Variations in concentrations and bioavailability of heavy metals in rivers caused by water conservancy projects: Insights from water regulation of the Xiaolangdi Reservoir in the Yellow River

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ABSTRACT

Water regulation of the Xiaolangdi Reservoir of the Yellow River was chosen as a case to investigate variations in concentrations and bioavailability of heavy metals caused by water conservancy projects in rivers. Water and suspended sediment (SPS) samples were collected at downstream sampling sites along the river during this period. Concentrations and speciation of Zn, Cr, Cu, Ni, and Pb in water and SPS samples were analyzed, and their bioaccumulation was studied with *Daphnia magna*. This study indicated that the exchangeable and carbonate-bound fractions of heavy metals in SPS decreased along the studied stretch, and the dissolved heavy metal concentrations increased along the river with 1.6–15 folds. This is because sediment resuspension increased along the river during water regulation, giving rise to the increase of heavy metal release from SPS. The dissolved Zn, Cu, Ni, and Pb concentrations were significantly positively correlated with SPS concentrations, and their increase along the river was greater than Cr. The body burdens of heavy metals in *D. magna* exposed into samples collected from the reservoir outlet were 1.3–3.0 times lower than those from downstream stations, suggesting that the heavy metal bioavailability increased during water regulation. This should be considered in the reservoir operation.

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Introduction

Heavy metals have aroused widespread concerns due to their abundance and persistence in environments as well as their toxicity to and bioaccumulation in organisms (Fan et al., 2016; Wu et al., 2010). Some researchers have mentioned that the eco-environmental risks of heavy metals in aquatic environments are not dependent on their total concentrations but on their bioavailable fraction (Alonso et al., 2004; Mota and Simões, 1996). Therefore, bioavailability has become a valid indicator to evaluate environmental risks of heavy metals. Distribution and transfer of heavy metals among different phases in rivers could significantly change their bioavailability, further influencing water quality. Once heavy metals enter rivers, they prefer to be bound with sediment. If sediment resuspension takes place due to the change of hydrodynamic conditions, these heavy

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metals can be released from sediment to the overlying water and become bioavailable. A lot of research have showed that sediment resuspension or deposition affected heavy metal fractions and distribution (Bi et al., 2014; Echols et al., 2008; Radakovitch et al., 2008; Wang et al., 2011; Zheng et al., 2013). For example, Superville et al. (2014) demonstrated that sediment resuspension caused by shipping increased the electro-labile Pb and Zn concentrations of the Deûle River (France). Therefore, sediment resuspension might change heavy metal bioavailability in rivers by changing their fractions and distribution.

Variations of hydrodynamic conditions in rivers could be caused by natural factors including waves, flood, and storms (Yang et al., 2003), as well as anthropogenic factors such as dredging (Je et al., 2007), ship traffic (Superville et al., 2015), and water conservancy projects' operation (Dong et al., 2015). There are lots of reservoirs, dams, and power stations in rivers for better utilization of water resources. The water with low suspended sediment (SPS) concentration upstream of the dams would scour the downstream river channel, leading to sediment resuspension. Therefore, these water conservancy projects could alter hydrodynamic conditions, and further influence transport and distribution of heavy metals in rivers. Nevertheless, research about the effect of water conservancy projects on heavy metal fractions and bioavailability in large rivers is rarely reported.

Water regulation of the Xiaolangdi Reservoir aims to reduce the severe sediment deposition along the lower reach of the Yellow River. During this period, high-speed water flow with low SPS concentration discharged from the dam outlet to scour downstream river channel, leading to suspension of downstream sediment along the river. This is similar to reservoir regulation of most water conservancy projects in rivers around the world. Bi et al. (2014) reported the particulate Mn, Pb, Zn, V, Cr, and Ni concentrations at the last hydrological station for the Yellow River and their fluxes into the Bohai Sea during water-sediment regulation in 2009. Nevertheless, the impact of such a large-scale sediment resuspension event caused by the water regulation on transport and bioavailability of heavy metals along the river is not well understood.

Therefore, in the present research, water regulation of the Xiaolangdi Reservoir was selected as a case to study variations in concentrations, speciation, and bioavailability of heavy metals caused by water conservancy projects in rivers. Water and SPS samples in six sampling sites downstream of the Xiaolangdi Reservoir were collected along the Yellow River for four times during water regulation in 2013. The concentrations of Zn, Cr, Cu, Ni, and Pb in water phase were measured, and their concentrations and fractions in SPS phase were also determined. The temporal–spatial variations of these heavy metal concentrations were analyzed. Furthermore, a test organism (*Daphnia magna*) was chosen to investigate the bioaccumulation of heavy metals in river water. The body burdens of heavy metals in *D. magna* were determined to study the variations of heavy metal bioavailability in the river during water regulation. In addition, the fluxes of the water, sediment, and heavy metals during this period were estimated.

