

Temporal variation and spatial distribution of PAH in water of Three Gorges Reservoir during the complete impoundment period

Jingxian Wang · Bernhard Henkelmann · Yonghong Bi ·
Kongxian Zhu · Gerd Pfister · Wei Hu · Cedrique Temoka ·
Bernhard Westrich · Karl-Werner Schramm

Received: 29 September 2012 / Accepted: 11 December 2012 / Published online: 30 December 2012
© Springer-Verlag Berlin Heidelberg 2012

Abstract Bioavailable concentrations of polycyclic aromatic hydrocarbons (PAHs) were investigated in water of Three Gorges Reservoir (TGR) using semipermeable membrane devices during the period of completely impounding water. Σ PAH concentrations in water of TGR in the period of completely impounding water were 15–381 ngL⁻¹. Σ PAH

concentrations increased from town or counties to big industrialized cities in TGR, indicating urbanization effects on PAH pollution in the water. Tributaries in TGR have a certain contribution of PAH pollution to the mainstream of Yangtze River and their pollution could not be neglected. An obvious decrease of PAH concentration was observed after 175-m water impounding in 2011 in TGR. Several factors may account for this decrease, including execution of comprehensive treatment and management measures in TGR, less rainfall in 2011, and sedimentation effect caused by the dam. Passive sampling method has been successfully applied in the investigation of trace PAH in water of TGR and proved to be a useful and efficient tool for the management and sustainable development of the big reservoir. The results of the study provide valuable information about PAH pollution in the whole reservoir including some tributaries, and the pollution status is dynamically related with human activities. Therefore, PAH could be used as a marker compound or indicator in the network monitoring system to surveil and trace the pollution status in TGR.

Responsible editor: Leif Kronberg

J. Wang · B. Henkelmann · G. Pfister · C. Temoka ·
K.-W. Schramm
Molecular EXposomics (MEX), Helmholtz Zentrum München–
German Research Center for Environmental Health (GmbH),
Ingolstädter Landstr.1,
85764 Neuherberg, Germany

J. Wang (✉) · C. Temoka · K.-W. Schramm (✉)
Department für Biowissenschaften, Wissenschaftszentrum
Weihenstephan für Ernährung und Landnutzung, TUM,
Weihenstephaner Steig 23,
85350 Freising, Germany
e-mail: wjingxw@yahoo.com.cn
e-mail: schramm@wzw.tum.de

Y. Bi · K. Zhu
The State Key Laboratory of Freshwater Ecology and Biotechnology,
Institute of Hydrobiology, Chinese Academy of Sciences,
Wuhan 430072, People's Republic of China

W. Hu
Institute of Mineralogy and Geochemistry,
Karlsruhe Institute of Technology,
Adenauerring 20b,
76131 Karlsruhe, Germany

B. Westrich
Institute for Geotechnical Engineering, University of Stuttgart,
Pfaffenwaldring 35,
70569 Stuttgart, Germany

Keywords PAH · TGR · Water · SPMD · Dam

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are toxic or carcinogenic compounds (Douben 2003) and have severely impacted local ecosystems and human health (Mumford et al. 1987; Latimer and Zheng 2003; Shi et al. 2007; Neamtu et al. 2009; Hu et al. 2011). They are emitted into the atmosphere by various combustion sources (Fernandes and Brooks 2003) or released into the aquatic environment through the discharges

from human activities such as industrial or domestic sewage effluents (Burgess et al. 2003). PAHs are widely distributed in the environment and have become more prevalent in many developing countries including China (Oanh et al. 2005; Xu et al. 2006).

The Three Gorges Dam is the world's largest hydropower project. This project started in December 1994 and finished in May 2006, creating a 1,080-km² reservoir. The water impounding by the dam had gone through three stages. The first construction period is from 1994 to 1997 and the water level rose from 66 to 88 m. The second period of construction is from 1998 to 2004 and the water level went up to 135 m. The third period is from 2004 to 2009. In 2006, the water level reached 156 m, and after the completion of the project, the water level reached 175 m in 2009. The environmental impacts of the project are profound because the reservoir has inundated 632-km² terrain and has changed the original water distribution of the Yangtze basin. The transportation and fate of pollutants in the human-changed waterway will also change accordingly.

In the study of persistent organic pollutants (POPs) in Three Gorges Reservoir (TGR) in 2008 (Wang et al. 2009), PAHs were found to be the predominant POP compounds in the Three Gorges Reservoir, China. In order to determine contamination levels and distribution during the period of completely impounding water of TGR to the designed water level 175 m, extensive sampling programs were undertaken in May 2009 and May 2011, following up the sampling campaign in May 2008. The bioavailable contaminants were collected with semi-permeable membrane devices (SPMD) in the reservoir from the great dam to the upstream city Chongqing, and the 16 PAHs included in the US EPA list of priority pollutants were analyzed. The sampling in the three years was done during the water drawdown period of the reservoir (late April to early June). The purpose of the study was to investigate the spatial and temporal variation of bioavailable PAHs in TGR and analyze their sources for better understanding the sources, geochemical processes, transport, and fate of PAHs in TGR during the various stages of water impoundment.

