Effect of Water-Sediment Regulation of the Xiaolangdi Reservoir on the Concentrations, Characteristics, and Fluxes of Suspended Sediment and Organic Carbon in the Yellow River

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Abstract

Water-sediment regulation (WSR) of the Xiaolangdi Reservoir in the Yellow River is different from other water conservancy projects, with sediment resuspending along the river downstream of the reservoir during water regulation while some suspended sediment depositing during sediment regulation. In this study, samples were collected before, during, and after WSR to investigate the effect of WSR on the suspended sediment and organic carbon downstream of the reservoir. The suspended sediment concentration ($[SPS]$) increased with the river flow velocity (V) as a power function ($[SPS]=1.348V^{2.519}$) during the three periods. The suspended sediment grain size decreased along the river during water and sediment regulations and after WSR; they were generally below 200 μm with the fine particles ($<50\text{ }\mu\text{m}$) of 68.0%-93.7% and positively correlated with the flow velocity. The black carbon content in suspended sediment elevated along the river during both water and sediment regulations, and it increased with 2-50 μm fraction during water regulation and with $<2\text{ }\mu\text{m}$ fraction during sediment regulation, suggesting that black carbon mainly exists in fine particles and is influenced by both suspended sediment source and characteristics. There was no significant difference in dissolved organic carbon (DOC) concentration during water regulation, sediment regulation, and after WSR, inferring that the effect of sediment resuspension/deposition on DOC concentration was insignificant. The contribution of DOC flux (27.3%) during WSR period to the annual flux was comparable to that (22.6%) of water, but lower than the sediment (32.5%) and particulate organic carbon (POC) (49.5%). This study suggests that WSR will exert significant influence on the concentrations, characteristics and fluxes of POC ($p<0.05$) and sediment ($p<0.05$) but have no significant influence on DOC ($p>0.1$) of the Yellow River.

Keywords: Suspended sediment, Organic carbon, Water-sediment regulation, Sediment resuspension-deposition, Yellow River, Water conservancy project

1. Introduction

Rivers play a vital role in the transport of water, sediment, and nutrients from terrestrial to marine ecosystems. The concentrations, characteristics, and fluxes of suspended sediment and organic carbon (OC) in rivers not only have remarkable effects on their transport from land to ocean but also exert a controlling influence on the fates of nutrients, organic pollutants, and heavy metals in rivers (Balakrishna and Probst, 2005; Dong et al., 2013; Wölz et al., 2010; Xia et al., 2013). Therefore, research on suspended sediment and OC is important for the study of water quality throughout the river system.

Anthropogenic activities, such as the operation of water conservancy projects, could change hydrodynamic condition of rivers, inducing sediment resuspension or suspended sediment deposition. This will further affect the discharge of water as well as the concentrations, characteristics, and fluxes of suspended sediment and OC (Dai and Liu, 2013; Meybeck et al., 2004; Yang et al., 2006; Yang et al., 2007). Many researchers have reported that hydropower dams and reservoirs have exerted influence on water discharge, sediment retention, and nutrient fluxes in large rivers around the world, such as the Mekong River (Kummu and Varis, 2007; Lu and Siew, 2006), the Danube River (Teodoru and Wehrli, 2005), the Indus River (Giasan et al., 2006), and the Yangtze River (Xu and Milliman, 2009). For example, more than 80% of water discharge from the Gwydir River (New South Wales, Australia) has been altered significantly by the Copeton Dam (Rolls et al., 2013). After the impoundment of the Three Gorges Dam in June 2003, the sediment discharge of the Yangtze River decreased by 60% (Xu and Milliman, 2009). Teodoru and Wehrli (2005) indicated that 5% of total nitrogen, 12% of total phosphorus, and 55% of suspended sediment for the Danube River was trapped in the Iron Gate I Reservoir.

In order to deal with the problems of the high suspended sediment concentration and severe sediment deposition along the Yellow River, the impoundment of the Xiaolangdi Reservoir began in October 1999, and the water-sediment regulation (WSR) of the reservoir has been in

operation since 2002. The WSR of the Xiaolangdi Reservoir aims at controlling flood, mitigating further infilling of sediment in the Sanmenxia (SMX) Reservoir, maintaining the reservoir capacity, and scouring the elevated river-bed in the lower reaches of the Yellow River. The WSR is divided into two periods: water regulation and sediment regulation. During water regulation, the overlying water with low suspended sediment concentration is released from the reservoir at a high flow velocity to scour the riverbed, resulting in sediment resuspension along the river downstream of the reservoir. During sediment regulation, the bottom water containing as much as 300 g/L of sediment is ejected from the reservoir at a high speed to maintain reservoir capacity (Hu et al., 2012), with some suspended sediment deposition along the lower reach. Therefore, the WSR of the Xiaolangdi Reservoir is clearly distinct from the operations of other water conservancy projects around the world. Thus, the effect of WSR on the concentrations, characteristics, and fluxes of suspended sediment and OC might be remarkably different from the other water conservancy projects.

The effect of WSR of the Xiaolangdi Reservoir on the fluxes of sediment and OC has been studied by several researchers (Yao et al., 2009; Zhang et al., 2015; Miao et al., 2016). For example, Zhang et al. (2013) mentioned that the contributions of the fluxes of dissolved organic carbon (DOC) and particulate organic carbon (POC) during WSR to the annual fluxes in 2008 were 35% and 56%, respectively. Yu et al. (2013) provided a good overview of the role of the Xiaolangdi dam in influencing the sediment flux of the Lower Yellow River and the effect of WSR on the suspended sediment concentration and median grain size. However, the effect of such large-scale sediment resuspension/deposition events like the WSR on suspended sediment and OC is not well understood. Especially, as sediment resuspension occurs during water regulation while suspended sediment deposits along the river during sediment regulation, the variations of concentrations and characteristics of suspended sediment and OC might be different during the two periods. However, there was no research report about the comparison of

the effects of water regulation and sediment regulation of the Xiaolangdi Reservoir. Furthermore, there is limited knowledge about the effect of hydrodynamic conditions on suspended sediment during WSR of the Xiaolangdi Reservoir.

