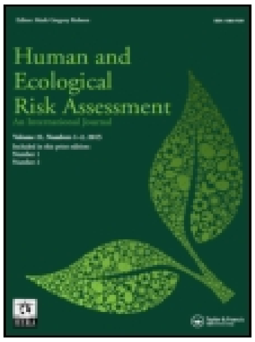

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Human and Ecological Risk Assessment: An International Journal

ISSN: 1080-7039 (Print) 1549-7860 (Online) Journal homepage: http://china.tandfonline.com/loi/bher20

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To cite this article: Yueling Qi, Anita Awino Owino, Victorine Anyango Makokha, Yun Shen, Di Zhang & Jun Wang (2016) Occurrence and risk assessment of polycyclic aromatic hydrocarbons in the Hanjiang River Basin and the Danjiangkou Reservoir, China, Human and Ecological Risk Assessment: An International Journal, 22:5, 1183-1196, DOI: 10.1080/10807039.2016.1147942

To link to this article: http://dx.doi.org/10.1080/10807039.2016.1147942

HUMAN AND ECOLOGICAL RISK ASSESSMENT
2016, VOL. 22, NO. 5, 1183–1196
http://dx.doi.org/10.1080/10807039.2016.1147942

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Occurrence and risk assessment of polycyclic aromatic hydrocarbons in the Hanjiang River Basin and the Danjiangkou Reservoir, China

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ABSTRACT
This study was conducted to investigate the occurrence, distribution, and source of 16 polycyclic aromatic hydrocarbons (PAHs) in the Hanjiang River Basin and the Danjiangkou (DJK) Reservoir. The concentrations of total PAHs in surface water, sediments, and bank soils ranged from 9.42 to 137.94 ng/l, 86.23 to 2514.93 ng/g, and 133.17 to 671.93 ng/g dry weight, respectively. The composition pattern of PAHs showed that 3-ring PAHs were dominated in all of the samples, while the proportion of high molecular weight PAHs (5- to 6-ring PAHs) in sediments and bank soil samples was almost three times higher than water. The source apportionment analysis showed that most of the PAHs in water were derived from sources of petroleum and combustion, while combustion was the predominant source of PAHs in sediments and bank soils. The methods based on toxic equivalency factors, risk quotient, and incremental lifetime cancer risk were used to assess the ecosystem risk and potential health risk of PAHs. The risk assessments showed that PAHs in the DJK Reservoir were out of potential health risk, but the ecological risk for majority of 16 PAHs was in the moderate level.

ARTICLE HISTORY
Received 23 November 2015
Revised manuscript accepted 26 January 2016

KEYWORDS
PAHs; occurrence; risk assessment; Danjiangkou Reservoir; South-to-North Water Diversion Project (SNWDP)

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a classical group of persistent organic pollutants containing two or more fused aromatic rings with common occurrence in the different environmental media. These compounds are generated by natural and anthropogenic processes. Human activity is the main source for the PAH input into the aquatic environment, including wastes from industrialized and urbanized areas, and the incomplete combustion of organic matter (Baumard *et al.* 1998; Chen *et al.* 2007b; Phillips 1999). PAHs are considered to be hazardous to human health, including highly mutagenic and carcinogenic PAHs with 4–7 rings, less mutagenic but highly toxic PAHs with 2 or 3 rings. The International

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Agency for Research on Cancer characterized several hundreds of PAHs including the marker of PAH benzo[*a*]pyrene (BaP) (Boffetta *et al.* 1997). Specially, 16 PAHs were listed as the priority pollutants by the US Environmental Protection Agency (USEPA) (Countway *et al.* 2003; Kim *et al.* 1999; Sun *et al.* 2009). For the past decades, the distribution, transport, source and potential risk to ecological systems and human health of the 16 priority PAHs have been extensively studied (Cachada *et al.* 2012; Mitra and Bianchi 2003; Ravindra *et al.* 2008; Shi *et al.* 2005; Zhang *et al.* 2013).

The Hanjiang (HJ) River is the biggest tributary of Yangtze River, situated in the central part of China. The HJ River Basin involved in provinces of Shaanxi, Hubei, Henan, Sichuan, Gansu, and Chongqing is of crucial importance in both economy and ecology of this region (Zhu *et al.* 2008). However, due to the rapid processes of urbanization and economic development, the water quality of the HJ River suffered a swift deterioration during the 1990s (Zhang and Ao 2004). The Danjiangkou (DJK) Reservoir located in the upper HJ River, consisting of the Dan Reservoir (DR) and the Han Reservoir (HR), was constructed since 1958 and finished until 2005, designed as the important water source of the Middle Route Project of the South-to-North Water Diversion Project (SNWDP). Tremendous and inevitable transformations have been delivered to the HJ River Basin following the completion of the DJK Reservoir and the operation of SNWDP. Though many environmental concerns had been raised, studies about the occurrence and the impact of PAHs pollution in this region have been limited to date (Chen *et al.* 2007a; Li *et al.* 2009; Wang and Ma 1999; Yang *et al.* 2006). The storage of the DJK Reservoir was mainly from the upstream of the HJ River Basin. The water quality in upper reach of the HJ River Basin and the DJK Reservoir has a profound influence on the human health of citizens in the Northern China.

Surface water, sediment and bank soil samples from the HJ River Basin and the DJK Reservoir were collected in this study. The aim of this study was to investigate the concentrations, distribution characteristic and sources of PAHs in the HJ River Basin and the DJK Reservoir. Assessing the ecological risk and human health risk through water consumption based on these primary results would provide references and advices for the environmental management.