1. Materials and methods

1.1. Sample collection and pretreatment

The Xiaolangdi Reservoir (112°26′46.5″E, 34°55′18.5″N) is the last reservoir in the main stream of the Yellow River. The distance between the reservoir and the estuary is about 800 km. The maximum reservoir capacity of the Xiaolangdi Reservoir is 12.65 km³. Water regulation was carried out during the period of June 19th–July 3rd, 2013. Water and SPS samples were collected on June 22th, 24th, 26th, and 28th. As shown in Fig. 1, six sampling sites including Xiaolangdi (XLD), Jiaogong (JG), Huayuankou (HYK), Aishan (AS), Luokou (LK), and Lijin (LJ) were selected along the river downstream of the Xiaolangdi dam. The XLD station (extremely close to the Xiaolangdi dam outlet) was selected as the first site to collect the water releasing from the reservoir immediately. The conductivity, dissolved oxygen (DO) concentration, pH, and temperature of the river water were measured by conductivity/DO/pH/temperature meters (Mettler Toledo, Schwerzenbach, Switzerland) *in-situ*. A total of 1.5 L river water sample was filtered by the pre-weighed 0.45-μm cellulose acetate membranes *in-situ* to determine dissolved heavy metal concentration and SPS concentration in river water. Then a large amount of river water sample was filtered by 0.45-μm cellulose acetate membranes to collect at least 1 g SPS for the determination of heavy metals in SPS at each site. Both the filtered water samples and the membranes wrapped in aluminum foil were kept at 4°C and transported to the laboratory quickly.

There are several small tributaries downstream of the Xiaolangdi Reservoir. The Yiluo River and the Qin River flow into the Yellow River between JG and HYK sites; the Jindi River and the Dawen River flow into the main river between HYK and AS sites (Fig. 1). The contributions of their annual water and sediment discharges to the Yellow River are only 8.3% and 0.3%, respectively (Dong et al., 2015), and the heavy metal concentrations in the river water of the tributaries are comparable to those of the main river (Wang et al., 2012). In addition, as the riverbed is above ground for the lower reaches of the Yellow River, heavy metals from municipal sewage and non-point sources could not be discharged into the river. Consequently, the variation of SPS and heavy metals in the river water during water regulation were mainly due to the sediment resuspension caused by the implementation of water regulation.

1.2. Physicochemical analysis of samples

The wrapped membranes were freeze-dried for 72 hr for moisture removal. Afterward, these membranes were weighed at room temperature to determine the SPS concentration in each water sample. Parts of dried SPS samples were sieved through a 2-mm sieve to determine their grain size, total organic carbon (TOC) content, and black carbon (BC) content. Their grain size distribution was measured with a Laser Particle Size Analyzer (Microtrac S3500, Montgomeryville, PA), which was classified into three categories: clay (<2 μm), silt (2–50 μm), and sand (>50 μm). The TOC and BC contents in SPS were determined with a Vario EL elemental analyzer (Elementar Analysensysteme
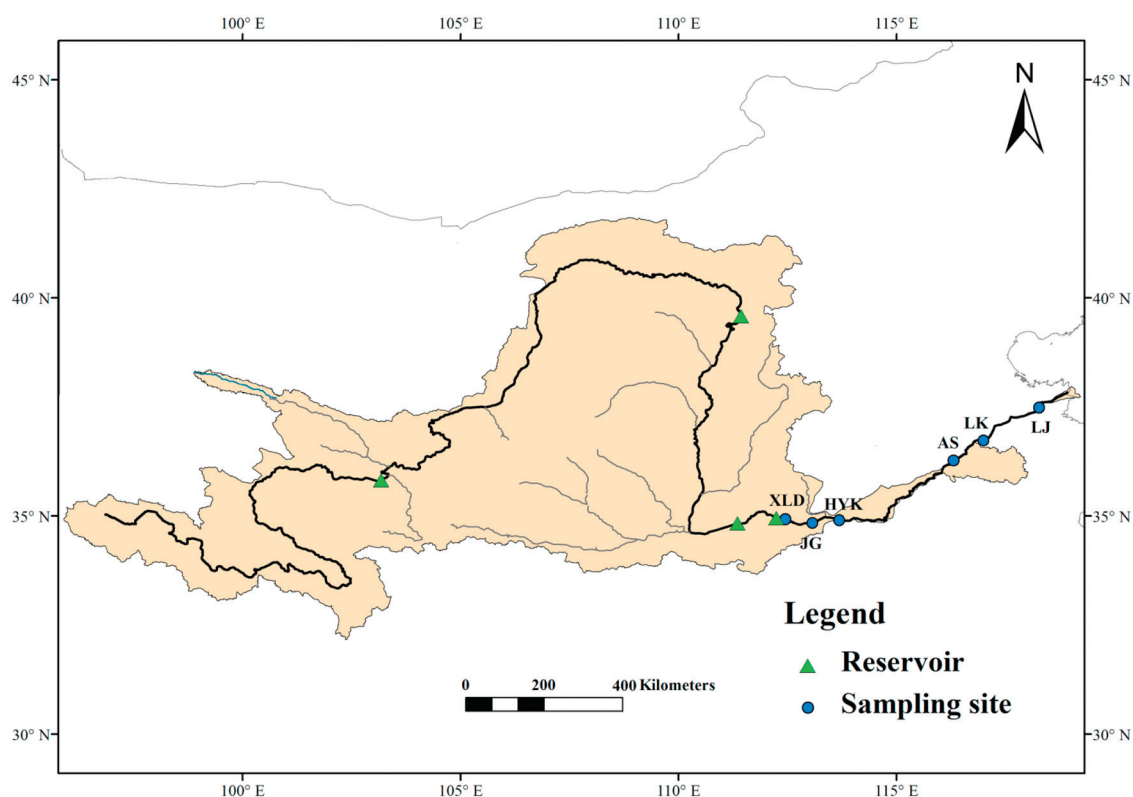
Fig. 1 – Sampling sites of the Yellow River during water regulation.

