

Spatial distribution and sources of polycyclic aromatic hydrocarbons (PAHs) in the reservoir sediments after impoundment of Manwan Dam in the middle of Lancang River, China

NanNan An¹ • Shiliang Liu¹ • Yijie Yin¹ • Fangyan Cheng¹ • Shikui Dong¹ • Xiaoyu Wu¹

Accepted: 16 April 2016 / Published online: 6 May 2016 - Springer Science+Business Media New York 2016

Abstract Polycyclic aromatic hydrocarbons (PAHs) have received increasing attentions owing to their carcinogenicity, teratogenicity and environmental toxicity. The studies on the spatial variations, sources identification and potential ecological risk assessment of PAHs in the reservoir sediments after dam construction are becoming new hotpots. Sixteen PAHs contamination levels were investigated from 15 sample sections in the sediments of Manwan Reservoir in the middle of Lancang River, China. Total concentrations of 16 PAHs ranged from 14.4 to 137.7 ng g^{-1} dw with a mean concentration of 70.68 ng g^{-1} dw. The areas with residential settlement at large tributaries and near dam had higher PAHs concentrations. In the sight of classification of PAHs pollution levels, the sediments of Manwan Reservoir could be considered as low to moderate PAHs polluted levels. One-way analysis of variance for spatial analysis revealed that there were no significant differences ($P < 0.05$) for 16 PAHs at the reservoir head, centre and tail. Moreover, no significant differences $(P<0.05)$ were found for most individual PAH at the mainstream and tributaries except that BaP showed significant differences $(P < 0.05)$ in the mainstream and tributaries. According to the diagnostic ratios, the possible pollution sources of PAHs in Manwan Reservoir might be mixed, primarily including the petroleum source and coal combustion. As compared with sediment quality guidelines, the observed concentrations of PAHs in all sample sections did not exceed the effects range low (ERL) and the threshold effect level (TEL) values, suggesting that there were little harmful biological toxic effects on the aquatic organisms in Manwan Reservoir. The study provided a comprehensive overview on the PAHs contaminations on the reservoir sediments in the middle Lancang River, which may have an important significances on the international river management.

Keywords Polycyclic aromatic hydrocarbons - Sediments · Ecological risk · Source identifications · Manwan Reservoir

Introduction

Sediments are a large sink of various types of chemical pollutants, and the information about their contamination levels are essential for evaluating the impacts of human activities on aquatic ecosystems (Beiras et al. [2003;](#page-8-0) Guevara et al. [2005](#page-8-0)). Among various environmental contaminants, polycyclic aromatic hydrocarbons (PAHs), which are regarded as priority pollutions by the US Environmental Protection Agency (USEPA) due to their carcinogenic, mutagenic and mutagenic (Santodonato [1997](#page-9-0); Mai et al. [2003](#page-8-0)), play significant roles in bioaccumulation and biomagnification on organisms and environment. PAHs origins primarily from anthropogenic sources, such as the discharge of crude oil and its by-products, and the combustion of coal or wood or other organic matter (Simpson et al. [1996\)](#page-9-0). Anthropogenic PAHs can enter to the water environment through direct and indirect discharge, surface runoff, atmospheric transport and deposition, finally be adsorbed by the sediment particles in the riverine ecosystem (Yunker et al. [2002](#page-9-0)). Even under proper conditions, sorbed PAHs will again release into the water body as an

 \boxtimes Shiliang Liu shiliangliu@bnu.edu.cn

State Key Laboratory of Water Environment Simulation, School of Environment, Beijing Normal University, Beijing, China

extended source that threaten the aquatic environment, which could result in "secondary pollution" (Hu and Aitken [2012;](#page-8-0) Zheng et al. [2014](#page-9-0)).

It is very essential to identify the pollution sources of PAHs for estimating their future ecological risk because of severe potential exposure risk on humans. PAHs source identification is comprehensive work since PAHs derived from various origins as a result of natural and anthropogenic inputs by various contaminated characteristics and transport pathways. Oil spills, domestic and industrial waste discharges and incomplete combustion of coal have caused significant accumulation of PAHs between different environmental media (Van Metre et al. [2000;](#page-9-0) Qiao et al. [2006;](#page-9-0) Ren et al. [2010](#page-9-0)). Diagnostic ratios have been frequently employed to distinguish PAHs sources (To-biszewski and Namieśnik [2012;](#page-9-0) Wang et al. [2013;](#page-9-0) Li et al. [2012\)](#page-8-0). The existing literatures have found the practicability of diagnostic ratios were on the basis of differences of thermodynamic stabilities between isomers of the same molecular mass in source apportionment. Some diagnostic ratios, including $Ant/(Ant + Phe)$, $Fla/(Fla + Pyr)$, $BaA/$ $(BaA + Chr)$, and InP/(InP + BghiP), were widely used to distinguish sources in the different environmental media (rivers, soils, atmosphere and sediments) (Wang et al. [2011;](#page-9-0) Yunker et al. [2002](#page-9-0)).

