Status, source and health risk assessment of polycyclic aromatic hydrocarbons (PAHs) in soil from the water-level-fluctuation zone of the Three Gorges Reservoir, China

Tianpeng Hu, Jiaquan Zhang, Chen Ye, Li Zhang, Xinli Xing, Yuan Zhang, Yongkui Wang, Wen Sun, Shihua Qi, Quanfa Zhang

A R T I C L E   I N F O

Article history:
Received 17 February 2016
Revised 30 July 2016
Accepted 26 September 2016
Available online 28 September 2016

Keywords:
Polycyclic aromatic hydrocarbons (PAHs)
Soil
The water-level-fluctuation zone
The Three Gorges Reservoir
Health risk assessment

A B S T R A C T

The paper discussed the distributions, sources and health risk of polycyclic aromatic hydrocarbons (PAHs) in the water-level-fluctuation zone (WLFZ) of the Three Gorges Reservoir (TGR), China, in where the rapid transfer of pollutants between the water and terrestrial environment caused by the cycle of water fluctuations is of great concern. Twenty-four soil samples were collected in two sampling campaigns, i.e., in September 2012 (the water levels started rising from 145 m) and in June 2013 (the water levels just fell to 145 m), and subsequently they were analyzed for 16 USEPA priority PAHs. Total PAH concentrations (Σ16PAHs) ranged from 18.40 to 392.29 ng·g⁻¹ (mean 87.66 ng·g⁻¹) in 2012, and 54.00 to 463.08 ng·g⁻¹ (mean 133.84 ng·g⁻¹) in 2013. The concentrations of ΣPAHs in soil sample in 2013 were significantly higher than those in 2012. The concentrations of ΣPAHs in the upstream counties (Banan, Changshou, Fuling and Fengdu) were significantly correlated with total organic carbon (TOC) and microbial biomass carbon (MBC), possibly due to the soil microbial mineralization or degraded PAHs and the semi-continuous inputs from anthropogenic sources. Source identification indicated that PAHs were mainly derived from river transport and combustion. The incremental lifetime cancer risks ranged from 10⁻⁶ to 10⁻⁸, indicating that the carcinogenic risk for the residents was negligible.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of ubiquitous persistent organic pollutants (POPs) (Alebic-Juretic, 2011). They are considered as one of the most serious pollutants due to their persistence in the environment, bioaccumulation and high toxicity (carcinogenic, teratogenic and mutagenic) (Deyerling et al., 2014). Due to their low solubility and high hydrophobic-lipophilic, PAHs in water environment are easily to be combined with suspended solids, then deposited into sediment, and in atmospheric environment final destination also are sediment and soil by atmospheric precipitation and rainfall (Jiang et al., 2014). However, PAHs in sediment and soil can enter water and atmosphere then causes secondary pollution (Sarria-Villa et al., 2016). So the sediment and soil are the sink and source of PAHs. PAHs in the environment from various processes, mainly originate from human activities, such as petroleum producing and leaks, coal and its refined product, and other organic matter combustion (Alebic-Juretic, 2011), many industrial processes (Peng et al., 2011), motor vehicle emissions (Lee and Dong, 2010), and small amounts are produced by forest fires and volcanic eruptions (Ravindra et al., 2008).