GmbH, Germany). The procedure in detail was provided in Appendix A. In addition, ~30 mL filtered water samples were transferred into brown glass bottles to determine the dissolved organic carbon (DOC) concentrations using a TOC analyzer (sievers900, USA).

1.3. Heavy metal bioaccumulation in D. magna

1.3.1. D. magna cultivation
The tested *D. magna*, cultured in laboratory conditions for 1 year, were provided by the Chinese Center for Disease Control and Prevention. The cultivation of *D. magna* was conducted with the artificial freshwater by following the guideline of Organization for Economic Cooperation and Development (OECD, 2008). As shown in our previous work (Dai et al., 2012; Zhang et al., 2014), the procedure has been provided in Appendix A.

1.3.2. Bioaccumulation of heavy metals in D. magna
The filtered water samples collected on June 22th, June 24th, June 26th, and June 28th were used. Every 10 Juvenile *D. magna* (~24 hr old) were exposed in each polypropylene beaker containing 200-mL water samples to accumulate heavy metals. The duration of exposure was 36 hr and *D. magna* were not fed during exposure. At the end of exposure, only the survivals were moved to polystyrene petri dish and carefully rinsed with artificial freshwater. In this study, the mortality rates of *D. magna* in the filtered water samples were 0%, thus, all these *D. magna* were gently dried by filter papers and weighed. Then the *D. magna* were freeze–dried for 72 hr to obtain their dry weights.

1.4. Heavy metal analysis

The filtered water samples were transferred into 50-mL centrifuge tubes. They were acidified immediately using HNO_3 63% (W/W) to pH ≤2. The dissolved heavy metal concentrations in water phases were determined by a Thermo X7 ICP-MS (Thermo Fisher Scientific, USA) after addition of the internal standard (Sc, In, Ge, and B) solution.

For the determination of heavy metal concentrations in SPS, the SPS samples were ground homogeneously and sieved though a 100-mesh sieve. After that, the SPS samples were added into Teflon beakers with 3 mL HNO_3, 3 mL HCl, and 2 mL HF. After 30 min, samples were processed using a MARS-XP microwave digestion system (CEM Corporation, USA). The detailed procedure of microwave digestion was as follows: heated up to 80°C and held for 3 min; 10°C/min to 120°C and held for 3 min; 10°C/min to 160°C and held for 3 min; 10°C/min to 180°C and held for 15 min; then naturally cooled to room temperature. A Thermo 6000 ICP-AES (Thermo Fisher Scientific, USA) was implemented to measure heavy metal concentrations. The absorption lines for Zn, Cr, Ni, Cu, and Pb were 213.8, 267.7, 221.6, 327.3, and 220.8 nm, respectively.

For different fractions of heavy metals, SPS samples were extracted using Tessier sequential extraction technique (Tessier et al., 1979), which classified the heavy metals in SPS into five fractions: the exchangeable (F1), carbonate-bound (F2), Fe-Mn oxides (F3), organic/sulphide (F4), and residual (F5) fractions (Islam et al., 2015). Details were provided in Appendix A. F5 was determined with the ICP-AES. Heavy metals in other fractions

were determined with an atomic absorption spectrophotometer (Hitachi, Z-2000).

To determine the heavy metal concentrations in *D. magna*, the dried *D. magna* were digested in 68% HNO_3 (Guaranteed reagent) at 110°C. After the digestion were cooled to room temperature, 2% HNO_3 were added, making the final volume be 2 mL. Heavy metal concentrations in digest were determined with the Thermo-X7 ICP-MS. Bioaccumulation concentrations of heavy metals in *D. magna* were expressed with their dry weights.

1.5. Quality assurance/quality control

The coefficients of determination for all standard curves were higher than 0.999. Detection limit for ICP-MS was 0.1 μg/L for Zn, Cr, Pb, Cu, and Ni. All samples were performed in triplicate. The relative standard deviation of the metal concentrations among the triplicates in this study was less than 5%. The National standard reference samples (sediment GBW08301) were used for quality control of SPS samples, and their results coincided well with the reference values with the standard deviations of <5%. The recoveries of the internal standards (Sc, In, Ge, and B) were over 90% for heavy metal in water phase and ≥85% for heavy metals in *D. magna*.

