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Spatial and Historical Occurrence, Sources, and Potential Toxicological Risk of Polycyclic Aromatic Hydrocarbons in Sediments of the Largest Chinese Deep Lake

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Abstract
Lake sediments are important reservoirs for polycyclic aromatic hydrocarbons (PAHs) in catchments. Knowledge of occurrence, sources, and toxicological risk of PAHs is crucial to abate their pollution and risk. We investigated the spatial and temporal occurrence, sources, and potential toxicological risks of 12 PAHs in the surface sediments and one sediment core of the largest deep lake (Lake Fuxian) of China. Our results indicated the average ΣPAH_{12} in the surface sediments of this lake was 1550.6 ± 231.4 ng g_{dw}^{-1}, much higher than those of most Chinese shallow lakes. The average ΣPAH_{12} in the lake area was higher than that in the estuaries. The average ΣPAH_{12} in the estuaries of influent rivers was higher than that of the outlet river. Coal combustion, gasoline combustion, and diesel combustion were the major sources, which contributed 68.5%, 19.8%, and 11.8% to the ΣPAH_{12}. The average total benzo[*a*]pyrene toxic equivalent concentration (TEQ^{carc}) of the six most carcinogenic PAHs was 317.1 ± 86.3 ngTEQ^{carc} g^{-1} in the surface sediments. The ΣPAH_{12} increased from 301.7 to 1964.4 ng g_{dw}^{-1} from 1945 to 2011 and significantly increased with the GDP and population of the catchment. The contribution of coal combustion to the concentrations of PAHs increased gradually with time. The total TEQ^{carc}, and the percentage of ΣPAH_{carc} to ΣPAH_{12} in the sediment core increased from 5.0 to 84.6 ngTEQ^{carc} g^{-1} and from 5.7 to 23.3%, respectively. Our study highlights the importance of such deep waters in burying PAHs and the increasing risk of PAHs from human activities.

Polycyclic aromatic hydrocarbons (PAHs) are a type of hydrophobic organic pollutants ubiquitously found in the environment due to their ongoing emissions from incomplete combustion of fossil fuels and biomass and pyrosynthesis of organic materials (Bzdusek et al. 2004; Harrison et al. 1996; Shen et al. 2013; Yunker et al. 2002). They are of great concern due to their persistence and mutagenic and carcinogenic toxicity. Knowledge of the temporal and spatial occurrence, sources, and toxicological risk of PAHs is crucial for effective abatement of their pollution and risk.

Lakes are important inland waters (Downing et al. 2006), which play important roles in supplying water, fishery, and entertainment for local residents (Yang et al. 2010). However, they also become the reservoirs of contaminants, such as PAHs due to the increasing human activities associated with the population growth and rapid economic growth in catchments (Li et al. 2016; Tao et al. 2010). Most of previous studies on the sources, occurrence, and potential risk of PAHs in lakes of China were performed in shallow lakes and surface sediments (Tao et al. 2010; Zhao et al. 2016). To date, the historical sources of PAHs, the shift of the sources, and the trends of the potential risk of PAHs in lake sediments have not been well addressed, especially in deep lakes in China (Guo et al. 2011; Xu et al. 2014). In contrast to shallow lakes, the sediments of deep lakes are not ready to be perturbed by waves and currents, and the bottom water temperature and oxygen content are lower (Antonopoulos and Gianniou 2003; Qin 2004; Weiss et al. 1991). The degradation of PAHs in deep lakes may thereby be much slower than shallow lakes. Additionally, the sediments of deep lakes have less disturbed record of chemical deposition than shallow lakes due to less perturbance by waves and currents. Consequently, the sediments of deep lakes may provide more valuable information on the sources, occurrence, and potential risk of PAHs.

Lake Fuxian is the largest deep lake in China, located at the central part of Yunnan Province on the Yunnan-Guizhou

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Plateau in Southwest China (Fig. 1). It covers a water surface area of 212 km^2, with the average and maximum depths of 89.6 m, and 155 m, respectively, and the water residence time of 167 years (Gu et al. 2017). It has the best freshwater quality in China with a water volume of 20.6 km^3, approximately 9.2% of the total volume of Chinese freshwater lakes (Dai et al. 2017). It receives water from more than 20 rivers, of which 7 are piedmont rivers flowing through cultivated fields in the northern watershed; the others are intermountain rivers with short lengths and steep gradients from hilly lands on the east and west of this lake. However, it has only one outflow river—Haikou River—on the east (Liu et al. 2014; Zhou et al. 2018). It is a oligotrophic lake and provides various natural resources for the local inhabitants (Zhou et al. 2018). However, it has been seriously influenced by anthropogenic activities, such as phosphate rock mining, coal-fired power generation, petrochemical processing, tobacco processing, biomass combustion, deforestation, and tourism since the 1980s (Dai et al. 2017; Liu et al. 2014). Previous study has indicated that this lake also suffered from the contamination of PAHs (Gu et al. 2017). However, little is known about the historical sources, the shift of the sources, the potential toxicological risks, deposition fluxes of PAHs, and the occurrence of PAHs in the surface sediments in the estuaries of influent and outlet rivers of this lake, and the comparison of the PAHs levels in sediments of this lake with other Chinese shallow lakes.

We investigated the spatial and historical occurrence, sources, source shift, and toxicological risk of 12 priority PAHs in the surface sediments of 15 sampling sites and 1 dated sediment core in Lake Fuxian and its tributary estuaries. The concentrations of the 12 PAHs in the surface sediments in different parts of this lake, and the estuaries of the influent and outlet tributaries were compared. The concentrations of the PAHs in the surface sediments of this lake also were compared with other shallow lakes in China. The PAHs sources in the surface sediments were quantitatively apportioned by principal component analysis (PCA) followed by multiple linear regression (MLR). The concentrations, deposition fluxes, and source shift of the 12 PAHs in the sediment core were investigated. benzo[*a*]pyrene toxic equivalent concentration (TEQ^{carc}) was applied to assess the potential toxicological risk of the PAHs in the surface sediments and the sediment core of this lake. This study will highlight the importance of such deep waters in burying PAHs and the increasing risk of PAHs in such deep waters posed by human activities.

Materials and Methods

Study Sites and Field Sampling

Sampling was performed in September 2011. The surface sediments (0–1 cm) were collected from 15 sites in the northern, southern, and western parts of Lake Fuxian and its 7 tributary estuaries using a gravity corer (Fig. 1; Table 1). One 22-cm sediment core was collected from the north center of the lake and was sliced every 0.50 cm at the depths of 0–4 cm, then 1.0 cm at the depths of 5.0–22 cm. After sampling, the samples were freeze-dried and stored at −20 °C until analysis. The core slices were measured for the activities of ^{137}Cs and ^{210}Pb using EG and G Ortec Gamma Spectrometry as the method used by Yao et al. (2013). ^{137}Cs was measured at 662 keV, whereas ^{210}Pb was determined via gamma emission at 46.5 keV and ^{226}Ra at 295 and 352 keV γ-rays emitted by its daughter isotope ^{214}Pb. The counter error increased with decreased activity of ^{210}Pb. For sediments with ^{210}Pb activity higher than 500 Bq/kg, the counter error is below 5%. ^{137}Cs was used to identify the 1963 nuclear weapons peak, which was used as part of a constant rate of supply (CRS) model to calculate a ^{210}Pb chronology for the core (Appleby 2002). The CRS model was chosen due to the complexity and heavily impacted nature of Lake Fuxian.

