surface	92	22.6–757.6	141.6	179.1	This research
Beijing	Farmland	9	5–297	58	87	Chen et al. (2005a)
Yangtze River Delta	Rural and suburban	30	8.6–3,881	219	397	Ping et al. (2007)
Hangzhou	Surface	3	60–616	220	298	Chen et al. (2004)
Guangzhou vegetable soils	Vegetable field	43	42–3,077	285	438	Chen et al. (2005b)
Beijing	Rural	47	16–3,884	345		Ma et al. (2005)
Guiyu (Shantou)	Surface	49	45–3,206	389	582	Yu et al. (2006)
Guiyang	Urban and suburban	13	61–1,560	511	567	Hu et al. (2006)
Dalian	Surface	24	219–18,724	1,104	1,946	Wang et al. (2007)
Pearl River Delta	Vegetable field	50	160–3,700	1,327	1,480	Cai et al. (2007)
Other countries						
Florida	Urban	40	83–2,371	543	731	Chahal et al. (2010)
Orleans	Suburban	19	527–3,753	731		Mielke et al. (2004)
Tarragona County, Spain	Urban, residential	24	112–1,002	736		Nadal et al. (2004)
New Orleans soils	Urban	107		1,821	5,100	Wang et al. (2008)
New Orleans	Inner-city	19	906–7,285	2,927		Mielke et al. (2004)
Detroit soils	Urban	106		3,436	7,843	Wang et al. (2008)

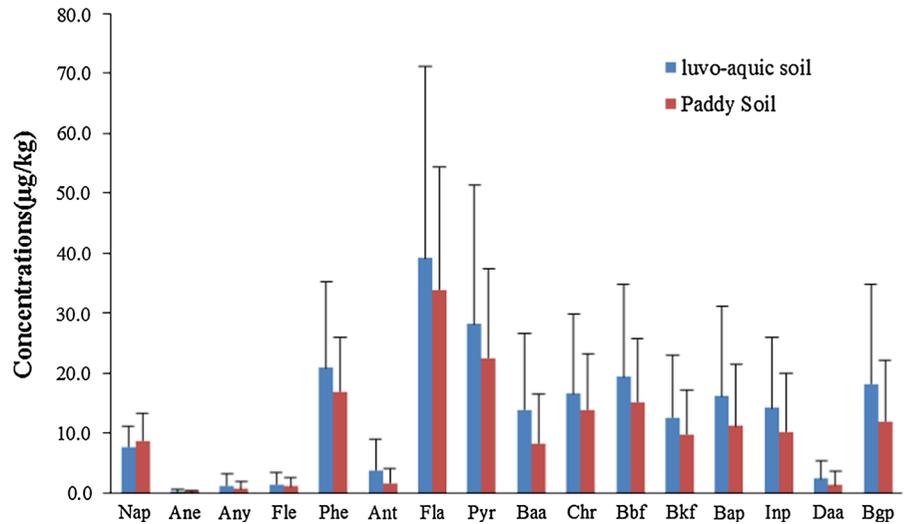
Pyr (13.3 %). The mean concentration of the sum of seven carcinogenic PAHs ( $\sum\text{Car-PAHs}$ ) including Baa, Chr, BbF, BkF, BaP, Inp and DbA in this study was  $7.5 \times 10^1 \mu\text{g}/\text{kg}$ , dm (USEPA 2002a).

Concentrations of  $\sum\text{PAHs}$  in this study were comparable with those reported for other areas of China and abroad (Table 3; Chen et al. 2004; Ma et al. 2005; Hu et al. 2006; Yu et al. 2006; Ping et al. 2007; Wang et al. 2007, 2008; Chahal et al. 2010). Median concentrations of  $\sum\text{PAHs}$  were greater than those in farmland soils from Beijing, China ( $5.8 \times 10^1 \mu\text{g}/\text{kg}$ , dm; Chen et al. 2005c). However, it is less than concentrations present in soils from other parts in China, including vegetable-growing areas near Guangzhou ( $2.9 \times 10^2 \mu\text{g}/\text{kg}$ , dm; Chen et al. 2005a), rural soils in Beijing ( $3.5 \times 10^2 \mu\text{g}/\text{kg}$ , dm; Chen et al. 2005a) and vegetable-growing areas of the Pearl River Delta ( $1.3 \times 10^3 \mu\text{g}/\text{kg}$ , dm; Cai et al. 2007). Median concentrations of  $\sum\text{PAHs}$  in the current study are also less than concentrations in suburban soils of Orleans, France ( $7.3 \times 10^2 \mu\text{g}/\text{kg}$ , dm; Mielke et al. 2004) and residential soils in Tarragona County, Spain ( $7.4 \times 10^2 \mu\text{g}/\text{kg}$ , dm; Nadal et al. 2004). The results of a hazard assessment showed that 73.9 %