In recent years, the studies on the environmental behaviors of PAHs have focused on the rivers, lakes and bays (Sun et al. [2009](#page-9-0); Huang et al. [2014;](#page-8-0) Yang et al. [2013](#page-9-0)), whereas, studies on the reservoir ecosystems in which landbased pollutants caused by numerous human activities after construction and operation of dams were deficient. Eight cascade dams have been planned or constructed along the mainstream of Yunnan section of Lancang River, which have emerged with the enormous effects of extensive hydropower development (Brian et al. [1996\)](#page-8-0). There were currently five large operated dams: the Gongguoqiao, Xiaowan, Manwan, Dachaoshan and Jinghong. The environmental consequences and ecological risk of the Manwan Reservoir in the mainstream of middle Lancang River have attracted increasing attention. Results from previous studies have indicated that the sediments quality was slightly threatened by heavy metals (e.g. Cd, Cr, Cu, Pb and Zn) and nutrient pollution (representative of phosphorus) in some localized areas in Manwan Reservoir, simultaneously influenced by natural and human activities (Liu et al. [2013](#page-8-0); Dong et al. [2016](#page-8-0)). Further, significant differences of spatial variations of some heavy metals and phosphorus fractions were found in the reservoir (Wang et al. [2012](#page-9-0); Liu et al. [2013\)](#page-8-0). Following the construction of Manwan Dam, the economic and population growth rates in Manwan Town over the past few years have seen tremendous increases. Therefore, the study on the spatial distributions and sources of PAHs in Manwan Reservoir would be an essential and typical example for toxicity assessment for the international river.

Little information is available about the occurrence, spatial distributions of PAHs, and toxicity risk assessment of PAHs in the sediments in Manwan Reservoir in the middle of the Lancang River. The objectives of this study are to: (1) explore the spatial variations and characteristics of PAHs in the sediments; (2) identify the possible sources of the PAHs; (3) evaluate the ecological toxicity assessment using sediment quality guidelines (SOGs).

Materials and methods

Study area

The Lancang River is the largest international river in Asia with a length of 4880 km, flowing through China, Laos, Myanmar, Thailand, Cambodia, and Vietnam. Its unique geographic features and hydraulic properties provide many advantages for hydropower cascade development along the mainstream (He et al. [2005](#page-8-0)). Fourteen cascade dams have been planned or constructed in the middle and lower reaches of Lancang River since the early 1980s. Of the constructed cascade dams along the mainstream of Lancang River, Manwan Dam has been first completed in 1995, which was a canyon reservoir located in a gorge flanked by high mountains. As the first multimillion kilowatt hydropower station in Yunnan Province, the total reservoir capacity is 1060×10^6 m³, with a normal water level of 994 m; the effective capacity is 257×10^6 m³ depending upon seasonal discharge regulation. The water area of the reservoir is 23.6 km^2 , and the width of the water surface is, on average, 337.1 m. The study area is located in the middle Lancang River (Fig. [1](#page-2-0)), is characterized by typical indian monsoon climates with a subtropical lowlatitude mountain climate (Bian and Wang [1991\)](#page-8-0). Average annual temperature is in the range of $18-20$ °C, and an annual rainfall ranges from 1000 to 1150 mm. In study area, dry and wet seasons are clear due to the uneven seasonal allocation of precipitation (Wang and Wang [2002](#page-9-0); Wang et al. [2012](#page-9-0)).

Sampling collection

Surficial sediment samples (0–15 cm) were collected using a stainless steel Van Veen grab sampler to investigate the spatial distributions of PAHs on January, 2015. The detailed sampling locations were shown in Fig. [1,](#page-2-0) including ten sampling sites (M1–M10) in the mainstream and five sampling sites (T1–T5) in the tributaries in Manwan Reservoir. Each sample in a cross-section was a mixture of three sampling sites: the left, middle and right of each

Fig. 1 Locations of the Manwan Reservoir and the 15 cross-sectional sediment sampling sites. M: the samples in the main stream (M1–M10); T: the samples in the tributaries $(T1-T5)$

Lancang River

section. Both the right and left sampling sites were selected from 1 m to the river shore. All of the sediments were freeze-dried in the laboratory using a freeze-dryer and stored at -20 °C for further experimental analysis.

Experimental analysis

5 g of freeze-dried (passed through 100-meshes nylon sieve) sediment were extracted using accelerated solvent extraction (ASE) (Dionex ASE 350) (Wang et al. [2007](#page-9-0); Yin et al. [2011](#page-9-0)). The samples were extracted in a 66 ml stainless steel vessel, which was bedded with 10 g of kieselguhr, then covered with 10 g of granular anhydrous $Na₂SO₄$ and 5 g copper powder. Extraction was performed with the mixture of a 1:1 (v/v) dichloromethane/acetone at 140 °C and 10 MPa for a 5 min heat-up followed by a 5 min static extraction. The vessel was then rinsed with 17 ml of the same solvent and the extracted analyses were purged from the sample cell using pressurized nitrogen through 60 s at 1500 psi. The whole procedure for one sample needed about 30 min and cycled twice. The combined extracts were evaporated on a rotary vacuum evaporator until 1 ml twice. Samples were allowed to pass through florida silica column. Then, 4:1 (v/v) *n*-hexane/ acetone mixture were added to column by 2 ml min^{-1} . Samples were concentrated again in a rotary evaporator to a volume of 5 ml. The concentrated extract was dried under nitrogen steam. The residue was dissolved in 1 ml of n-hexane, and hexamethylbenzene was added as internal standard before performing gas chromatography-mass spectroscopy (GC–MS) analyses (Yang et al. [2013\)](#page-9-0).

 $\frac{6}{1}$ Kilometers

PAHs were analyzed using GC–MS (GC–MS 2010QP-Ultra) coupled with a HP-5972 mass selective detector operated in the electron impact mode (70 eV) installed with a DB-5 capillary column $(30 \times 0.25$ mm diameter, 1 µm film thickness). Helium (99.999 %) was used as the GC carrier gas at a constant flow of 1.5 ml min^{-1} . An 1.0 µl concentrated sample was injected with splitless mode. The chromatographic conditions were as follows: injector temperature 300 °C; detector temperature 310 °C; oven temperature initially at 80 \degree C for 1 min, increased to $300 \degree C$, and held for 35 min. Chromatographic peaks of samples were identified by mass spectra and retention time. In this study, target analytes were 16 EPA priority PAH compounds as follows: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorine (Fla), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), 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 (InP), dibenzo[a,h] anthrancene (DahA), and benzo[g,h,i]perylene (BghiP). Method blanks, spiked blanks and sample duplicates were routinely analyzed with field samples in this case. The method detection limits were 0.4–1.2 ng g^{-1} , and the average recovery efficiency of four surrogate compounds was 90 \pm 15 % in all samples.

