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Distribution and partitioning of heavy metals in large anthropogenically impacted river, the Pearl River, China

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Abstract In order to evaluate the distribution and partitioning characteristics of heavy metals in the large anthropogenically impacted Pearl River Basin, the contents of "anthropophile" elements (Cr, Ni, Cu, Zn, Cd and Pb, which are clearly influenced by human activities) were determined, and their partitioning coefficients (K_d) between water and sediments and enrichment factors (EF) were calculated for samples collected at different locations along the Pearl River main stream. The modified BCR sequential extraction procedure (proposed by the European Community Bureau of Reference in 1993), which involves the successive extraction of metals in a decreasing order of reactivity, was applied. Sediment samples from the upper, middle, and lower reaches were included in this study. The results showed that the content of most metals in water and sediment samples gradually increases from upstream to downstream, suggesting a possible input from human activities as shown by their increasing high EF, ranged from 1.4 to 3.9 for Cu, from 1.4 to 6.7 for Zn, from 2.5 to 59.1 for Cd, and from 1.7 to 8.9 for Pb, respectively. The higher partition coefficients (K_d) for Cr, Zn, and Pb (10^5–10^6) indicated that they were mainly transported in solid phase, while parts of Ni, Cu, and Cd were transported in dissolved phase as they display relatively lower K_d in the range of 10^4–10^5. According to the results of the BCR leaching, the percentage of non-residual fraction of heavy metals in the sediments showed a decreasing order of Cd > Pb > Zn > Cu > Ni > Cr, implying that Cd and Pb were more active and bioavailable compared to the other four metals, and thus would be potentially more harmful to the watershed ecosystem.

Keywords Pearl River · Water and sediment · Heavy metals · Partitioning · Distribution

1 Introduction

Heavy metals such as Cr, Ni, Cu, Zn, Cd, and Pb have attracted increasing attention because of their persistence geochemistry, toxicity, and possible bio-accumulation in aqueous environments and ecosystems (Niu et al. 2009; Zhang et al. 2017; Meng et al. 2016; Li et al. 2017; Odukoya and Akande 2015). As critical environmental pollutants and potential "anthropophile" elements (Chen et al. 2014), these metals can be discharged into rivers by both natural and anthropogenic processes, and be transported in rivers through various carriers such as in dissolved phase, suspended particulate matters, sediments, and organisms (Yang et al. 2017a, b). During transport, heavy metals may undergo complex exchanges due to adsorption/desorption, precipitation/dissolution, complexation, redox reactions, and biouptake processes (Lin et al. 1984; Xie et al. 2012; Islam et al. 2015; Xiong et al. 2017), which in turn affect their environmental geochemical behavior and

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bioavailability. Understanding the distribution of metals among different phases is thus crucial for better evaluating the environmental impacts of these metals. Though the distribution of heavy metals has been widely studied in large rivers draining into relatively pristine basins, including the Mississippi River (Shiller 1997; Piper et al. 2006), the Amazon River (Gaillardet et al. 1997; Guinoiseau et al. 2017) and the Congo River (Dupre et al. 1996), and small rivers like the Seine River (Chen et al. 2014; Meybeck et al. 2007), the geochemical characteristics, and especially the distribution of metals in large anthropogenically impacted rivers, are rarely reported, which limits our knowledge on the riverine geochemistry of heavy metals and their transport to the ocean.

In this study, the Pearl River, a large anthropogenically impacted river located in the south of China, was studied in order to characterize the distribution and the partitioning of six typical "anthropophile" elements (Cr, Ni, Cu, Zn, Cd, and Pb) among different phases. Several studies reported the spatial distribution, pollution assessment, and sources of heavy metals in the water and sediments of the Pearl River. However, most studies focused only on the variations of total concentrations of certain metals either in a certain section of the river (Xu et al. 2009; Tang et al. 2015; Deng et al. 2017; Liu et al. 2017), or in one tributary (Zhou et al. 2013; Liu et al. 2011; Zhao et al. 2012) or in the estuary (Wang et al. 2004; Ip et al. 2007; Li et al. 2007; Fan et al. 2010; Pan and Wang 2012). Although these studies allowed for a better understanding of the geochemical background and the contents and the transports of metals in the Pearl River (Wang et al. 2007, 2013; Cai et al. 2016), little is known about the distribution and partitioning of metals amongst different phases (Li et al. 2007; Wu et al. 2016). Therefore, further research is needed to better characterize the distribution and the transport dynamics of metals and better constrain their ecological effect. In this study, we systematically investigated the distribution characteristics and chemical fractions of six typical "anthropophile" metals between water and suspended sediments, and amongst different sediment phases along the downstream gradient of the Pearl River, by means of the partitioning coefficient calculation and the BCR sequential digestion of solid samples (Tessier et al. 1979; Rauret et al. 1999; Quevauviller et al. 1997), which can provide useful information on the geochemical activity and bioavailability of heavy metals in rivers (Zhuang 2015; Yang et al. 2016a, b, c; Wang et al. 2016; Lin et al. 2017; Qiao et al. 2013; Yang et al. 2016a, b, c).

2 Methods and materials

2.1 Background of the Pearl River

The Pearl River is the third longest river in China, with an area of 454,000 km^2 within a range of E102°14′–115°53′/N21°31′–26°49′ (Lu et al. 2009) (Fig. 1). From west to east, it drains six provinces and two special administrative regions in southern China, including Yunnan, Guizhou, Guangxi, Guangdong, Hunan, Jiangxi, Hong Kong, and Macao. The annual mean precipitation is 1470 mm and mean annual runoff is about 320 billion m^3 yr^{-1}. Recently, with the implementation of China's reform and opening-up policy, the whole basin has encountered rapid urbanization and industrialization, accompanying rapid economic development and rapid population growth. These changes have also led to a series of environmental problems such as heavy metal pollution (Wang et al. 2013; Han et al. 2014; Zhao et al. 2017), which potentially threatens the local ecosystem.

2.2 Sampling

The distribution of sampling locations was shown in Fig. 1. Twelve samples were collected from upstream to downstream in the main stream of the Pearl River during a high flow cruise in June 2015. According to the watershed features (Zhen et al. 2016), the Pearl River was divided into the upper reaches (from the spring to Shilongzhen, Guangxi Province, including sampling M1-4), middle reaches (from Shilongzhen to Wuzhou, Guangxi Province, including sampling M5-9) and lower reaches (from Wuzhou to estuary, including sampling M10-12). Water samples and surface sediment samples were collected from each location.

The pH was measured in situ by portable Multiparameter (Multi 3430, WTW). Water samples were immediately filtered after collection through a 0.22 μm mixed cellulose esters membrane installed in a Teflon filtration system and then into previously acid-washed polypropylene (Nalgene) bottles. The filtered solutions for trace elements and cations analyses were acidified to a pH < 2 with ultra-pure HNO$_3$ and stored at 4 °C. The sediment sample was collected into a 50 ml polypropylene centrifuge tube and freeze-dried by a vacuum freeze dryer (FD-1, Beijing Tianlin Hengtai Technology Co., Ltd).

2.3 Materials and reagents

All reagents used in the experiments, including HNO$_3$, HF, CH$_3$COOH, HONH$_2$·HCl, H$_2$O$_2$, and CH$_3$COONH$_4$ were analytical grade (Sinopharm Chemical Reagent Co., Ltd.,
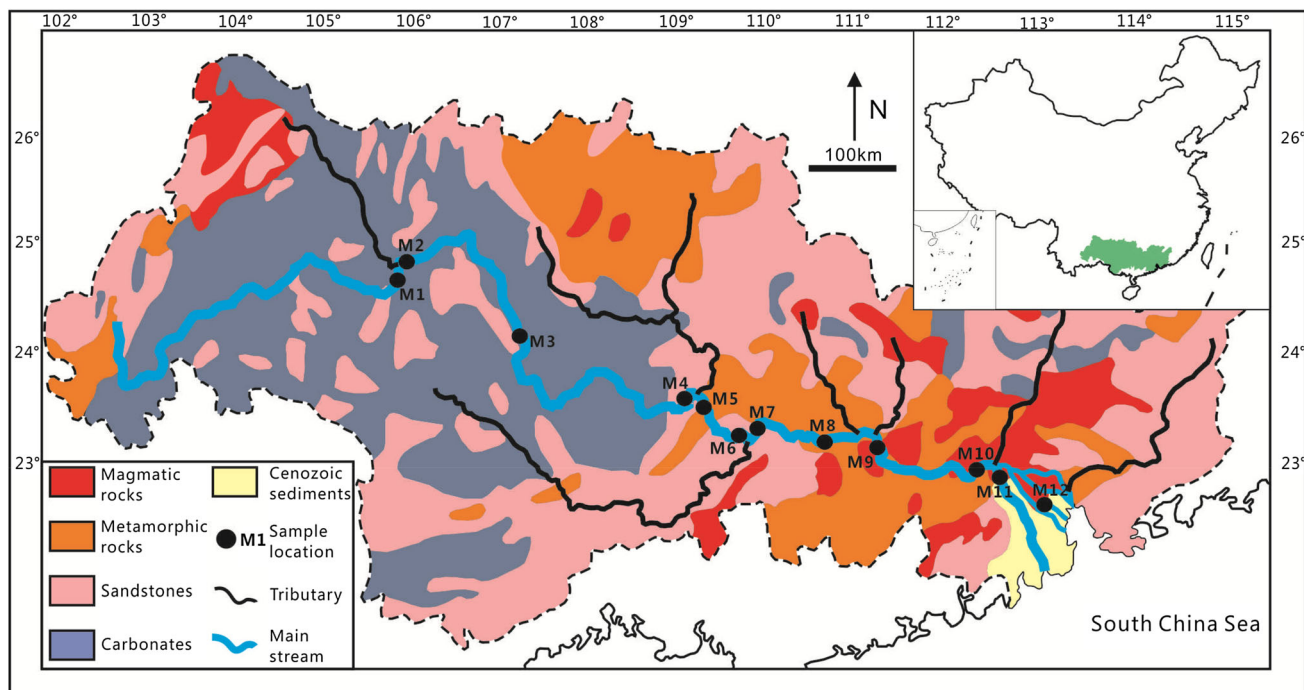
Fig. 1 Location of samples in the Pearl River, southern China

China). Deionized water obtained from the Millipore-Q water (Deionized Advantage A10, Merck Millibo) system was used in all preparations and experiments, including preparing 0.11 mol·L^{-1} CH$_3$COOH, 0.5 mol·L^{-1} HONH$_2$·HCl, 8.8 mol·L^{-1} H$_2$O$_2$ and 1 mol·L^{-1} CH$_3$COONH$_4$ for sequential extraction. In addition, sediment standard reference materials GSD-11 (GBW07311), GSD-3a (GBW07303a) and soil standard reference material GSS-7 (GBW07407) provided by the State Technology Supervision Administration Bureau, China were used in this study.