1.6. Statistical analyses

All statistical analyses were performed with IBM SPSS version 22 (SPSS Inc., IBM Company, Chicago, IL, USA). One-way ANOVA was carried out to test the temporal or spatial differences of all the groups, and the difference was considered significant when significance level was less than 0.05. The Spearman correlation coefficient was calculated and used to test the significance of the correlation between each pair of variables.

2. Results and discussion

2.1. Characteristics of suspended sediment and river water

The SPS concentrations increased from 0.04 g/L at XLD outlet to 10.1 g/L at LJ station, while the SPS particle size decreased along the river during water regulation (Table 1). This showed that, because the high-speed water flow with low SPS concentration releasing from the dam outlet was sufficient to scour riverbed during water regulation, more and more fine particles suspended into the overlying water along the studied stretch. In addition, as described in our previous study (Dong et al., 2015; Xia et al., 2016), the DOC concentrations in river water ranged between 5.27 and 7.12 mg/L, and there were no significant variations among the sites ($p > 0.05$). The pH values in the six sampling sites decreased from 7.80 to 6.82 along the river, and the DO concentration decreased from 7.88 to 4.27 mg/L along the studied stretch (Table 1). This is because the sediment resuspension during water regulation would accelerate the degradation of organic matter (Liu et al., 2016), leading to the decrease of DO and the production of CO_2 (Gibson et al., 2015). As a result, the pH value decreased along the river.

2.2. Temporal–spatial variations of particulate heavy metals

During water regulation, the average Zn, Cr, Cu, Ni, and Pb concentrations in SPS at six sampling sites were 124, 65.3, 28.2, 32.7, and 31.6 mg/kg, respectively. Among their five fractions (Tessier et al., 1979), the residual (F5) heavy metal is non-bioavailable, which cannot be released from the SPS. The order of the proportion of the heavy metal in F5 was Cr (79.7%) > Cu (64.7%) ≈ Ni (64.7%) > Pb (50.3%) > Zn (43.9%). This inferred that less Cr while more Pb and Zn could be released from the SPS to the overlying water. The exchangeable (F1) heavy metal is bioavailable; the carbonate-bound (F2) heavy metal can become bioavailable when pH value decreases. The proportion of Zn in F1 was higher than that of other studied metals (Fig. 2). The proportion of Pb in F2 reached 35.9% at dam outlet and the average value was 18.8% for all the sampling sites, which was approximately 2–13 times higher than those of other metals (Fig. 2). Furthermore, the pH values decreased along the river, thus, some particulate Pb in F2 could be dissolved into the overlying water and become bioavailable. These results indicated that Zn and Pb could be released from the SPS more easily during water regulation.

Heavy metals in exchangeable fraction (F1) and carbonate-bound fraction (F2) were bioavailable. As shown in Fig. 2, the proportions of heavy metals in F1 and F2 decreased along the river slightly and significantly ($p < 0.05$), respectively. Also, the heavy metal concentrations in F1 and F2 decreased along the river slightly and significantly ($p < 0.05$), respectively (Appendix A Fig. S1). For example, the concentration of carbonate-bound Zn in SPS decreased from 8.49 mg/kg at XLD outlet to 2.52 mg/kg at LJ ($p < 0.01$). This demonstrated that heavy metals in both the exchangeable fraction and carbonate-bound fraction released along the river and became dissolved heavy metals. This result further suggested that, during water regulation, the sediment in the downstream riverbed could be the source of heavy metals in the overlying water.

As shown in Appendix A Table S1, our results obtained in this study during water regulation were consistent with those collected during the same period reported by Bi et al. (2014). Compared with the particulate heavy metal concentrations in other rivers, the levels of heavy metals during water regulation were comparable to that in the Danube River (Europe) (Woitke et al., 2003), but lower than those in four rivers of France (Rhone River, Tet River, Aude River, and Orb River) (Radakovitch et al., 2008) and that in the Yangtze River (China) (Qiao et al., 2007). According to the result reported by Viers et al. (2009), the particulate heavy metal concentrations obtained in this study were much lower than the corresponding values in world rivers.

2.3. Spatial–temporal variations of dissolved heavy metals

2.3.1. Spatial variation of dissolved heavy metals
To study the spatial variations of dissolved heavy metal concentrations caused by water regulation, the average concentrations of heavy metals during four sampling times were calculated for the Xiaolangdi Reservoir outlet, downstream stations (JG, HYK, AS, and LK), and LJ station, respectively. The dissolved concentration of each heavy metal increased along the river, and the heavy metal levels at LJ station were 1.6–15 times higher than those at the reservoir outlet (Fig. 3). This

Table 1 – Characteristics of water and suspended sediment samples.