Statistical analysis

PAH concentrations in the sediments at different sites were subjected to an analysis of variance (ANOVA) in order to classify and test for significant differences ($P < 0.05$) by using statistical package of SPSS 18.0.

Results and discussions

Concentrations and spatial distributions of PAHs in the sediments

PAHs concentrations in the sediments of Manwan Reservoir

The total concentrations of 16 PAHs in the sediments ranged from 14.4 to 137.7 ng g^{-1} dw with a mean value of 71.51 ng g^{-1} dw. The highest concentrations of total PAHs were recorded at site M10 in the mainstream and site T3 in the tributary, while lowest values of PAHs were at site M6 in the mainstream and site T2 in the tributaries, respectively (Fig. 2a). Moreover, the pollution levels suggested by Baumard et al. [\(1998](#page-8-0)) can be used to classify the relative contamination levels. PAHs in the sediments from Manwan Reservoir can be identified as low to moderate pollution level. Only sites M8 and M10 in the mainstream and sites T3 and T4 in the tributaries were at moderate PAH pollution level, while other sample sites were characterized as low pollution level according to Table [1.](#page-4-0) This suggested that the existing PAHs concentrations did not pose heavy pollution on the sediments.

The 16 PAHs were divided into three groups on the basis of the number of their aromatic rings: 2, 3-ring; 4-ring; 5, 6-ring PAHs (Fig. 2b). The percentages were 24–93 % for 2, 3-ring PAHs, 7–42 % for 4-ring PAHs, and 0–53 % for 5, 6-ring PAHs, respectively. According to Fig. 2b, 2, 3-ring and 4-ring PAHs were predominate PAH congeners in the sediments measured throughout the Manwan Reservoir.

Comparing to the other rivers in China and other countries, the PAHs concentrations in the sediments from Manwan Reservoir were relatively lower than the other rivers in China such as Taihu Lake, Yellow River and Liao River. Meanwhile, the sediments contaminated by PAHs in Manwan Reservoir was close to those reported from Laizhou Bay, China and Lake Iznik, Turkey.

Spatial variations of PAHs in the sediments of Manwan Reservoir

In order to preferably analyze spatial distribution of PAHs, the first three cross-sectional samples (M1–M3) were selected to reveal changes as the reservoir tail. The next

1076 N. An et al.

seven cross-sectional samples (M4–M8, T1 and T2) were chosen as the reservoir center, and the last five cross-sectional samples (samples M9, M10, T3–T5) were chosen as the reservoir head close Manwan Dam.

The spatial distributions of PAHs in the sediments along the Manwan Reservoir were displayed in Fig. 3. The concentrations levels of Ant, Flu, Pyr, Chr, DahA, InP and BghiP showed a similar pattern with high concentrations observed at the reservoir centre and low concentrations observed at the reservoir tail and head. Most of the PAHs had the lowest values in the reservoir tail. Higher concentrations were found in the reservoir centre and head mainly because there were more tributaries in the centre and head, and these tributaries with emission would merge into the mainstream, in which were the confluence of the Mangshuai, Sanjiacun, and Jingfang rivers. The untreated sewage effluents from industrial or

municipal activities, upstream runoff from mining sites and agricultural land, and deposition of air pollutants resulted in the increase of contaminated levels in the sediments (Li et al. [2001\)](#page-8-0). Average concentrations of BaP were higher in the reservoir head than those in the reservoir centre and tail. In addition, BaP was often considered as a good marker for powered vehicles (Esen et al. [2008](#page-8-0)). There were some reservoir docks located at the reservoir centre and tail, more fishing vessels were operated and more vehicles were gathered to emission exhaust. Results of ANOVA showed that there were not significant differences for the 16 individual PAHs $(P\lt 0.05)$ at the reservoir centre, head and tail. No significant difference of the PAHs along the reservoir tail, centre and head, which verified that the construction and operation of the Manwan Dam did not significantly affect the spatial distributions of PAHs in the sediments.

Table 1 Comparisons of PAHs in different surface sediments in China and other countries

^a Number of PAH compounds analyzed in each study

^b Concentrations are the reported sums of the measured PAH, which vary for each study

 c Pollution levels (Baumard et al. [1998\)](#page-8-0), scale of level of contamination: low: 0–100; moderate: 100–1000; high: 1000–5000; very high: $>$ 5000 (Baumard et al. [1998\)](#page-8-0)

Fig. 3 Average concentrations of PAHs in the reservoir tail, centre and head of Manwan Reservoir (ng g^{-1} dw); The same small letter indicated that there were no significant difference between main stream and tributaries ($P < 0.05$); the different small letter indicated that there were significant difference between main stream and tributaries ($P < 0.05$)

Spatial variations of PAHs in the mainstream and tributaries of Manwan Reservoir

Figure 4 showed that results of statistical comparisons of the mainstream and tributaries using ANOVA. There were significant difference in BaP between mainstream and tributaries, while there were no significant differences in other individual PAH between mainstream and tributaries. The average concentrations of BaP in the tributaries were higher than those in the mainstream. Tributaries could carry and import more pollution into the mainstream and it was noteworthy that the PAHs contamination levels of tributaries were often very high (Song et al. [2010](#page-9-0)). Phe, Flu, Pyr, Chr and BaA could be originated from coal burning according to previous studies (Zuo et al. [2007](#page-9-0)). These individual PAH in the mainstream were higher than those in the tributaries, mainly due to the development of counties along the mainstream, including Yun County, Fengqing County, and Nanjian County with increasing coal burning activities crop residues for cooking, water heating, etc.