The water-level-fluctuation zone (riparian zone) is an effective sink for PAHs due to its integration and deposit of pollutants from both the terrestrial and aquatic environment (Ye et al., 2011). In the non-flood season, PAHs in the riparian zone generally come from natural weathering and anthropogenic activities, such as riverine discharge, industrial wastewater, and domestic sewage. In the flood season, PAHs in the aquatic environment with the inputs from shipping and human activities in the upper streams can accumulate to the riparian zone by flooding. Therefore, PAHs in the riparian zone have been affected by flooding through fluvial transport and frequent material exchanges between the aquatic and terrestrial system. Meanwhile, organic carbon...
fractions play an important role in controlling the adsorption of PAHs in soil, such as total organic carbon (TOC), black carbon (BC) and microbial biomass carbon (MBC) (Luo et al., 2015; Mahmoudi et al., 2013). The TOC and the MBC in soil are quite different between the non-flood season and the flood season for the change of water level. Furthermore, some microbes in soil can degrade certain PAHs (Johnsen et al., 2005; Kanaly and Harayama, 2000), and the various levels of the MBC may change the concentration of PAHs with the different types, quality, and oxidation or reduction conditions of soil. With the completion of the Three Gorges Dam, the Three Gorges Reservoir (TGR) inundates an area of 108,000 ha. The water level of the reservoir fluctuates from 145 m a.s.l. to 172 m a.s.l. in 2008, resulted in formation of the water-level-fluctuation zone (WLFZ) with a total area of 35,000 ha in the reservoir (Ye et al., 2011). There are concerns that PAHs from industrial activities and domestic consumption in the uplands may be carried to and accumulated in the WLFZ by floods (Floehr et al., 2015; Zhu et al., 2015). In this study, the objectives of the present study were to: a) investigate the concentrations and distribution of 16 priority PAHs in order to find out the characters of soil PAHs in a cycle change of water level fluctuation; b) determine the potential sources of the PAHs; and c) evaluate the potential cancer risks of PAHs using the incremental lifetime cancer risk approach. It can offer beneficial reference for the WLFZ ecological restoration and reconstruction.

2. Materials and methods

2.1. Sampling

The WLFZ was exposed to the air after submergence in May when the reservoir’s water level was 145 m. From September 2012 (the water level started rising from 145 m) to June 2013 (the water level just fell to 145 m), we selected 12 sampling sites based on the geographical characteristics of the WLFZ from upstream to downstream in the TGR (Fig. 1), and totally 24 soil samples were collected from the WLFZ of the TGR in September 2012 and in June 2013, to find out the changes of soil PAHs in a cycle of water level fluctuation. In each site, five sampling plots (1 m × 1 m) were randomly selected in a 100 m² field of the elevation from 165 m to 175 m. At each plot, we collected five topsoil samples (0–10 cm) and the samples were well mixed to form a composited sample. All the samples were wrapped in aluminum foil and stored in sealed polythene bags and freeze dried at −4 °C before analysis.

2.2. Analysis of PAHs

The procedures of preparing for the samples were similar to those described previously (Zhang et al., 2015). The soil samples were dried naturally, and then a 10 g soil sample was spiked with 1000 ng mixed-recovery surrogates (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12), and Soxhlet-extracted with 125 mL dichloromethane (DCM) for 24 h. Elemental sulphur was removed by adding activated copper sheets to the collection flasks. The sample extract was concentrated and the solvent exchanged with hexane and further reduced to 2–3 mL by a rotary evaporator (Heidolph-4000, Germany). A 1:2 (v/v) alumina/silica gel column (48 h extraction with DCM, then baked muffle for 12 h at 180 °C and 240 °C, both deactivated with 3% of its weight water before use) was used to cleanup the extract; then the PAHs were eluted with 30 mL of DCM/n-Hexane (v:v = 2:3). The eluate was concentrated to 0.2 mL under a gentle nitrogen stream (purity ≥ 99.999%). Prior to analysis, a known quantity of hexamethyldibenzene (1000 ng) was added to the eluate as an internal standard. All the soil samples were analyzed for 16 PAHs listed by the U.S. Environmental Protection Agency as priority PAHs: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorine (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).

The determination of PAHs was performed by a GC–MS (Agilent 7890 A-5975C) equipped with a DB-5 capillary column (30 m × 0.25 mm i.d × 0.25 μm film thickness). The carrier gas was high-purity helium at a constant flow rate of 1.0 mL/min. Mass selective detector operated in the electron impact mode at 70 eV. The chromatographic conditions were as follows: injector temperature and detector temperature were kept at 270 °C and 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⁻¹ and kept at 290 °C for 20 min.