Materials and methods

SPMD sampler and deployment in TGR

The materials and methods for the production of SPMD in this study were described in our previous paper (Wang et al. 2009). Briefly, the semipermeable membranes were prepared using lay-flat polyethylene tubing (from VWR Ismaning, Germany; 2.5 cm wide and 65 μm thick). The tubing was cut into 29-cm pieces, and 700 μL of triolein (Sigma, Munich, Germany, 99 %) was pipetted into each piece of tubing before sealing the ends. The triolein was spiked with 16 ¹³C-labeled PAHs as

performance reference compounds, which was different from our previous study (Wang et al. 2009) (PRC: naphthalene-¹³C₆, acenaphthylene-¹³C₆, acenaphthene-¹³C₆, fluorene-¹³C₆, phenanthrene-¹³C₆, anthracene-¹³C₆, fluoranthene-¹³C₆, pyrene-¹³C₃, benzo(a)anthracene-¹³C₆, chrysene-¹³C₆, benzo(b)fluoranthene-¹³C₆, benzo(k)fluoranthene-¹³C₆, benzo(a)pyrene-¹³C₄, indeno(1,2,3-c,d)pyrene-¹³C₆, benzo(g,h,i)perylene-¹³C₁₂, dibenzo(a,h)anthracene-¹³C₆). The prepared SPMDs were stored in closely aluminum foil-sealed heat-treated 10-mL glass vials at -28 °C and kept cooled during transportation until deployment.

The sampling sites spanned the whole reservoir from the upstream Chongqing to the great dam Maoping, covering more than 600-km-long distance. The sampling sites were MP (Maoping), GJB (Guojiaba), BD1 (Badong), BD2 (Badong), DN1 (Wushan), DN2 (Wushan), FJ (Fengjie), XJ1 (Yunyang), XJ2 (Yunyang), WZ (Wanzhou), CS (Changshou), and CQ (Chongqing) (Fig. 1). The first four sampling sites (MP, GJB, BD1, BD2) belong to Hubei area which covers about 100 km, and the rest sites belong to Chongqing area. CQ is the largest city in TGR with five million people and the second is WZ with 0.7 million people. CS is also an industrialized city with 0.3 million people and is located very close to CQ. MP, GJB, BD, and FJ are towns or counties with a total population of 0.3 million in these area (Ministry of Environmental Protection of China 2012). In Hubei area of TGR, between the sampling sites of MP and GJB, there is a big tributary Xiangxi River (XX) which is 97.3 km long. Between the sampling sites of BD1 and BD2, there is another tributary Shenglongxi River (SL). In late April to May 2009, the SPMDs were deployed for 14 and 25 days in seven sites (MP, GJB, BD1, BD2, WZ, CS, CQ) in the TGR. In late April to May 2011, five sites were added, among which, DN1, DN2, XJ1, and XJ2, were designed to monitor the contribution of tributaries Daning River (DN) and Xiaojiang River (XJ) to TGR pollution.

The SPMDs were deployed in stainless steel cages and immersed into the water at about 1-m depth. The samplers were mounted on boats or fastened to docks which were about 10–20 m from the riverbank. The SPMDs for the determination of blanks were prepared together with the other SPMD for sampling. SPMD blanks were transported to the sampling sites also in clean airtight jars, not deployed. After retrieval, the SPMDs were transported to the laboratory in the corresponding glass jars in the darkness and were kept in a freezer at -28 °C until processing.

Extraction, cleanup, and analysis

For chemical analysis, the SPMDs were cut into small pieces and extracted in 100 mL cyclohexane overnight at 200 rpm on a constant left-right shaker. The cleanup procedure of SPMD

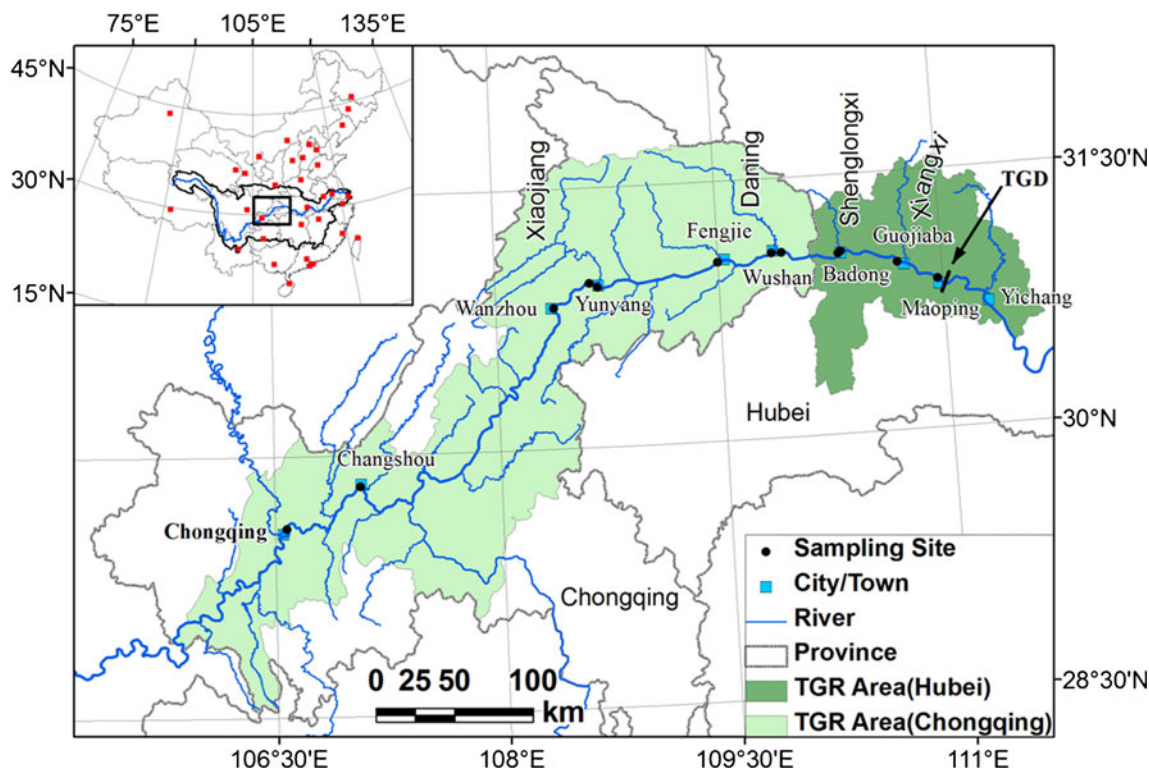


Fig. 1 Scheme of sampling sites. The sampling sites are MP (Maoping), GJB (Guojiaba), BD1 (Badong), BD2 (Badong), DN1 (Wushan), DN2 (Wushan), FJ (Fengjie), XJ1 (Yunyang), XJ2 (Yunyang), WZ (Wanzhou), CS (Changshou), and CQ (Chongqing)