Therefore, the present study was conducted to investigate the effect of the WSR on the concentrations and characteristics of suspended sediment and OC downstream of the Xiaolangdi Reservoir along the Yellow River. Water and suspended sediment samples in six sampling sites were collected during water regulation, during sediment regulation, and after WSR. The suspended sediment size and OC composition, including DOC and POC (black carbon and amorphous organic carbon), during the three periods were examined. The impacts of water regulation and sediment regulation on suspended sediment as well as OC transport along the studied stretch were compared, and the effect of hydrodynamic conditions on suspended sediment was also investigated. In addition, the fluxes of suspended sediment and OC were estimated during WSR.

2. Materials and methods

2.1 Study Area

The Yellow River, which originates from the Qinghai-Tibetan Plateau, is more than 5400 km long and has a drainage area of 752,443 km². Most of the Yellow River basin is located in arid and semiarid regions with an annual average temperature of 8-14 °C (Chen et al., 2005). The mean annual precipitation is highly variable across the river basin, increasing from 368 mm in the upper reaches to 530 mm in the middle reaches and to 670 mm in the lower reaches (Wang et al., 2006). However, the water primarily originates from the upper reaches of the river, while the sediment is primarily derived from the upper and middle reaches of the Yellow River, which is located in the Loess Plateau (from 100°54'E to 114°33'E and from 33°43'N to 41°16'N).

The Xiaolangdi Reservoir, which is 130 km long and has a water area of 272 km², is the most

downstream reservoir on the Yellow River. Its upstream drainage area occupies 92.3% of the Yellow River basin. The maximum reservoir capacity is 12.65 km³, and the capacity of WSR is 1.05 km³ (Li et al., 2007). The construction of the Xiaolangdi Reservoir was completed in October of 1997. Since 1999 and before the WSR operation in 2002, the suspended sediment-containing water released from the SMX Reservoir was trapped in the Xiaolangdi Reservoir, and there were 933 million tons of sediment trapped in the reservoir during this period (the Yellow River Sediment Bulletin, 2001). According to the data obtained from the Yellow River Conservancy Commission (YRCC), the annual water and sediment discharges downstream of the Xiaolangdi reservoir after its operation (2002-2013) are 16.5 km³ and 160 Mt, respectively; the annual water and sediment discharges before its operation (1950-2000) are 34.4 km³ and 870 Mt, respectively. The WSR is typically conducted in the summer and lasts approximately 20 days. In 2013, water regulation was conducted from June 19th to July 3rd, and sediment regulation occurred from July 3rd to July 10th.

2.2 Water and suspended sediment sampling

To investigate the characteristics and composition of suspended sediment and OC, water and suspended sediment samples were collected downstream of the Xiaolangdi Reservoir along the main river in 2013 during water regulation (June 22th, June 24th, June 26th, and June 28th), during sediment regulation (July 4th and July 8th), and after WSR (September 20th, low water season). The sampling sites (Fig. 1) included Xiaolangdi (2 km downstream of the Xiaolangdi dam, XLD), Jiaogong Bridge (JG), Huayuankou (HYK), Aishan (AS), Luokou (LK), and Lijin (LJ). In addition, to estimate the annual flux of OC into the Bohai Sea, water and suspended sediment samples were collected before WSR (June 15th, high water season) at the LJ station. To investigate the relationship between suspended sediment concentrations and the flow velocities, water samples were collected once every three days in June, July, and September of 2013 at the AS, LK, and LJ stations to determine the suspended sediment concentrations, and the flow

velocity of the river water was also determined. All of the water samples were collected at a depth of 0.5-1 m beneath the water surface with pre-cleaned brown bottles (2.5 L). The bottles were prepared as follows: the bottles were soaked in an acid solution for 24 h, then washed with tap water, distilled water and ultrapure water (three times for each water type), then dried in an oven (105 °C) and heated at 450 °C in a muffle furnace for 5 h. Six bottles were used at each site for each sampling.

Because the Lijin station is located approximately 100 km upstream of the river mouth and is not affected by tidal movement (Ran et al., 2013), the water and sediment discharges at the LJ station were determined daily to estimate the fluxes of water and sediment into the Bohai Sea. To investigate the water discharge, the flow velocities along ten vertical lines at the cross-section of Lijin were determined using a LS25-1 rotating element current meter (Chongqing Hydrometric Instrument Plant, Ministry of Water Resources, China). The depth of river water for each vertical line was measured by a fathometer to calculate the section area. Then, the water discharge was calculated as the sum of the discharges of each section. For the determination of sediment discharge, samples were collected using a DP-HSQ instantaneous suspended sediment sampler (Beijing, China). The water discharge at the cross-section, as mentioned above, was divided into five equal sections, and 1 L water sample was collected at each section at half of the water depth. The preliminary experiment showed that there was no significant difference in suspended sediment concentrations among different depths ($p>0.1$), indicating that the suspended sediment concentration and characteristics were the same as those collected at a depth of 0.5-1 m beneath the water surface and that water stratification in the river during this period might be insignificant. The five water samples were combined and settled for 24 h. After that, the water samples were in situ filtered through 0.45 μm membrane. After the suspended sediment sample was totally dried, its mass was determined to calculate the average suspended sediment concentration at the cross-section. Then, instantaneous sediment discharge was calculated using the instantaneous

water discharge and the suspended sediment concentration. Therefore, the daily sediment discharge was the time-weighted average of instantaneous sediment discharge with three samplings.