Sampling sites	pH	DO(ppm)	DOC (mg/L)[a]	SPS (g/L)[a]	d_{50}[a] (μm)	TOC[a] (‰)	BC[a] (‰)	Clay[b] (%)	Silt[b] (%)	Sand[b] (%)
XLD	7.80 ± 0.02	7.88	5.27 ± 2.68	0.04 ± 0.01	77.5	0.94 ± 0.72	0.26 ± 0.11	0.19 ± 0.38	30.8 ± 26.4	69.0 ± 26.6
JG	7.74 ± 0.04	7.71	5.54 ± 2.69	0.58 ± 0.58	36.6	1.54 ± 0.44	0.60 ± 0.15	0.67 ± 1.29	71.4 ± 13.0	27.9 ± 12.7
HYK	7.78 ± 0.00	7.51	5.62 ± 2.85	0.09 ± 0.03	37.5	3.05 ± 0.35	0.55 ± 0.27	0.07 ± 0.01	64.5 ± 2.24	35.4 ± 0.38
AS	7.51 ± 0.01	5.55	6.76 ± 0.43	5.01 ± 2.24	27.0	2.22 ± 0.26	0.63 ± 0.28	0.28 ± 0.18	80.4 ± 2.36	19.3 ± 2.47
LK	6.89 ± 0.01	4.80	6.82 ± 0.44	5.14 ± 1.57	31.9	2.00 ± 0.25	1.10 ± 0.27	3.01 ± 0.34	68.6 ± 3.74	28.4 ± 2.25
LJ	6.82 ± 0.02	4.27	7.12 ± 0.41	10.1 ± 0.54	17.0	3.22 ± 0.67	2.74 ± 0.68	0.98 ± 0.60	87.1 ± 4.04	11.9 ± 3.86

DO: dissolved oxygen concentration.
DOC: Dissolved organic carbon concentration in river water.
SPS: suspended sediment concentration in river water.
d_{50}: the medium value of suspended particle size.
TOC: Total organic carbon content in suspended sediment.
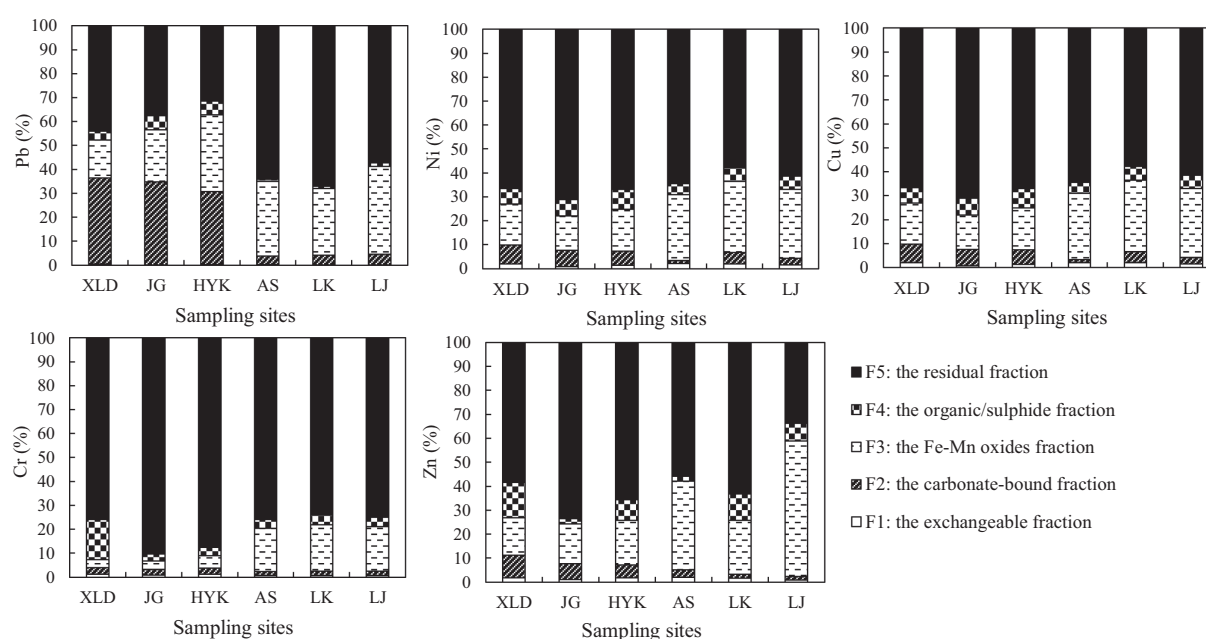BC: Black carbon content in suspended sediment.
[a] The values of DOC, SPS, d_{50}, TOC, and BC have been published in our previous study (Dong et al., 2015).
[b] The ratios of clay, silt, and sand in SPS have been published in our previous study (Xia et al., 2016).

indicated that parts of particulate heavy metals were released into the water phase and became dissolved heavy metals during sediment resuspension, which agreed with the particulate heavy metal result described in Section 2.2 that both the proportions and concentrations of the bioavailable heavy metals in SPS decreased along the river. Furthermore, the dissolved Ni, Cu, Zn, and Pb concentrations were positively correlated with SPS concentrations ($p < 0.05$) (**Appendix A Table S2**). This is because the SPS concentrations increased along the river downstream of the reservoir, resulting in the increase of heavy metal release from the particulates. Consequently, the spatial variation of heavy metal concentrations in river water during water regulation was closely related to the sediment resuspension and SPS characteristics.

