Effect of Water-Sediment Regulation of the Xiaolangdi Reservoir on the Concentrations, Bioavailability, and Fluxes of PAHs in the Middle and Lower Reaches of the Yellow River

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Abstract

The water-sediment regulation of the Xiaolangdi Reservoir is conducted to control the relationship between riverine runoff and sediment transport of the Yellow River; however, there is no research about the effect of water-sediment regulation on the bioavailability and fluxes of hydrophobic organic compounds (HOCs). In this study, water and suspended sediment (SPS) samples were collected downstream of the Xiaolangdi Reservoir before, during, and after the water-sediment regulation in 2013. The 16 priority polycyclic aromatic hydrocarbon (PAH) concentrations of freely dissolved, total dissolved, and SPS-associated were determined. During water regulation, water discharged from the reservoir at a high flow rate led to the resuspension of downstream sediment. During sediment regulation, the sediment ejected from the reservoir resulted in higher SPS concentrations than that during water regulation. Both the freely and total dissolved PAH concentrations in river water during sediment regulation were the highest,

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followed by the concentrations during water regulation and before regulation. The freely dissolved PAH concentrations in river water during the water-sediment regulation were 2-11 times higher than those before water-sediment regulation. This was due to the fact that the resuspended sediment during water-sediment regulation could release PAHs into water phase, and more contaminants were released from the SPS during sediment regulation than during water regulation. The fluxes of sediment and the 16 priority PAHs ($\Sigma_{16}\text{PAHs}$) during water-sediment regulation contributed to 32.4% and 35.7% of their annual fluxes, respectively, which were higher than the contribution (22.6%) of water discharge. This study suggested that the water-sediment regulation might reduce the long-term retention of sediment and PAHs in the reservoir. However, the environmental risk of PAHs as well as other contaminants downstream of the reservoir and in the estuary might increase during that period. Therefore, the effect of water-sediment regulation on the bioavailability and environmental risk of HOCs should be considered in the operation and management of the Xiaolangdi Reservoir in the future.

Keywords: Bioavailability, Polycyclic aromatic hydrocarbons (PAHs), Suspended Sediment (SPS), Dams, Water conservation project, Water quality

1. Introduction

The transport and distribution of hydrophobic organic compounds (HOCs) in different phases of rivers greatly affect their bioavailability and water quality. Once the HOCs enter rivers, they are preferentially associated with suspended sediment (SPS) which may further deposit as bottom sediment. If there are changes in the hydrodynamic conditions, bottom sediment may resuspend, and the HOCs in the sediment can be released to the water. Therefore, bottom sediments could act as both sink and source of HOCs, and the hydrodynamic condition is the key factor influencing the transition between sink and source. Li et al. (2006) suggested that SPS processes play an important role in the distribution of polycyclic aromatic hydrocarbons (PAHs) in different sections of the Yellow River. In addition, many studies have found that sediment resuspension and deposition could change the freely dissolved concentrations of HOCs and alter their bioavailability in waters (Dong et al., 2013; Eggleton and Thomas, 2004; Friedman et al., 2009; Pedersen et al., 2002; Schneider et al., 2007). For example, Cornelissen et al. (2008) indicated that the resuspension of dredged sediment had increased the bioavailability of PAHs by a factor of 37.5 and polychlorinated biphenyls by a factor of 2.9 in the waters of Oslo harbor, Norway.

The hydrodynamic conditions of a river vary with many factors, including anthropogenic activities like dredging (Hayes et al., 2000; Je et al., 2007), trawling (Durrieu de Madron et al., 2005; Ferré et al., 2008), and operation of water conservation projects, and natural factors like wind, storm, and tide (Ferré et al., 2008; Pusceddu et al., 2005). Among these factors, water conservation projects play a key role in influencing the hydrodynamic conditions of a river. To efficiently utilize water resources, many water conservation projects, including hydropower stations, reservoirs, and dams, have been built around the world. They have remarkable impacts on hydraulic regulation and sediment retention in riverine system (Nilsson et al., 2005; Syvitski et al., 2005). However, there are few reports about the effect of water conservation projects on

the bioavailability of HOCs and water quality of rivers.

Due to a high SPS concentration and different sources of water and sediment, water-sediment regulation of the Xiaolangdi Reservoir was conducted to solve the problem of imbalance between water and sediment for the Yellow River. The water-sediment regulation was divided into two periods: water regulation and sediment regulation. During water regulation, the overlying water with very little SPS was released from the Xiaolangdi Reservoir with a high flow discharge to scour the river channel and reduce SPS deposition. During sediment regulation, the bottom water containing as high as 300 g/L of sediment was ejected from the Xiaolangdi Reservoir at a high flow rate to maintain reservoir capacity (Hu et al., 2012). From 2002 to 2013, water-sediment regulation had been operated 14 times. For each period, the average fluxes of water and sediment into the Bohai Sea were 3.8 billion m³ and 62.0 million tons, respectively (Zhang and Wang, 2012). However, there is no research about the effect of the water-sediment regulation of the Xiaolangdi Reservoir on the concentrations, bioavailability, and risk of HOCs downstream of the reservoir.

Therefore, the present study was conducted to investigate the effect of water-sediment regulation on the distribution and bioavailability of PAHs downstream of the Xiaolangdi Reservoir. The water and SPS samples were collected before, during, and after water-sediment regulation. The total dissolved concentrations of the sum of 16 priority PAHs ($\Sigma_{16}\text{PAHs}$) in the water phase and their concentrations in the SPS phase were analyzed. The freely dissolved concentrations of PAHs were measured by negligible depletion solid phase micro-extraction (nd-SPME) to reflect their bioavailability. The temporal and spatial variations of PAH concentrations in different phases were studied, and the effects of water regulation and sediment regulation on the bioavailability of PAHs were compared. In addition, the flux of PAHs into the Bohai Sea during water-sediment regulation was estimated. The effect of water-sediment regulation on the environmental risks of PAHs downstream of the Xiaolangdi Reservoir was also

analyzed.