The procedural blanks, spiked blanks, and sample duplicates (analyzed at every ten samples) were analyzed in batch with field samples to evaluate the precision of the analyses. The PAHs found in the blanks were generally below the limits of detection (LOD), which was defined as three times of the signal-to-noise level in the blank sample. The variations in PAH concentrations in duplicate samples were < 15%. Minimum detection limits (MDLs) for the 16 PAHs were in the range of 0.07–0.58 ng·g⁻¹ dry weight. Representative average recoveries (arithmetic mean ± standard deviation, SD) were 57 ± 7, 85 ± 9, 105 ± 10, 113 ± 11% and 119 ± 10% for naphthalene-d₁₀, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂ and perylene-d₁₂, respectively.

2.3. Determination of TOC and MBC

The samples were pretreated with 10% HCl to remove carbonates. After the step of acid-pretreatment, the residues were centrifuged and rinsed with deionized water. The retentate were dried in an oven at 105 °C prior to analysis. The chloroform fumigation extraction method was used to determine MBC (Vance et al., 1987; Ye et al., 2014). A 5.0 g fresh soil was fumigated with ethanol-free chloroform and another 5.0 g was non-fumigated as blank then dark treatment for 24 h at 25 °C in an evacuated extractor. Sample blanks and duplicates were treated as quality control. Fumigated and non-fumigated soils were extracted with 20 mL 0.5 mol·L⁻¹ K₂SO₄ through horizontal shaking for 1 h. The extracts were filtered by a glass fiber microporous membrane filter with diameter of 0.45 μm, then frozen stored at −15 °C prior to analysis. The TOC and MBC were measured with a Multi N/C 2100-H1100 analyzer (Analytic Jena, Germany).

2.4. Risk assessment

The incremental life cancer risks (ILCRs) were taken as a flag to identify the different age classes and different exposure ways of the integrated lifetime risks that exposure to environmental PAHs pollution in the study area. The ILCRs exposure by ingestion, dermal contact, and inhalation were calculated as probabilities through the following equations, which were adapted from the USEPA standard models (Peng et al., 2011; Zhang et al., 2015):

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

(1)

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

(2)

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

(3)

In these equations, CS is the sum of BaP equivalent concentration (BaPₑₒₑ in ng·g⁻¹), BaPₑₒₑ is the product of the concentration of individual PAH compound and its corresponding toxic equivalence factor (TEF) (Table 2) (Xia et al., 2013); CSF is the carcinogenic slope factor (1/(mg/kg·d)); BW is the average body weight (kg); AT is the average life span (yr); ED is the exposure duration (yr); IRingestion is the ingestion rate of soil (mg·d⁻¹); IRinhalation is the inhalation rate (m³·d⁻¹); SA is the surface area of the skin that contacts the soil (cm²·d⁻¹); AF is the skin adherence factor for soil (mg·(cm²)⁻¹); ABS is the dermal absorption factor (chemical specific); and EF is the particle emission factor (m³·kg⁻¹). Details of the exposure parameters values which were used to derive the ILCRs are shown in Table 1 (Zhang et al., 2015).

Carcinogenic slope factors (CSF) based on the cancer-causing ability of BaP were parameterized as 7.3, 23 and 3.85 (1/(mg/kg·d)) for ingestion, dermal contact and inhalation, respectively (Peng et al., 2011). Cancer risks were estimated for three age groups: childhood (0–10 yrs), adolescence (11–18 yrs), and adulthood (19–70 yrs). Moreover, the cancer risks for males and females were calculated separately. Total risks were estimated as the sum of the individual risks for the three exposure routes.

2.5. Statistical analysis

Correlation analyses, principal component analyses (PCA), and other statistical procedures were calculated by SPSS 19.0 and figures were plotted by Origin 8.0.

3. Results and discussion

3.1. Concentrations of PAHs

The statistical data for the total PAHs (ΣPAHs) in soil from the WLZ of the TGR were summarized in Table 2. The total concentrations of 16 priority PAHs in soil varied from 18.40 to 392.29 ng·g⁻¹ (mean 87.66 ng·g⁻¹) in 2012 and varied from 54.00 to 463.08 ng·g⁻¹ (mean 133.84 ng·g⁻¹) in 2013. The ΣPAHs in soil sample collected in June 2013 is significantly higher than those in September 2012. In September 2012, the water level started rising from 145 m, and in June 2013 the water level just fell to 145 m, so the results indicated that the