was as previously described (Wang et al. 2009). Samples were spiked with a range of deuterated and ¹³C-labeled compounds to monitor the extraction and cleanup procedures. In brief, the extract was passed over anhydrous sodium sulfate to remove water. The volumes of the extraction solutions were reduced to one drop using vacuum rotary evaporation. The triolein was redissolved again with approximately 1–2 mL mixture of *n*-hexane/dichloromethane (1:1), and the samples underwent cleanup using a mixed column (a 3-cm-diameter column containing, from the bottom going upward, 10 g silica, 5 g alumina with 3 % H₂O, and 5 g anhydrous sodium sulfate). The extracts were eluted with 100 mL mixture of *n*-hexane and dichloromethane (1:1) and reduced to 1 mL. The residues were further purified through a C18 SPE cartridge for which acetonitrile was used as the eluting solvent. After adding a recovery standard, the extracts were concentrated with a gentle flow of nitrogen to 20 μL to be ready for analytical determination.

The analysis for the 16 PAHs listed as priority pollutants by the US EPA, namely, naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(*a*)anthracene, chrysene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, benzo(*a*)pyrene, indeno(1,2,3-*c,d*)pyrene, benzo(*g,h,i*)perylene, and dibenzo(*a,h*)anthracene, was performed by Agilent 5890 II plus MAT 95 using a Rtx-CLpesticides2 (30 m, ID 0.25 mm, film thickness 0.2 μm). Helium was used as the carrier gas with a head pressure of

16 psi. The GC/MS operating conditions were 47-eV EI ionization with the MS ion source temperature at 260 °C. The temperature program of GC was first hold at 60 °C for 1.5 min, then increased to 225 °C at 10 °Cmin⁻¹ and to 290 °C at 5 °Cmin⁻¹, and hold for 20 min at 315 °C. The temperature program of the injection port was increased to 120 °C at 12 °Cs⁻¹ and then maintained at 280 °C for 5 min. The sample was injected in a splitless mode with the cold injection system CIS 3. The temperature of transfer line was 300 °C.

QC/QA

Routine quality procedures were executed. These included the analysis of control samples and SPMD blank samples. The latter was also used to obtain the amounts of PRC prior to exposure. All of the results were blank-corrected using the average of all SPMD blanks. The method detection limits (MDLs) were calculated on the basis of three times the standard deviation of the blank values. A result is valid when the margin between the sample value and the average blank is larger than the MDL and is reported as a result after subtraction of the average blank value. Data below the MDL after subtraction of the average blank were taken as non-detectable and not included in further calculation. The MDL for the PAH analyzed was below 0.1 ng/L, except for

naphthalene, which MDL was between 19 and 24 ng/L because of contamination of the PE tube by this compound. Results for naphthalene were only available for the sampling sites CS and CQ in 2008 and 2009. The percentage of non-detectable PAH other than naphthalene was lower than 2 %. The average recoveries of all deuterated surrogates used for quantification ranged from 40 to 100 %. Recoveries at the lower end of the range were mainly determined for the higher volatile PAH. But they were still quantifiable with sufficient accuracy because of use of corresponding labeled internal standards. The correctness of the applied sample treatment and instrumental analysis for PAH was verified by several interlaboratory studies. From the results of these studies, a combined method uncertainty between 17 and 35 % was calculated.

Results and discussion

Amounts of PAH accumulated by SPMD

In our previous study in 2008 (Wang et al. 2009), six PRCs were spiked in SPMD and finally only anthracene- $^{13}\text{C}_6$ was usable to calculate PRC-based sampling rates (R_s) because other PRCs were too close to the initial amounts. In the improved SPMD in 2009 and 2011 field experiments, 16 $^{13}\text{C}_6$ -labeled PAHs were spiked which covered compounds of $\log K_{ow}$ from 3 to 6, and therefore more PRCs could possibly be used to calculate R_s . Ultimately, only four PRC compounds, namely, fluorene- $^{13}\text{C}_6$, phenanthrene- $^{13}\text{C}_6$, anthracene- $^{13}\text{C}_6$, and fluoranthene- $^{13}\text{C}_6$, could be used to calculate the sampling rate. There was not much difference among the results of aquatic concentration calculated from each of the R_s of the PRC compounds or from the average of the R_s (data not shown). In order to compare with the PAH concentrations measured in 2008 (Wang et al. 2009, 2012),

anthracene- $^{13}\text{C}_6$ was used again in the calculation for the PAH aquatic concentration in TGR in 2009 and 2011. The calculation method was based on the study of Huckins et al. (2006).

The results of total bioavailable PAH in TGR were shown in Table 1. In order to have a comprehensive vision of the temporal variation of PAH in TGR, the PAH concentrations measured in 2008 (Wang et al. 2009, 2012) were also included in Table 1. The total PAH in 2008 ranged from 15 to 354 ngL $^{-1}$, in 2009 from 17 to 381 ngL $^{-1}$ and in 2011 from 18 to 159 ngL $^{-1}$.

