



## Occurrence and source apportionment of polycyclic aromatic hydrocarbons in soils and sediment from Hanfeng Lake, Three Gorges, China

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### ABSTRACT

This study was conducted to investigate the pollutant status and the retention mechanism of polycyclic aromatic hydrocarbons (PAHs) in soils and sediment from bank–water-level-fluctuating zone (WLFZ)–water systems in Hanfeng Lake, Three Gorges, China. The concentrations of the 16 PAHs ranged from 21.8 to 1324 ng g<sup>-1</sup> dry wt for all 20 soil and sediment samples. These concentration levels were remarkably lower than those in soils and sediment collected domestically and worldwide. PAHs with two and three rings were found to be dominant in all the samples, with phenanthrene being most abundant. The spatial distribution of PAHs in bank soil, WLFZ soil, and sediment implied that the transfer and fate of PAHs in the bank soil–WLFZ soil–sediment systems were influenced by both water dynamic factors and physicochemical properties of PAHs. Diagnostic ratio analysis and principal component analysis suggested that the PAHs in the areas of Hanfeng Lake were primarily (>75%) derived from coal combustion and vehicle emissions. Use of natural gas, improving gasoline/diesel quality and phasing out old and nonstandard vehicles and ships are proposed to control PAH contamination and protect drinking water safety in the region.

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### Introduction

Polycyclic aromatic hydrocarbons (PAHs) represent a group of organic pollutants ubiquitous in the environment. PAHs originate from both natural and anthropogenic sources. The anthropogenic sources include those of petrogenic origin (crude oil, oil-refined products and coals) and those of pyrogenic origins related to incomplete combustion of coal, fossil fuel and biomass. Because of their persistence, potential for long-range transport, and health risks, PAHs have become contaminants of great concern worldwide.<sup>[1–3]</sup> There is currently a large body of data available regarding PAH contamination in different components of the environment, including the atmosphere, water, soil, and sediment.<sup>[4–7]</sup> Although PAH emissions from developed countries have been greatly reduced since the 1990 s,<sup>[8]</sup> no decrease in PAH levels has been identified to date,<sup>[9]</sup> and the main factor leading to this unexpected result has been identified as continuously increasing PAH emissions from developing countries, especially China and India.<sup>[10,11]</sup> For example, the PAH emissions from China reached 106,000 tons in 2007.<sup>[12]</sup>

As a developing country with a rapidly growing economy, China also has to face the potentially serious threat that PAHs pose to ecological and human health. Control of PAH emissions by adjusting energy consumption patterns has been shown to be an appropriate solution, and China has begun to take an effective action in the southeast by replacing

conventional energy types (e.g., coal and petroleum) with cleaner forms that produce almost no PAH emissions such as natural gas and liquefied petroleum gas.<sup>[13,14]</sup> However, coal combustion and biomass burning are still the main energy sources in the less-developed region of western China.<sup>[3]</sup>

As the largest hydropower project in the world, the Three Gorges Dam (TGD) in the Yangtze River has a length of 2335 m and a height of 185 m. Since its completion in 2009, the entire ecosystem structure and function of the catchments of the Three Gorges Reservoir (TGR) have been drastically altered by the annual rise and fall of water, and a substantial area (up to 348.9 km<sup>2</sup>) of water-level-fluctuating zone (WLFZ) or riverine floodplains has been formed. Because of changes in hydrological parameters (such as reduced water flow velocity), the intrinsic purification ability of water bodies has deteriorated and there have been adverse effects on the degradation and retention capacity for organic contaminants.<sup>[15]</sup> As the TGR was regulated as a strategic freshwater resource, some researchers have begun to focus on the pollution status of organochlorine pesticides, polychlorinated biphenyl, polychlorinated dibenzo-p-dioxins and dibenzofurans, polybrominated diphenyl ethers (PBDEs), and PAHs in water and sediment from the area.<sup>[15–20]</sup> However, the interconnection between aquatic and terrestrial habitats, WLFZs, has not received considerable attention, even though they may act as pollutant filters and sources of organic and inorganic pollutants.<sup>[21]</sup> The

WLFZ of Hanfeng Lake is the largest WLFZ in the TGR area, with an area of 45.2 km<sup>2</sup>. With the increase of industrial, agricultural and residential activities, the water quality of Hanfeng Lake has been severely threatened by increased fluxes of nutrients, metals, and organic contaminants in the riparian land around the lake in recent years. In the present study, Hanfeng Lake was selected to survey the pollution status and retention mechanism of PAHs in the bank–WLFZ–water system. In addition, the potential sources of PAHs in the study area were also differentiated and identified. This study was part of a comprehensive evaluation of the pollutant status of a series of persistent organic contaminants in bank–WLFZ–water systems in the area of the TGR.