Methods and materials

Chemicals

Mixture of 16 priority PAHs of the USEPA was purchased from AccuStandard, Inc., New Haven, CT, USA, including naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flr), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo[*a*]anthracene (BaA), chrysene, benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), BaP, dibenz[*a,h*]anthracene (DahA), benzo[*g,h,i*]perylene (BghiP) and indeno[1,2,3-cd]pyrene (InP). Anhydrous sodium sulfate (Na_2SO_4) was baked at 450°C for 4 h to remove moisture and organic impurities before use. Florisil with 60–100 mesh and neutral silica gel with 100–200 mesh were activated in a drying oven at 150°C for 10 h and 180°C for 12 h, respectively. The neutral silica gel was deactivated with 3% ultrapure water. Activated copper powder was prepared by washing with hydrochloric acid (2 N) and pure water, and finally stored in acetone. All organic solvents used were high-performance liquid chromatography (HPLC) grade (Fisher Scientific, Waltham, MA, USA).

Sample collection and preparation

A total of 48 surface water samples, 28 sediments (0–10 cm) and 18 bank soils (0–10 cm) were collected in December 2014. Twenty-eight surface water and 28 sediments were collected from upstream and downstream of the HJ River. Twenty surface water samples were collected in the DR and the HR of the DJK Reservoir, respectively. Eighteen soil samples were collected near the DJK Reservoir bank (Figure 1 and more detail supplied in Supplementary Material Table S1). Water samples were collected using precleaned Teflon bottles and transported to the laboratory stored at 4°C and extracted within 3 days. The sediments were sampled with a grab device and the bank soils were collected with a stainless steel shovel. Both sediment and bank soil samples were stored at –20°C before extraction.

Sample extraction and cleanup

Water samples were filtrated through 0.22-μm hydrophilic filters under vacuum to remove suspended particles. A solid-phase extraction (SPE) method was used to extract target PAHs from water samples. The C18 SPE cartridges (500 mg, Agilent, Inc., Santa Clara, CA, USA) were conditioned with 6 ml dichloromethane (DCM), 6 ml methanol and 3 ml pure water, successively. One liter of water sample was mixed with 100 ml 2-propanol, and percolated through the cartridge at the speed of 5 ml/min. The cartridge was dried for 3 h after extraction and then the cartridge was eluted with 20 ml DCM to yield a fraction containing PAHs. The eluent was concentrated to 50 μl under a gentle stream of high-purity nitrogen after 50 μl acetonitrile (ACN) was added as solvent keeper for HPLC analysis.

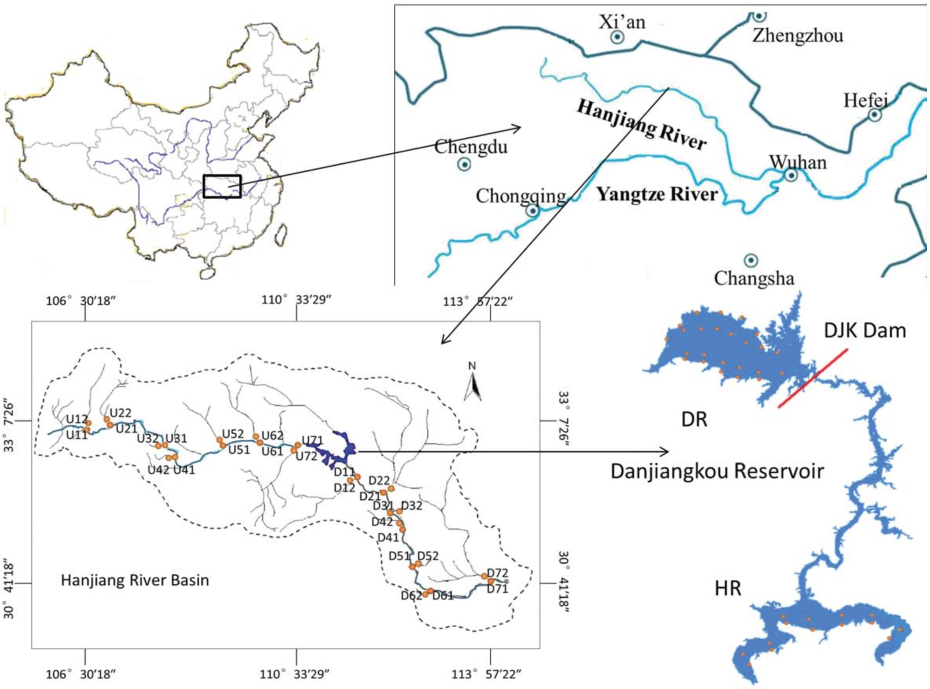

Figure 1. Sampling sites in the Hanjiang River Basin and the Danjiangkou Reservoir, China. DR: Dan Reservoir; DJK: Danjiangkou; HR: Han Reservoir.

The sediment and bank soil samples were lyophilized, ground to pass through a sieve of 2-mm stainless steel. One gram of sample was ground with 3 g C18 powder (SiliCycle, Inc., Quebec City, QC, Canada) for 5 min in a glass mortar. Then the mixture was transferred into a prepared 10 ml polyethylene syringe barrel column. The column was packed with a piece of 0.22-μm membrane filter, 1 g anhydrous sodium sulfate, 1 g Florisil, 1 g neutral silica gel and 2 g activated copper powder from the bottom to top. Another 0.22-μm membrane filter was laid on the top of the column after sample mixtures were loaded (Wang *et al.* 2011). The packed column was eluted with 20 ml DCM. The eluent was concentrated to 50 μl under a gentle stream of high-purity nitrogen after 50 μl ACN was added as solvent keeper for HPLC analysis.