of the concentrations of  $\sum\text{PAHs}$  were greater than  $100 \mu\text{g}/\text{kg}$ , dm, which were typical in the areas where no anthropogenic pollution sources occurred (Trapido 1999). These results indicated the anthropogenic contribution in this area.

Soils in Europe were classified, based on concentrations of  $\sum\text{PAHs}$ , as heavily contaminated ( $>1.0 \times 10^3 \mu\text{g}/\text{kg}$ , dm), contaminated (between  $6.0 \times 10^2$  and  $1.0 \times 10^3 \mu\text{g}/\text{kg}$ , dm), weakly contaminated (between  $2.0 \times 10^2$  and  $6.0 \times 10^2 \mu\text{g}/\text{kg}$ , dm) and not contaminated ( $<2.0 \times 10^2 \mu\text{g}/\text{kg}$ , dm; Malawska and Wiołkomirski 2001). Thus, in the present study, 69.6 % of soils were not contaminated ( $<2.0 \times 10^2 \mu\text{g}/\text{kg}$ , dm), 27.2 % were weakly contaminated ( $2.0 \times 10^2$ – $6.0 \times 10^2 \mu\text{g}/\text{kg}$ , dm), and only one sample with a concentration of  $7.6 \times 10^2 \mu\text{g} \sum\text{PAH}/\text{kg}$  was classified as a contaminated soil. However, the greatest concentration of  $\sum\text{PAHs}$  did not exceed  $4.0 \times 10^4 \mu\text{g}/\text{kg}$  (dm), which is the value set for remediation of soils (Van Brummelen et al. 1996). This result indicated that the concentrations of  $\sum\text{PAHs}$  in soils in the vicinity of Taizhou were not sufficiently great to require remediation/intervention, but 27.2 % of soils exhibited sufficient contamination to be of concern.

**Fig. 2** Concentrations of individual PAHs in fluvo-aquic soils and paddy soils in Taizhou



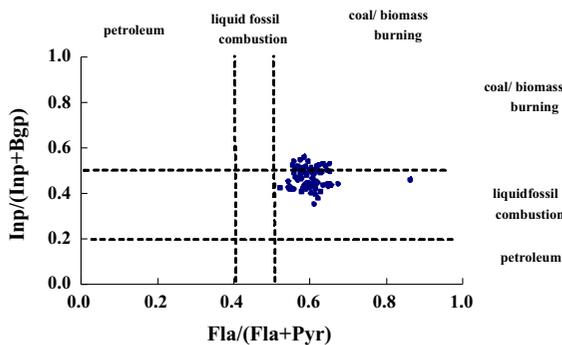
Concentrations of  $\sum$ PAHs in fluvo-aquic soils were significantly different from those in paddy soils (Fig. 2). Except for Nap, concentrations of individual PAH in fluvo-aquic soils were greater. In both types of soils,  $\sum$ PAHs were on average dominated by Fla, Pyr, Phe and BbF. This might be induced by the anaerobic rhizosphere of the flooded paddy soil, which might enhance the degradation of PAHs during vegetation period (Su and Yang 2009).