All polypropylene centrifuges tubes were soaked in 5% HNO$_3$ for 24 h and then rinsed repeatedly with deionized water. The PTFE digestion bombs and Teflon beakers were soaked in 20% HNO$_3$ for 24 h, then soaked in deionized water and rinsed repeatedly, and finally were placed in a ventilation cabinet to dry before using.

2.4 Solid sample digestion

The large mineral particles and plant impurities were removed and the particle mixture was uniformly ground to 200 mesh using an agate mortar. Twelve samples were chosen for entire digestion. 50 mg of sediment (and standards GSD-11, GSD-3a, GSS-7) materials were placed in pre-treated PTFE digestion bombs. 0.8 ml HF and 1 ml HNO$_3$ were added to the sealed bombs before heating at 170 °C for 48 h. After digestion, 0.8 ml H$_2$O$_2$ was added to the samples before evaporation at 120 °C. Afterward, the

residue was dissolved in 5 ml 40% HNO$_3$ and heated at 140 °C for 5 h. After cooling, the samples were diluted by adding deionized water for analysis. The concentration results derived from this entire digestion were compared to those of BCR leaching experiments for recovery and quality control (see below).

2.5 Sequential extraction of heavy metal in sediments

Three sediment samples from the upper, middle, and lower reaches of the Pearl River Basin (as well as standard materials GSD-11, GSD-3a, GSS-7) were selected for the modified BCR sequential extraction experiments (Rauret et al. 1999). This procedure led to the extraction of four separate fractions: exchangeable (or weak acid soluble-extractable), reducible (or iron-magnesium oxides), oxidizable (or organic-sulfide bound), and residual. The details of the procedure are given as follows:

1. The exchangeable fraction (F1): 250 mg of sediment and 10 ml of 0.11 mol·L^{-1} acetic acid were mixed in a 50 ml polypropylene centrifuge tube and stirred by a water bath oscillator (SHA-B, Changzhou Runghua Electric Co., Ltd) for 16 h at constant temperature of 30 °C before centrifugation (by a desktop high speed centrifuge, TG1650-WS, Shanghai Luxiangyi centrifuge instrument Co., Ltd) at 5750 r·min^{-1} for 20 min. The supernatant was carefully transferred to

a Teflon beaker. The residue was then washed with 10 ml of deionized water and centrifuged. The water supernatant was then recuperated and combined with the acetic acid supernatant. The final solution was evaporated to dryness at 100 °C. Finally, the residue was dissolved in 10 ml of 10% HNO_3 and transferred to a polypropylene centrifuge tube and stored at 4 °C for analysis.

2. The reducible fraction (F2): 10 ml of 0.5 mol·L^{-1} hydroxylamine hydrochloride was added to the residue derived from step (1) and the particles adhereding to the inner wall of the centrifuge tube were detached using sonication. The whole tube was stirred for 16 h at 30 °C. The separation of the extract, collection of the supernatant, and rinsing of residues were the same as described in step (1).

3. The oxidizable fraction (F3): 2.5 ml of 8.8 mol·L^{-1} hydrogen peroxide was slowly added to the residue from step (2), and the tubes were then covered and the residue was digested for 1 h at room temperature. The samples were then heated at 85 °C with a lid for 1 h and then evaporated until the volume of solution was less than 1 ml. Subsequently, another 2.5 ml of 8.8 mol·L^{-1} hydrogen peroxide was added to allow digestion at 85 °C with a lid for 1 h before evaporation to near dryness. Finally, 12.5 ml of 1 mol·L^{-1} ammonium acetate (adjusted to pH 2.0 ± 0.1 with HNO_3) was added to the residue and immediately stirred at 30 °C for 16 h. Then the extraction procedure was performed as described in step (1).

4. The residual fraction (F4): 4 ml HF and 4 ml HNO_3 were added to the residue obtained from step (3) and transferred to PTFE digestion bombs. The bombs were sealed and heated at 170 °C for 48 h. After cooling, 4 ml of hydrogen peroxide were added and then heated at 120 °C until near dryness. Finally, 10 ml 10% HNO_3 was added and the final solution was transferred to a polypropylene centrifuge tube and stored at 4 °C for analysis.

2.6 Concentration measurement and extraction recovery control

The contents of trace elements Cr, Ni, Cu, Zn, Cd, and Pb in water and different fractions derived from digestion and our sequential extraction were determined by inductively coupled plasma mass spectrometer (ICP-MS, NexION 300X, PE), and cations were determined by inductively coupled plasma optical emission spectrometer (ICP-OES, Wasst-mpx, Agilent) at the State Key Laboratory of Environmental Geochemistry (SKLEG), Chinese Academy of Sciences, Guiyang. The quality for concentration analysis was controlled by adding an external standard (Rh) and measurements of the well-calibrated international standards (1640a, NIST). The relative standard deviation was less than 5% for all elements.

The quality control for entire digestion and the sequential extraction procedure was assessed using blank samples, sample replicates, and standard reference materials (GSD-11, GSD-3a, GSS-7). Blank samples were treated following the same procedures with entire digestion and sequential extraction, and their contents of the six interest elements were negligible compared to the total mass of the six elements in samples. The standard deviations of the replicate samples were < 10%. The concentrations of heavy metals from entire digestion demonstrated a good agreement with their reference values, and the recovery rate of Cr, Ni, Cu, Zn, Cd, and Pb were 101% ± 3%, 101% ± 1%, 99% ± 1%, 91% ± 7%, 96% ± 3%, and 93% ± 7%, respectively.

The recovery of the sequential extraction was calculated as follows:

$$Recovery\,(\%) = [(C_{F1} + C_{F2} + C_{F3} + C_{F4})/C_{total\,content}] \times 100\% \tag{1}$$

where C represented the mass of heavy metals in different extracted fractions of the sediment. $C_{total\,content}$ represented the mass of heavy metals in entire digestion. The overall recoveries ranged from 72.0% to 108.1%, and were 84% ± 10%, 91% ± 3%, 92% ± 4%, 83% ± 1%, 99% ± 5%, and 99% ± 4% for Cr, Ni, Cu, Zn, Cd, and Pb, respectively.

3 Results

3.1 Concentration of metals in water and sediments

Total concentrations of metals in water and sediments are listed in Table 1 and shown in Fig. 2.

Concentration in water The concentrations of heavy metals in water ranged from 0.40 to 2.17 µg/kg (average: 0.80 µg/kg) for Cu, from 0.12 to 2.31 µg/kg (average: 0.62 µg/kg) for Zn, from 0.17 to 0.90 µg/kg (average: 0.42 µg/kg) for Ni, from 0.16 to 0.40 µg/kg (average: 0.24 µg/kg) for Cr, from 0.01 to 0.08 µg/kg (average: 0.03 µg/kg) for Pb, and from 0.005 to 0.096 µg/kg (average: 0.025 µg/kg) for Cd in the Pearl River.

Concentration of Cr in water slightly increased before the effluent Liujiang River (M4), then decreased overall downstream. Concentration of the other metals in water generally increased from upstream to downstream, with relatively higher concentrations observed after the

Table 1 Total metal concentrations in sediments and water and Kd values and EF values of heavy metals

Sampling locations	Concentrations of heavy metals in sediment (ppm) and water (ppb) and their Kd value and EF value											
	Cr				Ni				Cu			
	Sediment (ppm)	Water (ppb)	Kd	EF	Sediment (ppm)	Water (ppb)	Kd	EF	Sediment (ppm)	Water (ppb)	Kd	EF
M1	63	0.23	2.7×10^5	0.8	30	0.17	1.7×10^5	0.8	32	0.40	8.0×10^4	1.4
M2	49	0.26	1.9×10^5	1.2	18	0.21	8.7×10^4	0.9	19	0.43	4.3×10^4	1.5
M3	89	0.22	4.0×10^5	2.8	18	0.19	9.5×10^4	1.1	21	0.44	4.8×10^4	2.2
M4	94	0.40	2.3×10^5	1.6	38	0.23	1.7×10^5	1.3	36	0.49	7.2×10^4	2.0
M5	101	0.28	3.5×10^5	1.7	40	0.32	1.3×10^5	1.4	39	0.58	6.6×10^4	2.2
M6	71	0.34	2.1×10^5	1.9	24	0.32	7.4×10^4	1.2	35	0.63	5.6×10^4	3.1
M7	54	0.27	2.0×10^5	1.1	27	0.32	8.4×10^4	1.1	29	0.61	4.7×10^4	2.0
M8	81	0.16	5.0×10^5	1.1	37	0.52	7.0×10^4	1.0	44	0.70	6.3×10^4	2.0
M9	88	0.16	5.5×10^5	1.0	41	0.47	8.8×10^4	0.9	43	0.70	6.1×10^4	1.6
M10	81	0.18	4.5×10^5	1.7	37	0.60	6.1×10^4	1.6	44	1.06	4.2×10^4	3.1
M11	67	0.18	3.7×10^5	1.1	27	0.76	3.5×10^4	0.9	47	1.35	3.5×10^4	2.6
M12	60	0.16	3.9×10^5	1.0	26	0.90	2.9×10^4	0.9	69	2.17	3.2×10^4	3.9
Average	75	0.24	3.4×10^5		30	0.42	9.1×10^4		38	0.80	5.4×10^4	