The historical data of gross domestic product (GDP) and population of the lake catchment were collected from Statistic Bureau of Yuxi City.

Chemicals and Reagents

The studied 12 priority PAHs were naphthalene (Nap), acenaphthene (Ace), phenanthrene (Phe), anthracene (Ant), pyrene (Pyr), benzo[*a*]anthracene (BaA), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), dibenzo[*a*,*h*]anthracene (DahA), benzo[*ghi*]perylene (BghiP), and indeno[1,2,3-cd]pyrene (InP). The other four priority PAHs were not studied in this study due to their low recoveries or low resolution by GC–MS with our analytical methodology. Standard solution of these PAHs with purity > 97.5% was used for identification and quantification. All solvents used were of HPLC grade (Merck, Germany).

Chemical Analysis

One gram of dried ground sediment sample was Soxhlet extracted with 70 mL of *n*-hexane and dichloromethane (1:1, v/v) for 24 h. The extract was reduced to 3–5 mL with a rotary evaporator, then to 1–2 mL under a gentle nitrogen stream, and cleaned with a Waters gel permeation chromatography (GPC) as our previous study (Tao et al. 2018b). The eluate was evaporated, solvent-exchanged to *n*-hexane (100 μL), and analyzed immediately.

The PAHs were analyzed using a gas chromatography–mass spectrometry (Agilent 7890-5977) with a DB-5MS (0.25-μm film thickness, 30-m × 0.25-mm i.d.) capillary column and using electron ionization. One microliter of sample was splitlessly injected with an auto-sampler. The

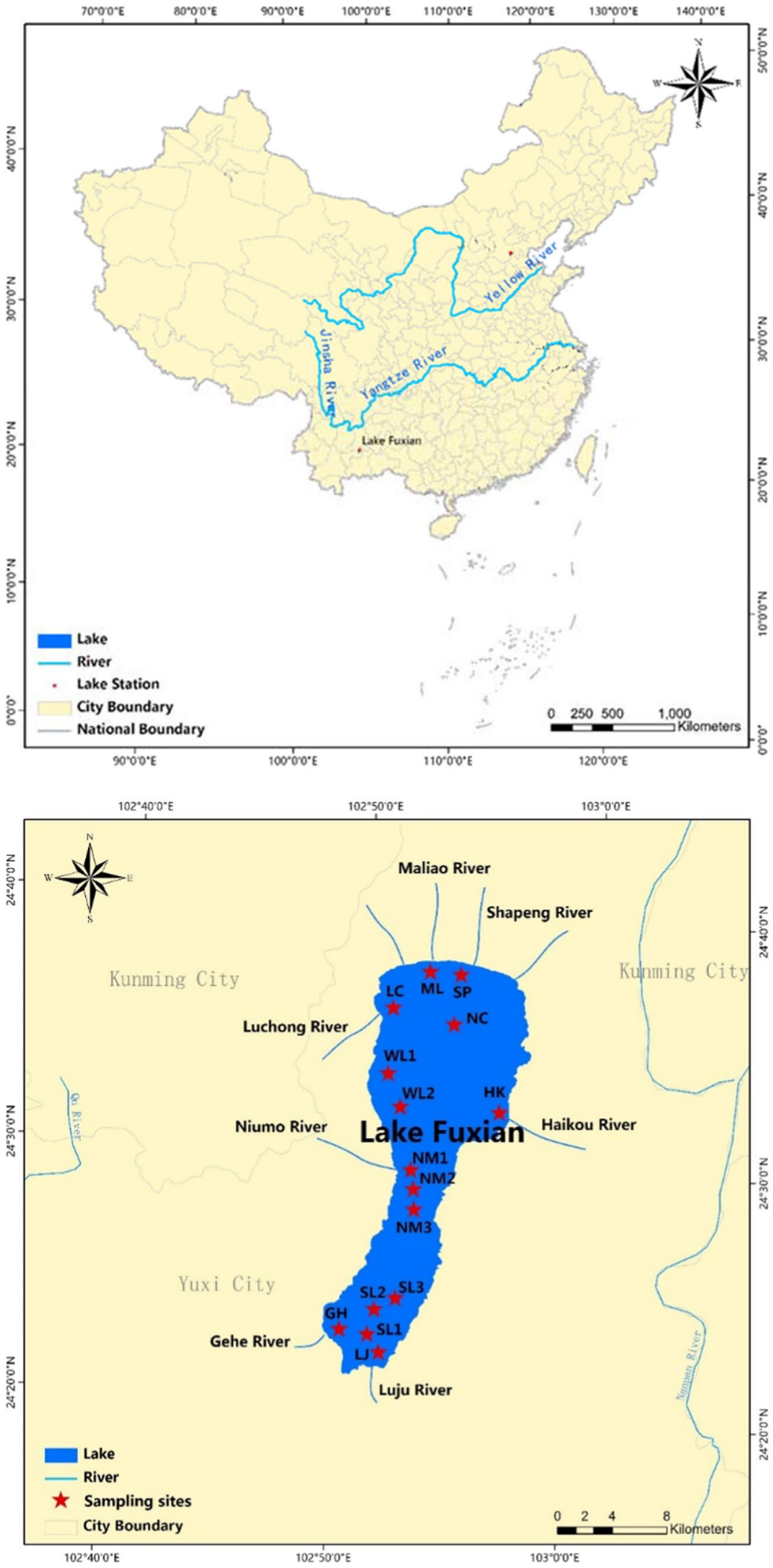

Fig. 1 The location of Lake Fuxian and the sampling sites in this lake. *NC* Northern Center, *WL1* Western Lake 1, *WL2* Western Lake 2, *SL1* Southern Lake 1, *SL2* Southern Lake 2, *SL3* Southern Lake 3, *SP* Shapeng River Estuary, *ML* Maliao River Estuary, *LC* Luchong River Estuary, *HK* Haikou River Estuary, *NM1* Niumo River Estuary 1, *NM2* Niumo River Estuary 2, *NM3* Niumo River Estuary 3, *LJ* Luju River Estuary, *GH* Gehe River Estuary