Source identification

Composition pattern of PAHs

PAHs composition pattern have provided most important information on sources identification in environmental samples (Yang et al. [2013\)](#page-9-0). According to the numbers of aromatic rings, the 16 PAHs were divided into two groups: the low molecular weight parent PAHs (LPAHs, 2, 3-ring) and high molecular weight parent PAHs (HPAHs, 4 to 6-ring). LPAHs are mainly from combustion (low-temperature pyrolysis) or petrogenic process, whereas HPAHs have a predominantly pyrolytic origin (Harrison et al. [1996;](#page-8-0) Mai et al. [2003\)](#page-8-0). As shown in Fig. [5](#page-6-0), HPAHs were dominant in the sediments in reservoir tail and reservoir center (except M6) and reservoir head (except M9 and T5), indicating that pyrogenic sources were predominant across the entire study region. At sites M6, T2, M9 and T5, LPAHs were dominant components, which resulted from the uneven distribution of the individual PAH along the reservoir. The sites M6, T2, M9 and T5 might be far from the large counties and industries resulting in the little polluted by human activities, including coal combustion and rural wastes discharge. The specific sources of PAHs would be further discussed with other evidence in the following section.

Isomeric ratios of PAHs

PAH isomer pairs ratios, such as $Ant/(Ant + Phe)$, $B(a)A/$ $(B(a)A + Chr)$ and Flu/(Flu + Pyr), are frequently used as distinct chemical tracers to distinguish possible sources of PAHs in environment (Mehdinia et al. [2014;](#page-8-0) Yang et al. [2013](#page-9-0); Doong and Lin [2004](#page-8-0)). Owing to the different origins of PAHs combined with the variable structures and compositions, the composition characteristics are employed to identify the pollution sources in environmental samples. According to Yunker et al. ([2002\)](#page-9-0), ratios of Ant/(Ant + Phe) are higher than 0.1 in the sampling sites, suggesting petrogenic inputs of PAHs are the main source, whereas it reveals that the environment are primarily contaminated by petroleum inputs. In addition, $Flu/(Flu + Pyr)$ ratios less than 0.4 are attributed to petrogenic sources; ratios of Flu/ (Flu $+$ Pyr) higher than 0.5 demonstrate that grass, wood, or coal combustion are the main sources of PAHs. If the ratios are between 0.4 and 0.5, PAHs possibly derive from combustion of petroleum. The $B(a)A/(B(a)A + Chr)$ ratios are another useful indicators in analyzing the attribution of PAH pollution. When $B(a)A/(B(a)A + Chr)$ ratios are lower than 0.2, between 0.2 and 0.35, higher than 0.35, indicated petroleum, petroleum combustion, and combustion origins of PAHs, respectively (Ping et al. [2007](#page-9-0); Bouloubassi et al. [2012\)](#page-8-0).

Fig. 4 Average concentrations of PAHs in the sediments from mainstream and tributaries of Manwan Reservoir (ng g^{-1} dw); The same small letters indicated that there were no significant difference between main stream and tributaries ($P < 0.05$); the different small letters indicated that there were significant difference between main stream and tributaries ($P < 0.05$)

According to Fig. 6, the ratios of Ant/(Ant $+$ Phe) at most sampling sites were lower than 0.1, suggesting that PAHs mainly originated from petroleum source, whereas the ratios of sites M5 and M8 were higher than 0.1, indicating that the PAHs source could be combustion activities.

The ratios of Flu/(Flu + Pyr) at sites T4, M10 were higher than 0.5, indicating that PAHs were primarily from

biomass and wood combustion. There were some heavy metal industries and populated area that have elevated levels of coal combustion activities (Zhao et al. [2012](#page-9-0)). Residential living and rural activities that use biomass fuel might be other sources of PAHs. The values of Flu/ (Flu + Pyr) at sites T3, M5 ranged from 0.4 to 0.5, suggesting that petroleum-related combustion were largely

Fig. 6 PAH isomer ratios in estimating possible sources in the sediments in Manwan Reservoir

responsible for the source of PAHs. These areas were close to reservoir docks and shipping activities and suffered from transportation traffic. Therefore, leakiness of gasoline from fishing vessels and ships and atmospheric deposition (from vehicle exhaust) can be considered as factors that are responsible for combustion emissions of PAHs. Moreover, Manwan Reservoir sediment were polluted by human activities, the sources on the sewage effluents and domestic wastewater were found (He et al. [2004\)](#page-8-0). While the ratios of most sites (e.g. M1, M2 and M9) in the mainstream lower than 0.4 indicated that PAHs were mainly from petrogenic processes.

For $B(a)A/(B(a)A + Chr)$, the ratios of sites M3 and T5 were between 0.2 and 0.35, implying that PAH were derived from mixed origins. The ratios of most sites (e.g. M5, M2, M7, T1 and T3) were higher than 0.35, suggesting that the coal combustions of PAH were the main source. These findings suggested that PAHs in the reservoir sediments could mainly derive from complex sources, including the petroleum and coal combustion. The results could be related with vehicle emission, as some sample sites are close to the highway, which is important for transportation. So PAHs pollution was possibly caused by automobile exhausts and street runoff. In addition, there were some heavy metals industries near the Manwan Reservoir which could burn more coals results in polluted gas (Li [1999\)](#page-8-0).

