

# Seasonal and spatial contamination statuses and ecological risk of sediment cores highly contaminated by heavy metals and metalloids in the Xiangjiang River

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**Abstract** To reveal seasonal and spatial variations of heavy metals and metalloids (HMMs) in sediment of the Xiangjiang River, a total of 24 water and 649 sediment samples were collected from six sampling stations in the Songbai section of the river which had been polluted by HMMs for 100 years. Their contamination statuses and ecological risk were determined by enrichment factor (EF), geo-accumulation index ( $I_{geo}$ ), pollution load index (PLI), and mean probable effect concentration quotients (mPECQs) analyses. The results revealed a unique seasonal distribution of metals in the sampling stations: The highest concentrations were revealed in the dry seasons (autumn and winter) and the lowest during the wet seasons (spring and summer). It exhibited a greater seasonal variation in the estuary sediment cores (sites ME and MW) than in the cores of other sites. Moreover, the highest

concentrations of the tested metals were also found in the estuary sediment cores in the dry seasons (autumn and winter). The highest vertical concentrations of Pb, Zn, Cu, Ni, As, Fe, and Mn were observed at the depths of 16–36 cm in all of the sampled sediment cores. The EF,  $I_{geo}$ , PLI, and mPECQs values of all samples in autumn were higher than in summer. Cd posed the highest ecological risk in all seasons, although its concentrations were lower compared to other studied elements. Our results will benefit to develop feasible sediment quality guidelines for government monitor and remediate the local sediments in the Xiangjiang River.

**Keywords** Sediment core · Heavy metals and metalloids · Seasonal variation · Xiangjiang River

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## Introduction

The prolonged impacts of heavy metals and metalloids (HMMs) in industrial emission on river ecosystem (especially on sediments) may last decades or more (Himmelheber et al. 2008; Birch et al. 2014; Bian et al. 2016; Ma et al. 2016). Once incorporated into sediments, HMMs are chemically and biologically bounded which affects their release and toxicity. The binding effects of the contaminants are highly associated with the environment factors of fluvial systems,

such as pH, temperature, electrical conductivity (EC), dissolved oxygen (DO), and flow rate (Bi et al. 2014; Liao et al. 2016; Ma et al. 2016; Ni et al. 2016). The environment factors are seasonally variant which cause seasonal changes of contamination statuses and ecological risk of pollutants in sediments (Elzwayie et al. 2017; Belabed et al. 2017). Therefore, it is reasonable to investigate seasonal variations of HMMs in sediments to assess their contamination levels and ecological risk.

The seasonal variations of HMMs in surface sediments have attracted increasing research interest (Ca Ador et al. 2000; Duman et al. 2007; Najamuddin 2016; Redwan and Elhaddad 2017). For example, higher levels of HMMs in surface sediments were shown in summer (Redwan and Elhaddad 2017; Belabed et al. 2017) or wet season (Najamuddin 2016) than in other seasons. A comprehensive four-season analysis also revealed that the highest seasonal values of heavy metals were observed in summer (Duman et al. 2007). The four-season analysis can provide a more detailed view into contamination trends than the studies only in two seasons, such as wet and dry seasons or summer and winter (Monteiro et al. 2016; Najamuddin 2016; Redwan and Elhaddad 2017). Moreover, it is globally found that surface sediments of estuaries were most severely polluted than other sites in a river in each season (Najamuddin 2016). In addition, a study of Tagus Estuary (Portugal) indicated that the seasonal variances of contaminants occur not only in the top layers, but also in the deeper layers of the sediments (Monteiro et al. 2016). Thus, it is necessary to more intensively investigate the characteristics of integrated sediment cores in all seasons to reveal the annual contamination trends.

Many geochemical and statistical indexes have been intensively applied to assess the pollution statuses and ecological risk of heavy metals and metalloids in sediments/soils (Jamshidi-Zanjani and Saeedi 2017; Chai et al. 2017; Liu et al. 2017; Chen et al. 2016; Kowalska et al. 2018; Sakan et al. 2015). Geo-accumulation index ( $I_{geo}$ ) is a widely utilized classical geochemical criterion to evaluate pollution degree of metals in sediments (Ranjbar Jafarabadi et al. 2017; Chai et al. 2017). Enrichment factor (EF) commonly indicates natural or anthropogenic sources of elements (Jamshidi-Zanjani and Saeedi 2017; Chen et al. 2016). However, they only focus on individual pollutant, while multi-metal contamination in

sediments is common. Unlike the indexes for individual metals, such as  $I_{geo}$  and EF, pollution load index (PLI) is a combination ecological risk assessment of total heavy metals and metalloids in sediments (Pandey et al. 2019). Mean probable effect concentration quotients (mPECQs) are also developed to evaluate the combined effects of multiple contaminants in sediments (MacDonald et al. 2000; Farkas et al. 2007; Liu et al. 2017).

The industrial emission of mining and smelting nonferrous metals is ranked as the primary pollutants in the Xiangjiang River, China. The biogeochemical and physicochemical properties and potential ecological risk of HMMs in its surface sediments during different individual seasons have been reported (Sun et al. 2012; Mao et al. 2013; Chai et al. 2010, 2017; Zhu et al. 2013; Wang et al. 2010, 2011; Li et al. 2018). However, the annual trends of contamination statuses and ecological risk in sediment cores are rarely explored. Here, we aim to reveal the seasonal variations of contamination statuses and ecological risk associated with HMMs in sediment cores of Songbai section which is one of major areas with vast contaminant input of the Xiangjiang river (Chai et al. 2017). The horizontal and vertical distributions of HMMs contents (e.g., Pb, Zn, Cd, Cu, Cr, As, Ni, Fe, and Mn), as well as water quality parameters (e.g., pH, EC, DO, TP,  $F^-$ , and  $SO_4^{2-}$ ) were seasonally investigated. The contamination statuses and ecological risk of the contaminants in sediments were determined by EF,  $I_{geo}$ , PLI, and mPECQs analyses. Moreover, the sources and correlation of the HMMs were revealed by principal component analysis (PCA) and Pearson's correlation. Our results provide support for government to administrate the quality of local sediments and facilitate treatment of heavy metal and metalloid pollution in the Xiangjiang River.

## Materials and methods

### Study area

The Songbai section of the Xiangjiang River (26°36'–26°39'N, 112°33'–112°39'E) locates on the upper and middle reaches of the river and lies in the southern Hengyang Basin, which is majorly composed of red rock layers of cretaceous and Paleogene. Red and purple soil hills are typical in the study area which are

quite fragile to soil erosion by rainfall. It is undermined by vegetation deterioration, mining, and smelting activities. The average rainfall and soil erosion modulus of the study area are 1, 223.4–1, 421.0 mm and 5505 t/km<sup>2</sup> a, respectively.

The Songbai area is well known for its dense distribution of Pb–Zn smelting factories. The Pb–Zn mines in Songbai area which ranks top 5 in China were found more than 900 years ago and the first modern Pb–Zn smelting plant in the area was built in 1905. As a result, the Songbai section has received HMMs for hundreds of years. The Xiangjiang River is one of the major branches of the Yangtze River and its metal contamination poses high ecological risk to the Yangtze river with the inputting water flow (Liu et al. 2017).