Instrumental analysis

PAHs were analyzed by a HPLC (Agilent 1220 Infinity LC) system. Athena PAHs special column (4.6 × 250 mm, 5 μm) was purchased from CNW, Inc. (Düsseldorf, Germany). The mobile phases were HPLC-grade ACN and pure water with linear gradient. The linear gradient was set up from 40% ACN to 100% in 25 min (kept 100% ACN for 10 min) and then 100% ACN to 40% in 10 min (kept 40% ACN for 15 min). The flow rate of the mobile phase was kept at 2.0 ml/min and the temperature of the column oven was 30 ± 0.8°C. Ten microliters of the sample solution was injected into HPLC system by an automatic injector and an ultraviolet detector was equipped to detect PAHs at 266 nm. Total organic carbon (TOC) content of all the samples was measured by the TOC analyzer (Elementar, Inc., Germany).

Ecological risk assessment

The ecological risk of PAHs in surface water, sediments and bank soils was evaluated using the risk quotient (RQ). RQ is based on scientifically derived risk limits: the maximum permissible concentrations (MPCs) and the negligible concentrations (NCs) (Kalf *et al.* 1997). When the concentrations were above MPCs, the risk of adverse effects was considered unacceptable. The NC was defined as the MPC/100 and took into account possible effects of combination toxicity due to the presence of other substances. However, there were no quality values such as MPCs and NCs available for six PAHs species (Acy, Ace, Flr, Pyr, BbF and DahA), so the quality values of congeners with the same toxicity equivalence factors (TEFs) (Nisbet and LaGoy 1992) were assigned to those compounds for risk assessment. The NCs and MPCs for 16 priority PAHs are listed in Supplementary Material Table S2.

RQ was defined using Eqs. (1)–(3):

$$\mathrm{RQ} = \frac{\mathrm{C_{PAHs}}}{\mathrm{QV}} \tag{1}$$

$$\mathrm{RQ_{NCs}} = \frac{\mathrm{C_{PAHs}}}{\mathrm{QV(NCs)}} \tag{2}$$

$$\mathrm{RQ_{MPCs}} = \frac{\mathrm{C_{PAHs}}}{\mathrm{QV(MPCs)}} \tag{3}$$

where $\mathrm{C_{PAHs}}$ is the mean concentration of certain PAHs in the medium; QV is the corresponding quality value of the PAHs species in the medium. QV(NCs) and QV(MPCs) are quality values of NCs and MPCs. When $RQ_{NCs} < 1$, the risk of single PAHs is negligible, while $RQ_{MPCs} \geq 1$ would indicate that ecological risk of the single PAHs is high and some control measures and remedial actions must be undertaken at once. When $RQ_{NCs} \geq 1$ and $RQ_{MPCs} < 1$, the ecological risk of the single PAHs is listed as middle level (Cao *et al.* 2010). However, this calculation method was not accurate to assess the risk of $\sum$PAHs, since it would neglect the ecosystem risk of individual PAHs. We adopted a new method from a previous research to remedy the problem (Cao *et al.* 2010). $RQ_{\sum PAHs}$, $RQ_{\sum PAHs(NCs)}$, and $RQ_{\sum PAHs(MPCs)}$ were defined using Eqs. (4)–(6):

$$RQ_{\sum PAHs} = \sum_{i=1}^{16} RQ_i (RQ_i \geq 1) \tag{4}$$

$$RQ_{\sum PAHs(NCs)} = \sum_{i=1}^{16} RQ_{NCsi} \quad (RQ_{NCsi} \geq 1) \tag{5}$$

$$RQ_{\sum PAHs(MPCs)} = \sum_{i=1}^{16} RQ_{MPCsi} \quad (RQ_{MPCsi} \geq 1) \tag{6}$$

Besides, an ecosystem risk classification of individual PAHs and $\sum$PAHs (Cao *et al.* 2010) was suggested based on the new method, which can be used to compare the ecosystem risk levels of PAHs in different media (Supplementary Material Table S3).

Human health risk assessment

BaP-equivalent concentration (BaPeq) is calculated to estimate the risk caused by exposure to multiple PAHs, which is defined by Eq. (7) (Liao and Chiang 2006):

$$BaPeq = \sum_{i=1}^{n} C_i \times TEF_i \tag{7}$$

where C_i is the concentration of PAH_i in water (mg/l) and TEF_i is the TEF of PAH_i relative to BaP, which was obtained from a previous study (Nisbet and LaGoy 1992).

There was rare health risk assessment for the DJK Reservoir except a study about the tributary of the DJK Reservoir (Zhou *et al.* 2009). Considering the poor efficiencies of drinking water purification from PAHs in traditional water plants (Wu *et al.* 2011), we reckoned that the PAHs concentrations in the final drinking water were the same with those in the reservoir. Citizens in Beijing and other cities in Northern China would drink the water from the DJK Reservoir over their entire lifetime after the completion of SNWTP. Therefore, the incremental lifetime cancer risk (ILCR) assessment recommended by USEPA to quantitatively estimate the risk of cancer in humans (USEPA 1989) was adopted in this study. The ILCR assessment of drinking water is defined Eq. (8) (Ma *et al.* 2013):

$$ILCR = \frac{BaPeq \times CSF \times IR \times EF \times ED}{BW \times AT} \tag{8}$$

where CSF is the carcinogenic slope factor of the ingested water (kg d)/mg, BaPeq is the total BaP-equivalent concentration in water (mg/l), IR is the ingestion rate of water (l/day), EF is the exposure frequency (days/year), ED is the exposure duration (year), BW is body weight (kg), and AT is the average life span (day).