---

Table 1

<table>
<thead>
<tr>
<th>Parameters used for the estimation of the incremental lifetime cancer risks (ILCRs).</th>
<th>Childhood</th>
<th></th>
<th></th>
<th></th>
<th>Adolescence</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th>Adulthood</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Male</td>
<td>Female</td>
<td></td>
<td></td>
<td>Female</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Male</td>
<td>Female</td>
<td></td>
</tr>
<tr>
<td>Body weight (BW)[^*]</td>
<td>kg</td>
<td>14.3</td>
<td>13.6</td>
<td>48.1</td>
<td>45.4</td>
<td>62.8</td>
<td>54.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ingestion rate (IRIngestion)</td>
<td>mg·d⁻¹</td>
<td>200</td>
<td>200</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exposure frequency (EF)</td>
<td>d·yr⁻¹</td>
<td>350</td>
<td>350</td>
<td>350</td>
<td>350</td>
<td>350</td>
<td>350</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exposure duration (ED)</td>
<td>yr</td>
<td>6</td>
<td>6</td>
<td>14</td>
<td>14</td>
<td>30</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average life span (AT)</td>
<td>d</td>
<td>LT × 365</td>
<td>LT × 365</td>
<td>LT × 365</td>
<td>LT × 365</td>
<td>LT × 365</td>
<td>LT × 365</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface area (SA)</td>
<td>cm²·d⁻¹</td>
<td>2800</td>
<td>2800</td>
<td>2800</td>
<td>2800</td>
<td>5700</td>
<td>5700</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dermal surface factor (AF)</td>
<td>mg·(cm²)⁻¹</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.07</td>
<td>0.07</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dermal absorption factor (ABS)</td>
<td>Unitless</td>
<td>0.13</td>
<td>0.13</td>
<td>0.13</td>
<td>0.13</td>
<td>0.13</td>
<td>0.13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inhalation rate (IRInhalation)</td>
<td>m³·d⁻¹</td>
<td>10.9</td>
<td>10.9</td>
<td>17.7</td>
<td>17.7</td>
<td>17.5</td>
<td>17.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particle emission factor (PEF)</td>
<td>m³·kg⁻¹</td>
<td>1.36 × 10⁶</td>
<td>1.36 × 10⁶</td>
<td>1.36 × 10⁶</td>
<td>1.36 × 10⁶</td>
<td>1.36 × 10⁶</td>
<td>1.36 × 10⁶</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[^*]: Values based on the 2002 National nutrition and health survey.
of the TGR soil samples varied from 12.98 to 165.75 ng·g⁻¹. The concentrations of low-molecular weight PAHs (LMW PAHs) in the WLFZ were 19.1%, 44.97%, 23.53%, 8.77%, and 3.64% in 2013, respectively. The concentrations of high-molecular weight PAHs (HMW PAHs) varied from 1.30 to 198.17 ng·g⁻¹, which would be transited longer distance. PAHs might have a higher proportion in the gas phase than those of HMW PAHs which would be transited longer distance. PAHs could undergo long-distance migration and come back to the soil. Hence, the compounds of 3-rings and 4-rings were the major components of PAHs in this area.

### Spatial distributions

The levels of PAHs in soil samples varied greatly among different sampling sites in the WLFZ of the TGR. As shown in Fig. 2, the mean concentrations (ng·g⁻¹) of PAHs decreased as the following order: S2 > S3 > S1 > S6 > S8 > S4 > S9 > S7 > S11 > S10 > S12 > S5 in 2012 and S3 > S2 > S4 > S8 > S1 > S12 > S5 > S9 > S7 > S6 > S11 > S10 in 2013. At upstream counties, such as Banan, Changshou, Fuling and Fengdu, the concentrations of PAHs were significantly higher than the middle and lower reaches counties, such as Zhongxian, Wanzhou, Yuyang, Fengjie, Wushan, Badong, Guizhou and Lanlingxi. The upstream counties were more close to the Chongqing urban where the industry is more developed than in the region dominated by agriculture in the middle and lower reaches counties. The highest concentration of PAHs was found at S2 in 2012 and S3 in 2013 because of the developed industrial activities and river transport.