2.3 Sample analysis

All of the water samples were in-situ filtered with 0.45 μm GF/F glass-fiber filters (Whatman, Maidstone, UK), which were preheated at 60 $^{\circ}\text{C}$ before use. After filtration, all of the water and suspended sediment samples were stored at 4 $^{\circ}\text{C}$ and quickly transferred to the laboratory. In the laboratory, the DOC concentration of the filtrate was analyzed using an elemental analyzer (Vario E1, Elementar Analysensysteme GmbH, Germany). Analytic precision and accuracy of DOC on triplicate injections were $<4.0\%$ and $<4.8\%$. The suspended sediment concentration of each water sample was determined by the measurement of the residue on the filter freeze-dried in a freezer dryer for 72 h until a constant weight was reached. After the suspended sediment samples were dried, they were sieved through a 2 mm sieve. The particle size of the suspended sediment samples, which was determined using a Microtrac S3500 Laser Particle Size Analyzer (Microtrac Inc., Montgomeryville, PA) based on the suitable standard operation procedure (refractive index, 1.59; measurement time, 20 s; flow, 90%), was classified into four categories: $<2\ \mu\text{m}$, 2-50 μm , 50-100 μm , and 100-2000 μm . The measurement error for the particle size was $\leq 1\%$.

To determine the total organic carbon (TOC) and black carbon (BC) contents in suspended sediment, the dried suspended sediment samples were grinded with an agate mortar to pass through a 100-mesh stainless steel sieve. An elemental analyzer (Vario E1, Elementar Analysensysteme GmbH, Germany) was used for the TOC analysis after the samples were treated with HCl (1:1, v/v). The BC content in samples was determined with the chemo-thermal oxidation method. Inorganic carbon in the suspended sediment samples was initially removed by HCl (1:1, v/v), and amorphous organic carbon (AOC) was subsequently removed in a thermal oxidation procedure at 375 $^{\circ}\text{C}$ in a tube furnace for 24 h in the presence of excess air. Then, the

BC content in suspended sediment was also determined with the elemental analyzer. Details of the method have been described in our previous work (Liu et al., 2010). The analytic precision based on triplicate analysis was $\pm 5\%$ for POC and BC. All of the sample analyses were performed in triplicate, and the results are expressed as the average $\pm$ standard deviation.

2.4 Data analysis and calculation of OC flux of the Yellow River

The data of annual water and sediment discharges from SMX to LJ before 2013 were quoted from the Yellow River Water Resources Bulletin (1998-2012) and the Yellow River Sediment Bulletin (2001-2012). In this study, statistical methods including regression analysis were conducted using Excel 2007. Correlation analyses and difference analyses at significance levels of 0.01 and 0.05 were performed using SPSS 22.

Because the LJ station is the last hydrometric station before the Yellow River flows into the Bohai Sea, the annual water discharge (D_W) and annual sediment discharge (D_{SPS}) into the sea were estimated with the following equations based on the data obtained at the LJ station in this study:

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

$$D_{SPS} = \sum_{j=1}^{365} (Q_{Wj} \times C_{SPSj}) \quad (2)$$

where Q_{Wj} and C_{SPSj} are the daily water discharge and suspended sediment concentration at the LJ station, respectively. The water discharge before (D_{Wb}), during (D_{Wd}), and after (D_{Wa}) WSR as well as the sediment discharge before (D_{SPSb}), during (D_{SPSd}), and after (D_{SPSa}) WSR were also calculated.

According to the DOC concentrations in the aqueous phase and the TOC contents in the suspended sediment phase, the fluxes of DOC (F_{DOC-D}) and POC (F_{POC-D}) into the Bohai Sea during WSR could be estimated as follows:

$$F_{DOC-D} = \sum_{i=1}^{22} (C_{DOCi} \times Q_{Wi}) \quad (3)$$

$$F_{POC-D} = \sum_{i=1}^{22} (P_{TOCi} \times Q_{SPSi}) \quad (4)$$

where C_{DOCi} is the DOC concentration (mg/L) in the water phase at the LJ station on the i^{th} day; P_{TOCi} is the TOC content (%) in the suspended sediment phase at the LJ station on the i^{th} day; and Q_{Wi} and Q_{SPSi} are the water and sediment discharges into the sea on the i^{th} day, respectively.

The annual DOC (F_{DOC-T}) and POC fluxes (F_{POC-T}) of the Yellow River could be estimated with the following equations:

$$F_{DOC-T} = F_{DOC-D} + F_{DOC-B} + F_{DOC-A} \quad (5)$$

$$F_{POC-T} = F_{POC-D} + F_{POC-B} + F_{POC-A} \quad (6)$$

where F_{DOC-B} and F_{DOC-A} are the DOC fluxes before and after WSR, respectively, and they could be estimated with the DOC concentrations in river water and the water discharges before/after WSR; F_{POC-B} and F_{POC-A} are the POC fluxes before and after WSR, respectively, and they could be calculated with the TOC contents in the suspended sediment and sediment discharges before/after WSR. Here, we used the data obtained on June 15th and on September 20th to represent the values before and after WSR, respectively.

3. Results and discussion

3.1 Relationship between suspended sediment concentrations and characteristics with hydrodynamic conditions

3.1.1 Suspended sediment concentrations during water and sediment regulations

According to the results shown in Fig.2a, the suspended sediment concentrations increased downstream of the Xiaolangdi Reservoir along the river during water regulation but decreased downstream of the reservoir during sediment regulation. This result is attributed to the fact that the overlying water containing little sediment at a high-flow velocity had a strong erosion

capacity during water regulation, leading to the resuspension of sediment, while suspended sediment discharged from the Xiaolangdi Reservoir during sediment regulation deposited along the river. Furthermore, the suspended sediment concentrations during sediment regulation were much higher than those during water regulation ($p<0.05$). The suspended sediment concentrations ranged from 0.04 to 10.0 g/L with a mean value of 3.48 g/L during water regulation, and ranged from 15.1 to 54.8 g/L with a mean value of 29.4 g/L during sediment regulation.

The average values of the suspended sediment concentrations during WSR were much higher than those (0.01-0.48 g/L, 0.24 g/L on average) after WSR ($p<0.05$) obtained in this study and those (0.43 g/L on average) before WSR ($p<0.05$) obtained in our previous research (Xia et al., 2013). The suspended sediment concentrations (3.02-19.0 g/L) at the LJ station during WSR in 2013 obtained in this study were comparable to those (6.3-10.6 g/L) during WSR in 2008 reported by Wang et al. (2012). Furthermore, the average suspended sediment concentration (3.48 g/L) during water regulation in the lower reaches of the Yellow River was approximately 20 times higher than that of other rivers in China, and 40 times higher than the average level of other large rivers around the world (Table S1). The average suspended sediment concentration (29.4 g/L) during sediment regulation was approximately two orders of magnitude higher than the average level of other large rivers around the world (Table S1). The high suspended sediment level of the Yellow River is due to severe erosion in the Loess Plateau (Zhang et al., 1990).