Ecological toxicity assessment

SQGs are significant tools to assess the ecological risks in river sediments. In this case, two sets of SQGs, including effects range low (ERL)/effects range median (ERM) and the threshold effect level (TEL)/the probable effect level (PEL) were applied to assess the ecological toxicity of individual PAH in the sediments. For the three ranges of chemical concentrations, adverse biological effects were expected rarely (<ERL/TEL), occasionally (>ERL/TEL and \leq ERM/PEL), and frequently (\geq ERM/PEL).

The measured concentrations of PAHs in this study area were compared with the ERL/ERM and TEL/PEL values (Table 2). Sixteen individual PAH concentrations were below the ERL and TEL in Manwan Reservoir. In the other words, PAHs in the sediments of Manwan Reservoir did not currently impose ecologically hazardous impacts on the sedimentary environment.

Conclusions

Sixteen PAHs concentrations were investigated in the sediments in Manwan Reservoir in the middle of Lancang River. The total concentrations of 16 PAHs were in the

Table 2 Comparisons of PAHs concentrations with the ERL/ERM and TEL/PEL guidelines values (ng g^{-1} dw)

| Compound | Mean | Min | Max | ERL | ERM | TEL | PEL |
|---------------|-------|--------------|------|------|--------|------|--------|
| Nap | 10.81 | 4 | 14 | 160 | 2100 | 34.6 | 391 |
| Acy | 0.25 | $\mathbf{0}$ | 2 | 44 | 640 | 6.71 | 88.9 |
| Ace | 0.25 | $\mathbf{0}$ | 0.8 | 16 | 500 | 5.87 | 128 |
| Fla | 1.88 | 1 | 2.6 | 19 | 540 | 21.2 | 144 |
| Phe | 10.45 | 2.6 | 17 | 240 | 1500 | 86.7 | 544 |
| Ant | 1.57 | $\mathbf{0}$ | 10.4 | 85.3 | 1100 | 46.9 | 245 |
| Flu | 4.56 | 0.2 | 10.2 | 600 | 5100 | 113 | 1494 |
| Pyr | 6.63 | 0.8 | 13.6 | 665 | 2500 | 153 | 1398 |
| BaA | 3.55 | $\mathbf{0}$ | 11 | 261 | 1600 | 74.8 | 693 |
| Chr | 4.6 | $\mathbf{0}$ | 11.8 | 384 | 2800 | 108 | 846 |
| BbF | 3.59 | $\mathbf{0}$ | 8.5 | 320 | 1880 | NA | NA |
| BkF | 2.96 | $\mathbf{0}$ | 6 | 280 | 1620 | NA | NA |
| BaP | 15.15 | $\mathbf{0}$ | 57.8 | 430 | 1600 | 88.8 | 763 |
| InP | 1.93 | $\mathbf{0}$ | 5.4 | | | 6.22 | 135 |
| DahP | 1.59 | $\mathbf{0}$ | 8.6 | 430 | 1600 | NA | NA |
| B ghiP | 1.93 | $\mathbf{0}$ | 4 | 63.4 | 260 | NA | NA |
| \sum PAHs | 71.51 | | | 4022 | 44,792 | 1684 | 16,770 |

range of 14.4–137.7 ng g^{-1} dw, with a mean value of 71.51 ng g^{-1} dw. In the mainstream, site M10 close to Manwan Dam was found with the highest PAHs concentration, additionally, site T4 in the largest tributary was detected with the highest PAHs concentration. Total concentrations of PAHs were considered as the low to moderate contamination level based on classification of pollution levels.

ANOVA was used to analyze the spatial variations of PAHs in the sediments in Manwan Reservoir. The concentrations of Ant, Flu, Pyr, Chr, DahA, InP, and BghiP in the reservoir centre were higher than those in the reservoir head and tail. And 16 PAHs had no significant differences between the reservoir head, centre and tail, indicating that the construction of Manwan Dam leaded to insignificant effects on the spatial distributions of PAHs. Moreover, there were not significant differences of most individual PAH between mainstream and tributaries, except for BaP.

Results from PAHs source identification have revealed that PAHs sources in Manwan Reservoir were complex, primarily including leakiness of gasoline and coal burning due to industries development and residential activities. This might be due to the complexity of the factors determining PAHs distribution in the sediment environment. Overall toxicity assessments inferred that PAHs in the sediments of investigated watershed might pose little biological effects on organisms in Manwan Reservoir in the middle of Lancang River.

These results on the spatial distributions, sources and potential toxicity assessments of PAHs in the sediments Acknowledgments This research was funded by National Natural Science Foundation of China (No. 41571173) and National Science and Technology Support Project (No. 2014BAK19B06-2).

Compliance with ethical standards

Manwan Reservoir.

Conflicts of interest Manwan Dam is managed by China Huaneng Group Corporation, a state-owned enterprise. The corporation gave us permission to conduct this sampling study, which did not involve any endangered or protected species. It was environmentally neutral and did not threaten the welfare of any species or that of the local population. Therefore, it was not related to ethical issues and no specific permissions were required for such activities. So there was no the potential conflicts of interest.

