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ORIGINAL ARTICLE

Geochemical distribution, fractionation, and sources of heavy metals in dammed-river sediments: the Longjiang River, Southern China

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Abstract In the present study, six sediment cores were collected from six river-dammed reservoirs to reveal the geochemical distribution of heavy metals (As, Cd, Pb, Sb, and Zn) in the Longjiang River, South China, which is highly impacted by nonferrous metal mining and smelting activities. The sediments were geochemically characterized, combining geochemical analysis, sequential extractions, and ^{210}Pb chronology. The results indicated that the river sediments were severely polluted by heavy metals in the order of Cd > Zn ≈ Pb ≈ Sb > As. These heavy metals generally exhibited relatively low enrichment in the upstream sediments because of the limited anthropogenic impact, but their abundances drastically increased in the midstream sediments due to local smelting activities. In downstream sediments, the heavy metal concentrations (except for Cd) decreased, owing to the effect of dam interception and detrital inputs. Cadmium levels tended to increase in downstream sediments, which were attributed to the intensive discharge of Cd during the pollution event in 2012. The sedimentary records were traced back to 1985, and a significant decrease of heavy metal enrichments could be found after the year 2000, suggesting the enhancement of environmental management in this period. The statistical results indicated that local metal smelting and mining activities were the main anthropogenic contributors for the enrichment of heavy metals in the dammed-river sediments. High enrichment factor and non-residual fractions of heavy metals in local sediments may pose a direct threat to aquatic organisms. Cd presents significant danger because of its extreme enrichment and high labile fractions.

Keywords Heavy metals · Fractionation · ^{210}Pb dating · Smelting and mining activities · Sediment cores · The Longjiang River

1 Introduction

Heavy metals can cause serious environmental problems due to their toxicity, persistence, and bioaccumulation (Du et al. 2009; Doğan et al. 2013; Gutiérrez et al. 2016). In recent decades, anthropogenic activities, such as industrial effluents, domestic sewage, agricultural runoffs, and gasoline combustion have introduced a great quantity of heavy metals into aqueous environments (e.g., rivers, lakes and reservoirs) through waste discharge and/or atmospheric deposition (Bing et al. 2011; Hu and Cheng 2016; Liu et al. 2017).

Rivers usually constitute critical resources of drinking water in the world, but these environments are sensitive to heavy metal pollution. Once heavy metals enter rivers, they are liable to be adsorbed by colloids and fine-grained particulates (i.e., organic matters, Fe–Mn oxides, clay minerals) (Du Laing et al. 2009), and then precipitated into

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the riverbed or transported further downstream. Many cascade dams have been constructed along rivers worldwide, which play important roles in trapping sediment particles (and therefore heavy metals), due to the rapid decrease of water flow (Yang et al. 2014a). Therefore, the sediments in cascade reservoirs may reflect the spatial and temporal distribution of heavy metals at a catchment scale. More importantly, the reservoir waters are usually used for agricultural irrigation and drinking water supply. Considering that sediments in reservoirs are the prolonged sources of heavy metals for overlying water (López et al. 2010; Wei et al. 2016), assessment of heavy metal pollutions in reservoir sediments are particularly important. Once the heavy metals exceed safe limits, they pose a long-term health risk to both aquatic organisms and humans (Shinn et al. 2009; Tao et al. 2012). Therefore, heavy metal pollution in river-dammed reservoirs has become one of the most important environmental topics in recent studies (Bing et al. 2016b; Wei et al. 2016). A number of researchers have utilized sediment cores or surface sediments from reservoirs to reconstruct historical records of contaminant inputs, constrain their origins, and assess their environmental effects (Grousset et al. 1999; van Griethuysen et al. 2005; Wang et al. 2015; Wei et al. 2016). Above all, a full understanding of heavy metal pollution in cascade reservoirs may help local reservoir water quality conservation and management.

Similarly, many rivers have experienced a dangerous pollution of heavy metal in South China. The heavy metal discharges—mainly originating from sulfide processing, tailing, and/or smelting waste discharges—have produced concern for the environmental impact of metal pollution incidents, for instance Tl pollution in the Beijiang River in Guangdong Province in 2010 (Xiao et al. 2012), Cd pollution in the Longjiang River and Tl pollution in the Hejiang River in Guangxi Province in 2012 and 2013, respectively (Dou et al. 2013; Chen et al. 2017). Among these rivers, the Longjiang River, a tributary of the Pearl River in north of Guangxi Province, is intensively dammed with cascade reservoirs. It has been suffered from heavy metal pollution caused by waste discharges from industrialized and urbanized activities in Hechi City and Yizhou City. The nonferrous metal mining and smelting activities in these cities, especially for Pb, Zn, and Sb, has been the local industry since 1980 (YCCH 2016). As a result, the Pb, Zn, and Sb mining and smelting activities have discharged large amounts of heavy metals such as As, Cd, Pb, Sb, and Zn into local rivers. Moreover, the Longjiang River experienced a serious Cd pollution emergency event on January 13, 2012. This accident discharged a large amount of wastewater (containing 30–40 t Cd) into the river without any treatment from an illegal plant using Cd-rich flue ash to refine indium. Consequent monitoring results revealed that the maximum concentrations of Cd and As in local river waters were up to 0.41 and 0.31 mg L^{-1}, respectively (Zhang et al. 2013). To prevent diffusion of the metal contaminants, a thousand tons of lime, caustic soda, and poly-aluminum chloride (PAC) were poured into the river to elevate the precipitation efficiency. Finally, it was estimated that about 18 t Cd was precipitated in the riverbed through flocculation-precipitation (Zhang et al. 2013). To date, little is known about heavy metal pollution in the dammed Longjiang River, which may affect the drinking water supply for millions of people in the Pearl River basin.