2. Materials and methods

2.1 Chemicals and glassware

Sixteen PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(123-cd)pyrene, dibenz(ah)anthracene, and benzo(ghi)perylene) and deuterated PAHs (*d*10-phenanthrene, *d*10-pyrene, and *d*12-chrysene) were obtained from JT Baker (Philipsburg, NJ, USA). The physical-chemical properties of the studied PAHs are listed in **Table S1 (Supplementary data)**. The recovery standard (2-fluorobiphenyl) and internal standard (*m*-terphenyl) were obtained from J&K Scientific Ltd. (New Haven, C.T., USA). HPLC grade dichloromethane (DCM), methanol, and hexane were supplied by J&K Scientific Ltd. (New Haven, C.T., USA). All glassware was prepared as follows: soaked in an acid solution for 24 h, afterward washed with tap water, distilled water, and ultrapure water (each for three times) in sequence; then dried in an oven (105°C) and heated at 450°C in a muffle furnace for 4 h.

2.2 SPME preparation for the determination of freely dissolved PAHs

Disposable glass fibers with a core of 110 µm in diameter and coated with a 30-µm layer of polydimethylsiloxane (PDMS) were obtained from Polymicro Technologies (Phoenix, Arizona, USA). Concentration of the PDMS coating was verified to be 13.55±0.02 µL/m fiber. The fibers were cut into required lengths (1 cm) with a quartz capillary cutting blade obtained from Polymicro Technologies. Then they were cleaned by sonicating in methanol and ultrapure water three times, and stored in ultrapure water before use.

The PDMS-water partition coefficients (K_{PDMS} , L/L) of PAHs serve as an essential

parameter for determining freely dissolved PAH concentrations in the water phase. Our preliminary experiments indicated that the effect of temperature on the K_{PDMS} was not significant in the range of 10-30°C. However, spiking PAHs into ultrapure water (low ionic strength) led to significant underestimated K_{PDMS} compared with previously reported values (Table S2). This might relate to the effect of ionic strength on PDMS-water distribution of HOCs (Jonker and Muijs, 2010). Therefore, in this study, artificial river water (ARW), containing 0.75 mM NaHCO₃, 1.50 mM CaCl₂, 1.50 mM MgCl₂, 0.20 mM KCl, and 0.50 mM NaN₃ in ultrapure water with a conductivity of 940 µs/cm, was prepared to mimic the Yellow River water with a conductivity of 947±37 µs/cm. The K_{PDMS} in the ARW was measured to determine the freely dissolved PAHs (C_{free} , ng/L) with the following equation:

$$C_{free} = \frac{C_{PDMS}}{(K_{PDMS} \times 10^9)} \quad (1)$$

where C_{PDMS} (µg/µL) is the PAH concentration in PDMS phase when the PAHs reach equilibrium between PDMS fiber and water phases. Details of the measurement of K_{PDMS} values are described in Supporting Information (SI 1.1), and 24 h was long enough for PAHs to reach equilibrium between PDMS fiber and water (Figure S1). K_{PDMS} values measured in the present study (both ARW and ultrapure water) are listed in Table S2, which are comparable to previous reported values using the same type of PDMS fibers.

2.3 Sample collection and pretreatment

The Yellow River is more than 5400 km long with a drainage area of 752443 km². The Xiaolangdi Reservoir is the last reservoir in the main river and the upstream drainage area occupies 92.3% of the Yellow River basin. The population of the Yellow River basin is 114 million, and the basin population downstream of the reservoir is 29 million. During water-sediment regulation in 2013, water regulation occurred from June 19th to July 3rd, and

sediment regulation occurred from July 3rd to July 10th. In this study, samples were collected before water-sediment regulation (June 15th of 2013), during water regulation (June 22th, June 24th, June 26th, and June 28th), and during sediment regulation (July 4th and July 8th). A total of six sampling sites were located along the middle and lower reaches of the Yellow River downstream of the Xiaolangdi Reservoir (Fig. 1), including Xiaolangdi (2 km downstream of the dam, XLD), Jiaogong Bridge (JG), Huayuankou (HYK), Aishan (AS), Luokou (LK), and Lijin (LJ). In addition, samples in the Xiaolangdi Reservoir (KQ) were collected at 0.5-1 m beneath the water surface on June 22th during water regulation and July 4th during sediment regulation to analyze the water quality of the reservoir.

To estimate the annual PAH flux of the Yellow River, the water and sediment discharges into the Bohai Sea were measured daily at LJ station. The velocity-area method described by Li et al. (2005) was used to determine water discharge. For the determination of sediment discharge, samples were collected using a DP-HSQ instantaneous type suspended sediment sampler. The details of the measurement are described in supporting information (SI 1.2). In addition, the PAH concentrations of the water samples collected on June 15th (before water-sediment regulation) and September 20th (after water-sediment regulation) at LJ station were determined.