Sampling sediment cores and fluvial water

Sediment cores were sampled at six representative sites in both sides of the Songbai section in 2015 (Fig. 1): The two stations ME and MW were selected along the estuary of the Jiao River and in midstream of the Xiangjiang River. The stations UE and UW

located upstream of the lead–zinc industrial area. The stations DE and DW were at downstream of the exit of the industrial area.

A 50-cm-long sediment core sample was taken in each sampling site and each season with a columnar bottom sampler (Beijing New Landmark Soil Equipment Co, Ltd., Beijing, China). The cores were sliced with a 2-cm interval, and each interval was homogenized after removing large debris and shells. Four water samples in a circle with 10 m of diameter and sediment core sampling point as center were randomly extracted, and their mixture was determined for the sampling site. A total of 24 water and 649 sediment samples were collected from the six sampling sites during spring (April, wet season), summer (July, wet season), autumn (October, dry season), and winter (December, dry season) seasons. The samples were delivered to our laboratory with ice bags.

Physicochemical characteristics analyses

The sediment samples were desiccated at 60 °C for 7 days, followed by desiccation at 110 °C for 2 days, and then they were homogenized, crushed, and passed

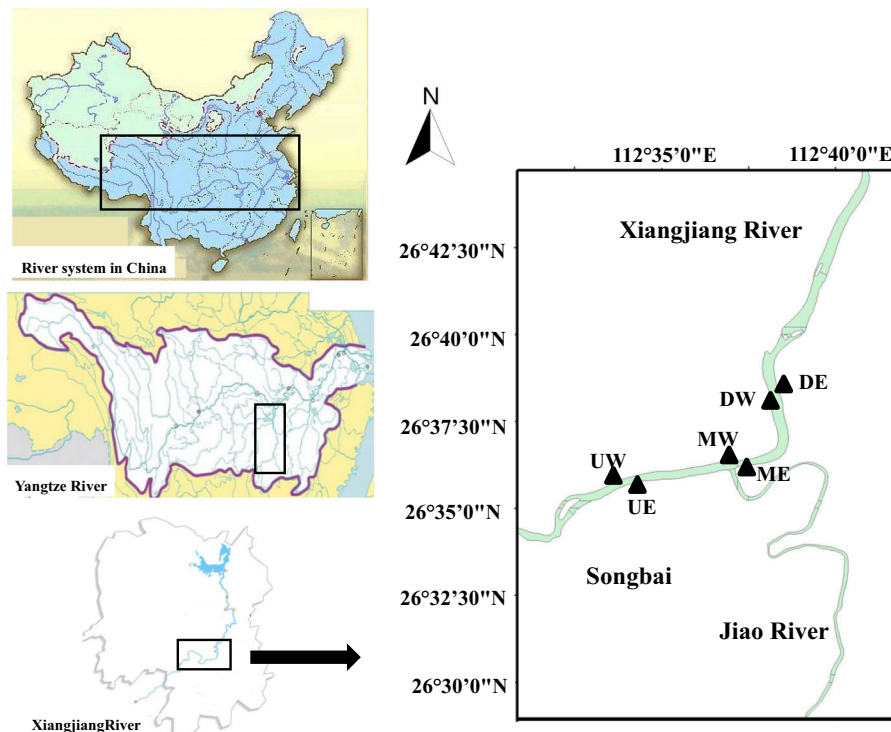


Fig. 1 Map showing the locations of the sampling sites in the Songbai section of the Xiangjiang River

through 150- $\mu\text{m}$  nylon sieves (100 meshes) for determining concentrations of the metals. 0.1 g of each sediment sample was digested in a Teflon tank mixed with 5 ml of HCl and 10 ml of  $\text{HNO}_3$  at 150 °C for 60 min. And then the mixture was digested with 5 ml of HF and 2 ml of  $\text{HClO}_4$  at 120 °C for 60 min. The digestion tank was cooled and the residue was dissolved with 1 ml of  $\text{HClO}_4$  and 1 ml of deionized water in a sealed shaker for 12 h. Finally, the solution was added to 50 ml with deionized water in a volumetric flask at room temperature. Each sample was performed with three replicates. The concentrations of Zn, Pb, Cu, Ni, Cd, Cr, Fe, and Mn were simultaneously measured with an inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7500 series, USA) (Yang et al. 2018a; Chai et al. 2018a, b). In addition, 0.5 g of the corresponding sediment sample was digested with 10 ml of aqua regia at 95 °C for 2 h, followed by adding 5 ml of HCl, 5 ml of thiocarbamide and aqua regia to 50 ml. The concentration of As was determined by an atomic fluorescence spectrophotometer (AFS-810, Beijing Titan Instrument Corp., Beijing, China) (Wu et al. 2015; Min et al. 2017).

Electrical conductivity, pH, temperature and dissolved oxygen of water samples were measured in situ by respective portable electrodes. Water samples were collected and stored with polypropylene bottles in an insulated cooler container. All samples were kept at 4 °C in the laboratory before chemical analysis.  $\text{F}^-$  and  $\text{SO}_4^{2-}$  were analyzed using an ion chromatograph (Metrohm).  $\text{BOD}_5$  was measured by 5-day BOD test.  $\text{NH}_4\text{-N}$  and TP were analyzed using spectrophotometry (Song et al. 2018).

In order to assure and control the quality of the analysis, laboratory quality assurance and control methods were performed, including standard reference materials, method blanks, and duplicates at intervals of 10 samples. China Stream Sediment Reference Materials (GBW07309 (GSD-9) and GBW07311 (GSD-11)) were used to examine the accuracy of the determination method, and the concentration of the standard reference materials was found to be within 88–105% of certified values.

Evaluating contamination statuses and potential ecological risk of heavy metals and metalloids

#### Enrichment factor (EF)

The enrichment factor (EF) was applied to assess the contamination levels of heavy metals and metalloids in sediments. The EFs is expressed as the following equation (Chai et al. 2017; Tamim et al. 2016):

$$EF = \frac{(C_m/C_{Fe})}{(B_m/B_{Fe})} \quad (1)$$

where  $(C_m/C_{Fe})$  and  $(B_m/B_{Fe})$  are the ratio between contents of a metal and Fe in a sediment sample and the reference soils, respectively. In this study, the metal contents in the soils of Hunan province in 1980s were used as the regional background values (Table 2). The stable elements as reference metals, such as Fe, Li, Al, Sc, V, and Mn, were used to calculate EF in previous studies (Chen et al. 2016; Jamshidi-Zanjani and Saeedi 2017; Mna et al. 2017; Sakan et al. 2015). Fe was selected as the reference element in the present study which is one of characteristic stable elements in the red soils of Human province. The classifications of EF index are as follows (Wang et al. 2015):  $EF \leq 1$ : no enrichment;  $1 < EF \leq 2$ : low enrichment;  $2 < EF \leq 5$ : moderate enrichment;  $5 < EF \leq 20$ : severe enrichment;  $20 < EF \leq 40$ : very severe enrichment;  $EF > 40$ : extremely severe enrichment.