The dissolved Ni, Cu, Zn, and Pb concentrations in river water were higher than Cr concentrations at most sampling sites (Fig. 4). Furthermore, the sequence of the dissolved concentrations of the five heavy metals in the overlying water was Pb < Cr < Cu < Ni < Zn at reservoir outlet, while the sequence was Cr < Cu < Ni < Pb < Zn at downstream stations and LJ station (Fig. 3). The increasing trends of dissolved Cr concentrations were less significant than those of Ni, Cu, Zn, and Pb. These results inferred that there were significant differences in the release along the river among the five heavy metals. According to the results mentioned in Section 2.2, the proportions of Cr in non-bioavailable fraction were the largest. The proportions of Pb, Zn, Ni, and Cu in bioavailable fractions were greater than Cr. Therefore, less Cr while more Pb and Zn released from the SPS during water regulation, which caused the greater increase trends of Pb, Zn, Ni, and Cu.

According to the results listed in **Appendix A Table S2**, there were significant relationships among dissolved Cu, Ni, and Pb ($p < 0.01$), suggesting that these three heavy metals might come from a similar source. Similar results were reported by Li et al.

Fig. 2 – Chemical fractions of heavy metals in suspended sediments at each sampling site.

■ F5: the residual fraction
▨ F4: the organic/sulphide fraction
□ F3: the Fe-Mn oxides fraction
▨ F2: the carbonate-bound fraction
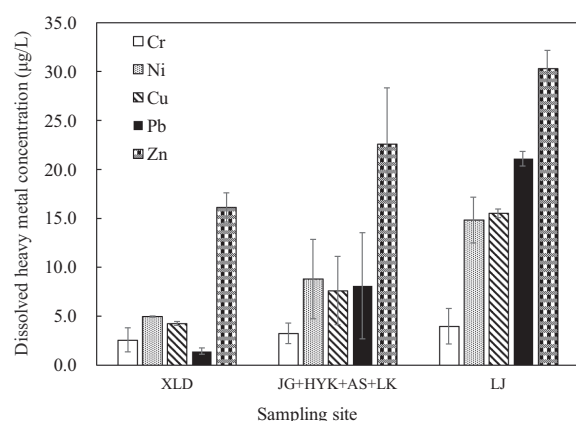□ F1: the exchangeable fraction

Fig. 3 – Spatial variations of dissolved heavy metal concentrations during water regulation.

(2009) that there were significant positive relationships among Cu, Zn, and Pb concentrations in the surface water of the Southern Yellow Sea. However, the dissolved Cr concentrations had no relationship with other heavy metals ($p > 0.05$). Some researchers also found the behaviors of Cr were different from other heavy metals. Magar et al. (2008) demonstrated that, compared with the release potentials for Cu, Pb, and Zn, the smaller potential for Cr release during dredging events might not have significant environmental risks.

2.3.2. Temporal variation of dissolved heavy metals
No significant difference was found in each heavy metal concentration at reservoir outlet among the four samplings ($p > 0.05$, Fig. 4a). For each heavy metal, the average level of the five stations (JG, HYK, AS, LK, and LJ) at downstream of the reservoir was determined for each sampling to characterize the temporal variation of dissolved heavy metals during water regulation. As shown in Fig. 4b, the dissolved Zn, Pb, Ni, Cu, and Cr concentrations at the five downstream stations (JG, HYK, AS, LK, and LJ) showed increasing trends with time, and reached the maximum values at the fourth sampling, indicating that the release of the four heavy metals increased during water regulation. This was consistent with the results of Section 2.3.1 and other studies (Magar et al., 2008; Zhang et al., 2013).

The heavy metal concentrations in the river water during water regulation were greater than those during non-water regulation period of the Yellow River reported by Zhang et al. (2013). The result inferred that the water regulation increased heavy metal bioavailability from reservoir downstream to the estuary. As listed in **Appendix A Table S3,** surface water environment quality standards of China (GB 3838-2002) classified water quality into five categories. The maximum values of dissolved Zn, Cu, and Pb concentrations in this work were lower than their corresponding limits of Class II (1.0×10^3 μg/L), Class II (1.0×10^3 μg/L), and Class III (50 μg/L), respectively. Most of the dissolved Ni levels in this research were lower than its corresponding limit of particular central drinking water surface source items (20 μg/L). Besides, the dissolved heavy metal concentrations during water regulation were compared with their maximum permissible concentrations (MPCs) established by the European Water Framework
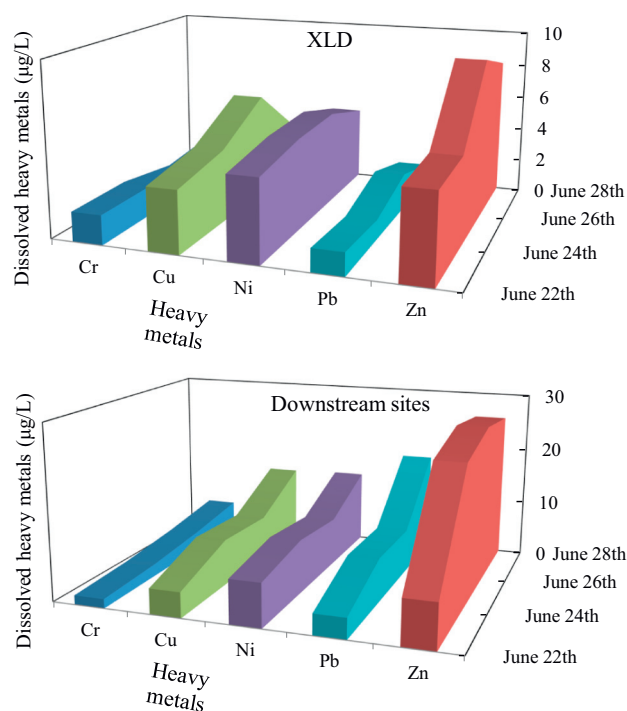

