JOURNAL OF ENVIRONMENTAL SCIENCES XX (2017) XXX–XXX

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JES JOURNAL OF ENVIRONMENTAL SCIENCES

www.jesc.ac.cn

Distribution and sources of polycyclic aromatic hydrocarbons and phthalic acid esters in water and surface sediment from the Three Gorges Reservoir

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ARTICLE INFO

Article history:
Received 28 June 2017
Revised 4 November 2017
Accepted 6 November 2017
Available online xxxx

Keywords:
Three Gorges Reservoir (TGR)
Polycyclic aromatic hydrocarbons (PAHs)
Phthalic acid esters (PAEs)
Water impoundment period
Water drawdown period
Sources

ABSTRACT

After the impoundment of the Three Gorges Reservoir (TGR), the hydrological situation of the reservoir has changed greatly. The concentration and distribution of typical persistent organic pollutants in water and sediment have also changed accordingly. In this study, the concentration, distribution and potential sources of 16 polycyclic aromatic hydrocarbons (PAHs) and 6 phthalic acid esters (PAEs) during the water drawdown and impoundment periods were investigated in water and sediment from the TGR. According to our results, PAHs and PAEs showed temporal and spatial variations. The mean ΣPAH and ΣPAE concentrations in water and sediment were both higher during the water impoundment period than during the water drawdown period. The water samples from the main stream showed larger ΣPAH concentration fluctuations than those from tributaries. Both the PAH and PAE concentrations meet the Chinese national water environmental quality standard (GB 3838-2002). PAH monomers with 2–3 rings and 4 rings were dominant in water, and 4-ring and 5–6-ring PAHs were dominant in sediment. Di-*n*-butyl phthalate (DBP) and di-2-ethylhexyl phthalate (DEHP) were the dominant PAE pollutants in the TGR. DBP and DEHP had the highest concentrations in water and sediment, respectively. The main source of PAHs in water from the TGR was petroleum and emissions from coal and biomass combustion, whereas the main sources of PAHs in sediments included coal and biomass combustion, petroleum, and petroleum combustion. The main source of PAEs in water was domestic waste, and the plastics and heavy chemical industries were the main sources of PAEs in sediment.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) and phthalic acid esters (PAEs) are two classes of ubiquitous, persistent toxic substances that are widely detected in air, water and sediment (Deyerling et al., 2014; Li et al., 2016; Liu et al., 2011, 2015; Net et al., 2015; Xu et al., 2013). PAHs mainly originate from the incomplete combustion of carbonaceous materials (Wang et al., 2015) and

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https://doi.org/10.1016/j.jes.2017.11.004
1001-0742/

are known to be toxic and carcinogenic compounds (Grote et al., 2005; Singh et al., 2017). PAEs are widely used as plasticizing agents in cellulosics and elastomers (Zhang et al., 2015), are released mainly by the plastics and cosmetics industries (Zhang et al., 2012) and are reported to be endocrine disruptors (Li et al., 2016; Xu et al., 2010). Due to their easy accumulation, high toxicity, and carcinogenic/endocrine disruption properties, PAHs and PAEs are of considerable concern worldwide. The control of PAHs and PAEs in surface water is also required according to China's environmental quality standards.

The Three Gorges Reservoir (TGR) on the Yangtze River is currently the world's largest hydraulic project, with a total water area of 1084 km^2 (Liu et al., 2012; Shen et al., 2014). The water quality in the TGR is essential for both human and ecological health in China (Zhu et al., 2015). The construction of the Three Gorges Project changed the natural flow conditions and the original water distribution of the Yangtze River (Wang et al., 2013). Consequently, the transportation and fate of pollutants changed accordingly. The slower flow rate reduced the diffusion and self-purification abilities of the pollutants (Xu et al., 2007). The water quality in the TGR has begun to deteriorate after impoundment (Xu et al., 2013; Zhao et al., 2011; Zhao et al., 2013a, 2013b).

The hydrodynamic conditions of the TGR vary greatly with reservoir operation. The reservoir operation of the TGR is divided into two periods: water drawdown period and water impoundment period. During the water drawdown period (usually from January to September), the water is released from the reservoir with a high discharge flow, and the water level drops from 175 to 145 m. During the water impoundment period (usually from September to December), the water level rises to 175 m and is maintained at this level, and the water flow rate is slow. The variation of hydrodynamic conditions between different water periods in a river has significant impact on the distribution, sources and fates of pollutants (Dong et al., 2015; Qi et al., 2014; Yang et al., 2010). Dong et al. (2015) indicated that both free and total dissolved PAH concentrations in water of the Xiaolangdi Reservoir were the highest during sediment regulation, followed by the concentrations during water regulation and before regulation.