#### Geo-accumulation index ( $I_{geo}$ )

A classical approach to estimate anthropogenic impacts on sediments is to calculate the geo-accumulation Index ( $I_{geo}$ ) of pollutants using the following formula (Muller 1969; Ranjbar Jafarabadi et al. 2017):

$$I_{geo} = \log_2 \left( \frac{C_m}{1.5C_n} \right), \quad (2)$$

where  $C_m$  and  $C_n$  are the contents of a metal in a sediment sample and background soils, respectively. The factor of 1.5 is used to minimize the geogenic effects on background values. The categories of  $I_{geo}$  are as follows:  $I_{geo} \leq 0$  (Class 1): unpolluted;  $0 < I_{geo} \leq 1$  (Class 2): unpolluted to moderately polluted;  $1 < I_{geo} \leq 2$  (Class 3): moderately polluted;  $2 < I_{geo} \leq 3$  (Class 4): moderately to heavily

polluted;  $3 < I_{geo} \leq 4$  (Class 5): heavily polluted;  $4 < I_{geo} \leq 5$  (Class 6): heavily to very extremely polluted;  $I_{geo} > 5$  (Class 7): extremely polluted.

*Pollution load index (PLI)*

The PLI was developed to assess comprehensive ecological risk (Tomlinson et al. 1980). Its calculation equation is given as follows:

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \cdots \times CF_n} \quad (3)$$

where CF is contamination factor of a metal, which is the ratio of contents of the metals in a sediment sample to in the reference; and n is the number of metals. The categories of PLI index are as follows:  $PLI < 1$ : uncontaminated;  $PLI \geq 1$ : contaminated.

*Multiple probable effect concentrations quality (mPECQs)*

The mPECQs, another classical method to evaluate ecological risk of multiple contaminants, was conducted to assess sediment quality (Liu et al. 2017). The formula is as follows:

$$mPECQs = \frac{\sum_{i=1}^n \frac{C_i}{PEC_i}}{n} \quad (4)$$

where  $C_i$  is the concentration of pollutant  $i$  in a sediment sample,  $PEC_i$  is the consensus-based probable effect concentration of the pollutant  $i$  (specifically, the PEC values of Cd, Pb, Zn, Cr, Cu, and As are 4.8, 129, 459, 111, 149, and 33 mg/kg, respectively) (MacDonald et al. 2000), and n is the number of HMMs. The categories of mPECQs as follows:  $mPECQs < 1$  (Class 1): non-toxic and the incidence of toxicity is relatively low ( $< 25\%$ );  $1 \leq mPECQs < 5$  (Class 2): the incidence of toxicity is 70–75%;  $mPECQs \geq 5$  (Class 3), toxic and the incidence of toxicity is more than 75% (MacDonald et al. 2000; Balistrieri et al. 2007).

*Statistical analyses*

The principal component analysis (PCA) was used to investigate the sources of HMMs in the sediment cores (Chai et al. 2017). PCA of annual mean of HMMs with the varimax rotation of the standardized component loadings was conducted by the eigenvalue

decomposition. The Kaiser–Meyer–Olkin (KMO) and Bartlett’s tests were performed to evaluate the validity of PCA. And the principal component values with an eigenvalue higher than 1 were retained until the cumulative variances higher than 85%. The relationship among HMMs was also analyzed by Pearson’s correlation matrix. PCA and Pearson’s correlation were performed with SPSS 19.0 statistical program (IBM, Inc., Armonk, NY).

**Results and discussion**

*Horizontal distributions of heavy metals and metalloids*

In the Songbai section of the Xiangjiang River, the average concentrations of Zn, Pb, Cu, Ni, Cd, Cr, As, and Mn in the surface sediment samples which were the top 10-cm layers of the sediment cores are given in Table 1. The confluence fields (sites ME and MW) of the Xiangjiang River and the Jiao River, which had received the treated effluents discharged from 90% smelting plants in the Songbai and Leiyang areas, had higher concentrations of Zn, Pb, Cu, Ni, Cd, Cr, and As than the other sampling sites in autumn and winter. But the seasonal variations of Mn and Fe were irregular. The highest concentrations of all of the tested metals were found at sites MW and ME in the dry seasons (autumn and winter), which implied that the effluents from smelting plants of Pb and Zn were likely to be a potential major source of heavy metals to the surrounding environment. The contents of the metals in the sediment samples of the Songbai section were dramatically higher than in the sediment samples from other fluvial ecosystems in Japan, India, Serbia, Peninsular Malaysia, and Portugal which flows through the major mining and industrially flourished cities (Shikazono et al. 2012; Patel et al. 2018; Sakan et al. 2016; Pal and Maiti 2018; Haris et al. 2017; Antunes et al. 2018). It indicated that the fluvial sediments of the Songbai section had possibly severely polluted by HMMs discharged by the densely distributed Pb–Zn smelting factories in this area.

The parameters (pH, EC, DO,  $F^-$ , and  $SO_4^{2-}$ ) in the water samples exhibited a significant trend of increasing and then dramatic decreasing from the upstream (UE and UW) to midstream (ME and MW), and to downstream (DE and DW), which shared a similar

**Table 1** Summary of the metal contents and chemical properties in the different surface sediments and water of the Songbai section