Table 1 The longitude and latitude of the sampling sites in Lake Fuxian

Sampling sites	Longitude (E)	Latitude (N)
Lake area		
Northern Center (NC)	102°54′3.25″	24°35′29.55″
Western Lake 1 (WL1)	102° 51′36.06″	24° 32′23.18″
Western Lake 2 (WL2)	102° 52′19.81″	24° 32′18.14″
Southern Lake 1 (SL1)	102° 51′43.09″	24° 21′43.37″
Southern Lake 2 (SL2)	102° 51′41.30″	24° 21′53.68″
Southern Lake 3 (SL3)	102° 51′43.14″	24° 22′39.67″
Estuaries		
Shapeng River Estuary (SP)	102°52′39.97″	24°37′42.94″
Maliao River Estuary (ML)	102°53′55.31″	24°37′33.60″
Luchong River Estuary (LC)	102°50′30.03″	24°33′16.96″
Haikou River Estuary (HK)	102°56′6.097″	24°31′15.24″
Niumo River Estuary 1 (NM1)	102°51′33.72″	24°27′18.48″
Niumo River Estuary 2 (NM2)	102°51′37.725″	24°27′18.24″
Niumo River Estuary 3 (NM3)	102°51′55.862″	24°27′10.987″
Luju River Estuary (LJ)	102°51′40.34″	24°21′42.70″
Gehe River Estuary (GH)	102°49′30.34″	24°22′49.60″

oven temperature was programed from 60 °C to 300 °C at the rate of 5 °C min^{-1} and then kept at 300 °C for 10 min. The post run was 2 min. The mass detector was operated at 70 eV, and the ion source temperature was 280 °C. The injector temperature was 300 °C. The PAHs were scanned in the full scan mode for the peak confirmation and quantified with characteristic ions in the selected ion monitoring mode (Tao et al. 2018b).

Quality Control and Statistical Analysis

The method for quality control was referenced to our previous study (Tao et al. 2018b). Calibration standards were prepared with seven concentration levels. Calibration standard and solvent blank were run with each set of analysis. The blank values were subtracted. The surrogate standards of naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12 were added to the samples before the extraction and were analyzed to evaluate the efficiencies of the sample processing and analysis. The recoveries of the surrogate standards varied from 71 to 103%. A standard reference material (SQCI-016, NSI Lab Solutions) was extracted and analyzed to confirm quantification accuracy. The recoveries of the PAHs in the reference material varied from 72 to 108%. Detection limits (defined as S/N > 3) were 0.5–1.0 ng g_{dw}^{-1} for the PAHs based on 1.00 g sediment and concentrated to 100 μL. PCA followed by MLR was used to quantitively apportion the sources of the PAHs in the surface sediments.

Calculation of Toxic BaP Equivalent (TEQ^{carc}) of Carcinogenic PAHs

BaP is the only PAH of which toxicological data are sufficient for derivation of a carcinogenic potency factor among all known potentially carcinogenic PAH (Peters et al. 1999). Toxic equivalence factor (TEF^{carc}) was applied to quantify the carcinogenicity of other PAHs relative to BaP and to estimate BaP-equivalent doses (Nadal et al. 2004; Tao et al. 2010). According to the data of USEPA, the calculated TEF^{carc} of BaA, BbF, BkF, BaP, DahA, and InP were 0.1, 0.1, 0.01, 1, 1, and 0.1, respectively (EPA 1993; Nisbet and LaGoy 1992).

Total toxic BaP equivalent (TEQ^{carc}) of the six most carcinogenic PAHs (BaA, BbF, BkF, BaP, DahA, and InP) in the surface sediments was calculated as (Tao et al. 2010):

$$TEQ^{carc} = \sum_{i} (C_i \times TEF_i^{carc}) \quad (1)$$

where C_i was the concentration of the carcinogenic PAH (ng g_{dw}^{-1}); TEF_i was the toxic equivalence factor of the carcinogenic PAH.

Results and Discussion

Occurrence of the PAHs in the Surface Sediments of Lake Fuxian

The concentration of the individual PAHs in the surface sediments in the southern, western, and northern parts of Lake Fuxian (the estuaries of the tributaries were not included) varied from 32.1 to 986.3 ng g_{dw}^{-1}, from 30.9 to 601.2 ng g_{dw}^{-1}, and from 13.2 to 306.5 ng g_{dw}^{-1} (Fig. 2). The average concentrations of ΣPAH_{12} in the surface sediments in the southern, western, and northern parts were 2798.6 ± 204.4 ng g_{dw}^{-1}, 1582.1 ± 294.7 ng g_{dw}^{-1}, and 1227.4 ng g_{dw}^{-1} (Fig. 2), which decreased in the order as: southern part > western part > northern part (Fig. 3). The average concentration of ΣPAH_{12} in the surface sediments of Lake Fuxian (the estuaries of the tributaries were not included) was 1869.4 ± 475.8 ng g_{dw}^{-1} (Fig. 4).

The concentration of the individual PAHs in the surface sediments in the estuaries of the tributaries varied from 10.7 to 601.2 ng g_{dw}^{-1} (Fig. 2). The average concentrations of ΣPAH_{12} in the surface sediments in the estuaries of the tributaries of Maliao River, Shapeng River, Luchong River, Haikou River, Niumo River, Gehe River, and Luju River were 1508.4, 1513.3, 788.6, 912.9, 1687.8, 811.6, and 1482.5 ng g_{dw}^{-1}, which decreased in the order as: Niumo

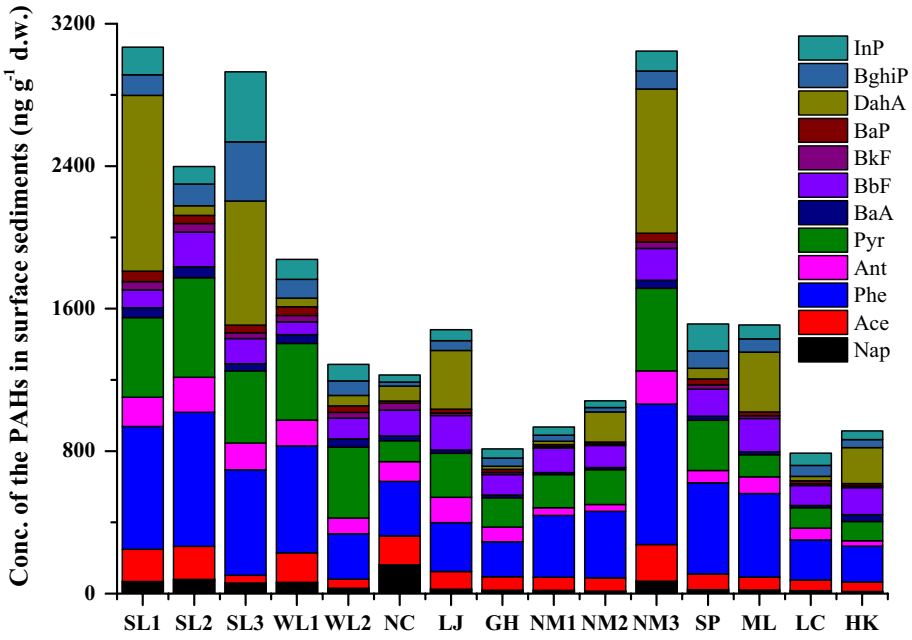

Fig. 2 Concentrations of the individual PAHs in the surface sediments of the sampling sites in Lake Fuxian