The present study aimed to explore the distribution, fractionation, and sources of heavy metals in dammed-river sediments, and to gain new insight into associated environmental risk. Six sediment cores were sampled from six reservoirs along the Longjiang River to investigate the contamination of heavy metals (As, Cd, Pb, Sb, and Zn) at a catchment scale. The evolution of heavy metals was reconstructed in one representative sediment core using ^{210}Pb chronology. Sequential extraction experiments were performed to determine the geochemical fractions of heavy metals, allowing assessment of the geochemical fractionation and mobility of heavy metals. Enrichment factors (EFs) were calculated to assess the contamination degree of heavy metals. Correlation analysis (CA) and specific elemental ratios were employed to identify the potential sources of heavy metals. This study provides novel data sets that could be used in an alliance of heavy metal-contaminated dammed-river sediments for better water quality management in catchments with cascade reservoir constructions.

2 Materials and methods

2.1 Study area

The Longjiang River is 367 km long, with a drainage area of 16,878 km^2. It belongs to the South Asia to Central Asia tropical monsoon area. The annual runoff of the mainstream is 12.2×10^9 m^3, and the volume in the flood season (from April to September) accounts for 85.4% (CERLAC 2013). The Carboniferous and Permian carbonates geologically dominate within the catchment and some metamorphic and magmatic rocks expose in the north. Six cascade hydropower stations (reservoirs), including Bagong (BG) upstream, Lalang (LL) midstream, and Yemao (YM), Luodong (LD), Sancha (SC), and Noumitan (NMT) downstream were constructed along the Longjiang River in 1976, 1971, 1997, 1971, 1995 and 1979, respectively. The total reservoir capacity of BG, LL, YM, LD, and NMT is 8, 102, 107, 62, and 62×10^7 m^3,

respectively, but no values were available in SC due to its no regulating capacity (Zhang 2002). Three main tributaries of the Longjiang River are the Dahuanjiang River, the Xiaohuanjiang River, and the Dongxiaojiang River, which annually contribute runoffs at 2.16×10^9, 2.31×10^9 and 0.76×10^9 m^3, respectively.

The local land is mainly covered by forest and grass within the catchment (Fig. S1). The concentrated urbanization is located at Hechi City and Yizhou City (Fig. S1). Along the mainstream course, the Pb–Sb–Zn smelters (Fig. 1), are located midstream and downstream. Along the three main tributaries, the urbanization is generally undeveloped (Fig. S1). However, the active mining activities upstream near the Dongxiaojiang River (Fig. 1), have resulted in increase of heavy metals into local river sediments (Lan et al. 2018).

2.2 Sampling and analysis

Six sediment cores were collected using a gravity-type PVC coring pipe (100 cm long and 5 cm in diameter) in July 2015 in the BG, LL, YM, LD, SC, and NMT reservoir, respectively. The length of the sediment cores of BG, LL, YM, LD, SC, and NMT was 34 cm, 58 cm, 54 cm, 54 cm, 30 cm, and 30 cm, respectively. Each sediment core was sliced into 2 cm layers and then stored in plastic bags. The samples were then transferred to the laboratory and stored at 3–5 °C until the samples were oven-dried (~ 50 °C) and ground by agate (< 74 μm).

Before being ground, each subsample (200 mg) was treated with 10% HCl and 10% H_2O_2 to remove carbonates and organic matters. A laser size analyzer (MALVERN, APA-2000, UK) was employed to analyze grain size. The grain size pattern of sediment samples was categorized using the system of Shepard (1954). The mineral compositions of selected subsamples were determined by X-ray diffraction (XRD, Empyrean, Netherlands).

Due to its long impoundment history, the LL core was selected for chronological determination. ^{210}Pb was obtained by gamma spectrometry (GX6020, DSA-1000, USA) at the State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. About 10 g samples were filled into plastic containers and sealed for a month allowing ^{226}Ra and ^{210}Pb to reach radioactive equilibrium. The test duration of each sample was 24 h. The radioactivity level of ^{210}Pb was determined by gamma emission at 46.5 keV, and ^{226}Ra was determined with 351.9 keV γ-rays emitted by its daughter nuclide ^{214}Pb. The standard materials from National Institute of Metrology, China, were used to calibrate the absolute efficiency of the detectors. Supported ^{210}Pb in each sample was assumed to be in equilibrium with the in-situ ^{226}Ra, and excess ^{210}Pb activities were determined from the difference between the total ^{210}Pb and

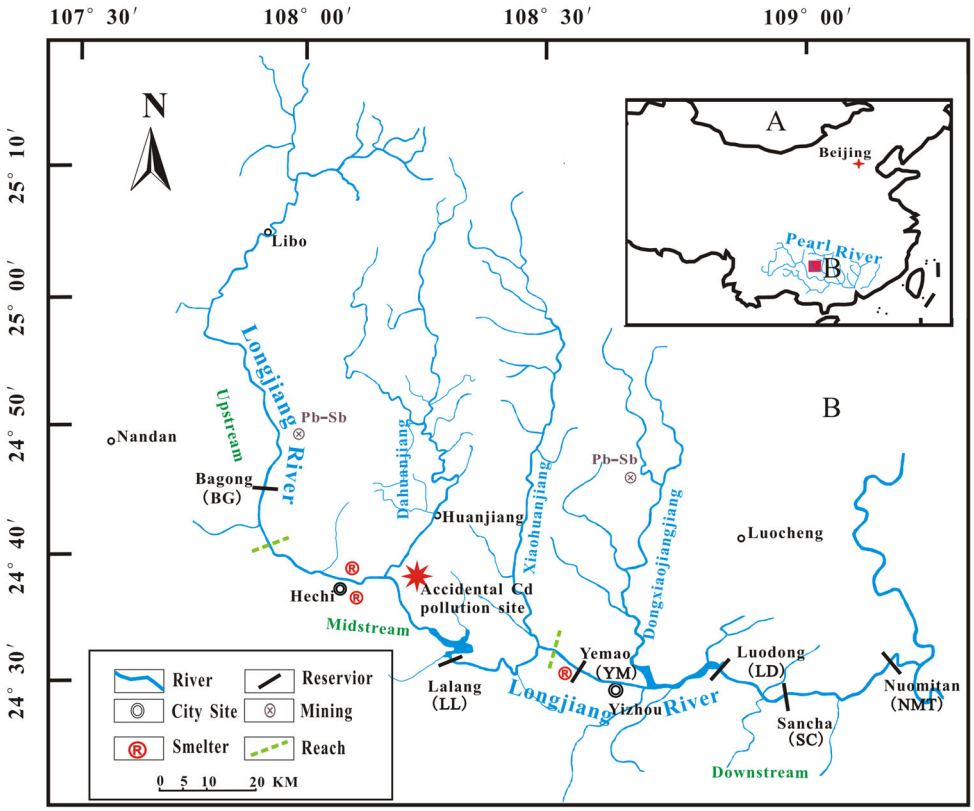

Fig. 1 Study area and sampling sites

supported ^{210}Pb activities. The measurement errors of ^{210}Pb and ^{226}Ra were all better than 15%.