Spatial pattern and composition of PAH in TGR

The results of PAH showed obvious spatial distribution in TGR that modest to dramatic increases in ΣPAH concentrations were seen in water of TGR from downstream to upstream during the five-time monitoring periods in the three years (Table 1). The concentrations of the total PAH in less urbanized Hubei area were characterized as homogeneous relative to most heavily populated cities in Chongqing area, which ranged from 16 to 42 ngL $^{-1}$ in the three years, whereas ΣPAH concentration increased obviously from WZ and showed the highest levels, 354 and 381 ngL $^{-1}$, in CS and CQ. The total PAH concentrations increased obviously from town or counties to big industrialized cities, suggesting that PAHs in water reflect the urbanization effects. CQ and CS may be a major PAH source to the downstream reservoir.

The composition of 16 priority PAHs (grouped by the ring number in compounds) was at similar percentages for five- and six-ring compounds in TGR from upstream to downstream (Fig. 2), whereas the three-ring and four-ring PAH portions were considerably higher in water from big city CQ and CS than from town or counties in Hubei area. Studies (Hong et al. 2012; Shen et al. 2009; McCready et al. 2000; Boonyatumanond et al. 2006) found that the composition of 16 priority PAHs in sediments was at similar

Table 1 ΣPAH concentrations for the 16 individual PAHs (in nanogram per liter) in water from dam to upstream of TGR in 2008, 2009, and 2011

	2008-1 May 4–11	2008-2 May 11–June 4	2009-1 Apr 29–May 13	2009-2 May 13–Jun 7	2011 Apr 24–May 19
MP (Maoping)	42	33	39	23	20
GJB (Guojiaba)	19	21	22	17	18
BD1 (Badong)	19	16	34	28	22
BD2 (Badong)	17	–	32	22	20
DN1 (Wushan)	–	–	–	–	32
DN2 (Wushan)	–	–	–	–	28
FJ (Fengjie)	–	–	–	–	34
XJ1 (Yunyang)	–	–	–	–	37
XJ2 (Yunyang)	–	–	–	–	36
WZ (Wanzhou)	15	26	58	46	43
CS (Changshou)	354	103	91	294	80
CQ (Chongqing)	166	–	129	381	159

An en dash indicates no data available because sampling was not done in these sites

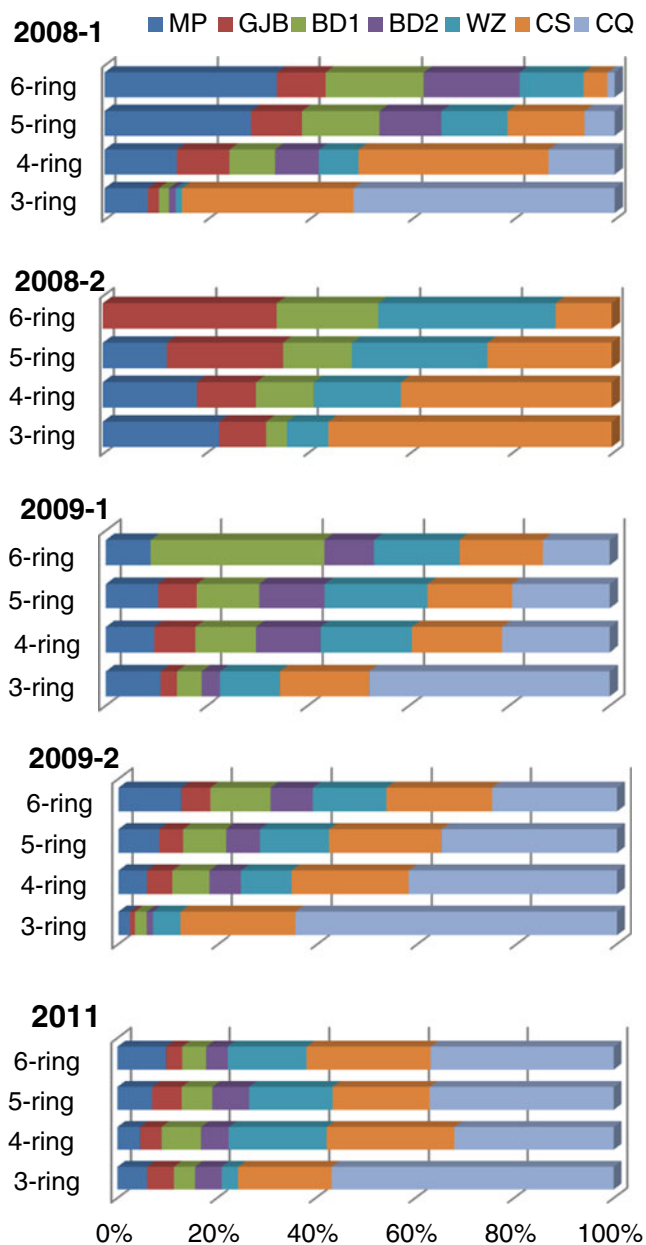


Fig. 2 Propositional composition of PAH in water from TGR in May of 2008, 2009, and 2011. The sampling sites are MP (Maoping), GJB (Guojiaba), BD1 (Badong), BD2 (Badong), WZ (Wanzhou), CS (Changshou), and CQ (Chongqing)

percentages for five- and six-ring compounds in both agricultural and urban section in rivers, while the four-ring PAHs were considerably higher in surface sediments in urban section. Hong et al. (2012) concluded that PAHs in sediment record urbanization effects on environmental changes. In our study, the distribution and composition of 16 priority PAHs in water of TGR also have an urbanization gradient from counties or towns to big cities.