**Profile analysis of PAHs**

The LMWPAHs (containing two-ring and three-ring PAHs) are natural or released from petrogenic sources, and the high molecular weight PAHs (HMWPAHs) (containing four-ring, five-ring and six-ring PAHs) are from pyrogenic source (Fernandes et al. 1997; Mastral and Callen 2000). The HMWPAHs constituted 81.1 % of the total PAHs in soils from the Taizhou region. The mean ratio of LMWPAHs to HMWPAHs was 1:4.3, which indicates that soils of the Taizhou region originated mainly from pyrogenic sources. The ratio of major combustion-specific compounds ( $\sum$ COMB, including Fla, Pyr, Baa, Chr, BbF, BkF, BaP, Inp and Bpe) to the total concentration of PAHs ( $\sum$ COMB/ $\sum$ EPA-PAHs) also indicates the sources of PAHs are combustion of fossil fuels (Crnković et al. 2007). In this study, the mean ratio of  $\sum$ COMB/ $\sum$ EPA-PAHs was 0.81, which further indicates that combustion was the primary source of PAHs in soils.

Ratios of Fla/(Fla + Pyr) were from 0.52 to 0.86 (Fig. 3), with a median of 0.60. Results of previous studies have suggested that combustion of coal and/or biomass (grass, wood) is the most likely source of PAHs when the ratio of Fla/Fla + Pyr is greater than 0.5 (Yunker et al. 2002). In the present study, for soils with detectable concentrations of Inp and Bpe, ratios of Inp/(Inp + Bpe) were from 0.35 to 0.56, with a median of 0.46. Results of previous studies also indicated that a Icp/(Icp + Bpe) ratio of 0.2–0.5 implies combustion of liquid fossil fuel such as gasoline, kerosene and crude oil, while a ratio greater than 0.5 implies combustion of coal and biomass (grass, wood; Zhang et al. 2005). Seventy percent of soils in the Taizhou region ratios between 0.2 and 0.5, which means that most of PAHs in soil were from combustion of liquid fossil fuel but also combustion of coal and biomass. These results are consistent with the life style of residents of Taizhou and consumption of fuel, and traffic patterns. Taken together, these results suggest that emission from pyrogenic sources (combustion of fossil fuel, coal and biomass) are the predominant source of PAHs.

In addition to the diagnostic ratios between PAHs, PCA was also used to identify major sources of pollutant emissions and to select statistically independent source tracers (Table 4). When the PCA was combined with varimax orthogonal rotation, the variance contribution rate, which explained more than 85 % of the variance, was extracted and three



**Fig. 3** Diagnostic ratios for source identification of PAHs in soil of Taizhou

components were identified. Component 1 consists mainly of Phe, four-ring and five-ring PAHs. This result indicated that compositions of PAHs observed in the study, the results of which are presented here, were characterized by greater molecular weight PAHs that are known to be carcinogens. These PAHs comprised 50.5–94.3 % of the  $\sum$ PAHs in soils. Results of previous studies indicated that Pyr, Chr, BbF, Fla, BkF, Phe and Ant are the primary PAHs released during combustion of coal (Harrison et al. 1996; Simcik et al. 1999). Moreover, Chr, BbF and BkF are indicators of domestic coal combustion in China (Chen et al. 2005b), and Chr, BaP, BbF, Inp, DBa and Bpe are indicators of emissions from internal combustion engines (Guo et al. 2003; Dallarosa et al. 2008). Inp and Baa are characteristic compounds that are indicators of combustion of gasoline and kerosene in internal combustion engines and from burning natural gas (Lim et al. 1999). Pyr and Fla are the main PAHs from combustion of straw (Jenkins et al. 1996). Based on the results of this analysis, it can be concluded that PAHs in soils of Taizhou are mainly from combustion of coal, gasoline natural gas, gasoline and diesel emissions from traffic, and burning of straw. Emissions from industry are probably decreasing due to enforcement of policies to eliminate outdated production capacity and optimization of industrial distribution in Taizhou (Geng et al. 2010). Automobile traffic might be a potential contribution in the future, since the total number of automobiles in Taizhou is now more than 256,000 and is increasing at a rate of 15 %. By 2015, the number will close to or exceed 510,000. At the same time, the annual year straw burning is also a major source which is out of