## Materials and methods

### Materials

A standard mixture of 16 priority PAH analytes designated by the United States Environmental Protection Agency (USEPA), such as naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenz[a,h]anthracene (DahA), and benzo[g,h,i]perylene (BghiP), was purchased from Supelco Company (Bellefonte, PA, USA) for qualitative and quantitative analyses. Five surrogate standards, naphthalene-*d*<sub>8</sub>, acenaphthene-*d*<sub>10</sub>, phenanthrene-*d*<sub>10</sub>, pyrene-*d*<sub>12</sub>, and chrysene-*d*<sub>12</sub>, were also obtained from Supelco Company. Hexamethylbenzene (HMB) was acquired from Dr. Ehrenstofer-Schafer. Bgm-Schlosser (Augsburg, Germany) and used as an internal standard.

### Sample collection and extraction

In the present study, soil samples were collected from the WLFZ of Hanfeng Lake, an anthropogenic lake formed in 2010 after the completion of the TGD. Because of annual fluctuation of the water level in the TGR, the water level of Hanfeng Lake now rises to 175 m during the water storage period (May–September) and drops to 145 m during the water drainage period (October–April). Twenty samples (including seven groups of samples each of which consisted of one bank soil, one WLFZ soil, and one sediment sample) were collected from Hanfeng Lake at seven sampling sites (S1–S7) along the water flow direction (Figure S1, Supplementary material). One WLFZ soil sample was not collected because of its landform. A stainless steel shovel was used to obtain bank soil and WLFZ soil samples, while sediment samples were collected with a Van Veen stainless steel grab sampler. The samples were placed into aluminum/polyethylene bags and transported to the laboratory on ice.

All the samples were freeze-dried, pre-cleaned, and homogenized by sieving through a stainless steel 80-mesh sieve, and then stored in brown glass bottles at –20°C until further analysis. Each sample (5 g) was spiked with surrogate standards and Soxhlet extracted for 48 h with 200 mL hexane/dichloromethane mixture (1:1, v:v). Sufficient activated copper sheets were

then added to remove elemental sulfur during the extraction. The extracts were subsequently concentrated using a rotary evaporator and solvent-exchanged with hexane, after which they were cleaned and fractionated using a multilayer silica/alumina column that was wet-loaded with 6 cm of aluminum, 12 cm of neutral silica gel, and 2 cm of anhydrous Na<sub>2</sub>SO<sub>4</sub>, from bottom to top. The fraction containing PAHs was eluted with 70 mL hexane/dichloromethane (1:1, v/v), then concentrated to 1 mL, transferred to a glass vial, and finally concentrated to 200 μL under a gentle steam of nitrogen gas and spiked with the internal standards before the instrumental analysis.

### Instrumental analysis

An Agilent GC/MS/MS-7000 A-QQQ system was used in electron impact (EI) and multiple reaction monitoring (MRM) mode to measure the PAHs. A 30-m DB-5 MS capillary column (250 μm i.d., 0.25 μm film thickness, J&W Scientific, Folsom, CA, USA) was used for the qualitative analysis. The gas chromatograph column temperature was programmed to increase from 80°C (held for 1 min) to 300°C at a rate of 10°C/min, after which it was held for 12 min. The temperatures of the injection port, ion source, transfer line, and quadrupole rods were 280, 230, 300, and 150°C, respectively. Helium was applied as the carrier gas at a flow rate of 1.2 mL/min. The injection was operated in a splitless mode and the injection volume was 1 μL.