	Metals contents in surface sediments (mg/kg)											Chemical properties in water (mg/L)							
	Zn	Pb	Cu	Ni	Cd	Cr	As	Mn	Fe%	T °C	pH	EC (µs/cm)	DO	BOD <sub>5</sub>	NH <sub>4</sub> -N	TP	F <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	
UW	Spring	724.67	459.62	108.51	51.72	34.35	319.16	112.71	1851.77	3.89	15	8.13	288	7.4	0.7	0.142	0.07	0.15	0.018
	Summer	561.82	387.38	59.10	29.98	18.49	149.95	96.61	1005.01	2.58	26	7.36	197	6.9	1.7	0.511	0.07	0.15	0.045
	Autumn	602.08	317.82	29.67	22.76	472.85	910.15	48.39	1431.85	2.83	22	8.11	320	7	0.5	0.231	0.04	0.22	0.009
	Winter	312.05	123.44	10.24	65.18	18.01	975.86	19.11	4400.68	4.06	14	8.02	178	7.5	1	0.124	0.06	0.19	0.015
UE	Spring	484.75	224.99	80.59	51.03	8.06	267.91	56.73	193.27	3.02	15	8.12	285	7.6	0.9	0.19	0.06	0.16	0.009
	Summer	614.55	240.25	64.70	43.44	30.02	398.73	84.93	2068.11	3.04	26	7.5	242	7.9	2.2	0.325	0.09	0.19	0.043
	Autumn	263.25	184.03	18.79	12.70	364.70	933.77	71.28	1057.81	2.42	22	8.08	326	7.1	1.1	0.208	0.04	0.15	0.019
	Winter	363.54	128.51	15.48	30.30	25.51	1036.25	68.49	2886.49	3.18	14	8.09	206	7.1	0.9	0.12	0.06	0.26	0.022
MW	Spring	190.11	259.17	31.62	29.35	2.82	234.50	36.71	2379.72	4.55	15	8.11	232	7.8	2.4	0.151	0.05	0.14	0.005
	Summer	1310.10	0.91	138.14	34.02	2.33	319.23	86.07	1230.55	1.71	26	7.71	267	6.5	1	0.205	0.04	0.25	0.029
	Autumn	1411.86	730.36	194.91	55.83	678.70	860.52	106.25	3939.24	5.75	22	8.11	274	6.5	0.9	0.134	0.06	0.32	0.026
	Winter	491.88	450.77	30.59	38.20	24.39	871.31	57.57	2213.41	3.21	14	8.28	261	7.4	0.7	0.166	0.08	0.41	0.014
ME	Spring	669.52	160.32	33.43	36.72	10.70	112.37	97.97	380.38	2.82	15	8.13	240	8	1.1	0.218	0.06	0.16	0.008
	Summer	459.76	67.24	45.68	29.11	2.76	285.91	78.65	434.72	2.53	26	7.71	264	6.6	1.3	0.166	0.04	0.24	0.028
	Autumn	3753.73	1111.12	449.95	36.46	1053.19	888.37	257.54	1230.17	2.47	22	8.15	270	6.4	0.5	0.137	0.06	0.34	0.028
	Winter	1291.27	529.66	45.84	42.45	51.07	901.42	75.99	1709.99	2.41	14	8.3	256	7.5	0.9	0.148	0.07	0.41	0.027
DW	Spring	493.19	108.17	70.60	66.08	9.91	184.83	81.83	765.59	4.45	15	8.08	249	8.5	1.2	0.154	0.04	0.12	0.007
	Summer	214.42	0.46	31.18	19.81	2.13	130.00	17.16	248.79	0.63	26	7.44	187	7.3	1.3	0.177	0.05	0.14	0.029
	Autumn	99.18	83.91	12.06	43.73	313.31	485.47	20.40	1660.30	3.83	22	7.83	189	6.8	2.7	0.161	0.05	0.21	0.038
	Winter	907.46	337.63	91.33	17.35	23.94	457.41	432.09	1280.97	2.47	14	8.09	188	6.4	0.5	0.191	0.05	0.25	0.018
DE	Spring	1294.34	388.70	100.61	80.79	25.53	194.83	353.34	5358.94	8.22	15	8.14	243	7.7	0.6	0.182	0.03	0.12	0.008
	Summer	560.17	1.85	279.88	45.27	5.26	167.01	948.48	4686.33	5.17	26	7.51	188	7	0.9	0.223	0.04	0.14	0.021
	Autumn	456.90	279.05	267.50	6.32	1711.00	454.53	781.22	879.92	2.04	22	7.9	183	7.2	2.5	0.158	0.07	0.19	0.029
	Winter	473.45	218.71	264.13	13.47	2.62	517.10	1371.78	1195.42	2.31	14	8.12	189	6.2	0.7	0.151	0.05	0.24	0.024
Mean	759.81	297.73	104.69	36.99	204.84	507.96	224.67	1898.98	3.29	19.25	7.96	238.42	7.18	1.18	0.19	0.06	0.21	0.02	
SD	721.43	247.24	108.45	17.17	405.91	312.60	333.00	1387.59	1.50	4.97	0.27	43.68	0.57	0.64	0.08	0.01	0.08	0.01	
Max	3753.73	1111.12	449.95	80.79	1711	1036.25	1371.78	5358.94	8.22	26	8.3	326	8.5	2.7	0.511	0.09	0.41	0.045	

**Table 1** continued

	Metals contents in surface sediments (mg/kg)										Chemical properties in water (mg/L)							
	Zn	Pb	Cu	Ni	Cd	Cr	As	Mn	Fe%	T °C	pH	EC (µs/cm)	DO	BOD <sub>5</sub>	NH <sub>4</sub> -N	TP	F <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
Min	99.18	0.46	10.24	6.32	2.13	112.37	17.16	193.27	0.63	14	7.36	178	6.2	0.5	0.12	0.03	0.12	0.005
CV%	94.95	83.04	103.60	46.42	198.16	61.54	148.22	73.07	45.43	25.81	3.36	18.32	7.95	54.29	41.80	26.04	38.52	50.71
BV	94.4	29.7	27.3	31.9	0.126	71.4	15.7	549	3.96	-	-	-	-	-	-	-	-	-

Cu, Hg, Cd, Cr, and Pb were not detected in water

SD Standard deviation, CV coefficient of variation, BV background values (China National Environmental Monitoring Center 1990), - not available

trend with Pb, Cd, Zn and Ni in the sediment samples (Table 1). Conversely, the lowest values of organics (BOD<sub>5</sub>) in the water samples were in the midstream, while the highest concentrations of HMMs in the corresponding sediment samples. This trend suggested that the elevated concentrations of metals in suspended solids were related to water quality parameters (Rodriguez-Freire et al. 2016).

The sampling sites DE and DW, which are situated at the downstream of Songbai and near a bend of the river, also had significantly higher average concentrations of Zn (1230 mg/kg), Pb (478 mg/kg), Cu (290 mg/kg), and As (1640 mg/kg). Lower concentrations of metals were showed in the east side sampling sites, UE and DE of the Xiangjiang River than the west side sites (with the exception of Zn in spring and As in winter), which were similar to the results of the previous studies on HMMs in this region (Chai et al. 2017). It is likely due to the special distributions of plants and residents. Over 80% of plants and residents are located on the east side of the section of the Xiangjiang River and over 80% of wastewater is discharged into the east branch.

Vertical distributions of heavy metals and metalloids

The vertical profiles of metals in the sediment cores are illustrated in Fig. 2. For all the sediment samples, lower metal concentrations and smaller concentration variations were observed in the upper layer of the sediment cores (depth of 0–10 cm). It suggested that the human-made contributions of HMMs in the Songbai section had recently declined, which was also supported by the previous studies (Chen et al. 2016; Qiu and Chen 2016).

Summarily, two distribution tendencies relating to metal contents in the sediment cores were observed. The vertical concentrations of Pb, Cu, Ni, Zn, As, Fe, and Mn increased from the surface to middle layers (depths of 16–36 cm), and then decreased in the deeper sediment layers. According to the <sup>210</sup>Pb dating results in previous studies, the average rate of sediment deposition in the Xiangjiang River was 5 cm/year (Dai et al. 2005; He et al. 2014). Thinking the settling velocity of sediment at this region, the layer with peak values corresponded to the year of 2012. The nonferrous metals production in the Xiangjiang River catchment rapidly increased since

1990s. In particular, over 50% of Pb in China were provided by the factories in Songbai area. The pollutants had been accumulated because of the small enterprise scale, lower technology level, and weaker consciousness of environmental protection. The discharging volumes of metal pollutants have been limited by the higher requirements of environmental protection and eliminating backward production from 2010 to 2012. As shown in the implementation plan for comprehensive control of water pollution in the Xiangjiang River issued by the government of Hunan province, 48 Pb–Zn smelting factories were closed down, 31 plants were stopped production, and 44 factories were renovated in the section of the Xiangjiang River, resulting in that 50% of total discharging volumes of metal pollutants was reduced in 2012. It corresponded to the vertical distribution trends of the major metals in the sediment cores in our study. The effects of the redox cycles of Fe and Mn on metals also potentially contribute the cluster distributions of Pb, Zn, Cu, Ni, and As. The redox boundary layer of the sediment cores focused on the depth of 10–30 cm which were also found enrichment of heavy metals. Many heavy metals are transported as Fe–Mn oxides or oxyhydroxides and accumulated in the redox boundary layer (Fernandes and Nayak 2014; Lu et al. 2016; Yang et al. 2018b).