Human and animal rights The study did not involve the human participants and animals

References

- Araghi PE, Bastami KD, Rahmanpoor S (2014) Distribution and sources of polycyclic aromatic hydrocarbons in the surface sediments of Gorgan Bay, Caspian Sea. Mar Pollut Bull 89(1–2):494–498. doi[:10.1016/j.marpolbul.2013.12.001](http://dx.doi.org/10.1016/j.marpolbul.2013.12.001)
- Baumard P, Budzinski H, Garrigues P, Sorbe JC, Burgeot T, Bellocq J (1998) Concentrations of PAHs (polycyclic aromatic hydrocarbons) in various marine organisms in relation to those in sediments and to trophic level. Mar Pollut Bull 36(12):951–960. doi[:10.1016/S0025-326X\(98\)00088-5](http://dx.doi.org/10.1016/S0025-326X(98)00088-5)
- Beiras R, Fernández N, Bellas J, Besada V, González-Quijano A, Nunes T (2003) Integrative assessment of marine pollution in Galician estuaries using sediment chemistry, mussel bioaccumulation, and embryo-larval toxicity bioassays. Chemosphere 52(7):1209–1224
- Bian FJ, Wang RY (1991) Characteristics and distribution of agro climatic resources in Yunnan torrid area. Trop Geogr 3:270–277 (in Chinese)
- Bouloubassi I, Roussiez V, Lorre A (2012) Sources, dispersal pathways and mass budget of sedimentary polycyclic aromatic hydrocarbons (PAH) in the NW Mediterranean margin, Gulf of Lions. Mar Chem 142–144(11):18–28
- Brian DR, Jeffrey VB, Jennifer P, David PB (1996) A method for assessing hydrologic alteration within ecosystems. Conserv Biol 10(4):1163–1174. doi:[10.1046/j.1523-1739.1996.100411](http://dx.doi.org/10.1046/j.1523-1739.1996.10041163.x) [63.x](http://dx.doi.org/10.1046/j.1523-1739.1996.10041163.x)
- Dong SK, Zhao C, Liu SL et al (2016) Speciation and pollution of heavy metals in sediment from middle Lancang-Mekong River influenced by dams [J]. Acta Sci Circumst 36(2):466–474
- Doong RA, Lin YT (2004) Characterization and distribution of polycyclic aromatic hydrocarbon contaminations in surface sediment and water from Gao-ping River. Taiwan Water Res 38(7):1733–1744. doi[:10.1016/j.watres.2003.12.042](http://dx.doi.org/10.1016/j.watres.2003.12.042)
- Esen F, Tasdemir Y, Vardar N (2008) Atmospheric concentrations of PAHs, their possible sources and gas-to-particle partitioning at a residential site of Bursa, Turkey. Atmos Res 88(3):243–255
- Guevara SR, Arribére M, Bubach D, Vigliano P, Rizzo A, Alonso M, Sánchez R (2005) Silver contamination on abiotic and biotic compartments of Nahuel Huapi National Park Lakes, Patagonia Argentina. Sci Total Environ 336(1–3):119–134. doi[:10.1016/](http://dx.doi.org/10.1016/jscitotenv200405020) [jscitotenv200405020](http://dx.doi.org/10.1016/jscitotenv200405020)
- Han F, Guo BD, Wang YY (2010) Distribution, sources and ecological risks assessment of PAHs in surface sediments in Liao River. Environ Prot Cycle Econ 12:62–66 (in Chinese)
- Harrison RM, Smith DJT, Luhana L (1996) Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, U.K. Environ Sci Technol 30(3):825–832. doi:[10.1021/es950252d](http://dx.doi.org/10.1021/es950252d)
- He DM, Zhao WJ, Chen LH (2004) Ecological change in the Manwan Reservoir area and its causes. Yunnan Univ Nat Sci 26(3):220–226 (in Chinese)
- He DM, Wu C, Peng H, Yang Z, Ou X, Cui B (2005) A study of ecosystem changes in longitudinal range-gorge region and transbiundary eco-security in southwest China. Adv Earth Sci 20(3):338–344 (in Chinese)
- Hu J, Aitken MD (2012) Desorption of polycyclic aromatic hydrocarbons from field-contaminated soil to a two-dimensional hydrophobic surface before and after bioremediation. Chemosphere 89(5):542–547. doi:[10.1016/j.chemosphere.2012.05.046](http://dx.doi.org/10.1016/j.chemosphere.2012.05.046)
- Hu NJ, Shi XF, Huang P, Liu JH (2011) Polycyclic aromatic hydrocarbons in surface sediments of Laizhou Bay, Bohai Sea. China. Environ Earth Sci 63(1):121–133. doi[:10.1007/s12665-](http://dx.doi.org/10.1007/s12665-010-0675-3) [010-0675-3](http://dx.doi.org/10.1007/s12665-010-0675-3)
- Huang L, Chernyak SM, Batterman SA (2014) PAHs (polycyclic aromatic hydrocarbons), nitro-PAHs, and hopane and sterane biomarkers in sediments of southern Lake Michigan, USA. Sci Total Environ 487(1):173–186. doi[:10.1016/j.scitotenv.2014.03.](http://dx.doi.org/10.1016/j.scitotenv.2014.03.131) [131](http://dx.doi.org/10.1016/j.scitotenv.2014.03.131)
- Li LJ (1999) Water quality status assessment and causal analysis of Lancang River. Acta Geogr Sin 54:127–134. doi:[10.1016/j.](http://dx.doi.org/10.1016/j.envpol.2006.05.029) [envpol.2006.05.029](http://dx.doi.org/10.1016/j.envpol.2006.05.029)
- Li X, Shen Z, Wai OWH, Li YS (2001) Chemical forms of Pb, Zn and Cu in the sediment profiles of the Pearl River Estuary. Mar Pollut Bull 42(3):215–223. doi[:10.1016/S0025-326X\(00\)00145-4](http://dx.doi.org/10.1016/S0025-326X(00)00145-4)
- Li QZ, Li GX, Luo ZX, Zhang X, Yan CY (2009) Pollution characteritics and ecological risk assessment of heavy metals and polycyclic aromatic hydrocarbons (PAHs) in sediment from Xiamen Bay. Environ Chem 6:869–875 (in Chinese)
- Li YB, Liu ZT, Feng L, Zhou JL (2011) Ecological risk assessment of PAHs in the sediments from Taihu Lake. Environ Chem 30(10):1769–1774 (in Chinese)
- Li WH, Tian YZ, Shi GL, Guo CS, Li X, Feng YC (2012) Concentrations and sources of PAHs in surface sediments of the Fenhe Reservoir and watershed, China. Ecotoxicol Environ Saf 75(1):198–206. doi:[10.1016/j.ecoenv.2011.08.021](http://dx.doi.org/10.1016/j.ecoenv.2011.08.021)
- Liu Q, Liu SL, Zhao HD, Deng L, Wang C, Zhao QH, Dong SK (2013) Longitudinal variability of phosphorus fractions in sediments of a canyon reservoir due to cascade dam construction: a case study in Lancang River. China. PLoS One 8(12):1–9. doi[:10.1371/journal.pone.0083329](http://dx.doi.org/10.1371/journal.pone.0083329)
- Machado KS, Figueira RC, Cocco LC, Froehner S, Fernandes CV, Ferreira PA (2014) Sedimentary record of PAHs in the Barigui River and its relation to the socioeconomic development of Curitiba, Brazil. Sci Total Environ 482–483(2):42–52. doi:[10.](http://dx.doi.org/10.1016/j.scitotenv.2014.02.106) [1016/j.scitotenv.2014.02.106](http://dx.doi.org/10.1016/j.scitotenv.2014.02.106)
- Mai BX, Qi SH, Zeng EY, Yang QS, Zhang G, Fu JM (2003) Distribution of polycyclic aromatic hydrocarbons in the coastal region off Macao, China: assessment of input sources and transport pathways using compositional analysis. Environ Sci Technol 37(21):4855–4863. doi[:10.1021/es034514k](http://dx.doi.org/10.1021/es034514k)
- Mehdinia A, Aghadadashi V, Fumani NS (2014) Origin, distribution and toxicological potential of polycyclic aromatic hydrocarbons