### Quality assurance/quality control

One procedure blank sample, one standard spiked blank sample, one standard spiked matrix sample, and one duplicate sample were analyzed for each batch of 12 samples to ensure quality control. The limits of detection were defined by a signal-to-noise ratio ≥5. Individual compounds were quantified using a six-point (50, 100, 250, 500, 1000, and 2500 ng/mL) calibration standard curve. Nap was not included in further discussions because of its low recovery of naphthalene-*d*<sub>8</sub> in the spiked blank and spiked matrix samples. The surrogate recoveries of acenaphthene-*d*<sub>10</sub>, phenanthrene-*d*<sub>10</sub>, pyrene-*d*<sub>12</sub>, and chrysene-*d*<sub>12</sub> were 73.6 ± 20.7, 85.2 ± 22.8, 82.1 ± 23.0, and 72.3 ± 31.9%, respectively. No detectable levels of PAHs were found in any of the blank samples, and reported concentrations were not corrected with blanks or recoveries.

## Results and discussion

### Concentration level and spatial distribution of PAHs

All the 16 USEPA priority PAHs were detected in all soil and sediment samples in the present study. We defined ΣPAHs as the total concentration of 15 USEPA priority PAHs (Nap was excluded because of its low recovery). Furthermore, the total concentration of seven carcinogenic PAHs, BaA, Chr, BbF, BkF, BaP, IcdP and DahA, was defined as Σ<sub>7</sub>PAHs. Table 1 shows the concentrations of the 15 individual PAHs, ΣPAHs, and Σ<sub>7</sub>PAHs for all the soil and sediment samples. As shown in Table 1, the concentration of ΣPAHs ranged from 79.7 to 473,

**Table 1.** Concentrations of polycyclic aromatic hydrocarbons (PAHs) (range and median) in the soil and sediment samples from Hanfeng Lake, Three Gorges (ng g<sup>-1</sup> dry wt).

Target analyte	Bank soil (n <sup>a</sup> = 7)	Fluctuating zone soil (n = 6)	Surface sediment (n = 7)
Acenaphthylene	0.33–1.59 (0.87)	<LOD <sup>b</sup> –5.61 (1.60)	0.25–2.79 (1.16)
Acenaphthene	0.24–2.64 (1.22)	0.48–7.12 (2.99)	0.33–7.30 (1.01)
Fluorene	5.36–45.8 (13.0)	8.25–62.9 (22.7)	4.11–85.8 (9.57)
Phenanthrene	35.6–224 (115)	62.7–453 (122)	10.8–251 (70.6)
Anthracene	1.32–11.0 (3.35)	0.45–9.09 (5.14)	0.64–11.0 (1.93)
Fluoranthene	7.20–34.1 (17.8)	5.26–99.3 (23.8)	3.23–51.7 (17.7)
Pyrene	3.84–31.4 (12.0)	2.31–87.2 (19.4)	1.17–50.6 (13.7)
Benz[a]anthracene	1.72–11.8 (7.19)	0.64–43.0 (10.9)	0.12–18.4 (5.64)
Chrysene	4.82–46.3 (22.7)	1.39–160 (38.1)	0.28–48.4 (19.4)
Benzo[b]fluoranthene	6.92–43.8 (28.6)	0.36–135 (16.0)	0.20–60.3 (16.4)
Benzo[k]fluoranthene	1.09–6.53 (3.98)	0.29–33.6 (3.21)	0.05–11.2 (3.37)
Benzo[a]pyrene	1.07–12.7 (3.41)	0.33–34.3 (8.77)	0.06–20.4 (3.44)
Indeno[1,2,3-cd]pyrene	2.48–17.0 (8.77)	0.35–101 (13.8)	0.08–25.1 (6.46)
Dibenzo[a,h]anthracene	1.47–10.1 (4.70)	0.28–60.7 (9.15)	0.06–11.8 (3.84)
Benzo[g,h,i]perylene	4.74–34.4 (14.3)	0.96–230 (28.5)	0.19–46.0 (12.2)
Σ <sub>7</sub> PAHs <sup>c</sup>	19.9–135 (66.2)	5.04–429 (134)	0.86–189 (58.5)
ΣPAHs	79.7–473 (285)	91.8–1324 (361)	21.8–692 (204)

<sup>a</sup>n means sample number.