River > Shapeng River > Maliao River > Luju River > Haikou River > Gehe River > Luchong River (Fig. 2). The average concentrations of ΣPAH_{12} in the surface sediments in the estuaries of the tributaries in the different parts of Lake Fuxian decreased in the order as: Western estuaries (Luchong River, and Niumo River) > Northern estuaries (Maliao River, and Shapeng River) > Southern estuaries (Gehe River, and Luju River) > Eastern estuary (Haikou River) (Fig. 4). It may be ascribed to the fact that most of the local industries are located in the northern and western parts of this lake, whereas the southern part of this lake is covered by agricultural fields and dense villages with less coal combustion. The southern part is characterized by shorter shorelines, less inflow rivers, and smaller and shallower (Dai et al. 2017). Haikou River is the only outflow river of Lake Fuxian, whereas all the other rivers are influent tributaries of Lake Fuxian. The result shows that the average concentrations of ΣPAH_{12} in the surface sediments in the estuaries of the influent rivers are higher than that of the outflow river. The average concentration of ΣPAH_{12} in the surface sediments in all the estuaries of the tributaries was 1311.6 ± 235.3 ng g_{dw}^{-1} and was lower than that in the lake (Fig. 4).

The average concentration of ΣPAH_{12} in the surface sediments of the 15 sampling sites, including the lake and estuaries of the tributaries was 1550.6 ± 231.4 ng g_{dw}^{-1} (Fig. 4), which was higher than those in the surface sediments of most shallow lakes in China, such as Lake Lugu (190.6 ng g_{dw}^{-1}), Lake Qilu (940.1 ng g_{dw}^{-1}), and Lake Chenghai (184.5 ng g_{dw}^{-1}) in the same area of Yunnan–Guizhou Plateau in Southwest China (Li et al. 2017), Lake Taihu (436.6–1230.8 ng g_{dw}^{-1}) (Tao et al. 2010) and most of other lakes (221.0–2418.8 ng g_{dw}^{-1}) at the middle and lower reaches of the Yangtze River in Eastern China (Li et al. 2016), Lake Baiyangdian (101.3–322.8 ng g_{dw}^{-1}) in North China (Hu et al. 2010), Lake Qinghai (239.4 ng g_{dw}^{-1}), and Lake Bositeng (100.4 ng g_{dw}^{-1}) in Northwest China (Li et al. 2017), and Lake Hulun (127.1 ng g_{dw}^{-1}), Lake Wudalianchi (248.6 ng g_{dw}^{-1}), and Lake Xinkai (125.3 ng g_{dw}^{-1}) in Northeast China (Li et al. 2017). However, the average concentration of ΣPAHs in the surface sediments of Lake Fuxian was lower than those from Michigan inland lakes (200–6200 ng g_{dw}^{-1}) (Kannan et al. 2005), and Lake Erie (224–5304 ng g_{dw}^{-1}) (Smirnov et al. 1998) in the United States.

DahA, Phe, Pyr, and BbF were the dominant congeners of the PAHs in the surface sediments of the 15 sampling sites (Fig. 5), which accounted for $27.1 \pm 1.5\%$, $17.2 \pm 1.5\%$, $12.8 \pm 2.8\%$, and $10.2 \pm 1.1\%$ of the concentration of ΣPAH_{12}. Higher concentrations of the individual PAHs were found in the surface sediments in the southern part of Lake Fuxian (Fig. 3).

Source Apportionment of the PAHs in the Surface Sediments of Lake Fuxian

Principal component analysis (PCA) followed by multiple linear regression (MLR) of the data was performed with SPSS 19.0 to apportion the sources of the PAHs in Lake Fuxian. Three principal components (PCs) were extracted, and the cumulative variance accounted for 89.6% of the total variance (Table 2). For each PC, the PAHs with relatively high loading values (exceeding 0.7) were marked with bold numbers (Table 2). Each type of PAH source might provide an individual profile or signature. PC1 was responsible for

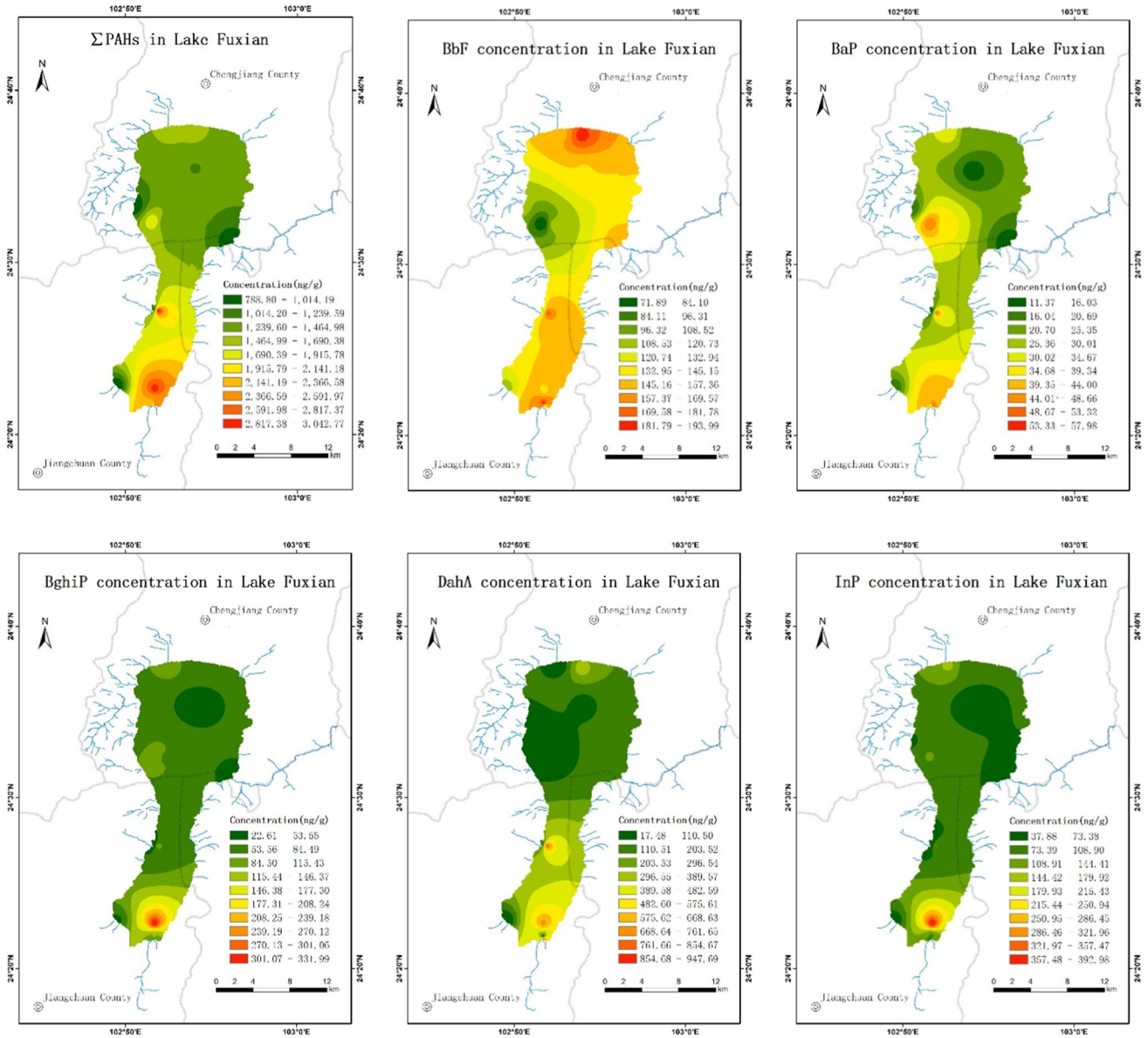

Fig. 3 Distribution of ΣPAH_{12} and individual PAHs in Lake Fuxian. BbF, BaP, BghiP, DahA, and InP were shown as the examples of the individual PAHs