The vertical variants of Cr and Cd (except in autumn) in all layers of the sediment cores tended to be smaller than other HMMs which had also been revealed in several previous studies (ElBishlawi et al. 2013; Lu et al. 2016; Mna et al. 2017). All metals (except Cr) had remarkably negative correlations with DOC in the sediment cores (ElBishlawi et al. 2013). Cr is mainly accompanied with coarse particles in sediments, whereas most other metals are mainly accumulated with fine-grained particles (Zhang et al. 2001; Lu et al. 2016). The distribution of fine-grained particles is relatively variant, whereas the coarse particles are evenly distributed at the top 50-cm sediment. Cd had a lower correlation with iron but showed essentially associated with organic matter and sulfides compared to other metals (ElBishlawi et al. 2013; Mna et al. 2017).

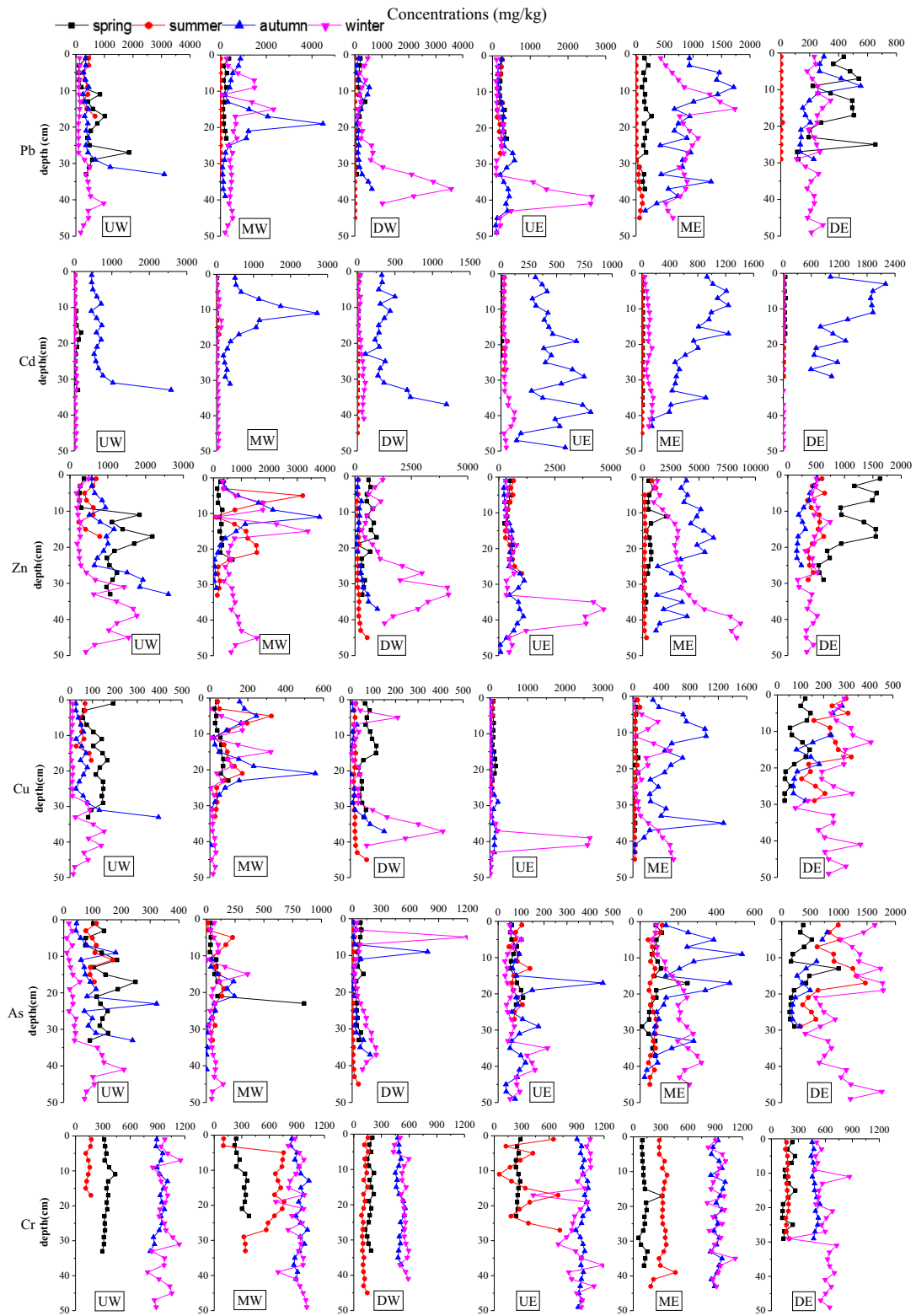
#### Seasonal variations of heavy metals and metalloids

The seasonal variations of the HMMs in the sampled sediment cores are also shown in Fig. 2 and Table 1.