<sup>b</sup>LOD means limit of detection.

<sup>c</sup>Σ<sub>7</sub>PAHs refer to the seven carcinogenic PAHs classified by the United States Environmental Protection Agency, including benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, and dibenzo(a,h)anthracene.

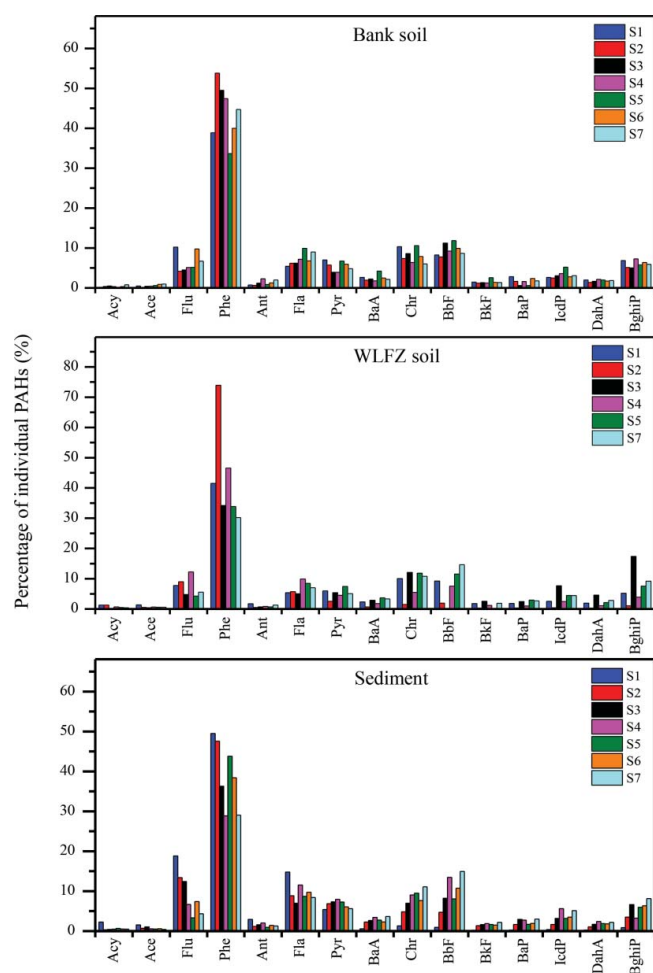
91.8 to 1324, and 21.8 to 692 ng g<sup>-1</sup> dry wt for bank soils, WLFZ soils and sediment samples, with median values of 285, 361, and 204 ng g<sup>-1</sup> dry wt, respectively. Additionally, the concentration of Σ<sub>7</sub>PAHs ranged from 19.9 to 135, 5.04 to 429, and 0.86 to 189 ng g<sup>-1</sup> dry wt with a median of 66.2, 134, and 58.5 ng g<sup>-1</sup> dry wt, respectively. In comparison, the concentrations of PAHs in the present study were much lower than those in sediment samples from Boston, MA, in the United States (7,300–35,800 ng g<sup>-1</sup> dry wt),<sup>[22]</sup> the western Baltic Sea in Sweden (mean: 4,882 ng g<sup>-1</sup> dry wt),<sup>[23]</sup> and Hanfeng Lake (2,936–8,282 ng g<sup>-1</sup> dry wt)<sup>[24]</sup> and the Macao Coast in China (294–12,741 ng g<sup>-1</sup> dry wt).<sup>[25]</sup> The levels were also markedly lower than those in soils from Dalian (219–18,727 ng g<sup>-1</sup> dry wt)<sup>[26]</sup> and Shanghai (442–19,700 ng g<sup>-1</sup> dry wt), China.<sup>[27]</sup> However, at sampling sites S3 and S5, comparatively high levels of PAHs (1,324 and 1,171 ng g<sup>-1</sup> dry wt, respectively) were also detected in WLFZ soils. These findings may reflect the convergence of water flows with higher levels of PAHs at these two sampling sites. In fact, site S3 was located at the confluence of the Nan River and Taoxi River, two main branches of the Hanfeng Lake catchment, while S5 was also situated at the place where the other tributary, the Dong River, converged. Widespread distribution of petroleum products has been found in the water of these tributaries.<sup>[28]</sup>