56.4% of the total variance, which was heavily weighted by BaP, BkF, Ant, Pyr, Phe, and BaA. It also had the largest weighting of DahA. This profile was indicative of coal combustion (Harrison et al. 1996; Larsen and Baker 2003; Simcik et al. 1999). Therefore, PC1 was inferred to indicate a combustion source of PAHs from coal. Lake Fuxian is located in one of the most populated and developed areas of Yunnan Province of China, it is reasonable to assign coal combustion as an important sources of the PAHs in this lake. PC2 accounted for 16.3% of the total variance and was heavily loaded on InP and BghiP. InP and BghiP were applied as the tracers for gasoline combustion (Larsen and Baker 2003; May and Wise 1984; Venkataraman et al. 1994). PC3 accounted for 9.7% of the total variance, which was heavily weighted by BbF. BbF was applied as a tracer for diesel combustion (Deng et al. 2013). Because Lake Fuxian is an important fishery location in Yunnan Province, diesel combustion from fishing boats and vehicles was assigned as the third contributor for the PAHs in Lake Fuxian.

Contributions of different PAH sources were further quantified by MLR analysis. By performing stepwise procedure, PC1 to PC3 representing the contributions of coal combustion, gasoline combustion from vehicles, and diesel combustion from fishing boats and vehicles were regressed against the sum of the PAHs. The MLR equation was expressed as:

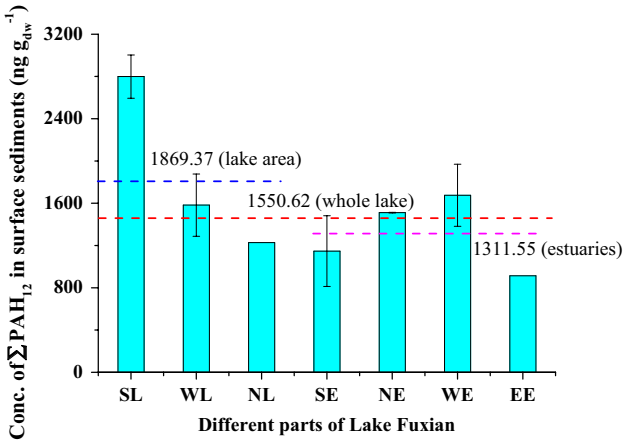

Fig. 4 Concentration of ΣPAH_{12} in the surface sediments in the different parts of Lake Fuxian. SL, southern lake, including the sites SL1, SL2, and SL3; WL, western lake, including the sites WL1, and WL2; NL, northern lake, including the site NC; SE, southern estuaries, including the sites LJ, and GH; NE, northern estuaries, including the sites SP, ML, and LC; WE, western estuaries, including the sites NM1, NM2, and NM3; EE, eastern estuaries, including the site HK

$$\sum \text{PAHs} = 0.846\text{PC1} + 0.245\text{PC2} + 0.146\text{PC3} \quad (r^2 = 0.928) \tag{2}$$

The average contribution of each type of PAH source was estimated with standardized coefficients in Eq. (2), which was 68.5% for coal combustion, 19.8% for gasoline combustion from vehicles, and 11.8% for diesel combustion from fishing boats and vehicles. The results of PCA and MLR supported the predominant coal and gasoline combustion sources of the PAHs in Lake Fuxian.

Higher concentrations of BaP, DahA, InP, and BghiP were found in the southern part of Lake Fuxian (Fig. 3), suggesting that the southern part of Lake Fuxian was more affected by both coal combustion and gasoline combustion. Higher concentrations of BaP and DahA also were found in the western part of Lake Fuxian (Fig. 3), suggesting the western part of Lake Fuxian was more affected by coal combustion. However, a higher concentration of BbF was observed in the northern part of Lake Fuxian (Fig. 3), suggesting that northern part of Lake Fuxian was more affected by diesel combustion from fishing boats and vehicles.

Potential Toxicological Risk of the PAHs in the Surface Sediments of Lake Fuxian

The total concentrations of the six most carcinogenic PAHs (BaA, BbF, BkF, BaP, DahA, and InP) in the surface sediments of the 15 sampling sites varied from 227.5 to 1402.3 ng g_{dw}^{-1} (Fig. 6a), with the mean of 589.9 ± 97.4 ng g_{dw}^{-1}, and accounted for $34.3 \pm 2.5\%$ of the concentration of ΣPAH_{12}. The average percentage of the carcinogenic PAHs in the surface sediments of the tributary estuaries was close to that in the lake, which was $36.0 \pm 2.9\%$ and $31.7 \pm 4.8\%$, respectively.

The TEQ^{carc} of the six most carcinogenic PAHs was calculated with Eq. (1). The total TEQ^{carc} in the surface sediments of the 15 sampling sites varied from 50.7 to 1077.9 ngTEQ^{carc} g^{-1} (Fig. 6b). The average total TEQ^{carc} in the surface sediments of Lake Fuxian was 317.1 ± 86.3 ngTEQ^{carc} g^{-1} ($n = 15$), which was much higher than those found in the surface sediments of different bays (East Taihu Bay (134.6 ngTEQ^{carc} g^{-1}), Xukou Bay (80.6 ngTEQ^{carc} g^{-1}), Meiliang Bay (76.8 ngTEQ^{carc} g^{-1}), and Gonghu Bay (57.3 ngTEQ^{carc} g^{-1})) of Lake Taihu (Tao et al. 2010) and the other 28 shallow lakes (12.9–472.9 ngTEQ^{carc} g^{-1}) at the middle and lower reaches of the Yangtze River in China (Li