This study included three age groups: children (0–10 years), teenagers (11–20 years) and adults (21–74.8 years); 74.8 years being the average life expectancy for Chinese were considered (China 2012b). A CSF of 7.3 (kg d)/mg for BaP exposure was adopted from a previous study (Wu *et al.* 2011), and other parameters used in this study are presented in Table 1.

Quality assurance and quality control

The average recovery of PAHs was monitored under a strict quality assurance and quality control to test the availability of the method before the sample analysis. Six replicate spiked water samples with a concentration of 20 ng/l for PAH congeners and six replicate spiked soil samples with a concentration of 10 ng/g were extracted and analyzed in the same way as all the other samples. Prior to and after every 10 samples, a solvent blank and matrix blank were analyzed through the entire procedure. A series of working standard solutions of PAHs with concentration gradient were detected to confirm and quantify every PAH compound.

Statistical analysis

SPSS 16.0 for Windows, Sigma Plot 10.0, and Microsoft Excel 2010 were used for statistical analysis. Pearson's correlation analysis was conducted to reveal the possible correlation among PAHs and TOC in samples.

Results and discussion

Results of limit of detection and recoveries

The limit of detection was determined as signal-to-noise ratio of 3:1. Peaks that were smaller than three times the background signal were not considered. The relative standard deviations for the method were less than 10%. The recoveries ranged from 76 ± ± 6% to 110 ± ± 8% for spiked water samples and ranged from 85 ± ± 7% to 103 ± ± 10% for spiked soil samples. Concentrations of PAHs in sediment samples were calculated with respect to the

Table 1. Parameters in the ILCR equation.

Parameters	Units	Children	Teenagers	Adults	Cited from
IR	l/day	0.447	0.718	1.227	USEPA (Moya *et al.* 2011)
EF	Days/year	365	365	365	/
ED	Year	7	10	54.8	/
BW	kg	24.1	51.1	63.1	The Central People's Government of the PRC (China 2012a)
AT	Day	27302	27302	27302	Ministry of Health of the PRC (China 2012b)

AT: average life span; BW: body weight; ED: exposure duration; EF: exposure frequency; IR: ingestion rate of water.

dry weight (dw). The method detection limits for water and soil samples ranged from 1.1 to 8.9 ng/l and 2.3 to 17.9 ng/g, respectively.

Occurrence and distribution of PAHs in surface water

The total concentration of 16 PAHs in all water samples ranged from 9.42 ng/l (DR11) to 137.94 ng/l (HR1) (Figure 2), with a mean concentration of 49.15 ng/l (Table 2). The concentrations of PAHs in source water and drinking water of China were in the range of 7.62–9662 ng/l (Wu *et al.* 2011). Compared with other rivers in China, the mean concentration of total PAHs in the HJ River was higher than that of Songhua River (33.9 ng/l) (Ma *et al.* 2013), and lower than that of the Mopanshan Reservoir in Harbin City (265 ng/l) (Liu *et al.* 2013) and Qiantang River (283.3 ng/l) (Chen *et al.* 2007b). The HJ River Basin and the DJK Reservoir were in the moderate level of PAHs pollution.

Sixteen target PAHs were present in majority of water samples and detectable ratio varied from 83.33% to 100%. The median concentrations of individual and total PAHs were lower than their mean concentrations, indicating that majority of the sites contained lower PAHs concentrations. Coefficients of variation (CV%) of majority of PAHs were below 100% except Fla (103%), Pyr (135%) and BkF (118%), suggesting small variation in the concentrations of PAHs at different sample sites (Table 2). The composition pattern of PAHs in water samples showed that 3-ring PAHs (Acy, Ace, Flr, Phe and Ant) played a dominant role in water samples (81.9%). Six-ring PAHs (BghiP and InP) concentrations were the lowest in all water samples, which only comprised 2.2% of total PAHs. The compositional profiles of PAHs in water samples were almost the same from different sampling areas. Low molecular weight PAHs (2- to 4-ring) were dominant in water samples with proportion 86.8%, 96.1%, 94.4% and 92.9%, respectively, from the DR, the HR, upstream and downstream of the HJ River, which could be attributed to the relatively high vapor pressure and water solubility of low molecular weight PAHs (Mackay *et al.* 2006). The mean concentrations of 16 target PAHs in water samples from different sample sites did not show