**Table 4** Rotated component eigenvalues and loadings of PAHs

Component	Component 1	Component 2	Component 3
Eigenvalue	11.069	1.588	0.939
Variance %	69.183	9.928	5.866
Cumulative %	69.183	79.111	84.977
Ace	0.334	0.037	0.866
Acy	0.637	0.453	0.195
Ant	0.579	0.184	0.147
Baa	0.932	−0.029	0.050
BaP	0.975	−0.140	0.084
BbF	0.970	−0.167	−0.082
Bpe	0.935	−0.235	−0.013
BkF	0.944	−0.205	−0.051
Daa	0.938	−0.195	−0.014
Chr	0.977	−0.121	−0.095
Fla	0.945	−0.055	−0.126
Flu	0.530	0.730	0.024
Inp	0.951	−0.175	−0.070
Nap	0.362	0.697	−0.261
Phe	0.822	0.308	−0.103
Pyr	0.986	−0.043	−0.029

control of the government (Qu et al. 2012). As a result, more attentions should be paid to control the estimation of PAHs from traffic and straw burning in the future.

#### Assessment of hazard posed by PAHs

The reference total carcinogenic potency was calculated as a sum of multiplied Dutch target concentrations with appropriate BaP<sub>eq</sub> (Kong et al. 2005). Total carcinogenic potency was compared with reference to estimating the toxicities and carcinogenicity of investigated sites. Carcinogenic potencies were 1.1–2.9 times greater than the reference value for more than 10 % of sample sites (five fluvo-aquic soil samples and eight paddy soil samples), which indicated greater carcinogenic burden of soils from these sites. Risks of cancer in humans due to injection of PAHs ranged from  $1.3 \times 10^{-9}$  to  $4.2 \times 10^{-7}$ , and the risk through dermal attach were from  $1.1 \times 10^{-9}$  to  $3.6 \times 10^{-7}$ . The cancer risks predicted for inhalation were even less, ranging from to  $2.6 \times 10^{-20}$  to  $8.4 \times 10^{-18}$ , which is consistent with results of previous studies (Man et al. 2013). All the estimated values were less

than  $10^{-6}$ , and qualitative descriptions of lifetime cancer risks were very small. However, all the factors included in assessments of risk were default values, and it is important to note this limitation of this study, which may induce uncertainty.

## Conclusions

PAHs were commonly occurred in soils of Taizhou. Concentrations of PAHs ranged from  $2.3 \times 10^1$  to  $7.6 \times 10^2$   $\mu\text{g}/\text{kg}$ , dm. According to the classification criteria of Maliszewska-Kordybach, most of the soils in Taizhou were not contaminated, while 27.2 % of samples were weakly contaminated and the rural area is not notably affected by PAHs. Concentrations were less than those found in other sites in China and abroad. Concentrations of PAHs were greater in fluvo-aquic soils than in paddy soils. HMWPAHs were predominant PAHs. Forensic ratios of Fla/(Fla + Pyr) were 0.52–0.86, which suggested that PAHs in soils in Taizhou were due to combustion. Ratios of concentrations of individual PAHs suggested that emission from pyrogenic sources, including, combustion of fossil fuel, coal and biomass, were the predominant sources. Results of PCA further showed that PAHs in soils of Taizhou mainly come from the combustion of coal, gasoline natural gas, gasoline and diesel emissions from traffic, and burning of straw, which is known to be a significant source in China (Qu et al. 2012). More attentions should be paid to the PAHs released from vehicle traffic and straw burning in the future. Fourteen percent of the sampling sites indicated carcinogen burden with the carcinogen activity factors 1.1–2.9 times greater than the reference ones. The estimated risk of cancer in humans due to PAH in soils was small.

**Acknowledgments** The authors thank Wenwu Yang, Liujiang Ni, Zongyang Zhang and Jiang Li from Taizhou Environmental Monitoring Station for soil sampling. The authors would like to thank Jiangsu provincial Environmental Monitoring Research Fund (1212) and National High Technology Research and Development Program (“863”Program) of China (SS2013AA062709). Prof. Giesy was supported by the program of 2012 “High Level Foreign Experts” (#GDW20123200120) funded by the State Administration of Foreign Experts Affairs, the People’s Republic of China to

Nanjing University and the Einstein Professor Program of the Chinese Academy of Sciences. He was also supported by the Canada Research Chair program, a Visiting Distinguished Professorship in the Department of Biology and Chemistry and State Key Laboratory in Marine Pollution, City University of Hong Kong.