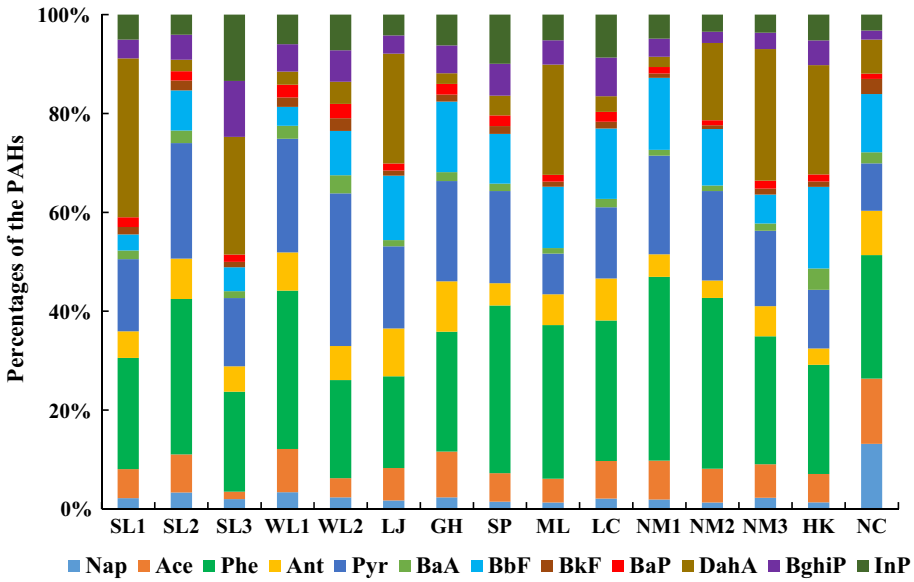

Fig. 5 The composition profiles of the PAHs in the surface sediments of the sampling sites

Table 2 Component loading after varimax rotation and cumulative variance of principal component analysis (PCA)

PAHs	Component		
	PC1	PC2	PC3
Nap	0.551	−0.504	−0.043
Ace	0.699	−0.655	0.054
Phe	**0.882**	−0.019	0.169
Ant	**0.904**	−0.151	0.198
Pyr	**0.899**	0.036	−0.118
BaA	**0.845**	−0.097	−0.228
BbF	0.062	−0.113	**0.938**
BkF	**0.915**	−0.251	−0.165
BaP	**0.934**	0.104	−0.172
DahA	0.628	0.287	0.297
BghiP	0.638	**0.713**	0.034
InP	0.592	**0.749**	0.003
Variance (%)	56.440	16.293	9.703
Cumulative variance (%)	56.440	72.733	82.436

et al. 2016), Bohai Sea (12.9–64.6 ngTEQ^{carc} g^{-1}), and the northern part of the Yellow Sea (6.0–68.8 ngTEQ^{carc} g^{-1}) in China (Li et al. 2015), Guba Penchenga, Barents Sea in Russia (18–300 ngTEQ^{carc} g^{-1}), and VadsØ Harbour (40–66 ngTEQ^{carc} g^{-1}), Jarfjord Harbour (19–35 ngTEQ^{carc} g^{-1}), and Korsfjord Harbour (18–60, ngTEQ^{carc} g^{-1}) in Norway (Savinov et al. 2003). The contribution of the six most carcinogenic PAHs to the total TEQ^{carc} in the surface sediments of the 15 sampling sites decreased in order as: DahA (64.9 ± 6.1%) > BaP (17.5 ± 8.2%) > InP (5.6 ± 1.0%) > BbF (3.2 ± 0.4%) > BaA (1.9 ± 0.4%) > BkF (0.05 ± 0.008%). DahA and BaP mainly derived from coal combustion posed high potential toxicological risk to Lake Fuxian.

Historical Occurrence, Sedimentary Flux, Sources, and Potential Toxicological Risk of the PAHs in Lake Fuxian

The concentration of ΣPAH_{12} in the sediment core increased from 301.7 to 1964.4 ng g_{dw}^{-1} in the period from 1945 to 2011 (Fig. 7), with three peaks appearing in 1968, 1982, and 2011. In contrast to previous studies in the lakes in developed countries, such as Michigan inland lakes (Kannan et al.

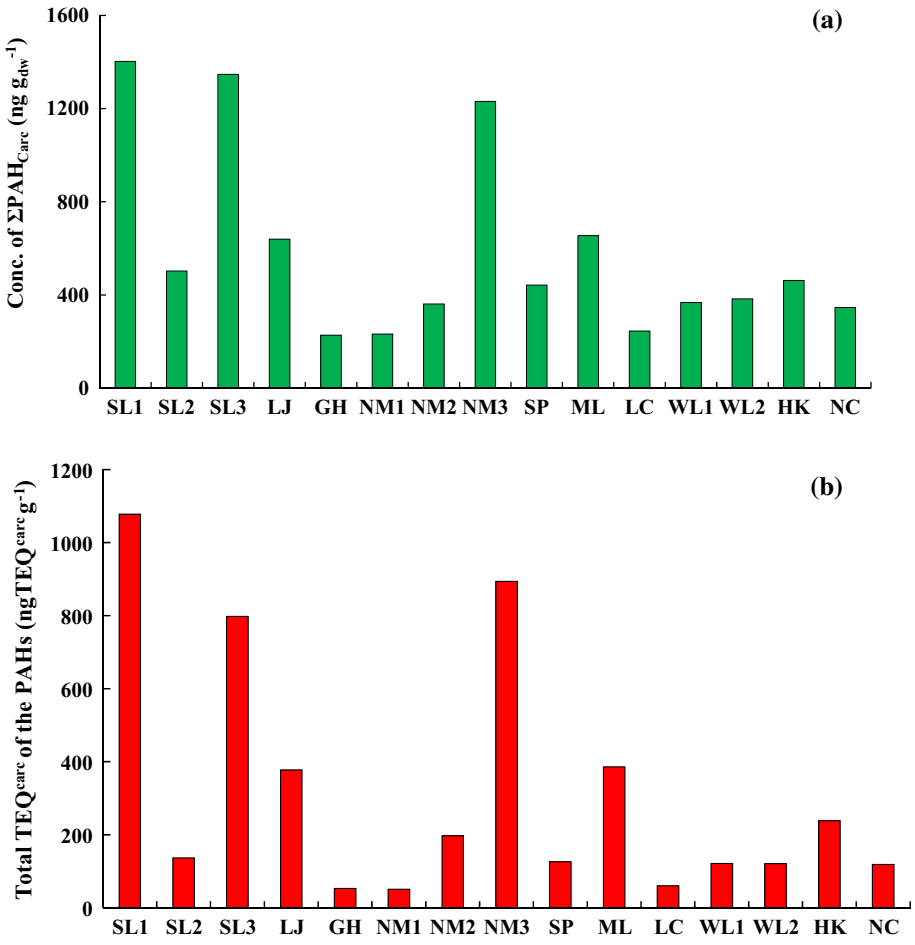

Fig. 6 The total concentration of the six most carcinogenic PAHs (ΣPAH_{carc}) in the surface sediments of the sampling sites (**a**), and the total toxic benzo[*a*]pyrene equivalent (TEQ^{carc}) of the six most carcinogenic PAHs in the sampling sites (**b**)