| Sampling locations	Concentrations of heavy metals in sediment (ppm) and water (ppb) and their Kd value and EF value														
	Zn				Cd				Pb				Distance to the Spring (km)	pH	DOC (mg/L)
	Sediment (ppm)	Water (ppb)	Kd	EF	Sediment (ppm)	Water (ppb)	Kd	EF	Sediment (ppm)	Water (ppb)	Kd	EF			
M1	76	0.12	6.3×10^5	1.4	0.2	0.01	2.4×10^4	2.5	23	0.01	2.0×10^6	1.7	831	8.57	2.7
M2	78	0.33	2.4×10^5	2.6	0.2	0.00	3.4×10^4	4.0	18	0.07	2.4×10^5	2.3	833	8.44	1.5
M3	48	0.20	2.4×10^5	2.1	0.2	0.01	3.6×10^4	7.3	13	0.02	7.6×10^5	2.1	1032	7.86	2.3
M4	133	0.23	5.8×10^5	3.1	1.4	0.02	8.9×10^4	23.9	31	0.03	1.1×10^6	2.8	1442	7.91	2.3
M5	179	0.42	4.3×10^5	4.2	2.7	0.02	1.2×10^5	48.3	42	0.03	1.3×10^6	3.9	1469	7.88	2.4
M6	131	1.09	1.2×10^5	4.8	1.3	0.03	5.1×10^4	36.2	50	0.06	8.9×10^5	7.1	1581	7.90	4.2
M7	151	0.32	4.8×10^5	4.3	1.6	0.02	8.5×10^4	35.0	42	0.02	2.7×10^6	4.8	1594	7.88	4.2
M8	226	0.85	2.7×10^5	4.3	2.5	0.03	9.7×10^4	35.5	67	0.02	4.0×10^6	5.0	1754	7.59	4.1
M9	259	0.31	8.5×10^5	4.1	2.5	0.02	1.4×10^5	29.9	61	0.02	3.1×10^6	3.8	1780	7.69	3.3
M10	226	0.37	6.1×10^5	6.7	2.3	0.02	9.9×10^4	50.0	57	0.01	7.0×10^6	6.7	1959	7.48	3.6
M11	215	0.84	2.6×10^5	4.9	1.8	0.04	4.9×10^4	30.8	73	0.02	3.8×10^6	6.6	1982	7.50	4.2
M12	217	2.31	9.4×10^4	5.2	3.3	0.10	3.4×10^4	59.1	95	0.08	1.2×10^6	8.9	2033	7.22	19.9
Average	162	0.62	4.0×10^5		1.7	0.03	7.1×10^4		47	0.03	2.3×10^6				
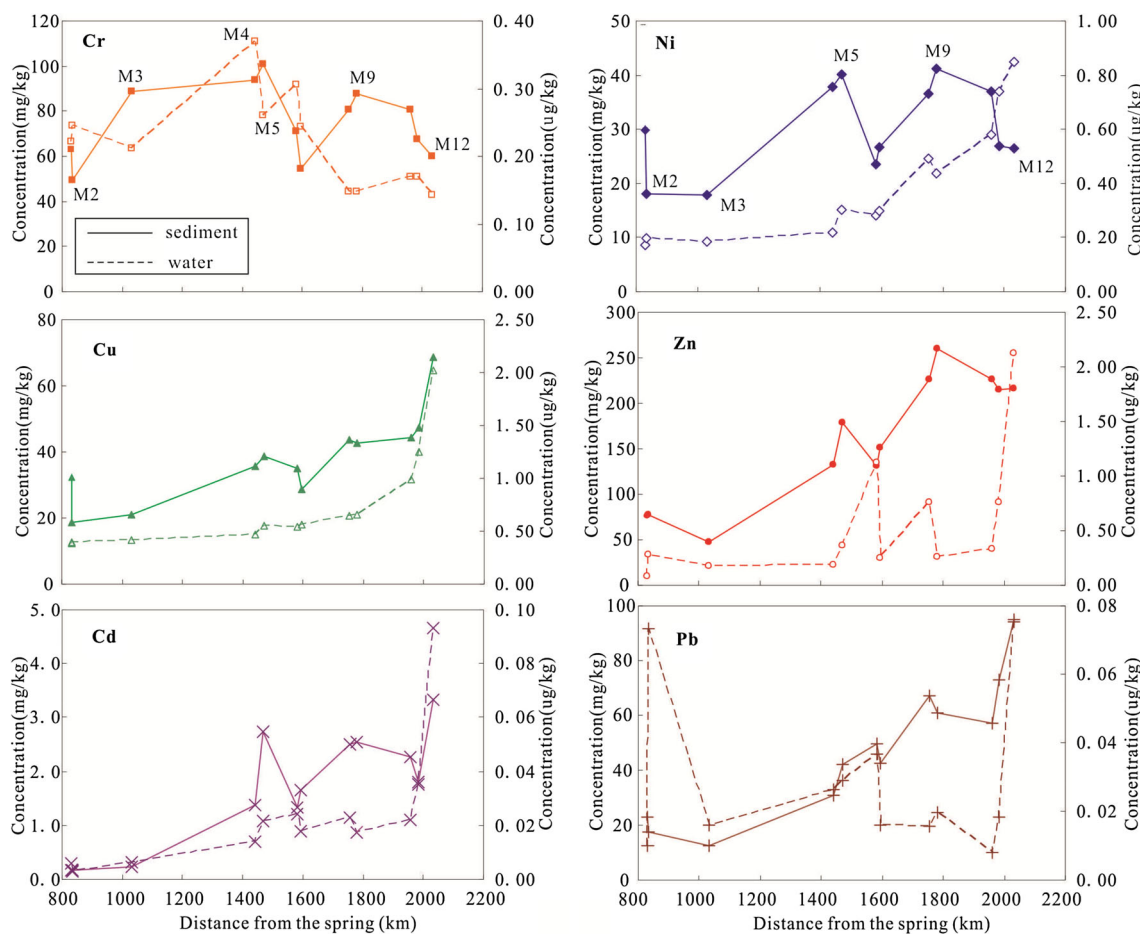
Fig. 2 Heavy metal contents of water and sediments in the Pearl River, southern China

confluence of the Beijiang River (M11) and at the estuary (M12) (Fig. 2). Of particular interest was that the Pb concentration showed a peak after the effluent Beipanjiang River (M2). These variations likely indicated the direct impact of tributary input on metal concentrations.

Concentration in sediments The total concentrations of heavy metals in sediments ranged from 48 to 259 mg/kg (average: 162 mg/kg) for Zn, from 49 to 101 mg/kg (average: 75 mg/kg) for Cr, from 13 to 95 mg/kg (average: 47 mg/kg) for Pb, from 19 to 69 mg/kg (average: 38 mg/kg) for Cu, from 18 to 41 mg/kg (average: 30 mg/kg) for Ni, and from 0.2 to 3.3 mg/kg (average: 1.67 mg/kg) for Cd in the Pearl River Basin. This result was consistent with the values reported in Xiong et al. (2017) on the Nanpan River in the upper reaches of the Pearl River and Cai et al. (2016) on Shunde waterways in the lower reaches of the Pearl River. Individual samples or the averages in the watershed systematically exhibited lower values than previous studies (Xiong et al. 2017; Cai et al. 2016; Niu et al. 2009; Liu et al. 2017; Xie et al. 2012; Yang et al. 2017a, b; Zhu and Wang 2012) (Table 2). These values were higher relative to the average values in the upper continental crust

(UCC) (Rudnick and Gao 2003), with the exception for Cr and Ni.

The spatial distribution of heavy metals in the sediments of the Pearl River Basin (Fig. 2) showed that from upstream to downstream (M1 to M12), the concentration of Cu, Zn, Cd, and Pb gradually increased, while those of Cr and Ni generally remained constant.

3.2 Enrichment factor (EF) of heavy metals in sediments

There were different factors that potentially influenced the enrichment or depletion of trace elements in river sediments (Chen et al. 2014). The enrichment factor (EF) was widely used to discriminate between anthropogenic and natural sources and to reflect the extent of environmental contamination (Zhao et al. 2017; Viers and Dupre 2009). In this study, the EF was calculated by comparing with UCC according to:

$$EF(X) = (X/Al)_{sample}/(X/Al)_{UCC} \tag{2}$$

where X was the concentration of interest element (Cr, Ni, Cu, Zn, Cd and Pb), using Al for normalization here. The concentrations of Zn, Cu, Cd, and Pb in the sediments were higher relative to the average values in the upper continental crust (UCC; Rudnick and Gao 2003), with the EF values increasing from upstream to downstream. The concentrations of Cr and Ni in the sediments are generally comparable to the average values in the upper continental crust, with the EF values remaining constant from upstream to downstream. Overall, most heavy metals have enrichment factors (EF) over 1 (Table 1).

3.3 Speciation distributions of heavy metals in sediments

The distribution of six heavy metals in different fractions of sediments was shown in Fig. 3. Cr, Ni, Cu, and Zn were mainly distributed in residual fraction, with the proportion of 73%–88%, 59%–67%, 36%–68%, and 33%–66%, respectively. The proportion of residual fraction decreased gradually from upstream to downstream, meanwhile the total proportion of exchangeable fraction, reducible fraction, and oxidizable fraction increased gradually downstream for Ni, Cu, Zn, and Cd. However, the total concentrations of these four elements in the residual fraction did not decrease significantly downstream (Table 3), and therefore the decreasing proportion of residual fraction was probably caused by the increased presence of metals in the other three fractions.