The flow velocity of the river water ranged from 0.6 to 3.2 m/s in this study. As shown in Fig.3a, the suspended sediment concentration ($[SPS]$, g/L) increased with the flow velocity of the river water (V , m/s) as a power function during the water-sediment regulation and non-WSR periods as follows ($n=144$, $r=0.95$, $p<0.01$):

$$[SPS] = 1.348V^{2.519} \quad (7)$$

Furthermore, during each period (water regulation, sediment regulation, and after WSR), the suspended sediment concentration also increased with the flow velocity of the river water as

power functions ($[SPS]=a \cdot V^b$) (Fig.3b). The b value was greatest during non-WSR period, followed by sediment regulation and water regulation periods, indicating that the effect of hydrodynamic condition on the suspended sediment concentration was most significant during non-WSR period. Ding et al. (2004) also reported that the major factor controlling the suspended sediment concentration in the Yangtze River was the flow velocity of river water. Such relationship observed in the Yellow River was consistent with the theoretical equation reported by Zhang (1989). Huang et al. (2012) reported that the suspended sediment concentration increased (from 0.165 to 4.22 g/L) with the flow velocity (from 0.15 m/s to 0.35 m/s) in a laboratory simulation experiment as a similar power function, which was consistent with the results obtained in this study. This infers that if the flow velocity of river water increases, an increasing amount of sediment would suspend into the water phase, indicating that the flow velocity of river water is the main factor for the variation of suspended sediment concentrations, especially for turbid rivers.

3.1.2 Suspended sediment particle size during water and sediment regulations

The particle size of the suspended sediment decreased downstream of the reservoir during water regulation, sediment regulation, and after WSR (Fig.2b and Table 1). This is because during water regulation, the flow velocity of river water would decrease along the river, and finer particles would resuspend and enter into the river water. During sediment regulation, large suspended particles would deposit faster along the river, thus leading to the decrease of particle size from XLD to LJ. After WSR, large suspended sediment would deposit along the river due to the decrease of flow velocity of river water. As shown in Fig. 3c, there was a significantly positive relationship between the suspended sediment particle size and the flow velocity of river water during the WSR and non-WSR periods ($p<0.01$), indicating that the particle size of suspended sediment decreased with the decrease of flow velocity of the river water.

According to the results shown in Table 1, during water regulation, the suspended sediment

particle size in the Yellow River was below 500 μm , and the average contributions of <2 μm , 2-50 μm , 50-100 μm , and >100 μm fractions in suspended sediment were 0.87%, 67.1%, 18.5%, and 13.5%, respectively. During sediment regulation, the suspended sediment particle size in river water was below 200 μm , and the average contributions of <2 μm , 2-50 μm , 50-100 μm , and >100 μm fractions were 9.64%, 84.1%, 5.35%, and 0.95%, respectively. During the non-WSR period, the suspended sediment particle size was below 200 μm , and the corresponding contributions were 10.0%, 65.6%, 16.9%, and 7.50%, respectively. Therefore, the contribution of 0-50 μm fractions in suspended sediment approximately ranged from 68.0% to 93.7% for the Yellow River in this study. Yu et al. (2013) reported that more than 50% of suspended sediment particle size was below 25 μm in the lower Yellow River during 2002-2012, which was comparable to our results. Some researchers also studied the suspended sediment particle size in other rivers. The average contributions of < 2 μm and 2-63 μm fractions in suspended sediment of the Yangtze River were 48.1% and 51.9%, respectively (Yu et al., 2011). For the Red River, the Maple River, the Sheyenne River, and the Wild Rice River, 75-99% of the suspended sediment was below 62 μm (Blanchard et al., 2011). Walling et al. (2000) reported that >95% of the suspended sediment was below 63 μm for the Humber River and the Tweed River (UK). Davide et al. (2003) indicated that 64-99% of the suspended sediment was particles with a size range of 0-63 μm for the Po River (Italy) under normal and high flow conditions. Therefore, according to their and our results, the suspended sediment particle size in rivers is generally below 200 μm , and the average contribution of fine particle (<50 μm) in suspended sediment might be 64-99%.

As shown in Table 1, the average contribution of < 50 μm fraction to the whole suspended sediment samples during sediment regulation (93.7%) was the highest, followed by that (75.6%) after WSR and that (68.0%) during water regulation. Furthermore, the average mean diameter (d_{50}) value of suspended sediment (13.63 μm) during sediment regulation was lower than that (37.91 μm) during water regulation. Zhang et al. (2013) also suggested that the suspended

sediment particle size during sediment regulation might be smaller than that during water regulation. This is attributed to the fact that the particle size of sediment ejected from the XLD reservoir during sediment regulation was smaller than that of resuspended sediment in the lower reach downstream of the reservoir during water regulation. The particle size of suspended sediment after WSR (d_{50} , 26.3 μm) for most sampling sites was smaller than that during water regulation. The reason could be explained as follows. For the XLD station, there was no significant difference in the particle size of suspended sediment between during water regulation and after WSR (Table 1) because both river water and sediment came from the XLD reservoir during these two periods. After WSR, the suspended sediment particle size downstream of the XLD reservoir decreased along the river (from HYK to LJ) faster than those during water regulation due to the lower flow velocity of river water.