Fig. 4 – Temporal variations of dissolved heavy metal concentrations at Xiaolangdi (XLD) outlet and at downstream sites (Jiaogong (JG), Huayuankou (HYK), Aishan (AS), Luokou (LK), Lijin (LJ)) during water regulation.

Directive (COUNCIL DIRECTIVE 98/83/EC 1998). The results showed that, considering all the four samplings at all sites, 4.5% and 22.7% of Ni and Pb values during water regulation exceeded their MPCs (Ni: 20 μg/L; Pb: 10 μg/L), respectively. According to the above mentioned, the potential risk of aquatic organism exposure to heavy metals in the Yellow River water during this period should be paid more attention, although water regulation had no significant effect on drinking water source along the studied stretch.

The dissolved heavy metal concentrations in other rivers are listed in Appendix A **Table S4.** The dissolved heavy metal concentrations obtained in this study were lower than the levels in the Tigris River (Turkey) (Varol et al., 2010), in the Guadiamar River (Spain) (Alonso et al., 2004), and in the River Soan (Pakistan) (Nazeer et al., 2014). The heavy metal concentrations during water regulation were comparable to that of the To Lich River (Vietnam) (Thuong et al., 2013), but higher than that in the Gomti River (India) (Singh et al., 2005) and the Yangtze River (China) (Yi et al., 2011).

2.4. Bioaccumulation of heavy metals in D. magna

Heavy metal bioaccumulation in aquatic organisms can directly reflect their bioavailability in the overlying water. The body burdens of heavy metals in *D. magna* cultivated in the filtered river water were determined in this study. As shown in Fig. 5, the concentrations of all heavy metals in *D. magna* with the filtered river water at the reservoir outlet were lower than that at the downstream sites (JG, HYK, AS, LK, and LJ). The body burdens of Cr, Cu, Ni, Pb, and Zn in *D. magna* at downstream

stations were 1.4, 1.4, 1.3, 1.9, and 3.0 times higher than those at the reservoir outlet, respectively. This demonstrated that heavy metal bioavailability downstream of the Xiaolangdi Reservoir increased during water regulation. The bioconcentration factor (BCF, L/kg) of heavy metals in *D. magna* can be calculated as follows in this study:

$$BCF = C_A/C_W \tag{1}$$

where C_A (mg/kg) is the heavy metal concentrations in *D. magna*; C_W (mg/L) is the dissolved concentrations of heavy metals in water phase. The mean values of BCFs of heavy metals at the six sampling sites were Cr < Cu < Pb < Ni < Zn during water regulation (Table 2), and the BCF values of these five heavy metals in *D. magna* obtained in this study were comparable to those reported by other researchers (McGeer et al., 2003; Miao et al., 2012).

In addition to the dissolved heavy metals in the river water, the heavy metals bound with SPS might also exert toxicity to *D. magna*. Our previous research has found that, with the same freely dissolved phenanthrene concentration, the immobilizations of *D. magna* with SPS (1–5 g/L) were 1.6–2.7 times higher than those without SPS (Zhang et al., 2014), and contaminants sorbed on SPS can also be partly bioavailable to aquatic organisms (Wang et al., 2011; Xia et al., 2016). Thus, the increase of both dissolved and particulate contents of heavy metals in river water caused by water regulation of the Xiaolangdi Reservoir would increase the eco-environmental risks of heavy metals in the lower reaches of the Yellow River.

2.5. Heavy metal fluxes during water regulation

Water discharge, sediment discharge, and heavy metal fluxes were estimated based on the data collected from LJ site, because it is the last hydrologic station of the Yellow River. The fluxes of dissolved ($F_{i(dissolved)}$) and particulate heavy metal i ($F_{i(particulate)}$)

during water regulation could be estimated with the following equations.

$$F_{i(dissolved)} = \sum_{i=1}^{15}(C_{Wi} \times Q_{Wi}) \tag{2}$$

$$F_{i(particulate)} = \sum_{i=1}^{15}(C_{SPSi} \times Q_{SPSi}) \tag{3}$$

where C_{Wi} (mg/L) and C_{SPSi} (mg/kg) were the dissolved and particulate heavy metal concentrations, respectively; Q_{Wi} (m³/d) and Q_{SPSi} (tons/d) were the daily water and sediment discharges during water regulation in 2013, respectively, as reported in our previous study (Dong et al., 2015). Water regulation was conducted for 15 days, equivalent to 4.1% of the year 2013. During water regulation, the water and sediment discharges were 3.35 billion/m³ and 30.0 million tons, respectively, which contributed to 14.2% and 17.3% of their annual discharges (2013), respectively (Dong et al., 2015).