The analysis for major elements (Al, Ca, Fe, Mn, and Ti) and heavy metals (As, Cd, Pb, Sb, and Zn) was done using ICP-AES (Varian VISTA, U.S.A.) and ICP-MS (Agilent 7700x, U.S.A.), respectively, after digestion by HNO_3-$HClO_4$-HF-HCl. The detected limits of Ca, Al, Fe, Mn, Ti, As, Cd, Pb, Sb, and Zn were 0.01%, 0.01%, 0.01%, 5 mg kg^{-1}, 0.005%, 0.2 mg kg^{-1}, 0.02 mg kg^{-1}, 0.5 mg kg^{-1}, 0.05 mg kg^{-1} and 2 mg kg^{-1}, respectively. The relative deviation was better than ± 10% for duplicate samples, and the recoveries of standard references (GBM398-4c, GBM908-10, and MRGeo08) were 95%–110%, for all the elements we investigated.

A sequential extraction method was applied to determine the geochemical fractions of heavy metals in two sediment cores (LL and NMT). More details about the extraction method have been reported previously (Ahnstrom and Parker 1999). Briefly, five successive fractions from 2 g samples were summarized as follows: F1 (soluble-exchange fraction), 15 mL 0.1 M $Sr(NO)_3$ (treated twice); F2 (specifically sorbed-carbonate bound), 30 mL 1.0 M NaOAc at pH 5.0 (treated once); F3 (oxidizable fraction), 5 mL 5% NaOCl at pH 8.5 (treated thrice); F4 (reducible fraction), 20 mL 0.2 M oxalate + 0.2 ascorbate (treated thrice); and F5 (residual fraction), in which the residues were digested by HNO_3-HF. A 5 mL 0.1 M NaCl rinse was used between each step and pooled with the front extract. The recovery rates of five heavy metals were approximately 90%–120%.

2.3 Enrichment factors calculation

Enrichment factors (EFs) is a useful indicator for evaluating anthropogenic impacts (Sutherland 2000; Liu et al. 2013; Chen et al. 2016). EF is defined as:

$$EF = (Me/Mi)_{sample}/(Me/Mi)_{reference}$$

where (Me/Mi) is the concentration ratio of targeted element (Me) to normalized elements (Mi, usually from natural sources and exhibiting conservative behavior) in the samples and references (uncontaminated background values). In previous studies, Al, Ti, Zr, and Cs have usually been selected as normalized elements (Sutherland 2000; Loska et al. 1997; N'Guessan et al. 2009; Liu et al. 2013). Considering that large amounts of limes and poly-aluminum chloride had been poured into the river during the emergency control for Cd pollution event, Ti was selected as the normalized element in this study. The geochemical abundance of the Guangxi soil (Ti, As, Cd, Pb, Sb, and Zn at 0.45%, 20.5 mg kg^{-1}, 0.27 mg kg^{-1}, 24.0 mg kg^{-1}, 2.93 mg kg^{-1}, and 75.6 mg kg^{-1}, respectively) were selected as reference background values (CNEMC 1990). EFs at 1.5 is considered a critical value for distinguishing the anthropogenic input and natural input (Wang et al. 2015, Wei et al. 2016). EFs can be classified as: no enrichment (< 1.5), moderate enrichment (1.5–5), significant enrichment (5–20), very high enrichment (20–40), and extreme enrichment (> 40) (Sutherland 2000).

3 Results and discussion

3.1 Physical–chemical characteristics of sediments

The vertical profiles of grain size compositions in the six sediment cores were shown in Fig. S2. Sediments were mainly composed of silt (74% on average) and clay (23% on average). Sand generally accounted for a minor fraction (2% on average), although a higher fraction was present in the 42-cm (73%) and 56-cm (54%) layer of the LL core. The mineralogy of the selected subsamples was dominated by quartz, followed by illite and kaolinite (Fig. S3). Calcite was only present in the subsamples of the BG core.

The vertical profiles of major element (Al, Ca, Fe, Mn, and Ti) concentrations in the six sediment cores are illustrated in Fig. S4. The concentrations of major elements in sediments were similar to their abundances in the upper continental crust, except for Ca, which was remarkable lower than its crustal abundance, owing to fact that it is prone to dissolve in water (Taylor and Mclennan 1985). Most major elements in the six sediment cores showed similar concentrations and generally exhibited a stable vertical distribution (Fig. S4), but Ca significantly elevated in upstream core (BG) (3.9–8.84%) with high contents of calcites. Moreover, significantly high concentrations of Fe (7.21%) and Mn (0.61%) were also observed at 26-cm layers of YM core, which were probably attributed to discharge of local Mn-smelters.

3.2 Geochemical distributions of heavy metals

The concentrations of heavy metals (As, Cd, Pb, Sb, and Zn) in the six sediment cores were listed in Table 1, and their vertical distribution are shown in Fig. S5. The heavy metal concentrations of the six cores (except As in upstream core BG) were higher than the background values of Guangxi soils (CNEMC 1990) and the upper crustal abundances (Taylor and Mclennan 1985) (Table 1). They were also higher than those values in the Yangtze River (Yang et al. 2014b), the Yellow River (Hu et al. 2015), and the Pearl River (Zhang and Wang 2001; Wang et al. 2011) (Table 1), suggesting severe heavy metal pollution occurred in the Longjiang River.