3.2 Contents and composition of OC during water and sediment regulations

3.2.1 Contents and composition of OC in suspended sediment

During both water and sediment regulations, the TOC content in suspended sediment phase increased from XLD to HYK downstream of the reservoir and then almost kept stable from HYK to LJ (Fig. 2c). As shown in Table 2 and Fig. S1, the TOC contents in suspended sediment phase ($0.48\% \pm 0.07\%$) during sediment regulation were higher than those ($0.25\% \pm 0.10\%$) during water regulation and those ($0.18\% \pm 0.07\%$) after WSR ($p < 0.01$). The spatio-temporal variations of TOC in suspended sediment were related to that of the particle size. As mentioned in section 3.1.2, the suspended sediment size during sediment regulation was much lower than that during water regulation, and the particle size of the suspended sediment decreased downstream of the reservoir during the two periods (Table 1). Further analysis showed that there was a negative correlation between the TOC content and suspended sediment size ($r = -0.749$, $p < 0.01$) (Fig. 4a). The results were in accordance with that reported by other researchers. Zhang et al. (2013) also showed that the TOC content in suspended sediment collected from the Yellow River in November 2006

decreased with the increase of suspended sediment size. Kukkonen et al. (2005) reported that 59.9%-94.5% of TOC in sediments of Lake Erie, Lake Huron, Lake Michigan, and West Bearskin Lake were associated with fine particles ($< 63 \mu\text{m}$). According to the results of our previous study (Li et al., 2006), the TOC contents in suspended sediment phase of the Yellow River before WSR were approximately 0.15%-0.30%, which was comparable to those after WSR obtained in this study. Compared with the TOC contents in suspended sediment of other rivers, the TOC content in the suspended sediment of the Yellow River was much lower than the levels in the global rivers such as the Amazon River, the Mississippi River, and the Po River (Table S1). This could be explained by the fact that the Yellow River sediments primarily come from the Loess Plateau, which consists of soils with fine sand (75-90%, 20-200 μm) and very low OC contents (Zhang, 2002; Song and Shi, 2010).

The TOC in suspended sediment could be divided into AOC and BC. The BC contents in suspended sediment ($0.04\% \pm 0.01\%$) during sediment regulation were lower than those ($0.06\% \pm 0.03\%$) after WSR and much lower than those ($0.12\% \pm 0.12\%$) during water regulation (Table 2), and the BC contents in suspended sediment phase downstream of the reservoir increased rapidly along the river during water regulation and increased slightly during sediment regulation (Table 2). The difference in BC content between the water and sediment regulations is because suspended sediment came from the reservoir during sediment regulation and from the lower reaches downstream of the reservoir during water regulation. As shown in Fig. 4b, there is a significantly negative relationship between BC content in suspended sediment (y) and d_{50} value (x) of suspended sediment during water regulation ($r=0.553$, $p<0.01$) and during sediment regulation ($r=0.767$, $p<0.01$), indicating that the BC content in suspended sediment increased with the decrease of suspended sediment size. Furthermore, no matter during water or sediment regulation, the BC content in suspended sediment increased with the decrease of $> 50 \mu\text{m}$ fraction in suspended sediment (Fig. 5c). The BC content in suspended sediment increased with the 2-50

μm fractions in suspended sediment during water regulation (Fig. 5b), while increased with $< 2 \mu\text{m}$ fractions during sediment regulation (Fig. 5a). That is to say, the effect of the 2-50 μm fractions (30.8%-87.1%) in suspended sediment on the BC content was significant during water regulation, and the effect of the $< 2 \mu\text{m}$ fractions (6.43%-14.1%) on the BC content was significant during sediment regulation. It suggests that the BC mainly exists in the fine particles ($< 50 \mu\text{m}$) of the Yellow River. Cornelissen et al. (2004) reported that about 50-90% of BC in lacustrine sediment of Finland and The Netherlands were in small size fractions ($< 63 \mu\text{m}$), which was consistent with our results. However, other researchers also reported that the sediment with a larger particle size contained a higher BC content. For example, Oen et al. (2006) indicated that the BC content in $> 75 \mu\text{m}$ fraction was the greatest in the sediments obtained from the Oslo Harbor and the Bergen Harbor. Rockne et al. (2002) observed that the greatest BC contents in the Piles Creek and Newtown Creek sediments were in the large size fractions of 63-125 μm and 300-500 μm , respectively. These might result from the different sources of BC between our and their studies (the analytic method for BC in our and their studies was CTO-375 method). As shown in Fig. 4b, for the suspended sediment during sediment regulation, the BC content was lower while the grain size was smaller than that during water regulation. This is due to the different sources for suspended sediment during these two periods. Therefore, the results suggest that both the suspended sediment source and characteristics are the main factors influencing the BC content in suspended sediment. In addition, the AOC content in suspended sediment were significantly correlated negatively with suspended sediment particle size ($r=0.725$, $p<0.05$) during sediment regulation (Fig. 4c), indicating that the AOC content of sediment in the XLD Reservoir was also related to the particle size.

The contribution of BC to TOC content in suspended sediment increased gradually from 23.4% at the XLD station to 94.6% at the LJ station during water regulation except for the HYK station, while the contribution were nearly constant ($8.3\% \pm 1.1\%$) during sediment regulation (Fig.

S1). The contributions ranged from 12.5% to 50.7% after WSR (Fig. S1). Because the hydrophobic organic compounds (HOCs) associated with BC are difficult to release into the water phase when the sediment resuspends into the aqueous phase, the suspended sediment with a lower BC content and a higher AOC content might release more contaminants into the water phase, leading to a higher ecological risk of HOCs. Therefore, the suspended sediment with higher TOC and lower BC contents during sediment regulation would release more HOCs into the river water, which has been proved in our previous research (Dong et al., 2015).

For comparison with DOC concentration, the POC concentration (POC_{water} , mg/L) in river water could be calculated as follows:

$$POC_{\text{water}} = TOC_{\text{SPS}} \times [SPS] \quad (8)$$

where TOC_{SPS} is the TOC content in suspended sediment phase (%), and $[SPS]$ is the suspended sediment concentration in the river water (mg/L). According to the values of TOC_{SPS} and $[SPS]$ in each sampling site, the calculated POC concentrations ranged from 0.02 to 19.7 mg/L during water regulation, from 43.9 to 318 mg/L during sediment regulation, and from 0.01 to 0.95 mg/L after WSR. In a similar way as the suspended sediment concentration, the POC concentrations in river water during sediment regulation were higher than those during water regulation and much higher than those after WSR ($p < 0.01$).