Temperature, pH, conductivity, and redox potential of the river water were determined in situ with a Mettler Toledo™ SevenGo meter (Mettler Toledo International, Schwerzenbach, Switzerland). The water sample was collected at each site with a 10 L pre-cleaned aluminum bucket. To analyze the SPS concentration, two liters of water sample were in situ filtered through a 0.45 µm glass fiber membrane (Whatman, Maidstone, England), which was preheated at 60 °C and weighed at room temperature before use. After filtration, the glass fiber membranes were sealed with aluminium foil and transported to the laboratory within 48 h. The membranes were placed in an oven at 60 °C until the samples were completely dried. Then each membrane was

weighed again to calculate the SPS concentration of the water samples. The filtrate obtained in situ was used for the determination of total and freely dissolved concentrations of PAHs. In general, the total dissolved HOCs are operationally defined as the HOCs which can pass through a 0.45 μm filter. The freely dissolved HOCs are commonly adopted to characterize their bioavailability. They are defined as the HOCs that are dissolved in the aqueous phase alone and in no way bound to any matrix (Pawliszyn, 1999). So the total dissolved HOCs include both the freely dissolved and the part combined with small colloids and dissolved organic carbon (DOC). As the total dissolved HOC concentration is not equivalent to its bioavailable concentration, SPME method was used to analyze the freely dissolved PAH concentrations in this study to better reflect the bioavailability of PAHs in river water during water-sediment regulation. The preliminary experiments indicated that the 0.45 μm glass fiber membrane had no substantial effect on PAH concentrations. The total dissolved PAHs of each river water sample were extracted in situ by solid phase extraction (SPE) using Oasis HLB cartridges (Waters, Milford, MA, USA), which were pre-conditioned with 10 mL DCM, 4 mL methanol, and 4 mL ultrapure water successively before extraction. Two liters of the filtered water sample with 50 ng/L 2-fluorobiphenyl were transferred to a 2.5 L-glass bottle, and a total of 100 mL methanol was added to enhance PAH extraction recoveries. Then the water sample in each bottle was passed through a SPE cartridge at a speed of 5 mL/min. After that, all the cartridges were subject to freeze-drying for over 72 h to remove moisture. Then the PAHs in each cartridge were eluted three times with 6 mL DCM each time. The eluents were combined, concentrated, and solvent-exchanged to 1 mL hexane under a soft nitrogen stream prior to GC/MS analysis.

In terms of freely dissolved PAHs, one piece of 1cm pre-cleaned PDMS fiber was introduced into each brown jar containing 800 mL of filtrate as obtained above. The jars were sealed with Teflon[®] caps and placed on a horizontal shaker at 120 rpm under 25 °C for 24 h. Upon equilibrium, fibers were removed from the jars, wiped dry with ashless paper, and placed in

200 μ L hexane (containing 5 ng of *m*-terphenyl as internal standard) for 24 h re-extraction of the PDMS-sorbed analytes before instrumental analysis. To confirm the feasibility of the nd-SPME method, the polyethylene devices (PEDs), which have been described in our previous work (Xia et al., 2013a) and Supplementary Information (SI 1.3), were suspended in river water to determine the freely dissolved concentrations of phenanthrene, pyrene, and chrysene in situ. According to the results shown in Figure S2, there was no significant difference between the freely dissolved concentrations of PAHs based on the PDMS placed in bottles and those based on the PEDs placed in river water; this indicated that the freely dissolved PAH concentrations in the water samples measured by nd-SPME could reflect the field concentrations.

For the determination of PAHs in SPS, a total of 2 g freeze-dried SPS sample was extracted using an accelerated solvent extractor (ASE300, Dionex Corp., USA). Each sample was extracted twice (under 100 °C and 1500 psi), using 66 mL hexane-acetone (1:1, v/v) for each time. Then the total extract was concentrated by a rotary evaporator and solvent exchanged with 5 mL of hexane before the clean-up procedure. The detail of the clean-up procedure can be found in our previous study (Liu et al., 2010). After that, samples were concentrated below 1 mL under a nitrogen stream prior to GC/MS analysis.

2.4 Calculation of PAH flux of the Yellow River

Because the Lijin station is the last hydrometric station before the Yellow River flows into the Bohai Sea, water and sediment discharges as well as the fluxes of PAHs were calculated with the data obtained at the Lijin station in this study. The annual water discharge (D_W) and annual sediment discharge (D_{SPS}) were calculated as follows:

$$D_W = \sum_{j=1}^{365} Q_{Wj} \quad (2)$$

$$D_{SPS} = \sum_{j=1}^{365} Q_{SPSj} \quad (3)$$

where Q_{Wj} and Q_{SPSj} are the daily water and sediment discharges at LJ station, respectively. The water discharge before (D_{Wb}), during (D_{Wd}), and after (D_{Wa}) water-sediment regulation as well as the sediment discharge before (D_{SPSb}), during (D_{SPSd}), and after (D_{SPSa}) water-sediment regulation were also calculated. The annual PAH flux (F_T) of the Yellow River could be estimated with the follow equation:

$$F_T = F_D + F_B + F_A \quad (4)$$

where F_D , F_B , and F_A are the PAH fluxes during, before, and after water-sediment regulation, respectively. The F_D (lasting for 22 days) can be estimated with the following equation:

$$F_D = \sum_{i=1}^{22} (C_{Wi} \times Q_{Wi}) + \sum_{i=1}^{22} (C_{SPSi} \times Q_{SPSi}) \quad (5)$$

where C_{Wi} and C_{SPSi} are the concentrations of $\sum_{16}$ PAHs in the water and SPS phases on the i^{th} day, respectively; Q_{Wi} and Q_{SPSi} are the water and sediment discharges into the sea on the i^{th} day, respectively, which were determined with daily measured data. Because the concentrations of $\sum_{16}$ PAHs in samples were not determined daily, the PAH concentrations of June 19th-21th and 23th were interpolated by those of June 22th, June 25th by June 24th, June 27th by June 26th, June 29th-July 3rd by June 28th, July 5th-July 7th by July 4th, and July 9th-10th by July 8th. The F_B and F_A were estimated as follows:

$$F_B = C_{Wb} \times D_{Wb} + C_{SPSb} \times D_{SPSb} \quad (6)$$

$$F_A = C_{Wa} \times D_{Wa} + C_{SPSa} \times D_{SPSa} \quad (7)$$

where C_{Wb} and C_{Wa} are the total dissolved concentrations of $\sum_{16}$ PAHs in the river water before and after water-sediment regulation; C_{SPSb} and C_{SPSa} are the concentrations of $\sum_{16}$ PAHs in the

SPS before and after water-sediment regulation. Here we used the data obtained on June 15th and on September 20th to represent the values before and after water-sediment regulation, respectively.