The proportions of non-residual fraction of elements in sediments showed large variation towards downstream, with the order of Pb (84.2%) > Cd (82.2%) > Zn (34.3%) > Ni (32.6%) > Cu (32.0%) > Cr (14.6%) in the upstream, of Cd (94.7%) > Pb (81.1%) > Zn (65.6%) > Cu (47.4%) > Ni (39.4%) > Cr (11.8%) in the midstream, and of Cd (96.0%) > Pb (83.7%) > Zn (67.5%) > Cu (63.6%) > Ni (40.6%) > Cr (27.4%) in the downstream of the Pearl River, respectively (Fig. 3). According to these values, Cd, Pb, and to a lesser extent Zn and Cu in the sediments were more active at midstream and downstream than upstream with a clearly increasing proportion of non-residual fractions.

4 Discussion

4.1 Potential sources of heavy metals in the Pearl River

The spatial concentration variations and relatively lower enrichment factors (< 2) of Cr and Ni were suggested to be mainly controlled by natural processes rather than anthropogenic contribution. The Pb, Cd, Zn, and Cu, however, were suggested to be dominantly enriched by anthropogenic activities, as they displayed much higher enrichment factors (> 1.5) toward downstream (Fig. 4). The enrichment of these heavy metals could be attributed to the importing of the tributaries, including the Liujiang River,

Table 2 Local and regional comparison of heavy metal contents in surface sediments of Pearl River Basin with other studies

| Sampling locations	Cr (mg/kg)	Ni (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	Cd (mg/kg)	Pb (mg/kg)	References
Local comparison							
Nanpan River	150	–	80	239	4.52	101	Xiong et al. (2017)
Nanpan River	58.7	25.6	28.3	69.3	0.51	16.6	Liu et al. (2017)
M1 (Nanpan River)	63	30	32	76	0.18	23	This study
Sanshui	131	69	100	525	26.07	136	Xie et al. (2012)
Jiujiang	124	53	62	441	6.29	78	Xie et al. (2012)
M11 (Sanshui)	67	27	47	215	1.81	73	This study
Shunde	111	30	98	312	1.72	92	Cai et al. (2016)
Shunde	130	69	178	810	36.23	458	Xie et al. (2012)
Guagnzhou	93	–	348	383	1.72	103	Niu et al. (2009)
Background of Guagnzhou	35	–	16	55	0.72	37	Niu et al. (2009)
M12 (Shunde)	60	26	69	217	3.32	95	This study
Regional comparison							
Average	–	41	86	213	3.82	79	Yang et al. (2017a, b)
Average	73	–	87	222	2.34	78	Zhu and Wang (2012)
Upper continental crust	92	47	28	67	0.09	17	Rudnick and Gao (2003)
Average	75	30	38	162	1.67	47	This study
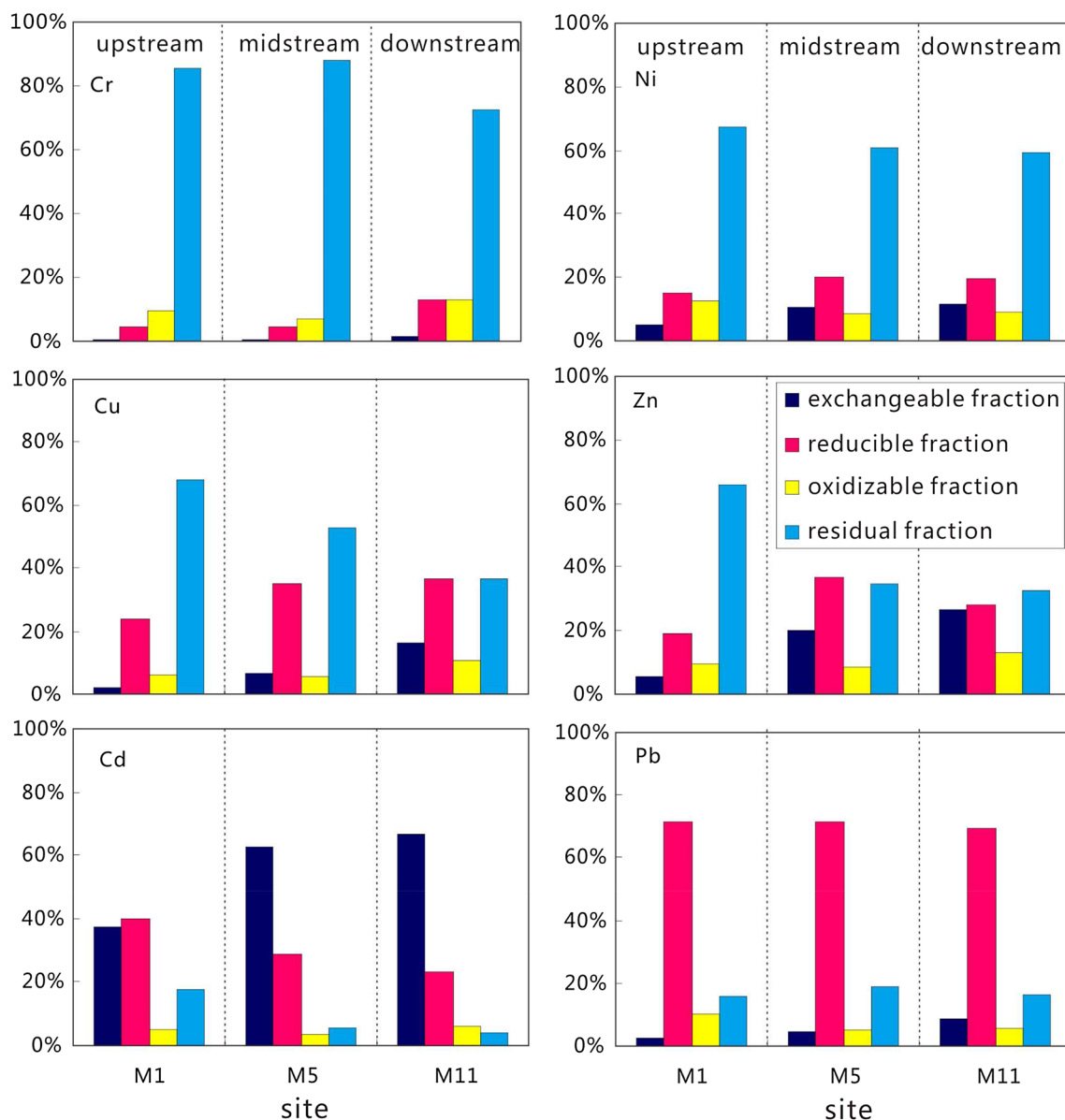
Fig. 3 Distribution of heavy metals in different chemical fractions in the sediments of the Pearl River, southern China

Guijiang River, Hejiang River, and Beijiang River, where a large amount of the mining and chemical industries and concentrated (Zhou et al. 2013; Dang et al. 2016; Ning et al. 2017; Wang et al. 2014; He et al. 2015; Xu et al. 2009). Although the main bedrock lithology in the basin changed from carbonate to silicate after M4 (Fig. 1), which would partially explain the Cr and Ni budgets in the Pearl River sediments, this lithological contribution with an increase of clay minerals (from silicate bedrocks) would be limited to the other four metals as they have much higher enrichment factors relative to the UCC (Rudnick and Gao 2003) (Fig. 4) which indeed was mainly composed of silicates (Gaillardet et al. 2003; Chen et al. 2014). The abrupt increase of several metals [e.g. EF (Cr) = 2.8 at the

sampling point M3] likely indicated a local contamination or a tributary contribution into the river section (Fig. 4).

The results of Pearson correlation analysis showed that Cr was only positively correlated with Ni, and there was no significant correlation between Cr and other elements (Table 4; Fig. 5). Cu, Zn, Cd, and Pb elements in sediments were significantly positively correlated (Table 4; Fig. 5), and their contents increased gradually from upstream to downstream, suggesting that these elements may be controlled by the same sources or processes. In fact, as discussed in the following section, Cu, Zn, Cd, and Pb were all byproducts of current mining and industrial activities, and their gradual increase downstream probably