Concentrations of heavy metals in the upstream core (BG) were low (Table 1). This is because the upstream area

Table 1 Heavy metal (As, Cd, Pb, Sb, and Zn) concentrations in the sediment cores of BG, LL, YM, LD, SC, and NMT

Sites	As ($mg \cdot kg^{-1}$)	Cd ($mg \cdot kg^{-1}$)	Pb ($mg \cdot kg^{-1}$)	Sb ($mg \cdot kg^{-1}$)	Zn ($mg \cdot kg^{-1}$)
BG					
Range	16.2–25.0	1.79–3.14	29.4–51.6	4.54–16.1	163–299
Mean ± SD	20.0 ± 2.1	2.37 ± 0.42	37.8 ± 6.0	7.71 ± 3.19	217 ± 39
LL					
Range	31.9–159	3.25–45.1	117–710	10.2–169	321–1890
Mean ± SD	82.1 ± 41.8	14.4 ± 14.4	360 ± 192	51.6 ± 47.7	1030 ± 437
YM					
Range	20.0–132	1.41–23.7	46.1–315	3.97–40.8	149–863
Mean ± SD	61.0 ± 29.0	8.03 ± 5.53	136 ± 76.6	16.1 ± 9.6	419 ± 208
LD					
Range	26.5–94.5	0.64–101	43.0–411	7.90–112	167–1290
Mean ± SD	42.1 ± 19.1	12.2 ± 20.8	140 ± 91.3	26.8 ± 28.2	479 ± 256
SC					
Range	15.3–61.3	1.34–21.9	26.5–100	4.67–17.8	97–461
Mean ± SD	33.0 ± 16.4	5.74 ± 5.28	62.8 ± 19.7	9.01 ± 4.42	267 ± 113
NMT					
Range	22.9–121.5	1.33–266	54.1–145	9.07–32.4	200–655
Mean ± SD	42.1 ± 29.5	40.8 ± 76.3	98.8 ± 23.3	17.7 ± 7.68	425 ± 126
BV					
Mean	20.5	0.27	24.0	2.93	75.6
UCC					
Mean	1.5	0.098	20	0.2	71
Yangtze River					
Mean	36.1	2.99	187	NA	208
Yellow River					
Mean	13.6	0.43	32.6	NA	94.1
Pearl River[1]					
Mean	NA	1.44	254	NA	370
Pearl River[2]					
Mean	44.9	NA	97.1	5.09	202

BV: background value of Guangxi soil in China from CNEMC (1990); UCC: Average values of upper continental crust from Taylor and Mclennan (1985); Yangtze River from Yang et al. (2014b); Yellow River from Hu et al. (2015); Pearl River[1] from Wang et al. (2011); Pear River[2] from Zhang and Wang (2001)

is mainly covered by forest and only slightly disturbed by anthropogenic activities (Fig. S1). Nevertheless, heavy metal concentrations drastically increased in midstream core (LL), indicating increasing anthropogenic inputs of heavy metals. The concentrated urbanization and industrialization in Hechi City, especially nonferrous smelting activities (Lan et al. 2018), could be the main reason (Fig. S1). Large amounts of heavy metals (i.e., As, Cd, Pb, Sb and Zn) would be released into environments during the sulfide processes (Filella et al. 2002; Gutiérrez et al. 2016).

In downstream cores (YM, LD, SC, and NMT), the heavy metals (except for Cd) concentrations tended to decrease. The average concentrations of As, Cd, Pb, Sb, and Zn in YM core apparently decreased 1.3, 1.8, 2.6, 3.2, and 2.5 times, lower than those in LL core, respectively. The decrease of heavy metal concentrations was likely caused by the dam interception and the dilution of detrital inputs, which play important roles in heavy metal distributions in river sediments (Wang et al. 2015). However, the concentrations of heavy metals (except for As) in LD core slightly increased, which were probably affected by the urban discharge of Yizhou City, and the confluence of the Dongxiaojiang River where Pb-Sb mining activities contributed to large Sb discharge (Lan et al. 2018). Heavy metal concentrations in the SC core apparently decreased but increased in the NMT core subsequently. This may be attributed to the land use variation around NMT reservoir which was dominated by arable land (Fig. S1). The

agricultural applications for fertilizers and pesticides could also be responsible for the elevated heavy metals in river sediments (N'Guessan et al. 2009).

The average Cd concentrations increased in downstream cores and the highest average Cd concentrations occurred in the NMT core (Table 1), which may indicate additional sources of Cd, rather than other heavy metals. Zn and Cd belong to the IIB group of the periodic table. Theoretically, Zn and Cd should be correlated if they are from the same sources, due to the close chemical behavior of these two metals (Gutiérrez et al. 2016). This is really the case for the six core sediments collected from the Longjiang River, as shown in Fig. 2. However, the downstream sediments showed anomalous high Cd/Ti ratios, which supported our hypothesis that additional Cd sources could occur at downstream. During the Cd pollution event in 2012, these four downstream reservoirs have been targeted for emergent cleanup for industrially discharged Cd, and consequently produced large amounts of Cd settlement in local river sediments. In addition, two layers with highest Cd concentrations (also the atypical values) in NMT core also contained high concentrations of Ca (3.07%–3.63%) and As (100–122 mg kg^{-1}) (Fig. S5), which was also consistent with the facts that thousand tons of lime were applied for Cd precipitation and that high concentrations of As were also detected in water during the pollution event, respectively (Zhang et al. 2013). Therefore, these findings demonstrated the elevated Cd in downstream cores was mainly ascribed to the Cd pollution event in 2012.

The profile of excessive ^{210}Pb ($^{210}Pb_{ex}$) activity in LL core was shown in Fig. S6. The vertical distribution of $^{210}Pb_{ex}$ activity globally exhibited an exponential decay with mass depth, suggesting that hydraulic sorting did not take place in the LL core. The average sediment rate was estimated at 1.93 cm yr^{-1} in the LL core, based on a constant initial ^{210}Pb concentration (CIC) model (Oldfield et al. 1978). Therefore, the LL core reflected a record of sediment accumulation that spanned approximately 30 years (1985–2015). According to previous literatures, the peak of sand volume at 42-cm coincided with the flood event in 1994 (Wei and Gui 2004), and the peak of sand volume at 56-cm coincided with the reconsolidation of the dam during 1985–1987 (CERLAC 2013), respectively. These two events may have increased the frequency of hydrological cycles in the reservoir, and thus more detrital inputs were generated from the riparian zone. Therefore, the two events perfectly matched to dating results, validating the CIC model.