A varied distribution of PAH concentrations was also observed among bank soil, WLFZ soil, and sediment (Figure S2). On the one hand, the levels of PAHs decreased in the order of bank soil > WLFZ soil > sediment for sampling sites S1 and S2. These two sites are located up- and midstream of the Nan River, and it was believed that a larger amount of surface sediment and suspended particulates was transferred downstream with the water flows, resulting in reduced levels of PAHs in sediment. Conversely, at sampling sites S3, S5 and S7, the levels of PAHs in WLFZ soils were larger than those in bank soils and sediment. These findings differed from our observation that PBDEs increased in the order of bank soil < WLFZ soil < sediment in the same area.<sup>[29]</sup> There are three

possible explanations for this discrepancy: (1) external PAHs source input: for example, water flows contaminated by petroleum products from the Nan River and Taoxi River increased the content of PAHs in WLFZ soil and sediment at sampling site S3; (2) high background level of PAHs: for example, sampling site S5 is located at the old town of Kaixian county, which had the largest population density and most vehicles before the completion of the TGD, and therefore the most serious PAH pollution among the seven sampling sites; and (3) redistribution of PAHs from sediment to WLFZ soil. PBDEs, especially BDE 209, are highly hydrophobic chemicals that are easily absorbed into soil particulates once released into bank soil or WLFZ soil. As a result, these chemicals are ultimately deposited in the sediment via soil erosion by rain and floodwater. PAH components, especially low-molecular-weight PAHs (e.g., Phe), have larger solubility in water, which can cause their partial desorption from surface sediment particulates, entry into water, and redistribution to WLFZ soil with the rising water level of Hanfeng Lake during the water storage period of the TGR. This explanation appears to be confirmed by the graph shown in Figure S3 in which the relative abundance of Phe in WLFZ soil was apparently higher than that in sediment, whereas the relative abundance of Σ<sub>7</sub>PAHs (high molecular weight PAHs) resembling more like that of BDE 209 showed no marked difference between WLFZ soil and sediment in all the seven sampling sites.

### Distribution patterns and diagnostic ratio analysis of PAHs

Figure 1 shows the distribution patterns of 15 priority PAHs in the studied samples. As shown in the figure, the PAH distribution pattern was consistent among the samples collected from bank soils, WLFZ soils and sediment. Phe was the predominant PAH component, accounting for 44.0, 43.4, and 39.1% of the total PAH concentration, respectively. In general, low-molecular-weight PAHs (including two- and three-ring compounds) showed a much higher percentage (60%) of the total PAHs