Table 3 Results of sequential extraction of heavy metal in surface sediments

| Heavy metals	Sampling locations	F1	F2	F3	F4	∑(F1 + F2 + F3 + F4)	Sample amount for sequential extraction (g)	Total digestion	Sample amount for total digestion (g)	Recovery rate (%)	Proportion of F1 (%)	Proportion of F2 (%)	Proportion of F3 (%)	Proportion of F4 (%)
Cr (ng)	M1	39	375	782	6986	8183	0.25	2285	0.05	73	0.5	4.6	9.6	85.4
	M5	61	704	1097	13,856	15,718	0.25	4367	0.05	72	0.4	4.5	7.0	88.2
	M11	137	1290	1312	7265	10,004	0.25	2702	0.05	74	1.4	12.9	13.1	72.6
Ni (ng)	M1	222	672	546	2983	4423	0.25	1061	0.05	85	5.0	15.2	12.3	67.4
	M5	761	1473	635	4404	7273	0.25	1420	0.05	102	10.5	20.3	8.7	60.6
	M11	590	990	463	2987	5029	0.25	1074	0.05	93	11.7	19.7	9.2	59.4
Cu (ng)	M1	106	1174	290	3342	4913	0.25	1221	0.05	82	2.2	23.9	5.9	68.0
	M5	517	2688	419	4019	7644	0.25	1441	0.05	106	6.8	35.2	5.5	52.6
	M11	1601	3556	1024	3536	9717	0.25	1917	0.05	101	16.5	36.6	10.5	36.4
Zn (ng)	M1	569	2076	1050	7062	10,757	0.25	2750	0.05	79	5.3	19.3	9.8	65.7
	M5	7078	12,771	2992	11,994	34,836	0.25	7808	0.05	89	20.3	36.7	8.6	34.4
	M11	9797	10,376	4746	12,001	36,920	0.25	6816	0.05	108	26.5	28.1	12.9	32.5
Cd (ng)	M1	16	18	2	8	44	0.25	9	0.05	98	37.2	40.0	5.1	17.8
	M5	431	199	23	37	690	0.25	138	0.05	101	62.4	28.9	3.4	5.3
	M11	323	112	31	19	485	0.25	91	0.05	107	66.6	23.2	6.3	4.0
Pb (ng)	M1	109	3402	496	752	4760	0.25	982	0.05	99	2.3	71.5	10.4	15.8
	M5	415	6544	470	1728	9158	0.25	2101	0.05	87	4.5	71.5	5.1	18.9
	M11	1471	11,717	908	2740	16,835	0.25	3658	0.05	92	8.7	69.6	5.4	16.3
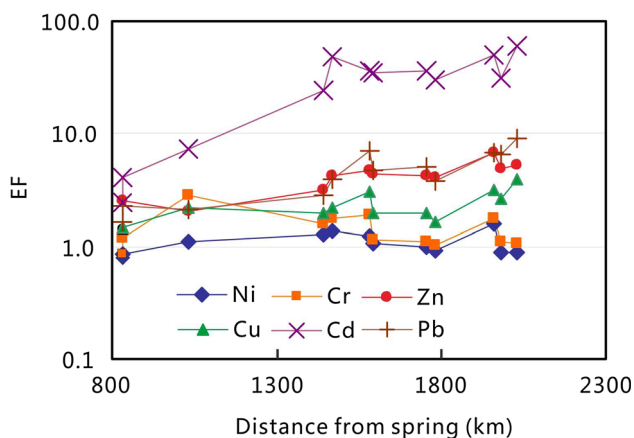
Fig. 4 Spatial variation of enrichment factors (EF) of heavy metals in the Pearl River, southern China

indicated an increase of such anthropogenic input (Wen et al. 2013).

4.2 Partitioning of metals between dissolved and particulate loads

The solid-solution-interaction of heavy metals can be described in terms of partition coefficient K_d, which is defined as the ratio of the adsorbed and/or the total particulate concentration (C_s) to the dissolved concentration (C_w) of the same chemical component (Benoit and Rozan 1999; Fu et al. 2013), and was qualitatively used for investigating the distribution of heavy metals between water and particulate. Some researchers have described K_d as an important physicochemical characteristic parameter of heavy metal pollution in water environment (Li et al.

2011; Benoit and Rozan 1999). Under the physical and chemical conditions of natural rivers, the partition coefficient of heavy metals between water and particulate could potentially be used to assess the migration ability and the potential ecological effects that ensue (Chen and Zhou 1992). Though heavy metals are principally accumulated and transported in sediments in river systems (Chen et al. 2014; Deng et al. 2017; Xu et al. 2009), dissolved metals (including colloidal form) are more bioavailable and thus potentially display much direct environmental effect. The partition coefficient of a metal can be calculated as follows:

$$Kd = \frac{Cs}{Cw} \qquad (3)$$

where C_s (mg·kg^{-1}) was elemental concentration of solid phase and C_w (mg·L^{-1}) was the total concentration remaining in water at equilibrium.

The mean partitioning coefficients of Cr, Ni, Cu, Zn, Cd, and Pb in the Pearl River were 3.4×10^5, 9.1×10^4, 5.4×10^4, 4.0×10^5, 7.1×10^4 and 2.3×10^6, respectively (Table 1). The ranges of K_d for each element were consistent with the results reported for the upper reaches of the Xijiang River (Liu et al. 2017). Similar findings were also reported for the Seine River Basin in France (Chen et al. 2009). The high partition coefficients (e.g. above 10^5) indicated that the elements migrated mainly in the form of particulate phase, while the relatively lower values (e.g. below 10^4) would suggest that the transportation in dissolved phase is becoming more important (Guéguen and Dominik 2003). A comparison of the range of the partition coefficients for the six investigated metals was illustrated in Fig. 6. The partition coefficient of Cr, Zn, and Pb varied from 1.9×10^5 to 5.5×10^5, 9.4×10^4 to 8.5×10^5 and

Table 4 The results of Pearson correlation analysis between heavy metals in the Pearl River Basin

	Cr	Ni	Cu	Zn	Cd	Pb
Pearson correlation coefficient of heavy metal elements in sediments (n = 12)						
Cr	1					
Ni	.637*	1				
Cu	0.046	0.392	1			
Zn	0.209	.664*	.765**	1		
Cd	0.283	.616*	.835**	0.896	1*	
Pb	− 0.076	0.313	.931**	0.859	0.857	1**
Pearson correlation coefficient of heavy metal elements in water (n = 12)						
Cr	1					
Ni	− .673*	1				
Cu	− 0.546	.934**	1			
Zn	− 0.312	.716**	.830**	1		
Cd	− 0.407	.828**	.947**	.926**	1	
Pb	0.045	0.193	0.4	.595*	0.498	1

*Correlation is significant at the 0.01 level

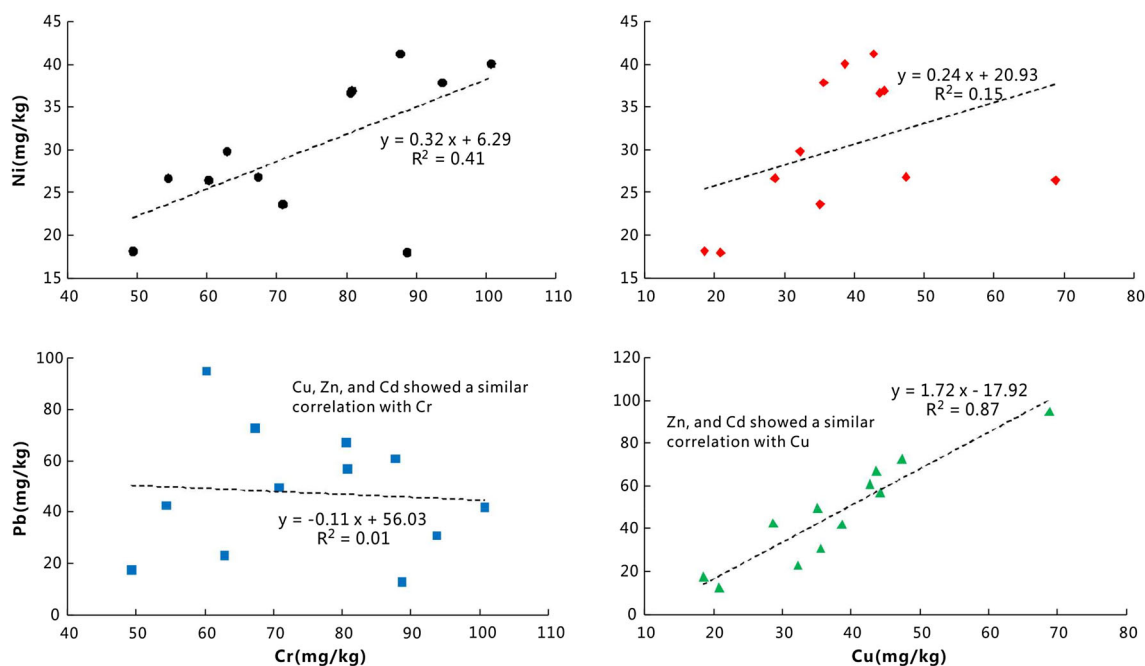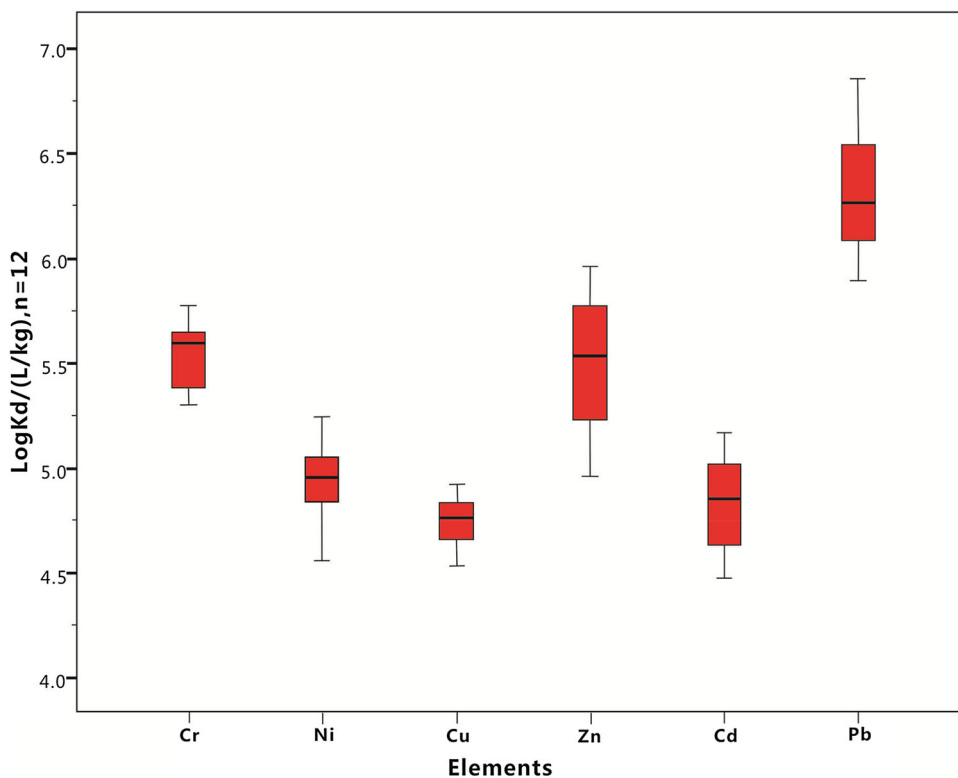**Correlation is significant at the 0.01 level

Fig. 5 Relationship between heavy metals in the Pearl River, southern China

Fig. 6 Diagrams showing partition coefficients of heavy metals in the Pearl River, southern China

2.4×10^5 to 7.0×10^6, respectively, indicating that these three metals were more concentrated (and migrated) in particles, compared to the other three metals Ni, Cu, and Cd, whose partition coefficients ranged from 2.9×10^4 to

1.7×10^5, 3.2×10^4 to 8.0×10^4 and 2.4×10^4 to 1.4×10^5, respectively.