2.5 GC/MS analysis of PAHs

PAHs were analyzed using a Varian 3800 gas chromatography-4000 ion trap mass spectrometry (GC/MS) system equipped with a Varian FactorFourTM highly inert capillary column VF-5ms (30m×0.25mm diameter, and 0.25µm film thickness). The injection port temperature was maintained at 280°C. Highly purity Helium (99.9999%) was used as the carrier gas and kept at a constant flow rate of 1.0 mL/min. Sample extracts (1.0 µL) were injected in splitless mode. The GC oven temperature was held at 80°C for 2 min, then ramped at 15°C/min to 230°C and held for 2 min. The temperature was then programmed to increase to 290°C at 8°C/min and held for 2 min. Ionization was performed in electron impact (EI) mode and the ion source temperature was fixed at 200 °C. For identification of each target chemical, full scan mode from 35 to 550 amu was first performed and identification was based on both retention time and characteristic ions. The quantification of each individual PAH and recovery standard was calculated based on internal standard method using the Varian WorkStation software.

2.6 Organic carbon, black carbon, and particle size analysis

For the determination of DOC in water sample, a total of 40 mL of the supernatant was transferred into a brown sample bottle. The DOC concentration was determined by an elemental analyzer (Vario El, Elementar Analysensysteme GmbH, Germany). The contents of total organic carbon (TOC) and black carbon (BC) of the SPS samples were also determined by the elemental analyzer after they were pretreated with the method as described in our previous work ([Liu et al., 2010](#)). In addition, the particle size of each SPS sample was determined with a Microtrac S3500

251 Laser Particle Size Analyzer (Microtrac Inc., Montgomeryville, PA).

252 **2.7 Quality assurance/quality control**

253 The correlation coefficients for calibration curves of PAHs with GC/MS were all higher than
254 0.99. The method detection limits (MDLs) of PAHs in water samples ranged from 0.4 to 6.5 ng/L
255 (Table S3), which were calculated using six duplicates of blank samples according to the IUPAC
256 method (MDL=mean+3SD). The PAHs in blank SPME fibers and SPE cartridges were below
257 detection limits. As shown in Table S4, the recoveries of 16 PAHs and 2-fluorobiphenyl in spiked
258 solution, spiked SPS, and spiked polyethylene ranged from 80.5% to 105.4% (N=36), from
259 72.1% to 95.9% (N=48), and from 62.1% to 75.9% (N=24), respectively. The recovery of
260 2-fluorobiphenyl, which was used as recovery standard, ranged from 74.8% to 90.2% in real
261 water samples, from 65.9% to 89.3% in real SPS samples, and from 60.2% to 79.8% in
262 polyethylene samples. All the data were corrected with the recoveries of recovery standard. The
263 use of SPME achieved a depletion ratio of less than 1.8% of the freely dissolved concentrations
264 for the 16 PAHs in water, which was less than 5% and could be considered negligible. A 24-h
265 extraction of the PDMS fibers was long enough for PAHs to desorb from PDMS, and the results
266 showed that no PAHs were detected in a second extraction of fibers using 200 μ L fresh hexane.
267 All the samples were in triplicate, and the results are expressed as average $\pm$ standard deviation.

268 **3. Results and discussion**

269 **3.1 Effect of water-sediment regulation on PAH concentrations in different** 270 **phases**

271 **3.1.1 Total and freely dissolved PAHs in the water phase**

272 As shown in Figure 2, the total dissolved concentrations of $\sum_{16}$ PAHs in river water before
273 water-sediment regulation were lower than those during water regulation, and much lower than

274 those during sediment regulation for each sampling site ($p < 0.05$). For example, the total
 275 dissolved concentration of $\sum_{16}\text{PAHs}$ at JG station was 149 ± 56.3 ng/L before water-sediment
 276 regulation, and it increased to 256 ± 32.6 ng/L during water regulation and 608 ± 69.7 ng/L during
 277 sediment regulation. The reason could be analyzed as follows. During water regulation, the water
 278 discharged from the reservoir at a high flow rate led to the resuspension of downstream sediment.
 279 During sediment regulation, the sediment ejected from the Xiaolangdi Reservoir resulted in high
 280 SPS concentrations downstream of the reservoir. Both the resuspended sediment during water
 281 regulation and the sediment ejected from the reservoir during sediment regulation could release
 282 contaminants into the water phase, leading to the higher total dissolved concentrations of
 283 $\sum_{16}\text{PAHs}$ during water-sediment regulation than those before water-sediment regulation. In
 284 addition, the SPS concentrations as well as the silt and sand particle concentrations during
 285 sediment regulation were higher than those during water regulation (Table 1, Table S5). Therefore,
 286 the SPS during sediment regulation released more PAHs than during water regulation, resulting in
 287 the higher total dissolved concentrations of $\sum_{16}\text{PAHs}$. This is also supported by the result shown
 288 in Figure S3 that there was a significant positive relationship between total dissolved
 289 concentrations of $\sum_{16}\text{PAHs}$ and SPS concentrations for all sampling sites ($n=36$, $r=0.89$, $p < 0.01$).