## 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*, 1033–1039.
- Banger, K., Toor, G. S., Chirenje, T., & Ma, L. (2010). Polycyclic aromatic hydrocarbons in urban soils of different land uses in Miami, Florida. *Soil and Sediment Contamination*, *19*, 231–243.
- Cabrerizo, A., Dachs, J., Moeckel, C., Ojeda, M. A.-J., Caballero, G., Barceló, D., et al. (2011). Ubiquitous net volatilization of polycyclic aromatic hydrocarbons from soils and parameters influencing their soil–air partitioning. *Environmental Science and Technology*, *45*, 4740–4747.
- Cai, Q., Mo, C., Li, Y., Zeng, Q., Katsoyiannis, A., Wu, Q., et al. (2007). Occurrence and assessment of polycyclic aromatic hydrocarbons in soils from vegetable fields of the Pearl River Delta, South China. *Chemosphere*, *68*, 159–168.
- Chahal, M. K., Toor, G. S., & Brown, P. (2010). Trace metals and polycyclic aromatic hydrocarbons in an urbanized area of Florida. *Soil and Sediment Contamination*, *19*, 419–435.
- Chen, L., Ran, Y., Xing, B., Mai, B., He, J., Wei, X., et al. (2005a). Contents and sources of polycyclic aromatic hydrocarbons and organochlorine pesticides in vegetable soils of Guangzhou, China. *Chemosphere*, *60*, 879–890.
- Chen, Y., Sheng, G., Bi, X., Feng, Y., Mai, B., & Fu, J. (2005b). Emission factors for carbonaceous particles and polycyclic aromatic hydrocarbons from residential coal combustion in China. *Environmental Science and Technology*, *39*, 1861–1867.
- Chen, Y., Wang, C., & Wang, Z. (2005c). Residues and source identification of persistent organic pollutants in farmland soils irrigated by effluents from biological treatment plants. *Environment International*, *31*, 778–783.
- Chen, B., Xuan, X., Zhu, L., Wang, J., Gao, Y., Yang, K., et al. (2004). Distributions of polycyclic aromatic hydrocarbons in surface waters, sediments and soils of Hangzhou City, China. *Water Research*, *38*, 3558–3568.
- Chen, L., Yang, F., Xu, J., Hu, Y., Hu, Q., Zhang, Y., et al. (2002). Determination of selenium concentration of rice in China and effect of fertilization of selenite and selenate on selenium content of rice. *Journal of Agricultural and Food Chemistry*, *50*, 5128–5130.
- Crnković, D., Ristić, M., Jovanović, A., & Antonović, D. (2007). Levels of PAHs in the soils of Belgrade and its environs. *Environmental Monitoring and Assessment*, *125*, 75–83.