PAHs are the predominant toxic organic compounds in the TGR (Floehr et al., 2015; Wang et al., 2013; Zhu et al., 2015). Zhu et al. (2015) investigated the concentrations and sources of PAHs in surface water from the TGR during the water drawdown period (March and April) in 2012. They determined that PAH pollution in the TGR originates from petroleum, coal and biomass combustion. Wang et al. (2013) studied the temporal and spatial variation of PAHs in water from the TGR during the water drawdown period (April to June) in 2008, 2009 and 2011. They observed an obvious decrease of PAH concentration in water after 175-m water impounding in 2011. Floehr et al. (2015) found that PAHs were the key organic pollutants in sediments from the TGR, and pose an ecotoxicological risk. Although some researchers have examined the concentration and source of PAHs in the TGR, there are no reports on the concentrations and sources of PAHs during different water periods in the TGR.

PAEs were also reported to be one of the main organic pollutant classes in the TGR before the 175-m impoundment (Guo et al., 2006; Xu et al., 2007). The concentrations of di-n-butyl phthalate (DBP) and di-2-ethylhexyl phthalate (DEHP) in 2005 were 0.83–2.21 μg/L and 0.66–3.60 μg/L, respectively (Xu et al., 2007). No relevant reports can be found concerning the PAE concentrations in water and sediments from the TGR after the 175-m impoundment of the TGR. Additionally, the sources of PAEs in water and sediment from the TGR are also not known.

In this study, the concentration, distribution and potential sources of PAHs and PAEs in surface water and sediment from the TGR in 2015 were investigated. Samples during both the water drawdown period (June) and water impoundment period (December) were collected to study the temporal variations and sources of PAHs and PAEs during different water periods. In total, 16 PAHs and 6 PAEs included in the US EPA list of priority pollutants were analyzed in both the water and sediment samples. Our results can also be used as reference levels for future PAH and PAE pollution monitoring programs in water and sediment from the TGR.

1. Materials and methods

1.1. Chemicals and reagents

In this study, the 16 target PAHs are naphthalene (Nap), acenaphthene (Ace), acenaphthylene (Acy), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-c,d]pyrene (InP), dibenzo[a,h]anthracene (DahA) and benzo[g,h,i] perylene (BghiP). The 6 target PAEs are dimethyl phthalate (DMP), diethyl phthalate (DEP), di-*n*-butyl phthalate (DBP), butyl benzyl phthalate (BBP), di-2-ethylhexyl phthalate (DEHP), and di-*n*-octyl phthalate (DNOP). Standard mixed stock solutions of the PAHs and PAEs were supplied by AccuStandard Inc. (USA, 99%), and a PAH recovery standard (fluoranthene-d10) was also purchased from AccuStandard Inc. (USA). Chromatographic-grade methylene dichloride, acetone and ethyl acetate were obtained from Fisher Chemical (USA). Chromatographic-grade n-hexane was purchased from TEDIA (USA).

1.2. Sample collection

The locations of the sampling sites are shown in Fig. 1, which includes 12 sites (M1 to M12) in the main stream and 8 sites (T1 to T8) in tributaries of the Yangtze River. Both surface water samples and surface sediments were collected from all the sites in June 6–13 (water drawdown period) and December 14–21 (water impoundment period) in 2015. The tributary sampling sites (T1–T8) from upstream to downstream include the Wujiang River, Quxi River, Xiaojiang River, Modaoxi River, Meixi River, and Daning River.

The surface water samples were taken from the top layer (0–50 cm) using a pre-cleaned stainless-steel barrel. Four-liter water samples were filtered through 0.45-μm membranes and stored in pre-cleaned 4-L brown glass containers, then each water sample was spiked with the PAH recovery standard (fluoranthene-d10, 1.0 μg). The surface sediment samples were collected using a pre-cleaned grab sampler and stored in sealable bags. All water and sediment samples were transported to the

Please cite this article as: Lin, L., et al., Distribution and sources of polycyclic aromatic hydrocarbons and phthalic acid esters in water and surface sediment from the Three..., J. Environ. Sci. (2017), https://doi.org/10.1016/j.jes.2017.11.004