### Correlations analysis

Correlation analysis between the individual PAHs was used as a means to assessing whether particular compounds may derived from the same source (Xing et al., 2011). Correlation coefficients matrix come back to the soil. Hence, the compounds of 3-rings and 4-rings were the major components of PAHs in this area.

### Spatial distributions

The levels of PAHs in soil samples varied greatly among different sampling sites in the WLFZ of the TGR. As shown in Fig. 2, the mean concentrations (ng·g⁻¹) of PAHs decreased as the following order: S2 > S3 > S1 > S6 > S8 > S4 > S9 > S7 > S11 > S10 > S12 > S5 in 2012 and S3 > S2 > S4 > S8 > S1 > S12 > S5 > S9 > S7 > S6 > S11 > S10 in 2013. At upstream counties, such as Banan, Changshou, Fuling and Fengdu, the concentrations of PAHs were significantly higher than the middle and lower reaches counties, such as Zhongxian, Wanzhou, Yuyang, Fengjie, Wushan, Badong, Guizhou and Lanlingxi. The upstream counties were more close to the Chongqing urban where the industry is more developed than in the region dominated by agriculture in the middle and lower reaches counties. The highest concentration of PAHs was found at S2 in 2012 and S3 in 2013 because of the developed industrial activities and river transport.

### Correlations analysis

Correlation analysis between the individual PAHs was used as a means to assessing whether particular compounds may derived from the same source (Xing et al., 2011). Correlation coefficients matrix come back to the soil. Hence, the compounds of 3-rings and 4-rings were the major components of PAHs in this area.

### Spatial distributions

The levels of PAHs in soil samples varied greatly among different sampling sites in the WLFZ of the TGR. As shown in Fig. 2, the mean concentrations (ng·g⁻¹) of PAHs decreased as the following order: S2 > S3 > S1 > S6 > S8 > S4 > S9 > S7 > S11 > S10 > S12 > S5 in 2012 and S3 > S2 > S4 > S8 > S1 > S12 > S5 > S9 > S7 > S6 > S11 > S10 in 2013. At upstream counties, such as Banan, Changshou, Fuling and Fengdu, the concentrations of PAHs were significantly higher than the middle and lower reaches counties, such as Zhongxian, Wanzhou, Yuyang, Fengjie, Wushan, Badong, Guizhou and Lanlingxi. The upstream counties were more close to the Chongqing urban where the industry is more developed than in the region dominated by agriculture in the middle and lower reaches counties. The highest concentration of PAHs was found at S2 in 2012 and S3 in 2013 because of the developed industrial activities and river transport.

### Correlations analysis

Correlation analysis between the individual PAHs was used as a means to assessing whether particular compounds may derived from the same source (Xing et al., 2011). Correlation coefficients matrix come back to the soil. Hence, the compounds of 3-rings and 4-rings were the major components of PAHs in this area.
among the individual PAHs (Table 3) showed that 2-, 3-, 4-, 5- and 6 rings were significantly correlated with each other in 2012, especially for LMW PAHs. The vapor pressures of semi-volatile organic compounds, such as PAHs, are the key factor to determine their vapor-particle partition, which implies the vapor pressure can affect the tendency of these compounds that were migrated through long-term atmospheric transport and then get back to soils, directly or indirectly (Agarwal et al., 2009). LMW PAHs have higher vapor pressure, so they can escape to atmosphere more easily than the HMW PAHs (Chung et al., 2007).

The soil texture, TOC, soil microbial community, and the physical and chemical properties of PAHs have a great influence on the persistence of PAHs in soil. Those factors jointly determine the persistent time of PAHs in the residues in soil (Brändli et al., 2008; Reilley et al., 1996). Moreover, TOC has been shown to be important for the sorption, sequestration, and fate of PAHs (Günther et al., 1996), and the MBC is the most active part of soil organic carbon and it is moving fast, poor stability and much easier to be changed (Günther et al., 1996). TOC concentrations in soil varied from 3617.32 mg·kg⁻¹ to 18,768.56 mg·kg⁻¹, with a mean value of 8930.53 mg·kg⁻¹ in 2012, and from 1959.48 mg·kg⁻¹ to 38,335.77 mg·kg⁻¹, with a mean value of 8700.53 mg·kg⁻¹ in 2013. The concentrations of MBC in our study ranged from 17.04 to 179.5 mg·kg⁻¹, with a mean value of 48.93 mg·kg⁻¹ in 2012, and ranged from 56.89 to 437.65 mg·kg⁻¹, with a mean value of 181.09 mg·kg⁻¹ in 2013.