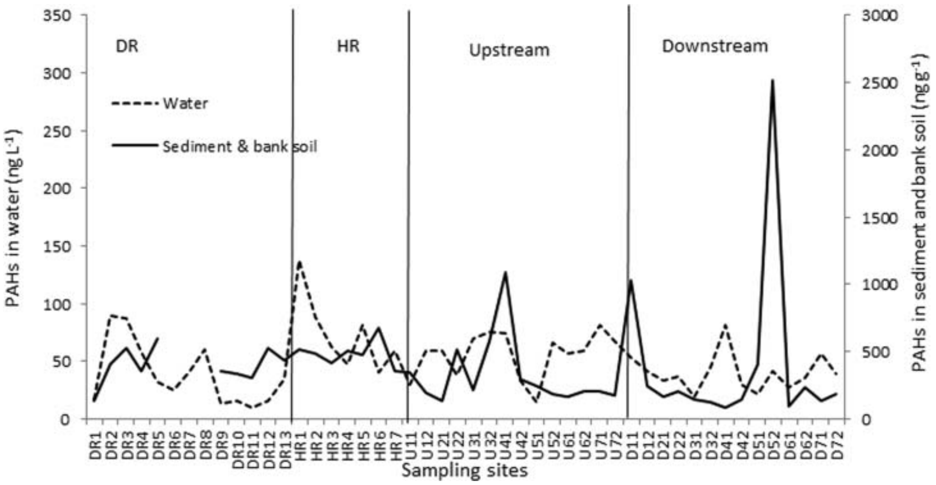

Figure 2. Spatial distribution pattern of total PAHs in water, sediment, and bank soil. DR: Dan Reservoir; HR: Han Reservoir; PAH: polycyclic aromatic hydrocarbon.

Table 2. PAHs concentrations in all samples.

		Water (ng/l) (N = 48)				Sediment (ng/g) (N = 28)				Bank soil (ng/g) (N = 18)			
	Rings	Mean ± SD	Median	DR%	CV%	Mean ± SD	Median	DR%	CV%	Mean ± SD	Median	DR%	CV%
Nap	2	1.46 ± 1.37	0.96	96	94	34.67 ± 9.75	30.45	89	82	5.41 ± 28.58	0.00	32	180
Acy	3	2.26 ± 1.82	1.93	100	80	24.40 ± 2.51	11.90	100	101	5.43 ± 24.68	5.07	100	46
Ace	3	7.85 ± 5.46	6.60	100	70	38.76 ± 27.68	17.07	100	125	16.89 ± 48.59	11.97	96	164
Flr	3	6.30 ± 4.68	5.54	100	74	39.64 ± 9.82	40.52	100	24	18.92 ± 9.66	18.36	96	52
Phe	3	22.60 ± 15.23	20.49	100	67	97.85 ± 72.79	95.82	94	32	84.86 ± 31.22	58.73	100	86
Ant	3	1.25 ± 1.09	0.96	83	87	92.19 ± 115.45	89.57	89	61	98.45 ± 56.17	71.89	100	117
Fla	4	1.63 ± 1.68	0.91	96	103	10.95 ± 79.18	10.10	100	48	25.96 ± 5.24	6.06	93	305
Pyr	4	1.11 ± 1.50	0.70	94	135	10.82 ± 49.18	10.91	100	64	15.16 ± 6.93	3.15	93	324
BaA	4	0.49 ± 0.19	0.48	96	39	1.65 ± 26.65	0.60	67	121	10.17 ± 2.00	2.54	75	262
Chr	4	0.68 ± 0.44	0.53	98	64	2.13 ± 27.97	0.67	72	176	8.70 ± 3.74	0.90	57	322
BbF	5	0.90 ± 0.50	0.82	100	56	5.01 ± 50.64	1.54	67	154	15.99 ± 7.70	1.10	54	317
BkF	5	0.56 ± 0.66	0.37	98	118	1.38 ± 31.46	0.00	39	186	11.65 ± 2.56	1.49	57	270
BaP	5	0.54 ± 0.33	0.45	100	60	57.46 ± 30.86	3.73	78	145	8.39 ± 83.19	0.36	54	368
DahA	5	0.43 ± 0.08	0.39	100	19	1.09 ± 35.72	0.80	56	119	8.02 ± 1.30	0.00	21	445
BghiP	6	0.61 ± 0.50	0.39	94	83	8.65 ± 34.40	5.67	89	91	15.88 ± 7.89	5.52	100	217
InP	6	0.48 ± 0.34	0.37	92	71	1.77 ± 47.88	1.09	61	170	15.56 ± 3.01	0.00	46	308
$\sum$PAHs		49.15 ± 25.85	43.52	100	53	365.43 ± 487.59	203.03	100	133	428.41 ± 124.38	424.99	100	29

Ace: acenaphthene; Acy: acenaphthylene; Ant: anthracene; BaA: benzo[*a*]anthracene; BaP: benzo[*aa*]pyrene; BbF: benzo[*b*]fluoranthene; BghiP: benzo[*g,h,i*]perylene; BkF: benzo[*k*]fluoranthene; Chr: chrysene; CV%: coefficient of variation; DahA: dibenz [*a,h*]anthracene; DR%: detectable ratio; Fla: fluoranthene; Flr: fluorene; InP: indeno[1,2,3-cd]pyrene; Nap: naphthalene; PAH: polycyclic aromatic hydrocarbon; Phe: phenanthrene; Pyr: pyrene.

significant differences (Supplementary Material Table S4). The highest levels of total 16 PAHs were found in the HR with a mean concentration of 73.72 ng/l, followed by upstream of the HJ River with 55.83 ng/l, downstream of the HJ River with 40.16 ng/l and the lowest concentration was found in the DR with 38.42 ng/l.