Temporal variation

The first time of impounding water in TGR to reach a water level of 135 m was in June 2003. After the flood season in 2006, the water level reached to 156 m, and during this primary operation period, the lowest water level was 135 m. Until 2008, the engineering construction of the Three Gorges project was near to completion. In November 2008, the reservoir started to retain water to a water level of 172.8 m. In October 2009, the second time of storing water in the reservoir started and the water level rose to 171.4 m. In October 2010, the third time of water storage in the reservoir started and for the first time the water level rose to the designed height of 175 m. From now on, the Three Gorges project goes into its normal operation period with water level fluctuations from 145 to 175 m. Our sampling campaign in May 2008 was exactly in the primary operation period. The second sampling campaign in May 2009 was just after the first time of storing water to 172.8 m, and the third sampling campaign in May 2011 was after the first time of storing water to the designed height of 175 m. There were obvious temporal variations of PAH concentration in TGR for the five-time monitoring in the three years (Table 1). The Σ PAH concentration of 2008–1 at the majority of sites was higher than 2008–2, and the water flow of 2008–1 was lower than 2008–2 (Table 2). Similar variation was observed in 2009— Σ PAH concentration of 2009–2 was generally higher than 2009–1 and the water flow was lower than 2009–1. 2008–2 and 2009–1 had similar water flow, and Σ PAH concentrations in these two periods were also similar. It is obvious that high flow volume of water dilutes pollutant concentration in 2008 and 2009. However, 2011 was an exception, because Σ PAH concentrations were lower compared to the other two years whereas water flow volume was also much lower. Other factors discussed below may have

Table 2 Water flow and water physiochemical parameters during the measurement

	2008-1	2008-2	2009-1	2009-2	2011
Inflow water ($m^3 s^{-1}$)	9,475	10,720	10,293	12,512	6,525
Outflow water ($m^3 s^{-1}$)	9,785	10,710	11,613	14,298	6,658
Water level (m)	149.5	147.6	157.4	151.9	155.8
Water temperature ($^{\circ}C$)	21.1	22.7	20.1	21.6	18.9
pH	7.9	8.1	8.6	8.8	7.8
DO (mgL^{-1})	6.1	4.8	6.8	7.2	7.2

Water flow is the average value of everyday’s flow in and out of TGR at 8:00 a.m. during the sampling period

contributed to the decrease of Σ PAH concentration in water of TGR in 2011.

The sources of PAH include shipping activities, urban runoff, and wastewater discharge. The industrial wastewater discharge in 2010 was lower than in 2008 and 2009 (Table 3) (Ministry of Environmental Protection of China 2012). The wastewater treatment capacity improved every year because the number of urban sewage treatment plant in TGR is increased from 56 in 2008 to 71 in 2010. Until April 2011, there are 155 wastewater treatment plants running in TGR and treatment ability reaches to 25 million tons/day (Xinhua Net 2011a). Therefore, the large-scale construction of wastewater treatment plant and management measures for reducing wastewater discharge and saving energy in TGR could have contributed to the decrease of pollution in 2011.

It was reported that there were more than 400,000 ships and boats passing through TGR in 2008 and in order to mitigate the pressure of moving around the dam of the Yangtze shipping, the construction of express highway started in February 2009 (China Three Gorges Project News 2009). The express highway was completed and opened to traffic in January 2011, and at the same time, the roll-on and roll-off ships for moving around the dam were stopped running in TGR (China News Net 2011). These nonstandard ships have problems of low-energy efficiency, poor shipping status, potential safety hazards, etc. (Xinhua Net 2011b). They also do not have wastewater treatment facilities and have constituted a threat to water resources. Stopping these ships from running would undoubtedly reduce environmental pollution to some extent in TGR. This measure should also have its contribution to the decrease

of Σ PAH concentration in Hubei area of TGR in 2011. However, construction of the express highway to replace the use of roll-on and roll-off ships may have temporarily contributed to the decline in Σ PAH concentrations but could in the future become a large contributor to Σ PAH concentrations with increased growth in vehicular traffic, and more attention should be paid on this potential.

The third reason may be due to rainfall and urban runoff. The rainfall was less in spring 2011 and higher in spring 2009 and 2008 compared with normal years (China National Climate Center 2011). Less rainfall is associated with lower pollutant impact by wet deposition. As a matter of fact, dry deposits are highly polluted in urban atmosphere (Lohmann et al. 2011). Bomboi and Hernandez (1991) demonstrated that urban runoff was a major contributor to wastewater pollution for PAH. Less rainfall in spring 2011 may partly have caused lower Σ PAH concentration in CQ and CS than in 2008 and 2009.

PAHs are semivolatile and those of high molecular weight tend to become attached to particles. Greater scavenging of PAH by particles from water happens in areas with higher suspended sediment loads. After 135-m water impounding in 2004–2005, the concentration of suspended solids in TGR from Wanzhou to the dam has decreased greatly, and the closer the water is to the dam, the more the suspended solids decrease. The decreased percentages after 135-m water impounding were 33 % in WZ, 71 % in BD, and 86 % in MP. After the first time of 175-m water impounding in 2009, the decreased percentages compared with the 135-m water impounding were 43 % in WZ, 77 % in BD, and 90 % in MP (Yin et al. 2011). A large amount of suspended solids takes PAH from water to suspended sediment. This should have the potential to decrease PAH in downstream of TGR compared with upstream CS and CQ and have also caused PAH to decrease after 175-m water impounding. Compared to CQ, Σ PAH concentration in WZ decreased by 55–91 %, in BD decreased by 74–93 %, and in MP decreased by 70–94 % in the five monitoring periods. Sediment settling becomes slow downstream of WZ, and the decrease in PAH concentration also becomes slow. In Hubei area, about 100 km from BD to MP, the Σ PAH concentration was almost constant compared to that in the upstream area. Therefore, the urbanized cities CQ and CS are major PAH sources to the downstream reservoir as mentioned above and suspended sediments scavenge quite a bit of PAH to the river bottom from WZ to the downstream area. Yin et al. (2011) also found that the water quality in TGR has improved after 175-m water impounding as assessed by Surface Water Environmental Quality Standard (GB3838-2002) and attributed the reason to the sedimentation effects arising from the increase of water level and decrease of velocity. Part of pollutants settled with deposition of suspended solids and entered into sediment.