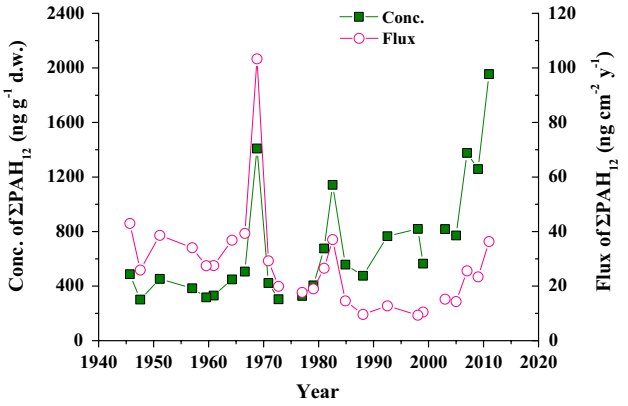

Fig. 7 The concentration and sedimentation flux of ΣPAH_{12} in the sediment core of Lake Fuxian

2005) and Lake Washington (Wakeham et al. 2004) in the United States, Lake Stora Frillingerl in Sweden (Elmquist et al. 2007), and a small rural lake in the United Kingdom (Gevao et al. 1998), an increasing trend of the PAH concentration was observed in Lake Fuxian in recent decades (Fig. 7). The concentration of ΣPAH_{12} in the sediment core in Lake Fuxian significantly increased with the historical GDP and population of the lake catchment (Fig. 8), which was consistent with previous studies on distribution of PAHs in sediment cores of Lake Taihu (Liu et al. 2009) and Michigan inland lakes (Kannan et al. 2005), and the study on spatial occurrence of PAHs in surface sediments of 28 shallow lakes at the catchment of Yangtze River in China (Li et al. 2016). The results indicated that local human activities may dominate the concentrations of PAHs in the sediments of Lake Fuxian. The sedimentary flux of ΣPAH_{12} varied from 9.6 to 103.3 ng cm^{-2} y^{-1}, which decreased gradually during the period from 1945 to 1999, then rebounded since the year of 2003 (Fig. 7). The average sedimentary flux of ΣPAH_{12} was 27.9 ± 3.8 ng cm^{-2} y^{-1} in the period from 1945 to 2011. The maximum sedimentary flux appeared in the late 1960s. The ratios of PAH congeners (Ant/(Ant + Phe) and InP/(InP + BghiP)) in the sediment core varied from 0.11 to 0.29, and from 0.64 to 0.75, and generally increased with time from 1945 to 2011 (Fig. 9), which suggested that the contribution of coal combustion to the concentrations of PAHs in the sediment core increased gradually during this period (Yunker et al. 2002). The ratios of both Ant/(Ant + Phe) and InP/(InP + BghiP) increased dramatically in the late 1990s (Fig. 9). Furthermore, lower concentration of ΣPAH_{12} appeared in the late 1990s (Fig. 7). The results suggested that the sources of the PAHs in Lake Fuxian shifted dramatically in the late 1990s, which may be ascribed to the shift of local energy consumption especially for the transition from biomass to petroleum and coal in rural areas (Tao et al. 2018a).

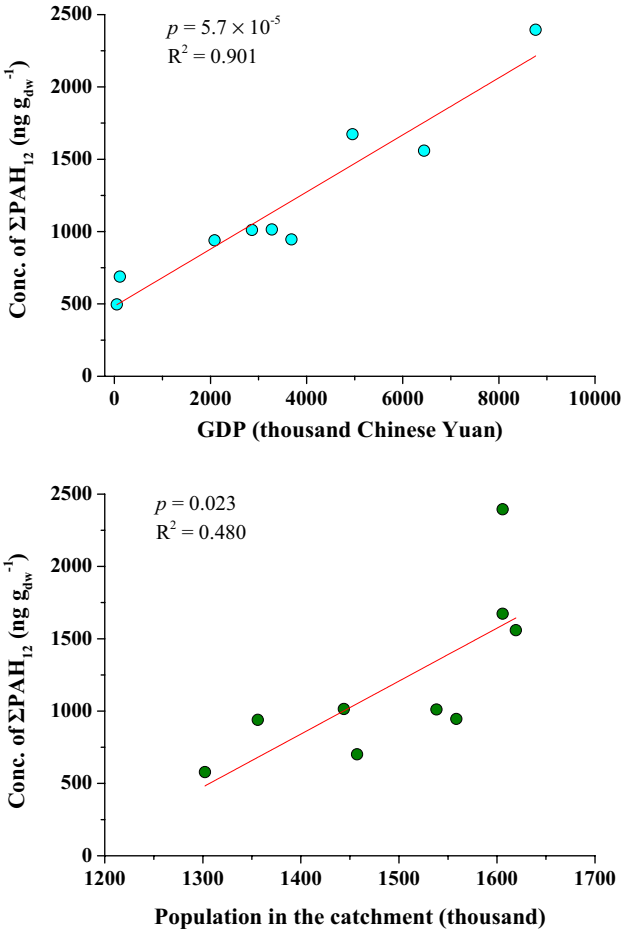

Fig. 8 Correlations between the concentration of ΣPAH_{12} in the sediment core of Lake Fuxian and the historical gross domestic product (GDP) and population of the catchment

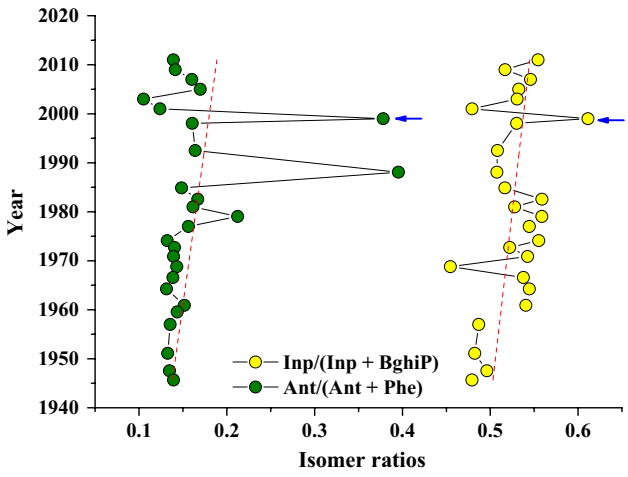

Fig. 9 The concentration ratios of PAH congeners in the sediment core of Lake Fuxian

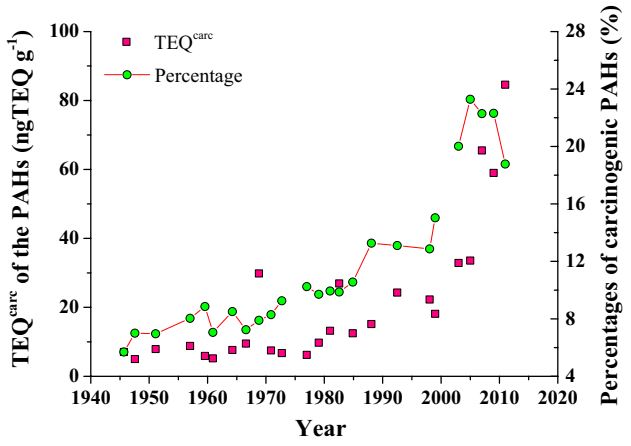

Fig. 10 The total toxic benzo[*a*]pyrene equivalent (TEQ^{carc}) of the six most carcinogenic PAHs, and the percentages of ΣPAH_{carc} to the ΣPAH_{12} in the sediment core of Lake Fuxian