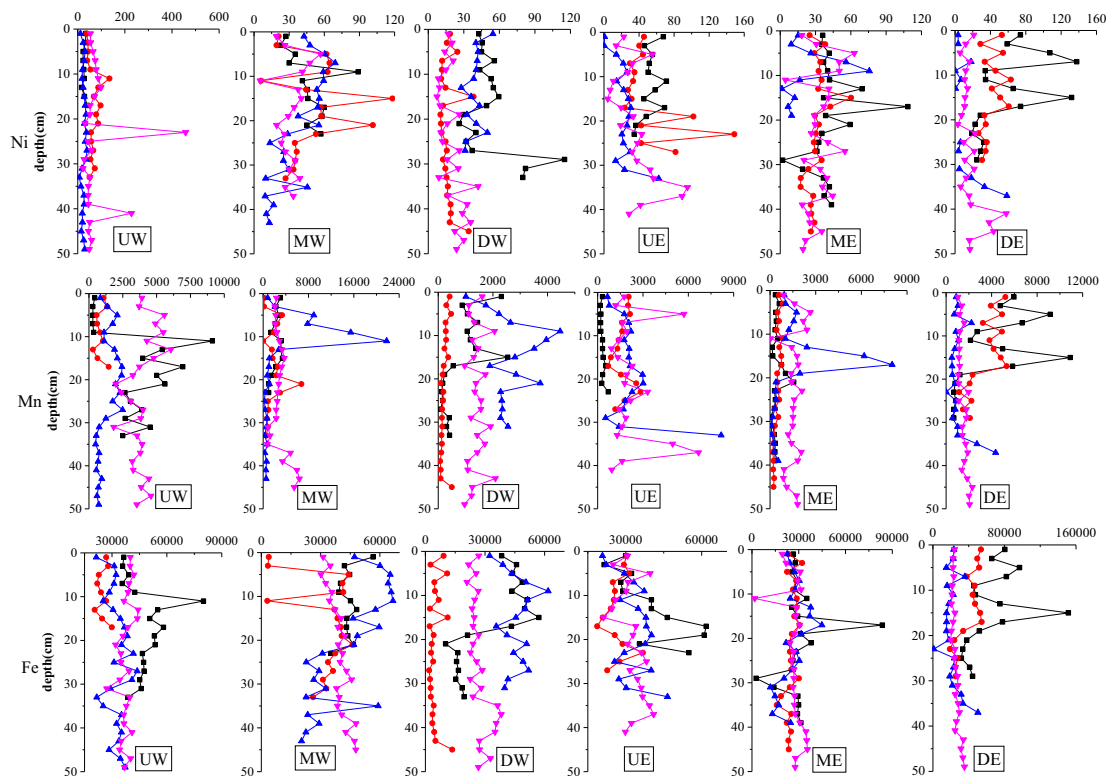
Spring is a warm-rainy season in the Songbai area. The concentrations of Pb, Zn, Cd, Cu, and As were generally lower in depths of 10–20 cm than in other layers of the sample cores in spring, except that Fe was the highest. Summer is a wet season in which floods are frequently shown in the Songbai section. Consequently, the concentrations of metals in the sediment samples were lower in summer than in winter. But the concentrations of Ni, Fe, and Mn were higher in summer. The seasonal highest values of HMMs at sites MW and ME were observed at autumn. And at upstream sites (UE and UW), the concentrations of HMMs also increased with increasing depths in autumn, while the concentrations of Pb, Zn, As, Cu, and Cd decreased at site DE. The highest concentrations of Pb, Zn, Cu, As and Cr were 3.57, 8.68, 2.66, 1.79 and 1.28 g/kg during winter, respectively (Fig. 2). Similarly, in autumn, the concentrations of the five metals (Pb, Zn, Cu, Cd, and As) increased as the depth at all sites except site DE. Higher concentrations of Pb, Zn, Cu, Cr, and As in the sediment samples were shown in winter than in other seasons, but lower Ni, Fe, and Mn was found.

Overall, the distributions of metals followed the order:  $Fe > Mn > Zn > Cr > Pb > Cd > As > Cu > Ni$  in all the sampling stations and exhibited a unique seasonal pattern with the highest values in the dry seasons (autumn and winter) and the lowest during the wet seasons (spring and summer). Moreover, the amplitude of variations of mean concentrations of HMMs (except Cr) was narrow between four seasons in sites UE, UW, DE, and DW. But the concentrations of HMMs in sites ME and MW (estuary region) were significantly seasonally variant. The seasonal variations are possibly owing to different processes which include: (1) resuspension of sediments mainly contributed to the seasonal variations. The monsoon accelerated the flow of the Xiangjiang River in summer and spring, leading to increasing speed of water flow and volume of the resuspended sediments (Wang et al. 2014). (2) pH values of sediments also determined its adsorption on HMMs. The sediment samples with higher pH value have the ability to absorb more HMMs compounds (Duivenvoorden et al. 2017). The mean pH value ( $pH = 7.54$ ) during the wet seasons were lower than in the dry seasons ( $pH = 8.09$ ), which was possibly attributed to naturally increased intakes of red soils particles (acid soil,  $pH = 3.52$ ) from soil erosion causing by intensive





**Fig. 2** Vertical variations of the nine metals in the sediment cores of the Songbai section in 2015



**Fig. 2** continued

rainfall. Our results indicated that the metals were strongly bound to the sediment particles under alkaline conditions. (3) Dilution and oxidation driving were possibly associated with the seasonal variations (Redwan and Elhaddad 2017). The volume of water flow in the wet seasons is higher than in the dry seasons. During high-flow periods, the surface of the sediment is flushed with oxygen, driving redox metals into the subsurface. During low-flow periods, oxygen is quickly consumed, and redox processes are close to the sediment surface.

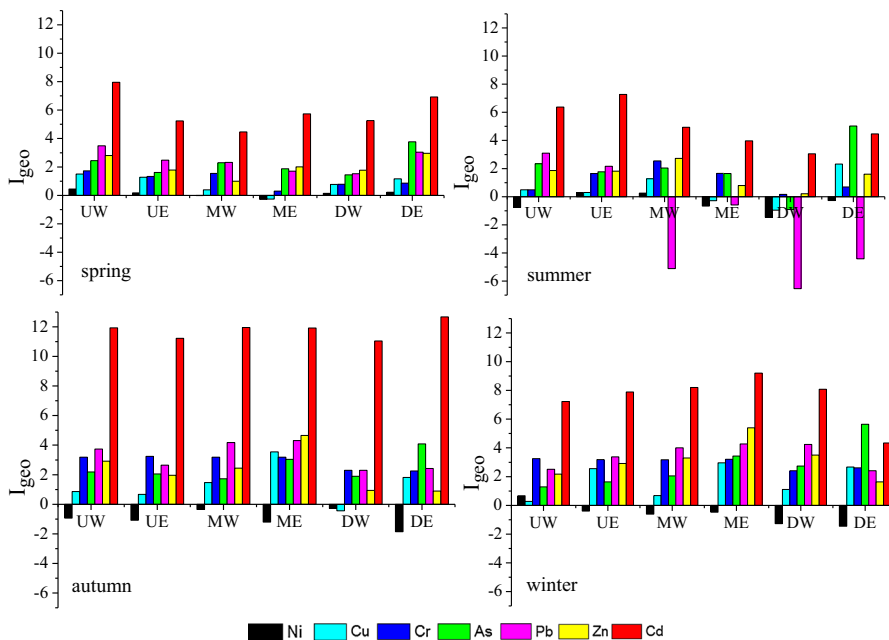
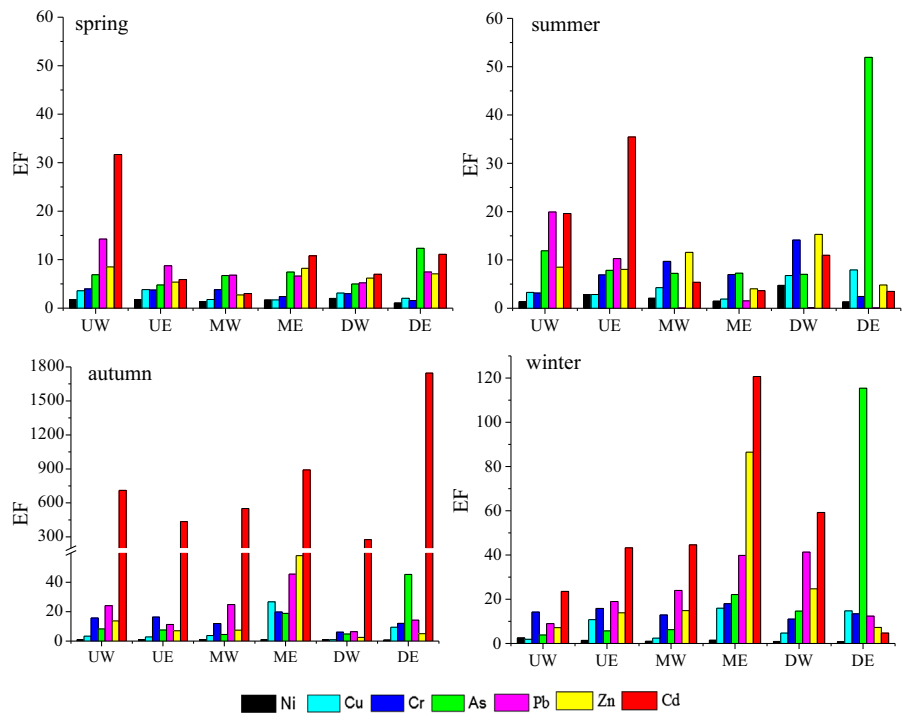
#### Contamination statuses and potential ecological risk