Table 3 Wastewater discharge and treatment in 2008, 2009, and 2011 in TGR

	2008	2009	2010
Total discharge of industrial effluent (million ton)	558	486	319
Hubei area	22	34	36
Chongqing area	536	452	283
Total discharge of urban sewage (million ton)	593	623	615
Hubei area	16	27	28
Chongqing area	577	596	587
Number of urban sewage treatment plant	56	70	71
Hubei area	8	14	14
Chongqing area	48	56	57
Annual treatment capacity (million ton)	515	558	590
Hubei area	13	25	27
Chongqing area	502	533	563

Data cited from reports of Ministry of Environmental Protection of China (2012) on the ecological and environmental monitoring results of the Three Gorges Project

The contribution of tributaries

The \sum PAH concentration in MP was 23, 12, 17, 6, and 2 ng L⁻¹ higher than in GJB, respectively, in the five-time monitoring period (Table 1), indicating that Xiangxi River (XX) had PAH pollution input to the mainstream of Yangtze River. It was reported that green algae bloom occurred every year since water impounding occurred in TGR from 2003 to 2010 (Three Gorges News Net 2012). The most serious one occurred in June 2008 with 25-km length of green algae in the river. In order to control algal bloom, comprehensive treatment and management measures have been taken, including releasing filter-feeding fish fries as algae biological controller, cleaning up algae by mechanical treatment and chemical substance, and discharging domestic sewage after being treated to meet the state's discharge standards (Three Gorges News Net 2012). No green algae bloom occurred in 2011, and this may be due to these measures. Our results show that the contribution of \sum PAH concentration from Xiangxi River in 2011 was very low compared to 2008 and 2009. The reason for the decrease of PAHs in Xiangxi River may also be the result of the comprehensive treatment and management for the river. \sum PAH concentrations in BD1 were 2 ngL⁻¹ higher than in BD2 in 2008, 2 and 6 ngL⁻¹ higher in 2009, and 2 ngL⁻¹ higher in 2011 (Table 1), indicating that Shenlongxi River (SL) also had PAH pollution input to the mainstream but its contribution was lower than XX river. In 2011, four sampling sites were added to monitor PAH contribution of the tributaries Daning River (DN) and Xiaojiang River (XJ). After the two tributaries, \sum PAH concentration in the mainstream increased by 4 and 1 ngL⁻¹, respectively (Table 1). Among the four monitored tributaries in 2011, XJ contributed the lowest PAH of 1 ngL⁻¹ to the mainstream and DN contributed the highest PAH of 4 ngL⁻¹ among the four rivers. The annual average flow of the four tributaries is 65 m³s⁻¹ for XX, 20 m³s⁻¹ for SL, 106 m³s⁻¹ for DN, and 127 m³s⁻¹ for XJ. Compared with the flow of the mainstream Yangtze (Table 2), their inputs are small and the discharge at the two sites of each tributary is approximately equal. Therefore, percentages of increased total PAH concentrations in the mainstream after the four tributaries were 11, 10, 14, and 2.8 % in 2011 for XX, SL, DN, and XJ, respectively. Pollution from tributaries could not be neglected.

Source analysis

Ratios of PAH with similar molecular weights have been used as indices for source apportionment (Yunker et al. 2002; Liu et al. 2008). If anthracene/anthracene+phenanthrene (ANT/(ANT+PHE)) <0.1 and benz(a)anthracene/benz(a)anthracene+chrysene (BaA/(BaA+CHR)) <0.2, a petrogenic source is suggested; for a pyrogenic source, ANT/(ANT+PHE) would be >0.1 and BaA/(BaA+CHR) >0.35 (Yunker et al. 2002).

Fluoranthene/fluoranthene+pyrene (FLUO/(FLUO+PYR)) <0.4 is for a petrogenic source between 0.4 and 0.5 for liquid fossil fuel (vehicle and crude oil) combustion (Yunker et al. 2002), and indeno(1,2,3-*c,d*)pyrene/indeno(1,2,3-*c,d*)pyrene+benzo(*g,h,i*)perylene (INP/(INP+BghiP)) <0.2 is possibly for a petrogenic source between 0.2 and 0.5 for liquid fossil fuel (vehicle and crude oil) combustion (Yunker et al. 2002). The ANT/(ANT+PHE) in TGR was higher than 0.1 except CQ (Table 4). The BaA/(BaA+CHR) was smaller than 0.2 except CQ and CS in 2008 and 2009. In 2011, the ratio of most sites was higher than 0.2. The source was neither pure petrogenic nor pure pyrogenic; thus, it should be their mixture. The sources had obviously changed in 2011 since the ratio of BaA/(BaA+CHR) was much higher than in 2008 and 2009. But the cause of the change in sources in 2011 is unknown. It may be related with the newly running express highway for moving around the dam, and further study is needed to clarify it. FLUO/(FLUO+PYR) was less than 0.4 except CQ and CS, indicating that PAH in the downstream of TGR was characterized as petrogenic source. The ratio in CS was between 0.4 and 0.5 and CQ was higher than 0.5, indicating that the source in CS was mainly from liquid fossil fuel (vehicle and crude oil) combustion and that in CQ was characteristics of coal,