The partitioning coefficients showed large variations for single elements, and even some interesting trends with water pH (Fig. 7), which may be caused by either the

Fig. 7 Relationship between partition coefficients of heavy metals and the pH values in the Pearl River, southern China
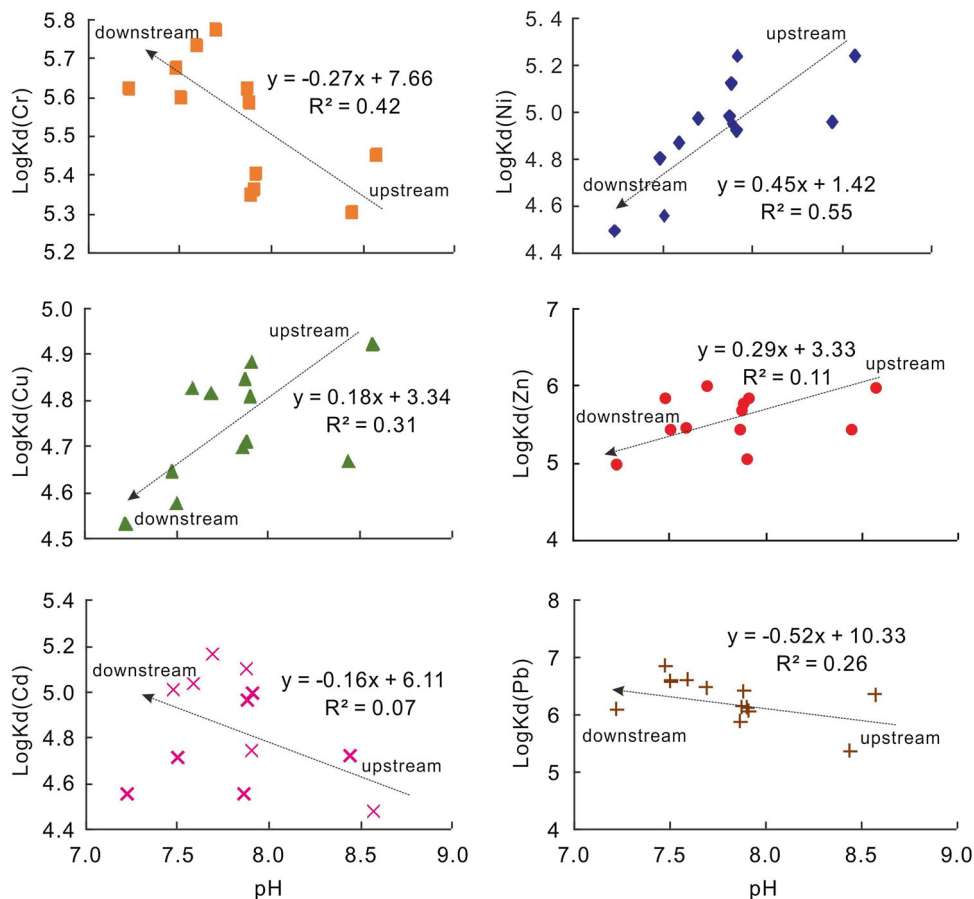
change in source contribution or in situ exchange processes triggered by, for example, biological processes or adsorption/precipitation characteristics of sediments directly or indirectly controlled by pH. From upstream to downstream, the K_d values of Cr increased gradually as the pH decreased, showing a significant negative correlation with pH, whereas K_d values of Ni and Cu clearly decreased with pH from upstream to downstream, indicating particulate forms were favored at high pH for those two metals. The K_d value of Zn, Cd, and Pb remained almost constant from upstream to downstream and showed no correlation with pH. These distinct variation trends suggested that, under acid conditions, Cr would be enriched in sediment toward downstream, whereas particulate Ni and Cu may gradually decrease.

From upstream to downstream, the DOC (Table 1) generally showed an increasing trend. However, Zn, as an essential nutrient for organisms, did not display a corresponding variation in its K_d value, thus excluding the influence of biological processes on metal K_d changes. The element partitioning may be also influenced by river water pH. In fact, all waters displayed a gradual decrease of the pH downstream (Fig. 7), resulting from either the major lithology change from carbonate in the upper reaches to

silicates in the lower reaches, or most likely the increasing contribution of anthropogenic inputs (e.g. mining wastes, waste waters, industrial discharges) with relatively low pH (Cong and Zhao 2003). As acid condition was not conducive for metal adsorption, and under low pH condition heavy metals in the particles would be readily released into the water, resulting in a lower K_d value. Therefore, the adsorption may impact K_d and thus partially explain the K_d trend with pH, at least for metals Ni or Cu. However, the different trends illustrated by other metals would suggest that such in situ exchange effect was not dominant Though further systematic study is needed to better assess the mechanisms causing the change of metal distribution with pH downstream the Pearl River, our results showed that (see the above discussion) the upstream–downstream variation of metal partitioning was likely derived from the contribution of different sources.

4.3 Distributions of heavy metals amongst solid phases and the potential ecological effects

Although the contents of heavy metals in the Pearl River water were classified as human drinking water reference (I) according to the environmental quality standards for

surface water (GB 3838-2002), and the heavy metal contents in the sediment were also below the aquatic sediment quality guidelines (Chen et al. 2001), heavy metals contained in sediment particles could be released into the overlying water again under certain conditions, forming "secondary pollution," which is also likely to be potentially harmful to the riverine ecosystem. From the above analysis results it was clear that heavy metals were transported in the Pearl River mainly in solid phase, with mean K_d range from 5.4×10^4 to 2.3×10^6. However, not all heavy metals contained in sediments have an environmental impact; it depended on their chemical speciation/ fraction. In the following section we further discuss the distribution of heavy metals in different sediment fractions with a goal of elucidating the proportion of adsorbed metals and their ecological effects.

In the four chemical fractions derived from our BCR experiments, the metals in exchangeable fraction were much more active and thus easily uptaken by biota, especially when the acidity changed. The reducible fraction referred to metals in the oxides, and the elements of oxidizable fraction were mainly bound to sulfides or organic matter. The fact that the heavy metals in these two fractions can be indirectly assimilated by organisms indicated a relatively weak migration potential and environmental effects compared to the first fraction (Hu et al. 2014). In the residual fraction, metal was considered to be a component of the crystal lattice of minerals, and was thus not bioavailable and had a poor environmental mobility (Zhang et al. 2017). Therefore, the distributions of elements in variable chemical fractions of sediments were pivotal for assessing the potential biological toxicity and environmental impact of heavy metals in aquatic ecosystems (Islam et al. 2015).

The exchangeable fraction mostly referred to metals adsorbed onto sediments (Zhang et al. 2017). In this study, all six metals showed an increase proportion of exchangeable species downstream (Fig. 3), contrasted with the downstream pH decrease that would strengthen adsorption effect. This indicated that the K_d variation was not mainly derived from riverine adsorption. Moreover, except for Cr, the exchangeable fraction of the other five metals was relatively low (< 20% for Zn and Cu and even < 10% for Ni, Cr, and Pb), confirming again the limited impact of adsorption on particulate metal budget.

Cr and Ni were mainly distributed in the residual fraction, and their proportion remained quasi constant from upstream to downstream. This suggested that the distribution of Cr and Ni were relatively insensitive to the variation of surrounding conditions (Nemati et al. 2011). The extremely low proportion of Cr in non-residual fraction in all samples may be resulted from the refractory behavior of Cr during surface weathering processes and its inability to

form precipitate or complex with carbonates or Fe/Mn oxide-hydroxide (Sundaray et al. 2011).

The proportion of Cu in residual fraction decreased from upstream to downstream, whereas the proportion of non-residual fractions increased from upstream to downstream. This suggested that Cu became more mobile and bioavailable in the middle and downstream. In contrast to the residual fraction, the reducible fraction and both other fractions of Cu became more important downstream. The decrease trend of K_d would thus mainly be controlled by the decline of Cu in residual phase. Therefore, the change of Cu K_d and its distribution among chemical fractions were not mainly affected by the pH, but may be influenced by the sources.

Similar to Cu, except for the residual fraction, the reducible phase was another important Zn carrier in river sediment. This result was consistent with previous observations (Li et al. 2001; Yu et al. 2010) that Fe/Mn oxides might be an important transporter of metals. Zn (and Cu) bounded to Fe/Mn oxides may be explained by the fact that the amorphous sesquioxides have a greater ability to adsorb and retain heavy metals such as Zn onto their specific surface area (Ahdy and Youssef 2011). The similarity between the atomic radius of Zn and Fe made the above exchange possible (Ahdy and Youssef 2011). Zn in the exchangeable fraction could be interpreted by its co-precipitation with the carbonates due to similar mineral structure and ionic radius of Zn and Ca (Crocket and Winchester. 1966) and Zn associated with calcite (either tetrahedrally coordinated Zn (II) adsorbed at the calcite surface or octahedrally coordinated Zn (II) incorporated in the calcite structure) was reported (Priadi et al. 2011). Parts of Zn were carried by sulfide, which was consistent with previous research (Qiao et al. 2013). The occurrence of significant quantities of Zn sulfide in suspended matter was also proved in the anthropogenically impacted Seine River (Priadi et al. 2011; Chen et al. 2014). Carbonates may be derived from natural processes prior to joining the river system in the basin, but sulfide was likely input by human activities (Liu et al. 2017; Deng et al. 2017).