Occurrence and distribution of PAHs in sediments and bank soils

The concentrations of PAHs in sediments from different sampling sites ranged from 86.23 ng/g dw (D41) to 2514.93 ng/g dw (D52), with the mean value of 365.43 ng/g dw. The concentrations of PAHs in bank soils from different sample sites ranged from 133.17 ng/g dw (DR1) to 671.93 ng/g dw (HR6), with the mean value of 428.41 ng/g dw (Figure 2). For Ibirité Reservoir (Belo Horizonte, Minas Gerais, Southeastern Brazil) and its tributaries, the total PAHs concentration was 129.5 ± 47.8 and 311.3 ± 326.3 ng/g, respectively (Mozeto *et al.* 2014). The mean concentration of total PAHs in surface sediment was 35.16 ng/g dw in Congo River Basin (Mwanamoki *et al.* 2014). The concentrations of total PAHs in Songhua River of China was 178 ng/g in sediment and 209 ng/g in soil (Ma *et al.* 2013), Qiantang River with 313.1 ng/g in sediment (Chen *et al.* 2007b) and Mopanshan Reservoir was 325.9 ng/g in sediment (Liu *et al.* 2013). Compared with these results, the HJ River Basin had a higher level for PAHs in sediment and bank soil.

The detectable ratio of 16 target PAHs varied from 37.5% to 100% with the mean value of 77.47% (Table 2). Although the detectable ratio of PAHs in sediment and bank soil was not as high as that in water, 16 priority PAHs were still detectable in most samples. The median concentration of $\sum$PAHs in sediments (203.03 ng/g) was significantly lower than the mean value of $\sum$PAHs (365.43 ng/g), indicating that most of the sites contained relatively low PAHs concentrations. By contrast, the median concentration of $\sum$PAHs in bank soils (424.99 ng/g) was almost the same as the mean value of $\sum$PAHs (428.41 ng/g). In addition, the CV% for $\sum$PAHs in bank soils was 29%, which was much smaller than that in sediments with 133%, indicating great variation in the concentration of $\sum$PAHs in upstream and downstream of the HJ River. The compositional profiles of PAHs with different rings in sediments and bank soils are presented in Supplementary Material Figure S1b and it could be seen that 3-ring PAHs contributed the most to the total PAHs (64.38%). Five-ring and 4-ring PAHs were the second and the third parts, accounted for 13.4% and 11.92% of total PAHs, respectively. Although there were some differences in the composition pattern of PAHs between the water, sediment and bank soil samples, low molecular weight PAHs (2–4 rings) were still abundant in the sediment and bank soil samples. However, the proportion of high molecular weight PAHs (5–6 rings) increased to 19.37% in sediment and bank soil samples, about three times higher than 7.18% in water. This could be explained by the fact that the organic matters in sediment and soil were able to absorb high molecular weight PAHs more efficiently than those with low molecular weight because the former have low water solubility and high hydrophobicity. Due to the low solubility of high molecular weight PAHs in water, they are liable to be absorbed mainly by organic matters of soil and sediment (Chiou *et al.* 1998; Mackay *et al.* 2006).

The mean concentrations and ranges of 16 target PAHs in sediment and bank soil samples at different sampling areas are given in Supplementary Material Table S5. There was the highest mean concentration of 16 PAHs 487.33 ng/g dw in the HR, range of total PAHs concentration was from 350.13 to 671.93 ng/g. Concentrations in three sampling sites of U41 (1087.81 ng/g), D11 (1023.86 ng/g) and D52 (2514.93 ng/g) were >1000 ng/g in upstream and downstream of the HJ River (Figure 2). Site U41 (Yuehe River) was located near Jianmin town and had a dock for ferry. Site D11 (Nanhe River) was situated near Gucheng county and there was a ferry station. Site D52 (Fanjiatai River) was located in Fanjiatai town near an industrial area. It could be inferred that the wastewater discharge from industrial area, daily sewage outfalls from cities and the emission from vehicles should be the main sources of PAHs.

Correlations analysis between concentrations of PAHs and TOC

Some studies have reported a significant correlation between PAHs concentrations and TOC for highly contaminated sites (Wang *et al.* 2010) and organic carbon was an important factor for PAHs retention in soils (Cachada *et al.* 2012). The scatter plot between $\sum$PAHs concentration and TOC in water, sediments and bank soils are shown in Supplementary Material Figure S2 and the data for TOC are shown in Table S1. There were poor correlations between PAHs concentration and TOC in water, sediment and bank soil samples. A poor correlation has also been reported in other researches, where there was continuous input of PAHs source (Wang *et al.* 2010). When the values of TOC were low, the correlation would show variable behavior (Saba *et al.* 2012). Hence, the results could be explained by the fact that the distribution of PAHs did not reach the equilibrium state due to the continuous input of various PAHs contaminants and the low level of TOC in the research area.

Source apportionment of PAHs

Most of the PAHs contaminants in the environment are derived from anthropogenic activities, which are classified into pyrolytic and petrogenic sources. Pyrolytic PAHs are formed as a consequence of incomplete combustion, whereas petrogenic PAHs are mainly derived from crude oil and its refined products (Li *et al.* 2015). Based on previous researches (Yunker *et al.* 2002), the ratios of Fla/(Fla + Pyr) and Ant/(Ant + Phe) were adopted in this study to infer the possible sources. PAHs with Fla/(Fla + Pyr) >0.5 were mainly from combustion of grass, wood and coal, while PAHs were mainly from combustion of petroleum when the ratio was between 0.4 and 0.5 and they were typical of petroleum contamination when Fla/(Fla + Pyr) <0.4. PAHs with Ant/(Ant + Phe) <0.1 were mainly from petroleum contamination, while Ant/(Ant + Phe) >0.1 were typical of combustion sources (Li *et al.* 2006).