Table 4 Ratios of PAH with similar molecular weights

Location	MP	GJB	BD1	BD2	WZ	CS	CQ
ANT/(ANT+PHE)							
2008-1	0.11	0.14	0.18	0.17	0.17	0.13	0.10
2008-2	0.14	0.13	0.17	–	0.20	0.16	–
2009-1	0.13	0.13	0.13	0.14	0.11	0.14	0.07
2009-2	0.14	0.14	0.20	0.12	0.10	0.25	0.08
2011	0.11	0.10	0.12	0.22	0.16	0.13	0.09
BaA/(BaA+CHR)							
2008-1	0.07	0.04	0.03	0.03	0.09	0.21	0.29
2008-2	0.08	0.05	0.03	–	0.07	0.18	–
2009-1	0.06	0.03	0.03	0.03	0.06	0.22	0.23
2009-2	0.07	0.02	0.03	0.02	0.09	0.18	0.21
2011	0.28	0.23	0.05	0.25	0.06	0.35	0.39
FLUO/(FLUO+PYR)							
2008-1	0.33	0.29	0.30	0.32	0.30	0.53	0.76
2008-2	0.33	0.38	0.24	–	0.26	0.45	–
2009-1	0.23	0.25	0.24	0.21	0.34	0.47	0.58
2009-2	0.29	0.19	0.22	0.20	0.37	0.45	0.52
2011	0.35	0.37	0.31	0.29	0.17	0.38	0.67
INP/(INP+BghiP)							
2008-1	0.37	0.37	0.40	0.38	0.37	0.43	0.42
2008-2	–	0.39	0.39	–	0.40	0.36	–
2009-1	–	–	0.48	0.63	0.62	0.56	0.66
2009-2	0.51	0.55	0.45	0.57	0.58	0.48	0.56
2011	0.50	–	0.56	0.36	0.46	0.46	0.47

grass, or wood combustion (Yunker et al. 2002). Ratio of INP/(INP+BghiP) in 2008 was between 0.2 and 0.5, and 83 % of the ratio in 2011 was between 0.2 and 0.5, indicating that the possible source was liquid fossil fuel (vehicle and crude oil). But 75 % of the ratio in 2009 was higher than 0.5 and suggests combustion of biomass and coal (Yunker et al. 2002). During the monitoring period in 2009, rainfall was higher than the other two years, indicating that rainfall causes higher impact of pollutant scavenging from air masses originating from urban cities.

Downstream and upstream of TGR have different PAH sources. Chongqing and Changshou are big cities in the upstream area of TGR. Local discharge, ship activities, and air pollution may have been the main source of PAH. In the downstream area, especially Hubei area of TGR, the main source of PAH may be ship activities and oil spillage.

Conclusion

PAHs in TGR were investigated employing SPMD during the drawdown season in late April and early June of the completely impounding water years in TGR. The successful application of passive sampler in TGR provides an efficient method for monitoring and surveillance of trace pollutants in TGR. The results of the study showed a clear distribution pattern of PAH in different areas of TGR and the variation in different water impounding years, and the pollution status is dynamically related with anthropogenic activities, suggesting that PAH could be used as a marker compound or indicator in the network monitoring system to surveil and trace the industrial pollution status in TGR.

The total PAH concentrations increased from town or counties to big industrialized cities, indicating urbanization effects on PAH pollution in water. Different composition of 16 priority PAHs in cities and towns in TGR suggests different pollution sources from industrialized cities to rural area. A decrease in PAH concentration was observed after 175-m water impounding in TGR. Several reasons contribute to this decrease. Comprehensive treatment and management measures like construction of wastewater treatment plants and phasing out old and nonstandard ships resulted largely to reduce wastewater discharge. The dry weather in 2011 may caused less impact of pollutants into the water of TGR from the atmosphere. Sedimentation is another important reason for decreasing pollution in water after 175-m water impounding because of the increase of water volume and slow down of water velocity.

The normal 175-m water impounding operation is just the start, for the transfer and fate of pollutants in the anthropogenically modified waterway will change greatly. Intensive monitoring should be executed in TGR to watch the transfer and fate of pollutants and provide valuable information for managing and

controlling pollution. More attention should be paid on sediment quality because sedimentation causes transfer of pollutants into sediment. Our study only reflects PAH pollution in TGR in the drawdown period of a year during which, normally, water quality is at best compared to other seasons (dry season from November to April, flood season from June to August, and impoundment from September to October). Monitoring should be considered in other periods of the TGR operation cycle.

Acknowledgments This project was funded by the German Ministry of Education and Research (BMBF 02WT1132). We are grateful to two anonymous reviewers for their valuable comments on an earlier draft of this article.