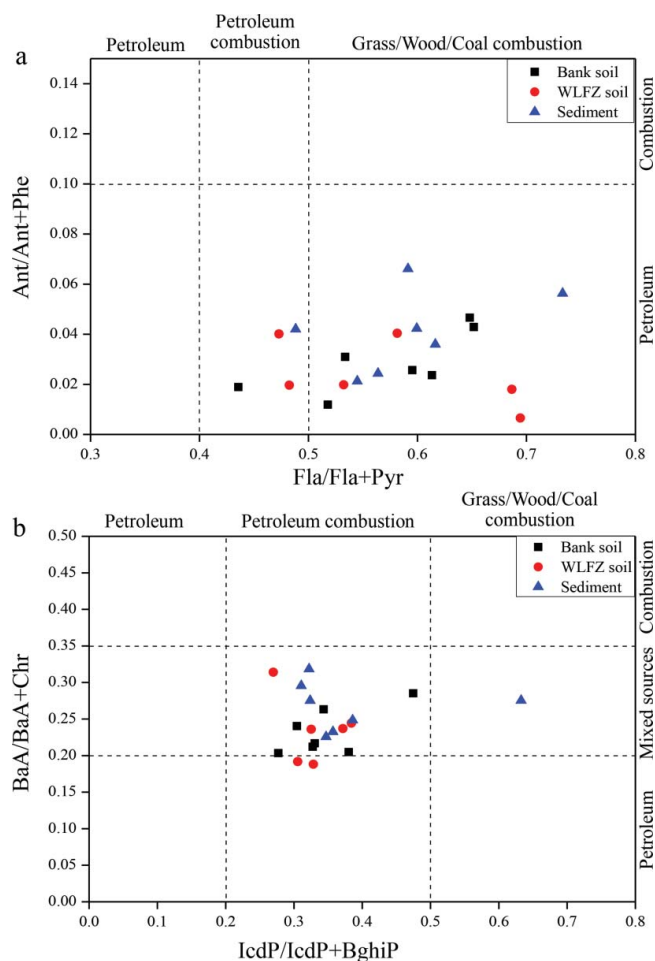


**Figure 1.** Relative percentages of individual polycyclic aromatic hydrocarbons (PAHs) in all the three types of samples from the seven sampling sites (S1–S7). WLFZ = water-level-fluctuating zone; WLFZ soil sample of S6 is not available.

than high-molecular-weight PAHs (including four-, five- and six-ring compounds), which comprised 40% of the total PAH concentration. This result is not surprising, as agricultural production is dominant in the study area, and coal and biomass (grass and wood) were the main energy sources.<sup>[28]</sup> Environmental PAHs in agricultural production areas have been reported from coal burning and biomass burning,<sup>[30,31]</sup> and low-molecular-weight PAHs were the dominant PAH components emitted.<sup>[32]</sup>

Diagnostic ratios were frequently applied to differentiate varied pollution sources of PAHs from samples collected in different environmental compartments.<sup>[3,33,34]</sup> Generally, the ratios of several PAH components, including Ant/Ant + Phe, Fla/Fla + Pyr, BaA/BaA + Chr, and IcdP/IcdP + BghiP, were widely used diagnostic tools. Values of Ant/Ant + Phe < 0.1, Fla/Fla + Pyr < 0.4, BaA/BaA + Chr < 0.2, and IcdP/IcdP + BghiP < 0.2 usually imply a petrogenic source, while values of Ant/Ant + Phe > 0.1, Fla/Fla + Pyr > 0.4, and IcdP/IcdP + BghiP > 0.2 would suggest pyrogenic origins.<sup>[35–38]</sup> The Fla/Fla + Pyr was between 0.4 and 0.5, coupled with an IcdP/IcdP + BghiP value between 0.2 and 0.5, suggesting a fossil fuel combustion origin.<sup>[35,37]</sup> In the present study, most ratios of Fla/Fla + Pyr were higher than or close to 0.5, regardless of whether samples were collected from bank soil, WLFZ soil, or sediment

(Fig. 2a), indicating that they originated from grass, wood, or coal combustion.<sup>[35]</sup> In other words, coal burning and biomass (grass and wood) burning may be the dominant origins of PAHs in the region. These findings were similar to those reported by Guo et al.,<sup>[3]</sup> who found that coal or biomass burning was the main source of pollution of sediment PAHs collected from lakes in western China, and was in accordance with the fact that coal and biomass (grass and wood) were the main energy sources in the areas of Hanfeng Lake.<sup>[28]</sup> On the other hand, as shown in Figure 2b, most ratios of IcdP/IcdP + BghiP + BghiP were clustered between 0.3 and 0.4, suggesting that liquid fossil fuel combustion/petroleum combustion may also contribute a large portion of PAHs emitted in the study area. This suggestion is also supported by a BaA/BaA + Chr value between 0.2 and 0.35, which indicates a mixed source of petroleum and combustion. These results are partially supported by the idea that high-temperature combustion processes, such as the combustion of fuels in engines, emit higher molecular weight PAH compounds.<sup>[39]</sup> However, considering that diagnostic ratios provide only qualitative information about PAH pollution sources, and their values may easily change to different extents during phase transfers and environmental degradation processes,<sup>[34]</sup> they are usually used together with multivariate statistic methods to identify the sources of PAHs.



**Figure 2.** Cross-plots of polycyclic aromatic hydrocarbons (PAHs) for the ratios of (a) Ant/Ant + Phe vs. Fla/Fla + Pyr and (b) BaA/BaA + Chr vs. IcdP/IcdP + BghiP in soils and sediment from Hanfeng Lake, Three Gorges.