Many researches confirmed that soil microbial can mineralize organic pollutants, and can use the sorption of PAHs in soil to metabolism, so a continuous input of fresh contaminants would prevent the processes of sorption-desorption from reaching an equilibrium state (Chiou et al., 2001). However, as shown in the Table 3 the correlations were not significant among TOC, MBC and individual PAHs in 2012 and 2013. Many research had been confirmed that soil microbial can mineralize organic pollutants, and can use the sorption of PAHs in soil to metabolism, so a continuous input of fresh contaminants would prevent the processes of sorption-desorption reaching an equilibrium state (Chiou...
et al., 2001). The lack of correlation relationships between PAHs and TOC were also reported in previous studies (Jiang et al., 2009; Zhang et al., 2006) and the possible reason for the lack of correlations were soil microbial degradation (Fu et al., 2012).

### 3.4. Molecular diagnostic ratios of PAHs

Sources of PAHs in the environment mainly are petroleum and combustion (Yunker et al., 2002). Two of the main artificial sources of PAHs are combustion biomass/coal and the incomplete combustion of petroleum products (Bucheli et al., 2004; Maliszewska-Kordybach et al., 2008). In generally, LMW PAHs are from low temperature transformation and leakage of petroleum, and HMW PAHs are from the combustion (Jenkins et al., 1996; Yang et al., 2012). The ratios of molecular PAHs can be used to characterize the nature of potential PAH emission sources which have been spacially proved (Yunker et al., 2002). The ratio of BaA/(BaA + Chr) > 0.35 implies petroleum combustion source, and values <0.2 imply petroleum source, values between 0.2 and 0.35 imply petroleum combustion source. Furthermore, IcdP/(IcdP + BghiP) ratios > 0.5 indicate biomass or coal combustion source (Bucheli et al., 2004; Maliszewska-Kordybach et al., 2008), ratios < 0.2 indicate petroleum source and between 0.2 and 0.5 indicates petroleum combustion source (especially liquid fossil fuel vehicles and crude oil) (Devi et al., 2014). In this study, the ratios values of IcdP/(IcdP + BghiP) and BaA/(BaA + Chr) were used to identify sources of PAHs in soil from the WLFZ of the TGR.

The ratios of IcdP/(IcdP + BghiP) and BaA/(BaA + Chr) in soil from the WLFZ were showed in the scatterplot (Fig. 4). The ratios of BaA/(BaA + Chr) > 0.35 implies biomass or coal combustion source, and BaA/(BaA + Chr) < 0.2 implies petroleum combustion source. Furthermore, IcdP/(IcdP + BghiP) > 0.5 indicates biomass or coal combustion source, and values <0.2 imply petroleum source, values between 0.2 and 0.35 imply petroleum combustion source. Therefore, IcdP/(IcdP + BghiP) and BaA/(BaA + Chr) were used to identify sources of PAHs in soil from the WLFZ of the TGR.

### 3.5. Principal component analysis (PCA)

As shown in the Fig. 5, two principal components for the accumulated variance contribution rates above 95% were extracted, which accounted for 97.56% and 96.64% of the total variance in 2012 and 2013, respectively. In 2012, PC1 explained 92.44% of the total variance, and all individual PAHs were characterized by strong loadings except DBA. Fla, Pyr, BaA and BaP and Chr are typical markers for coal combustion (Larsen and Baker, 2003; Simcik et al., 1999), while BbF and BkF are markers for fossil fuels combustion (Rogge et al., 1993). BaA and Chr often derive from the combustion of both diesel fuels and natural gas (Khallili et al., 1995). IcdP, BaP and BghiP are connected with traffic emission (Fraser et al., 1997). Therefore, PC1 obviously represents pyrogenic combustion. PC2 accounted for 5.12% of the total variance in the data: it was loaded only with DBA. This factor probably represents traffic in that DBA which have been associated with ship/vehicle emissions.