290 Similar to the total dissolved of $\sum_{16}\text{PAHs}$, the freely dissolved concentrations of $\sum_{16}\text{PAHs}$ in
 291 river water during sediment regulation were higher than those during water regulation, and much
 292 higher than those before regulation (Figure 2). For example, the freely dissolved pyrene
 293 concentrations during water regulation and sediment regulation were 2 and 7 folds higher than
 294 those before regulation, respectively. The freely dissolved concentration of HOCs is commonly
 295 used as an indicator of their bioavailability (Wang et al., 2011; Xia et al., 2013b). Therefore, the
 296 water-sediment regulation could increase the concentrations of bioavailable PAHs downstream of
 297 the reservoir. As shown in Figure S4, the ratios of freely to total dissolved concentrations of
 298 $\sum_{16}\text{PAHs}$ were $53.6 \pm 16.2\%$ before water-sediment regulation, $60.5 \pm 16.3\%$ during water

regulation, and $52.4\pm18.4\%$ during sediment regulation. The results indicated that there was no significant difference in the ratios among the three periods. Furthermore, the ratios of freely to total dissolved concentrations of phenanthrene ($60.6\pm11.6\%$), pyrene ($39.8\pm25.6\%$), and chrysene ($23.7\pm8.1\%$) obtained in this research were comparable to those of the Yongding River, the Haihe River, and the Yellow River in our previous study (Xia et al., 2013a).

3.1.2 PAHs in the SPS phase

The PAH concentrations in the SPS during sediment regulation were higher than those during water regulation at each sampling site (Figure 2). This might be attributed to the fact that the SPS during sediment regulation was from the sediment of the Xiaolangdi Reservoir (KQ) and the SPS during water regulation was from the sediment downstream of the reservoir; these two sediments from different sources had different PAH concentrations, with the former higher than the latter (Figure S7). Besides, as shown in Table 1, the particle size of the SPS during sediment regulation was smaller than that during water regulation, and the TOC contents of the SPS of the former were higher than the latter. That is to say, the SPS during sediment regulation had larger specific surface areas and more sorption sites. Therefore, after desorption caused by sediment resuspension, the PAH concentrations in unit SPS during sediment regulation were still higher than those during water regulation. Feng et al. (2008) and Yang et al. (2008) have conducted simulation experiments to study the PAH release during sediment resuspension, and found that the PAH concentrations in SPS increased with the decrease of SPS particle size.

3.1.3 Distribution of PAHs between the SPS and water phases

The distribution coefficient (K_d , L/kg) of each PAH between the SPS and water phases was calculated with the following equation:

$$K_d = C_s / C_w \quad (8)$$

where C_s is the PAH concentration in the SPS phase (ng/kg), and C_w is the total dissolved PAH

concentration in the water phase (ng/L). The OC-normalized distribution coefficient (K_{OC}) was calculated by the following equation:

$$K_{OC} = K_d / f_{oc} \quad (9)$$

where f_{oc} is the TOC content of SPS ($\text{kg}_{OC}/\text{kg}_{SPS}$). As shown in [Figure S5](#), there was no significant difference in the log K_d value for each PAH between sediment regulation and water regulation periods ($p > 0.1$). However, the log K_{OC} value of each PAH during sediment regulation was lower than that during water regulation ([Table 3](#)). In general, the K_d values are affected by the contents and composition of TOC in SPS as well as PAH characteristics, while the K_{OC} values are influenced by the TOC composition (such as BC content) and PAH characteristics. In this study, the BC contents of SPS increased from XLD to LJ during water regulation, while keeping constant during sediment regulation. Furthermore, the BC contents during sediment regulation were lower than those during water regulation ([Table 1](#)); this resulted in the higher log K_{OC} values of PAHs during water regulation because the sorption capacity of BC is higher than amorphous organic carbon ([Accardi-Dey and Gschwend, 2003](#)). In addition, the increased BC during water regulation inferred that the PAHs associated with SPS were less bioavailable than during sediment regulation. Besides, the OC-normalized distribution coefficients of PAHs obtained in this study were comparable to those between SPS and water in the Xijiang River reported by [Deng et al. \(2006\)](#). In addition, as shown in [Figure S6](#), there is a positive relationship between log K_{OC} and log K_{OW} values ($p < 0.01$), suggesting that the characteristics of PAHs are the main factor for their distribution between SPS and river water during water or sediment regulation.

3.2 Spatial variation of PAH concentrations during water-sediment regulation

As shown in [Figure 3](#), during water regulation, the total and freely dissolved PAH concentrations in the water of the Xiaolangdi Reservoir were lower than those downstream of the reservoir except for HYK on June 22th, LK on 24th, and LJ on 24th and 28th. In addition, for both

total and freely dissolved PAH concentrations, the average values of the six sampling sites downstream of the reservoir were higher than those of the reservoir for each sampling. During sediment regulation, the total and freely dissolved PAH concentrations in the water of the reservoir were lower than those downstream of the reservoir for each sampling. There was a slightly decreasing trend in both total and freely dissolved concentrations of PAHs along the river downstream of the reservoir from June 26th to July 8th ($p < 0.05$), with only small disorders at the HYK and AS stations (Figure 3). The reason can be analyzed as follows. During water regulation, the PAH concentrations in SPS increased from XLD to LJ by 17%-81% (Figure S7). Furthermore, the particle size of the SPS decreased and the BC contents of SPS increased from XLD to LJ (Table 1). Therefore, the PAHs might be released from the coarse particles and then re-sorbed by the smaller particles with higher BC contents along the river, resulting in the decrease of PAH concentrations in the water phase from XLD to LJ. During sediment regulation, the SPS and DOC concentrations decreased from XLD to LJ (Table 1). Parts of the DOC and colloids might also be deposited with the deposition of SPS by flocculation. Therefore, the PAHs combined with both DOC and colloids would also deposit, leading to a decreasing trend in PAH concentrations in the water phase during sediment regulation. Consequently, the spatial variation of PAH concentrations in river water during water-sediment regulation was related to the sediment resuspension/deposition and SPS characteristics.