in surface sediments from the Bushehr coast, the Persian Gulf. Mar Pollut Bull 90(1–2):334–338. doi:[10.1016/j.marpolbul.](http://dx.doi.org/10.1016/j.marpolbul.2014.09.021) [2014.09.021](http://dx.doi.org/10.1016/j.marpolbul.2014.09.021)

- Ping LF, Luo YM, Zhang HB, Li QB, Wu LH (2007) Distribution of polycyclic aromatic hydrocarbons in thirty typical soil profiles in the Yangtze River Delta region, east China. Environ Pollut 147(2):489–515. doi:[10.1016/j.envpol.2006.05.027](http://dx.doi.org/10.1016/j.envpol.2006.05.027)
- Qiao M, Wang CX, Huang SB, Wang DH, Wang ZJ (2006) Composition, sources, and potential toxicological significance of PAHs in the surface sediments of the Meiliang Bay Taihu Lake China. Environ Int 32(1):28–33. doi:[10.1016/jenvint](http://dx.doi.org/10.1016/jenvint200504005) [200504005](http://dx.doi.org/10.1016/jenvint200504005)
- Ren JL, Zhang J, Li DD, Cheng Y, Liu SM (2010) Behavior of dissolved inorganic arsenic in the Yellow Sea and East China Sea. Deep Sea Res II(57):1035–1046. doi[:10.1016/jdsr22](http://dx.doi.org/10.1016/jdsr2201002005) [01002005](http://dx.doi.org/10.1016/jdsr2201002005)
- Santodonato J (1997) Review of the estrogenic and antiestrogenic activity of polycyclic aromatic hydrocarbons: relationship to carcinogenicity. Chemosphere 34(4):835–848. doi[:10.1016/](http://dx.doi.org/10.1016/S0045-6535(97)00012-X) [S0045-6535\(97\)00012-X](http://dx.doi.org/10.1016/S0045-6535(97)00012-X)
- Simpson CD, Mosi AA, Cullen WR, Reimer KJ (1996) Composition and distribution of polycyclic aromatic hydrocarbon contamination in surficial marine sediments from Kitimat Harbor Canada. Sci Total Environ 181(3):265–278. doi[:10.1016/0048-9697\(95\)](http://dx.doi.org/10.1016/0048-9697(95)05026-4) [05026-4](http://dx.doi.org/10.1016/0048-9697(95)05026-4)
- Song YX, Ji JF, Mao CP, Yang ZF, Yuan XY, Aokyo GA (2010) Heavy metal contamination in suspended solids of Changjiang River—environmental implications. Geoderma 159(3–4):286– 295. doi:[10.1016/jgeoderma201007020](http://dx.doi.org/10.1016/jgeoderma201007020)
- Sun JH, Wang GL, Chai Y, Zhang G, Li J, Feng J (2009) Distribution of polycyclic aromatic hydrocarbons (PAHs) in Henan Reach of the Yellow River Middle China. Ecotoxicol Environ Saf 72(5):1614–1624. doi[:10.1016/jecoenv200805010](http://dx.doi.org/10.1016/jecoenv200805010)
- Tobiszewski M, Namieśnik J (2012) PAH diagnostic ratios for the identification of pollution emission sources. Environ Pollut 162(1):110–119. doi:[10.1016/jenvpol201110025](http://dx.doi.org/10.1016/jenvpol201110025)
- Unlu S, Alpar B, Ozturk K, Vardar D (2010) Polycyclic aromatic hydrocarbons (PAHs) in the surficial sediments from Lake Iznik (Turkey): spatial distributions and sources. Bull Environ Contam Toxicol 85(6):573–580. doi:[10.1007/s00128-010-0134-6](http://dx.doi.org/10.1007/s00128-010-0134-6)
- Van Metre PC, Mahler BJ, Furlong ET (2000) Urban sprawl leaves its PAH signature. Environ Sci Technol 32(19):4064–4070. doi:[10.](http://dx.doi.org/10.1021/es991007n) [1021/es991007n](http://dx.doi.org/10.1021/es991007n)
- Wang P, Wang JL (2002) Basic climatic characteristics in the Manwan hydropower station reservoir area of lancang River, Yunnan Province, China. J Yunnan Norm Univ 6:57–61 (in Chinese)
- Wang WT, Meng BJ, Lu XX, Liu Y, Tao S (2007) Extraction of polycyclic aromatic hydrocarbons and organochlorine pesticides from soils: a comparison between Soxhlet extraction, microwave-assisted extraction and accelerated solvent extraction