### Table 3

<table>
<thead>
<tr>
<th>PAHs/2012</th>
<th>2-Rings</th>
<th>3-Rings</th>
<th>4-Rings</th>
<th>5-Rings</th>
<th>6-Rings</th>
<th>∑PAHs</th>
<th>MBC</th>
<th>TOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petroleum</td>
<td>0.946**</td>
<td>0.983**</td>
<td>0.995**</td>
<td>0.995**</td>
<td>0.995**</td>
<td>0.995**</td>
<td>0.995**</td>
<td>0.995**</td>
</tr>
<tr>
<td>Petroleum combustion</td>
<td>0.946**</td>
<td>0.983**</td>
<td>0.995**</td>
<td>0.995**</td>
<td>0.995**</td>
<td>0.995**</td>
<td>0.995**</td>
<td>0.995**</td>
</tr>
<tr>
<td>Biomass &amp; coal combustion</td>
<td>0.946**</td>
<td>0.983**</td>
<td>0.995**</td>
<td>0.995**</td>
<td>0.995**</td>
<td>0.995**</td>
<td>0.995**</td>
<td>0.995**</td>
</tr>
<tr>
<td>TOC</td>
<td>0.796**</td>
<td>0.855**</td>
<td>0.941**</td>
<td>0.859**</td>
<td>0.932**</td>
<td>0.980**</td>
<td>0.996**</td>
<td>0.983**</td>
</tr>
<tr>
<td>∑PAHs</td>
<td>0.479**</td>
<td>0.480**</td>
<td>0.484**</td>
<td>0.846**</td>
<td>0.962**</td>
<td>0.992**</td>
<td>0.995**</td>
<td>0.992**</td>
</tr>
<tr>
<td>MBC</td>
<td>0.516</td>
<td>0.492</td>
<td>0.087</td>
<td>0.480</td>
<td>0.087</td>
<td>-0.180</td>
<td>1</td>
<td>-0.190</td>
</tr>
<tr>
<td>TOC</td>
<td>0.140</td>
<td>0.087</td>
<td>-0.122</td>
<td>-0.039</td>
<td>-0.084</td>
<td>-0.064</td>
<td>-0.180</td>
<td>1</td>
</tr>
</tbody>
</table>

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

**Fig. 4.** Molecular indices used to identify PAHs sources in soil from the WLFZ of the TGR.
Similarly, in 2013, PC1 explained 89.95% of the total variance, and it was characterized by strong loadings with all sixteen PAHs except Ant. Thus, PC1 still represents mixed sources. PC2 was loaded only with Ant. Ant is a marker of wood combustion (Duval and Friedlander, 1981) and Ant is one of the LMW PAHs, so PC2 was approximately linked to low-temperature transformation or combustion (Jenkins et al., 1996; Yang et al., 2012). Ant accounted for the numerous part of the PAH research carried out in Chicago, USA of emissions from coke ovens, and gasoline engines (Khalili et al., 1995). Thus, PC2 apparently represents low-temperature transformation or combustion sources.

3.6. Health risk assessments

The incremental life cancer risks (ILCRs) account for the potential health risks to different age groups caused by soil-borne PAH exposure through direct ingestion, dermal contacts and inhalation collectively of the two years soil samples collected from the WLFZ of the TGR. As presented in the Fig. 6A & C, the differences of the ILCRs between two years soil sample were slight, the average value of ILCRs in 2013 samples were a little higher than that in 2012 samples, suggesting that the potential health risks had a tendency to increase. The health risks of PAHs for the three exposure routes decreased as follows: dermal contacts > direct ingestion > inhalation collectively. In practice, the health risks exposure through the direct inhalation orders of magnitude between $10^{-11}$ and $10^{-12}$, about $10^{-5}$ to $10^{-6}$ times lower than those exposure through ingestion collectively and dermal contact. Therefore, the cancer risks exposure through the direct inhalation were so low that it would be negligible compared with those exposure through the rest two routes in this study. The health risks to the same age group between different genders were not distinct. What’s more, the ILCRs of adolescence were less than children or adulthood, suggesting that adolescents were less susceptible to the damage of PAHs cancer risk compared to the rest two age groups. Especially, children were more sensitive to the health risk of pollutants (Xia et al., 2013).