There are several tributaries downstream of the Xiaolangdi Reservoir. The Yiluo River and the Qin River flow into the Yellow River between JG and HYK; the Jindi River and the Dawen River flow into the main river between HYK and AS. The contributions of their annual water discharge and sediment discharge to the Yellow River are only 8.3% and 0.3%, respectively, and the PAH concentrations in the river water of the tributaries are slightly higher than those of the main river (Li et al., 2006), which will lead to the slight increase of PAH concentrations in river water of the main stream. This might be the reason for the small disorders of PAH concentrations

in the water phase along the river mentioned above.

3.3 Flux of PAHs during water-sediment regulation

3.3.1 PAH flux into the Bohai Sea

During water-sediment regulation, the water discharge into the Bohai Sea at the Lijin station was 5.3 billion m³ and the sediment discharge was 56.1 million tons. The fluxes of PAHs in the dissolved and particulate phases were estimated at 1.06 tons and 10.03 tons, respectively. Therefore, the total flux of PAHs during water-sediment regulation was 11.1 tons, and the PAH flux in the total dissolved phase contributed to 9.5%. Before water-sediment regulation (during January 1st-June 18th), the water and sediment discharges were 6.5 billion m³ and 13.1 million tons, respectively, and the PAH flux was 1.8 tons including 0.8 tons in dissolved phase. After regulation, the water and sediment discharges were 11.5 billion m³ and 103.7 million tons, respectively, and the PAH flux was 18.2 tons including 2.7 tons in dissolved phase. Therefore, the annual flux of PAHs was the sum of the three periods, which was estimated to be 31.1 tons. Besides, the calculation of PAH flux during non water-sediment regulation based on only two samplings might result in the uncertainty of the annual PAH flux. However, according to previous research, there was no significant difference in PAH concentrations between dry and wet seasons (Lang et al., 2008; Li et al., 2006). Therefore, the uncertainty about the obtained annual PAH flux caused by the few samplings in this study might be negligible. In addition, Wang et al. (2007) estimated the PAH flux of the Yellow River to be 70.5 tons using the method that the riverine flux was assumed to positively correlate with the regional total emission of PAHs; this value was comparable to that obtained in our study. Water-sediment regulation of the Xiaolangdi Reservoir lasted for 22 days, accounting for 6.0% of the whole year. However, the contribution of PAH flux during water-sediment regulation to the annual flux was 35.7% (11.1/31.1×100%).

3.3.2 Comparison with other rivers

As shown in **Table 2**, for the total dissolved concentrations of $\sum_{16}\text{PAHs}$, the levels in the Yellow River were much lower than those in the Jialing River (Xu et al., 2012), and were comparable to the levels in the Seine River (Bourgeault and Gourlay-Francé, 2013) and at the Datong station in the Yangtze River Estuary (Qi et al., 2014). However, the PAH levels in the present study were much higher than those in the Pearl River Estuary (Wang et al., 2007), the Niagara River (Michor et al., 1996), the Danube River (Maldonado et al., 1999), the lower reach of the Mississippi River (Mitra and Bianchi, 2003), and the lower Brisbane River (Shaw et al., 2004). For the freely dissolved concentrations of $\sum_{16}\text{PAHs}$, the levels in this study were much higher than those in the Danube River (Vrana et al., 2014) and the Seine River (Bourgeault and Gourlay-Francé, 2013), but were comparable to the levels in the Morava River (Prokeš et al., 2012), and were lower than the levels in the Willamette River (USA) (Sower and Anderson, 2008).

The concentrations of $\sum_{16}\text{PAHs}$ in the SPS phase during water-sediment regulation ranged from 98 to 329 ng/g, which were comparable to those (31-514 ng/g) in the upper and middle reaches of the Yellow River (Zhang and Zhang, 2010), and higher than those in the Danube River Estuary (Maldonado et al., 1999). However, the concentrations of $\sum_{16}\text{PAHs}$ in the SPS phase obtained in the present research were much lower than those in the Pearl River Delta (Wang et al., 2007), in the Yangtze River (Qi et al., 2014), and in the Mississippi River (Mitra and Bianchi, 2003). Because the loess with low TOC contents contributes to 90% of the sediment of the Yellow River, the TOC contents in the SPS obtained in this study were lower than those for other rivers. Similar results about the Yellow River have been reported by other researchers (Li et al., 2006; Zhang et al., 2013). This might explain the lower PAH concentrations in the SPS of the Yellow River than many other large rivers around the world.

Many researchers have reported the fluxes of $\sum_{16}\text{PAHs}$ from rivers to seas. As shown in **Table 4**, the annual flux of PAHs of the Yellow River was lower than the Yangtze River (Qi et al., 2014)

and Humen tidal channel (China) (Yang et al., 2004), but was comparable to the Heilongjiang River (Wang et al., 2007), the Pearl River (Wang et al., 2007), the Rhone River (Lipiatou et al., 1997), and the Mississippi River (Mitra and Bianchi, 2003; Wang et al., 2004). Furthermore, the contribution of the dissolved PAH flux to their total flux of the Yellow River was lower than that of the Yangtze River (Qi et al., 2014) and the Ebro River (Lipiatou et al., 1997), but was comparable to that of the Mississippi River.

3.4 Effect of water-sediment regulation on the environmental risk of PAHs for the Yellow River

According to the results shown in section 3.3, the water discharge, sediment discharge, and PAH flux during the water-sediment regulation contributed to 22.6%, 32.4%, and 35.7% of their annual discharges, respectively. Therefore, both the contribution ratios of sediment transport load and PAH flux during water-sediment regulation were higher than that of water discharge, indicating that the water-sediment regulation is beneficial to the ejection of sediment and PAHs from the Xiaolangdi Reservoir as well as downstream of the reservoir. Consequently, as to the long-term effect, the water-sediment regulation could reduce the retention of sediment and PAHs in the reservoir.