Two stages could be discerned based on the distribution of heavy metal concentrations in dating cores (Fig. 3A). The first stage was from 1985 to 1999 (corresponding to 58–32 cm), and heavy metal concentrations were extremely high, with average value of 118, 21.1, 503, 81.1, and 1305 mg kg^{-1} for As, Cd, Pb, Sb, and Zn, respectively. In this stage, China has experienced a rapid economic growth that produced severe environmental problems (Xue and Zeng 2010). Similarly, Guangxi Province has experienced a rapid economic growth (Wang et al. 2015; YCCH 2016). Nonferrous metal smelting released a large amount of heavy metals to the rivers (Xu et al. 2016). This can be proven by the low percentage of qualified industrial discharged wastewater of Guangxi Province at the same period (Fig. 3B). Therefore, the high enrichment of heavy metals in the Longjiang River during this stage might be

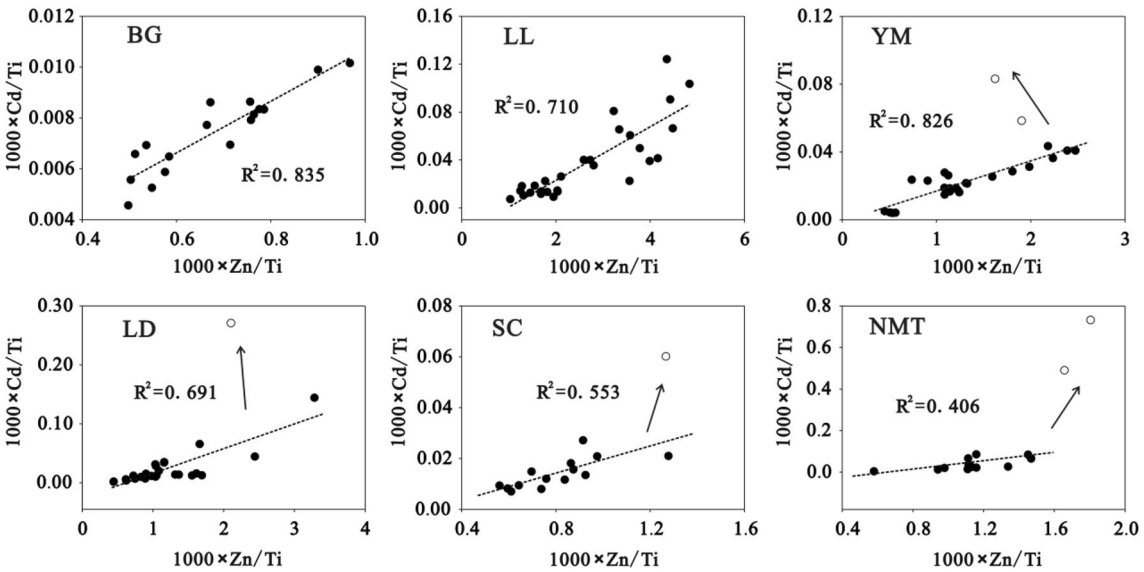

Fig. 2 Relationship between the ratios of Zn/Ti and Cd/Ti in the sediments of BG, LL, YM, LD, SC and NMT core, respectively. The empty circles in downstream cores (YM, LD, SC, and NMT) exhibited different trends due to obviously high Cd inputs from pollution events

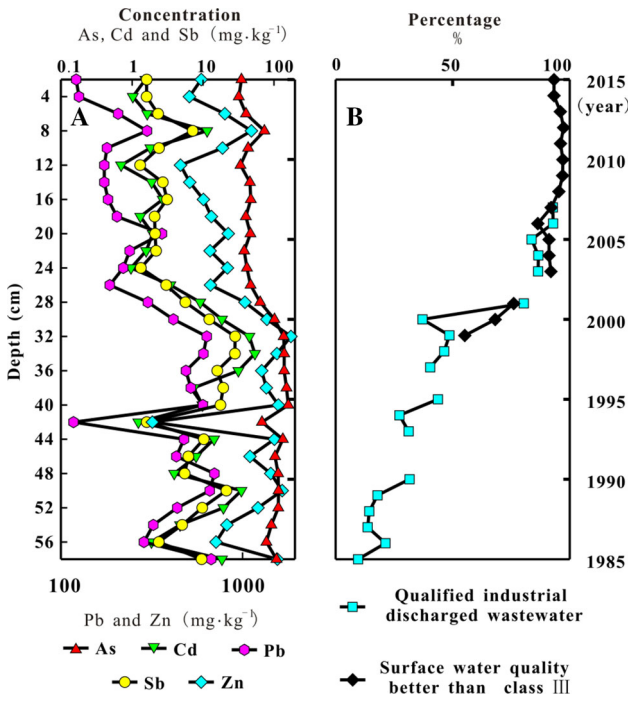

Fig. 3 **A** Vertical profiles of heavy metal (As, Cd, Pb, Sb, and Zn) concentrations in the LL core; **B** Annual percentage of qualified industrial wastewater discharged in Guangxi (BSEG 1985–2015); Annual percentage of surface water better than class III in Guangxi (BSEG 1997–2015). The classes of water quality are divided according to SEPA (2002). Class III refers to water in the second-grade protection zone of a centralized drinking water source, fish and shrimp overwintering ground, migration route, aquaculture area, swimming area, etc

due to the inadequacy of environmental supervision and low efficiency of wastewater treatments. This then resulted in large amounts of unqualified wastewater being directly discharged into river without proper treatment in the early stage of the economic boom. Similar results also suggested a significantly high enrichment of heavy metals in this stage from other areas in China based on the recorded sediment cores (Bing et al. 2011, 2016a; Zhao et al. 2013; Zhang et al. 2015). Two distinct decreases occurred in the layers of 42-cm (1994) and 56-cm (1986), both due to dilution by high silty sand fractions.