In this study, the ratios of Ant/(Ant + Phe) for the water ranged from 0.0 to 0.63 and 77.1% of them were <0.1. Ratios of Fla/(Fla + Pyr) ranged from 0.0 to 1.00 and 29.2% of them were <0.5. Most of the PAHs in water samples were derived from mixed sources of petroleum and combustion (Supplementary Material Figure S3a). However, the ratios of Ant/(Ant + Phe) for the sediment ranged from 0.0 to 0.99 and 93.5% of them were >0.1, clearly indicating a combustion source in sediment. Ratios of Fla/(Fla + Pyr) ranged from 0.02 to 0.93 and 80.4% of them were >0.4, 73.9% >0.5, suggesting that combustion of biomass and coal could be the main pollution sources of PAHs in sediment (Supplementary Material Figure S3b). As there was no significant positive correlation between the PAHs concentrations in water, sediment and bank soil, we assumed that PAHs in water reflected the current status of contamination, whereas PAHs in sediment and soil were mainly attributed to historical contamination. It could be explained that the HJ River Basin was contaminated by agricultural activity and the runoff of soils in the history, while with the development of the industry, the discharge of wastewater from factory, the water transportation and domestic sewage have also become the important sources of PAHs pollutants.

Ecological risk assessment

The RQs for 16 PAHs in surface water, sediment and bank soil are shown in Table 3. In surface water samples, the mean values of RQ_{NCs} of Ace, Flr, Phe, Ant, Pyr, BaA, BbF, BkF, BaP, BghiP and InP in the DR; Ace, Flr, Phe, BaA, BbF, BkF and InP in the HR; Ace, Flr, Phe, Ant, Pyr, BaA, BbF, BaP and BghiP in upstream of the HJ River and Ace, Flr, Phe, Ant, Pyr, BaA, BbF, BghiP and InP in downstream of the HJ River were >1.0, and RQ_{MPCs} of individual PAHs were all <1.0, indicating that Ace, Flr, Phe, Ant, Pyr, BaA, BbF, BkF, BaP, BghiP and InP widely showed moderate-level ecological risk in the HJ River Basin.

For sediment and bank soil samples, the mean values of RQ_{MPCs} of individual PAHs were all <1.0 except for Ant in upstream of the HJ River ($RQ_{MPCs} = 1.15$), which indicated that contamination with Ant was much severe. The mean values of RQ_{NCs} of Nap, Acy, Ace, Flr, Phe and Ant in the DR; Nap, Flr, Phe, Ant and BaP in the HR; Nap, Phe, Ant and BaA in upstream of the HJ River and Nap, Phe, Ant, Fla, BaA, BbF, BaP and DahA in downstream of the HJ River were >1.0, indicating that low molecular weight PAHs showed more ecological risk potential.

RQ_{MPCs} of $\sum$PAHs in water, sediment and bank soil in the HJ River Basin were zero except that in sediment at upstream of the HJ River and RQ_{NCs} of $\sum$PAHs in all the three media were >1.0 but <800 (Table 3). Overall, the results indicated that PAHs in the HJ River Basin were in low ecological risk and at upstream of the HJ River the ecological risk in sediment was at moderate level (based on Supplementary Material Table S3). The mean ecological risk in sediment ($RQ_{\sum PAHs(NCs)} = 115.5$) was 4.2 times than that in water ($RQ_{\sum PAHs(NCs)} = 27.2$) and bank soil ($RQ_{\sum PAHs(NCs)} = 147.0$) was 5.4 times more that in water, indicating PAHs in sediment and bank soil had much severe potential ecological risk than in

Table 3. PAHs risk quotients of surface water, sediment, and bank soil samples.

	In water								In sediment and soil							
	DR (N = 13)		HR (N = 7)		Upstream (N = 14)		Downstream (N = 14)		DR (N = 11)		HR (N = 7)		Upstream (N = 14)		Downstream (N = 14)	
PAHs	RQ_{NCs}	RQ_{MPCs}	RQ_{NCs}	RQ_{MPCs}	RQ_{NCs}	RQ_{MPCs}	RQ_{NCs}	RQ_{MPCs}	RQ_{NCs}	RQ_{MPCs}	RQ_{NCs}	RQ_{MPCs}	RQ_{NCs}	RQ_{MPCs}	RQ_{NCs}	RQ_{MPCs}
Nap	0.1	0	0	0	0.2	0	0.1	0	34.6	0.3	9.4	0.1	5.2	0.1	2.5	0
Acy	0.7	0	0.9	0	0.8	0	0.6	0	1.1	0	0.7	0	0.3	0	0.2	0
Ace	1.4	0	4.5	0	3.2	0	2.3	0	2.2	0	0.3	0	0.5	0	0.8	0
Flr	1	0	4.5	0	2.3	0	1.7	0	1.4	0	1.6	0	0.8	0	0.6	0
Phe	5.7	0.1	12.6	0.1	8.6	0.1	5.6	0.1	19.2	0.2	19.2	0.2	16.5	0.2	16.8	0.2
Ant	2.2	0	0.9	0	2.2	0	1.4	0	66.5	0.7	93.1	0.9	115.3	1.2	48.8	0.5
Fla	0.4	0	0.2	0	0.7	0	0.7	0	0.4	0	0.4	0	0.4	0	1.6	0
Pyr	3.2	0	0.8	0	1	0	1.2	0	0.3	0	0.7	0	0.3	0	0.9	0
BaA	3.4	0	6.9	0.1	5.3	0.1	4.7	0	0.5	0	0.3	0	2.3	0	5.9	0.1
Chr	0.3	0	0.1	0	0.2	0	0.2	0	0	0	0	0	0	0	0.1	0
BbF	3.1	0	1.2	0	2.3	0	1.9	0	0.3	0	0.1	0	0.3	0	1	0
BkF	1.9	0	2.3	0	0.9	0	0.9	0	0	0	0.1	0	0.2	0	0.8	0
BaP	1.7	0	0.7	0	1	0	0.9	0	0.1	0	5.3	0.1	0.5	0	6	0.1
DahA	0.9	0	0.8	0	0.8	0	0.8	0	0	0	0	0	0.1	0	6.1	0.1
BghiP	3.6	0	0.7	0	1.8	0	1.5	0	0.1	0	0.2	0	0.1	0	0.3	0
InP	1.8	0	1.1	0	0.9	0	1.1	0	0	0	0	0	0.1	0	0.4	0
∑PAHs	27.9	0	33.2	0	25.7	0	21.4	0	125	0	128.6	0	139.3	1.2	82.8	0