3.2.2 DOC concentration in river water

During both water and sediment regulations, there were no significant variations of DOC concentrations downstream of the reservoir along the river ($p > 0.1$, Fig. 2d). According to the results shown in Table 2, there was no significant difference in the average DOC concentrations during water regulation, sediment regulation, and after WSR ($p > 0.1$). The results indicated that the effect of sediment resuspension/deposition on the DOC concentrations was insignificant. In addition, the XLD station is only 2 km away from the XLD dam, and there are no tributaries or

wastewater flowing into the river along this river section; therefore, the DOC concentration at the XLD station can approximately represent the DOC level of the water discharged from the reservoir. According to the data obtained from the XLD station, the DOC concentration in the water containing high suspended sediment concentration discharged from the XLD reservoir during sediment regulation was 6.95 ± 0.05 mg/L, which was nearly equivalent to the levels (6.84 ± 0.19 mg/L) in the water released from the reservoir during water regulation. This result suggests that the DOC in the surface water, bottom water, and pore-water of the reservoir almost reached equilibrium in the reservoir. During water regulation, the suspended sediment concentration increased from 0.04 to 10.0 g/L along the river downstream of the XLD reservoir due to sediment resuspension, while the DOC concentration in the river water only ranged from 6.84 ± 0.19 mg/L to 7.12 ± 0.41 mg/L (Fig.2d and Table 2). Additionally, no matter during water regulation or during sediment regulation, there was no significant relationship between suspended sediment concentration and DOC concentration in the river water for each sampling ($p > 0.1$). The reason could be analyzed as follows. The suspended sediment and sediment mainly come from the Loess Plateau, and the soluble OC in the loess has been dissolved into the river water once they enter into the river channel. Therefore, for the sediment in the watercourse, effect of their resuspension/deposition on the DOC concentrations is insignificant. In addition, although the DOC level in pore water of the sediment might be higher than that in overlying water (Lai et al., 2015), the effect of DOC releasing from the pore water on the DOC concentrations in overlying water during sediment resuspension might be insignificant due to the small amount of pore water during water regulation.

The ratio of DOC to POC can reflect which form is dominant in the OC in the river. The ratios in global rivers are generally more than 1 or nearly 1 (Degens et al., 1991). In this study, the ratios of DOC to POC concentrations ranged from 0.38 to 434 during water regulation, and ranged from 0.03 to 0.21 during sediment regulation (Table S2). The results indicated that the

dominant form of OC in this river was POC during sediment regulation; during water regulation, DOC was the dominant form from XLD to HYK, and POC substituted for DOC downstream of the HYK station. Furthermore, the logarithm values of the ratios of DOC to POC concentrations correlated negatively with the logarithm values of suspended sediment concentrations, according to the following equation:

$$\log[DOC / POC] = -1.13\log[SPS] + 0.40 \quad (r=0.974, N=40, p<0.01) \quad (9)$$

where $[SPS]$ is the suspended sediment concentration in the river water (g/L), and $[DOC/POC]$ is the ratio of DOC concentration to POC concentration (dimensionless). When the suspended sediment concentration was 2.24 g/L, the ratio (DOC/POC) was equal to 1. There might be exchange or phase transition between DOC and POC during the sediment transport from the river to the sea along the studied stretch. As no significant spatial variation of DOC concentration downstream of the reservoir along the river was found (Fig. 2d), there was no apparent exchange between DOC and POC. In this study, we did not include sampling in reference rivers; this might cause some uncertainties about the results of suspended sediment and OC patterns driven by the WSR. However, during non-WSR period, the water and suspended sediment release from the Xiaolangdi Reservoir, and there are only four small tributaries (the Yiluo River, the Qin River, the Jindi River, and the Dawen River) downstream of the Xiaolangdi Reservoir, accounting for 8.3% and 0.3% of the water and sediment discharges of the Yellow River, respectively. In addition, there were no significant spatial variations of DOC concentrations in the river water as well as the TOC and BC contents in suspended sediment along the river during non-WSR periods according to the results obtained in this study and our previous research (Xia et al., 2013) ($p>0.1$). Therefore, it can be deduced that the spatial variations of suspended sediment and OC during WSR are mainly driven by the reservoir modifications.

3.3 Effect of WSR on the water discharge as well as suspended sediment and OC fluxes

3.3.1 Fluxes of water and suspended sediment into the Bohai Sea

According to the data obtained in this study, during WSR, 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 annual sediment and water discharges are estimated to be 172.8 million tons and 23.5 billion m³, respectively, similar to the average of annual sediment (160 million tons) and water discharges (16.5 billion m³) for 2002-2013 (Yellow River Sediment Bulletin 2002-2013). Therefore, the contributions of sediment and water discharges during WSR (22 days) to their annual discharges in 2013 were approximately 32.5% and 22.6%, respectively.

The fluxes of water and sediment discharged by other rivers around the world are listed in Table S3. The water discharge of the Yellow River in 2009 reported by Wang et al. (2012) was 19.3 billion m³, which agreed with the results obtained in this study. The yields or specific fluxes of water in km³/km²/yr and sediment in t/km²/yr, equivalent to mm/yr and g/m²/yr, respectively, were calculated. The water yield of the Yellow River was much lower than those of most rivers around the world. The sediment yield of the Yellow River was much higher than those of other large rivers. The net contribution (0.96%) of sediment discharge from the Yellow River to the total sediment transported by rivers worldwide reported by Milliman and Farnsworth (2013) was much higher than the contribution (0.07%) of water discharge.