However, during the water-sediment regulation, the PAH concentrations in the water phase downstream of the reservoir were higher than those before and after the water-sediment regulation. This indicated that the water-sediment regulation of the Xiaolangdi Reservoir might increase the bioavailability of PAHs downstream of the reservoir as well as in the estuary during that period. In addition, the total dissolved concentration of each PAH in the river water was compared with its maximum permissible concentration (MPC) established by the Dutch Government, which could serve as a generic environmental quality standard (IWINS, 1997). The results indicated that the total dissolved concentrations of pyrene and benz(a)anthracene exceeded

their MPCs at some sampling sites during the water-sediment regulation. Considering all the samplings at the six sites, 16.7% of the total dissolved benz(a)anthracene concentration exceeded its MPC during water regulation; 33.3% and 25.0% of pyrene and benz(a)anthracene exceeded their MPCs during sediment regulation, respectively (Figure 4). During water-sediment regulation, the freely dissolved PAH concentrations of the river water were 2-11 times higher than those before water-sediment regulation (Figure S8). This could increase the potential risk of fish and other organism exposure to PAHs in the river water.

This study suggested that the water-sediment regulation might reduce the environmental risk of PAHs in the reservoir in the long-term. However, a large amount of sediment would resuspend and release PAHs and other HOCs into the river water during water-sediment regulation, resulting in the increase of bioavailability and potential risk of PAHs as well as other HOCs to aquatic organisms downstream of the reservoir and in the estuary during that period. Therefore, the effect of water-sediment regulation on the bioavailability and environmental risk of PAHs as well as other contaminants should be considered in the operation and management of the Xiaolangdi Reservoir in the future.

Acknowledgements

This study was supported by the National Science Foundation for Innovative Research Group (No: 51421065), National Science Foundation for Distinguished Young Scholars (No: 51325902), and the National Science Foundation of China (No: 51279010).

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Figure captions

Figure 1 Sampling sites of the Yellow River during water-sediment regulation (Reservoir 1: Sanmenxia Reservoir; Reservoir 2: Xiaolangdi Reservoir; The blue line upstream the AS site is the east line project of the South-to-North Water Diversion, which passes across the Yellow River with a tunnel at 70 m beneath the riverbed of the Yellow River.)

Figure 2 Temporal variations of $\sum_{16}\text{PAHs}$ in water and SPS phases at each site before and during water and sediment regulation (A: before water-sediment regulation; B: during water regulation; C: during sediment regulation, there was no data for JG and HYK because the SPS samples were not much enough for the determination of PAHs during water regulation.)

Figure 3 Spatial variations of $\sum_{16}\text{PAHs}$ in water and SPS phases during water-sediment regulation (KQ: the PAH concentrations in the water of the reservoir; DA: the average PAH concentrations of the six sampling sites downstream of the reservoir)

Figure 4 Comparison of dissolved concentrations of pyrene and benz(a)anthracene in river water during water-sediment regulation and their maximum permissible concentrations (MPCs) (the solid lines in the plots represent the MPCs of individual PAH)

Figure 1 Sampling sites of the Yellow River during water-sediment regulation

(1: Sanmenxia Reservoir; 2: Xiaolangdi Reservoir (KQ); the blue line upstream the AS site is the east line project of the South-to-North Water Diversion, which passes across the Yellow River with a tunnel at 70 m beneath the riverbed of the Yellow River.)

Figure 2 Temporal variations of $\Sigma_{16}\text{PAHs}$ in water and SPS phases at each site

before and during water-sediment regulation

(A: before water-sediment regulation; B: during water regulation; C: during sediment regulation.

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Figure 3 Spatial variations of $\Sigma_{16}\text{PAHs}$ in water phases during water-sediment regulation (KQ: the PAH concentrations in the water of the reservoir; DA: the average PAH concentrations of the six sampling sites downstream of the reservoir)

Figure 4 Comparison of dissolved concentrations of pyrene and benz(a)anthracene in river water during water-sediment regulation and their maximum permissible concentrations (MPCs) (the solid lines in the plots represent the MPC of individual PAH)

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Table 1 DOC concentration, SPS concentration and median grain size (d50), TOC and BC contents of SPS during water-sediment regulation

Sampling site	Distance from Estuary (km)	Water regulation					Sediment regulation				
		DOC (mg/L)	SPS (g/L)	d ₅₀ (μm)	TOC (‰)	BC (‰)	DOC (mg/L)	SPS (g/L)	d ₅₀ (μm)	TOC (‰)	BC (‰)
Xiaolangdi (XLD)	864	5.27±2.68	0.04±0.01	77.5	0.94±0.72	0.26±0.11	6.91±0.05	54.75±1.82	30.8	3.03±0.14	0.25±0.09
Jiaogong (JG)	788	5.54±2.69	0.58±0.58	36.6	1.54±0.44	0.60±0.15	6.69±0.14	47.87±16.5	27.3	3.62±1.06	0.32±0.00
Huayuankou (HYK)	731	5.62±2.85	0.09±0.03	37.5	3.05±0.35	0.55±0.27	6.80±0.33	20.61±0.16	14.2	4.83±0.51	0.34±0.04
Aishan (AS)	402	6.76±0.43	5.01±2.24	27.0	2.22±0.26	0.63±0.28	6.39±0.62	18.29±6.19	12.3	3.63±0.30	0.41±0.09
Luokou (LK)	298	6.82±0.44	5.14±1.57	31.9	2.00±0.25	1.10±0.27	6.13±1.03	15.11±4.65	11.1	3.82±0.97	0.30±0.05
Lijin (LJ)	104	7.12±0.41	10.05±0.54	17.0	3.22±0.67	2.74±0.68	6.00±0.51	19.02±7.09	12.5	4.64±0.01	0.34±0.03