The second stage was from 2000 to 2015 (corresponding to 30–2 cm). Heavy metal concentrations significantly decreased and remained stable after 2000 with average values of 48.6, 8.16, 227, 24.0, and 774 mg kg^{-1} for As, Cd, Pb, Sb, and Zn, respectively. At this stage, the Chinese government introduced the "sustainable development" policy for the first time, and strict controls on environmental pollution were performed by local governments across the country (Dai et al. 2007; YCCH 2016). The decrease of heavy metal concentrations in the studied core since 2000 suggested that heavy metal pollution has been effectively controlled due to proper environmental management. The annually qualified ratios of industrial wastewater and surface water quality in Guangxi province were also significantly improved since 2000 (Fig. 3B). Similar studies also indicated decreased heavy metal pollution after 2000 based on the recorded sediment cores (Dai et al. 2007; Bing et al. 2016a; Liu et al. 2017), which suggested that the decrease of heavy metals during this period could be attributed to direct government guidance and supervision, as well as improvement of wastewater treatment.

3.3 Geochemical fractionation of heavy metals

Previous studies suggest that it is important to constrain their geochemical fractionation prior to evaluate the pollution status of heavy metals in sediments, because bulk concentrations are insufficient (Wang et al. 2015). Sequential extraction experiments are thought to be an effective way to assess the geochemical fractionation of heavy metals in sediments (Najamuddin et al. 2016). The geochemical fractions of heavy metals in the selected sediment cores (LL and NMT) were shown in Fig. 4 and exhibited a similar distribution.

The exchangeable fractions (F1) of heavy metals in sediments were relatively low (lesser than 8.5%). Heavy metals associated with F1 include weakly adsorbed metals retained on a solid surface by relatively weak electrostatic interaction, and they are considered the most easily released fraction in environments (Filgueiras et al. 2002).

Heavy metal associated with carbonate bound fractions (F2) usually precipitate or coprecipitate with carbonates (Filgueiras et al. 2002). The average percentage of As, Cd, Pb Sb, and Zn in F2 was 7.06, 60.9, 33.3, 10.5, and 18.6%, respectively. Among them, Cd and Pb were dominant in F2. Heavy metals associated with F2 were considered to be easily transported and transformed, and absorbed by aquatic organisms (Clemens 2006; Li et al. 2014), which suggests that Cd and Pb may possess high potential bioavailability in the Longjiang River.

Heavy metal associated with oxidizable fractions (F3) are generally considered to be associated with organic matters by complexations or bioaccumulation processes (Wang et al. 2015). The average percentage of As, Cd, Pb Sb, and Zn in F3 was 2.32, 25.6, 27.3, 2.52, and 27.0%, respectively. Heavy metals associated with oxidizable phases are assumed to remain in soils or sediments for longer period, but they may be mobilized by decomposition processes (Xu 2016). Such processes would frequently occur in the Longjiang River with a monsoon climate accompanied by hydrological events during flood season (from April to September), and this may cause large amounts of sediment move into aerobic water, leading

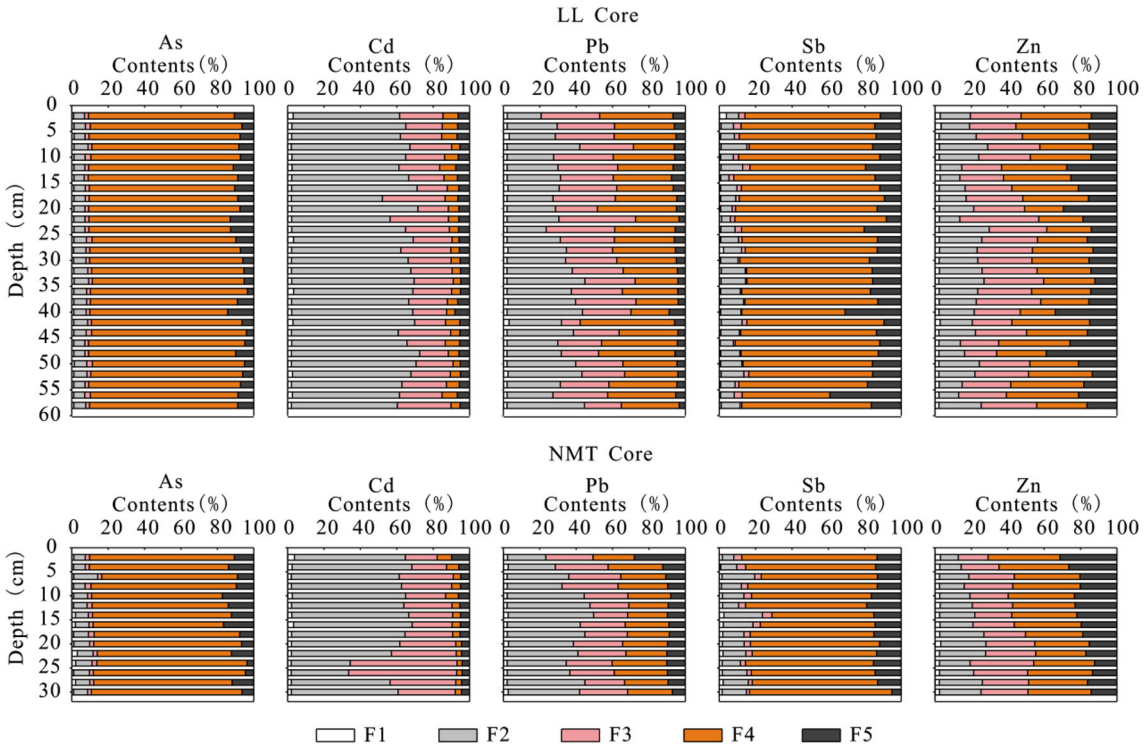

Fig. 4 Geochemical fractions of heavy metals (As, Cd, Pb, Sb, and Zn) contents in LL and NMT core. F1, F2, F3, F4, and F5 mean exchangeable, carbonate bound, oxidizable, reducible and residual fraction, respectively

heavy metals, especially Cd, Pb, and Sb, to be released into the Longjiang River.