- Dallarosa, J., Teixeira, E. C., Meira, L., & Wiegand, F. (2008). Study of the chemical elements and polycyclic aromatic hydrocarbons in atmospheric particles of PM10 and PM 2.5 in the urban and rural areas of South Brazil. *Atmospheric Research*, *89*, 76–92.
- Fernandes, M., Sicre, M.-A., Boireau, A., & Tronczynski, J. (1997). Polyaromatic hydrocarbon (PAH) distributions in the Seine River and its estuary. *Marine Pollution Bulletin*, *34*, 857–867.
- Fu, J., Zhou, Q., Liu, J., Liu, W., Wang, T., Zhang, Q., et al. (2008). High levels of heavy metals in rice (*Oryza sativa* L.) from a typical E-waste recycling area in southeast China and its potential risk to human health. *Chemosphere*, *71*, 1269–1275.
- Gao, Y., & Zhu, L. (2004). Plant uptake, accumulation and translocation of phenanthrene and pyrene in soils. *Chemosphere*, *55*, 1169–1178.
- Geng, J., Lu, Y., Wang, T., Giesy, J. P., & Chen, C. (2010). Effects of energy conservation in major energy-intensive industrial sectors on emissions of polychlorinated dibenzop-dioxins and polychlorinated dibenzofurans in China. *Energy Policy*, *38*, 2346–2356.
- Guo, H., Lee, S., Ho, K., Wang, X., & Zou, S. (2003). Particle-associated polycyclic aromatic hydrocarbons in urban air of Hong Kong. *Atmospheric Environment*, *37*, 5307–5317.
- Harrison, R. M., Smith, D., & Luhana, L. (1996). Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, UK. *Environmental Science and Technology*, *30*, 825–832.
- Hu, J., Zhang, G., & Lui, C.-Q. (2006). Pilot study of polycyclic aromatic hydrocarbons in surface soils of Guiyang city, People's Republic of China. *Bulletin of Environmental Contamination and Toxicology*, *76*, 80–89.
- IARC (International Agency for Research on Cancer). (1987). IARC monographs on the evaluation of the carcinogenic risk of chemicals to humans. Supplement 7, IARC, Lyons.
- 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*, 2462–2469.
- Kong, K., Cheung, K., Wong, C., & Wong, M. (2005). The residual dynamic of polycyclic aromatic hydrocarbons and organochlorine pesticides in fishponds of the Pearl River delta, South China. *Water Research*, *39*, 1831–1843.
- Lim, L. H., Harrison, R. M., & Harrad, S. (1999). The contribution of traffic to atmospheric concentrations of polycyclic aromatic hydrocarbons. *Environmental Science and Technology*, *33*, 3538–3542.
- Long, G., & Ng, M. K. (2001). The political economy of intra-provincial disparities in post-reform China: A case study of Jiangsu province. *Geoforum*, *32*, 215–234.
- 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.
- Malawska, M., & Wiołkomirski, B. (2001). An analysis of soil and plant (*Taraxacum officinale*) contamination with heavy metals and polycyclic aromatic hydrocarbons (PAHs) in the area of the railway junction Iława Główna, Poland. *Water, Air, and Soil pollution*, *127*, 339–349.
- Man, Y. B., Kang, Y., Wang, H. S., Lau, W., Li, H., Sun, X. L., et al. (2013). Cancer risk assessments of Hong Kong soils contaminated by polycyclic aromatic hydrocarbons. *Journal of Hazardous Materials*, *261*, 770–776.
- Mastral, A. M., & Callen, M. S. (2000). A review on polycyclic aromatic hydrocarbon (PAH) emissions from energy generation. *Environmental Science and Technology*, *34*, 3051–3057.
- Mielke, H. W., Wang, G., Gonzales, C. R., Powell, E. T., Le, B., & Quach, V. N. (2004). PAHs and metals in the soils of inner-city and suburban New Orleans, Louisiana, USA. *Environmental Toxicology and Pharmacology*, *18*, 243–247.
- Musa Bandowe, B. A., Rückamp, D., Bragança, M. A., Laabs, V., Amelung, W., Martius, C., et al. (2009). Naphthalene production by microorganisms associated with termites: Evidence from a microcosm experiment. *Soil Biology & Biochemistry*, *41*, 630–639.
- Nadal, M., Schuhmacher, M., & Domingo, J. (2004). Levels of PAHs in soil and vegetation samples from Tarragona County, Spain. *Environmental Pollution*, *132*, 1–11.
- Ping, L., Luo, Y., Zhang, H., Li, Q., & Wu, L. (2007). Distribution of polycyclic aromatic hydrocarbons in thirty typical soil profiles in the Yangtze River Delta region, east China. *Environmental Pollution*, *147*, 358–365.
- Qu, C., Li, B., Wu, H., & Giesy, J. P. (2012). Controlling air pollution from straw burning in china calls for efficient recycling. *Environmental Science and Technology*, *46*, 7934–7936.
- Shi, W., Zhang, F., Zhang, X., Su, G., Wei, S., Liu, H., et al. (2011). Identification of trace organic pollutants in freshwater sources in Eastern China and estimation of their associated human health risks. *Ecotoxicology*, *20*, 1099–1106.
- 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*, 5071–5079.
- Su, Y. H., & Yang, X. Y. (2009). Interactions between selected PAHs and the microbial community in rhizosphere of a paddy soil. *Science of the Total Environment*, *407*, 1027–1034.
- Subramanyam, V., Valsaraj, K., Thibodeaux, L., & Reible, D. (1994). Gas-to-particle partitioning of polycyclic aromatic hydrocarbons in an urban atmosphere. *Atmospheric Environment*, *28*, 3083–3091.
- Trapido, M. (1999). Polycyclic aromatic hydrocarbons in Estonian soil: Contamination and profiles. *Environmental Pollution*, *105*, 67–74.
- Tsai, P., Shih, T., Chen, H., Lee, W., Lai, C., & Liou, S. (2004). Assessing and predicting the exposures of polycyclic aromatic hydrocarbons (PAHs) and their carcinogenic potencies from vehicle engine exhausts to highway toll station workers. *Atmospheric Environment*, *38*, 333–343.
- USEPA. (1996a). Method 3540C, test methods for evaluating solid waste, physically chemical methods. SW-846 annual. US Environ. Protect. Agency. Revision 3.
- USEPA. (1996b). *Test methods for evaluating solid waste, physical chemical methods, methods 8270-C for semi-volatile organic compounds by Gas Chromatography Mass Spectrometry GC-MS, SW-846* (3rd ed.). Washington, DC: U.S. Government Printing Office.