The contamination statuses and potential ecological risk of HMMs in the sampled sediment cores were evaluated by EF,  $I_{geo}$ , PLI and mPECQs analyses. As shown in Fig. 3, the mean EF values of Pb, Zn, Cu, Cd, Cr, and As in the six sediment cores were more than 1, indicating that these metals had been caused contamination in the sediment samples of the Xiangjiang River. The EF values of metals ranked as the following

order: Cd > Pb > Zn > As > Cr > Cu. The results indicated that the lowest concentration of Cd caused most severe potential ecological risk in this region. The similar results were revealed by the previous studies in the same area (Mao et al. 2013; Chai et al. 2017). The EF values of metals in autumn and winter were greater than in spring and summer, indicating that the enrichment variations were potentially positively associated with monsoon. Such high enrichment can possibly be attributed to the anthropogenic sources of metals. In this study, EF values of Ni (except DW in summer) were less than 1, suggesting that contamination of Ni is not a major concern in the Songbai section of the Xiangjiang river (Fig. 3).

Comparing the results of  $I_{geo}$  with EF analyses, it revealed that Cd was the most acute pollution in the sediment samples, posing a serious environmental risk (Fig. 4). The degree of Cd contamination measured by  $I_{geo}$  was over 5 in the four seasons. The mean  $I_{geo}$  values of Pb (Class 4), Zn (Class 3), Cr (Class 3), As (Class 3), and Cu (Class 2) were also higher in autumn and winter than in spring and summer, respectively.

**Fig. 3** EF values of the HMMs at all sites in four seasons

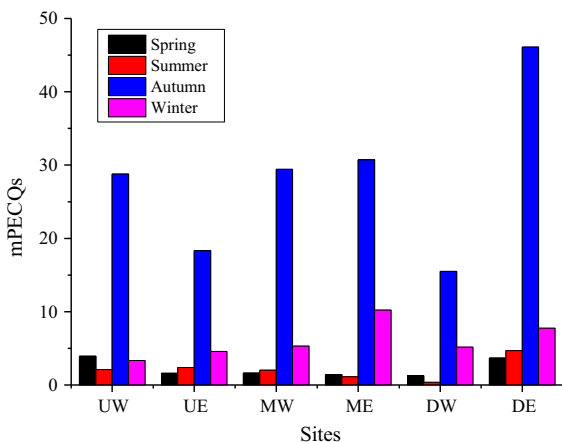
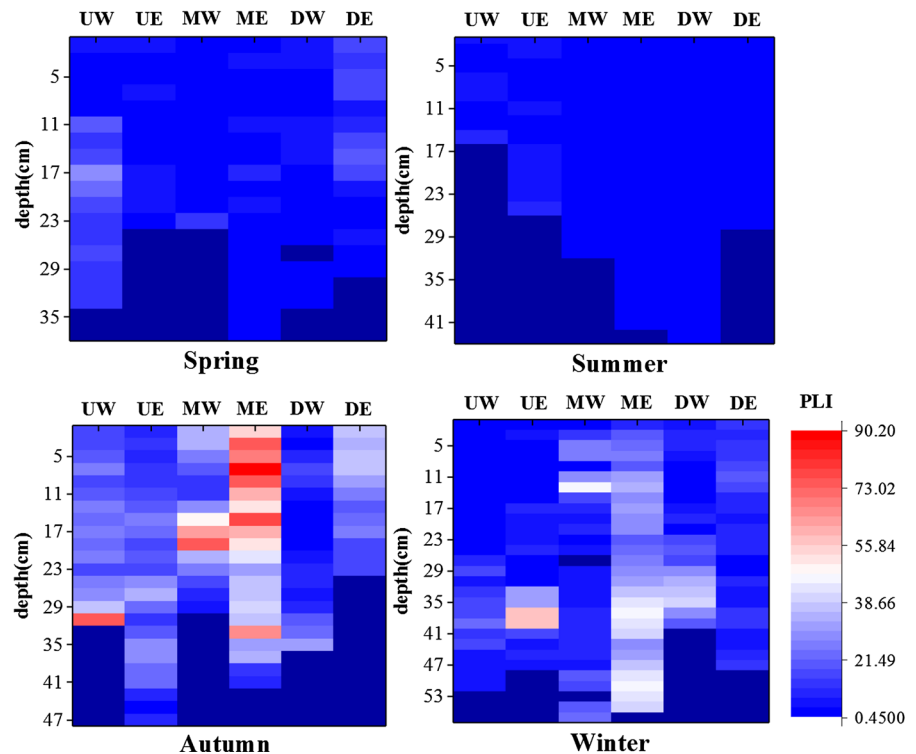


**Fig. 4**  $I_{geo}$  values of the HMMs at all sites in four seasons

Figure 5 presents the vertical profiles of PLI values of the major pollution metals (Pb, Zn, Cu, Cd, Cr and As) in the sediment cores. The site UE exhibited a

slightly increasing trend from the upper to lower layers, in which the highest PLI value was shown in the layer of 38–42 cm depth in winter. A decreasing

**Fig. 5** PLI values of the HMMs at all sampling sites in the four seasons



**Fig. 6** Mean mPECQs values of the HMMs at all sampling sites in four seasons

trend from the upper to the lower layers was shown in the sites ME and DE. The most severe ecological risk of the site ME (PLI = 90.1) and DE (PLI = 37.2) was at the depth of 8–10 cm and 2 cm in autumn, respectively. The season orders of the mean PLI and mPECQs values of all sites were as followed: autumn > winter > spring > summer (Fig. 6). The

**Table 2** Loadings of the nine metals on principal components (PCs) in the sediment cores

Elements	PC1	PC2	PC3	PC4
Zn	.778	.107	-.021	-.543
Pb	.824	.236	-.253	-.112
Cu	.789	-.053	.431	-.218
Ni	-.455	.736	-.048	-.283
Cd	.531	-.178	-.250	.683
Cr	.757	.258	-.236	.188
As	.173	-.139	.932	.198
Mn	.117	.874	.195	.278
Fe%	-.091	.883	.109	.158
Eigenvalues	3.020	2.272	1.289	1.078
% of total variance	33.558	25.250	14.319	11.982
Cumulative %	33.558	58.808	73.127	85.109

mean mPECQs values in winter (class 3) were 10 times higher than that in summer (class 2).