Heavy metal associated with reducible fraction (F4) are typically scavenged by Mn oxides, and amorphous and crystalline Fe oxides (Li et al. 2014). The average percentages of As, Cd, Pb, Sb, and Zn in this fraction were 80.5, 5.49, 30.1, 70.6, and 32.8%, respectively. As and Sb were dominant in this fraction, followed by Pb and Zn. Similar results have also reported the dominance of As and Sb in F4 in other studies, which suggested this could be attributed to the specific geochemical behaviors of As and Sb (Beauchemin et al. 2012; Wang et al. 2016). Generally, heavy metals associated with this fraction are barely soluble under natural conditions, but are thermodynamically unstable under anoxic circumstances and are attacked by benthic organisms (Filgueiras et al. 2002; Wang et al. 2015).

Heavy metal associated with residual fractions (F5) are likely to be incorporated in alumino-silicate minerals, and they are quite stable and unable to be released into water under natural conditions (Wei et al. 2016). The average percentages of As, Cd, Pb, Sb, and Zn in this fraction were 8.86, 5.66, 7.16, 15.1, and 19.1%, respectively. Compared with the mobilized fractions, heavy metals associated with F5 were relatively low. Previous studies suggested the elevated heavy metal in mobilized fractions could be due to more anthropogenic contributions (Wei et al. 2016),

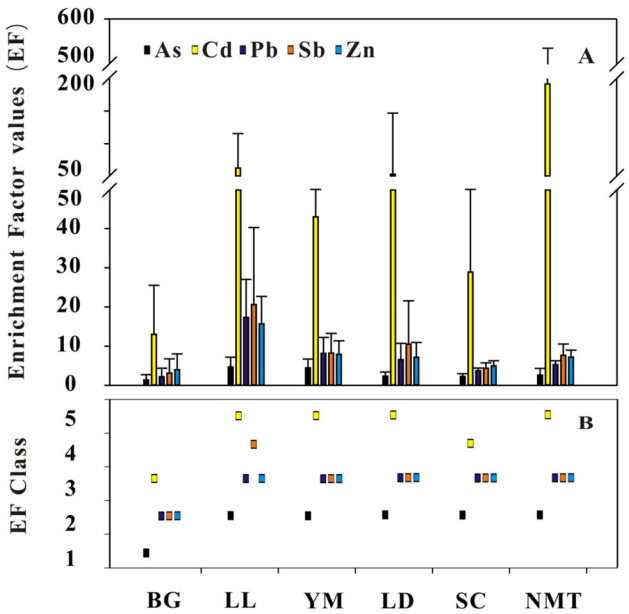

Fig. 5 Enrichment factors of heavy metals (As, Cd, Pb, Sb, and Zn) and classification in the sediment cores from the Longjiang River. EF Class 1. no enrichment, 2. moderate enrichment, 3. significant enrichment, 4. very high enrichment, 5. extreme enrichment

indicating that very high amounts of heavy metals were derived from anthropogenic activities in the Longjiang River.

3.4 Assessment of heavy metal pollutions

The calculated EFs and pollution degrees of heavy metals in the six sediment cores were shown in Fig. 5. The mean EFs of heavy metals (except As in BG) in the six sediment cores were all higher than 1.5, revealing that heavy metals mainly originated from anthropogenic inputs. In general, the average EFs of five heavy metals in six sediment cores varied in the order of Cd (12.5–192) > Zn (4.0–15.7) ≈ Pb (2.2–17.4) ≈ Sb (3.6–20.6) > As (1.4–4.7). Spatially, the EFs of heavy metals were relatively low in the upstream core (BG), and then drastically increased in midstream core (LL). Subsequently, most heavy metal EFs decreased in downstream cores (YM, LD, SC, and NMT). And the pollution degrees upstream were under none to significant, and moderate to extreme midstream while they were still in moderate to extreme downstream. The highest EFs of As (9.5, significant), Pb (36, very high), Sb (71, extreme), and Zn (29, very high) were located on the LL core. However, Cd (1235, extreme) was located on the NMT core. Like their concentrations, the variations of EFs could be explained by low anthropogenic impacts upstream and increasing anthropogenic inputs in the midstream and downstream areas.

EFs of As, Cd, Pb, Sb, and Zn before 2000 were relatively high, with the average values of 6.8 (significant), 94.2 (extreme), 24.5 (very high), 32.9 (very high), and 20.5 (very high), respectively. There was, however, a significant decrease after 2000, with the average values of As, Cd, Pb, Sb, and Zn of 2.6 (moderate), 37 (very high), 11 (significant), 9.7 (significant), and 11 (significant), respectively. Despite the clear decrease of EFs after 2000, the pollution degrees and the potential mobility of heavy metals were still high, which suggests more strictly controlled policies on the point sources of heavy metals should be carried out.

Since the bioavailability and toxicity of heavy metals in sediments depend on their chemical forms and total concentrations (Wei et al. 2016), it could be inferred that heavy metals with the high EFs and high labile fractions in sediments have high potential of mobility and bio-toxicity in aquatic ecosystems. In addition, Cd, which was the most enriched in the sediments and mainly occurred in easily released fractions, could pose the highest ecological risk to the Longjiang River.

3.5 Source identification of heavy metals

The correlation coefficients among the sedimentary parameters (clay and silt fractions), major elements (Al, Ca, Fe, Mn, and Ti), and heavy metals (As, Cd, Pb, Sb, and Zn) in six sediment cores were listed in Table S1. In the BG core, As, Pb and Sb generally displayed significant positive correlation ($p < 0.05$) with Al and Ti. Al and Ti usually come from natural weathering process, indicated that natural materials are one of the important sources of these heavy metals in the BG reservoirs. Though, Cd was only correlated with Zn ($p < 0.01$). The potential sources of Cd and Zn may originate from sulfide weathering or the agricultural activities, which are dispersedly distributed upstream (Fig. S1). In the LL core, the five heavy metals were significantly correlated with each other ($p < 0.01$), and also correlated with Fe and Mn ($p < 0.05$), indicated they may have a common origin. It is well known that the wastes from mining and smelting activities not only enrich these heavy metals but also contain high amounts of Fe and Mn (Wang et al. 2015). In downstream cores, As, Cd, Pb, Sb, Zn, Fe, and Mn were also generally correlated with each other ($p < 0.05$). However, the five heavy metals were also correlated with lithospheric elements (Al and Ti) in SC core, which suggested the natural detritus were also one of the important sources of heavy metals in the sediments of SC reservoirs, and thus decreased the heavy metal concentrations (Table 1).