### Principal component analysis and potential sources of PAHs

Fifteen priority PAHs (excluding Nap) were employed in principal component analysis (PCA) with Varimax rotation to explore and quantify sources of PAHs in the present study. PCA of PAHs resulted in two components (75.7 and 15.5%) and explained 91.2% of the total variance among samples. As shown in Figure 3, PCA distinguished three groups of PAHs. In the first principal component (PC1), two groups of PAHs (Groups 2 and 3) contributed 75.7% of the total variance. Group 2 was characterized by high loading of Ant, Flu, Fla, Phe, Pyr, BaA, and Chr, which clearly indicated a predominance of coal combustion in the areas of Hanfeng Lake.<sup>[40–42]</sup> Moreover, the high loading of Ace and BaP also indicated vehicle emissions of PAHs.<sup>[36]</sup> Based on the specific water dynamic factors in bank–WLFZ–water systems in Hanfeng Lake, the Group-2 PAHs apparently represented a combined contribution from both coal combustion and vehicle emissions. In addition, enriched BkF was proposed to indicate diesel vehicle exhausts, while IcdP has also been found in both diesel and gas engine emissions.<sup>[40,43,44]</sup> Therefore, the Group-3 PAHs (including BkF, IcdP, DahA, and BghiP) in PC1 can be attributed to vehicle sources, including diesel and gasoline engine emissions from vehicular or ship activities. In summary, this principal component (PC1) appears to represent the combined contribution from both coal combustion and vehicle emissions. However, PCA apparently failed to distinguish the two sources from each other.

The second principal component (PC2) was found to be responsible for 15.5% of the total variance, and was strongly influenced by the Group-1 PAHs (including Acy and BbF). Although elevated levels of Acy, Ace, Flu, Phe and Ant have generally been attributed to coal combustion,<sup>[41]</sup> high loading of Acy may also indicate coke production.<sup>[32]</sup> Therefore, the predominance of Acy in PC2 may indicate a partial contribution of PAHs from coking based on the fact that there are large coal reserves of 1.2 billion tons and an annual output of 2.2 million tons for Kaixian county.<sup>[28]</sup> Combination of the results drawn from the PCA with diagnostic ratios indicated that coal combustion and vehicle emissions were probably the main

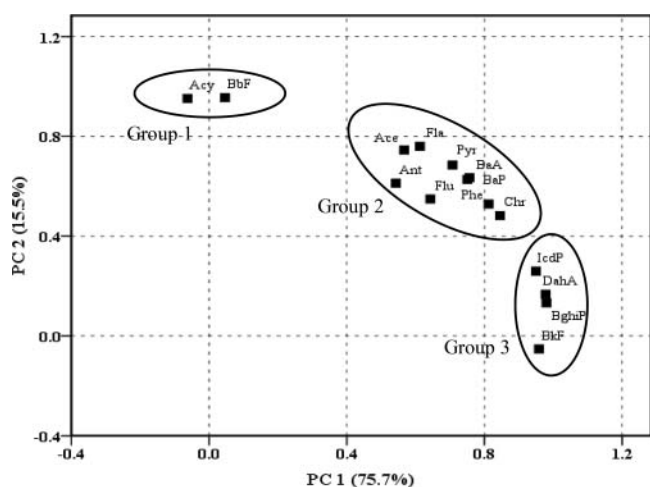


Figure 3. Principal component analysis of 15 individual polycyclic aromatic hydrocarbons (PAHs).

sources of PAHs in soils and sediment in Hanfeng Lake. Based on the source information observed in the study area, two effective measures should be taken to control PAHs contamination and protect the area: (1) replace coal burning with clean energy sources such as natural gas and (2) control vehicle emissions by improving gasoline/diesel quality and phasing out old and non-standard vehicles and ships in areas impacting Hanfeng Lake.