3.3.2 Fluxes of OC into the Bohai Sea

During water regulation, the fluxes of DOC and POC into the Bohai Sea are estimated to be 0.02 million tons and 0.10 million tons, respectively. During sediment regulation, the fluxes of DOC and POC into the Bohai Sea are estimated to be 0.01 million tons and 0.17 million tons, respectively. The annual fluxes of DOC and POC exported to the Bohai Sea by the Yellow River were estimated at 0.11 million tons and 0.55 million tons, respectively. Besides, the estimation of OC flux during non-WSR period based on only two samplings might lead to the uncertainty of the annual OC flux (Underwood, 1992). However, according to the results of previous research

(Wang et al., 2012; Zhang et al., 2013), there was no significant difference in OC concentrations during non-WSR period. Therefore, the uncertainty about the obtained annual OC flux caused by the few samplings in this study might be negligible. The contribution of DOC flux during WSR to the annual flux was 27.3%, which was comparable to the contribution of water discharge (22.6%). The contribution of POC flux during WSR to the annual flux was 49.5%, which was higher than the contribution of water discharge. This indicates that the Xiaolangdi Reservoir acts as a sink for POC upstream of the reservoir during non-WSR, while it becomes an important source of the POC flux downstream of the reservoir during WSR. The contributions of the WSR period to annual DOC and POC exports in 2013 obtained in this study were lower than those (35% and 56%) in 2008 described by Zhang et al. (2013). This is because although the water (5.25 billion m³) and sediment discharges (56.1 million tons) during WSR in 2013 were comparable to those (4.28 billion m³ and 59.8 million tons) in 2008, the annual water (23.5 billion m³) and sediment discharges (173 million tons) in 2013 were much higher than those (14.5 billion m³ and 77.1 million tons) in 2008.

As shown in Table S3, the DOC yield within the Yellow River (0.15 g C/m²/yr) was much lower than those for the Yangtze River (Wang et al., 2012), the Pearl River (Ni et al., 2008), the Congo River (Coynel et al., 2005), the Amazon River (Moreira-Turcq et al., 2003), and the Mississippi River (Bianchi et al., 2007). The POC yield within the Yellow River (0.73 g C/m²/yr) was slightly lower than those for the Yangtze River, the Pearl River, the Amazon River, and the Mekong River (Hoa et al., 2007), but higher than those for the Mississippi River and Ebro River. The net contribution of OC from the Yellow River to the coastal ocean was approximately 0.15% of the total organic carbon transported by rivers worldwide.

3.3.3 Effect of the WSR on the suspended sediment and OC fluxes of the Yellow River

According to the data obtained from the YRCC, the annual sediment discharge in 2013 decreased to 19.9% of the average level before the operation of the XLD Reservoir (1950-2001).

In addition to the effect of the XLD reservoir, other factors like the water-soil conservation practices over the Loess Plateau and climate change might also contribute to the decrease of sediment discharge. According to the research of Wang et al. (2007), the climate change, especially precipitation reduction which affects soil erosion, was responsible for 30% of sediment reduction; the water-soil conservation practices, including terrace, planting grass, afforestation, and warp land dam, performed upstream of the SMX Reservoir became effective in the late 1970s and contributed to 40% of sediment reduction.

According to the sediment budget estimated using the data obtained from the YRCC (Table S4), the sediment discharge at the SMX station decreased from 794 million tons for 1980-2001 to 341 million tons for 2002-2013, and the sediment discharge at the XLD station decreased from 743 million tons to 79.1 million tons. The decrease in sediment discharge (89.4%) at the XLD station was higher than that at SMX station (57.1%), indicating that 262 million tons of sediment was trapped in the XLD reservoir each year. Miao et al. (2016) also reported that there was sediment trapped in the reservoir. Considering the amount of sediment retention (933 million tons) for 1999-2001 (Yellow River Sediment Bulletin 2002), the annual sediment retention for 1999-2001 was 311 million tons, which was higher than the value (262 million tons) after WSR operation for 2002-2013. This indicated that the WSR of the reservoir was beneficial for the release of sediment trapped in the reservoir into the sea to maintain the reservoir capacity. In addition, the annual sediment discharges were 79.1, 110, and 160 million tons at the XLD, HYK, and LJ stations for 2002-2013, respectively. The sediment discharge increased from XLD to LJ, showing sediment erosion from XLD to LJ along the river. Therefore, the WSR of the XLD Reservoir has significant effects on sediment releases from the reservoir and on sediment erosion along the lower reaches of the river. However, as mentioned above, large amounts of coarse sediment (262 Mt/yr) are still accumulating in the reservoir, suggesting that more measures should be conducted to maintain XLD reservoir capacity.

According to the results of Zhang et al. (1992), the annual fluxes of DOC and POC into the Bohai Sea by the Yellow River were 0.2 million tons and 6.1 million tons before the operation of the XLD reservoir. Compared with their results, the DOC and POC fluxes in 2013 have decreased by 45.0% and 91.8%, respectively, suggesting that the OC flux decreased after the operation of XLD Reservoir. This was mainly attributed to the sediment reduction as mentioned above. The decreasing ratio of POC flux was comparable to that (80.1%) of sediment discharge. However, the decreasing ratio of DOC flux was much lower than that of POC flux. This is because the effect of XLD Reservoir on the DOC concentration was less than that on the POC concentration. The results obtained in the present study suggest that although the WSR is beneficial for the discharge of OC in the reservoir to the sea, large amounts of OC are still trapped in the reservoir.

4. Conclusions

This study showed that the suspended sediment concentrations increased along the river downstream of the XLD Reservoir during water regulation but decreased during sediment regulation. The suspended sediment concentrations during sediment regulation were higher than those during water regulation and after WSR. Furthermore, suspended sediment concentration ($[SPS]$) increased with the flow velocity of river water (V) as a power function ($[SPS]=a \cdot V^b$) before, during, and after WSR ($p<0.01$). The suspended sediment grain size were generally below 200 μm , and the average contributions of fine particles ($< 50 \mu\text{m}$) were 68.0-93.7% for the Yellow River; they decreased downstream of the reservoir during water regulation, sediment regulation, and after WSR due to the decrease of flow velocities. Furthermore, the suspended sediment particle size was positively correlated with the flow velocity ($p<0.01$) during and after WSR. During both water and sediment regulations, the TOC and BC contents in suspended sediment increased with the decrease of suspended sediment grain size. However, both the suspended sediment grain size and the BC contents during sediment regulation were lower than those during water regulation due to the different sources for suspended sediment during these

two periods. Further analysis found that the BC contents increased with 2-50 μm fractions during water regulation and with $< 2 \mu\text{m}$ fractions during sediment regulation. This inferred that BC mainly exists in fine particles ($< 50 \mu\text{m}$) of the Yellow River and is affected by both suspended sediment source and characteristics. Because no significant difference in the DOC concentration in river water among water regulation, sediment regulation, and after WSR were found, the effect of resuspension/deposition of the sediment along the river on the DOC concentrations is insignificant. The contribution of DOC flux (27.3%) during WSR to the annual flux was comparable to that (22.6%) of water, but lower than the sediment (32.5%) and POC (49.5%), suggesting that the effect of WSR on DOC concentration, characteristics, and flux was less than that on POC. This study suggests that WSR will exert significant influence on concentrations and composition of POC and suspended sediment but have no significant influence on DOC of the Yellow River.