During water regulation, the dissolved Cr, Cu, Ni, Pb, and Zn fluxes were 12.6, 47.3, 44.2, 63.4, and 76.3 tons, respectively; their particulate fluxes were 2.84×10^3, 837, 1.07×10^3, 627, and 2.80×10^3 tons, respectively. The heavy metal fluxes during water regulation were dominated by particulate fluxes. The particulate Cu, Cr, Pb, and Zn fluxes during water regulation obtained in this study were comparable to the results reported by others (Wang, 2012; Bi et al., 2014). The particulate Cu, Cr, Pb, and Zn during water regulation obtained in this study respectively contributed to 19.7%, 31.2%, 15.9%, and 26.9% of their average annual particulate fluxes reported by Wang (2012) who considering the sediment and heavy metal fluxes during the water-sediment regulation. The results above showed that both the contributions of sediment flux and particulate heavy metal fluxes during water regulation to their annual fluxes were greater than the contribution of water discharge. This suggests that water regulation is conducive to delivering the downstream sediment and heavy metals to the sea.
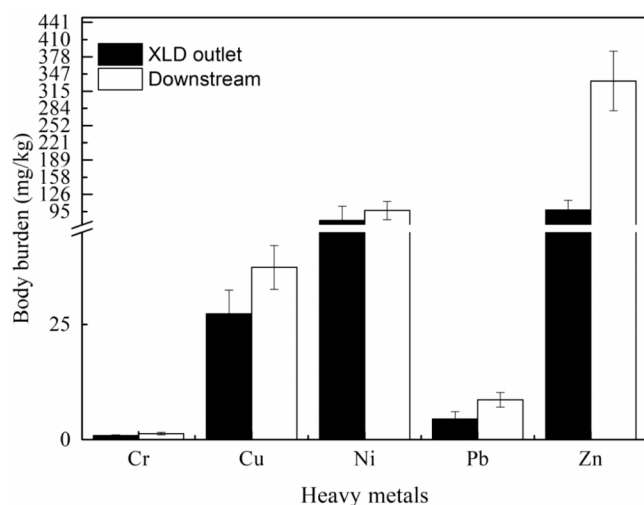
3. Conclusions

The results revealed that, due to sediment resuspension induced by water regulation of the Xiaolangdi Reservoir, the SPS concentrations increased while SPS particle size decreased along the downstream river stretch. In river water, a decrease of pH values along the river was observed. This was because sediment resuspension during water regulation accelerated organic matter degradation, leading to CO_2 production.

Fig. 5 – Comparison of heavy metal concentrations in *Daphnia magna* between Xiaolangdi (XLD) outlet site and downstream sites.

Table 2 – Bioconcentration factors (BCFs, L/kg) of heavy metals in *Daphnia magna* at different sites.

Sampling site	Zn	Cr	Cu	Ni	Pb
XLD	4.44×10^3	401	2.44×10^3	2.41×10^4	2.89×10^3
JG	1.30×10^4	485	1.46×10^3	6.14×10^3	3.44×10^3
HYK	1.90×10^4	426	4.18×10^3	4.59×10^4	1.32×10^3
AS	4.49×10^4	1.59×10^3	1.02×10^3		2.25×10^3
LK	3.91×10^4	250	953	2.41×10^4	497
LJ	1.54×10^4	158	336	4.27×10^3	60.1
Mean	2.27×10^4	551	1.73×10^3	2.09×10^4	1.74×10^3

The proportions of heavy metals in exchangeable and carbonate-bound fractions decreased along the river, indicating some heavy metal release from the SPS. Correspondingly, the dissolved heavy metal concentrations in river water increased along the river, and the heavy metal levels at LJ station (near the estuary) were 1.6–15 times higher than that at the reservoir outlet. This was because the SPS concentrations increased along the studied stretch, resulting in an increase of the heavy metal release. The increasing trends of the five heavy metals have significant differences; less Cr while more Pb and Ni released from the SPS during water regulation. In addition, no significant difference was found in dissolved concentrations of each heavy metal at reservoir outlet among the four samplings ($p > 0.05$). However, the average dissolved heavy metals at downstream stations have increasing trends with time, and reached their maximum values for the last sampling. The average body burdens of Cr, Cu, Ni, Pb, and Zn in *D. magna* for the samples at the downstream stations were 1.4, 1.4, 1.3, 1.9, and 3.0 times higher than that at the dam outlet. These results showed that the bioavailability of heavy metals increased during water regulation. In addition, both the contribution ratios of sediment flux (17.3%) and particulate heavy metal fluxes during water regulation to their annual particulate fluxes (15.9%–31.2%) were greater than the corresponding contribution of water discharge (14.2%). This study suggests that the bioavailability and environmental risk of heavy metals downstream of the Xiaolangdi Reservoir might increase during water regulation of the reservoir.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jes.2018.02.009.

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