- USEPA. (2002a). Polycyclic organic matter. US Environmental Protection Agency. <http://www.epa.gov/ttn/atw/hlthef/polycycl.html>
- USEPA. (2002b). Polycyclic organic matter. US Environmental Protection Agency. <http://www.epa.gov/ttn/atw/hlthef/polycycl.html>
- Van Brummelen, T., Verweij, R., Wedzinga, S., & Van Gestel, C. (1996). Enrichment of polycyclic aromatic hydrocarbons in forest soils near a blast furnace plant. *Chemosphere*, *32*, 293–314.
- von Waldow, H., MacLeod, M., Scheringer, M., & Hungerbühler, K. (2010). Quantifying remoteness from emission sources of persistent organic pollutants on a global scale. *Environmental Science and Technology*, *44*, 2791–2796.
- Wang, Z., Chen, J., Qiao, X., Yang, P., Tian, F., & Huang, L. (2007). Distribution and sources of polycyclic aromatic hydrocarbons from urban to rural soils: A case study in Dalian, China. *Chemosphere*, *68*, 965–971.
- Wang, G., Zhang, Q., Ma, P., Rowden, J., Mielke, H. W., Gonzales, C., et al. (2008). Sources and distribution of polycyclic aromatic hydrocarbons in urban soils: Case studies of Detroit and New Orleans. *Soil & Sediment Contamination*, *17*, 547–563.
- Wania, F., & Mackay, D. (1996). Peer reviewed: Tracking the distribution of persistent organic pollutants. *Environmental Science and Technology*, *30*, 390A–396A.
- White, P. A., Rasmussen, J. B., & Blaise, C. (1998). Genotoxic substances in the St. Lawrence system I: Industrial genotoxins sorbed to particulate matter in the St. Lawrence, St. Maurice, and Saguenay Rivers, Canada. *Environmental Toxicology and Chemistry*, *17*, 286–303.
- Wilcke, W. (2000). Synopsis polycyclic aromatic hydrocarbons (PAHs) in soil—a review. *Journal of Plant Nutrition and Soil Science*, *163*, 229–248.
- Wild, S. R., & Jones, K. C. (1995). Polynuclear aromatic hydrocarbons in the United Kingdom environment: A preliminary source inventory and budget. *Environmental Pollution*, *88*, 91–108.
- Yu, X., Gao, Y., Wu, S., Zhang, H., Cheung, K., & Wong, M. (2006). Distribution of polycyclic aromatic hydrocarbons in soils at Guiyu area of China, affected by recycling of electronic waste using primitive technologies. *Chemosphere*, *65*, 1500–1509.
- 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*, 489–515.
- Zhang, X., Tao, S., Liu, W., Yang, Y., Zuo, Q., & Liu, S. (2005). Source diagnostics of polycyclic aromatic hydrocarbons based on species ratios: A multimedia approach. *Environmental Science and Technology*, *39*, 9109–9114.