In river sediments, the sources of heavy metals could not be easily identified because the hydrodynamic conditions accelerated the homogeneity of the sediments and obscured heavy metal source signals (Bing et al. 2016b). Previous studies considered that specific elemental ratios could further constrain the sources of heavy metals (Bi et al. 2006; Bing et al. 2016b). Elements with similar geochemical behavior may provide important geochemical signatures of initial sources. Two groups of couple

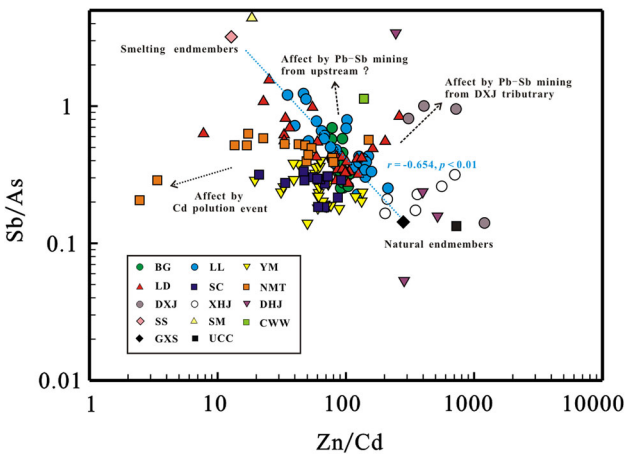

Fig. 6 Zn/Cd versus Sb/As in the sediments of six sediment cores (BG, LL, YM, LD, SC, and NMT) from the Longjiang River. Tributaries (DXJ, XHJ, and DHJ) from Lan et al. 2018; SS: soils impacted by smelting dusts near the smelters in Hechi City (Xiang et al. 2011); SM: smelting wastewater collected from Hechi City (unpublished data); CWW: city wastewater collected from Hechi City (unpublished data). GXS: background values of Guangxi soil in China (CNEMC 1990); UCC: average values of upper continental crust (Taylor and Mclennan 1985). The blue dash line is the linear trend of the subsamples of LL core ($r = 0.654$, $p < 0.01$)

elements, Zn and Cd, As and Sb, both have similar geochemical behaviors (Filella et al. 2002; Gutiérrez et al. 2016), respectively, and their ratios of Zn/Cd versus Sb/As in six sediment cores might be able to reveal the original signal of heavy metal endmembers, and further constrain their sources in the six sediment cores.

The results of Zn/Cd versus Sb/As in six sediment cores were shown in Fig. 6. Source-specific materials, including sediments of three tributaries (Lan et al. 2018), Guangxi soil in China (CNEMC 1990), UCC (Taylor and Mclennan 1985), smelting and city wastewater (unpublished data), and soils impacted by smelting dust in Hechi City (Xiang et al. 2011) were also shown in Fig. 6. This figure gives a broad picture on what the main heavy metal sources were presented in the Longjiang River. In the BG core, a large variation of Sb/As ratios may be affected by Pb-Sb mining activities (Fig. 1). Nonetheless, the plots of Zn/Cd versus Sb/As for LL core distributed around the linear trend between natural endmembers and smelting wastes ($p < 0.01$) indicates the mixing model of these two sources. This result further suggested smelting activities could be the main contributors to the increase of the heavy metal enrichments midstream.

Most of the plots of Zn/Cd versus Sb/As in downstream cores were very close to the linear trend displayed by LL core (Fig. 6). This further indicated the heavy metal pollutions derived from midstream were still prominent in downstream reservoirs. Conversely, some values of subsamples of LD core were close to the values of Pb–Sb mining impacted sediment of the Dongxiaojiang River (Fig. 6), indicating that Pb–Sb mining from the Dongxiaojiang River was also one of the sources downstream. Additionally, the plots of Zn/Cd versus Sb/As in downstream cores generally exhibited low ratios of Sb/As and Zn/Cd (Fig. 6), which might be due to the effect of the Cd pollution event in 2012.

4 Conclusions

The Longjiang River has suffered different degrees of heavy metal (As, Cd, Pb, Sb, and Zn) pollution, and Cd pollution was the most severe. The mean EF values of five heavy metals were all higher than 1.5 (except As in upstream), revealing the anthropogenic inputs. The low concentrations of heavy metals in the upstream core (BG) indicate the limited impact of anthropogenic activities. However, heavy metal concentrations in midstream core (LL) drastically increased and reached the highest values (except Cd) due to the active smelting activities. In downstream cores (YM, LD, SC and NMT), most heavy metal concentrations clearly decreased due to the effect of dam interception and natural attenuation. However, an additional source of Cd was observed in downstream sediments, which originated from the Cd pollution event in 2012. The heavy metals in upstream core were under no to moderate pollution degrees while they were in moderate to extreme moderate pollution degrees in midstream and downstream cores. One turning point exists within 1985–2015 for the Longjiang River sedimentary series, which can define two stages, prior to 2000 and after 2000. The first stage was the time when Hechi City developed rapidly, and the Longjiang River suffered high enrichment of heavy metals (significant to extreme) due to an inefficient model of economic growth. The second stage was characterized by the enhancement of environmental regulations and wastewater treatments, and the heavy metal enrichments tended to decrease (moderate to very high). The geochemical fractionation results indicated that Cd was primarily associated with carbonate-bound fractions, As and Sb prevailed in the reducible fraction while Pb and Zn were comparatively distributed in carbonate-bound, oxidizable, reducible and residual fractions, respectively. The high enrichments and non-residual fractions of heavy metals, especially Cd, in sediments posed high ecological risk to aquatic organisms. The anthropogenic sources of heavy metals in the sediments were mainly related to smelting and mining activities within the catchment, which could be the main contributors for the increase of the heavy metals. In addition, although the environmental control and natural attenuation effects have sustainably decreased the heavy metal concentrations, the pollution degrees and mobilities of heavy metal remained high in the dammed-river sediments. Therefore, more caution should be paid on the environmental management for river-dammed reservoirs in the Longjiang River.

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