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Table 2 Comparison of PAHs level in the Yellow River with other rivers around the world

River name (Country)	Dissolved PAH concentration in water phase		$\sum_{16}$ PAHs in SPS	references
	Total (ng/L)	freely (ng/L)	SPS (ng/g)	
Yellow River (China)	101-803	66.2-468	98.1-329	In this study (during water-sediment regulation)
	121-208	38.0-128		In this study (before water-sediment regulation)
Yellow River (China)	179-369		54.3-154.5	Li et al., 2006 (in the middle and lower reaches)
Yellow River (China)	96.6-476.84		31-514	Zhang and Zhang, 2010 (in the upper and middle reaches)
Yangtze River (China)	320-630		1830-9150	Qi et al., 2014 (at Datong station)
Yangtze River (China)	242-6345		4677	Feng et al., 2007 (in Wuhan section)
Jialing River (China)	812-1586			Xu et al., 2012
Pearl River (China)	10.8-323		100-3840	Wang et al., 2007
Brisbane River (Australia)	5-12			Shaw et al., 2004
Mississippi River (USA)	12-77		1100-7000	Mitra and Bianchi, 2003 (in the lower reach)
Mississippi River (USA)	62.9-114.7			Zhang et al., 2007
Niagara River (Canada)	16.8			Michor et al., 1996
Danube River Estuary	1.30		0.5-5.6	Maldonado et al., 1999
Danube River (Austria and Slovakia)		5-72		Vrana et al., 2014
Seine River (France)	8.9-271.8	3.5-105.9	4000-64000	Bourgeault and Gourlay-Francé, 2013
Morava River (Czech Republic)		25-203		Prokeš et al., 2012
Willamette River (USA)		440 ± 422		Sower and Anderson, 2008

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Table 3 The $\log K_{OC}$ (OC-normalized distribution coefficient) values of PAHs during water-sediment regulation at each site

PAHs	$\log K_{OW}$	$\log K_{OC}$ (During water regulation)					$\log K_{OC}$ (During sediment regulation)						
		XLD	AS	LK	LJ	Mean	XLD	JG	HYK	AS	LK	LJ	Mean
Nap	3.3	4.78	4.36	4.90	4.73	4.69	4.52	4.15	4.04	4.26	4.48	4.72	4.36
Acy	3.94	5.73	5.17	5.42	5.60	5.48	5.71	5.62	5.83	5.35	5.31	5.66	5.58
Ace	4.03	5.43	4.95	5.25	5.51	5.29	5.23	4.79	5.15	4.92	5.01	5.35	5.08
Fle	4.18	5.47	5.14	5.37	5.66	5.41	5.32	4.99	5.33	5.35	5.24	5.71	5.32
Phe	4.57	6.14	5.54	5.78	5.99	5.86	5.77	5.29	5.49	5.63	5.50	5.88	5.59
Ant	4.54	5.61	5.27	5.33	5.71	5.48	5.00	4.72	5.23	5.19	5.02	5.07	5.04
Flu	5.22	6.18	5.61	5.63	6.11	5.88	5.52	5.15	5.45	5.40	5.36	6.08	5.49
Pyr	5.18	6.23	6.28	6.39	6.07	6.24	5.91	4.72	4.46	5.40	5.82	5.69	5.33
BaA	5.61	6.54	5.69	5.41	5.39	5.76	6.15	5.68	5.79	5.61	5.59	5.38	5.70
Chr	5.91	6.04	5.06	5.30	5.86	5.57	5.92	5.86	5.82	5.47	5.63	5.70	5.73

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Table 4 Comparison of PAH flux of the Yellow River with other rivers around the world

River name (Country)	Water discharge (10 ⁹ m ³ /yr)	SPS (mg/L)	PAH flux (t/yr)				references
			total	particulate	dissolved	dissolved/total(%)	
Yellow River (China)	5.25	20-5.96×10 ⁴	11.1	10.03	1.06	9.5	in this study (during water-sediment regulation)
Yellow River (China)	23.5		31.1	26.6	4.5	14.4	in this study (annual flux)
Yellow River (China)	57		70.5				Wang et al., 2007
Yangtze River (China)	980		368.9			About 50	Qi et al., 2014
Heilongjiang River (China)	350		30.2				Wang et al., 2007
Xijiang River (China)			19.4				Deng et al., 2006
Pearl River (China)	350		33.9				Wang et al., 2007
Humen tidal channel (China)			247.9	13.8	234.1	94.4	Yang et al., 2004
Qiantang River (China)	9.48				11.4		Chen et al., 2007
Mississippi River (USA)	58		28.2	25.2	3.0	10.6	Mitra and Bianchi, 2003; Wang et al., 2004
Seine River (France)	13.7	9-17	8.4	0.27	8.14	96.8	Fernandes et al., 1997
Rhone River (France)	53.9		7.4-33	5.8-29	1.6	5.2-21.6	Lipiatou et al., 1997; Gómez-Gutiérrez et al., 2006
St. Lawrence River (Canada)			6.5				Mackay and Hickie, 2000
Niagara River (USA, Canada)	18.9		3.2				Michor et al., 1996; Halfon and Allan, 1995
Danube River (Europe)	210		0.3				Humborg, 1997; Maldonado et al., 1999
Ebro River (Spain)	9.3		1.3	0.9	0.4	30.8	Lipiatou et al., 1997; Gómez-Gutiérrez et al., 2006
Chenab River (Pakistan)	59		52.8				Farooq et al., 2011