Interestingly, Cd was mainly distributed in exchangeable fraction and reducible fraction, with the proportion of 37%–67% and 23%–40%, respectively. However, the proportion of reducible fraction decreased gradually from upstream to downstream, whereas the proportion of exchangeable fraction increased significantly toward downstream. Two mechanisms may be responsible for this variation: (1) Cd has special affinity with carbonates and would precipitate simultaneously with the carbonate minerals at alkaline environments/high pH (Ahdy and Youssef 2011), and (2) Cd has special geochemical characteristics on the Earth's surface: it exists in the form of sulphide when the environmental is reduced, and in the form of

oxides in the strong oxidation environment. The Cd oxide is easily oxidized to $CdSO_4$ and then transferred into aqueous solution in the strong oxidation environment (Yang et al. 2016a, b, c). In this study, the increasing percentage of exchangeable fraction was considered to be only affected by the source, because the downstream environment was weaker in oxidation from the perspective of the distribution of reducible fraction; therefore, Cd was easier to convert from oxide to sulfide under these circumstances. In weak oxidation environment in the middle and lower reaches, Cd was difficult to oxidize from an oxidizable fraction to a reducible fraction or even to $CdSO_4$ and then co-precipitated with carbonate in the form of ions. Finally, as discussed above, it was concluded that the increase in the exchangeable fraction was affected by the source rather than the transition from other fractions caused by changes in redox conditions in the river system. The global enrichment of Cd in the surface soil layer of the whole basin would be an important contributor (Li et al. 2007; Zhen et al. 2016). Furthermore, the proportion of Cd in residual fraction decreased gradually from upstream to downstream, indicating that Cd in the downstream was more prone to migrating and had thus higher pollution potential for aqueous environments.

Pb was mainly distributed in reducible fraction, which accounted for 70%–71% of total Pb. Residual fraction accounted only for 16%–19%. In fact, Pb could easily form stable complexes with Fe and Mn oxides. Pb could not only adsorb to manganese and iron during oxide/hydroxide co-precipitation, but also interact with Fe or with itself to form a stable and solid compound (Zhang et al. 2017). Therefore, it could explain the relatively high proportion of reducible Pb.

In summary, Cd and Pb have the strongest geochemical mobility among the six heavy metals analyzed in the Pearl River, and may bring potential ecological and biological risks once the river conditions change. At the opposite side of the spectrum, the geochemical activities of Cr and Ni were the weakest and have the weakest environmental effect.

5 Conclusions

In this study, the distribution of six anthropophile elements (Cr, Ni, Cu, Zn, Cd, and Pb) was investigated based on the concentration measurement and the modified BCR leaching experiments with a goal to evaluate the potential ecological and biological risks induced by these heavy metals in the Pearl River. Except for Cr, the content of other metals in water gradually increases from upstream to downstream, and the fluctuation of concentration clearly indicates that the concentration is affected by the tributary

remittance. The fact that the contents of Cu, Zn, Cd, and Pb in sediments increased gradually downstream and their relatively higher enrichment factors suggested an increasing anthropogenic contribution derived from human activities, such as mining and industry. The relative constant variations of Cr and Ni concentrations (and thus EFs) would indicate a main natural contribution (e.g. by weathering processes) rather than anthropogenic input. All metals displayed higher partition coefficients (K_d) between sediment and water (in the range of 10^4–10^6), indicating that they were mainly transported in solid form. The relatively lower K_d values for Ni, Cu, and Cd (in the range of 10^4–10^5) implied a more potential ecological risk effect of these metals, as their dissolved phases are more important. The large ranges and geographical variations of K_d for these six metals were likely caused by the contribution of different sources rather than in situ exchange processes. Our results showed that K_d values of Cr continuously increased from upstream to downstream; conversely, Ni and Cu decreased toward downstream, whereas Zn, Cd, and Pb remained almost constant. Our BCR experiments demonstrated that Cr, Ni, Cu, and Zn were mostly concentrated in residual fraction, while Cd was mainly in exchangeable fraction and Pb in reducible fraction. Except for Pb, the proportion of non-residual fractions for metals Cr, Ni, Cu, Zn, and Cd increased towards downstream, implying increasing biogeochemical mobility and potential environmental effects of these metals in the lower Peal River reaches, a region with high population and important economic activities. Though systematic work is needed to better identify the exact contributing sources and mechanisms controlling the exchange of metals among different riverine phases, our study clearly demonstrated that the distribution and partitioning should be taken into account when investigating the geochemistry of metals and their potential ecological effects in a river system.

References

Ahdy HHH, Youssef DH (2011) Fractionation analysis of some heavy metals in sediments of the north-western part of the Red Sea, Egypt. Chem Ecol 27:427–443

Benoit G, Rozan TF (1999) The influence of size distribution on the particle concentration effect and trace metal partitioning in rivers. Geochimica et Cosmochimica Acta 63(1):113–127

Cai YM, Chen WP, Peng C, Wang TY, Xiao RB (2016) Spatial distribution and potential ecological assessment of heavy metals

in soil and sediments in Shunde waterway. Environ Sci 37:1763–1770 (in Chinese with English abstract)

Chen JS, Zhou JY (1992) Research on heavy metal pollution in the water environment of China. China Enviromental Science Press, Beijing

Chen JS, Wang LX, Hong S, Fan WH (2001) The difference and the cause analyses of the aquatic sediment quality guidelines for heavy metals. Environ Chem 05:417–424

Chen JB, Gaillardet J, Louvat P, Huon S (2009) Zn isotopes in the suspended load of the Seine River, France: isotopic variations and source determination. Geochim Cosmochim Acta 73:4060–4076

Chen JB, Gaillardet J, Bouchez J, Louvat P, Wang YN (2014) Anthropophile elements in river sediments: overview from the Seine River, France. Geochem Geophys Geosyst 15:4526–4546

Cong ZY, Zhao FH (2003) Current situation and prospect of the research on acid mine drainage. China Min Mag 03:15–18

Crocket JH, Winchester JW (1966) Coprecipitation of zinc with calcium carbonate. Geochim Cosmochim Acta 30(10):1093–1109

Dang YF, Zhao YL, Deng R, Liang YJ (2016) Investigation and source analysis of heavy metal pollution of Duliujiang River. GUANGDONG WEILIANG YUANSU KEXUE 23:12–19

Deng QC, Wang XF, Yin J, Deng CB (2017) Spatial distribution and source analysis of heavy metals in sediments of the upstream Xijiang Basin within nonferrous metal accumulation areas. Res Environ Sci 30:1221–1229 (in Chinese)

Dupre B, Gaillardet J, Rousseau D, Allegre CJ (1996) Major and trace elements of river-borne material: the Congo Basin. Geochim Cosmochim Acta 60:1301–1321

Fan X, Cui B, Zhao H, Zhang Z, Zhang H (2010) Assessment of river water quality in Pearl River Delta using multivariate statistical techniques. Proc Environ Scis 2:1220–1234

Fu J, Tang XL, Zhang J, Balzer W (2013) Estuarine modification of dissolved and particulate trace metals in major rivers of East-Hainan, China. Cont Shelf Res 57:59–72

Gaillardet J, Dupre B, Allegre CJ, Negrel P (1997) Chemical and physical denudation in the Amazon River Basin. Chem Geol 142:141–173

Gaillardet J, Viers J, Dupre B (2003) Trace elements in river waters. Treatise Geochem 5:225–272

Guéguen C, Dominik J (2003) Partitioning of trace metals between particulate, colloidal and truly dissolved fractions in a polluted river: the Upper Vistula River (Poland). Appl Geochem 18:457–470

Guinoiseau D, Gelabert A, Allard T, Louvat P, Moreira-Turcq P, Benedetti MF (2017) Zinc and copper behaviour at the soil-river interface: new insights by Zn and Cu isotopes in the organic-rich Rio Negro basin. Geochim Cosmochim Acta 213:178–197

Han C, Qin Y, Zheng B, Ma Y, Zhang L, Cao W (2014) Sediment quality assessment for heavy metal pollution in the Xiang-jiang River (China) with the equilibrium partitioning approach. Environ Earth Sci 72:5007–5018

He Y, Zhang Y, Zhu M (2015) The pollutant infiltration pathways and measures to control groundwater pollution in the Guijiang River drainage systems. Carsologica Sin 34:387–394 (in Chinese with English abstract)

Hu DX, Wu SR, Liu YY, Wang H, Wang XD, Li QB (2014) Determination of chemical species of cadmium, arsenic and lead in mineral yard soil by modified BCR and ICP-AES method. Rock Miner Anal 3:369–373 (in Chinese with English abstract)

Ip CCM, Li XD, Zhang G, Wai OW, Li YS (2007) Trace metal distribution in sediments of the Pearl River Estuary and the surrounding coastal area, South China. Environ Pollut 147:311–323

Islam MS, Ahmed MK, Raknuzzaman M, Habibullah-Al-mamun M, Islam MK (2015) Heavy metal pollution in surface water and sediment: a preliminary assessment of an urban river in a developing country. Ecol Ind 48:282–291

Li XD, Shen ZG, Wai OWH, Li YS (2001) Chemical forms of Pb, Zn and Cu in the sediment profiles of the Pearl River Estuary. Mar Pollut Bull 3:215–223

Li Q, Wu Z, Chu B, Zhang N, Cai S, Fang J (2007) Heavy metals in coastal wetland sediments of the Pearl River Estuary, China. Environ Pollut 149:158–164

Li GL, Liu GJ, Jiang MM, Wang RW, Zheng LG (2011) Partition characteristics and correlation of heavy metal between sediment and surface water from Chaohu Lake. J Univ Sci Technol China 41:9–15

Li HB, Gu YG, Wang R, Lu HB (2017) Contamination, fractionation and biological risk related to metals in surface sediments from the largest deep freshwater lake in China. Arch Environ Contam Toxicol 72:78–87