Generally, a value of ILCR less than or equal to $1.0 \times 10^{-6}$ was taken for non-significant or essentially negligible and as with some normal human activities such as diagnostic X-rays or radiation (Asante-Duah, 2002); while the ILCR in the range of $1.0 \times 10^{-6}$ to $1.0 \times 10^{-4}$ means that the potential health risks to human; whereas a greater value (ILCR above $1.0 \times 10^{-4}$) is higher risks (Chen and Liao, 2006). In this study...
study, the total ILCRs for the three age groups ranged between 10⁻⁹ and 10⁻⁶, indicated that the carcinogenic risk for the residents who are exposed to the soil in our study area is essentially negligible. As presented in Fig. 6B & D, the highest value of the total ILCRs was measured at S2 and S3 in 2012 and 2013 respectively, approximately 10³ times higher than the S9. In the mass of the total ILCRs for the areas with the high PAH concentrations tend to be more serious cancer risks. But the sampling site S9 in 2012 and S10 in 2013 with the least total ILCRs did not have the minimum lPAHs concentration, it was because of the Bap at those two sampling sites were less than all other sites. The cancer risk of PAHs was characterized by the total BaPeq. The total BaPeq was ranged from 0.06 to 30.46 ng·g⁻¹ in 2012 and between 0.82 ng·g⁻¹ and 32.34 ng·g⁻¹ in 2013 (Table 1), The seven carcinogenic PAHs contaminants BaPeq values accounted for the vast majority of the total BaPeq, ranged from 80% to 98%, suggesting that the seven carcinogenic PAHs contaminants were the primary sources to the total BaPeq in soil, and Bap made the biggest contribution to the total BaPeq, with the value of 50% of the total BaPeq, Bap has been used as a tracer for traffic emission (Khairy and Lohmann, 2013; Sadiktsis et al., 2012), therefore, we can safely infer that the industrial emissions and river transport of PAHs play an important role on cancer risks.

4. Conclusions

Sixteen priority PAHs contaminants in soil from the WLZF of the TGR were analyzed to investigate the spatial distributions, possible sources and potential health risks to the residents. The total concentrations of 16 priority PAHs in soil were 18.40–392.29 ng·g⁻¹ (mean 87.66 ng·g⁻¹) in 2012 and 54.00–463.08 ng·g⁻¹ (mean 133.84 ng·g⁻¹) in 2013. The results indicated that the total PAHs were obviously increased after a fluctuation cycle. The concentrations of PAHs in the upper were significantly higher than those in the middle and lower reaches counties. The highest concentrations of PAHs were found at the upstream counties near the Chongqing main urban zone. The compounds of 3 rings and 4 rings were the major components of PAHs in these area. There were no significances between the individual PAHs and TOC or MBC in 2012 and 2013, possibly due to soil microbial mineralized or degraded PAHs and the semi-continuous inputs from anthropogenic sources.

Source identification indicated that the river transport industry emissions and combustion were the major sources for PAHs in soil from the WLZF of the TGR. In our study, the total ILCRs ranged from 10⁻⁹ to 10⁻⁶ indicate that the carcinogenic risk for the residents who are exposed to the soil in our study area is essentially negligible. However, attentions should be attracted on the sites of high BaP or DBA concentrations because Bap made the biggest contribution to the total BaPeq and it had no minimum safety concentration limits for the risk, especially for children.

Acknowledgments

The research was supported by the Open Fund of State Key Laboratory of Biogeology and Environmental Geology (No. GBL21309), the fund of Executive Office of the State Council Three Gorges Construction Committee, China (No. SX2010-014), the National Natural Science Foundations of China (No. 41303090, No. 41503112), and the Outstanding Youth Science and Technology Innovation Team Projects of Hubei Polytechnic University (No. 13zxz07).

References