The total concentration of the six carcinogenic PAHs in the sediment core increased from 21.1 to 367.0 ng g_{dw}^{-1} in the period from 1945 to 2011. Their percentage to the concentration of ΣPAH_{12} increased from 5.7 to 23.3% (Fig. 10). The total TEQ^{carc} in the sediment core increased gradually from 5.0 to 84.6 ngTEQ^{carc} g^{-1} (Fig. 10). The results indicated the increasing potential toxicological risk of the PAHs in the sediments of Lake Fuxian in the period from 1945 to 2011. The average contribution of the six most carcinogenic PAHs to the total TEQ^{carc} in the sediment core decreased in the order as: BaP ($46.9 \pm 1.5\%$) > DahA ($20.6 \pm 2.0\%$) > InP ($15.9 \pm 0.7\%$) > BbF ($8.8 \pm 0.4\%$) > BaA ($7.3 \pm 0.4\%$) > BkF ($0.6 \pm 0.002\%$). The contributions of BbF, BkF, and InP to the total TEQ^{carc} in the sediment core significantly increased with the time in the period from 1945 to 2011 (Fig. 11). BbF, BkF, and InP are mainly derived from the combustion of coal, gasoline, and diesel. The results thereby indicated the combustion of coal, gasoline, and diesel enhanced the potential risks of the PAHs in the sediments of Lake Fuxian from 1945 to 2011. While the contribution of BaA to the total TEQ^{carc} in the sediment core decreased with the time. The contribution of DahA decreased with time before the beginning of the 1980s then increased. In contrast, the contribution of BaP increased with time before the beginning of the 1980s then decreased. The results also showed that the proportions of the individual PAHs within the total PAH concentrations had changed from 1945 to 2011, suggesting a shift in the sources of the PAHs during this period.

Conclusions

Our results indicated that the average concentration of ΣPAH_{12} in the surface sediments of this deep lake (Lake Fuxian) was higher than those of most shallow lakes assessed in China. The average concentration of ΣPAH_{12} in surface sediments of the lake was higher than that in the estuaries. The average concentration of ΣPAH_{12} in the surface sediments of the estuaries of influent rivers was higher than that of the outlet river. We identified the relative contribution of human activities, including coal combustion, gasoline combustion, and diesel combustion, to the occurrence of the PAHs in the surface sediments of this lake. The average concentration of ΣPAH_{12}, the total TEQ^{carc} of the six most carcinogenic PAHs, and the ratio of ΣPAH_{carc} to ΣPAH_{12} increased gradually in the period from 1945 to 2011 and were related to the historical GDP and population of the catchment. The sources of the PAHs in this lake have shifted in the past decades especially in 1999. The contribution of coal combustion to the concentrations of PAHs in the sediment core increased gradually with time. Our study highlighted the importance of such deep lakes in burying PAHs, and the increasing risk of PAHs due to the combustion of coal, gasoline, and diesel caused by human activities. Our study may help to mitigate the pollution and risk of PAHs in Lake Fuxian and the catchment.

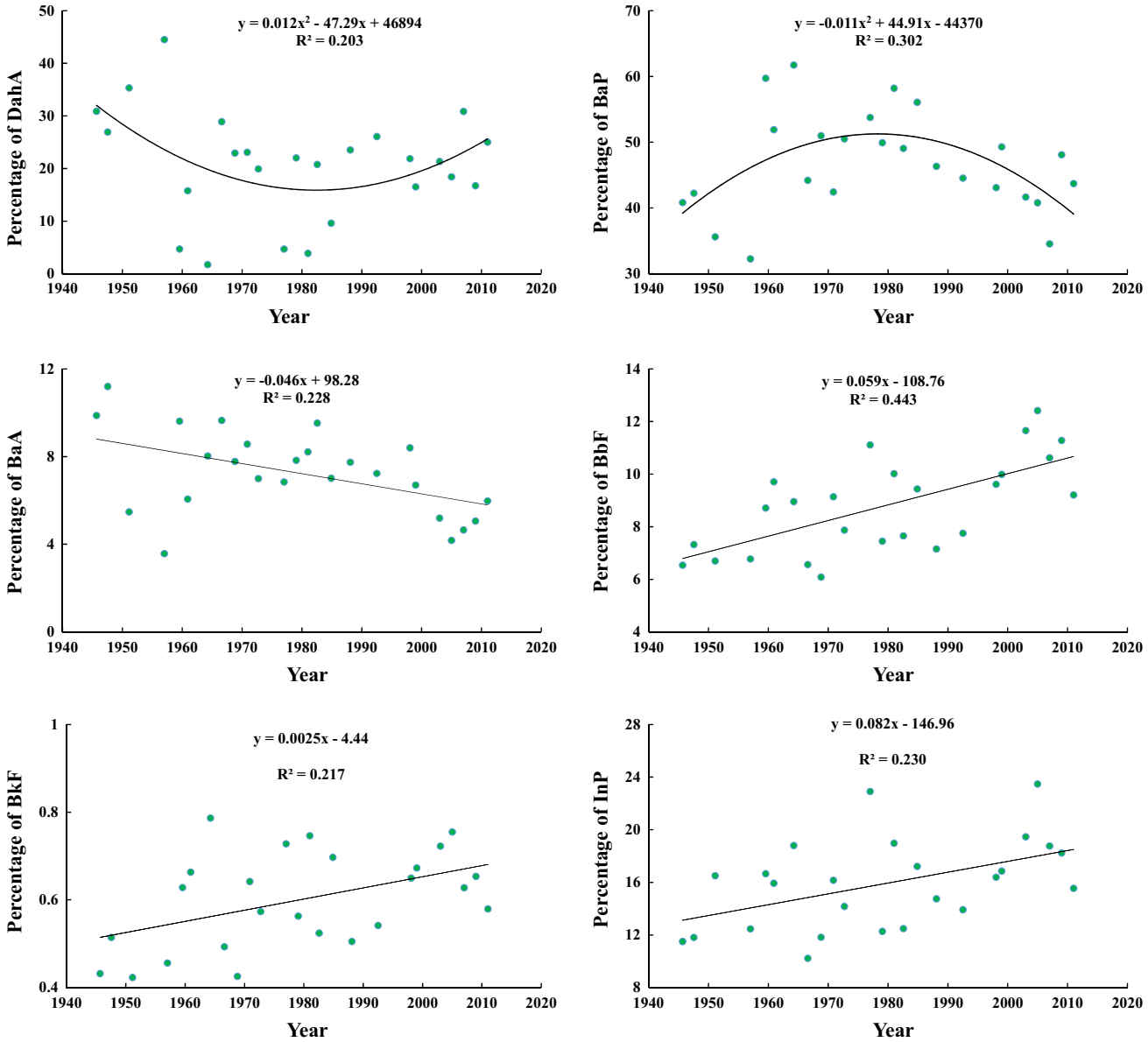

Fig. 11 The temporal trend of the individual contribution of the six most carcinogenic PAHs to the ΣPAH_{carc} in the sediment core of Lake Fuxian

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