Based on the results of EF,  $I_{geo}$ , PLI, and mPECQs described previously, two contamination characteristics of the nine HMMs could be highlighted: (1) metal

**Table 3** Pearson’s correlation coefficient between the nine metals in the sediment cores of the Songbai section in different seasons

		Pb	Cd	Zn	Cu	As	Cr	Ni	Fe	Mn
Spring	Pb	1								
	Cd	0.074	1							
	Zn	0.105	.354**	1						
	Cu	.689**	– 0.109	0.061	1					
	As	0.248	.350*	.502**	0.146	1				
	Cr	.699**	– 0.176	– 0.053	.779**	0.202	1			
	Ni	0.131	– .354*	– 0.152	0.152	– 0.175	.289*	1		
	Fe	.367**	– .280*	– 0.03	.348*	– 0.016	.338*	.644**	1	
	Mn	– 0.117	– .298*	0.116	– 0.091	0.209	– 0.087	.303*	.404**	1
Summer	Pb	1								
	Cd	.780**	1							
	Zn	.530**	.571**	1						
	Cu	.454**	.578**	.879**	1					
	As	0.115	0.134	0.235	.294*	1				
	Cr	– 0.044	– 0.039	0.105	0.023	– 0.075	1			
	Ni	.357**	.387**	.294*	.276*	0.051	0.046	1		
	Fe	0.066	0.192	.300*	.441**	– 0.031	– 0.11	0.243	1	
	Mn	.740**	.836**	.648**	.660**	0.121	– 0.124	.450**	.407**	1
Autumn	Pb	1								
	Cd	.829**	1							
	Zn	.829**	.742**	1						
	Cu	.895**	.782**	.782**	1					
	As	.649**	.737**	.587**	.654**	1				
	Cr	– 0.272	– 0.063	– 0.194	– 0.175	– 0.111	1			
	Ni	0.293	0.127	0.044	0.257	0.294	0.188	1		
	Fe	– 0.257	0.031	– 0.144	– 0.243	0.138	.493**	0.285	1	
	Mn	– 0.163	0.107	0.079	– 0.062	0.168	.392*	0.163	.764**	1
Winter	Pb	1								
	Cd	.670**	1							
	Zn	.484**	.788**	1						
	Cu	.779**	.422**	.373**	1					
	As	.494**	.829**	.861**	0.242	1				
	Cr	– 0.044	0.071	0.066	– 0.14	0.094	1			
	Ni	0.23	0.052	0.113	0.038	0.111	0.174	1		
	Fe	– 0.133	– 0.205	0.108	0.105	– 0.069	– 0.022	.604**	1	
	Mn	0.01	– 0.195	– 0.068	– 0.118	– 0.08	.307*	.727**	.595**	1

\*Correlation is significant at the 0.05 level (two-tailed)

\*\*Correlation is significant at the 0.01 level (two-tailed)

contamination in the sampled sediments of the Xiangjiang River was obviously presented seasonal variations. The ecological risk in autumn was higher than in summer. The results revealed that seasonal

regulation on industrial wastewater discharging into the Xiangjiang River should be strengthened, especially in the dry seasons (autumn and winter). (2) Cd posed the highest ecological risk in all seasons with

low concentrations. The possible reasons are that the chemical form of Cd transport more easily and is more sensitive to anthropogenic activities (Yang et al. 2009), which has higher values of toxic factor than other HMMs (Hou et al. 2013).

#### Sources of heavy metals and metalloids in the sediment cores

The results of PCA in the sediment cores are presented in Table 2. Four components explained 85.11% of the total variances. Nine metals were assembled in four groups according to their PCA coefficients. The first principal component explained the most variance (33.56%) and had strong positive loadings on Cr, Cu, Zn, and Pb. The second principal component accounted for 25.25% of total variances and included Ni, Mn and Fe. The third principal component explained 14.32% of the total variances on As. The fourth principal component, accounting for 11.98% of the total variances, comprised of Cd. The results indicated that PC1 potentially described the primary pollution sources of the Songbai section of the Xiangjiang river. It matched with the fact that the Pb–Zn mining and smelting industries were aggregated in the Songbai area (Chai et al. 2017).

The results of Pearson correlation analyses of the HMMs in the sediment samples are summarized in Table 3. The concentrations of Ni in the sediment samples are strongly correlated with Fe and Mn in all seasons except autumn, suggesting that Ni is derived primarily from natural sources because Fe and Mn are major stable elements in the Xiangjiang River basin. Moreover, the concentrations of Ni in sampled sediments nearly equaled to its reference content which was also supported by results of EF and  $I_{geo}$  analyses. In contrast, Cu, Pb, Zn, Cd, and As were weakly associated with Fe and Mn, but exhibited a significant positive correlation ( $p < 0.01$ ) with each other, implying that they had an identical source. Combining with the results of PCA, the anthropogenic input was a possible source of them. The activities related to Pb–Zn mining and smelting industries are responsible for Cu, Cd, Pb and Zn enrichment in the sediments and water of the Xiangjiang River (Qi et al. 2016; Chai et al. 2017).

#### Conclusion

The Xiangjiang River has been polluted by HMMs for 100 years, especially in the Songbai section where numerous Pb–Zn smelting factories are clustered. However, the seasonal variations of contamination statuses and ecological risk of the sediment cores are rarely investigated. This study revealed that the distribution of metals followed the order: Fe > Mn > Zn > Cr > Pb > Cd > As > Cu > Ni in all of the sampling stations and exhibited a unique seasonal pattern with the highest values in the dry seasons (autumn and winter) and the lowest during the wet seasons (spring and summer). A great amplitude of seasonal variations in the estuary sediment cores (sites ME and MW) was directly linked to both the special geographical locations and the anthropogenic activities. The highest concentrations of all of the tested metals were found at sites MW and ME in the dry seasons (autumn and winter). The highest concentrations of Pb, Zn, Cu, Ni, As, Fe, and Mn were observed at the depths of 16–36 cm in the sediment cores, which was possibly associated with that the pollutants discharged by the Pb–Zn smelting industry in the Songbai area had been limited since 2010. The EF,  $I_{geo}$ , PLI, and mPECQs values of the sediment cores of the Songbai section were higher in autumn than in summer and Cd was the most severe metal pollutant in this section. It is very difficult to intensively uncover the seasonal trends of distribution of HMMs in the sediment cores, especially in the estuary. But future studies may focus on how the specific geochemical, hydrological, and environmental factors influence the chemical composition, structure, and morphology of sediment cores in the Xiangjiang River.

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#### Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

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