techniques. Anal Chim Acta 602(2):211–222. doi[:10.1016/](http://dx.doi.org/10.1016/jaca200709023) [jaca200709023](http://dx.doi.org/10.1016/jaca200709023)

- Wang CP, Sun HW, Chang Y et al (2011) PAHs distribution in sediments associated with gas hydrate and oil seepage from the Gulf of Mexico. Mar Pollut Bull 62:2714–2723
- Wang C, Liu SL, Zhao QH, Deng L, Dong SK (2012) Spatial variation and contamination assessment of heavy metals in sediments in the Manwan Reservoir Lancang River. Ecotoxicol Environ Saf 82(4):32–39. doi:[10.1016/jecoenv201205006](http://dx.doi.org/10.1016/jecoenv201205006)
- Wang XT, Miao Y, Zhang Y, Li YC, Wu MH, Yu G (2013) Polycyclic aromatic hydrocarbons (PAHs) in urban soils of the megacity Shanghai: occurrence, source apportionment and potential human health risk. Sci Total Environ 447(1):80–89. doi[:10.1016/jscitotenv201212086](http://dx.doi.org/10.1016/jscitotenv201212086)
- Yang D, Qi SH, Zhang Y, Xing XL, Liu HX, Qu CK, Liu J, Li F (2013) Levels, sources and potential risks of polycyclic aromatic hydrocarbons (PAHs) in multimedia environment along the Jinjiang River mainstream to Quanzhou Bay China. Mar Pollut Bull 76(1–2):298–306. doi:[10.1016/jmarpolbul201308016](http://dx.doi.org/10.1016/jmarpolbul201308016)
- Yin H, Tan Q, Chen Y, Lv GB, Hou XD (2011) Polycyclic aromatic hydrocarbons (PAHs) pollution recorded in annual rings of gingko (Gingko biloba L): determination of PAHs by GC/MS after accelerated solvent extraction. Microchem J 97(2):138– 143. doi[:10.1016/jmicroc201008004](http://dx.doi.org/10.1016/jmicroc201008004)
- Yuan H, Li T, Ding X, Zhao G, Ye S (2014) Distribution, sources and potential toxicological significance of polycyclic aromatic hydrocarbons (PAHs) in surface soils of the Yellow River Delta China. Mar Pollut Bull 83(1):258–264. doi[:10.1016/jmarpolbul](http://dx.doi.org/10.1016/jmarpolbul201403043) [201403043](http://dx.doi.org/10.1016/jmarpolbul201403043)
- Yunker MB, Macdonald RW, Vingarzan R, Reginald HM, Goyette D, Sylvestre S (2002) PAHs in the Fraser River Basin: a critical appraisal of PAH ratios as indicators of PAH source and compositions. Org Geochem 33(4):489–515. doi:[10.1016/S0146-](http://dx.doi.org/10.1016/S0146-6380(02)00002-5) [6380\(02\)00002-5](http://dx.doi.org/10.1016/S0146-6380(02)00002-5)
- Zhang L, Qin Y, Zheng B, Lin T, Li Y (2013) Polycyclic aromatic hydrocarbons in the sediments of Xiangjiang River in southcentral China: occurrence and sources. Environ Earth Sci 69(1):119–125. doi:[10.1007/s12665-012-1939-x](http://dx.doi.org/10.1007/s12665-012-1939-x)
- Zhao QH, Liu SL, Deng L, Yang ZF, Dong SK, Wang C, Zhang ZL (2012) Spatio-temporal variation of heavy metals in fresh water after dam construction: a case study of the Manwan Reservoir, Lancang River. Environ Monit Assess 184(7):4253–4266. doi[:10.1007/s10661-011-2260-y](http://dx.doi.org/10.1007/s10661-011-2260-y)
- Zheng Y, Lin ZR, Li H, Ge Y, Zhang W, Ye YB, Wang XJ (2014) Assessing the polycyclic aromatic hydrocarbon (PAH) pollution of urban stormwater runoff: a dynamic modeling approach. Sci Total Environ 481(2):554–563. doi[:10.1016/jscitotenv201402097](http://dx.doi.org/10.1016/jscitotenv201402097)
- Zuo Q, Duan YH, Yang Y, Wang XJ, Tao S (2007) Source apportionment of polycyclic aromatic hydrocarbons in surface in Tianjin, China. Environ Pollut 147(2):303–310. doi[:10.1016/](http://dx.doi.org/10.1016/jenvpol200605029) [jenvpol200605029](http://dx.doi.org/10.1016/jenvpol200605029)