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Table 1 Average particle size of suspended sediment (SPS) samples collected during and after water-sediment regulation

period	Particle size of SPS	%						
		XLD	JG	HYK	AS	LK	LJ	Mean
Water regulation (n=12)	<2 μm	0.19±0.38	0.67±1.29	0.07±0.01	0.28±0.18	3.01±0.34	0.98±0.60	0.9±1.10
	2-50 μm	30.8±26.4	71.4±13.0	64.5±2.24	80.4±2.36	68.6±3.74	87.1±4.04	67.1±2.24
	50-100 μm	33.9±4.29	21.8±10.3	23.1±5.34	11.9±1.77	16.9±2.03	3.49±1.62	18.5±2.24
	>100 μm	35.1±23.6	6.15±5.54	12.4±7.58	7.42±2.36	11.5±1.74	8.42±2.64	13.5±2.24
	d ₅₀ (μm)	77.6	36.6	37.5	27.0	31.9	17.0	37.9
Sediment regulation (n=6)	<2 μm	6.43±1.42	8.93±0.24	14.1±2.62	9.01±0.11	7.74±1.69	11.6±2.72	9.64±2.78
	2-50 μm	83.5±1.70	87.7±0.75	78.2±3.48	85.1±1.25	83.1±4.59	86.6±3.77	84.0±3.36
	50-100 μm	8.63±2.24	2.96±0.86	5.57±4.11	4.68±0.45	8.50±0.51	1.77±1.03	5.35±2.82
	>100 μm	1.47±2.24	0.40±0.34	2.07±1.99	1.16±0.70	0.62±0.18	0.02±0.15	0.96±0.75
	d ₅₀ (μm)	19.9	13.1	8.60	13.1	15.4	11.0	13.6
After regulation (n=3)	<2 μm	0		4.95	9.93	14.2	20.9	10.0±8.09
	2-50 μm	17.1		84.1	71.4	76.5	79.1	65.6±27.5
	50-100 μm	53.0		8.54	15.9	6.96	0	16.9±20.9
	>100 μm	29.9		2.43	2.78	2.28	0	7.48±12.6
	d ₅₀ (μm)	79.4		21.8	16.7	8.78	4.95	26.3

Table 2 Organic carbon contents and composition in suspended sediment (SPS) and water samples during and after water-sediment regulation

period	OC	%						
		XLD	JG	HYK	AS	LK	LJ	mean
Water regulation (n=12)	TOC in SPS (%)	0.11±0.09	0.17±0.05	0.34±0.04	0.259±0.02	0.23±0.04	0.37±0.07	0.25±0.10
	BC in SPS (%)	0.03±0.01	0.07±0.02	0.05±0.00	0.08±0.03	0.19±0.03	0.35±0.12	0.12±0.12
	DOC in river water (mg/L)	6.84±0.19	6.88±0.16	7.03±0.44	6.76±0.43	6.82±0.44	7.12±0.41	6.19±1.89
Sediment regulation (n=6)	TOC in SPS (%)	0.36±0.01	0.44±0.13	0.61±0.08	0.45±0.04	0.45±0.11	0.59±0.01	0.48±0.07
	BC in SPS (%)	0.03±0.01	0.04±0.00	0.04±0.00	0.05±0.01	0.04±0.01	0.05±0.00	0.04±0.01
	DOC in river water (mg/L)	6.95±0.05	6.69±0.14	6.80±0.33	6.39±0.62	7.13±1.03	6.00±0.51	6.65±0.56
After regulation (n=3)	TOC in SPS (%)	0.17	0.229	0.09	0.20	0.11	0.26	0.18±0.07
	BC in SPS (%)	0.03	0.03	0.04	0.07	0.04	0.12	0.06±0.03
	DOC in river water (mg/L)	7.58	7.15	7.45	6.61	7.28	6.33	7.07±0.49

TOC: total organic carbon;

BC: black carbon;

DOC: dissolved organic carbon.

Figure captions

Figure 1 Sampling sites of the Yellow River downstream of the Xiaolangdi reservoir during and after water-sediment regulation (SMX: the Sanmenxia Reservoir; XLD: the Xiaolangdi Reservoir; JG: Jiaogong Bridge; HYK: Huayuankou; AS: Aishan; LK; Luokou; LJ: Lijin)

Figure 2 Spatial variations of suspended sediment (SPS) concentrations, D_{50} values, POC (particulate organic carbon) contents, and DOC (dissolved organic carbon) concentrations during water and sediment regulations

Figure 3 Relationships between the flow velocities of river water with concentrations and particle size of suspended sediment during water regulation (WR), sediment regulation (SR), water-sediment regulation (WSR) and non-WSR (the data were obtained from AS, LK and LJ station)

Figure 4 Relationships between particle size of SPS (D_{50}) with BC content in suspended sediment (SPS) as well as total organic carbon (TOC) and amorphous organic carbon (AOC) contents during water and sediment regulations

Figure 5 Relationships between BC content in suspended sediment (SPS) with different fractions ($< 2 \mu\text{m}$, $2\text{-}50 \mu\text{m}$, and $>50 \mu\text{m}$) in SPS during water and sediment regulations

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Figure 5 Relationships between BC content in suspended sediment (SPS) and different fractions in SPS (< 2 μm , 2-50 μm , and >50 μm) during water and sediment regulations