Lin ZQ, Zheng JL, Huang JZ (1984) A study on the chemical forms of heavy metals in suspension in Zhujiang river. Trop Oceanol 3:50–57 (in Chinese with English abstract)

Lin CQ, Hu GR, Yu RL, Han L (2017) Speciation and ecological risk of heavy metals in surface sediments from Jiulong River. Environ Sci 38:1002–1009 (in Chinese with English abstract)

Liu JL, Feng XB, Zhu W, Li ZG, Yin RS (2011) Distribution characteristics and pollution assessments of heavy metals in Dongjiang river sediments. Chin J Ecol 30:981–986 (in Chinese with English abstract)

Liu J, Li SL, Chen JB, Zhong J, Yue FJ, Liang Y (2017) Temporal transport of major and trace elements in the upper reaches of the Xijiang River, SW China. Environ Earth Sci 76:299

Lu FH, Ni HG, Liu F, Zeng EF (2009) Occurrence of nutrients in riverine runoff of the Pearl River Delta, South China. J Hydrol 376:107–115

Meng Q, Zhang J, Zhang Z, Wu T (2016) Geochemistry of dissolved trace elements and heavy metals in the Dan River Drainage (China): distribution, sources, and water quality assessment. Environ Sci Pollut Res 23:8091–8103

Meybeck M, Lestel L, Bonté P, Moilleron R, Colin JL, Rousselot O (2007) Historical perspective of heavy metals contamination (Cd, Cr, Cu, Hg, Pb, Zn) in the seine river basin (France) following a DPSIR approach (1950-2005). Sci Total Environ 375:204–231

Nemati K, Bakar NKA, Abas MR, Sobhanzadeh E (2011) Speciation of heavy metals by modified BCR sequential extraction procedure in different depths of sediments from Sungai Buloh, Selangor, Malaysia. J Hazard Mater 192:402–410

Ning ZP, Lan XL, Huang ZY, Chen HY, Liu YZ, Xiao TF, Zhao YL (2017) Spatial distribution characteristics, sources and potential ecological risk of heavy metals in sediments of the Hejiang River. China Environ Sci 37:3036–3047

Niu H, Deng W, Wu QH, Chen X (2009) Potential toxic risk of heavy metals from sediment of the Pearl River in South China. J Environ Scis 21(8):1053–1058

Odukoya AM, Akande O (2015) Metal contamination assessment in the urban stream sediments and tributaries of coastal area southwest Nigeria. Chin J Geochem 34:431–446

Pan K, Wang WX (2012) Trace metal contamination in estuarine and coastal environments in China. Sci Total Environ 421–422:3–16

Piper DZ, Ludington S, Duval JS, Taylor HE (2006) Geochemistry of bed and suspended sediment in the Mississippi river system: provenance versus weathering and winnowing. Sci Total Environ 362:179–204

Priadi C, Bourgeault A, Ayrault S, Gourlay-France C, Tusseau-Vuillemin MH, Bonte P, Mouchel JM (2011) Spatio-temporal variability of solid, total dissolved and labile metal: passive vs.

discrete sampling evaluation in river metal monitoring. J Environ Monit 5:1470–1479

Qiao YM, Yang Y, Gu JG, Zhao JG (2013) Distribution and geochemical speciation of heavy metals in sediments from coastal area suffered rapid urbanization, a case study of Shantou Bay, China. Mar Pollut Bull 68:140–146

Quevauviller P, Rauret G, López-Sánchez JF, Rubio R, Ure A, Muntau H (1997) Certification of trace metal extractable contents in a sediment reference material (CRM 601) following a three-step sequential extraction procedure. Sci Total Environ 205(2):223–234

Rauret G, Lópezsánchez JF, Sahuquillo A, Rubio R, Davidson C, Ure A (1999) Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. J Environ Monit 1:57–61

Rudnick RL, Gao S (2003) Composition of the continental crust. In: Rudnick RL (ed) Treatise on geochemistry 3: the crust. Elsevier, Amsterdam, pp 1–64

Shiller AM (1997) Dissolved trace elements in the Mississippi river: seasonal, interannual, and decadal variability. Geochim Cosmochim Acta 61:4321–4330

Sundaray SK, Nayak BB, Lin S, Bhatta D (2011) Geochemical speciation and risk assessment of heavy metals in the river estuarine sediments—a case study: Mahanadi Basin, India. J Hazard Mater 186:1837–1846

Tang X, Duan DD, Huang W, Ran Y (2015) Distribution and partitioning of heavy metals in particulate and colloid phases in different kinds of water in the downstream Pearl River. Ecol Environ Sci 24:2017–2021 (in Chinese)

Tessier A, Campbell PGC, Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. Anal Chem 51:844–851

Viers JB, Dupre Gaillardet J (2009) Chemical composition of suspended sediments in World Rivers: new insights from a new database. Sci Total Environ 407(2):853–868

Wang ZH, Lin Q, Li CH, Huang HH, Yang ML, Gan JL et al (2004) Variation features and ecological assessment of heavy metals from Pearl River estuary. J Fish Sci China 11:214–219 (in Chinese with English abstract)

Wang SS, Cao ZM, Lan DZ, Zheng ZC, Li GH (2007) Concentration distribution and assessment of several heavy metals in sediments of west-four Pearl River Estuary. Environ Geol 55:963–975

Wang SL, Xu XR, Sun YX, Liu JL, Li BH (2013) Heavy metal pollution in coastal areas of South China: a review. Mar Pollut Bull 76:7–15

Wang SP, Wang YH, Zhang RJ, Xu DQ (2014) Spatial variation and source analysis of heavy metals in surface sediments of the Hejiang River, China. Appl Mech Mater 522–524:71–74

Wang J, Liu GJ, Lu LL, Liu HQ (2016) Metal distribution and bioavailability in surface sediments from the Huaihe River, Anhui, China. Environ Monit Assess 188:1–13

Wen YB, Yang ZF, Xia XQ (2013) Dissolved and particulate zinc and nickel in the Yangtze River (China): distribution, sources and fluxes. Appl Geochem 31:199–208

Wu QH, Zhou HC, Tam NFY, Tian Y, Tan Y, Zhou S et al (2016) Contamination, toxicity and speciation of heavy metals in an industrialized urban river: implications for the dispersal of heavy metals. Mar Pollut Bull 104:153–161

Xie WP, Wang SB, Zhu XP, Chen KC, Pan DB, Hong XY et al (2012) Residues and potential ecological risk assessment of metal in sediments from lower reaches and estuary of Pearl River. Environ Sci 33:1808–1815 (in Chinese with English abstract)

Xiong Y, Ning ZP, Liu YZ, ZhaoYL WuSL, Liu W (2017) Distribution and Pollution Evaluation of Heavy Metals in Sediments in the Nanpan River Basin (Yunnan Section). Earth Environ 45:171–178

Xu ZC, Yang XY, Wen Y, Chen GH, Fang JD (2009) Evaluation of the heavy metals contamination and its ecological risk of the sediments in Beijiang River's upper and middle reaches. Environ Sci 30:3262–3268 (in Chinese with English abstract)

Yang F, Hao ZH, Zhang SY, Liu HZ, Wang CW, Ling QC (2016a) Environment geochemistry of heavy metals in the alluvial soils of Yangtze River in Wuhan city. Acta Geol Sin 90:1955–1964 (in Chinese with English abstract)

Yang QL, Hu GR, Yu RL, He HX, Lin CQ (2016b) Distribution, fractionation, and contamination assessment of heavy metals in offshore surface sediments from western Xiamen Bay, China. Acta Geochimica 35:355–367

Yang SL, Zhao N, Zhou DQ, Wei R, Yang B, Pan B (2016c) The concentration and chemical speciation of arsenic in the Nanpan River, the upstream of the Pearl River, China. Environ Sci Pollut Res 23:6451–6458

Yang JX, Zhang YF, Zhu LY (2017a) Pollution and risk assessment of typical heavy metals in river sediments of seven major watershed in China. Res Environ Sci 30:423–432 (in Chinese with English abstract)

Yang SL, Zhao N, Wang DW, Lu M, Yang B (2017b) Multi-media Behavior of Pb and Zn in Nanpan River, Upstream of Pearl River, China. Southwest China J Agric Sci 30:1619–1624

Yu XJ, Yan Y, Wang WX (2010) The distribution and speciation of trace metals in surface sediments from the Pearl River Estuary and the Daya Bay, Southern China. Mar Pollut Bull 8:1364–1371

Zhang G, Bai J, Xiao R, Zhao Q, Jia J, Cui B et al (2017) Heavy metal fractions and ecological risk assessment in sediments from urban, rural and reclamation-affected rivers of the Pearl River Estuary, China. Chemosphere 184:278–288

Zhao YL, Liu SY, Liu W (2012) Water environment and health risk assessment of the Guijiang basin. Pearl River 33:39–41 (in Chinese)

Zhao GM, Ye SY, Yuan HM, Ding XG, Wang J (2017) Surface sediment properties and heavy metal pollution assessment in the pearl river estuary, China. Environ Sci Pollut Res Int 24:2966–2979

Zhen G, Li Y, Tong Y, Yang L, Zhu Y, Zhang W (2016) Temporal variation and regional transfer of heavy metals in the Pearl (Zhujiang) River, China. Environ Sci Pollut Res Int 9:8410–8420

Zhou YC, Zhi CY, Wang L, You QP (2013) Health risk assessment of heavy metals pollution in Liujiang River. J Anhui Agric Sci 41:4370–4372 (in Chinese)

Zhu QQ, Wang ZL (2012) Distribution characteristics and source analysis of heavy metals in sediments of the main river systems in China. Earth Environ 40:305–313

Zhuang W (2015) Review on geochemical characteristics and the ecological risk of heavy metals in the sedimentary environment. Environ Sci Technol 38:196–2041