References

- Bomboi M, Hernandez A (1991) Hydrocarbons in urban runoff: their contribution to the wastewaters. *Water Res* 25:557–565
- Boonyatumanond R, Wattayakorn G, Togo A, Takada H (2006) Distribution and origins of polycyclic aromatic hydrocarbons (PAHs) in riverine, estuarine, and marine sediments in Thailand. *Mar Pollut Bull* 52:942–956
- Burgess RM, Ahrens MJ, Hickey CW (2003) Geochemistry of PAHs in aquatic environments: source, persistence and distribution. In: Douben PET (ed) *An ecotoxicological perspective*. Wiley, New York, pp 35–46
- China National Climate Center (2011) Climate assessment for the spring of 2011 (March to May) Three gorges ecology and environmental monitoring quarterly, no. 2, Local Climate Station. Accessed 13 June 2011
- China News Net (2011). It will be lights out for non standard roll on & off ships of moving around the dam in March 2011. <http://www.ctg.com.cn/xwzx/news.php?mnewsid=46118&mtxt=%C8%FD%CF%BF%BF%E2%7F8%BA%BD%D4%CB>. Accessed 21 January 2011
- China Three Gorges Project News (2009). The construction of express highway for moving around the three gorges dam was in an all-round way and the construction of land-and-water coordinated transport for the three gorges project commenced on full scale. <http://www.ctg.com.cn/xwzx/news.php?mnewsid=31948&mtxt=%C8%FD%CF%BF%BF%E2%7F8%BA%BD%D4%CB>. Accessed 13 February 2009
- Douben PET (ed) (2003) *PAHs: an ecotoxicological perspective*. Wiley, New York
- Fernandes MB, Brooks P (2003) Characterization of carbonaceous combustion residues: II. Non-polar organic compounds. *Chemosphere* 53:447–458
- Hong Y, Yu S, Yu G, Liu Y, Li G, Wang M (2012) Impacts of urbanization on surface sediment quality: evidence from polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) contaminations in the Grand Canal of China. *Environ Sci Pollut Res* 19:1352–1363
- Hu NJ, Shi XF, Huang P et al (2011) Polycyclic aromatic hydrocarbons (PAHs) in surface sediments of Liaodong Bay, Bohai Sea, China. *Environ Sci Pollut Res* 18:163–172
- Huckins JN, Petty JD, Booij K (2006) *Monitors of organic chemicals in the environment: semipermeable membrane devices*. Springer, New York

- Latimer JS, Zheng J (2003) The sources, transport and fate of PAHs in the marine environment. In: Douben PET (ed) PAHs: an ecotoxicological perspective. Wiley, New York, pp 9–34
- Liu Y, Ling CN, Zhao JF, Huang QH, Zhu ZL, Gao HW (2008) Distribution and sources of polycyclic aromatic hydrocarbons in surface sediments of rivers and an estuary in Shanghai, China. *Environ Pollut* 154:298–305
- Lohmann R, Dapsis M, Morgan EJ, Dekany V, Luey PJ (2011) Determining air-water exchange, spatial and temporal trends of freely dissolved PAHs in an urban estuary using passive polyethylene samplers. *Environ Sci Technol* 45:2655–2662
- McCready S, Slee DJ, Birch GF, Taylor SE (2000) The distribution of polycyclic aromatic hydrocarbons in surficial sediments of Sydney Harbour, Australia. *Mar Pollut Bull* 40:999–1006
- Ministry of Environmental Protection of China (2012) Bulletin on the ecological and environmental monitoring results of the Three Gorges Project. <http://english.mep.gov.cn/download/Documents/>. Accessed 12 April 2012
- Mumford JL, He XZ, Chapman RS, Cao SR, Harris DB, Li XM et al (1987) Lung-cancer and air-pollution in Xuanwei. *China Science* 235:217–220
- Neamtu M, Ciomasu IM, Costica N et al (2009) Chemical, biological, and ecotoxicological assessment of pesticides and persistent organic pollutants in the Bahlui River, Romania. *Environ Sci Pollut Res* 16(Suppl 1):S76–S85
- Oanh NTK, Albina DO, Ping L, Wang XK (2005) Emission of particulate matter and polycyclic aromatic hydrocarbons from selected cook stove-fuel systems in Asia. *Biomass Bioenergy* 28:579–590
- Shen Q, Wang KY, Zhang W, Zhang SC, Wang XJ (2009) Characterization and sources of PAHs in an urban river system in Beijing, China. *Environ Geochem Health* 31:453–462
- Shi Z, Tao S, Pan B, Liu WX, Shen WR (2007) Partitioning and source diagnostics of polycyclic aromatic hydrocarbons in rivers in Tianjin, China. *Environ Pollut* 146:492–500
- Three Gorges News Net (2012) Fish—scavenger: eat water bloom in Xiangxi river and grow to be green food. <http://ok10000.com.cn/News/hy/21.html>. Accessed 20 March 2012
- Wang J, Bi Y, Pfister G, Henkelmann B, Zhu K, Schramm K-W (2009) Determination of PAH, PCB, and OCP in water from the Three Gorges Reservoir accumulated by semipermeable membrane devices (SPMD). *Chemosphere* 75:1119–1127
- Wang J, Bi Y, Pfister G, Henkelmann B, Zhu K, Schramm K-W. 2012. Erratum to “Determination of PAH, PCB, and OCP in water from the Three Gorges Reservoir accumulated by semipermeable membrane devices (SPMD)”. [*Chemosphere*, 75, 1119–1127]. 10.037.
- Xinhua Net (2011a). Water quality of Chongqing area in TGR is stable and is improving since impounding water of the Three Gorges Project. <http://www.ctg.com.cn/xwzx/news.php?mnewsid=47313&mtxt=%CE%DB%CB%AE%B4%A6%C0%ED%B3%A7>. Accessed 2 May 2011
- Xinhua Net (2011b). All of the non standard roll on & off ships for moving around the Three Gorges Dam stop running from today. <http://www.ctg.com.cn/xwzx/news.php?mnewsid=48321>. Accessed 2 July 2011
- Xu SS, Liu WX, Tao S (2006) Emission of polycyclic aromatic hydrocarbons in China. *Environ Sci Technol* 40:702–708
- Yin S-Y, Lou B-F, Liu H, Lan J, Yuan L, Zhang Q, Zang X-P (2011) Analysis of water quality of the Yangtze River within the Three Gorges Reservoir area during construction period. *Res Environ Yangtze Basin* 20:305–310
- Yunker MB, Macdonald RW, Vingarzan R, Mitchell RH, Goyette D, Sylvestre S (2002) PAHs in the Fraser River Basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Org Geochem* 32:489–515