### Conclusion

PAHs in soils and sediment from the areas of Hanfeng Lake were preliminarily investigated in the present study. The results demonstrated that the concentrations of PAHs in the study areas were much lower than those in other areas, both domestically and worldwide. In all soil and sediment samples, two- and three-ring PAH compounds accounted for more than 60% of the total PAH concentrations, and Phe was the predominant component. The levels of PAHs decreased in the order of bank soil > WLFZ soil > sediment for sampling sites S1 and S2, but the level in WLFZ soils was apparently larger than those in bank soils and sediment for sampling sites S3, S5 and S7. These findings indicate that both water dynamic factors and physico-chemical properties of PAHs compounds directly influenced the transfer and fate of PAHs in the continuous bank soil–WLFZ soil–sediment system. Source identification of PAHs showed that PAHs in the areas of Hanfeng Lake probably mainly originated from coal combustion and vehicle emissions.

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## Supplementary Materials

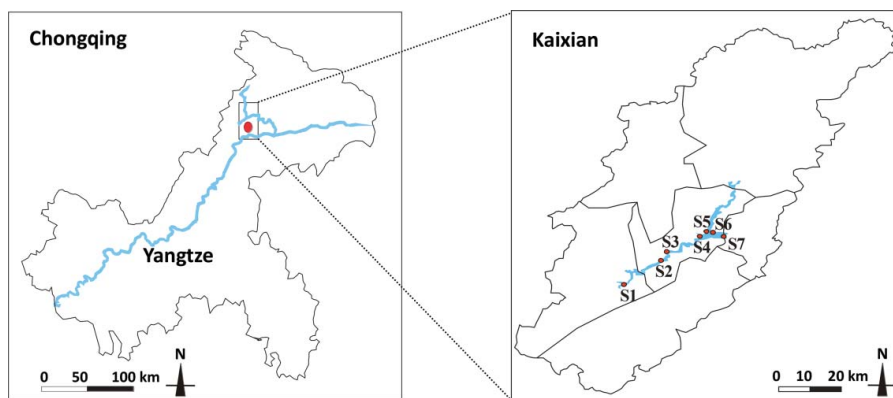


Fig. S1. Sampling sites at Hanfeng Lake, Three Gorges.

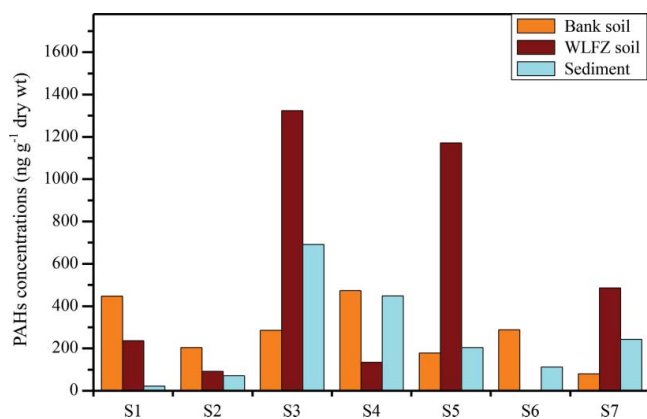


Fig. S2. Concentrations of polycyclic aromatic hydrocarbons (PAHs) in all the three types of samples from the seven sampling sites. WLFZ = water level fluctuating zone; WLFZ soil sample of S6 is not available.

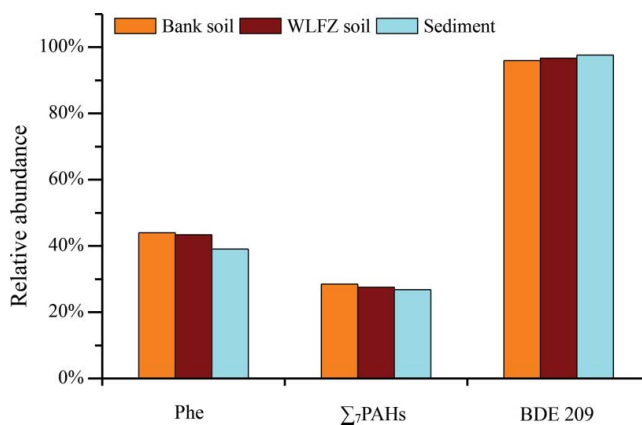


Fig. S3. Comparison of relative abundance for Phenanthrene (Phe), high molecular weight PAHs ( $\Sigma_7$ -PAHs), and BDE 209 in all the seven sampling sites. WLFZ = water level fluctuating zone.