Ace: acenaphthene; Acy: acenaphthylene; Ant: anthracene; BaA: benzo[*a*]anthracene; BaP: benzo[*aa*]pyrene; BbF: benzo[*b*]fluoranthene; BghiP: benzo[*g,h,i*]perylene; BkF: benzo[*k*]fluoranthene; Chr: chrysene; DahA: dibenz[*a,h*]anthracene; DR: Dan Reservoir; Fla: fluoranthene; Flr: fluorene; HR: Han Reservoir; InP: indeno[1,2,3-cd]pyrene; Nap: naphthalene; PAH: polycyclic aromatic hydrocarbon; Phe: phenanthrene; Pyr: pyrene; RQ_{MPCs}: risk quotient for the maximum permissible concentrations; RQ_{NCs}: risk quotient for the negligible concentrations.

water. However, there was no significant difference between the DJK Reservoir and upstream or downstream of the HJ River in water, sediment and bank soil.

Human health risk assessment

In the present study, the total BaPeq of 16 PAHs in water samples ranged from 0.75 to 2.45 ng/l with a mean value of 1.15 ng/l. BaPeq in all water samples were below the guideline value of 2.8 ng/l for surface water regulated by the Environmental Quality Standard for Surface Water in China (GB3838-2002) and 10 ng/l for drinking water regulated by the Standards for Drinking Water Quality in China (GB5749-2006).

The potential cancer risk posed by water consumption from the DJK Reservoir is listed in Table 4. Generally, a high potential health risk was recognized when the ILCR value was

Table 4. ILCR values for different sampling areas.

	BaPeq (ng/l)				
Sampling areas	Range	Means	ILCR values for children	ILCR values for teenagers	ILCR values for adults
DR (N = 13)	0.75–2.45	1.49 ± 0.63	2.69E-09	2.04E-09	1.54E-08
HR (N = 7)	0.85–1.43	0.98 ± 0.23	2.69E-09	1.35E-09	1.02E-08
Upstream (N = 14)	0.86–1.43	1.08 ± 0.17	1.95E-09	1.48E-09	1.12E-08
Downstream (N = 14)	0.81–1.24	1.00 ± 0.15	2.58E-09	1.37E-09	1.04E-08
Total (N = 48)	0.75–2.45	1.15 ± 0.41	2.08E-09	1.58E-09	1.20E-08

BaPeq: BaP-equivalent concentration; DR: Dan Reservoir; HR: Han Reservoir; ILCR: incremental lifetime cancer risk.

$>10^{-4}$. When the values were between 10^{-6} and 10^{-4}, the potential risk reckoned lower (Liao and Chiang 2006). There was no significant difference between the DJK Reservoir and the HJ River for each age group. However, the mean ILCR value for adults (1.20×10^{-8}) was higher than that for children (2.08×10^{-9}) and teenagers (1.58×10^{-9}), indicating that adults had the highest cancer risk. Obviously, the increased duration of exposure (54.8 years) is the main reason. In this study, all of the ILCR values were rather $<10^{-6}$, indicating a negligible carcinogenic risk posted by PAHs through drinking water from the DJK Reservoir. Nevertheless, only PAHs were investigated in this study and the risk of other contaminants need to be further assessed to ensure the safety of drinking water resource.

Conclusions

The total concentrations of 16 PAHs in the HJ River and the DJK Reservoir ranged from 9.42 to 137.94 ng/l, with mean concentration of 49.15 ng/l in water, 86.23–2514.93 ng/g dw, with the mean value of 365.43 ng/g dw in sediments and 133.17–671.93 ng/g dw, with the mean value of 428.41 ng/g dw in bank soils. Compared with other study areas, the concentrations of PAHs were in the moderate level for water, but in a higher level for sediment and bank soil. The poor correlation between the PAHs concentration and the TOC indicted that there was continuous input of PAHs source in these areas. Most of the PAHs pollution in water samples was derived from mixed sources of petroleum and combustion, while combustion was the predominant source of PAHs in sediment and bank soil samples. The ecological risk for majority of 16 PAHs was in the moderate level and some measures need be undertaken. Nevertheless, the human health risk assessment showed that PAHs through drinking water consumption from the DJK Reservoir was out of potential cancer risk.

Funding

This project was supported in part by Knowledge Innovation Program of the Chinese Academy of Sciences (No. Y455436K02), the Hundred Talents Program of the Chinese Academy of Sciences (No. Y329671K01), and Sino-Africa Joint Research Center (No. Y323731K02).

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